

An Exploration Into TADF For OLEDs: A Case Study Based On Novel Synthesised Solution-Processable Molecules

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*Getting an education was a bit like a communicable sexual disease.
It made you unsuitable for a lot of jobs,
and then you had the urge to pass it on.*

— Terry Pratchett, *Hogfather*

The Abstract

Work is presented on new molecules designed for Organic Light Emitting Diodes (OLEDs). The molecules synthesised here-in are designed to be solution processable, and display the property of Thermally Activated Delayed Fluorescence (TADF). In the process of characterising these molecules, investigation into the methodology of the field of TADF is conducted and recommendations are made for change. The recommendations presented are: a more thorough way of interpreting transient fluorescence data that does not assume that $k_{RISC} \ll k_{ISC}$; the use of the optimised T_1 state to simulate the excited state geometry in certain circumstances; and caution about using the photoluminescence spectra at 77 K to calculate the energy of the triplet state.

The molecules synthesised are carbazole substituted DMAC-TRZ, a new 1,3-Bis(N-carbazolyl)benzene (i.e. mCp) like host, and a 10H-phenoxazine based compound with substitution para to the nitrogen (a previous synthetic challenge). Of these compounds the carbazole substituted DMAC-TRZ compounds are the focus of most of the work. Unlike DMAC-TRZ, the synthesised solution processable compounds are shown to have H-aggregate like properties when in pure film. Data is also presented that 3 key geometries are necessary to describe the DMAC group beyond the previously described two geometries. Evidence that a transition occurs between two of these geometries in the excited state is presented based on T_1 simulations. It is further suggested that the substitution of groups like carbazole on DMAC may prevent this transition.

Two of the compounds based on the DMAC-TRZ donor-acceptor show extremely narrow singlet-triplet energy gap. This appears to lead to the situation where cooling to 77 K has a greater effect on the rate of fluorescence, than the Reverse Inter System Crossing (RISC) rate. This can be seen as direct experimental evidence that vibronic coupling plays a part in the rate of fluorescence.

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Preface

This thesis represents the blood, sweat, and toil of 4.5 years at Sheffield University. As such it is rather long! It has been split into 4 parts: the introduction, the work on CBZ substituted DMAC-TRZ (See text for meaning of these acronyms), the work beyond DMAC-TRZ, and the supplementary information. Of these parts, 1–3 are designed to be read in a book like manner. The final part — the supplementary information — is designed to be referred to when necessary. It is hoped that those reading it will at least learn something about the field of thermally activated delayed fluorescence. In fact the thesis should in totality represent a pretty good guide to get from graduate level to understand the field of thermally activated delayed fluorescence for OLEDs.

Three deviations from the traditional format of a thesis should be noted. Firstly there is not 1 single conclusion for the entire document. The work on DMAC-TRZ and the work beyond it are two separate subjects, and hence not possible to mesh into a single conclusion chapter. There are two conclusion chapters, one for part 2, and the other for part 3. A second deviation is the experimental is in the appendices. It should be stressed that this is not some scheme to get under the word limit. The reason the experimental is in the supplementary information is that it is not written in a "book" like manner. i.e. it is not designed to be read from front to back. A final change is that a results chapter has been moved to the appendices. This chapter was originally part of the 3rd part, and was moved last minute. This was done because no novel conclusions were drawn or novel data presented. As such this chapter does not represent anything new, but is a representation of some of the work done during this PhD. It is moved here to try to spare the examiners from having to read it. It is however there, and available to be read.

As for the quality of the work within this thesis, every effort has been made to not make any errors, and correctly reference. Nonetheless, it is inevitable mistakes have been made. This is why no single work should ever be used to examine a field. No one is infallible. There are however improvements that could be made if there was more time. Not all references have been chased back to the original work which is being referenced. This is particularly true for work which borders on text-book

knowledge and is outside the authors specialisation. A specific example would be the referencing for H and J aggregation. As with all multi-disciplinary areas of study, it is simply not possible to chase down every bit of information from every specialism.

This work has been produced to the best of the authors ability. However, as with all things, a line is necessary to be drawn where "good enough is good enough". This being a quote from Psychoanalyst Donald Winnicott on raising children. Perfection is an impossible ideal to strive towards. All anyone can do is the best they can. Here is mine.

Part I

Introduction

Chapter 1

An Introduction To The Science Of OLEDs

"Let there be light"

—Unknown, *Genesis 1:3, The Bible*

*"Knowing your own ignorance is
the first step to enlightenment."*

—Patrick Rothfuss,
The Wise Man's Fear

"To begin, begin"

—William Wordsworth

Light has always been important to mankind. In the developed world, with artificial light available at a flick of a switch, the importance of producing light is easily forgotten; it is, however, not hard to find the remnants of its historic significance in the legacy of the English language. Those considered smart are called "bright", the rational and well-informed "enlightened" and the period where our modern understanding of the world began, and science in the modern sense started, is called "the enlightenment". Indeed how many creation myths within the first few lines talk about the creation of light or its separation from dark?

The importance of artificial light to the human species goes well beyond its application in allowing work to continue after sunset. Modern anthropologists believe our very evolution may be shaped by our ability to generate light.¹ It is noted that humans are relatively unique amongst primates in staying awake beyond dusk. From

this observation, it is believed in early human civilisation people would stay awake after dark with the aid of artificial light to socialise, and protect against predators, with this socialising being possibly linked to the development of language. Between the extended period awake, and our rather advanced language, it seems possible that artificial light shaped modern humans biology significantly.¹

While light has always been important, the development of efficient lighting is even more pressing with the additional challenge of climate change. Across the EU, it is estimated that between 8 % and 23 % of household electricity is expended on lighting.² Of course this is only a small portion of national energy usage, with a 2020 report suggesting UK lighting takes up only 0.7 % of total energy usage.^{3*} Even though this value is small, with the aim to reach net zero emissions becoming an international goal,⁴ all steps to conserve electricity must be taken.

In addition to the need for more efficient lighting, the efficient lighting systems must be produced cheaply. While for many in the developed world, the expense of efficient lighting will be minimal, it is worth remembering that large amounts of the developing world still do not have access to mains electricity. When electricity is unavailable, it is claimed that inefficient candles, battery torches, or kerosene lamps are commonly used.⁵ While charities exist which seek to remedy this situation,^{5,6} it really does stress the need for cheapness in efficient lighting solutions.

Organic light emitting diodes (OLEDs) are at the forefront of efficient lighting solutions.⁷ However, much work still needs to be done to make them cheap, and long-lasting.⁷ This thesis will look at several types of molecule used in OLEDs. Specifically, this thesis present work on solution processable (ie. made from solutions of the compounds, not via vacuum deposition) light emitting molecules, and molecular hosts which contain them. The emitting molecules investigated will be designed to emit light via a process known as Thermally Activated Delayed Fluorescence (TADF). TADF is known to form cheap efficient devices,⁸ and solution processing, allows for cheap manufacture.⁷ In order to introduce this work, the topics which make up this field will be discussed in this chapter, namely: "Favourable Properties For Displays And Lighting", "Designing An Organic Light Emitting Diode", "Thermally Activated Delayed Fluorescence", and "Solution Processing"

*The total includes all consumed fuel and generated electricity, across all sectors. This value is calculated from the headline 143.7 Mtoe energy usage and 11 TW h lighting energy usage listed in the report. Televisions, consumer electronics, and computers, which all involve some degree of light emission, accounts for an approximate further 0.6 %.



Figure 1.1: The applications of OLEDs. Namely an OLED display (left),⁹ and OLED lights (right).¹⁰

1.1 Favourable Properties For Displays And Lighting

The main applications of Organic Light Emitting Diodes (OLEDs) are in displays (ie. monitors, televisions, and mobile phone screens) and in lighting. When these applications are considered, some general characteristics to aim for can be predicted. Similar to both displays and lighting, is that the molecules must be efficient, cheap, bright, and stable. However, the aims in regards to colour differ. In displays, it may be qualitatively considered that the devices need red, green, and blue emitters in order to cover the whole emission spectra, where as lighting requires a single emission, pretty close spectrally to sunlight. Each of these criteria will be explored in this section. ie. Colour, Brightness, Efficiency, Price, and Stability.

1.1.1 Colour

Colour is a complex topic. There are entire books written on the subject.¹¹ Here a brief overview will be given, stressing the pertinent points for OLEDs. This will be by no means comprehensive.

1.1.1.1 CIE Coordinates

The desired colour of light emitters varies greatly between those used for lighting, and those used for displays. In all cases, the discussion of colour relies heavily on knowledge of "Commission Internationale de l'éclairage" colour space (CIE Colour Space). The original (1931) Commission Internationale de l'éclairage work studied the human eye's response to colour, and built on work by J. Guild and W. D. Wright.¹³ The experiments aimed to see how colours could be reproduced using 3 wavelengths of light at 700, 546.1, and 435.8 nm (ie. red, green and blue or R, G and B).¹³ The results were calibrated such that white light was obtained with

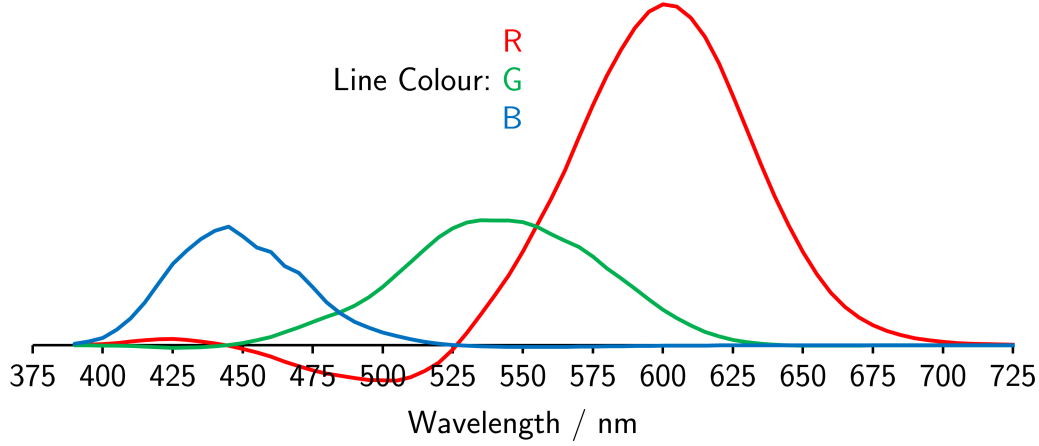


Figure 1.2: The fitting functions from RGB colour space.¹²

equal parts of each wavelength, and red being 1 cd m^{-2} .¹³ This system provides RGB colour space. The problem with colour defined in this fashion, is that it defines some colours with negative values. ie. a colour might consist of 10 R, 100 G, and -10 B.¹³ What is meant by a negative colour here, is that some light had to be added to the observed colour, to match it with the combination of red, green and blue colours defined this way.¹³ This investigation provided R, G, and B colour matching functions for the CIE coordinates, which can be found quite easily online,¹²

A function of these RGB coordinates can be used to express every colour and every brightness.¹³ However, using negative values is not ideal. As such the Commission Internationale de l'éclairage drew up a conversion to a set of coordinates with: no negative values, produce white light when each parameter is equal, and letting one coordinate (Y here) be proportional to luminance.¹³ This is the X, Y, Z coordinates. The colour matching functions are defined in the following equation, where $\bar{x}$ is the colour matching function of X, and $\bar{r}$ for R etc.¹³

$$\bar{x}(\lambda) = 0.49\bar{r}(\lambda) + 0.31\bar{g}(\lambda) + 0.20\bar{b}(\lambda) \quad (1.1)$$

$$\bar{y}(\lambda) = 0.17697\bar{r}(\lambda) + 0.81240\bar{g}(\lambda) + 0.01063\bar{b}(\lambda) \quad (1.2)$$

$$\bar{z}(\lambda) = 0.00\bar{r}(\lambda) + 0.01\bar{g}(\lambda) + 0.99\bar{b}(\lambda) \quad (1.3)$$

These XYZ functions also have their own colour matching functions.^{12,14} These values, produced in 1931, were all based off a block of colour making up a 2° angle of the eye's vision.¹³ However the eye acts differently, and more accurately at greater angles.¹³ In 1964, it was recommended that results using results for angles greater than 4° should be used, and hence the 1964 CIE coordinates were produced. The 1964 values, however compromise the additivity of values (In the 1931 values $10X + 10X = 20X$).¹³

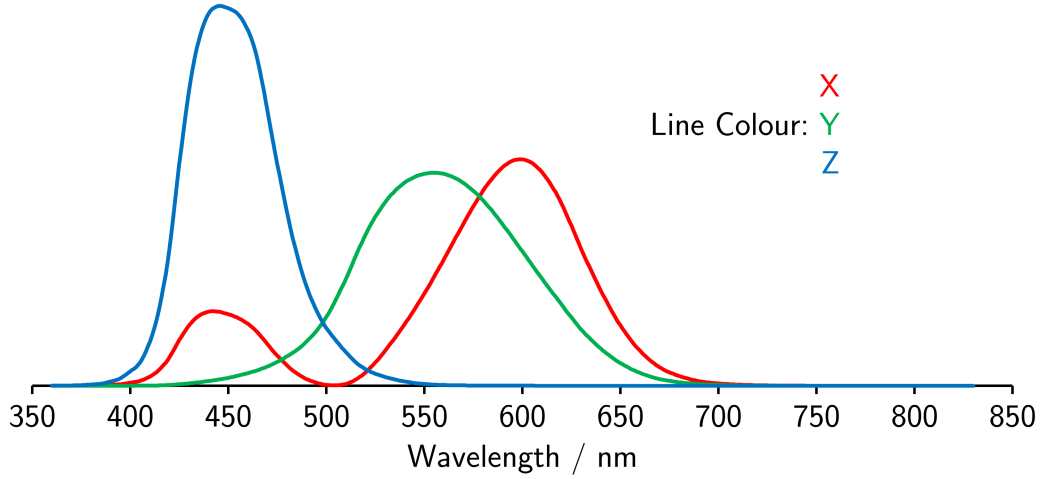


Figure 1.3: The fitting functions from XYZ colour space.¹²

In order to plot colour, chromaticity diagrams are often drawn. A full selection of XYZ coordinates, represents both brightness and colour. It is the relative amount of XYZ which represents colour. As such, the following definitions are often made:

$$x = \frac{X}{X + Y + Z} \quad (1.4)$$

$$y = \frac{Y}{X + Y + Z} \quad (1.5)$$

$$z = \frac{Z}{X + Y + Z} \quad (1.6)$$

It is only necessary to plot two of the parameters x , y , z and represent colour because, for example, $z = 1 - y - x$. By convention x and y are plotted. An example of one such chromaticity plot, from a relatively modern review on TADF is shown in figure 1.4.

While the XYZ functions allow for all colours to be expressed, a disadvantage is that some colours do not exist which may be written as a XYZ coordinate. Fundamentally there cannot be "negative light", and as such XYZ coordinates which require this to be the case, do not exist. While the area requiring "negative light" may seem difficult to define, it is possible by considering the fundamentals of XYZ coordinates. Because of the additive nature of XYZ coordinates, this means that all shades of colour formed by two different wavelengths of light have (x,y) chromaticity coordinates on the line which connects the (x,y) coordinates of pure light. That is if light source n has (x,y) coordinates $(0.1,0.2)$ and light source m has coordinates $(0.2,0.1)$, and both light sources have the same value of $X + Y + Z$, all combinations of this light, in the manner $(1-c)n + cm$ must fall on the line $(0.1+0.1c, 0.2-0.1c)$ for $0 \leq c \leq 1$. This means that all observable light must fall between the "pure colours"

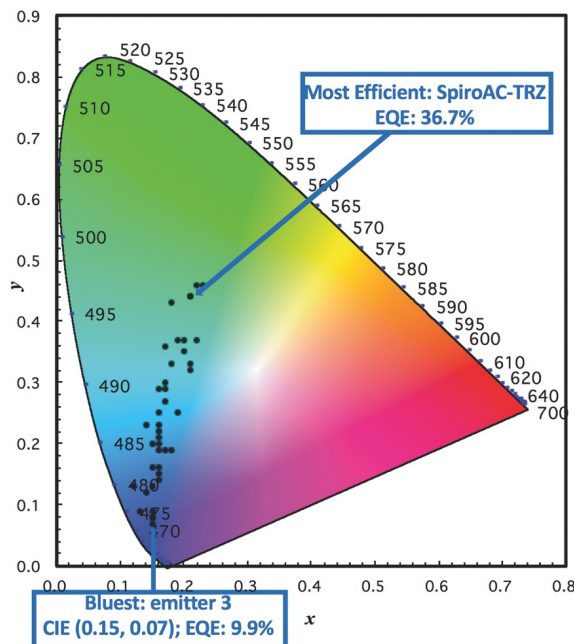


Figure 1.4: A diagram showing the 1931 CIE colour space, and the distribution of "blue" OLEDs colour. Reproduced from "Purely Organic Thermally Activated Delayed Fluorescence Materials for Organic Light-Emitting Diodes" by M. Y. Wong and E. Zysman-Coleman, under the provisions of a creative commons license (See link). No changes were made to the diagram.

which we observed. A pure colour may be considered as a infinitesimally wide peak at a given wavelength. The area bounded by these "pure colours" are observable colours, and this is why CIE chromaticity plots are often bounded by numbers representing the wavelength of light (see figure 1.4). The area of observable colour is referred to as "spectrum locus".¹³

1.1.1.2 Displays

In current display technology, there is a movement towards high dynamic range.¹⁵ High dynamic range is defined as having an accessible colour palette between the (x,y) colorimetry coordinates of (0.708, 0.292), (0.170, 0.797), (0.131, 0.046).¹⁵ This correspond to monochromatic 630 nm light, 532 nm light, and 467 nm light.¹⁵ These CIE coordinates are the target of any research on displays.

1.1.1.3 Lighting

For lighting, the case is much more complex than for displays. In terms of colour, the desired wavelength is approximately that of white light. However, the exact desired hue of light varies from time of day, as it is known that varying the hue similarly to sunlight is beneficial to our health.¹⁶ The shade of light is often represented in terms of the colour correlated temperature, which is the most similar black body

radiation temperature to the light produced. Calculation of this value has been summarised in the literature.¹⁷ It is claimed (without evidence) that temperatures in the range of 2500–6500 K are appropriate for lighting.⁷ While this claim is un-evidenced, commercial lightbulbs tend to have temperature in this region, although perhaps to slightly lower minimum values.^{18,19}

$$u = \frac{4X}{X + 15Y + 3Z} \quad (1.7)$$

$$v = \frac{6Y}{X + 15Y + 3Z} \quad (1.8)$$

$$(1.9)$$

$$U^* = 13W^*(u - u_n) \quad (1.10)$$

$$V^* = 13W^*(v - v_n) \quad (1.11)$$

$$W^* = 25Y^{1/3} - 17 \quad (1.12)$$

Beyond the shade of light, it is desirable that objects which are illuminated have the colour that they do in sunlight. In order for this to happen, the spectral profile of the light produced must be similar to that of sunlight. The standard unit to measure this is the CIE colour rendering index (CRI); the process of calculating the CRI is beyond this work, but it will still be sketched however. In order to measure the CRI, the ability to reproduce 8 test colours is examined. 8 standard test colours are illuminated, (test colour, defined using "Munsell colours", are listed in "Measuring Colour" by R. Hunt, and M. Pointer)²⁰ and their CIE coordinate in U*V*W* colour space recorded (See above for definition, where u_n is the u value for a reference white).¹¹ The CIE coordinates under a reference light source is used as a reference to calculate the CRI. For colour correlated temperature over 5000 K, the standard illuminant D (A CIE standard theoretical light source, used to compute colours, with various temperature) with temperature chosen to match the light source is used as a reference light source. For light sources with colour correlated temperature below 5000 K a Planckian radiator is used. The difference (d_i for the i th test colour) between the CIE coordinates under the reference light, and under the tested light in U*V*W* colour space is used to calculate the CRI using the following equation, where R_a is the colour rendering index.²⁰

$$R_a = 100 - 4.6 \left(\frac{d_1 + d_2 + d_3 + d_4 + d_5 + d_6 + d_7 + d_8 + d_9}{8} \right) \quad (1.13)$$

This should give a value of 100 for perfect reproduction of colour, but it is claimed⁷ that values greater than 80 are sufficient for lighting. A rough guide is provided in the literature⁷, with incandescent lighting giving CRI = 100, Compact fluorescent lamps 70, and sodium lamps (orange street lights) 24. The US department for energy set a target of >90 CRI for OLED lighting devices for 2020.²¹

1.1.2 Brightness

Before getting into the desired brightness, the units must be discussed. Those of a chemistry background working in the field of OLEDs can surely be forgiven for not knowing their candelas from their lumens (Surely mole of photons is the only logical way of defining the amount of light emitted? This is a non-SI unit known as the "Einstein"). There are 3 key quantities which are relevant to the discussion of light emitters: luminous flux (ϕ_v) measured in lumens (lm = cd sr); the luminous intensity (I_v) measured in candela (cd); and illuminance measured in lux (lx = lm m⁻²). Because **luminous** flux, **luminous** intensity, and **illuminance**, sound so similar, it is most clear to refer to them by the unit used to measure them, i.e. lumen, candela, and lux.²²

When describing an emitter, lumens and candela are most useful. Lumens (lm) are a measure of the total amount of observable light emitted from a device weighted by human observability, where as a candela (cd) is the same quantity per solid angle emitted. The human observability of light is given by the luminosity functions, proportional to the Y value in XYZ coordinates. A solid angle is the measure of a proportion of the area of a sphere, and its SI unit is the steradian (sr), or the square radian. 1 Steradian (1 sr) correspond to an area on the surface of a sphere the size of the radius of the sphere squared. An entire sphere has a solid angle of 4π steradian (sr). A candle roughly emits 1 candela in all directions, giving a luminous flux of $4\pi \approx 12.6$ lm. A more thorough equation is shown below in spherical coordinates, where θ is the inclination to the z-axis, and φ is the angle to the x-axis. Note the $\sin(\theta)$ is from the Jacobian of the integration of the area of a sphere; this jacobian is further divided by r^2 to give the equation below, because the solid angle not the area is desired.²²

$$\phi_v = \int_0^{2\pi} \int_0^\pi I_v(\theta, \varphi) \sin(\theta) d\theta d\varphi \quad (1.14)$$

Of course when we look at the amount of light incident on the eye, the amount of light is going to be the total amount of light per area. When additionally weighting for the eyes sensitivity, the measurement in lux or lm m⁻² is given. It is calculated as one might imagine, the amount of lumens from a light-source which land on a

certain area.²²

An additional complication is that it would be a mistake to imagine OLEDs emit an equal distribution of light in all directions akin to a candle. The major issue here is that OLEDs are flat devices which emit light from one face. While the angular distribution profile of OLED emission does vary from molecule to molecule,²³ an approximation that is used in the literature is a Lambertian surface.²⁴ This is a crude approximation at best. A lambertian surface emits as if it is a perfect scatterer, or in other words that light is emitted in a random direction. While one might imagine that this means that equal light is emitted in all directions pointing away from the OLED, this is not the case. The reason for this, is because when viewed from an angle, the LED is less in the field of view. A qualitative experiment to demonstrate this is by looking at a coin and imagining one side of the coin to emit light. If one looks at it 90° from the surface, a large coin is seen, and so lots of light would reach the eye from the imagined glowing face. As the angle is changed to 0°, the coin face shrinks in the eye, before becoming invisible. So a decrease in the total light hitting the eye from the hypothetical light emitting face would be expected. Hence the lambertian distribution is given by the amount of light per solid angle being proportional to the area of the OLED surface seen, or for $I_v = I_{v,0}$ at 90° to the surface.

$$I_v = I_{v,0} \cos(\theta) \quad (1.15)$$

This means for a surface which has a brightness of 1 cd perpendicular to the surface, the luminous flux may be calculated as being $\pi \approx 3.14$ lm, as follows:

$$\phi_v = \int_0^{2\pi} \int_0^{\pi/2} I_{v,0} \cos(\theta) \sin(\theta) d\theta d\varphi = \int_0^{2\pi} \int_0^{\pi/2} I_{v,0} \sin(2\theta) d\theta d\varphi = I_0 \pi \quad (1.16)$$

The reason it is necessary to introduce these parameters is because depending on application, different things are desired. For displays, the brightness when viewed from the front is desired (luminous intensity, candela), and for lighting the total light output is desired (luminous flux, lumen). R. Lenk, and C. Lenk²⁵ suggest lighting should have brightness in the region of 500–800 lm, where as D. Chitnis et al.⁷ suggest 1000–4000 lm. A glance at the website of a local hardware store suggests for most applications 500–4000 lm is most appropriate.^{26,27} Of course this does not say how large an OLED emitter is involved, but one can imagine in order to fit in a lightbulb it must be no larger than a few centimetres squared. Online articles²² suggest OLEDs must have brightness of around 8,000 lm m⁻² (Note this unit is not

Lux! see footnote).*

NVD a supplier of displays suggests²⁸ that LCD displays tend to be of brightnesses of 250–350 cd m⁻², and manufacture up to 800 cd m⁻². This provides a ballpark figure to aim for. For a 1 cm by 1 cm test OLED this would be a brightness of ~ 0.03 cd, which if it was assumed to be lambertian, would be ~ 0.1 lm perpendicular to the surface.

While brightness is itself important, another desirable characteristic is that the colour of the OLED does not change with brightness. This is particularly true for displays, where varying the brightness is very important. However, dimmable OLEDs for lighting are also desirable, although also a current electrical design challenge.²⁹

1.1.3 Efficiency

When the efficiency of lighting is considered, what is observed is that the peak efficiency of various common lighting solutions are on the order of 10 lm W⁻¹, and 100 lm W⁻¹.⁷ The problem with these figures, are that the highest efficiencies are for lighting solutions which act poorly for both displays and lighting. Namely Sodium Lamps are claimed to have a peak efficiency of 190 lm W⁻¹, but have a low colour rendering index, are combustible, and require time to warm up.⁷ The second most efficient lighting solution that is listed by S.J. Dhoble et al. is LED lighting (28–150 lm W⁻¹).⁷ LED lighting is the major competitor for OLED lighting. The US department of energy had set a goal of 200 lm W⁻¹ as a 2020 goal for solid state lighting ie. OLEDs and LEDs.²¹ A separate target of 50 lm W⁻¹ for stable white OLED devices with no outcoupling enhancement (see section 1.2.3) is also listed.²¹

1.1.4 Price

It is claimed that the major barrier to OLEDs being used in lighting remains price.^{21,30,31} A 2015 US Department of energy report put the price per 1000 lm as \$ 200 for OLEDs, and \$1 for LEDs.²¹ While it is believed that large scale production may yield improvements,^{21,31} simplification of the manufacturing process is naturally a target. One of the cost barriers is that most devices are made by vacuum deposition, a process where the desired compound is sublimed onto the OLED surface. It is reported that in industrial vacuum deposition a large proportion of the compound is wasted.³² According to the US department of energy, the 2015 yields for vacuum deposition were above 50 % but still below the ideal 95 %.²¹ Further device consistency is lacking.²¹ It is claimed that both roll-to-roll (R2R) processing,²¹ and solution processing,³² have the potential to lower these production costs.

*This is per m² of OLED. This unit is sometimes referred to as nits to distinguish it from lux, but is considered a non-SI unit.

Roll-to-roll processing is where an OLED is built up on a flexible substrate by being passed over successive rollers, which add layers to build up the OLED.³³ While roll-to-roll processing is cheaper than vacuum methods, strict control on the tension of the flexible substrate must be maintained, as well as strict temperature control. Further, when glass is used to encapsulate, handling must be delicate to avoid breakages.²¹ Solution processing uses a variety of techniques (spin coating, drop casting, inkjet printing) to add compound in solution to the OLED device. The solvent evaporates leaving the compound alone on the device. Problems still need to be overcome however. It is claimed that, for production via solution processing, solvents may damage layers on which they are deposited and curing and drying steps are claimed to be time consuming.²¹ In addition there is a known disparity in efficiency of devices formed by vacuum methods, and solution methods.²¹

1.1.5 Stability

A final desirable property is stability. If a device has the correct colour, brightness, and price, but only lasts a day, it is not commercially viable. For lighting, a L_{70} stability (the time taken for luminous flux to fall to 70 %) of greater than 50,000 hrs is desired for OLEDs at brightness of $10,000 \text{ lm m}^{-2}$.²¹ Stability remains an issue for OLEDs for lighting.^{34,35} For displays OLEDs have in recent years gained considerable market-share.³⁶ This suggests current stability goals have been reached, but this is not the full story. It is known that highly efficient blue emitters, are usually unstable,²¹ and as such they are often replaced with less efficient, longer lived compounds.^{21,37} LG electronics is quoted as saying that the current stability of OLED displays is 100,000 h,³⁷ although running conditions are not expanded upon. As such a lifetime of 100,000 h at brightness on similar order to other displays should be targeted.

1.2 Structure And Function Of An Organic Light Emitting Diode

The criteria for what is a good Organic Light Emitting Diode (OLED) has just been listed, parametrised via colour, brightness, efficiency, price and stability. While this criteria is useful, it is unhelpful without the knowledge of how an OLED works. This is what this section will discuss. The precise details on how to make each component on a molecular level will be glossed over, because this is beyond the scope of this thesis. The general design and functionality will be sketched however.

Generally, an OLED is made up of several thin ($\sim 10\text{--}100 \text{ nm}$) layers of material

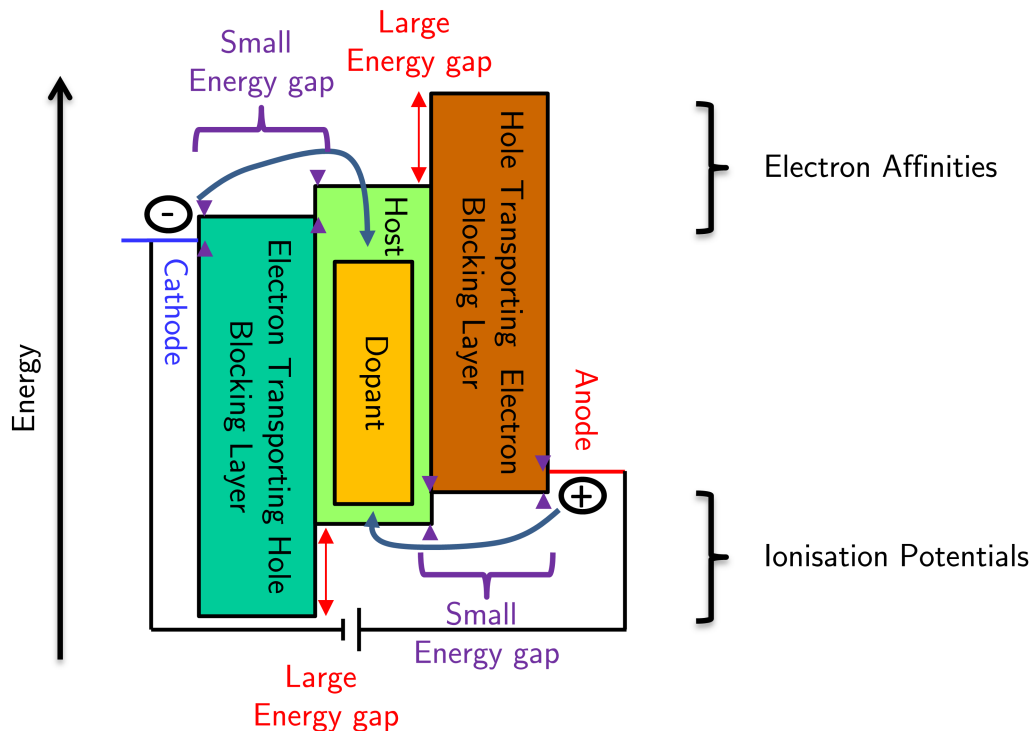


Figure 1.5: An example of the energy levels in a device demonstrating via the use of boxes with the upper bar representing electron affinity, and the lower ionisation energy.

between a cathode and an anode. Each layer of material has its own purpose, but generally seek to ensure that as much light is emitted from the desired compound as possible. Further, it is desired to keep the applied voltage and current to a minimum. An example of an OLED design is shown in figure 1.5

It is worth considering the name Organic Light Emitting Diode, and examining the meaning of it. Organic refers to the compounds which make it up (excluding the anode and cathode), as being made up of mostly "organic" molecules, which chemists may interpret as meaning made up predominantly of nitrogen, hydrogen, and carbon. It should be noted that OLED devices often contain heavy metal complexes, which chemists conventionally refer to as "inorganic". The use of "organic" here is to distinguish itself from more standard LEDs, which are semiconductors made in large part of heavier inorganic compounds (examples listed³⁸ are SiC, GaAs, AlGaAs, GaAsO_m GaO_m GaN, LnGa_mN, AlGaLnP). "Light emitting" is a rather obvious part of the OLED name; however diode is more complex. A diode is a device which preferably conducts electricity in one direction.

While it may seem arbitrary to design a device which emits light to also be a diode, the diode characteristic follows naturally from trying to get the device to work efficiently. It is hoped that this will become clear as how devices are optimised are explained. As such the following sections will describe how an OLED works, in terms of how light is generated, how the OLED is made efficient, and how light

leaves these device. It is hoped that in describing these design characteristics, much of the design strategy for OLEDs will be elucidated.

1.2.1 Light Emission

Fundamentally, OLEDs are designed to emit light. Hence it is helpful to outline how light is emitted in an OLED. In an OLED charges are injected into either side of a device, and then travel through it. A charge travelling through a device is called a polaron. This is a slight simplification, as polarons also describe the deformation caused by the charge, but is nonetheless used somewhat interchangeably in the literature. Conventionally positive charges are referred to as *holes*, and negative charges *electrons*.

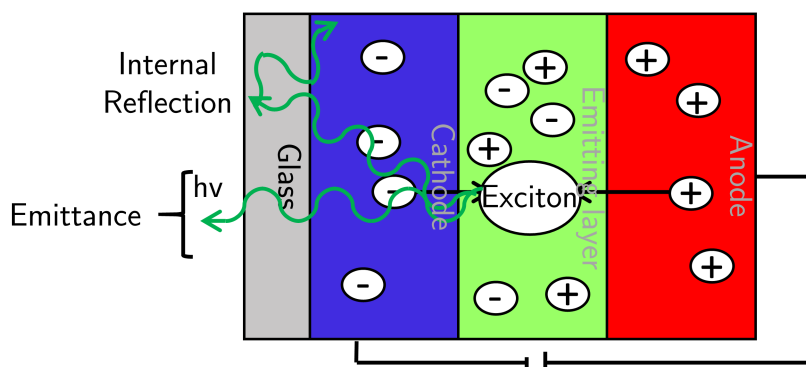


Figure 1.6: A simplified view of the processes in OLEDs

In a device, oppositely charged polarons collide, and combine, forming a single neutrally charged region, with higher energy than the surrounding area. This higher energy is usually reflected in a molecule being in an electronically excited state, and is referred to as an exciton. The excited state usually follows Kasha's rule ("polyatomic molecular entities luminescence with appreciable yield only from the lowest excited state of a given multiplicity."),³⁹ and hence lose energy until they are either in a S_1 or T_1 state.

Generally when polarons combine, they form singlet and triplet in a 1:3 ratio.⁴⁰ The 1:3 ratio corresponds to the single degeneracy of singlets and triple degeneracy of triplets, suggesting each state is formed randomly. A major problem in the design of OLEDs is that the triplets formed are inherently non-radiative (they require the breaking of the spin selection rule to emit). A major focus of research is hence making triplets emit. The two most popular strategies are TADF, which thermally interconverts triplets to singlets, and phosphorescent (triplet emitting) compounds, which introduce highly phosphorescent heavy metals to allow triplet emission.

1.2.2 Optimising Charge Combination, And Turn On Voltage

Ideally polarons combine on compounds designed to emit light in an OLED device. Further this combination is done with a minimum amount of voltage applied. However it is entirely possible that the charges pass through the OLED device, or combine in layers which are not desired to emit. In addition the voltage applied to make this happen may be much higher than would be ideal. Devices are usually designed in order to prevent charge recombination in parts of the OLED where it is not desired, and to lower the operational voltage of the device. These design goals are realised by using other layers in the device. An example of an OLED structure, and the energy levels involved are shown in figure 1.5

While much of the mathematics and theory of the electronic properties within an OLED are beyond the scope of this thesis, they are summarised in greater depth in the literature.⁴¹ However, when multiple layers are introduced, it is worthwhile considering the way the electronic charges distribute themselves in the layers. OLED devices are generally designed such that the energy levels for electrons move to higher and higher energy and holes to lower and lower energy. The theory behind the change in energy levels is rarely explored in the literature, but the processes which occur will be explained here using the concepts of: the "Schottky junction" between the metal electrodes and a semiconductor; and "band bending", which describes how semiconductors behave when they are in contact with each other.

When two materials are brought together, as in the connection between the layers in an OLED, the Fermi-energy* is equilibrated (ie. the thermodynamic work to remove an electron becomes the same in the two materials.). This occurs because it is energetically favourable for electrons to move from a compound with a large Fermi energy to one with a small one. In undoped semi-conductors (intrinsic semiconductors), where the degeneracy of the conduction band and the valence band are the same, the Fermi-level lies at the midpoint of the conductance and valence band.

The material in the (metallic) electrodes of an OLED are chosen such that the Fermi level is close to but above the valence band of the electron injecting side. The ordering of energy levels is reversed on the hole injecting side. Because the Fermi energy is approximately at the midpoint of the valence and conduction bands, it allows a predictable transfer of charges. Because the fermi level is lower on the semiconductor on the electron injecting side, it is energetically favourable to transfer electrons from the metal onto the semiconductor. Hence the first semiconductor layer on the electron transporting side, has a negative charge close to the cathode,

*The fermi level is the thermodynamic work required to add 1 electron to a body. Note that "thermodynamic work" accounts for both entropy and enthalpy, and as such may fall between the bands corresponding to the ground and first excited state (ie. the valence band and the conductance band.)

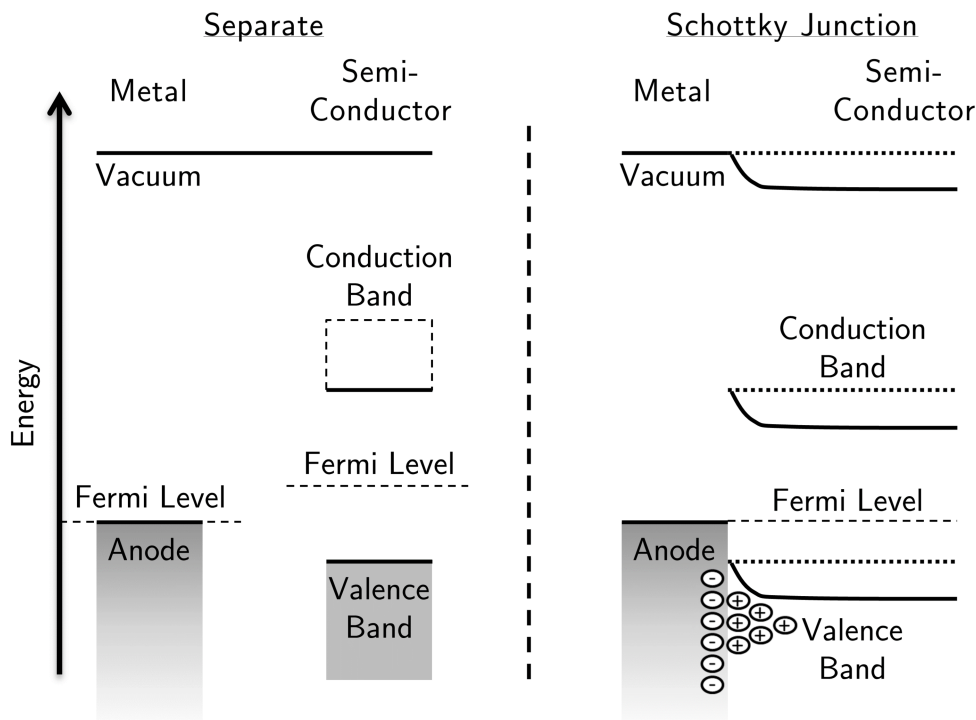


Figure 1.7: A Schottky junction, based on the diagrams in "Electronic Processes in Organic Semiconductors" by A. Köhler and H. Bässler.⁴²

and the first hole transporting layer has a positive charge on the hole injecting side. When charges are transferred in this way, what is referred to as a Schottky junction is formed and is summarised in figure 1.7. It is this junction that causes OLEDs to conduct charge in only one direction.

The movement of charges in only one direction in a Schottky junction may be understood by imagining the case shown in figure 1.7. Either an excess of positive charge or negative charge may be added to the anode, ie. the forward and reverse bias case respectively. When a positive charge is added to the anode, this eliminates a negative charge built up on the anode, but this in turn creates a net positive charge at the junction, encouraging a charge to move away from the interface. Hence charge is conducted. When a negative charge is added, this causes a build up of negative charge on the anode, which binds the free positive charge carriers on the semiconductor more tightly. Further, because free charges do not inherently exist in an organic semiconductor, charges may not be generated away from the interface. Hence charges are only able to move in one direction across the junction.

The Fermi level must also be equilibrated at the interface of the semiconducting layers, but because each layer is also equilibrated with its adjacent layers, the change in the energy levels becomes complex to interpret. The actual effects of this are rarely explored in the literature, but the theory of how bands change is referred to as "band bending" and is summarised in figure 1.8. Nonetheless there is a tendency

to design OLEDs such that there is a gradual increase in the energy of electrons, as well as holes. It is claimed⁴² that doing this decreases the potential needed to inject charges between layers, and may in fact make the process thermally accessible. This increased amount of charge injection is what gives (in-part) the "hole transporting" or "electron transporting" name to layers; of course the layers must also conduct holes to be a "hole transporting layer", and electrons for an "electron transporting layer". A layer with a large conductivity does not, however, inherently improve a device as conductivity is not additive (unlike resistance).

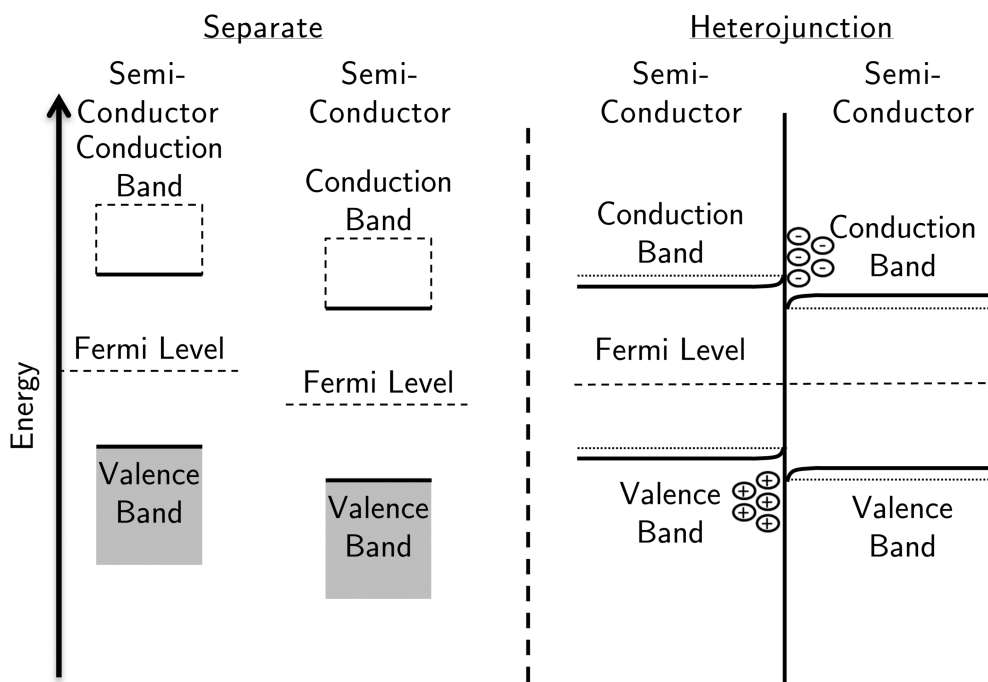


Figure 1.8: An example of the band bending observed in a heterojunction, based on the diagrams in "Electronic Processes in Organic Semiconductors" by A. Köhler and H. Bässler.⁴²

An additional purpose of additional layers in an OLED device is to block the flow of charges out of the emitting layer. This is done by introducing a considerable energy barrier to the movement of charges out of the emitting layer as demonstrated in figure 1.5. It is this property which leads to them being referred to as electron/hole blocking.

1.2.3 Outcoupling

Three things are necessary for an OLED to work, excitons to be formed by the combination of charges, these excitons to emit light, and for this light to be emitted from the device. While it may seem trivial for the light to leave the device, it is not. It is frequently claimed that the ratio of light emitted from the device to light

generated in the device is only 20 %.^{43,44} This 20 % value is only approximate, as it assumes: an isotropic distribution of emitters, that the effective refractive index of the device is 1.6, and neglects photonic structuring effects.^{45,46} Nonetheless the 20 % value demonstrates that a large amount of light is wasted because it is not emitted from a device.

Numerous methods of designing OLED devices in order to increase the outcoupling (ie. the amount of light which leaves the device) have been researched,⁴⁷ with varying degrees of commercial viability.^{21,48} Since the focus of this thesis is developing molecules for the emitting layer, a method of increasing extraction via the design of the emitting molecules should be stressed. When emitting molecules align such that the transition dipole moment of emission is in the same plane as the OLED device, an increase in outcoupling of about 20 % has been claimed.²³ A claimed disadvantage of this design aim is that it does not work effectively in solution processed molecules.²³

1.3 Thermally Activated Delayed Fluorescence

The focus of this thesis is developing molecules for the emitting layer. In the emitting layer charges combine to form singlets and triplet in a 1:3 ratio (discussed briefly in section 1.2.1). A large amount of triplet is a problem because singlets are relatively easy to make emit light, and triplets difficult. A leading modern method of making triplets emit is Thermally Activated Delayed Fluorescence or E-type fluorescence. Thermally Activated Delayed Fluorescence is almost always abbreviated to TADF. TADF works by making the singlet and triplet states close enough in energy to thermally interconvert. Of course such a transition breaks El-Sayd’s rule, and when a small singlet-triplet energy gap is targeted, a decrease in fluorescent rate is often observed. The methodology of working past these problems will be explored in this section.

TADF fundamentally is aimed at replacing phosphorescent compound which have long been studied as dopants to allow triplet emission. It is commonly claimed that the mostly iridium and platinum compounds used as phosphorescent molecules in OLEDs are expensive, rare, and toxic. It is questionable how expensive these compounds are, since it is claimed that only 2 % of the cost of OLEDs was the cost of these molecules in 2015,²¹ or \$2 per m² of OLED. The metallic materials are certainly rare making up just 0.001 ppm (Ir), and 0.005 ppm (Pt) of the earths crust according to the CRC.⁴⁹ The toxicity is somewhat problematic to prove, since it is difficult to generalise between all molecules containing a single atom. It is however true that both iridium⁵⁰ and platinum⁵¹ have been used in chemotherapy drugs.

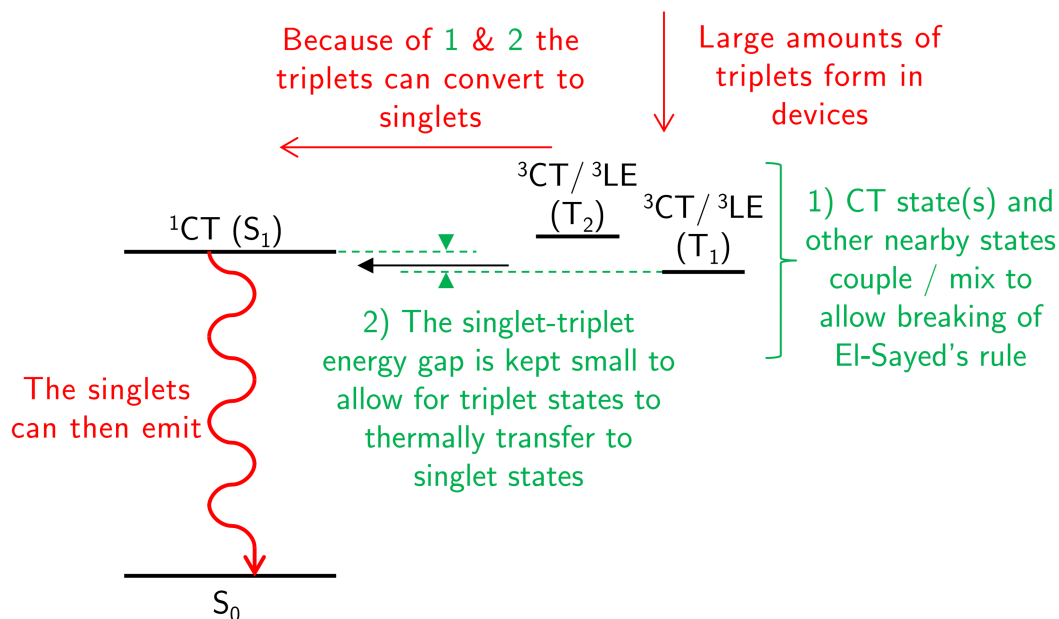


Figure 1.9: How TADF works as shown on a Jablonski diagram. CT and LE are used to refer to charge transfer states and locally excited states.

Since chemotherapy drugs are used to kill cells, this certainly suggests that at least some iridium and platinum complexes are highly toxic.

1.3.1 Minimising The Singlet-Triplet Gap

The fundamental design strategy of TADF, is to minimise the singlet-triplet energy gap.⁸ This allows for conversion from singlets to triplets via thermal activation (Note that triplet to singlet conversion is usually disallowed by El-Sayed's rule, this will be expanded upon in section 1.3.3).⁸ In order to practically design a narrow singlet-triplet energy gap, the traditional consensus has been to design molecules whose lowest excited state is a charge transfer state.⁸ A charge transfer state is an excited state where charge has been transferred from one part of a molecule to another relative to the ground state. The electron transfer is usually one heterocycle to another. The reason for the design philosophy of low energy charge transfer states is to minimise the exchange energy.

The exchange energy is the difference in energy between the singlet and triplet states due to the enforced antisymmetry of the electrons.* The belief that charge transfer states reduces the exchange energy is due to the calculation of this value in a Hartree-Fock style calculation. The Hartree-Fock style exchange energy can be said to apply if it is assumed that: electrons do not interact; that the mean-

*Because electrons are fermions, they are inherently antisymmetric with respect to the interchange of two electrons. This means when two electrons are swapped, the sign of the wavefunction is reversed. Enforcing this antisymmetry causes a difference in energy between singlets and triplets.

field approximation applies; and a Slater determinant containing one virtual orbital provides a good approximation to real singly excited states. The energy gap between singlets and triplets (ΔE_{ST}), as caused by enforcing the antisymmetry in the Hartree-Fock formalism is as follows (See section B.1.1 for proof). In this equation, the wavefunction of the Highest Occupied Molecular Orbital (HOMO), occupied by electron n is $\phi_H(n)$ and likewise $\phi_L(n)$ for the Lowest Unoccupied Molecular Orbital (LUMO). J is the exchange energy, and r_x the location of electron x . Both chemists and physicists notation for the exchange energy is shown, to aid readers from both backgrounds.

$$\Delta E_{ST} = 2J = 2(\phi_H\phi_L|\phi_L\phi_H) = 2 \int_{-\infty}^{\infty} \phi_H(1)^* \phi_L(1) \frac{1}{|r_1 - r_2|} \phi_L(2)^* \phi_H(2) d\tau \quad (1.17)$$

$$\Delta E_{ST} = 2J = 2 \langle \phi_H\phi_L | \phi_H\phi_L \rangle = 2 \int_{-\infty}^{\infty} \phi_H(1)^* \phi_L(2)^* \frac{1}{|r_1 - r_2|} \phi_H(1) \phi_L(2) d\tau \quad (1.18)$$

This equation approaches zero as the separation between the HOMO and LUMO wavefunctions increases, since it depends on the inverse of the separation of the two. Hence the aim of this method has been to separate these wavefunctions. Qualitatively the target of separating the wavefunctions is often summarised in saying "the desire is to minimise the overlap of HOMO and LUMO".

In order to minimise the overlap between HOMO and LUMO, it tends to be assumed that the wavefunctions of heterocycles do not change as they are connected. Hence each heterocycle can be chosen independently. In addition it tends to be assumed that the energy of the 1 electron wavefunction can be approximated by the cyclic voltammetric ionisation potential (I_E), and electron affinity (E_A). This means the energy gap can be tuned. A final assumption is often that the lowest excited state in separate heterocycles (ie. the lowest locally excited state) correspond to the energy gap of the ionisation potential and the electron affinity of that separate heterocycle. In other words the locally excited state on each heterocycle corresponds to its individual $I_E - E_A$ gap. All these assumptions mean that if two heterocycles are connected, and one has the lowest ionisation energy of the pair, and the other the highest electron affinity, a charge transfer state should be the lowest energy excited state which could be formed. This series of assumption is summarised in figure 1.10. All these approximations are very crude however, and should not be relied upon.

A lot of assumptions have been made in order to gain this somewhat crude understanding of TADF, and in recent years some of these have been brought into question.

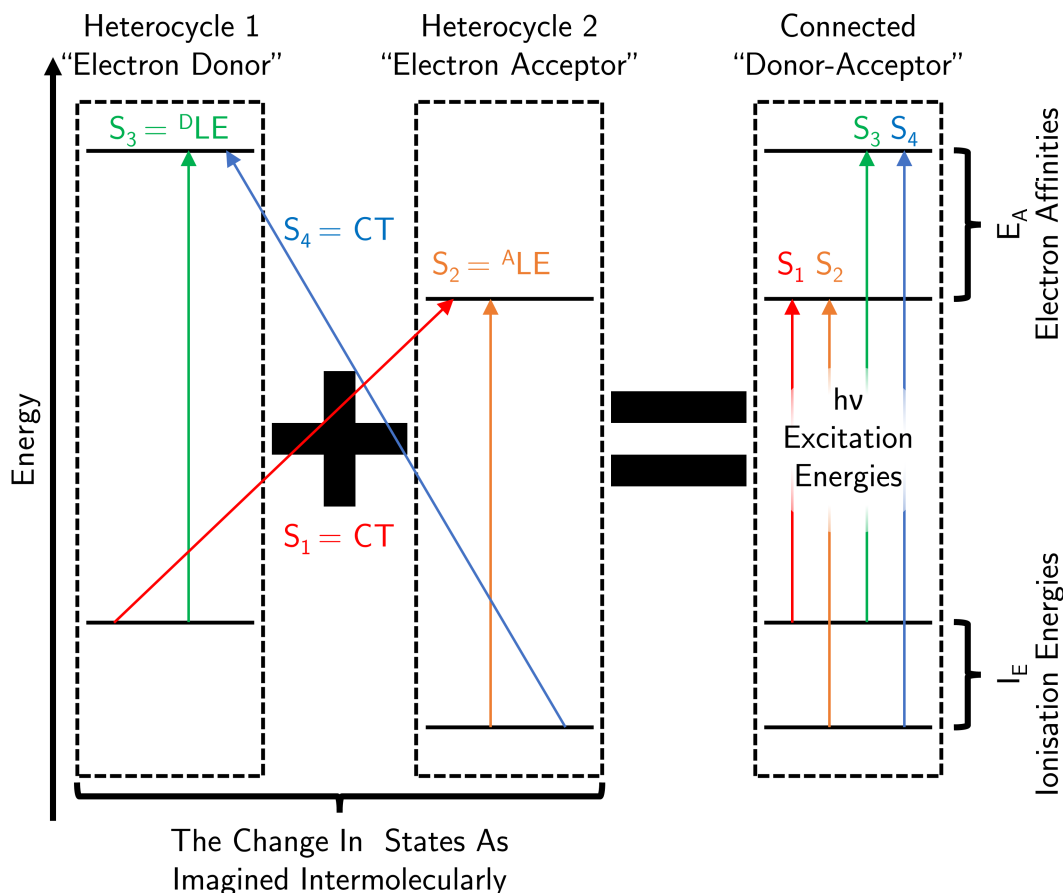


Figure 1.10: A representation of the approximations commonly made when two heterocycles are brought together to form a donor-acceptor. The I_E and E_A energy gap in both the donor and acceptor are shown arbitrarily, and hence the ordering of ^ALE , and ^DLE may be reversed.

The most significant work has been done by the researcher Piotr de Silva,^{52,53} and the W. Domcke et al.⁵⁴ Perhaps the most egregious approximation is simply defining the singlet-triplet energy gap as that in equations 1.17–1.18. This is because the assumption to reach this equation, that "a Slater determinant containing one virtual orbital provide a good approximations to real singly excited states" is simply untrue.

It is text book knowledge that the minimum level of theory to model excited state is Configuration Interaction Singles (CIS / CI-singlets),^{53,55} Further higher levels of theory are preferable. Configurational interactions recalculates the excited states by mixing other Hartree-Fock calculated excited states; for CI-singles, all singly excited Hartree-Fock orbital are used, with higher levels including doubly, triply etc. states.

There has been recent work, which has shown that the singlet-triplet energy gap can invert. The inversion of the energy gap means that the triplet is higher in energy than the singlet state.^{52,54} According to equations 1.17–1.18 an inversion of the singlet-triplet energy gap would be expected to be forbidden. This provides

strong experimental evidence that using equations 1.17–1.18 alone does not work.

When a single additional singly excited Hartree-Fock state is included, the energy gap between singlets and triplets is as follows.⁵³ Note that chemists notation is used in the definitions

$$\begin{aligned} \Delta E_{ST} = & K_{LE} + K_{CT} \\ & - \sqrt{\frac{1}{4}(\Delta E + K_{LE} + K_{CT})^2 - K_{CT}(\Delta E + K_{LE} + (t + K_X))^2} \\ & + \sqrt{\frac{1}{4}(\Delta E + K_{LE} + K_{CT})^2 - K_{CT}(\Delta E + K_{LE} + (t + K_X))^2} \end{aligned} \quad (1.19)$$

$$K_{CT} = (\phi_H \phi_L | \phi_L \phi_H) \quad (1.20)$$

$$K_{LE} = (\phi_H \phi_L + 1 | \phi_L + 1 \phi_H) \quad (1.21)$$

$$t = t' + K'_x = \langle \phi_H | h | \phi_{L+1} \rangle \quad (1.22)$$

$$K_X = (\phi_H \phi_L + 1 | \phi_L \phi_H) \quad (1.23)$$

When it is understood that CIS calculations also include all other singly excited states, it may be observed that even to the lowest level of theory, the S–T energy gap is very complex. However, the inversion of the singlet and triplet states can only be modelled if doubly excited states are included⁵² or alternatively spin-polarisation is accounted for by treating the spins as occupying separate orbits.^{54*}

1.3.2 Maintaining Fluorescent Rate

The conventional wisdom of separating the donating and accepting components in order to reduce the singlet-triplet energy gap has one major downside: a reduction in fluorescent rate.^{57,58} In fact it is claimed in some systems that the rate of fluorescence is on par with the rate of conversion of triplets to singlets.⁵⁹ The rate of fluorescence is given by the following equation according to Fermis golden rule. In this equation the rate of fluorescence (k_f) is given in terms of the density of states (ρ), the initial state (Ψ_i), the final state (Ψ_f) and the dipole operator.

*W. Domcke was contacted, and confirmed that both the inclusion of doubly excited states in restricted Hartree-Fock, and the use of unrestricted Hartree-Fock orbitals are modelling the same effect. Spin polarisation appears as separate from correlation in unrestricted Hartree-Fock, but appears as correlation in the restricted form of the calculation.⁵⁶

$$k_f = \frac{2\pi}{\hbar} |\langle \Psi_f | \mu | \Psi_i \rangle|^2 \rho \quad (1.24)$$

It is commonly claimed that from equation 1.24 it is obvious that the overlap of initial and final states is necessary for fluorescence. It however is felt that this needs expanding upon here, and this is done in section B.3.1.5. So fundamentally there is a trade off in TADF, where fluorescent rate is decreased at the expense of utilising triplets. This is problematic because long lived excited states are known to interact to cause detrimental processes. Long lived excited states have been linked with a roll off in efficiency at high currents, and a reduction in device stability. It is known that long lived excited states interact with other excitons and polarons, to not only eliminate the excited state (Roll-off)⁶⁰ but also create high energy species which can damage the device.^{61,62,63}

1.3.3 Breaking El-Sayed's Rule And Vibronic Coupling

Conversion between the lowest energy singlet state, and the lowest energy triplet state is often forbidden via El-Sayed's rule.^{64,65} This states that in order to have fast intersystem crossing ($S_n \rightarrow T_n$) there must be a change in orbital type.⁶⁶ This may be understood in terms of conservation of angular momentum. Electron spin is an angular momentum that is fundamental to an electron. In a singlet state the spin quantum number (s) is 0 and so the angular momentum (S) is zero. For a triplet state $s = 1$ so the spin angular momentum (S) via the following formula is $\hbar\sqrt{2}$. In order to compensate for this change in angular momentum, the angular momentum of the orbital must also change.

$$S = \hbar\sqrt{s(s+1)} \quad (1.25)$$

The conversion of triplets to singlets can be seen as the singlet to triplet process described above in reverse, and hence requires the same properties. The reverse of intersystem crossing is usually referred to as "Reverse InterSystem Crossing" or "RISC" and is fundamental to TADF. TADF is however designed to have a charge transfer state as its lowest singlet energy, creating a high lying charge transfer triplet state as outlined in section 1.3.1. This high lying triplet state is desirable to be the lowest energy triplet in order to minimise the singlet-triplet energy gap. This implies that El-Sayed's rules should curtail the rate of reverse inter-system crossing, as both singlet and triplet are a CT state of the same character. Further it is known that the experimental rate of reverse intersystem crossing and fluorescence can be of similar magnitudes.⁵⁹ This suggests the breaking of El-Sayed's rule is a fundamental problem for TADF.

Thus far, three problems have been highlighted for TADF, the competition between fluorescent rate, and the singlet-triplet energy gap, and breaking El-Sayed's rule. Both of these problems may be severely reduced via a combination of vibronic coupling, and mixing of states.^{57,53} As has previously been stated (see section 1.3.1), there is growing evidence that describing the singlet and triplet transition simply in terms of a HOMO to LUMO transition does not give a full picture of the states. As such, the mixing of other orbitals must be considered. This mixing of orbitals means that the singlet and triplet states may not be entirely the same character, and this allows for the breaking of El-Sayed's rule.⁵³ Further, the relatively unemissive singlet charge transfer state may mix with relatively more emissive nearby locally excited states, boosting the fluorescent rate.

It however seems unlikely that orbitals will often mix to reduce the singlet-triplet energy gap, and increase the fluorescent rate, in the ground state. A tendency may be predicted to expand the singlet-triplet energy gap and not increase the singlet fluorescence rate. A large number of states are locally excited in character, ie. with large orbital overlaps, meaning they produce low lying triplet energies and high lying singlet energies. As such mixing to stabilise the 1st excited state is likely larger for triplets, and smaller for singlets. This arrangement of energy levels is summarised in figure 1.11.

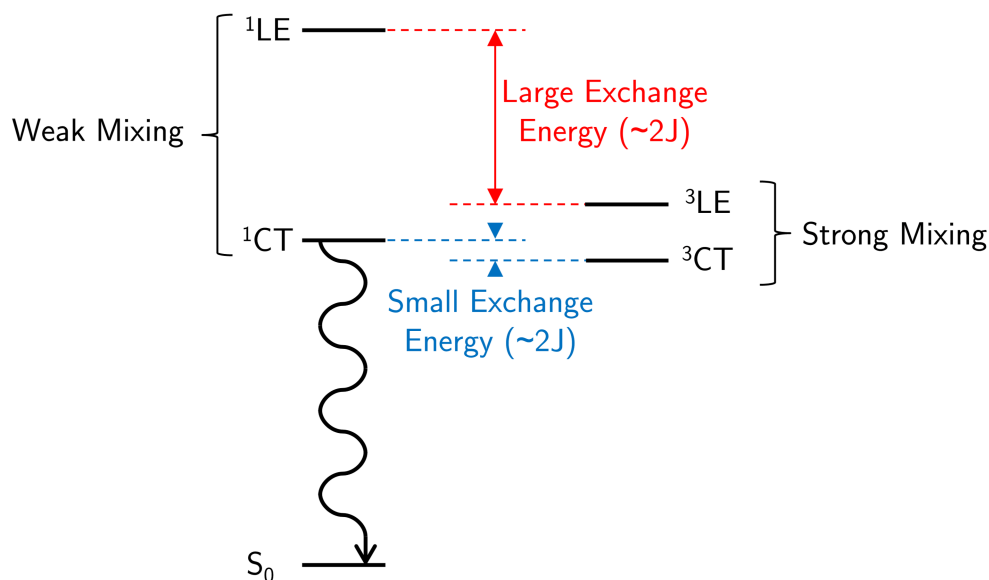


Figure 1.11: A hypothesised issue with the mixing of the locally excited (LE) and charge transfer (CT) states, heavily favouring triplet mixing, but not singlet mixing.

Much of the understanding so far has been based on the molecule existing at a single unchanging geometry. A single geometry, however, does not entirely describe the 1st excited state. The molecules in an excited state are free to move, both their ground vibrational state, and within excited vibrational states on the order

of kT (26 meV) from the ground state. Within each state, a random distribution of geometries will be observed, with probability corresponding to the square of the nuclear wavefunction. In the amorphous solid state (as in OLEDs) the vibrations will be restricted. However numerous different ground state geometries will also exist. Because excitons can diffuse in devices, to the numerous solid state geometries, a similar range of geometries in the restricted solid state, and unrestricted gaseous phase can be predicted.

The numerous geometries accessible in OLEDs, as well as the direct interaction between the vibrations and the electronic states may allow for triplet to singlet conversion at a lower singlet-triplet energy gap, and emission to occur at a higher rate.* It is in fact textbook knowledge that phosphorescence, which also requires spin-orbit coupling, is encouraged in organics by out-of-plane vibrations (ie. where two conjugated rings vibrate about the dihedral angle which connects them).⁶⁹ The rationale for this effect appears to be mixing different orbitals by breaking the symmetry.^{69,70}

Within the field of TADF, the vibronic coupling is expressed most frequently in terms of the components of the following equation.⁷¹ In this equation the Hamiltonian for spin orbit coupling including vibronic effects (H_{SO-VIB}) is expanded in terms of the spin orbit coupling without vibronic effects (H_{SO}), the wavefunction of various states (Ψ_{S_n} for the n th singlet state, and Ψ_{T_n} for the n th triplet state), the energy of these states (E_{S_n} for the n th singlet state, and E_{T_n} for the n th triplet state), and the nuclear configuration along a certain normal mode (Q_a for the a th normal mode). All nuclear configurations are measured relative to the reference coordinate (usually the lowest energy ground state geometry) Q_0 , and all differentials are calculated at this position. $\mathcal{T}$ is defined below in terms of the electrostatic wavefunction H_{es} .

*It may be thought by the reader that vibrations may directly interact with excited states in order to allow singlet to triplet conversion. This is not directly possible, because vibrations do not have angular momentum. However vibrations do sometimes have regional angular momentum, e.g. in the case of an out-of-plane twist ie. where two conjugated rings vibrate about the dihedral angle which connects them. If hypothetically some of this regional angular momentum was used, this would leave a net rotation, and so it is in theory a rovibronic (rotational-vibrational-electronic) transition. Such transitions have only been researched incidentally in TADF,⁶⁷ but is a rather complex phenomena, with study usually restricted to small (6 atom or less) molecules.⁶⁸

$$\begin{aligned}
\langle \Psi_{S_1} | \hat{H}_{SO-VIB} | \Psi_{T_1} \rangle &= \langle \Psi_{S_1} | H_{SO} | \Psi_{T_1} \rangle + \left[\sum_a \frac{\partial \langle \Psi_{S_1} | H_{SO} | \Psi_{T_1} \rangle}{\partial Q_a} Q_a \right]_{Q_0} \\
&+ \frac{1}{2} \sum_a \sum_b \left[\frac{\partial^2 \langle \Psi_{S_1} | H_{SO} | \Psi_{T_1} \rangle}{\partial Q_a \partial Q_b} Q_a Q_b \right]_{Q_0} \\
&+ \sum_n \frac{\langle \Psi_{S_1} | H_{SO} | \Psi_{T_n} \rangle \langle \Psi_{T_n} | \mathcal{T}_N | \Psi_{T_1} \rangle}{E_{T_n} - E_{S_1}} \\
&+ \sum_m \frac{\langle \Psi_{S_1} | H_{SO} | \Psi_{S_m} \rangle \langle \Psi_{S_m} | \mathcal{T}_N | \Psi_{T_1} \rangle}{E_{S_m} - E_{T_1}}
\end{aligned} \tag{1.26}$$

$$\tau = \sum_a \left[\frac{\partial H_{es}}{\partial Q_a} \right]_{Q_0} \tag{1.27}$$

This equation for the vibronic effects on spin-orbit coupling is based on earlier work on benzene.⁷² Here a brief description the process of gaining this equation will be discussed; however the process of expanding Hamiltonians vibronically is explained in greater detail in other works.⁷³ The derivation of the first few terms of the equation 1.26 is to Taylor expand Fermi's golden rule, about nuclear coordinates. (terms 1-3) The equation is thus modelling the various geometries which may undergo reverse inter-system crossing. A proof for terms 1–3 is expanded on in section B.1.2. Terms 4–5 come from the mixing of the triplet and singlet states with other sates, when the vibronic effects are considered, as explained by higher order terms in perturbation theory. In addition, the electrostatic Hamiltonian is modelled by its first derivative.⁷¹ The proof for terms 4–5 and perturbation theory is shown in section B.1.3, with a more focused rate of transition proof in sections B.1.3.3 and B.1.3.4. Strictly speaking terms 4–5 and 2–3 come from two different types of expansion in vibronic coupling,⁷³ although it is asserted that "in practice these terms can hardly be told apart, and which terms dominate will depend on the system under study".⁷¹ In practice the simulations are often restricted to several key vibrational modes.⁵⁹

"Conical intersections" or equivalently "avoided crossings" have also been highlighted as potentially important for reverse intersystem crossing.⁷¹ Conical intersections are where the wavefunctions of potential wells of electronic states cross. Theoretically these crossing are theoretically forbidden and in reality "avoided crossings" are formed. Theoretically the nuclear potential tends towards infinity at a conical intersection (hence why they are forbidden), and this means that strong vibronic coupling occurs in this region, firmly breaking the Born-Oppenheimer approxima-

tion.* Avoided crossing are predicted when vibronic coupling is accounted for, and conical intersections when they are not. The Strong vibronic coupling in the region around the avoided crossing are of course relevant to equation 1.26.

1.4 Solution Processing

So far, targets for final OLED devices have been discussed, as have how to make OLEDs, and how to design molecules for TADF. However, it is necessary to not only make good devices, but also make them cheaply (see section 1.1.4 for more details).^{21,30,31} A leading strategy towards cheap OLED devices is solution processing.³² Solution processing is where the OLED devices are made by precipitating chemicals from solution, as opposed to via vacuum deposition. Vacuum deposition works via sublimation (solid $\rightarrow$ gas) followed by deposition (gas $\rightarrow$ solid) under vacuum onto the OLED device.

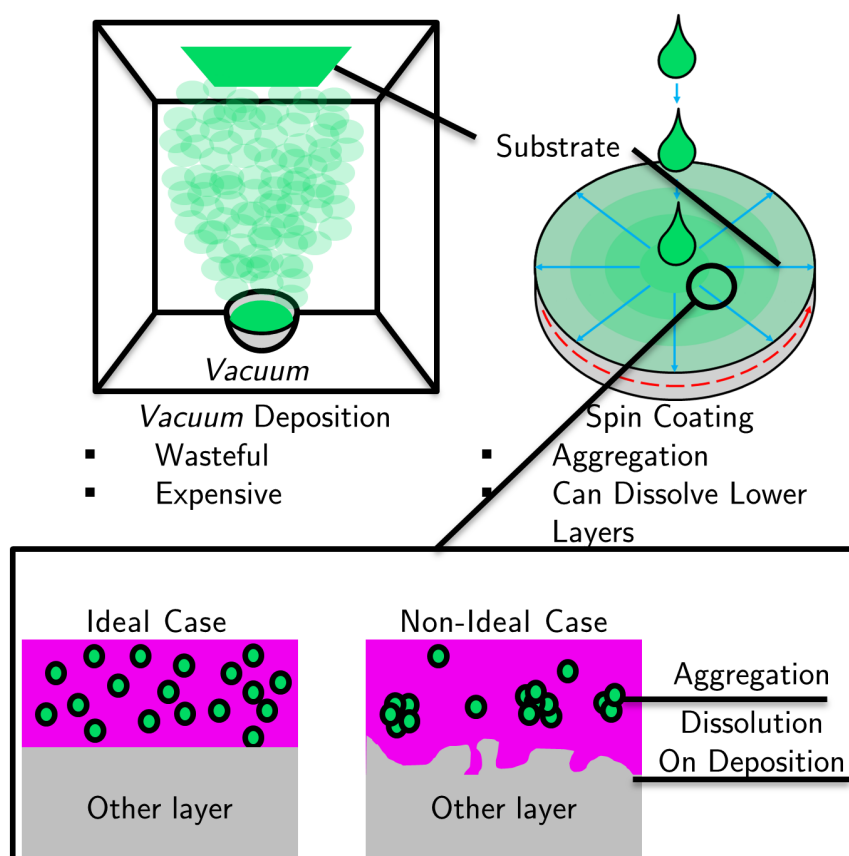


Figure 1.12: A summary of *vacuum* deposition *versus* spin coating.

It is desirable to use alternative methods to vacuum processing because it is wasteful of the compounds it processes. It is claimed that the usage of compound

*This states it is correct to represent "the complete wavefunction as a product of an electronic and a nuclear part, where the two wave-functions may be determined separately by solving two different Schroedinger equations."³⁹

is well under the desired 95 % usage.²¹ Problems with solution processing include damaging lower layers, and lower efficiency in devices.²¹ In addition the time spent curing the device is undesirable.²¹ It is entirely possible to design systems where this reduction in efficiency and the damaging of layers do not occur.

It is worth considering why the efficiency of solution processed devices is so much lower than in the vacuum deposited devices. Experimentally it has been found that even when identical molecules are used, vacuum processing still often performs better than solution processing,^{74,75} although this is not always the case.^{76,75} It is claimed that in addition to the dissolution of other layers in devices, phase separation (ie. aggregation) is a key problem for solution processed devices.⁷⁷ Aggregation can lead to reduced band gaps and triplet energies, as well as a range of other effects.⁷⁸ An additional design specification is that in order to be solution processable the compounds must go into solution.

So in order to create solution processable molecules it is necessary to have: low aggregation; molecules that will go into solution; and finally a solvent in which it can be deposited, without disrupting the other layers. In the literature, general design strategies in order to obtain these properties have been proposed. Evidence has been presented that phase separation is reduced by decreasing the length of solubilising groups and increasing the rigidity of components (unfortunately likely reducing solubility).^{77,79} In addition it has been proposed that increasing the mass of molecules may allow for "orthogonal processing".^{80,76,81} Orthogonal processing is where molecules are deposited consecutively in solutions which do not dissolve the layer below. It has been claimed that large mass molecules are insoluble in alcohol solution, allowing for the surrounding layers to be formed of compounds only soluble in alcohol.^{80,76,81,82}

Another strategy to prevent aggregation is putting both host and emitting molecules in a single polymer. This means that the way in which the TADF molecules interact are controlled. Many examples of this strategy exist in the literature.⁸³

It has further been claimed that for small molecules, hook-like groups enable the formation of good films under solution processing.⁸⁴ While Hook-like is not explicitly defined in the cited document, it appears to refer to groups which can interact strongly in many directions. These interactions may allow for the molecules to interact with one-another outside of the optimum crystalline geometry. In addition it may be argued that this could prevent aggregation, by allowing for unfavourable interactions, however this does contrast with the claim that short solvating groups prevents phase separation.^{77,79}

Generally strategies towards increasing the ability of solution processing can be separated into two categories, "increasing the mass", and "increasing the solubility".

These will be further discussed.

1.4.1 Increasing The Mass

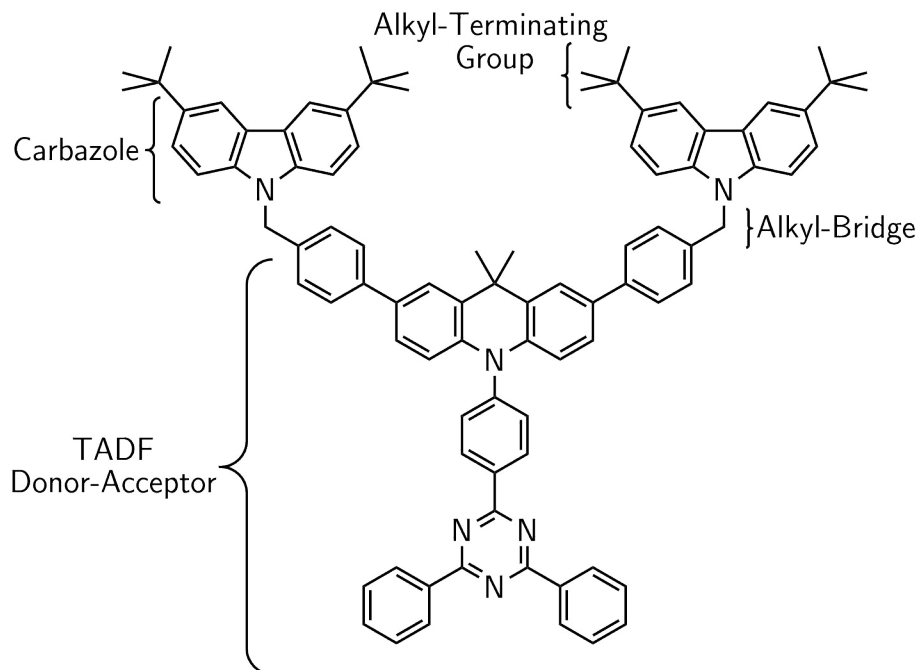


Figure 1.13: An example of a molecule designed for solution processing,⁸⁵ with labelled optional alkyl groups often included in the design.

It has been claimed that molecules with masses greater than 700–1000 Da tend not to be soluble in alcohol.^{80,76,81,82} Devices have been made using molecules such as these, which are fully solution processed, and with external quantum efficiencies (efficiencies measured in terms of polaron pairs injected, vs photons of light emitted) as high as 16.1 %.⁸¹ Generally when components are added to increase the mass, carbazole (see figure 1.13) is used.⁸³ Evidence has been presented that molecules with carbazole attached have improved charge transporting properties, and reduced interaction strength.^{86,87} Further carbazole is often used in host molecules,⁸⁸ due to its frequently asserted good hole transporting properties,^{89,90} high stability,⁸⁹ high triplet energies^{87,90} and solubility.⁸⁹

1.4.2 Increasing The Solubility

Alkyl chains are often added to increase solubility. Carbazole has two sites commonly used to add alkyl groups, 1) between the nitrogen and the TADF compound, 2) para to the nitrogen off the carbazole compound.⁸³ An example of a molecule with both these substituents is shown in figure 1.13. While substituting in both ways serve to increase solubility, they both have other effects which differ from one another.

Carbazole is known to undergo irreversible oxidation through sites para to its nitrogen.⁹¹ In order to prevent this, alkyl substituents are commonly placed there.⁹¹ These substituents have additionally been linked with reducing stokes shift,⁹¹ and improving film morphology.⁹² Additional improvements of: increasing the glass transition temperatures;⁹¹ improving the external quantum efficiency (EQE: the device efficiency), and the roll-off (ie. the reduction in efficiency at high current);⁷⁵ and reducing the amount of exciton-polaron annihilation;⁹¹ have been claimed. Various groups have been trialled to substitute para to carbazole's nitrogen, and overall the tert-butyl group was found superior for electrochemical stability.⁷⁵

Interaction between carbazole and the electronic properties of the donor-acceptor involved in TADF are also relatively commonplace.^{93,94} It is often desirable to prevent the interaction between carbazole and the donor-acceptor, because this changes the properties in a somewhat unpredictable way. The use of a non-conjugated alkyl chain to separate the two is useful in this regard.

1.5 Aims Of This Thesis

The initial aims of this thesis, were to make several new solutions processable molecules, and to characterise them. In the process of this task, the aims changed to investigate the methodology of TADF, and suggest improvements. It is felt that both of these aims were achieved, although the new molecules made were less efficient than desired.

1.6 Scope Of This Thesis

In this thesis, the bulk of the work will be on three different TADF emitters, where two are designed for solution processing, and a third will act as a previously published standard. These molecules will be characterised, and the process of characterisation examined to provide suggestions for improvement of the methodology in the field of TADF. These methodological suggestions will span steady-state spectrometry, transient spectrometry, and computational simulation. This will take up chapters 2 through 6.2, and will make up part II of this thesis.

Beyond the work on the these three main molecules, additional work will be presented on the development of new molecules for solution processed OLEDs. Synthetic methods to create a new design of a solution processable emitter will be presented in chapter 7. Additionally a new host will be developed in chapter 8. While this work on new molecules remains incomplete, it is hoped it will remain of interest to the reader. All work beyond the three main molecules, will be separated

into a part of its own (part III) or relegated to the supplementary information.

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Part II

A Study Of Carbazole Substituted DMAC-TRZ TADF Molecules

Chapter 2

Introduction: Design And Synthesis

*"It's the not the destination,
It's the journey"*

—Ralph Waldo Emerson

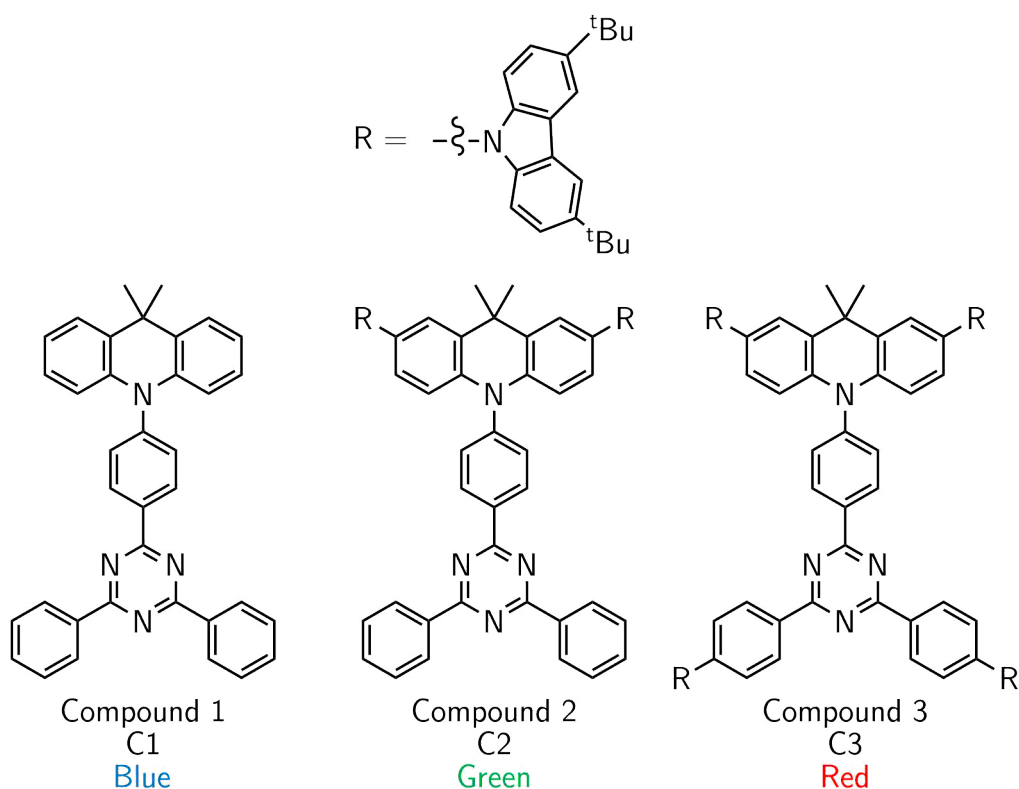


Figure 2.1: The compounds discussed in this chapter, the names that will be used to refer to them, and the colour most commonly used in graphs of them.

This part will deal with the study of the base molecule 6-[4-(9,9-dimethyl-9,10-dihydroacridin-10-yl)phenyl]-2,4-diphenyl-1,3,5-triazine (DMAC-TRZ / C1) and several synthesised derivatives (C2, C3), designed for solution processing. These struc-

tures are summarised in figure 2.1. It is the study of these molecules which will make up the bulk of this thesis.

Due to the quantity of work within this part of the thesis, it will be separated into three distinct results chapters, designed to act as stand-alone investigations. These chapters will be a study of the steady state spectra with other general characterisation, a study of the transient photoluminescent spectra, and a computational study. These sections will be tied together by a general introduction chapter (this one) and conclusion, but will each have their own introduction and conclusions. It is hoped that this will help the reader digest the information.

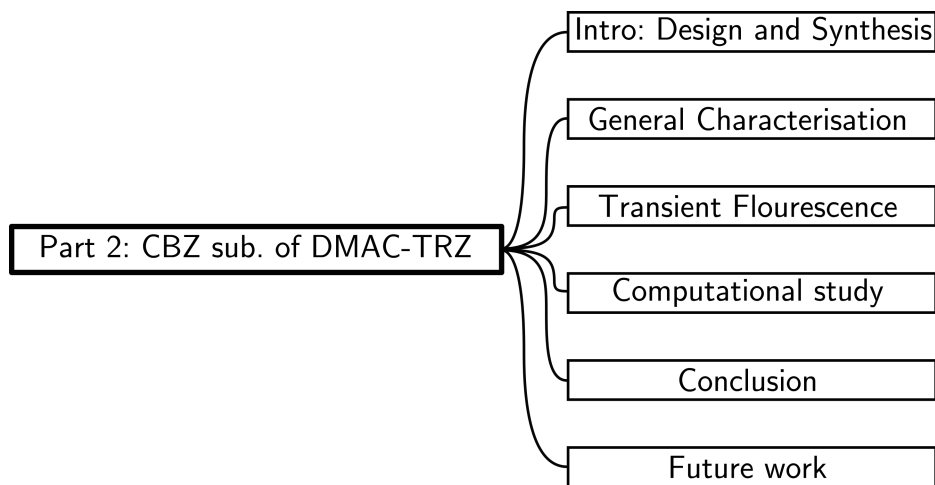


Figure 2.2: The layout of this part of the thesis.

More generally this section will deal with the consequences of geometry, low singlet triplet energy gap, and interfering electron donor groups (henceforth "electron" will be dropped, donor groups are defined in the glossary) in TADF molecules. The geometry of DMAC will be highlighted as key, and an additional geometric form will be introduced, to add to the well known two geometries of this fragment written about in the literature.^{1,2} It will be noted that the singlet-triplet energy gap in C2 and C3 are low, assigned as due to the interference of the carbazole donor, and the consequences of this will be explored.

Interpretation of these results will lead to proposed changes to the computational and photophysical methodology within the field of TADF. It will be noted that counter to the conventional wisdom of CAM-B3LYP^{3,4} functional being inappropriate for use for the computational study of TADF, when used for the geometrical relaxed T_1 state, it provides superior results to the standard B3LYP functional. Inherent within this theory is the proposition that geometrically relaxed T_1 states should be calculated for TADF compounds, which while claimed to require substantial additional calculation³, was not found herein.

The proposed change in photophysical methodology will result from it being

noted that the existing methods of interpretation of transient fluorescence are based almost entirely around the interpretation of rate limiting functions.⁵ Results will be shown which break the assumption of the most common rate limiting model, and so a non-rate limiting approach will be introduced. This non-limiting approach will then be used to interpret simultaneously the changes in rate constants, relative starting intensity of delayed and pulse fluorescence and decay area, in order to assign the changes between molecules.

A final topic of discussion will be calling into doubt the conventional wisdom of TADF proceeding by a biexponential decay. It will be shown that a stretched exponential fit provides a much better fit to data. While it will be found beyond the scope of this thesis to fully interpret these results, papers will be referenced which may guide the reader.

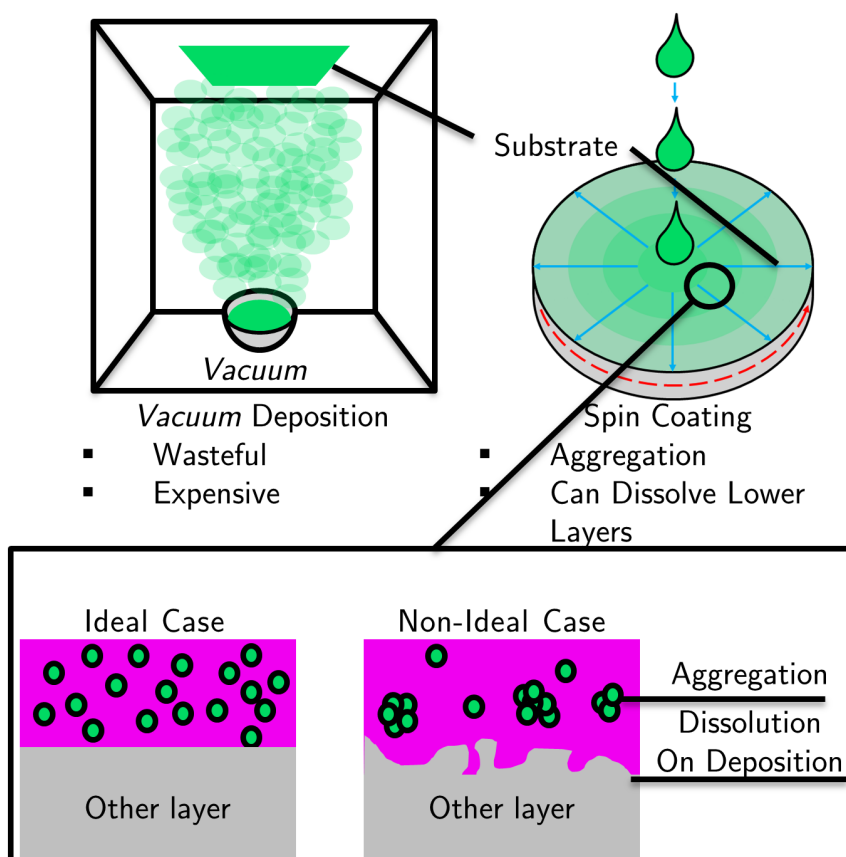


Figure 2.3: A summary of *vacuum* deposition *verses* spin coating.

Fundamental to this section is the reason and process for designing molecules to be solution processable. This was the initial design aim for the molecules discussed in this chapter. While solution processing has already been discussed, (see section 1.4) this will be briefly recapped here. The most conventional technique for device manufacture is *via vacuum* deposition. This is fundamentally expensive due to the large amount of compound that is wasted in this process.⁶ Solution processing is a

way of using less compound.⁷

Designing for solution processing is however in itself problematic. Fundamental problems occurring within solution processing are phase separation⁸ (ie. aggregation) and dissolution of other layers on deposition.⁷ These processes are represented schematically in figure 2.3. Conventionally phase separation is prevented by reducing the length of any solubilising groups, or increasing rigidity and bulk of the components,^{8,9} and dissolution of other layers may be prevented by increasing the molecular mass^{10,11,12}. It has been claimed that increased molecular mass prevents solubility in alcohol, allowing for deposition of other layers in compound only soluble in alcohol.^{10,11,12,13} The process of depositing layers in solvents which do not dissolve the other layers, is referred to as orthogonal deposition.

2.1 The Design

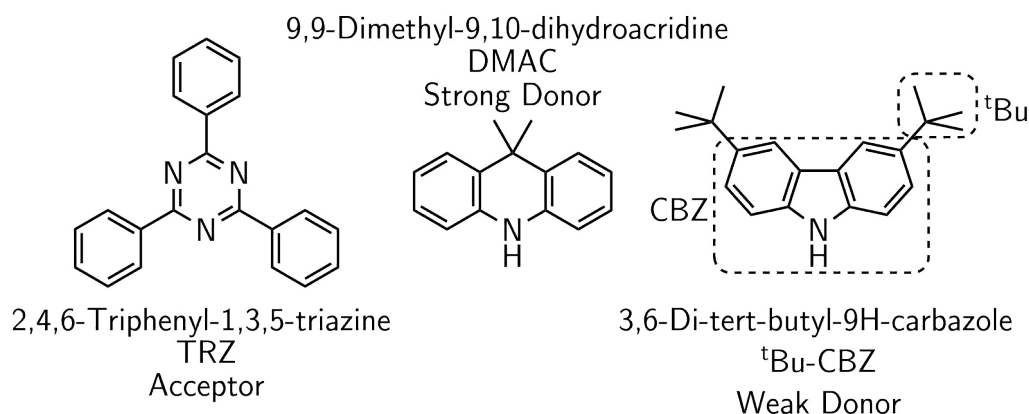


Figure 2.4: The components which make up the molecules studied.

The molecules studied in this chapter (see figure 2.1 prior to this section) are based around a single core donor-acceptor compound, made up of a 9,9-dimethyl-9,10-dihydroacridine (DMAC) donor, and a 2,4,6-triphenyl-1,3,5-triazine (TRZ) electron acceptor (henceforth "electron" will be dropped, the definition of electron acceptor is given in the glossary). To this base molecule, 3,6-di-tert-butyl-9H-carbazole (^tBu-CBZ) is added through substitution of hydrogen atoms (relative to the structures shown, although not synthetically). These components are summarised in figure 2.4. The reason these structures are chosen, specifically for the design of solution processable devices, can be separated into 3 topics, which will each be dealt with in turn:

1. Why the DMAC-TRZ core?
2. Why the carbazole substitution of DMAC and TRZ?

3. Why the 3,6-di-tert-butyl substitution of Carbazole?

DMAC-TRZ is a remarkably good TADF emitter. The efficiency of emission is usually measured in terms of the photoluminescent quantum yield (PLQY) of compounds in film, as well as the external quantum efficiency (EQE), and internal quantum efficiency of a device of these compounds. The PLQY measures the amount of photons emitted to photons absorbed, and the EQE measures the amount of photons emitted in a device compared to charge pairs combined. The IQE measures the photons formed in a device. The maximum PLQY and IQE is 100 %, and the maximum EQE is commonly asserted^{15,16} for TADF devices to be ~ 20 % for the isotropic case (assumes the effective refractive index ≈ 1.6 and neglecting photonic structure effects and waveguiding)^{17,18}.

For DMAC-TRZ,¹⁴ an EQE of 27.4 % and solid state PLQY of 90 %. This EQE exceeds the commonly asserted^{15,16} maximum EQE. While the EQE is so high due to preferable alignment,¹⁴ which it has been reported are often broken up on solution processing¹⁹, the IQE remains high. Its blue-green colour is not perfect for display technology, (with a CIE coordinate of (0.21, 0.50), compared to the desired blue (0.131,0.046) or green (0.170,0.797)* used as the colour gamut in modern ultra-high definition displays²⁰) it is possible that combined with a red emitter, it could find use in lighting. Beyond practical interest, the compound is also of academic interest. Both DMAC and TRZ components are part of other high efficiency devices (see figure 2.4).²¹ A selection of these are shown in figure 2.5. So any conclusions from the study of these molecules may in turn be applied to other systems using these components.

The principle reason for adding carbazole is to increase the weight of the molecules; however it also should imbue additional favourable properties. Evidence has been presented that molecules with attached carbazole have reduced strength of interactions^{25,26} and improve charge transporting properties^{25,26} in certain systems. It is also frequently asserted that carbazole has good hole transport properties,^{27,28} stability (both morphological and thermal),²⁷ high triplet energies,^{26,28} and solubility²⁷. These assertions are partially evidenced by the pervasiveness of carbazole in hosts for OLEDs.²⁹ It is also cheap.³⁰ Most solutions processable small molecules add carbazole to their structures for these reasons.

Tertiary butyl groups are 3,6 substituted on the carbazole in order to improve the molecular properties. Evidence has been presented showing 3,6-tert butyl substitution reduces Stokes shift,³¹ prevents irreversible oxidation to which carbazole is susceptible,³¹ as well as improving solubility,³² and film morphology.³² Further it has been found to increase the glass transition temperature,³¹ and improve EQE and

*see section 1.1.1.1 for details on CIE coordinates

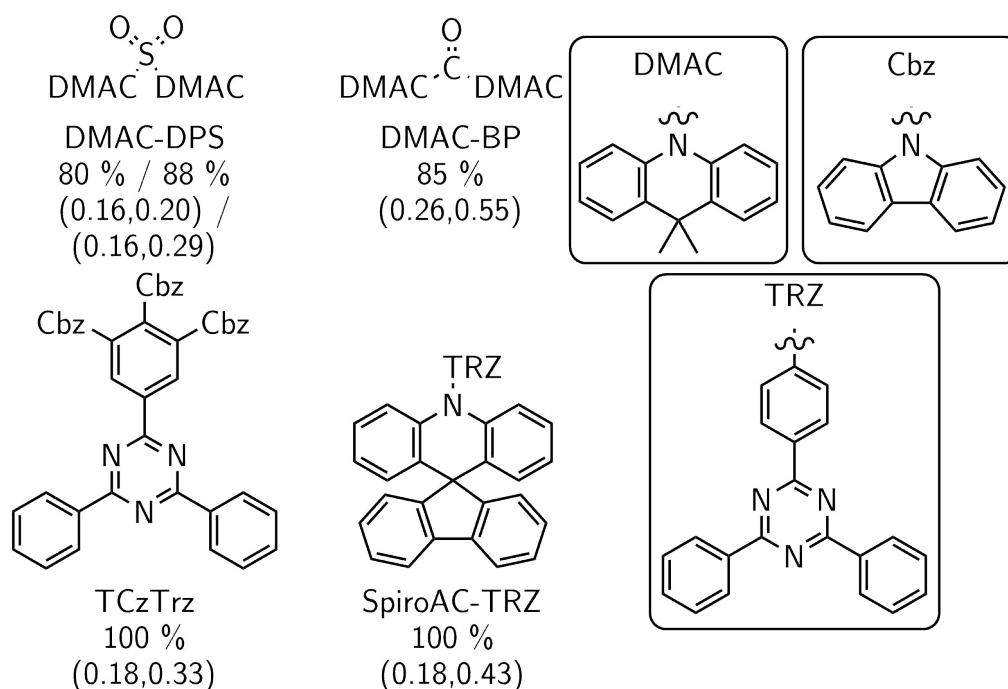
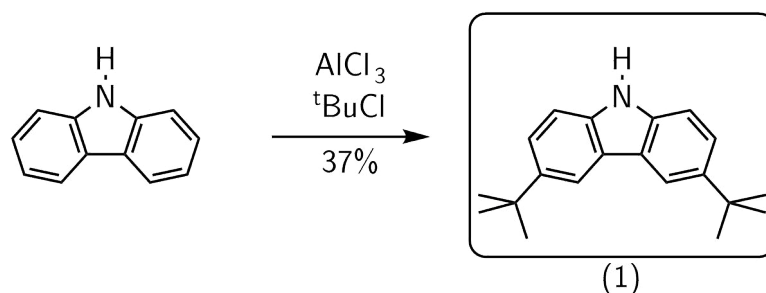


Figure 2.5: Example of molecules with high solid state PLQY, with listed PLQY and CIE coordinates.^{21,22,23,24,14}

roll-off in some molecules.³³ It has been suggested that it may reduce exciton-polaron annihilation by increasing intermolecular distance.³¹ Other terminating groups have been trialled, but of those, t-Bu groups were found to be superior due to their electrochemical stability.³³ While, as previously stated, groups with conformational disorder work against the prevention of phase separation^{8,9}, it is believed that the positive attributes out-weigh the negative.

2.2 The Synthesis

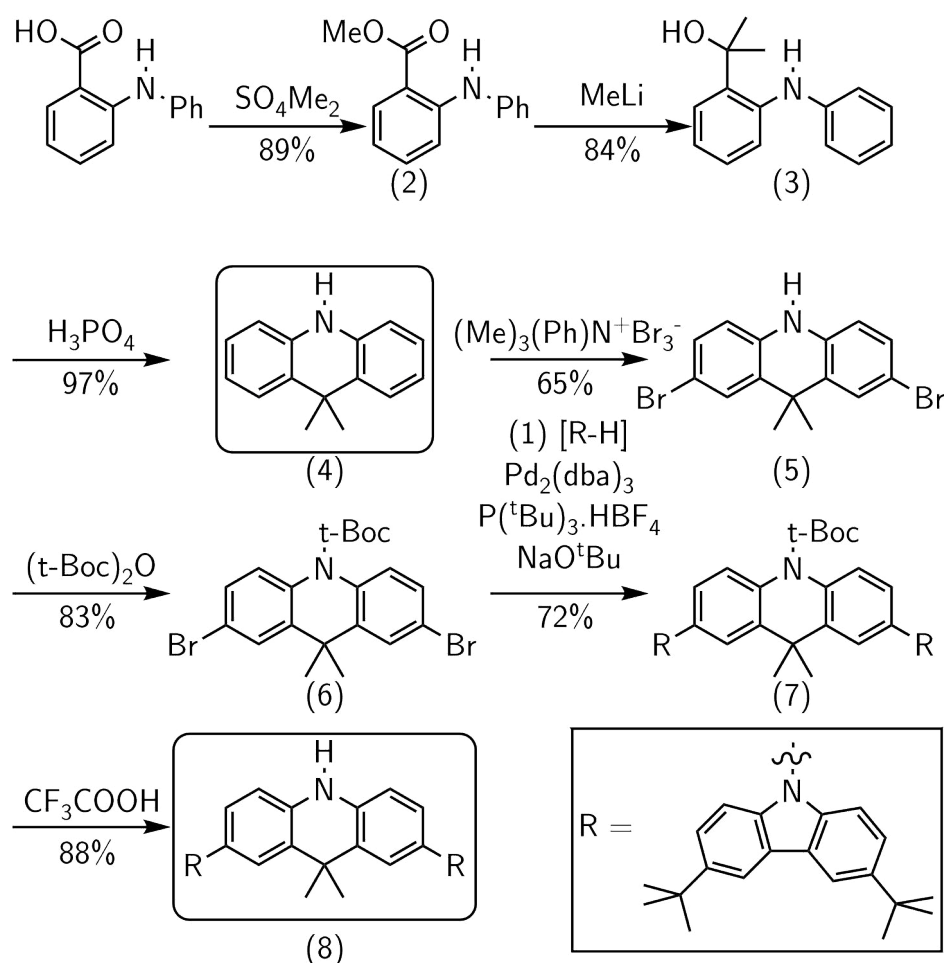


Scheme 2.1: The synthetic scheme for carbazole alkylation. Rounded boxes indicate molecules used later in the synthesis, square boxes show abbreviated groups.

Having discussed the design, it is now necessary to discuss briefly how the chemicals studied were made. Largely the description of the methods used will be left

for the experimental. However here a brief description of the types of reaction done will be discussed, and why they were chosen over other methods. Largely the choice of synthetic steps will be found to be simply that it worked on similar molecules; however, there will be exceptions. Further while the syntheses are based on others, this does not mean they are identical. Changes to purification, compound ratios, and solvent ratios have all been made to try to optimise the procedures. These will not be discussed here, unless they are so significant as to represent a radical change in the synthetic methods. As the synthesis has little influence over the rest of this thesis, the synthetically disinterested reader may skip this section, safe in the knowledge that it will spoil little of what follows.

The synthesis itself will be split in to 4 diagrams (schemes (2.1) to (2.4)). The synthesis of the carbazole components, DMAC components, acceptor (TRZ) components, and the synthesis of the final molecules respectively. This is to prevent the diagrams involved from running over several pages, as well as to break down the synthesis into manageable components for the reader.

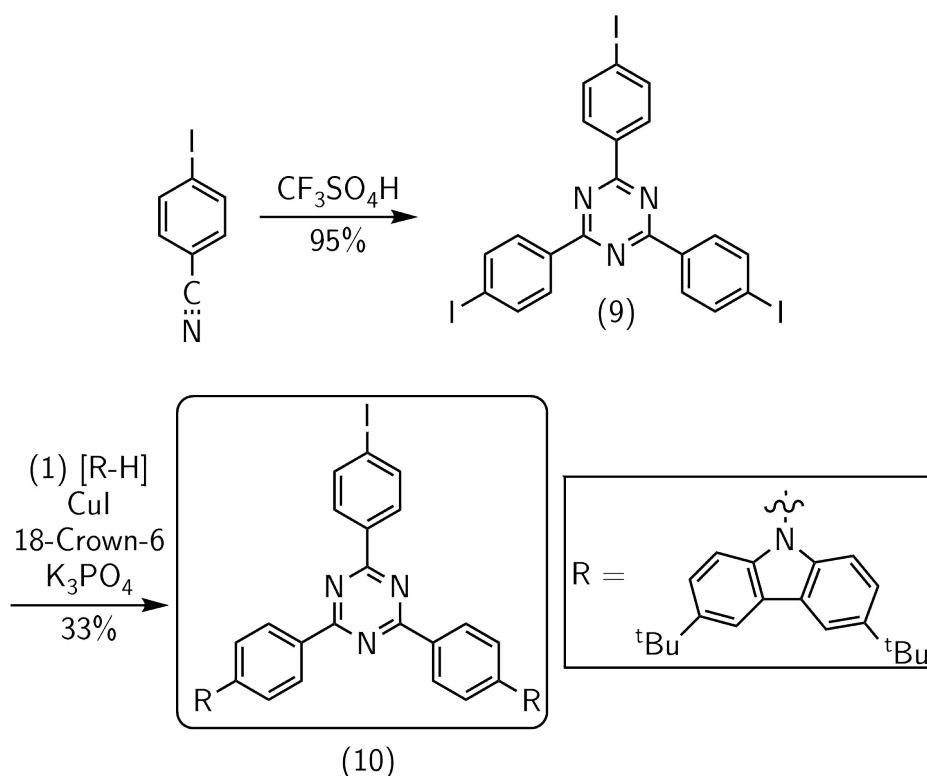


Scheme 2.2: The synthetic scheme for electron donor components. Rounded boxes indicate molecules used later in the synthesis, square boxes show abbreviated groups.

The synthesis of the carbazole components are shown in scheme 2.1. Initially the carbazole is reacted *via* a Friedel-Crafts alkylation to form compound (1). This reaction is based on a literature procedure using the same molecule.³⁴ While the yield is low (37 %), much higher yields are possible (up to 95 % yield),^{35,36} but require an alternative solvent (nitromethane).

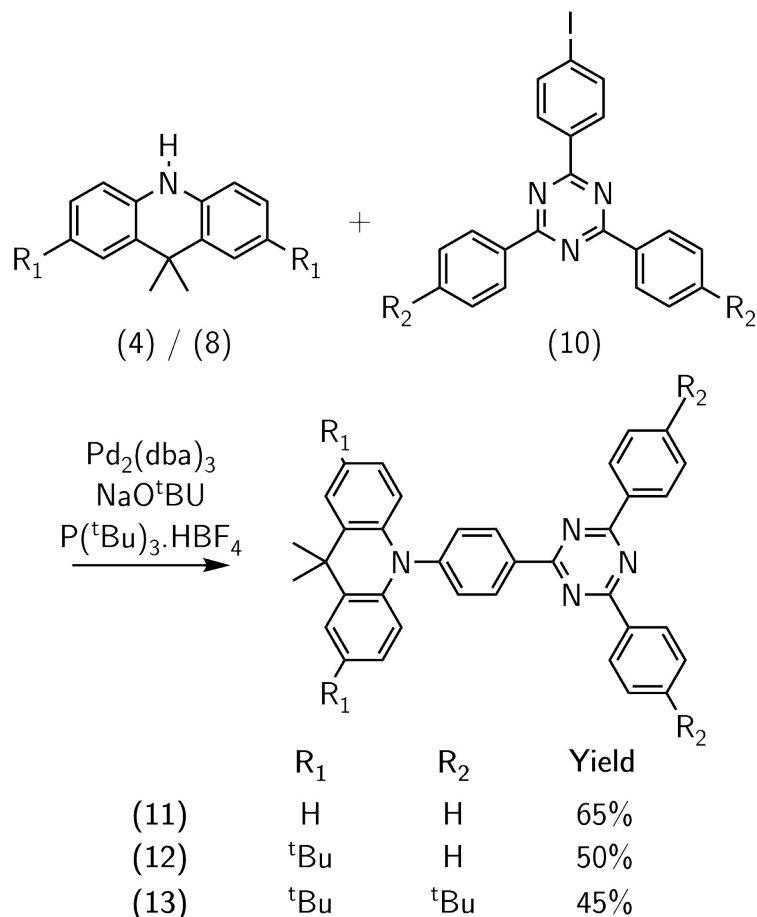
The formation of the DMAC components are shown in scheme 2.2. The subsequent reactions forming compounds (2-4) are based on a standard literature synthesis of DMAC.³⁷ The reactions are, in order, a methylation of a carboxylic acid, a methylation of an ester, and a ring closing condensation reaction. All yields are high, although it is recommended that those reproducing this procedure do not use dimethyl sulfate (SO_4Me_2). This compound is a volatile³⁸ likely carcinogen^{39,38} that was not fully quenched with water. An alternative safer synthesis is given by C. Adachi *et al.*⁴⁰

The bromination to form (5) occurs using the brominating agent Phenyl-trimethyl-ammonium perbromide. This synthesis is based on an already published synthesis.³⁷ The use of this brominating agent instead of the standard N-bromo-succinimide is suspected not to make any material difference. The low yield is suspected from the instability of the crude, and the potential for alternative brominating sites on the starting material.



Scheme 2.3: The synthetic scheme for electron acceptor components. Rounded boxes indicate molecules used later in the synthesis, square boxes show abbreviated groups.

After brominating, a tert-butyloxycarbonyl (t-boc) protecting group is added (compound 6). This is based on a related synthesis⁴¹, where it is shown that the protecting group is stable under Buchwald-Hartwig conditions. The Buchwald-Hartwig coupling forming (7) is done using standard Buchwald-Hartwig conditions. The subsequent removal of the protecting group is done using the cited paper.⁴² The yields for each of these steps is high, perhaps quantitative for all but the Buchwald-Hartwig coupling. The origin of this low yield is unclear.



Scheme 2.4: The synthetic scheme for donor-acceptor coupling.

The scheme for the formation of the acceptor groups is shown in scheme 2.3. The initial reaction using trifluoromethanesulfonic acid to form (9) is based on the procedure reported by Stock *et al.*⁴³ This is a trimerisation reaction. Other reactions attempted using procedures from Yamamoto *et al.*²⁵ These procedures did not work, it is believed likely this is due to them not specifying the use of dry solvents/conditions. At time of synthesis it was felt that it was pointless to enforce dry conditions due to the inevitably non-dryness of the acid. In hindsight this may have been an error since pK_a of trifluoromethanesulfonic acid is stronger than water, instantaneously protonating it.⁴⁴ Originally the reaction was trialed with bromine replacing the iodine. However this product was found unsuitable for subsequent

coupling due to long reaction times.

The subsequent coupling reaction forming compound (10) is an Ullman reaction. This reaction was originally attempted with the brominated trimer (in dioxane not o-dichloromethane). This reaction however did not complete after a week at reflux. The more modern Buchwald-Hartwig was also attempted, and while it was found to be faster, it favoured the formation of the triply substituted compound.

The final steps in the synthesis (ie. the donor-acceptor couplings) are shown in scheme 2.4. Each reaction was a Buchwald-Hartwig coupling, although the conditions varied slightly. It is unclear why the yield for this reaction changes so much between the compounds studied.

Characterisation data for each of these reactions are included in section A.3, and NMR of the final products in the section A.4. The NMR suggests relatively pure products, although the elemental analysis suggests slight impurity. Relatively sharp peaks are observed in the differential scanning calorimetry (see section B.3.1.9), consistent with purity. All products were purified using column chromatography, with product (13) also purified using HPLC. Recrystallisation was attempted, for some of the later compounds in the synthesis, but proved unsuccessful. Inherent in the design of solution processing molecules is design motifs which prevent crystallisation i.e. solubilising groups. It is felt that recrystallisation was most likely inhibited by these same design motifs.

There was a qualitative increase in solubility along the series C1–3. In fact when forming films of the compounds, the poor solubility of C1 in solvents like toluene hampered the range which could be made. This poor solubility was not found in C2 and C3.

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Chapter 3

General Characterisation Of Carbazole Substituted DMAC-TRZ Molecules

*“Gardens are not made by singing
'Oh, how beautiful!'
and sitting in the shade.”*

— Rudyard Kipling, *Complete Verse*

Now the synthesis of the molecules has been discussed, the characterisation of these molecules must begin. In order to remind the reader of the molecules which will be discussed in this chapter, as well as the naming conventions, figure 3.1 is included. It caused great irresoluteness whether to begin with the characterisation of these molecules, or the simulations of them. The simulations give the reader a better handle on what is going on, but tend to suggest the author is overly reliant on them for the conclusions. The way these chapters are written, it should be possible for the reader to begin with these computations if they so desire and where necessary they will be referred ahead to it.

Within this chapter the general steady state characterisation, as well as material characterisation will be discussed. It is felt this should provide the reader with a general understanding of these molecules, before the more complex computations and transient decays are discussed. This chapter will include absorption and fluorescence spectra in film and solution (ambient & 77K), as well as cyclic voltammetry data. Further, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) will be discussed. The aim of this chapter is to determine the energy levels of the molecules studied, and whether the molecules will be good in devices (excluding

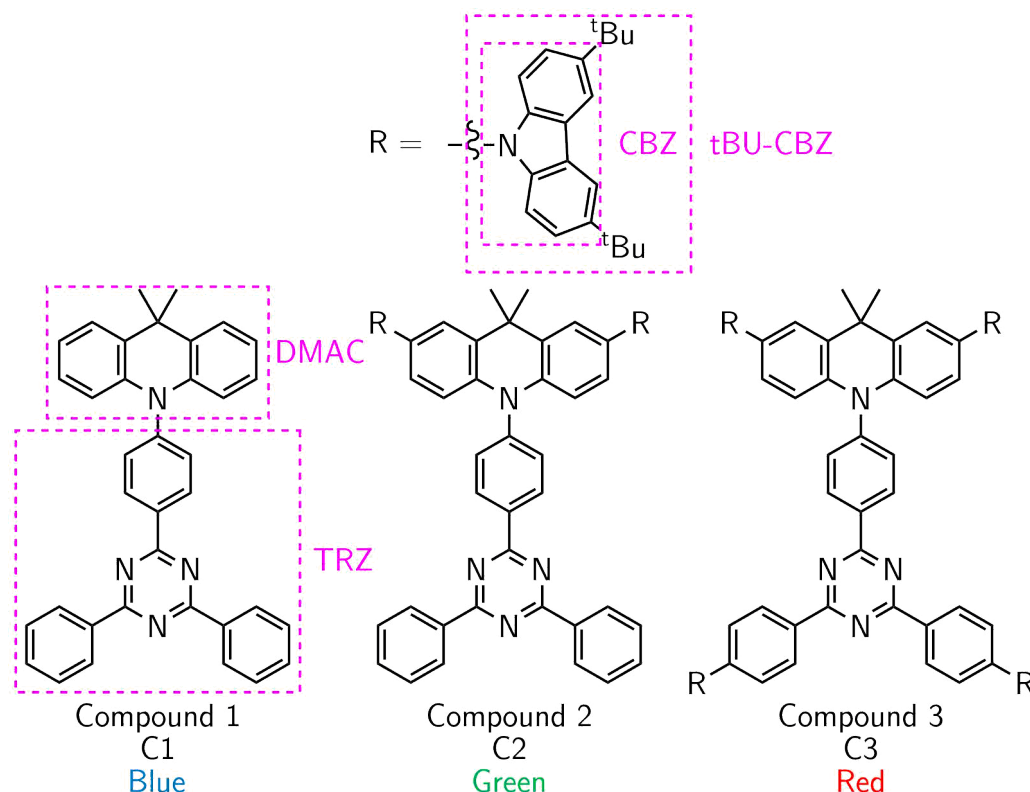


Figure 3.1: The structures of the compounds discussed, the components which make them up and the names and colours which correspond to them.

considerations of roll-off which are based on transient measurements).

It is found that there is a general narrowing of the band gap going down the molecular series C1, C2 and C3; however the magnitude of this change depends on whether the compounds are viewed in the solid or solution state. The narrowing of the band gap will be rationalised by the interference of the CBZ donor with the DMAC-TRZ donor-acceptor pair. The difference between solid state and solution state band gaps will be rationalised by the blocking of conformational changes, in the solid state, for C2 and C3. This will be further evidenced by the computational and transient studies which will make up the rest of this part of this thesis.

The TGA and DSC measurements will predict that these compounds are stable both morphologically and physically, and thus suitable for devices. Device data is currently being completed, so is not possible to include herein.

3.1 Introduction

A variety of techniques are employed in the first instance to characterise TADF compounds. TADF, as previously described in label 1.3, operated principally as shown in figure 3.2. The states involved can then be characterised by the processes shown in figure 3.3. The relevance of each measurement and its assumptions will be

discussed here.

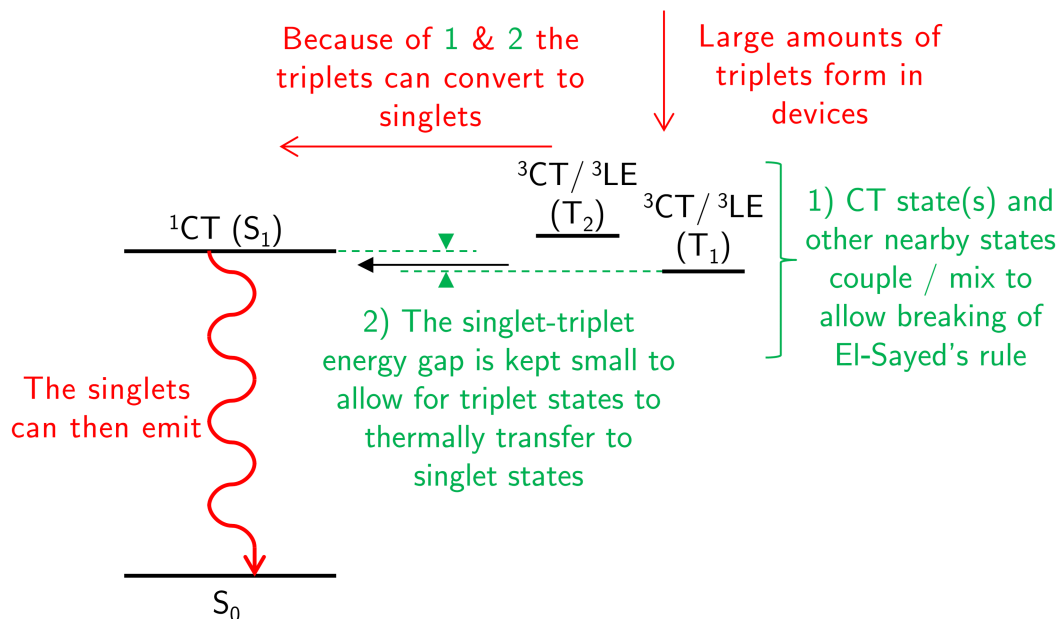


Figure 3.2: How TADF works as shown on a Jablonski diagram.

While figure 3.3 implies that the absorption and emission wavelengths are the same for a given vibrational transition, this is not true. Upon initial excitation the matrix which holds the molecules relaxes causing there to be shift (known as the Stokes' shift) between the absorption and emission. While usually the shift causes reduction in energy (*ie.* a red shift), this is not necessarily true as the matrix may relax itself to lower energy at the expense of raising the energy of the excited state. It should also be noted that the vibrational progression extends to higher energies for absorption and lower energies for emission. This is because emission and absorption occur from the ground state and low lying vibrational states. Low lying vibrational states are accessible if they lie within several KT of the ground state, and a thermal equilibrium will be reached.

As just described the absorption and emission energies are different; however both are relevant. In both, the ground *vibrational* state to ground *vibrational* state (The states with thick lines in figure 3.3) transition is of greatest relevance. While this value is easy to estimate when a clear progression of peaks is visible, for charge transfer states (CT states) this is usually not the case. Charge transfer states are usually characterised as having broad featureless peaks. While no justification is usually given for this featurelessness, inhomogeneous broadening is known to increase with solvent reorganisation energy, which is likely greater for a CT transition.¹ Because the ground state transition cannot be measured, it is necessary to take the onset as a crude approximation of it. Charge transfer states are usually the lowest energy absorption and emission state in TADF molecules by design. The lowest

energy state being designed to be CT in nature is certainly true singlet states, and this often makes it true for triplet states. A fundamental design aim of TADF is a narrow singlet-triplet gap, and this is achieved by having a charge transfer state as the lowest energy excited singlet state because it reduces the exchange energy (see section 1.3.1). Additionally it is necessary for other states in the triplet regime to not be significantly lower in energy than this state.

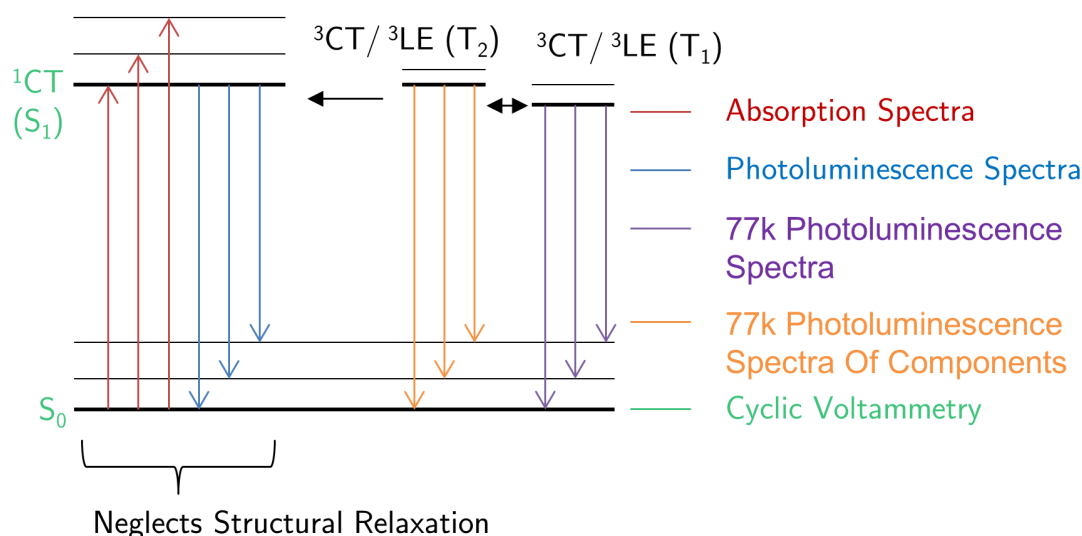


Figure 3.3: The processes which can be used to characterise the TADF process and what they characterise, as shown on a Jablonski diagram. Structural relaxation upon excitation is broadly ignored, but is most relevant when comparing emission and absorption.

Once the absorption and emission onsets have been obtained they may be interpreted. The absorption energy gives the energy gap, without nuclear rearrangement of the matrix, and the emission gives wavelength with it. This means the absorption spectra is relevant to the device manufacture as it suggests how much energy must be put into the device. The difference between the emission and the absorption gives an idea of the energy loss due to matrix relaxation which is relevant to the energy efficiency of the device. These values can easily be obtained *via* the use of steady state absorption and emission spectra, on the solutions and films of these compounds.

The difference between absorption and emission in solutions and films are also relevant to the study of these compounds. The emission of films is the best guess of the device emission, and the solution emission gives an idea of the effect of polarity and decreased steric confinement. The effect of polarity can confirm the charge transfer nature of the lowest energy excited state. The solution spectra may also give hints as to the tendency of the molecules to aggregate.

Traditionally the energy gap between the triplet and ground state is estimated by taking the emission at 77 K (boiling point of liquid nitrogen). It is assumed

at 77 K that any TADF will be limited, and further non-radiative decay will be reduced. Usually this is sufficient for phosphorescence to be visible. While it will be found herein that this is not necessarily true, the results will still be presented.

Thus far only the relative energies in the TADF system have been discussed. The absolute energies are also relevant to device design. Figure 3.4 provides a sketch of the energy levels in device design. Within OLED devices, electrons and holes (ie. the absence of electrons / positive charges) are injected into either side of the devices, and ideally combine in the emitting layer. In order to ensure these charges meet in the emitting layer, the energy must prevent the electrons or holes from leaving the emitting layer from the other side from where they were injected. In addition, in order to minimise the turn-on voltage, it is desirable to gradually raise the energy of the electrons and holes (See section 1.2 for more details).

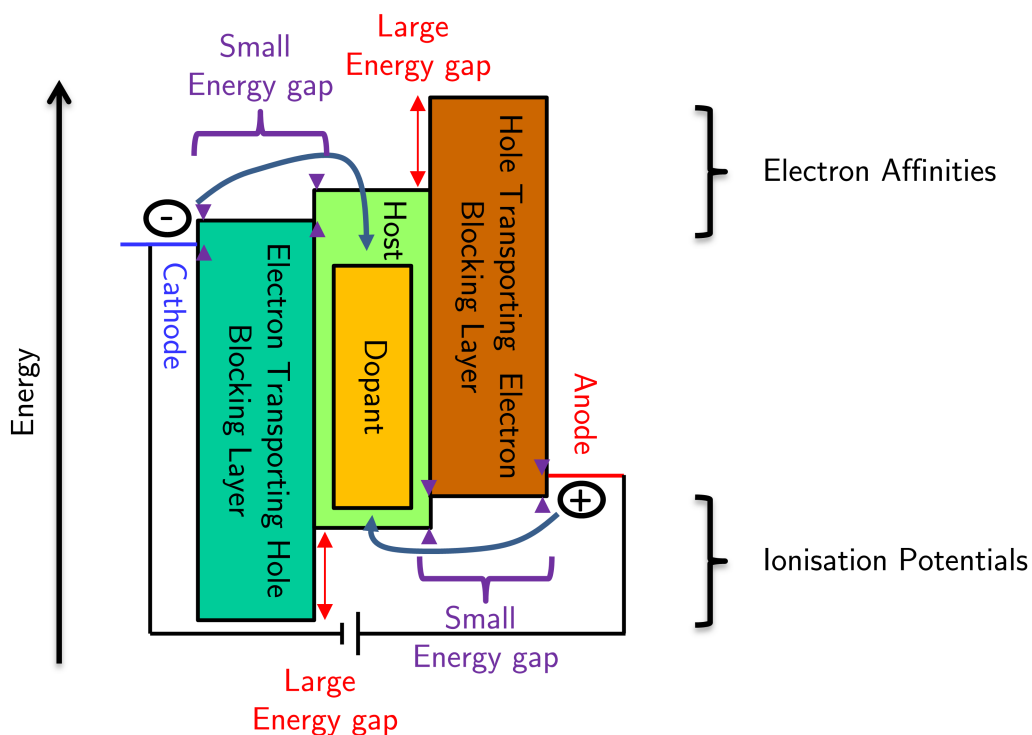


Figure 3.4: An example of the energy levels in a device demonstrating via the use of boxes with the upper bar representing electron affinity, and the lower ionisation energy.

The absolute energies of ionisation and electron affinity are often estimated *via* cyclic voltammetry. Cyclic voltammetry provides the potential of a redox reaction between the relaxed ionised and relaxed non-ionised couple, relative to a reference electrode/chemical. Standard potentials then exist (although are debated)² to convert this to a potential relative to *vacuum*. Further these potentials are then used to approximate the energy of the highest energy electron in the S_0 and S_1 states, often referred to (erroneously) as the HOMO and LUMO respectively.

From these estimates S_0 and S_1 states, the energy of the triplet states are esti-

mated by adding the energy of the phosphorescence energy to the S_0 state. This has also been done for the components of the molecule to estimate the location of nearby LE states.³

3.2 Cyclic Voltammetry

As previously stated, the absolute energies of the S_0 and S_1 states are estimated *via* cyclic voltammetry. As a result it is perhaps best to begin with these measurements. Figure 3.5 shows examples of the cyclic voltammetry data for the compounds studied and B.3.1.1 shows a more thorough study. The reason why the methodology in use here is chosen is also discussed in section B.3.1.1.

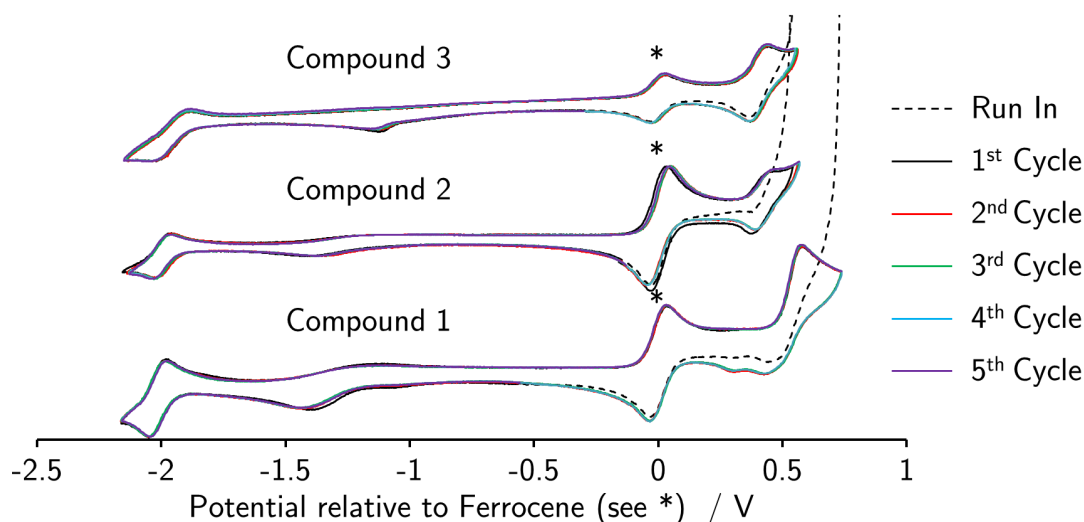


Figure 3.5: The voltammograms of compound 1, 2 and 3. These were run with conditions listed in the experimental and at a scan rate of 50 mV s⁻¹. The y-axis represents current, but this is not shown. The impurity seen at approximately -1.25 peak appears⁴ most likely to be from the following reaction $H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$. However it did appear to reduce on bubbling argon. The cause of this is unclear, but is possibly related to the loss of H_2 or water evaporation. The voltammogram was obtained in N,N-dimethylformamide.

The redox events are assigned as quasi-reversible, and the absence of a Nicholson parameter^{5*} of 1 suggests the results cannot provide the thermodynamic ionisation energy and electron affinity. This is further discussed in the supplementary information (see B.3.1.1). Nonetheless, the potentials relative to ferrocene for the chemicals are listed in table 3.1 and are treated as the best guess of the ionisation energy and electron affinity. The values of the potential are also given relative to vacuum,

*The Nicholson parameter is a measure of the ratio of the heights of forward and reverse current peaks. A value of 1 suggests that the compound is reduced and subsequently oxidised without degradation of the compound. In addition it suggests that both reduction and oxidation are rapid enough that they proceeded based on the diffusion rate of compound to the electrode, not the rate of oxidation/reduction at the electrode.

using the standard 4.80 V value.* While this 4.80 eV is known to be incorrect,² it remains the standard in the field of organic electronics. Alternative values with more scientific basis are listed in section B.3.1.1.

Table 3.1: The potentials for oxidation (Ox.) and reduction (Red.) relative to ferrocene (Fc) and *vacuum* (Vacc.) (−4.80 V) for compounds C1–3. The values are taken from the slowest scan rate voltammograms with discernable peaks. See tables B.1 and B.2 for all measured potentials.

Compound	E(Fc) / V (Red. / Ox.)	E(Vacc., −4.80 V) / V (Red. / Ox.)
C1	−1.99 / 0.49	−2.81 / −5.29
C2	−2.00 / 0.41	−2.80 / −5.21
C3	−1.96 / 0.40	−2.84 / −5.21

The changes in potential (and hence estimated S_0 and S_1 levels) are perhaps best shown diagrammatically, this is shown in figure 3.6. What can be observed is a reduction of the ionisation energy from C1 to C2, and no change from C2 to C3, and no significant change in the electron affinity, except a slight increase from C2 to C3.[†] These changes are small, although greater than the resolution of cyclic voltammetry which is on the order of mV in ideal conditions.^{8,9} It should be stressed that conditions are not ideal here (i.e. the reductions/oxidations are not reversible, and the Nicholson parameter is not 1). As such the small change in electron affinity could be argued to be within error, but is consistent with other work in this section.

The change in ionisation potential can easily be explained by the addition of tBU-CBZ. When this is added to DMAC (C1 → C2), a decrease in the energy required for ionisation is observed, and as both are electron donating species, it could be expected for their wavefunctions to mix and act together in donating electrons. The narrowing of the band gap here, will also be observed in the absorption and emission spectra in solution of these compounds (although not in film as will later be discussed). Calculations (see chapter 5) will also back up that the donation of electrons will occur from both DMAC and tBU-CBZ. No change for when tBU-CBZ is added to TRZ is rationalised as, when it adds here, it is too far away from DMAC to mix. Of course any mixing of the wavefunctions of DMAC is not ideal, this suggests the existing DMAC-TRZ TADF core, which is known to be good at TADF, is disrupted. It is perhaps not surprising that these wavefunctions mix, having been reported in

*The values for C1 has already been reported and are consistent with the earlier values by the Chun-Chih Wu group⁶ (2.78, 5.30 eV) but differs from their later values (3.12, 5.61 eV)⁷. The cause of this discrepancies appears related to the referencing with ferrocene. The discrepancy however averages at 0.33 eV and they report the ferrocene potential at 0.46 eV compared to the Ag|AgCl(sat.)⁶ reference electrode used in both.

[†]Note: sign convention is such that it is energy required to ionise and energy released by electron capture.

other examples in the literature.^{10,11} In these literature examples, the effects were not too detrimental to the TADF system.

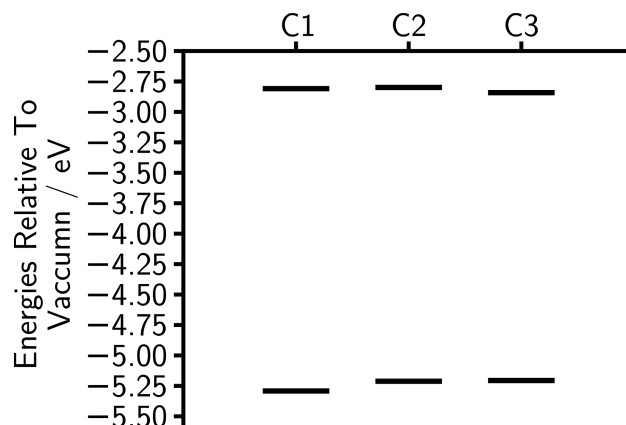


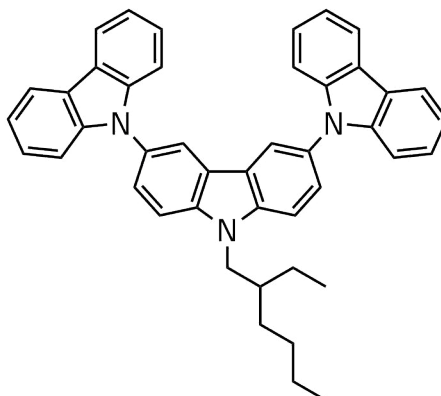
Figure 3.6: The ionisation energies and electron affinities of C1–3 using 4.80 eV ferrocene potential relative to *vacuum*.

The change in electron affinity is less easy to rationalise. It seems most likely that the addition of tBU-CBZ to TRZ stabilises the anion by increasing conjugation, but this is not what would be expected by adding a donating group to the acceptor group. A slight reduction in S_1 energy in both relaxed and un-relaxed forms will be predicted by simulations and seen in solution absorption and emission, which would be consistent with these results. Further the computational simulations predict some run in of the acceptor orbitals into CBZ. As such, this is how it is assigned. It should be noted here by the reader that this change is less than the change in ionisation energy;. A reduction in the $C2 \rightarrow C3$ change relative to $C1 \rightarrow C2$ in the will turn out to be a common theme in the *solution* measurements of these compounds. The reduction for C2/C3 relative to C1/C2 is consistent with the electron donating CBZ interacting more strongly with the donating DMAC.

3.3 The Absorption And Photoluminescence Spectra Of The Compounds Of Interest

It has just been shown according to cyclic voltammetry there is a slight narrowing of the energy gap along the series $C1 \rightarrow C3$. This appears to be due to changes in the ionisation energy when tBU-CBZ is added to DMAC, and change in the electron affinity when it is added to TRZ. The change in the ionisation energy appears greater than the electron affinity. In this section the emission of all compounds (see figure 3.1) will be investigated, in both film and solution, and what will be found is the solution measurements match well to cyclic voltammetry. The film results will not match so well. The emission of frozen solutions at 77 K will also be presented and

will be found inconsistent with being the emission of triplet states in C2 and C3, and inconsistent with literature results for C1.



Full name: 3,6-di(9-carbazolyl)-9-(2-ethylhexyl)carbazole
Formal abbreviated name: TCz1
Name herein: Host 1
Abbreviated name herein: H1

Figure 3.7: The structure and naming convention of the host molecule used in this chapter. Different naming conventions are used in this document than in the literature, as it is felt that it helps the reader for names to follow application as opposed to structure or convention.

The films studied are a pure films and a 10 % blend with host 1 (see figure 3.7). A variety of solvents are also used for solution measurements. For 77 k frozen solutions the emission of a single frozen glassy solvent matrix will be looked at. As has previously been stated, the emission and absorption take place with and without relaxation of the excited state respectively. The onsets of these spectra are used to estimate band gaps of the compounds with relaxed and non-relaxed excited states. The non-relaxed state gives approximately the energy which must be input, and the emission gives the energy that will be output. The best approximations are given by film emission; however, emission in solution provides information about aggregation, polarity dependence, and emission with less steric confinement.

First the emission in films will be discussed, as it is the simpler system, and then solutions; finally, the emission in frozen 77 K solutions will be shown. It will be initially assumed that the lowest energy absorption and emission is charge transfer like, and then evidence in the form of solution spectra will be presented. Notable observations will include the continuous reduction of energy of emission along the series C1–C3; the blocking of conformational relaxation in the solid state for C2 and C3; and the inability to obtain the absorption onset for C3 due to the TRZ-CBZ charge transfer absorption. Further results for the 77 K phosphorescence spectra will be shown, and suggested to incorrectly describe the singlet-triplet gap in each

and every case. This assignment will be justified with reference to the literature and other sections.

3.3.1 The Films

Prior to studying the films, their formation must briefly be discussed. The films studied in the bulk of this thesis will be spin coated for the mixed films, and drop cast for the pure films. This is because there is evidence for phase separation in the dropcast mixed films, which naturally cannot occur in the pure films. This will not be discussed further in the bulk of this thesis but more can be read in section B.3.1.3.1.

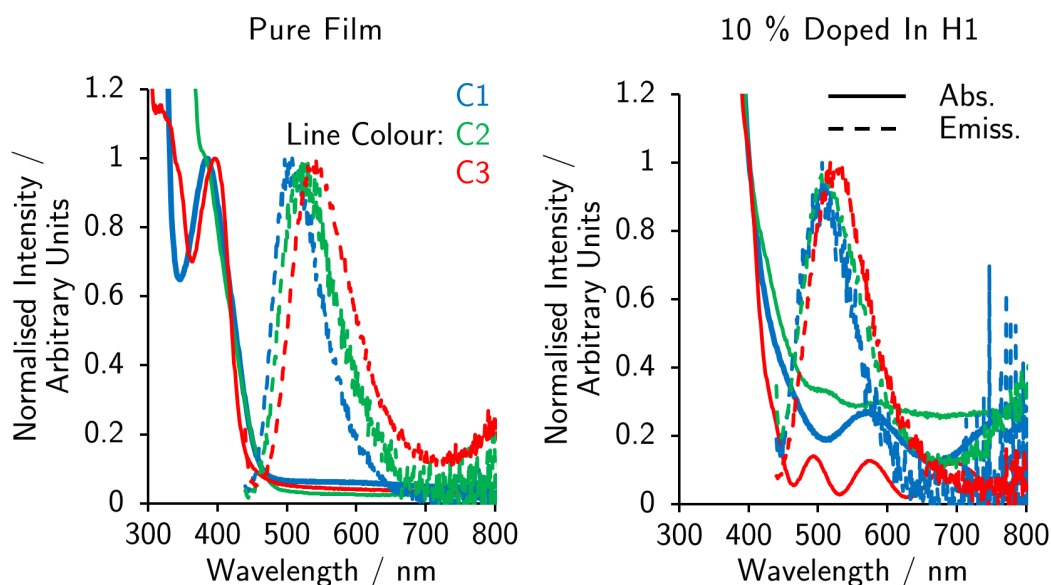


Figure 3.8: The normalised absorption (abs.) and emission (emiss.) spectra of C1-3 in pure films and 10 % doped in H1. The photoluminescence spectra are excited at 430 nm. The doped films were repeated 3 times, with slightly different but consistent oscillation observed in all. The films with the lowest oscillation are displayed.

An additional consideration is the excitation dependence of emission. Photoluminescence is acquired by first exciting the sample of interest and then viewing the light that is emitted. Generally, according to Kasha's law, emission occurs from the lowest excited state, and this causes the emission to be excitation independent. In the solid state, however, the molecules are frozen in a variety of geometries, and may not be able to transfer energy between themselves to reach the lowest energy geometry. As a result, an excitation dependence is possible. The excitation dependence of the films is shown in section B.3.1.3.2 with little dependence.

Further to the film composition and its excitation dependence, in the mixed films, what is actually emitting and absorbing may be questioned. The absorption and emission of the host H1 is shown in section B.3.1.2 and the compound in solution

in the subsequent section. It will be observed that there is great similarity between the emission and absorption in films and solution of C1–3, but little between the films of C1–3 and the pure host. Therefore, it will be concluded that it is not the host emitting. In addition, the excitation spectra shown in section B.3.1.4.4 are consistent between solution and films.

All this means that the emission and absorption spectra can be compared in their own right. The spectra are shown in figure 3.8. Immediately visible is the oscillation in the doped film absorption. This fluctuation is assigned as an artefact of the film.¹² The fluctuation is not due to the actual film absorption, but prevents meaningful interpretation of absorption of the doped film.*

Differences in the emission also exist between the doped and pure films, and this can largely be assigned as resulting from the different environments of the molecule, as well as what will be assigned as H-aggregate like properties of C2 and C3 in pure film (discussed further in section 3.3.2). The environments the molecules are in are important since they change the polarity and the steric crowding felt by the molecules in film. As a result, while the pure films remain interesting, they are not treated as directly comparable with regards to emission, as the matrix differs from molecule to molecule: not true for doped films.

The reasoning that only the molecules in common host should be compared in order to be compatible also applies to the absorption spectra. However, due to the absence of interpretable spectra for doped films, the pure films are taken as the best guess of film absorption. Figure B.18 (which will be discussed later) supports this approximation, demonstrating that the variation in absorption peak is small in comparison to emission with change in polarity. Further, sterics in different matrices should matter less for absorption, since the excitations occur from the ground states, and when films are formed, the molecules will tend towards a geometry which stabilises the ground state. Since the ground state geometry is approximately common regardless of matrix, the matrix should not matter too much here. However the H-aggregate like properties of C2 and C3 (as will be discussed in section 3.3.2), will weaken any conclusion based on this comparison. Nonetheless the pure films remain a best guess of solid state properties.

As has previously been stated (see section 3.1), of greatest importance is the comparison of these films is the low energy onset for absorption and the high energy onset for fluorescence (see section B.3.1.3.3 for diagrammatic calculation); these are compared in figure 3.9. When the onsets are compared, 5 notable observations can be seen: that the absorption of compound 3 is blue shifted relative to 1 and 2, not predicted by cyclic voltammetry (CV); the emission of C1–C3 are very close

*if these measurements were repeated, the reflectance spectra would also be recorded to try to correct for this effect.

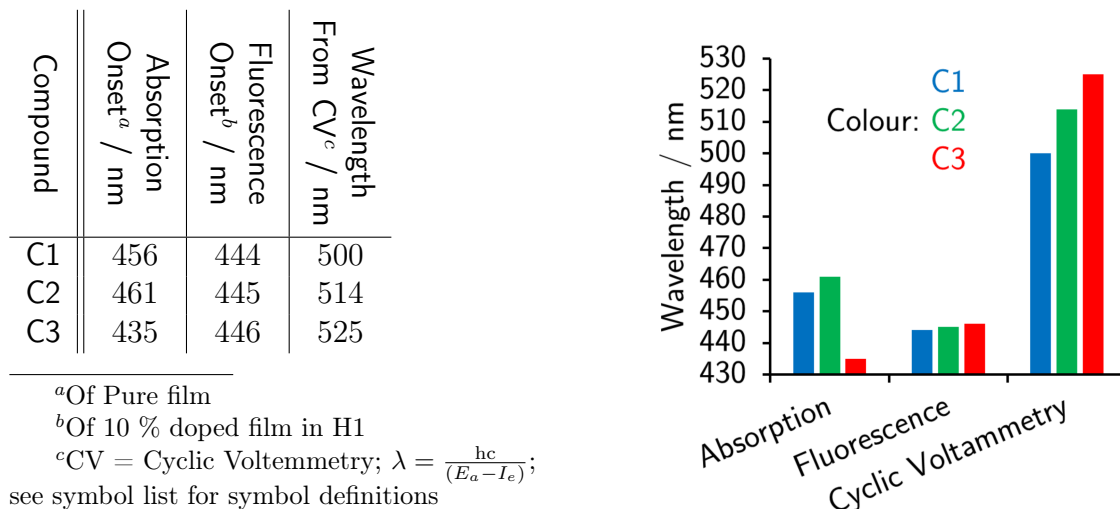


Figure 3.9: A table of the onset of the absorption of pure films and emission of doped films, and a graph demonstrating the changes between these values. Note the use of wavelengths is not ideal since in scales with the inverse of energy. Comparisons using energy can be seen in chapter 5.

together — not predicted by CV; the onset of C1 and C2 is blue shifted relative to the absorption; the estimated wavelength from cyclic voltammetry is very different to the observed wavelengths; and while the shift in energy of the absorption going from C1 to C2 is similar, the magnitude is less than what would be expected based on CV. These will be discussed in order.

The fact that the onset of the absorption of compound 3 is blue shifted relative to 1 and 2 is assigned to a non-S₁ absorption being observed. This would mean this absorption is of sufficient strength to make the first excited state indistinguishable from itself and background. It is noted that the position has similarities with the CBZ-TRZ charge transfer state,¹³ with absorption peak of 397 nm in toluene (commonly used to approx film) compared to 396 nm in pure film. In the solution spectra section (see the following section) it will be noted that the molecular absorption coefficient of similar value to the CBZ-TRZ (and far exceeding the observed DMAC-TRZ value). Finally, in the computational section, results consistent with this will be produced when using the CAM-B3LYP functional (see chapter 5 in particular section 5.5).

It is notable that the emission spectra are very close together. This is despite the cyclic voltammetry results suggesting they should be spread out. The change from C1 to C2 in absorption spectra is however, much larger, although still smaller than for cyclic voltammetry and cannot be compared to the C3 lowest energy absorption for reasons just discussed. Later it will be shown that there is significantly more change in the emission spectra of solution spectra. The reason for this disparity will be discussed later in section 3.3.5 where trends will be discussed across all mea-

surements of the energy gap. Ultimately, it will be suggested that in the solid state conformational change is blocked by tBU-CBZ substitution on DMAC, significantly reducing the change in energy gap from C1 $\rightarrow$ C2.

For C3 the lack of change in emission spectra relative to C2 is significantly harder to rationalise than C1 $\rightarrow$ C2. This is particularly the case due to the absence of visible lowest excited state absorption, which makes it impossible to tell definitively whether the effect stems from a reduced ability to change conformation or an expanded emission band gap. It is not easy to see why an increased band gap size would be caused by being in the solid state, so it is tentatively assigned herein as being due to an extension of the previously assigned rearrangement of DMAC, being further blocked by the increased steric restraint on the TRZ end of the molecule.

As has previously been stated the onset of fluorescence in compounds 1 and 2 is blue shifted from absorption. This negative Stokes shift is most likely due to the errors incurred on approximating the $v=0 \rightarrow v=0$ (vibrational ground state to ground state) transition via the onset, but may be a feature of the relaxation of these compounds. As has been stated prior (see section 3.1), it is possible that the energy gap between the ground and excited state is expanded upon relaxation. This can occur when it is favourable to stabilise the matrix at the expense of the doped molecule.

It is not felt that ordering of the energy gaps is necessarily made inconsistent by these absorption and emission energies, as has just been discussed. However the large difference in estimated and actual wavelength is perhaps of concern, suggesting that cyclic voltammetry underestimates the energy gap. This difference is attributed to the approximations of cyclic voltammetry (CV), namely solvent effects are discounted, which are in fact very important for charge stabilisation. Further approximation such as the formation of charges in CV not being accounted for are also expected to contribute.

As previously noted there is a reduction in the magnitude of the shift in absorption energy for C2 relative to C1, relative to energies gained from cyclic voltammetry. This effect can either be due to the approximations of cyclic voltammetry, or the possible H aggregation of the pure film which will be discussed in the next section. It will be seen that toluene solution has in fact greater shift in the energy relative to cyclic voltammetry, pointing in the direction of the latter.

While the onsets have been previously discussed, and are the best guess for energy gaps, the absorption and fluorescence peaks remain the most repeatable measure. These are tabulated in table 3.2 for films.

Table 3.2: A table of the peaks of the absorption of pure films and emission of doped films, when excited at 430 nm. Flourescence errors are calculated via averaging over several excitation frequencies of the same sample. Errors in absorption could not be calculated, due to lack of repeats. It is noted, however, that for toluene solution the standard deviation varied between 0.5–6 nm. The standard deviation for toluene absorption likely gives a ballpark estimate for the standard error for a single measurement of film absorption.

Compound	pure film abs. peak	doped film fluor. peak
C1	384	508 ± 1
C2	380	509 ± 2
C3	395	524 ± 3

3.3.2 The Solution Spectra

The change in the film spectra has just been discussed, and what has been found is the results differ quite greatly from cyclic voltammetry. The change in band gap from C1 to C2 is much smaller than expected for emission, and the C3 absorption is unusually blue shifted relative to C1 and C2. Nonetheless there does seem to be a reduction in energy gap across the series C1 to C3 when emission is observed. The absorption discrepancy for C3 is assigned to the CBZ-TRZ charge transfer state dominating the spectra.

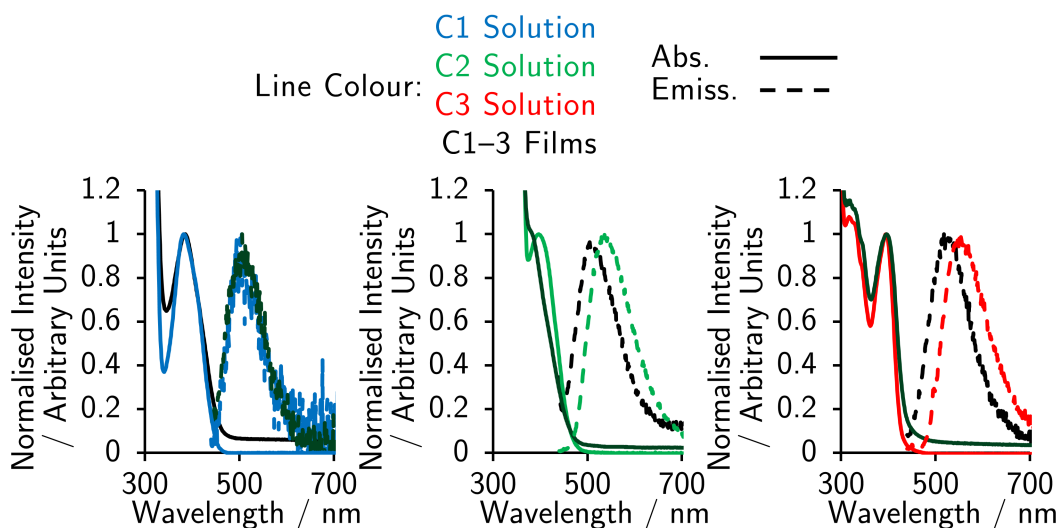


Figure 3.10: The normalised absorption (abs.) and emission (emiss.) spectra of C1–3 in toluene solution and films. The photoluminescence spectra are excited at 430 nm, and the concentrations of solutions are as appropriate to the features they show. The film absorption is measured in pure films, and emission in doped films, see section 3.3.1 for details.

Here solution absorption and emission spectra will be discussed, then compared with the cyclic voltammetry and film results. It will be found that the change in energy is more cyclic voltammetry like than the film results. Further, the C3 absorption anomaly will be reproduced and be characterised to a greater extent as

being like the CBZ-TRZ charge transfer state. The effect of polarity will be studied, and will weakly suggest that there is an increase in the change of dipole upon excitation across the series C1–C3. This increase in change in polarity is consistent with a greater separation of donating and accepting electron densities. Since the tBU-CBZ is added to the exterior of the molecule and seemingly contributes to electron donating and accepting in the charge transfer state, an increase in polarity would be expected. In addition, evidence that ordered aggregation occurs in the pure films will be discussed.

To begin with, the emission and absorption in toluene solution is compared with the pure film absorption and 10 % doped film emission, (films chosen based on previous section) this is because toluene is deemed most likely to have a polarity similar to that of H1 (the host used in this chapter) and C1–C3. This comparison is done in figure 3.10. The concentration dependence of each of these spectra are compared in section B.3.1.4.2 showing no dependence beyond self absorption, suggesting no concentration induced effects, and providing evidence against ordered aggregation occurring in solution.

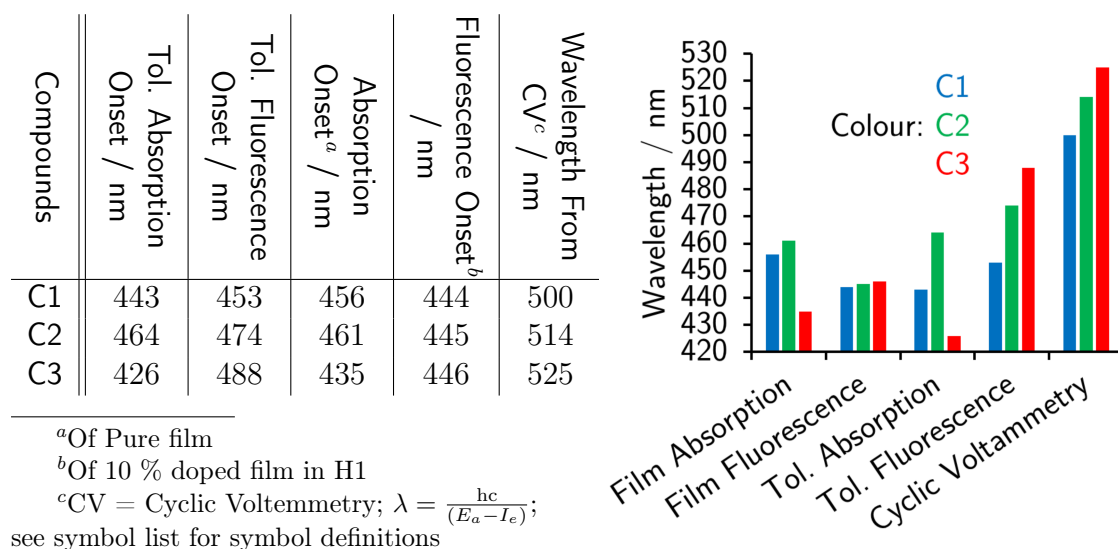


Figure 3.11: A table of the onset of the absorption of pure films and toluene solution and emission of doped films and toluene solution, and a graph demonstrating the changes between these values, with an additional comparison to cyclic voltammetry data. Note the use of wavelengths is not ideal since in scales with the inverse of energy. Comparisons using energy can be seen in chapter 5.

When the toluene and film emission are compared, large differences are observed. The C1 spectra are broadly the same; however, a red shift is observed in C2 and C3. This change approximately reproduces the change in band gap from C1 to C2 and C3 that would be expected by cyclic voltammetry (CV), as is shown in figure 3.11. Further, as in CV, the change from C1 → C2 is greater than for C2 → C3. The reproduction of CV results in solution, but not in film, suggest the inconsistency in

film is steric or aggregation based in nature, and not related to the approximations in cyclic voltammetry. The likely steric nature of this effect is further explored in section B.3.1.4.7

As well as the emission spectra, the absorption spectra are also important. The absorption spectra are also shown in figure 3.10, and the results seem consistent for C1 and C3 although a slight broadening of the peaks is observed in both cases. However, the peak for C2 is quite different appearing to shift to higher energy. It is possible, however, that this change is simply caused by broadening of the peak, consistent with the increased variety of environments available in the solid state. This is consistent since overlapping Gaussian functions tend to form peaks closer to each other than they are when separated. A second possibility is that a H aggregate is formed.¹⁴

H-aggregates would also be expected to reduce the intensity of fluorescence. While it will later be shown that C1, C2 and C3 have similar quantum yields in doped film (64 %, 59 % and 51 % respectively), it will be observed that the pure films of C2 and C3 have significantly reduced PLQY (54 %, 28 % and 29 % for C1–3 respectively), further, the prompt decay rate show a reduction when in pure film (for C2 and C3 $\tau_{pf} = 27, 24$ ns in respective doped films and $>28, 31$ ns in respective pure films). This seems to suggest H-aggregation in pure films which is suppressed in doped films. C3, however, shows no sign of aggregation effects in regards to shift in absorption spectra of pure films. It is possible that no effect observable in the absorption spectra, due to it being dominated by the CBZ-TRZ absorption, and this state may be arranged in such away as to not have its absorption spectra changed by aggregation,¹⁵ this seems unlikely however.

The apparent red shift in the emission of C2 and C3 (see figure B.16) in pure films may also be due to H-aggregation, although this could be due to differing matrices.¹⁴ The mixed nature of the results causes considerable uncertainty in the nature of the pure films, so no clear answer as to whether H-aggregation occurs in them, as a result they will be labelled as having H-aggregate like properties.

Table 3.3: The molar absorption coefficient of the lowest energy peak for C1–3 as calculated for Toluene solution. Spectra were recorded at concentration of 1, 10, 100, 1000 μM , and all spectra with absorptivity below 0.05 were averaged for the result.¹⁶ In addition, a spectra from a degassed solution with absorptivity below 0.05 was averaged.¹⁶

Compound	$\epsilon(\text{Tol.}) / 10^3 \text{ M}^{-1} \text{ cm}^{-1}$
C1	2.5 ± 0.2
C2	2.2 ± 0.2
C3	48.6 ± 0.6

Along with peak shape and position, the absorption spectra gives information about the molar absorption coefficient. The molar absorption coefficient can be

seen as a function of the probability of the molecule absorbing a photon via a certain transition. The molar absorption coefficients are compared in table 3.3 in toluene, where the low absolute values for C1 and C2 are highly consistent with a charge transfer (CT) state. CT states have low molar absorption coefficient as the absorption of light is governed by the following equation,^{*} with ϵ the molar absorption coefficient, ν the wavenumber, Ψ_i the initial state Ψ_f the final state and μ the dipole operator. The precise formula is calculable using equations 5.2, 5.3, and 5.6 shown later.

$$\int \epsilon(\bar{\nu}) d\bar{\nu} \propto \langle \Psi_f | \mu | \Psi_i \rangle^2 \rho \quad (3.1)$$

A slight increase in molar absorption coefficient is observed from C2 to C1, which is consistent with earlier conclusion that there is increased separation between electron donating and accepting parts of the formed charge transfer state. The increased separation would be expected to lower the molecular absorption coefficient. However, this difference is small, and the error bars overlap. In addition, changes in vibronic coupling will likely have an strong influence on such a small change. Vibronic coupling is the change in electronic properties with vibrations (ie. change in nuclear coordinates). Because the molecular absorption coefficient is low, it may be expected that changes in geometry will be important in making the transition faster.

The change in the molar absorptivity from C2 to C3 is far too large to be justified by vibronic coupling itself. As previously stated the absorption position bears striking resemblance to the reported CBZ-TRZ charge transfer (CT) (396 nm in toluene here vs 397 nm there) state;¹³ this is also true for the molar absorption parameter, calculated as being approximately¹³ $30 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ per CBZ-TRZ donor acceptor pair [†] When considering the presence of 2 possible CBZ-TRZ CT transition in C2 this provides an estimated measured molar absorptivity of $60 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. While there is a difference between this reported value and the value reported herein, they are certainly of similar order. The difference may also be due to error or vibronic coupling.

Thus far only the emission and absorption of toluene has been discussed, this is not the only solvent studied. Generally the emission in other solvents was not that interesting and thus will be left for the supplementary information (see B.3.1.4.1).

^{*}While it is frequently claimed that it is obvious from the equation shown that overlap is required between initial and final states, this from experience is beyond the information given in the average undergraduate chemistry course. A brief description of why this is believed to be the case is given in section B.3.1.5.

[†]Molar absorptivity was not reported in this paper,¹³ but the absorption spectra was, this allowed calculation of this relative to the carbazole LE state at $\sim 290 \text{ nm}$ with absorptivity of $\sim 20,000 \text{ M}^{-1} \text{ cm}^{-1}$ per carbazole.¹⁷

With the other spectra the expected red shift of emission with increased polarity was observed for all compounds. When the main peak was red shifted, a weak bluer peak was observed in every case. This peak may be from locally excited states (i.e. a non-charge transfer state), or from impurities. It is tentatively assigned that this bluer peak is from impurities due to the observed batch dependence for certain compounds(see section B.3.1.4.8). The impurity peak appears to become visible due to the quenching of TADF emission (see quantum yields in section 3.3.4). Due to the low concentration of this impurity, and imperceptibility in film absorption and emission, it is henceforth ignored.

Table 3.4: The change in dipole estimated via the Lippert-Mattaga method. See "Principles Of Fluorescence Spectroscopy" by J. Lakowicz for calculation.¹⁸

Compound	$(\mu_E - \mu_G) / D$
C1	4.4 ± 0.7
C2	5.1 ± 0.8
C3	6.6 ± 1.0

While alone the solution spectra are not hugely interesting, collectively they can be used to draw a Lippert-Mattaga plot which allows for the estimation of change in polarity upon excitation. The plots are shown in section B.3.1.4.5, and the overall results are summarised in table 3.4. The large absolute value of change in polarity for each compound is consistent with a charge transfer excitation, due to the large increase in polarity these involve. Unfortunately, the uncertainty in this data set is rather large. While there is a probable increase in change in polarity across the series, the uncertainty in this assignment is large, this is particularly true for C2, where the error bars overlap with both C1 and C3. Nonetheless this increase in change in polarity is further evidence of increase in charge separation with added carbazole groups, consistent with them competing with both the donor acceptor.

While the onsets have been previously discussed, and are the best guess for energy gaps, the absorption and fluorescence peaks remain the most repeatable measure. These are tabulated in table 3.5 for films.

Table 3.5: A table of the peaks of the absorption and emission of toluene solution. The results are averaged over all excitations, and all appropriate concentrations of those measured (1, 10, 100, 1000 μ M). A minimum error of 0.5 nm was enforced due to sampling every nm.

Compound	Tol abs. peak	Tol film fluor. peak
C1	381 ± 2	500.9 ± 0.8
C2	393 ± 3	536.4 ± 0.5
C3	395.6 ± 0.5	557 ± 3

3.3.3 77 K Photoluminescence Spectra

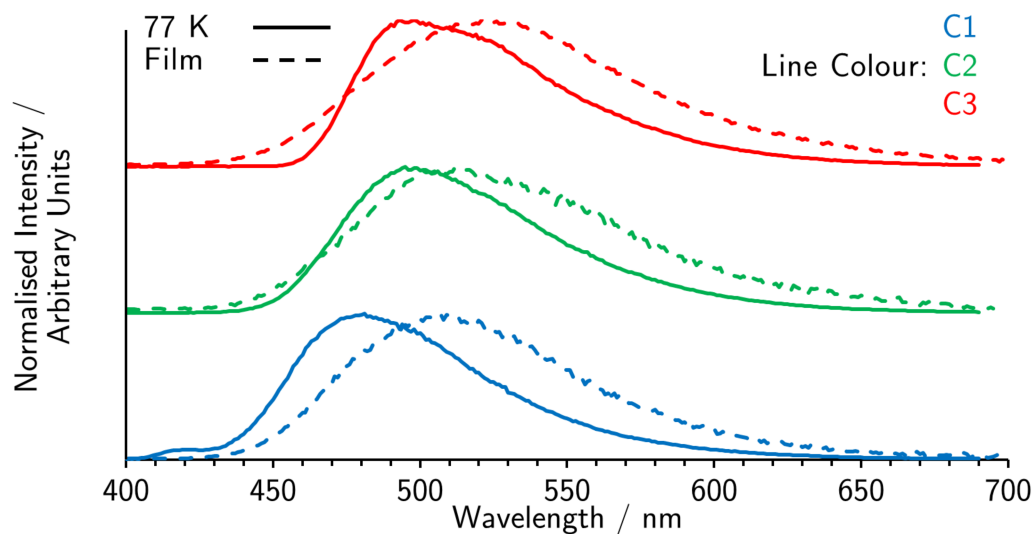


Figure 3.12: The normalised photoluminescence spectra of C1–3, 10 % doped in film with H1 (film), and at 10 μ M in frozen glassy solution (1:1 diethyl ether:ethanol) at 77 K (77 K). The samples are excited at 350 nm.

So far the data from the cyclic voltammetry and the absorption and emission of films and solutions of C1–C3 has been presented. What has been found is consistent across all measurements there is the reduction in band gap across the series, although this effect appears suppressed in film measurements. This is assigned as from the blocking of conformational rearrangement in film. Further weak evidence has been presented of an increase in polarity across the series. It is hence assigned that tBU-CBZ mixes with the donating and accepting orbitals, decreasing the band gap. It has also been observed in solution, both according to cyclic voltammetry and solution spectra, that this narrowing in band gap is most significant for the change from C1 $\rightarrow$ C2. Finally it has been noted that the pure solid state films of C2 and C3 have data consistent with likely H-aggregation.

Here the spectra of compound 1–3 when cooled to 77 K in frozen solution (1:1 diethylether:ethanol) are compared. This solution is chosen because it has been noted to form a glass when frozen; this means that there is little scattering, allowing for emission spectra to be obtained.¹⁹ The spectra when cooled to 77 K is traditionally referred to as the "phosphorescence spectra" and is used to measure the energy gap between the ground state and the first triplet excited state. The triplet emission is justified by the quenching of the non-radiative decay of the triplet state, and quenching of the thermal activation required for TADF. In order to ensure that what is observed here is not prompt fluorescence, a time gap (200 μ s) is inserted between excitation and detection. Despite this, the results will suggest TADF is not

quenched in C2 and C3, and further the energy gap predicted for C1 will be found too high.

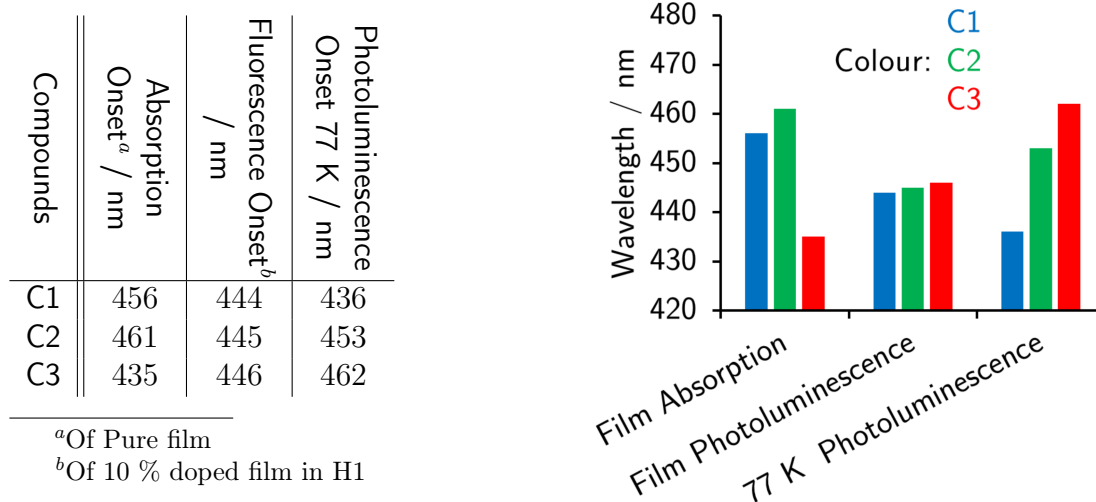


Figure 3.13: A table of the onset photoluminescent spectra at 77K compared to the absorption of pure films and emission of doped films at room temperature. A graph demonstrating the changes is also shown.

It is felt that when comparing the solution emission to fluorescent emission, the most apt comparison is to the film emission. This is because both film and frozen solution are rigid matrices and as has previously been stated, the rigidity of the matrix appears to have a significant effect on the emission of the compounds studied herein. The comparison spectra are shown in figure 3.12 with comparison of onsets shown in 3.13. It is immediately obvious when comparing the film and the frozen solution spectra, that while a normal shift is observed for C2 and C3 — ie. a red shift indicating the T_1 state is lower in energy than S_1 — this is not the case for C1. This is further highlighted in figures 3.13 and 3.14 which show the onsets and conventionally calculated singlet-triplet energy gaps from them.

Prior to discussing the singlet triplet energy gaps calculated for C2 and C3, the unusual gap for C1 should be discussed. While it has been shown to be physically possible for TADF molecules to have triplet energy higher than their singlet energies^{20,21}, if this were the case, it would not be expected that triplets state would be significantly populated. It is known that this molecule is a successful TADF compound due to early reports by the Wu group.^{6,7} It has also previously been measured^{6,7} that the singlet triplet energy gap is in the range 0.05 — -0.06 eV (ie. a shift in onset in the opposite direction to measured). The cause of the discrepancy is of interest. It is noted that the measurements previously done were in film^{6,7} and so the solid state solvation of the matrix could be the cause, and further a longer time delay of 10 ms was used, which may select phosphorescence better. Neither of

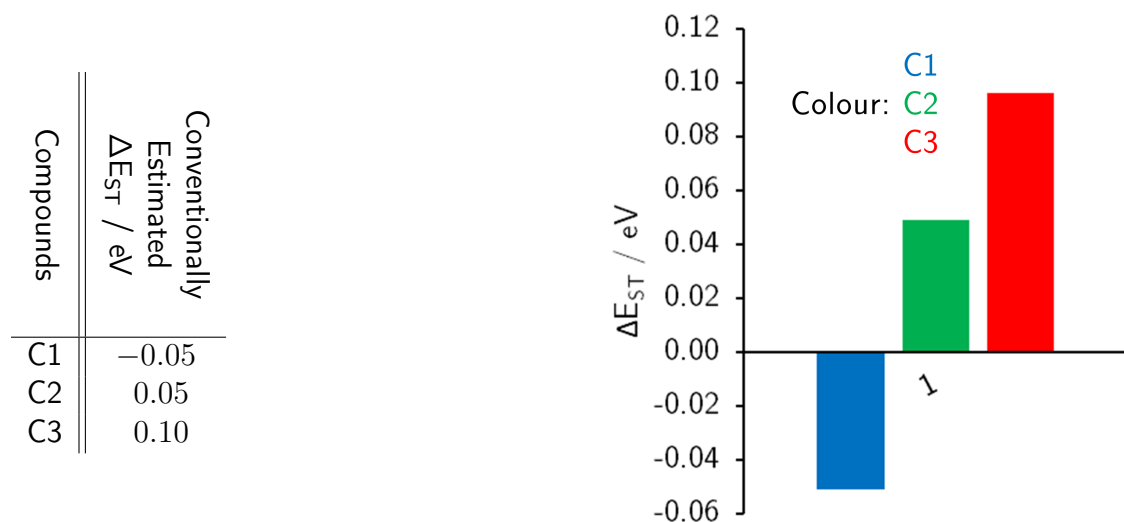


Figure 3.14: A table of the difference in energy between singlet and triplet states, estimated by the conventional method using the difference in energy of the film and frozen solution spectra, using the onset wavelengths to calculate energy. A graph demonstrating the changes is also shown.

these were possible with the equipment in use here. Since the reported values are in common medium ie. in doped film, this suggests that the cited results are better, and so will be henceforth used.

The shift in C2 and C3 values is curious. This curiosity arises when one considers what one might expect the values to be in this case. The previous data seems to suggest that the CBZ group is interacting with the donating and accepting groups to increase the electron donating and accepting abilities of both. Along with this, there is weak evidence of an increase in polarity. All of this suggests that the separation of electron donating and accepting components in the first excited state increases along the series C1→C2→C3. Further computational evidence for this will be presented in chapter 5.

An increase in donor-acceptor separation may be expected to reduce the energy gap between singlets and triplets. This is because the energy gap (ΔE_{ST}) is given by the following equation, when no mixing with other states is assumed,²² and where the symbols are defined: J the exchange energy, $\phi_H(n)$ the highest occupied molecular orbital represented as a vector in the space of a basis set, occupied by electron n , $\phi_L(n)$ the lowest occupied molecular orbital, occupied by electron n , r_n the position of electron n , and τ meaning all space:

$$\Delta E_{ST} = 2J = 2(\phi_H\phi_L|\phi_L\phi_H) = 2 \int_{-\infty}^{\infty} \phi_H(1)^*\phi_L(1) \frac{1}{|r_1 - r_2|} \phi_L(2)^*\phi_H(2)d\tau \quad (3.2)$$

$$\Delta E_{ST} = 2J = 2 \langle \phi_H \phi_L | \phi_H \phi_L \rangle = 2 \int_{-\infty}^{\infty} \phi_H(1)^* \phi_L(2)^* \frac{1}{|r_1 - r_2|} \phi_H(1) \phi_L(2) d\tau \quad (3.3)$$

The equation has been given in both chemists notation (equation 3.2) and physicists notation (equation 3.3), to aid readers from both backgrounds. While recent research has called these equations into question,²² suggesting that in certain circumstances the mixing of states can dominate the energy gap, the existing conventional wisdom remains that this equation dominates. By noting the coulomb interaction involves a term for inter-electron distance between the HOMO and LUMO, it can be seen that the overlap in HOMO and LUMO would be expected as being key in this interaction. To first approximation it is approximated that the electron donating component and the electron accepting component correspond to the HOMO and LUMO respectively (neglects all mixing of orbitals in the excited state, corresponding to theory level below CIS in computational chemistry, see sections 1.3.1 for more details). Given this approximation, it can be seen that the increased separation of electron donating and accepting components would be expected to narrow the gap between singlets and triplets.

So, it has just been predicted that the current experimental results suggest that the gap between singlet and triplet will narrow for C2 and C3 relative to C1. Further evidence will be presented in sections 4.3.2 and 4.3.3, which show that there is no apparent quenching of delayed fluorescence in C2 and C3. However, this does not explain the apparent red shift of triplet emission, which suggests the opposite effect. It is useful to go back to the initial assumption used to justify the emission being phosphorescence. They are:

1. The quenching of triplets is reduced to make them visible.
2. TADF is quenched.

It is possible that with the narrowed energy gap TADF is not quenched, and hence what is being observed is TADF. Further it is known that in TADF there is an initial red shift and a subsequent blue shift^{23,24} in the emission, where the latter blue shift is caused by the molecules with large singlet-triplet gap, within the distribution of states within the solid state, taking longer to decay. It is possible that the bluer emitting species are increasingly separated, at low temperatures, causing the observed blue shift. Indeed, subsequent transient studies at reduced temperatures will see that delayed fluorescence is not suppressed relative at 77 K,

suggesting TADF is still present.* Further some computational studies will suggest the energy gap between singlets and triplets is comparable to kT at 77 K. Since no other explanation for the unusual shift in C2 and C3 photoluminescence at 77 K can be readily thought of, it is taken that this shift is due to the distribution of states in the excited state band. It is further possible that the differing medium causes these effects.

While the onsets have been previously discussed, and are the best guess for energy gaps, the absorption and fluorescence peaks remain the most repeatable measure. These are tabulated in table 3.6 for films.

Table 3.6: A table of the peaks of photoluminescence at 77 K of compounds. Frozen glassy solution (1:1 diethyl ether:ethanol) are shown at a concentration of 10 μM . Spectra are excited at 350 nm, 400 nm, and 430 nm, and averaged for mean and errors. It should be noted slight excitation dependence was observed which contributes to the large errors.

Compound	Tol film fluor. peak
C1	482 ± 3
C2	496 ± 3
C3	498 ± 2

3.3.4 Film And Solution PLQY

Thus far in this chapter, it has been shown that the energy gap along the series C1–3 narrows, first (C1→C2) via change in the energy of the donating components and then (C2→C3) the energy of the accepting components. A concomitant increase in polarity of the excited state along the series C1-3 is also observed. This increase in polarity and decrease in energy gap is consistent with an increase in separation of donating components from C1 to C2 and possibly from C2 to C3. This conclusion is contrasted with the photoluminescence spectra at 77 K, but as the transient decay and computational study are also consistent with a narrowing of the singlet-triplet energy gap, this is treated like an outlier. An additional observation has been shifts in peaks consistent with H-aggregation in C2, and it has been noted that while some evidence for this in C3 exists, not all observed effects are seen. It has been postulated that these unseen effects may be hidden in C3 due to the domination of the CBZ-TRZ CT state in the absorption spectra.

*The diligent reader will spot a contradiction here, if the long lived bluer states are quenched, it would be expected that delayed fluorescence would be partially quenched. It will however be shown in the transient studies that it increases. An increase in delayed fluorescence can most likely only be caused by a reduction in pulse fluorescent rate, reducing the visibility of this quenching by causing the opposite effect (i.e. a reduction in pulse fluorescent rate causes an apparent increase in relative delayed fluorescence intensity). A long lived component will also be observed in the delayed fluorescence, which may be due to these non-emissive states.

For each of the film and solution spectra, a *photoluminescent quantum yield* (PLQY) was obtained. These values are important as they serve as an indicator as to whether the electroluminescent quantum yield is good (*i.e.* the quantum yield relevant to OLED devices — TADF’s application). Further, when combined with the other measurements of TADF, it may suggest what changes to existing TADF systems are favourable and dis-favourable in terms of devices. A full tabulations of results is shown in table B.8; comparisons of subsections of this data will be henceforth discussed.

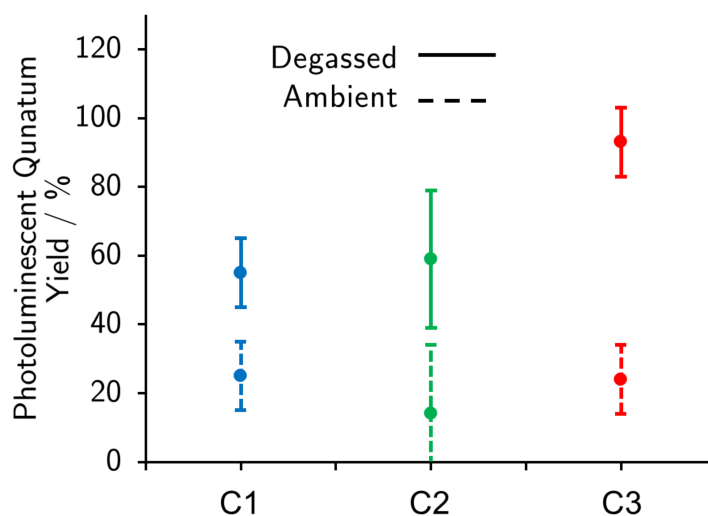


Figure 3.15: The PLQY of C1-3 in toluene

First the compounds in solution should be compared. While the comparison in all solutions studied will be left for the supplementary information (see figure B.32), as due to the large uncertainty in PLQYs measurements, a precise meaning is difficult to parse. All they seem to show is a general tendency for degassed solutions to be more efficient than non-degassed (expected for any system with triplets, as oxygen is a well known quencher especially of triplets).²⁵ Within the solutions, generally all compounds give the highest quantum efficiency in toluene (with the possible exception of C1 in non-degassed solution but this is within error, see section B.3.1.7). These assertions are demonstrated diagrammatically in figure B.32 in the supplementary information, but are weakened by many of the data points being within error of each other.

The comparison in toluene is most interesting of the solvent measurements. This is because the polarity matches closest to film, and further because the PLQYs are sufficiently large for comparison to be made which are greater than 1 standard deviation. The PLQYs measured in toluene are compared in figure 3.15, and show the expected increase on degassation. Most interesting is the apparent increase in PLQY from C2 to C3 in degassed solution; this is particularly so because the

previous work in this chapter seems to point towards the change from C1 to C2 as having the greatest effect on the photophysical properties of the molecule. This inevitably calls into question the validity of this result and this will be reinforced when considering the transient fluorescence and the computational studies which will follow in this chapter. These will suggest the change in photophysical properties along the series C1, C2, C3 is most likely greatest going from C1 to C2.

This inconsistency between the solution PLQY and all other work is perplexing. It is noted here that the error bars are quite large, and may be larger yet (The smaller errors bars in C1 and C3 will be called into question in the experimental, i.e. section A.1.7), and this may be the cause of this result. However, it is worth attempting to explain this result. It is entirely possible that the increased sterics in C3 due to the tBU-CBZ on the TRZ component decreases the rate of non-radiative decay. Further, the increased delocalisation of TRZ onto CBZ, as previously predicted, may help prevent quenching. Sterics seems the most likely cause of the increase. In part, evidence for sterics being the cause comes from C1, where the emission in film displays much higher PLQY than solution when under assumed degassed condition (84 % in film according to the literature⁶ vs 60 % in solution reported here).

Simply putting down the difference between the compound to sterics is quite vague. Further discussion of the conformations of these molecules will be left to the computational section of this thesis (see chapter 5). It should be noted by the reader that certain conformations of DMAC have been linked with having greater overlap of donating and accepting components which are not good for TADF.²⁶ This is because the formed species acts as a triplet trap.²⁶ It is possible that in solution this conformational change is allowed, but is blocked in the solid state.

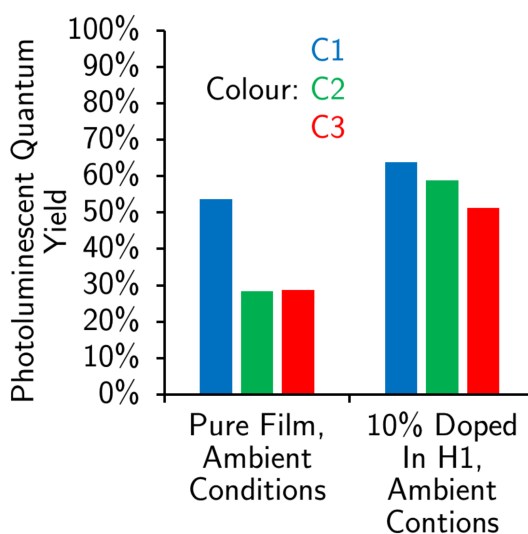


Figure 3.16: The PLQY of C1-3 in pure film and 10 % doped in H1.

The PLQY in films in ambient conditions are compared in figure 3.16; the use

of ambient condition must immediately be addressed. Due to a lack of appropriate equipment, the PLQY measurements could only be obtained in ambient conditions (*i.e.* with oxygen present). The effect of this may be demonstrated by comparing the PLQY of C1 to that of previously published data. It has been previously published⁶ that C1 has a PLQY of 83 % in pure film relative to 54 % reported here. This reduction is attributed as being most likely due to the ambient conditions (although details of the acquisition conditions are not specified in the cited paper). A crude approximation is hence made here that the degassed PLQY is a constant percentage greater for all compounds, while this will not in reality be true, it is likely approximately true, and allows comparison of this data.*

When the film PLQY in figure 3.16 are compared, several changes are obvious, firstly C2 and C3 have significantly lower PLQY in pure film than C2 and C3, representing considerable quenching relative to their doped films. Secondly for the PLQY in doped films there is a consistent decrease in efficiency across the series C1-3. The first point is interesting because with a narrowed singlet-triplet gap, it might be expected that C2 and C3 have more efficient TADF than C1 and hence less quenching in pure film.

The reduction in PLQY for pure films may be interpreted as being due to the previously stated H-aggregate like properties of C2 and C3; in H-aggregates it is known that there is a reduction in the rate of singlet emission rate. A corresponding reduction in singlet emission rate will be observed in transient studies. Slower singlet decay rate allows for the probability of decay via non-radiative pathways to increase.

It is further possible that the increase is due to intramolecular interactions in pure film accelerating the decay. Exciton pair interactions are of particularly greater likelihood in pure films (e.g triplet triplet annihilation, singlet-triplet annihilation, singlet-triplet annihilation). However, as the rates decrease in transient studies this does not seem likely.

The reduction of the PLQY for doped films along the series C1-3 must also be justified. As previously stated the singlet triplet gap narrows between C1 and C2 and C3, and this favours fast TADF. This suggests that the ratio of radiative singlet decay to non-radiative decay must be the cause of this change. This is perhaps easiest to explain by a reduction in singlet radiative decay rate, as previously stated this depends on the overlap of donating and accepting components, and this overlap appears to decrease along this series. Counter to this proposal for the case of C2 → C3, an increase in prompt decay rate will be seen in going from C2 to C3, but it will

*It is possible that this discrepancy is instead related to sample purity or preparation. It has been found beyond the scope of this document to test this. It is noted that the published films are formed by sublimation. Sublimation has been linked to better organic electronic device properties (in solar cells) in certain materials;^{27,28,29} however it is unclear to what extent this generalises.

not be clear that this is from an increased singlet decay rate. Increased non-radiative decay rate likely also plays a factor, and is a probable cause of this effect although a mechanism for this will be hard to parse.

3.3.5 Differences Between Solution And Films

So far, evidence has been presented for a continued narrowing of the band gap along the series C1–C3, and reduction in the PLQY in film along the series. Polarity seems to increase along the series, suggesting an increased separation in donating and accepting wavefunctions on the molecules. This increase in separation is attributed to the reduction in PLQY in doped film for C1 to C2, via means of reducing radiative decay rate. While the photoluminescent spectra at 77 K did not show evidence for a narrowing of the singlet-triplet energy gap, it was proposed via comparison to the literature, as well as the transient decay and computational results shown later, that the energy gaps do in fact narrow. An increase in non-radiative decay is also proposed as the cause of the reduction in PLQY from C2 to C3. H-aggregate like effects have been seen in the pure film of C2 and C3, likely causing the reduction of PLQY in pure films, by means of reducing radiative decay rate. When the emission of solutions have been compared to those in the solid state throughout this document, there has been an apparent suppression of the reduction in band gap along the series C1, C2, C3. This lack of change in solid state band gaps is what this section deals with.

It has been suggested throughout that the reason for the lessening of change, of the emission band gap, in the solid state, is due to steric effects for doped film and H-aggregation for pure film. The data, however, has been presented in a piecemeal fashion. This has been due to the complexity of presenting a large amount of interconnected data in a way which is understandable to the reader. It is felt that this section is necessary in order to collate the information which has been presented.

To begin with, the absorption and PLQY of pure film will be compared with the solution spectra (see 3.17). While the absorption is red-shifted in both solution and pure film for C1 and C2 for all spectra, this effect seems reduced in the solid state. For pure film this has been assigned as likely being due to H-aggregation, because of the concomitant reduction in PLQY (see figure 3.17), reduction in pulse fluorescence rate (see figure 4.9) and red shifting of the emission of pure film, relative to doped film (see figure B.12). The C3 absorption has been assigned as being dominated by the CBZ-TRZ charge transfer state due to similarity in molar absorption coefficient, and toluene absorption peak (see section 3.3.2)

For doped film, while the absorption spectra is impossible to interpret due to an artefact from the films thickness¹² (see figure 3.8), the emission and PLQY can

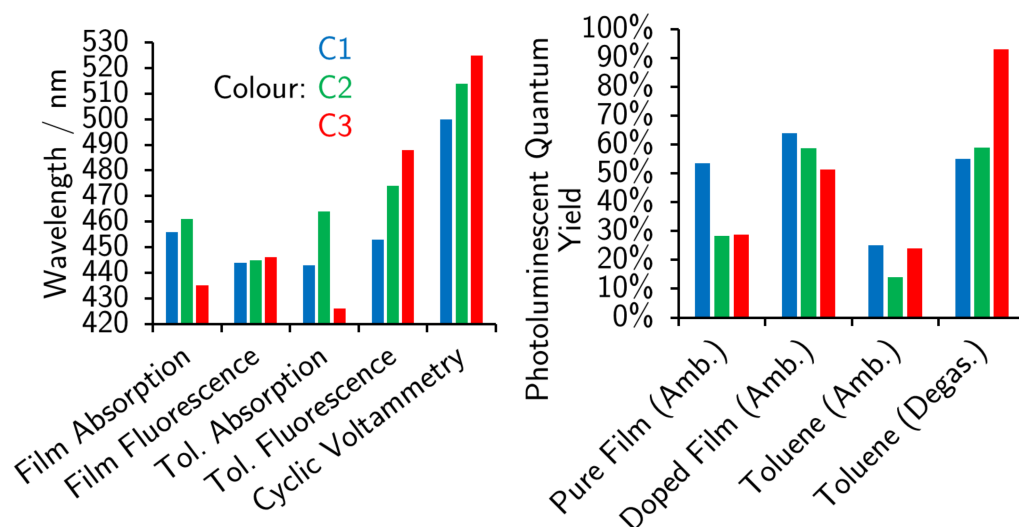


Figure 3.17: A comparison of the onsets of fluorescence (of doped film for film) and absorption (of pure film for film, see section 3.3.1), and calculated cyclic voltammetry equivalent (left) and PLQY of C1-3 in toluene in ambient (Amb.) and degassed (Degas.) conditions and C1-3 10 % doped in H1 (right).

be compared. The reduction in PLQY along the series C1–3, is much less than in pure films (see figure 3.17) suggesting the H-aggregation is suppressed or eliminated. Despite the suppression of H-aggregation, the shift in the emission of the compounds has significantly reduced shift along the series C1–3 relative to solution. This is despite solution spectra, phosphorescence spectra (see section 3.3.3), cyclic voltammetry (see section 3.2) and polarity changes (see 3.4) suggesting that there is increased delocalisation along this series.

The observation of a strong reduction in band gap in all solution spectra, but not doped film, suggests electronically there should be a more significant narrowing of the band gap along this series. The only explanation that seems possible is sterics. This steric effect is likely from the added bulk of the tBU-CBZ groups preventing the geometric relaxation of the excited state. This will be supported by the computational section of this thesis (see chapter 5), where it will be shown that these compounds naturally change geometry in the excited state, between two yet defined geometries. Further the unlikeliness of the results being electronic in nature is further discussed in section B.3.1.4.7.

3.4 Spectra Of Components

The changes which occur in the compound C1–3 upon S_1 excitation and emission have now been quite thoroughly investigated. The general narrowing of the band gap has been discussed, as has the suspected narrowing of the singlet-triplet energy

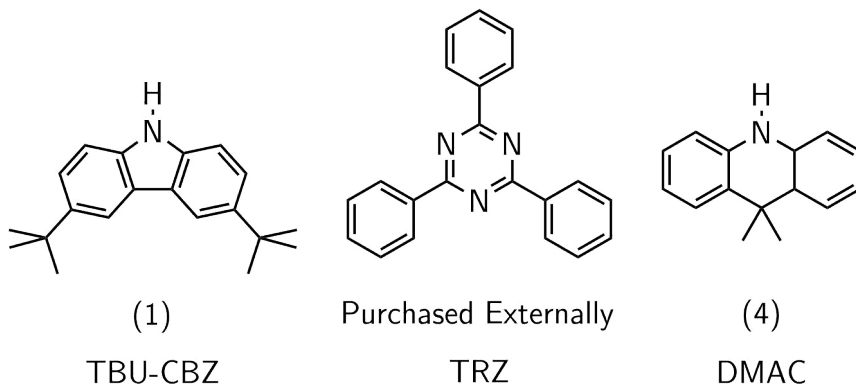


Figure 3.18: The components of the molecules C1–3 which are studied in this chapter. The names and the reaction from which they are obtained are listed below. Refer to section 2.2 for reactions

gap, the changes in polarity, the H-aggregation properties of the pure film of C2 and C3, as well as the apparent blocking of conformational relaxation in C2 and C3.

The S_1 state is not the only state relevant to TADF however. As has been discussed in the introduction (see section 3.1 and figure 3.2) and the general thesis introduction (see section 1.3.3) in order for the reverse intersystem crossing from T_1 to S_1 to occur, which is so fundamental to TADF, El-Sayed’s rule must be broken. In order to break El-Sayed’s rule, mixing or coupling to nearby states is necessary. For these states to mix or couple, their triplet states must be close in energy to the lowest energy triplet state. In order to estimate the location of these singlet and triplet states the photoluminescence of the component molecules can be measured at 77 K. This is what will be discussed in this section. It will be tentatively suggested that DMAC has the lowest energy triplet state, although the clarity of the data will be found wanting.

Herein “components” are defined as the units likely to be orthogonal in the structures presented and hence forming discrete un-mixing units of conjugation. Computational structures and crystal structures of similar molecules (see section 5.2) are used as a basis for this. The components used herein are shown in figure 3.18. It is perhaps notable the three phenyl groups attached to the triazine are included in the Trz component; this is because computationally and crystallographically (in a similar molecule) they are relatively planar, which is rationalised herein because they lack the usually ortho-ortho C-H steric restriction of phenyl-phenyl and phenyl-heterocycle connections (see figure 3.19).*

Firstly the absorption and fluorescent emission will be discussed, these are detailed in figure 3.20. The exciton dependence is shown in figure B.34. No fluorescent emission was visible for Trz. While tBu-Cbz gives a quite conventional

*Conventionally the lone pair on the triazine nitrogen may be considered to cause steric repulsion. This is further expanded on in section 5.2

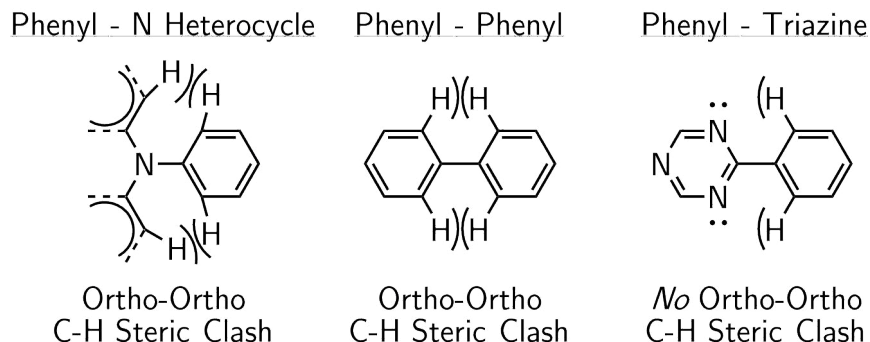


Figure 3.19: A demonstration of the likely reason for planarisation of phenyl groups with triazine, and not other groups.

emission spectra, independent of concentration and with no excitation dependence, in DMAC excitation dependence is seen. It is unclear qualitatively whether the excitation dependence is due to excitation of differing states, or due to the excitation of an impurity. It is normally expected that Kasha's rule is followed. As such, it is taken that the difference is due to an impurity. In order to excite the maximum amount of the desired compound, the results with the main absorption peak excited will be used. It should be noted, however, that at lower excitation energies, there is a lower emission peak. The spectra resulting from excitation of the main peak is, as a result, the only one included in this section of the thesis. It should be noted that while in other sections it is claimed that there are up to three geometries of DMAC, each emitting differently, this is unlikely to be the cause of these effects, since the spectra are taken in solution, allowing for these structure to interconvert.

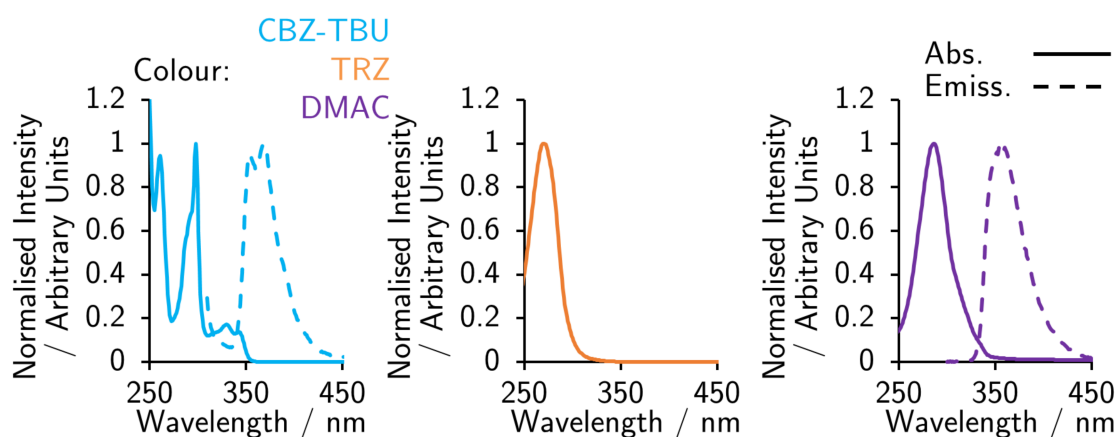


Figure 3.20: The absorption and emission spectra of the components at room temperature in 100 μM solutions of 1:1 diethyl ether:ethanol. Excitation was done at 300 nm, and 285 nm for tBU-CBZ, and DMAC respectively.

The phosphorescent spectra are now considered (summarised in figure 3.21), with excitation dependence shown in figure B.35. tBU-Cbz is seen to have emission almost coincidental to its fluorescent emission, it is thusly concluded either the

triplet singlet energy gap is very small so as to make them appear coincidental *ie.* TADF occurs from a CT state, or the phosphorescence is not observed. A slight blue shift is also observed, but it is unclear whether this could be due to noise, or the differing emission of molecules in the main band. A final possibility is that it may be due to differing slit widths. DMAC has a clearer emission peak, although the onset is made less clear at higher excitation. It is believed this may be due to the impurity which may be present and the lower excitation is used, as such the low excitation value is shown here. Trz also has an excitation dependence, with much higher energy emission seen at higher excitations. Tentatively the lower energy peak visible at lower energy excitations is chosen as correct, as the excitation corresponds to a peak in absorption, and hence is most likely from the desired compound.

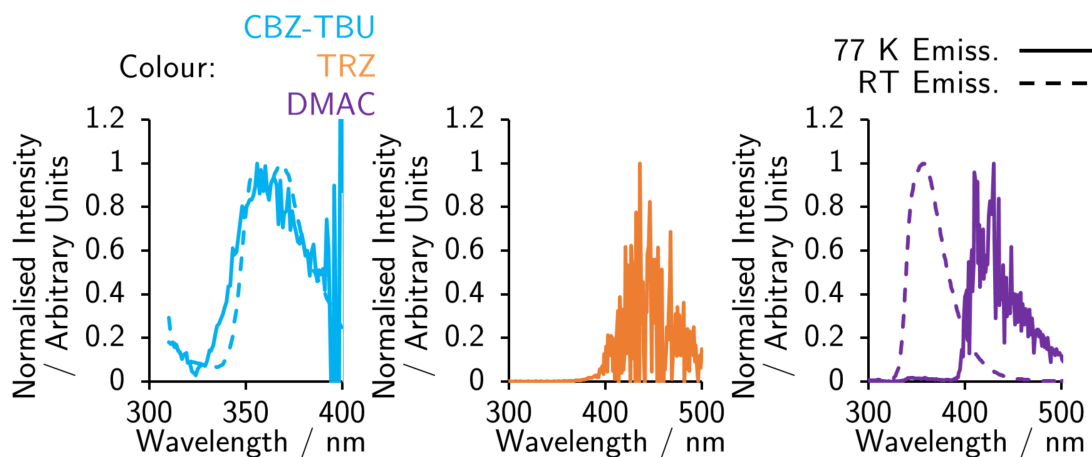


Figure 3.21: The room temperature and 77 K emission spectra of the components at room temperature in 100 μM for DMAC and tBU-CBZ and 10 μM for trz, solutions of 1:1 diethyl ether:ethanol. 77 K spectra obtained after a 200 μs delay with spectra then averaged over a period before re-exciting. Excitation was done at 300 nm, 270 nm, and 285 nm for tBU-CBZ, TRZ, and DMAC respectively.

The onsets of the phosphorescent spectra are shown in figure 3.22 and calculated in figure B.36. It is noted that DMAC has the lowest energy onset. Further even if the assertion regarding Trz, that the lower energy phosphorescence emission is correct, is wrong, this still holds. However if the assumed result for DMAC is wrong where the phosphorescent emission at lower energy excitation is believed to be incorrect, the result is invalidated. The results do hint towards the DMAC ^3LE state being the most likely excited state to be involved in the emission.

Due to the unusual fluorescence properties of these compounds, any conclusions drawn from them will be tentative at best. Due to the poor quality of these results, it is debatable whether they should be part of this thesis; they are included herein, in order to show the reader that these measurements have been attempted, more than for the conclusions drawn from them.

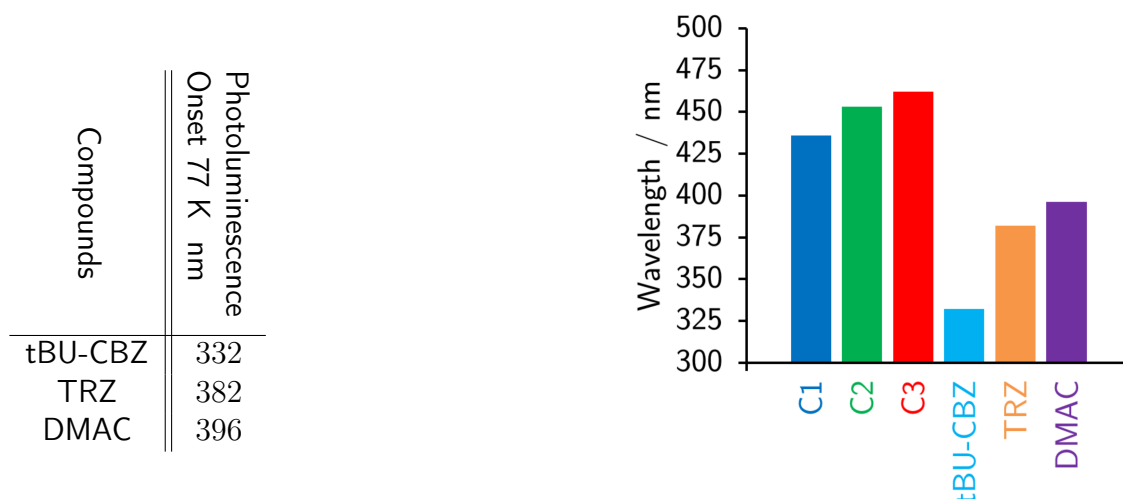


Figure 3.22: A table of the onsets of photoluminescence at 77 K for each compound, as calculated in figure B.36 and a graphical comparison to the onset acquired for the compounds of interest for this chapter.

3.5 Thermal Properties

While all the previous information provides a good understanding of the photo-physics of the system, and shows that the molecules likely are TADF active, and so suitable for OLEDs, the results do not show that morphological and chemical stability of the films is sufficient for devices. In order for these results to be discussed the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) must be examined. What will be reinforced (particularly for TGA) is that the change is greatest for $C1 \rightarrow C2$ and smaller for $C2 \rightarrow C3$.

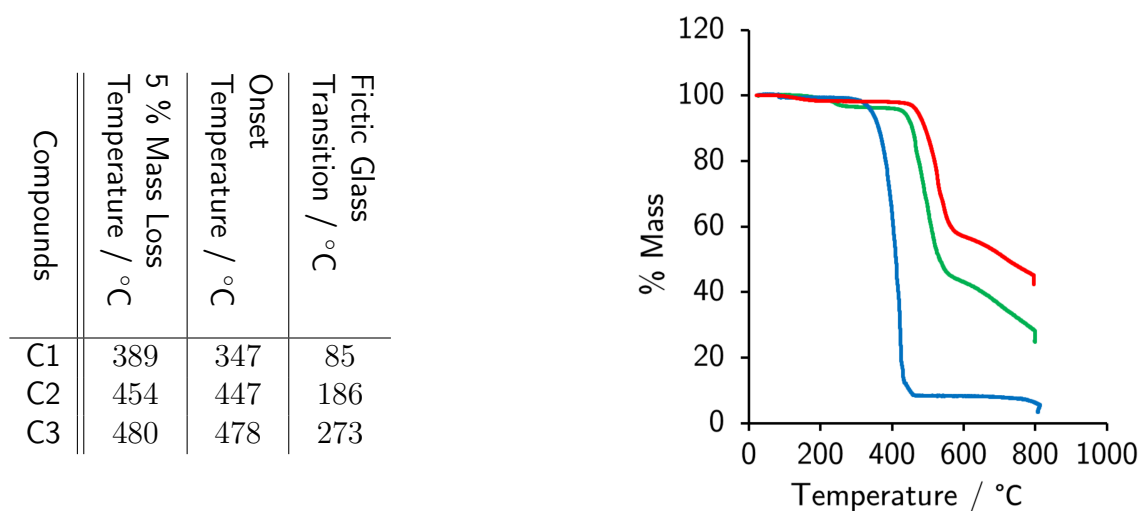


Figure 3.23: A table of the onsets of photoluminescence at 77 K for each compound, as calculated in figure B.36 and a graphical comparison to the onset acquired for the compounds of interest for this chapter. The average fictic glass transition, is also shown from all discernable runs

TGA measured the mass loss on heating of the molecules and the results for C1–3 are shown in figure 3.23 with the tabulated onsets of degradation. What is observed is a general stabilisation of the compounds along the series C1–3 and high stabilities throughout. This is assigned as being due to the sterics of tBU-CBZ blocking interactions and degradation processes. This stabilisation is surprising based on the electronic characteristics of these molecules; as previously discussed (see section 3.2) the ionisation energy and the electron affinity are increased when carbazole is added. It might be expected based on these changes that degradation would be easier, as it is easier to take electron off the molecules, as well as add them, since this is not observed, it is believed the effects are most likely sterics. Note this sterical effect may be either from blocking the pathway to degradation, or the increased delocalisation preventing the desired reaction, due to the change in shape this causes. This change appears greatest for C1 $\rightarrow$ C2, consistent with earlier results, and suggesting that DMAC may be key in the degradation, since this is where carbazole is added. The onset of decomposition is high in each of these compounds, and so they seem suitable for devices.

The DSC measurements are somewhat harder in principle to interpret than TGA data. This is because a variety of different features are shown via this method. However of highest interest to devices, is the lowest temperature at which a morphological change takes place; this is because it is at this temperature morphological change can change devices. In each case glass transitions are the first observed morphological change, and these are tabulated in figure 3.23.* There is a general increase in the glass transitions, and this can be explained by the increased size of the molecules, causing more steric blocking of the vibrational modes. In all cases the transitions are sufficiently high to not worry about this morphological change in standard devices operation, although C1 falls rather close.

3.6 Conclusion

C1–3 have been investigated by means of cyclic voltammetry, absorption and fluorescence spectra of films and solutions, emission of frozen solution at 77 K, DSC, and TGA. Key characteristics apparent from these measurements are a general narrowing of the energy gap along the series C1–3, apparently most prevalent for C1 $\rightarrow$ C2. This narrowing of the energy gap is somewhat undesirable, as it means moving away from the most desirable blue coloured OLED, to the less desirable green OLED. Along with this narrowing there is an apparent increase in the change in polarity upon excitation and a suggested reduction in the singlet-triplet energy gap. While

*The "fictic" glass transition is used, as it is the best guess for the location of the "thermodynamic" glass transition.³⁰

this change in the energy gap would seem desirable, as it in theory should increase the rate of reverse intersystem crossing, the desired effect is not observed in film *photoluminescent quantum yield (PLQY)*. This is rationalised as due to a concomitant reduction in emission rate, allowing for a greater ratio of non-radiative decay. This simultaneous proposed reduction in emission rate, narrowing of the singlet-triplet energy gap, and narrowing of the energy gap, is consistent with the greater separation of the electron donating and accepting parts of the molecules, with additional tBU-CBZ, in turn consistent with the donating and accepting wavefunctions spreading onto tBU-CBZ.

The reduction in the singlet-triplet energy gap is not explicitly shown here-in via means of spectral observation. The photoluminescence spectra at 77 K (commonly referred to as phosphorescence spectra) in fact suggests an increase in singlet triplet energy gap. However it is noted that the measured triplet energy for C1 is rather different from literature values, and that for C2 and C3 the results are inconsistent with almost all other results. It will be shown in the subsequent chapter that the rate of decay for C2 and C3 are inconsistent with a large singlet-triplet gap, having not been quenched at 77 K. Further it will be shown that when the compounds are simulated computationally, the singlet-triplet gap is generally reduced along the series C1–3.

Further observations are the poor PLQY of pure films of C2 and C3, assigned as most likely being due to H-aggregation and the suppression of energy levels shifts in the solid state photoluminescent emission spectra of C2 and C3 in doped films. This suppression in energy shifts is assigned as being due to a blocking of relaxation due to sterics. Finally, there was an observed increase in thermal and morphologically stability along the series C1–3. The cause of the H-aggregation in pure films is much harder to narrow down to a single cause.

Overall the effects of the addition of carbazole to DMAC-TRZ core are seen to be somewhat detrimental to the overall efficiency of the resulting compound for TADF. The molecules become less efficient, of longer wavelength, and become impractical to form pure films out of. However, these downsides are not sufficient to rule them out of devices and there are upsides of increased morphological and thermal stabilities. Further the additional mass imbued by the additional tBU-CBZ groups likely improve solution processing.

While the topics of geometry and exciton lifetime of these compounds has been touched upon in this chapter, they have not been fully explored. Both of these are highly relevant to how these compounds behave, both theoretically and in devices. With exciton lifetime, it is broadly excepted that the roll-off³¹ and degradation^{32,33,34} of devices is related to how long excitons last in devices. For the geometry of the

compounds, while it has previously been noted that conformational change appears blocked in C2 and C3 in films, the precise mechanism has not been discussed. This mechanism is important, as it may generalise to all molecules which include DMAC in them, or with DMAC like structures. The geometry of these compounds, along with ab initio calculations will be explored in chapter 5

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Chapter 4

Transient Fluorescence And The Interpretation With Fast RISC

*"Question everything.
Learn something.
Answer nothing."*

—Euripides

As has been stated in the introduction to this part of the thesis, the results on DMAC-TRZ are split into 3 chapters, the general characterisation, the computational study and the transient fluorescence. All these chapters are on the same set of molecules (see figure 4.1). It has also been stated that the reader can either start with the computational chapter or the general characterisation chapter. This chapter however builds largely on the information in the general characterisation, so it is vital that this is read first.

In this chapter the transient fluorescence data will be discussed, as well as the fitting of said data and its interpretation. It will be found that the current most common methods of fitting and interpretation are not sufficient to analyse these molecules, and recommendations will be made for change in methodology. While it will be found beyond the scope of this thesis to fully integrate the newly proposed methods, it is hoped that others will carry on this work.

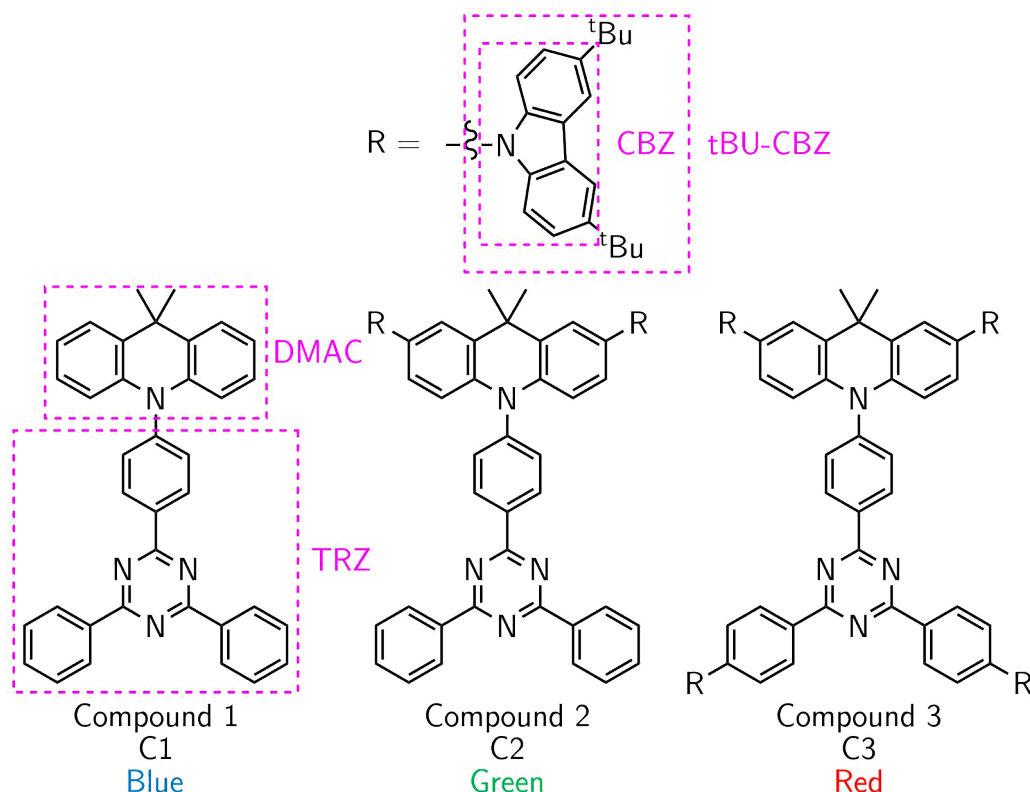


Figure 4.1: The structures of the compounds discussed, the components which make them up and the names and colours which correspond to them.

4.1 Introduction

Transient fluorescence is a study of how the emission of a molecule changes with time. It involves exciting the molecule with a short laser pulse at a given frequency and then detecting the output light at different times. Transient fluorescence is widely considered to be a measure of the lifetime of excited states in a molecule which is important for TADF, as long lived excited states are often linked with detrimental processes. Long lived excited states are usually thought to increase the degradation of compounds^{1,2,3} and reduce the efficiency at high currents⁴ (i.e. the roll off). The mechanism for this is usually the formation of high energy species via various bi-exciton elimination processes (i.e. singlet-singlet, triplet-triplet or singlet-triplet annihilation) or exciton-polaron elimination processes.

The study of transient fluorescence in molecules which undergo *thermally activated delayed fluorescence* (TADF) is itself rather complex. This complexity results from the variety of processes which can occur in TADF molecules which to first approximation are those summarised in figure 4.2. In this figure k_{s-nr} , k_{s-r} are the radiative and non-radiative decay rate respectively of singlets, k_{t-nr} , k_{t-r} are the same for triplets, k_{ISC} the intersystem crossing rate and k_{RISC} the reverse intersystem crossing rate. These processes lead to the following set of differential equations

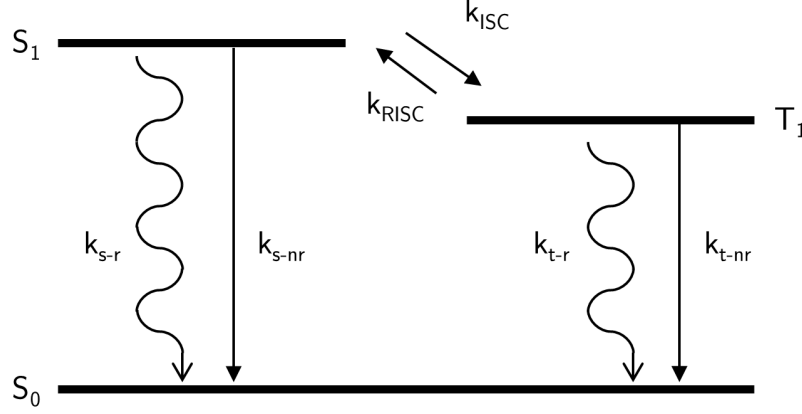


Figure 4.2: The constants which principally effect TADF, where ISC is "intersystem crossing" and RISC is "reverse intersystem crossing", s-r is radiative singlet decay, s-nr non-radiative, and similarly for t-r and t-nr for triplets. In this diagram the states shown strictly correspond to all the vibrational and rotational states within a electronic state. Excited vibrational states (hot states) will naturally have influence on the rates of all transitions.

with the symbology previously listed, and $[S_1]$ the concentration of excitons in the S_1 state, $[T_1]$ the concentration of excitons in the T_1 , at t the time:

$$\frac{d[S_1]}{dt} = -(k_{s-nr} + k_{s-r} + k_{ISC})[S_1] + k_{RISC}[T_1] \quad (4.1)$$

$$= -(\bar{k}_S + k_{ISC})[S_1] + k_{RISC}[T_1] \quad (4.2)$$

$$= -k_S[S_1] + k_{RISC}[T_1] \quad (4.3)$$

$$\frac{d[T_1]}{dt} = -(k_{t-nr} + k_{t-r} + k_{RISC})[T_1] + k_{ISC}[S_1] \quad (4.4)$$

$$= -(\bar{k}_T + k_{RISC})[T_1] - k_{ISC}[S_1] \quad (4.5)$$

$$= -k_T[T_1] - k_{ISC}[S_1] \quad (4.6)$$

While it is expected that the definitions of $\bar{k}_S$, $\bar{k}_T$, k_S and k_T are obvious, they are defined explicitly below. Effectively k_S and k_T are the rates of decay processes for singlet and triplets respectively with TADF (note this neglects formation of singlets and triplets from each other), and $\bar{k}_S$ and $\bar{k}_T$ are the decay process "bar" the TADF processes.

$$\bar{k}_S = k_{s-nr} + k_{s-r}; \bar{k}_T = k_{t-nr} + k_{t-r} \quad (4.7)$$

$$k_S = k_{s-nr} + k_{s-r} + k_{ISC}; k_T = k_{t-nr} + k_{t-r} + k_{RISC} \quad (4.8)$$

This set of differential equations has* been solved to give the following equations for pulse and delayed fluorescence.^{5,6,7,8}

$$[S_1] = (a_{PF} e^{-k_{PF}t} + a_{DF} e^{-k_{DF}t}) \quad (4.9)$$

$$k_{PF}, k_{DF} = \frac{k_S + k_T}{2} \left(1 \pm \sqrt{1 + 4 \frac{k_{ISC}k_{RISC} - k_S k_T}{(k_S + k_T)^2}} \right) \quad (4.10)$$

These equations are themselves rather hard to interpret qualitatively. Further when it is considered that the decays are fit to an equation of the form of equation 4.9, it can be observed that fundamentally an equation of 6 variables (see eq. 4.8 and 4.10) is being fit to an equation with 4 parameters. This discrepancy in degrees of freedom leads to an inevitable degree of hand-waving. The full equation also requires the total light emitted to be measured which is rarely done in practice, reducing the number of real parameters to 3. It is possible, in principle, to relate the PLQY to these parameters, increasing the amount of parameters fit back to 4, but this is still not sufficient to solve these equations.

In order to try to interpret these equations further, it is common to take limiting cases of these equations. The method in the highest cited review on TADF⁵ involves assuming $k_{s-nr}, k_{s-r}, k_{ISC} \gg k_{t-nr}, k_{t-r}, k_{RISC}$ leading to the following equations.

$$k_{PF} = k_S \quad (4.11)$$

$$k_{DF} = k_T - \left(\frac{k_{ISC}}{k_S} \right) \quad (4.12)$$

While these assumptions may be commonly expected in TADF, with the compounds studied herein they are unsuitable. This unsuitability stems from the lack of quenching in TADF upon cooling to 77 K as will be shown in this section. TADF is normally quenched when cooled to 77 K due to a reduction in k_{RISC} which requires thermal activation. According to Marcus theory (See any physical chemistry text book) the value of k_{RISC} is related to the value of k_{ISC} via the following equation, where ΔE_{ST} is the singlet-triplet energy gap, T the temperature, and k the Boltzmann constant.[†]

$$k_{RISC} = k_{ISC} e^{\frac{-\Delta E_{ST}}{kT}} \quad (4.13)$$

*A slightly different formulation is shown here, which may be trivially converted to those in the cited papers

[†]In principle this gives another degree of freedom from which to interpret the decay, but not a sufficient number to solve it.

In this equation k_{ISC} is usually treated as a constant (vibronic coupling or a large activation energy may break this approximation) and so in order for there to be little reduction in k_{RISC} when cooling, $kT \gg \Delta E_{ST}$. This means $k_{ISC} \approx k_{RISC}$, breaking one of the key tenants of this approximation.

Recent research⁹ has suggested that $\bar{k}_S$ competes with k_{ISC} , in some systems, which is problematic since simple limiting cases exist for either $k_S k_T \gg k_{ISC} k_{RISC}$ and $k_S k_T \approx k_{ISC} k_{RISC}$ (see sections B.3.2.2.1 and B.3.2.2.2). It is believed this is the first time the later limiting equation has been published in the field of TADF. As a result the only reasonable inequality would seem to be $\bar{k}_S \gg \bar{k}_T$. Which does not allow for much simplification of the equations shown.

Hence in this document, it is felt that the only way forward is to work with the whole of equation 4.10. It is also felt that while often only the time constants are compared for TADF molecules, the relative intensities of pulse and delayed fluorescence should be compared. This chapter contains initially work to understand these equations in the subsequent section.

Finally while all of this work is based on the processes shown in figure 4.2, additional processes can occur. At large exciton concentrations bi-exciton processes such as triplet-triplet annihilation (TTA) singlet-triplet annihilation (STA) and singlet-singlet annihilation (SSA) become significant. These processes are rarely included in the fitting of TADF data, although there has been some progress in this direction⁶ at the limit of slow ISC and RISC.

4.2 Interpretation Of Equations

As has just been discussed, TADF transient decays are usually interpreted using simplified forms of the basic TADF equation.^{5,6,7,8} Because there is hence no appropriate method to interpret the equations, it was decided a new approach must be taken. The TADF decay was originally solved by Berberan-Santos et al.⁸ with maths based on excimer kinetics. Usually it is considered that the rate constants are of greatest importance when interpreting these equations. The calculated rate constants are as follows:

$$k_{PF}, k_{DF} = \frac{k_S + k_T}{2} \left(1 \pm \sqrt{1 + 4 \frac{k_{ISC} k_{RISC} - k_S k_T}{(k_S + k_T)^2}} \right) \quad (4.14)$$

It should be noted that these rate constants are generated when phosphorescence is included in the decay. As such, for a selection of identical molecules with active TADF and phosphorescent pathways, only two exponential decays should be observed. This is despite it being commonly claimed that additional decays within the

data are from phosphorescence.^{10,11} However this assertion is not necessarily wrong; the additional decays could be from sets of molecules which are not TADF active. It is unclear what influence this self selection would cause.

An additional observation is that the sum of the pulse fluorescent rate, and the delayed fluorescence rate yields the sum of all processes which occur in TADF, ie.

$$k_{PF} + k_{DF} = k_S + k_T \quad (4.15)$$

The rate constant is not the only observable which can be extracted from the transient photoluminescent decays of TADF compounds. Figure 4.3 shows an ideal TADF decay, and the additional information which can be extracted from it. Decay rates, relative areas and relative starting intensities may be extracted using fitting, and the photoluminescent quantum yield may further give information on the decay. While these values are inter-related, with areas and PLQY being obtainable by integrating the decay, the information still aids the assignment of changes in the fundamental constants which define them, since the degree with which change in decay rate and starting intensity cancels each other out in the area calculations serves as a test of which parameter changes.

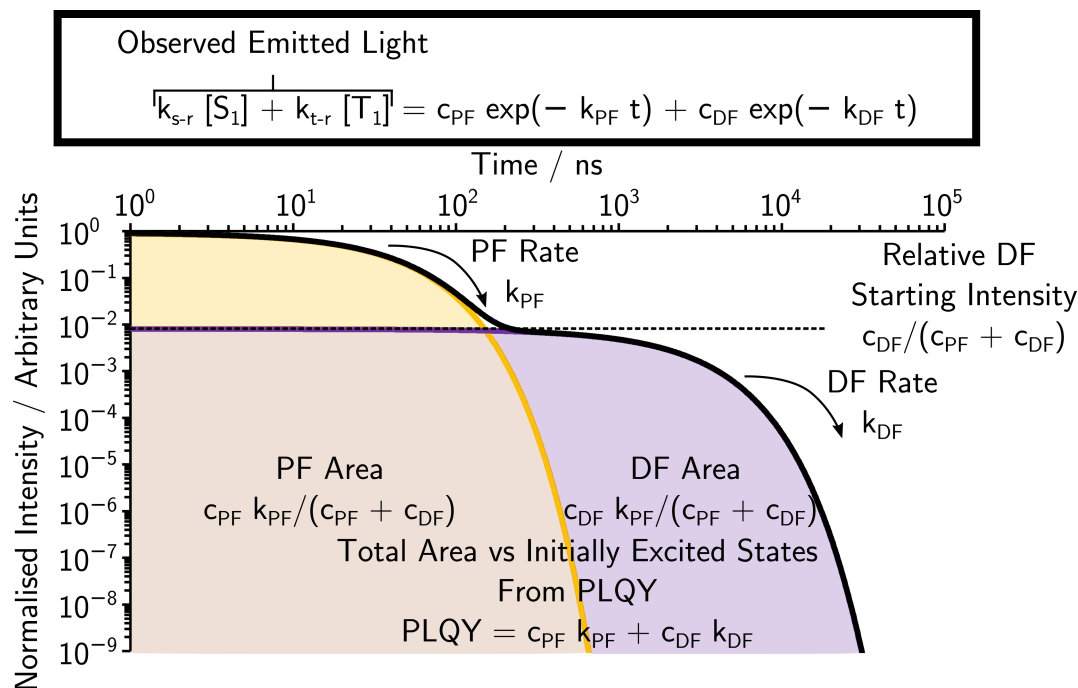


Figure 4.3: The parameters from the fit. Note: Fits are usually normalised resulting in the $(c_{PF} + c_{DF})$ normalisation parameter.

It may be shown that the starting intensities (I_{PF} , I_{DF}) are given by the following equation (See section B.3.2.1 for proof from equations from Berberan-Santos et al.⁸):

$$I_{PF} = \frac{c_{PF}}{c_{PF} + c_{DF}} = \frac{k_{s-r} \left(\frac{k_S - k_T}{2} \right) \left(1 + \sqrt{1 + 4 \frac{k_{ISC} k_{RISC}}{(k_S - k_T)^2}} \right) - k_{t-r} k_{ISC}}{k_{s-r} (k_S - k_T) \sqrt{1 + 4 \frac{k_{ISC} k_{RISC}}{(k_S - k_T)^2}}} \quad (4.16)$$

$$I_{DF} = \frac{c_{DF}}{c_{PF} + c_{DF}} = - \frac{k_{s-r} \left(\frac{k_S - k_T}{2} \right) \left(1 - \sqrt{1 + 4 \frac{k_{ISC} k_{RISC}}{(k_S - k_T)^2}} \right) - k_{t-r} k_{ISC}}{k_{s-r} (k_S - k_T) \sqrt{1 + 4 \frac{k_{ISC} k_{RISC}}{(k_S - k_T)^2}}} \quad (4.17)$$

While figure 4.3 shows the area calculated from the normalised decay, what is really of interest is the relative area of delayed (A_{DF}) and pulse regions (A_{PF}). This is because only the relative areas are actually known, since only a small sample of the emitted light is collected. The formulas for this are shown as follows:

$$A_{PF} = \frac{1}{2} + \frac{k_{s-r} k_T (k_S - k_T) - k_{ISC} (2k_{RISC} k_{s-r} + k_{t-r} (k_T + k_S))}{(2k_{t-r} k_{ISC} + 2k_{s-r} k_T) (k_S - k_T) \sqrt{1 + \frac{k_{ISC} k_{RISC}}{(k_S - k_T)^2}}} \quad (4.18)$$

$$A_{DF} = \frac{1}{2} - \frac{k_{s-r} k_T (k_S - k_T) - k_{ISC} (2k_{RISC} k_{s-r} + k_{t-r} (k_T + k_S))}{(2k_{t-r} k_{ISC} + 2k_{s-r} k_T) (k_S - k_T) \sqrt{1 + \frac{k_{ISC} k_{RISC}}{(k_S - k_T)^2}}} \quad (4.19)$$

And the photoluminescent quantum yield (PLQY) by the following equation:

$$PLQY = \frac{k_{t-r} k_{ISC} + k_{s-r} k_T}{k_T k_S - k_{ISC} k_{RISC}} \quad (4.20)$$

$$= 1 - \frac{k_{t-nr} k_{ISC} + k_{s-nr} k_T}{k_T k_S - k_{ISC} k_{RISC}} \quad (4.21)$$

Of course each of these equations is fairly uninterpretable. A process of taking partial derivatives of them, to see if they increase or decrease with certain parameter changes was attempted, the results were no easier to interpret than the starting equations. To attempt to understand the equations, the equations were plotted for several test functions as shown in section B.3.2.3. The reason why the test functions are chosen is in part based on the breakdown of the function shown in figure 4.4. Further it is noted that the function $k_{ISC} k_{RISC}$ appears to turn TADF on and off. It is felt this is the minimum amount of graphs which are needed in order to interpret the data, for example it is noted a pure increase in k_{s-nr} gives an increase in $k_S + k_T$ and a decrease in k_{s-r} , k_{t-r} , $k_{t-nr} + k_{t-r}$, $k_{ISC} k_{RISC}$ and k_{RISC} at constant $k_S + k_T$. As such it is unique in the changes predicted. However, as previously noted, since

we are fitting to 4 variables, with a system of 6, this will not lead to a certain assignment.

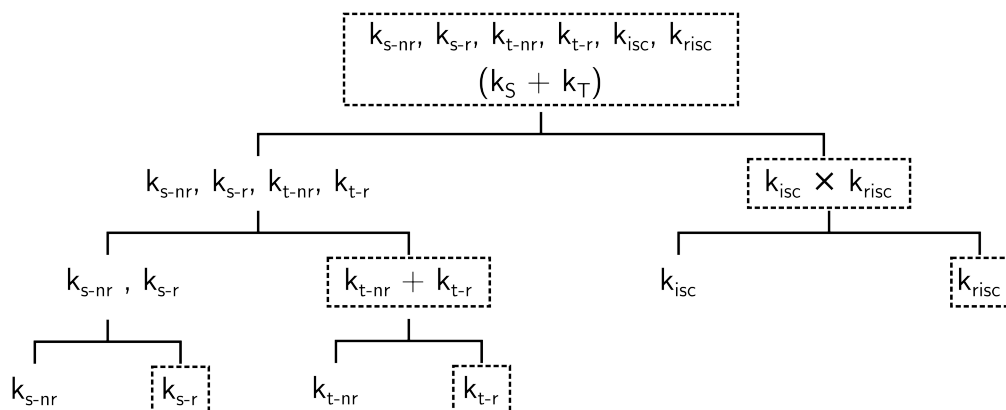


Figure 4.4: The breakdown of the functions dictating decay rate, area, intensity and photoluminescent quantum yield for prompt and delayed fluorescence regions.

Within table 4.1 some parameters only change when there are large in proportion of the total decay (labelled "High") and others only when they are low (labelled "Low"). Of particular note are the changes dependent on the triplet decay rate ($k_{t-nr} + k_{s-nr}$), as this is hardly ever large in comparison to the other decay constants, these will be ignored. It is felt that the only way to interpret the changes between values is by using this table, and matching changes. This will be how this document will continue.

It should be noted that the results from this table cannot be used to assign changes with 100 % accuracy. The face 6 variables are being measured by 4 parameters prevents this. However it is possible to say that the results are consistent or inconsistent with a previous hypothesis, and this does support the results if they are consistent.

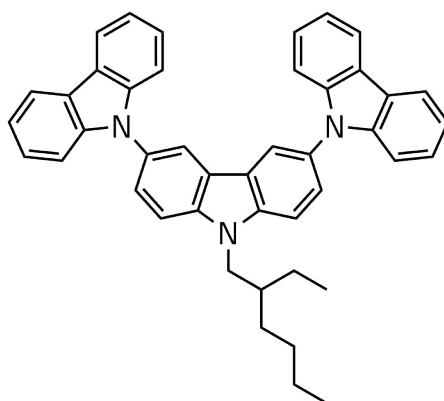
Table 4.1: The changes observed in transient fluorescence when changing certain parameters of the TADF decay. This summarises the data shown in section B.3.2.3

Changed Parameter With Varied $k_S + k_T$	PF Rate	DF Rate	DF % Area (A_{PF})	DF % Initial Intensity (I_{DF})	% PLQY
$\uparrow k_S + k_T$	$\uparrow$	$\uparrow$	—	—	—
Changed Parameter With Constant $k_S + k_T$	PF Rate	DF Rate	DF % Area (A_{PF})	DF % Initial Intensity (I_{DF})	% PLQY
$\uparrow k_{ISC}k_{RISC}$	$\downarrow$ Low $\uparrow$ High	$\uparrow$ Low $\downarrow$ High	$\uparrow$	$\uparrow$	$\downarrow$
$\uparrow k_{RISC}$	$\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$
$\uparrow k_{t-r} + k_{t-nr}$	$\downarrow$	$\uparrow$	$\downarrow$ Low $\uparrow$ High ^a	— Low $\uparrow^a$ High	$\downarrow$
Changed Parameter With Constant $k_S, k_T,$ $k_{ISC},$ and k_{RISC}	PF Rate	DF Rate	DF % Area (A_{PF})	DF % Initial Intensity (I_{DF})	% PLQY
$\uparrow k_{s-r}$	—	—	$\downarrow$	$\sim \downarrow^b$	$\uparrow$
$\uparrow k_{t-r}$	—	—	$\uparrow$	$\sim \uparrow^b$	$\uparrow$

^aUnlikely since this only happens at high triplet rate in comparison to singlet rate.^bLittle change observed.

4.3 Results

A theoretical framework has just been shown for the interpretation of the transient decay data. In this section the actual results will be discussed within this framework. The work will be presented in sections corresponding to each compound order, along the series C1, C2, C3, with each compound being studied in pure film, 10% doped in H1 (see figure 4.5), and frozen solution (1 : 1 Ethanol : Diethyl ether) cooled to 77 K. Each compound will be compared to the previous one in the series (i.e. C3 to C2, and C2 to C1), so changes in value and how they relate to molecular structure can be compared.



Full name: 3,6-di(9-carbazolyl)-9-(2-ethylhexyl)carbazole
 Formal abbreviated name: TCz1
 Name herein: Host 1
 Abbreviated name herein: H1

Figure 4.5: The structure and naming convention of the host molecule used in this chapter. Different naming conventions are used in this document than in the literature, as it is felt that it helps the reader for names to follow application as opposed to structure or convention.

In this document the decays will be fitted to the equation 4.9 and interpreted via the use of the table shown in 4.1. The nature of the fitting procedure used is discussed in B.3.2.4. While this method of interpretation is not perfect, it is felt it provides a "best guess" within modern theory as to the changes between molecules. The rates of decay will be given as their time constants, related via the following equation. It is felt that time constants allow a more qualitative understanding of the system for the reader. The rate constants and the time constants will be swapped between freely, so it is advised the reader is careful about which is being discussed.

$$\tau = \frac{1}{k} \quad (4.22)$$

In the mixed films, it may be questioned what is emitting. It is shown in section

B.3.2.5 that the host is in fact excited at the used wavelenth. In addition, fluorescence may be observed in pure film. However, the pure host decay does have significantly different initial fluorescence, and does decays much faster than the compounds shown here-in. Therefore it will henceforth be assumed that the host emission is entirely quenched by exciton transfer to the TADF materials (C1–3).

4.3.1 Transient Emission Of Compound 1

Compound 1 is used as the starting point for looking into these molecules. This is because it has been studied by others and is a highly efficient TADF emitter.^{12,13} The structure of compound 1 is reiterated in figure 4.6. In this document, this compound has previously been studied and it was found that it behaved rather similar to most TADF emitters, i.e. emission occurred from a TADF state, and singlet-triplet energy separation was low but discernable (0.05 eV).

The compound has also been studied in the literature^{13,12}. It was found to have a prompt decay rate of 20.3 ns and 26.3 ns for doped and pure film respectively and delayed decay rate of 1.9 μ s and 3.6 μ s respectively. The results found herein are shown in figure 4.7 and are rather different from these values. It is unclear why this is the case but may be related to the use of single photon counting in the cited measurements as opposed to full spectrum graphing shown here, or the use of different fitting procedures,* or fitting using less of the decay. Indeed data is recorded herein on the timescale of 100 μ s and the data presented in the cited papers are on the order of 10 μ s. It is found herein (see B.3.2.4) curtailing the plot appears to shorten the time constant, so this may only really explain the doped film difference. Further the differing hosts in doped film will likely have an effect. It is further possible that the film formation conditions or purity could be responsible for this discrepancy, although this could not be experimentally determined.

In addition to the difference in decay constants, there is also a difference in the photoluminescent quantum yield (PLQY) shown in figure 4.7. It has previously been discussed in section 3.3.4 that this is most likely due to the PLQY being taken in ambient conditions here, and in de-oxygenated condition in the literature. It was assumed then, as a crude approximation, that upon degassation a constant PLQY is added across all species, this is once again used.

*fitting procedure is not specified in cited document

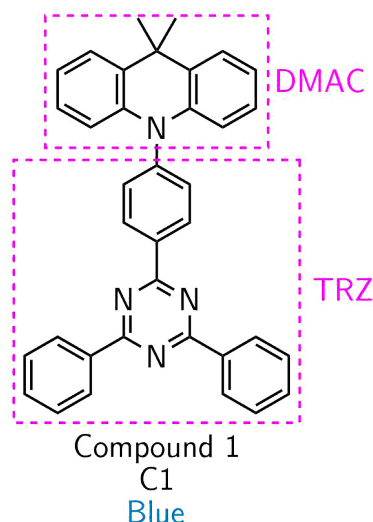


Figure 4.6: The structure of compound 1 with the components labelled.

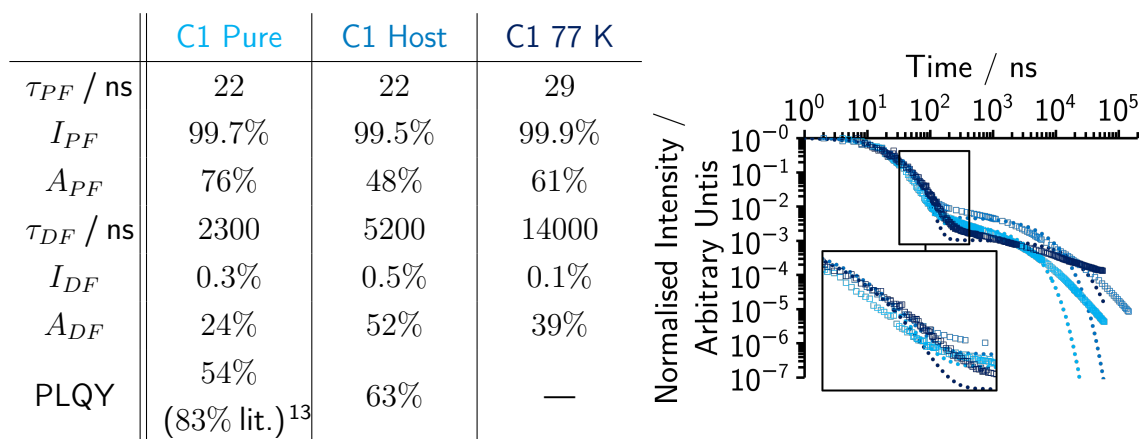


Figure 4.7: The transient decays of C1 (hollow squares) the fit (solid circles) and a table of the parameters taken from the fit. An enlarged version of the decays are shown in section B.3.2.6.

Table 4.2 shows the parameters obtained for C1. In order to try to interpret the changes, the characteristic changes in parameters in table 4.2 are compared with those for varying the single parameters listed. In going from C1 in host (C1-H) to C1 in pure film (C1-nH i.e. no-host) and starting from the top of table 4.2, first $k_s + k_t$ may be compared to. There is a observed increase in overall sum of rate constants (i.e. $k_s + k_t$) due to the increase in PF rate and DF rate. However this change is in reality likely within error (Note that τ_{PF} is many orders of magnitude shorter than τ_{DF} , also note equation 4.15). The change in the ratio of $k_{RISC}k_{ISC}$ is rather indeterminable, not strongly matching with the changes observed. For the change (C1-H) to (C1-nH), there does seem likely an increase in the triplet decay rate, most likely the non-radiative decay rate. This is what would be expected for compound with a lack of host, since the lack of separation may increase the

likelihood of the compounds interacting with themselves or excitons eliminating.

For sample at 77 K (C1-77 K), it was felt that comparing the cooled sample to doped film was most appropriate, because in both cases the films are held in a lattice. In the study of TADF, when a compound is reduced in temperature, what is normally expected is that the reverse intersystem crossing rate decreases. This decrease is due to the dependence on thermal energy expressed in equation 4.13. When the results are compared we see the change is easiest to assign with a reduction in the overall rates ($k_S + k_T$) and a reduction in the ratio of $k_{ISC}k_{RISC}$ rate to the overall rate of k_{RISC} . It seems highly likely based on these results that the k_{RISC} rate is reduced on cooling. Note this is consistent with a measurable difference in the singlet and triplet energy and so inconsistent with previous photoluminescent spectra at 77 K ie. "phosphorescence spectra" see section 3.3.3.

4.3.2 Transient Emission Of Compound 2

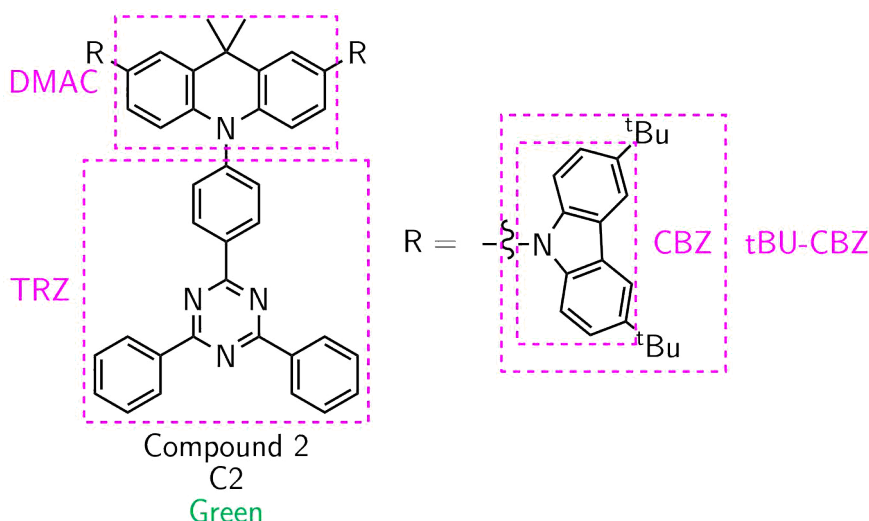


Figure 4.8: The structure of compound 3 with the components labelled.

It has just been assigned for C1 that the change on going from pure film to doped film is most consistent with increased triplet non-radiative decay, and when cooled to 77K decreased RISC rate. Here C2 will be examined. For simplicity, the results of compound 1 and 2 will be compared in blends with the host (H) directly, corresponding to the "ideal" TADF emission conditions. Subsequently the results of C2 in pure film (nH) and cooled to 77 K will be compared only to C2 in doped film.

Relative to C1, compound 2 (shown in figure 4.8) has previously been shown (section 3) to have all the characteristics of increased separation of donating and accepting wavefunctions with the exception of a decreased singlet-triplet energy

Table 4.2: The changes in decay parameters with changed environment of C1, compared with the changes observed in transient fluorescence when changing certain parameters of the TADF decay. Assigned changes in parameters which can sum to form the overall observed changes are shown via means of colour matched arrows.

Observed changes	PF Rate	DF Rate	DF % Area (A_{PF})	DF % Initial Intensity (I_{DF})	% PLQY
C1(H)→C1(n-H)	~	↑	↓	↓	↓
C1(H)→C1(77 K)	↓	↓	↓	↓	?
Changed Parameter With Varied $k_S + k_T$	PF Rate	DF Rate	DF % Area (A_{PF})	DF % Initial Intensity (I_{DF})	% PLQY
↑ $k_S + k_T$ ↑↓	↑	↑	—	—	—
Changed Parameter With Constant $k_S + k_T$	PF Rate	DF Rate	DF % Area (A_{PF})	DF % Initial Intensity (I_{DF})	% PLQY
↑ $k_{ISC}k_{RISC}$?↓	↓ Low	↑ Low	↑	↑	↓
↑ High	↑ High	↓ High	↑	↑	↑
↑ k_{RISC} ?↓	↓	↑	↑	↑	↑
↑ $k_{t-r} + k_{t-nr}$ ↑	↓	↑	↓ Low	↑ ^a	↓
↑ High ^a			↑ High ^a		
Changed Parameter With Constant $k_S, k_T, k_{ISC},$ and k_{RISC}	PF Rate	DF Rate	DF % Area (A_{PF})	DF % Initial Intensity (I_{DF})	% PLQY
↑ k_{s-r}	—	—	↓	~↓ ^b	↑
↑ k_{t-r}	—	—	↑	~↑ ^b	↑

^aUnlikely since this only happens at high triplet rate in comparison to singlet rate.

^bLittle change observed.

gap (which proved indeterminable). This included a possible increase in polarity (section 3.3.2) and the donating component appears more conjugated (see section 3.2), narrowing the energy gap with the first excited state. The lack of an observable narrowing of the singlet-triplet energy gap when the photoluminescent spectra at 77 K was observed has previously been called into question (see section 3.3.3).

When in pure film, it has been shown there is a blue shift in absorption (see section 3.3.2) and a reduced photoluminescent quantum yield (PLQY), consistent with H-aggregation (see section 3.3.2). From this, it would be expected that significant differences would be observed in the decay characteristics of C2 compared to C1, in all situations. This will be shown to be the case in this section. Each of these decays of C2 and the C1 in host decay are compared in figure 4.9.

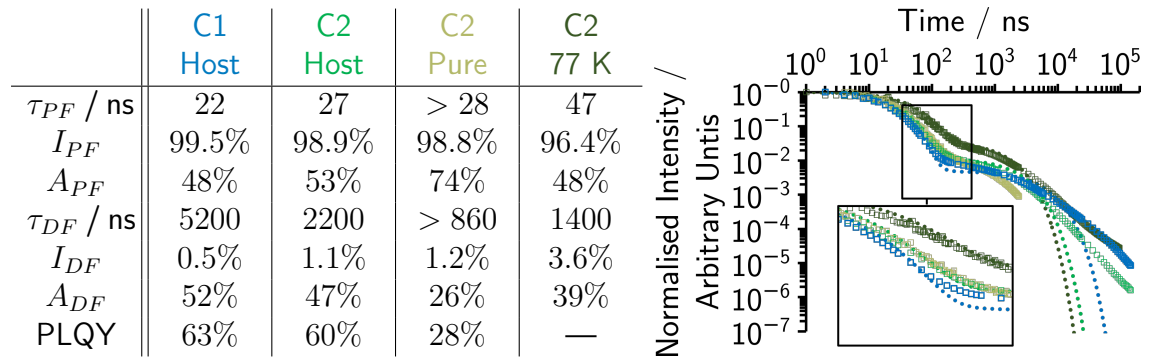


Figure 4.9: The transient decays of C2 (hollow squares), with C1 in host to show changes. The fit (solid circles) and a table of the parameters taken from the fit are also shown. An enlarged version of the decays are shown in section B.3.2.6.

Prior to discussing the comparison with C1, it is first necessary to discuss whether the singlet-triplet energy is in fact narrowed. The change on cooling to 77 K is particularly interesting in this regard. As has been previously stated cooling to 77 K is usually causes a reduction in k_{RISC} (See equation 4.13). However here the changes are quite different to this. While an overall reduction in the sum of rate constants appears to be observed, the changes in the other parameters are not consistent with a decrease in the ratio of k_{RISC} rate to the total rates. The increase in delayed fluorescence area and initial delayed fluorescence intensity suggests if anything an increase in the ratio of k_{RISC} and $k_{RISC}k_{ISC}$ and hence the reduction likely comes from elsewhere. An increase in the relative amount of triplet decay also seems to be indicated, suggesting a reduction in singlet decay rate, and likely radiative singlet decay rate. It is believed that a decrease in the radiative singlet decay rate is most likely because the PLQY in doped film in ambient conditions is found to be similar to C1. In addition it is believed that the PLQY for C1 has a much larger PLQY when not measuring in ambient conditions (84 %).¹³

The question then becomes what causes this change. A decrease in k_{r-s} could

be due to a decrease in structural variability to conformations with higher emission rate ie. a decrease in vibronic coupling. This is quite a curiosity in TADF, since it is often assumed that the radiative rate remains constant upon cooling and the TADF is quenched, allowing for the observation of the triplet state. The lack of quenching of TADF suggests quite strongly that the energy gap between singlets and triplets is so small that it is not quenched.

The previous chapter suggest an increased separation of charge from C1 to C2. An increase in charge separation is usually associated with an increase in the reverse intersystem crossing rate (k_{RISC}) for C2, and reduced singlet emission rate (k_{s-r}). It may be shown trivially from equation 4.14, that the sum of the prompt and delayed rate constants gives the sum of the total rate (equation 4.15), and hence via the data listed in table 4.9, it is possible to show that the overall sum of rate constants decreases with a change from C1 to C2. Hence it may be predicted that the reduction in singlet decay rate would dominate the change. When comparison is made to the changes tabulated in figure 4.3, it can be seen that this is possibly the case, the change in parameters can be seen as largely being a combination of increased $k_{ISC}k_{RISC}$ ratio, and of $k_{t-nr} + k_{t-r}$ rate, considering a decrease in rate would be expected, this would suggest the singlet decay is likely. Since the literature photoluminescent quantum yield for C1 is high¹³, this would suggest substantial reduction in decay rate can only come from the reduction in radiative decay rate. It is possible that the non-radiative decay rate decreases similarly, explaining why the delayed fluorescence initial intensity does not change as predicted by a pure increase in k_{s-r} as a ratio of $k_S + k_T$.

Unfortunately comparing C2 in host to pure film is quite difficult as insufficient transient decay was recorded. It does not seem possible to make any reasonable predictions about the results here. Subsequently it will be shown that C3 behaves quite similarly to C2 in transient decay, and it is believed hence, that it's pure film decay may be a good approximation for C2's. The decrease in prompt rate is likely indicative of an overall reduction of rate (prompt fluorescence is usually sufficiently faster than the delayed fluorescence, to dominate the aforementioned sum of them, giving the sum of rate constants), and it is possible that the reduction in delayed fluorescence intensity is indicative of a reduction in singlet radiative decay rate. This would be the predicted change if the theorised H-aggregation does occur.

4.3.3 Transient Emission Of Compound 3

It has just been shown that when going from C1 to C2, the change in rates is consistent with an increase in reverse intersystem crossing rate, and a decrease in singlet decay rate. When the compound is cooled to 77 K there is a decrease in

Table 4.3: The changes in decay parameters with changed environment of C2, compared with the changes observed in transient fluorescence when changing certain parameters of the TADF decay. Assigned changes in parameters which can sum to form the overall observed changes are shown via means of colour matched arrows.

Observed changes	PF Rate	DF Rate	DF % Area (A_{PF})	DF % Initial Intensity (I_{DF})	% PLQY
C1(H)→C2(H)	↓	↑	↓	↑	↓
C2(H)→C2(n-H)	↓	?	?	↑	↓
C2(H)→C2(77 K)	↓	↑	↑	↑	?
Changed Parameter With Varied $k_S + k_T$	PF Rate	DF Rate	DF % Area (A_{PF})	DF % Initial Intensity (I_{DF})	% PLQY
↑ $k_S + k_T$ ↓↓↓	↑	↑	—	—	—
Changed Parameter With Constant $k_S + k_T$	PF Rate	DF Rate	DF % Area (A_{PF})	DF % Initial Intensity (I_{DF})	% PLQY
↑ $k_{ISC}k_{RISC}$ ↑↑	↓ Low ↑ High	↑ Low ↓ High	↑	↑	↓
↑ k_{RISC} ↑	↓	↑	↑	↑	↑
↑ $k_{t-r} + k_{t-nr}$ ↑↑	↓	↑	↓ Low ↑ High ^a	↑ ^a	↓
Changed Parameter With Constant $k_S, k_T, k_{ISC},$ and k_{RISC}	PF Rate	DF Rate	DF % Area (A_{PF})	DF % Initial Intensity (I_{DF})	% PLQY
↑ k_{s-r} ↓↓↓	—	—	↓	~↓ ^b	↑
↑ k_{t-r}	—	—	↑	~↑ ^b	↑

^aUnlikely since this only happens at high triplet rate in comparison to singlet rate.

^bLittle change observed.

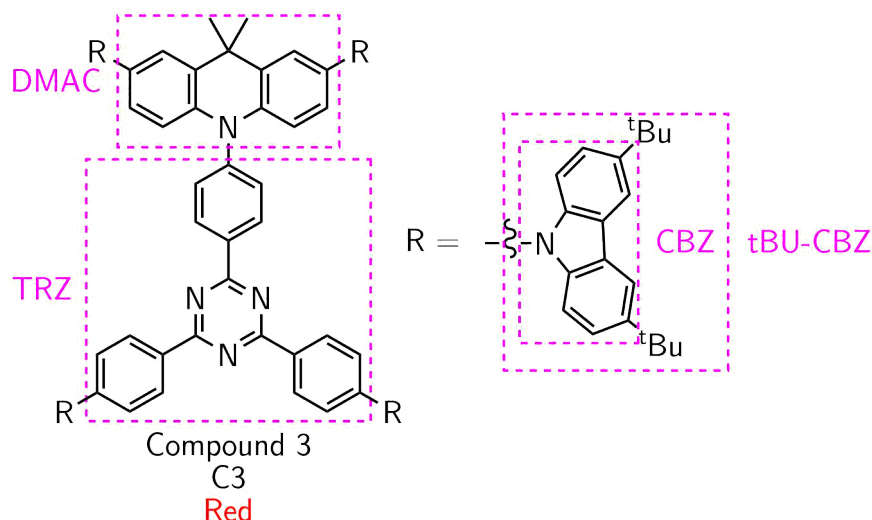


Figure 4.10: The structure of compound 3 with the components labelled. An enlarged version of the decays are shown in section B.3.2.6.

the singlet decay rate, unusual for TADF but consistent with an extremely narrow singlet-triplet energy gap.

The change from C2 to C3 has already been investigated in this thesis using steady state measurements (see section 3). It was found during the steady state measurements, that there was an apparent narrowing of the band gap in C3 (see sections 3.2, 3.3.1, and 3.3.2), consistent with an increased delocalisation of the acceptor away from the donor (i.e. onto the newly attached tBU-CBZ groups). Given this, a further reduction in the singlet decay rate and an increase in the reverse intersystem crossing rate may be predicted for C3. While photoluminescent spectra at 77 K did not support this hypothesis, it will be found that C3 is not quenched at 77 K consistent with an extremely narrow singlet-triplet energy gap.

It has also previously been postulated that H-aggregation may occur in the pure film of C3. Evidence for this included a reduction in PLQY (see 3.3.4), and a red shift in emission, but notably lacked a blue shift in absorption (see section 3.3.2). The lack of blue shift in absorption had been partially rationalised by the domination of the absorption spectra by the CBZ-TRZ charge transfer state, which is of higher energy than the S_1 state (section 3.3.2). If H-aggregation does occur, a reduction in the singlet radiative decay rate would be observed.

The decays corresponding to C3 are shown in figure 4.11, and what can initially be observed is the remarkable similarity of the C2 and C3 decays. This is true both in pure and doped film, and suggests the change in the TADF mechanism is small between the two, and that the decay of C2 in pure film may be modelled pretty closely by C3 (including H-aggregation effects). It will be noted (See section 4.3.5.1) however that the power dependence for C3 in pure film shows some sign of

saturation from bimolecular processes, and so any interpretation of C3 in pure film should be treated with caution.

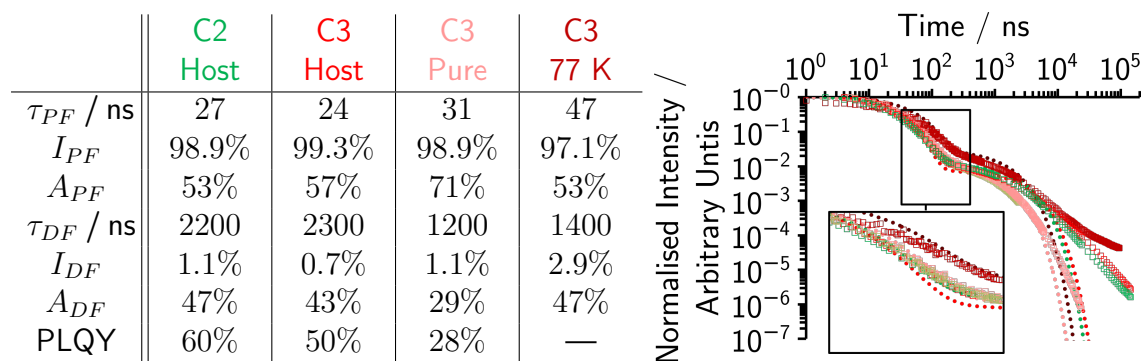


Figure 4.11: The transient decays of C3 (hollow squares), with C2 in host shown, to show changes, and C2 in pure film (same colouring as figure 4.9) to show the similarity to C3 in pure film. The fit (solid circles) and a table of the parameters taken from the fit are also shown.

When going from C2 to C3 in blends with the host, there appears to be an increase in the sum of decay rates. This is because, as previously mentioned, according to equation 4.14, the sum of the prompt and decay rates gives the sum of all decay rates. This suggests that the dominant change between the two compounds is an increase in one or more rate constants. When the changes in area, rate, starting intensity, and PLQY are also compared (as in table 4.4), however, no single change in graphed parameter replicates these changes. A decrease in RISC would seem the most likely parameter to replicate the changes in the graphs, this is inconsistent with an increase in overall rate.

A reduction in k_{RISC} or of $k_{RISC}k_{ISC}$ rate does lead to similar changes in measurable parameters as is observed, but is inconsistent with there being an increase in the sum of rates. It is however possible that all parameters increase by similar proportions, while leaving either k_{RISC} or of $k_{RISC}k_{ISC}$ at the same or similar rate. While this is felt as the easiest way to interpret this data, it would be unusual, and difficult to rationalise in terms of changes to the molecular structure. However, other interpretations may be possible. A possible rationalisation is that while the fit is quite different between C2 and C3 in host, the data points in the decay are rather similar. It is impossible to qualitatively tell whether this is due to problems with the fit, or is an accurate best guess. While it seems a reduction in the ratio of k_{RISC} or of $k_{RISC}k_{ISC}$ is the most likely cause of any change, due to the smallness of the change, it is hence left as a tentative conclusion.

The change from doped C3 to pure C3 decreases the overall sum of rates. The changes in parameters seem to most closely match an increase in the relative proportion of triplet decay. This, in principle, suggests a slowdown of all other processes.

Table 4.4: The changes in decay parameters with changed environment of C3, compared with the changes observed in transient fluorescence when changing certain parameters of the TADF decay. Assigned changes in parameters which can sum to form the overall observed changes are shown via means of colour matched arrows.

Observed changes	PF Rate	DF Rate	DF % Area (A_{PF})	DF % Initial Intensity (I_{DF})	% PLQY
C2(H)→C3(H)	↑	↓	↓	↓	↓
C3(H)→C3(n-H)	↓	↑	↓	↑	↓
C3(H)→C3(77 K)	↓	↑	↑	↑	?
Changed Parameter With Varied $k_S + k_T$	PF Rate	DF Rate	DF % Area (A_{PF})	DF % Initial Intensity (I_{DF})	% PLQY
↑ $k_S + k_T$ ↑↓	↑	↑	—	—	—
Changed Parameter With Constant $k_S + k_T$	PF Rate	DF Rate	DF % Area (A_{PF})	DF % Initial Intensity (I_{DF})	% PLQY
↑ $k_{ISC}k_{RISC}$ ↑	↓ Low ↑ High	↑ Low ↓ High	↑	↑	↓
↑ k_{RISC} ↓↑	↓	↑	↑	↑	↑
↑ $k_{t-r} + k_{t-nr}$ ↑↑	↓	↑	↓ Low ↑ High ^a	↑ ^a	↓
Changed Parameter With Constant $k_S, k_T, k_{ISC},$ and k_{RISC}	PF Rate	DF Rate	DF % Area (A_{PF})	DF % Initial Intensity (I_{DF})	% PLQY
↑ k_{s-r} ↓↓	—	—	↓	~↓ ^b	↑
↑ k_{t-r} ↓	—	—	↑	~↑ ^b	↑

^aUnlikely since this only happens at high triplet rate in comparison to singlet rate.

^bLittle change observed.

H-aggregation possibly causes part of this change. H aggregation is known to reduce the radiative rate of molecules. Changes in k_{RISC} and k_{ISC} could occur when going from doped film to pure film due to changes in the solid state solvation or vibronic space of the molecules, effecting the ability for El-Sayed’s rule to be broken (See section 1.3.3). An increased triplet decay rate may also be present, resulting from non-radiative decay from the interaction of the nearby molecules with similar energy levels. When C3 is cooled to 77 K, the change in parameters is similar to that observed for C2. Hence it will not be discussed further here.

4.3.4 Spectral Shifts In Transient Emission Of All Compounds

The decay of the integrated spectra of C1–3 has just been discussed, and what has been found is that C1 acts like a regular TADF molecule, with a decreased in k_{RISC} rate on cooling to 77 K and an increase in non-radiative decay when in pure film relative to doped film. C2 has been shown to have decay consistent with increased k_{RISC} rate and decreased k_{s-r} rate, consistent with an increase of donor and acceptor wavefunction. Further, C2’s results are consistent with the energy gap between singlets and triplets being so small that when cooled to 77 K the rate of reverse intersystem crossing is not reduced.

In contrast to the others, results from C3 are harder to interpret. Relative to C2, C3 appears to have an accelerated decay rate of $S_1 \rightarrow S_0$, and $T_1 \rightarrow S_0$, compared to the rate of intersystem crossing. However, the results for C3 compared to C2 are tentative, due to the change appearing clearly in the fit, but not the data. Previous results (see chapter 3)suggested that the changes from C2 to C3 were dominated by increased separation of the donating and accepting wavefunctions; the fact that the transient data does not back this up adds to the uncertainty of the results. A separation of donating and accepting wavefunctions would imply increased reverse intersystem crossing rate, and reduced singlet emission rate.

Similar to C2, C3 was not quenched on cooling to 77 K, and the results from pure films of C2 and C3 also appeared to be similar. The difference between the doped and pure film of C3 seemed most consistent with a reduction in all the overall rates, with a slight relative increase in triplet decay. This decrease is inconsistent with the H-aggregation postulated to occur in pure films of C2 and C3.

Of course the integrated spectra decays are not the whole picture; and the spectra at each time point is recorded. An example of how the spectra changes with time is shown in figure 4.12, with the rest shown in section B.3.2.7. What is noticeable across all spectra is an initial red shift, and, in those with longer timescales ($>10,000$ ns) included, a gradual blue shift is observed. This is an effect quite characteristic of TADF which was recently reported by Penfold et. al.¹⁴ and summarised quite

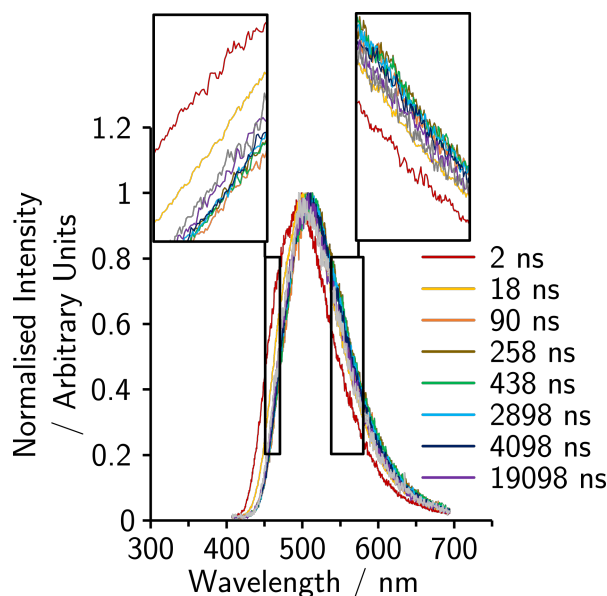


Figure 4.12: Photoluminescence spectra of C1, 10 % doped in H1, at different time delays. Inserts shown magnification of the changes in the low and high wavelength regions.

succinctly by S. Tumkevicius et al.¹⁵

The initial red then subsequent blue shift occurs because in the solid state there are a range of conformations which each decay at differing rate. The initial red shift is caused by states with higher singlet triplet energy gap and thus greater donor and acceptor orbital overlap, decaying quickly. This increased decay rate is due to a larger oscillator strength from the donor-acceptor overlap. Molecules with large singlet-triplet energy gap have inherently bluer singlets and hence the redder states live longer. The blue shift on the other hand, which occurs in the TADF portion, is caused by the states with smaller singlet-triplet energy gap having faster singlet to triplet energy transfer but lower singlet energy. This means in delayed fluorescence the redder states decay quicker, and the bluer states are long lived.

Further to the prior described effect, there is a noticeable change in spectral shape for compound 1 at short timescale. This is demonstrated in figures 4.12 and in B.54, and is present in both pure and mixed host compound films. Three possibilities exist for why this occurs, vibronic relaxation, structural relaxation, and multiple states with slow interconversion. The timescales according to Lakowicz¹⁶ for the first one is 10 ps, the second is actually a consequence of vibrational relaxation. The latter also usually occurs at 10^{-12} s. The most likely is two states, or two distinct geometries in the solid state with differing initial decay rates. This corresponds to the computational results, which will be discussed in the section 5.5.

While the red and blue shift is commonly rationalised by the distribution of states at room temperature, it is not expected to see these effects at 77 K, as TADF is not expected at 77 K. Figure 4.13 shows the change in the C1 spectra at 77 K,

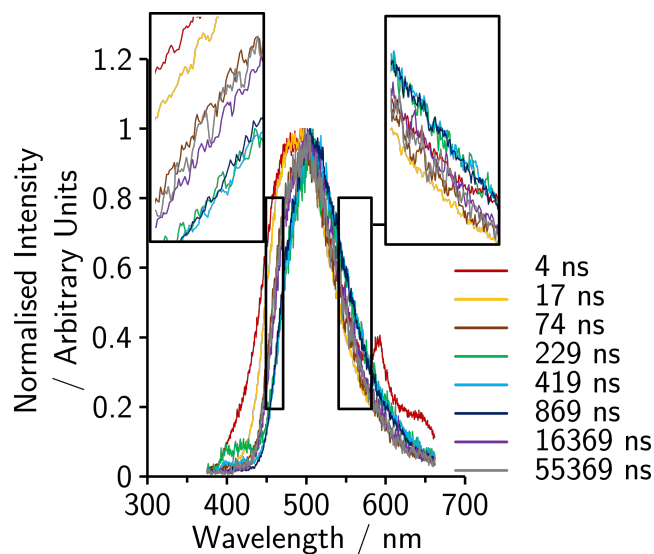


Figure 4.13: Photoluminescence spectra of C1, in frozen solution (1:1 diethyl ether : ethanol), at different time delays. Inserts shown magnification of the changes in the low and high wavelength regions.

with similar shifts seen for the other compound (see figure B.53). These shifts do seem indicative of TADF playing a part in the decay of all compounds, but it is unclear to what extent phosphorescence plays a part in the C1 decay. While it is possible that similar shifts could occur in phosphorescence, this is not something that is characteristic of it.

Readers will also observe the additional peak in the fluorescence of compound 1 at short time scales (not present in other compounds). This cannot be explained easily. It most likely corresponds to impurities or aggregates but also could be a different state. The fact that, despite it being the lowest in energy, it is phenomenally short lived (disappearing after 14 ns), suggests that it is a local property at a very small part of the sample, perhaps due to contamination. As a result it will not be discussed further.

4.3.5 Confirmation Of A TADF Mechanism and Alternative Fits

Throughout this section the compounds have been assumed to operate under TADF. While it is common to make this assumption, it is not necessarily valid. In this section it will be shown that these decays do most likely operate under TADF, although questions will be raised about the fits used.

There are 3 main ways in which the mechanism for TADF is verified. Firstly, there is the effect of cooling on the spectra which usually quenches the “thermal activation”. While this is seen in one of the decays (C1), it is not observed for the

others, and hence it is surmised that the energy gap is too small at 77 K to quench C2 and C3. Further, other mechanisms can be thermally activated. The classic alternative mechanism for delayed fluorescence of Triplet-Triplet Annihilation (TTA), may also require thermal activation, and thermal activation of phosphorescence is theoretically possible. The second way of confirming TADF is studying the power dependence of the decay, at a given time or over the whole spectra. The rate of Triplet-Triplet annihilation does not scale linearly with the amount of triplets,¹⁷ whereas it does for TADF. A final approach is to look at fitting, where bi-exponential decay is expected for TADF, this is not expected for TTA. The precise nature of this decay will be discussed later.

Herein the power dependence will first be discussed, and be shown to be TADF-like in most circumstances. Subsequently the fits will be discussed, and shown to be somewhat TTA like. This discrepancy will be justified by two possibilities. 1) the distribution of states, 2) A possible unknown in the decay of TADF molecules. However the results are interpreted to suggest TADF type decay.

4.3.5.1 Power Dependence

In order to definitively prove that the delayed fluorescence observed is TADF and not TTA, the power dependence of the films is often measured. For a pure TADF system, the amount of triplets formed is proportional to the amount of light absorbed (assuming saturation is not approached), and the amount which decay is proportional to the number of triplets, so a linear power dependence would be expected. For TTA, the number of triplets formed is proportional to the amount of light absorbed, and the rate of formation of singlets is given by the square of the number of triplets. This is complicated by several factors however, which will now be discussed. When TTA dominates as a triplet decay pathway and it is significantly slower than radiative emission and intersystem crossing is negligent, this gives the following equations for the decay.¹⁷ Where I_{DF} is the intensity of delayed fluorescence, γ_{TT} is the rate constant, $[T]$ is the concentration of triplets at time t , $[T]_0$ is the initial concentration of triplets and f is the fraction of TTA recombinations which emit.

$$I_{DF} = \frac{1}{2}f\gamma_{TT}[T]^2 \quad (4.23)$$

$$= \frac{1}{2}f\gamma_{TT} \frac{[T]_0^2}{(1 + \gamma_{TT}[T]_0 t)^2} \quad (4.24)$$

What can be observed is that at $t \ll 1/(\gamma_{TT}[T]_0)$ the power goes with the square of the initially excited triplets, and for $t \gg 1/(\gamma_{TT}[T]_0)$ there is no dependence (half

life = $1/(\gamma_{TT}[T]_0)$). Hence results must be taken at short time to have a noticeable effect.¹⁷ In the ideal case the power dependence is taken over the entire decays. This makes it very apparent if there is a change. However, it is considerably more work. A compromise is used here. The full decay is recorded at two substantially different powers for the compounds in host with the lower value being the one used in the analysis (20 nJ). For pure film a plot of intensity verses power at a single point in time in the decay is recorded. The approximate mid-point in this range of powers is used in the full-analysis and fitting previously discussed, where a power of 1000 nJ is used. The compounds in frozen solution at 77 K are effectively more diffuse within its matrix, making TTA slower, and as the purpose of these plots was to quench TADF, a power dependence was not ran.

An additional issue with power dependencies is that of saturation. While it is often assumed the number of excited states is proportional to the number of photons entering the material, which is in turn proportion to the power applied, this is not always the case. When the number of excited states is no longer proportional to power, this is called saturation. There are several ways a material can saturate, either the photons can run out of molecules to excite (bleaching), or decay processes can begin to compete with the excitation. The bleaching of the ground state is likely an exponential decrease in the increase of fluorophores. An exponential is assigned because the rate of absorption of light is proportional to the number of molecules (which decreases with excitation), and the probability of a molecule absorbing light (which is constant).

When the cause of saturation is from the competition of decay processes with excitation, the number of excited state does not increase with increased excitation pulse length. Increasing the power does however, increase the number of excited states, because the rate of excitation must equal the rate of decay. When saturation has been reached, the power dependence is determined by the exciton concentration dependence of the decay process. For a bimolecular process such as TTA, the rate is dependent on the square of the exciton concentration. This means the number of excited states at saturation increases with the square root of states excited (i.e. power) in the excitation pulse.¹⁷ The square root dependence can be visualised by observing that the decay processes speed up much faster (quadratic) than the excitation processes (linear) with increased power. The process of coming to this result mathematically is expressed below. The symbols are defined as previously, with I_{EX} being the rate of excitation, $[T]_{limit}$ being the limiting triplet concentration, and t the time. It should be noted the equations assume the laser pulse is continuous, allowing for saturation to be reached.

$$\frac{d[T_1] + [S_1]}{dt} = I_{EX} - \gamma_{TT}[T]^2 \quad (4.25)$$

$$[T]_{limit} = \left(\frac{I_{EX}}{\gamma_{TT}} \right)^{0.5} \quad (4.26)$$

These equations mean that when a log-log plot of power dependence is plotted without bimolecular saturation ($[T] \propto I_{EX}$), a gradient of 1 is indicative of TADF ($I_{DF} \propto [T]$), a gradient of 2 of TTA ($I_{DF} \propto [T]^2$). For bimolecular saturation ($[T]^2 \propto I_{EX}$) a gradient of 0.5 for TADF ($I_{DF} \propto [T]$) would be observed and 1 ($I_{DF} \propto [T]^2$) for TTA. Because such low power is used in the decays recorded, it is not believed that saturation would occur, and this simplifies the proceeding discussion. As such the nature of the processes dominating the decay can be observed from a log-log plot.

The power dependencies of compound 1 are shown in figure 4.14 as an example of the other decays. All other decays are shown in section B.3.2.9. Section B.3.2.9 shows most power dependencies to be similar, except for compound 3 in pure film, which is hence shown in figure 4.15. In doped film, what is observed, is that there is no real change with varied power, indicating TADF-like delayed fluorescence. In pure film an approximately linear increase in power is observed. For pure films, the intensity a certain time period after excitation is plotted. The time used, however, is not ideal, being on the order of a single half life in time after the initial pulse. It is felt, however, that a deviation from the linear gradient would still be expected for TTA. Hence an assignment of TADF is given.

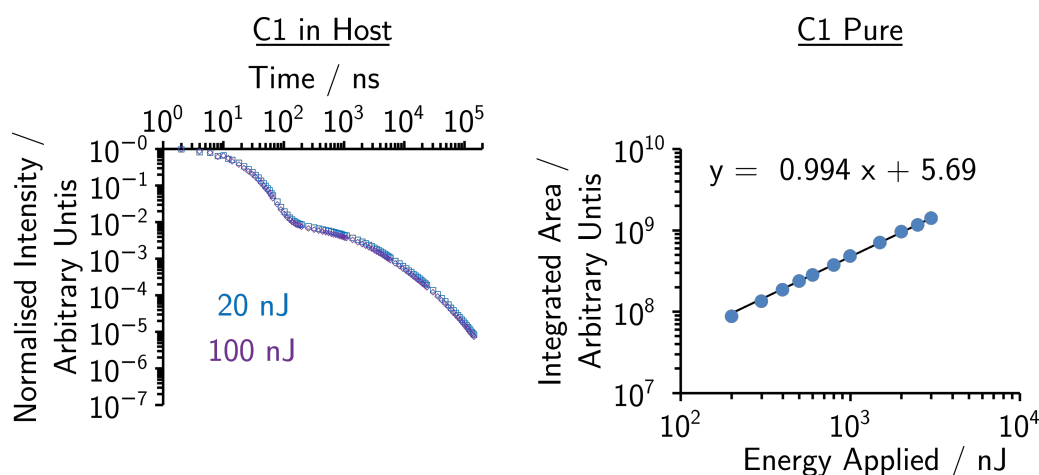


Figure 4.14: The total decay of C1 at two different power (left) and the integrated area at ~ 3990 ns after an excitation at 410 nm. A black fitting line is shown for the power.

For all other compounds, similar decays when 10 % doped in H1 are observed. Similarly, gradients close to linearity are observed when in pure film with no change

is observed at higher power, with the exception of compound 3. For compound 3, a gradient lower than linearity is observed. It is believed the reason for this is that saturation may be being reached. However, at saturation, it is expected that a TTA dominated system would have a gradient of 1. As the gradient is significantly less than this, it is believed that TTA does not dominate the decay, and only the number of molecules excited.

Since it is likely that bimolecular processes are causing saturation in C3 in pure film, the values from the decay should be treated with caution. It is possible that there are other causes of the non-linear power dependence, such as the effect of local heating, so the measurements are not perfect. It is also further noted in figure 4.15, that lower powers appear to give values closer to the desired linearity. Unfortunately the decay swaps to non-linearity at powers just below 1000 nJ, which is used in the full analysis and fitting previously discussed. The fact that the full analysis and fitting of C2 is quite similar to C3, despite C2 having linear power dependence, and C3 not leads to the conclusion that it is unlikely TTA is having a strong effect here. Hence the analysis and fitting of the C3 transient decays is included, but caution should be taken with the results.

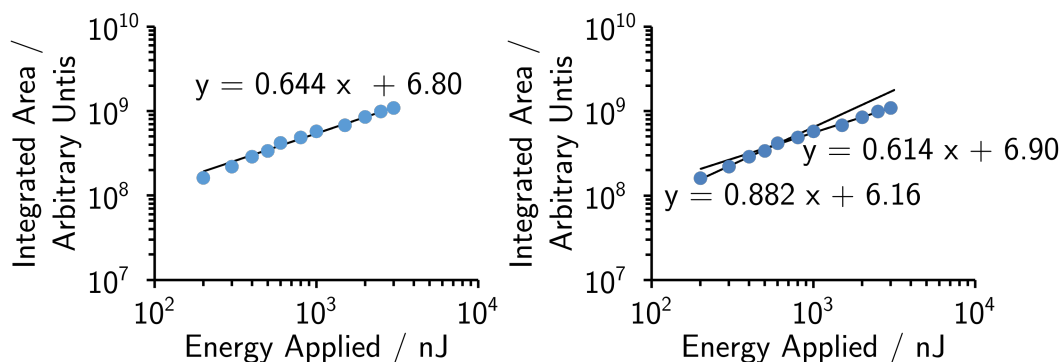


Figure 4.15: The integrated area at ~ 3990 ns after an excitation at 410 nm of C2 in pure film. A black fitting line is shown for the power, fitted over the whole data series (left) and over two distinct parts (right).

4.3.5.2 Fit

What has just been shown is that the power dependence appears TADF-like in all studied molecules, with the possible exception of C3 in pure film. The results from this film are hence advised to be treated with caution. Despite it being shown that in all likelihood the decays progress by TADF, the diligent reader will note that the decays of C1–3 appear to have power law like tails to them which are poorly fit by a bi-exponential decay. This section will be about the fits for the decays, and how perhaps better ones can be used. It is beyond the scope of this publication to

fully implement new fits, but it will be noted that better fits are given by stretched exponential fits but not triplet-triplet annihilation (TTA) like fits. In order to show this the compounds in host will be used as a test case. While stretched exponentials are common in other photophysical fields,^{18,19} they have not been fully explored in the field of TADF.

As has just been stated, a pure TTA decay of triplets progresses via the following equation:

$$I_{DF} = \frac{1}{2} f \gamma_{TT} [T]^2 \quad (4.27)$$

$$= \frac{1}{2} f \gamma_{TT} \frac{[T]_0^2}{(1 + \gamma_{TT} [T]_0 t)^2} \quad (4.28)$$

Of course in the system that is looked at here the decay is accompanied via prompt and delayed fluorescence from TADF, which by itself gives a bi-exponential decay. While the solution of the rate equation involving both TADF and TTA is quite complex, here it is approximated by the following equation, where symbols are defined as previous and I_{emiss} being the intensity of emission

$$I_{emiss} = (a_{PF} e^{-k_{PF}t} + a_{DF} e^{-k_{DF}t}) + \frac{1}{(a_{TTA} + b_{TTA}t)^2} \quad (4.29)$$

This is not entirely without evidence. It has been found that within the approximation of slow ISC and RISC, as well as otherwise slow triplet decay, inverse and inverse square terms are generated.⁶ When this function is fit to, the graphs shown in 4.16 are formed. This fit appears to match the data much better than a bi-exponential decay, despite it being shown by the power dependence that TTA is unlikely to dominate the TADF decay. An improvement in fit should be evidenced by a reduction of $\frac{\chi^2}{N}$ goodness of fit parameter, which was 2×10^6 , 4×10^6 , and 1×10^6 , in the prior fits and now have the values shown in the figure. The reader will note that the fits are actually worse for the TTA fits than the standard bi-exponential fits used in the prior sections. It should be noted that the starting values of the fits are partially responsible for this, but it does demonstrate how a qualitatively good fit can actually be bad when uncertainties are taken into account.

An alternative fit is the stretched exponential fit. Stretched exponentials are common to fit to in other areas of photochemistry such as transient absorption.¹⁹ Stretched exponentials are associated with distributions of states emitting, although other interpretations do exist.¹⁹ The following equation is used to fit to stretched exponentials:

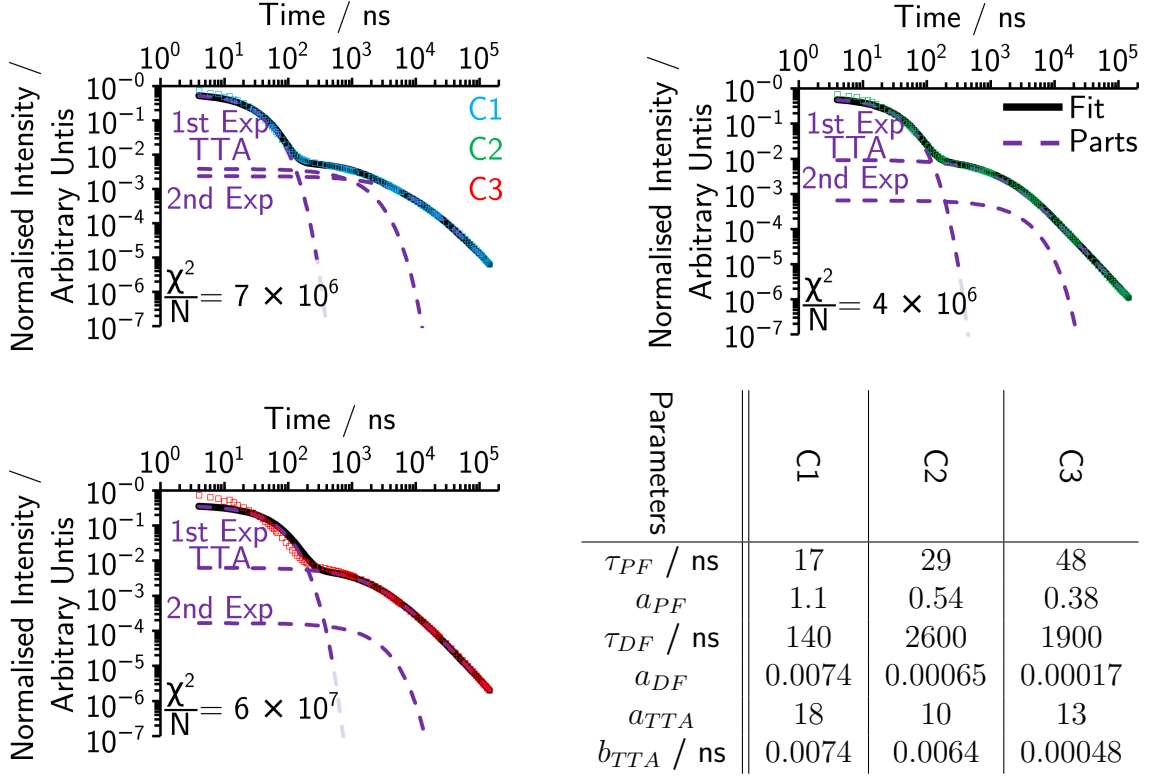


Figure 4.16: The decays of compounds 1–3 doped 10 % in H1, when fitted to equation 4.29, including a triplet-triplet annihilation function. Parameters are tabulated, and χ^2 fitting parameter is listed.

$$I_{emiss} = (a_{PF} e^{(-k_{PF}t^{\gamma_{PF}})} + a_{DF} e^{(-k_{DF}t^{\gamma_{DF}})}) \quad (4.30)$$

It should be noted that the interpretation of the parameters gained from this fit are non-trivial, with both the "stretch parameter" γ and the value similar to the rate constant k or time constant τ being needed to calculate the average rate parameter.¹⁸ Further interpretation of these results will be found beyond the scope of this publication.

The stretched exponential fits are shown in figure 4.17, and the parameters used in fitting are tabulated are also shown. While qualitatively it may appear they fit the data less well than the crude approximation to TTA decay, the χ^2/N goodness of fit parameter suggests otherwise. The χ^2 goodness of fit is in fact better than both the TTA fit and the standard bi-exponential fit. This lends credence to the commonly claimed, but rarely justified assertion that these power law like long lived states are from the distribution of states, and not a bimolecular process. While these fits do lend credence, they are not a proof and so a degree of doubt is possible.

It is noted that the main thing which is poorly fit in the stretched exponential decay is the long lived states. It is expected that two stretched bi-exponential decays with a TTA component may give the best fit, since the TTA decay fits these

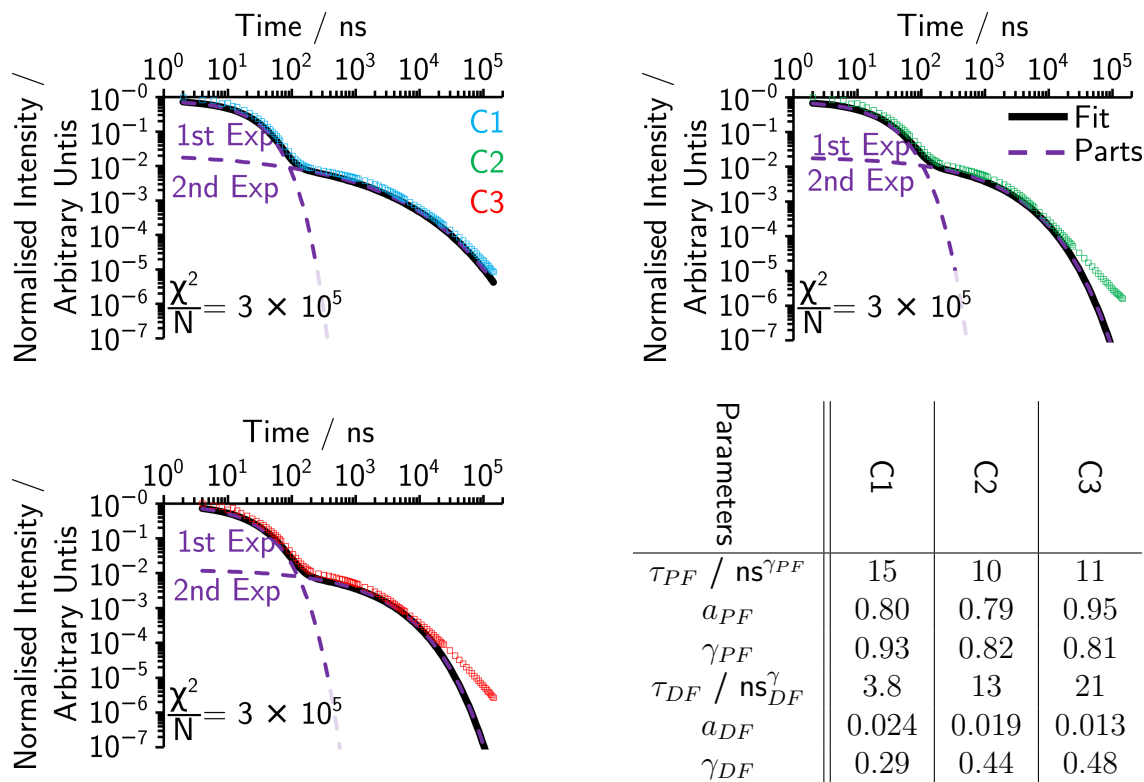


Figure 4.17: The decays of compounds 1–3 doped 10 % in H1, when fitted to equation 4.30 including stretched exponential functions. Parameters are tabulated, and χ^2 fitting parameter is listed.

long lived states very well. However, it is beyond the scope of this publication to implement such a fit.

4.4 Conclusion

This chapter has shown via power dependencies that the photoluminescent decay of C1–3 most likely proceed via TADF (with the possible exception of C3 in pure film), and while it has been shown that better fits may be obtained by the use of stretched exponentials, it has been found beyond the scope of this thesis to implement such a fit. Instead the classic bi-exponential decay has been used to fit the data, the pooriness of these fits naturally weakens the strength of any conclusions drawn from them, but are still interpreted as a best-guess as to the changes between the molecules.

When interpreting these fits, it was found that none of the literature approximations for the photoluminescent decay were appropriate, so a new method of interpreting the fits was developed. This new method involves looking at the changes in the areas, starting intensities, and time constants generated by the fit. Further the change in photoluminescent quantum yield is considered. These values are plotted

for several test functions, and the change in size compared. It is felt this is the only reasonable way of interpreting these results.

Further, when the TADF equations were interpreted, it was found that for a set of identical molecules which can undergo both TADF and phosphorescence, the phosphorescence and TADF is indistinguishable in the decays. This goes against the commonly asserted interpretation that additional decays are from phosphorescence. However, this interpretation is not ruled out. The additional decays could be from molecules which do not undergo TADF, and only phosphorescence. Unfortunately, it is not clear what influence this will have on the results.

The data when fitted allowed interpretation of the changes when going from one molecule to the next. This keyed in to the previous narrative of an increased separation of donating and accepting components for C1 to C2 but less so for C2 to C3. For C1, what was observed upon going to C2 was consistent with a reduction in singlet decay rate, and increase in reverse inter-system crossing rate predicted for a greater separation of donating and accepting components of the molecule. A greater separation of these components has also been seen to be consistent with the general characterisation chapter, and will be found to be consistent with the computational chapter. The change from C2 to C3 was quite small, and is interpreted as being due to an increase in singlet and triplet decay with constant reverse intersystem crossing and intersystem crossing rate. This change is unexpected, and cannot be assigned as being due to an increase in separation of donor and acceptor. The precise cause of the change cannot be determined. The lack of strong increase in intersystem crossing rate may suggest that reverse intersystem crossing cannot be made faster at this point by narrowing the singlet and triplet energy gap. This would suggest that it is the probability of transfer between states which dominates the reverse intersystem crossing rate and not the probability of there being enough energy for the transition.

When the photoluminescent decays of the compounds when cooled to 77 K were examined, while the expected decrease in reverse intersystem crossing was observed for C1, this was not observed for C2 and C3. For C2 and C3 results consistent with an apparent reduction in the singlet decay rate was observed. A cause for this sort of reduction could be decreased vibrations at low temperatures reducing the vibronic coupling which allows emission. If these results are indicative of the actual change, it is believed that this would be the first known example of "thermally activated fluorescence" in a E-type fluorescence molecule, (ie. one that undergoes TADF). The distinction between "thermally activated delayed fluorescence" and "thermally activated fluorescence", is that the step which is temperature dependent is the fluorescence and not the transfer from triplet to singlet states where the singlet

undergoes non-activated fluorescence. The lack of apparent reduction in the reverse intersystem crossing rate is taken as evidence for the narrowing of the singlet triplet energy gap going from C1 to C2.

When the compounds were in pure film, an increase in overall decay rates was observed for C1 and a decrease for C2 and C3. For C1, the expected result of increased triplet decay, likely from non-radiative sources was observed; however, for C2 and C3, a decrease in rates was observed. While the full decay of C2 was not obtained, the decay is similar to C3, which was used to interpret both, and it was shown that a general reduction in all rates except triplet decay was observed. This is not inconsistent with a reduction in singlet rate, but consistent with earlier H-aggregation-like properties in C2 and C3. This conclusion is weakened by signs of saturation in C3, suggesting a bi-molecular decay pathway. However, due to the similarity of C2 and C3, it is felt that most likely this result holds.

During the photoluminescent decay, it was observed the spectra shifted, in all cases, in a similar manner to earlier reports of TADF decay. While this is to be expected at room temperature, it is a surprise at 77 K. While it is easy to rationalise for C2 and C3, where the TADF appears not to be quenched at 77 K, for C1 it is harder. It is suspected that some residual TADF processes still occur at 77 K as a result for C1.

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Chapter 5

Computations and modelling the S_1 state with T_1

*"Everything is vague
to a degree you do not realize
till you have tried to make it
precise"*

—Bertrand Russel

Various calculations were ran on the compounds studied; this chapter deals with these calculations. As has been stated in the introduction, this chapter may be used as a starting point for access to the experimental results on DMAC-TRZ derivatives. Other chapters will be referred to where appropriate, following a similar approach to other chapters. The fundamental problem of this work on DMAC-TRZ derivatives is the interrelatedness of all of the data, which makes both writing and reading of this document difficult. It is hoped that reiterating the conclusions of the chapters and providing section details of where these conclusions come from will aid the reader in interpreting the data.

The calculations studied in this chapter will involve the ground state singlet optimised geometries of C1–3 (see figure 5.1) and their calculated excited states using B3LYP and CAM-B3LYP functionals. Further, the calculation of the excited state in the ground state triplet state (T_1 state) will also be discussed, and it will be postulated that due to the charge transfer nature of the S_1 and T_1 state, the T_1 optimised state is likely a good approximation for the excited singlet state. This will allow approximate calculations of excitation energies corresponding to absorption and emission spectra.

Evidence will be presented, for the compounds studied, that for ground state singlet geometries, B3LYP appears to work better; however for the excited state

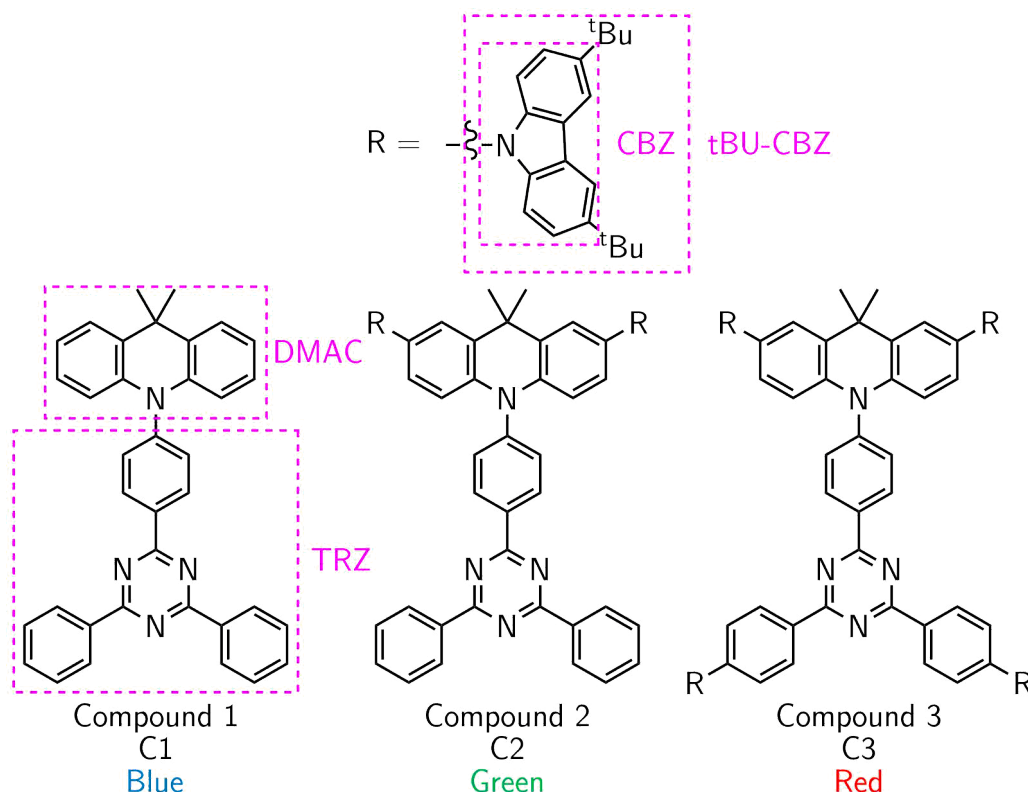


Figure 5.1: The structures of the compounds discussed, the components which make them up and the names and colours which correspond to them.

geometry as calculated in the T_1 state CAM-B3LYP appears better. It will be postulated that the reason for CAM-B3LYP's worse performance when comparing excitation energies will be due the Hartree-Fock exchange, which partially substitutes for the Becke 1998 exchange in CAM-B3LYP,¹ lacking the static correlation energy believed to be present in the Becke 1998 exchange.² Alternatively a lack of exploration of the full set of thermally accessible geometries will be suggested, as well as a the exchange energy being calculated slightly differently in CAM-B3LYP and B3LYP.

The results will further demonstrate there are 3 key geometries to DMAC (see figure 5.1 for what is meant by DMAC), and that there is an increased separation of donating and accepting components in the excited state along the series C1–3. Further a reduction in singlet-triplet energy gap will be observed. The increased separation results from extra conjugation onto the CBZ group, particularly present for the DMAC donor and concomitant with this increased conjugation will be a general narrowing of the absorption/ emission energy, consistent with solutions spectra. Data will also be presented that the reduction in change in energy gap (see section 3.3.5) in doped film may be due to blocking the change in geometries in the solid state.

5.1 Introduction: Computational Methods And Geometry

5.1.1 The Functionals

The computational study of molecular excited states involves first putting a molecule into a certain geometry, relaxing it to its minima, and then calculating the excited states of the molecules. In order to do these calculations, the energy of the molecule and its excited states must be calculated. The energy may be calculated by a variety of methods, such as Hartree-Fock (HF), density functional theory (DFT) or post-Hartree-Fock methods; however, for large molecules, such as the ones studied herein, only DFT and Hartree-Fock are practical. Generally, in the situation where only DFT and HF are practical, mixed functionals are considered the most preferable (e.g. B3LYP or CAM-B3LYP).

From these hybrid functionals, the electron density and energy of the excited states may be calculated using time-dependent density functional theory (TD-DFT).^{*} From these calculations, it is possible to calculate the change in electron density upon excitation, as well as the energy needed for the excitation.

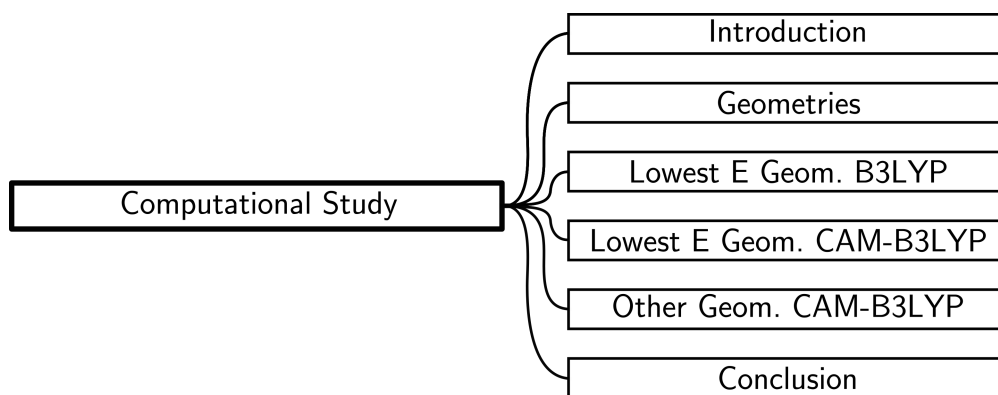


Figure 5.2: The structure of the computational section.

Generally, for these hybrid calculations, B3LYP is considered the standard method to use. However, B3LYP is known to struggle in calculating charge transfer states.^{3,4,5} Charge transfer (CT) states are fundamental to the design of TADF molecules, as they allow for a small gap in energy between the singlets and triplets (see 1.3.1) presenting a problem. B3LYP struggles with CT states because it is made up of 80% DFT and 20% Hartree-Fock exchange,^{6,7} and the DFT proportion uses the generalised gradient approximation for the exchange energy.⁸ The generalised gradient

^{*}The precise way in which these work is beyond the scope of this thesis, they are outlined however in many books on computational chemistry. Frank Jensen's introduction to Computational Chemistry gives a brief description.

approximation fails to replicate the true long range electron-electron interaction energy.⁸ This discrepancy is because in the overall DFT calculation, a self interacting coulombic term (ie. an electron interacting with itself) is included which is by its nature unphysical; the exchange term is ideally designed to cancel this completely.⁸ In the case of the generalised gradient approximation it does not do this, and this is particularly observed at long self-interaction distances.⁸

While the reader may assume that the electrons are usually relatively localised so long distance interactions with itself should not matter, this is not true with the energy change on exciting an electron to a charge transfer (CT) state is considered.^{3,4,5} A CT state, by its nature, involves transferring an electron from one part of a molecule to another, meaning the electron travels a long distance. The consequence of these effects is that CT states are incorrectly shown as being over-stabilised in the CT state.⁸

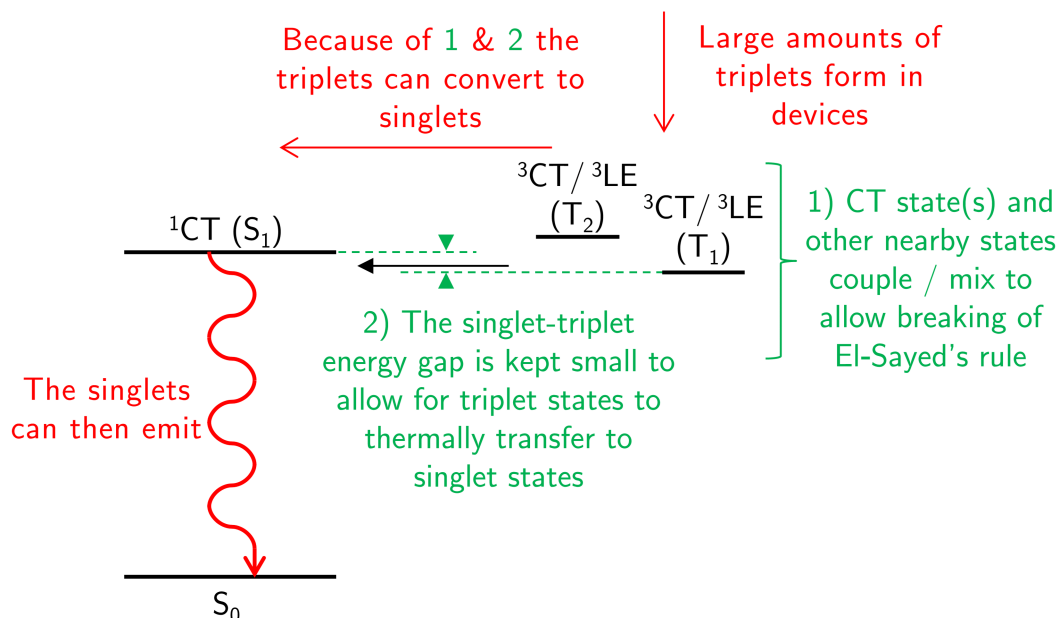


Figure 5.3: How TADF works as shown on a Jablonski diagram.

CAM-B3LYP corrects for this over-stabilisation of CT states by splitting the exchange energy into two parts, a short range component (modelled by the generalised gradient approximation model Becke1998) and a long range part (modelled by the Hartree-Fock exchange) which correctly cancels the exchange.^{8,1} The ratio of these components is weighted upon the inter-electron distance.¹ Throughout these calculations the correlation is left unchanged and modelled by a combination of VMN5 and LYP correlations.^{1,9*} It may be postulated that this creates a problem, since it has been found that the exchange and correlation do not neatly separate

*In the Gaussian (software used herein) implementation of B3LYP, a similar correlation is used where VMN5 is replaced with VMN3.^{1,9}

into functions used to model them, and this will be used to justify some changes in this section.² This creates a problem when the Becke1998 exchange is swapped for the Hartree-Fock, because the Becke1998 contains some static exchange, and the Hartree-Fock exchange does not.²

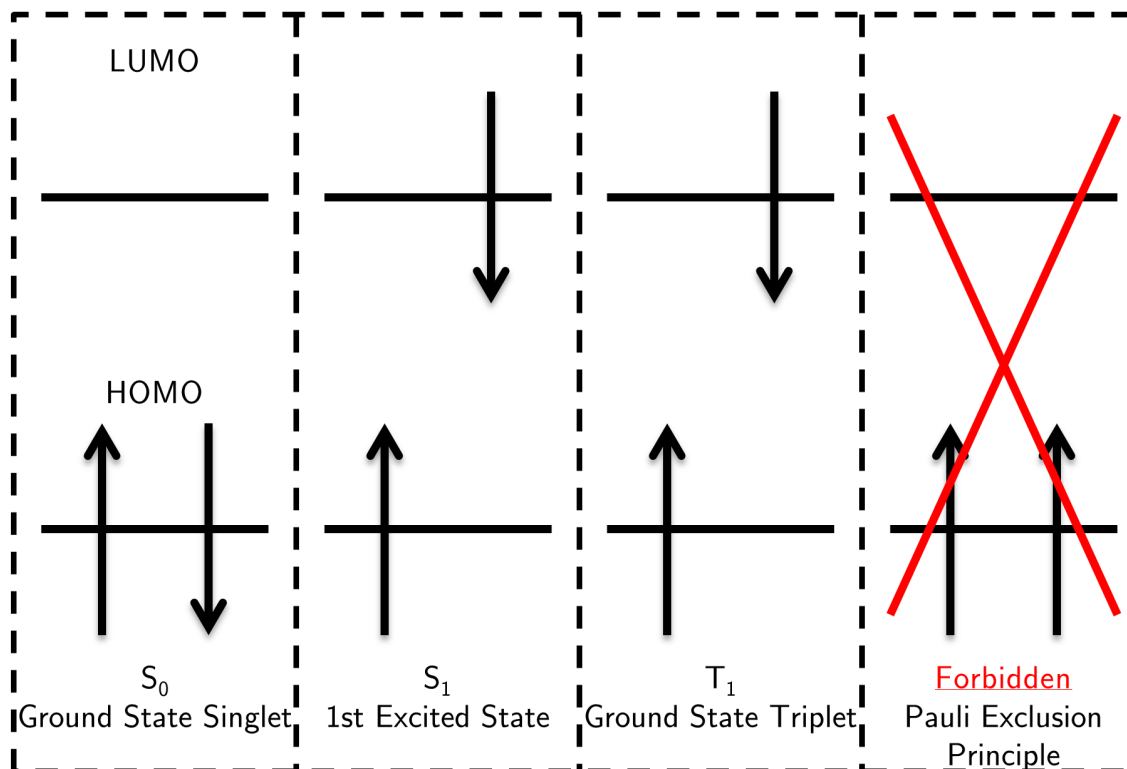


Figure 5.4: The ground state singlet, triplet and 1st excited state under the approximation that each state is made from its non-interacting one electron wavefunctions. The HOMO is the highest occupied molecular orbital, and the LUMO is the lowest unoccupied molecular orbital. Note the functionals used do not use the orbital approximation.

Within the field of TADF, the use of CAM-B3LYP has already been studied. A variety of different claims have been associated with it. It has been claimed that CAM-B3LYP "dramatically overestimates the $E_{VA}(S_1)$ [Assumed the vertical absorption energy, but undefined in paper]" by Adachi et al.¹⁰ and overestimates the singlet-triplet energy gap in a case according to Penfold¹¹. In this document it is found both the vertical absorption energy and the singlet-triplet energy gap are problems in all functionals; nonetheless it is found that in certain circumstances CAM-B3LYP is better and in others B3LYP is better. Since the ground state triplet and 1st excited singlet will be found to be similar (both energetically and in the shape of the orbitals), it is suggested that the approximation of the 1st excited singlet state by the ground state singlet is inappropriate and that the ground state triplet is better. A separate source¹² appears to show CAM-B3LYP behaves well in simulations, although it is not one of the two functionals they recommend for the study of TADF

5.1.2 The Approach In This Section

Originally when these calculations were ran, B3LYP was used on the lowest energy ground state geometry. From here it was found that while this replicated the changes between molecules, some discrepancies were present in all parameters. As a result CAM-B3LYP was used, with additional SCRF solvation approximation with a toluene solvent used to approximate solid state solvation, and the Tamm-Dancoff approximation was used. These calculations qualitatively appeared to over-correct for the discrepancies in the changes in energy.

The use of the Tamm-Dancoff approximation should be addressed. The approximation neglects the change in the orbital interaction strengths upon excitation due to mixing of doubly excited states.¹³ It has been noted that using this approximation appears to give better triplet energies in TADF molecules;¹² however theoretical calculations of some molecules appear to require the missing doubly excited states.^{14,15} This is noted for the CAM-B3LYP calculations ran, but in practice does not effect the interpretation of the results.

When the calculation in the lowest energy conformation was ran, it was found that only using this geometry was insufficient to understand these molecules. As a result, the several non-ground state conformations are ran. Since it was initially believed CAM-B3LYP was a more appropriate functional, this was used to investigate them.

While using additional geometries did yield interesting results, it did not solve all of the problems, so the calculations were re-ran in the ground state triplet (T_1) geometry. These results did improve understanding, and are believed to be of particular relevance to the methodology in the field of TADF; however, inaccuracies do remain in all calculations.

Of course while this summarises the calculations ran, it does not state the information collected from them. In order to explore this, it is perhaps useful to discuss what values obtainable via these calculations are useful to the study of TADF. The location of the electron density which is both donated and accepted on undergoing the charge transfer excitation is useful to know, as it helps explain changes between molecules, by showing which parts of the molecule are involved.* The energy gap (E_{ST}) between the S_1 and T_1 states are useful to know, as these give the relative rate of reverse inter-system crossing (k_{RISC}) relative to intersystem crossing (k_{ISC}) (see equation 5.1 derived from understanding that the RISC is ISC in reverse and the Arrhenius equation).

*From the change in electron density one can observe increased conjugation, reducing energy gap. Separation of donating and accepting components is also associated with a decrease in singlet-triplet energy gap, and in oscillator strength, for reasons to be discussed

$$k_{RISC} = k_{ISC} e^{\frac{-\Delta E_{ST}}{kT}} \quad (5.1)$$

As well as the singlet-triplet energy gap, the excitation energy between the ground state, and the S_1 state is useful, as it allows estimation of the absorption and emission energies. Further the oscillator strength (f) is useful, as this defines the molar absorption parameter (ε), and is related to the rate of fluorescent decay (k_{s-r}). The equations for these can be found in any physical chemistry text book (possibly requiring reference to Einstein parameters) and the version from B. Valeur¹⁶ and P. Atkins et al.¹⁷ are shown below,* Where g_1 is the degeneracy of the ground state, g_2 the degeneracy of the excited state, ν is the frequency, and n is the index of refraction. The fundamental constants of the mass of the electron (m), the speed of light (c), elemental charge (e), Avogadro's constant (N_a), and the permittivity of free space (ϵ_0) are also used.

$$f = \frac{10^3 \ln(10) m c^2}{N_a \pi e^2 n} \int \varepsilon(\bar{\nu}) d\bar{\nu} \quad (5.2)$$

$$k_{s-r} = \frac{2\pi \nu^2 e^2 g_1}{\epsilon_0 m c^3 N_a g_2} f \quad (5.3)$$

In order to understand the importance of geometry in these calculations, it is worth dividing all the desired measurements into the ideal geometries they would be simulated under. The absorption occurs from the relaxed ground state geometry, the emission from the relaxed S_1 geometry, and the singlet-triplet energy gap is from the relaxed S_1 to the relaxed T_1 geometry. The problem is that it is common knowledge that calculating relaxed excited state geometries is difficult, meaning only S_0 and T_1 are practically calculated.[†] Further, while the fully relaxed geometry will likely be able to be reached in solution, it will not necessarily be possible in amorphous film. Partially this is rectified in film, because the excitons may diffuse to the structure of lowest energy geometry, but it is not necessarily true that the lowest energy geometry will be present in sufficient number (if at all) to allow the emission to be from the optimum geometry.

As has previously been stated, the approximation of S_1 by T_1 will be proposed here-in, with the suggestion that this may be applied somewhat generally to the field

*The values used for the fundamental constant here are a little odd in the case of equation 5.2, the numeric form of this equation is given in several sources^{16,18,19} as either $\frac{4.32 \times 10^{-9}}{n} \int \varepsilon(\bar{\nu}) d\bar{\nu}$ or $\frac{4.39 \times 10^{-9}}{n} \int \varepsilon(\bar{\nu}) d\bar{\nu}$, and this number can only be provided by using an alternative form of the electron charge ie. $e_{alt} = \sqrt{\frac{e^2}{4\pi\epsilon_0}}$, however even then this number is a factor of 10 out. Further while the text claims it is unit-less, this gives a unit of m^2 .

[†]A further problem not explicitly addressed here, is that the simulations run as if the molecules are at 0 K. In reality a thermal distribution of molecular geometries are produced, and these interact with light.

of TADF. In order to make a claim of generality, the fundamental design principles of molecules for TADF must be discussed, and it must be demonstrated that the claim follows from them. The design of TADF molecules involves making the S_1 state a CT state, this is because it is believed that it narrows the energy gap between singlets and triplets.²⁰ This energy gap, when mixing with other states is neglected, is given by the following formula, where the energy gap is ΔE_{ST} , J is the exchange energy, $\phi_H(n)$ the highest occupied (Hartree-Fock) molecular orbital represented as a vector in the space of a basis set, occupied by electron n , $\phi_L(n)$ the lowest occupied (Hartree-Fock) molecular orbital, occupied by electron n , r_n the position of electron n , and τ means all space. Both chemists notation (upper) and physicist notation (lower) are shown to allow readers from both backgrounds to understand this work.

$$\Delta E_{ST} = 2J = 2(\phi_H\phi_L|\phi_L\phi_H) = 2 \int_{-\infty}^{\infty} \phi_H(1)^* \phi_L(1) \frac{1}{|r_1 - r_2|} \phi_L(2)^* \phi_H(2) d\tau \quad (5.4)$$

$$\Delta E_{ST} = 2J = 2 \langle \phi_H\phi_L | \phi_H\phi_L \rangle = 2 \int_{-\infty}^{\infty} \phi_H(1)^* \phi_L(2)^* \frac{1}{|r_1 - r_2|} \phi_H(1) \phi_L(2) d\tau \quad (5.5)$$

This energy gap is reduced by separating the HOMO and LUMO making the $(r_1 - r_2)$ large. Often it is approximated that the charge transfer transition is purely this transition.²¹ Strictly this is calculating excited states at a level of theory below configurational interactions singlets level, ie. it excluded all singly excited states except the HOMO to LUMO.^{21,22} While this is considered too low a level of theory to calculate excited states computationally,²² experimentally it is often found to correlate with some experimental data¹¹ (although often Kohn-Sham orbitals are thought of instead of Hartree-Fock), and is broadly used in the field of TADF. It is, however, currently being brought into question.^{21,14,15} Indeed it is text book knowledge that for Hartree-Fock orbitals the LUMO tends towards zero energy gap with the HOMO.²³ Recently it has been claimed this may not be the case for DFT, with the HOMO LUMO energy gap corresponding to the first absorption energy^{24,25} but withholds such conclusion for the mixed functionals commonly used.²⁵

The reality of the ground state charge transfer is that the transition corresponds to a combination of orbital transitions, and these each effect the energy gap between singlets and triplets. Several recent exploration of how this effects the energy gap either by adding a single additional singly excited state²¹ and including a single additional doubly excited state¹⁵ demonstrates how complex the energy gap may become. Considering the ideal full-CI calculation contains all excited states (singly, doubly, tritely etc.) it would perhaps be senseless to make predictions of the singlet

triplet energy gap. Nonetheless qualitatively it has long been observed that the overlap of the hybrid DFT and HF HOMO and LUMO correlates with the energy gap, and has recently been shown via simulation.¹¹

Further, it is commonly stated that the fluorescent rate decreases (k_f) as the overlap between the HOMO and LUMO decreases. This is based on the following formula where Ψ_i is the initial state, Ψ_f is the final state, μ is the dipole operator and ρ the density of states. Here it is apparent that the approximation of the HOMO and LUMO as being the only orbital changes which matter between the initial and final state. While it is commonly claimed to be obvious that it follows from equation 5.6 that the HOMO and LUMO need to overlap, it is not felt this is the case here, and this is expanded on in section B.3.1.5.

$$k_f = \frac{2\pi}{\hbar} \langle \Psi_i | \mu | \Psi_f \rangle^2 \rho \quad (5.6)$$

While generally the use of HOMO and LUMO overlap is used in the study of TADF, it may be strongly argued that HOMOs and LUMOs do not exist. Hartree-Fock HOMOs and LUMOs are 1 electron orbitals excluding all configurational interactions. These orbitals are convenient to calculate and allow the electron density of the states, with configurational interactions included, to be expressed in terms of them. For DFT 1 electron orbitals are also used, but do include electron correlation; they are still calculated for convenience in order to express the overall changes in terms of them. As a result it may be argued that what should be studied is the change in electron density on excitation.

The change in electron density is made of a sum of changes in orbitals which, in the case of singly excited states, each have exchange contributions contributing to the total energy. The exchange contribution from a singly excited state may be generally expressed by swapping the HOMO and LUMO in equations 5.4 and 5.5 for the source of the excited electron and its destination. As a result the overlap in total change in electron density, if only singly excited states are considered, may be a better measure of the total exchange energy. To first approximation doubly or higher excited states may be neglected, as is common in CI excited state calculations, but it should be noted they may also cause significant changes to the orbital energies.¹⁵ Note, a problem with this approach is it includes cross terms (ie. singly excited state 1 will have calculated electron correlation with singly excited state 2, but this is not true in reality).

In terms of the oscillator strength, the HOMO and LUMO are not used in the equation to calculate it. Further, what is being calculated is the ability of an applied dipole to interconvert two electronic states. As such it is wholly appropriate to use the change in electron density to look at this value.

It has just been discussed that a decrease in the overlap in donating and accepting electron densities approximately decreases the singlet triplet energy gap when only singly excited states are calculated. This corresponds to CI-singles, a commonly used method of calculating excited states. Because separation of donating and accepting parts of the molecule defines a CT states, this is why they are desired in TADF. While it is desirable to keep the excited states slightly overlapped in order to increase the oscillator strength, generally in good TADF compounds, the orbitals are mostly separated. Because a small energy gap between singlets and triplets implies that the energetic landscape of both triplets and singlet states are similar, this allows the approximation of the S_1 state by the T_1 on the basis of very few approximations. The approximations made are

1. The S_1 and T_1 states both originate from the same CT states, hence disregarding the differences in spin, they would be the same,
2. There is little mixing with other excited states, hence they do not differ from the original CT state significantly ,
3. The small energetic difference between the CT states does not dramatically influence the orbital shape difference between S_1 and T_1 , hence the states remain practically identical.

Each of these can be verified via looking at change in density between the S_1 and T_1 states, where if they are similar then the approximations hold. The 2nd assertion, that there is little mixing between orbitals, is weakened by the fact it has been hypothesised that mixing with other states is key to allowing the TADF. It is common knowledge that the transition between two states of the same type is disallow via El-Sayed's rule. Put simply El-Sayed's rule forbids this transition because there is no change in orbital angular momentum, and this means that change in spin angular moment cannot be compensated via spin-orbit coupling. Mixing with other states²¹ or vibronic mechanisms²⁶ can allow this (see section 1.3.3). However it is unclear how much mixing with other states is required to bypass this rule. Preliminary research suggests not much mixing between states is needed;²¹ as a result it is possible that all approximations hold.

Regardless of whether the lack of mixing holds generally for TADF, it remains possible to check this by checking the change in density between the S_1 and T_1 states. A large mixing with other states would be expected to cause a large difference between these densities. In this document, these will be calculated by looking at the difference in the change in density between the $S_0 \rightarrow S_1$ transition and the $S_0 \rightarrow T_1$ transition. It is shown below that this gives the change in electron density for S_1 to

T_1 , where ρ_{S_0} is the S_0 electron density, ρ_{S_1} the S_1 electron density, and ρ_{T_1} the T_1 electron density.

$$(\rho_{S_1} - \rho_{S_0}) - (\rho_{T_1} - \rho_{S_0}) = \rho_{S_1} - \rho_{T_1} \quad (5.7)$$

While the T_1 state has been calculated in the field in the field of TADF.²⁷ It is believed this is the first document to observe it may approximate S_1 . While this postulate will be used herein, it is beyond the scope of this thesis to study a wide range of TADF molecules to confirm it experimentally. It is acknowledged that this is a weakness of this thesis and so it may be interpreted as a first preliminary test of it.

In this section, first the geometries to be studied will be discussed, then the lowest energy conformation using B3LYP will be considered, in both ground and excited state geometries, then the same with CAM-B3LYP, and finally an investigation into the different geometries using CAM-B3LYP will be discussed. What will be found is that CAM-B3LYP performs better at comparing excited states, whereas B3LYP performs better in the ground state. It will also be concluded that there are 3 geometries important to DMAC and that conversion between two geometries is likely blocked for C2 and C3 in the solid state.

The computational results will also suggest that the CBZ component of C2 and C3 competes severely with the electron donation of DMAC group in the first excited CT state. This competition leads to reduction in the absorption and fluorescence energies. Further it is shown there is much weaker competition between the CBZ and TRZ in electron accepting, however it is still there and narrows the energy gap. The singlet-triplet energy gap also narrows consistent with experiment. Each of these observations are consistent with the rest of the work in this thesis.

5.2 The Geometries

The beginning of any piece of computational work is the geometries from which the compound will be studied. A good starting place for the geometries of a compound is the Cambridge structural database (a database of crystal structures).²⁸ Immediately, when compounds similar to the compounds studied herein are searched for, similar structures are found which provide the basis of computational simulation. When this work began, there was no exact structure in the database so the similar structures²⁹ shown in figure 5.5 were used. Since completion of this work, a new geometry has been uploaded of the precise structure.³⁰ The new geometry is shown in figure 5.6 and is not overly dissimilar to the ones in figure 5.5.

However, while these structures provide a good starting point, it must be remem-

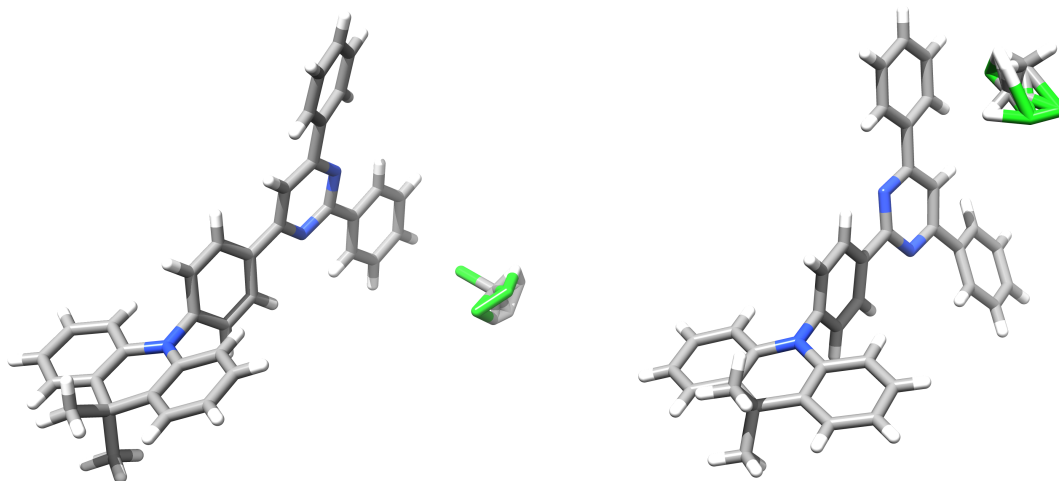


Figure 5.5: Diagram of related structures, "YAWGIP"²⁹ (left), and "YAWGEL"²⁹ (right) from the Cambridge Structural Database.

bered that they correspond to materials in a crystalline morphology. In devices, and in film, the material is used in an amorphous form, by rapidly depositing from solution. In this amorphous form many different geometries of the structures exist, in which some may interchange via vibrations (dependent on the amount of free space, and size of the change), and others may not. Further, within the solid state, excitons may diffuse by means of Föster (singlets) and Dexter (singlets and triplets) transfer. Excitons tend towards the lowest energy structure in the film. In the process of this diffusion, various geometries will emit, and hence they must still be investigated.

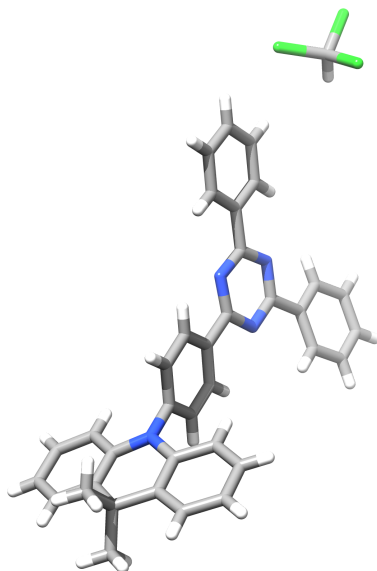


Figure 5.6: Diagram of newly published C1 crystal structure structure; "PUDFIG"³⁰ in the Cambridge structural database.

In order to investigate the other possible geometries in the film, some approximations must be made. As a compound drops out of solution, it will go from having

thermal distribution of states in solution, to having a fixed geometry in the solid state. Unfortunately, in computational chemistry, only local minima within the potential energy surface can be easily and accurately considered, and so it seems reasonable to deal with all "key geometries" of the compound at their minima. Using the minima is an approximation, as is what is decided as a "key geometry". Inevitably, deciding what geometries are significant is mostly done by chemical intuition; this is not perfect and allows for the influence of human error, but allows for rapid calculations at low costs. Alternative methods do exist where large quantities of geometries are created via Monte Carlo or Molecular Dynamics (MD) techniques; however, these simulations are beyond the scope of this publication.

The crystallographic database can further help to identify "key geometries". In the database alternative geometries of the components of the molecule in other structures can be viewed, and it may be postulated from this that these geometries are likely form-able in the measured compounds. Here-in, "component" is defined such that the groups found approximately orthogonal in the crystal structures correspond to a component. The rationale for this separation based on molecular orthogonality, is that conjugation is approximately symmetry forbidden through an orthogonal connection between heterocycles. This means that to first approximation they are electronically independent of each other. This provides 3 components, DMAC, TRZ, and tBU-CBZ, as shown in figure 5.7.*

This designation of components shown in 5.7 does follow from the crystallographic structure shown in figures 5.5 and 5.6. Of possible note are the phenyl groups attached to the triazine (C_3N_3 heterocycle), and why they are grouped with the TRZ component. A quick search on the crystallographic database will demonstrate to the reader that the TRZ component usually lies with the phenyl groups planar to the triazine group and that attached heterocycles tend to be at angles close to 90° to this. This is rationalised here-in by sterics — and lack thereof of triazine — in the ortho-ortho connection of the heterocyclic rings in these molecules. The steric effects are summarised in figure 5.8.

It is noted that sterics may be expected between the triazine and the attached phenyl groups, due to the presence of a lone pair. The lone pair in triazine is conventionally thought of as being in the remaining unbonded sp_2 orbital. It should be noted that electrons act as waves, and their location may be difficult to fully place. This lone pair may interact with the C-H anti-bonding orbital on the phenyl, or bend or bifurcate away from the hydrogen atom. Regardless, the position of this lone pair does not appear that to dominate the geometry. However, there is likely more flexibility in its positioning than implied by these stationary structures. It has

*It will be found later that conjugation does run through these connections, and so this is itself a crude approximation

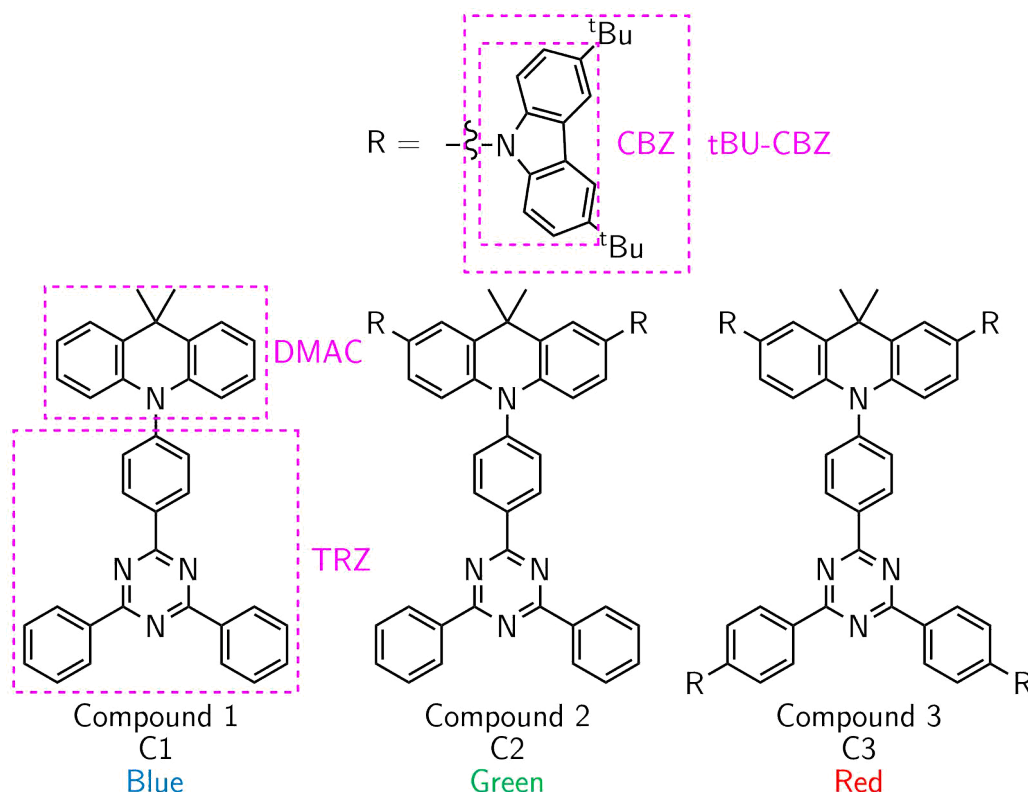


Figure 5.7: The structures of the compounds discussed, the components which make them up and the names and colours which correspond to them.

been measured that 1,4 substituted phenyls may flip on the timescales of 910 ns³¹ and 5 ms³² in the solid state dependent on structure. While a full flip may or may not be on the timescale of TADF, this does suggest conformational variability. Investigation into this by M. Bryce et al.³³ has suggested variability in the phenyl position may be influential in TADF design.

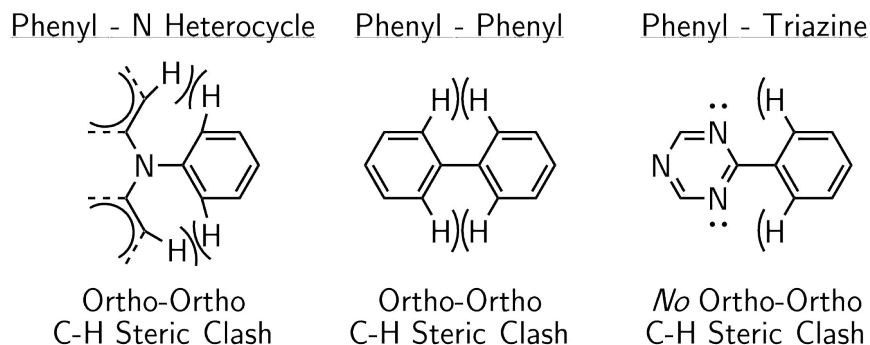


Figure 5.8: A demonstration of the likely reason for planarisation of phenyl groups with triazine, and not other groups.

When the geometries of tBU-CBZ and TRZ are examined in the Cambridge crystallographic database, the geometries tend to a single conformation, that is they are planar. As a result, the geometries of tBU-CBZ and TRZ are not varied

in this document. For DMAC however, the geometries vary quite significantly. Previously in the literature 2 different geometries of DMAC have been discussed in two separate papers,^{34,35} these are called "planar" and "crooked" according to Zhang et al.³⁵ and "quasi-equatorial" and "quasi-axial" according to Su et al.³⁴ in an adamantane substituted DMAC.

On further investigation of the crystallographic database, there appears to be varying bending between the two phenyl rings of DMAC, along the N - - C(CH₃)₂ axis. This bending is present in the "quasi-equatorial" structure, but not in the "planar" structure (see figure 5.9). When geometric relaxation is applied to the ground state of the bent and unbent structures of C1 and C2 studied here-in (C3 is not varied geometrically in this document) and the common place approximation of the ^tBU group as a methyl group is used,* two different ground state geometries are produced. This suggests that the "planar" and "quasi-equatorial" geometries are in-fact different. The "quasi-axial" and "crooked" geometries however appear qualitatively the same in the literature and hence are not treated as different here. This suggests that there are in fact 3 "key geometries" to DMAC, and it is believed that this is the first observation of this. It is found all DMAC containing entries fit into these 3 geometries, with what will be established as the "planar-orthogonal" geometry,^{36,37,38,39,40,41,42} the "boat-orthogonal" geometry^{36,43,37,44,45,46,29,47,48,49,50,51,40,52,53,54,41,55} and the "boat-aligned" geometry^{56,57} having entries from cited papers.

While these 3 geometries are now specified, the nomenclature for referring to them must be examined. The current nomenclature is, as summarised in figure 5.9, a mix of two naming conventions which are somewhat incompatible. The nomenclature developed by Zhang et al.³⁵ referring to both "planar" and "crooked" structures refers purely to the DMAC molecule, and not how it connects to the acceptor, precluding a full description of the structures. The nomenclature developed by Su et al.³⁴ refers to the boat like conformation of the central C5N ring (with reference to the standard cyclo-hexane conformations - see any organic chemistry textbook) in DMAC, and describes whether the connection to the acceptor is more axial or equatorial like. This description is unsuitable in the case that DMAC is planar. As a result a new nomenclature is proposed here-in.

The principle aim of nomenclature is to provide clear and unambiguous designation of objects. As a result, 3 new names are suggested. "*Planar-Orthogonal*" is suggested to be equivalent to the "Planar" by Zhang et al.³⁵, where "Planar" refers to the planarity of DMAC, and orthogonal the orthogonality with the acceptor. A possible cause of confusion is that the donor can be "Planar" with the acceptor, but it is felt that since DMAC cannot be orthogonal to itself, it should be clear that

*Note: the approximation of the ^tBU group as a methyl group will be used throughout this computational section

"Planar" corresponds with DMACs shape and "Orthogonal" with its arrangement with the acceptor. "*Boat-Aligned*" is used as equivalent to the "crooked" geometry proposed by Zhang et al.³⁵ and the "Quasi-Axial" proposed by Su et al.³⁴. The "Boat" in "Boat-Aligned" corresponds to the boat like geometry of DMAC, and the "Aligned" with the alignment of donor and acceptor in the same plane. It is noted that the donor and acceptor are not fully aligned, due in part to the "Axial" like nature of the structure. Nonetheless it will be shown that conjugation can run through this structure, and so for qualitative interpretation it may as well be. It is not felt there is room for misinterpretation since "Boat" clearly refers to the boat conformation of DMAC, and DMAC in itself cannot be "Aligned"; it must be aligned with another species such as the acceptor. Finally "Boat-Orthogonal" is suggested as the equivalent of the "Quasi-Equatorial" structure presented by Su et al.³⁴, with the reason for naming previously described for the other structures. It is not felt that any ambiguity exists in the "Boat-Orthogonal" name. This naming convention is summarised in figure 5.9.

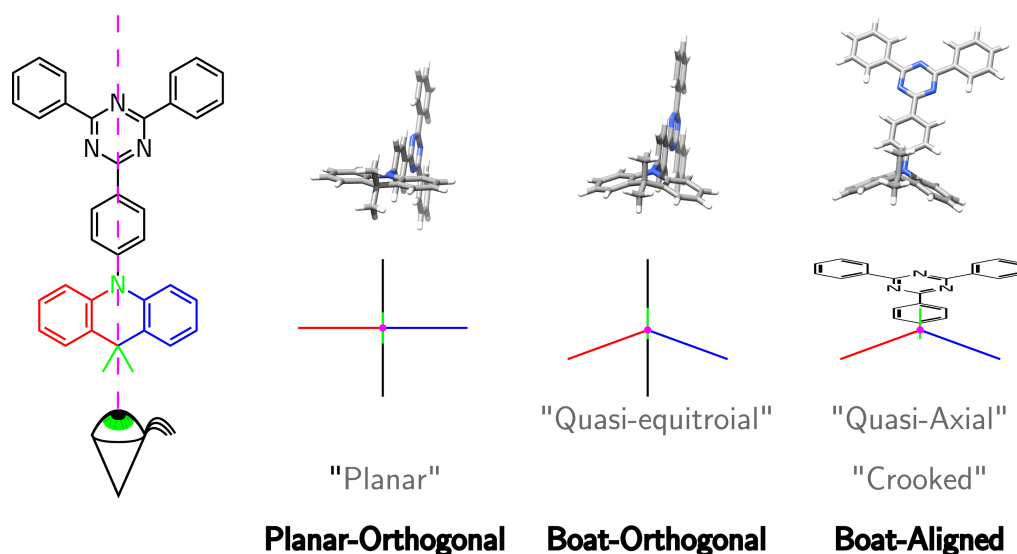


Figure 5.9: The structures of the geometries with old naming conventions shown in grey and new ones in black. The computational structures as well as a schematic representation are also shown.

It should be noted that a modern paper⁵⁸ has recently stressed the difference, between the "boat-orthogonal" and "planar-orthogonal" geometries, and suggested that the degree of planarity may play a difference in some electronic properties. However they use the naming convention of "Crooked" and "Planar" and cite Zhang et al.³⁵ As such the distinction of three geometries is not made.

The energetics of C1 in the ground state, in each of these 3 geometries using

CAM-B3LYP functional are compared in 5.10.* The geometries are visualised in figure 5.9 for C1, and in figure 5.26 for C2. It can be observed that the ground state geometry is the boat-orthogonal geometry, however the planar-orthogonal geometry is close in energy and within thermal energy at room temperature. Of course it is unclear if this is true in the solid state, as all calculations are carried out as if in the gas phase, with some solution like properties. Nonetheless this ground state geometry, which matches the crystal geometries shown in figure 5.6, will be the focus of this investigation. The planar-orthogonal geometry will also be investigated for C1 and C2; it is rationalised that C2 and C3 are rather similar at the DMAC end of the molecules, so it is less important to investigate this. For the boat-aligned geometry only C1 will be investigated, as it is felt this highlights the key features of this geometry. Existing work in the literature has also been done pointing towards the boat-aligned geometry being a triplet quencher³⁵ and related to the degradation of the compounds.⁵⁹

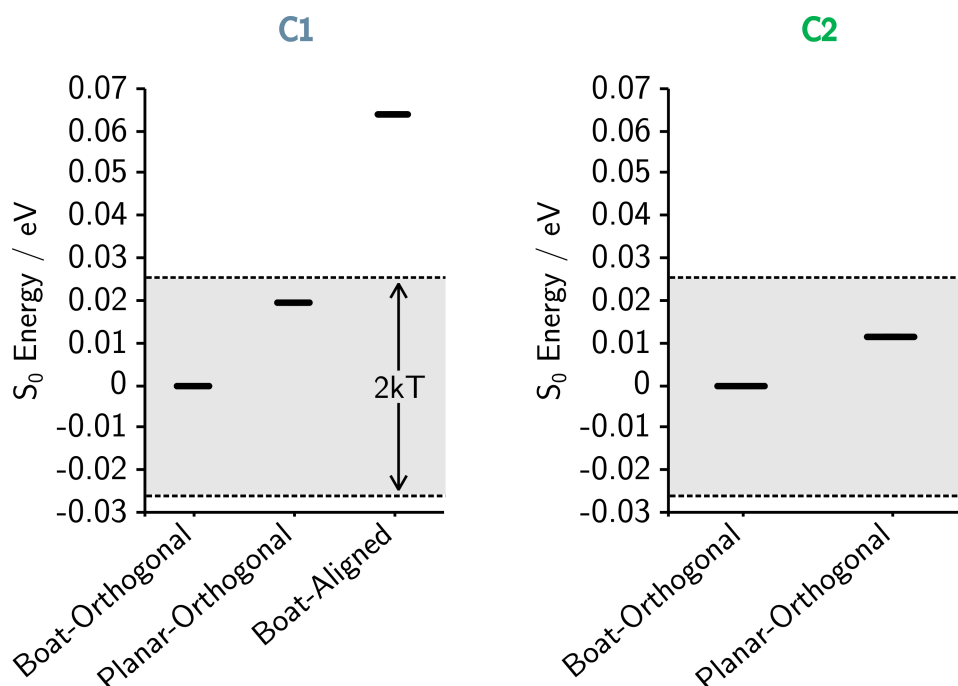


Figure 5.10: The energies of the optimised ground state in various geometries of C1 and C2, and with kT shown at room temperature.

While so far the geometries of the components have been varied, the relative

*CAM-B3LYP is used because it is found to reproduce the closeness in energy between the CBZ-TRZ Charge transfer state, and DMAC-TRZ CT state, this will be discussed further in section 5.4

geometries of the components has not been varied.* It is felt that these torsional changes are less necessary than the ones within the component, as qualitatively it seems that the only likely other torsional minima would be the mirror image of the existing one (see figure 5.11). This mirror image is likely similar electronically to the existing structure, so it is not investigated here.

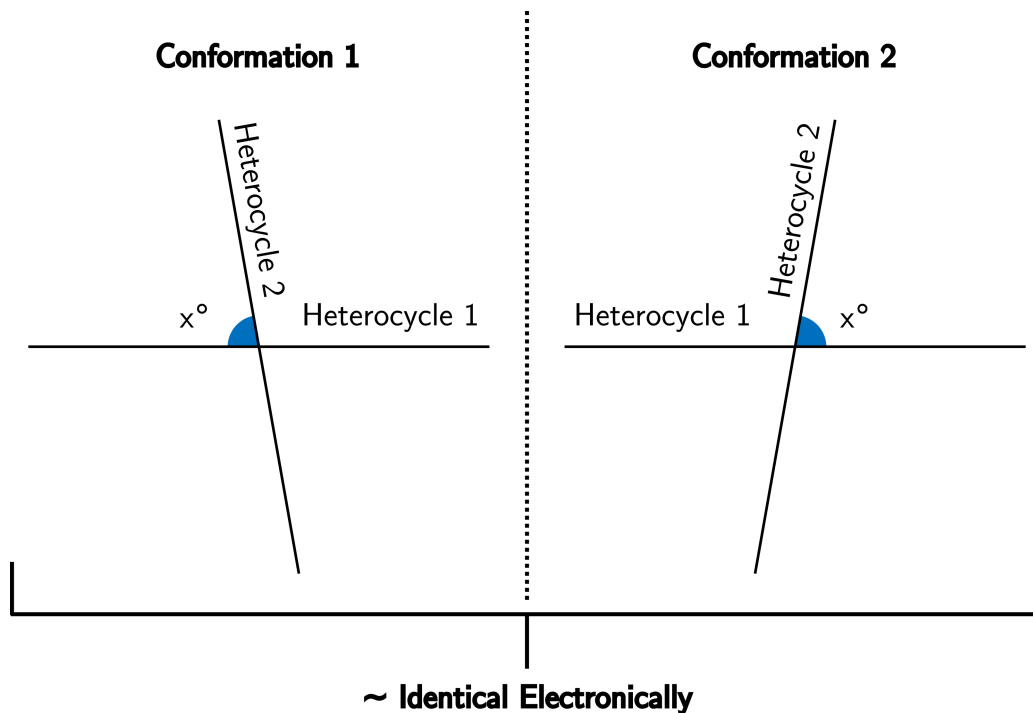


Figure 5.11: The conformations approximated as being the same in this document.

Originally when these calculations were first ran, the focus was on the lowest energy geometry, ie. the boat-orthogonal geometry. Having ran calculations with this geometry, it was found that experiment and theory did not fully match up. As a result the other geometries were introduced, in the minimum amount of other geometries, in order to justify the discrepancy. Having ran these calculations, it was decided that it would be worthwhile to calculate these compounds in the ground state triplet geometry, and postulated that this may better approximate the S_1 geometry. Each of these sets of results will now be discussed.

*It may be argued that the relative geometry of the TRZ and the DMAC component have been varied in the boat-aligned geometry. There is no evidence such a geometry exists for the CBZ component attached to the DMAC component (ie. with the CBZ component planar to the DMAC component). However, it may be argued that this should be simulated. It is found that the boat-aligned geometry is too high in energy to be significantly populated thermally in both the S_0 and S_1 state. At most this state can act as a triplet quencher, and this is unlikely considering the likely considerable energy barrier to formation of this species (overcoming the ortho-ortho strain as shown in figure 5.8). As a result, it is not felt necessary to simulate this geometry.

5.3 Boat-Orthogonal — The Lowest Energy Geometry — With B3LYP

It has just been shown that there are three "key geometries" to the molecules studied, where "key geometries" are defined via chemical intuition. These three geometries are summarised in figure 5.9, and are called boat-orthogonal, planar-orthogonal, and boat-aligned. It has further been shown that the lowest energy geometry is the boat-orthogonal geometry for C1 and C2 (see figure 5.10) and it is assumed that this is the same for C3 due to similarity at the DMAC end of the molecule. It should be noted that the planar-orthogonal geometry is very close in energy, such as to allow for significant occupation of this state, and the boat-aligned is somewhat further away, but, if at equilibrium, should allow some occupation. While the interchange between the boat-orthogonal geometry and planar-orthogonal appears likely to happen readily (*at least in solution*), the interchange of either of these with the boat-aligned is likely difficult, due to having to overcome the ortho-ortho steric interaction summarised in figure 5.8.

In this section, the lowest energy conformation — the boat-orthogonal geometry — will be discussed. The energy of the ground and excited states will be calculated using the B3LYP functional, in both the ground state (S_0) and the ground state triplet (T_1). What will be found is that the ordering of the energy gaps matches with experiment, and so do the trends in singlet triplet energy gaps. The energy gap between singlets and triplets will however be consistently overestimated in the T_1 geometry and underestimated in the S_0 and the changes in energy between the emission/absorption will also be underestimated throughout. Further, the change in energy of the transitions are underestimated. The oscillator strengths are overestimated in the T_1 state and, and underestimated S_0 state.

5.3.1 The Ground State Singlet (S_0) Geometry

The B3LYP S_0 geometry calculations were the first to be ran on the chemicals studied herein. The energies of the S_1 excitations are shown in figure 5.12. Within this figure it is immediately noticeable that similar trends are observed between the experimental changes in energy gap and the calculated ones. It should be noted that the experimental energy gaps use onset potentials, which are a poorly evidenced approximation of the 0-0 vibrational transition for absorption or fluorescence, so should be treated with a degree of caution (this is further discussed in section 3.1).

It should also be noted in the experimental energies that the absorption onset of C3 is assigned as being due to the CBZ-TRZ charge transfer (CT) state (see

figure 5.7 for component labels). This assignment is done in section 3.3.2. It is not believed that the CBZ-TRZ CT state is the lowest energy absorption peak, and is instead believed that the absorption masks the lowest energy absorption peak as is discussed in 3.3.2; further, this prevents the obtaining of the lowest energy absorption onset. As a result, the absorption onset for C3 is estimated to shift similarly to its fluorescence. Further the CBZ-TRZ CT state can be compared with calculations with reference to the changes of energy density in the higher states (see figure B.11), and the resulting energies are tabulated and graphed in figure 5.12.

While it is the case that the changes in energy are similar in direction to experiment (as shown in figure 5.12), the magnitude of these changes are somewhat different. The changes from C1 $\rightarrow$ C2 are overestimated, for C2 $\rightarrow$ C3 are similar but slightly underestimated and for C3 (S_0 - S_1) $\rightarrow$ C3 (S_0 -(CBZ-TRZ CT)) are once again overestimated. Further the energy of the transitions is too low in simulations.

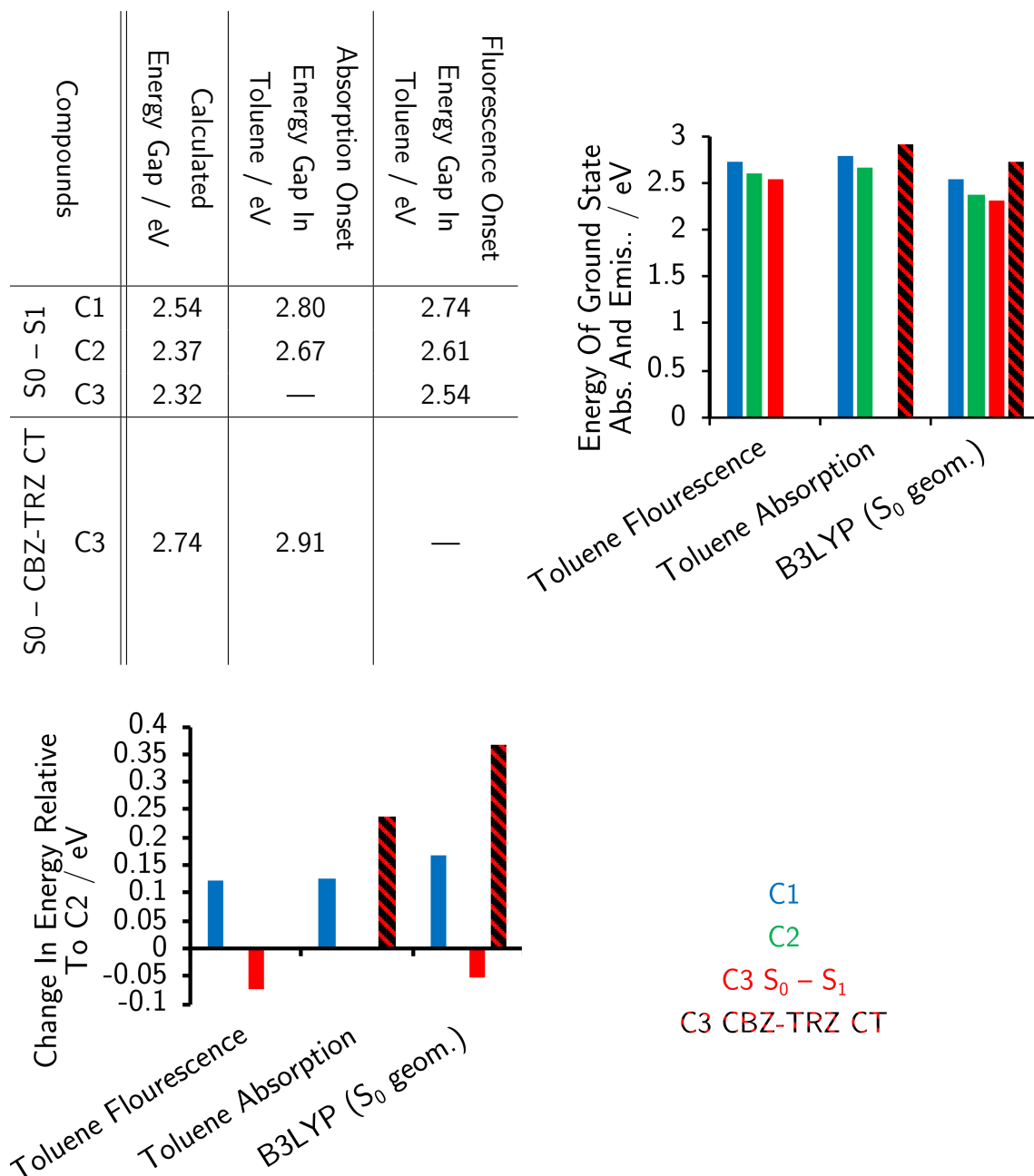


Figure 5.12: A table of energy changes as estimated by *B3LYP* calculations in the S_0 geometry (top left). The changes graphed (top right), and the changes shown relative to the C2 transition, normalised for each data set (bottom left).

The problem with the total energy being too low seems most consistent with the aforementioned (see section 5.1.1) problem that *B3LYP* has with CT states, where they are over-stabilised.⁸ It is possible this is also the cause of the general overestimation of changes between compounds. Other explanations do exist, however, the changes could be from transitions occurring from other geometries. A further explanation would be the lowest states being "dark" ie. none or little interacting with light. As will be discussed the oscillator strength in these calculations is rather low,

and so this could be interpreted as the low energy states being "dark", or the geometry changing to a location where it is more allowed. The lack of nearby states with higher oscillator strength (see section B.3.3.1.1), however, suggests "dark" states are unlikely to be the cause.

It should be noted (see section B.3.3.1.1) that there is a large number of states between the CBZ-TRZ state and the first excited state, which could be interpreted as weakening the hypothesis that this dominates the absorption spectra of C3. It should be noted that the oscillator strength of the CBZ-TRZ is at least 2 orders of magnitude greater than all states lower in energy than it. As such it remains likely that the CBZ-TRZ would dominate the spectra.

Table 5.1: The calculated (*B3LYP*, S_0 geom.), and approximate experimental toluene oscillator strength, and singlet triplet energy gap (not in toluene), of the various transitions in the compounds studied. The approximate experimental values are taken assuming the peak and full-width at half height of the oscillator strength in wavenumbers are the same in both wavelength and wavenumber, strictly incorrect due to the Jacobian correction.⁶⁰ Further the peaks are approximated as Gaussians with these properties. It is hoped this is sufficient for a rough order calculation. The numerical equation for oscillator strength shown in various text books is used.^{61,18,16} Note: The Jacobian correction⁶⁰ is applied to the molar absorption coefficients maxima used

Compound (Transition)	$f_{Calc.}$	$f_{Exp.-Abs.-Aprox.}$	$\Delta E_{ST-Calc.}$ / eV	$\Delta E_{ST-Exp.}$ / eV
C1(S1-S0)	0.0000	0.036 ± 0.003	0.007	0.05
C2(S1-S0)	0.0004	0.030 ± 0.003	0.004	$\lesssim 0.007$
C3(S1-S0)	0.0004	—	0.004	$\lesssim 0.007$
C3(CBZ-TRZ/S5-S0)	0.4940	0.461 ± 0.006	—	—

As has just been described the energies of the transitions roughly match experiment, it is interesting to see the change in density to which they correspond. The $S_1 \leftarrow S_0$ states are shown in figure 5.13, with higher states shown in section B.3.3.1.1. What is immediately obvious is that the a DMAC-TRZ CT state dominates the first excited in each and every compound. Further it can be observed that both the donating and accepting orbitals run into the carbazole groups attached to the DMAC and TRZ components respectively. Of these the donating components appears to run in more significantly.

The increase in conjugation for along the series C1–3 for the $S_1 \leftarrow S_0$ transition is consistent with the reduction in energy gap seen across the series. Further the larger increase for $C1 \rightarrow C2$ and less for $C2 \rightarrow C3$ is consistent with the changes in energy and the rest of the data generated.

On top of the energy levels and orbital distributions, the singlet-triplet energy gap and the oscillator strengths can be compared with experiment. This is done in table 5.1, with oscillator strength calculated approximately via the method described

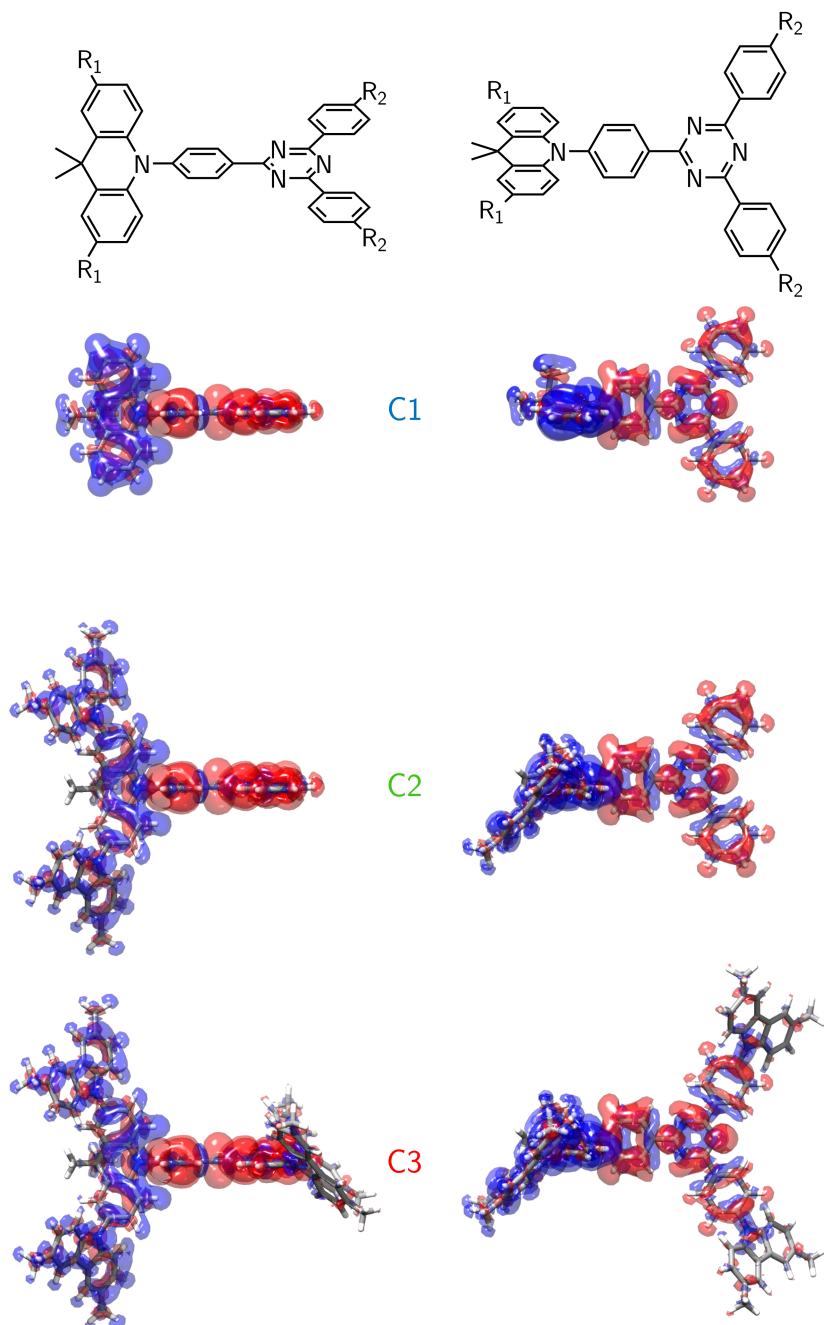


Figure 5.13: The change in electron density as calculated using *B3LYP* for $S_0 \rightarrow S_1$ in the S_0 geometry. Two arrangements are shown with the geometries shown via chem-draw structures. Blue represents electron loss, red electron gain. Cut-offs are set to $0.4 \text{ me r}_{\text{Bohr}}^{-3}$ throughout to allow a comparison of magnitudes.

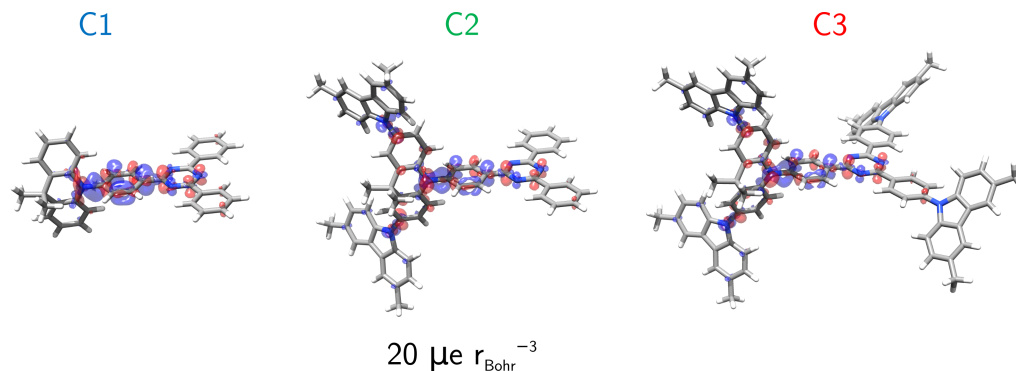


Figure 5.14: The change in electron density, as calculated using *B3LYP* in the S_0 geometry, for $T_1 \rightarrow S_1$. Blue represents electron loss, red electron gain. Cut-offs are set to $0.02 \text{ me } r_{\text{Bohr}}^{-3}$, to allow full comparison.

in the caption. It should be noted that the energy gaps for all compounds were not successfully found via comparison of emission at 77 K to room temperature emission as discussed in section 3.3.3, with it being found in sections 4.3.2 and 4.3.3, that the delayed fluorescence is not quenched at 77 K for C2 and C3. As such it is assumed that the energy gap is less than kT at 77 K temperature, where T is temperature, and k is the Boltzmann constant for C2 and C3. For C1 an average of literature values is used^{62,63} which use a superior method of calculating the singlet-triplet energy gap (discusses in section 3.3.3).

It is apparent when comparing the oscillator strength between experiment and calculation that it is an order of magnitude too low (more for C1), and that the singlet-triplet energy gap for C1 is also an order of magnitude too low (although C2 and C3 seem correct). While a simple Arrhenius equation interpretation of the energy gaps, would predict a 2 fold reduction in rate cooling from room temperature to 77 K for the C1 energy gap calculated, which is not that dissimilar to the changes in rates and intensities in the transient studies (see section 4.3.1), the transient rates are complex, and do not yield to such simple interpretations (see section 4.2).

It could be postulated based on the singlet-triplet energy gaps provided by this method, that C1 is not quenched. The shift in emission observed experimental could be purely from different molecules in the S_1 band emitting at different times. It is noted that the shift in emission is of similar order as is observed in C2 and C3, but to lower energy (see section 3.3.3).

However, as has been previously stated (see section 5.1.2) the ground state geometry is not qualitatively appropriate for calculating the singlet-triplet energy gap, and as such this may explain the inconsistencies. The inconsistencies in the oscillator strength seem the most likely caused by changes in geometry via thermally accessible vibration allowing an increase, however it may be due to the functional used.

Fundamental to TADF is the transfer of excited states from the T_1 state to the S_1 state. This transition requires El-Sayed's rule to be broken, ie. some process must allow there to be an appropriate change in angular momentum for this transition to take place. Leading theories are that a change in vibrational state may allow this²⁶, or that a mixing with other states can allow this.²¹ If mixing with states causes the T_1 and S_1 states to be different, this should theoretically be visible by subtracting these changes in electron density. These subtracted electron densities are shown here-in in figure 5.14.

In order for the differences in electron density to be visible the cut off of the change in electron density for the $S_1 \rightarrow T_1$ transition had to be lowered from the standard $0.4 \text{ me } r_{\text{Bohr}}^{-3}$ to $0.02 \text{ me } r_{\text{Bohr}}^{-3}$ showing the similarity of the orbitals. Nonetheless a difference in electron density is observed, and it is curious to observe it is mostly located on the bridging phenyl, with small additional changes on the DMAC and triazine rings. This is particularly curious given it is known that the phenyl ring has a rather large vibronic coupling as measured by the Huang-Rhys parameter.^{64,65} This helps demonstrate the importance of the bridging phenyl in TADF molecular construction.

5.3.2 The Ground State Triplet (T_1) Geometry

What has just been shown are the calculations of the compounds using the S_0 geometry. Similar changes in S_1 excitation energies were observed between experiment and calculations, but that these changes tended to exaggerate the magnitude, and the overall magnitude of the energies were too low. These discrepancies were suggested to be due to the well known short coming of B3LYP in calculating charge transfer states.⁸ Further, in the calculations, the singlet-triplet energy gaps were found to be low in the case of C1, and the orientational polarisability too low in all cases. In addition little difference between the singlet and triplet orbitals was observed, weakening the case for breaking El-Sayed's rule via orbital mixing. Of course the calculations were ran in the S_0 , which may be argued as being unsuitable for calculation of all excited state values (see section 5.1.2), and this will be explored here.

In this section the compounds will be calculated in the T_1 geometry ie. the ground state triplets, which has been argued (see section 5.1.2) as being more appropriate for the excited state. The molecules were relaxed to their minima from this state from the S_0 geometry, and the new geometries are shown in figure 5.15. What is immediately obvious is that while the boat-orthogonal (see figure 5.9 for definition of these geometries) geometry is maintained for C1, it is not maintained for C2 and C3, and instead these molecules convert to the planar-orthogonal geometry. This will

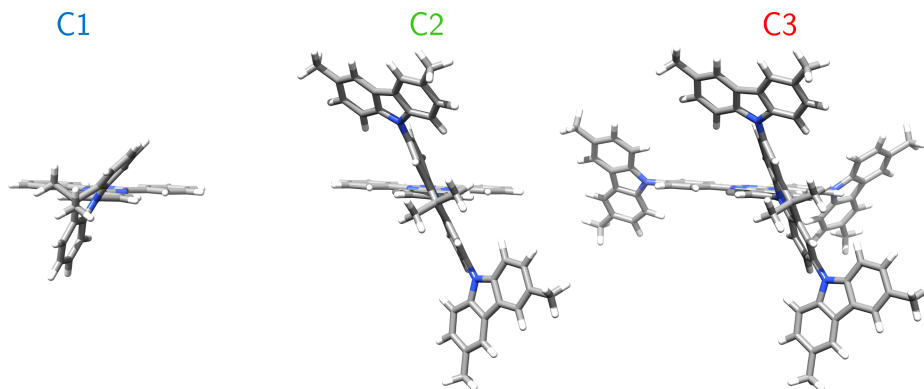


Figure 5.15: The geometries of the compounds when optimised from the S_0 geometry while in the S_1 state using the B3LYP functional.

be found to be partially consistent even when calculated via CAM-B3LYP, where all molecules convert to planar-orthogonal geometry. This result shows that major conformational changes occurs in the excited state.

The energies of the calculated S_0 to S_1 transitions are shown in figure 5.16. The changes and energies follow a similar trend to the S_0 geometry, and once again over-estimate the changes, especially from C1 to C2, and underestimated the energy gap. Once again this is attributed to the underestimation of charge transfer state energies within B3LYP,^{1,8,66} supported by the increased separation of electron donation and acceptance along the series C1, C2, C3, as shown in figure 5.17. Similarly to the S_0 geometry the donating electron density is shown to spread from the DMAC donor and to the CBZ component, and similarly, but to a lesser extent, accepting electron density is spread from the TRZ component to the CBZ component. These changes are used to justify the changes in energy shown in figure 5.16.

When the oscillator strength and the singlet triplet energy gap are compared in figure 5.2, significantly contrasting results are shown compared to the earlier S_0 geometry. The singlet-triplet energy gap is shown to be much larger than would be expected experimentally in all cases, and as is the oscillator strength.* This is especially surprising given that this suggests the excited states are more locally excited like, and B3LYP favours CT states.

An explanation for the raised oscillator strength and singlet-triplet energy may lie in the approximation of the S_1 and T_1 as the same. A tendency for triplet states to increase the singlet-triplet energy gap can be imagined when the geometries are minimised. This is because, if a change in geometry were to increase the exchange energy, not only would the triplet be stabilised (and thus the geometry change would be implemented), the S_1 state would be destabilised. While the triplet stabilisation

*The experimental oscillator strength is also a maximum value — reinforcing the inaccuracy of these values.

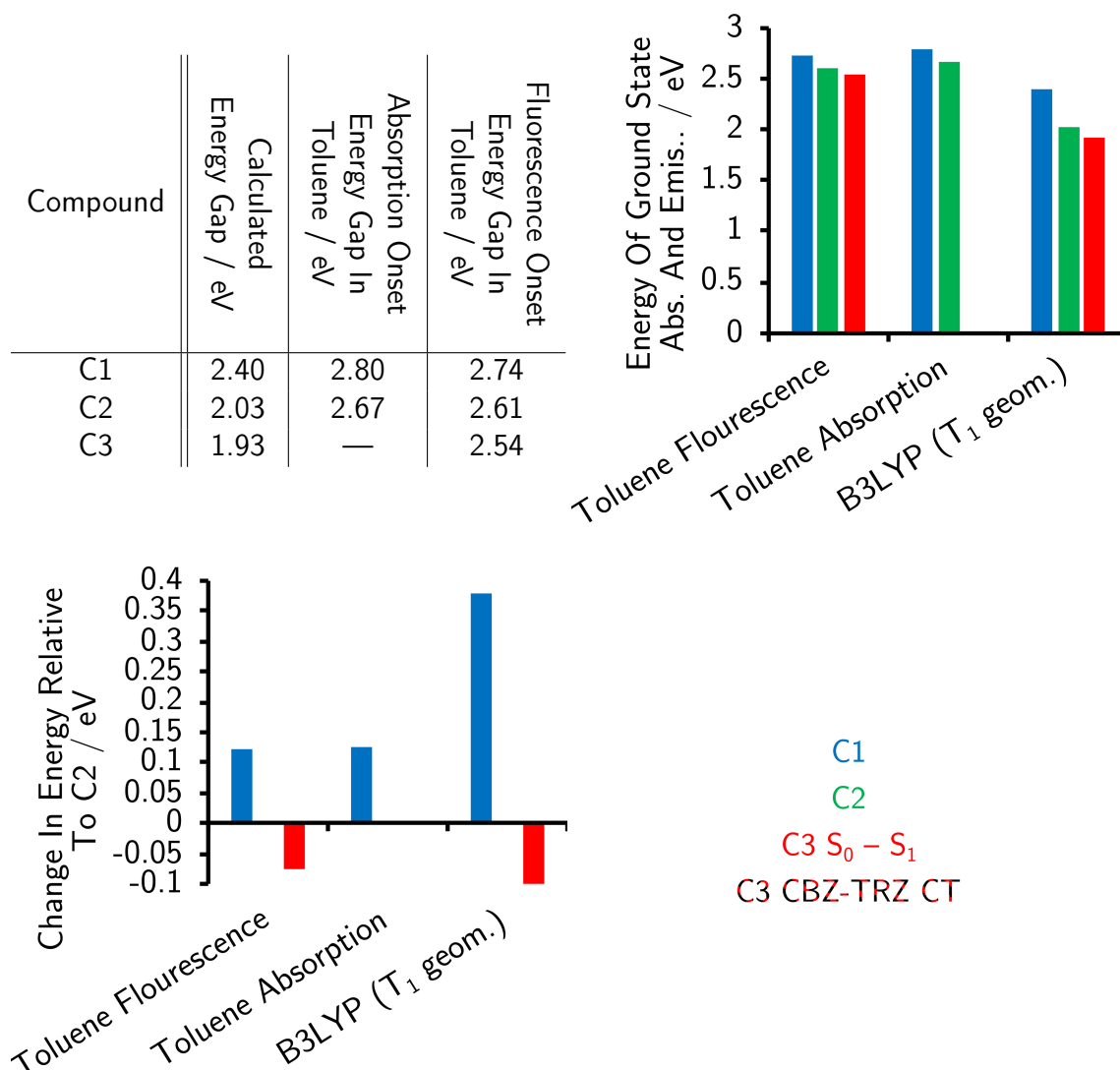


Figure 5.16: A table of energy changes as estimated by *B3LYP* calculations in the T_0 geometry (top left). The changes graphed (top right), and the changes shown relative to the C2 transition, normalised for each data set (bottom left).

will be a correct representation of the triplet energy, the destabilisation of the singlet will not be a correct representation of the singlet energy at its minima. This is interpreted as a weakness in approximating all excited states as the triplet state.

An additional cause of an increased singlet triplet energy gap may be a lack of doubly excited states in the excited states. It is known that doubly excited states cause a reduction in the singlet-triplet energy gap and may cause inversion¹⁵ and claimed¹⁵ on the basis of work by P. Elliot et al.⁶⁸ that TD-DFT does not fully account for this. This has also been shown experimentally.^{15,14} It is beyond the scope of this publication to go through this work in any sort of detail, and this is left to the reader.

In addition to the energies, the oscillator strength, and the singlet-triplet energy gap, the differences between the electronic excited states can be examined.

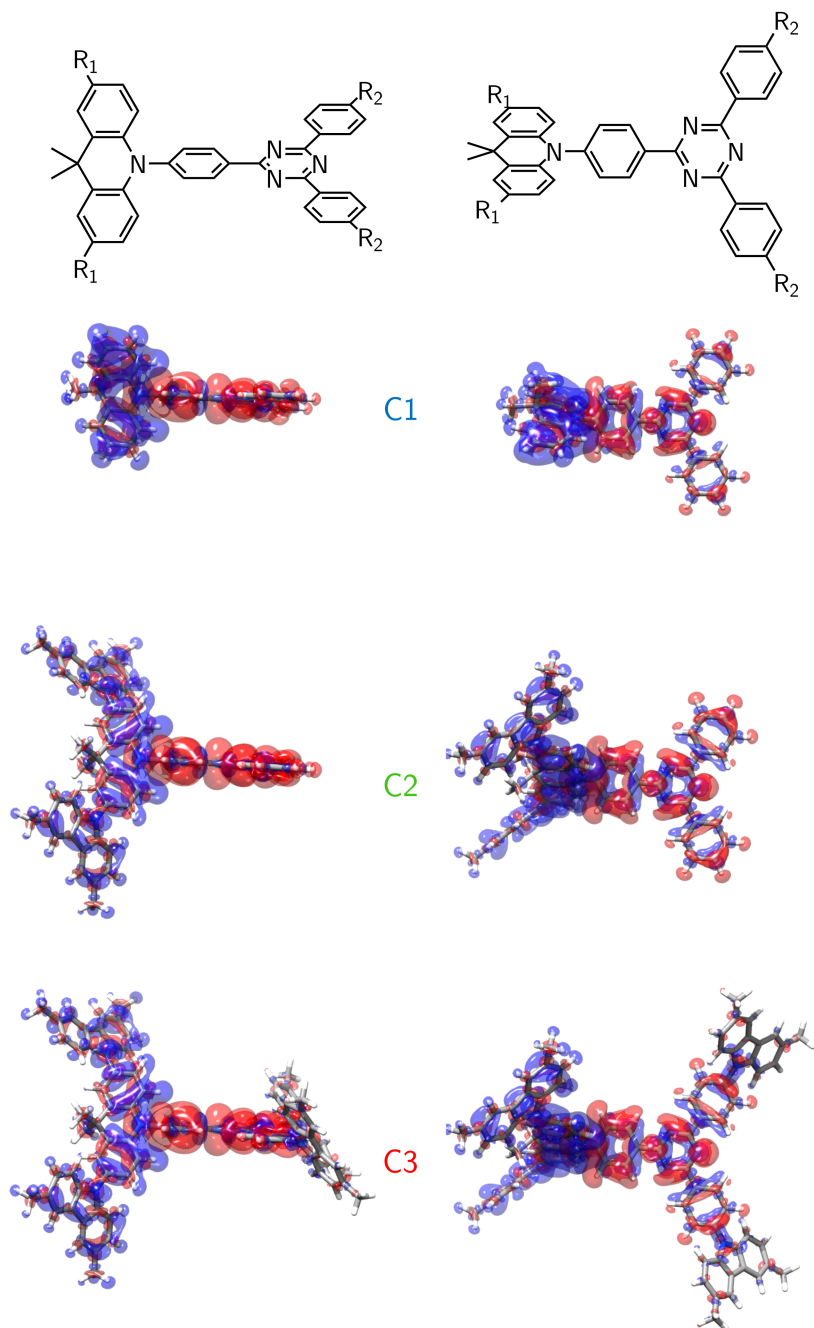


Figure 5.17: The change in electron density as calculated using *B3LYP* in the T_1 geometry for $S_0 \rightarrow S_1$ for the TADF compounds synthesised. Two arrangements are shown with the geometries shown via chem-draw structures. Blue represents electron loss, red electron gain. Cut-offs are set to $0.4 \text{ me } r_{\text{Bohr}}^{-3}$ throughout to allow a comparison of magnitudes.

Table 5.2: The calculated, and approximate experimental oscillator strength, and singlet triplet energy gap, of the various transitions in the compounds studied. Calculations were ran using *B3LYP* in the T_1 geometry. The approximate experimental values are calculated using approximate formula from A. Köhler⁶⁷ where $f = \frac{1}{\tau_0 n^3 \bar{\nu} (cm^{-2})^2}$. The time constants are approximated by the pulse fluorescent rate (note this means it is a maximum), the wavenumber from the maximum in wavelength (neglects jacobian correction), and the refractive index approximated as glass's (1.6). It is hoped this is sufficient for a rough order calculation. The experimental singlet-triplet energy gap values are sourced as described in section 5.3.1.

Compound (Transition)	$f_{Calc.}$	$f_{Exp.-Emiss.-Aprox.}$	$\Delta E_{ST-Calc.}$ / eV	$\Delta E_{ST-Exp.}$ / eV
C1(S1-S0)	0.2779	0.03	0.374	0.05
C2(S1-S0)	0.1661	0.02	0.166	$\lesssim 0.007$
C3(S1-S0)	0.1730	0.03	0.135	$\lesssim 0.007$

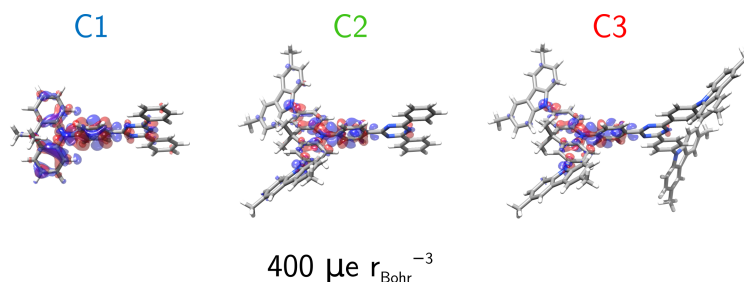


Figure 5.18: The change in electron density as calculated from *B3LYP* in the T_1 geometry for $T_1 \rightarrow S_1$. Blue represents electron loss, red electron gain. Cut-offs are set to $0.4 me r_{Bohr}^{-3}$, to allow full comparison.

A selection of other excited states are shown in section B.3.3.1.2, but of greatest importance is the difference between the S_1 and the T_1 states. As previously mentioned, difference between these two states may allow the breaking of El-Sayed's rule.²¹ The difference between these states are shown in figure 5.18. Unlike in the previous section, it is not necessary to adjust the electron cut-offs from the standard $0.4 me r_{Bohr}^{-3}$ in order to make them visible. This shows that there is significantly more mixing of states, allowing the breaking of El-Sayed's rule, in the ground state triplet geometry.

Similar to the ground state singlet geometry, the difference between the S_1 and the T_1 states is mostly located on the bridging phenyl group, and the DMAC group, although the proportion on the TRZ end of the molecule appears reduced. Once again this shows the importance of the bridging phenyl group in these molecules.

5.4 Boat-Orthogonal — The Lowest Energy Geometry — With CAM-B3LYP

So far all three compounds have been investigated via B3LYP in both the ground state singlet (S_0) geometry and the ground state triplet (T_0) geometry. While this has done a reasonable job of replicating experimental results, consistently the singlet excitations energy appear to be too low. Further the changes between C1 and C2 have consistently been exaggerated. As a result, it was thought interesting to try the CAM-B3LYP functional to try to fix these problems. CAM-B3LYP is meant to correct for the over-stabilisation of charge transfer in B3LYP.^{1,8,66}

When applying CAM-B3LYP it will be found that this appears to qualitatively over-correct for the problems in B3LYP. It is believed that this is likely the case because the CAM-B3LYP works by using the Hartree-Fock correlation in place of the Becke 1988 correlation for long range electron interactions.¹ The Becke 1988 is also what the B3LYP functional is designed to use. It has been shown that Becke 1988 also contains contribution to the static correlation, which the correlation function in B3LYP must naturally lack for it to work well.² It is assumed this must also be the case for CAM-B3LYP, and so when the Hartree-Fock exchange is swapped for Becke 1988 there must be a lack of static exchange.

A slight problem with the logic that the exchange and correlation behave the same in B3LYP and CAM-B3LYP, is that B3LYP uses a slightly different correlation to CAM-B3LYP in the software used (Gaussian) herein (0.19 VMN3 + 0.81 LYP vs 0.19 VMN5 + 0.81 LYP respectively*).^{1,71,9,70} VWN5 and VWN3 are different parametrisations of the same formula,^{71,9} VWN3 has been found to behave better in simulations,⁹ but VWN5 is recommended by the authors of the original paper.⁷¹ For the sake of this document, it will be assumed that the correlations behave similarly, but this is acknowledged as a weakness in the arguments used herein, and may be the actual source of any errors.

Static exchange must be defined for the reader. Electron correlation is the energetic stabilisation which occurs from modelling electrons using functions beyond

*Some confusion may be caused by the fact VWN and VWN3 are used interchangeably in the literature.⁹ Further it is implied on the Gaussian website that VWN3 is used in the Gaussian software⁶⁹, however an email confirmed that VWN5 is used here.⁷⁰

a single determinant of 1 electron non-interacting orbital.* There are two ways in which stabilisation can occur from this, adding more determinants (static correlation), and making the orbitals behave as if they interact with each other (dynamic correlation). In reality both of these are solved (at least using the configurational interactions method for Hartree-Fock), by adding additional determinants. However it can be imagined that resulting orbitals which are made up of 2 base Hartree-Fock non-interacting orbitals in large quantities are likely resulting from static correlation, and ones that are mostly 1 orbital with lots of other small determinants are likely from dynamic correlation.†

It is suggested here-in that a sign of static exchange may be a significant difference in the electron density between the S_1 and T_1 states, particularly for the T_1 geometry. Under the approximation that the S_1 and T_1 are the same except for spin, it could be imagined that the dynamic correlation would be similar. However, with locally excited states having triplet energies much lower than their singlet energies, it would be expected that static correlation in the triplet state would be more likely than in the singlet state,‡ and would cause the difference between S_1 and T_1 states. Unfortunately, this would only show the difference in static correlation and not the total amount. While if it was assumed the orbitals produced from the functional were 1 electron non-interacting orbitals, the amount of mixing would help show if static correlation was occurring, unfortunately in DFT a correlation term is included, making this not valid. Therefore, it is not possible to show the total amount of static correlation in each state.

5.4.1 The Ground State Singlet (S_0) Geometry

As with B3LYP, originally the compound were calculated with CAM-B3LYP optimised in their S_0 geometry. The energy of the calculated excited states are shown in figure 5.19 and compared to experiment. It is immediately obvious when comparing the excited states that the two changes have occurred compared with B3LYP: firstly the energy gaps are now too big rather than too small, and secondly the changes

*This is not fantastically explained. The most basic approach to calculating energetic states is to model the compound using Hartree-Fock calculations. Hartree-Fock calculations model the electronic states as a single determinant of molecular orbital. Molecular orbitals are 1 electron non-interacting orbitals. Beyond Hartree-Fock, there is a variety of methods to improve these calculations, such as configurational interactions, which adds additional determinants of additional excited states, in order to lower the total energy. There are also additional methods beyond the scope of this publication such as Møller-Plesset perturbation theory and coupled cluster theory. These methods are all considered to address the correlation energy.

†DFT is much more complex as terms which account for correlation are included in the base functional, as a results determination of whether static exchange occurs or dynamic does, is very difficult

‡Note: mixing of electronic states happens most when the difference in energy between states is low. See cited paper.²¹

between the compounds are now far too small.

The increase in $S_0 \rightarrow S_1$ energy gaps is expected, as CAM-B3LYP is meant to remove the excess stabilisation in the CT states.^{1,8,66} Further the reduction in the change in energy is expected, since charges become more separated along the series C1-3 in B3LYP. However, the magnitude of these effects seem far greater than would be expected. 3 justifications are possible, the aforementioned lack of static correlation; the wrong geometry is used ie. thermal activation to a geometry where absorption occurs happens in the real molecules; or finally the aforementioned problems with the VWN5 correlation function used in CAM-B3LYP.

Of course the assumption has just been made that the separation of donator and acceptor increases along the series C1-3 in CAM-B3LYP as well as B3LYP. It is indeed shown that there remains an increase in electron separation along the series for CAM-B3LYP in figure 5.20. This would be consistent with a greater proportion of the HF exchange in the calculations; however does not rule out the other possibilities.

When the predicted singlet-triplet energy gaps are compared with experiment in figure 5.3, it is observed they are far too large, this is because the lowest triplet states are not CT states. This can be observed in the supplementary information (see section B.3.3.2.1), and is not necessarily wrong, considering the ground state is modelled here not the excited state. The oscillator strength however is also far too low, and is inconsistent (the reader will note this is the same as in B3LYP). Once again this could either be due to geometric change occurring before absorption, or the functional being wrong.

Table 5.3: The calculated (CAM-B3LYP, S_0 geom.), and approximate experimental toluene oscillator strength, and singlet triplet energy gap (not in toluene), of the various transitions in the compounds studied. The approximate experimental values are taken assuming the peak and full-width at half height of the oscillator strength in wavenumbers are the same in both wavelength and wavenumber, strictly incorrect due to the Jacobian correction.⁶⁰ Further the peaks are approximated as Gaussians with these properties. It is hoped this is sufficient for a rough order calculation. The numerical equation for oscillator strength shown in various text books is used.^{61,18,16} Note: The Jacobian correction⁶⁰ is applied to the molar absorption coefficients maxima used. The experimental singlet-triplet energy gap values are sourced as described in section 5.3.1.

Compound (Transition)	$f_{Calc.}$	$f_{Exp.-Abs.-Aprox.}$	$\Delta E_{ST-Calc.}$ / eV	$\Delta E_{ST-Exp.}$ / eV
C1(S1-S0)	0.0001	0.036 ± 0.003	0.553	0.05
C2(S1-S0)	0.0006	0.030 ± 0.003	0.323	$\lesssim 0.007$
C3(S1-S0)	0.0011	—	0.329	$\lesssim 0.007$
C3(CBZ-TRZ/S5-S0)	1.1090	0.461 ± 0.006	—	—

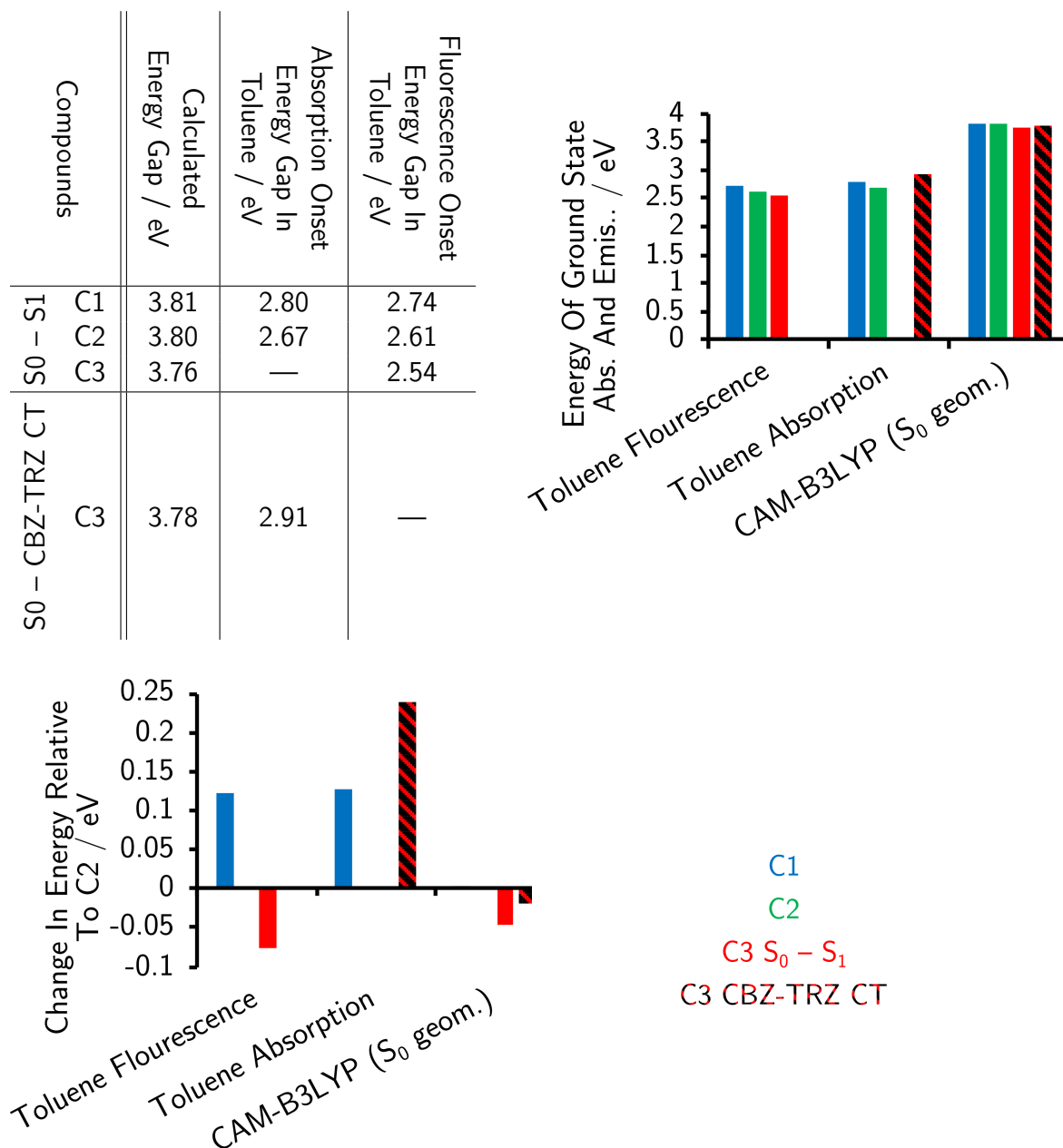


Figure 5.19: A table of energy changes as estimated by *CAM-B3LYP* calculations in the *S₀ geometry* (top left). The changes graphed (top right), and the changes shown relative to the C2 transition, normalised for each data set (bottom left).

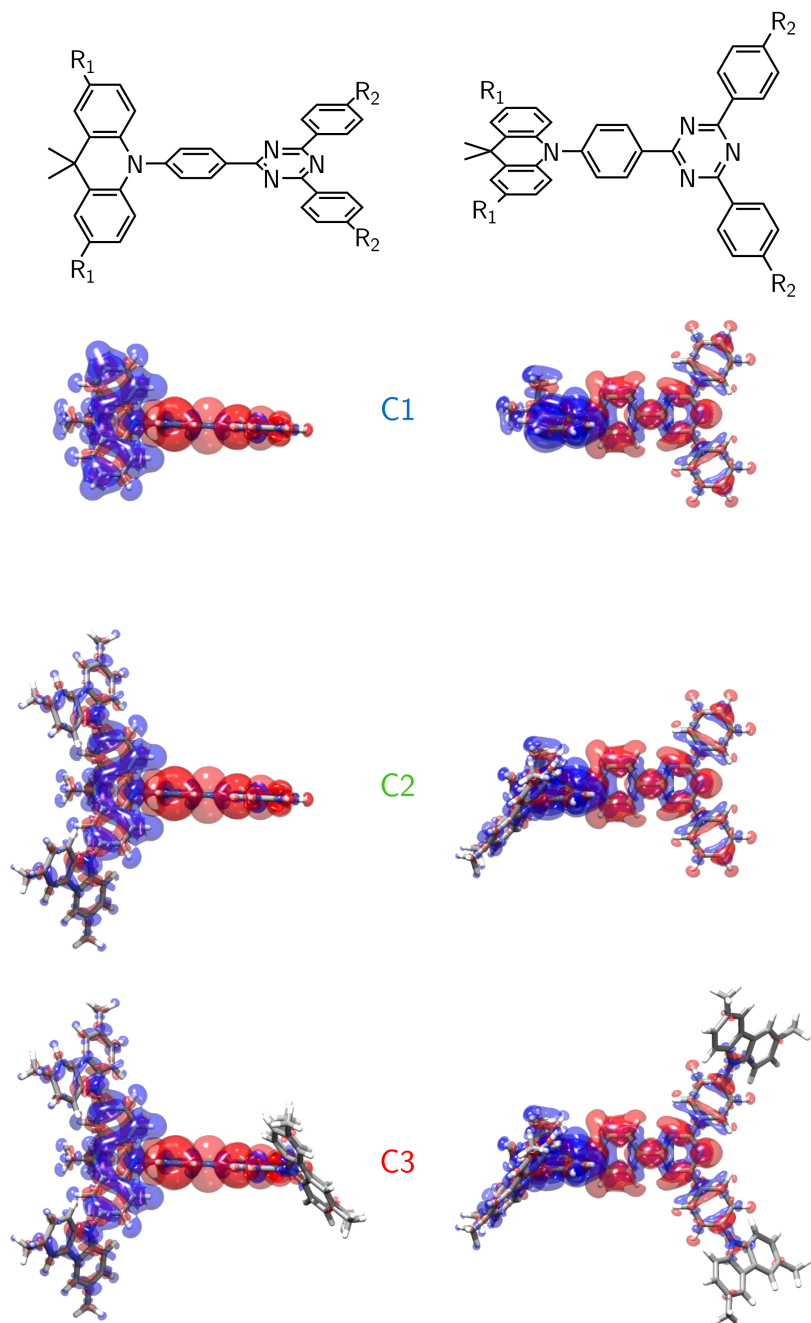


Figure 5.20: The change in electron density as calculated from *CAM-B3LYP* for $S_0 \rightarrow S_1$ in the S_0 geometry. Two arrangements are shown with the geometries shown via chem-draw structures. Blue represents electron loss, red electron gain. Cut-offs are set to $0.4 \text{ me r}_{\text{Bohr}}^{-3}$ throughout to allow a comparison of magnitudes.

5.4.2 The Ground State Triplet (T_1) Geometry

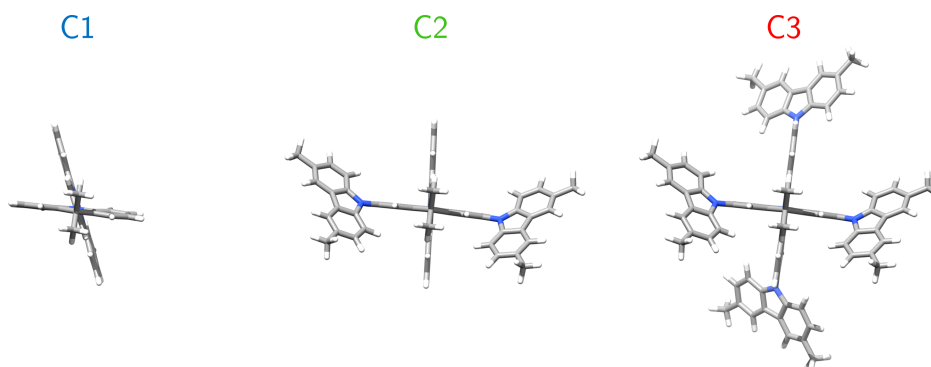


Figure 5.21: The geometries of the compounds when optimised from the T_1 geometry while in the S_1 state using the *CAM-B3LYP* functional.

Interestingly when the geometry is changed to the minima of the T_1 state, the changes in energy become more like experiment, this is shown in figure 5.22. Of further note is the change in geometry in this state. As is shown in figure 5.21, all 3 compounds swap from their boat-orthogonal S_0 geometry to the planar-orthogonal geometry. A minima corresponding to the boat-orthogonal geometry could not be found, so it is assumed not to be there. The diligent reader will remember that only the C2 and C3 geometries changed under B3LYP. This goes to show the significance of functional but little beyond this.

It is particularly interesting that the energetic changes in the excited state are arguably the closest aligned to experiment for CAM-B3LYP in the T_1 geometry, but arguably the worst aligned for the S_0 geometry. It is unclear precisely why this is the case. A case could be made that the ground state changes geometry and the excited state does not, or that because the ground state triplet is a CT state, the CAM-B3LYP performs better in minimisation, but there is no clear indisputable evidence for either. As a result, it is not possible to recommend one functional over another in this work based purely on this.

When the changes in the $S_0 \rightarrow S_1$ electron density are compared, as shown in figure 5.23, it is observed that the changes in density are mostly DMAC-TRZ charge transfer. This is consistent with all prior calculations. Further, it can be observed that for both donor and accepting parts of the molecule the electron density spreads onto the CBZ groups. Once again this is consistent with the rest of the work in this chapter.

The S_1 - T_1 energy gap are tabulated in figure 5.4, and it is observed that similar to most other calculations this energy gap is overestimated. However when the changes in density are observed (see section B.3.3.2.2), all triplet transitions are similar to the singlet ones. This suggests that unlike in the S_0 geometry, CAM-

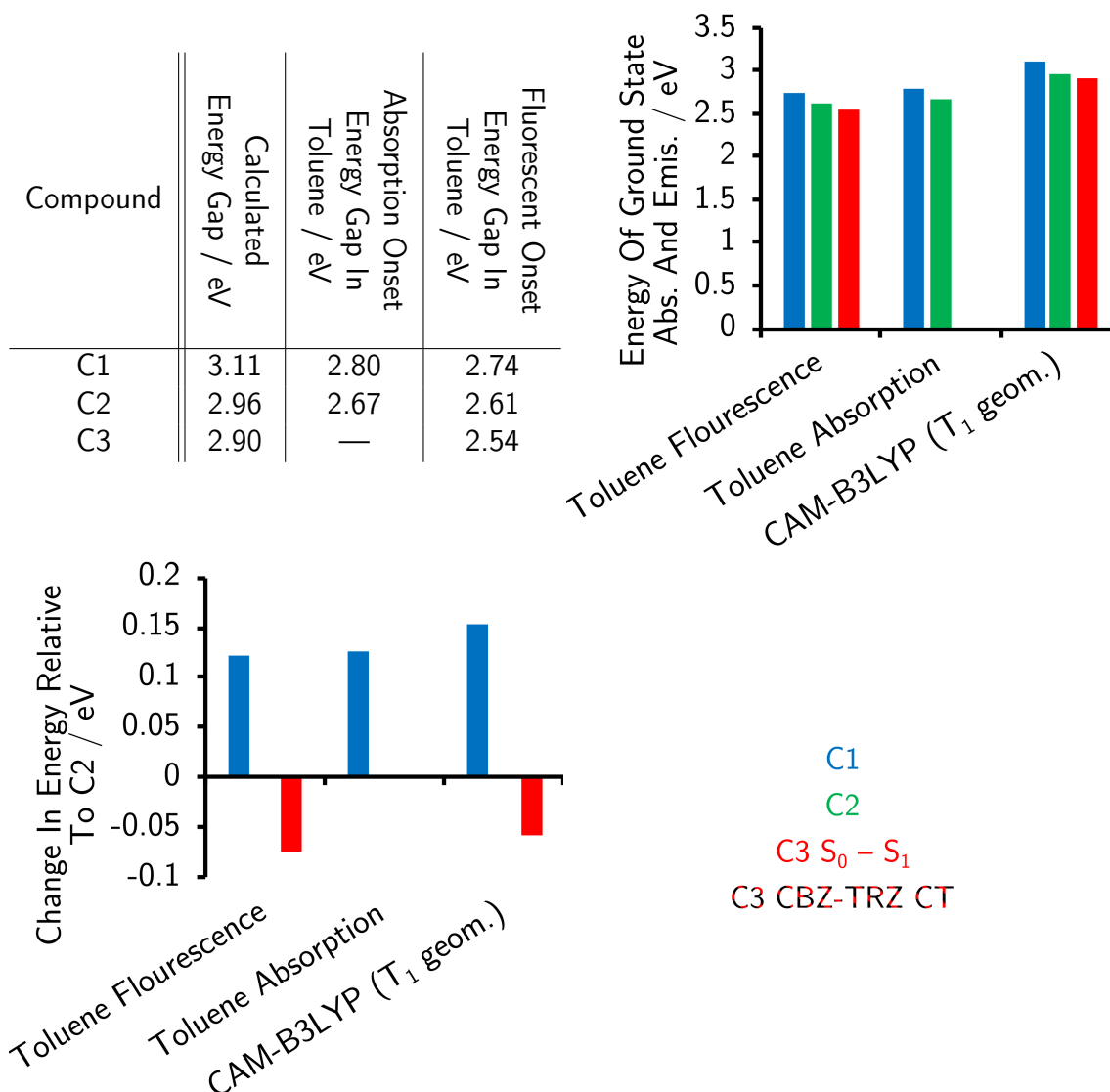


Figure 5.22: A table of energy changes as estimated by *CAM-B3LYP* calculations in the T_1 geometry (top left). The changes graphed (top right), and the changes shown relative to the C2 transition, normalised for each data set (bottom left).

B3LYP produces the right states as those which are lowest in energy and this does not cause the energy gaps to be too large.*

It is notable that the CAM-B3LYP functional is the first to show the C1 singlet-triplet energy gap to be an order of magnitude greater than C2 and C3, consistent with experiment. It is however also true that all singlet-triplet energy gaps are an order of magnitude too large. This discrepancy can perhaps be attributed to the use of the Tamm-Dancoff approximation in this case, which neglects doubly excited states. It is known that this may, in certain molecules, destabilise the triplet states.^{13,12}

*It is possible that the ground state triplet is an LE state in C2 and C3 as this state is not observed experimentally; however this would have to be near degenerate to the singlet CT state, so the triplet CT state would also have to be close by. Note: it is possible that the triplet CT state is above the singlet CT state^{15,14} in energy, but is unlikely to be much above.

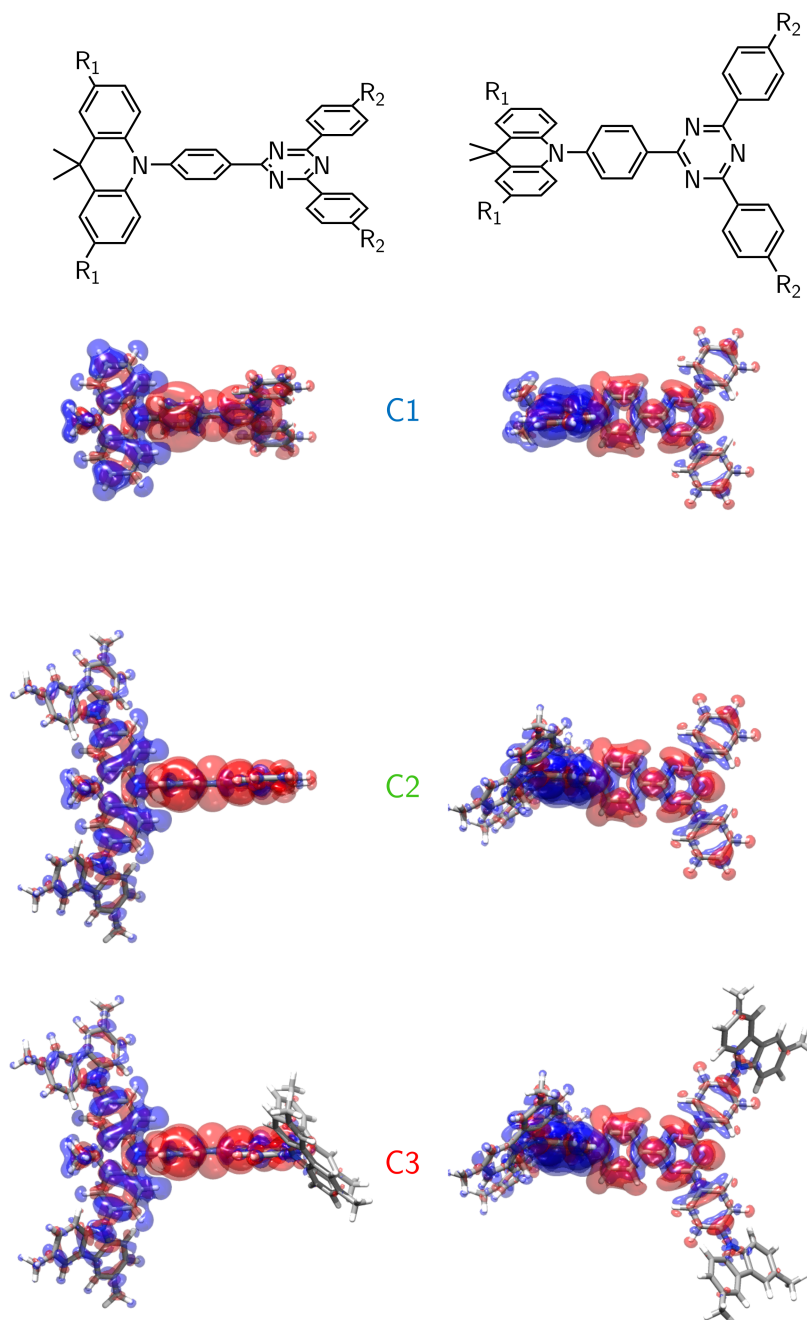


Figure 5.23: The change in electron density as calculated using *CAM-B3LYP* in the T_1 geometry for $S_0 \rightarrow S_1$ for the TADF compounds synthesised. Two arrangements are shown with the geometries shown via chem-draw structures. Blue represents electron loss, red electron gain. Cut-offs are set to $0.4 \text{ me } r_{\text{Bohr}}^{-3}$ throughout to allow a comparison of magnitudes.

Table 5.4: The calculated, and approximate experimental oscillator strength and singlet triplet energy gap, of the various transitions in the compounds studied. Calculations were ran using *CAM-B3LYP* in the T_1 geometry. The approximate experimental values are calculated using approximate formula from A. Köhler⁶⁷ where $f = \frac{1}{\tau_0 n^3 \bar{\nu} (cm^{-2})^2}$. The time constants are approximated by the pulse fluorescent rate (Note: this represents the maximum possible singlet emission rate and hence the largest possible oscillator strength), the wavenumber from the maximum in wavelength (neglects jacobian correction), and the refractive index approximated as glass's ($n = 1.6$). It is hoped this is sufficient for a rough order calculation. The experimental singlet-triplet energy gap values are sourced as described in section 5.3.1.

Compound (Transition)	$f_{Calc.}$	$f_{Exp.-Emiss.-Aprox.}$	$\Delta E_{ST-Calc.}$ / eV	$\Delta E_{ST-Exp.}$ / eV
C1(S1-S0)	0.2754	0.03	0.411	0.05
C2(S1-S0)	0.0041	0.02	0.022	$\lesssim 0.007$
C3(S1-S0)	0.0001	0.03	0.010	$\lesssim 0.007$

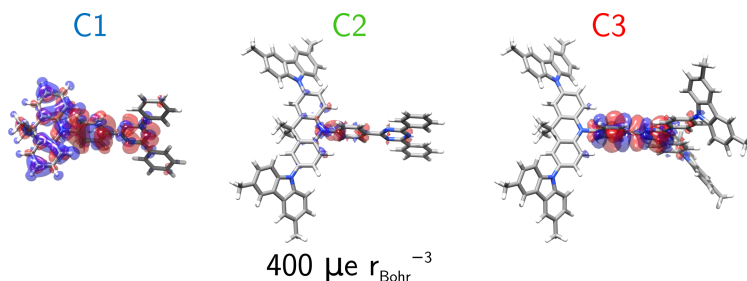


Figure 5.24: The change in electron density as calculated using *CAM-B3LYP* in the T_1 geometry for $S_0 \rightarrow S_1$ for the TADF compounds synthesised. Two arrangements are shown with the geometries shown via chem-draw structures. Blue represents electron loss, red electron gain. Cut-offs are set to $0.4 me r_{Bohr}^{-3}$ throughout to allow a comparison of magnitudes.

However it should be noted all the previous criticism of the CAM-B3LYP method used here-in could also explain it, ie. viewing only the ground state geometry, the lack of static correlation, and the use of VWN5 correlation, as well as any other conceivable problem with the functional. Further the tendency for charge transfer triplet states to exaggerate the singlet triplet energy gap, as discussed in section 5.3.2, also still applies.

As well as the singlet-triplet energy gaps, the oscillator strengths are compared in figure 5.4. The oscillator strengths are shown to vary wildly compared to the maximums provide by experiment. For C1 the oscillator strength is shown to be 2 orders of magnitude larger than the *maximum* experimental values. it is possible that there is only a very small region where the oscillator strength is this high. Thus it is possible, when the entire thermally accessible region is considered, that only a very small proportion of molecules are able to decay at this rate, accounting for this discrepancy. While this would explain the results, it is unlikely that the majority

of other thermally accessible geometries have much lower oscillator strength. This seems to point to a mistake in the calculations, although the cause is unclear.

The inconsistency in oscillator strength could result from any number of reasons related to the functional; however one particular issue related to the setup of this work should be addressed. It is noted that the change in electron density is quite different for $S_0 \rightarrow S_1$ compared to, $\rightarrow T_1$ as shown in figures 5.24 and B.70. This weakens the approximation that the S_1 state can be modelled by the T_1 state. Nonetheless the shifts in energetics are similar to experiment, and so this will be treated as only a problem in the changes in density.

It is noted that the relaxed geometry in the C1 state has an angle of approx. $\sim 70^\circ$ between the DMAC, and TRZ groups in the C1 geometry, which is approx. $\sim 90^\circ$ in all other planar geometries, under all CAM-B3LYP calculations.* It is believed this TRZ-DMAC angle may be key to this increase in the oscillator strength, due to making the states more overlapped. An increased tendency to form LE states would be consistent with the previously described "over-correction" of the CAM-B3LYP, from neglecting the static correlation. However while this may be true, the energy changes shown here are the most consistent. As a result it is much harder to draw any thorough clear cut conclusions on the validity of this decrease of angle.

Finally the differences in the S_1 and T_1 electron density should be discussed and these are summarised in figure 5.24. It is immediately noticeable that the difference in electron density are located mostly on the bridging phenyl, and that it is quite significant. An electron cut-off of $0.4 \text{ me } r_{\text{Bohr}}^{-3}$ was only needed to observe it, the same density that is used to observe the un-subtracted transitions. In addition the triazine consistently contributed to the change in electron density, and in the case of C1, the DMAC group further contributes.

5.5 Other Geometries With CAM-B3LYP

What has just been shown is that when compound 1–3 are investigated by CAM-B3LYP, the change in energy of the $S_0 \rightarrow S_1$ transition is broadly consistent with experiment. However the magnitude of these changes are only consistent in the optimised T_1 geometry. Further evidence is given that the electron density changes are consistently DMAC-TRZ charge transfer for the S_1 transitions (see figure 5.25 for component naming) states, with minor contribution of CBZ in C2 and 3. When all calculations are considered, there are some changes in the energy values given for $S_0 \rightarrow S_1$ transitions. For B3LYP the S_1 excitation energies are consistently too

*Interesting for B3LYP T_1 calculations yields an angle of $\sim 60^\circ$ between DMAC and TRZ in the excited state. This is despite the more charge-transfer like T_1 state with a $\sim 90^\circ$ angle being less destabilised in the CAM-B3LYP geometry. This does not yield to simple explanations.

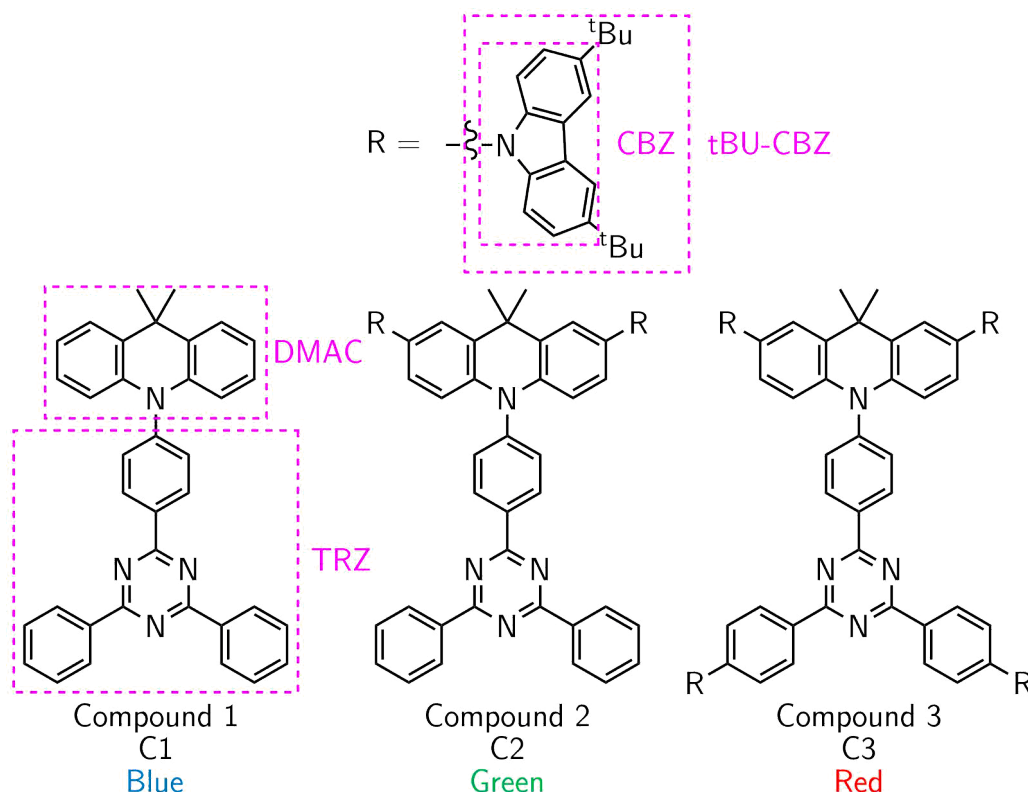


Figure 5.25: The structures of the compounds discussed, the components which make them up and the names and colours which correspond to them.

small, and the changes between transitions too large (with exception of C2-C3). For CAM-B3LYP the energies are consistently too large, and the changes are far too small in the S_0 geometry, and approximately correct in the T_0 geometry.

Further to the S_1 excitation energies, the T_1 excitation energies were calculated, and this allowed calculation of the singlet-triplet energy gaps. The singlet-triplet energy gaps were consistently too large with the exception of the B3LYP S_0 geometry calculation (which if decided were valid would imply that the C1 geometry was not quenched at 77 K). A number of effects may cause this, including the inherent inaccuracies in the functional, only using the lowest energy conformation, and the lack of doubly excited state character in the TD-DFT, particularly when the Tamm-Dancoff approximation is used. A further possibility that in the T_0 geometry, it is energetically favourable for the exchange energy to be higher. This hypothesis is supported by the observation that the oscillator strength is too low in 6–7/8 of S_0 geometries, and too high in 4/6 T_1 geometries.

The best results energetically were found for CAM-B3LYP in the excited T_1 geometry, and in this geometry all compounds have swapped from the boat-orthogonal, to the planar-orthogonal geometry. Because of this, and that CAM-B3LYP is designed to fix the problems of B3LYP,¹ this functional was used to investigate the other geometries, in hope that it would explain the inconsistency in the ground

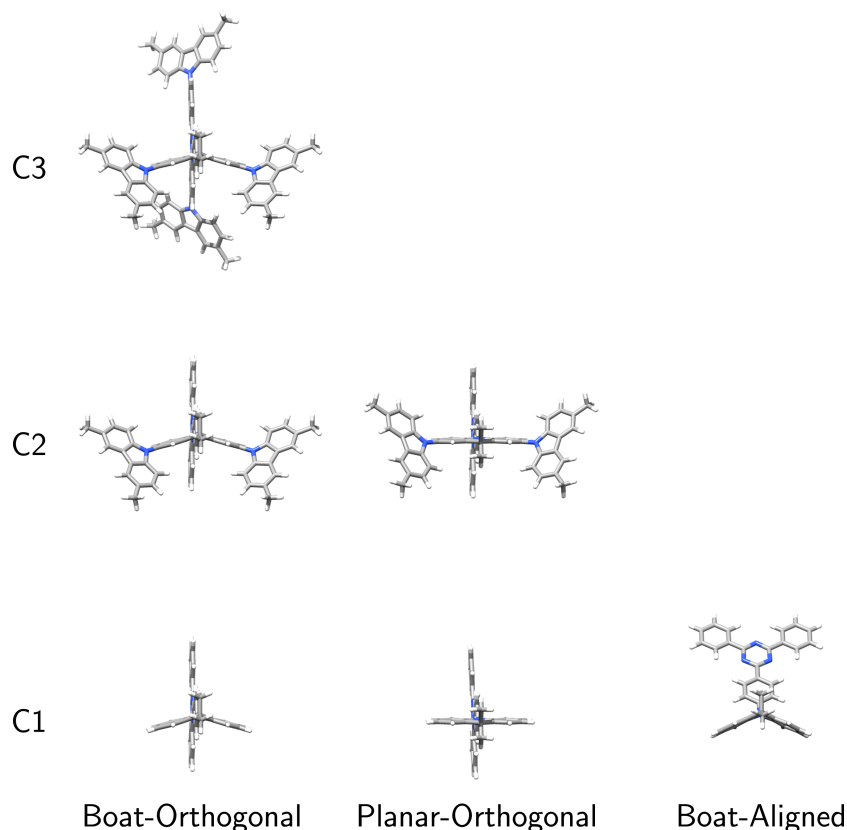


Figure 5.26: The geometries of the compounds when optimised in the S_0 state using the CAM-B3LYP functional, under the various geometries studied.

state. While this will be found not to be the case, the excitation energy difference between the planar-orthogonal and boat-orthogonal geometries will be found to be similar with the differences between doped film and solution spectra.

The geometries studied are summarised in figure 5.26. It was decided to focus on the planar-orthogonal geometry here-in and so this is calculated for C1 and C2. It was decided that this would be sufficient for a preliminary investigation. In addition the boat-aligned geometry was simulated for C1. There have been a number of reports on this geometry, pointing towards it being a triplet quencher³⁵ and being involved in degradation.⁵⁹

The energies of these ground states are shown in figure 5.27, and it is immediately observable that the boat orthogonal geometry and planar-orthogonal are very close in energy, and perhaps thermally accessible at room temperature. A simple Boltzmann equation assuming equal degeneracy would predict occupation of 64 %, 30 %, and 5 % for boat-orthogonal, planar-orthogonal and boat-aligned, and 61% and 39% for boat-orthogonal and planar orthogonal in C2. These results could only be predicted to be true in solution however, with the solid state being much harder to model.

The excitation energies for the S_1 excitation are tabulated in table 5.5, and

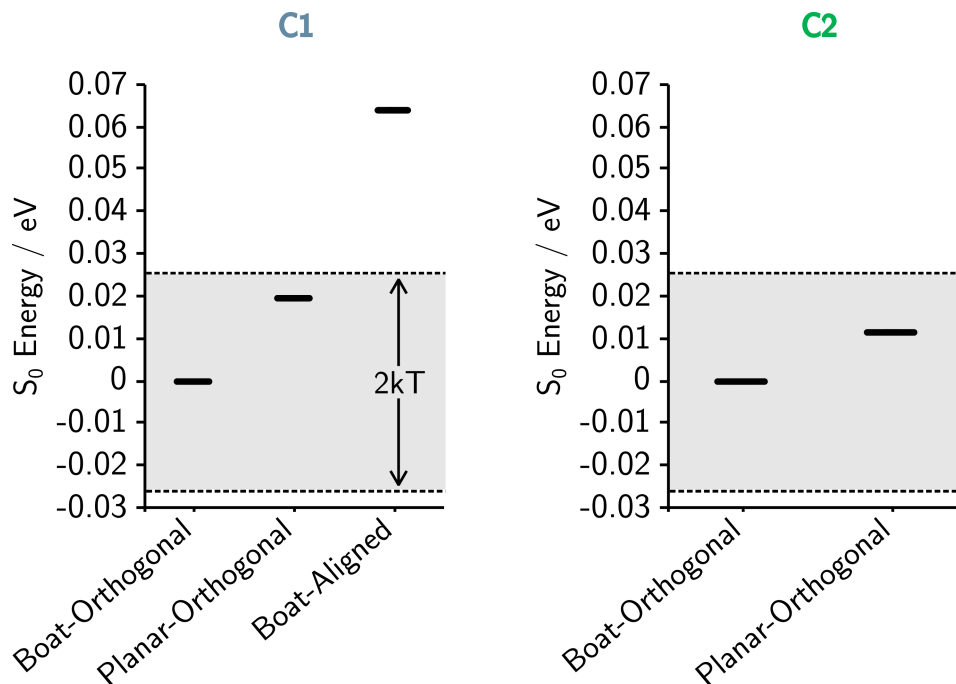


Figure 5.27: The energies of the optimised ground state in various geometries of C1 and C2, and with kT shown at room temperature.

graphed in figure 5.28. It is immediately obvious that a change in from the boat-orthogonal geometry to the planar-orthogonal geometry cannot make the results more consistent with experiment. It is, in fact, observed when optimised in the S_0 state, in this geometry*, that the C2 excitation energy is greater than the C1 energy. This is surprising considering when optimised in the T_1 state in this geometry, such strong alignment between calculations and experiment is observed. What is observable is a considerable narrowing of the S_1 – S_0 energy gap in this state (~ 0.2 eV) above and beyond the energy required to rearrange to it (~ 0.015 eV).[†]

The Boat-Aligned geometry on the other hand has a much larger energy gap, even taking into account the energy required to change geometry. This is consistent with the excited state being more LE like, destabilising the singlet state in favour of the triplet state. The changes in electron density are consistent with this, and are shown in section B.3.3.2.3.

When the oscillator strengths are compared in table 5.6, it is immediately observable that it consistently decreases in the planar-orthogonal geometry and increases in the boat-aligned geometry. The scale of the decrease is hard to parse, as the oscillator strength in the planar-orthogonal geometry is too low for the software to calculate. The decrease in the planar-orthogonal geometry is particularly interesting because in the optimised T_1 geometry, the oscillator strength in the planar-

*As opposed to optimised in the T_1 state, as shown in the prior section.

[†]It is noted that a slight excitation dependence was observed in the solid state, although the strength of this dependence is not significant enough to assign it as being due to this.

Table 5.5: The energy changes as estimated by *CAM-B3LYP* calculations in the S_0 geometry.

Compounds		Calculated Boat-Orthogonal Energy Gap / eV	Calculated Planar-Orthogonal Energy Gap / eV	Calculated Planar-Aligned Energy Gap / eV	Absorption Onset Energy Gap In Toluene / eV	Fluorescent Onset Energy Gap In Toluene / eV
S1 – S0	C1	3.81	3.63	3.99	2.80	2.74
	C2	3.80	3.65	—	2.67	2.61
	C3	3.76	—	—	—	2.54
S0 – CT	1C					
	ZBZ-TRZ					
S0 – S0	CT					
	C3	3.78	—	—	2.91	—

orthogonal geometry is 3 order of magnitude greater in the C1 geometry, and 1 order of magnitude greater in the C2 geometry. This is believed, in the case of C1, to be in part due to the decreasing of the angle between DMAC, and TRZ from $\sim 90^\circ$ to $\sim 70^\circ$, but the cause of the change is less obvious for C2. The structure of C1 and C2, in their planar-orthogonal geometries — when optimised in the S_1 and T_1 states — are shown in figure 5.29. The lower oscillator strength in the S_0 optimised geometries is however consistent with the earlier hypothesis weakness of optimised T_1 geometries. It is hypothesised that the T_1 geometries are more likely to overestimate the oscillator strength, as it is energetically favourable for the triplet to increase the exchange energy (ie. become more like a locally excited state).

The energy gaps between this predicted S_1 and T_1 states were also calculated and are shown in table 5.7. The singlet triplet gap appears to narrow when in the planar-orthogonal geometry, and it in fact swaps the ordering of C1 and C2. This is contrary with the experimental singlet-triplet energy gap, but as the ground state singlet geometry is being used to model the excited singlet and triplet in this calculation, this is probably an error in methodology. The results are consistent with the decrease in oscillator strength, suggesting that the boat-orthogonal geometry is more CT like.

It is frankly fascinating how the calculated properties change, between the optimised S_0 and T_1 geometries, with such minor changes in the the base molecules. The structures are shown in figure 5.29 and show remarkably similar geometries. This is

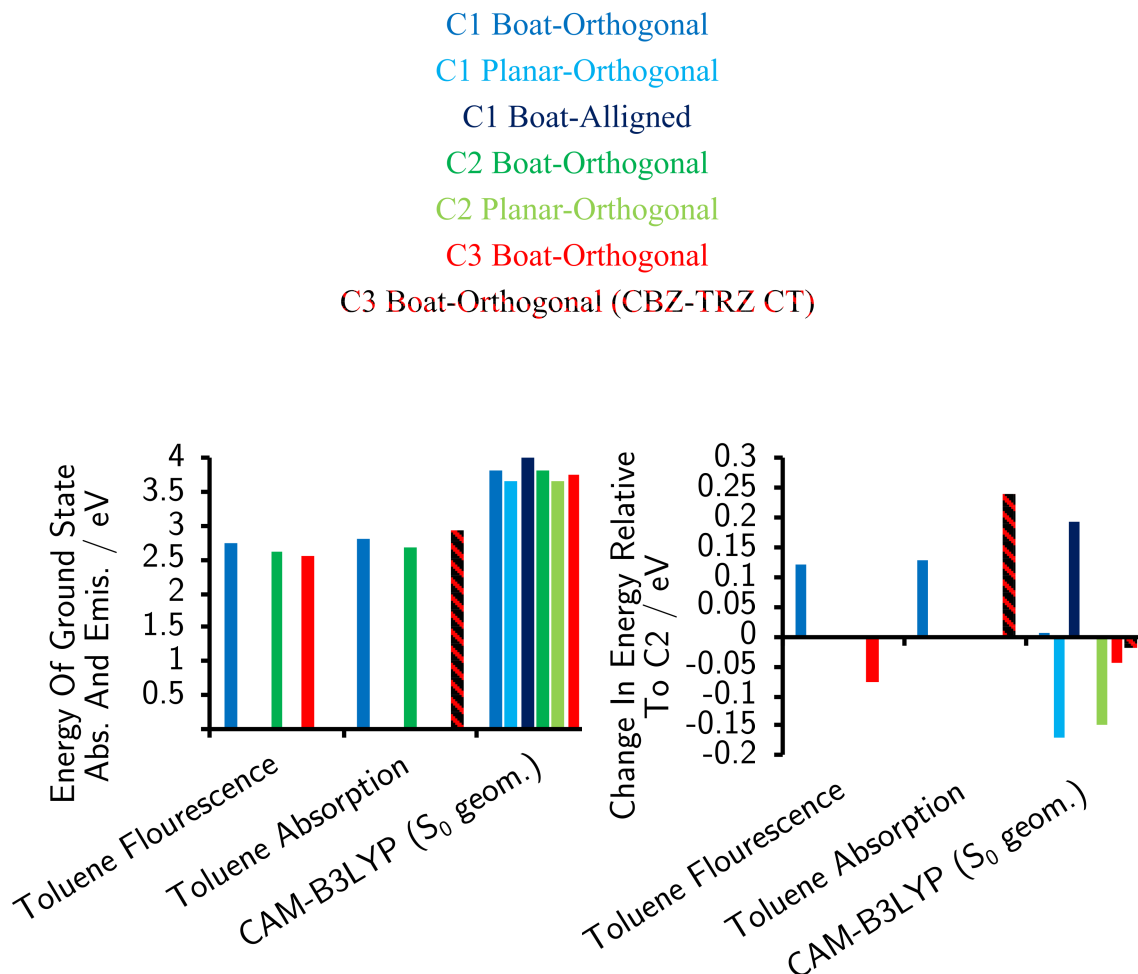


Figure 5.28: The energy changes as estimated by *CAM-B3LYP* calculations in the S_0 geometry. The changes graphed (left) and the changes shown relative to the C2 transition (right), normalised for each data set.

particularly true for C2. As previously noted there is a decrease in the DMAC-TRZ dihedral angle from $\sim 90^\circ$ to $\sim 70^\circ$ for C1 in the T_1 geometry. The only remarkable change for C2, however, is a slight movement to planarize the CBZ states when in the T_1 geometry. Nonetheless the energy gap between the S_0 states in the S_0 and T_1 optimised geometry are large (~ 0.35 eV, as tabulated in table 5.8).

It is of note that the energy gap between the planar-orthogonal geometry and boat-orthogonal geometry is of similar magnitude in C1 and C2, see figure 5.30. It has been noted experientially that the fluorescent onsets are shifted significantly less between C1–3 in doped film than in solution between the molecules. The difference in the S_1 excitation energies in the planar-orthogonal geometry and boat-orthogonal geometry fluorescent are compared with the difference between the onsets in doped film and toluene solution in figure 5.30. It is notable that difference

Table 5.6: The calculated (CAM-B3LYP, S_0 geom.), and approximate experimental toluene oscillator strength, of the various transitions of all geometries in the compounds studied. The approximate experimental values are taken assuming the peak and full-width at half height of the oscillator strength in wavenumbers are the same in both wavelength and wavenumber, strictly incorrect due to the Jacobian correction.⁶⁰ Further the peaks are approximated as Gaussians with these properties. It is hoped this is sufficient for a rough order calculation. The numerical equation for oscillator strength shown in various text books is used.^{61,18,16} Note: The Jacobian correction⁶⁰ is applied to the molar absorption coefficients maxima used

Compound (Transition)	$f_{Calc.}$			$f_{Exp.-Abs.-Approx.}$
	Orthogonal Boat	Planar	Aligned Boat	
C1(S1-S0)	0.0001	0.0000	1.4276	0.036 ± 0.003
C2(S1-S0)	0.0006	0.0000	—	0.030 ± 0.003
C3(S1-S0)	0.0011	—	—	—
C3(CBZ-TRZ/S5-S0)	1.1090	—	—	0.461 ± 0.006

Table 5.7: The calculated (CAM-B3LYP, S_0 geom.), and experimental toluene singlet triplet energy gaps of all geometries of the compounds studied.

Compound (Transition)	$\Delta E_{ST-Calc.}$ / eV			$\Delta E_{ST-Exp.}$ / eV
	Orthogonal Boat	Planar	Aligned Boat	
C1(S1-S0)	0.553	0.156	0.8818	0.05
C2(S1-S0)	0.323	0.218	—	$\lesssim 0.007$
C3(S1-S0)	0.329	—	—	$\lesssim 0.007$
C3(CBZ-TRZ/S5-S0)	1.1090	—	—	0.4
—	—	—	—	—

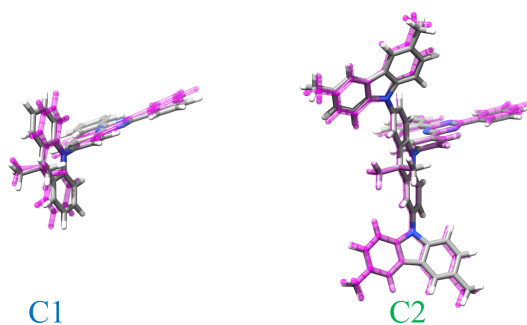
in energy between the two geometries is similar in magnitude to the changes in C2 and C3, with C1 being considerably lower.

The similarity in the in the magnitude of the energy difference between films/toluene solution and planar-orthogonal/boat-orthogonal geometries in compound 2 and 3 is significant, as it could be seen to imply that it is this geometric change that is blocked in doped film. It is noted that the geometric change from boat-orthogonal to planar-orthogonal is small in C1, and large in C2 and C3, because the tBU-CBZ groups must be moved. The geometric change is best shown in figure 5.26, but is actually more significant, as the ^tBu groups are replaced with methyl groups for the sake of simulation. It has already been shown here-in that in both B3LYP and CAM-B3LYP C2 and C3 convert to the planar-orthogonal geometry when minimised in the T_1 state.

It is this observation that demonstrates the usefulness of calculating the T_1 state. In doing this it was possible to observe a likely geometric change which happens in

Table 5.8: The energy of the planar-orthogonal geometry in both S_0 and T_1 geometries relative to the lowest energy (boat-orthogonal) geometry, in either compound.

Compounds	S_0 Geometry Energy / eV	T_1 Geometry Energy / eV
C1	0.019	0.337
C2	0.011	0.365
C3	—	0.370

**Figure 5.29:** The planar-orthogonal of the compounds when optimised in the S_0 (atomic colouration) and the T_1 (purple) states using the *CAM-B3LYP* functional.

the excited state. Under the approximation that the S_1 state behaves similarly, this allows the assigning of a key difference between solution and doped film. Assigning this difference may allow the design of bluer DMAC molecules which do not show the red shift observed in C1 for swapping geometry. Further the red shift in C2 and C3 from the additional conjugation of S_1 onto the CBZ groups may be blocked in further design iterations.

Nonetheless several assumptions have been made in this assignment, and these must be stressed here and where possible mitigated. Firstly, that sterics as opposed to electronic factors (ie. solid state solvation) are the cause of the difference between solid state and solution; secondly that this is the steric change that is blocked, and not another; thirdly that the molecules start in the boat-orthogonal geometry; and finally that the CAM-B3LYP functional can be trusted in this manner.

It is true that the doped film onset is blue shifted relative to toluene (see section 3.3.5), and compounds 2 and 3 are predicted to respond more readily to polarity (see section 3.3.2). It may be predicted that the effect is from polarity. However the changes are much more significant than would be predicted. This is shown in

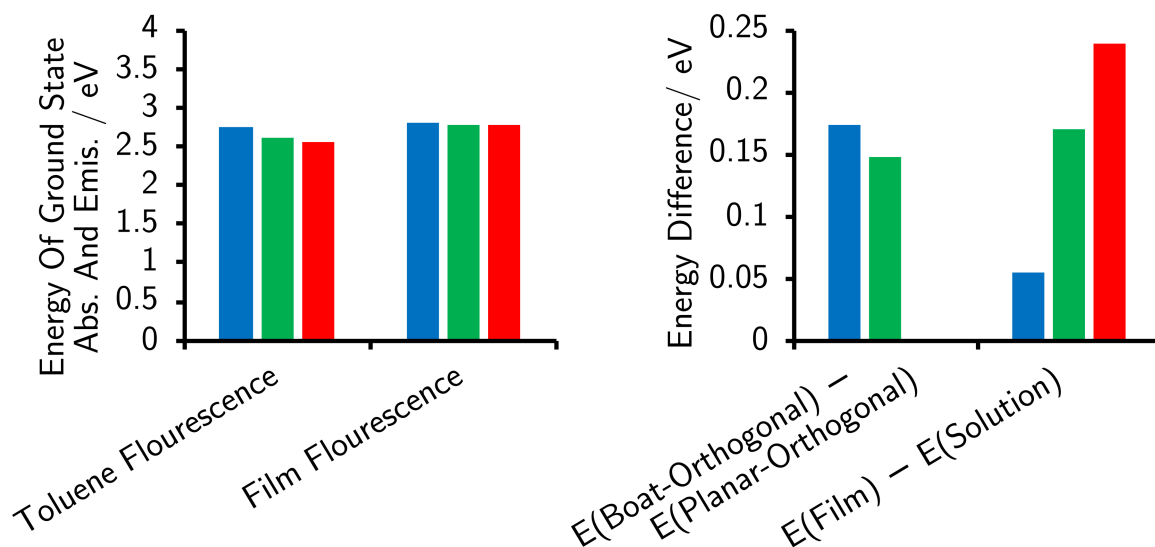


Figure 5.30: The change in energy of photoluminescence in films and toluene solution (left), and the difference between the two compared to the calculated difference in energy between Planar-Orthogonal and Boat-Orthogonal geometries.

section B.3.1.4.7.

The assumption that the change in energy is most likely from the proposed boat-orthogonal to planar-orthogonal geometric change can be justified, in part, from looking at the changes in electron density. The change in electron density in the planar-orthogonal geometry on S_1 excitation under CAM-B3LYP (shown in figures B.75, and B.77) is very similar to the change in electron density in the boat-orthogonal geometry (see figure 5.20). This would indicate similar geometric relaxation would stabilise them both. When the optimised, lowest energy, ground state (ie. boat-orthogonal), and the optimised excited (T_1) are compared (see figure 5.31) most geometric changes are minor outside the planarisation of DMAC, and so they would not be blocked via the sterics of the solid state. This is with the exception of the change in DMAC-TRZ angle observed in certain compounds; however it is notable this is not observed in C2 and C3, under CAM-B3LYP. With this born in mind, and the fact that C2's boat-orthogonal planar-orthogonal energy gap matches the energy difference observed, it seems this change in energy is most likely.

The assumption that the molecules start in the boat-orthogonal geometry is perhaps the most difficult to justify completely and is a major weakness in understanding the film-solution energy difference this way. As has previously been discussed the S_0 energies of the planar-orthogonal and boat-orthogonal geometries are sufficiently close to allow thermal occupation of both in solution. It is possible, that in film, this is not true, but this is not shown to be the case here-in. Nonetheless it seems that this geometric change could be blocked in film, and the energy change corresponding to this matches between theory and experiment. Further when the

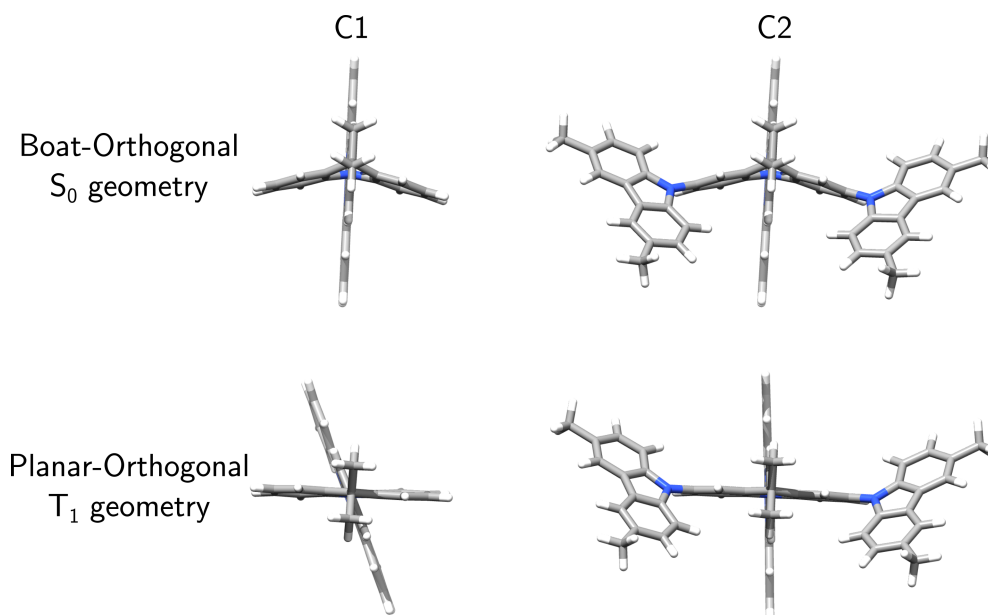


Figure 5.31: A comparison of the optimised boat-orthogonal structure in the S_0 state, and the optimised T_1 state as calculated by CAM-B3LYP. The optimised T_1 state represents minima from both planar-orthogonal and boat-orthogonal starting geometries; however it is planar-orthogonal in nature.

crystal structure of C1 is observed (see fig 5.32), it is seen to be boat like, if not to the extent of the calculations, either confirming the boat structure, or suggesting vibrational conversion between the two, leading to an average structure. However, because of this weakness the assignment is kept as being tentative.

CAM-B3LYP has proven unreliable at reproducing the absorption energies in the S_0 , and so it may be argued from this that the conclusions from geometric change should be disregarded. This un-reliability has been assigned as either being due to the differing correlation function (VWN5 vs VWN3), lack of static correlation in the replacement exchange function, or lack of simulated geometries. The reproduction of shifts in the T_1 geometry appears to point to the lack of geometries being the cause, however the overestimations of all S_1 energies appears to point to problems with a lack of static exchange, or the correlation function. This also cannot be completely resolved, and is a further weakness in this argument.

5.5.1 The Ground State Triplet In Other Geometries

Finally in these new geometries the ground state triplet was investigated. For the planar-orthogonal geometries, the results converged to the same results that have already been presented in the boat-orthogonal T_1 geometry, and so this will not be further discussed here-in. The boat-aligned geometry however did not converge.

The boat-aligned results did not present anything particularly new or interesting.

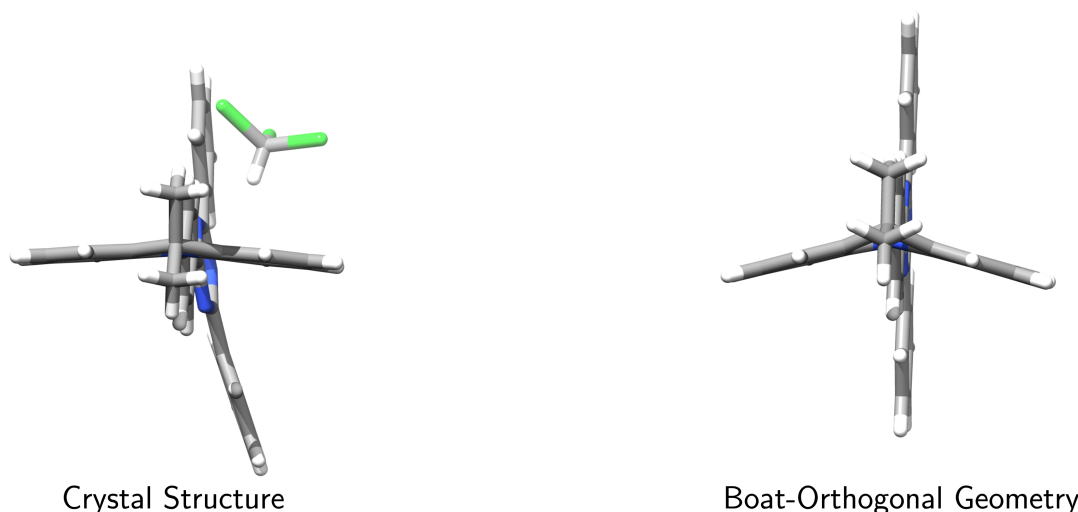


Figure 5.32: A comparison of the PUDFIG crystal structure of C1, and the computed and optimised (S_0 state, CAM-B3LYP functional) boat-orthogonal geometry.

Table 5.9: The relative energies of the various key states in the various key geometries in C1. The energies are given relative to the lowest energy S_1 energy ie. the planar-orthogonal one.

Electronic states	Relative S_1 Energy / eV	Relative T_1 Energy / eV
Planar-Orthogonal	0.000	−0.411
Boat-Aligned	0.467	−0.585

As has been previously stated, this geometry has previously been discussed as being linked to the degradation of compounds³⁵, and as a triplet quencher.⁵⁹ The S_1 state is too high in energy to be thermally accessible, and the T_1 structure is low in energy and may act as a triplet quencher. The singlet and triplet state energies are summarised in table 5.9.

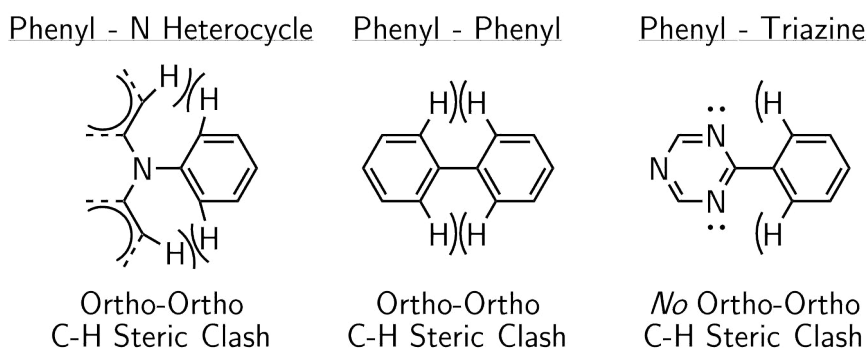


Figure 5.33: A demonstration of the likely reason for planarisation of phenyl groups with triazine, and not other groups.

It should be noted that there is likely a considerable kinetic barrier to the formation of the boat-aligned structure, this is because the the ortho-ortho steric repulsion must be overcome between the DMAC and TRZ groups. This steric repulsion

is shown in figure 5.33. It should be noted that both ortho hydrogens on DMAC are on one side of the bridging phenyl, and as such create a large amount of strain.

5.6 Conclusions

Overall in this chapter a computational investigation has been undertaken into 3 DMAC-TRZ TADF compounds. These compounds, in both the ground state singlet and triplet states, were optimised and their excited states calculated, using both B3LYP and CAM-B3LYP. Three geometries were identified as being key to the function of these molecules, and these were also investigated.

The geometries identified have been previously published but, two structures previously considered the same are identified as different. The geometries have been renamed to allow for clarity in identifying them. They have been given new names the "boat-orthogonal", "planar-orthogonal", and "planar-aligned" geometries. While little has been done to further the understanding of the planar-aligned geometry, it has been suggested that the transition from the boat-orthogonal to the planar-orthogonal geometry may be blocked in film when bulky groups are attached to DMAC, such as the CBZ-tBU group used herein. This lack of geometric relaxation appears to lead to a blue shift in the emission.

When the geometries were optimised and the excited states calculated, several trends were observed over almost all sets of results. Firstly there appeared to be greater separation of donating and accepting components with increased CBZ-tBU groups, due to the CBZ group competing with the DMAC electron donator, and TRZ electron acceptor, with a more significant effect observed for DMAC. With this increased separation, a decrease in singlet-triplet energy gap and a concomitant decrease in the oscillator strength was also observed. A final common observation was that the difference in the electron density between the T_1 and S_1 states was mostly located on the bridging phenyl groups, but commonly has contributions from both DMAC and TRZ.

Despite similarities in certain results, there was key and consistent differences when the same "key geometry" was optimised and the excited states calculated using different functionals. B3LYP consistently underestimated the excitation energies and the changes in energy between states, with CAM-B3LYP doing the opposite. Four possible reasons for this are suggested, which are different correlation functions, lack of static correlation in CAM-B3LYP destabilising CT states excessively, over-stabilisation of CT states in B3LYP due to incomplete cancellation of the self interaction function, and finally a lack of geometries calculated. In all functionals, it was noted that there was likely insufficient doubly excited states included in the

calculations, but this is particularly true for the CAM-B3LYP calculation where the Tamm-Dancoff approximation was made, and this will likely also have an influence in inconsistencies in these calculations.

It was further proposed in this work that the T_1 geometry would be better for calculating the excited state properties of the molecules, and this was investigated. It was found the T_1 calculations appeared useful in showing geometry change in the excited states, but had a tendency to overestimate the oscillator strength. However it should be further noted that the S_0 geometry calculations tended to underestimate these values. This suggests neither geometry is perfect, and that there is use in calculating the T_1 state, namely in observing geometry changes. The trends in the T_1 calculation of the oscillator strength were rationalised because there is an energetic preference for the T_1 geometry to have overlapped donating and accepting orbitals, increasing the exchange interaction, and the oscillator strength.

The singlet-triplet energy gaps were also calculated, and were too high in all T_1 calculations. This may be justified similarly to the oscillator strength. In the S_0 geometry, the B3LYP calculation of the singlet-triplet energy gaps appeared correct for C2 and C3, and possibly too low in C1; in the CAM-B3LYP they were too high. The CAM-B3LYP S_0 calculation appeared to calculate the locally excited states as the lowest energy triplet state, inconsistent with experiment, explaining this entirely, but it is unclear why B3LYP appeared to calculate these values so well. It is possible that because of the stabilisation of CT states in B3LYP that the S_1 and T_1 are essentially calculated with zero mixing, and no inherent predilection for being a charge transfer state or locally excited state from the optimisation; thus in this case calculated correctly. But equally there is no proof for this.

Overall this chapter helps with the understanding of the experimental results, and reinforces conclusion made from them. Further it allows for the proposal of a change in common TADF methodology; namely the calculation of T_1 states.

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Chapter 6

Overall Conclusion And Future Work On The Carbazole Substituted DMAC-TRZ TADF

6.1 Conclusions

*"Doubt is an uncomfortable
condition, but certainty is a
ridiculous one"*

— Voltaire

Overall results have been presented that show, the effects of adding tBU-CBZ groups to the DMAC and TRZ groups of a DMAC-TRZ donor acceptor TADF dye. An increase of donor acceptor separation is observed with increased substitution of tBU-CBZ groups. This result is consistent across almost all steady state measurements, transient fluorescence measurements, and computational chemistry calculations. It is broadly consistent, across the data, that the change when adding tBU-CBZ to DMAC is more significant than when it is added to TRZ (Note: the addition to TRZ occurred when tBU-CBZ is already added to DMAC). The results are also consistent with a reduction in film emission efficiency along this series, as well as a red shift in emission spectra.

The experimental results show a significant narrowing of the singlet-triplet energy gap with substitution of tBU-CBZ to DMAC, preventing quenching at 77 K in both C2 and C3. This effect leads to the novel case of the singlet decay rate decrease being the most significant change when cooling to 77 K, as measured by transient fluorescence. The narrowing of the singlet-triplet energy gap is not backed up by the measurements of steady-state photoluminescence at 77 K. This is attributed to

TADF not being quenched in C2 and C3, and either the same for C1, or too short a delay after excitation or matrix effects.

It was found that the addition of tBU-CBZ to the DMAC-TRZ TADF dye appeared to cause H-aggregation in pure films. This has a rather detrimental effect, given that C1 has previously been found to perform well in pure films. Efficient pure films are a target for device simplification. This conclusion was shown to be consistent with steady state and transient results.

It was also found when simulating the compounds that the previous literature assignment of two key geometries (conformations) of DMAC is insufficient, and an additional conformation is required to explain the results. Three key geometries of the DMAC moiety are proposed, and a new naming convention was suggested to aid their identification. Results consistent with a transition between two of them in the excited state were presented; further evidence that this transition is blocked in film was demonstrated.

Beyond the characterisation of molecules, several changes to the general TADF methodology were proposed and implemented. These were: a new way of interpreting transient fluorescence data; the use of stretched exponential fits (not fully implemented herein); and the calculation of T_1 states to model the excited states of TADF molecules. These will now be expanded upon.

It was noted that the current interpretation of the transient fluorescence of TADF compounds relied on several assumptions which were not necessarily true in all cases, with no other alternative strategy available. A method using graphing and summarising the changes in magnitude was presented here-in to try to get around this problem. Further in transient fluorescence, it was found that the standard bi-exponential fit did not fit data well, with stretched exponentials doing a much better job. This is suggested, with the possible inclusion of other TTA like terms, for the fitting of transient decaying in the future .

It was postulated that the standard calculation of only S_0 like geometries for TADF may cause problems for making of predictions on the excited state. It was proposed that the T_1 optimised geometries may act well as substitutes, given several caveats written in the bulk of this thesis. This method proved key in finding geometric changes in the excited states, but did tend to overestimate the oscillator strength and singlet-triplet energy gap.

6.2 Future Work

"He who lives by the crystal ball
soon learns to eat ground glass."

—Edgar R. Fiedler, *The Three Rs
of Economic Forecasting-Irrational,
Irrelevant and Irreverent*

The aim of the present study on this set of molecules has been to build up a case study on them. This case study has highlighted numerous recommended changes in methodology in TADF, and has highlighted the importance of additional geometric distinctions on the DMAC heterocycle. However, this case study could be expanded and the certainty of the conclusions drawn from it increased.

H-aggregation has been assigned as the most likely cause of a fleet of effects within the solid state pure films, but the nature of this aggregate has not been identified. This remains a target, and would allow for a stronger assignment of this effect. If a solution could be found which exhibited the formation of this aggregate, NMR techniques could be used to identify the nature of it. It is possible in the solid state, that solid state NMR could also be employed to identify if the resulting aggregate was partially crystalline, and some information on its structure.

Within the spectroscopic work, it has been shown that the fitting functions used in the field are not sufficient, and the use of a stretched exponential, possibly in conjunction with an inverse square function has been suggested. This work could not be completed within the time frame of this project; however further investigation in this direction could potentially be beneficial to the entire field of TADF.

Within the computational work on this system, a continuous problem was that it is known that many different thermally accessible geometries contribute to the absorption and fluorescence of the molecules. An investigation which generates a large number of different thermally accessible geometries and simulates them may be useful in this case. It is possible to generate a large number of structures using molecular dynamics simulation or Monte-Carlo calculations, and then model these with DFT. Further in the calculations used herein, a continuous suspected problem was the lack of doubly excited state character in the excited states calculated. The use of CISD in a repeat of these calculations would fix this, and help draw clearer conclusions. All of these suggestions would require a significant amount of computational power, perhaps beyond the scope of modern computational methods.

It has been suggested from this work that both the "boat-orthogonal" and "planar-orthogonal" geometries are key to describing the photophysics of these sys-

tems. However experimental observations of these geometries has not been possible. Currently the data fits this description, but this does not constitute a proof that both geometries are significant. As a result, proper experimental observation would be highly beneficial. This would take the form of finding a spectroscopic signature of each geometry, likely when they are fixed within a crystal structure, and then checking for this signature in films, or when excited using transient methods. Both transient visible or infra-red spectra seem ideal candidates for this.

A further issue with the computations is the varying angle between DMAC and TRZ between calculations. It is not necessarily clear whether the current simulated geometries are at global or local minima with respect to this angle, and calculations to clarify this would be useful.

Finally, in terms of the design of solution processable molecules, it is noted that the addition of tBU-CBZ groups lower the photoluminescent quantum yield (PLQY). As a result, it would be beneficial to create a system where this does not occur. This will be explored further in chapter 7. There is also uncertainty in the PLQY measurements as a result of measurement under ambient conditions (in air). Ideally these measurements would be repeated under inert conditions.

Part III

Beyond DMAC-TRZ

Chapter 7

A Study Of Substitution Para to Nitrogen In 10H-Phenoxazine

"Ever tried.

Ever failed.

No matter.

Try again.

Fail again.

Fail better."

— Samuel Beckett, *Worstward Ho!*

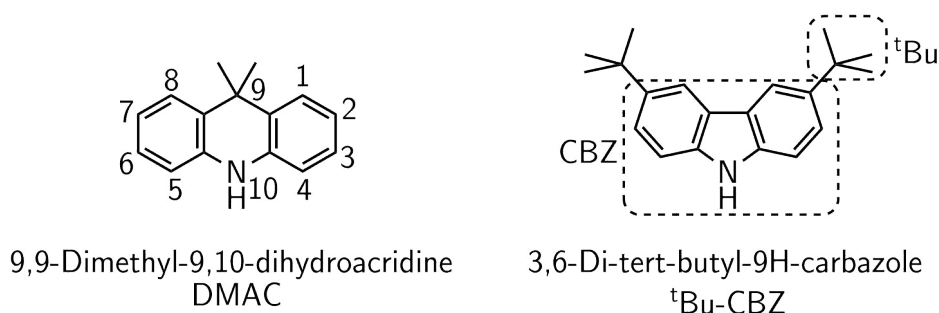


Figure 7.1: Diagram of the structure of DMAC, and ^tBu-CBZ. IUPAC numbering on DMAC is shown.

Prior to starting this section, a shout-out must be made to Miss Holly Bradshaw, a summer student supervised by the author. Without her, this chapter, would not be possible. Her work on the synthesis on characterisation of the derivatives involving the integrated and protecting group based directing groups make up the bulk of this chapter.

Throughout the previous part of this thesis, the 2,7 substitution of 9,9-dimethyl-9,10-dihydroacridine (DMAC) by 3,5-bis(1,1-dimethylethyl)-carbaz-9-yl (^tBu-CBZ)

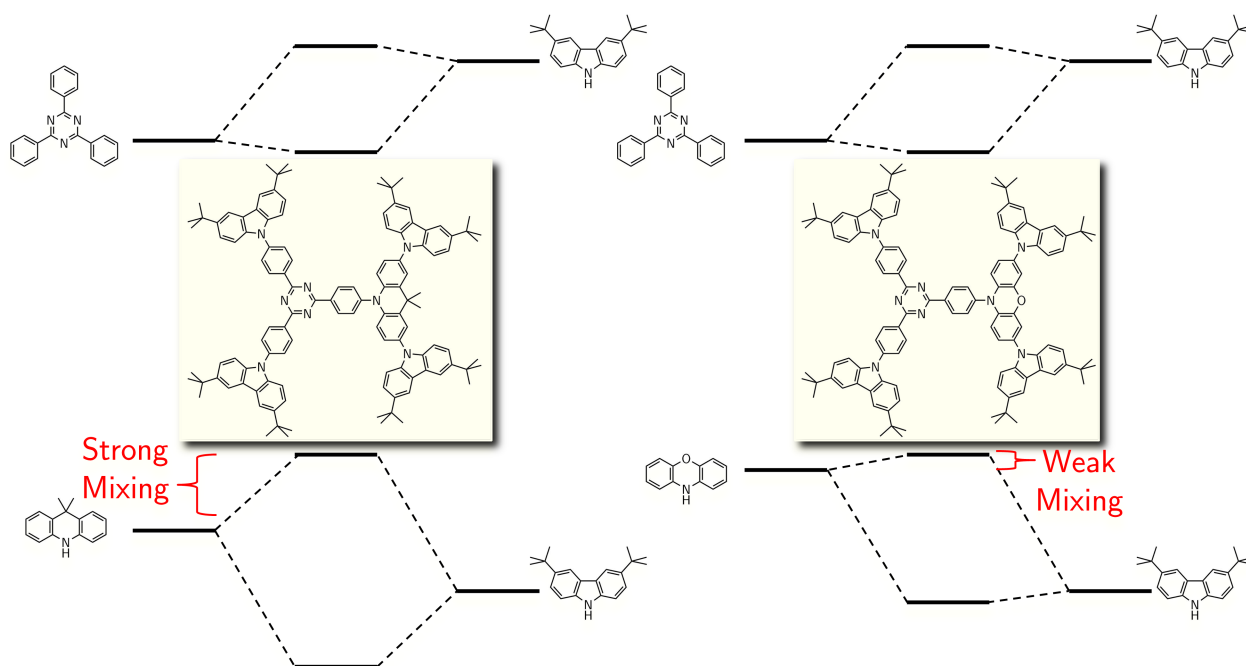


Figure 7.2: A schematic diagram showing the proposed reduction in mixing between donor and *t*Bu-CBZ for a PHX-TRZ system (right) vs a DMAC-TRZ system (left).

has been investigated (see figure 7.1 for structures). The problem with substituting DMAC with *t*Bu-CBZ is that *t*Bu-CBZ interferes negatively with DMAC.^{1,2} The interference of DMAC with *t*Bu-CBZ stems from the CBZ group contributing to the electron donation, and leads to too large a separation of donating and accepting components.

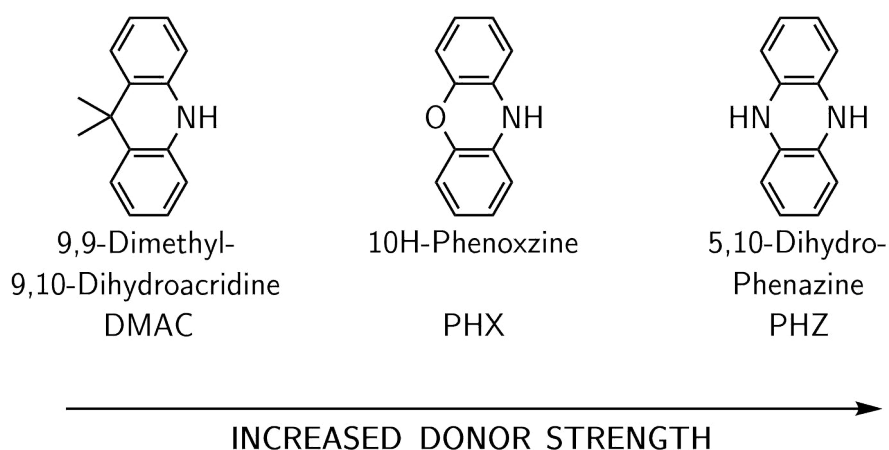


Figure 7.3: A comparison of similar donors with increased donating strength.

The reason why *t*Bu-CBZ is substituted is explored in section 2.1. Put simply *t*Bu-CBZ has been shown to have a raft of different favourable properties,^{3,4} and is claimed to have even more.^{1,5,4} On top of *t*Bu-CBZ's favourable properties, it is cheap⁶ and is hence used in the majority of hosts currently used in OLEDs.⁷ 2,7 functionalisation is desired in particular since the bridging phenyl is so often

found in successful TADF molecules,⁸ as such it is unclear to what extent the free movement of it is key to TADF. It is true that studies exist which suggest the steric constraining of it may be beneficial⁹ but it is unclear how much this generalises. It is also true that 1,8 substitution would also be unlikely to interfere, and few literature examples of this type of substitution could be found for the donors of a similar type to DMAC.^{10,11,12}

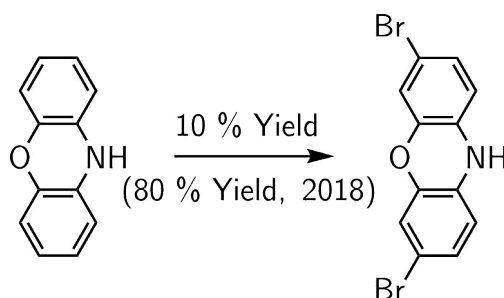


Figure 7.4: The maximum yields of bromination of 10H-phenoxazine both at the commencement of this project and midway through.^{13,14}

Because ^tBu-CBZ has such favourable properties, it is desirable to use it in compounds, but prevent the interference with the donor. It may be qualitatively predicted that a stronger donor would be effected less by ^tBu-CBZ (ie. a donor which requires less energy to donate an electron), because of less mixing of states, and this is shown schematically in figure 7.2. Thankfully there are other donors of similar structure with stronger electron donating abilities; these are shown in figure 7.3.

The problem with non-DMAC donors is functionalising them. Usually when functionalising a heterocycle, halogens are substituted for use in a subsequent coupling reaction. There is no published procedure for PHZ, (see figure 7.3 for abbreviations) and when this work began, the highest yields published for PHX was 10 %.¹³ A 10 % yield is too low to allow for practical laboratory synthesis of derivatives. During this work a procedure with 10H-phenoxazine and an 80 % yield was published, but has yet to be reproduced.¹⁴ As the work in this chapter predated this method, it will be treated as if it had not been published for most of this chapter, although it is suspected that this method is superior to all the work presented here-in.

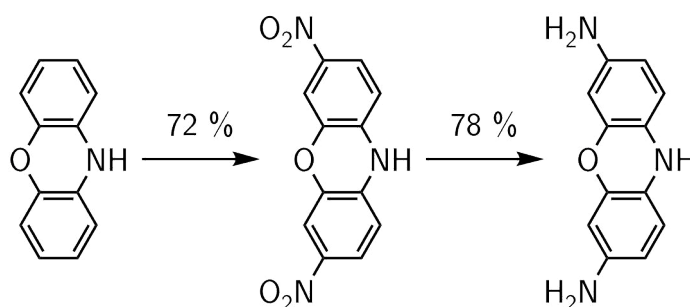
The topic of this chapter is to attempt the functionalisation of stronger donating heterocycles like PHX or PHZ. It was decided that PHX would be the focus because PHZ has been shown to behave poorly in devices.⁸

While the synthesis of 2,7 substituted derivatives on the base 10H-phenoxazine was observed (pre 2018) to be low yielding, several possibilities exist for alternative methods. Alternative functionalisation methods could be employed, as well as at-

taching "directing groups" to increase the yield. These directing groups may be a part of the final molecule, or act as protecting groups, added and then taken off.

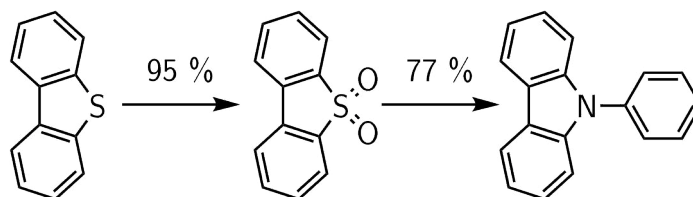
The exploration of alternative procedures for para substitution of 10H-phenoxazine will be the subject of the rest of this chapter. First a synthesis using alternative functionalisation will be explored, then one using a "directing" group key to the molecule, and then one using a "directing" protecting group. Moderate success was only found for the "directing" protecting group.

7.1 Nitro/Amine functionalisation



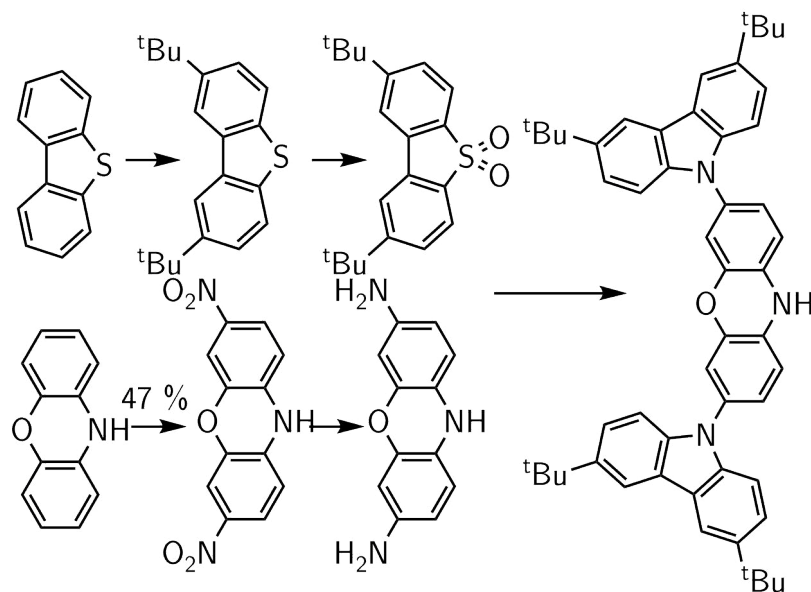
Scheme 7.1: The claimed yield for reaction with 10H-phenoxazine, by G. Calzaferri et al.

The original strategy employed to attempt to functionalise 10H-phenoxazine was based around a report by G. Calzaferri et al.¹⁵ G. Calzaferri et al. reported that nitration occurred in much greater yield than the original bromination paper. The nitro group were then converted to an amine via means of reduction with iron and hydrochloric acid. The reported reaction are summarised in scheme 7.1.



Scheme 7.2: The claimed yields for the formation of carbazole products from dibenzothiophene. The procedure is proposed by A. Osuka et al.,¹⁶ although the first reaction is not explicitly done by them. Here the yield by E. Kalandia et al.¹⁷ is presented.

A separate paper showed that carbazole could be formed via the deprotonation of the amine and reaction with 5,5-dioxide-dibenzothiophene (see scheme 7.2).¹⁶ It was estimated by reference to the literature that the pKa of the amine groups attached to phenoxazine were greater than the secondary amine in phenoxazine, so it was not planned to employ a protecting group.



Scheme 7.3: The planned synthesis

As such the reaction procedure shown in scheme 7.3 was planned. Unfortunately the results reported by G. Calzaferri et al.¹⁵ for the nitration and subsequent reduction could not be replicated. Much lower yield was found for the first step, and the second step produced an impure product. As such this synthesis was abandoned at the first step. This was done early in the PhD and it is unclear to what extent synthetic incompetence played a part, although later investigation of the procedures suggest this was not the case.

7.2 Functionalisation Via Directing Groups

While the yield of bromination of PHX was low in the literature (pre 2018), when the PHX was substituted at the amine position, much higher yields were observed. The structures which give higher yield from bromination are summarised in figure 7.5. This is of course prior to the 80 % reported yield for the bromination of the base 10H-phenoxazine by T. D. James et al.¹⁴ This observation of higher yields in substituted 10H-phenoxazine provided the basis for another approach to the functionalisation of 10H-phenoxazine.

If the synthesis could be engineered to have similar groups attached to 10H-phenoxazine, as in figure 7.5, when the bromination occurs, it would seem likely that the yield would be increased. This is the approach taken in this section. The attached group can be due to being necessary in the final molecule, or via means of a protecting group. Both of these will be explored in-turn.

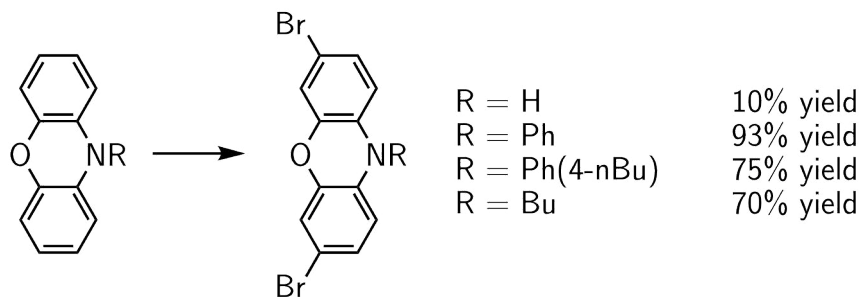


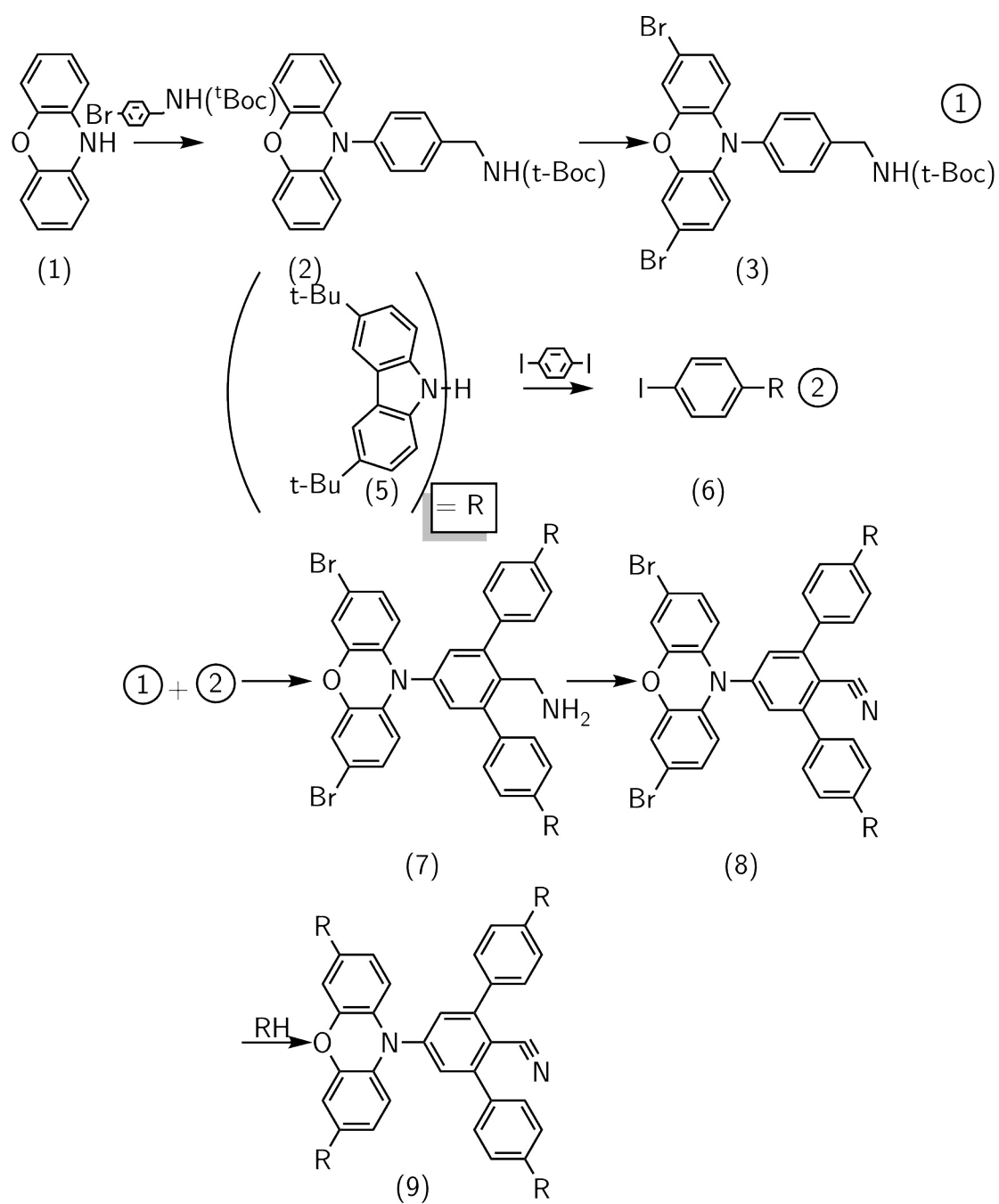
Figure 7.5: The yields of various reactions pre 2018.^{18,19,20}

7.2.1 Functionalisation Mediated By An Inbuilt Phenyl Group

It is shown in figure 7.5 that bromination of 10H-phenoxazine with substituted amine gave better yields (pre 2018). Here a synthesis is proposed where amine substitution is incorporated. Further the group substituted (a phenyl group) remains present in the final molecule. This synthesis is summarised in scheme 7.4, and involves making a 10H-phenoxazine - cyano donor-acceptor, which has been found to perform well in the literature.²¹

Unfortunately when the synthesis shown in figure 7.4 was attempted, the first reaction was found not to form the desired product, in-fact no clear primary product could be isolated. It is suspected that fragmentation or other decomposition of the starting materials occurred during this Buchwald-Hartwig coupling. There is a report that carbamate protecting groups when protecting un-conjugated amines are unstable while both at high temperatures and basic conditions.²² Hence it is believed the decomposition results from the carbamate, since hot and basic conditions are employed with Buchwald-Hartwig coupling. After the initial synthesis step could not be accomplished, this scheme was abandoned.

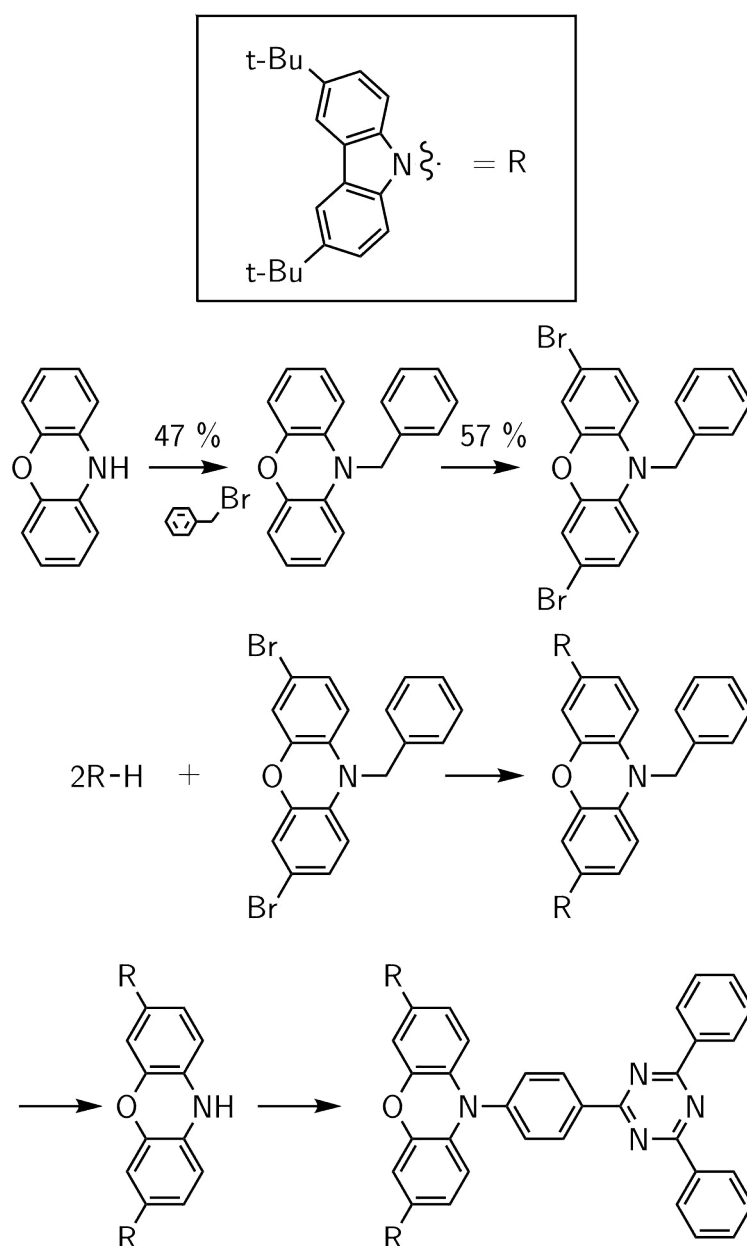
The reaction scheme generally uses rather standard reactions. Namely Buchwald-Hartwig coupling, nucleophilic substitution, bromination, acid catalysed hydrolysis, and oxidation. Each of these are based on literature reactions.^{23,24,25,26,27,21} A more unusual reaction is the coupling of the carbazole substituted phenyl group (ie. formation of compound (7) in figure 7.4). This reaction is also based on a literature reaction,²¹ and is based on reports that the amine nitrogen can act as a directing group for coupling under certain conditions.^{28,29}



Scheme 7.4: The planned synthesis using an inbuilt phenyl directing group.

7.2.2 Functionalisation Mediated By A Benzyl Protecting Group

A final attempt at the functionalisation of 10H-phenoxazine involved protecting the 10H-phenoxazine with a benzyl protecting group. The plan was to follow the reaction scheme shown in scheme 7.5. In the proposed reaction scheme the benzyl group would act as a directing group for bromination as well as a protecting group for the subsequent Buchwald-Hartwig coupling. Moderate success was found following this method, and the yields shown in scheme 7.5 was accomplished. Unfortunately due to time restraints this synthesis could not be completed.



Scheme 7.5: The planned synthesis using a benzyl protecting directing group. Experimental yields for the steps completed are shown.

The structure of benzyl protected brominated benzyl protected product was confirmed by means of singlet crystal X-ray diffraction, and yielded the structure shown in figure 7.6. This gives emphatic proof that bromination occurred at the desired site. During working on this project a separate report on the functionalisation via benzyl protecting group was reported by T. D. James et al.³⁰ This separate report showed 75 % yield for protection and 48 % yield for subsequent bromination.

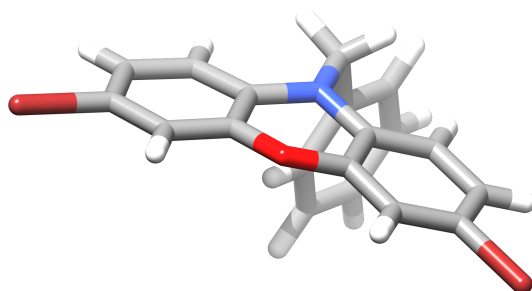


Figure 7.6: The obtained crystal structure for brominated and benzyl-protected 10H-phenoxazine.

It was not possible within the time-frame of this project to prove that no side reactions occur during the Buchwald-Hartwig coupling to ^tBu-CBZ. It also was possible to demonstrate removal of the benzyl protecting group. Neither of these things were attempted in the other published work using this method of functionalisation.³⁰

7.3 Conclusions

Positive results towards a method of brominating 10H-phenoxazine via means of benzyl protection have been presented, having attempted a number of alternative methods. These results do not definitively prove benzyl protection as a strategy, as they neglect to show that the benzyl group is stable under buchwald-Hartwig coupling, or can be removed from the 10H-phenoxazine.

Nonetheless, this work is made irrelevant due to a recent publication of a bromination with much higher yields yield by T. D. James et al.¹⁴ This bromination occurs on the base 10H-phenoxazine, and serves to show the bromination developed by C. J. Chang et al.¹³ was poorly developed. It is true that the bromination by T. D. James et al.¹⁴ has yet to be repeated. This work will be relevant if the work by T. D. James et al.¹⁴ proves irreproducible, but this seems unlikely.

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Chapter 8

A Study Of A New Solution Processable Host Molecule

*"If at first you don't succeed,
try, try again.
Then quit.
There's no point in being a damn
fool about it."*

— Unknown

This chapter would not have been possible without the diligent work of various masters students throughout this PhD, namely Miss Lauren Jackson, Mr JinTao Zhu, and Mr Douglass Crackett. These masters students worked on all the synthesis and characterisation shown.

As has previously been discussed in chapter 2, when devices using TADF are formed, it is often beneficial to use a host to contain the emissive compound. The use of a host is to separate the emissive species to prevent unfavourable interactions such as exciplexes, aggregates, and bimolecular exciton elimination.

The use of a host is easiest when devices are formed by *vacuum* methods. However solution methods are cheaper and so are desirable. The problem with hosts in solution processed devices is that aggregation may occur negating the positive effects they have. This is summarised in figure 8.1.

While no precise design characteristics have been suggested for solution processable host molecules, they do exist for hosts in general. It has been claimed^{1,2} that hosts need to have:*

1. Larger band gap than the doped TADF molecule, to allow exciton/polaron

*Note the desired properties has been adjusted to remove mention of the "HOMO" and "LUMO". It is found here-in that these are poorly defined concepts, and best avoided.

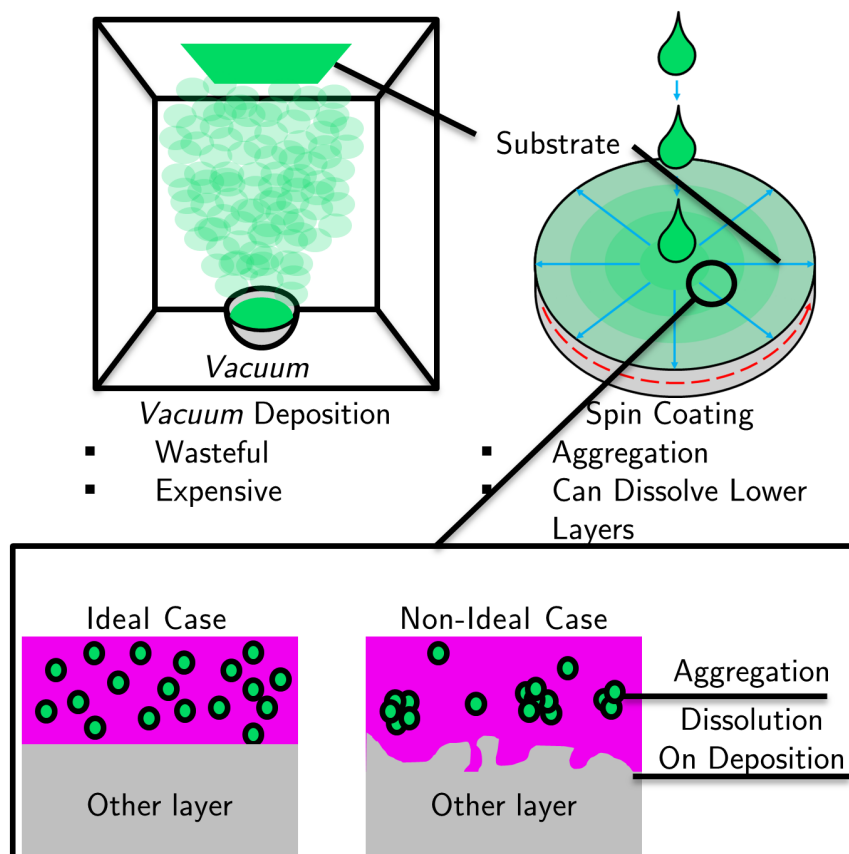


Figure 8.1: A summary of *vacuum* deposition and spin coating.

transfer to the doped TADF molecule;

2. High enough triplet energy to make it energetically favourable for the triplets to stay on the TADF compound;
3. Suitably aligned ionisation energy and electron affinity, to allow for efficient transfer into the emitting layer;
4. bipolar charge transport to balance the densities of hole and electron in the emitting layer;
5. High morphological stability;
6. Form good films.

Precisely what is meant by these criteria is vague at best. However some practical values may be obtained by further research in the literature. In particular the criteria for blue OLEDs is of particular interest. Blue OLEDs are the highest energy OLEDs and so hosts designed for these will work for all others. Further there is a continuing interest in blue OLEDs, as they are claimed to be a particular industrial challenge.³

When the spectral sensitivity of the eye is examined, it may be observed that the blue sensitivity tails off at approximately 380 nm.⁴ 380 nm corresponds to a energy of 3.26 eV, and provides the desired minimum band gap for hosts for blue emitters. 3.26 eV is also pretty close to the largest band gap of blue emitters tabulated by M. Y. Wong and E. Zysman-Colman, corresponding to 3.35 eV.³ In the original criteria it states the "band gap" must be higher, which usually implies the difference in ionisation energy, and electron affinity. However the fluorescence onset energy is felt to be better than the gap between the ionisation energy and electron affinity, because, with the fluorescence, less egregious approximations are being made. The assumption that the difference between the ionisation energy and electron affinity gives the band gap is based on assuming that electrons do not interact with each other. When the fluorescence energy is used, the assumption made is that the energy gap produced corresponds to the lowest energy gap. A reduction in energy gap is usually observed for fluorescence, known as a "stokes shift". The stokes shift results from the relaxation of the matrix which contains the molecule. While this does not necessarily reduce the energy gap to the minimum one possible, it does usually move closer to it than the absorption spectra.

The energy of triplet excitation may be considered similarly. The design of TADF molecules involves minimising the singlet-triplet energy gap, and as such, to a good approximation,³ the minimum excitation energy of the triplet state may be considered the same as the singlet. As such the phosphorescent onset should also be greater than 3.26 eV or 3.35 eV depending on the measure.

"Suitably aligned" ionisation energies and electron affinities (criteria 3) refers to two different criteria. Firstly the host energy levels must be suitably aligned relative to the other layers in the device, and secondly with regards to the dopant. With regard to the other layers, devices are designed such that the injected holes move to higher and higher energy, as well as the electrons, in such a fashion to expand the band gap. This design allows the devices to begin emitting light as soon as the turn on voltage is exceeded.⁵ Additional layers are included to make this increase in energy gradual, which is often stated as reducing the turn on voltage.^{5*} Devices are also often designed so that a large energy gap from a layer blocks the movement of charges out of the emitting layer. The design elements of devices are shown in figure 8.2. There must be materials with suitable energies to act as the other layers in devices. However, as there is a large number of commercial materials suitable for these other layers,⁶ this is less of an issue in host design.

The second criteria for suitable alignment of energy levels, is suitable alignment with the dopant. If the dopants ionisation energy or electron affinity fall significantly

*A reason for this cannot be found, but may be understood in terms of the inverse region in Marcus theory being reached at large energy separation between the layers.

outside the host's it may be favourable to form an undesired exciplex. As such, a broad energy gap is desirable to allow many dopants. However a large energy gap increases the turn on-voltage, so a happy medium must be strived for. This criteria seems fundamentally vague and hard to quantify, so quantification will not be attempted.

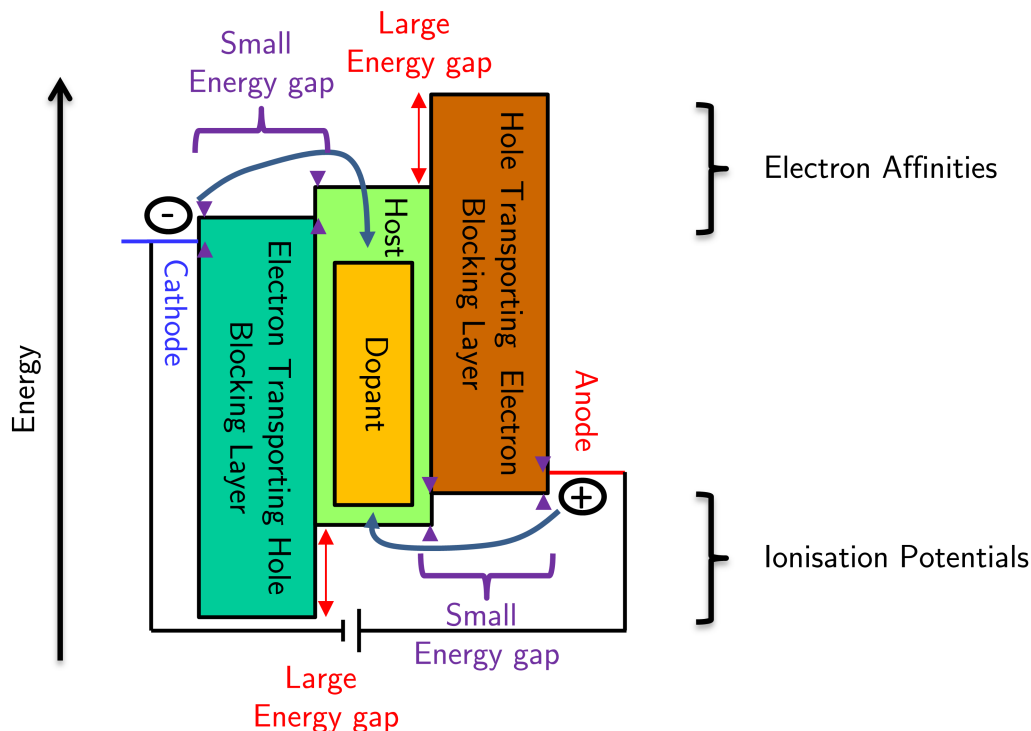


Figure 8.2: An example of the energy levels in a device demonstrating via the use of boxes with the upper bar representing electron affinity, and the lower ionisation energy. It stresses the tendency of electrons to move to lower energies and holes to higher ones.

The bipolar charge transport property is also hard to design around. While no general recommended conductivities can be found in the literature, a host "CBP" will be examined as an ideal case. It was claimed that CBP (4,4'-N,N'-Dicarbazolylbiphenyl) was the most common host for phosphorescent compounds⁷ in 2010. Electron and hole mobilities are usually studied using the "Poole-Frenkel mobility" which fits to mobility (μ) to the following equation. In the equation μ_0 is the zero-field mobility, β the Poole-Frenkel slope, and E the electric field.

$$\mu = \mu_0 e^{\beta\sqrt{E}} \quad (8.1)$$

While the "Poole-Frenkel mobility" parameters are not helpful in designing devices, the mobility of an ideal device with switch on voltage 2 V and approximate thickness 100 nm gives a practical benchmark. Here CBP has an electron mobility⁸ of $\sim 5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and hole mobility⁸ of $\sim 1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This suggests carrier mobilities on the order $10^{-3} - 10^{-4}$ are sufficient, and this provides a bench-

mark. It is possible lower values will work perfectly fine, but an actual minimum value is beyond the scope of this thesis.

In terms of morphological stability and the formation of good films, (criteria 5–6) the criteria is much more vague. Morphological stability is generally considered as being achieved if no glass transitions, crystallisation, or melting events occur close to room temperature. Generally melting and crystallisation does not occur until much higher temperatures, so glass transitions are the focus of the research.

While glass transitions are the focus of the research, it should be noted that, in bulk, a glass transitions does not change the shape, or structure of a solid, and instead changes the response to outside stimuli. A glass transition, according to statistical thermodynamics, corresponds to another vibrational mode becoming thermally accessible. Generally the worry is that this may allow the movement of the molecules in such a way as to allow a degree of crystallisation^{9,10} or mixing with other layers.^{9*} Both of these have been observed in small molecules in thin films.⁹ Theoretically, glass transitions should not lead to crystallisation or mixing of layers and experimental examples and counter examples are presented in an excellent review by Sebastian Scholz et al.¹¹ As such the relevance of glass transitions may be questioned. Nonetheless, as it is convention within in the field, and because an unpredictable change in properties is expected at a glass transition, it is considered a sign of morphological stability if it is high.

An additional question about the glass transition is how high is high enough. While it is true that the higher the temperature a morphological change occurs, the better a device may be, it has been suggested that 70–90 °C is a reasonable minimum value.^{12,11} It is unclear if there is experimental data backing up such an assertion.

The final criteria is that the host "forms good films". Generally what is meant by a "good film" is characterised in terms of low surface roughness and a lack of pin holes in the structure. Once again quantifying this is difficult. It is known that rough films are susceptible to cause catastrophic failure of devices via short-circuits,¹¹ as well as charge leaking.¹³ When the roughness of ITO was examined,¹³ it was found that there was a significant increase in charge leaking with roughness of 16.4 nm verses 10.8 nm. Here the roughness is measured via the peak-to-valley roughness (ie. the maximum height minus the lowest). As such a roughness less than or equal

*It should be noted that a glass transition does not correspond to a release/intake in energy, as such these changes are hard to justify based on it. It should noted, however, that a glass transition is normally measured on a powder of a compound, where as the devices are thin films. It is possible that this morphological change may mean that it is energetically favourable, and permissible, for the additional vibration that a glass transition corresponds to either cause crystallisation or mix layers. No doubt if it were possible to run DSC on the device a endothermic or exothermic peak would be observed corresponding to energy released/taken in upon crystallisation/phase change.

to 10.8 nm is proposed as suitable, although tentatively.

For pin-holes, it has been asserted that they allow a process where by oxygen and water can make its way into a device.¹⁴ So all pin holes are ideally avoided.

While criteria has just been presented for what constitutes a smooth pin-hole free film, this does not say how to achieve this. It has been claimed that "hook-like" alkoxyide and alkyl groups may keep films smooth and pin-hole free in solution processed hosts.¹⁰ Unfortunately what is meant by "hook-like" is not defined in the paper. It is noted that tert-butyl groups are described as "hook-like" because they form "C-H... π intermolecular interactions", and claiming "This C-H... π interaction thus interlaces with π - π stacking chains, resulting in a packing motif quite similar to the conformation of polymer chains, thus suppressing intermolecular aggregation"; as such it is taken that "hook-like" means able to interact strongly with surrounding molecules in a random and multidirectional fashion, so as to allow molecules to stick together outside of its most stable crystalline state.

It is now possible to present a new list of criteria with numerical values.

1. Lager singlet and triplet emission onset energy than 3.35 eV or 3.26 eV;
2. Ionisation energy and electron affinity which may be matched with other layers and dopants in a device;
3. Hole and electron charge transport approximately of the order $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ or higher;
4. Glass transition, melting point, and crystallisation temperatures all above 70°C but more ideally 90°C;
5. Be pin-hole free and with a peak-to-valley surface roughness of 10.8 nm or less.

While all these criteria are good for both *vacuum* and solution processed films, it is worth thinking about what additional problems may occur in solution processed films. When solution processed devices are formed, the host or dopant may aggregate, and aggregation can lead to reduced band gaps and triplet energies. An additional problem is that the layer below the host-dopant layer may also dissolve as it is deposited. Further the host layer may be dissolved upon subsequent layer deposition.

It has been implied by Y. Qiu et al.,¹⁰ that alkyl and alkoxy groups which interact strongly in random directions may improve film quality in solution processed devices. If alkyl and alkoxide groups do interact in this way, it is likely these will prevent phase separation and aggregation. As for dissolution of the layers, it has been shown by K. Matuika, K. Albrecht, K. Yamamoto and K. Fujita that heavier molecules tend

not to be soluble in alcohol.^{15,16,17,18} It has been claimed that molecules with mass greater than 800-1000 Da are sufficient to imbue this property.^{15,16,17,18} Examples exist of efficient devices of fully solution processable devices (e.g. EQE = 16.1 %) ¹⁷ that have been manufactured using this orthogonal processing methods.^{16,17}

8.1 A Design Of A New Host For Solution Processing

Given the sheer complexity of fulfilling all of the desired properties of hosts, often tried and tested methods are modified in order to generate new OLEDs. An example of a tried and tested method for hosts are carbazole based ones.⁷ CBP has been claimed to be a common host for green and red phosphorescent material.⁷ For blue OLEDs mCP and similar compounds are commonly proposed as alternatives (See figure 8.3 for structures of CBP and mCP).⁷ Blue OLEDs are the focus of this work, and so mCP will be used as the basis of a new host molecule

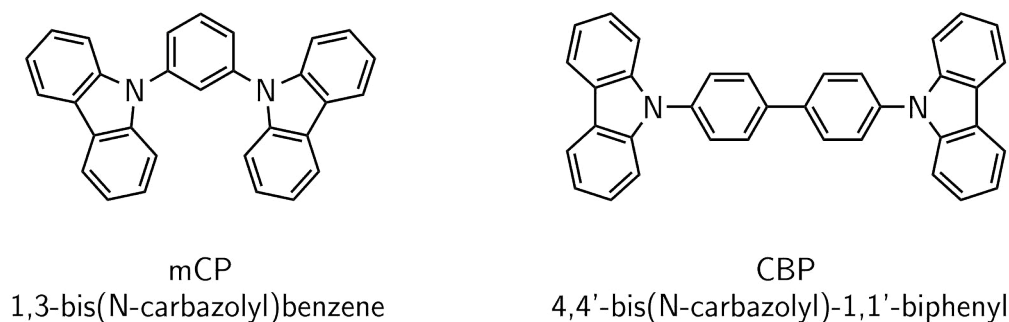


Figure 8.3: The structures and full IUPAC names of mCP and CBP.

When the previous criteria are compared with the values for mCP, the following results are observed.

Table 8.1: The "desired" host properties claimed here-in compared with mCP's.^{19,20,21,22}

Criteria	Desired	mCP
First Excitation Energy	> 3.35 eV or > 3.26 eV	> 3.5 eV
Triplet Energy	> 3.35 eV or > 3.26 eV	2.90 ± 0.1 eV ^a
Electron conductivity ^b	$\sim 10^{-4}$ cm ² V ⁻¹ s ⁻¹ or higher	3×10^{-4} cm ² V ⁻¹ s ⁻¹
Hole Conductivity	$\sim 10^{-4}$ cm ² V ⁻¹ s ⁻¹ or higher	4×10^{-4} cm ² V ⁻¹ s ⁻¹
Lowest Glass Transition	> -70 °C	55 °C.

^athis is calculated using the high energy peak. While in theory this is a better method, most others use the onset. As such this value may be slightly higher than reported.

^bfor a 100 nm device with a 2 V potential

As shown in table 8.1, mCP does not reach the desired triplet energy or glass transition temperature. However, its commonness suggests that the lack of fulfilment

of these criteria is not overly detrimental to the device performances. As such it will still be used to design new host molecules for solution processing. In this section the target molecule ("NH1") will be the one shown in figure 8.4.

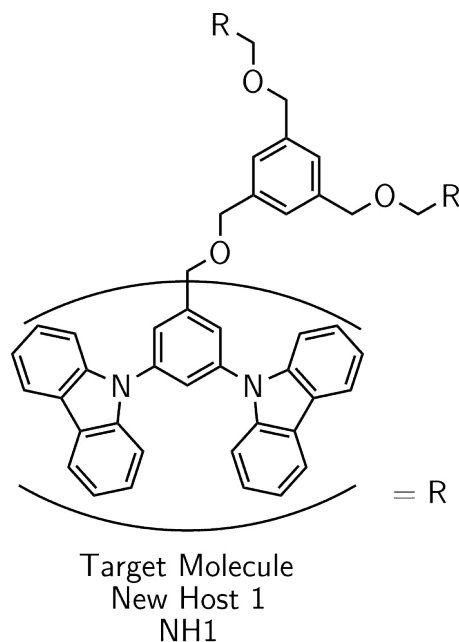


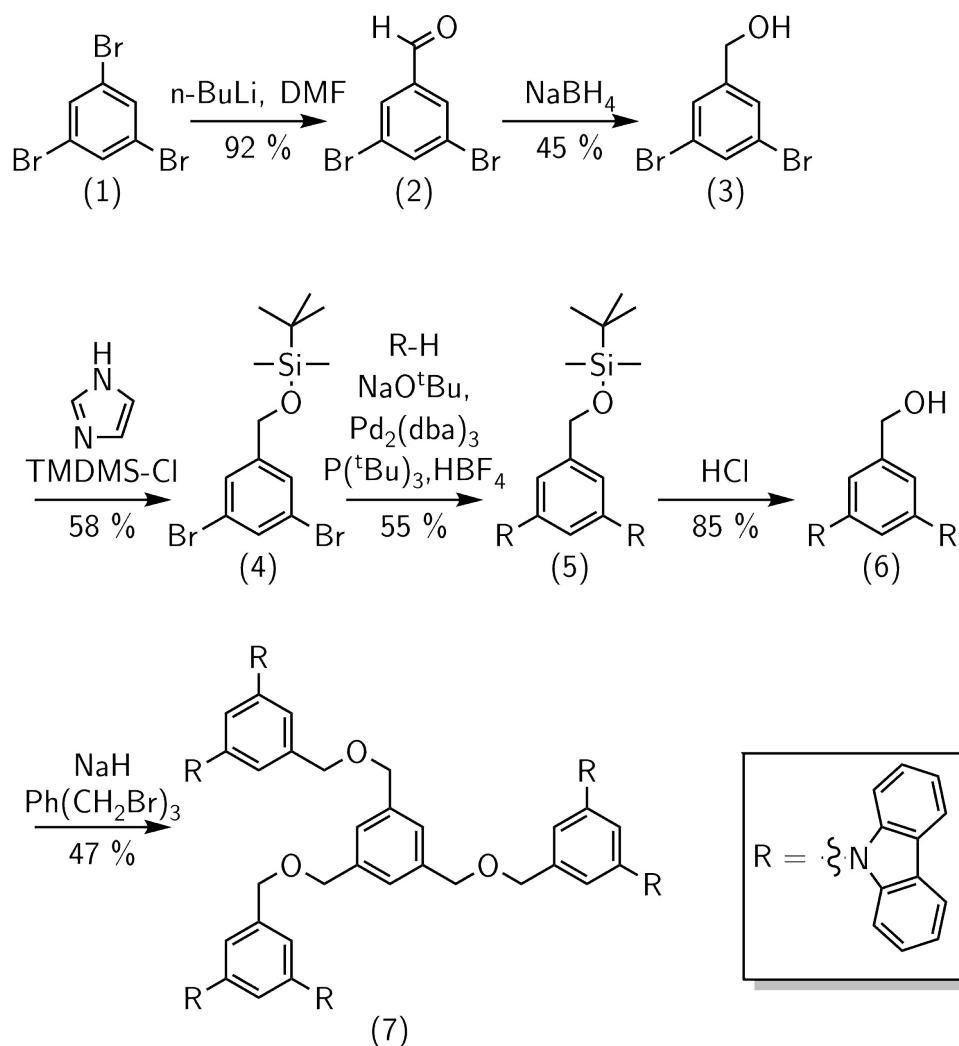
Figure 8.4: The Target molecule for this section, and the name ("New Host 1") and abbreviation ("NH1") used here-in.

The target molecule ("NH1") is selected because it increases the total molecular weight to 1429 Da, which is higher than 800-1000 Da suggested in the literature for alcohol resistance.^{15,16,17,18} In addition it was hoped that the alkoxide connection between the mCP like exterior, and phenyl interior will allow for the mCP groups to act like "hook" like groups. That is the alkoxide bridges will be orientated randomly, allowing for the more rigid mCP groups to interact randomly with surrounding molecules. It was hoped that making mCP a "hook-like" group would allow for good film formation, and prevent aggregation and phase separation. Finally it was hoped that the energy gaps would be similar to those in mCP. Electronic similarity to mCp is hopefully achieved by making mCP the component of greatest conjugation in the molecule.

8.2 The Synthesis Of A Solution Processed Host

NH1, shown in figure 8.4, was synthesised via the synthetic route shown in scheme 8.1. In this section the reactions will be addressed in turn, and the reason they were chosen discussed. The synthetically disinterested reader may skip this section.

The syntheses are mostly based upon the work of D. H. Choi et al.²³ with the remaining reaction (formation of (7) in figure 8.1) being a simple nucleophilic



Scheme 8.1: The synthesis of NH1 with reagents and yields shown.

substitution. The syntheses designed by D. H. Choi et al.²³ involves the initial lithiation of (1) followed by nucleophilic substitution on DMF to form (2). This is then reduced by sodium borohydride to (3). The compound is then protected via a silyl group, forming (4).

The silyl protecting group used is most likely introduced to prevent undesired processes occurring in the Buchwald-Hartwig coupling. Buchwald-Hartwig coupling is used to form product 4 from product 5. The coupling reaction was not attempted without the silyl protecting group here-in, and it is assumed that this was trialled by D. H. Choi et al.²³ The silyl group proved hard to purify efficiently via column chromatography, consistent with its degradation under acid conditions (Silica is known to be acidic).²⁴ It is believed that the acidic degradation of the silyl group causes the non-ideal yields shown. It is unclear how the much higher yields reported by D. H. Choi et al.²³ were achieved given they also use column chromatography for purification.

Compound (5) is de-protected to form (6), and attached to the phenyl core via nucleophilic substitution to form (7). The yields of all steps in the synthetic scheme are lower than would be desired, and are assigned as being due to the presence of acid sensitive groups, and polar protonatable groups in compounds 3-6.

8.3 Initial Characterisation: Absorption Spectra

After the successful synthesis of NH1, initial characterisation of the molecules was attempted via absorption spectra. The absorption spectra is shown in figure 8.5, with concentration dependence, and onset calculation shown in the supplementary information (section B.4.2). The onset of absorption occurs at 347 nm. While the absorption spectra of mCP could not be found, it is believed that the spectra is likely similar because the reported maxima is the same (340 nm)²⁵ as is observed here-in.

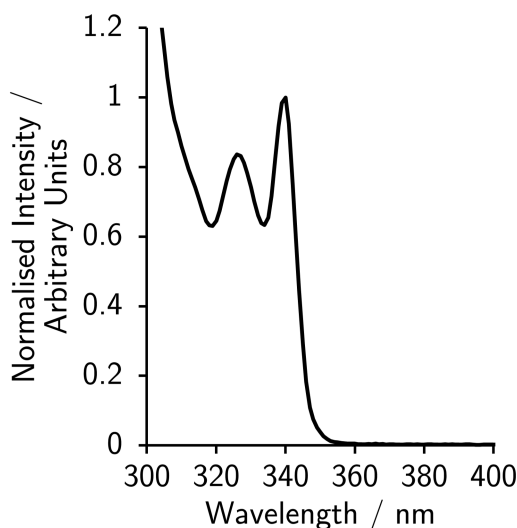


Figure 8.5: The absorption of NH1 at 10 μ M in toluene.

The absorption of mCP and NH1 being similar is preliminarily quite a promising result, as it suggests that the electronic properties are quite similar to mCP. However there was not enough time in this project to conduct further study.

8.4 Conclusion

A new host molecule is synthesised based on mCP. Further an initial characterisation via absorption spectra was conducted, which suggests that the electronic properties are similar to mCP. A more thorough examination still needs to be carried out, but this gives good tentative results.

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Chapter 9

Conclusions And Future Work Beyond DMAC-TRZ

9.1 Conclusions

In the work beyond DMAC-TRZ, a strategy of functionalising 10H-phenoxazine has been explored, as well as the synthesis and initial characterisation of a new host molecule. While the work on functionalisation of 10H-phenoxazine via benzyl protecting group has already been published, and a better method proposed, the methods shown here-in are a good starting point if the published methods prove unreproducible. It was confirmed that benzyl substitution allows good yield for substitution para to the nitrogen atom in 10H-phenoxazine.

A new host molecule, based on the symmetric substitution of mCP about a 1,3,6-trialkoxymethyl-benzene core is shown. Preliminary analysis via absorption spectra shows that the molecule behaves similar to mCP, which is a desired result. Further characterisation remains necessary however.

9.2 Future Work

A potential new host has been synthesised and partially characterised via UV-Vis spectrometry. In order for the ability of the new host to be tested, the host must be characterised via several other techniques: the ionisation potential, and electron affinity must be confirmed via cyclic voltammetry; the triplet energy must be calculated via observation of the phosphorescent emission; the morphological and physical stability must be confirmed via DSC and TGA; and additionally the fluorescence spectra must be recorded. It would also be useful to measure: its conductivity to both electrons and holes; how smooth the film is and confirm it to be pinhole free; and to make a solution processed device out of it, ideally using orthogonal solvent

depositions (ie. depositing layers in solvents which do not dissolve the layer below).

Finally there is much scope for developing new host compounds for solution processing. Ideally new hosts would be as good as vacuum processed hosts.

Part IV

Appendices

Appendix A

On Experimental Methods

"I am now persuaded that my first supply was impure, and that it was that unknown impurity which lent efficacy to the draught"

— Robert Lewis Stevenson, *Strange Case Of Dr. Jekyll and Mr. Hyde*:
On the final downfall of Dr. Jekyll,
and every chemists nightmare.

In this section the experimental techniques and synthetic methods employed in this thesis will be discussed. Knowledge of the apparatus and the techniques will be assumed. The work will be split into "Electronic And Physical Characterisation Of Final Molecules", "Characterisation And Purification Of Synthetic Products", and "Synthetic Methods". "Electronic And Physical Characterisation Of Final Molecules" will outline all methods used to characterise the electronic states of the target molecules synthesised; "Characterisation And Purification Of Synthetic Products" will outline all methods used for all compounds in the syntheses; and "Synthetic Methods" will outline how the molecules are synthesised.

A.1 Electronic And Physical Characterisation Of Final Molecules

A.1.1 Fluorescence Spectra

Fluorescent spectra at room temperature were obtained on FluoroMax 3 or 4 spectrometers, with the slit-width and integration time varied to prevent saturation. When the uncorrected detector registered greater than 5×10^5 counts per second

(cps), saturation was considered to be reached. 5×10^5 cps is considerably lower than the manufacturers published saturation limit of 2×10^6 , but is consistent with results from the Prof. Julia Weinstein's group (Sheffield University). Occasionally the 5×10^5 cps value was exceeded, but only when spectra below this value was found to be comparable, proving that saturation was not occurring. Glass and Quartz cuvettes were used as appropriate. For films spectra, quartz coated glass substrates from Ossila were used.

When solutions were cooled to 77 K, a Cary Eclipse spectrometer was used. Appropriate slit-widths, integration times, and excitation pulses were used to gain signal, but not saturate the detector. It should be noted that rather large slits widths were often necessary to gain interpretable spectra, on the order of 10 nm. In addition the time gaps listed were inserted between excitation and detection.

In order to cool the samples to 77 K, the solutions were placed in a quartz NMR tube, inside a home-made stick dewar filled with liquid nitrogen. The dewar was made out of quartz, and similar in design to the "Liquid nitrogen finger dewar" supplied by Bruker. The dewar consisted of two connected hollow tubes, one larger than the other, closed at the thin end, and open at the thick end. The lower tube was transparent; the upper tube silvered. The lower tube fit the NMR tube with space for the liquid nitrogen to flow round and maintain its temperature, whereas the upper acted as a bath, maintaining an excess of liquid nitrogen. The tube itself was made of two tubes of quartz, with a vacuum produced between the layers.

Prior to the collection of low temperature spectra, room temperature absorption spectra were collected to check for aggregation. In all cases, no-signs of aggregation were observed.

All solvents used were of HPLC grade or above.

A.1.2 Absorption Spectra

Solution absorption spectra was obtained using a Cary 50 UV-vis spectrometer, using both 1 mm and 10 mm glass and quartz cuvettes. While effort was made to keep the absorbance below 1, this was not possible for all shown spectra. Where the absorbance exceeded this value, it is noted with the spectra. All solvents used were of HPLC grade or above. For films a Cary 60 UV-vis spectrometer was used.

A.1.3 Cyclic Voltammetry

Cyclic voltammetry was obtained using a home-made 3 electrode cell by Prof. Jim A. Thomas (Sheffield University). This used a commercial potentiostat (PAR Versastat 4), and home-made platinum working and counter electrodes. A silver quasi reference

electrode was also used. The electrodes were arranged to minimise the distance between the quasi-reference electrode and working electrode. Grubbs dried N,N-dimethylformamide was used as a solvent, with 0.1 M TBAP electrolyte and the relevant compound at 1 mM. The software versastudio was used to obtain results from the setup.

A.1.4 Transient Fluorescence

All transient fluorescence was recorded using a time-resolved photoluminescence. The setup is based on a laser system (Solstice, Spectra-Physics) delivering pulses with pulse lengths of 90 fs (FWHM) at 800 nm and at a repetition rate of 1 kHz. Excitation pulses of 400nm were created by frequency-doubling of fundamental at 800nm.

A.1.5 Computational Analysis

All computational analysis was conducted using Gaussian 09, and GaussView 5 software. All compounds were initially optimised, and there frequencies calculated. The compounds which did not fully optimise or which had negative frequencies were re-ran, with a combination of the following changes: 1) geometry changed, 2) Tight optimisation conditions, 3) Hessian calculated at the start of the optimisation. Gaussian has two exit points for the optimisation process 1) that the maximum force, Root mean square force, maximum displacement, and root mean square displacement are lower than a certain threshold value, 2) that the maximum and root mean square force were two orders of magnitude smaller than the threshold value. Where possible the first listed exit point for optimisation was aimed for, with the optimisation being repeated with a number of the aforementioned changes if this did not occur. Occasionally it proved impossible to fulfil the first optimisation exit condition, in which case the second was settled for.

In the text, two different sets of results are shown, one with B3LYP functional, and the other with CAM-B3LYP. The differing Gaussian input commands are shown in table A.1.

A.1.6 Photoluminescent Quantum Yields Of Films

Photoluminescent Quantum Yield (PLQY) measurements of films were taken via means of an integrating sphere. The values given are the average of 3 values obtained from the same film by exciting at 405 nm.

Table A.1: The "key words" provided to Gaussian for optimisation and TD-DFT calculations, using both CAM-B3LYP and B3LYP functionals.

Functional	Optimisation	TD-DFT (<i>y</i> ="singlet"/"triplet", <i>x</i> ="1","2", ... ie. state looked at)
B3LYP	opt freq b3lyp/6-311g(d,p) geom=connectivity empiricaldispersion=gd3 int=ultrafine pop=regular	td=(<i>y</i> ,nstates=20,root= <i>x</i>) b3lyp/6-311g(d,p) geom=connectivity density=current empiricaldispersion=gd3 int=ultrafine pop=regular volume
CAM-B3LYP	opt freq cam-b3lyp/6-311g(d,p) scrf=(solvent=toluene) geom=connectivity empiricaldispersion=gd3 int=ultrafine pop=regular	cam-b3lyp/6-311g(d,p) geom=connectivity density=current empiricaldispersion=gd3 int=ultrafine pop=regular tda=(<i>y</i> ,nstates=20, root= <i>x</i>) volume

A.1.7 Photoluminescent Quantum Yields Of Solutions

Photoluminescent Quantum Yield (PLQY) measurements of solutions were taken via means of comparison to quinine sulphate (in 0.1 M H₂SO₄ solution). The method used was that outlined by J. R. Lakowicz.¹ All the compounds had their absorptions kept below an absorption of 0.05.² Excitation was done at 350 nm and 366 nm for both the quinine sulphate solution and the compound with measured PLQY, and the corresponding quantum yield of the quinine sulphate standard (Q_R) was used.^{3,4} This allowed for calculation of the quantum yield by the following formula, where the intensity of fluorescence is given by I for the compound, and I_R for the quinine sulphate reference, and similarly for absorption (A) and refractive index (n).

$$Q = Q_R \frac{I}{I_R} \frac{A_R}{A} \frac{n^2}{n_R^2} \quad (\text{A.1})$$

When degassing was required, a process of freeze thaw degassation was applied. This involved freezing the solutions in liquid nitrogen, removing the gas via high *vacuum* pump, allowing the solution to melt, and then repeating the process. This process was repeated 5 times. After completion the container was filled with argon gas, and the degassed solvent used by means of syringing to a cuvette which was flushed with argon, and sealed via means of an air tight top and parafilm. It is noted that Quinine Sulphate does not need degassation, and so this was not applied

to these solutions.⁵

The error of the produced PLQY ϕ was obtained by repeated PLQY measurements of a group of compounds (not listed here) against quinine sulphate, which was generalised to these compounds. These calculations were carried out by Oleksandra Korchenska, of the Jenny Clark (Sheffield University), and Ahmed Iraqi (Sheffield University) groups. The error when comparing this single compound to itself were generalised to all results. When the compounds of interest were studied, they were excited at both 350 nm and 366 nm. When both excitation at 350 nm and 366 nm both provided results suitable for the PLQY calculation, these results were averaged, and the reported errors reduced, consistent with an average. This method fundamentally assumes that the errors are not caused between different samples, or from different absorption spectra runs. As such this reduction in errors may be questioned.

Quinine sulphate was used as a standard because it is the amongst the most common for PLQY measurements and widely available.⁵ In addition the excitation for which it is standardised is highly appropriate for the compounds studied here-in.

A.1.8 Differential Scanning Calorimetry

All differential scanning Calorimetry was carried out using Perkin-Elmer Pyris 1 DSC and TA Instruments DSC25 calorimeters. All scans were ran at scan rate of 10 °C min⁻¹. A combination of sealed and unsealed cells were used in scans. Multiple scans were always ran, sometimes with the first run differing quite significantly from the others. In all cases the reported glass transitions were averages of similar runs (ie. excluding the initial run if it was significantly different). Both cooling and heating glass transitions were combined when this was possible.

A.1.9 Thermogravimetric Analysis

All thermogravimetric analysis (TGA) data was acquired on a Perkin Elmer Pyris 1 TGA system, under nitrogen atmosphere. Scan rates were at 10 °C min⁻¹. Occasionally drops in mass prior to the main degradation were observed. Drops in mass outside the main degradation were assigned as being due to solvent loss, and this was confirmed by analysing the compound prior to and after the DSC scans (Note: the DSC scans always exceeded this value). No change was observed in the NMR prior to, and after heating above these low temperature mass-loss events, and as such partial degradation is ruled out, and solvent loss is assigned. The 5 % mass losses described are mass losses compared to after any solvent losses.

A.2 Characterisation And Purification Of Synthetic Products

Here all the methods used to characterise and purify the synthetic products are listed. The characterisation data is reported using the methods described by the RSC.⁶ However, some differences to the RSC methods exist, and these will also be expanded upon.

A.2.1 Nuclear Magnetic Resonance

All nuclear magnetic resonance measurements were recorded on a combination of Bruker spectrometers, namely: Avance 400 (DPX-400), Avance 400, Avance III HD 400, Avance III 400 and Avance III HD 500. For all cases ^1H and ^{13}C spectra were collected, and in most DEPT ^{13}C spectra were ran. Where possible, additional CH/CH_3 *vs* C/CH_2 assignments are made, as per the recommendations by J. Leonard, B. Lygo, and G. Procter⁷ as well as D. F. Taber.⁸ All NMR were referenced against known solvent peaks prior to interpretation.⁹

All J couplings are given in Hz. J couplings are reported as observed on the spectra, and are tentatively assigned. Assignments are made using the notation $J_{x,y}$ where coupling is observed on the peak of hydrogen "x" due to coupling to hydrogen "y". Slight differences in the observed values are written explicitly, breaking slightly with convention (ie. $J_{x,y}$ is not necessarily written as equal to $J_{y,x}$). The break in convention from not enforcing $J_{x,y} = J_{y,x}$ is done so the reader may make valid assignments differing to the those written down. All science is open to interpretation, but differing views cannot be made if data is withheld or manipulated in a way hidden from the reader.

Efforts were made to assign the hydrogen NMR with a degree of certainty, where necessary employing 2D or alternate spectra types. This is not true for ^{13}C NMR spectra, and the ^{13}C assignments are provided to show the reader that the correct number of carbon environments are present. Nonetheless assignment are best guesses based on the information available. Occasionally additional 2D spectra were used in the assignments, but were not found necessary to include here-in. All assignable solvent peaks were ignored in the assignment,⁹ as well as reasonably weak impurities peaks.

Some slight changes in style may be observed in section A.3.4 and A.3.5, as this work was largely completed by students supervised by the author and not the author. These have been adapted to be as similar as possible to the style otherwise used.

A.2.2 Elemental Analysis

Elemental analysis was carried out for CHN/S analysis using an Emementar vario MICRO cube. The tolerance of this system is $\pm 0.3\%$, and this is reflected in the reported data. For Br, Cl, and I analysis a schroniger flask combustion method is employed. The sample is combusted, and the the gases absorbed and titrated to determine the ratios. Similarly the Br/Cl/I analysis data was produced with a tolerance of $\pm 0.3\%$.

A.2.3 Infra-Red Spectra

All fourier transfer infra-ref (FT-IR) absorption spectra were recorded on Perkin-Elmer Paragon 1000 and Spectrum RX-1 spectrometers. Samples were analysed using ATR or thin film in NaCl discs. The peaks were assigned using literature tables,⁶ and the knowledge that aromatic overtones occur in the region of 2000–1700 cm^{-1} . Slight changes in methodology may be seen in sections A.3.4 and A.3.5, due to this being based on the works of students supervised by the author.

A.2.4 Melting Points

All melting points were carried out using Gallenkamp Melting Point Apparatus.

A.2.5 Column Chromatography

Column chromatography was performed by combining several literature methods.^{10,11} The quantity of silica used was based on that reported by J. Leonard, B. Lygo, and G. Procter.¹⁰ It was found however that the quantities listed were too low, and as such, these were increased by 150 % in the case of loading with column eluent, and 200 % in the case of using dry loading. Dry loading used a ratio of 1:10 by mass of compound:adsorbant.

The columns were optimised in two separate ways depending on the difference in retention factor of desired compound and impurity. For large separation ($\Delta R_f > 0.3$) the lowest R_f compound was optimised as being 0.35. For smaller separation ($\Delta R_f > 0.3$), the average R_f was set to 0.35. This is consistent with the method presented by W. C. Still, M. Kahn, and A. Mitra.¹¹

It is noted that a theoretical description of the chromatographic dependence on R_f exists.¹² In this work it is recommended that an R_f that is in the range of 0.18–0.30 for optimal separation of compounds.¹² However different ranges are given in the same book, potential recommending ranges up to 0.50.¹²

The flow rate of the columns was maintained by continuous flow of air into the column. The column itself was partially sealed, with a suba-seal with several needles in it, allowing for the slow release of air at high pressures. The flow rate was optimised to be approximately 5 cm min^{-1} , through an approximately 15 cm long column, as per the recommendations of W. C. Still, M. Kahn, and A. Mitra.¹¹ It is noted that an improved design for maintaining flow rate using an "aquarium diaphragm" pump has been recommended,¹² and this is further recommended to the reader.

A.2.6 Thin Layer Chromatography

TLCs were run on "TLC Silica gel 60 F254" aluminium backed plates, purchased from Merck. UV light was used for visualisation.

A.2.7 Mass Spectrometry

A variety of machines were used to obtain mass-spectrometry data. A magnetic sector instrument VG AutoSpec spectrometer was used for EI and CI spectra, and a Walters LCT instrument was used for ES spectra. GC-MS with both EI and CI modes were run on a Perkin Elmer Turbomass spectrometer. All peaks with intensity greater than 10 % of the main peak were listed, and their assignments attempted. Slight changes in methodology will be observed for section A.3.4 and A.3.5, due to these sections being based on the works of students supervised by the author. Namely in section A.3.5 the intensity of mass-spec peaks was not recorded.

A.2.8 X-Ray Crystallography

X-ray crystallography structures were obtained on a combination of SMART 1000 and SMART Apex 2 detectors, supplied by Bruker. All X-ray structures were obtained at 100 K. Positions of hydrogen atoms was determined primarily via assuming standard bond-lengths and geometry, although these structures were checked against the electron density map. For hydrogens, electron density maps were used mostly to determine the position in polar groups, such as NH and OH.

A.3 Synthetic Methods

This section outlines all synthetic procedures used in this thesis. It will be subdivided into sections based on the target molecules for certain chapters, and then further subdivided, where necessary, into the heterocycles made, or the attempt at

a synthesis. It should be assumed that all reactions were carried out in ambient conditions, with un-dried solvents, unless stated otherwise.

A.3.1 Materials

All materials used were produced by commercial suppliers unless otherwise stated. All dry solvents were produced using Grubbs apparatus unless otherwise stated.

A.3.2 DMAC-TRZ

This section deals with the synthesis of all compounds synthesised in part II. In short it will deal with the synthesis of the target molecules shown in figure A.1. This synthesis shall be split into sections on each heterocycle/groups of heterocycles shown in figure A.1, namely ^tBu-CBZ, TRZ, and DMAC

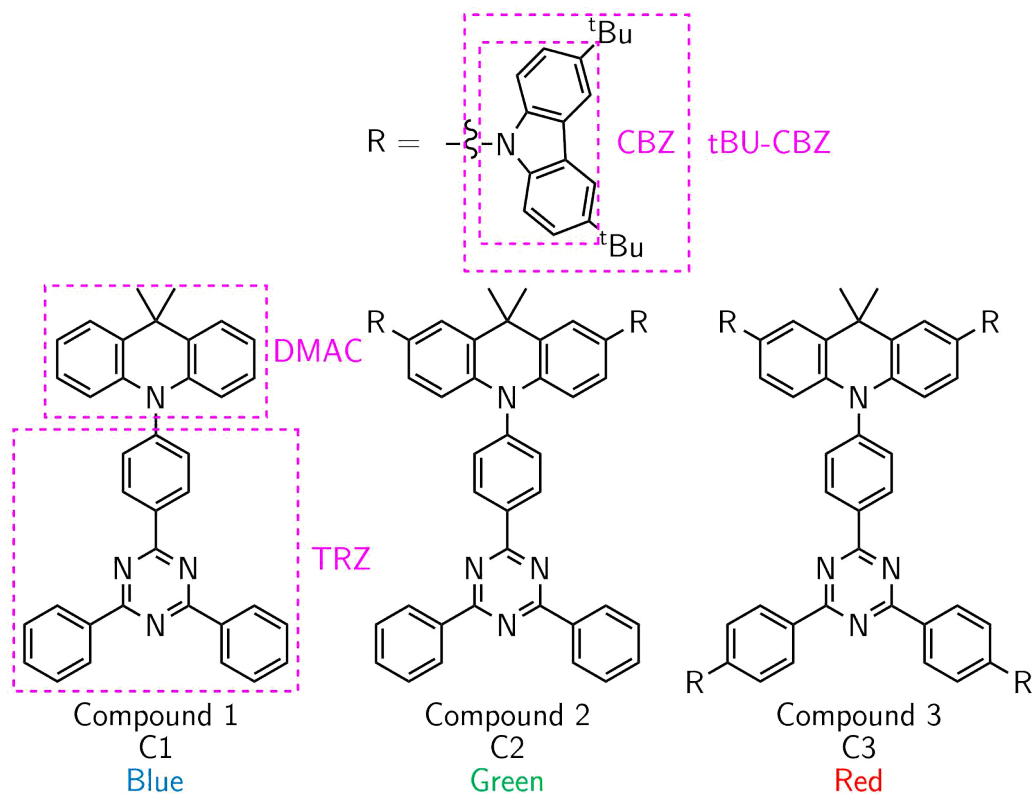
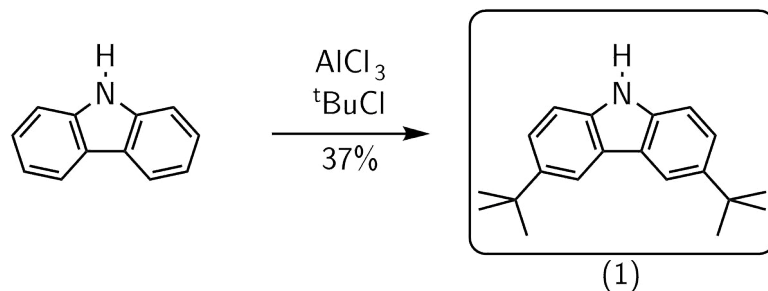
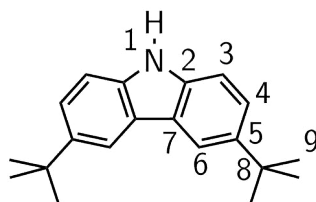


Figure A.1: The structures of the compounds discussed, the components which make them up and the names which correspond to them.



Scheme A.1: The synthetic scheme for carbazole alkylation. Rounded boxes indicate molecules used later in the synthesis, square boxes show abbreviated groups.

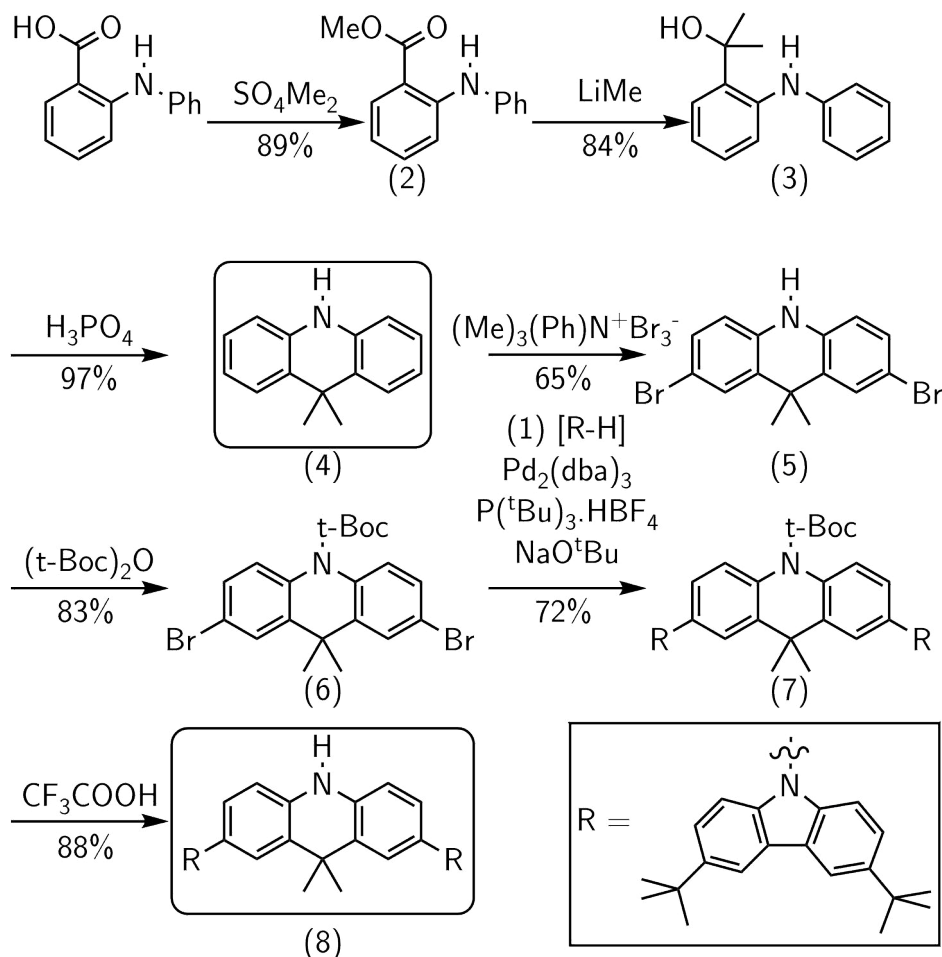
A.3.2.1 ^tBu-CBZ



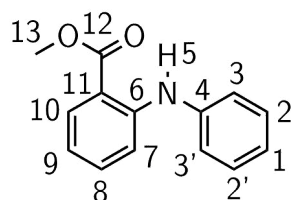
A.3.2.1.1 (1) 3,6-bis(1,1-dimethylethyl)-9H-Carbazole: The synthesis followed a similar process to that previously in the literature.¹³ To 10.00 g (59.8 mmol, 1.0 equiv.) of 9H-carbazole, and 7.98 g (59.9 mmol, 1.0 equiv.) of anhydrous aluminium trichloride, 200 ml of anhydrous dichloromethane was added, while under Ar atmosphere. The flask was connected to a NaOH bubbler, as it had previously been reported that copious gas was released (this was not observed herein).¹³ Subsequently the flask was cooled to 0 °C, and a solution of 13.2 ml (11.2 g, 121 mmol, 2.0 equiv.) of tertbutylchloride dissolved in 40 ml dry dichloromethane was added, forming a brown solution. The reaction was then stirred at room temperature for 20 h remaining brown throughout, before being poured onto 200 g of iced water. The product was then extracted with 3 × 100 ml of dichloromethane, and washed with 200 ml of water and 200 ml of brine. The product was then dried over MgSO₄, before recrystallisation from ethanol. The product was dried by heating (60 °C) under high vacuum. This provided 6.14 g (22.0 mmol, 37 % yield) of a white powder. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, J_{6,4} = 1.9, 2H, H-6), 7.85 (s, 1H, H-1), 7.47 (dd, J_{4,3}, J_{4,6} = 8.5, 1.9, 2H, H-4), 7.34 (d, J_{3,4} = 8.5, 2H, H-3), 1.46 (s, 18H, H-9). ¹³C NMR (101 MHz, CDCl₃) δ 142.3 (C-2), 138.2 (C-7), 123.7 (C-4), 123.3 (C-5), 116.3 (C-6), 110.1 (C-4), 34.8 (C-8), 32.2 (C-9). $\tilde{\nu}_{max}$ / cm⁻¹: 3412 (m, N-H), 3050 (vw, C-H), 2951 (m, C-H), 2902 (m, C-H), 2863 (m, C-H), 1754 (vw, Aromatic Overtone), 1628 (vw, Aromatic), 1611 (vw, Aromatic), 1575 (vw, Aromatic), 1493 (m), 1471 (m), 1392 (w), 1360 (m), 1330 (w), 1299 (m), 1263 (m), 1250 (m), 1202 (m), 1138 (m), 1102 (m), 1034 (m), 922 (m), 880 (m), 834 (m), 816 (s), 690 (m),

643 (w), 617 (s), 545 (vw), 485 (m), 455 (m). ES-MS: m/z 281 ($[M+H+1]^+$, 6 %), 280 (100, $[M+H]^+$), 279(1, $[M]^+$). Found: C, 85.8; H, 8.6; N, 4.9. Calc. for $C_{20}H_{25}N$: C, 86.0; H, 9.0; N, 5.01. Mp 216–219 °C.

A.3.2.2 DMAC

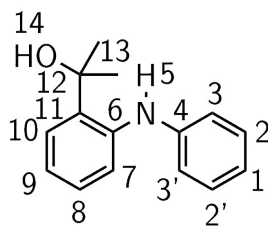


Scheme A.2: The synthetic scheme for electron donor components. Rounded boxes indicate molecules used later in the synthesis, square boxes show abbreviated groups.



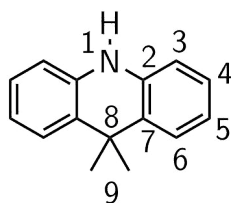
A.3.2.2.1 (2) Methyl 2-(phenylamine) benzoate The procedure used is similar to one that is previously published.¹⁴ Alternative safer procedures are recommended.¹⁵ 15.0 ml (18.0 g, 143 mmol, 1.70 equiv.) of dimethylsulphate was added

to a solution of 18.00 g (84.40 mmol, 1.0 equiv.) of N-phenyl anthanilic acid, and 12.42 g (89.88 mmol, 1.1 equiv.) of potassium carbonate in 270 ml of acetone. This resulted in a cloudy yellow solution which was refluxed for 2 h, remaining cloudy yellow throughout. Subsequently the reaction was quenched onto 200 g of crushed ice. The aqueous layer was then extracted with 2×300 ml of chloroform, before being dried over MgSO_4 and solvent removed under reduced pressure. The resulting oil was then purified via column chromatography using an eluent of 10 % ethyl acetate: 90 % 40:60 petroleum ether. The product was subsequently dried by heating (60°C) under high vacuum. This yielded 17.07 g (75.12 mmol) of a yellow oil giving a 89 % yield. On refrigeration, a yellow glassy solid was formed, which remained solid at room temperature. Note: Due to toxicity of the reagents, and their persistence after quenching, it is not recommended herein that this step is repeated.¹⁵ Further note: the compound should be stored under refrigeration.¹⁶ ^1H NMR (400 MHz, DMSO) δ 9.32 (s, 1H, H-5), 7.90 (dd, $J_{10,9}$, $J_{10,8} = 8.0, 1.6$, 1H, H-10), 7.46–7.29 (m, 3H, H-2, H-8), 7.29–7.19 (m, 3H, H-3, H-7), 7.09 (tt, $J_{1,2/2'}$, $J_{1,3/3'} = 7.3, 1.1$, 1H, H-1), 6.81 (ddd, $J_{9,8}$, $J_{9,10}$, $J_{9,7} = 8.1, 7.2, 1.1$, 1H, H-9), 3.85 (s, 3H, H-13). ^{13}C NMR (101 MHz, DMSO) δ 168.0 (C/ CH_2 , 12-C), 146.7 (C/ CH_2 , 11-C), 140.4 (C/ CH_2 , C-4), 134.4 (CH/ CH_3 , C-8), 131.3 (CH/ CH_3 , C-10), 129.5 (CH/ CH_3 , C-2), 123.2 (CH/ CH_3 , C-1), 121.5 (CH/ CH_3 , C-3), 117.6 (CH/ CH_3 , C-9), 114.1 (CH/ CH_3 , C-7), 112.0 (CH/ CH_3 , 6-C), 51.9 (CH/ CH_3 , 13-C). $\tilde{\nu}_{\text{max}}$ / cm^{-1} : 3322 (s, br, NH), 3033 (CH), 2950 (CH, s), 2844 (CH, w), 1686 (C=O, s), 1593 (s), 1578 (s), 1515 (s), 1453 (s), 1426 (s), 1360, 1260 (s), 1233 (s), 1190, 1163, 1141, 1084, 1046 (w), 1028 (w), 966 (w), 885 (w), 796 (w). ESI-MS: m/z 229 ($[\text{M}+\text{H}+1]^+$, 16%), 228 (100, $[\text{M}+\text{H}]^+$), 197 (3, $[\text{M}-\text{OMe}+1]^+$), 196 (19, $[\text{M}-\text{OMe}]^+$). Found: C, 73.8; H, 5.9; N, 5.9. Calc. for $\text{C}_{15}\text{H}_{13}\text{NO}_2$: C, 74.0; H, 5.8; N, 6.2. Mp $57\text{--}59^\circ\text{C}$.



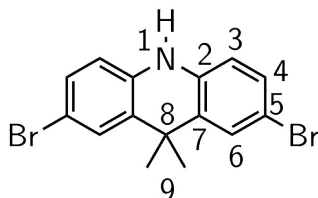
A.3.2.2.2 (3) α - α -dimethyl-2-(phenylene)-benzoate The procedure used is similar to one that is previously published.¹⁴ A solution under argon was made up of 6.00 g (26.4 mmol, 1.0 equiv.) of methyl 2-(phenylamino)benzoate in 60 ml of dry THF, and cooled to -78°C . To this solution 25.5 ml of 3.1 M (79 mmol, 3.0 equiv.) methyl lithium in diethoxymethane was added over a period of 30 min. The mixture was then stirred at -78°C for a further 30 min before being returned to room

temperature, and allowed to stir for an extra 1 hour. The cloudy yellow mixture was then poured onto 100 g of crushed ice, extracted with 3×70 ml of chloroform, and dried over Na_2SO_4 . The product was purified using a column chromatography with eluent 10% EtOAc, 90 % 40:60 petroleum ether. The product was recovered under reduced pressure, and then dried by heating (60°C) under high vacuum. This yielded 5.05 g (22.2 mmol, 84 % yield) of a thick brown oil. ^1H NMR (400 MHz, DMSO) δ 8.49 (s, 1H, H-5), 7.30–7.19 (m, 4H, H-2, H-7, H-10), 7.16 (td, $J_{8,7}$, $J_{8,9}$, $J_{8,10}$, = 7.7, 7.7, 1.5, 1H, H-8), 7.00 (dd, $J_{3/3',2/2'}$, $J_{3/3',1/1}$ = 8.6, 1.0, 2H, H-3, H-3'), 6.90–6.77 (m, 2H, H-10, H-9, H-1), 5.78 (s, 1H, H-14), 1.53 (s, 6H, H-13). ^{13}C NMR (101 MHz, DMSO) δ 143.8 (C/ CH_2 , C-4), 141.8 (C/ CH_2 , C-6), 136.2 (C/ CH_2 , C-11), 129.3 (CH/ CH_3 , C-2), 127.3 (CH/ CH_3 , C-10), 126.0 (CH/ CH_3 , C-8), 120.1 (CH/ CH_3 , C-1), 119.6 (CH/ CH_3 , C-7), 118.5 (CH/ CH_3 , C-9), 116.5 (CH/ CH_3 , C-3), 72.3 (CH/ CH_3), 29.6 (C/ CH_2). $\tilde{\nu}_{\text{max}}$ / cm^{-1} : 3531 (vw, OH), 3356 (m, NH), 3044 (w, Aromatic CH Stretch), 2976 (w, CH_3 Asymmetric Stretch), 2932 (vw, CH_3 Symmetric Stretch), 1930 (vw, Aromatic Overtone), 1589 (s), 1577 (s), 1512 (s), 1497 (s), 1474 (m), 1454 (m), 1441 (m), 1424 (m), 1383 (w), 1365 (w), 1338 (w), 1309 (s), 1257 (m), 1219 (w), 1176 (w), 1165 (w), 1154 (w), 1128 (m), 1107 (w), 1080 (w), 1048 (w), 1028 (w), 995 (w), 946 (w), 936 (w), 886 (m), 845 (w), 744 (s), 692 (s), 646 (w), 618 (w), 583 (m), 561 (w), 501 (m), 426 (w), 411 (w). ESI-MS: m/z 230 ($[\text{M}+\text{H}+2]^+$, 1 %), 229 (11, $[\text{M}+\text{H}+2]^+$), 228 (69, $[\text{M}+\text{H}]^+$), 212 (1, $[\text{M}-\text{OH}+2]^+$), 211 (17, $[\text{M}-\text{OH}+1]^+$), 210 (100, $[\text{M}-\text{OH}+\text{H}]^+$), 194 (2, $[\text{M}-2\text{Me}]^+$). Found: C, 79.2; H, 7.1; N, 6.7. Calc. for $\text{C}_{15}\text{H}_{13}\text{NO}_2$: C, 79.2; H, 7.5; N, 6.2.



A.3.2.2.3 (4) 9,9-dimethyl-10H-acrydine synthesis The procedure used is similar to one that is previously published.¹⁴ To 5.05 g (22.2 mmol) of 2-(2-(phenylamino)phenyl)propan-2-ol 80 ml of 85 % phosphoric acid was added, which was stirred and heated to 35°C forming an cloudy orange solution, and left for 2 h. The cloudy orange mixture was then poured onto 100 g of ice, and the precipitate filtered, and washed with 3×60 ml of deionised water. The product was then dried in a vacuum oven overnight, yielding 4.52 g (21.5 mmol, 97 %) of a brown powder. ^1H NMR (400 MHz, CDCl_3) δ 7.40 (dd, $J_{6,5}$, $J_{6,4}$ = 7.8, 1.3, 2H, H-6), 7.12 (td, $J_{4,5}/J_{4,3}$, $J_{4,6}$ = 7.7, 1.4, 2H, H-4), 6.94 (td, $J_{5,4}/J_{5,6}$, $J_{5,3}$ = 7.8, 1.0, 2H, H-5), 6.71 (dd, $J_{3,4}$, $J_{3,5}$ = 7.9, 1.0, 2H, H-3), 6.15 (s, Br, H-1), 1.60 (s, 6H, H-9). ^{13}C NMR (101 MHz,

CDCl₃) δ 138.6 (C/CH₂, C-2), 129.2 (C/CH₂, C-7), 126.8 (CH/CH₃, C-4), 125.6 (CH/CH₃, C-6), 120.7 (CH/CH₃, C-3), 113.5 (CH/CH₃, C-5), 36.3 (C/CH₂, C-8), 30.7 (CH/CH₃, C-9). $\tilde{\nu}_{max}$ / cm⁻¹: 3356 (m, NH), 3045 (w, Aromatic CH Stretch), 2959 (m, CH₃ Asymmetric Stretch), 2918 (w, CH₃ Symmetric Stretch), 1793 (vw, Aromatic Overtone), 1606 (m), 1580 (m), 1508 (m), 1477 (s), 1451 (s), 1386 (m), 1361 (w), 1317 (s), 1243 (m), 1214 (m), 1160 (w), 1148 (w), 1132 (w), 1105 (w), 1094 (w), 1037 (m), 932 (w), 886 (m), 857 (w), 848 (w), 744 (s), 689 (m), 658 (m), 616 (w), 574 (m), 541 (m), 504 (s), 475 (m). ESI-MS: m/z 211 ([M+H+1]⁺, 9 %), 210 ([100, M+H]⁺), 195 (8, [M-Me+1]⁺) 194 (59, [M-Me]⁺). APCI: m/z 211 ([M+H+1]⁺, 16 %), 210 ([100, M+H]⁺), 195 (1, [M-Me+1]⁺) 194 (5, [M-Me]⁺), EI-MS: m/z 209 ([M]⁺, 9%), ([M-Me]⁺, 100 %). Found: C, 85.8; H, 7.3; N, 6.4. Calc. for C₁₅H₁₃NO₂: C, 86.1; H, 7.2; N, 6.7. Mp 112–117 °C.



A.3.2.2.4 (5) 2,7-dibromo-9,10-dihydro-9,9-dimethyl-acridine The procedure used is similar to one that is previously published.¹⁴ A solution was made of 1.00 g (4.78 mmol, 1.0 equiv.) of 9,9-dimethyl-10H-acridine in 20 ml of tetrahydrofuran. To this solution, 3.59 g (9.55 mmol, 2.0 equiv.) of trimethylphenylammonium tribromide was added, in a singlet portion, causing a change from a pink-orange colour to a dark brown with a white precipitate. The vessel was stirred at room temperature for 6 h, before being poured onto 60 ml of deionised water. The crude product was then extracted using 2 × 60 ml of ethyl acetate, dried over MgSO₄, and the solvent removed under vacuum (instability of the crude at high temperature was observed, so it was not heated above 50 °C). The product was then purified using column chromatography on silica with a 1:7 ethyl acetate to petroleum ether. Finally the product was dried by heating (60 °C) under high vacuum for 1 h.; this provided a 1.14 g (3.11 mmol, 65 % yield) of a green crystal. ¹H NMR (400 MHz, DMSO) δ 9.19 (s, 1H, H-1), 7.46 (d, $J_{6,4}$ = 2.1, 2H, H-6), 7.22 (dd, $J_{4,3}$, $J_{4,6}$ = 8.5, 2.1, 2H, H-4), 6.73 (d, $J_{3,4}$ = 8.5, 2H, H-3), 1.47 (s, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 137.3 (C/CH₂, C-5), 130.9 (C/CH₂, C-7), 129.8 (CH/CH₃, C-4), 128.6 (CH/CH₃, C-6), 115.3 (CH/CH₃, C-3), 113.1 (C/CH₂, C-2), 36.7 (C/CH₂, C-8), 30.5 (CH/CH₃, C-9). $\tilde{\nu}_{max}$ / cm⁻¹: 3400 (w, N-H), 2951 (w, CH₃ Asymmetric Stretch), 1723 (w, Aromatic Overtone), 1603 (m), 1568 (w), 1495 (w), 1472 (s), 1454 (s), 1404

(s), 1352 (m), 1318 (w), 1291 (s), 1245 (s), 1153 (m), 1126 (m), 1093 (s), 1077 (s), 1003 (m), 916 (m), 887 (m), 875 (m), 863 (s), 845 (m), 802 (s), 746 (m), 726 (m), 674 (m), 653 (s), 590 (s), 536 (s), 491 (s), 454 (s). ESI-MS: m/z 370 ($[M+H+2]^+$, 35 %), 369 (9, $[M+H+1]^+$), 368 (100, $[M+H]^+$), 366 (43, $[M+H-2]^+$), 354 (13, $[M-CH_3+2]^+$), 352 (31, $[M-CH_3]^+$), 350 (14, $[M-CH_3-2]^+$). Found: C, 49.0; H, 3.6; N, 3.8; Br 43.5. Calc. for $C_{15}H_{13}Br_2N$: C, 49.0; H, 3.6; N, 3.8; Br 43.8. Mp 125–135 °C.

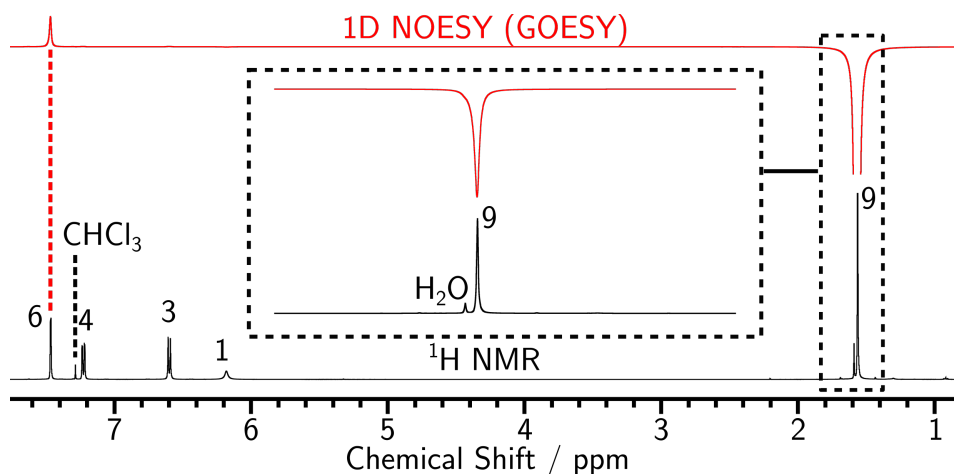
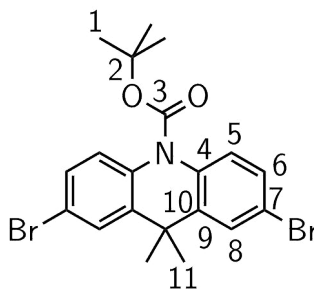


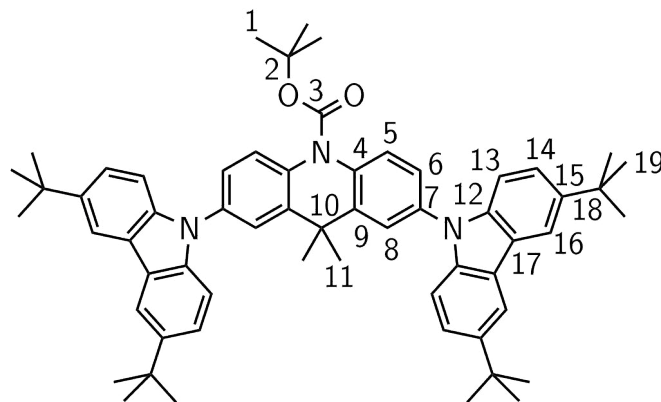
Figure A.2: A comparison of the GOESY spectra and 1H NMR of compound (5) shown in figure A.2.

In order to prove the 2,7 substitution it was necessary to also run further NMR spectra. The NMR shown in figure A.2 definitively proves the above structure. This is because it shows through space correlation between hydrogen on position 9 and position 6. As the peak assigned to hydrogen 6 is a doublet with low coupling constant (2.1 Hz), it is most likely that there are no hydrogens on the adjacent carbons. This is consistent with the bromination occurring on the 5 position as opposed to the 4 position, which would otherwise be qualitatively indistinguishable via NMR.



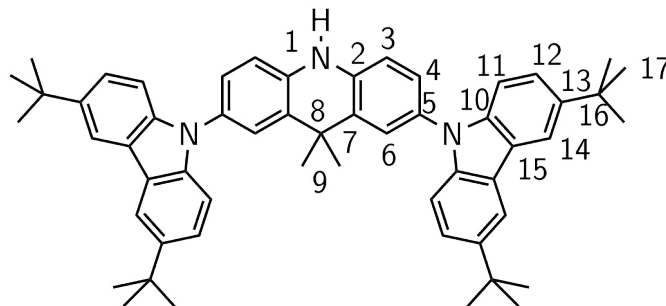
A.3.2.2.5 (6) 2,7-dibromo-9,9-dimethyl-9,10-dihydroacridine-10(9H)-carboxylic acid tert-butyl ester The procedure used is similar to one

that is previously published.¹⁷ 1.10 g (3.01 mmol, 1.0 equiv.) of 2,7-dibromo-9,10-dihydro-9,9-dimethyl-acridine and 0.128 g (1.04 mmol, 0.35 equiv.) of 4-dimethyl-amininopyridine were dissolved in 11 ml of dry THF under argon, and a solution of 0.981 g (4.49 mmol, 1.49 equiv.) of tert-butyl-dicarbonate in 2 ml of dry THF under argon was added. No colour change from the initial brown solution was observed. The resulting solution was stirred for 3 h, remaining brown throughout, before quenching with 10 ml of deionised water, which after stirring for 30 min causing precipitation of a white powder. The product was then filtrated off and washed with 3×10 ml of water and 3×10 ml of ethanol. The product was then dried by heating (60 °C) under vacuum for 1 h, to give 1.17 g (2.49 mmol, 83 % yield) of a white powder. ¹H NMR (400 MHz, DMSO) δ 7.58 (d, $J_{8,6} = 2.1$, 2H, H-8), 7.53 (d, $J_{5,6} = 8.6$, 2H, H-5), 7.47 (dd, $J_{6,5}, J_{6,8} = 8.6, 2.1$, 2H, H-6), 1.48 (s, 6H, H-11), 1.46 (s, 9H, H-1). ¹³C NMR (101 MHz, CDCl₃) δ 152.1 (C/CH₂, C-3), 142.9 (C/CH₂, C-7), 137.3 (C/CH₂, C-4), 129.1 (CH/CH₃, C-5), 127.1 (CH/CH₃, C-6), 126.4 (CH/CH₃, C-8), 119.0 (C/CH₂, C-9), 82.7 (C/CH₂, C-2), 38.0 (C/CH₂, C-10), 28.3 (CH/CH₃, C-1), 26.6 (CH/CH₃, C-11). $\tilde{\nu}_{max}$ / cm⁻¹: 2977 (w, CH₃ Asymmetric Stretch), 2929 (w, CH₃ Symmetric Stretch), 1706 (s, C=O), 1600 (vw), 1494 (m), 1461 (s), 1405 (m), 1390 (m), 1365 (m), 1328 (s), 1310 (s), 1293 (m), 1268 (s), 1253 (s), 1229 (s), 1217 (m), 1163 (s), 1148 (s), 1097 (m), 1086 (s), 1078 (s), 1045 (m), 1021 (s), 951 (s), 919 (m), 866 (m), 853 (s), 830 (s), 810 (s), 778 (s), 761 (m), 749 (s), 736 (m), 678 (m), 663 (m), 585 (w), 552 (m), 522 (s), 504 (s), 465 (m). APCI: m/z 469 ([M+2]⁺, 8%), 467 (27, [M]⁺), 465 (10, [M-2]⁺), 414 (44, [M-tBu+2H+2]⁺), 413 (15, [M-tBu+2H+1]⁺), 412 (100, [M-tBu+2H]⁺), 411 (52, [M-tBu+2H-1]⁺), 410 (54, [M-tBu+2H-2]⁺), 368 (11, [M-BOC+2H]⁺). Found: C, 51.6; H, 4.5; N, 2.9; Br 34.1. Calc. for C₂₀H₂₁Br₂NO₂: C, 51.4; H, 4.5; N, 3.0; Br 34.2. Mp 190–192 °C.



A.3.2.2.6 (7) 2,7-(3,6-di-tert-butyl-9H-carbazole-9yl)-9,9-dimethyl-9,10-dihydroacridine-10(9H)-carboxylic acid tert-butyl ester 1.10 g of

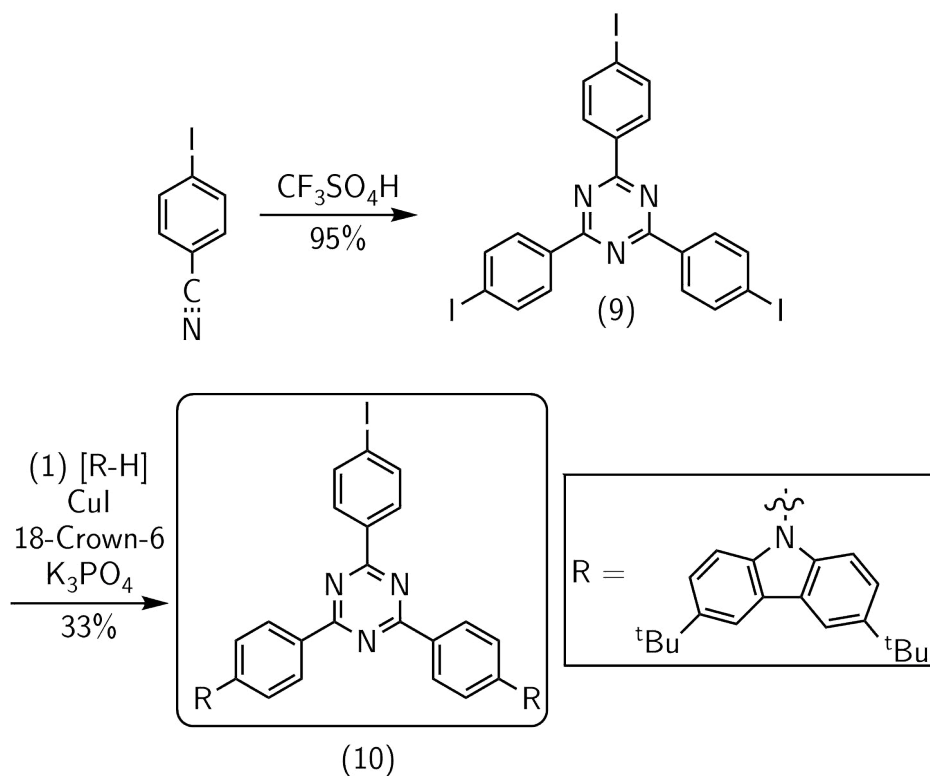
2,7-dibromo-9,9-dimethyl-9,10-dihydroacridine-10(9H)-carboxylic acid tert-butyl ester (2.36 mmol, 1.00 equiv), 1.32 g of 3,6-di-tert-butylcarbazole (4.71 mmol, 2.00 equiv.), 0.108 g of tris(dibenzylideneacetone)dipalladium(0) (0.118 mmol, 0.050 equiv.), 0.034 g tri-*t*-butylphosphonium tetra-fluoroborate (0.119 mmol, 0.050 equiv.), 0.905 g sodium *t*-butoxide (5.14 mmol, 4.00 equiv.) were dissolved in 35 ml of dry toluene forming a purple solution. The solution was formed under argon. After refluxed for 11.5 h, the reaction was cooled to room temperature for 1 h, forming a dark brown solution, the reaction was quenched on 100 ml of deionised water. The organic layer was extracted with 4 × 100ml chloroform. Then the extracts were combined, dried over sodium sulphate, filtered and evaporated under reduced pressure. The crude product was purified by suspending in 20 ml of 40:60 petroleum ether, filtering off and washing with 3 × 20ml of 40:60 petroleum ether, 3 × 20ml of butanol, and 3 × 20ml of methanol, and the resulting powder dried by heating (60 °C) under vacuum for 1 h, to yield 1.46 g (1.69 mmol, 72 % yield) of a pale brown powder of 2,7-(3,6-Di-tert-butyl-9H-carbazole-9yl)-9,9-dimethyl-9,10-dihydroacridine-10(9H)-carboxylic acid tert-butyl ester. ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, J_{16,14} = 1.6, 4H, H-16), 7.89 (d, J_{5,6} = 8.6, 2H, H-5), 7.61 (d, J_{8,6} = 2.2, 2H, H-8), 7.53 – 7.43 (m, 6H, H-6, H-14), 7.37 (d, J_{13,14} = 8.6, 4H, H-13), 1.67 – 1.60 (m, 15H, H-1, H-11), 1.47 (s, 36H, H-19). ¹³C NMR (101 MHz, CDCl₃) δ 152.7 (C/CH₂, C-3), 143.0 (C/CH₂, C-12), 142.6 (C/CH₂, C-4), 139.4 (C/CH₂, C-18), 137.0 (C/CH₂, C-7), 135.5 (C/CH₂, C-9), 126.9 (CH/CH₃, C-5), 124.4 (CH/CH₃, C-6), 123.8 (CH/CH₃, C-1), 123.4 (C/CH₂, C-17), 121.7 (CH/CH₃, C-8), 116.4 (CH/CH₃, C-16), 109.3 (CH/CH₃, C-13), 82.7 (C/CH₂, C-2), 38.3 (C/CH₂, C-10), 34.9 (C/CH₂, C-18), 32.2 (CH/CH₃, C-19), 28.5 (CH/CH₃, C-1), 27.1 (CH/CH₃, C-11). $\tilde{\nu}_{max}$ / cm⁻¹: 3043 (vw, Aromatic CH Stretch), 2959 (m, CH₃ Asymmetric Stretch), 2903 (w, CH₃ Symmetric Stretch), 2867 (w, CH₃ Symmetric Stretch), 1867 (vw, Aromatic Overtone), 1719 (s, C=O), 1634 (vw), 1605 (w), 1579 (vw), 1487 (s), 1456 (m), 1413 (vw), 1393 (w), 1364 (m), 1323 (s), 1293 (m), 1262 (s), 1233 (s), 1202 (w), 1161 (s), 1152 (s), 1131 (m), 1105 (w), 1097 (w), 1081 (w), 1045 (w), 1027 (w), 979 (vw), 953 (w), 924 (w), 897 (w), 879 (m), 851 (w), 841 (m), 808 (s), 765 (w), 756 (w), 741 (m), 724 (vw), 705 (vw), 680 (vw), 659 (m), 635 (vw), 614 (m), 596 (w), 577 (vw), 564 (vw), 527 (m), 514 (w), 503 (w), 483 (w), 470 (w), 448 (w), 420 (m), 407 (w). ES-MS: *m/z* 866 (6 %, [M+2]⁺), 865 ([M+1]⁺, 45), 864 ([M]⁺, 100), 810 ([M-*t*Bu+2H+1]⁺, 20), 809 ([M-*t*Bu+2H]⁺, 52). Found: C, 80.8; H, 7.6; N, 4.6 Calc. for C₆₉H₆₉N₃O₂: C, 83.4; H, 7.9; N, 4.6. Mp 232–236 °C



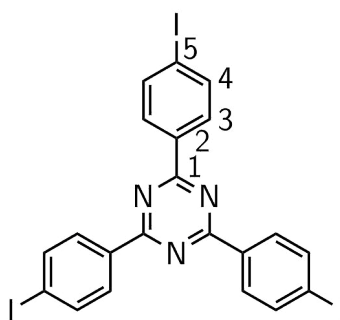
A.3.2.2.7 (8) 2,7-(3,6-di-tert-butyl-9H-carbazole-9-yl)-9,9-dimethyl-9,10-dihydroacridine This procedure was based on a similar procedure in the literature.¹⁸ 0.650 g (752 μmol) of 2,7-(3,6-di-tert-butyl-9H-carbazole-9-yl)-9,9-dimethyl-9,10-dihydroacridine-10(9H)-carboxylic acid tert-butyl ester was dissolved in 15 ml of dichloromethane, forming a dark brown solution. Subsequently, 12 ml of trifluoroacetic acid was added under stirring, which darkened the solution. The solution was then heated to reflux for 30 min before cooling for 5 min forming a deep black-brown solution. After cooling, the solution was quenched with 15 ml of deionised water and subsequently neutralised with 10 % NaHCO_3 solution (~ 120 ml). The product was then extracted with $4 \times 100\text{ml}$ of dichloromethane and dried using MgSO_4 . Finally, the solvent was removed under reduced pressure and then dried by heating (60°C) under high vacuum for 1 h. This yielded 0.506 g (663 μmol , 88 % yield) of a red brown powder. ^1H NMR (400 MHz, Acetone) δ 8.73 (s, 1H, H-1), 8.30 (d, $J_{14,12} = 1.6$, 4H, H-14), 7.65 (d, $J_{6,4} = 2.2$, 2H, H-6), 7.51 (dd, $J_{12,11}, J_{12,14} = 8.7, 2.0$, 4H, H-12), 7.39 – 7.28 (m, 6H, H-4, H-11), 7.19 (d, $J_{3,4} = 8.4$, 2H, H-3), 1.76 (s, 6H, H-9), 1.45 (s, 36H, H-17). ^{13}C NMR (101 MHz, CDCl_3) δ 142.6 (C/ CH_2 , C-10), 139.9 (C/ CH_2 , C-15), 137.3 (C/ CH_2 , C-5), 131.2 (C/ CH_2 , C-7), 130.0 (C/ CH_2 , C-2), 125.9 (CH/ CH_3 , C-4), 124.8 (CH/ CH_3 , C-6), 123.7 (CH/ CH_3 , C-12), 123.1 (C/ CH_2 , C-13), 116.4 (CH/ CH_3 , C-14), 114.7 (CH/ CH_3 , C-3), 109.2 (CH/ CH_3 , C-11), 37.0 (C/ CH_2 , C-7), 34.9 (C/ CH_2 , C-16), 32.2 (CH/ CH_3 , C-17), 31.1 (CH/ CH_3 , C-9). $\tilde{\nu}_{\text{max}} / \text{cm}^{-1}$: 3396 (w, NH) 3043 (w, Aromatic CH Stretch), 2956 (m, CH_3 Asymmetric Stretch), 2903 (m, CH_3 Symmetric Stretch), 2865 (w, CH_3 Symmetric Stretch), 2324 (w, Aromatic Overtone), 2161 (w, Aromatic Overtone), 2051 (w, Aromatic Overtone), 1980 (w, Aromatic Overtone), 1868 (vw, Aromatic Overtone), 1747 (w, Aromatic Overtone), 1610 (w, Aromatic Stretch), 1591 (w), 1488 (s), 1475 (s), 1461 (s), 1392 (m), 1362 (m), 1325 (m), 1294 (s), 1262 (s), 1235 (m), 1202 (m), 1183 (m), 1148 (w), 1127 (m), 1105 (w), 1085 (w), 1034 (m), 923 (w), 906 (w), 877 (m), 840 (w), 808 (s), 765 (w), 741 (m), 703 (w), 658 (m), 613 (s), 591 (w), 573 (w), 547 (w), 524 (w), 504 (m), 470 (m), 451 (m), 423 (m), 419 (m), 402 (w). ESI: m/z 765 (15 %, $[\text{M}+2]^+$), 764 ($[\text{M}+1]^+$, 51), 763($[\text{M}]^+$, 100), 762 ($[\text{M}-\text{H}]^+$, 57). Found: C, 85.8; H, 7.8; N, 5.2

Calc. for $C_{55}H_{61}N_3$: C, 86.5; H, 8.1; N, 5.5. Mp 199–222 °C. Exact Mass - ESI +:
Found: 764.4932; Calc. for $C_{55}H_{61}N_3$: 764.4938; PPM difference: 0.84.

A.3.2.3 TRZ

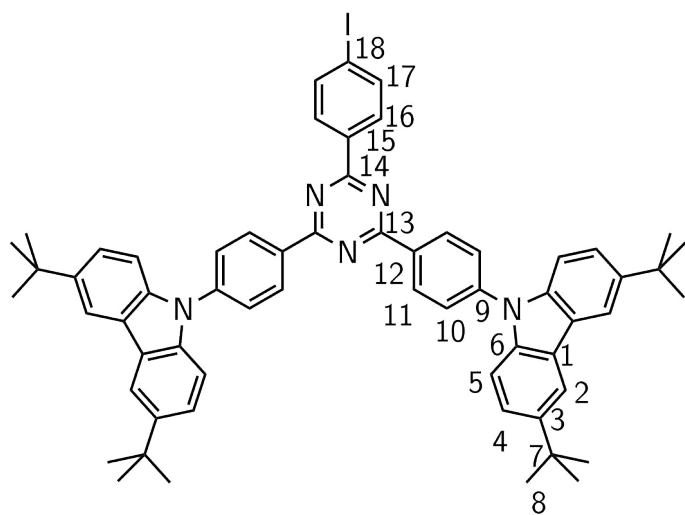


Scheme A.3: The synthetic scheme for electron acceptor components. Rounded boxes indicate molecules used later in the synthesis, square boxes show abbreviated groups.



A.3.2.3.1 (9) 2,4,6-tris(4-iodophenyl)-1,3,5-triazine This procedure was based on a similar procedure in the literature.¹⁹ To 10.00 g (13.10 mmol) of 4-iodobenzonitrile, 17.5 ml of trifluoromethanesulfonic acid was added, and the resulting red-orange solution was stirred for 24 h. The reaction was then quenched by adding to 60 ml of water, and neutralised with 5 M NaOH solution. The precipitate was then filtered off and washed with 3×30 ml of water, 3×30 ml of Ethanol and

3 × 30 ml of chloroform and finally was dried by heating (60 °C) under high vacuum for 1 h. This yielded 9.49 g (4.15 mmol) of a brown-white powder and giving a 95 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.44 (d, J_{3,4} = 8.5, 6H, H-3), 7.93 (d, J_{4,3} = 8.5, 6H, H-4). ¹³C not possible due to lack of solubility. $\tilde{\nu}_{max}$ / cm⁻¹: 3064 (m, Aromatic CH Stretch), 2117 (w, Aromatic Overtones), 1927 (m, Aromatic Overtones), 1800 (m, Aromatic Overtones), 1632 (w, Aromatic Overtones), 1585 (s, Triazine), 1573 (s, Triazine), 1525 (s), 1504 (s), 1482 (s), 1396 (s), 1367 (s), 1354 (s), 1293 (s), 1231 (s), 1176 (s), 1148 (m), 1101 (m), 1055 (s), 1004 (s), 972 (m), 961 (m), 859 (m), 840 (s), 801 (s), 703 (s), 670 (s), 639 (m), 628 (s), 520(m). APCI: m/z 688 (100 %, [M+H]⁺), 230, ([C₆H₄I(CN)]⁺, 22). Found: C, 36.5; H, 2.1; N, 5.9; I, 54.6 Calc. for C₂₁H₁₂I₃N₃: C, 36.7; H, 1.8; N, 6.1; I, 55.4. Mp > 360 °C.

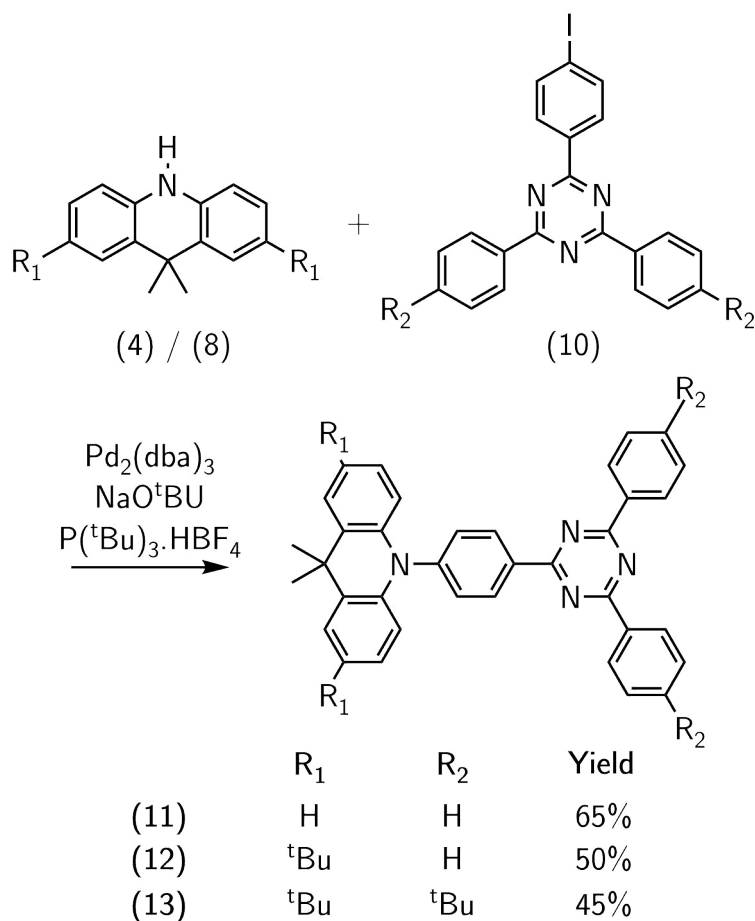


A.3.2.3.2 (10) 2-(4-iodophenyl)-4,6-di(4-(3,6-di-tert-butyl-carbazole))-phenyl-1,3,5-triazine 4,6-Tris(p-iodophenyl)1,3,5-triazine (1) (1.500 g, 2.18 mmol, 1.0 equiv.), 3,6-ditert-buthylcarbazole (1.22 g, 4.37 mmol, 2.0 equiv.) and 18-crown-6 (0.150 g, 0.568 mmol, 0.26 equiv.) were dissolved in o-dichlorobenzene (50 ml) and the resulting solution was heated to reflux under argon. Reflux was maintained until all material was in solution (brown-orange colour). Subsequently the solution was cooled to just below reflux and K₂CO₃ (1.55 g, 11.2 mmol, 5.1 equiv) and Cu (0.413 g, 6.50 mmol, 3.0 equiv.) were added. The mixture was subsequently stirred for 48 h at reflux, and then reaction mixture was cooled for 1 h forming a green-brown solution. The resulting mixture was filtered through a glass frit, and the residue was washed with chloroform (3 × 100 ml). From the resulting solution the solvent was evaporated under reduced pressure and the product purified by silica gel column chromatography, using a graduated column from 17 % toluene to 22 %, with petroleum ether making up the

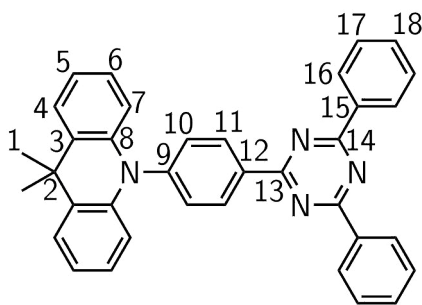
remaining amount. Dry loading onto diatomaceous earth was employed to load the column. After the product was dried by heating (60 °C) under high vacuum for 1 h, this afforded 0.359 g (0.363 mmol) of 2-(4-iodophenyl)-4,6-di(4-(3,6-di-tert-butyl-carbazole)-phenyl)-1,3,5-triazine as yellow crystals giving 33 % yield. ^1H NMR (400 MHz, CDCl_3) δ 9.01 (d, $J_{11,10} = 8.6$, 4H, H-11), 8.57 (d, $J_{17,16} = 8.5$, 2H, H-17), 8.17 (s, 4H, H-2), 7.98 (d, $J_{16,17} = 8.5$, 2H, H-16), 7.84 (d, $J_{10,11} = 8.6$, 4H, H-10), 7.56 – 7.48 (m, 8H, H-4,5), 1.49 (s, 36H, H-8). ^{13}C NMR (126 MHz, CDCl_3) δ 171.3 (C/ CH_2 , C-14), 171.2 (C/ CH_2 , C-13), 143.6 (CH/ CH_3 , C-3), 142.5 (C/ CH_2 , C-12), 138.8 (C/ CH_2 , C-6), 138.1 (CH/ CH_3 , C-16), 135.8 (C/ CH_2 , C-15), 134.0 (C/ CH_2 , C-9), 130.7 (CH/ CH_3 , C-11), 130.6 (CH/ CH_3 , C-17), 126.3 (CH/ CH_3 , C-10), 124.02* (C/ CH_2 , C-1), 123.98* (CH/ CH_3 , C-5), 116.5 (CH/ CH_3 , C-2), 109.6 (CH/ CH_3 , C-4), 100.5 (C/ CH_2 , C-18), 34.9 (C/ CH_2 , C-7), 32.1 (CH/ CH_3 , C-8). $\tilde{\nu}_{\text{max}}$ / cm^{-1} : 3046 (vw, Aromatic C-H Stretch), 2952 (m, Aromatic C-H Stretch), 2902 (w, Aromatic C-H Stretch), 2864 (w, Aromatic C-H Stretch), 1604 (m, Aromatic Overtone), 1587 (m, Aromatic Overtone), 1571 (m, Aromatic Overtone), 1507 (s), 1488 (s), 1470 (s), 1410 (m), 1394 (m), 1361 (s), 1323 (s), 1295 (s), 1259 (m), 1230 (m), 1202 (m), 1174 (m), 1149 (m), 1104. ES-MS: m/z 991 (30 %, $[\text{M}+\text{H}+1]^+$), 990 ($[\text{M}+\text{H}]^+$, 100), 857 (6), 713 ($[\text{M}-(\text{NC}_{12}\text{H}_6(\text{t-Bu})_2)+2\text{H}]^+$, 12), 587 ($[\text{M}-(\text{NC}_{12}\text{H}_6(\text{t-Bu})_2)-\text{I}+2\text{H}]^+$, 8), 320 (52). Found: C, 74.0; H, 6.1; N, 7.1; I, 12.8. Calc. for $\text{C}_{61}\text{H}_{60}\text{N}_3\text{I}$: C, 72.6; H, 6.0; N, 6.7; I, 14.2. Mp 272–287 °C. Exact Mass - ES^+ : Found: 990.3970; Calc. for $\text{C}_{61}\text{H}_{61}\text{N}_5\text{I}$: 990.3972; PPM difference: -0.2.

*This number is given to an additional number of significant figures, to allow it to be distinguished from the other peak shown at this significance. It is noted that this is beyond the reliability of the solvent references, so inherently unreliable.⁹

A.3.2.4 Final Molecules



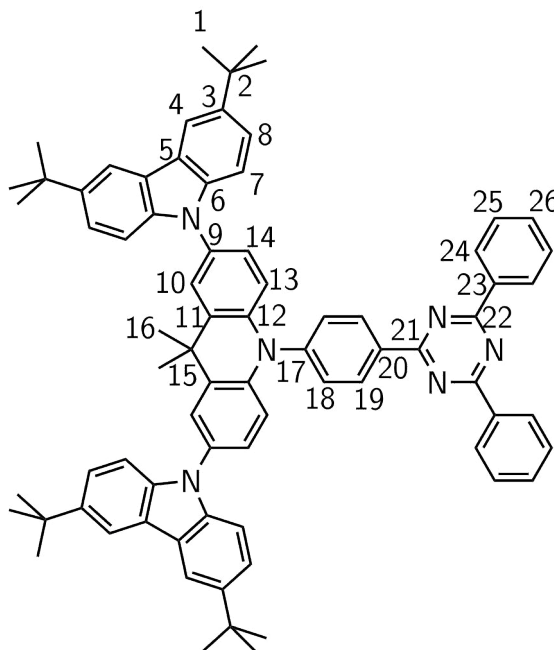
Scheme A.4: The synthetic scheme for donor-acceptor coupling. Rounded boxes indicate molecules used later in the synthesis, square boxes show abbreviated groups.



A.3.2.4.1 (11) 4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl-9,10-dihydro-9,9-dimethyl-Acrydine 0.300 g (1.433 mmol, 1.0 equiv.) of 9,9-dimethyl-9,10-dihydroacridin, 0.612 g (1.577 mmol, 1.10 equiv.) of 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine, 0.413 g (4.30 mmol, 3.0 equiv.) of sodium tert-butoxide, 0.033 g (36 μ mol, 0.025 equiv.) of tris(dibenzylideneacetone)dipalladium(0) and 0.0416 g (36 μ mol, 0.10 equiv.) tri-*t*-butylphosphonium-tetra-fluoroborate were

combined and dissolved with 20 ml of dry toluene under argon forming a purple solution. The solution was subsequently heated to form a yellow/black solution, it was left at reflux for 12 h, forming a brown-black solution, before being allowed to cool, and quenched on 40 ml of deionised water. The crude product was subsequently extracted with 4×40 ml of chloroform, and the resulting solution dried over MgSO_4 , filtered, and the solvent removed under vacuum. The resulting product was then purified using column chromatography on silica with eluent 30 % chloroform: 70 % 40:60 petroleum ether. The product was then dried by heating (60°C) under vacuum (1 h), to yield 0.480 g (0.930 mmol, 65 % yield) of a pale yellow powder. ^1H NMR (400 MHz, CDCl_3) δ 9.03 (d, $J_{11,10} = 8.5$, 2H, H-11), 8.82 (dd, $J_{16,17}$, $J_{16,18} = 8.1$, 1.6, 4H, H-16), 7.69 – 7.53 (m, 8H, H-10,17,18), 7.50 (dd, $J_{7,6}$, $J_{7,5} = 7.4$, 1.8, 2H, H-7), 7.05 – 6.91 (m, 4H, H-5,6), 6.38 (dd, $J_{4,5}$, $J_{4,6} = 7.9$, 1.5, 2H, H-4), 1.73 (s, 6H, H-1). ^{13}C NMR (101 MHz, CDCl_3) δ 172.0 (C/ CH_2 , H-14), 171.2 (C/ CH_2 , H-13), 145.4 (C/ CH_2 , H-12), 140.7 (C/ CH_2 , H-15), 136.21* (C/ CH_2 , H-9), 136.18* (C/ CH_2 , H-3), 132.8 (CH/ CH_3 , H-18), 131.7 (CH/ CH_3 , H-11), 131.7 (CH/ CH_3 , H-6), 130.3 (C/ CH_2 , H-8), 129.2 (CH/ CH_3 , H-16), 128.9 (CH/ CH_3 , H-17), 126.6 (CH/ CH_3 , H-4), 125.5 (CH/ CH_3 , H-10), 121.0 (CH/ CH_3 , H-5), 114.3 (CH/ CH_3 , H-7), 36.2 (C/ CH_2 , H-2), 31.5 (C/ CH_2 , H-1). $\tilde{\nu}_{\text{max}} / \text{cm}^{-1}$: 3064 (w, CH Aromatic Stretch), 3031 (w, CH Aromatic Stretch), 2963 (w, C-H sp_3 Stretch Asymmetric), 2856 (w, C-H sp_3 Stretch Symmetric), 1920 (w, Aromatic Overtone), 1812 (w, Aromatic Overtone), 1588 (m), 1571 (w), 1518 (s), 1513 (s), 1510 (s), 1488 (m), 1474 (s), 1464 (s), 1445 (s), 1408 (m), 1364 (s), 1328 (s), 1270 (s), 1171 (m), 1158 (m), 1146 (m), 1113 (m), 1099 (m), 1089 (m), 1068 (m), 1047 (m), 1025 (m), 1018 (m), 1001 (m), 993 (w), 976 (w), 927 (m), 842 (m), 836 (m), 808 (w), 792 (w), 769 (s), 741 (s), 737 (s), 700 (m), 694 (s), 683 (s), 665 (m), 646 (s), 636 (m), 622 (m), 605 (m), 578 (m), 554 (m), 546 (m), 519 (m), 479 (m), 454 (m), 438 (w), 428 (m), 405 (m). ESI: m/z 517 (43 %, $[\text{M}+1]^+$), 516 ($[\text{M}]^+$, 100). Found: C, 80.7; H, 5.4; N, 10.3. Calc. for $\text{C}_{36}\text{H}_{28}\text{N}_4$: C, 83.7; H, 5.5; N, 10.8. Mp 226–230 $^\circ\text{C}$. Exact Mass - ESI $^+$: Found: 517.2384; Calc. for $\text{C}_{36}\text{H}_{28}\text{N}_4$: 517.2387; PPM difference: 0.52.

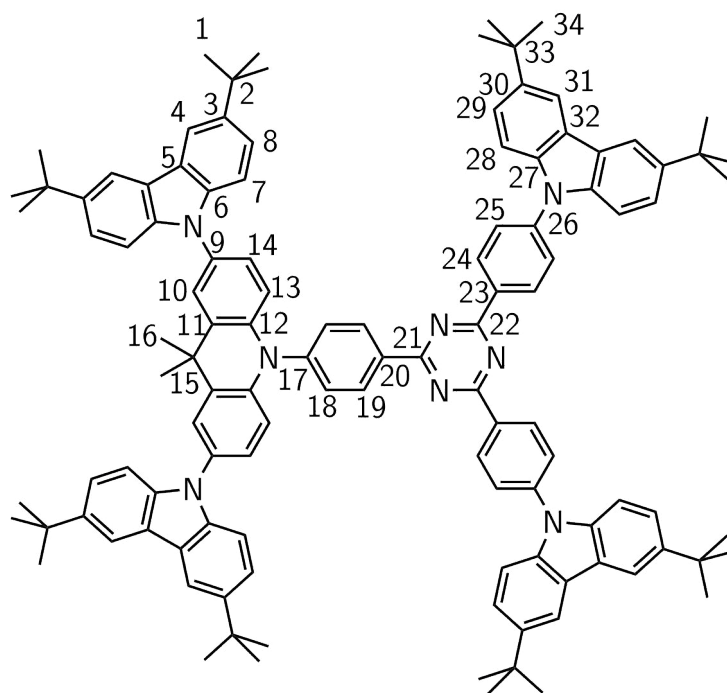
*This number is given to an additional number of significant figures, to allow it to be distinguished from the other peak shown at this significance. It is noted that this is beyond the reliability of the solvent references, so inherently unreliable.⁹



A.3.2.4.2 (12) 10-[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-2,7-(3,6-di-tert-butyl-9H-carbazole-9yl)-9,9-dimethyl-9,10-dihydroacridine

2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (0.260 g, 671 μmol , 1.10 equiv.), tris(dibenzylideneacetone)dipalladium (0) (14 mg, 16 μmol , 0.026 equiv.), tri-tert-butylphosphonium tetrafluoroborate (18 mg, 63 μmol , 0.10 equiv.) sodium tert-butoxide (0.253 g, 1.83 mmol, 3.00 equiv.), and 10-(4-4,6-di[4-(3,6-di-tert-butyl-carbazole)phenyl]-1,3,5-triazin-2-ylphenyl)-3,7-(3,6-di-tert-butyl-carbazole)]10H-phenoxazine (0.450 g, 610 μmol , 1.0 equiv.), were dissolved in dry toluene (20 mL) under argon. The mixture was refluxed for 91 h. After cooling for 1 h, the reaction mixture was poured into 40 ml of deionised water and extracted with chloroform (40 ml x 3). The organic phase was dried over anhydrous MgSO_4 , filtered and the solvent removed under reduced pressure. The crude product was purified by silica gel column chromatography with a graduated 22.5 % to 25.0 % toluene and 77.5 % to 75 % petroleum ether. Finally, the product was dried by heating (60 $^{\circ}\text{C}$) under high vacuum for 1 h. This procedure yielded 0.319 g (305 μmol , 50 % yield) of 10-[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-2,7-(3,6-Di-tert-butyl-9H-carbazole-9yl)-9,9-dimethyl-9,10-dihydroacridine as a yellow orange powder. ^1H NMR (400 MHz, CDCl_3) δ 9.14 (d, $J_{19,18} = 8.5$, 2H, H-19), 8.84 (dd, $J_{24,25}, J_{24,26} = 8.1, 1.6$, 4H, H-24), 8.15 (d, $J_{4,6} = 1.7$, 4H, H-4), 7.77 (d, $J_{18,19} = 8.5$, 2H, H-18), 7.70 – 7.58 (m, 8H, H-10,14,25), 7.47 (dd, $J_{8,7}, J_{8,4} = 8.7, 1.9$, 4H, H-8), 7.33 (d, $J_{7,8} = 8.6$, 4H, H-7), 7.20 (dd, $J_{26,25}, J_{26,24} = 8.7, 2.3$, 2H, H-26), 6.61 (d, $J_{13,14} = 8.7$, 2H, H-13), 1.79 (s, 6H, H-16), 1.47 (s, 36H, H-1). ^{13}C NMR (101 MHz, CDCl_3) δ 172.0 (C/ CH_2 , C-22), 171.1 (C/ CH_2 , C-21), 144.9 (C/ CH_2 , C-20), 142.6 (C/ CH_2 , C-6), 139.7 (C/ CH_2 , C-4), 139.5 (C/ CH_2 , C-9), 136.9 (C/ CH_2 , C-17), 136.1 (C/ CH_2 ,

C-23), 132.9 (CH,CH₃, C-26), 132.1 (CH/CH₃, C-19), 131.7 (CH/CH₃, C-18), 131.5 (C/CH₂, C-11/12), 131.1 (C/CH₂, C-11/12), 129.2 (CH/CH₃, C-24), 128.9 (CH/CH₃, C-25), 125.3 (CH/CH₃, C-10), 124.5 (CH/CH₃, C-14), 123.7 (CH/CH₃, C-8), 123.2 (C/CH₂, C-5), 116.4 (CH/CH₃, C-4), 115.3 (CH/CH₃, C-41), 109.3 (CH/CH₃, C-7), 36.8 (C/CH₂, C-15), 34.9 (C/CH₂, C-2), 32.2 (CH/CH₃, C-1), 31.8 (CH/CH₃, C-16). $\tilde{\nu}_{max}$ / cm⁻¹: 3050 (w, CH Aromatic Stretch), 2955 (m, CH₃ Symmetric Stretch), 2903 (m, CH₃ Asymmetric Stretch), 2865 (w, CH₃ Asymmetric Stretch), 1868 (w, Aromatic Overtone), 1748 (w, Aromatic Overtone), 1603 (w), 1588 (m), 1511 (s), 1482 (s), 1446 (s), 1427 (m), 1411 (m), 1392 (m), 1363 (s), 1317 (m), 1294 (s), 1262 (s), 1234 (m), 1202 (m), 1176 (m), 1147 (m), 1129 (m), 1104 (w), 1085 (w), 1069 (w), 1034 (m), 1026 (m), 1018 (m), 1002 (w), 923 (w), 897 (w), 877 (m), 840 (m), 808 (s), 770 (m), 743 (s), 694 (m), 684 (m), 672 (m), 659 (m), 646 (m), 636 (m), 614 (m), 572 (w), 538 (m), 499 (w), 470 (m), 422 (m), 411 (w), 406 (w). MALDI: m/z 1073 (29 %, [M+2]⁺), 1072 ([M+1]⁺, 82), 1071 ([M]⁺, 100), 1057 ([M-Me+1]⁺, 11), 1056 ([M-Me]⁺, 13). Found: C, 85.2; H, 7.3; N, 7.3; Calc. for C₇₆H₇₄N₆: C, 85.2; H, 7.0; N, 7.3. Mp 220–260 °C. Exact Mass - ES +: Found: 1071.6040; Calc. for C₇₆H₇₅N₆: 1071.6053; PPM difference: -1.2.



A.3.2.4.3 (13) 10-[4-(4,6-di-[4-(9H-3,6-di-tert-butyl-carbazol-9-yl)phenyl]-1,3,5-triazin-2-yl)phenyl]-2,7-(3,6-di-tert-butyl-9H-carbazole-9-yl)-9,9-dimethyl-9,10-dihydroacridine 0.400 g (0.404 mmol, 1.0 equiv.) of 2-(4-iodophenyl)-4,6-di-[4-(9H-3,6-di-tert-butyl-carbazol-9-yl)phenyl]-1,3,5-triazine,

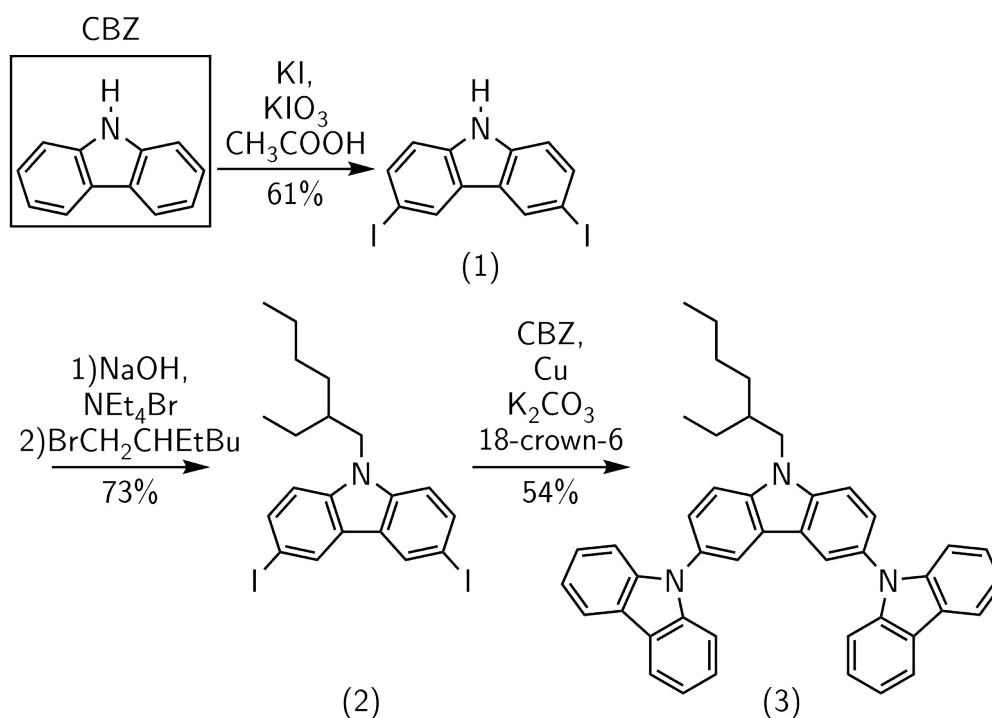
0.340 g (0.445 mmol, 1.1 equiv.) 10-(4-(4,6-di[4-(3,6-di-tert-butyl-carbazole)phenyl]-1,3,5-triazin-2-yl)phenyl)-3,7-(3,6-di-tert-butyl-carbazole)]10H-phenoxazine, 0.0026 g (2.8 μ mol, 0.0070 equiv.) of tris(dibenzylideneacetone)dipalladium(0), 0.0033 g (11 μ mol, 0.028 equiv.) of tri-tert-butylphosphine tetrafluoroborate, and 0.0582 g (0.606 mmol, 1.5 equiv.) of sodium tert-butoxide were combined, and 12 ml of dry toluene was added under argon. This formed a maroon solution with a precipitate. The resulting solution was heated to reflux and stirred forming a yellow brown solution, it remained at reflux for 88 h, before being cooled for 1 h, and quenched on 50 ml of deionised water. The product was extracted from the resulting mixture using 3×100 ml of ethylacetate. Subsequently the solution was dried with MgSO_4 before removing the solvent under vacuum. The product was then purified using column chromatography, with a 23 % toluene, 77 % 40:60 petroleum ether eluent and precipitated from a minimum amount of chloroform into 400 ml of methanol, and then further purified via HPLC, using 80 % THF, and 20% water on C_{18} functionalised silica, and finally precipitation in 360 ml of methanol from chloroform. Finally, the product was dried by heating (60 $^{\circ}\text{C}$) under high vacuum for 1 h. This procedure yielded 0.297 g (0.183 mmol) of 10-[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-2,7-(3,6-Di-tert-butyl-9H-carbazole-9yl)-9,9-dimethyl-9,10-dihydroacridine, as a yellow powder, providing a 45 % yield. ^1H NMR (400 MHz, CDCl_3) δ 9.21 (d, $J_{19,18} = 8.5$, 2H, H-19), 9.09 (d, $J_{24,25} = 8.7$, 4H, H-24), 8.18 (d, $J_{4,8}/J_{31,29} = 1.0$, 4H, H-4/31), 8.15 (d, $J_{4,8}/J_{31,29} = 1.6$, 4H, H-4/31), 7.87 (d, $J_{25,24} = 8.7$, 4H, H-25), 7.82 (d, $J_{18,19} = 8.5$, 2H, H-18), 7.68 (d, $J_{10,14} = 2.3$, 2H, H-10), 7.59 – 7.50 (m, 8H, H-(7/28),(8/29)), 7.48 (dd, $J_{8,7}/J_{29,28}$, $J_{8,4}/J_{29,31} = 8.7$, 1.9, 4H, H-8/29), 7.34 (d, $J_{7,8}/J_{28,29} = 8.6$, 4H, H-7/28), 7.22 (dd, $J_{14,13}, J_{14,10} = 8.8$, 2.3, 2H, H-14), 6.65 (d, $J_{13,14} = 8.7$, 2H, H-13), 1.80 (s, 6H, H-16), 1.49 (s, 36H, H-1/34), 1.47 (s, 36H, H-1/34). ^{13}C NMR (126 MHz, CDCl_3) δ 171.5 (C-22), 171.3 (C-21), 145.2 (C-20), 143.7 (C-6/27), 142.7 (C-23), 142.6 (C-6/27), 139.8 (C-3/30), 139.5 (C-9), 138.8 (C-3/30), 136.7 (C-17), 134.1 (C-26), 132.2 (C-19), 131.8 (C-18), 131.5 (C-11/12), 131.2 (C-11/12), 130.8 (C-24), 126.4 (C-25), 125.4 (C-14), 124.6 (C-10), 124.03* (C-5/8/29/32), 124.01* (C-5/8/29/32), 123.7 (C-8/29), 123.2 (C-5/32), 116.6 (C-4/31), 116.4 (C-4/31), 115.4 (C-13), 109.6 (C-7/28), 109.3 (C-7/28), 36.8 (C-15), 34.9 (C-2/33), 34.9 (C-2/33), 32.21* (C-1/34), 32.16* (C-1/34), 31.9 (C-16). $\tilde{\nu}_{\text{max}} / \text{cm}^{-1}$: 3047 (w, CH Aromatic Stretch), 2956 (m, CH_3 Symmetric Stretch), 2903 (m, CH_3 Asymmetric Stretch), 2866 (w, CH_3 Asymmetric Stretch), 2324 (w, Aromatic Overtone), 2161 (w, Aromatic Overtone), 2051 (w), 1979 (w), 1868 (vw), 1742 (vw), 1604 (m), 1589

*This number is given to an additional number of significant figures, to allow it to be distinguished from the other peak shown at this significance. It is noted that this is beyond the reliability of the solvent references, so inherently unreliable.⁹

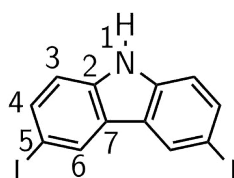
(w), 1505 (s), 1487 (s), 1471 (s), 1424 (m), 1410 (m), 1392 (m), 1362 (s), 1321 (s), 1295 (s), 1261 (s), 1232 (m), 1202 (m), 1173 (m), 1149 (m), 1130 (w), 1105 (m), 1082 (w), 1034 (m), 1017 (m), 946 (w), 921 (w), 896 (w), 877 (m), 841 (m), 827 (m), 808 (s), 757 (m), 741 (m), 729 (w), 700 (w), 685 (w), 654 (m), 635 (w), 612 (m), 596 (m), 539 (m), 512 (w), 470 (m), 419 (m). MALDI: m/z 1628 (6 %, $[M+H+2]^+$), 1627 ($[M+H+1]^+$, 18), 1626 ($[M+H]^+$, 13), 1614 ($[M-Me+H+3]^+$, 15), 1613 ($[M-Me+H+2]^+$, 53), 1612 ($[M-Me+H+1]^+$, 100), 1611 ($[M-Me+H]^+$, 72). Found: C, 82.5; H, 7.3; N, 6.3. Calc. for $C_{116}H_{120}N_8$: C, 85.7; H, 7.4; N, 6.9. Mp 290–303 °C. Exact Mass - ES^+ : Found: 1625.9749; Calc. for $C_{116}H_{121}N_8$: 1625.9714; PPM difference: 2.1.

A.3.3 H1

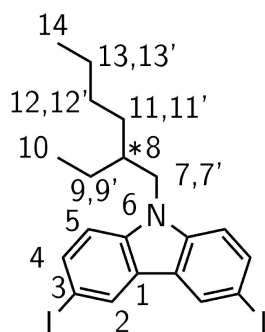
This section deals with the synthesis of the host discussed in part II.



Scheme A.5: The synthetic scheme for donor-acceptor coupling. Rounded boxes indicate molecules used later in the synthesis, square boxes show abbreviated groups.

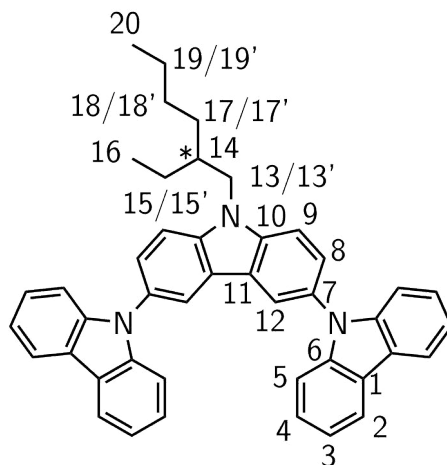


A.3.3.0.1 (1) 3,6-diiodocarbazole A mixture of 5.00 g of 9H-carbazole (29.9 mmol, 3.0 equiv.), and 85 ml of acetic acid, was formed which was a orange solution with suspended particles. To this solution 6.62 g of potassium iodide (39.9 mmol, 4.0 equiv.) was added, followed by 4.27 g of potassium iodate (20.0 mmol, 2.0 equiv.), forming a deep red brown solution with suspended particles. The solution was subsequently heated to reflux forming a deep purple solution, with refluxing purple liquid. The resulting solution was refluxed from 5 h, until the refluxing liquid ran clear, and the solution was a red-brown colour, with suspended precipitate. Subsequently, the solution was cooled, for 1 h which caused further precipitation. The precipitate was filtered off, and washed with 4×50 ml of acetic acid, and 3×100 ml of deionised water. The residue was then dried overnight in a vacuum oven resulting in 7.60 g of a grey-brown powder (18.2 mmol, 61 % yield). ^1H NMR (400 MHz, CDCl_3) δ 8.32 (d, $J_{6,4} = 1.7$, 2H, H-6), 8.09 (s, 1H, H-1), 7.68 (dd, $J_{4,3}, J_{4,6} = 8.5, 1.7$, 2H, H-4), 7.21 (d, $J_{3,4} = 8.5$, 2H, H-3). ^{13}C NMR (101 MHz, CDCl_3) δ 138.6 (C/ CH_2 , C-7), 134.9 (CH/ CH_3 , C-6), 129.5 (CH/ CH_3 , C-4), 124.7 (C/ CH_2 , C-2), 112.8 (CH/ CH_3 , C-3), 82.6 (C/ CH_2 , C-5). $\tilde{\nu}_{\text{max}} / \text{cm}^{-1}$: 3411 (s, NH), 1870 (m, Aromatic Overtone), 1738 (m, Aromatic Overtone), 1595 (m), 1560 (m), 1469 (s), 1426 (s), 1378 (m), 1317 (m), 1282 (s), 1262 (m), 1242 (s), 1187 (m), 1135 (m), 1128 (m), 1044 (m), 1012 (s), 936 (m), 893 (s), 869 (s), 804 (s), 800 (s), 779 (m), 758 (m), 722 (m), 680 (m), 630 (m), 618 (m), 583 (m), 564 (s), 478 (m), 436 (m), 423 (s), 413 (s). EI: m/z 420 (14 %, $[\text{M}+1]^+$), 419 ($[\text{M}]^+$, 100), 293 ($[\text{M}-\text{I}]^+$, 9), 292 ($[\text{M}-\text{IH}]^+$, 28), 265 ($[\text{M}-\text{I}_2\text{H}_2]^+$, 20), 264 ($[\text{M}-\text{I}_2\text{H}_3]^+$, 17). Found: C, 34.2; H, 1.8; N, 3.2; I, 59.80; Calc. for $\text{C}_{12}\text{H}_7\text{I}_2\text{N}$: C, 34.4; H, 1.7; N, 3.3; I, 60.6. Mp 199–200 °C. Exact Mass - ESI $^+$: Found: 419.8738; Calc. for $\text{C}_{12}\text{H}_7\text{NI}_2$: 419.9741; PPM difference: 0.52.



A.3.3.0.2 (2) 9-(2-ethylhexyl)-3,6-diiodo-9H-carbazole This procedure was based on a similar procedure in the literature.²⁰ To a mixture of 5.00 g (11.9 mmol, 1.0 equiv.) of 3,6-diiodocarbazole and 0.716 g (17.8 mmol, 1.5 equiv.) of freshly powdered NaOH, 25 ml of acetone was added. This formed a orange-brown

solution with suspended particles. Subsequently 0.115 g (0.357 mmol, 0.030 equiv.) terabutylammonium bromide, was added making the solution cloudy, with no perceivable change in amount of precipitate. The solution was then heated to 50 °C, and 3.2 ml (18 mmol, 1.5 equiv.) of 2-ethylhexylbromide was added. The solution was then heated to reflux for 4 h, forming a orange solution with yellow precipitate. The solution was then cooled for 1 h, and the solvent removed en-vacuo, via a combination of rotary evaporation and vacuum distillation. The resulting residue was then redissolved in 150 ml of toluene, and washed with 3×100 ml of saturated NaCl solution, dried over MgSO_4 , and the solvent removed under vacuum. The crude product was then purified via means of column chromatography using a 1 : 3 toluene : 40:60 petroleum ether eluent, and dry loading onto diatomaceous earth. The product was dried by heating (60 °C) under high vacuum for 1 h. This yielded 4.65 g (8.75 mmol, 73 % yield) of a orange-brown solid. ^1H NMR (400 MHz, CDCl_3) δ 8.33 (d, $J_{2,4} = 1.6$, 2H, H-2), 7.70 (dd, $J_{4,5}, J_{4,2} = 8.6, 1.7$, 2H, H-4), 7.16 (d, $J_{5,4} = 8.6$, 2H, H-5), 4.15 – 4.04 (m, 2H, H-7,7'), 2.12 – 1.78 (m, 1H, H-8), 1.45 – 1.14 (m, 8H, H-9,9',11,11',12,12',13,13'), 0.96 – 0.80 (m, 6H, H-10,14). ^{13}C NMR (101 MHz, CDCl_3) δ 139.6 (C/ CH_2 , C-3), 134.3 (CH/ CH_3 , C-2), 129.0 (CH/ CH_3 , C-4), 123.7 (C/ CH_2 , C-6), 111.0 (CH/ CH_3 , C-5), 81.8 (C/ CH_2 , C-1), 47.2 (C/ CH_2 , C-7), 39.2 (CH/ CH_3 , C-8), 30.9 (C/ CH_2 , C-11), 28.7 (C/ CH_2 , C-9), 24.3 (C/ CH_2 , C-13), 22.99 (C/ CH_2 , C-12), 14.2 (CH/ CH_3 , C-10), 11.0 (CH/ CH_3 , C-14). $\tilde{\nu}_{\text{max}}$ / cm^{-1} : 3052 (w, CH Aromatic Stretch), 2953 (m, CH_3 Asymmetric Stretch), 2927 (m, CH_2 Asymmetric Stretch), 2867 (m, CH sp_3 Symmetric Stretch), 2854 (m, CH sp_3 Symmetric Stretch), 1869 (w, Aromatic Overtone), 1852 (w, Aromatic Overtone), 1736 (w, Aromatic Overtone), 1616 (w), 1606 (w), 1582 (m), 1560 (w), 1466 (s), 1453 (s), 1427 (s), 1378 (m), 1346 (m), 1314 (m), 1283 (s), 1257 (m), 1244 (m), 1220 (s), 1204 (m), 1148 (m), 1132 (m), 1045 (m), 1014 (s), 973 (w), 959 (w), 936 (w), 928 (w), 900 (w), 872 (s), 818 (m), 802 (s), 793 (s), 759 (w), 737 (m), 723 (m), 653 (w), 628 (s), 581 (m), 566 (m), 561 (s), 500 (m), 483 (m), 466 (w), 422 (m), 406 (w). APCI: m/z 533 (12 %, $[\text{M}+1]^+$), 532 ($[\text{M}]^+$, 100). Found: C, 45.5; H, 4.4; I, 47.5; N, 2.5; Calc. for $\text{C}_{20}\text{H}_{23}\text{I}_2\text{N}_1$: C, 45.2; H, 4.4; I, 47.8, N, 2.6. Mp 98–102 °C.

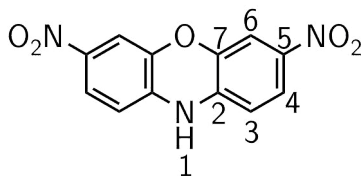


A.3.3.0.3 (3) 3,6-di(9-carbazolyl)-9-(2-ethylhexyl)-carbazole This procedure was based on a similar procedure in the literature.²¹ A mixture was formed under argon, consisting of: 1.89 g (11.3 mmol, 3.0 equiv.) of 9H-carbazole, 2.87 g (45.2 mmol, 12 equiv.) of copper, 12.49 g (90.37 mmol, 24 equiv.) of potassium carbonate, 0.498 g (1.88 mmol, 0.50 equiv.) of 18-crown-6 and 2.00 g (3.77 mmol, 1.0 equiv.) of 9-(2-ethylhexyl)-3,6-diiodo-9H-carbazole. To this mixture 35 ml of 1,2-dichlorobenzene, which was degassed via application of vacuum and argon three times, was added. This formed a yellow solution with grey powder suspended. The reaction was then heated to reflux under argon, forming a yellow-orange solution with a cloudy grey-brown suspension. The solution remained at reflux for 26 h forming a dark brown solution with orange residue, before being cooled, leaving the solution unchanged. The inorganic residue was then filtered off, and flask and filtrate washed with 3×50 ml of chloroform. The solvent was subsequently removed under reduced pressure, and the crude product purified via flash chromatography, using a graduated column from 1 : 2 40:60 petroleum ether : chloroform, to 1 : 1, and dry loading onto diatomaceous earth. Subsequently the product was precipitated from minimum chloroform into 500 ml methanol. This method was repeated twice on the filtrate, with prior solvent removed from the precipitate under high vacuum. Subsequently one final precipitation using only 100 ml of methanol was completed. The final product was dried by heating (60 °C) under high vacuum for 1 h. The combined solids yielded 1.23 g (2.02 mmol, 54 % yield) of a cream coloured powder. ^1H NMR (400 MHz, DMSO) δ 8.57 (d, $J_{12,8} = 1.9$, 2H, H-12), 8.25 (d, $J_{2,3} = 7.7$, 4H, H-2), 7.92 (d, $J_{9,8} = 8.7$, 2H, H-9), 7.69 (dd, $J_{8,9}, J_{8,12} = 8.7, 1.9$, 2H, H-8), 7.41 (t, $J_{4,5}, J_{4,3} = 7.6$, 4H, H-4), 7.34 (d, $J_{5,4} = 8.1$, 4H, H-5), 7.27 (t, $J_{3,2}, J_{3,4} = 7.4$, 4H, H-3), 4.49 (d, $J_{13/13',14} = 7.3$, 2H, H-13,13'), 2.22 – 2.14 (m, 1H, H-14), 1.56 – 1.19 (m, 8H, H-15,15',17,17',18,18',19,19'), 0.97 (t, $J_{16,15}, J_{16,15'} = 7.4$, 3H, H-16), 0.85 (t, $J_{20,19}, J_{20,19'} = 7.1$, 3H, H-20). It should be noted that the spectra in chloroform is different to the previously published one, and is as follows: ^1H NMR (400 MHz, CDCl_3) δ 8.22

(t, $J_{12,8} = 1.1$, 2H, H-12), 8.16 (d, $J_{2,3} = 7.7$, 4H, H-2), 7.69 – 7.61 (m, 4H, H-8,9), 7.43 – 7.35 (m, 8H, H-4,5), 7.32 – 7.26 (m, 4H, H-3), 4.46 – 4.28 (m, 2H, H-13a,13b), 2.30 – 2.18 (m, 1H, H-14), 1.53 – 1.31 (m, 8H, H-15,15',17,17',18,18',19,19'), 1.05 (t, $J_{16,15}, J_{16,15'} = 7.4$, 3H, H-16), 0.94 (t, $J_{20,19}, J_{20,19'} = 7.2$, 3H, H-20). ^{13}C NMR (101 MHz, CDCl_3) δ 142.0 (C/ CH_2 , C-6), 140.8 (C/ CH_2 , C-10), 129.4 (C/ CH_2 , C-7), 126.03* (CH/ CH_3 , C-8), 125.98* (CH/ CH_3 , C-4), 123.5 (C/ CH_2 , C-11), 123.2 (C/ CH_2 , C-1), 120.4 (CH/ CH_3 , C-2), 119.9 (CH/ CH_3 , C-12), 119.8 (CH/ CH_3 , C-3), 110.5 (C/ CH_2 , C-10), 109.9 (CH/ CH_3 , C-5), 48.1 (C/ CH_2 , C-13), 39.8 (CH/ CH_3 , C-14), 31.2 (C/ CH_2 , C-17), 29.0 (C/ CH_2 , C-15), 24.7 (C/ CH_2 , C-18), 23.3 (C/ CH_2 , C-19), 14.2 (CH/ CH_3 , C-20), 11.2 (CH/ CH_3 , C-16). $\tilde{\nu}_{\text{max}}$ / cm^{-1} : 3050 (w, CH Aromatic Stretch), 2956 (m, CH_3 Asymmetric Stretch), 2927 (m, CH_2 Asymmetric Stretch), 2857 (m, CH sp_3 Symmetric Stretch), 1886 (w, Aromatic Overtone), 1769 (w, Aromatic Overtone), 1626 (m), 1596 (m), 1574 (w), 1495 (s), 1486 (s), 1478 (s), 1450 (s), 1379 (w), 1335 (m), 1315 (m), 1287 (m), 1231 (s), 1172 (m), 1157 (m), 1146 (m), 1118 (m), 1060 (w), 1025 (m), 1014 (m), 999 (m), 979 (w), 918 (m), 876 (m), 847 (w), 833 (w), 808 (m), 746 (s), 722 (s), 694 (m), 666 (m), 656 (m), 638 (m), 619 (m), 616 (m), 576 (m), 567 (m), 560 (m), 527 (m), 498 (m), 445 (w), 425 (m), 402 (w). APCI: m/z 611 (43 %, $[\text{M}+\text{H}+1]^+$), 610 ($[\text{M}+\text{H}]^+$, 100), 609 ($[\text{M}]^+$, 64). Found: C, 85.5; H, 6.3; N, 6.5; Calc. got $\text{C}_{44}\text{H}_{39}\text{N}_3$: C, 86.7; H, 6.5; N, 6.9. Mp 173–176 °C. Exact Mass - ESI^+ : Found: 610.3204; Calc. for $\text{C}_{44}\text{H}_{39}\text{N}_3$: 610.3217; PPM difference: 2.1.

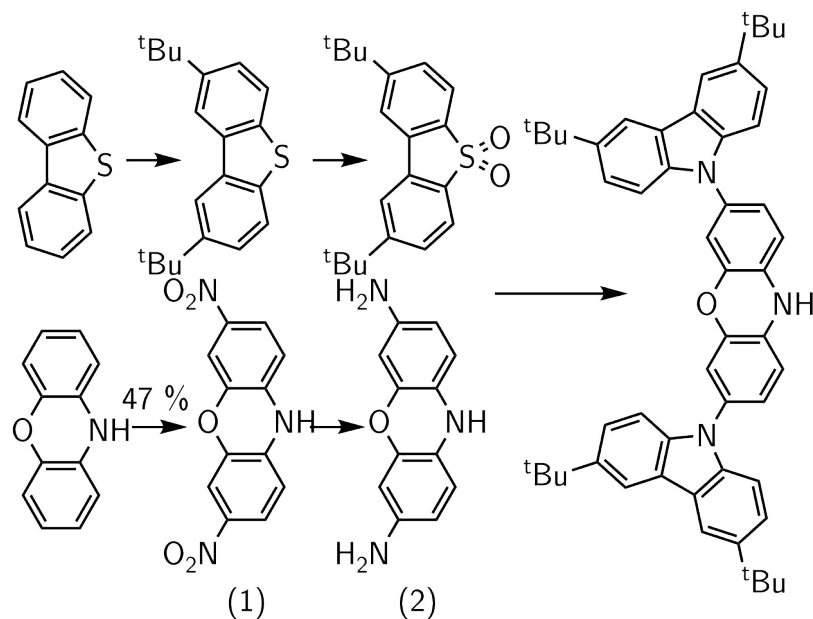
A.3.4 Attempt To Functionalise 10H-phenoxazine

A.3.4.1 Attempt 1: Nitro/Amine Functionalisation



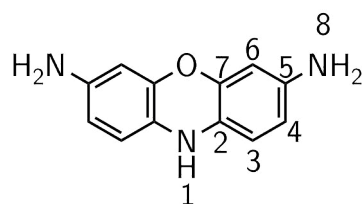
A.3.4.1.1 (1) 3,7-dinitro-10H-phenoxazine This procedure was based on a similar procedure in the literature.²² 5.00 g (27.3 mmol, 1.0 equiv.) of phenoxazine was dissolved in 150 ml of a 2 : 2 : 1 dichloromethane : trifluoroacetic acid : trifluoroacetic anhydride solution, under argon. The reaction was cooled to 0 °C, and then 4.37 g (54.6 mmol, 2.0 equiv.) of NH_4NO_3 was added slowly. The reaction was kept at

*This number is given to an additional number of significant figures, to allow it to be distinguished from the other peak shown at this significance. It is noted that this is beyond the reliability of the solvent references, so inherently unreliable.⁹

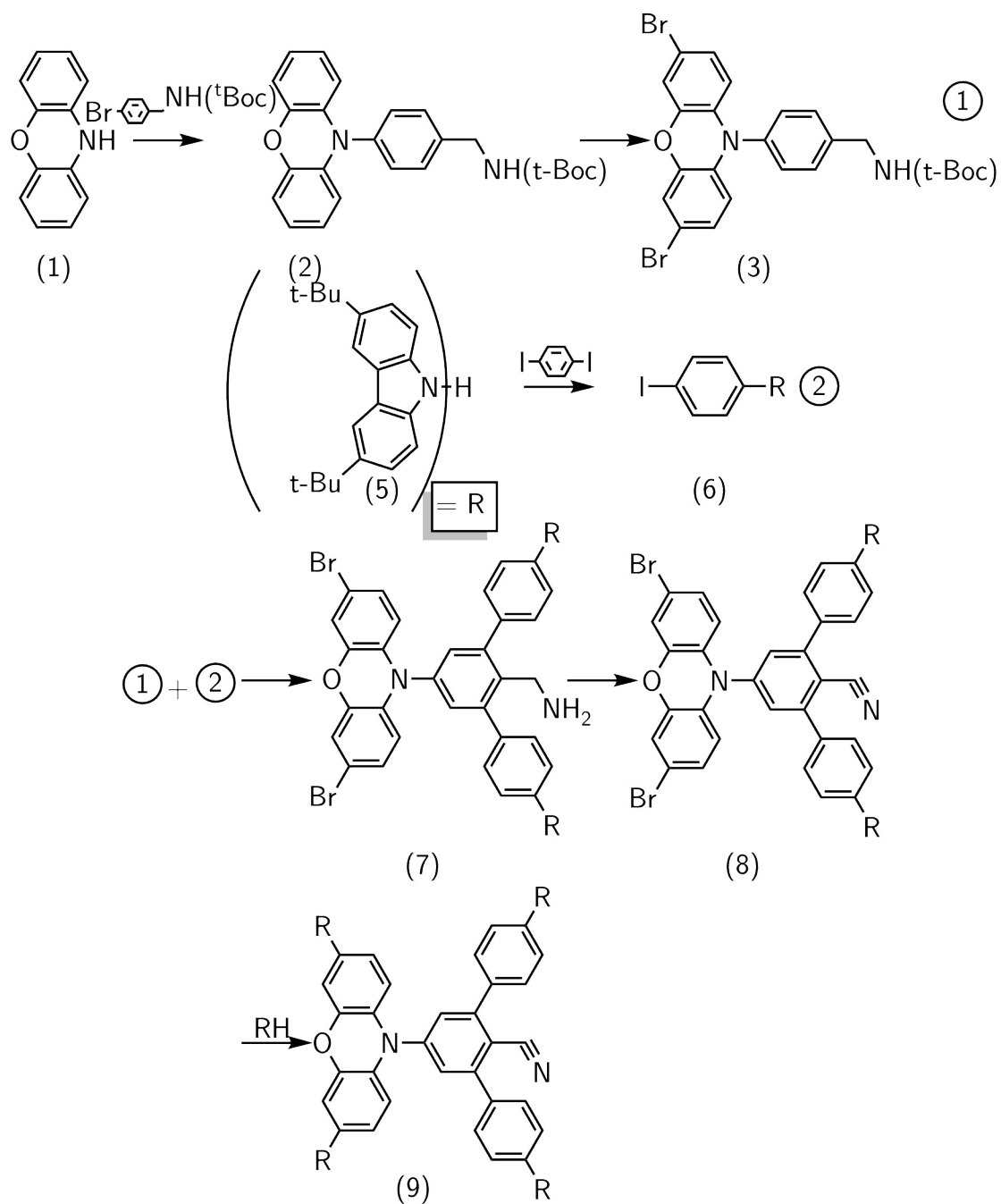


Scheme A.6: The planned synthesis, attempted syntheses are numbered.

0 °C for 30 min, before being allowed to warm to room temperature, and left for 16 h. The product was extracted with 5 x 200ml of dichloromethane followed by 5 x 200ml of ethyl acetate. It was then purified by column chromatography on silica, using a graduated column from 2 : 3 ethyl acetate: 40:60 petroleum ether, with 1 % triethylamine, to a 1 % triethylamine, in ethyl acetate solution. 3.52 g (12.9 mmol) of a red crystalline product were recovered, giving a yield of 47 %. ^1H NMR (400 MHz, DMSO) δ 10.14 (s, 1H, H-1), 7.74 (dd, $J_{4,2}$, $J_{4,6}$ = 8.8, 2.5, 2H, H-4), 7.39 (d, $J_{6,4}$ = 2.4, 2H, H-6), 6.62 (d, $J_{3,4}$ = 8.8, 2H, H-3). ^{13}C NMR (101 MHz, DMSO) δ 142.0 (C-2), 141.2 (C-6), 137.2 (C-4), 122.0 (C-7), 113.5 (C-3), 110.4 (C-5). ES-MS: m/z 273 ($[\text{M}]^-$, 2 %), 272 (100, $[\text{M}-\text{H}]^-$). $\tilde{\nu}_{\text{max}}$ / cm^{-1} : 3330 (m, N-H), 3094 (w, C-H), 1633 (vw), 1571 (s), 1497 (s), 1404 (m), 1309 (s), 1275 (s), 1237 (s), 1212 (s), 1200 (s), 1140 (s), 1127 (s), 1069 (s), 968 (s), 925 (s), 883 (s), 874 (s), 857 (s), 845 (m), 831 (s), 820 (s), 814 (s), 766 (w), 740 (s), 719 (s), 711 (s), 657 (m), 552 (s), 535 (s), 505 (s). Found: C, 52.7; H, 2.9; N, 14.6. Calc. for $\text{C}_{12}\text{H}_7\text{N}_3\text{O}_5$: C, 52.4; H, 3.3; N 15.3.

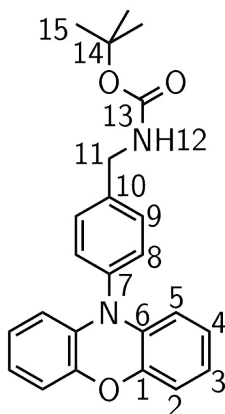


A.3.4.1.2 (2) 3,7-diamino-10H-phenoxazine This procedure was based on a similar procedure in the literature.²² To a mixture of 0.320 g (1.17 mmol, 1 equiv.) of 3,7-di-nitro-10H-phenoxazine and 0.350 g (6.27 mmol, 5.4 equiv.) of iron in 30 ml of ethanol, 2.4 ml of 37 % hydrochloric acid was added. The reaction was refluxed for 1 h then the reaction mixture was filtered, and the solvent removed under vacuum. The residue was then washed with water and diethyl ether. A suitable solvent for recrystallization or for column chromatography could not be found to purify. GC-MS suggested a very impure mixture with the predominant peak being the product. ESI: m/z 242.1 (30 %), 212.1 (100, $[M-H]^+$).



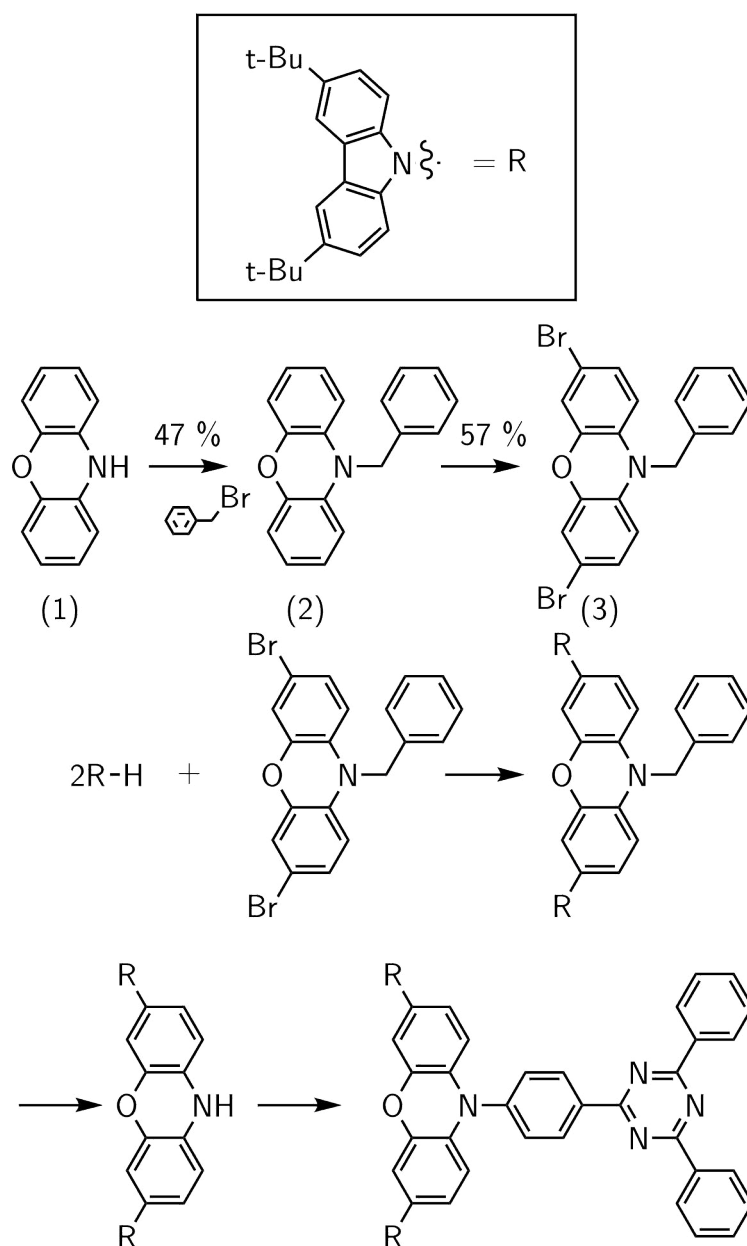
Scheme A.7: The planned synthesis using an inbuilt phenyl directing group.

A.3.4.2 Attempt 2: Functionalisation Mediated By An Inbuilt Phenyl Group

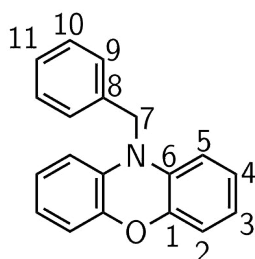


A.3.4.2.1 (2) [4-(10H-phenoxazin-10H-yl)benzyl] carbamic acid tert-butyl ester A solution of (4-bromobenzyl)carbamic acid tert-butyl ester, (2.51 g, 8.7 mmol) in toluene (100 ml) under argon was formed. To this solution 10H-phenoxazine (1.76 g, 9.62 mmol), Pd(OAc)₂ (0.049 g, 0.22 mmol), tri-tert-butylphosphonium tetrafluoroborate (0.25 g, 0.86 mmol), ^tBuOK (2.94 g, 26 mmol) was added. This gave a black solution. After stirring at reflux for 65 h, the reaction mixture was cooled for 30 min, and diluted with water (100 ml), and the product extracted with ethyl acetate (11 × 100 ml). The organic layer was washed with brine (100 ml), and the combined organic extracts were dried over sodium sulfate and concentrated under vacuum to give a thick brown oil. The residue was then purified by column chromatography, eluting with a 1:4 mixture of ethyl acetate and petroleum ether, to yield no significant amount of a primary product.

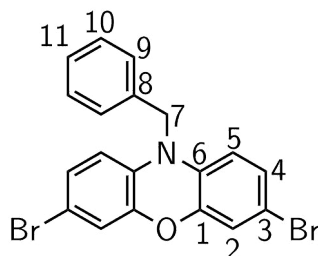
A.3.4.3 Attempt 3: Functionalisation Mediated By A Benzyl Protecting Group



Scheme A.8: The planned synthesis using a benzyl protecting directing group. Experimental yields for the steps completed are shown.



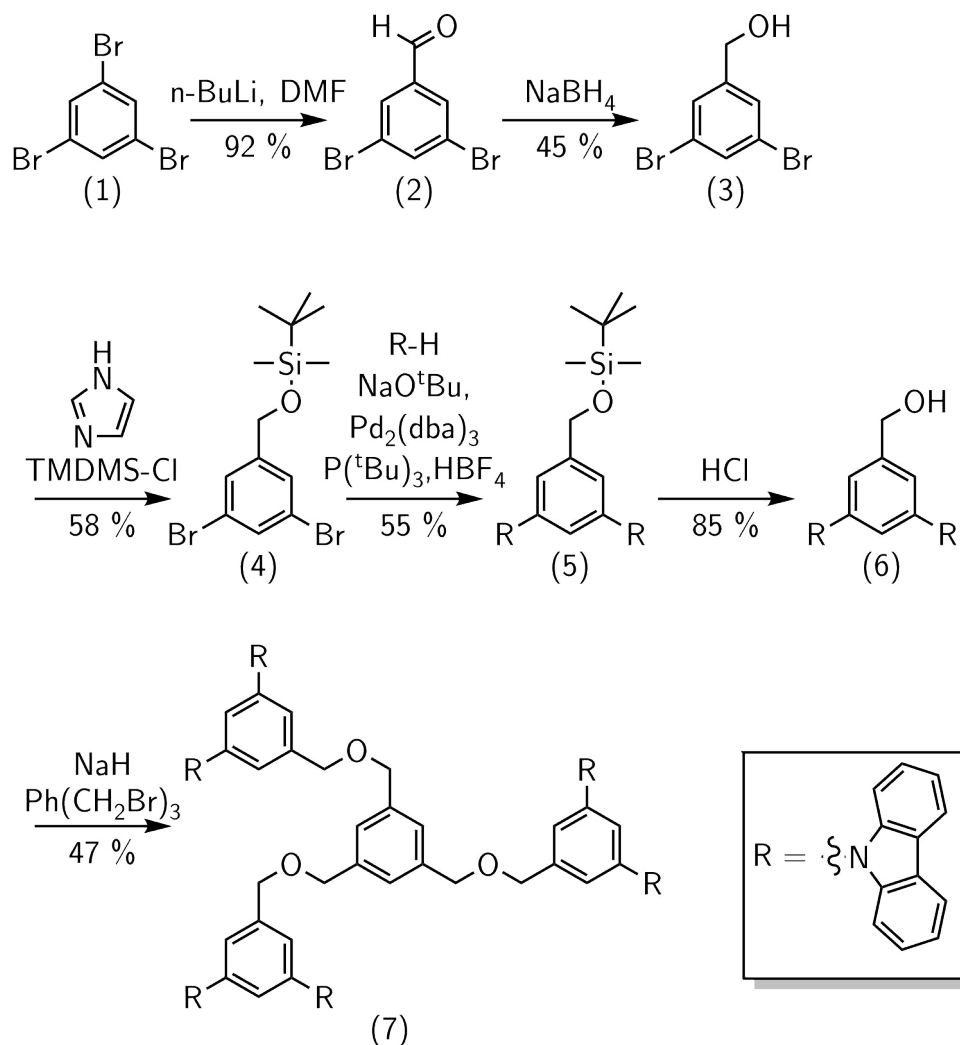
A.3.4.3.1 (2) 10-benzyl-10H-phenoxazine KOH (pellets, 1.92 g, 34.3 mmol) was dissolved in acetone (4.1 ml) and the resulting solution was stirred at room temperature for 30 min. 10H-phenoxazine (1.00 g, 5.46 mmol) was then added and the solution stirred for a further 4 h. On addition of 10H-phenoxazine the blue mixture turned dark brown immediately. Additional acetone (4.1 ml) containing (bromomethyl)benzene (1.41 g, 0.97 ml, 8.22 mmol) was added into the above solution (no colour change was observed) and the resulting system was sealed after 30 min and allowed to react overnight. Subsequently the reaction mixture was poured into water (70 ml), the solid was filtered off, and washed with water (8×10 ml) and methanol (1×50 ml). The product was purified using column chromatography, using 1 : 15 mixture of ethyl acetate : petroleum ether (40:60) eluent. The product was then dried by heating (60 °C) under high vacuum for 1 h, to yield, as a cream-white solid, 10-benzyl-10H-phenoxazine (47 % yield, 0.638 g, 2.33 mmol). ^1H NMR (400 MHz, CDCl_3) δ 7.38–7.26 (m, 5H, H-9–11), 6.73–6.63 (m, 6H, H-3–5), 6.33 (d, $J_{2,3} = 7.1$, 2H, H-2), 4.75 (2H, H-7). ^{13}C NMR (101 MHz, CDCl_3) δ 145.3 (C/ CH_2 , C-8), 136.4 (C/ CH_2 , C-6), 134.0 (C/ CH_2 , C-1), 129.1 (CH/ CH_3 , C-10), 127.3 (CH/ CH_3 , C-11), 126.1 (CH/ CH_3 , C-9), 123.8 (CH/ CH_3 , C-2), 121.4 (CH/ CH_3 , C-4), 115.4 (CH/ CH_3 , C-5), 112.3 (CH/ CH_3 , C-3), 49.4 (C/ CH_2 , C-7).



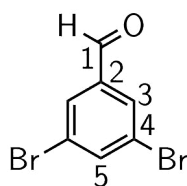
A.3.4.3.2 (3) 3,7-dibromo-10-benzyl-10H-phenoxazine To a stirred pale yellow solution of 10-benzyl-10H-phenoxazine (0.451 g, 1.65 mmol) in CH_2Cl_2 (30 ml), a solution of n-bromosuccinimide (0.588 g, 3.3 mmol) in CH_2Cl_2 (25 ml) was added dropwise over 15 min, giving a dark pink solution. The mixture was stirred for 60 min in the absence of light at room temperature. The combined dark blue filtrate was washed with H_2O (4×100 ml), dried (Na_2SO_4), and solvent was removed under reduced pressure. Finally the product was dried by heating (60 °C) under high vacuum for 1 h to give 3,7-dibromo-10-benzyl-10H-phenoxazine (0.406 g, 57 %), as a grey-brown powder. ^1H NMR (400 MHz, CDCl_3) δ 7.36 (t, $J_{10,9}, J_{10,11} = 7.3$ 2H, H-10), 7.29 (d, $J_{11,10} = 7.1$, 1H, H-11), 7.24 (d, $J_{9,10} = 7.0$, 2H, H-9), 6.83–6.79 (m, 4H, H-2,4), 6.18 (d, $J_{9,10} = 7.0$, 2H, H-5), 4.71 (s, 2H, H-7). ^{13}C NMR (101 MHz, CDCl_3) δ 145.5 (C/ CH_2 , C-8), 135.2 (C/ CH_2 , C-6), 132.8 (C/ CH_2 ,

C-1) 129.3 (CH/CH₃, C-10), 127.7 (CH/CH₃, C-11), 126.8 (CH/CH₃, C-9), 126.0 (CH/CH₃, C-5), 118.7 (CH/CH₃, C-4), 113.5 (CH/CH₃, C-2), 113.0 (C/CH₂, C-3), 49.3 (C/CH₂, C7).

A.3.5 New Host 1

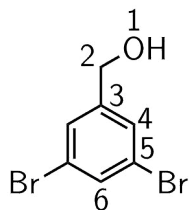


Scheme A.9: The synthesis of new host 1 (NH1) with reagents and yields shown.



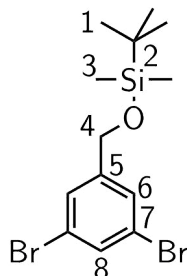
A.3.5.0.1 (2) 3,5-dibromo-benzaldehyde This procedure was based on a similar procedure in the literature.²³ 1,3,5-tribromobenzene (15.00 g, 47.6 mmol,

1.0 equiv.) was dissolved in anhydrous diethyl ether (250 ml) under argon. After stirring, the yellow solution was cooled down to $-78\text{ }^{\circ}\text{C}$, and 2.5 M n-BuLi solution in hexane (19.1 ml, 47.6 mmol, 1.0 equiv.) was added dropwise. After this, dry DMF (7.9 ml, 95 mmol, 2 equiv.) diluted in dry diethyl ether (10 ml) was added dropwise. This solution was stirred for 1 h at $-78\text{ }^{\circ}\text{C}$, forming an orange solution. The solution was then allowed to reach $0\text{ }^{\circ}\text{C}$ and HCl (10 %, 100 ml) added until the solution has pH greater than 7. The mixture was extracted using chloroform ($2 \times 250\text{ ml}$) and dried over MgSO_4 . The solvent was then removed under reduced pressure and ran through a silica plug using chloroform. Finally, the solvent was removed and the product was dried under high vacuum ($60\text{ }^{\circ}\text{C}$, 1 h) to obtain the colourless solid 3,5-dibromo-benzaldehyde (11.53 g, 92 % yield); ^1H (400 MHz, CDCl_3) δ 9.90 (s, 1H, H-1), 7.94 (d, $J_{3,5} = 1.7$, 2H, H-3), 7.92 (t, $J_{5,3} = 1.6$, 1H, H-5). ^{13}C (100 MHz, CDCl_3) δ 189.4 (C-1), 139.7 (C-3), 131.4 (C-5), 128.5 (C-2), 124.1 (C-4). EI: m/z 263 ($[\text{M}-\text{H}]^+$), 235 ($[\text{M}-\text{CHO}]^+$), 155 ($[\text{M}-\text{CHO}-\text{Br}]^+$), 75 ($[\text{C}_6\text{H}_3]^+$). $\tilde{\nu}_{\text{max}} / \text{cm}^{-1}$: 3066 (Ph-H), 2844 and 2736 (-CHO), 1690 (C=O). Found: C, 32.1; H, 1.8; Br, 58.6; Calc. for $\text{C}_7\text{H}_4\text{Br}_2\text{O}$ C, 31.9; H, 1.5; Br, 60.6. Mp $77\text{--}81\text{ }^{\circ}\text{C}$.

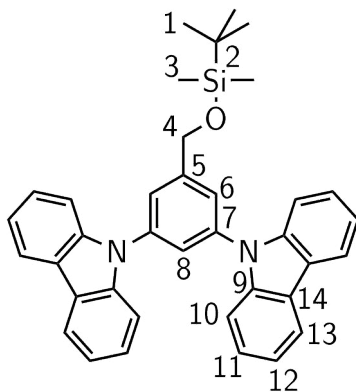


A.3.5.0.2 (3) 3,5-dibromobenzenemethanol This procedure was based on a similar procedure in the literature.²³ 3,5-dibromo-benzaldehyde (3.00 g, 11.3 mmol 1 equiv.) was dissolved in ethanol (50 ml) and dichloromethane (50 ml). This formed a yellow solution. To this solution Sodium borohydride (858 mg, 22.7 mmol, 2.0 equiv.) was added slowly while stirring. The reaction mixture was stirred at room temperature for 3 h. Subsequently, the mixture was quenched on to water (100 ml) and the product extracted with ethyl acetate ($3 \times 100\text{ ml}$), and washed with brine. The resulting solution was dried using anhydrous MgSO_4 and the solvent removed to produce a pale yellow solid. Purified via silica gel column chromatography, was then conducted, using petroleum ether and ethyl acetate in a 5:1 ratio. Subsequently the product was dried in a vacuum oven for 24 h. The produced of 1.37 g of 3,5-dibromobenzenemethanol (45 % yield, 5.16 mmol) was obtained as a white solid. ^1H (400 MHz, CDCl_3) δ 7.58 (s, 1H, H-8), 7.46 (s, 2H, H-7), 4.67 (d, $J_{2,1} = 2.9$, 2H, H-2), 1.77 (s, 1H, H-1). ^{13}C (101 MHz, CDCl_3) δ 144.8 (C-5), 133.2 (C-3), 128.5 (C-6), 123.2 (C-4), 63.9 (C-2). $\tilde{\nu}_{\text{max}} / \text{cm}^{-1}$: 3298 (CH₂-OH), 3067, 2918 (Ph-H), 1202 (CH). Found: C, 32.4; H, 2.6; Br, 58.9; Calc. for: $\text{C}_7\text{H}_6\text{Br}_2\text{O}$:

C, 31.6; H, 2.3; Br, 60.1. EI: m/z 266 ($[M]^+$), 249 ($[M-OH]^+$), 235 ($[M-CH_2OH]^+$), 157 ($[C_6H_5Br]^+$), 77 ($[C_6H_5]^+$). Mp 104–112 °C.

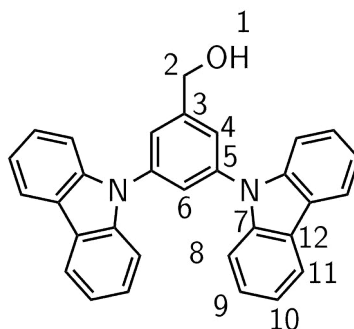


A.3.5.0.3 (4) tert-butyl((3,5-dibromobenzyl)oxy)dimethyl silane This procedure was based on a similar procedure in the literature.²³ Imidazole (0.486 g, 7.14 mmol, 1.1 equiv.) and 3,5-dibromobenzenemethanol (1.2 g, 6.5 mmol, 1.0 equiv.) were dissolved in anhydrous dichloromethane (60 ml) under argon. Tert-butyldimethylsilyl chloride (1.02 g, 6.77 mmol) was added to the mixture and stirred at room temperature for 4 h. After the completion of the reaction, the white solution was quenched on 75 ml of water and extracted by dichloromethane (3×75 ml). The organic layers were combined and dried over Na_2SO_4 and the solvent removed and the product dried under high-vacuum at 60 °C for 1 h, to get the light brown oil (1.43 g, 3.76 mmol, 58 %). 1H (400 MHz, $CDCl_3$) δ 7.53 (s, 1H, H-8), 7.39 (s, 2H, H-6), 4.67 (s, 2H, H-4), 0.94 (s, 9H, H-1), 0.10 (s, 6H, H-3); ^{13}C (101 MHz, $CDCl_3$) δ 145.6 (C-7), 132.5 (C-5), 127.8 (C-8), 122.9 (C-6), 63.7 (C-4), 26.0 (C-1), 18.5 (C-3), -5.2 (C-2). EI⁺ m/z 380 ($[M]^+$), 365 ($[M-CH_3]^+$), 323 ($[M-C_4H_9]^+$), 293 ($[M-C_4H_9-(CH_3)_2]^+$), 293 ($[M-OSi(CH_3)_2C_4H_9]^+$), 170 ($[M-OSi(CH_3)_2C_4H_9-Br]^+$). $\tilde{\nu}_{max}$ / cm^{-1} : 2954 ($-CH_3$), 2885 ($-CH_3$), 2929 (Ph-H), 2857 (Ph-H), 1425 (Si- CH_3), 1254 (Si- CH_3), 1112 (CH_2-O-Si), 1091 (CH_2-O-Si). Found: C, 41.3; H, 5.1; Br, 39.6; Calc. for $C_{13}H_{20}Br_2OSi$: C, 41.1; H, 5.3; Br, 42.0.*



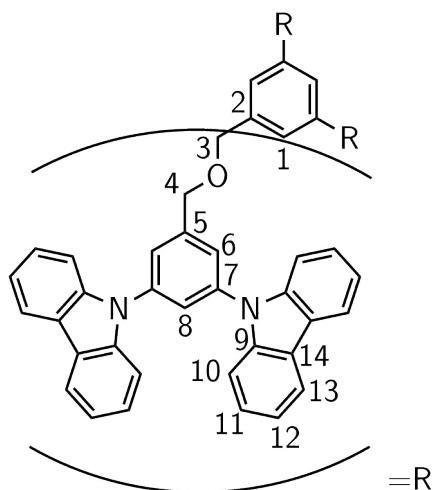
*This sample was additionally purified via column chromatography with hexane eluent.

A.3.5.0.4 (5) 9,9'-[5-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]methyl]-1,3-phenylene]bis-9H-carbazole This procedure was based on a similar procedure in the literature.²³ Tert-butyl((3,5-dibromobenzyl)oxy)dimethyl silane (1.0 g, 2.8 mmol, 1.0 equiv.), carbazole (0.936 g, 5.6 mmol, 2.0 equiv.), sodium-tert-butoxide (1.26 g, 13 mmol, 4.6 equiv.), tris(dibenzylidene acetone)dipalladium(0) ($\text{Pd}_2(\text{dba})_3$, 0.238 g, 0.26 mmol, 0.093 equiv) and tri-tert-butylphosphonium tetrafluoroborate ($\text{P}(\text{tBu})_3\cdot\text{HBF}_4$, 0.076 g, 0.26 mmol, 0.093 equiv) were dissolved in 6 ml of anhydrous toluene under argon. The purple solution was then stirred and heated to reflux for 48 h. The solution was quenched in water (100 ml) and extracted by dichloromethane (3×150 ml). The combined organic layers were washed with brine (150 ml), dried over Na_2SO_4 and concentrated under reduced pressure. The brown crude oil was purified via silica gel column chromatography (1:3 DCM:hexane graduated to 2:3) and dried under high vacuum (60 °C, 1 h). 9,9'-[5-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]methyl]-1,3-phenylene]bis-9H-carbazole (0.851 g, 1.54 mmol, 55 %) was obtained as a transparent solid. ^1H (400 MHz, CDCl_3) δ 8.16 (d, $J_{13,12} = 7.7$, 4H, H-13), 7.70 (s, 1H, H-8), 7.69 (s, 2H, H-6), 7.56 (d, $J_{8,9} = 8.2$, 4H, H-10), 7.44 (t, $J_{11,10}, J_{11,12} = 7.3$, 4H, H-11), 7.32 (t, $J_{12,11}, J_{12,13} = 7.4$, 4H, H-12), 4.97 (s, 2H, H-4), 0.97 (s, 9H, H-1), 0.17 (s, 6H, H-3); ^{13}C (101 MHz, CDCl_3) δ 145.7 (C-7), 140.6 (C-9), 139.3 (C-5), 126.3 (C-11), 123.7 (C-8), 123.4 (C-6), 123.2 (C-14), 120.6 (C-13), 120.4 (C-10), 109.9 (C-12), 64.4 (C-4), 26.1 (C-1), 18.3 (C-2), -5.1 (C-3); EI^+ m/z 552 ($[\text{M}]^+$), 495 ($[\text{M}-\text{C}_4\text{H}_9]^+$), 465 ($[\text{M}-\text{C}_4\text{H}_9-2\text{CH}_3]^+$), 421 ($[\text{M}-\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9]^+$), 387 ($[\text{M}-\text{C}_{12}\text{H}_8\text{N}]^+$). $\tilde{\nu}_{\text{max}} / \text{cm}^{-1}$: 2952 ($-\text{CH}_3$), 2883 ($-\text{CH}_3$), 2927 (Ph-H), 2854 (Ph-H), 1461 (Si- CH_3), 1227 (Si- CH_3), 1332 ($\text{R}_2\text{N}-\text{CR}_2$), 1311 ($\text{R}_2\text{N}-\text{CR}_2$), 1109 ($\text{CH}_2-\text{O}-\text{Si}$), 1095 ($\text{CH}_2-\text{O}-\text{Si}$). Found: C, 79.7; H, 6.5; N, 4.8 ; Calc. for $\text{C}_{37}\text{H}_{36}\text{N}_2\text{OSi}$: C, 80.4; H, 6.6; N, 5.1. Mp 51–55 °C.



A.3.5.0.5 (6) 3,5-di(9H-carbazol-9-yl)phenylmethanol This procedure was based on a similar procedure in the literature.²³ A solution was made in 12.0 ml of tetrahydrofuran of 9,9'-[5-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]methyl]-1,3-phenylene]bis-9H-carbazole (0.74 g, 1.34 mmol) . A solution of HCl (4.0 ml,

3M) was added dropwise over 15 min and stirred at overnight at room temperature. Subsequently, the mixture was extracted with dichloromethane (3×50 ml) and washed with water (50 ml). The extracted DCM solution were dried with anhydrous MgSO_4 . The solvent was subsequently removed, and the crude product purified by precipitation from dichloromethane to hexane (100 ml). The product was finally dried under high-vacuum (60 °C, 1 h) to produce (3,5-di(9H-carbazol-9-yl)phenyl)methanol (0.497 g, 1.13 mmol, 85 % yield) as a white solid. ^1H (400 MHz, CDCl_3) δ 8.16 (d, $J_{11,10} = 7.7$, 4H, H-11), 7.75 (s, 1H, H-6), 7.71 (s, 2H, H-4), 7.54 (d, $J_{8,9} = 8.2$, 4H, H-8), 7.44 (t, $J_{9,8}, J_{9,10} = 7.2$, 4H, H-9), 7.31 (t, $J_{10,9}, J_{10,11} = 7.4$, 4H, H-10), 4.97 (d, $J_{2,1} = 5.6$, 2H, H-2), 1.99 (s, 1H, H-1). ^{13}C (101 MHz, CDCl_3) δ 144.8 (C-5), 140.6 (C-7), 139.5 (C-3), 126.2 (C-9), 124.1 (C-6), 123.8 (C-4), 123.6 (C-12), 120.5 (C-11), 120.4 (C-8), 109.8 (C-10), 64.5 (C-2). EI^+ m/z 436 ($[\text{M}-2\text{H}]^+$), 406 ($[\text{M}-\text{H}-\text{CH}_2\text{OH}]^+$). $\tilde{\nu}_{\text{max}} / \text{cm}^{-1}$: 3308 (O-H), 3052 ($\text{R}_2\text{C}-\text{CH}_2$), 2922 (Ph-H), 2863 (Ph-H), 1324 ($\text{R}_2\text{N}-\text{CR}_2$), 1307 ($\text{R}_2\text{N}-\text{CR}_2$), 1028 (CH_2-OH). Found: C, 84.2; H, 5.2; N, 6.1; Calc. for $\text{C}_{31}\text{H}_{22}\text{N}_2\text{O}$: C, 84.9; H, 5.1; N, 6.4. Mp 144-147 °C.



A.3.5.0.6 (7) 1,3,5-tris[3,5-di((9H-carbazol-9-yl)-phenylmethoxy)-methyl]-benzene 3,5-di((9H-carbazol-9-yl)-phenyl)-methanol (0.708 g, 1.62 mmol, 1.0 equiv.) was dissolved in DMF (5.6 ml) and subsequently cooled to 0 °C with stirring. To this solution NaH (60 % dispersion in mineral oil, 0.0783 g, 1.93 mmol, 1.2 equiv.) was added, and the formed mixture stirred for 10 min. To this solution, 1,3,5-tris(bromomethyl)benzene (0.1903 g, 0.53 mmol, 0.33 equiv.) was added, and the cooling removed, such that mixture was allowed to warm to room temperature. The room temperature solution was subsequently stirring for 25.5 hours. To quench the reaction 20 ml of water was added, causing the formation via precipitation of a white solid. The solid was filtered off, and washed with water and dried in a vacuum oven for 67 hours. This product was purified via column

chromatography using a chloroform eluent. The solvent was removed, and the product dried by heating to 60 °C for 1 h under high vacuum. A yellow/white solid was formed of 1,3,5-tris[3,5-di((9H-carbazole-9-yl)phenylmethoxy)methyl]benzene (0.359 g, 0.25 mmol, 47 %). ^1H (400 MHz, CDCl_3) δ 8.14 (d, $J_{13,12} = 7.5$, 12H, H-13), 7.74 (s, 3H, H-8), 7.67 (s, 6H, H-6), 7.54 (d, $J_{10,11} = 8.0$, 12H, H-10), 7.44 (s, 3H, H-1), 7.43 (t, $J_{11,10}$, $J_{11,12} = 7.5$, 12H, H-11), 7.31 (t, $J_{12,11}$, $J_{12,13} = 8.0$, 12H, H-12), 4.70 (s, 6H, H-3), 4.68 (s, 6H, H-4). ^{13}C (101 MHz, CDCl_3) δ 142.3 (C-7), 140.5 (C-9), 139.3 (C-5), 138.6 (C-2), 126.6 (C-11), 126.2 (C-1), 124.5 (C-8), 124.1 (C-6), 123.6 (C-14), 120.5 (C-13), 120.4 (C-10), 109.7 (C-12), 72.6 (C-4), 71.5 (C-3). m/z 1453 ($[\text{M}+\text{Na}+1]^+$). $\tilde{\nu}_{\text{max}} / \text{cm}^{-1}$: 3049 (w, CH_2 Asymmetric Stretch), 2856 (w, CH_2 Symmetric Stretch), 1594 (s), 1492 (m), 1480 (m), 1462 (s), 1442 (s), 1390 (w), 1332 (s), 1311 (s), 1227 (s), 1155 (m), 1090 (m), 1027 (m), 1003 (m), 923 (m), 852 (w), 789 (w), 745 (s), 722 (s), 704 (s), 667 (m), 647 (m), 617 (m), 565 (m), 547 (w), 527 (w), 434 (m), 421 (s). MALDI: m/z 1432 ($[\text{M}+3]^+$, 12 %), 1431 (41, $[\text{M}+2]^+$), 1430 (100, $[\text{M}+1]^+$), 1429 (83, $[\text{M}]^+$), 971 (21), 841 (15, $[\text{M}-\text{CH}_2\text{PhCBZ}_2-2\text{H}]^+$), 554 (19, $[(\text{CBZ})_2\text{PhCH}_2\text{OCH}_2\text{Ph}(\text{CH}_2)_2]^+$), 422 (86, $[(\text{CBZ})_2\text{PhCH}_2]^+$). Found: C, 84.8; H, 5.0; N, 5.8. Calc. for $\text{C}_{102}\text{H}_{72}\text{N}_3\text{O}_6$: C, 85.7; H, 5.1; N, 5.9. Mp 136–150 °C.

A.4 NMR Of Target Molecules

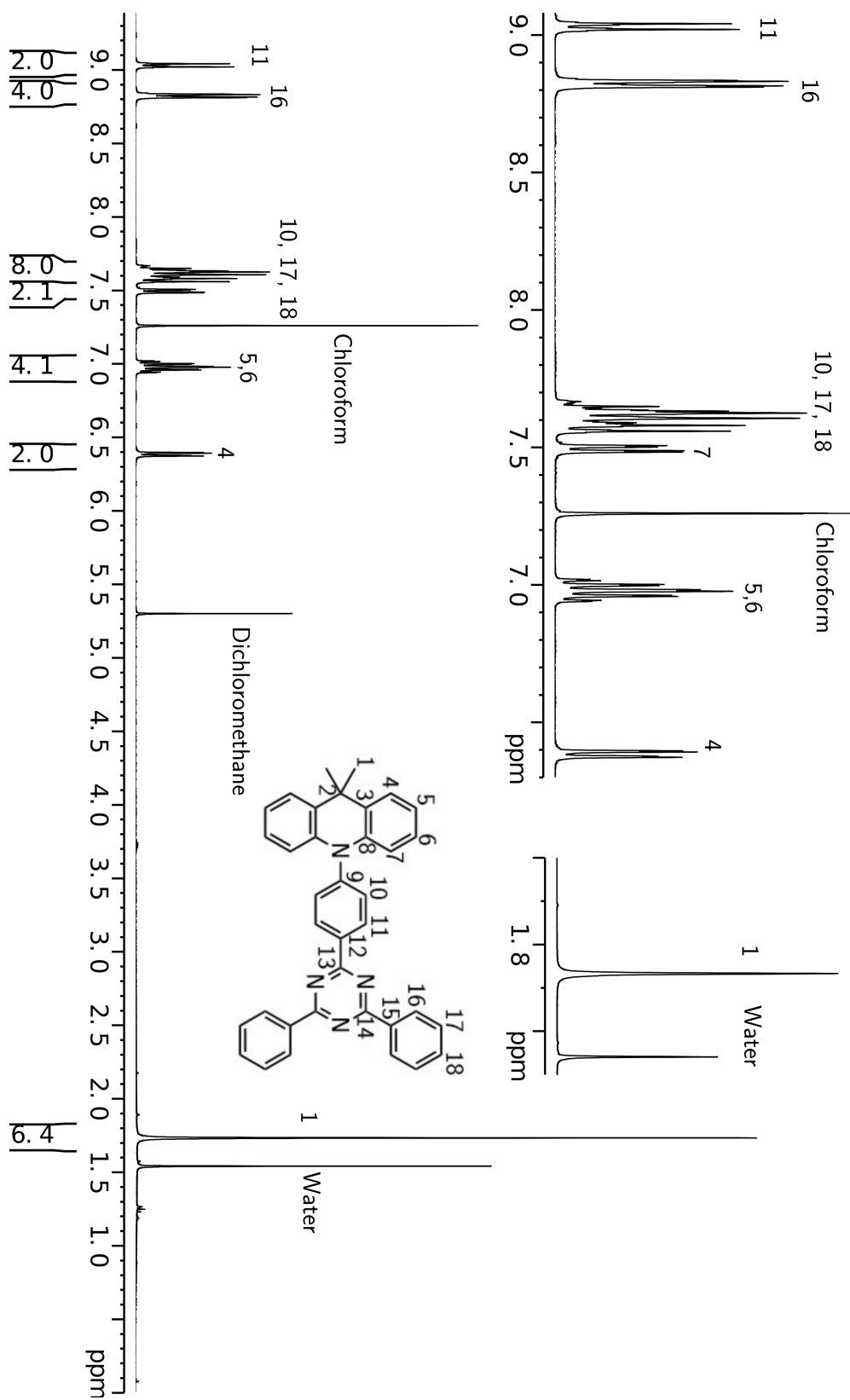
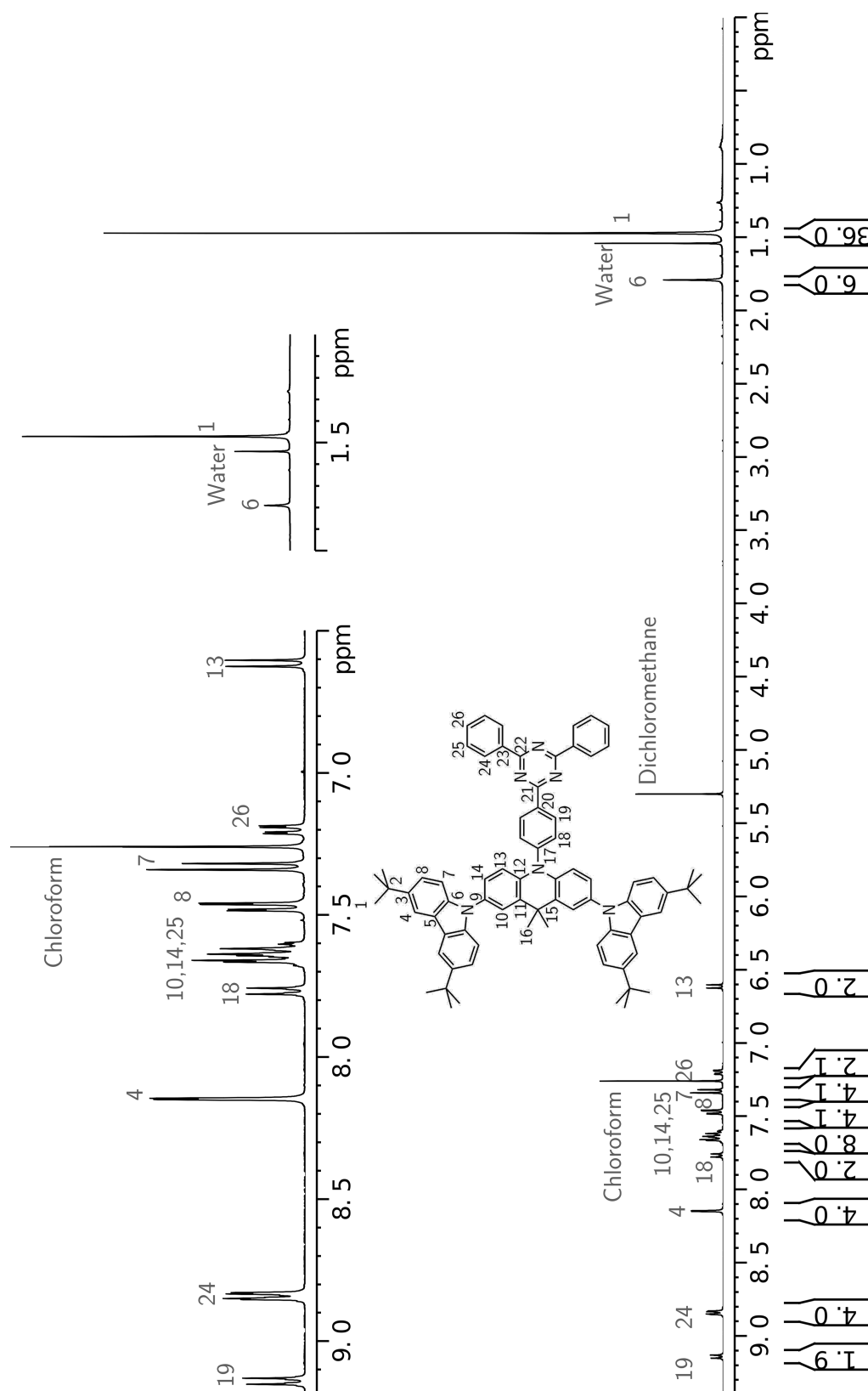


Figure A.3: The ^1H NMR of compound 1, with all hydrogens assigned

Figure A.4: The ^1H NMR of compound 2, with all hydrogens assigned

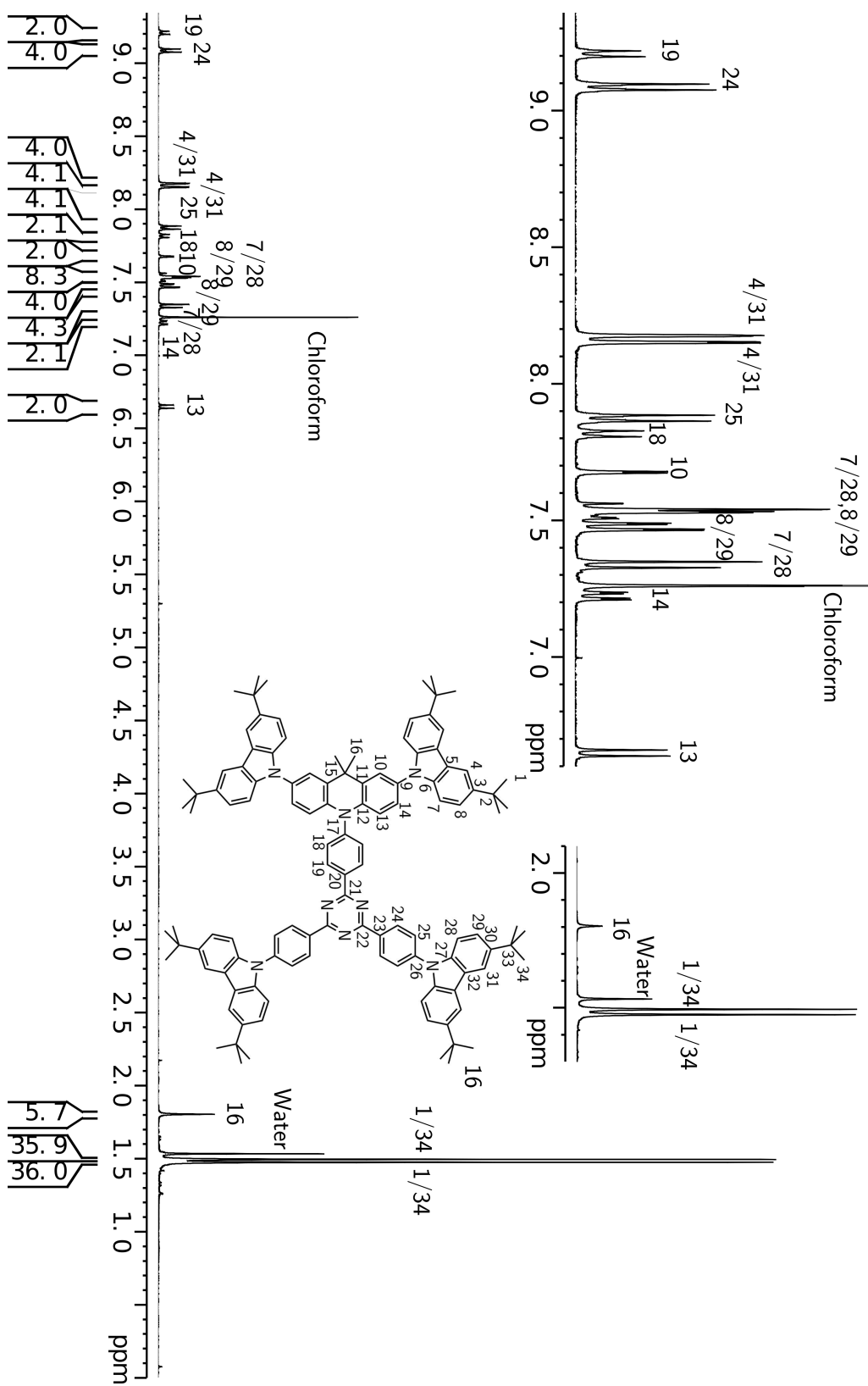


Figure A.5: The ^1H NMR of compound 3, with all hydrogens assigned



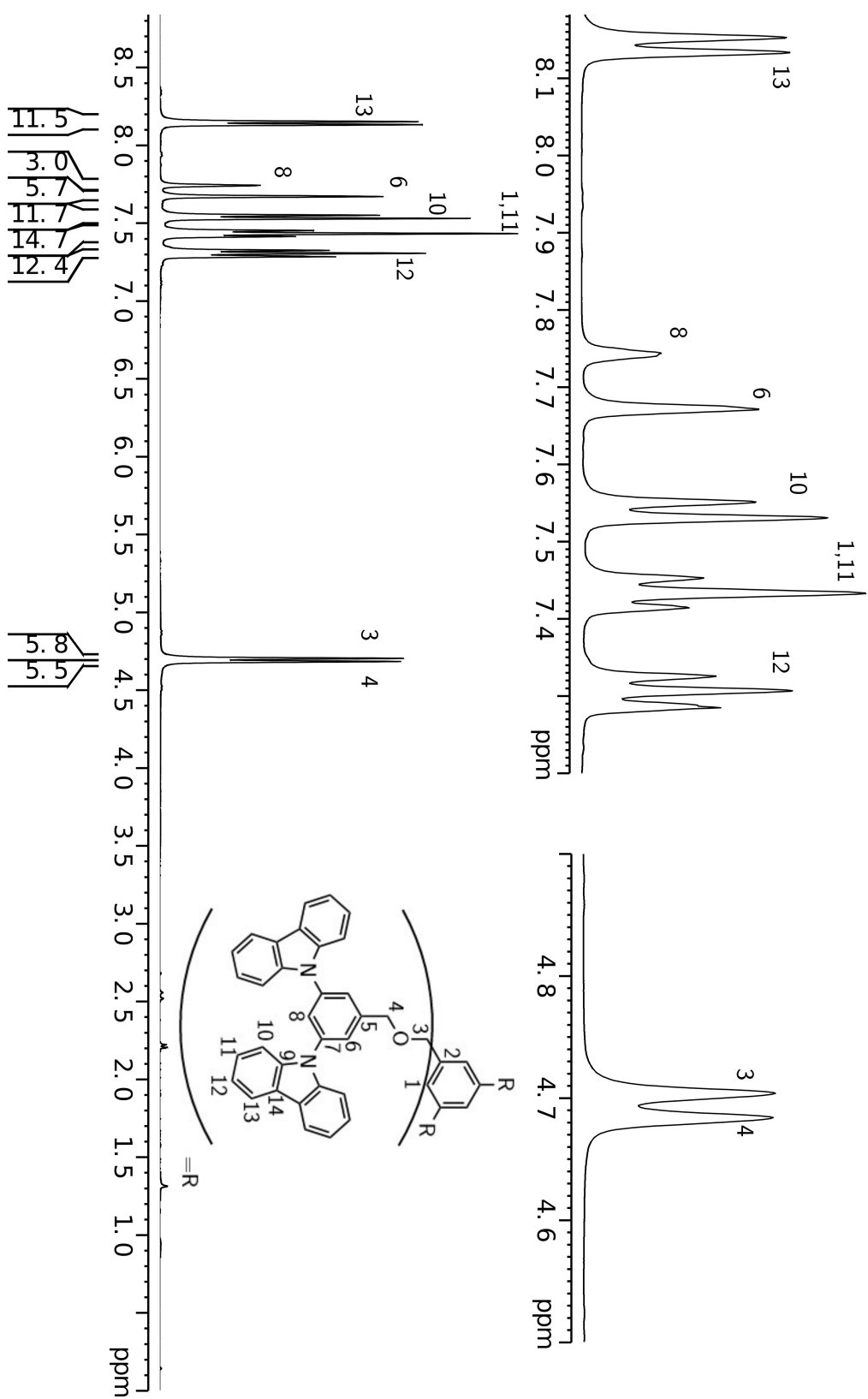


Figure A.7: The ^1H NMR of new host 1, with all hydrogens assigned

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Appendix B

Supplementary Information

*"All the small things,
True care truth brings"*

— Blink 182, *All The Small Things*

B.1 The Introduction

B.1.1 Singlet-Triplet Energy Gap Hartree-Fock

For excited states within computational chemistry, often the determinants with one or more occupied orbitals, swapped with virtual orbitals are used to try to express the excited state.¹ When one virtual orbital is swapped with one occupied orbital, this is called a singly excited state, if two then a doubly etc.¹ Note these are distinct from real excited states, because, in-part, the number of virtual orbitals is different from the number of actual excited states.¹ In fact it is text-book knowledge that as the number of virtual states increases, the energy gap between the lowest energy singly excited state and the ground state tends towards zero.² In order to try to force a distinction the singly excited state in Hartree-Fock will be referred to as "singlet excited state" or "singly excited slater determinant" and the real excited states as "real singly excited states". The real excited states must be calculated at a level of theory beyond Hartree-Fock, at a minimum of Configurational-Interaction singles ie. using all singly excited determinants.¹

Nonetheless, within the field of TADF, the energy gap between the real singlet and triplet states is often approximated by the value given when using a pure Hartree-Fock method, and conflates the hartree-fock generated singly excited state, with a real singly excited state.^{3,4} This will be described here. For 2 wavefunctions ($\phi_H(x)$ and $\phi_L(x)$ for the HOMO and LUMO respectively) and two spins (α and

β), it is possible to generate 16 different determinants, which collapse to 6 different unique non-zero determinants. Note that $\Phi \equiv -\Phi$ for the sake of this distinction. From these determinants it will be possible to express one function, corresponding to a singly excited singlet, and 3 degenerate functions for a singly excited triplet. The 16 determinants are shown below.

$$\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_H(1)\alpha(1) & \phi_H(1)\alpha(1) \\ \phi_H(2)\alpha(2) & \phi_H(2)\alpha(2) \end{vmatrix}; \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_L(1)\alpha(1) & \phi_H(1)\alpha(1) \\ \phi_L(2)\alpha(2) & \phi_H(2)\alpha(2) \end{vmatrix} \quad (\text{B.1})$$

$$\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_H(1)\alpha(1) & \phi_H(1)\beta(1) \\ \phi_H(2)\alpha(2) & \phi_H(2)\beta(2) \end{vmatrix}; \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_L(1)\alpha(1) & \phi_H(1)\beta(1) \\ \phi_L(2)\alpha(2) & \phi_H(2)\beta(2) \end{vmatrix} \quad (\text{B.2})$$

$$\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_H(1)\alpha(1) & \phi_L(1)\alpha(1) \\ \phi_H(2)\alpha(2) & \phi_L(2)\alpha(2) \end{vmatrix}; \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_L(1)\alpha(1) & \phi_L(1)\alpha(1) \\ \phi_L(2)\alpha(2) & \phi_L(2)\alpha(2) \end{vmatrix} \quad (\text{B.3})$$

$$\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_H(1)\alpha(1) & \phi_L(1)\beta(1) \\ \phi_H(2)\alpha(2) & \phi_L(2)\beta(2) \end{vmatrix}; \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_L(1)\alpha(1) & \phi_L(1)\beta(1) \\ \phi_L(2)\alpha(2) & \phi_L(2)\beta(2) \end{vmatrix} \quad (\text{B.4})$$

$$\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_H(1)\beta(1) & \phi_H(1)\alpha(1) \\ \phi_H(2)\beta(2) & \phi_H(2)\alpha(2) \end{vmatrix}; \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_L(1)\beta(1) & \phi_H(1)\alpha(1) \\ \phi_L(2)\beta(2) & \phi_H(2)\alpha(2) \end{vmatrix} \quad (\text{B.5})$$

$$\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_H(1)\beta(1) & \phi_H(1)\beta(1) \\ \phi_H(2)\beta(2) & \phi_H(2)\beta(2) \end{vmatrix}; \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_L(1)\beta(1) & \phi_H(1)\beta(1) \\ \phi_L(2)\beta(2) & \phi_H(2)\beta(2) \end{vmatrix} \quad (\text{B.6})$$

$$\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_H(1)\beta(1) & \phi_L(1)\alpha(1) \\ \phi_H(2)\beta(2) & \phi_L(2)\alpha(2) \end{vmatrix}; \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_L(1)\beta(1) & \phi_L(1)\alpha(1) \\ \phi_L(2)\beta(2) & \phi_L(2)\alpha(2) \end{vmatrix} \quad (\text{B.7})$$

$$\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_H(1)\beta(1) & \phi_L(1)\beta(1) \\ \phi_H(2)\beta(2) & \phi_L(2)\beta(2) \end{vmatrix}; \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_L(1)\beta(1) & \phi_L(1)\beta(1) \\ \phi_L(2)\beta(2) & \phi_L(2)\beta(2) \end{vmatrix} \quad (\text{B.8})$$

These 16 determinants can be reduced to the 6 possible functions as follows:

$$\begin{aligned} & \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_H(1)\alpha(1) & \phi_H(1)\alpha(1) \\ \phi_H(2)\alpha(2) & \phi_H(2)\alpha(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_H(1)\beta(1) & \phi_H(1)\beta(1) \\ \phi_H(2)\beta(2) & \phi_H(2)\beta(2) \end{vmatrix} \\ & = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_L(1)\alpha(1) & \phi_L(1)\alpha(1) \\ \phi_L(2)\alpha(2) & \phi_L(2)\alpha(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_L(1)\beta(1) & \phi_L(1)\beta(1) \\ \phi_L(2)\beta(2) & \phi_L(2)\beta(2) \end{vmatrix} \\ & = \frac{1}{\sqrt{2}} (\beta(1)\beta(2)(\phi_L(1)\phi_L(2) - \phi_L(2)\phi_L(1))) = 0 \end{aligned} \quad (\text{B.9})$$

$$\begin{aligned}
\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_H(1)\alpha(1) & \phi_H(1)\beta(1) \\ \phi_H(2)\alpha(2) & \phi_H(2)\beta(2) \end{vmatrix} &= -\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_H(1)\beta(1) & \phi_H(1)\alpha(1) \\ \phi_H(2)\beta(2) & \phi_H(2)\alpha(2) \end{vmatrix} \\
&= \frac{1}{\sqrt{2}}(\phi_H(1)\phi_H(2)(\alpha(1)\beta(2) - \beta(1)\alpha(2)))
\end{aligned} \tag{B.10}$$

$$\begin{aligned}
\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_L(1)\alpha(1) & \phi_L(1)\beta(1) \\ \phi_L(2)\alpha(2) & \phi_L(2)\beta(2) \end{vmatrix} &= -\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_L(1)\beta(1) & \phi_L(1)\alpha(1) \\ \phi_L(2)\beta(2) & \phi_L(2)\alpha(2) \end{vmatrix} \\
&= \frac{1}{\sqrt{2}}(\phi_L(1)\phi_L(2)(\alpha(1)\beta(2) - \beta(1)\alpha(2)))
\end{aligned} \tag{B.11}$$

$$\begin{aligned}
\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_H(1)\alpha(1) & \phi_L(1)\beta(1) \\ \phi_H(2)\alpha(2) & \phi_L(2)\beta(2) \end{vmatrix} &= -\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_L(1)\beta(1) & \phi_H(1)\alpha(1) \\ \phi_L(2)\beta(2) & \phi_H(2)\alpha(2) \end{vmatrix} \\
&= \frac{1}{\sqrt{2}}(\alpha(1)\beta(2)\phi_H(1)\phi_L(2) - \beta(1)\alpha(2)\phi_L(1)\phi_H(2))
\end{aligned} \tag{B.12}$$

$$\begin{aligned}
\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_H(1)\beta(1) & \phi_L(1)\alpha(1) \\ \phi_H(2)\beta(2) & \phi_L(2)\alpha(2) \end{vmatrix} &= -\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_L(1)\alpha(1) & \phi_H(1)\beta(1) \\ \phi_L(2)\alpha(2) & \phi_H(2)\beta(2) \end{vmatrix} \\
&= \frac{1}{\sqrt{2}}(\beta(1)\alpha(2)\phi_H(1)\phi_L(2) - \alpha(1)\beta(2)\phi_L(1)\phi_H(2))
\end{aligned} \tag{B.13}$$

$$\begin{aligned}
\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_H(1)\alpha(1) & \phi_L(1)\alpha(1) \\ \phi_H(2)\alpha(2) & \phi_L(2)\alpha(2) \end{vmatrix} &= -\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_L(1)\alpha(1) & \phi_H(1)\alpha(1) \\ \phi_L(2)\alpha(2) & \phi_H(2)\alpha(2) \end{vmatrix} \\
&= \frac{1}{\sqrt{2}}(\alpha(1)\alpha(2)(\phi_H(1)\phi_L(2) - \phi_L(1)\phi_H(2)))
\end{aligned} \tag{B.14}$$

$$\begin{aligned}
\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_H(1)\beta(1) & \phi_L(1)\beta(1) \\ \phi_H(2)\beta(2) & \phi_L(2)\beta(2) \end{vmatrix} &= -\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_L(1)\beta(1) & \phi_H(1)\beta(1) \\ \phi_L(2)\beta(2) & \phi_H(2)\beta(2) \end{vmatrix} \\
&= \frac{1}{\sqrt{2}}(\beta(1)\beta(2)(\phi_H(1)\phi_L(2) - \phi_L(1)\phi_H(2)))
\end{aligned} \tag{B.15}$$

It is notable that two of these functions are not antisymmetry namely $\frac{1}{\sqrt{2}}(\beta(1)\alpha(2)\phi_H(1)\phi_L(2) - \alpha(1)\beta(2)\phi_L(1)\phi_H(2))$ and $\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)\phi_H(1)\phi_L(2) - \beta(1)\alpha(2)\phi_L(1)\phi_H(2))$. This can be solved by adding and subtracting these functions to form (with additional re-normalisation) $\frac{1}{2}(\alpha(1)\beta(2) - \beta(1)\alpha(2))(\phi_H(1)\phi_L(2) + \phi_H(2)\phi_L(1))$ and $\frac{1}{2}(\alpha(1)\beta(2) + \beta(1)\alpha(2))(\phi_H(1)\phi_L(2) - \phi_H(2)\phi_L(1))$ respectively. The orbital occupations that these states belong to are shown in figure B.1.

What is of interest to this work is the orbital energy difference between the

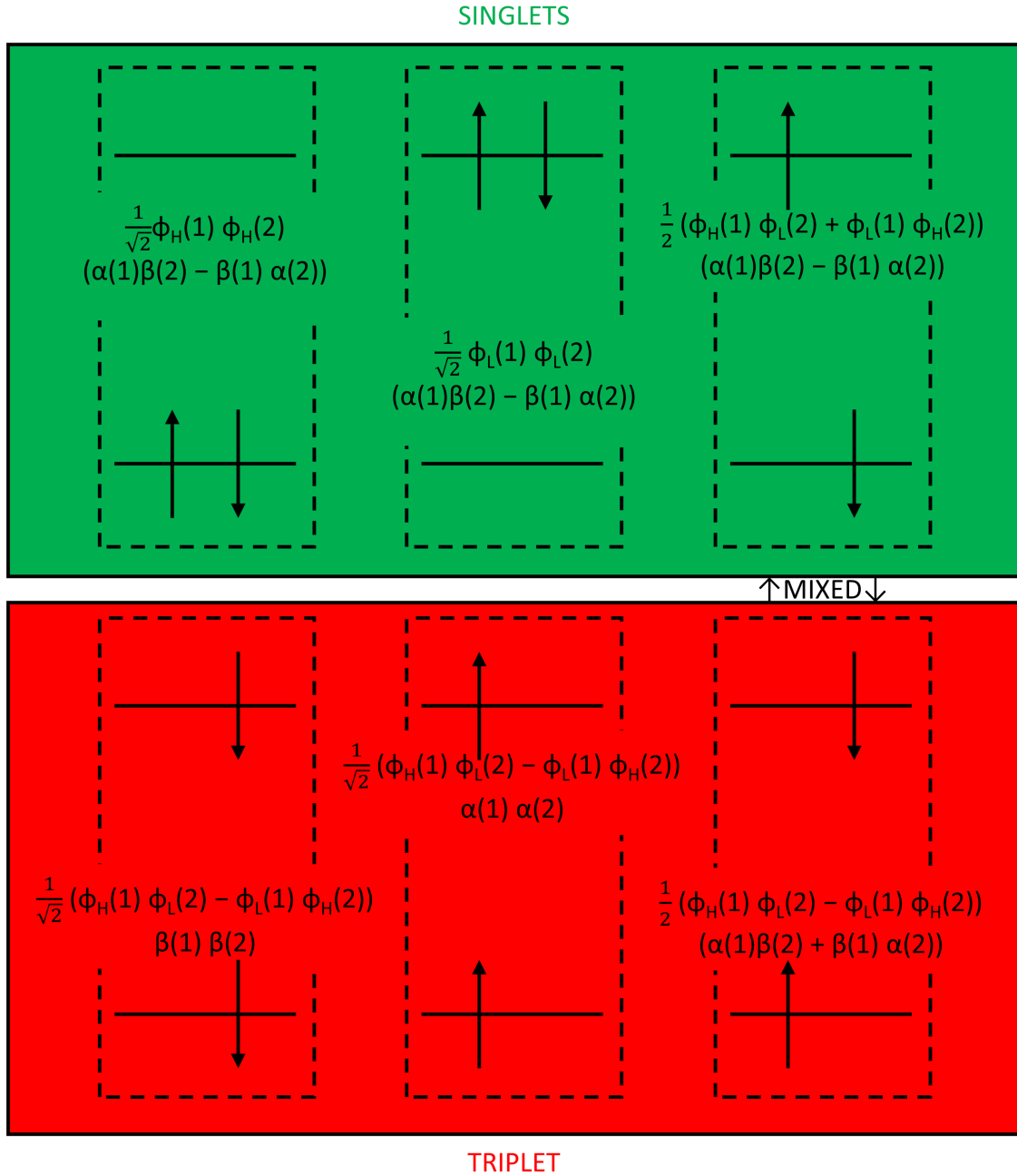


Figure B.1: All possible state generated by the double occupation of 2 spin sates(α , β), and 2 single electron orbitals (ϕ_H , ϕ_L)

singlet and triplet excited states (ie. with single HOMO and LUMO occupation). The energies of each electronic state may be calculated via the expectation of the total wave-function ie. $\langle \Phi | H_e | \Phi \rangle$. Usually this is expressed in terms of the nuclear repulsion operator (V_{nn}), and the 1 electron (h_i) and 2 electron ($g_{i,j}$) operators described below, where the nuclear repulsion operator is independent of electrons, the 1 electron function acts on an individual electron (i), and the 2 electron function on two electron (i,j). The 1 electron function contains the kinetic energy and nuclear attraction energy, and the two electron operator contains the electron-electron repulsion.

$$h_i = -\frac{1}{2} \nabla_i^2 - \sum_A^{N_{nuclei}} \frac{Z_A}{R_A - r_i} \quad (\text{B.16})$$

$$g_{i,j} = \frac{1}{r_i - r_j} \quad (\text{B.17})$$

$$H_e = \sum_i^{N_{elec}} h_i + \sum_{j>i}^{N_{elec}} g_{i,j} + V_{nn} \quad (\text{B.18})$$

It may be shown that the energies of the singlet and triplet state correspond to the following equations using this property. This relies on the knowledge that electrons are indistinguishable, and hence that e.g. $\langle \phi_H(1) | h_i | \phi_H(1) \rangle = \langle \phi_H(2) | H_e | \phi_H(2) \rangle$, and that the 1 electron orbitals used are orthogonal, so that: $\langle \phi_H(1) \phi_L(2) | h_i | \phi_H(2) \phi_L(1) \rangle = \langle \phi_H(2) | \phi_L(2) \rangle \langle \phi_H(1) | h_i | \phi_L(1) \rangle = 0$.

$$\langle \Phi_{S_1} | H_e | \Phi_{S_1} \rangle \quad (\text{B.19})$$

$$\begin{aligned} &= \langle \phi_H(1) | h_i | \phi_H(1) \rangle + \langle \phi_L(1) | h_i | \phi_L(1) \rangle + \langle \phi_H(1) \phi_L(2) | g_{i,j} | \phi_H(1) \phi_L(2) \rangle \\ &\quad + \langle \phi_H(1) \phi_L(2) | g_{i,j} | \phi_H(2) \phi_L(1) \rangle \end{aligned} \quad (\text{B.20})$$

$$\begin{aligned} &\langle \Phi_{T_1,-1} | H_e | \Phi_{T_1,-1} \rangle = \langle \Phi_{T_1,0} | H_e | \Phi_{T_1,0} \rangle = \langle \Phi_{T_1,+1} | H_e | \Phi_{T_1,+1} \rangle \\ &= \langle \phi_H(1) | h_i | \phi_H(1) \rangle + \langle \phi_L(1) | h_i | \phi_L(1) \rangle + \langle \phi_H(1) \phi_L(2) | g_{i,j} | \phi_H(1) \phi_L(2) \rangle \\ &\quad - \langle \phi_H(1) \phi_L(2) | g_{i,j} | \phi_H(2) \phi_L(1) \rangle \end{aligned} \quad (\text{B.21})$$

Hence the energy difference is:

$$\langle \Phi_{S_1} | H_e | \Phi_{S_1} \rangle - \langle \Phi_{T_1,0} | H_e | \Phi_{T_1,0} \rangle = 2 \langle \phi_H(1) \phi_L(2) | g_{i,j} | \phi_H(2) \phi_L(1) \rangle \quad (\text{B.22})$$

B.1.2 Taylor Expansion Of Fermis Golden Rule For Vibronic Coupling About Normal Modes

Fermis Golden rule states that the rate of transition between two state is as follows, where $k_{i \rightarrow f}$ is the rate of transfer between the initial state (Ψ_i) and the final state (Ψ_f) as the results of a perturbing hamiltonian (H'), where ρ is the density of states.

$$k_{i \rightarrow f} = \frac{2\pi}{\hbar} \langle \Psi_f | H' | \Psi_i \rangle^2 \rho \quad (\text{B.23})$$

However usually the two states used are purely electronic, occurring at a single unchanging geometry. This neglects the variety of geometries available for spin orbit coupling. In order to model the changes that occur due to this, the equation is usually expanded using a Taylor expansion about this base geometry, with normal modes as the parameter expanded over. A taylor expansion in several variables of the function $f(x_1, \dots, x_n)$ about the point where $(x_1, \dots, x_n) = a_1, \dots, a_n$, is as follows:

$$\begin{aligned} f(x_1, \dots, x_n) \approx & f(a_1, \dots, a_n) + \sum_{j=1}^n \frac{1}{1!} \frac{\partial f(a_1, \dots, a_n)}{\partial x_j} (x_j - a_j) \\ & + \sum_{j=1}^n \sum_{k=1}^n \frac{1}{2!} \frac{\partial^2 f(a_1, \dots, a_n)}{\partial x_j \partial x_k} (x_j - a_j)(x_k - a_k) + \dots \end{aligned} \quad (\text{B.24})$$

In order to expand fermis golden rule in this manner, a set of coordinates along the normal mode must be created. These coordinates are usually written as Q_n where n is the relevant normal mode. A value of Q_n may be seen as the movement of all atoms a unit vectors distance in the direction of normal mode n, relative to a defined standard position Q_0 . If the position of each nucleus is written as a vector, where each column corresponds to a different atomic nucleus, and the cartesian location is expressed in terms of (x,y,z) coordinate represented by their $\hat{i}$, $\hat{j}$, $\hat{k}$ unit vectors, this means that the nuclear position would change by the following formula:

$$\begin{pmatrix} C_{x-1}\hat{i} + C_{y-1}\hat{j} + C_{z-1}\hat{k} \\ C_{x-2}\hat{i} + C_{y-2}\hat{j} + C_{z-2}\hat{k} \\ \vdots \\ C_{x-m}\hat{i} + C_{y-m}\hat{j} + C_{z-m}\hat{k} \end{pmatrix} + \begin{pmatrix} D_{x-1}\hat{i} + D_{y-1}\hat{j} + D_{z-1}\hat{k} \\ D_{x-2}\hat{i} + D_{y-2}\hat{j} + D_{z-2}\hat{k} \\ \vdots \\ D_{x-m}\hat{i} + D_{y-m}\hat{j} + D_{z-m}\hat{k} \end{pmatrix} = Q_0 + Q_n \quad (\text{B.25})$$

This allows the the spin orbit coupling including vibronic coupling (H_{SO-VIB}) to be expressed in terms of the spin orbit coupling without (H_{SO}). The following formula expands (H_{SO-VIB}) in terms of H_{SO} , where $[f(x)]_{Q_0}$ is used to express the

calculation of the function at the position Q_0

$$\begin{aligned}
 \langle \Psi_f | H_{SO-VIB} | \Psi_i \rangle &\approx [\langle \Psi_f | H_{SO-VIB} | \Psi_i \rangle]_{Q_0} \\
 &+ \sum_{j=1}^n \frac{1}{1!} \left[\frac{\partial \langle \Psi_f | H_{SO-VIB} | \Psi_i \rangle}{\partial Q_j} \right]_{Q_0} (Q_j) \\
 &+ \sum_{j=1}^n \sum_{k=1}^n \frac{1}{2!} \left[\frac{\partial^2 \langle \Psi_f | H_{SO-VIB} | \Psi_i \rangle}{\partial Q_j \partial Q_k} \right]_{Q_0} (Q_j)(Q_k) \\
 &+ \dots
 \end{aligned} \tag{B.26}$$

In order to simplify this, the defining $Q_0 = \underline{0}$ where $\underline{0}$ is the zero vector is possible. This means all normal modes are written relative to the reference geometry (Q_0). In addition, it may be observed that $[\langle \Psi_f | H_{SO-VIB} | \Psi_i \rangle]_{Q_0} = \langle \Psi_f | H_{SO} | \Psi_i \rangle$, ie. the value with no spin orbit coupling. An additional approximation is also made, that $\left[\frac{\partial \langle \Psi_f | H_{SO-VIB} | \Psi_i \rangle}{\partial x_j} \right]_{Q_0} = \left[\frac{\partial \langle \Psi_f | H_{SO} | \Psi_i \rangle}{\partial x_j} \right]_{Q_0}$ this is akin to assuming that the spin orbit operator is not itself dependent on the vibronic coupling, and that it is only the wave function that is. These approximations lead to the following set of equations:

$$\langle \Psi_f | H_{SO-VIB} | \Psi_i \rangle \approx \langle \Psi_f | H_{SO} | \Psi_i \rangle \tag{B.27}$$

$$+ \sum_{j=1}^n \frac{1}{1!} \left[\frac{\partial \langle \Psi_f | H_{SO} | \Psi_i \rangle}{\partial Q_j} \right]_{Q_0} (Q_j - Q_0) \tag{B.28}$$

$$+ \sum_{j=1}^n \sum_{k=1}^n \frac{1}{2!} \left[\frac{\partial^2 \langle \Psi_f | H_{SO} | \Psi_i \rangle}{\partial Q_j \partial Q_k} \right]_{Q_0} (Q_j - Q_0)(Q_k - Q_0) \tag{B.29}$$

$$+ \dots \tag{B.30}$$

Taking the first three terms of this equation leads to the three first terms in equation 1.26.

B.1.3 Perturbation Theory To 2nd order: Fermis Golden Rule And Beyond

B.1.3.1 Perturbation Theory To 2nd Order

In order to calculate the rate of transfer between two states, Fermi's golden rule is often employed. Fermi's golden rule states that the rate of transition between two state is as follows, where $k_{i \rightarrow f}$ is the rate of transfer between the initial state (Ψ_i)

and the final state (Ψ_f) as the results of a perturbing hamiltonian (H').

$$k_{i \rightarrow f} = \frac{2\pi}{\hbar} \langle \Psi_f | H' | \Psi_i \rangle^2 \quad (\text{B.31})$$

The derivation of this equation, however, leaves higher order terms which can be added to any model, in order to get a higher level of accuracy. The derivation of Fermis golden rule requires, however, knowledge of perturbation theory, and this will be addressed first in this section.

First, consider a quantum system, where the Hamiltonian (H_0) is known, as is the eigenfunctions ($\Psi_{0,n}$), and the eigen values ($E_{0,n}$). To this system a small change in potential is applied, with value H' . In addition let us introduce a parameter λ , which will multiply the value of H' . This value of λ is 1, however introducing it allows us to employ a mathematical trick, but in order to do this, it must be stated that λ can vary between 0 and 1. Once again, this is artificial, and in nature it is 1. This allows the following equation to be written, in terms of the new hamiltonian (H) of the system:

$$H = H_0 + \lambda H' \quad (\text{B.32})$$

The applied potential (H') allows for the old eigenvectors to mix (Note: these form a complete set, and so any new eigenvector can be expressed in terms of them), and what is desired is the new wavefunction (Ψ_n), and eigenvalues (E_n). In order to express these new functions, they are written as a taylor expansion. The equation for a taylor expansion is as follows, where $f(x)$ is the function, expanded about at position $x = a$.

$$f(x) \approx f(a) + \frac{1}{1!} \frac{df(a)}{dx} (x - a) + \frac{1}{2!} \frac{d^2 f(a)}{dx^2} (x - a)^2 + \dots \quad (\text{B.33})$$

The Taylor expansion is done about $\lambda = 0$, and this is why λ must be written as being variable between 0 and 1. Note: a taylor expansion works best for values close to where the expansion is done. However in nature λ is 1. This means that the results of the taylor expansion must be similar between when $\lambda = 0$ and 1, and hence the perturbation must be small. The perturbation being small is the fundamental assumption of perturbation theory. Expanding about $\lambda = 0$ gives the following equations:

$$\Psi_n \approx \Psi_{0,n} + \frac{1}{1!} \frac{d\Psi_{0,n}}{d\lambda}(\lambda) + \frac{1}{2!} \frac{d^2 \Psi_{0,n}}{d\lambda^2}(\lambda)^2 + \dots \quad (\text{B.34})$$

$$E_n \approx E_{0,n} + \frac{1}{1!} \frac{dE_{0,n}}{d\lambda}(\lambda) + \frac{1}{2!} \frac{d^2 E_{0,n}}{d\lambda^2}(\lambda)^2 + \dots \quad (\text{B.35})$$

In these equations, the λ parameters remain important. When equation B.32 is looked back on, it is noted that λ and the perturbation H' are multiplied. Further when λ is 0 there is no perturbation, where as when it is 1 there is the full perturbation. This means that when λ is squared, one can expect the square of H' to be applied. Because squared numbers make up a lower proportion of bigger number when they are both squared, this means that the terms containing λ^2 are smaller than those with λ , and further consecutive terms become more and more insignificant.

When the new hamiltonian is considered, the following equation is produced:

$$\begin{aligned} (H_0 + \lambda H') \left(\Psi_{0,n} + \frac{1}{1!} \frac{d\Psi_{0,n}}{d\lambda} \lambda + \frac{1}{2!} \frac{d^2\Psi_{0,n}}{d\lambda^2} \lambda^2 + \dots \right) \\ = \left(E_{0,n} + \frac{1}{1!} \frac{dE_{0,n}}{d\lambda}(\lambda) + \frac{1}{2!} \frac{d^2E_{0,n}}{d\lambda^2}(\lambda)^2 + \dots \right) \left(\Psi_{0,n} \right. \\ \left. + \frac{1}{1!} \frac{d\Psi_{0,n}}{d\lambda}(\lambda) + \frac{1}{2!} \frac{d^2\Psi_{0,n}}{d\lambda^2}(\lambda)^2 + \dots \right) \end{aligned} \quad (\text{B.36})$$

from here, terms in terms of λ can be grouped. Henceforth the equations will only be shown up to second order (λ^2)

$$\lambda^0 H_0 \Psi_{0,n} = \lambda^0 E_{0,n} \Psi_{0,n} \quad (\text{B.37})$$

$$\lambda^1 \left(H_0 \frac{d\Psi_{0,n}}{d\lambda} + H' \Psi_{0,n} \right) = \lambda^1 \left(E_{0,n} \frac{d\Psi_{0,n}}{d\lambda} + \Psi_{0,n} \frac{dE_{0,n}}{d\lambda} \right) \quad (\text{B.38})$$

$$\lambda^2 \left(H_0 \frac{d^2\Psi_{0,n}}{d\lambda^2} + H' \frac{d\Psi_{0,n}}{d\lambda} \right) = \lambda^2 \left(E_{0,n} \frac{d^2\Psi_{0,n}}{d\lambda^2} + \frac{d\Psi_{0,n}}{d\lambda} \frac{dE_{0,n}}{d\lambda} + \Psi_{0,n} \frac{d^2E_{0,n}}{d\lambda^2} \right) \quad (\text{B.39})$$

Prior to proceeding with simplifying these equations, the "intermediate normalisation" must be enforced. Currently, there is no reason to believe that $\Psi_{0,n}$ is orthogonal to its derivatives. However, if the "intermediate normalisation" is enforced, then it become so. It is noted that Ψ_n may be normalised in any way desired. As such, instead of the standard normalisation, using $\langle \Psi_n | \Psi_n \rangle = 1$, the normalisation $\langle \Psi_{0,n} | \Psi_n \rangle = 1$ is used. This allows the following maths

$$\langle \Psi_{0,n} | \Psi_n \rangle = \langle \Psi_{0,n} | \Psi_{0,n} + \frac{1}{1!} \frac{d\Psi_{0,n}}{d\lambda} \lambda + \frac{1}{2!} \frac{d^2\Psi_{0,n}}{d\lambda^2} \lambda^2 + \dots \rangle \quad (\text{B.40})$$

$$1 = \langle \Psi_{0,n} | \Psi_{0,n} \rangle + \langle \Psi_{0,n} | \frac{1}{1!} \frac{d\Psi_{0,n}}{d\lambda} \lambda \rangle + \langle \Psi_{0,n} | \frac{1}{2!} \frac{d^2\Psi_{0,n}}{d\lambda^2} \lambda^2 + \dots \rangle \quad (\text{B.41})$$

$$1 = 1 + \langle \Psi_{0,n} | \left| \frac{1}{1!} \frac{d\Psi_{0,n}}{d\lambda} \lambda \right\rangle + \langle \Psi_{0,n} | \left| \frac{1}{2!} \frac{d^2\Psi_{0,n}}{d\lambda^2} \lambda^2 + \dots \right\rangle \quad (\text{B.42})$$

$$0 = \lambda \langle \Psi_{0,n} | \left| \frac{1}{1!} \frac{d\Psi_{0,n}}{d\lambda} \right\rangle + \lambda^2 \langle \Psi_{0,n} | \left| \frac{1}{2!} \frac{d^2\Psi_{0,n}}{d\lambda^2} + \dots \right\rangle \quad (\text{B.43})$$

Because each individual term in λ is a single dot product between $\Psi_{0,n}$ and its derivative, and because λ can be varies between 0 and 1, this means that each individual dot product must be zero, and hence the $\Psi_{0,n}$ is orthogonal to all of its derivatives. ie.

$$\langle \Psi_{0,n} | \left| \frac{d^m \Psi_{0,n}}{d\lambda^m} \right\rangle = 0 \text{ for } m > 0 \quad (\text{B.44})$$

From here the first order energy equation (equation B.38) can be solved by multiplying left by the complex conjugate of the unperturbed wavefunction ($\langle \Psi_{0,n} |$). This involves knowing that $\langle \Psi_{0,n} | \Psi_{0,n} \rangle = 1$, $\langle \Psi_{0,n} | \left| \frac{d\Psi_{0,n}}{d\lambda} \right\rangle = 0$ and $\langle \Psi_{0,n} | H_0 \left| \frac{d\Psi_{0,n}}{d\lambda} \right\rangle = E_n \langle \Psi_{0,n} | \Psi_{0,n} \rangle^*$

$$\langle \Psi_{0,n} | H' | \Psi_{0,n} \rangle = \frac{dE_{0,n}}{d\lambda} \quad (\text{B.45})$$

Additionally the change in wavefunction to first order can be calculated by multiplying equation B.38 left by a complex conjugate of an orthogonal wavefunction of the unperturbed wavefunction ($\langle \Psi_{0,m} |$), this leads to

$$\langle \Psi_{0,m} | \left| \frac{d\Psi_{0,n}}{d\lambda} \right\rangle = \frac{\langle \Psi_{0,m} | V | \Psi_{0,n} \rangle}{E_n - E_m} \quad (\text{B.46})$$

Because the solutions to the unperturbed wavefunctions form a complete set, this means that any wavefunction can be expressed in terms of them. This means the following is true:

$$\left| \frac{d\Psi_{0,n}}{d\lambda} \right\rangle = \sum_m |\Psi_{0,m}\rangle \langle \Psi_{0,m} | \left| \frac{d\Psi_{0,n}}{d\lambda} \right\rangle \quad (\text{B.47})$$

However from the intermediate normalisation we know $\langle \Psi_{0,n} | \left| \frac{d\Psi_{0,n}}{d\lambda} \right\rangle = 0$ hence

$$\left| \frac{d\Psi_{0,n}}{d\lambda} \right\rangle = \sum_{m \neq n} |\Psi_{0,m}\rangle \langle \Psi_{0,m} | \left| \frac{d\Psi_{0,n}}{d\lambda} \right\rangle \quad (\text{B.48})$$

from equation B.46, we then have

$$\left| \frac{d\Psi_{0,n}}{d\lambda} \right\rangle = \sum_{m \neq n} |\Psi_{0,m}\rangle \frac{\langle \Psi_{0,m} | V | \Psi_{0,n} \rangle}{E_n - E_m} \quad (\text{B.49})$$

*Note: this is because of the hermitian properties of the operators, meaning $\langle \Psi_{0,n} | H_0 = E_n \langle \Psi_{0,n} |$ because $\langle \Psi_{0,n} | H_0 = (\langle \Psi_{0,n} | H_0^\dagger) = (H_0 | \Psi_{0,n})^\dagger = (E_n | \Psi_{0,n})^\dagger = E_n^\dagger \langle \Psi_{0,n} | = E_n \langle \Psi_{0,n} |$

And hence the new wavefunction can be calculated.

The second order wavefunction and energy can also be calculated from equation B.39. The energy is calculated by multiplying left by $\langle \Psi_{0,n} |$, this yields upon rearrangement, and simplification, and employing the results of the intermediate normalisation:

$$\frac{d^2 E_{0,n}}{d\lambda^2} = \langle \Psi_{0,n} | H' | \frac{d\Psi_{0,n}}{d\lambda} \rangle \quad (\text{B.50})$$

Using the result from equation B.69 this may be expressed as

$$\frac{d^2 E_{0,n}}{d\lambda^2} = \sum_{k \neq n} \frac{\langle \Psi_{0,n} | H' | \Psi_{0,m} \rangle \langle \Psi_{0,m} | H' | \Psi_{0,n} \rangle}{E_n - E_k} \quad (\text{B.51})$$

In order to express the wavefunction, a slight simplification in notation must be made, this is as follows:

$$| \frac{d\Psi_{0,n}}{d\lambda} \rangle = \sum_{m \neq n} | \Psi_{0,m} \rangle \frac{\langle \Psi_{0,m} | V | \Psi_{0,n} \rangle}{E_n - E_m} \quad (\text{B.52})$$

$$= \sum_m | \Psi_{0,m} \rangle \langle \Psi_{0,m} | | \frac{d\Psi_{0,n}}{d\lambda} \rangle \quad (\text{B.53})$$

$$= \sum_m c_{m,n,1} | \Psi_{0,m} \rangle \quad (\text{B.54})$$

$$c_{m,n,1} = \langle \Psi_{0,m} | | \frac{d\Psi_{0,n}}{d\lambda} \rangle \quad (\text{B.55})$$

$$= \frac{\langle \Psi_{0,m} | V | \Psi_{0,n} \rangle}{E_n - E_m} \quad (\text{B.56})$$

$$| \frac{d^2 \Psi_{0,n}}{d\lambda^2} \rangle = \sum_m | \Psi_{0,m} \rangle \langle \Psi_{0,m} | | \frac{d^2 \Psi_{0,n}}{d\lambda^2} \rangle \quad (\text{B.57})$$

$$= \sum_{m \neq n} | \Psi_{0,m} \rangle \langle \Psi_{0,m} | | \frac{d^2 \Psi_{0,n}}{d\lambda^2} \rangle \quad (\text{B.58})$$

$$= \sum_m c_{m,n,2} | \Psi_{0,m} \rangle \quad (\text{B.59})$$

$$c_{m,n,2} = \langle \Psi_{0,m} | | \frac{d^2 \Psi_{0,n}}{d\lambda^2} \rangle \quad (\text{B.60})$$

When equation B.39 is multiplied left by $\langle \Psi_{0,k} |$ ie. an orthogonal wavefunction to $\langle \Psi_{0,n} |$, and the equation is simplified, the following equation is gained:

$$c_{k,n,2} = \frac{1}{E_k - E_n} \left(c_{k,n,1} \frac{dE_{0,n}}{d\lambda} - \sum_m c_{m,n,1} \langle \Psi_{0,n} | V | \Psi_{0,m} \rangle \right) \quad (\text{B.61})$$

substituting in for $c_{x,n,1}$ from equation B.56, and $\frac{dE_{0,n}}{d\lambda}$ from equation B.67 yields:

$$c_{k,n,2} = \frac{1}{E_k - E_n} \left(\frac{\langle \Psi_{0,k} | V | \Psi_{0,n} \rangle}{E_n - E_k} \langle \Psi_{0,n} | H' | \Psi_{0,n} \rangle - \sum_m \frac{\langle \Psi_{0,m} | V | \Psi_{0,n} \rangle}{E_n - E_m} \langle \Psi_{0,n} | V | \Psi_{0,m} \rangle \right) \quad (\text{B.62})$$

Hence

$$\frac{d^2 \Psi_{0,n}}{d\lambda^2} = \sum_k \frac{1}{E_k - E_n} \left(\frac{\langle \Psi_{0,k} | V | \Psi_{0,n} \rangle}{E_n - E_k} \langle \Psi_{0,n} | H' | \Psi_{0,n} \rangle - \sum_m \frac{\langle \Psi_{0,m} | V | \Psi_{0,n} \rangle}{E_n - E_m} \langle \Psi_{0,n} | V | \Psi_{0,m} \rangle \right) \Psi_{0,k} \quad (\text{B.63})$$

B.1.3.2 Perturbation Theory With Multiple Perturbations

While the prior description only contains one perturbation, it is entirely possible to use several perturbations, or a series in the formalism. This is what is explored here. The hamiltonoian used will be as follows

$$H = H_0 + \lambda H'_1 + \lambda H'_2 + \dots \quad (\text{B.64})$$

This can be directly substituted into the equations already calculated using

$$H' = H'_1 + H'_2 + \dots \quad (\text{B.65})$$

and this yields the following equations:

$$\frac{dE_{0,n}}{d\lambda} = \langle \Psi_{0,n} | H' | \Psi_{0,n} \rangle \quad (\text{B.66})$$

$$= \sum_s \langle \Psi_{0,n} | H'_s | \Psi_{0,n} \rangle \quad (\text{B.67})$$

$$\left| \frac{d\Psi_{0,n}}{d\lambda} \right\rangle = \sum_{m \neq n} |\Psi_{0,m}\rangle \frac{\langle \Psi_{0,m} | V | \Psi_{0,n} \rangle}{E_n - E_m} \quad (\text{B.68})$$

$$= \sum_s \sum_{m \neq n} |\Psi_{0,m}\rangle \frac{\langle \Psi_{0,m} | H'_s | \Psi_{0,n} \rangle}{E_n - E_m} \quad (\text{B.69})$$

$$\frac{d^2 E_{0,n}}{d\lambda^2} = \sum_{k \neq n} \frac{\langle \Psi_{0,n} | H' | \Psi_{0,m} \rangle \langle \Psi_{0,m} | H' | \Psi_{0,n} \rangle}{E_n - E_k} \quad (\text{B.70})$$

$$= \sum_s \sum_{k \neq n} \frac{\langle \Psi_{0,n} | H'_s | \Psi_{0,m} \rangle \langle \Psi_{0,m} | H'_s | \Psi_{0,n} \rangle}{E_n - E_k} \quad (\text{B.71})$$

$$+ \sum_s \sum_{q \neq s} \sum_{k \neq n} \frac{\langle \Psi_{0,n} | H'_s | \Psi_{0,m} \rangle \langle \Psi_{0,m} | H'_q | \Psi_{0,n} \rangle}{E_n - E_k} \quad (\text{B.72})$$

$$\frac{d^2 \Psi_{0,n}}{d\lambda^2} = \sum_k \frac{1}{E_k - E_n} \left(\frac{\langle \Psi_{0,k} | V | \Psi_{0,n} \rangle}{E_n - E_k} \langle \Psi_{0,n} | H' | \Psi_{0,n} \rangle \right. \quad (\text{B.73})$$

$$\left. - \sum_m \frac{\langle \Psi_{0,m} | V | \Psi_{0,n} \rangle}{E_n - E_m} \langle \Psi_{0,n} | V | \Psi_{0,m} \rangle \right) \Psi_{0,k} \quad (\text{B.74})$$

$$= \sum_s \sum_k \frac{1}{E_k - E_n} \left(\frac{\langle \Psi_{0,k} | H'_s | \Psi_{0,n} \rangle}{E_n - E_k} \langle \Psi_{0,n} | H'_s | \Psi_{0,n} \rangle - \right. \quad (\text{B.75})$$

$$\left. \sum_m \frac{\langle \Psi_{0,m} | H'_s | \Psi_{0,n} \rangle}{E_n - E_m} \langle \Psi_{0,n} | H'_s | \Psi_{0,m} \rangle \right) \Psi_{0,k} \\ + \sum_{q \neq s} \sum_q \sum_k \frac{1}{E_k - E_n} \left(\frac{\langle \Psi_{0,k} | H'_s | \Psi_{0,n} \rangle}{E_n - E_k} \langle \Psi_{0,n} | H'_q | \Psi_{0,n} \rangle \right. \quad (\text{B.76})$$

$$\left. - \sum_m \frac{\langle \Psi_{0,m} | H'_s | \Psi_{0,n} \rangle}{E_n - E_m} \langle \Psi_{0,n} | H'_q | \Psi_{0,m} \rangle \right) \Psi_{0,k} \quad (\text{B.77})$$

Of particular interest in these expansions are the cross terms shown as the final terms in the equations for $\frac{d^2 E_{0,n}}{d\lambda^2}$ and $\frac{d^2 \Psi_{0,n}}{d\lambda^2}$. These terms are not present in the original perturbation interpretation.

An additional change may be that that the perturbation is not known, and so this itself must be expanded in terms of λ . This will not be discussed in this thesis, but may explain some of the versions of perturbation theory in the literature.

B.1.3.3 Fermi's Golden Rule, And Incorporating Higher Orders

Thus far how the various wavefunction change according to perturbation theory has been discussed. However, what is of interest is the rate of transfer between two state, an initial one, and a final one, under the application of a perturbation. This is most commonly expressed via Fermis golden rule. Fermi's golden rule states that the rate of transition between two state is as follows, where $k_{i \rightarrow f}$ is the rate of transfer between the initial state (Ψ_i) and the final state (Ψ_f) as the results of a perturbing hamiltonian (H').

$$k_{i \rightarrow f} = \frac{2\pi}{\hbar} \langle \Psi_f | H' | \Psi_i \rangle^2 \quad (\text{B.78})$$

The proof for Fermi's this is somewhat in depth, requiring knowledge of the time dependent schrodinger equation and a perturbation theory expansion. As such the proof of Fermis golden rule will only be sketched here.

Initially, prior to the application of light, the Hamiltonian is in discrete states ie. the eigenvectors of the system. The time dependent Hamiltonian is as follows, where $\Psi_{n,t,0}$ is a *time dependent* eigenvectors of the unperturbed hamiltonian (H_0)

$$i\hbar \frac{\partial}{\partial t} |\Psi_{n,t,0}\rangle = H_0 |\Psi_{n,t,0}\rangle \quad (\text{B.79})$$

This equation can be solved to split the hamiltonian into time dependent and time-independent component $\Psi_{n,t_0,0}$. For the sake of this proof, it will be assumed at $t = t_0 \implies \Psi_{n,t,0} = \Psi_{n,t_0,0}$, where the latter has no time dependence. In the following equation, several new terms are introduced $E_{n,0}$ is the eigenvector for $\Psi_{n,t_0,0}$ and $\omega_{n,0} = \frac{E_{n,0}}{\hbar}$:

$$|\Psi_{n,t,0}\rangle = e^{-\frac{iE_{n,0}(t-t_0)}{\hbar}} |\Psi_{n,t_0,0}\rangle = e^{-i\omega_{n,0}(t-t_0)} |\Psi_{n,t_0,0}\rangle \quad (\text{B.80})$$

When the perturbation from light is applied, the following hamiltonian is formed, where H' is the new wavefunction:

$$i\hbar \frac{\partial}{\partial t} |\Psi_{n,t,0}\rangle = (H_0 + H') |\Psi_{n,t,0}\rangle \quad (\text{B.81})$$

In practice the previous equation is said to be unsolvable even for simple perturbations. In order to progress with these proof, it is helpful to create a new set of vectors of the time dependent system . This allows the formation of vectors which do not change with time under the unperturbed hamiltonian, and are as follows:

$$|\Phi_{n,t}\rangle = e^{-\frac{iH_0(t-t_0)}{\hbar}} |\Phi_n(t)\rangle \quad (\text{B.82})$$

Note: The exponential of an operator is defined by its Taylor series expansion. It may be observed that the prior equation can be substituted into equation B.79 and it still holds, however there remains time dependence in wavefunction. If it is defined that $|\Phi_{n,t=t_0}\rangle = \Psi_{n,t_0,0}$, it may be observed that this function is equally capable of showing the time dependence of the unperterbed wavefunction because equation B.79 holds, the problem is that $\Phi_n(t)$ is not known, this will be the aim of the rest of the proof. Particularly we want to know how this wavefunction progresses when the perturbation is applied. THis may be done by substituting this new eigenvector value into equation B.81, and cancelling equal terms, the following equation is formed:

$$i\hbar \frac{\partial}{\partial t} |\Phi_n(t)\rangle = e^{+i\frac{H_0 t}{\hbar}} H' e^{-i\frac{H_0 t}{\hbar}} |\Phi_n(t)\rangle = H'(t) |\Phi_n(t)\rangle \quad (\text{B.83})$$

In this equation, a new time dependent function is defined $H'(t) = e^{+i\frac{H_0 t}{\hbar}} H' e^{-i\frac{H_0 t}{\hbar}}$. In order to calculate how the wavefunction progresses, all that needs to be done is to integrate this equation, this is done as follows

$$\int_{t_0}^t i\hbar \frac{\partial}{\partial t} |\Phi_n(t)\rangle dt = \int_{t_0}^t H'(t) |\Phi_n(t)\rangle dt \quad (\text{B.84})$$

$$|\Phi_n(t)\rangle = |\Phi_n(t_0)\rangle + \frac{1}{i\hbar} \int_{t_0}^t H'(t) |\Phi_n(t)\rangle dt \quad (\text{B.85})$$

Of course this remaining integral is unsolvable, but the following expansion may be made, by expanding $|\Phi_n(t)\rangle$ recursively (Note it appears on both sides of the equation B.85)

$$\begin{aligned} |\Phi_n(t)\rangle = & |\Phi_n(t_0)\rangle \\ & + \frac{1}{i\hbar} \int_{t_0}^t H'(t) \left(|\Phi_n(t_0)\rangle \right. \\ & \quad \left. + \frac{1}{i\hbar} \int_{t_0}^t H'(t) \left(|\Phi_n(t_0)\rangle \right. \right. \\ & \quad \left. \left. + \dots \right. \right. \\ & \quad \left. \left. + \frac{1}{i\hbar} \int_{t_0}^t H'(t) |\Phi_n(t)\rangle \right) dt^\infty \end{aligned} \quad (\text{B.86})$$

Because the perturbation H' is small, it may be treated as a perturbation theory expansion as follows

$$|\Phi_n(t)\rangle = |\Phi_{0,n}(t)\rangle + |\Phi_{1,n}(t)\rangle + |\Phi_{2,n}(t)\rangle + \dots \quad (\text{B.87})$$

$$|\Phi_{0,n}(t)\rangle = |\Phi_n(t_0)\rangle \quad (\text{B.88})$$

$$|\Phi_{1,n}(t)\rangle = \frac{1}{i\hbar} \int_{t_0}^t H'(t) (|\Phi_n(t_0)\rangle) dt \quad (\text{B.89})$$

$$|\Phi_{2,n}(t)\rangle = \frac{1}{i\hbar} \int_{t_0}^t H'(t) \frac{1}{i\hbar} \int_{t_0}^t H'(t') (|\Phi_n(t_0)\rangle) dt' dt \quad (\text{B.90})$$

The probability magnitude in state $\Psi_{m,t_0,0}$ after initial perturbation is now given by the following equation

$$\langle m | |\Phi_n(t)\rangle \quad (\text{B.91})$$

Note the actual probability of transition is the normalised square of this value. From here the probability from each order of the wavefunction can be calculated. However in order to do this, the effect of the operators $e^{+i\frac{H_0 t}{\hbar}}$ and $e^{-i\frac{H_0 t}{\hbar}}$ must be

examined. It may be shown that $e^{+i\frac{H_0 t}{\hbar}} \Psi_{m,t_0,0} = e^{+i\frac{E_{m,0} t}{\hbar}} \Psi_{m,t_0,0}$ and similarly for negative form where $E_{m,0}$ is the eigenvalue of the $\Psi_{m,t_0,0}$ eigenfunction of H_0 . This is shown below using the expansion of the operator:

$$e^{+i\frac{H_0 t}{\hbar}} \Psi_{m,t_0,0} = \sum_{n=0}^{\infty} \frac{(iH_0 t)^n}{n!} \Psi_{m,t_0,0} = \sum_{n=0}^{\infty} \frac{(iE_{m,0} t)^n}{n!} \Psi_{m,t_0,0} = e^{+i\frac{E_{m,0} t}{\hbar}} \Psi_{m,t_0,0} \quad (\text{B.92})$$

This allows for the following expansions:

$$\langle \Psi_{m,t_0,0} | \Phi_{0,n}(t) \rangle = \langle \Psi_{m,t_0,0} | \Psi_{n,t_0,0} \rangle = 0 \quad (\text{B.93})$$

$$\begin{aligned} \langle \Psi_{m,t_0,0} | \Phi_{1,n}(t) \rangle &= \frac{1}{i\hbar} \int_{t_0}^t \langle \Psi_{m,t_0,0} | H'(t) | \Psi_{n,t_0,0} \rangle dt \\ &= \frac{1}{i\hbar} \int_{t_0}^t \langle \Psi_{m,t_0,0} | H'(t) | \Psi_{n,t_0,0} \rangle dt \\ &= \frac{1}{i\hbar} \int_{t_0}^t \langle \Psi_{m,t_0,0} | e^{+i\frac{H_0 t}{\hbar}} H' e^{-i\frac{H_0 t}{\hbar}} | \Psi_{n,t_0,0} \rangle dt \\ &= \langle \Psi_{m,t_0,0} | H' | \Psi_{n,t_0,0} \rangle \frac{1}{i\hbar} \int_{t_0}^t e^{+i\frac{(E_{m,0}-E_{n,0})t}{\hbar}} H' dt \\ &= \langle \Psi_{m,t_0,0} | H' | \Psi_{n,t_0,0} \rangle \frac{1}{i\hbar} \frac{e^{+i(\omega_{m,0}-\omega_{n,0})t} - 1}{i(\omega_{m,0} - \omega_{n,0})} \\ &= \langle \Psi_{m,t_0,0} | H' | \Psi_{n,t_0,0} \rangle \frac{1}{i\hbar} e^{+i\frac{(\omega_{m,0}-\omega_{n,0})t}{2}} \frac{e^{+i\frac{(\omega_{m,0}-\omega_{n,0})t}{2}} - e^{-i\frac{(\omega_{m,0}-\omega_{n,0})t}{2}}}{i(\omega_{m,0} - \omega_{n,0})} \\ &= \langle \Psi_{m,t_0,0} | H' | \Psi_{n,t_0,0} \rangle \frac{i}{\hbar} e^{+i\frac{(\omega_{m,0}-\omega_{n,0})t}{2}} \frac{\sin(\omega_{m,0} - \omega_{n,0})t/2}{(\omega_{m,0} - \omega_{n,0})/2} \end{aligned} \quad (\text{B.94})$$

$$|\langle \Psi_{m,t_0,0} | \Phi_{1,n}(t) \rangle|^2 = |\langle \Psi_{m,t_0,0} | H' | \Psi_{n,t_0,0} \rangle|^2 \frac{1}{\hbar^2} \left(\frac{\sin(\omega_{m,0} - \omega_{n,0})t/2}{(\omega_{m,0} - \omega_{n,0})/2} \right)^2 \quad (\text{B.95})$$

From here, it is necessary to consider the squared term of the form $\frac{\sin^2(\alpha t)}{\alpha^2}$ with variation in α^2 . As $t \rightarrow \infty$ the plot of this function vs α tends towards a delta function. In addition it may be shown that this delta function has a linear dependent on t. The following equation can be written, although the proof of this is beyond the scope of this work.

$$\lim_{t \rightarrow \infty} \frac{1}{t} \frac{\sin^2(\alpha t)}{\alpha^2} = \pi \delta_{\alpha} = 2\pi \delta_{2\alpha} \quad (\text{B.96})$$

This allows the following equation to be made

$$\frac{|\langle \Psi_{m,t_0,0} | \Phi_{1,n}(t) \rangle|^2}{t} = |\langle \Psi_{m,t_0,0} | H' | \Psi_{n,t_0,0} \rangle|^2 \frac{2\pi}{\hbar^2} \delta_{\omega_{m,0}-\omega_{n,0}} \quad (\text{B.97})$$

This is simply Fermis golden rule.

Deviations from Fermi's golden rule are given by the higher order results. For this work, only the second order result must be discussed, namely:

$$\langle \Psi_{m,t_0,0} | \Phi_{2,n}(t) \rangle = \langle \Psi_{m,t_0,0} | \frac{1}{i\hbar} \int_{t_0}^t H'(t) \frac{1}{i\hbar} \int_{t_0}^t H'(t') (|\Phi_n(t_0)\rangle) dt' dt \quad (\text{B.98})$$

From here the identity operator may be added, to allow solving this equation. That is $\mathbb{1} = \sum_k |\Psi_{k,t_0,0}\rangle \langle \Psi_{k,t_0,0}|$

$$\langle \Psi_{m,t_0,0} | \Phi_{2,n}(t) \rangle = \langle \Psi_{m,t_0,0} | \sum_k \frac{1}{(i\hbar)^2} \int_{t_0}^t \int_{t_0}^t H'(t) |\Psi_{k,t_0,0}\rangle \langle \Psi_{k,t_0,0} | H'(t') (|\Phi_n(t_0)\rangle) dt' dt \quad (\text{B.99})$$

From here, using a similar procedure from the first order equations, this can be written

$$\langle \Psi_{m,t_0,0} | \Phi_{2,n}(t) \rangle = \sum_m \frac{1}{(i\hbar)^2} \langle \Psi_{m,t_0,0} | H' | \Psi_{m,t_0,0} \rangle \langle \Psi_{m,t_0,0} | H' | \Phi_n(t_0) \rangle \quad (\text{B.100})$$

$$\int_{t_0}^t \int_{t_0}^t e^{+i\frac{E_{m,0}t}{\hbar}} e^{-i\frac{E_{k,0}t}{\hbar}} e^{+i\frac{E_{k,0}t'}{\hbar}} e^{+i\frac{E_{n,0}t'}{\hbar}} dt' dt \quad (\text{B.101})$$

From here intergration can be done via setting $t_0 = 0$

$$\langle \Psi_{m,t_0,0} | \Phi_{2,n}(t) \rangle = \sum_m \frac{1}{(i\hbar)^2} \frac{\langle \Psi_{m,t_0,0} | H' | \Psi_{m,t_0,0} \rangle \langle \Psi_{m,t_0,0} | H' | \Phi_n(t_0) \rangle}{E_{k,0} - E_{n,0}} \quad (\text{B.102})$$

$$\int_{t_0}^t e^{+it'\frac{E_{m,0}-E_{n,0}}{\hbar}} - e^{+it'\frac{E_{m,0}-E_{k,0}}{\hbar}} dt \quad (\text{B.103})$$

$$\begin{aligned} \langle \Psi_{m,t_0,0} | \Phi_{2,n}(t) \rangle &= \sum_m \frac{1}{(i\hbar)^2} \frac{\langle \Psi_{m,t_0,0} | H' | \Psi_{m,t_0,0} \rangle \langle \Psi_{m,t_0,0} | H' | \Phi_n(t_0) \rangle}{E_{k,0} - E_{n,0}} \\ &e^{+it\frac{E_{m,0}-E_{n,0}}{2\hbar}} \left(e^{+it'\frac{E_{m,0}-E_{n,0}}{2\hbar}} - e^{-it'\frac{E_{m,0}-E_{n,0}}{2\hbar}} \right) \\ &- e^{+it\frac{E_{m,0}-E_{k,0}}{2\hbar}} \left(e^{+it'\frac{E_{m,0}-E_{k,0}}{2\hbar}} - e^{-it'\frac{E_{m,0}-E_{k,0}}{2\hbar}} \right) \end{aligned} \quad (\text{B.104})$$

By analogy to the previous part, this leads to

$$\frac{|\langle \Psi_{m,t_0,0} | \Phi_{2,n}(t) \rangle|^2}{t} = \sum_m \quad (\text{B.105})$$

$$\begin{aligned} & \left| \frac{\langle \Psi_{m,t_0,0} | H' | \Psi_{m,t_0,0} \rangle \langle \Psi_{m,t_0,0} | H' | \Phi_n(t_0) \rangle}{E_{k,0} - E_{n,0}} \right|^2 \frac{2\pi}{\hbar^2} \delta_{\omega_{m,0}=\omega_{n,0}} \\ & + \sum_m \left| \frac{\langle \Psi_{m,t_0,0} | H' | \Psi_{m,t_0,0} \rangle \langle \Psi_{m,t_0,0} | H' | \Phi_n(t_0) \rangle}{E_{k,0} - E_{n,0}} \right|^2 \frac{2\pi}{\hbar^2} \delta_{\omega_{m,0}=\omega_{k,0}} \end{aligned}$$

B.1.3.4 Higher Order Result, With Multiple Perturbations

There may be more than one perturbation causing the transition, and this may be modelled via the same techniques. The results can be seen simply from the prior results if the following substitution is made

$$H' = H'_1 + H'_2 \quad (\text{B.106})$$

This substitution is particularly of interest for the second order results. This is because terms of the form below are made:

$$\left| \frac{\langle \Psi_{m,t_0,0} | H'_1 | \Psi_{m,t_0,0} \rangle \langle \Psi_{m,t_0,0} | H'_2 | \Phi_n(t_0) \rangle}{E_{k,0} - E_{n,0}} \right|^2 \frac{2\pi}{\hbar^2} \delta_{\omega_{m,0}=\omega_{n,0}} \quad (\text{B.107})$$

$$\left| \frac{\langle \Psi_{m,t_0,0} | H'_1 | \Psi_{m,t_0,0} \rangle \langle \Psi_{m,t_0,0} | H'_2 | \Phi_n(t_0) \rangle}{E_{k,0} - E_{n,0}} \right|^2 \frac{2\pi}{\hbar^2} \delta_{\omega_{m,0}=\omega_{k,0}} \quad (\text{B.108})$$

B.2 Experimental

B.3 Carbazole Substituted Acrydine-Tryazine TADF Molecules

B.3.1 General Characterisation

B.3.1.1 Cyclic Voltammetry

Cyclic voltammetry was ran on all compounds with a quasi-reference electrodes. It was decided that the voltammograms should be run with ferrocene added. Below is the reason why (fig. B.2). While the voltammograms were run both and without the ferrocene, there was found to be shift when ferrocene was added, ranging from slight (compound 1) to major (compound 2). While the data was collected for compound 3, it was not seen necessary to make a graph of this, as the point has been made. The reason for this movement may be attributed to the changing electrode reduction couple working at the reference electrode. Traditionally the couple is said to be from $\text{Ag} \rightleftharpoons \text{Ag}_2\text{O}$ at the surface, with surface oxidised species causing the reference potential⁵ (although no evidence can be found for this). However it is known that the reference potential changes as additional species are added to the electrochemically active vessel.⁶ This has been assigned⁶ as to being due to the added species creating new reductive pairs with silver, which in turn changes the location of the silver reference electrode.

It should be noted both reductive and oxidative events can be observed. The voltammograms were run using varied scan rates, and multiple runs, this was done to confirm reproducibility, and find the most accurate standard potential as will be discussed later.

Prior to showing all the results, it is important to show an example voltammogram without the downscaling scaling necessary to fit many on a single graph. This is shown in figure B.3. Several none ideal features can be observed; these are 1) non-flat baseline 2) broad baseline 3) the features between -0.5 and -1 V. These will be addressed in order. 1) the non-flat baseline can be attributed due to ohmic effects, ideally these can be reduced by putting the reference and working electrode closer together, and may be reduced by subtracting a background with similar electrode spacing. The former was done to the best of ability, the latter could not be done, due to the tendency of the reference electrode potentials to move about with species added. 2) the broad baseline can also be reduced one of two ways. Firstly a reference can be ran (which as previously stated is impossible). Secondly a purer solvent can be used. This would require manual purification of solvent, which was not done here for the sake of time. 3) the features in the -0.5 and -1 V region are assigned to impurities/oxygen. It was noticed that there was change in these features,

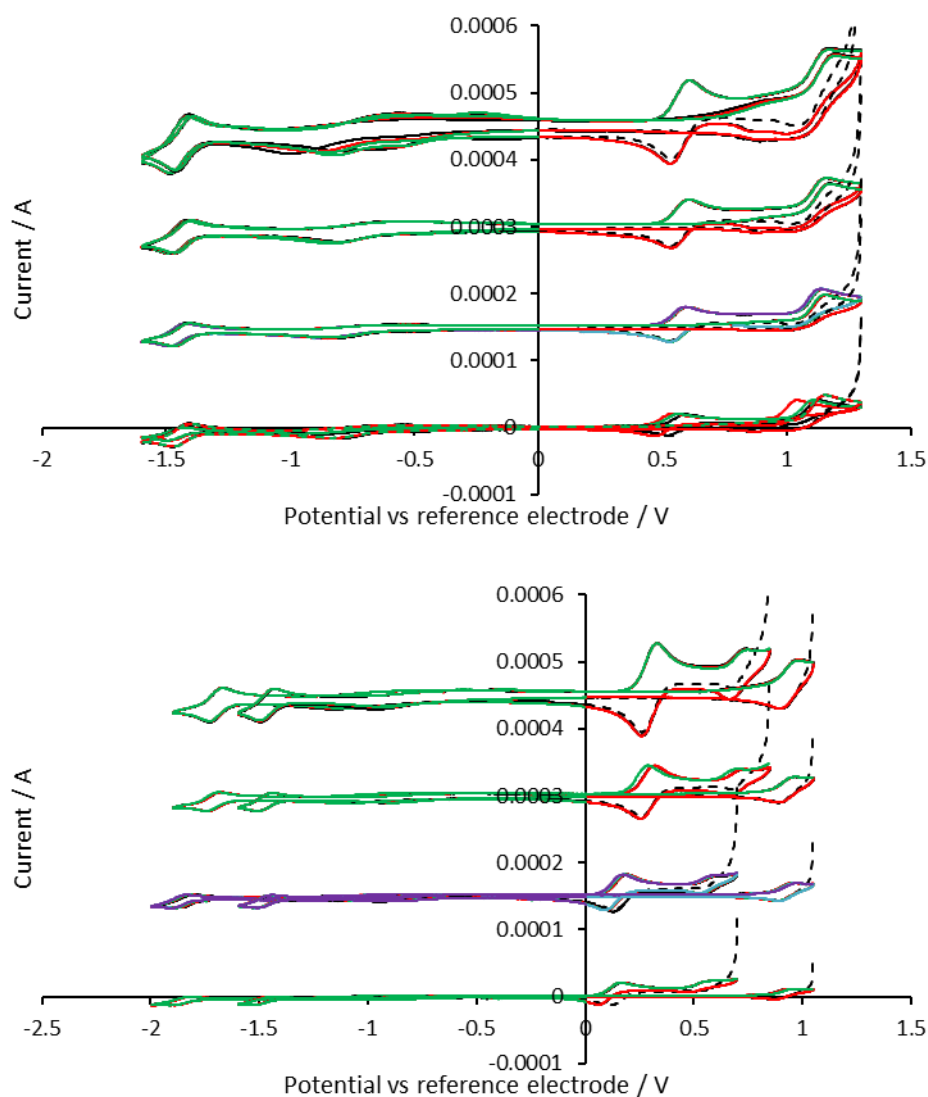


Figure B.2: Voltammograms of compound 1 (upper) and compound 2 (lower). These were run with wire Pt working, and counter electrodes, and silver wire reference electrodes. The voltammograms were ran at 20, 50, 100, and 300 mV s⁻¹ corresponding to the bottom to top graphs respectively in an individual diagram. The “run in” is shown in dashed black, the first run black, second red, third green, fourth blue, and fifth purple. Graphs with larger scan rates are offset with multiples of 1.5×10^{-4} A.

suggesting at least one to be due to oxygen/water, the other may be due to the known impurities induced via grubbs-purification. While these peaks are non-ideal, it is felt that because they are separated from the other peaks in the voltammogram quite significantly, they should not effect the results.

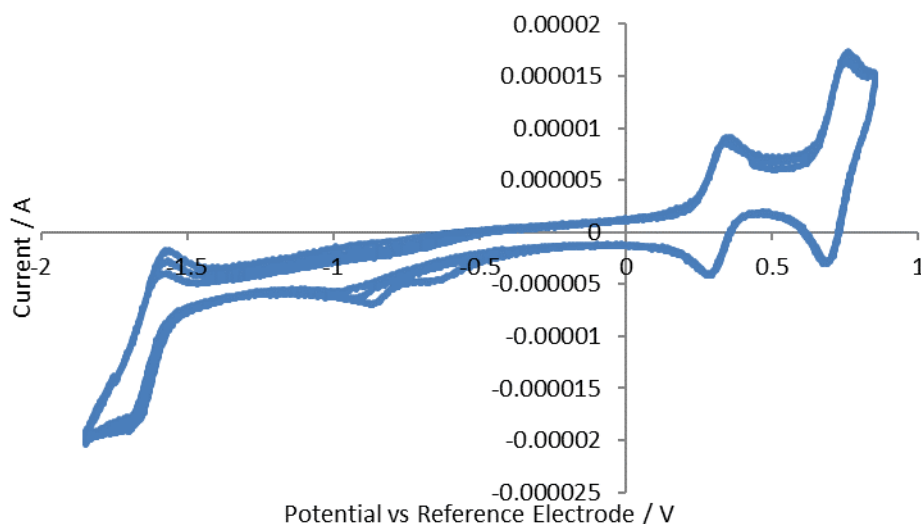


Figure B.3: The voltammograms of compound 3 at a scan rate of 20 mV s^{-1} . These were run with wire Pt working, and counter electrodes, and silver wire reference electrodes over a total of three whole scans. However the initial run-in is only from $+0.85$ to 0 V is removed for clarity.

While it has been stated that the background is impossible to take, it should be demonstrated what the spectra looks like with this subtraction. This is shown in figure B.4 and demonstrates the problem. While the data necessary for subtraction was collected for all other compounds, this was the only one it was calculated for. It was figured further work would only waste time.

A second point which should be addressed is that the standard potential is used as opposed to the onset potential. It is claimed⁷ that the onset potential is used due to an observation that the onset potential correlated with the calculated polymer band energies,⁸ it is further claimed in this paper that "these values are for the polymer and correspond to the first oxidation or reduction potential of the polymer (removal or addition of one electron). Therefore, the E_{ox} [ie. the oxidation potential] and E_{red} [ie. the reduction potential] values would correspond to onset values in terms of the observed oxidation or reduction of polyacetylene". There is no evidence to the later point, since in the onset region, the Nernst equation is approached, which indicates that 0 A is approached exponentially, therefore it must go beyond the energy of first oxidation and reduction. Further, the logical fallacy "causation does not imply correlation" must be noted to the first point.

For compounds in solution, it has been claimed⁹ that the average of the peak an-

odic and cathodic peaks gives the ionisation energy/electron affinity of a compound in solution. This is based on an observation by Nicholson et al.¹⁰ which calculates using thermodynamics and kinetics, assuming a single energy state in solution, the predicted shape of a voltammogram under reversible conditions. It is calculated¹⁰ that for a reductive run followed by an oxidative run of a reversible redox reaction, that the cathodic peak should be $-28.50/n$ mV from the polarographic half wave potential (with n = number of stoichiometric electrons involved with the oxidation/reduction and assuming diffusion constants of all species are equal). Further the peak anodic current is shifted by 34.4–29.3 mV from the half wave potential for switching potential 65–300 mV from the half wave potential. This suggests that an average of the cathodic peak potential and anodic peak wave potential should give the half wave potential with an error only on the order of 1 mV. The half-wave potential approximates the standard potential for the limit of the diffusion constants of oxidised and reduced species being equivalent in solution.

One may draw on the onset of these voltammograms on the diagram in the cited¹⁰ reference and show that the onset is in fact 100 mV ie. 0.1 V off desired half wave potential (see figure B.5).*. Since this value is large, the onset potential is essentially disproved for a single energy state, and so there is no reason to believe it would work for a series of energy states arranged in a band. This does not mean that on average the results will not "correlate".

While this only discusses the results for a reversible voltammogram, it is often claimed that the average of the peaks is also true when the voltammogram is for a quasi reversible system. It is claimed that the error induced by the quasi reversible case is usually low, but increases with peak separation.⁹

The results for each compound with ferrocene are shown in figure B.6, the results are relatively standard, and hence there is not much to discuss. What is a problem, although is not necessarily clear in the diagrams provided, is that the peaks are not necessarily clear on the slower scan rates. This is a problem as it prevents the standard potential from being accurately estimated. In these cases the maximas were estimated by eye, but were not used in assigning the standard potentials, as will be discussed later.

For the sake of ease of comparison, the scans with scan rate of 50 mV s⁻¹ are collated within electro-5. This nicely demonstrates the changes in band gap from compound 1 to 2, with narrowing in band-gap dominated by the change in the HOMO. For compound 3 the results are somewhat obscured, because of broadening

*note: the graphed quantity on the x axis is, before the switching potential, approx. $E = E_i - E^\circ - vt$ when $n = 1$ and the diffusion constant are approximately the same. After the switching potential it is $E_\lambda - vt = E - 2vt$. E is the electrode potential, E_i is the initial potential, E° the standard potential, E_λ is the switching potential, and v the scan rate and t time. Potentials are given in mV

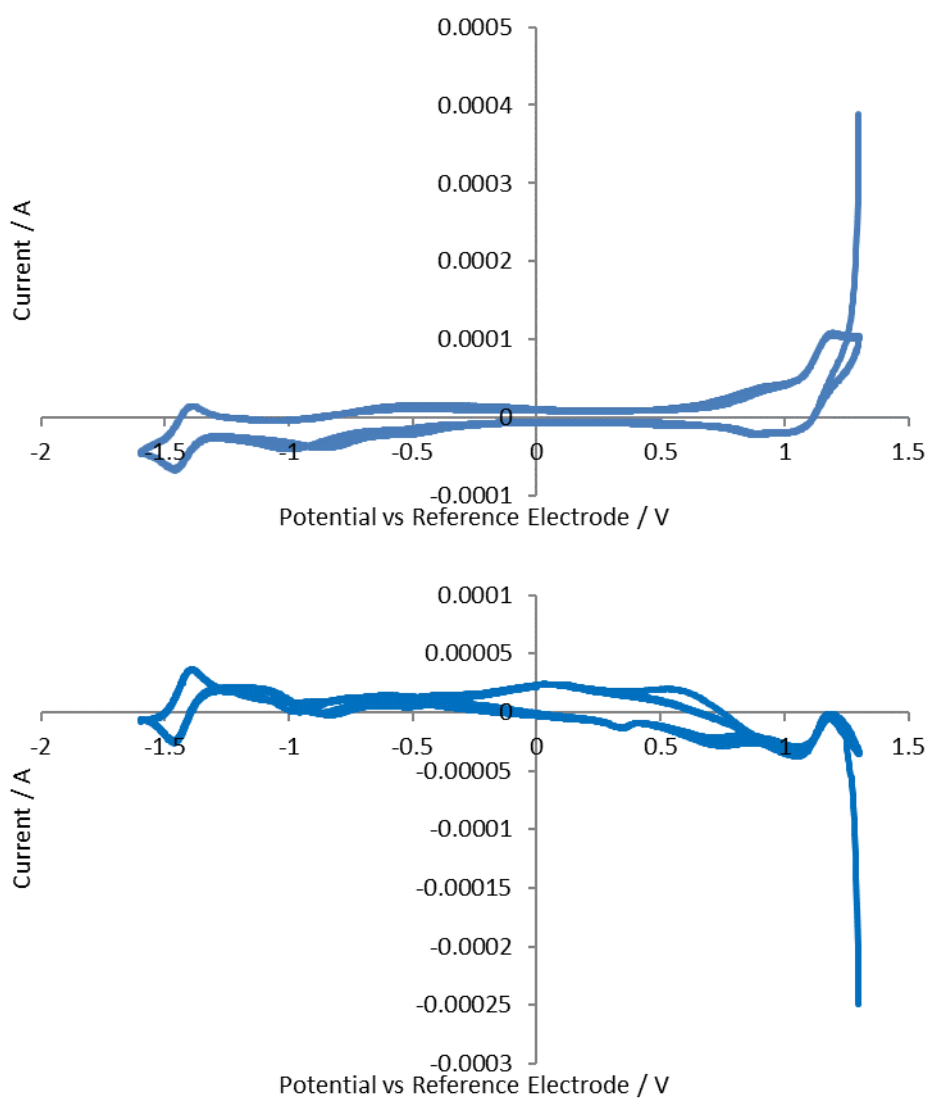


Figure B.4: Voltammogram of compound 1 without (upper) and with (lower) background subtraction. The scan is done at 300 mV s^{-1} without ferrocene.

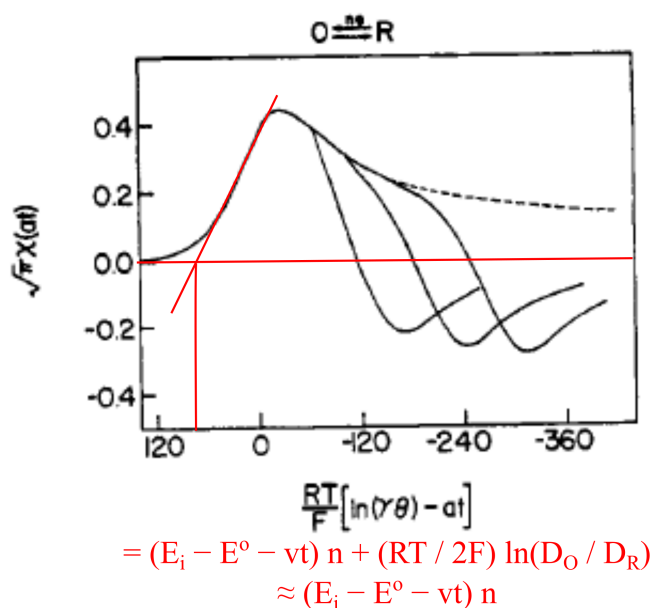


Figure B.5: The onset potential, relative to the polarographic half wave potential, assuming that number of stoichiometric electrons is 1, and that the diffusion constants of oxidised and reduced species are approximately equal. Adapted with permission from Richard S. Nicholson and Irving Shain. *Theory of Stationary Electrode Polarography: Single Scan and Cyclic Methods Applied to Reversible, Irreversible, and Kinetic Systems*. Analytical Chemistry, 36(4):706–723, 1964. Copyright (2020) American Chemical Society. Note the labelled x axis is only true until the switching potential is reached, this is further discussed in the footnote in the text.

in the separation of the reduction peaks, but it can perhaps be seen that there is a slight narrowing in band gap due to a decrease in energy here. The broadening of separation of peaks is itself interesting, as it indicates a slowing of the reduction, possibly due to steric hindrance from attached carbazole

The results obtained from all of these graphs are shown in table B.1, which are then summarised to their key standard potentials and referenced against vacuum in table B.2. As per normal the difference in the peaks is seen to decrease with decrease scan rates. This means the voltammogram approaches the reversible ideal, at the cost of resolution of the maxima and minima necessary for standard potential assignment. This reaches the point in several scans where the peak and minimum potential must be estimated by eye. All voltammograms are thusly assigned as quasi-reversible. The results for the Nicholson parameter are curious as they consistently are above 1 and decreasing. Theoretically one would not expect these values to exceed 1,¹¹ as this indicates there is more oxidized/reduced species, than non-oxidized reduced. However this may be rationalised due to the un-even baseline, and the fact both reduction and oxidation appear to take place close to the solvent potential limits. The absence of a value of 1, means that the estimations of the half-wave potential are uncertain at best.

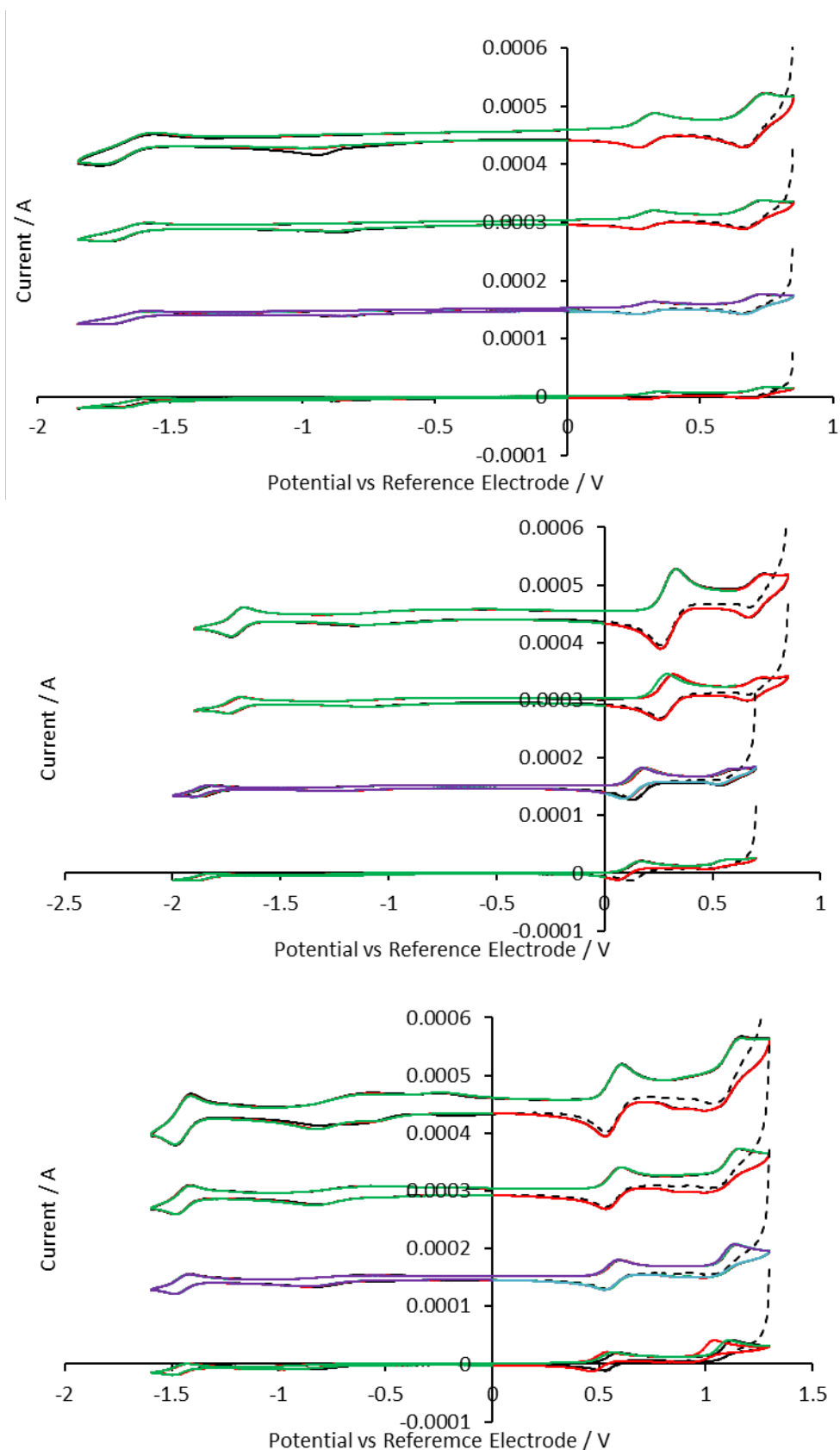


Figure B.6: The voltammograms of compound 1 (bottom), 2 (middle) and 3 (top). These were run with wire Pt working, and counter electrodes, and silver wire reference electrodes. The voltammograms were run at 20, 50, 100, and 300 mV s⁻¹ corresponding to the bottom to top graphs respectively in an individual diagram. The “run in” is shown in dashed black, the first run black, second red, third green, fourth blue, and fifth purple. Graphs with larger scan rates are offset with multiples of 1.5×10^{-4} A.

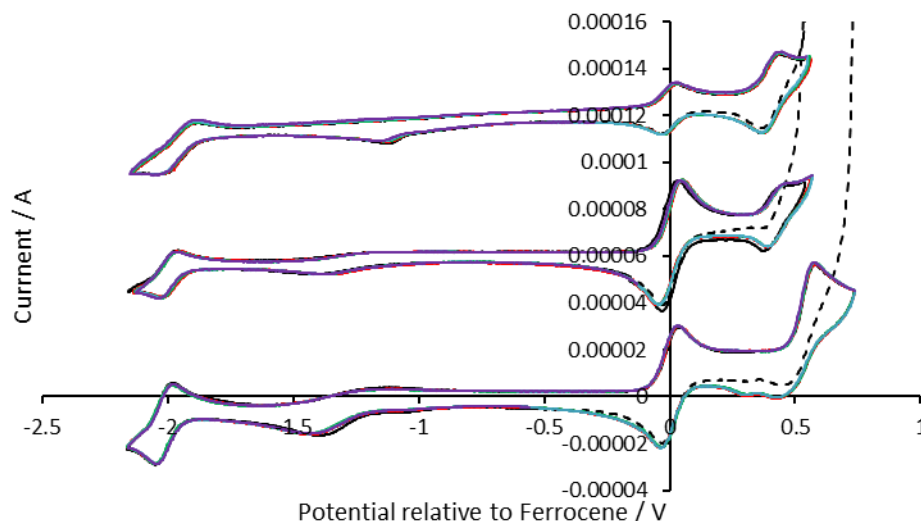


Figure B.7: The voltammograms of compound 1 (bottom), 2 (middle) and 3 (top). These were run with wire Pt working, and counter electrodes, and silver wire reference electrodes and referenced relative to ferrocene. This reference was updated for each individual run based on the whole ferrocene couple in each. The voltammograms were ran at 50 mV s^{-1} . The “run in” is shown in dashed black, the first run black, second red, third green, fourth blue, and fifth purple. Graphs of different compounds are offset with multiples of $1.5 \times 10^{-4} \text{ A}$.

When the data is summarised in table B.2, the minimum scan rate with non-estimated maxima and minima are used. Several different scales are used to calculate the energy relative to *vacuum* as the energy gaps of the standard reduction potentials and vacuum potential are not fully known. Basically the most commonly cited values is -4.8 eV , however this value is known to be wrong.⁷ In the same review they suggest using values 5.1 eV , and 5.39 eV .

$$\bar{x} = \frac{\sum_{i=1}^n (x_i \sigma_i^{-2})}{\sigma_i^{-2}} \quad (\text{B.109})$$

A case can be made against the 5.1 eV and 5.39 eV values, and instead the values should be $5.14 \pm 0.03 \text{ eV}$, $5.43 \pm 0.05 \text{ eV}$. Basically the reasoning for this is they⁷ appears to use both data reported with error bars and without to reach these values; however it is believed here-in that data without error bars should be discarded, and those with error bars should be averaged by a standard weighted mean calculations (weighted on their uncertainties) this gives values listed earlier. The weighted mean equation is shown above with $\bar{x}$ the resulting mean, x_i and σ_i the mean and standard deviation of each individual data point. The calculated standard deviation $\sigma_{\bar{x}}$ is shown calculated below.

$$\sigma_{\bar{x}} = \sqrt{\frac{1}{\sum_{i=1}^n (\sigma_i^{-2})}} \quad (\text{B.110})$$

B.3.1.2 Host Absorption And Emission

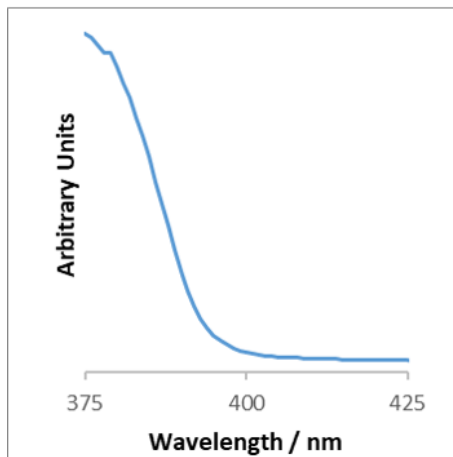


Figure B.8: The absorption of H1 in film.

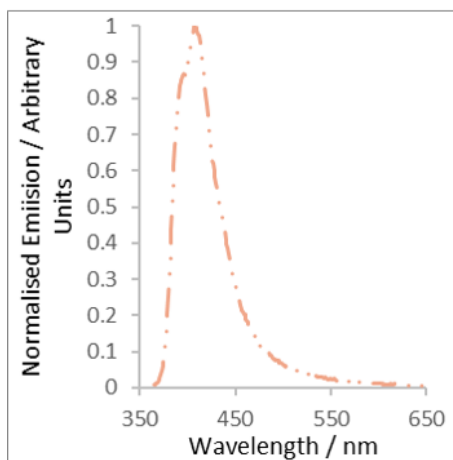


Figure B.9: The emission of H1 in film when excited at 355 nm.

B.3.1.3 Film Spectra

B.3.1.3.1 Phase Separation The compounds which are herein investigated have been measured in film. Both in a 10 % mix with the host and part of pure system, as well as both drop cast and spin coated systems. The absorptions are compared in figure B.10. While there is clear distortion in the absorption spectra from interference effects due to the films thickness,¹² a rough comparison is possible. Unfortunately due to the lack of solubility of the host, as well as shortage of

Table B.1: Standard potentials and errors from a single solution over multiple runs of compound 1-3 (C1-3). The standard potentials are taken from minimum scan rate results with clear maxima, see table 1, for further info. The results for various potentials of the Normal Hydrogen Electrode relative to vacuum are shown, as there is uncertainty in this.

Compound	Speed	Oxidation Standard Potential / V	Oxidative Peak Sifference / V	ipa/ipc	Reductive Standard Potential / V	Reductive Peak Difference / V	ipc/ipa
1	300	0.5142 ± 0.0015	0.1739 ± 0.0011	1.256 ± 0.012	-2.0177 ± 0.0004	0.0742 ± 0.0012	1.3064 ± 0.0079
	100	0.5098 ± 0.0024	0.1609 ± 0.0005	1.073 ± 0.001	-2.0139 ± 0.0006	0.0684 ± 0.0012	1.2972 ± 0.0045
	50	0.5027 ± 0.0004	0.1513 ± 0.0169	0.952 ± 0.002	-2.0149 ± 0.0005	0.0693 ± 0.0008	1.2434 ± 0.0004
	20	0.4923 ± 0.0128	0.1319 ± 0.0024	0.746 ± 0.018	-1.9912 ± 0.0063	0.0675 ± 0.0004	1.0869 ± 0.0085
2	300	0.4086 ± 0.0009	0.0738 ± 0.0034	2.337 ± 0.056	-1.9938 ± 0.0007	0.0589 ± 0.0023	1.2962 ± 0.0013
	100	0.4121 ± 0.0025	0.0704 ± 0.0034	2.167 ± 0.043	-1.9943 ± 0.0011	0.0628 ± 0.0011	1.2319 ± 0.0085
	50†	0.4253 ± 0.0017	0.0762 ± 0.0086	1.713 ± 0.021	-2.0008 ± 0.0013	0.0688 ± 0.0015	1.1472 ± 0.0110
	20‡	0.4164 ± 0.0011	0.1043 ± 0.0015	1.337 ± 0.018	-1.9724 ± 0.0047	0.0712 ± 0.0015	1.0379 ± 0.0056
3	300	0.4064 ± 0.0014	0.0859 ± 0.0002	1.566 ± 0.003	-1.9593 ± 0.0015	0.2069 ± 0.0011	1.2437 ± 0.0159
	100	0.4018 ± 0.0013	0.0754 ± 0.0007	1.491 ± 0.012	-1.9593 ± 0.0006	0.1655 ± 0.0023	1.0184 ± 0.0095
	50	0.4064 ± 0.0005	0.0730 ± 0.0082	1.465 ± 0.007	-1.9583 ± 0.0020	0.1593 ± 0.0019	0.9000 ± 0.0069
	20*	0.4060 ± 0.0025	0.0708 ± 0.0007	1.392 ± 0.007	-1.9556 ± 0.0014	0.1321 ± 0.0059	0.4929 ± 0.0115

Table B.2: Standard potentials and errors from a single solution over multiple runs of compound 1-3 (C1-3). The standard potentials are taken from minimum scan rate results with clear maxima, see table 1, for further info. The results for various potentials of the Normal Hydrogen Electrode relative to vacuum are shown, as there is uncertainty in this.

	-4.80 eV			-5.43 $\pm$ 0.05 eV			-5.14 $\pm$ 0.03 eV	
	Homo Estimation / V	LUMO Estimation / V		Homo Estimation / V	LUMO Estimation / V		Homo Estimation / V	LUMO Estimation / V
C1	5.292 $\pm$ 0.013	2.809 $\pm$ 0.005		5.92 $\pm$ 0.05	3.44 $\pm$ 0.05		5.63 $\pm$ 0.03	3.15 $\pm$ 0.03
C2	5.212 $\pm$ 0.003	2.799 $\pm$ 0.001		5.84 $\pm$ 0.05	3.43 $\pm$ 0.05		5.55 $\pm$ 0.03	3.14 $\pm$ 0.03
C3	5.206 $\pm$ 0.003	2.842 $\pm$ 0.002		5.84 $\pm$ 0.05	3.47 $\pm$ 0.05		5.55 $\pm$ 0.03	3.18 $\pm$ 0.03

material, it was not possible to change the thicknesses in order to stop this effect. Disregarding this distortion, the absorption spectra remain approximately the same in both drop cast and spin coated spectra.

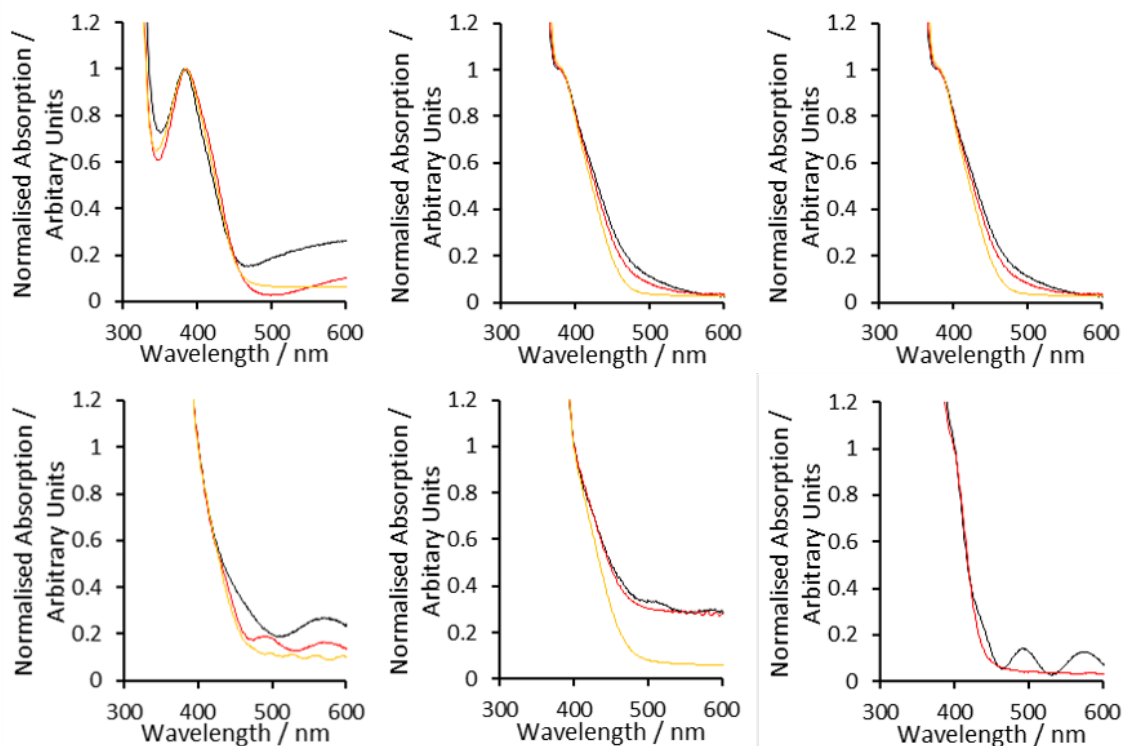


Figure B.10: The absorption of films 1-3 (left to right) in pure and 10 % doped films (top and bottom respectively). The red and orange films correspond to drop cast films of differing thicknesses, and the black film spin coated.

While the absorption spectra remain somewhat unchanged, the emission spectra changes (see figure B.11) for spin coated and drop cast film of the doped substrate, with negligible change in the pure films. It can be hypothesised that there can be three main causes for shifts in emission spectra based on the film formation conditions. These are differing aggregation, differing degrees of relaxation of the glassy film and phase separation. All of which are possible.

A strong possibility is phase separation occurring in spin coated films. This is because it is noted that pure films are red shifted relative to the doped ones. In figure B.12 it can be seen that there is a movement of the drop cast doped films, relative to the spin coated doped films, towards that of the pure films. This movement is particularly observed in compound 2, where almost complete matching is observed. Given this, it is believed that phase separation is the most likely cause of the shift in compound 2 and likely compound 3's. For C1, the effect is less easy to discern.

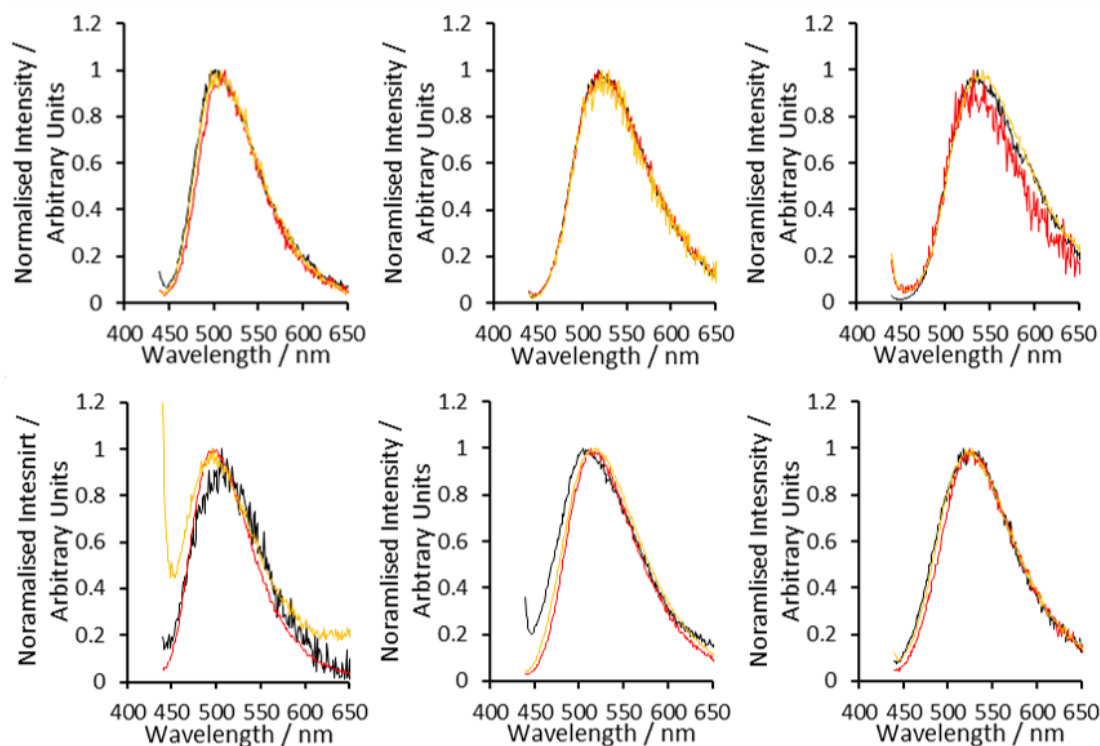


Figure B.11: The emission of compounds 1-3 (left to right) in pure and 10 % doped films (top and bottom respectively). The red and orange graphs correspond to two drop cast films of differing concentrations, and the black graphs corresponds to the spin coated film, all of which are excited at 430 nm.

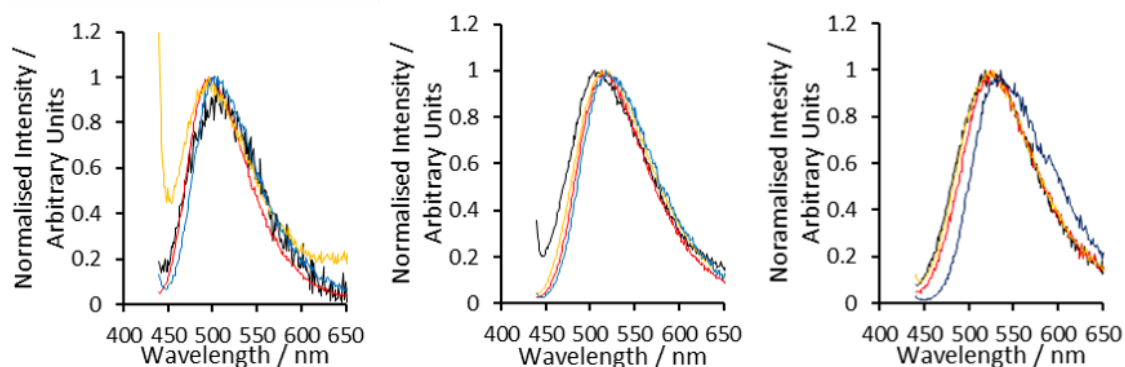


Figure B.12: The emission of compounds 1-3 (left to right). The red and orange graphs correspond to two drop cast films of differing concentrations, and the black graphs corresponds to the spin coated film, all of which in in 10 % doped films. The blue graph corresponds to the emission in pure film. All spectra are excited at 430 nm.

B.3.1.3.2 Excitation dependence While only the spectra excited at 430 nm excitation are shown in thus far, no excitation dependence is observed as shown in figure B.13. This is both for spin coated and drop cast films.

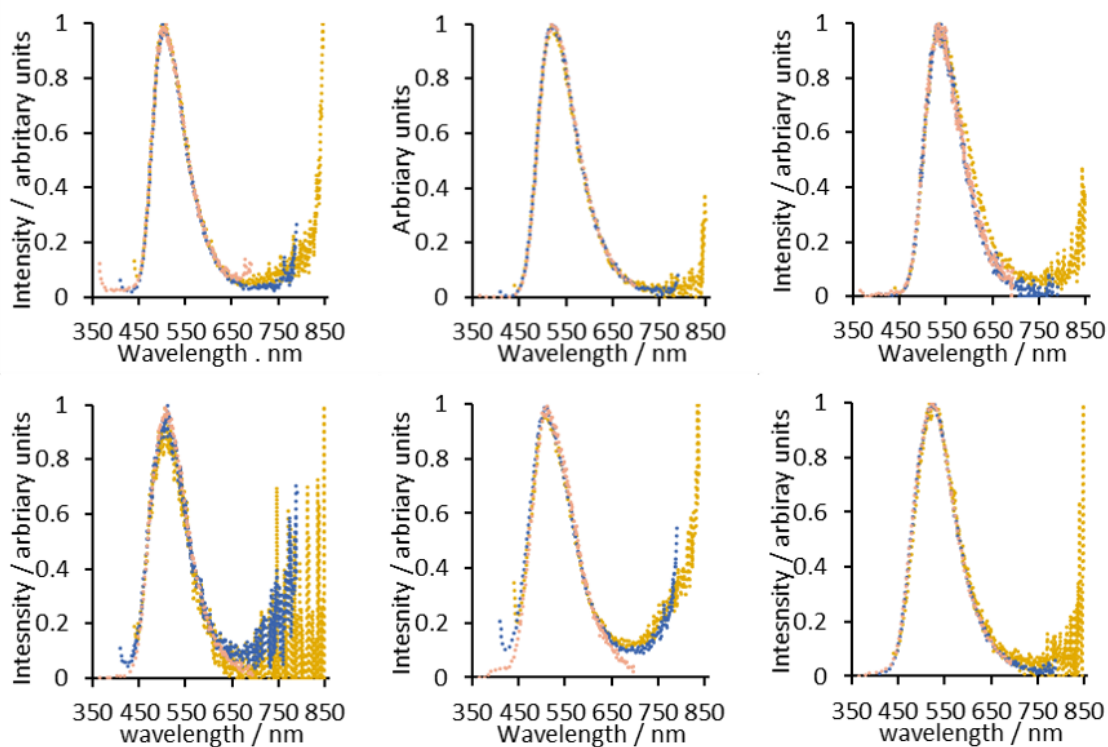


Figure B.13: The photoluminescent emission spectra of the pure films (top) and 10 % doped in H1 (bottom) of a) (left) compound 1 b) (centre) compound 2 and c) (right) compound 3 with changing excitation wavelength. The spectra with excitation at 355 (red), 400 (blue) and 430 (yellow) is shown.

B.3.1.3.3 Onsets

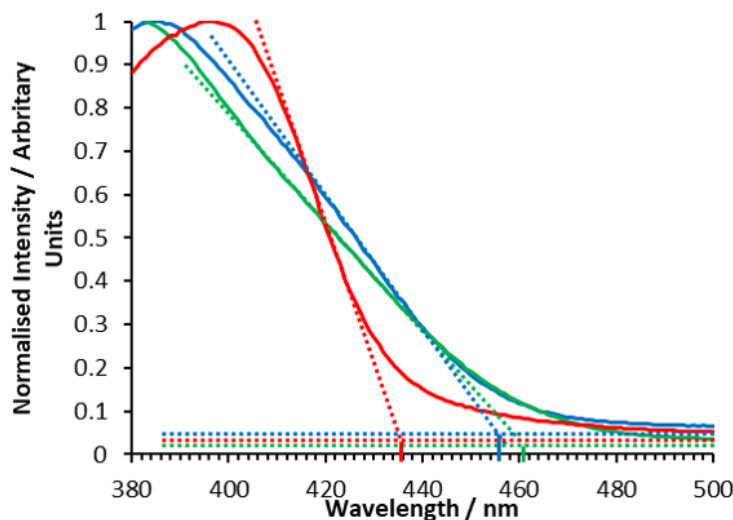


Figure B.14: The onset of the absorption spectra of compounds 1 (blue), 2 (green) and 3 (red) in drop cast pure film. The spectra are shown with solid lines, and the extrapolation line, from points of inflection are shown in dotted lines. The extrapolation of the baseline (from points off the chart), are also shown. The crossing points are marked with lines which are the same as the spectra. All films are formed via the drop-cast method.

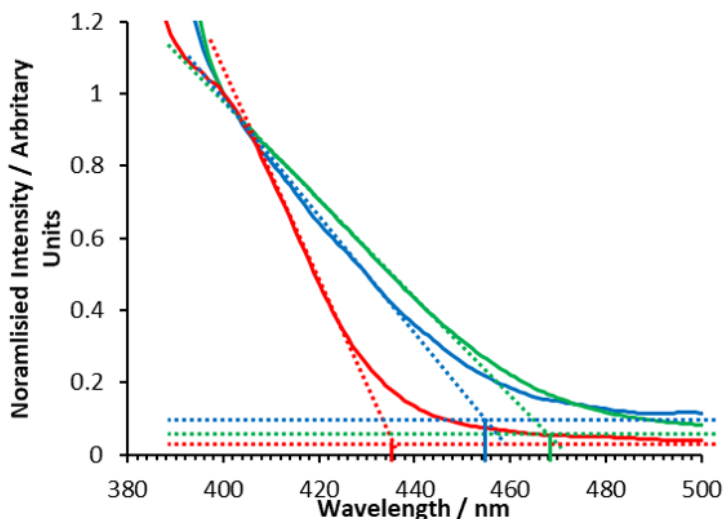


Figure B.15: The onset of the absorption spectra of compounds 1 (blue), 2 (green) and 3 (red) in drop cast 10 % doped film. The spectra are shown with solid lines, and the extrapolation line, from points of inflection are shown in dotted lines. The extrapolation of the baseline (from points off the chart), are also shown. The crossing points are marked with lines which are the same as the spectra. All films are formed via spin-coating

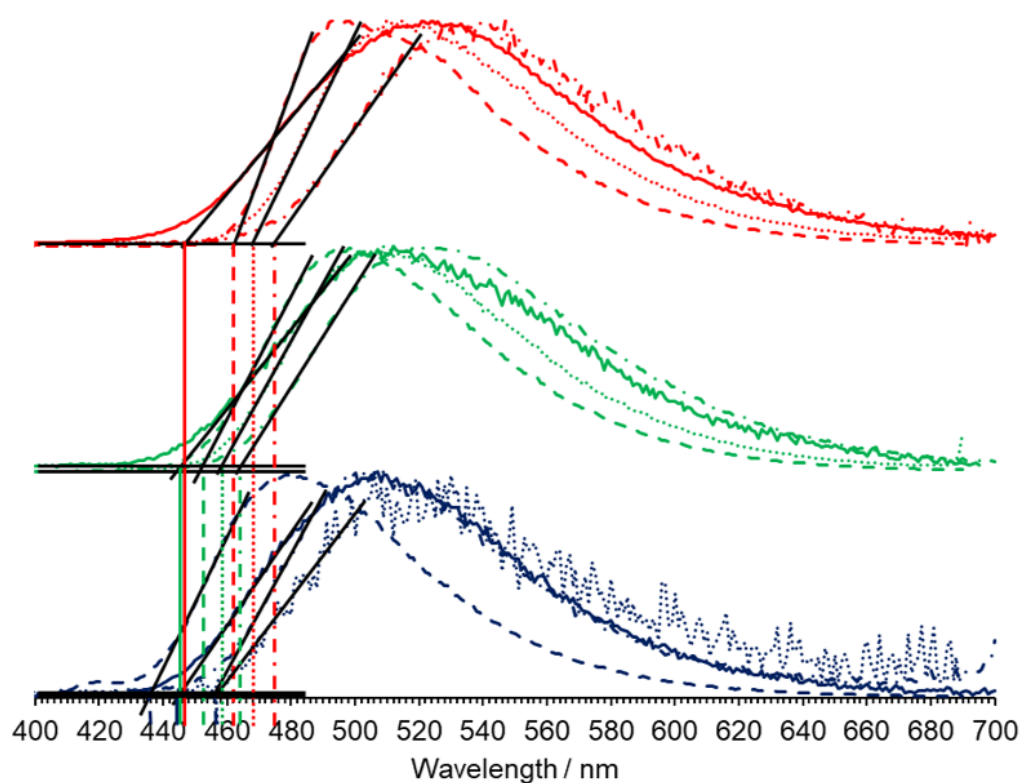


Figure B.16: the photoluminescent emission spectra in 10 % doped film (solid line), pure film (dot-dashed) and 10 μ M solutions frozen at 77K in a 1:1 mix of diethyl ether to ethanol solution, both with (dashed line) and without (dotted line) a 200 μ s delay. This is shown for compounds 1 (red), 2 (blue), and 3 (green). The intensity in all spectra are normalised on their maxima. The onset is also shown for each value. All spectra are excited at 350 nm

B.3.1.4 Solution Spectra

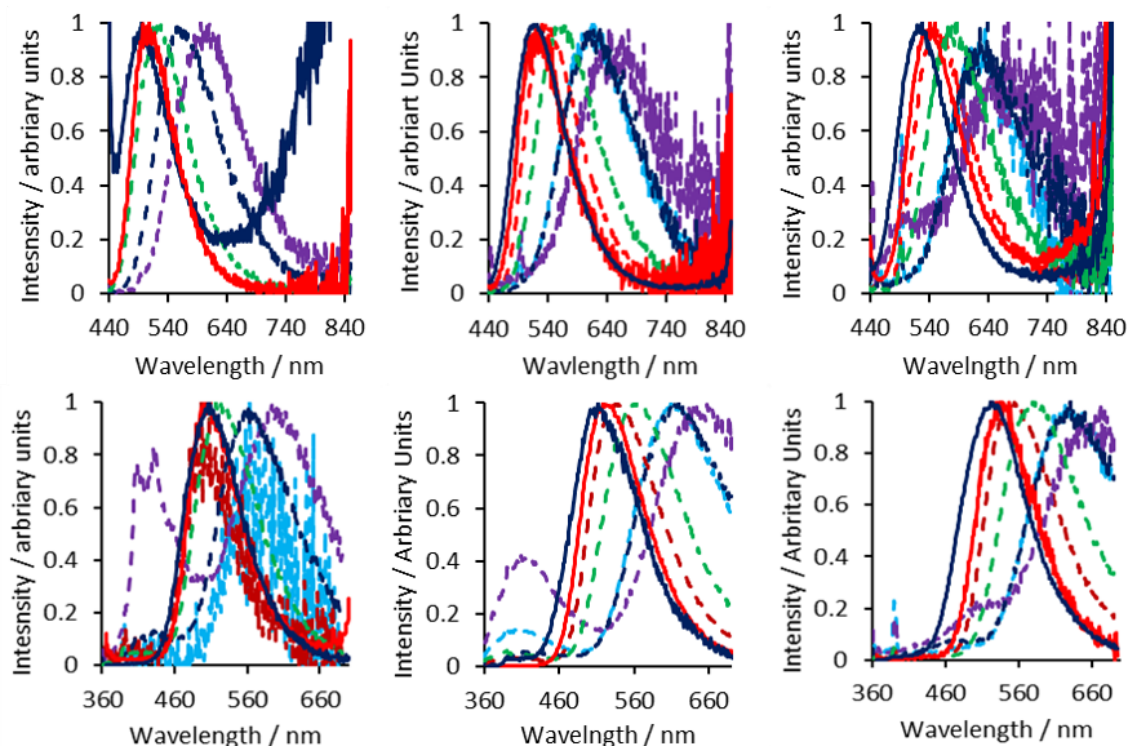


Figure B.17: The photoluminescent emission spectra of a) (left) compound 1 b) (centre) compound 2 and c) (right) compound 3. The following spectra are shown, pure film (red), doped film (blue), toluene (red-dashed), diethyl ether (green-dashed), thf (turquoise-dashed), chloroform (deep blue-dashed), DCM (purple-dashed). All spectra shown are excited at 430 nm (top) and 350 nm (bottom). The solutions of compound 1 and 2 are 10 μM , and for compound 3 are 1 μM .

B.3.1.4.1 Fluorescence And Absorption In All Solutions

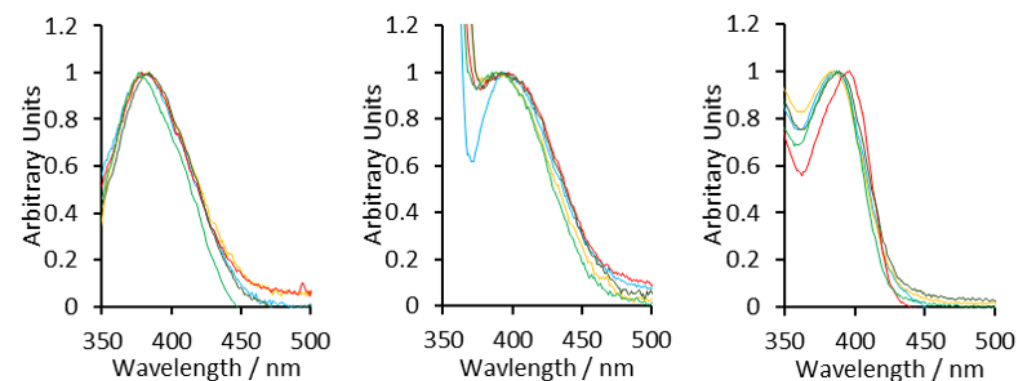


Figure B.18: The absorption spectra of a) (left) compound 1 b) (centre) compound 2 and c) (right) compound 3. The following spectra are shown, toluene (red), diethyl ether (green), thf (turquoise), chloroform (deep green), DCM (purple). The solutions of compound 1 and 2 are 10 μM , and for compound 3 are 1 μM .

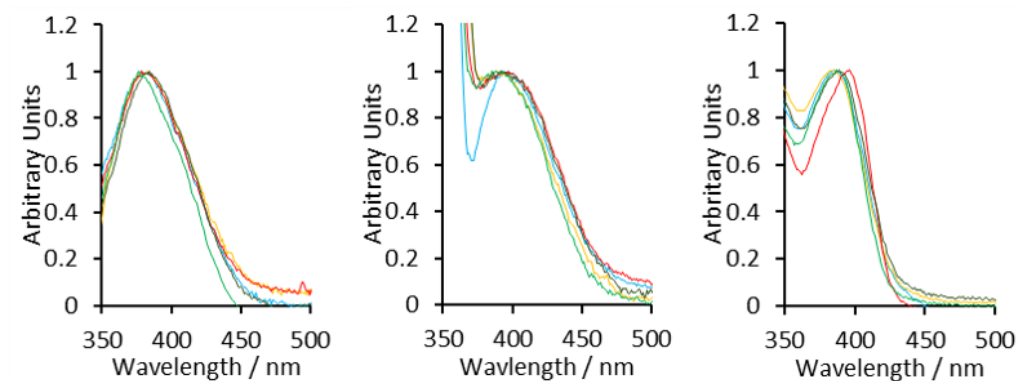


Figure B.19: An extended C3 solution spectra. The following spectra are shown, toluene (red), diethyl ether (green), thf (turquoise), chloroform (deep green), DCM (purple). The solutions are 1 μM .

B.3.1.4.2 Concentration Dependence In Toluene

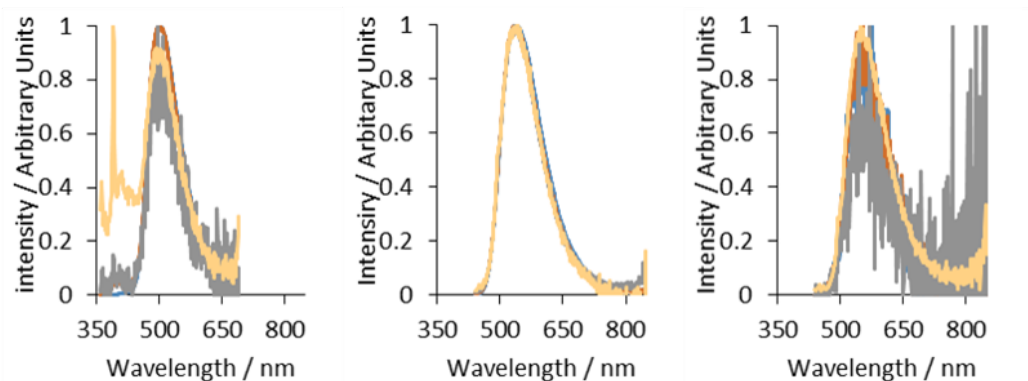


Figure B.20: The photoluminescent emission spectra of a) (left) compound 1 b) (centre) compound 2 and c) (right) compound 3 in toluene. All spectra shown are excited at 430 nm with the exception of C1 which is excited at 430 nm. The solutions are at 1 μM (yellow), 10 μM (grey), 100 μM (red), 1000 μM (blue).

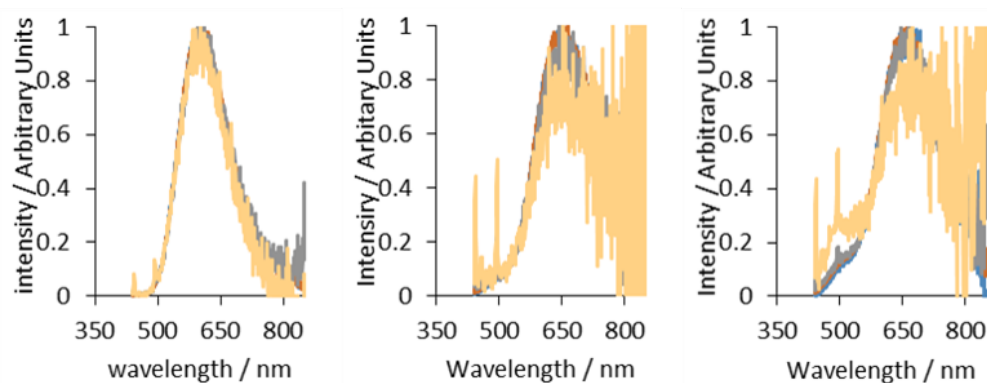


Figure B.21: The photoluminescent emission spectra of a) (left) compound 1 b) (centre) compound 2 and c) (right) compound 3 in dichloromethane. All spectra shown are excited at 430 nm with the exception of C1 which is excited at 430 nm. The solutions are at 1 μM (yellow), 10 μM (grey), 100 μM (red), 1000 μM (blue).

B.3.1.4.3 Concentration Dependence In DCM

B.3.1.4.4 Excitation plots Excitation spectra are consistent with the absorption spectra, as shown in the following figures. At high concentration, change consistent with reabsorption is observed.

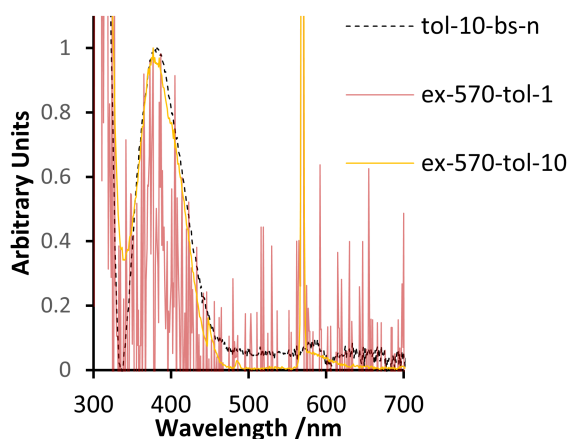


Figure B.22: The excitation spectra (ex-), for toluene solutions of concentration $x / \text{mol dm}^{-3}$ (tol- x) of C1. The absorption spectra is also shown (dashed line).

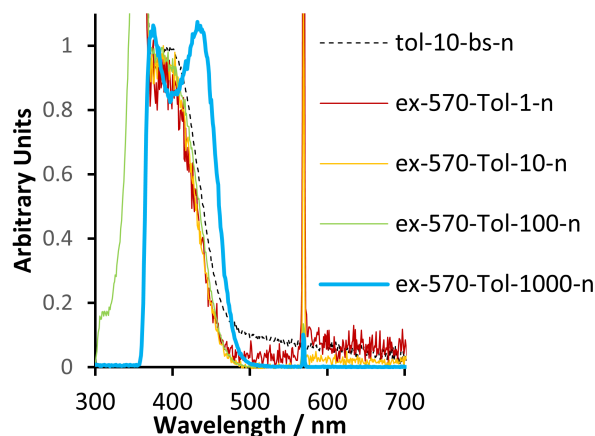


Figure B.23: The excitation spectra (ex-), for toluene solutions of concentration $x / \text{mol dm}^{-3}$ (tol- x) of C2. The absorption spectra is also shown (dashed line).

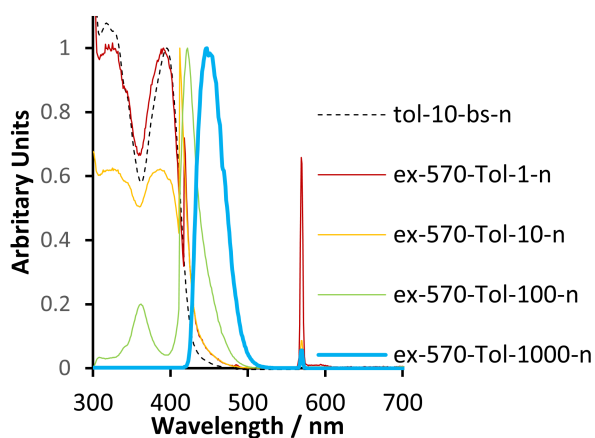


Figure B.24: The excitation spectra (ex-), for toluene solutions of concentration $x / \text{mol dm}^{-3}$ (tol- x) of C3. The absorption spectra is also shown (dashed line).

B.3.1.4.5 Lippert-Mattaga Plots The solvent dependence of the compounds may be modelled via the Lippert-Mattaga equation. This models the solvent effects as linearly dependent on the "orientational polarisability" of the solvents.¹³ The orientational polarisability is calculated via the equation below, where n is the refractive index, and ε is the dielectric constant. These values are taken from industry supplier values. It should be noted that the refractive index is dependent on the wavelength used, but it is approximated as the value given by suppliers.

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon} - \frac{n^2 - 1}{2n^2 + 1} \quad (\text{B.111})$$

The relation between stokes shift in wavenumber (ie. $\bar{\nu}_A - \bar{\nu}_F$) and orientational polarisability is given in the following equation.¹³ In this equation, μ_E is the dipole of the excited state, and μ_G of the ground state; C is a constant and a is the Onsager radius. Note this results in a value of polarity given in SI units, and the final value is given in Debye units (D).

$$\bar{\nu}_A - \bar{\nu}_F = \frac{2\Delta f}{hc} \frac{(\mu_E - \mu_G)^2}{a^3} + C \quad (\text{B.112})$$

What follows are the plotted solvent values of stokes shift, with orientational polarisability dependence, and a table of results from these.

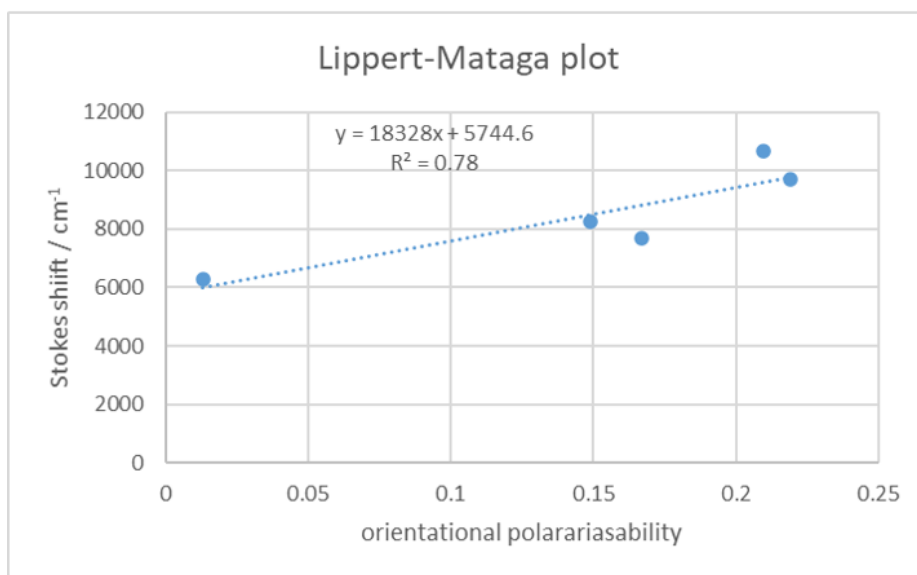


Figure B.25: The Lippert-Mattaga plot for compound 1. A trend-line from least square fitting, and resulting equations, are shown.

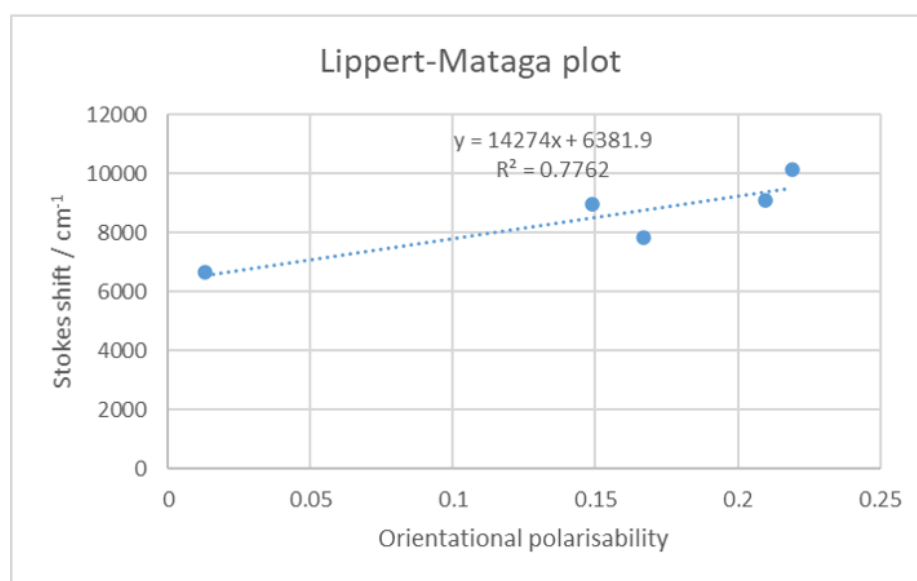


Figure B.26: The Lippert-Mattaga plot for compound 2. A trend-line from least square fitting, and resulting equations, are shown.

Table B.3: The tabulated parameters for the orientational polarisability. The Onsager Radius is provided by "volume" command in Gaussian.

Compound	Gradient	Onsager Radius / Å	Estimated Polarity / D
C1	14260	6.26	4.4±0.7
C2	14274	7.53	5.1±0.8
C3	15902	8.56	46.6±1.0

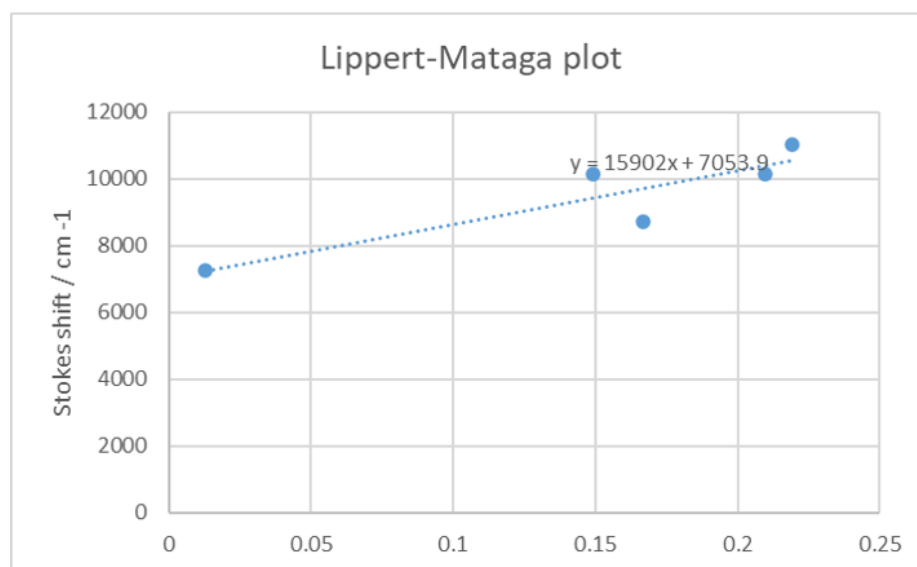


Figure B.27: The Lippert-Mattaga plot for compound 3. A trend-line from least square fitting, and resulting equations, are shown.

B.3.1.4.6 All Molar Absorptivities The molar absorptivities are listed here. Note non-ideal spectra are shown as well as the ideal one. It is common knowledge that an absorption greater than 1 causes inconsistencies in the absorption spectra. This is observed in all the large concentration spectra. At low concentrations, the baseline begins to cause inconsistencies in the results. The ideal concentrations are 10 μM and 100 μM for C1 and C2, and 1 μM and 10 μM for C3.

Table B.4: The tabulated molar absorptivities for C1–3.

Concentration C1 / μM	$\varepsilon_{\text{Toluene}}$ / $\text{M}^{-1} \text{cm}^{-1}$	$\varepsilon_{\text{Diethylether}}$ / $\text{M}^{-1} \text{cm}^{-1}$	ε_{DCM} / $\text{M}^{-1} \text{cm}^{-1}$	ε_{THF} / $\text{M}^{-1} \text{cm}^{-1}$	$\varepsilon_{\text{Chloroform}}$ / $\text{M}^{-1} \text{cm}^{-1}$
1	2700	6700	790	—	6940
10	2200	3300	2800	2100	2400
100	2300	2900	2710	2400	2400
1000	2400	—	—	2400	2200
Concentration C2 / μM	$\varepsilon_{\text{Toluene}}$ / $\text{M}^{-1} \text{cm}^{-1}$	$\varepsilon_{\text{Diethylether}}$ / $\text{M}^{-1} \text{cm}^{-1}$	ε_{DCM} / $\text{M}^{-1} \text{cm}^{-1}$	ε_{THF} / $\text{M}^{-1} \text{cm}^{-1}$	$\varepsilon_{\text{Chloroform}}$ / $\text{M}^{-1} \text{cm}^{-1}$
1	12000	—	7200	—	—
10	2400	2000	2000	2100	1800
100	2000	—	2100	—	—
1000	1800	—	1800	—	—
Concentration C3 / μM	$\varepsilon_{\text{Toluene}}$ / $\text{M}^{-1} \text{cm}^{-1}$	$\varepsilon_{\text{Diethylether}}$ / $\text{M}^{-1} \text{cm}^{-1}$	ε_{DCM} / $\text{M}^{-1} \text{cm}^{-1}$	ε_{THF} / $\text{M}^{-1} \text{cm}^{-1}$	$\varepsilon_{\text{Chloroform}}$ / $\text{M}^{-1} \text{cm}^{-1}$
1	48000	49000	51000	49000	50000
10	42000	—	45000	—	—
100	33000	—	99000	—	—
1000	34000	—	99000	—	—

B.3.1.4.7 Polarity Or Sterics: The Difference Between Solution And Film Spectra In order to examine the polarity dependence the emission and absorption of various compounds were measured. The results are summarised in tables B.5 for C1, B.6 for C2, and B.7 for C3. The results are further expressed in figures B.28, and B.29.

The dependence on orientational polarisability for all compounds is shown in figure B.28. What may be noted in this diagram is the the film peaks are quite closely grouped in contrast to the solution peaks. This tight grouping would appear to take a rather large extrapolation of the orientational polarasiability fits in order to be achieved, and this points against the reduction in shifts being from polarity.

The reduction in shifts being unlikely to be from polarity is shown much more clearly in figure B.29. In this figure the differences between the compounds peaks in solution are shown. There is a clear reduction in change in both doped films, and pure films. In fact high polarity — likely not present in film — would be required to come close to replicating the films changes in solution. In addition, this contrasts with the peak position, which would require low polarity to be replicated, as is shown in figure B.28.

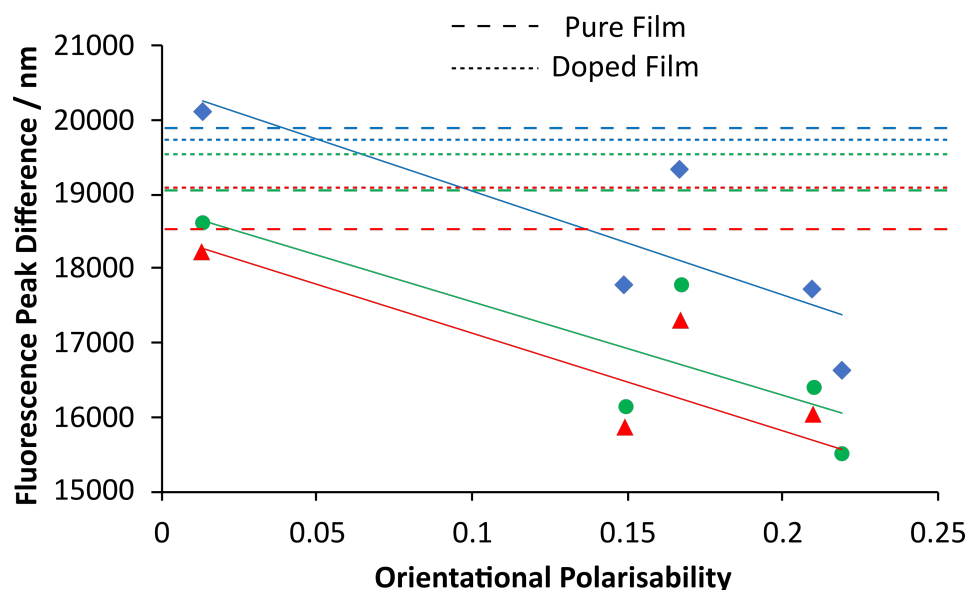


Figure B.28: The change in peak fluorescence with orientational polarisability for 10 μM (C1 and C2), and 1 μM (C3) solutions of compound 1–3. The solution peaks are fit using the line shown. The film emissions are shown for both pure and doped films using dashed lines to indicate the unknown equivalent orientational polarisability of films.

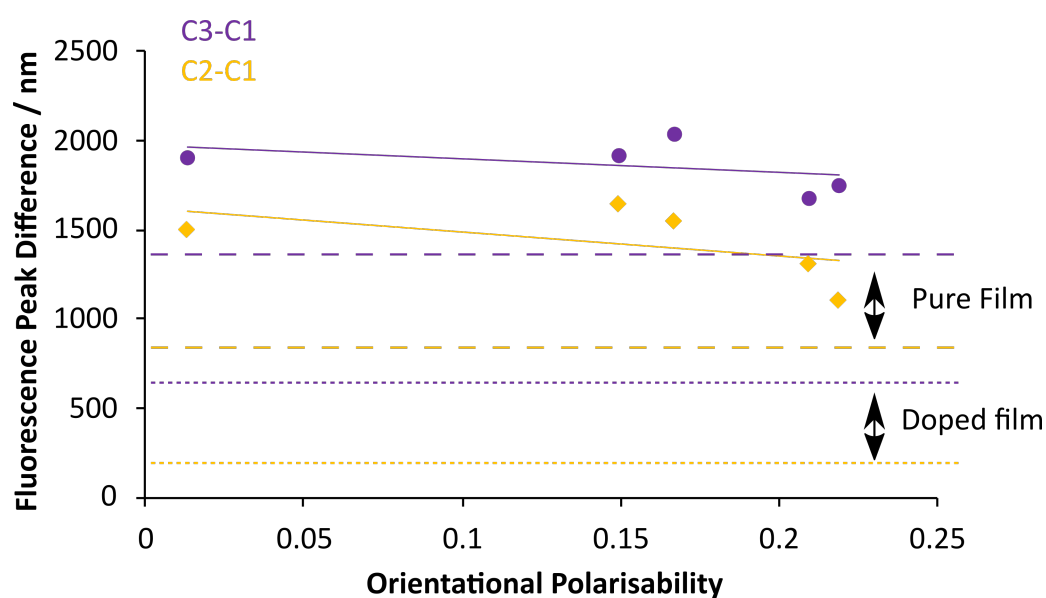


Figure B.29: The difference in peak fluorescence between C1 and C3, and C1 and C2. The difference is plotted for a variety of solvents with varying orientational polarisability. Solutions are 10 μM (C1 and C2), and 1 μM (C3). The solution differences are fit using the line shown. The film emission differences are shown for both pure and doped films using dashed lines to indicate the unknown equivalent orientational polarisability of films.

Table B.5: The fluorescence maxima and absorption maxima (bracketed) of C1. Measurements taken in tetrahydrofuran(THF), Toluene (TOL), dichloromethane (DCM), and chloroform (CHCl_3), under both degassed (-dg) an non-degassed conditions. Fluorescence is with 350 nm excitation.

Concentration / μM	THF	TOL	DCM	CHCl_3	DEE	THF-dg	TOL-dg	DCM-dg	CHCl_4 -dg
1			605 (381)	552 (384)	525 (377)			603(366)	565 (368)
10	575 (381)	502 (382)	601 (379)	562 (384)	517 (377)	570 (377)	498 (375)	604 (379)	567 (384)
100	578 (381)	501 (382)	598 (383)	567(383)	520 (377)	573 (383)	502 (383)	604 (382)	568 (384)
1000	571 (381)	499 (382)	601	563 (384)		573 (383)	505 (384)	600 (383)	

Table B.6: The fluorescence maxima and absorption maxima (bracketed) of C2. Measurements taken in tetrahydrofuran(THF), Toluene (TOL), dichloromethane (DCM), and chloroform (CHCl₃), under both degassed (-dg) an non-degassed conditions. Fluorescence is with 350 nm excitation.

Concentration / μM	THF	TOL	DCM	CHCl ₃	DEE	TOL-dg	DCM-dg
1		537 (384)	642 (390)				
10	609 (394)	537 (397)	644 (388)	619 (392)	562 (388)	542 (390)	646 (388)
100 1000		533 (398)	670 (391)				

Table B.7: The fluorescence maxima and absorption maxima (bracketed) of C3. Measurements taken in tetrahydrofuran(THF), Toluene (TOL), dichloromethane (DCM), and chloroform (CHCl_3), under both degassed (-dg) an non-degassed conditions. Fluorescence is with 350 nm excitation.

Concentration / μM	THF	TOL	DCM	CHCl_3	DEE	TOL-dg	DCM-dg
1	623 (385)	549 (396)	672 (385)	630 (389)	578 (387)	559 (396)	650 (384)
10		547 (395)	660 (384)				
100		537	668				
1000			679				

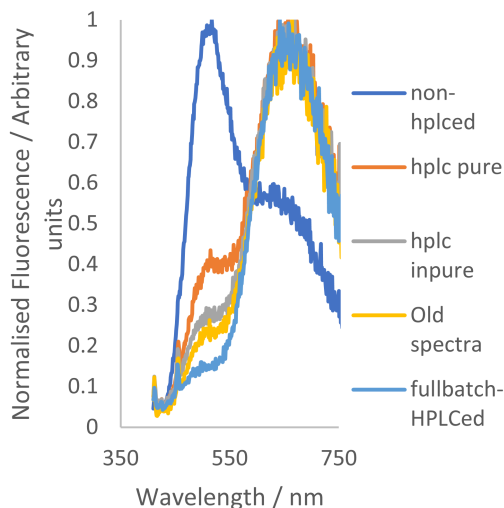


Figure B.30: The batch dependence of the blue peak for compound 3 in 1 μM DCM solutions. The spectra are obtained by excitation at 400 nm. One batch that has previously been purified by HPLC, is compared with a various HPLC fractions of a new batch which is also purified by HPLC.

B.3.1.4.8 Batch Dependence Of High Energy Solution Peak

B.3.1.5 On The Dipole Matrix Element

The dipole matrix element is as follows, where Ψ_i is the initial state, Ψ_f the final state, and μ the dipole operator.

$$\langle \Psi_i | \mu | \Psi_f \rangle \quad (\text{B.113})$$

The dipole matrix element is key to the calculation of both radiative rates (k) and the molar absorption coefficient (ε) for materials. The equations for these relation are as follows, where ρ is the density of states, $\bar{\nu}$ is the wavenumber and n is the number of moles.

$$\frac{4.32 \times 10^{-9}}{n} \int \varepsilon(\bar{\nu}) d\bar{\nu} = \langle \Psi_i | H_1 | \Psi_f \rangle^2 \rho \quad (\text{B.114})$$

$$k = \frac{2\pi}{\hbar} \langle \Psi_i | \mu | \Psi_f \rangle^2 \rho \quad (\text{B.115})$$

These equations follow from Fermi's Golden rule, and this will be initially shown in this section for the rate. Numerous text discuss the derivation for the molar absorptivity equation (e.g. see Further information sections 16 and 17 in "Molecular Quantum Mechanics" by Atkins and Friedman¹⁴ for relations with the oscillator strength), and so this will not be discussed. Fermi's golden rule is predicated on a perturbation (H_1) being applied to the initial Hamiltonian (H_0). It being the initial

Hamiltonian which produces the initial (Ψ_i) and final states (Ψ_f) as eigenvectors. The sum of the perturbing and initial Hamiltonian produces a new total Hamiltonian (H_{tot}). Fermi's golden rule for a general rate of transmission (k), and with the additional symbol of ρ equalling the density of states, is shown below.

$$H_{tot} = H_0 + H_1 \quad (\text{B.116})$$

$$k = \frac{2\pi}{\hbar} \langle \Psi_i | H_1 | \Psi_f \rangle^2 \rho \quad (\text{B.117})$$

In the case of light absorption, the perturbation is the electric field generated by light, which oscillates sinusoidally. The wavelength of the visible light (~100–1000 nm) is far greater than the size of the average molecule (~1–100 Å or 0.1–10 nm), and as such the sinusoidal perturbation can be approximated as linear (see Taylor series expansion of sine). The energy of a particle in an electrical field is its charge multiplied by the field, but it is the change of energy across the molecule which is important to perturb the Hamiltonian. As such "dipole operator" (μ) defined below is the perturbing energy.

$$E = \sum_i E_{Field}(i) q_i \quad (\text{B.118})$$

$$= \sum_i (x + c) q_i \quad (\text{B.119})$$

$$= \sum_i (x q_i) + \sum_i (c q_i) \quad (\text{B.120})$$

$$= \underbrace{\sum_i (x q_i)}_{\text{changes wavefunction}} + \underbrace{\sum_i (c \sum_i (q_i))}_{\text{does not changes wavefunction}} \quad (\text{B.121})$$

$$H_1 = \mu = \sum_i (\hat{r} q_i) \quad (\text{B.122})$$

It is commonly claimed that there must be overlap of the initial and final states in order for decay to occur. Unfortunately no proof as to why overlap between the initial and final state requires overlap could be found, and hence what follows is the author's best guess as to why this is the case. It is highly likely that this description is not 100 % correct but it is included anyway as it is felt preferable to simply claiming it is so, as per much of the other literature. It is felt at the least that this will allow a starting point for those who wish to study this further. As for text-book descriptions, it is claimed by A. Köhler and H. Bässler that¹⁵ "The rate of an electronic transition and thus the intensity of the resulting absorption or

emission signal, to zero order approximation, depends on the spatial overlap of the initial and final wavefunctions." No description of what is meant by "zero order" is given. If they mean the integral with no dipole operator, this is zero since the initial and final states are orthogonal.

A separate description is given by p. Atkins and J. De Paula in "Atkins Physical Chemistry" where they claim¹⁶ "because the integrand in the transition dipole is proportional to the overlap of the initial and final wavefunctions, it is zero unless the two wavefunctions have non-zero functions in all space." However wavefunctions do not ever equal zero, they only tend towards it. Further this neglects that the transition dipole operator may fundamentally change the initial wavefunctions due to the initial wavefunction not necessarily being an eigenfunction of it as an operator. This means that it is not necessarily true that the initial and final states directly multiply. It may be shown mathematically that they do however, and this is the subject of this section.

The starting point of a derivation of the effect of overlap begins with the dipole operator. The dipole operator is the particle charge (q_i) multiplied by the particle position($\hat{r}_i$) operator, summed over all charges(i). The dipole operator can thus be expressed as the sum of the position operators ($\hat{r}_{e,j}$) for each individual electron (j) multiplied by the electron charge ($q_{e,k}$) and the position operator ($\hat{r}_{n,k}$) of the nuclei (k) multiplied by the nuclear charge ($q_{n,k}$). This equation is summarised as follows. It is worth noting that the initial and final states may be split into electronic and nuclear components as well

$$\mu = \sum_i (\hat{r}_i(q_i)) \quad (\text{B.123})$$

$$= \sum_j (\hat{r}_{e,j}q_{e,j}) + \sum_k (\hat{r}_{n,k}(q_k)) \quad (\text{B.124})$$

$$\Psi_i = \psi_{i,n}\psi_{i,e} \quad (\text{B.125})$$

$$\Psi_f = \psi_{f,n}\psi_{f,e} \quad (\text{B.126})$$

This allows an initial simplification of the dipole matrix element, based on the electronic states upon excitation being orthogonal to the starting state.

$$\langle \Psi_i | \mu | \Psi_f \rangle = \langle \psi_{i,n} \psi_{i,e} | \sum_j (\hat{r}_{e,j} q_{e,j}) + \sum_k (\hat{r}_{n,k} (q_k)) | \psi_{f,n} \psi_{f,e} \rangle \quad (\text{B.127})$$

$$\begin{aligned} &= \langle \psi_{i,n} \psi_{i,e} | \sum_j (\hat{r}_{e,j} q_{e,j}) | \psi_{f,n} \psi_{f,e} \rangle \\ &+ \langle \psi_{i,n} \psi_{i,e} | \sum_k (\hat{r}_{n,k} (q_k)) | \psi_{f,n} \psi_{f,e} \rangle \end{aligned} \quad (\text{B.128})$$

$$\begin{aligned} &= \langle \psi_{i,e} | \sum_j (\hat{r}_{e,j} q_{e,j}) | \psi_{f,e} \rangle \langle \psi_{i,n} | \psi_{f,n} \rangle \\ &+ \langle \psi_{i,n} | \sum_i (\hat{r}_{j,n} (q_k)) | \psi_{f,e} \rangle \langle \psi_{i,e} | \psi_{f,e} \rangle \end{aligned} \quad (\text{B.129})$$

$$= \langle \psi_{i,e} | \sum_j (\hat{r}_{e,j} q_{e,j}) | \psi_{f,e} \rangle \langle \psi_{i,n} | \psi_{f,n} \rangle \quad (\text{B.130})$$

The right bra-ket just returns the nuclear overlap — giving the vibronic structure. Hence the focus will be on the left bra-ket henceforth. The position operator gives eigenvalues only for localised functions (ie. a dirac delta functions in space), since it multiplies the values by the position vector ($\mathbf{r}$), which varies with position, so reforming the function with only a multiplication of a constant, only for a fully localised function. Since in practice all wavefunctions are delocalized they will not be eigenfunctions of the system. Non-eigenvectors give results corresponding to probability distributions of the eigenvalues. Note eigenvalues of the perturbation will be marked with a bar, and those of the un-perturbed Hamiltonian without.

$$\mu \bar{\Psi} = \lambda \bar{\Psi} \text{ for } \bar{\Psi} = \delta_{r1}, \delta_{r2} \dots, \text{ and } \lambda = \mathbf{r}_1, \mathbf{r}_2 \dots \quad (\text{B.131})$$

Since all wavefunctions can be expressed as a weighted sum of eigenfunction for a given operator, it is possible to express the final wavefunction in terms of the position operator's eigenvalues.

$$\psi_{e,f} = \sum_s c_{s,f} \bar{\Psi}_{s,f} \quad (\text{B.132})$$

Having made this definition, the maths can now be approached begining in equation :

$$\langle \psi_{i,e} | \sum_j (\hat{r}_{e,j} q_{e,j}) | \psi_{f,e} \rangle = \langle \psi_{i,e} | \sum_j (\hat{r}_{e,j} q_{e,j}) | \sum_s c_{s,f} \bar{\Psi}_{s,f} \rangle \quad (\text{B.133})$$

$$= \langle \psi_{i,e} | \sum_{j,s} q_{e,j} c_{s,f} \hat{r}_{j,e} \bar{\Psi}_{s,f} \rangle \quad (\text{B.134})$$

$$= \langle \psi_{i,e} | \sum_{j,s} q_{e,j} c_{s,f} \mathbf{r}_s \bar{\Psi}_{s,f} \rangle \quad (\text{B.135})$$

The sum over all electrons (j) of the charge ($q_{e,j}$) and the position ($\mathbf{r}_s$) is interesting since for each value of the perturbation's eigenfunction (s) a non-zero value is only returned at the location of delta function which the eigenfunction corresponds. Here it sums over all charges at this location. As such it can be seen as the electron density (ρ_e) multiplied by the general position vector ($\mathbf{r}$). While this function is a vector, it is a vector in position space, as opposed to the wavefunction space, and as such it may be brought out to the front of the bra-ket.

$$\langle \psi_{i,e} | \sum_{j,s} q_{e,j} c_{s,f} \mathbf{r}_s \bar{\Psi}_{s,f} \rangle = \langle \psi_{i,e} | \sum_s \rho_e c_{s,f} \mathbf{r} \bar{\Psi}_{s,f} \rangle \quad (\text{B.136})$$

$$= \langle \rho_e \mathbf{r} \psi_{i,e} | \sum_s c_{s,f} \bar{\Psi}_{s,f} \rangle \quad (\text{B.137})$$

$$= \langle \rho_e \mathbf{r} \psi_{i,e} | \psi_{f,e} \rangle \quad (\text{B.138})$$

From this resulting equation, it is now obvious that the initial and final states overlap, since they now directly multiply.

B.3.1.6 Photoluminescence at 77K

The excitation dependence of the phosphorescence was investigated for all three compounds (see figure 1), and the results are shown in figure 2. Originally it was desired to investigate this to try and explain the perceived blue shift phosphorescence relative to the fluorescence spectra. it was felt that an excitation dependence would suggest there being two active states which effect the triplet states. However in reality this is more likely to be due to the various geometries frozen in solution and their band gaps will be excited in different proportions at different excitation wavelength, and as a result any dependence is most likely not as a results of two states. That being said, there is a clear dependence on excitation wavelength on the phosphorescence spectra of the three compounds, as shown in figure 2. It should be notes that the peak observed at 430 nm on the 430 nm excitation spectra is believed to be due to excitation pulse. However, the peak on compound 1 at 350 excitation,

which is to the left of the main peak, is from an unknown source.

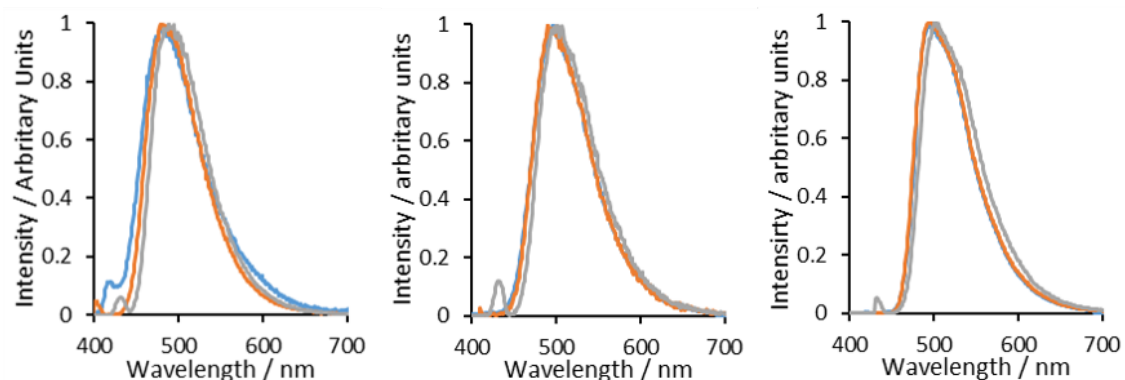


Figure B.31: The phosphorescence spectra of compound 1 (left), compound 2 (centre) and compound 3 (right), when excited at 350 nm (blue), 400 nm (orange) and 430 nm (grey). The spectra are obtained with 0.2 ms delay time, 5 ms gate time, and assuming 0.02 s decay time. To detect the spectra, a 10 nm excitation slit width, 5 nm emission slit width, and a 0.1 s averaging time were used.

B.3.1.7 Film and Solution PLQY

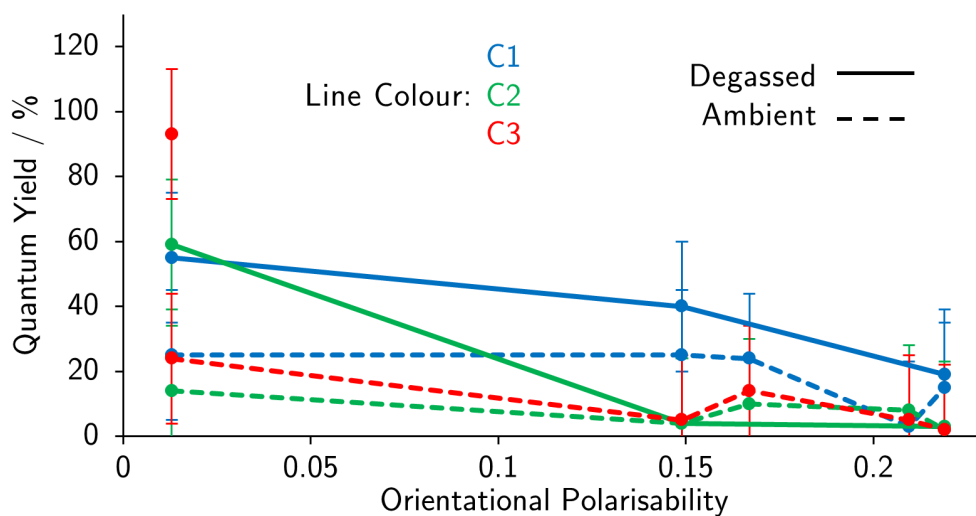


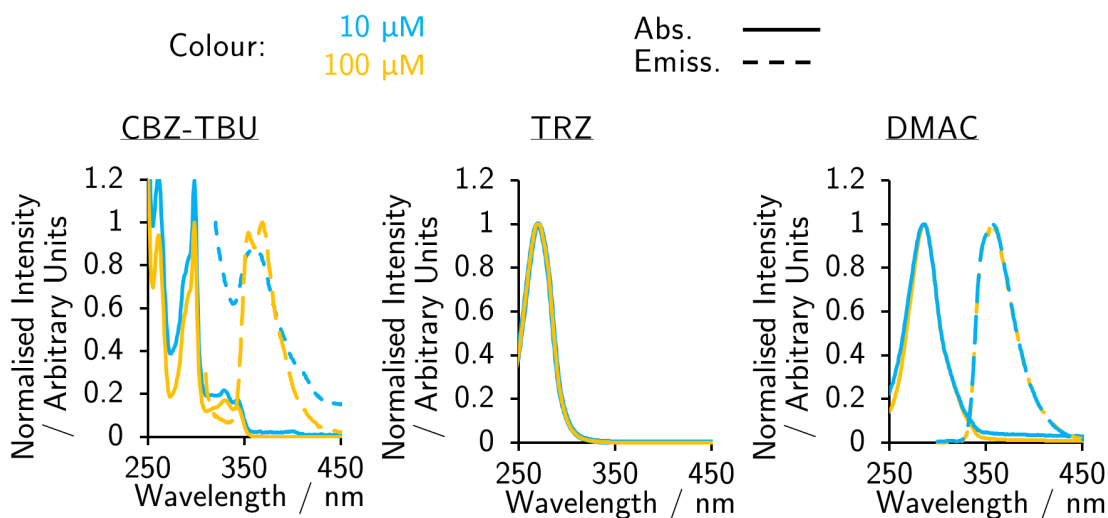
Figure B.32: The PLQY of C1-3 in various solutions, the orientational polarisability of the solvents is tabulated in figure B.8.

Table B.8: The photoluminescent quantum yield (PLQY) of C1-3 in various solutions and film. Errors calculated by assuming they are the same as a standard, and with multiple observations of the same sample acting as independent observations.

Compounds	Toluene PLQY / %	Chloroform PLQY / %	Diethyl Ether PLQY / %	Tetrahydrofuran PLQY / %	Dichloromethane PLQY / %	Pure Film PLQY / %	Doped Film ^a PLQY / %
C1 (Ambient)	30 ± 10	30 ± 10	20 ± 10	0 ± 10	20 ± 10	54	64
C1 (Degassed)	60 ± 10	40 ± 10	—	—	20 ± 10	—	—
C2 (Ambient)	10 ± 20	0 ± 20	10 ± 20	10 ± 20	0 ± 10	28	59
C2 (Degassed)	60 ± 20	0 ± 20	—	—	0 ± 20	—	—
C3 (Ambient)	20 ± 10	0 ± 10	10 ± 10	0 ± 10	0 ± 10	28	51
C3 (Degassed)	60 ± 10	40 ± 10	—	—	20 ± 10	—	—

^a10 % doped in H1

B.3.1.8 Spectra of components

**Figure B.33:** The concentration dependence of the components of C1-3.

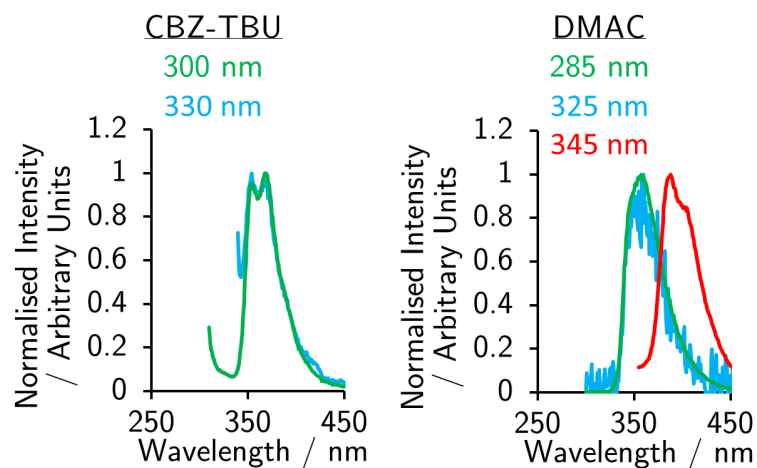


Figure B.34: The excitation dependence of the room temperature photoluminescence of the components of C1-3.

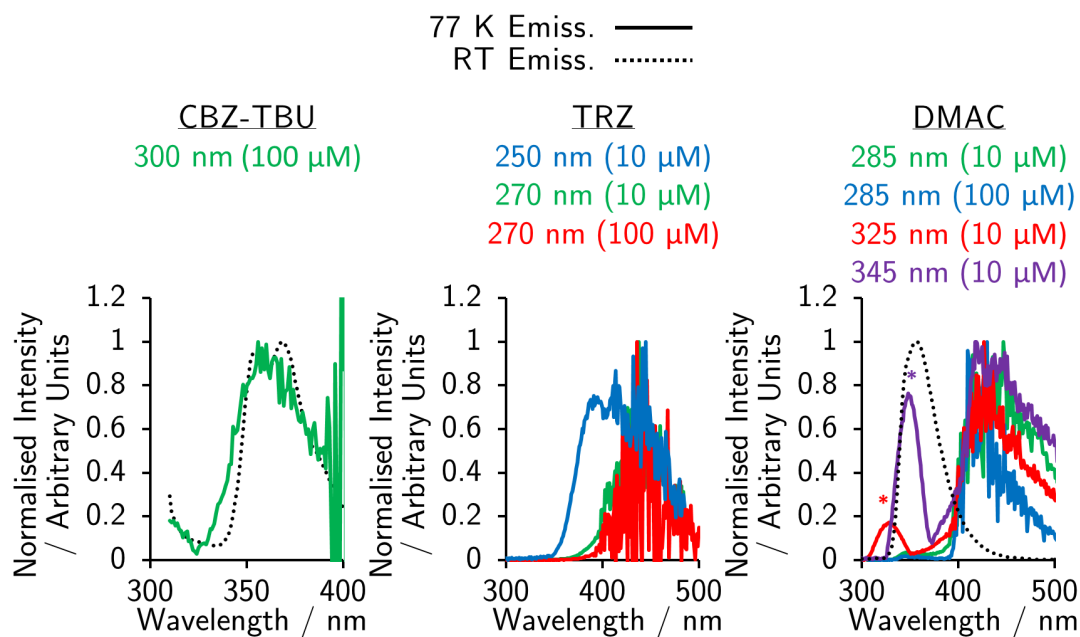


Figure B.35: The excitation dependence of the photoluminescence at 77 K of the components of C1-3. * indicates excitation pulse wavelength.

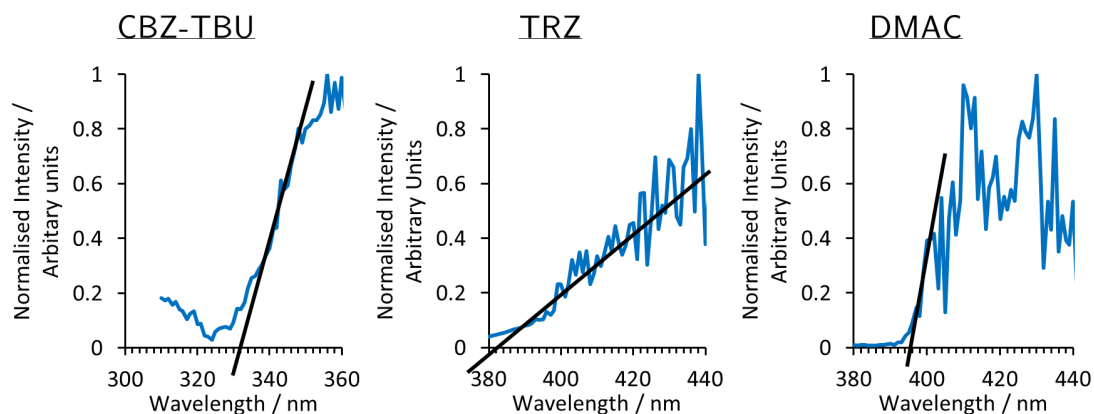


Figure B.36: The onset of phosphorescence for the components of C1-3.

B.3.1.9 Thermal Properties

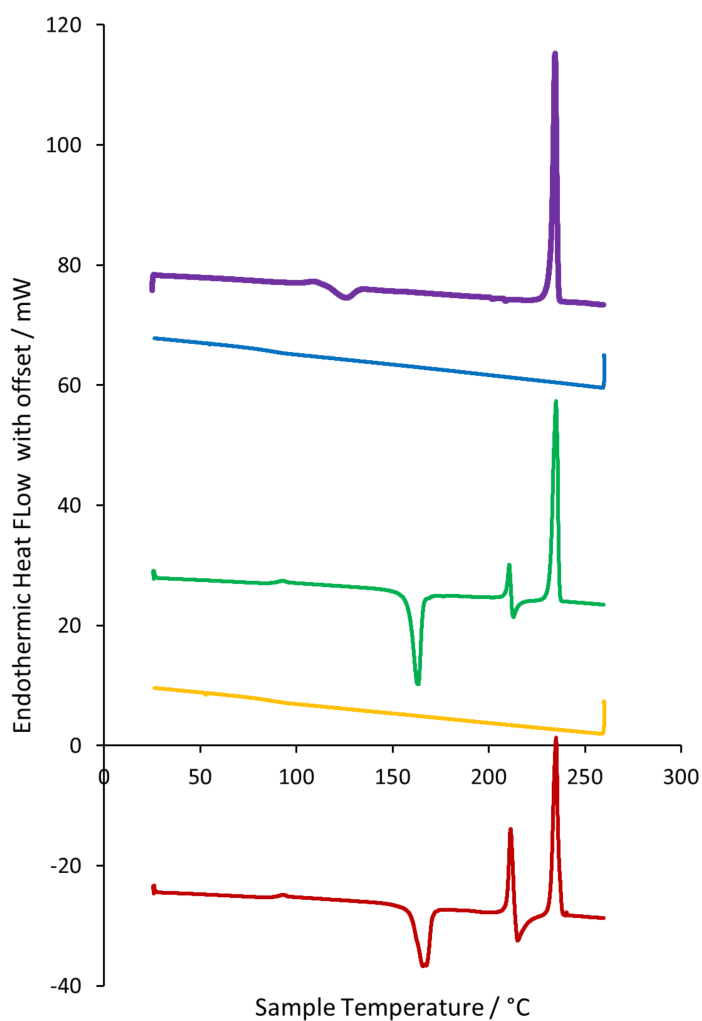


Figure B.37: The DSC run for C1, with offset runs. The DSC run starts with initial heating at the top and the swaps between cooling on subsequent runs.

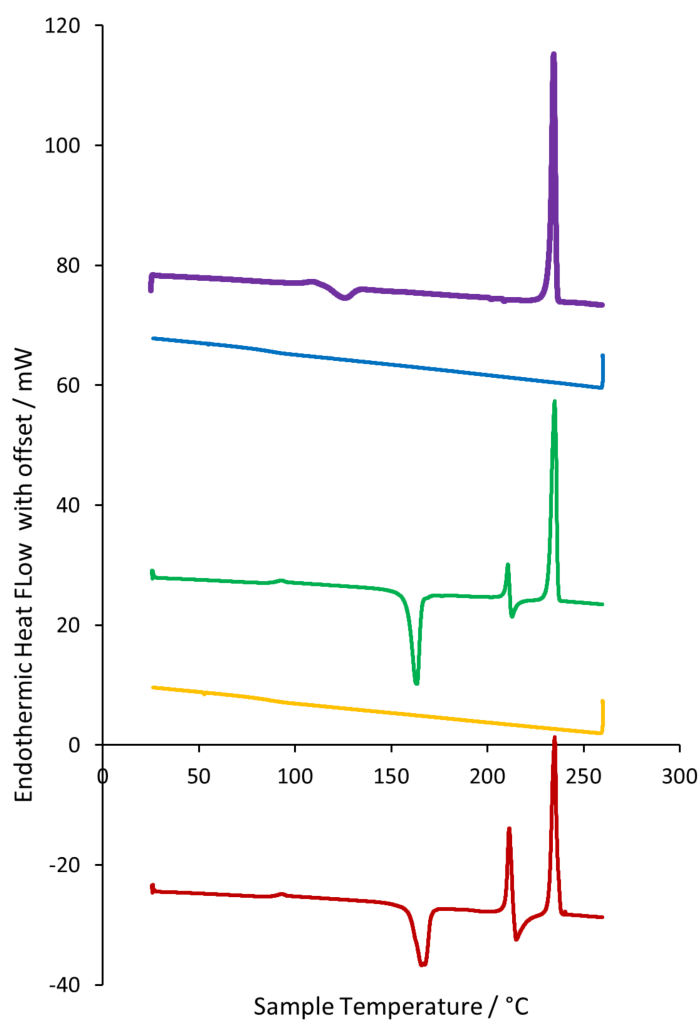


Figure B.38: The DSC run for C2, with offset runs. The DSC run starts with initial heating at the top and the swaps between cooling on subsequent runs.

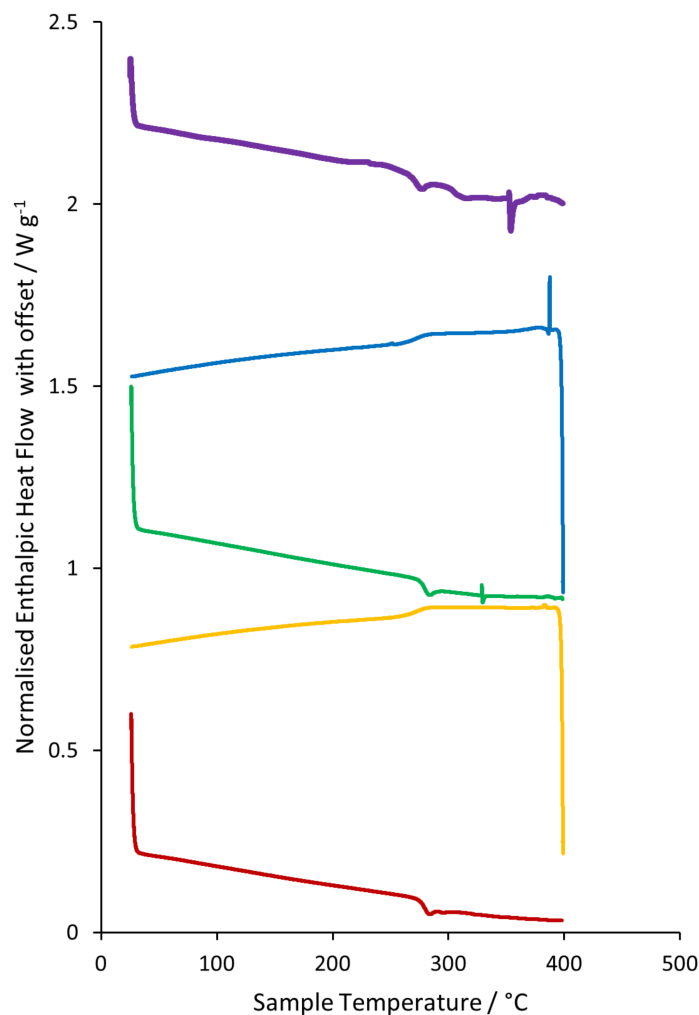


Figure B.39: The DSC run for C3, with offset runs. The DSC run starts with initial heating at the top and the swaps between cooling on subsequent runs.

B.3.2 Transient Fluorescence

B.3.2.1 Full Interpretation of Equations

$$k_{PF}, k_{DF} = k_S, 0 \quad (\text{B.139})$$

Alternatively put

$$k_{PF}, k_{DF} = \left(\frac{k_S + k_T}{2} \right) \pm \frac{1}{2} \sqrt{(k_S - k_T)^2 + 4k_{ISC}k_{RISC}} \quad (\text{B.140})$$

$$[S_1] = \frac{[S_1]_0}{k_{PF} - k_{DF}} ((k_S - k_{DF}) e^{-k_{PF}t} + ((k_{PF} - k_S) e^{-k_{DF}t})) \quad (\text{B.141})$$

$$[T_1] = \frac{[S_1]_0 k_{ISC}}{k_{PF} - k_{DF}} (e^{-k_{PF}t} - e^{-k_{DF}t}) \quad (\text{B.142})$$

F is the intensity of emitted light

$$F = k_{s-r}[S_1] + k_{t-r}[T_1] \quad (\text{B.143})$$

$$F = \left(\frac{[S_1]_0 k_{ISC}}{k_{PF} - k_{DF}} \right) [e^{-k_{PF}t}(k_{s-r}(k_S - k_{DF}) - k_{ISC}k_{t-r}) + e^{-k_{DF}t}(k_{s-r}(k_{PF} - k_S) + k_{ISC}k_{t-r})] \quad (\text{B.144})$$

$$F_{PF} = \left(\frac{[S_1]_0 k_{ISC}}{k_{PF} - k_{DF}} \right) e^{-k_{PF}t}(k_{s-r}(k_S - k_{DF}) - k_{ISC}k_{t-r}) \quad (\text{B.145})$$

$$F_{DF} = \left(\frac{[S_1]_0 k_{ISC}}{k_{PF} - k_{DF}} \right) e^{-k_{DF}t}(k_{s-r}(k_{PF} - k_S) + k_{ISC}k_{t-r}) \quad (\text{B.146})$$

I is the relative intensity

$$I_{PF} = \frac{F_{PF}(t=0)}{F_{PF}(t=0) + F_{DF}(t=0)} \quad (\text{B.147})$$

$$I_{PF} = \frac{k_{s-r}(k_S - k_{DF}) - k_{ISC}k_{t-r}}{(k_{s-r}(k_S - k_{DF}) + k_{ISC}k_{t-r}) + (k_{s-r}(k_{PF} - k_S) - k_{ISC}k_{t-r})} \quad (\text{B.148})$$

$$I_{PF} = \frac{k_{s-r}(k_S - k_{DF}) - k_{ISC}k_{t-r}}{k_{s-r}(k_{PF} - k_{DF})} \quad (\text{B.149})$$

$$I_{DF} = \frac{F_{DF}(t=0)}{F_{PF}(t=0) + F_{DF}(t=0)} \quad (\text{B.150})$$

$$I_{DF} = \frac{k_{s-r}(k_{PF} - k_S) + k_{ISC}k_{t-r}}{(k_{s-r}(k_S - k_{DF}) + k_{ISC}k_{t-r}) + (k_{s-r}(k_{PF} - k_S) - k_{ISC}k_{t-r})} \quad (\text{B.151})$$

$$I_{DF} = \frac{(k_{s-r}(k_{PF} - k_S) + k_{ISC}k_{t-r})}{k_{s-r}(k_{PF} - k_{DF})} \quad (\text{B.152})$$

When noting that the intensity (F) are exponentials, it may be seen that the relative area of the pulse fluorescence decay (A_{PF}) is expressed below (normalised over total area).

$$A_{PF} = \frac{F_{PF}(t=0) \div k_{PF}}{F_{PF}(t=0) \div k_{PF} + F_{DF}(t=0) \div k_{DF}} \quad (\text{B.153})$$

$$A_{PF} = \frac{F_{PF}(t=0)k_{DF}}{F_{PF}(t=0)k_{DF} + F_{DF}(t=0)k_{PF}} \quad (\text{B.154})$$

$$A_{PF} = \frac{1}{2} \frac{(F_{PF}(t=0)k_{DF} + F_{DF}(t=0)k_{PF}) + (F_{PF}(t=0)k_{DF} - F_{DF}(t=0)k_{PF})}{F_{PF}(t=0)k_{DF} + F_{DF}(t=0)k_{PF}} \quad (\text{B.155})$$

$$A_{PF} = \frac{1}{2} + \frac{1}{2} \frac{(F_{PF}(t=0)k_{DF} - F_{DF}(t=0)k_{PF})}{F_{PF}(t=0)k_{DF} + F_{DF}(t=0)k_{PF}} \quad (\text{B.156})$$

$$A_{PF} = \frac{1}{2} + \frac{1}{2} \frac{k_{DF}(k_{s-r}(k_S - k_{DF}) - k_{ISC}k_{t-r}) - k_{PF}(k_{s-r}(k_{PF} - k_S) + k_{ISC}k_{t-r})}{k_{DF}(k_{s-r}(k_S - k_{DF}) - k_{ISC}k_{t-r}) + k_{PF}(k_{s-r}(k_{PF} - k_S) + k_{ISC}k_{t-r})} \quad (\text{B.157})$$

To continue, some substitutions must be made

$$a = k_{s-r}k_s \quad (\text{B.158})$$

$$b = k_{s-r}k_{DF} \quad (\text{B.159})$$

$$c = k_{s-r}k_{PF} \quad (\text{B.160})$$

$$d = k_{ISC}k_{t-r} \quad (\text{B.161})$$

$$f = \frac{k_S + k_T}{2} \quad (\text{B.162})$$

$$g = \frac{1}{2} \sqrt{(k_S - k_T)^2 + 4k_{ISC}k_{RISC}} \quad (\text{B.163})$$

$$A_{PF} = \frac{1}{2} + \frac{1}{2} \frac{(f - g)(a - b - d) - (f + g)(c - a + d)}{(f - g)(a - b - d) + (f + g)(c - a + d)} \quad (\text{B.164})$$

$$A_{PF} = \frac{1}{2} + \frac{1}{2} \frac{-b(f - g) - c(f + g) + (a - d)(f - g) + (-d + a)(f + g)}{-b(f - g) + c(f + g) + (a - d)(f - g) + (d - a)(f + g)} \quad (\text{B.165})$$

$$A_{PF} = \frac{1}{2} + \frac{1}{2} \frac{-k_{s-r}k_{DF}^2 - k_{s-r}k_{PF}^2 - 2fd + 2fa}{-k_{s-r}k_{DF}^2 + k_{s-r}k_{PF}^2 + 2gd - 2ga} \quad (\text{B.166})$$

$$A_{PF} = \frac{1}{2} + \frac{1}{2} \frac{-k_{s-r}((f - g)^2 + (f + g)^2) - 2fd + 2fa}{-k_{s-r}(f - g)^2 + k_{s-r}(f + g)^2 + 2gd - 2ga} \quad (\text{B.167})$$

$$A_{PF} = \frac{1}{2} + \frac{1}{2} \frac{-2k_{s-r}(f^2 + g^2) + 2f(a - d)}{4k_{s-r}fg + 2gd - 2ga} \quad (\text{B.168})$$

$$A_{PF} = \frac{1}{2} + \frac{1}{2} \frac{-2k_{s-r}(f^2 + g^2) + 2f(a - d)}{2g(2k_{s-r}f + d - a)} \quad (\text{B.169})$$

$$A_{PF} = \frac{1}{2} + \frac{1}{2} \frac{-2k_{s-r}((\frac{k_S+k_T}{2})^2 + (\frac{1}{2}\sqrt{(k_S-k_T)^2 + 4k_{ISC}k_{RISC}})^2) + 2\frac{k_S+k_T}{2}(k_{s-r}k_S - k_{ISC}k_{t-r})}{\sqrt{(k_S-k_T)^2 + 4k_{ISC}k_{RISC}}(2k_{s-r}(\frac{k_S+k_T}{2}) + k_{ISC}k_{t-r} - k_{s-r}k_S)} \quad (\text{B.170})$$

$$A_{PF} = \frac{1}{2} + \frac{1}{2} \frac{-2k_{s-r}(\frac{1}{2}(k_S^2 + k_T^2) + k_{ISC}k_{RISC}) + (k_S + k_T)(k_{s-r}k_S - k_{ISC}k_{t-r})}{\sqrt{(k_S-k_T)^2 + 4k_{ISC}k_{RISC}}(k_{s-r}k_T + k_{ISC}k_{t-r})} \quad (\text{B.171})$$

$$A_{PF} = \frac{1}{2} + \frac{1}{2} \frac{-k_{s-r}k_S^2 - k_{s-r}k_T^2 - k_{s-r}k_{ISC}k_{RISC} + k_Sk_{s-r}k_S - k_Sk_{ISC}k_{t-r} + k_Tk_{s-r}k_S - k_Tk_{ISC}k_{t-r}}{\sqrt{(k_S-k_T)^2 + 4k_{ISC}k_{RISC}}(k_{s-r}k_T + k_{ISC}k_{t-r})} \quad (\text{B.172})$$

$$A_{PF} = \frac{1}{2} + \frac{1}{2} \frac{-k_{s-r}k_T^2 - k_{s-r}k_{ISC}k_{RISC} + k_S^2k_{s-r} - k_Sk_{ISC}k_{t-r} + k_Tk_{s-r}k_S - k_Tk_{ISC}k_{t-r}}{\sqrt{(k_S-k_T)^2 + 4k_{ISC}k_{RISC}}(k_{s-r}k_T + k_{ISC}k_{t-r})} \quad (\text{B.173})$$

$$A_{PF} = \frac{1}{2} + \frac{1}{2} \frac{k_{s-r}k_T(k_S - k_T) - k_{ISC}(k_{s-r}k_{RISC} + k_{t-r}(k_S + k_T))}{\sqrt{(k_S + k_T)^2 + 4k_{ISC}k_{RISC}}(k_{s-r}k_T + k_{ISC}k_{t-r})} \quad (\text{B.174})$$

It may be proved trivially that, for the delayed fluorescence relative area, using similar maths, the following

$$A_{DF} = \frac{1}{2} - \frac{1}{2} \frac{(F_{PF}(t=0)k_{DF} - F_{DF}(t=0)k_{PF})}{F_{PF}(t=0)k_{DF} + F_{DF}(t=0)k_{PF}} \quad (\text{B.175})$$

This is similar enough to equation B.156, and as such may be simplified similarly to

$$A_{DF} = \frac{1}{2} - \frac{1}{2} \frac{k_{s-r}k_T(k_S - k_T) - k_{ISC}(k_{s-r}k_{RISC} + k_{t-r}(k_S + k_T))}{\sqrt{(k_S + k_T)^2 + 4k_{ISC}k_{RISC}}(k_{s-r}k_T + k_{ISC}k_{t-r})} \quad (\text{B.176})$$

The PLQY is easier to calculate, as this simply follows from the total amount of molecules which emit (ie. integrated un-normalised intensity), divided by the total number of originally excited states.

$$PLQY = \frac{F_{PF}(t=0) \div k_{PF} + F_{DF}(t=0) \div k_{DF}}{[S_1]_0} \quad (\text{B.177})$$

$$PLQY = \frac{F_{PF}(t=0)k_{DF} + F_{DF}(t=0)k_{PF}}{[S_1]_0 k_{PF} k_{DF}} \quad (B.178)$$

It may be observed that the numerator in this previous equation is identical to one of the denominator in equation B.156. The same simplification applies with the exception of taking out the parts of the equation which cancel in the fraction (see bracketed factor in equation B.144). As such the equation can be simplified as below. Note that the earlier defined symbols f and g are also used.

$$PLQY = \frac{(2g)(k_{s-r}k_T + k_{ISC}k_{t-r})([S]_0)}{[S_1]_0 k_{PF} k_{DF} (k_{PF} - k_{DF})} \quad (B.179)$$

$$PLQY = \frac{(2g)(k_{s-r}k_T + k_{ISC}k_{t-r})([S]_0)}{[S_1]_0 (f+g)(f-g)(2g)} \quad (B.180)$$

$$PLQY = \frac{(2g)(k_{s-r}k_T + k_{ISC}k_{t-r})}{(f+g)(f-g)(2g)} \quad (B.181)$$

$$PLQY = \frac{(k_{s-r}k_T + k_{ISC}k_{t-r})}{f^2 + g^2} \quad (B.182)$$

$$PLQY = \frac{(k_{s-r}k_T + k_{ISC}k_{t-r})}{\left(\frac{k_S + k_T}{2}\right)^2 + \frac{1}{4}((k_S - k_T)^2 + 4k_{ISC}k_{RISC})} \quad (B.183)$$

$$PLQY = \frac{(k_{s-r}k_T + k_{ISC}k_{t-r})}{k_S k_T + k_{ISC}k_{RISC}} \quad (B.184)$$

B.3.2.2 Limiting interpretations of the equations

B.3.2.2.1 Slow k_{ISC} And k_{RISC} When the ISC and RISC rate are slow, easy simplification is possible. Here the following equations apply, forming the case with no TADF.

$$k_{PF}, k_{DF} = k_S, k_T \quad (B.185)$$

Alternatively put

$$[S_1] = [S_1]_0 e^{k_S t} \quad (B.186)$$

$$[T_1] = \frac{[S_1]_0 k_{ISC}}{k_S - k_T} (e^{-k_{PF} t} - e^{-k_{DF} t}) \quad (B.187)$$

$$I_{PF} = 1 \quad (B.188)$$

$$I_{DF} = 0 \quad (\text{B.189})$$

$$A_{PF} = 1 \quad (\text{B.190})$$

$$A_{DF} = 0 \quad (\text{B.191})$$

$$PLQY = \frac{k_{s-r}}{k_T} \quad (\text{B.192})$$

B.3.2.2.2 Fast k_{ISC} , k_{RISC} This essentially returns the equilibrium case,

$$k_{PF}, k_{DF} = k_{ISC} + k_{RISC}, 0 \quad (\text{B.193})$$

Alternatively put, ie. when multiplied by $(f + g)/(f + g)$ in the delayed fluorescence rate

$$k_{DF} = \frac{k_{RISC}(k_{s-r} + k_{s-nr}) + k_{ISC}(k_{t-r} + k_{t-nr})}{k_{ISC} + k_{RISC}} \quad (\text{B.194})$$

$$[S_1] = \frac{[S_1]_0}{k_{ISC} + k_{RISC}} (k_{ISC} e^{-k_{PF}t} + k_{RISC} e^{-k_{DF}t}) \quad (\text{B.195})$$

$$[T_1] = \frac{[S_1]_0 k_{ISC}}{k_{DF} - k_{PF}} (e^{-k_{PF}t} - e^{-k_{DF}t}) \quad (\text{B.196})$$

$$I_{PF} = \frac{k_{s-r}(k_{ISC}) - k_{ISC}k_{t-r}}{k_{s-r}(k_{ISC} + k_{RISC})} \quad (\text{B.197})$$

$$I_{DF} = \frac{(k_{s-r}k_{RISC} + k_{ISC}k_{t-r})}{k_{s-r}(k_{PF} - k_{DF})} \quad (\text{B.198})$$

$$A_{PF} = \frac{1}{2} - \frac{1}{2} \frac{k_{s-r}k_{ISC}^2 + k_{t-r}^2k_{ISC}k_{t-r}k_{RISC} + k_{ISC}}{(k_{ISC} + k_{RISC})(k_{s-r}k_{RISC} + k_{ISC}k_{t-r})} \quad (\text{B.199})$$

$$A_{PF} = \frac{1}{2} + \frac{1}{2} \frac{k_{s-r}k_{ISC}^2 + k_{t-r}^2k_{ISC}k_{t-r}k_{RISC} + k_{ISC}}{(k_{ISC} + k_{RISC})(k_{s-r}k_{RISC} + k_{ISC}k_{t-r})} \quad (\text{B.200})$$

$$PLQY = \frac{(k_{s-r}k_{RISC} + k_{ISC}k_{t-r})}{k_{ISC}k_{RISC} + k_{ISC}k_{RISC}} \quad (\text{B.201})$$

B.3.2.2.3 $k_{s-nr}, k_{s-r}, k_{ISC} \gg k_{t-nr}, k_{t-r}, k_{RISC}$ Implicit in this calculation is that k_{s-nr}, k_{s-r} and k_{ISC} are of similar order. Further that k_{t-nr}, k_{t-r} , and k_{RISC}

$$k_{PF}, k_{DF} = k_S, 0 \quad (\text{B.202})$$

Alternatively put, ie. when multiplied by $(f + g)/(f + g)$ in the delayed fluorescence rate

$$k_{PF}, k_{DF} = k_S, k_{t-nr} + k_{t-r} + k_{RISC} \left(1 - \frac{k_{ISC}}{k_{ISC} + k_{s-nr} + k_{ISC}} \right) \quad (\text{B.203})$$

$$[S_1] = \frac{[S_1]_0}{(e^{-k_{PF}t} + \left(\frac{k_T}{k_S} - \frac{k_{ISC}k_{RISC}}{k_S^2} \right) e^{-k_{DF}t})} \quad (\text{B.204})$$

$$[S_1] \approx [S_1]_0 e^{-k_{PF}t} \quad (\text{B.205})$$

$$[T_1] = \frac{[S_1]_0 k_{ISC}}{k_S} (e^{-k_{PF}t} - e^{-k_{DF}t}) \quad (\text{B.206})$$

$$I_{PF} = \frac{k_{s-r}k_S}{k_{s-r}k_{PF}} \quad (\text{B.207})$$

Note, the following

$$I_{DF} = \frac{(k_{s-r}(k_{PF} - k_S) + k_{ISC}k_{t-r})}{k_{s-r}k_{PF}} \approx 0 \quad (\text{B.208})$$

$$A_{PF} = \frac{1}{2} + \frac{1}{2} \frac{k_{s-r}k_Tk_S - k_{ISC}k_{s-r}k_{RISC} + k_{ISC}k_{t-r}k_S}{k_S(k_{s-r}k_T + k_{ISC}k_{t-r})} \quad (\text{B.209})$$

$$A_{PF} = \frac{1}{2} - \frac{1}{2} \frac{k_{s-r}k_Tk_S - k_{ISC}k_{s-r}k_{RISC} + k_{ISC}k_{t-r}k_S}{k_S(k_{s-r}k_T + k_{ISC}k_{t-r})} \quad (\text{B.210})$$

$$PLQY = \frac{(k_{s-r}k_T + k_{ISC}k_{t-r})}{k_Sk_T + k_{ISC}k_{RISC}} \quad (\text{B.211})$$

B.3.2.3 Plotting Equations For The General Case

So in reality the situation will be in-between each of the literature limiting cases.^{4,17,18,19} Some singlets will decay radiative and non-radiatively initially, and some will go to triplets. The ratio of singlets to triplets will vary significantly depending on the parameters involved. It is possible to get an idea of how these parameters change by plotting the general equations without approximating parameters. This will be

broken down into sections on the rate constant, the relative starting intensity, and one on a combination of area and PLQY.

B.3.2.3.1 Rate The rate constants are calculable via the equations shown below

$$k_{PF}, k_{DF} = \left(\frac{k_S + k_T}{2} \right) \pm \frac{1}{2} \sqrt{(k_S - k_T)^2 + 4k_{ISC}k_{RISC}} \quad (\text{B.212})$$

When the equations is written in this form several things become apparent

- TADF is effectively turned on or off by $k_{ISC} \times k_{RISC}$ (Note that it has been shown when this is set to 0, the non-TADF system is produced. See section B.3.2.2.1.)
- The equation shown a degree symmetry with respect to exchange of the pairs k_{ISC}, k_{RISC} ; and $(k_{s-nr} + k_{s-r}), (k_{t-nr} + k_{t-r})$.
- The pulse and delayed fluorescence show linear increase with the linear multiplication increase of all parameters (ie. $k_{ISC-new} = ck_{ISC-old}$, $k_{s-r-new} = ck_{s-r-old}$, ... where c is a constant multiplied with all parameters). Note that the ks+kt contains all parameters in a linear sum, and the linear increase cancels exactly for $(k_{ISC}k_{RISC} - k_Sk_T)/(k_S + k_T)^2$ as both top and bottom increase by the square of the multiplied factor.
- The radiative and non radiative rate of decay are only ever expressed as their sum. So functionally they are indistinguishable
- There is no separate phosphorescent decay constant. This means if the phosphorescence peak is indistinguishable or nearly indistinguishable from the TADF peak, it should not be possible to separate out its decay for a group of electronically identical molecules.

As a result it was concluded 4 parameters should be plotted

- $k_{ISC} \times k_{RISC} / \max(k_{ISC} \times k_{RISC})$ with constant $(k_{s-nr} + k_{s-r}), (k_{t-nr} + k_{t-r})$ and k_{ISC} to k_{RISC} ratio,
- k_{RISC} / k_{ISC} constant $(k_{s-nr} + k_{s-r}), (k_{t-nr} + k_{t-r})$ and k_{ISC} ratio,
- $(k_{t-nr} + k_{t-r}) / (k_{s-nr} + k_{s-r})$ constant $(k_{s-nr} + k_{s-r}), k_{ISC}$ and k_{RISC} ratio,
- $k_S + k_T$ with constant ratio of parameters, in order to confirm linearity.

In order to ensure comparability, $k_S + k_T = 1$ is enforced throughout, except when $k_S + k_T$ is varied. The results of these graphs are shown in figure B.40, with confirmation of the aforementioned limiting cases, as well as a breakdown of values shown in figure B.41. These graphs largely yield to the standard qualitative description of these systems. For when k_{RISC} and k_{ISC} are varied, an initial increase in delayed fluorescence, over several orders of magnitude corresponds to the switching on of RISC, and thus faster decay than the standard triplet decay, this then peaks, as RISC and singlet emission begin to compete with each other. The emission rate then declines. For the pulse fluorescence the reverse is true, as RISC begins to increase pulse fluorescence decreases, as it takes up a larger proportion of the decay constants. This is only true when RISC is large in comparison to ISC. This initial decrease is followed by an increase, as the prompt decay becomes more the rate that singlets and triplets reach equilibrium, instead of the rate that the initially excited singlets decay. This increase for fast RISC is unexpected within previous descriptions of this system.

The dependence on the ratio of k_{RISC} to k_{ISC} behaves broadly as expected with increased RISC causing increased DF and decreased PF. There is a caveat that this effect is most prominent when k_{ISC} is of the order of k_S . This however can once again be explained by the two limiting cases of fast RISC and slow RISC, in the slow ISC regime (ie. with $k_{ISC} \ll k_S$ here), the effects is minimised because RISC remains slow throughout. For fast ISC (ie. with $k_{ISC} \gg k_S$) the effect of increased reverse intersystem crossing is minimised because the pulse fluorescence begins to correspond to the decay of the system to equilibrium instead of the decay of initial singlets.

$(k_{t-nr} + k_{t-r})$ similarly has expected and unexpected results. As it increases, and reaches a point where it $\approx k_{RISC}$, delayed fluorescence increased. A corresponding decrease in pulse fluorescence is also observed for fast $(k_{t-nr} + k_{t-r})$, this corresponds to a reduction in the amount of $(k_{s-nr} + k_{s-r})$, k_{ISC} , and k_{RISC} present as it increases. Interestingly this effect decreases for slow RISC, which can be assigned the increased amount of intersystem crossing and singlet decay in the ratio.

As expected we see that varying $k_S + k_T$ yields a linear graph. In fact it is notable the prompt fluorescence only varies significantly (ie. by greater than 4/3) for changes in $k_S + k_T$. The next greatest change occurs when triplet decay is fast which is unlikely. On the other hand, the delayed rate goes through several order of magnitude of change for change in parameter ratios. This suggests perhaps that prompt fluorescence is most sensitive to the wholesale change of parameters instead of their relative values.

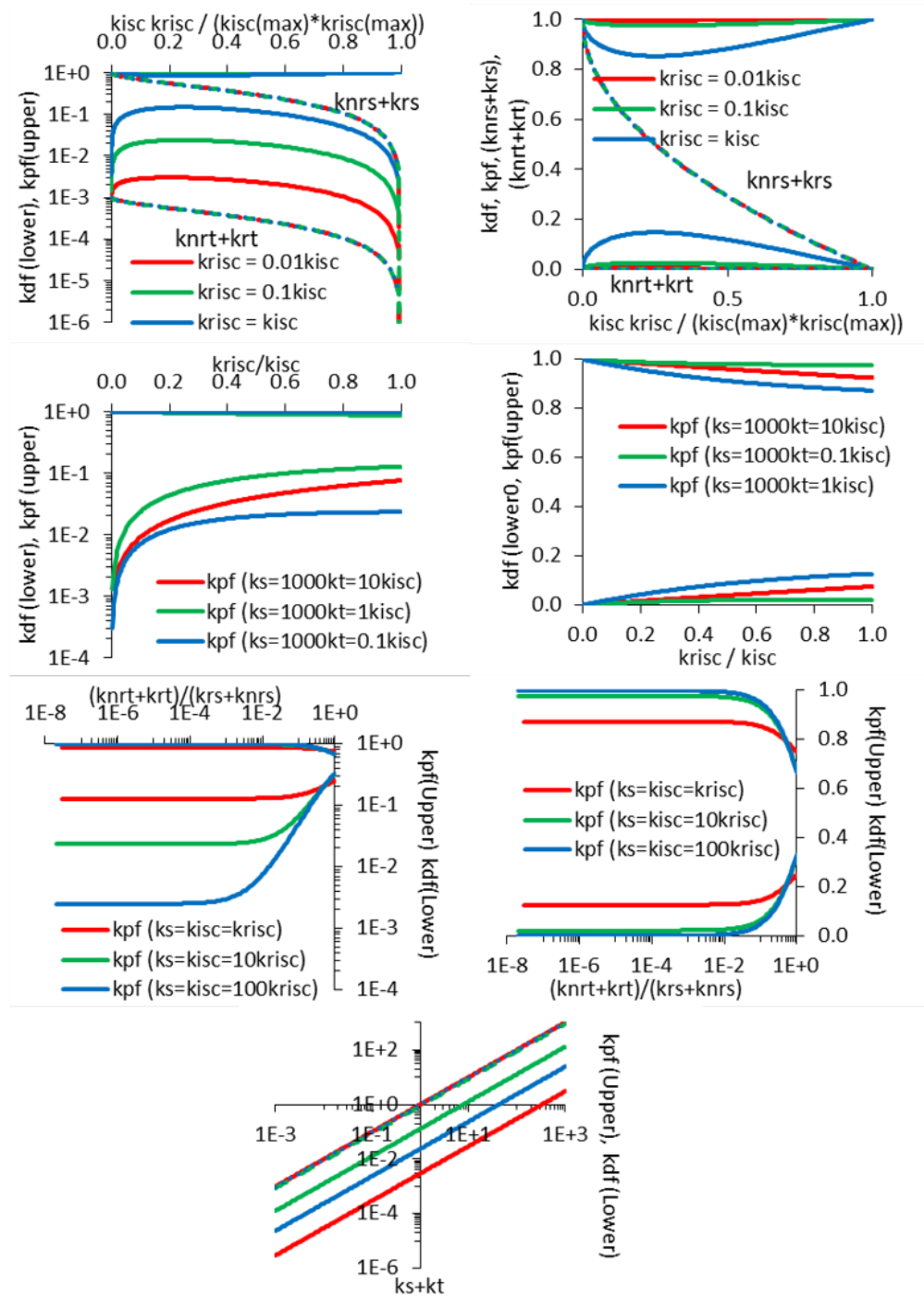


Figure B.40: The change in prompt and delayed fluorescence decay rate with change in various rate constants. $k_S + k_T = 1$ has been enforced except when $k_S + k_T$ is varied. There is a slight change in notation, with rate being written without subscripts and $k_{t-nr} = knrt$ etc.

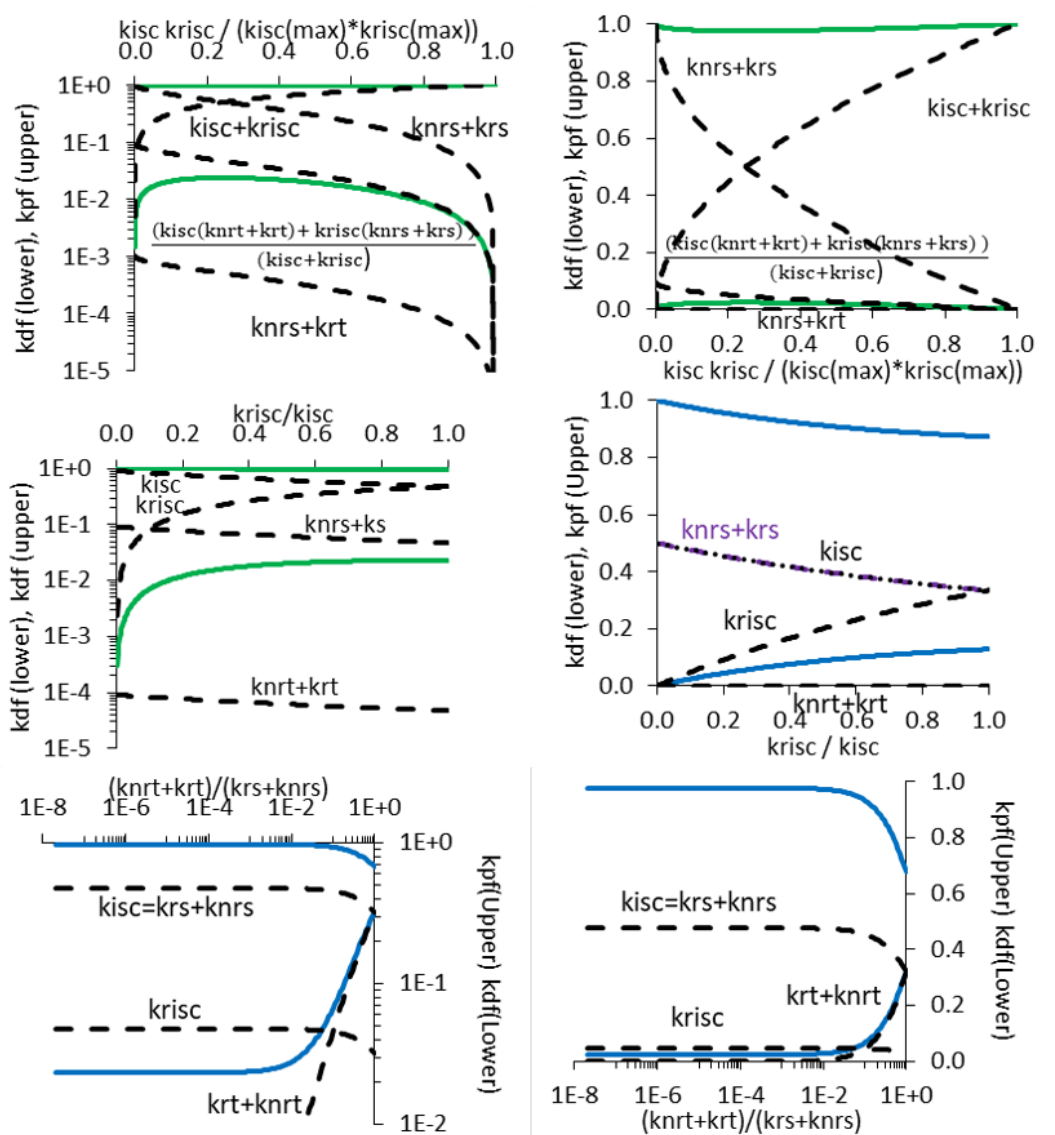


Figure B.41: The change in prompt and delayed fluorescence decay rate with change in various rate constants. $k_S + k_T = 1$ has been enforced except when $k_S + k_T$ is varied. Additional plotted lines showing limiting cases, as well as components are also shown. Graph lines are selected from figure B.40. There is a slight change in notation, with rate being written without subscripts and $k_{t-nr} = k_{nrt}$ etc.

B.3.2.3.2 Area And PLQY In addition to decay constants, there exists several other observables which can be readily compared in order to investigate the decay constants of the system. These are the starting intensities of the pulse and delayed fluorescence decays, and the integrated area of the decay. These have been calculated in section B.3.2.1. Here the area and the PLQY are examined.

Of course each of these equations are quite hard to explain qualitatively, and so plotting can be employed, first the percentage area and PLQY are plotted in figure B.42 and B.43 respectively. In order to plot these formula, assumptions regarding the relative rate of radiative and non-radiative rates must be undertaken. For this purpose the following approximations are made. They are to reflect the much higher PLQY expected for singlet emission than triplet emission. This is with the exception of when these parameters are explicitly varied. It should be noted that both singlet and triplet radiative decay is counted in the PLQY.

$$\frac{k_{s-r}}{k_{s-r} + k_{s-nr}} = 0.95 \quad (\text{B.213})$$

$$\frac{k_{t-r}}{k_{t-r} + k_{t-nr}} = 0.05 \quad (\text{B.214})$$

The results of the percentage area generally follow what we would qualitatively expect. As the RISC and ISC increase, so does the amount relative amount of delayed fluorescence. The rate of increase is initially slower for $k_{RISC} \approx k_{ISC}$, but then increases faster. This change is justified by the large difference in k_{RISC} and k_{ISC} , the turn on of RISC essentially quenching the system, and not leading to the equilibrium case, until higher rates. This causes a greater initial increase/decrease, but slows the changes for faster RISC. For PLQY only the initial turning on of ISC is relevant, and becomes more relevant the lower the RISC rate relative to ISC.

For decay area vs k_{RISC}/k_{ISC} when k_{RISC} is greater than the non-radiative decay rate an increase is observed, and an additional increase when k_{RISC} and k_{ISC} approach equality. The first increase can be justified by the increase in delayed fluorescence when RISC is enabled, and the second can be justified by the system changing such that pulse fluorescence corresponds to bringing the system to equilibrium and then emitting by delayed fluorescence. Additionally, the multiple of k_{RISC} and k_{ISC} is greater when they are equal, this will contribute to the second change. The changes are greatest for fast ISC, and this is easy to justify as the amount of excitons engaging in delayed fluorescence increases with ISC. For PLQY there is a large increase when $k_{RISC} \approx k_{t-nr} + k_{t-r}$.

When triplet emission rate is changed, an initial increase in the pulse fluorescence area is observed followed by a decrease. The initial increase can be justified by the

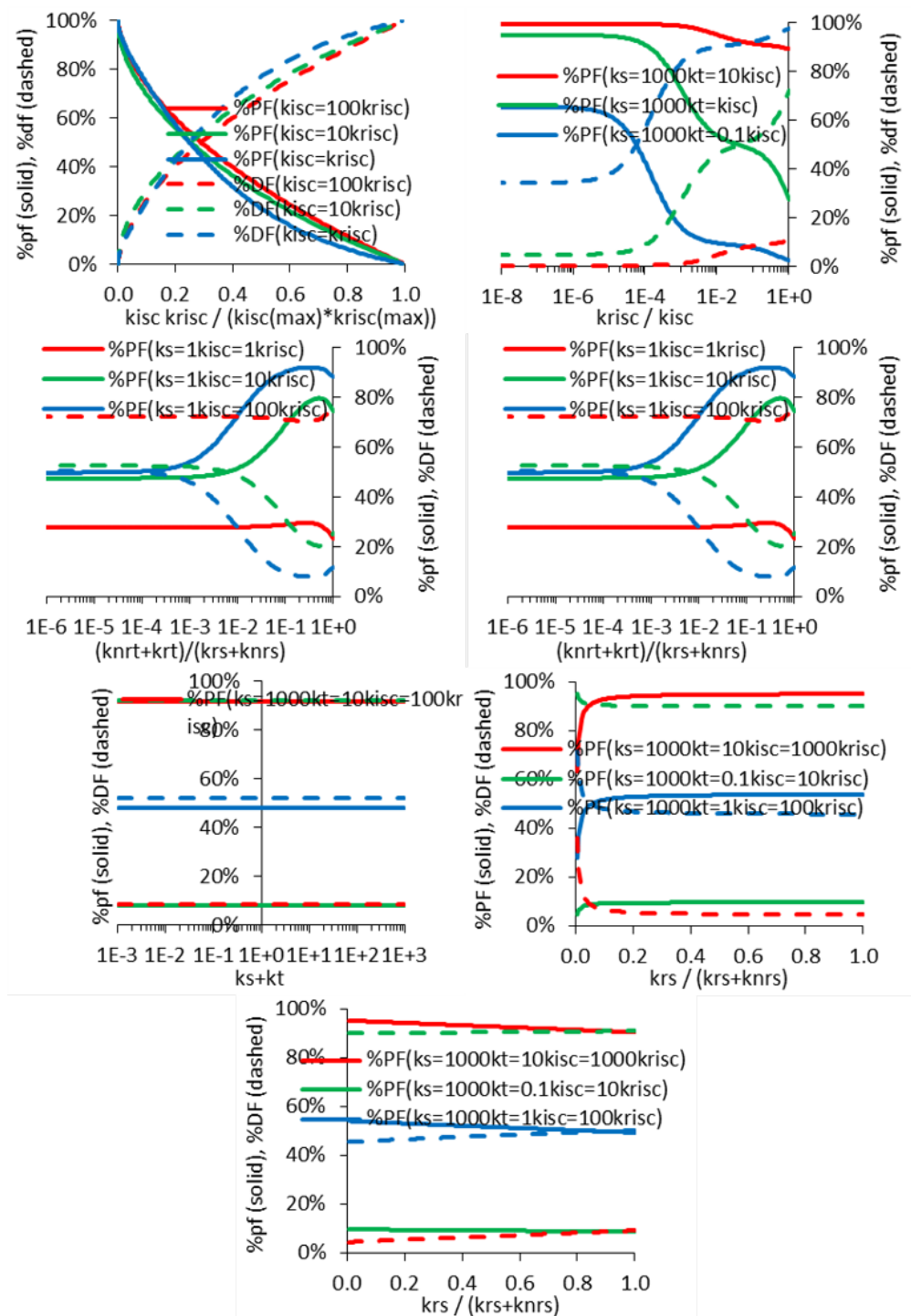


Figure B.42: The change in prompt and delayed fluorescence area with change in various rate constants. $k_S + k_T = 1$ has been enforced except when $k_S + k_T$ is varied. $\frac{k_{s-r}}{k_{s-r}+k_{s-nr}} = 0.95$ and $\frac{k_{t-r}}{k_{t-r}+k_{t-nr}} = 0.05$ are also used unless explicitly varied. There is a slight change in notation, with rate being written without subscripts and $k_{t-nr} = k_{nr}$ etc.

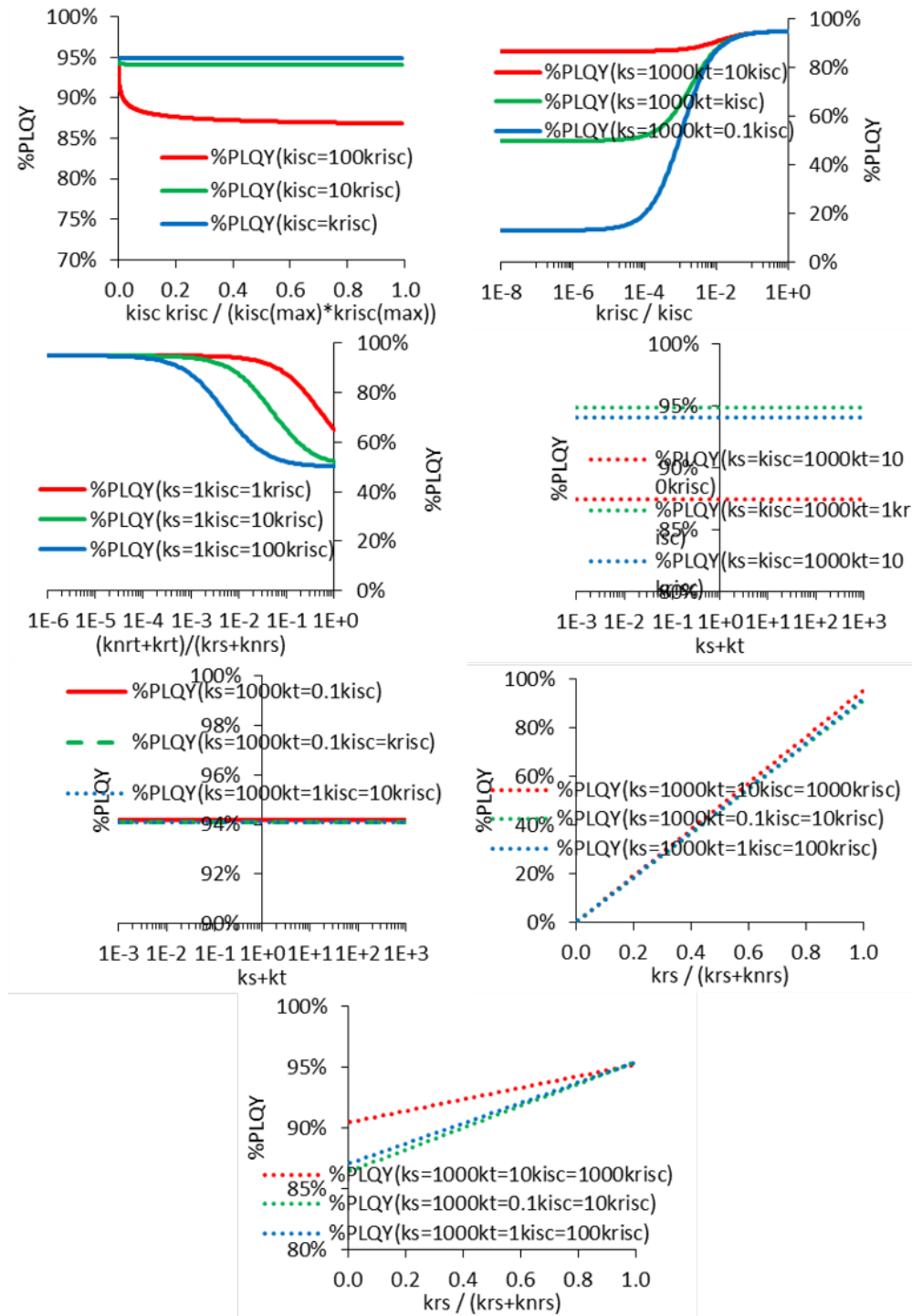


Figure B.43: The change in photoluminescent quantum yield (PLQY) with change in various rate constants. $k_s + k_T = 1$ has been enforced except when $k_s + k_T$ is varied. $\frac{k_{s-r}}{k_{s-r}+k_{s-nr}} = 0.95$ and $\frac{k_{t-r}}{k_{t-r}+k_{t-nr}} = 0.05$ are also used unless explicitly varied. There is a slight change in notation, with rate being written without subscripts and $k_{t-nr} = knrt$ etc.

additional quenching in the delayed fluorescence; the decrease at large triplet rate can be understood by both k_T and k_s contributing equally to the singlet rate, hence at fast k_T , the non-radiative rate from this will dominate. The PLQY naturally decreases at about $k_{RISC} \approx k_{t-nr} + k_{t-r}$, as most triplets begin to decay non-radiatively.

As expected there is no dependence when all rates are changed by multiplication by a constant, this is also the same for PLQY.

A final set of dependences which is investigated is the change with changes non-radiative and radiative decay ratios in the singlet and triplet regimes. Note, it is the ratio, and not the magnitude that is varies. As expected the ratio of prompt increases as the ratio of radiative singlet rate increases, and this increases is greatest when the singlet radiative ratio is similar to the triplet one. The terminal value approached is given by the other parameters. The delayed ratio increases with triplet radiative ratio, but the increase is much more gradual than in singlets. This reflects the much slower triplet rate used, and the fact triplets are not initially populated. PLQY increases with increases in both singlet and triplet ratio, and as expected this is greatest for singlets.

B.3.2.3.3 Intensities The initial intensity of each component with changing parameters is shown in figure B.44. With increased kisc krisc, the amount of pulse fluorescence decreases. This corresponds to the an decrease in decay of the singlet states, and an increase in emission rate of the delayed component. Naturally this is fastest for fast RISC. The change with respect to k_{RISC} mirrors this in explanation, as similarly there is a decrease with in % PF when it increases. The change is also shown to be greatest for fast ISC.

When the rate of triplet decay is increased, there is also a corresponding decrease pulse fluorescence component. This can be understood when looking at the pulse fluorescence, and seeing that the rate can be approximated as $k_S + k_T$. So a large k_T may accelerate the rate of decay. It should be noted a decrease is only observed when $k_{t-nr} + k_{t-r}$ is of a similar order to $k_{s-nr} + k_{s-r}$. As this usually does not occur, the results are in reality approximately constant.

As would be expected, the change in initial intensity is unaffected by increase of all parameters by multiplying by a constant.

Finally the ratio of radiative to non-radiative decays are varied. As expected increased singlet ratio increases singlet emission ratio, and increased triplet ratio increases delayed about.

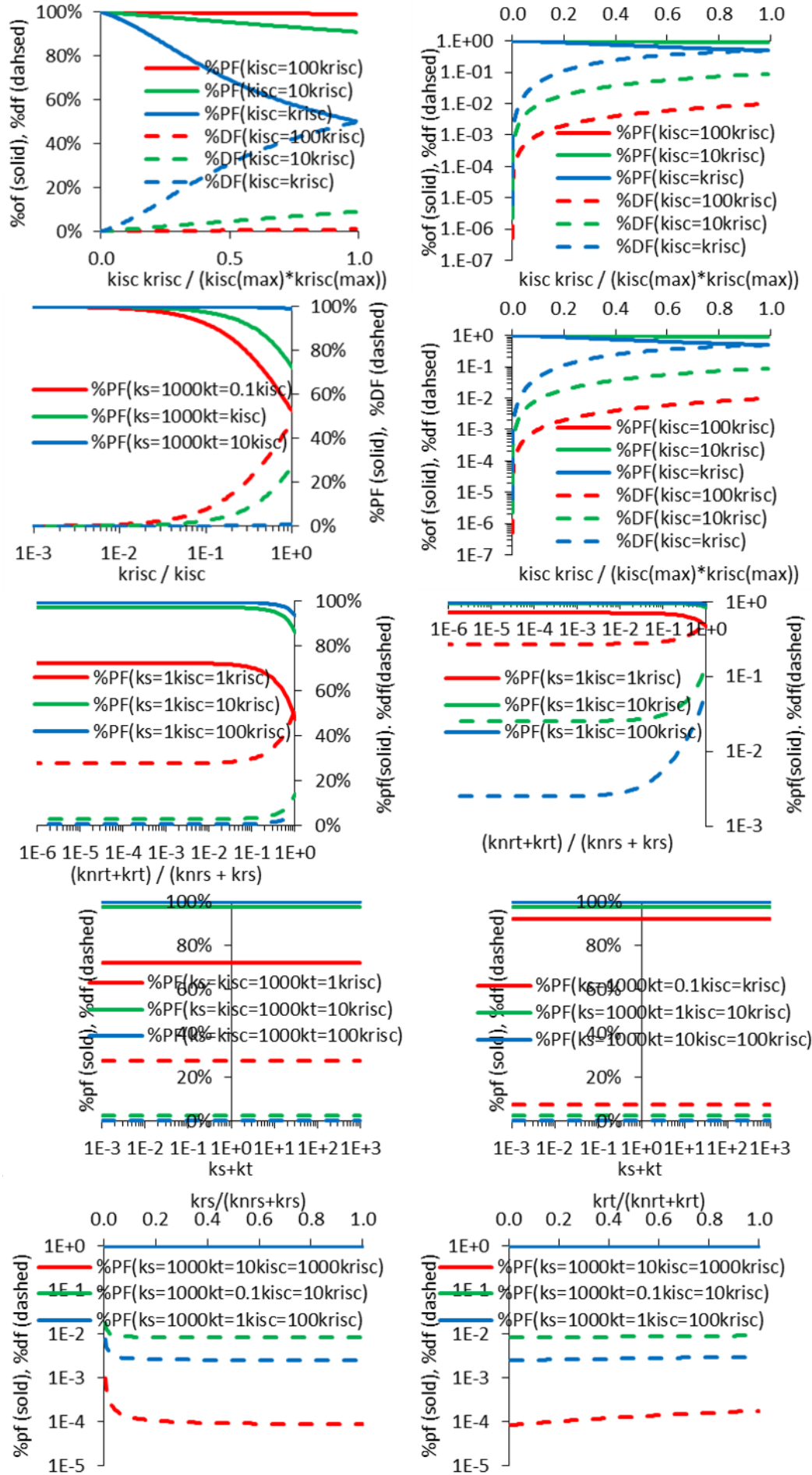


Figure B.44: The change in starting intensities with change in various rate constants. $k_S + k_T = 1$ has been enforced except when $k_S + k_T$ is varied. $\frac{k_{s-r}}{k_{s-r} + k_{s-nr}} = 0.95$ and $\frac{k_{t-r}}{k_{t-r} + k_{t-nr}} = 0.05$ are also used unless explicitly varied. There is a slight change in notation,

B.3.2.4 Fitting Procedure

Prior to going into detail of the results which have been collected, it is first necessary to discuss the fits used. The fit used was a minimisation of χ^2 parameter fit. That is the minimisation of the following parameter where x is the data, $f(x)$ is the thing fitted to, and σ is the standard deviation. The standard deviation of the sums used in the fit are estimated from that given by the background standard deviation, and the number of data point used in the sums (ie. the area integrated over in the spectra) (N). The first 4 ns (from the peak) of the decay were excluded to prevent errors.

$$\chi^2 = \frac{(x - f(x))^2}{\sigma^2} \quad (\text{B.215})$$

$$\sigma = \frac{\sigma_{\text{background}}}{\sqrt{N}} \quad (\text{B.216})$$

In most of this document, the equation fit to ($f(x)$) was a simple bi-exponential decay. See below. In the equation shown A_1 , A_2 , τ_1 , and τ_2 are the values altered to fit. Other fits have been used, and will be discussed as and when they are.

$$f(x) = A_1 e^{-\frac{x}{\tau_1}} + A_2 e^{-\frac{x}{\tau_2}} \quad (\text{B.217})$$

In the decays shown within this document it can be observed that there is strong deviation from a biexponential decays at long timescale. This has been observed also in the literature and is commonly attributed (without experimental or theoretical justification) to the variation in decays between molecules. Hence, a case can be made that the points fitted to should be appended, in order to prevent the influence of these results to the fit. The problem lies when the fit at different timescales is compared (see figures B.45 and B.46). The fit appears to approach a certain value as more data points are used. This seems to indicate the only reliably comparable way to plot fits is to use the maximum length available. An additional problem is that the length of the data gathered varies depending on the decay. Further with each decay being different in shape a certain degree, differing dependencies may be expected. Loosely the decays can be grouped into groups with a similar shape. These groups are listed in table B.9 with abbreviations C2 = compound 2, nh = no host (ie. pure films), h = host (ie. 10% doped in H1), and 77 K indicating the compound has been frozen in glassy solution (1:1 mix of ethanol:diethylether) at 77K. Examples of each of these groups and their variance on time included in decay are shown in figures B.45 and B.46.

When the changes in fitting parameters are further compared, it may be observed

Table B.9: The "groups" of compounds with similar decay shape. For abbreviations see text

group 1	group 2	group 3	group 4	group 5	group 6
c1-nh	c1-h	C2-nh	C2-h	C1-77K	C2-77K
		C3-nh	C3-h		C3-77K

that C2-nh and C1-77K do not reach steady values. The results of this are that the decays of neither the fits of C2-nh and C1-77K can be fully trusted. However for C1-77K it is found the key points of the resulting fit can be interpreted. C2-nh is also rather similar in its decay to C3-nh, so an approximation of these two as the same will be proposed.

A sensible method of using the fits seems to be to use parameters where the fits are long enough to give results accurate results to a certain number of significant figures. Here 2 s.f. will be used. When the fit is not stable to this number of s.f. an inequality will be shown, which assumes the results extrapolate to a steady values.

It should be noted also how high the χ^2/N parameter is throughout these fits, as this is a common feature across all compounds. A value higher than 1 for this parameter is considered high, and as a result it could be considered that these fits are inappropriate. However this fit is currently the best guess of a reasonable fit for TADF and is commonly used in the literature. Therefore for the sake of maintaining comparability and with the absence of an alternative, it will be used here.

While the consensus in the literature is that the use of a bi-exponential decay is the best for TADF compounds, some alternative fits will be discussed in section 4.3.5.2.

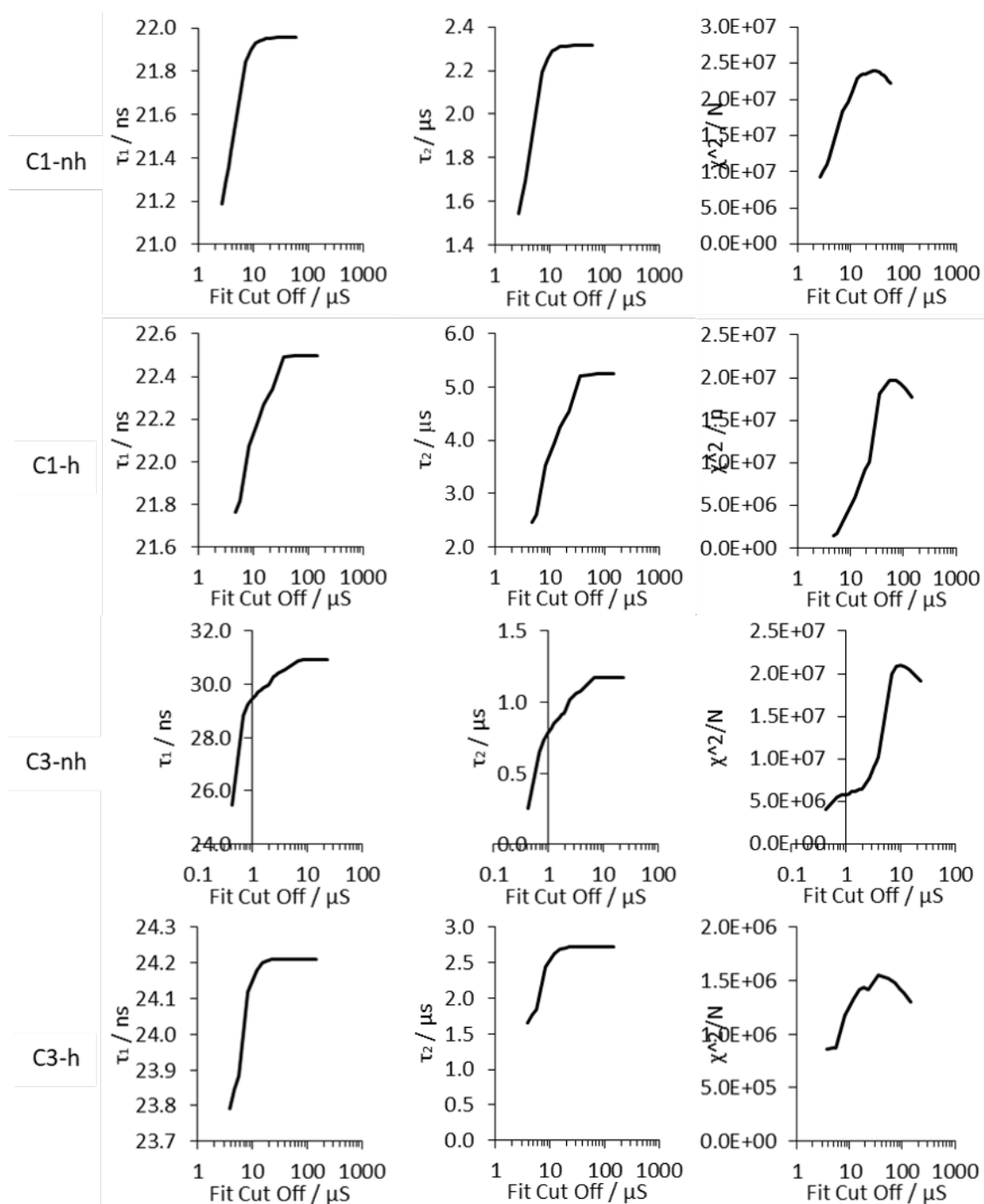


Figure B.45: Fitted parameters for the decay (see eq. B.217) of the whole spectra of an example of a decay from each group of decays of films (see table B.9) with varied maximum time included.

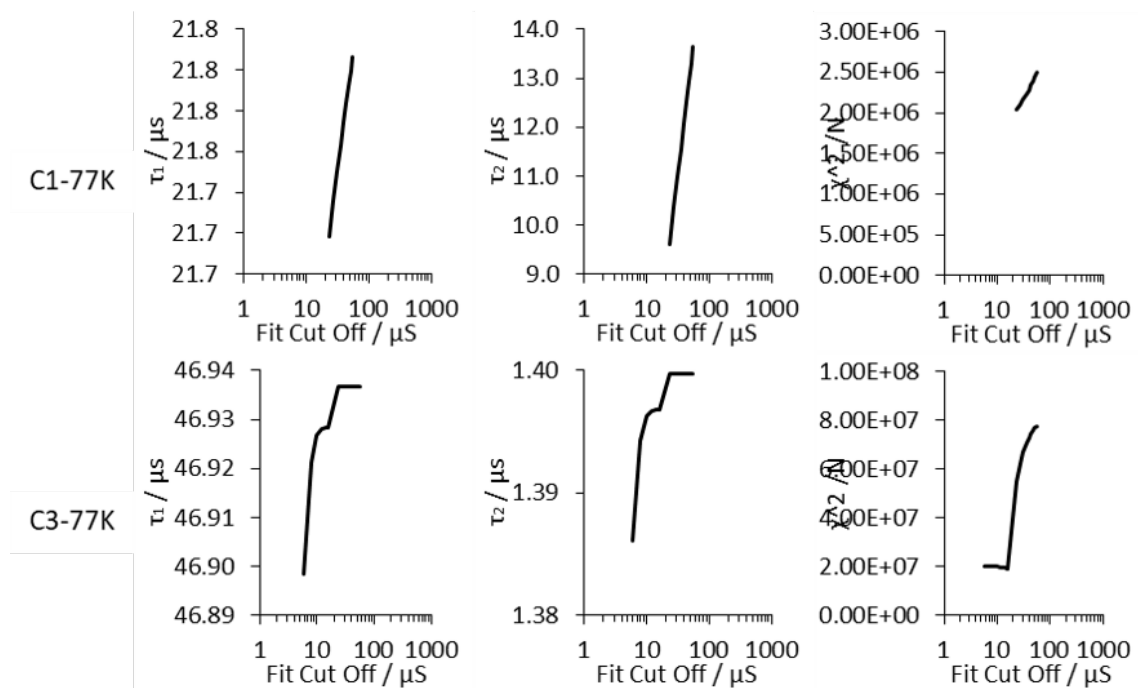


Figure B.46: Fitted parameters for the decay (see eq. B.217) of the whole spectra of an example of a decay from each group of decays of frozen solutions (see table B.9) with varied maximum time included.

B.3.2.5 Host Emission

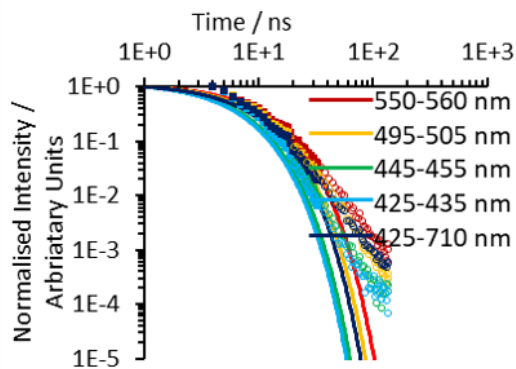


Figure B.47: The decay of the host upon excitation of 410 nm, for integration in regions shown. The fitting parameters for a mono-exponential decay. The data is shown using various symbols, for each individual run on the transient decay apparatus and the fit using a solid line.

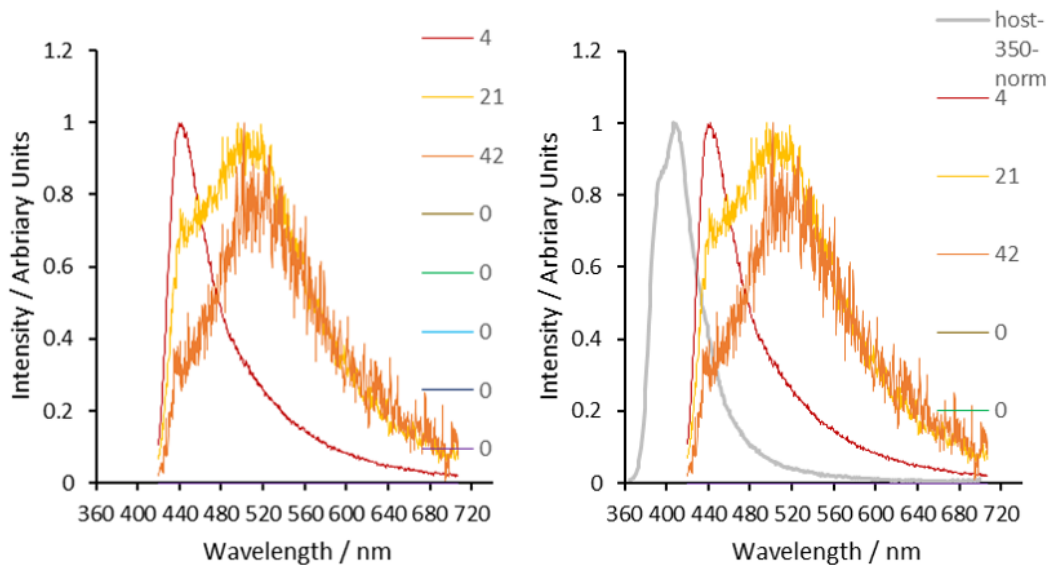


Figure B.48: : The spectra of the host when excited at 410 nm. The time of each spectra is shown in the nanoseconds to the right of the spectra.*NOTE the graphs have longer time scale results but these are noisy and so excluded for clarity.

B.3.2.6 Enlarged decays

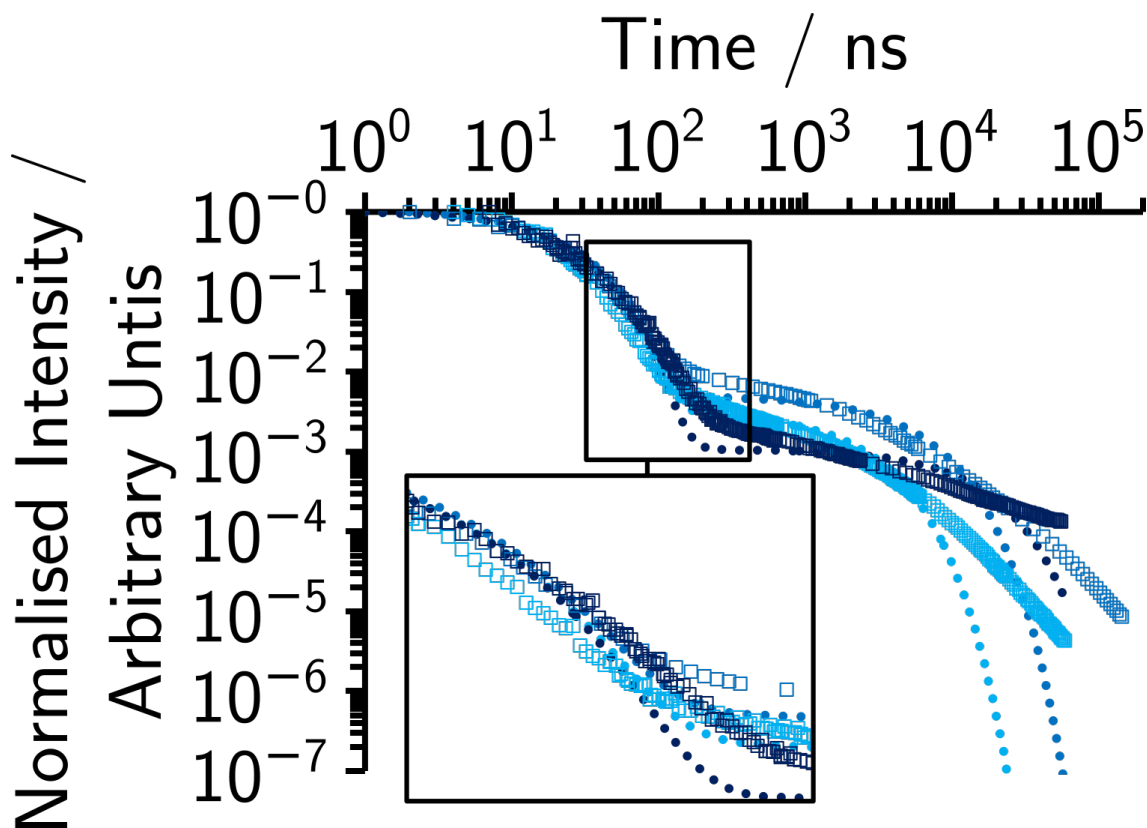


Figure B.49: The transient decays of C1 (hollow squares) the fit (solid circles).

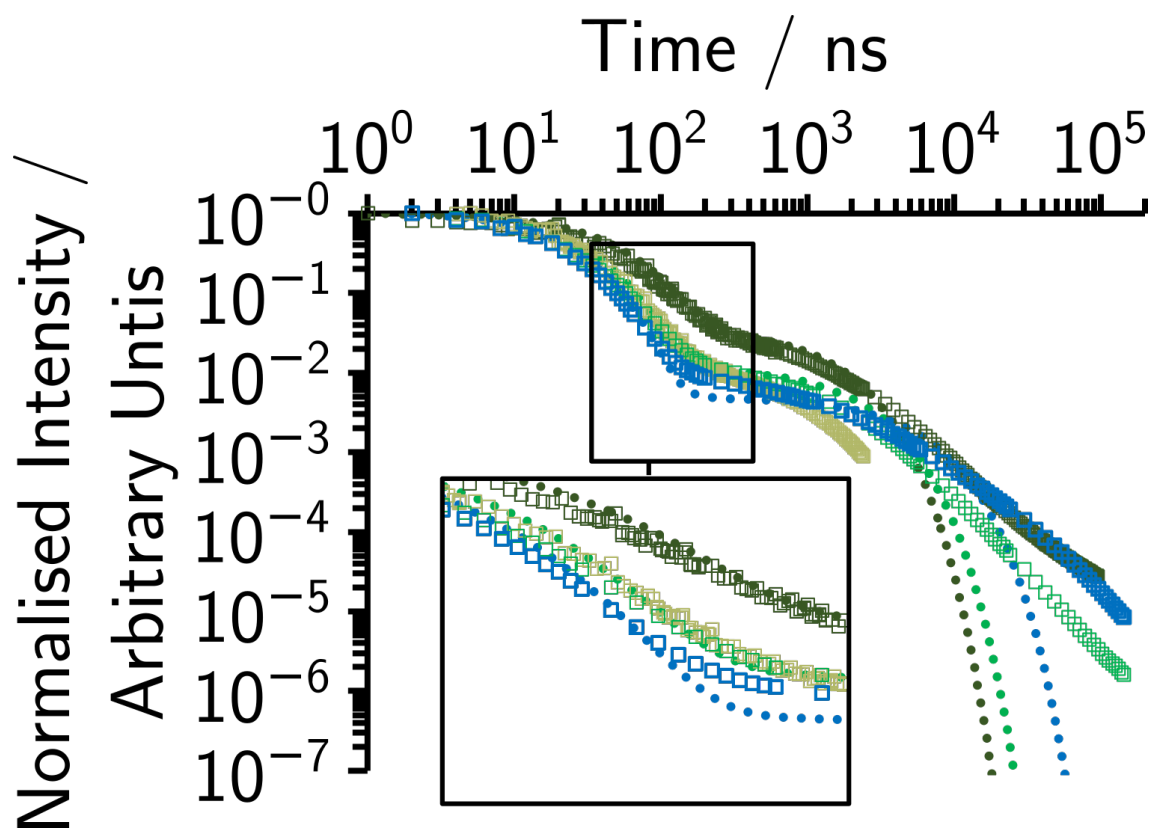


Figure B.50: The transient decays of C2 (hollow squares), with C1 in host to show changes.

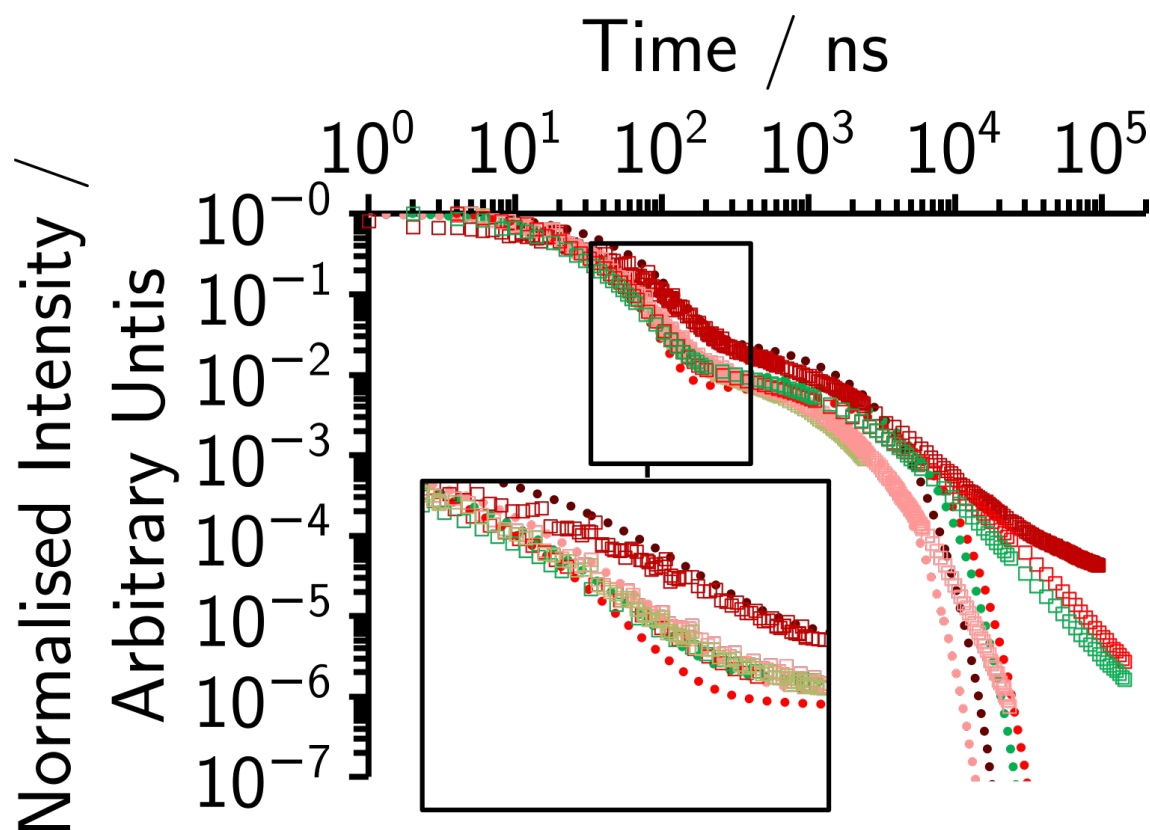
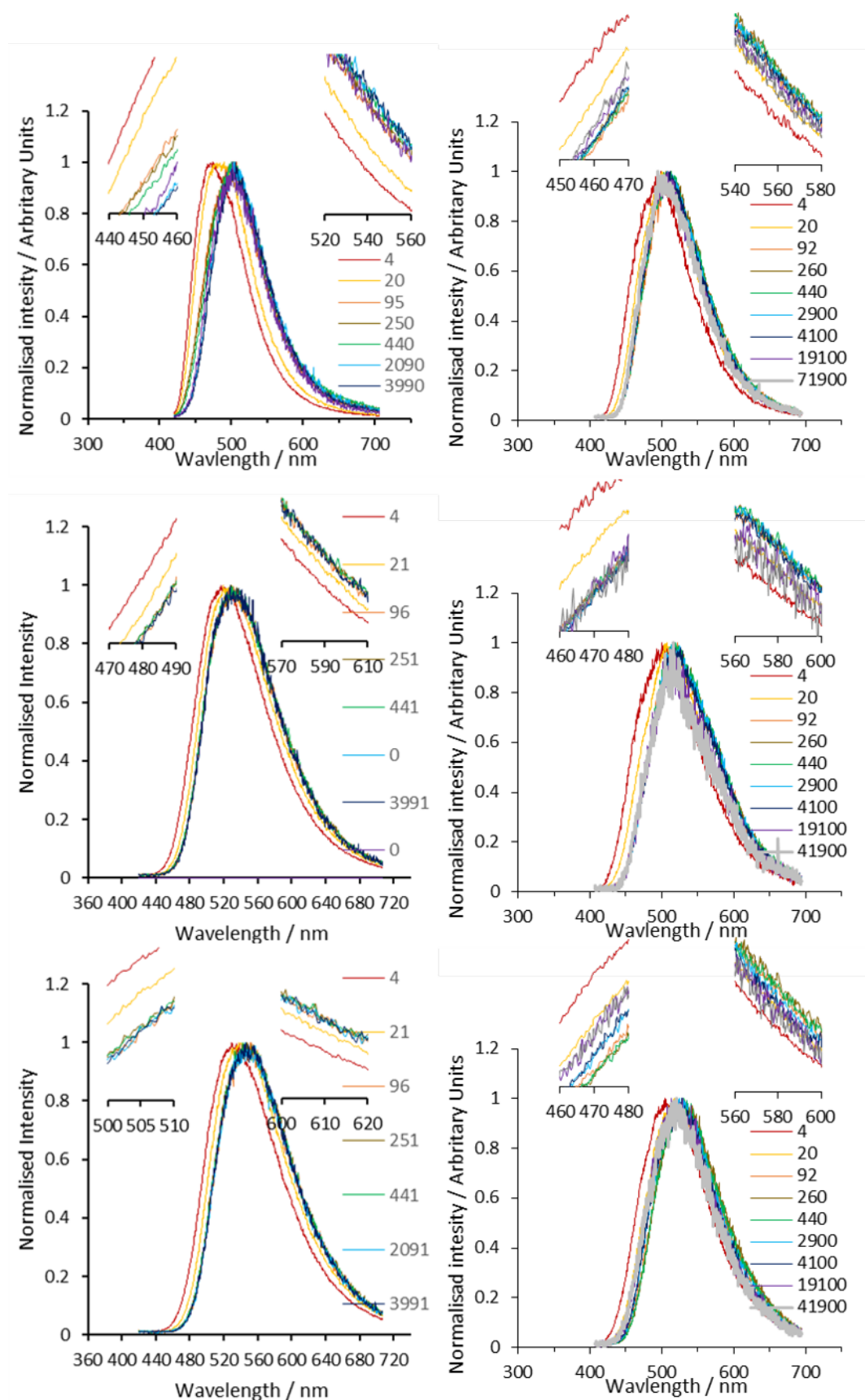


Figure B.51: The transient decays of C3 (hollow squares), with C2 in host shown, to show changes, and C2 in pure film (same colouring as figure 4.9) to show the similarity to C3 in pure film. The fit (solid circles) are also shown.

B.3.2.7 Transient Spectra



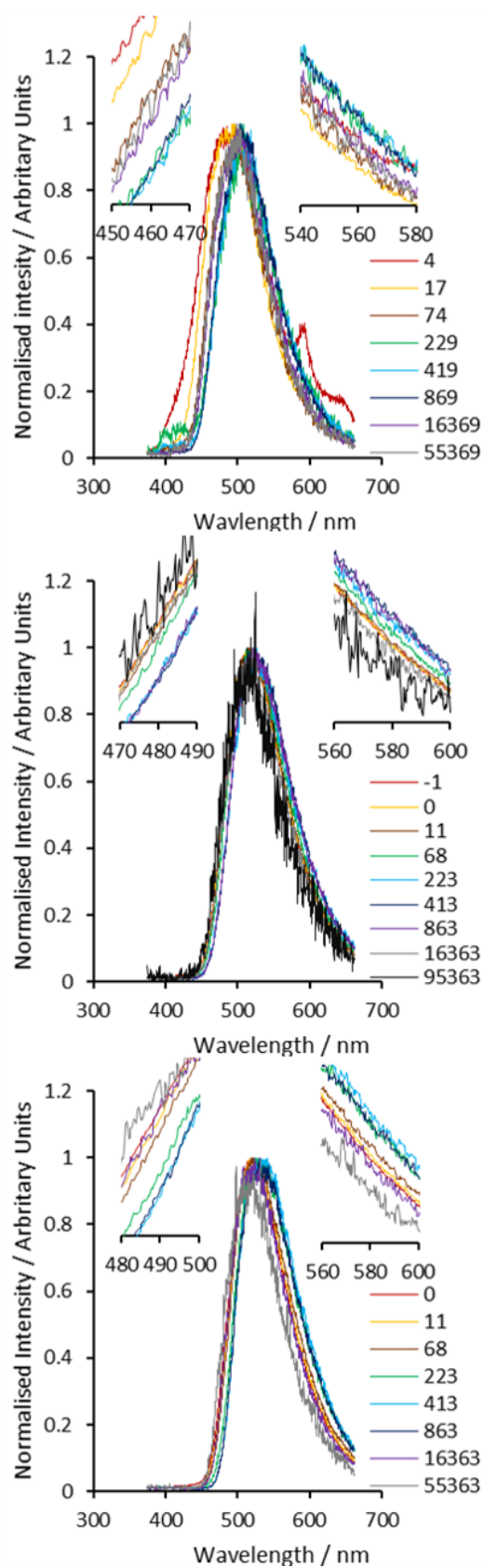


Figure B.53: The emission spectra at different times for decay of compounds 1 (top), 2 (middle), and 3 (bottom) at 77K, when excited at 355 nm, in glassy frozen solution, made of a 1:1 mix of ethanol:diethylether. The inserts show magnifications at the low, and high energy sides of the spectra in order to stress shifts.

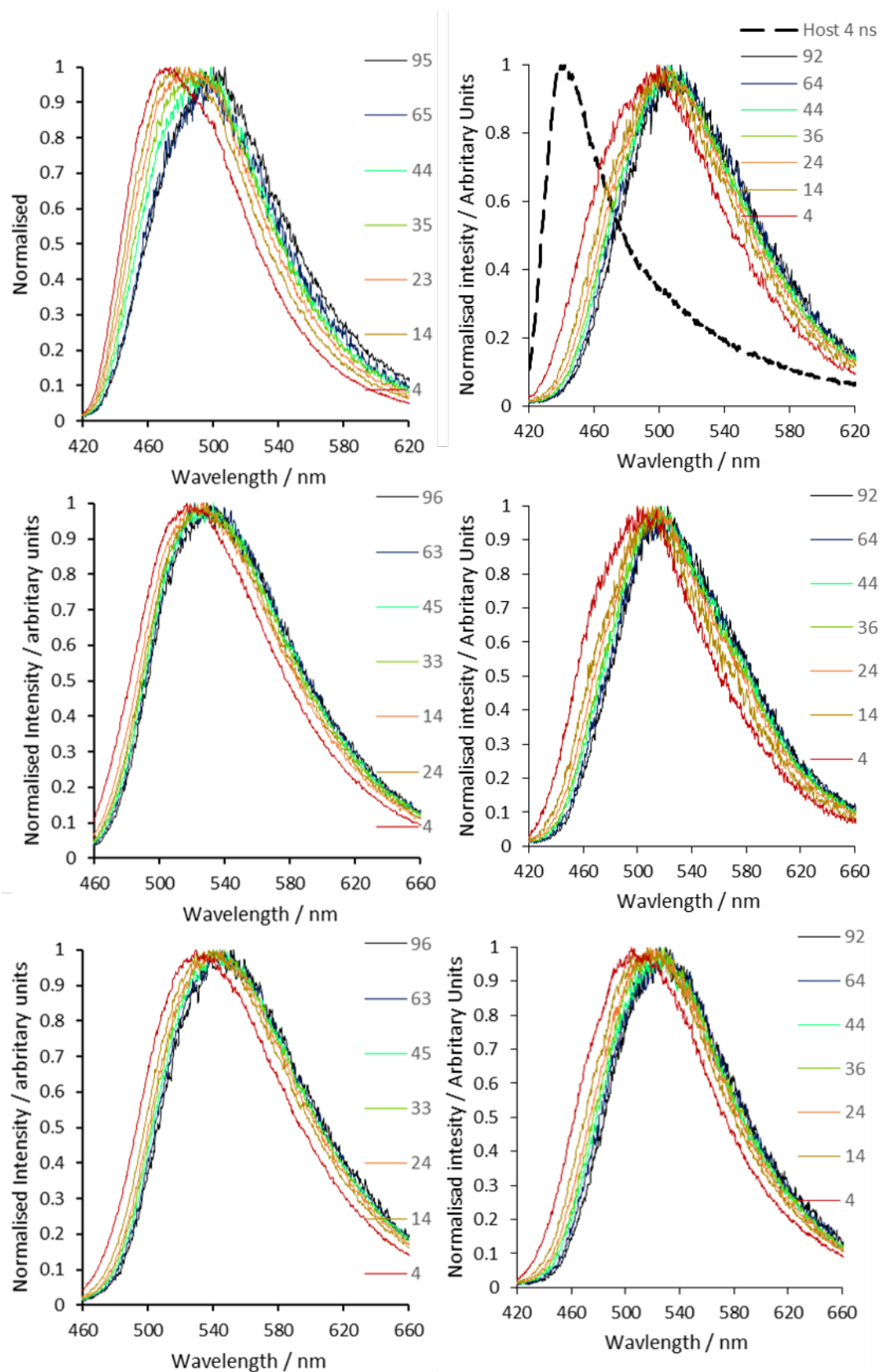


Figure B.54: The spectra at short timescale of compound 1 (top) compound 2 (middle), and compound 3 (bottom), with (right) and without (left) host, when excited at 410 nm. The time of each spectra is shown in the nanoseconds to the right of the spectra.

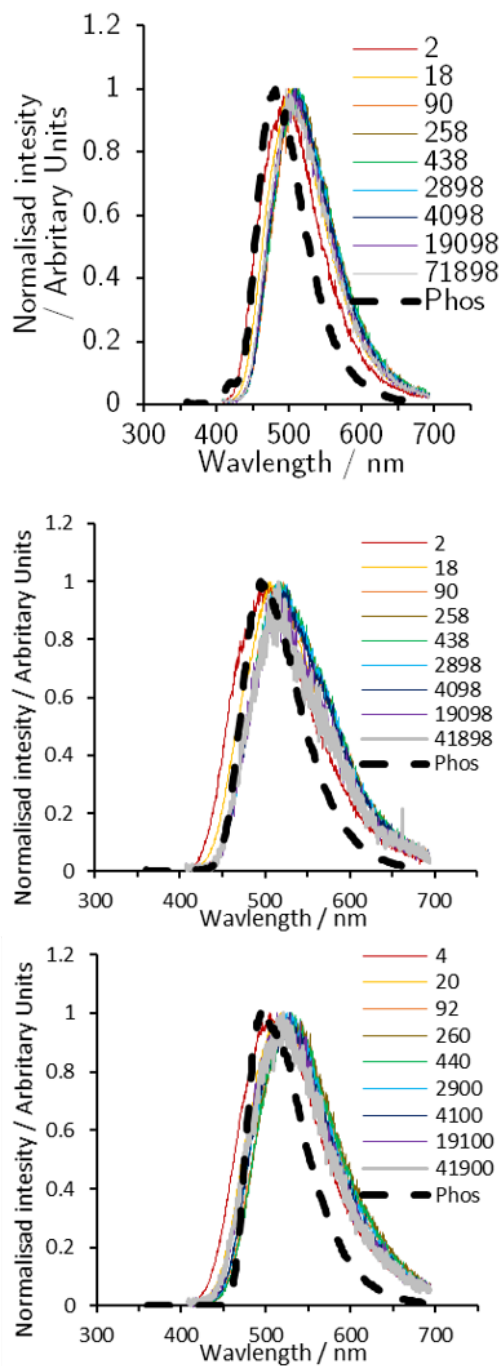


Figure B.55: The transient spectra compared with phosphorescence spectra from section 3.3.3 of compound 1 (top) compound 2 (middle), and compound 3 (bottom), in host, when excited at 410 nm. The time of each spectra is shown in the nanoseconds to the right of the spectra.

B.3.2.8 Change In Decays Across spectra

In this section the decays in different regions of the spectra are examined, as in the diagrams shown in the diagrams. The general trend is consistent with the initial red shift of decays, corresponding to shorter lifetime at shorter wavelengths. In addition, generally there is a blue shift at long time scales, corresponding to longer delayed fluorescence decay in the blue region. Of course there is true for all spectra in terms of the results of the fits. However there is in all cases a dispersion of decays (not fits) in the early times, and a regrouping at longer times (C1 at 77 K may be an exception). As such it is felt that the lack of consistency in the results is most likely due to errors in the fit.

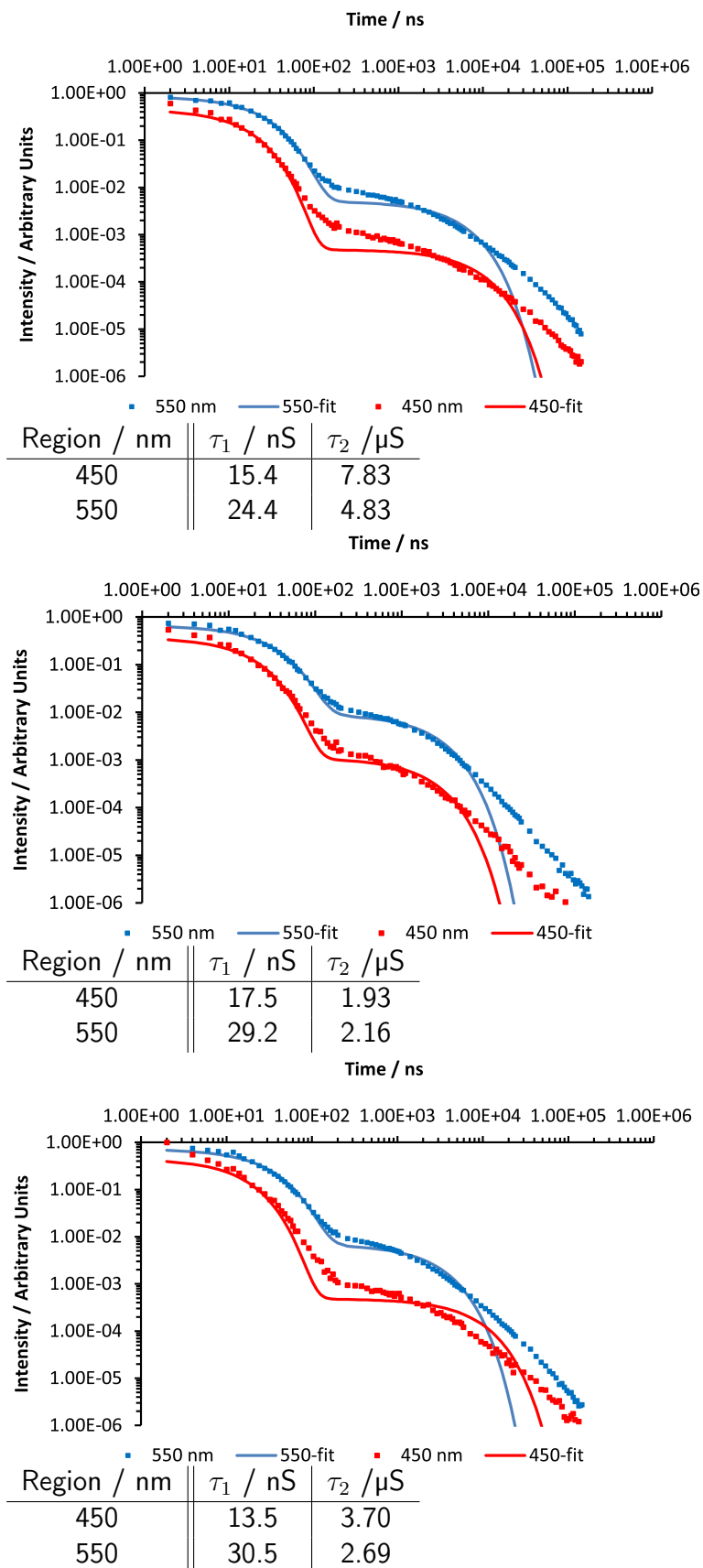


Figure B.56: The decays of pure films of C1 (top), C2 (middle) and C3 (bottom) when recording at different wavelengths. The fitting parameters are also shown in tables following the spectra. Spectra were obtained via excitation at 410 nm.

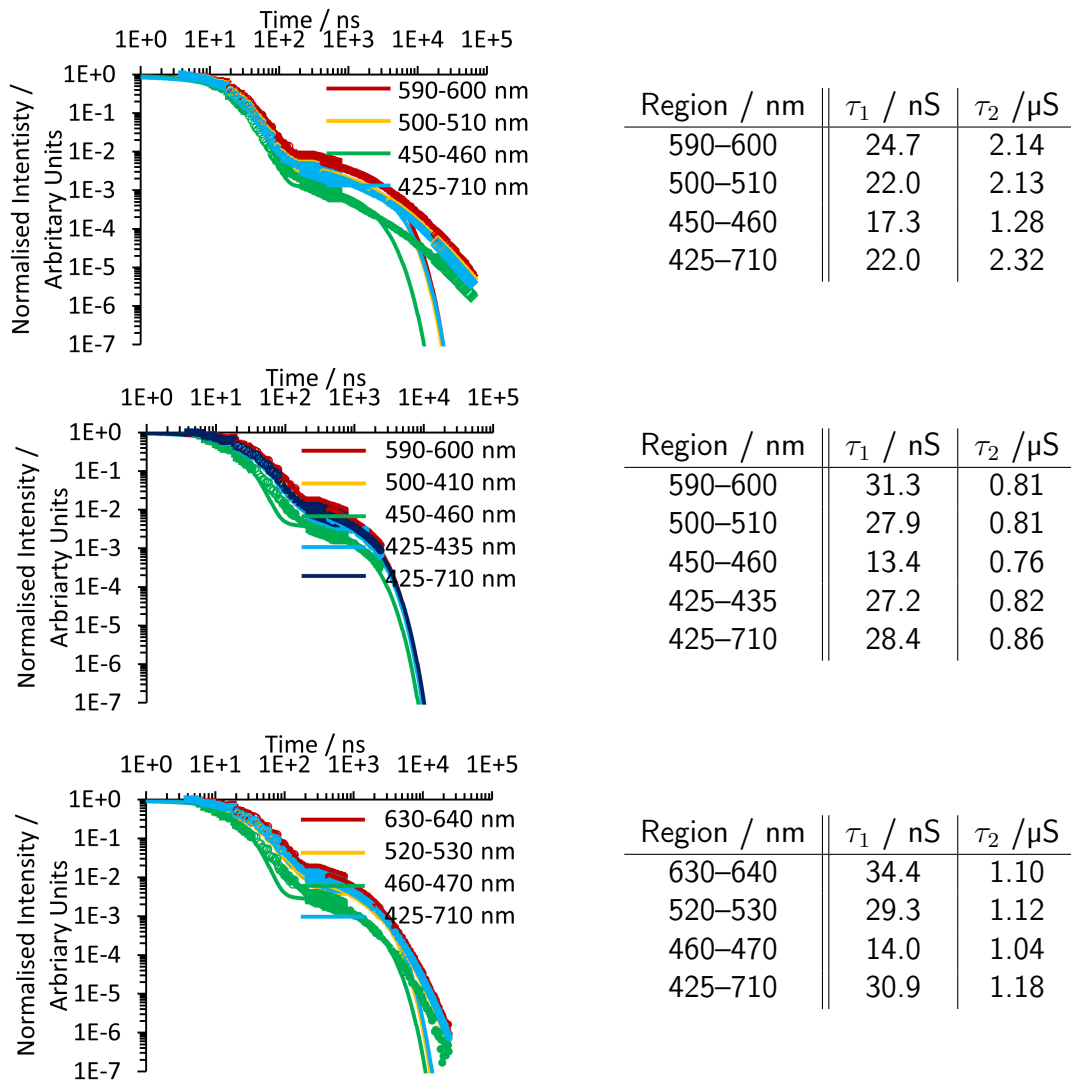


Figure B.57: The decays of pure films of C1 (top), C2 (middle) and C3 (bottom) when recording at different wavelengths. The fitting parameters are also shown in tables following the spectra. Spectra were obtained via excitation at 410 nm.

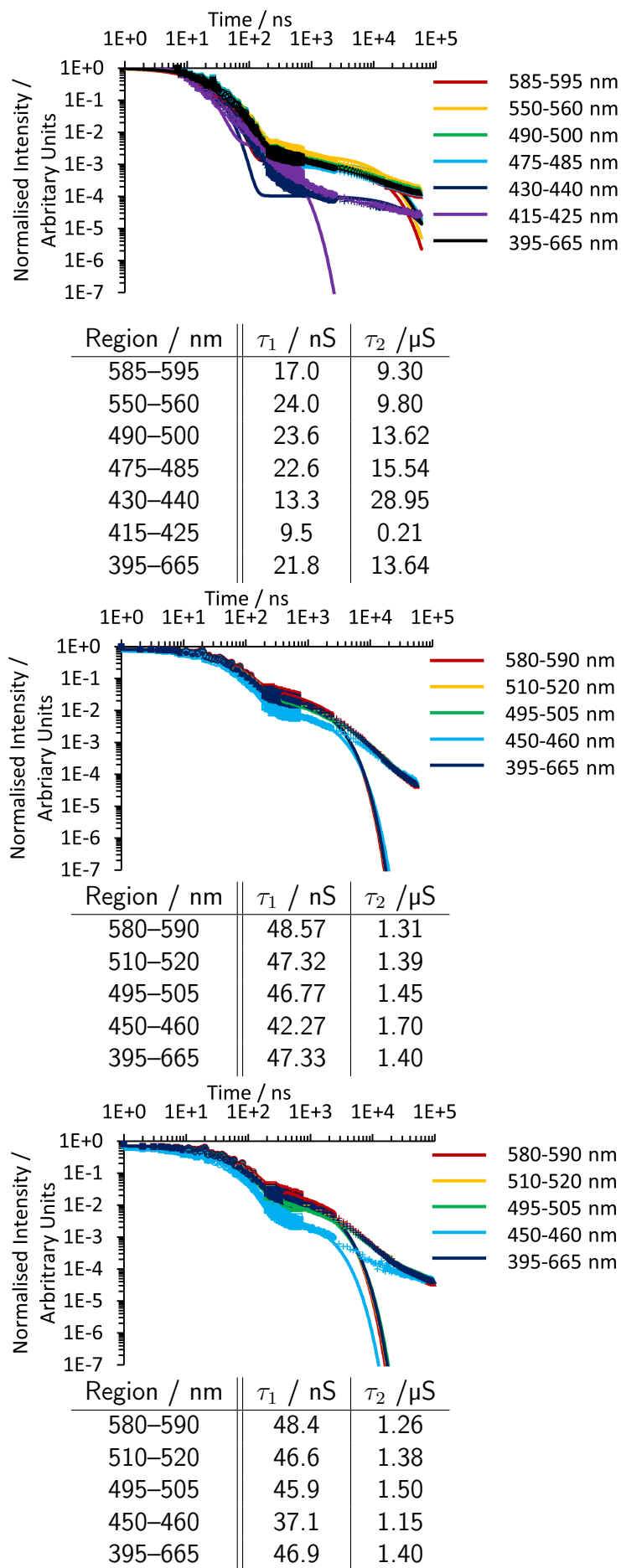


Figure B.58: The decays of pure films of C1 (top), C2 (middle) and C3 (bottom) when recording at different wavelengths. The fitting parameters are also shown in tables following the spectra. Spectra were obtained via excitation at 355 nm.

B.3.2.9 Power Dependencies

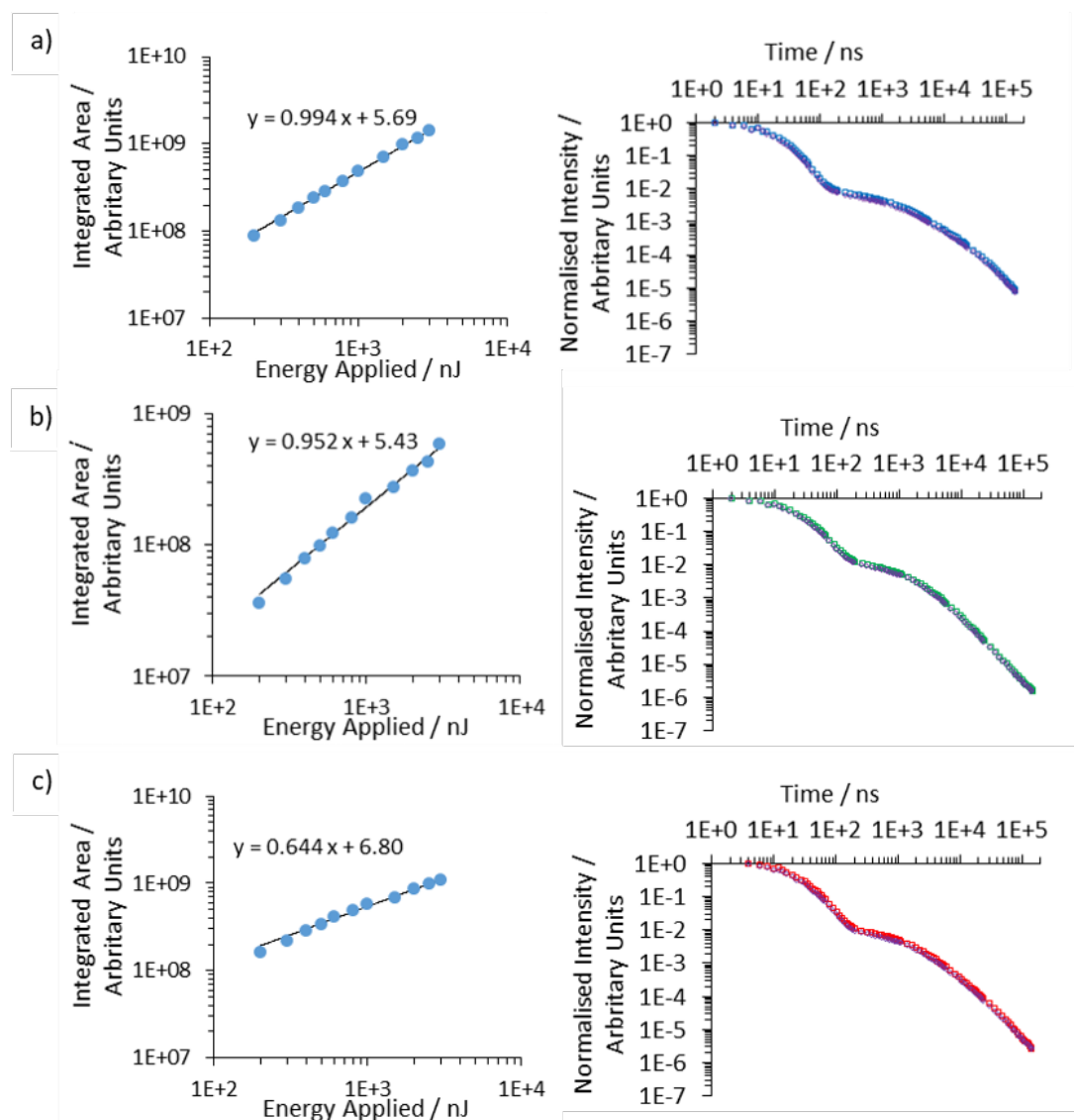


Figure B.59: Shown left is the Intensity of the spectra of compound 1 (top), 2 (middle) and 3 (bottom), in pure film. The integration is done after a delay of 3990 ns after excitation at 410 nm, and is integrated between 425 – 710 nm. The data is shown in blue the fits in black. Shown right is the decay in doped film of compounds ordered as previous. The decays are taken at two powers 20 nJ (compound colour) and 100 nJ (purple).

B.3.3 Computations

B.3.3.1 Boat-Orthogonal — The Lowest Energy Geometry — With B3LYP

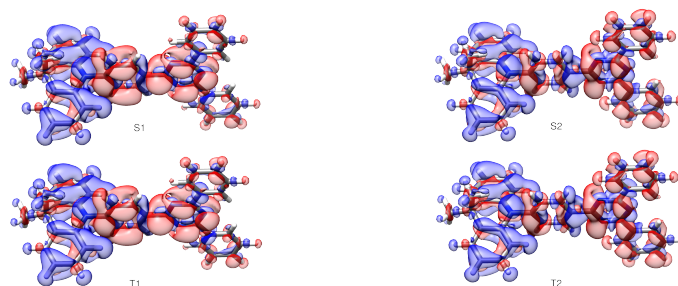


Figure B.60: Change in electron density as calculated from B3LYP in the S_0 geometry for various states of compound 1. Blue represents electron loss, red electron gain. Cut-offs are the default provided by Chimera.

Table B.10: The calculated oscillator strengths and energy gaps for various states of C1, calculated for B3LYP, in the S_0 Geometry.

transition	Oscillator Strength	Change In Energy / eV
$S_0 \leftarrow S_1$	0.0000	2.5415
$S_0 \leftarrow S_2$	0.0000	2.7901

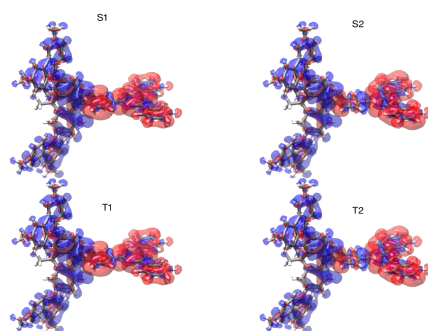


Figure B.61: Change in electron density as calculated from B3LYP in the S_0 geometry for various states of compound 2. Blue represents electron loss, red electron gain. Cut-offs are the default provided by Chimera.

B.3.3.1.1 The Ground State Singlet (S_0) Geometry

Table B.11: The calculated oscillator strengths and energy gaps for various states of C2, calculated for B3LYP, in the S_0) Geometry.

transition	Oscillator Strength	Change In Energy / eV
$S_0 \leftarrow S_1$	0.0004	2.3724
$S_0 \leftarrow S_2$	0.0001	2.5792

Table B.12: The calculated oscillator strengths and energy gaps for various states of C3, calculated for B3LYP, in the S_0) Geometry.

transition	Oscillator Strength	Change In Energy / eV
$S_0 \leftarrow S_1$	0.0004	2.3217
$S_0 \leftarrow S_2$	0.0001	2.4763
$S_0 \leftarrow S_3$	0.0035	2.6298
$S_0 \leftarrow S_4$	0.0006	2.7231
$S_0 \leftarrow S_5$	0.4940	2.7407

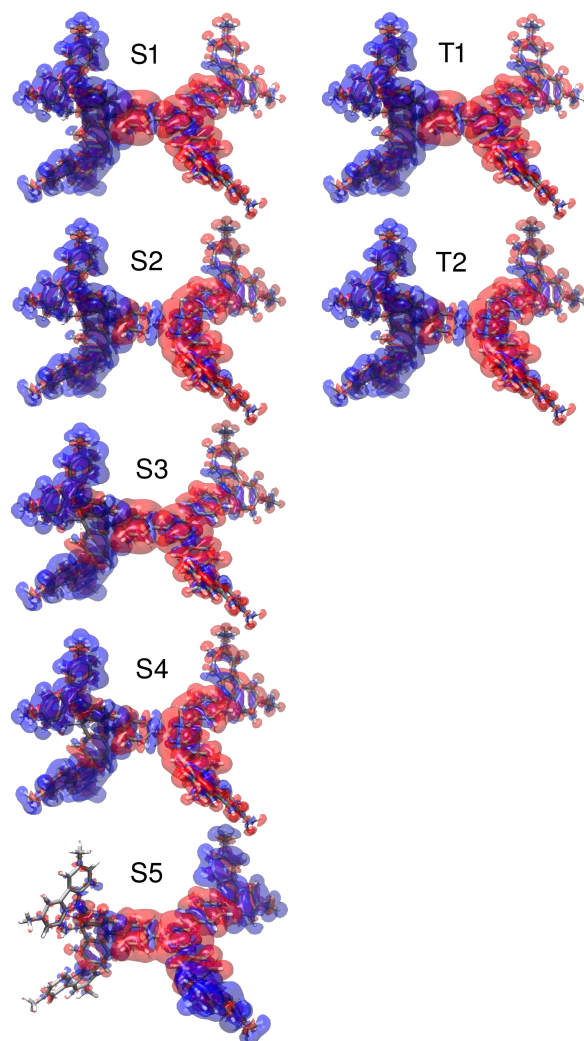


Figure B.62: Change in electron density as calculated from B3LYP in the S_0 geometry for various states of compound 3. Blue represents electron loss, red electron gain. Cut-offs are the default provided by Chimera.

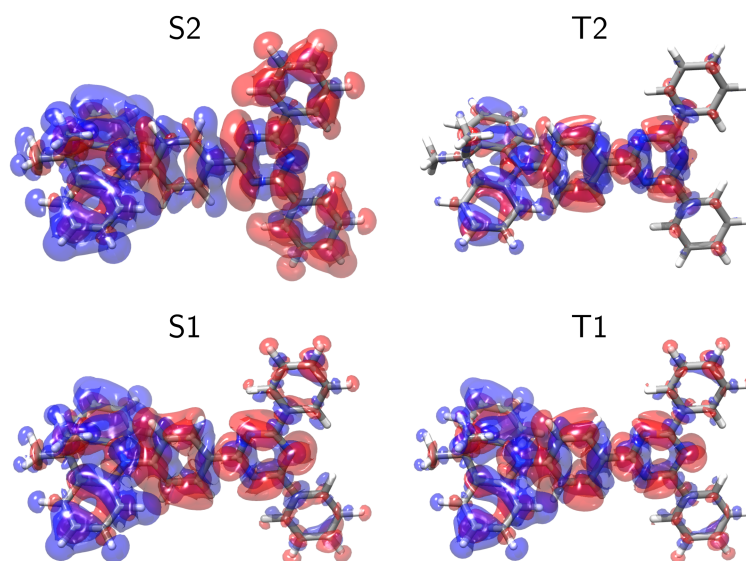


Figure B.63: Change in electron density as calculated from B3LYP in the T₁ geometry for various states of compound 1. Blue represents electron loss, red electron gain. Cut-offs are set to $0.4 \text{ me } r_{\text{Bohr}}^{-3}$.

B.3.3.1.2 The Ground State Triplet (T₁) Geometry

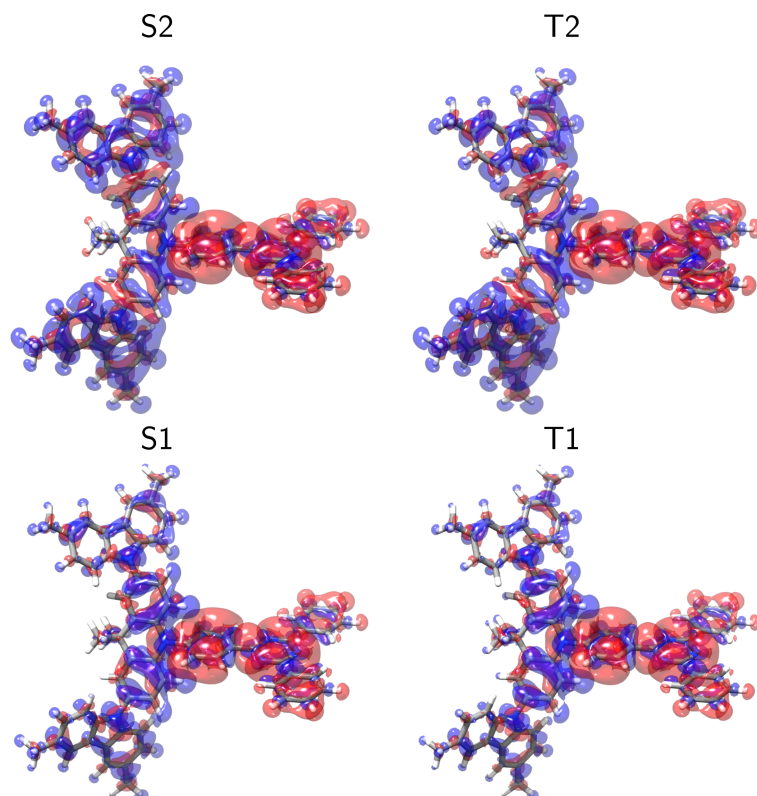


Figure B.64: Change in electron density as calculated from B3LYP in the T_1 geometry for various states of compound 2. Blue represents electron loss, red electron gain. Cut-offs are set to $0.4 \text{ me } r_{\text{Bohr}}^{-3}$.

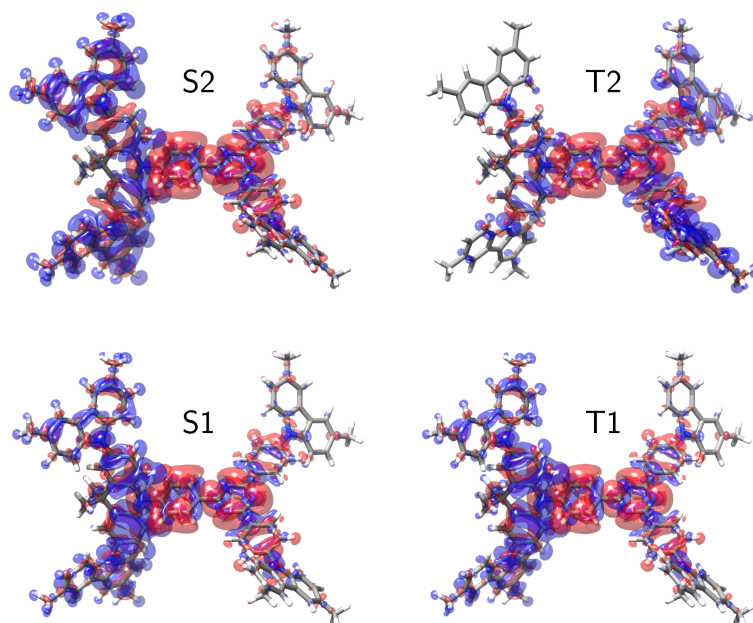


Figure B.65: Change in electron density as calculated from B3LYP in the T_1 geometry for various states of compound 3. Blue represents electron loss, red electron gain. Cut-offs are set to $0.4 \text{ me } r_{\text{Bohr}}^{-3}$.

B.3.3.2 Boat-Orthogonal — The Lowest Energy Geometry — With CAM-B3LYP

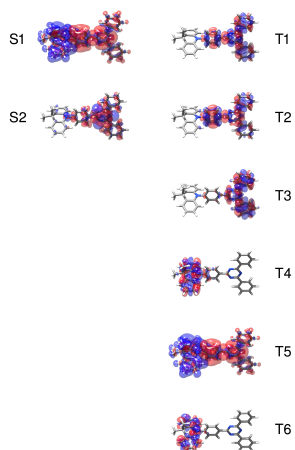


Figure B.66: Change in electron density as calculated from CAM-B3LYP in the S_0 geometry for various states of compound 1. Blue represents electron loss, red electron gain. Cut-offs are the default provided by Chimera.

B.3.3.2.1 The Ground State Singlet (S_0) Geometry

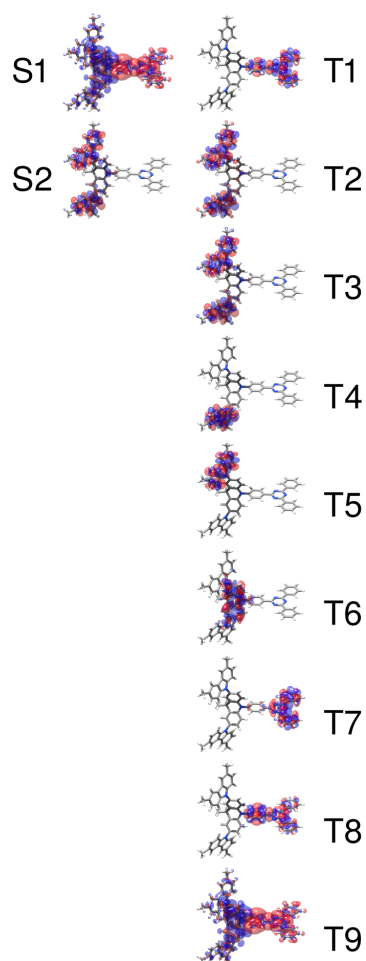


Figure B.67: Change in electron density as calculated from CAM-B3LYP in the S_0 geometry for various states of compound 2. Blue represents electron loss, red electron gain. Cut-offs are the default provided by Chimera.

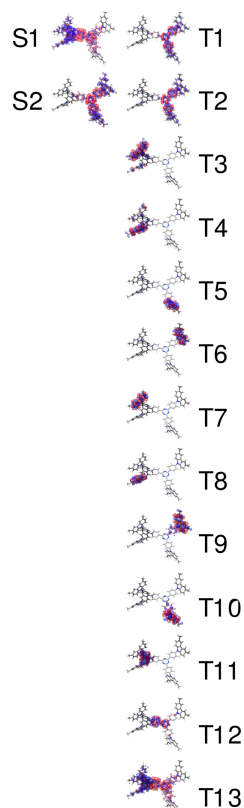


Figure B.68: Change in electron density as calculated from CAM-B3LYP in the S_0 geometry for various states of compound 3. Blue represents electron loss, red electron gain. Cut-offs are the default provided by Chimera.

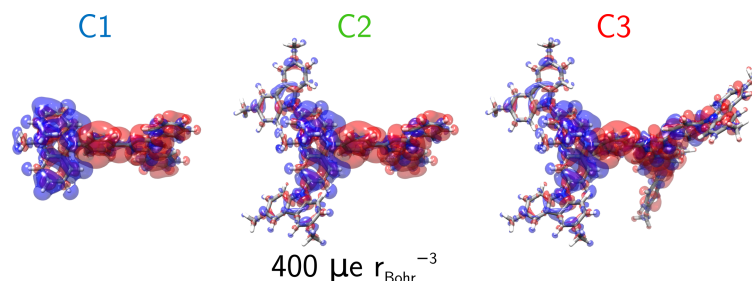


Figure B.69: The change in electron density, as calculated using CAM-B3LYP in the S_0 geometry, for $T_1 \rightarrow S_1$. Blue represents electron loss, red electron gain. Cut-offs are set to $0.4 \text{ me } r_{\text{Bohr}}^{-3}$, to allow full comparison.

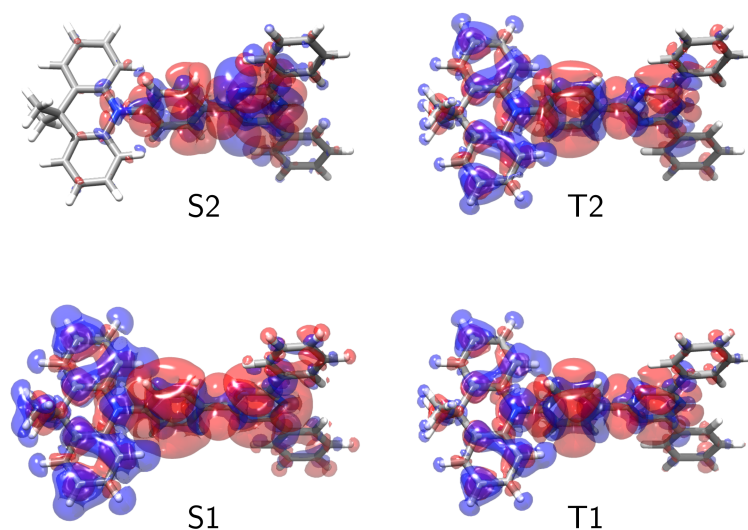


Figure B.70: Change in electron density as calculated from CAM-B3LYP in the T₁ geometry for various states of compound 1. Blue represents electron loss, red electron gain. Cut-offs are set to $0.4 \text{ me } r_{\text{Bohr}}^{-3}$.

B.3.3.2.2 The Ground State Triplet (T₁) Geometry

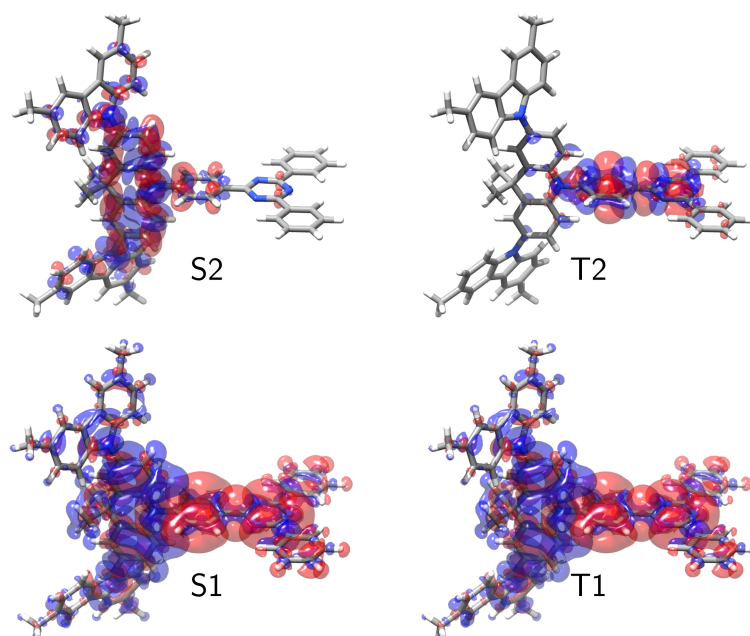


Figure B.71: Change in electron density as calculated from CAM-B3LYP in the T₁ geometry for various states of compound 2. Blue represents electron loss, red electron gain. Cut-offs are set to 0.4 me r_{Bohr}^{-3} .

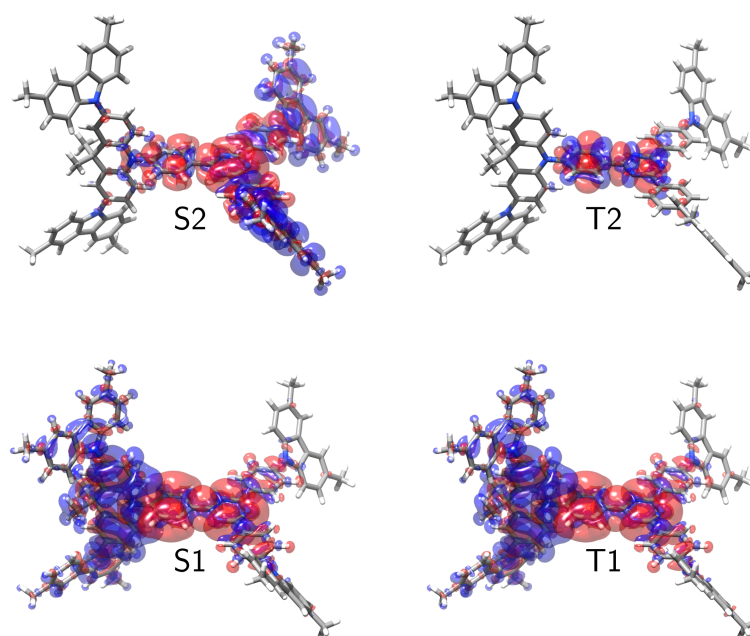


Figure B.72: Change in electron density as calculated from CAM-B3LYP in the T₁ geometry for various states of compound 3. Blue represents electron loss, red electron gain. Cut-offs are set to 0.4 me r_{Bohr}^{-3} .

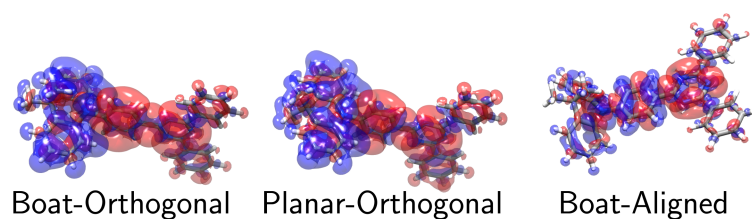


Figure B.73: The change in electron density as calculated using *CAM-B3LYP* in various S_0 optimised geometries for $S_0 \rightarrow S_1$ for C1. Blue represents electron loss, red electron gain. Cut-offs are set to $0.4 \text{ me } r_{\text{Bohr}}^{-3}$, to allow full comparison.

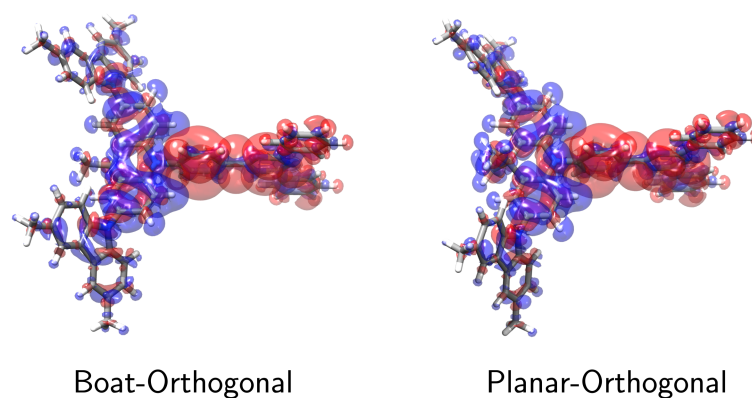


Figure B.74: The change in electron density as calculated using *CAM-B3LYP* in various S_0 optimised geometries for $S_0 \rightarrow S_1$ for C2. Blue represents electron loss, red electron gain. Cut-offs are set to $0.4 \text{ me } r_{\text{Bohr}}^{-3}$, to allow full comparison.

B.3.3.2.3 Other Geometries

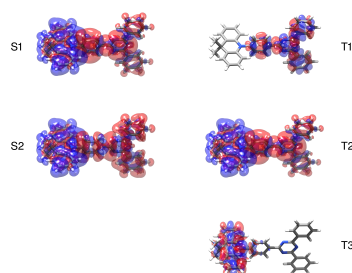


Figure B.75: The change in electron density as calculated using *CAM-B3LYP* in the planar-orthogonal geometry of C1. The S_0 optimised geometries is used. Blue represents electron loss, red electron gain. Cut-offs are set to $0.4 \text{ me r}_{\text{Bohr}}^{-3}$, to allow full comparison.

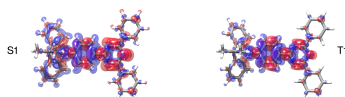


Figure B.76: The change in electron density as calculated using *CAM-B3LYP* in the boat-aligned geometry of C1. The S_0 optimised geometries is used. Blue represents electron loss, red electron gain. Cut-offs are set to $0.4 \text{ me r}_{\text{Bohr}}^{-3}$, to allow full comparison.

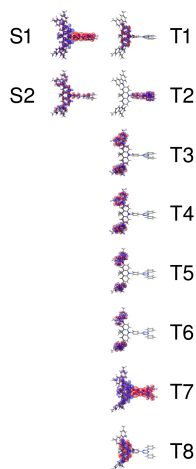


Figure B.77: The change in electron density as calculated using *CAM-B3LYP* in the planar-orthogonal geometry of C2. The S_0 optimised geometries is used. Blue represents electron loss, red electron gain. Cut-offs are set to $0.4 \text{ me r}_{\text{Bohr}}^{-3}$, to allow full comparison.

B.4 A New Solution Processable Host Molecule

B.4.1 The summarised "HOMO" and "LUMO" data from "Purely Organic Thermally Activated Delayed Fluorescence Materials for Organic Light-Emitting Diodes"

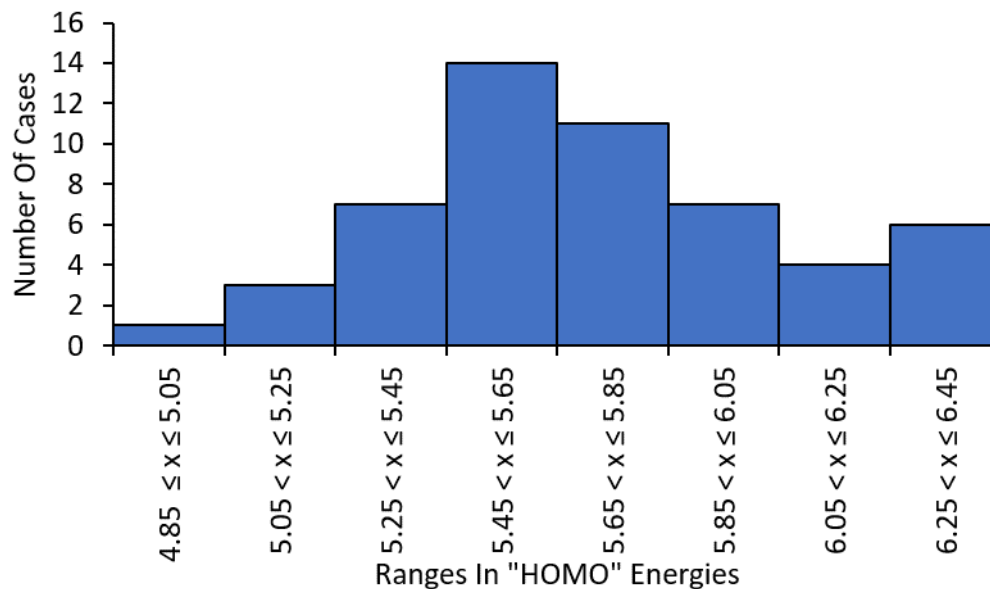


Figure B.78: A summary of the "HOMO" energies for blue emitters provided by M. Y. Wong and E. Zysman-Colman.²⁰

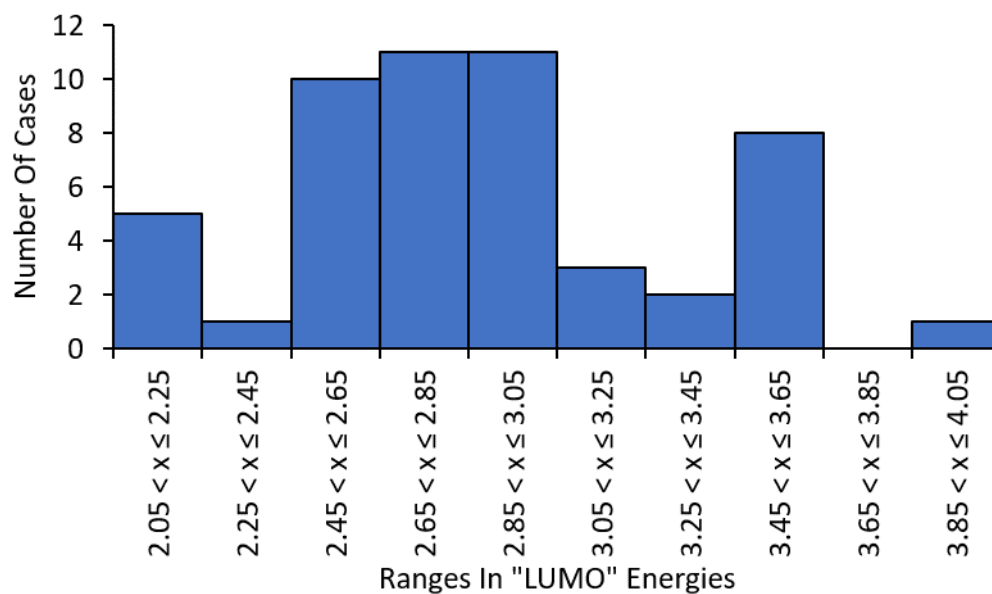


Figure B.79: A summary of the "LUMO" energies for blue emitters provided by M. Y. Wong and E. Zysman-Colman.²⁰

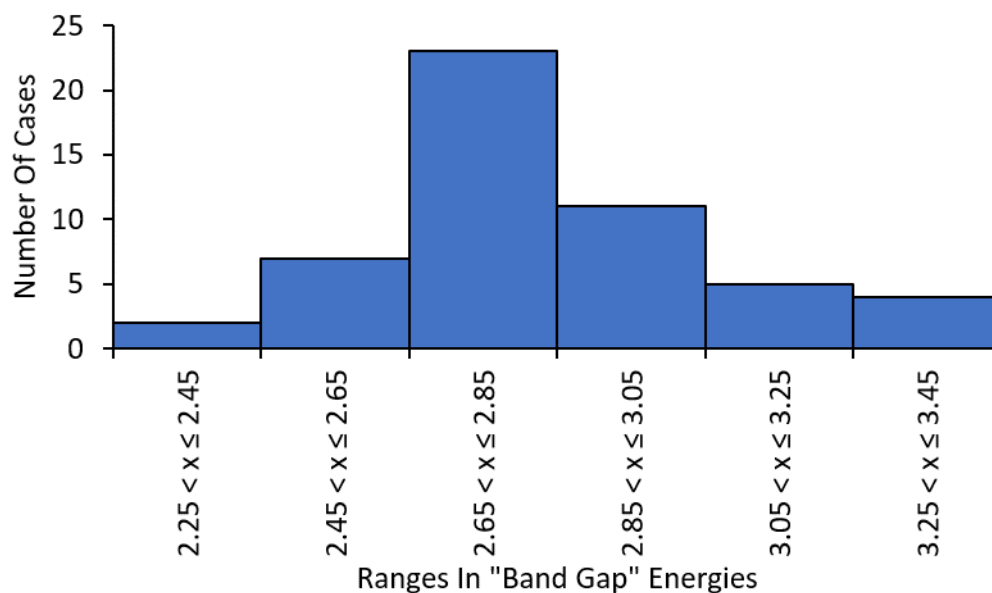


Figure B.80: A summary of the band gap energies for blue emitters calculated by subtracting the reported "HOMO" and "LUMO" energies provided by M. Y. Wong and E. Zysman-Colman.²⁰

B.4.2 Absorption

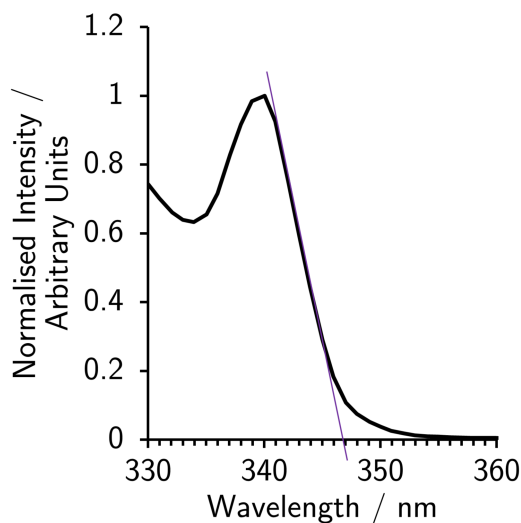


Figure B.81: The onset of absorption of NH1 at 10 μM in toluene.

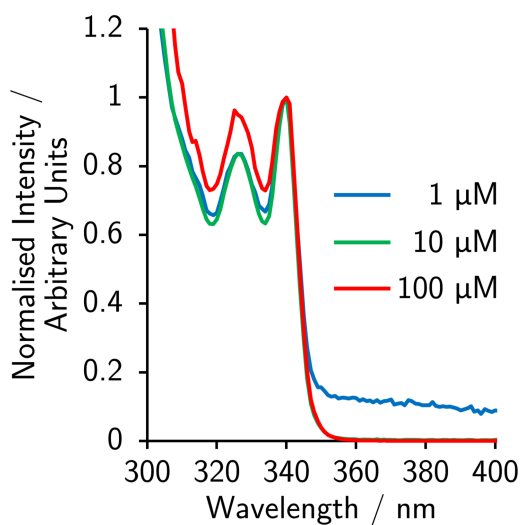


Figure B.82: The absorption of NH1 at various concentrations in toluene. Note the absorption at 100 μM exceeds an absorbance of 1. As such it should be interpreted tentatively, and this likely explains the discrepancy with other concentrations.

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*The scene end badly,
as you might imagine
in a cavalcade of anger and fear.
There will be feasting and dancing
In Jerusalem next year.*
— The Mountain Goats, *This Year*

*You can hide 'neath your covers and study your pain
Make crosses from your lovers, throw roses in the rain
Waste your summer praying in vain
For a saviour to rise from these streets
Well now I'm no hero that's understood
All the redemption I can offer, girl, is beneath this dirty hood
With a chance to make it good somehow
Hey what else can we do now?
Except roll down the window and let the wind blow back your hair.*
— Bruce Springsteen, *Thunder Road*