

The important thing in science is not so much to obtain new facts as to discover new ways of thinking about them

– Sir Lawrence Bragg

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Abstract

Overview

The previously unobserved dynamic motions exhibited by the indium carboxylate metal-organic framework (MOF) $(\text{Me}_2\text{NH}_2)[\text{In}(\text{ABDC})_2]$ are studied through various crystallographic techniques combined with gravimetric and volumetric adsorption measurements.

Chapter 1

The relevant literature in the field of MOFs is introduced to provide a suitable background for subsequent analysis. Particular attention is paid to the effects of functionalization, the analysis of gas sorption through *in situ* crystallographic studies, and the dynamic behaviours of currently known flexible frameworks. These areas are of particular relevance to the work discussed in the rest of the thesis.

Chapter 2

The structural changes that occur to the as-synthesised framework during solvent removal are studied. These results reveal that the MOF undergoes a rare continuous breathing motion, causing its pores to close on increased solvent loss. The behaviour is shown to occur in a single-crystal-to-single-crystal process and be reversible on uptake of atmospheric water vapour. The behaviour of the framework is analysed compared to known flexible frameworks currently reported in the literature.

Chapter 3

The dynamic motion of the framework on solvent loss is explored for other known laboratory solvents, revealing substantial solvent-dependence in the behaviour. The framework is shown to close during loss of more polar solvents, DMF and acetone, but not with less polar solvents, CHCl_3 and THF. A further dynamic response of the material is also introduced by the coordination of water molecules into the building unit of the framework.

Chapter 4

The relevance of the dynamic motion is addressed showing a significant impact on the gas adsorption properties of the MOF, including the overall uptake, the adsorption profile and the relative CO_2 vs CH_4 selectivity. Introduction of stepped-shape isotherm is also shown by only partially desolvating the framework. This allows for defined phase transitions not seen in the fully desolvated frameworks and has been followed by *in situ* crystallographic techniques.

Chapter 5

Modifications to the framework are reported, converting the contained amine group to a methyl amide and exchanging the organic counter ion for a Ag^+ ion. The modified MOFs are shown to demonstrate similar flexible behaviours, but with changes to the dimensionality of the motions.

Chapter 6

The behaviour of the material is summarised.

Authors Declaration

The work presented in this thesis, with the exception of the gravimetric and volumetric gas adsorption measurements, is the original work of the author. The adsorption measurements and subsequent fitting were carried out in collaboration with Craig McAnally and Dr. Ashleigh Fletcher at the University of Strathclyde. All other work was conducted at the University of Sheffield or at Diamond Light Source in the period between September 2012 and October 2015. The views expressed in the thesis are entirely those of the author and not those of the University of Sheffield.

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Commonly used Abbreviations

ABDC	=	2-aminobenzene-1,4-dicarboxyalte
AMBDC	=	2-acetylamino benzene dicarboxyalte
ATR	=	Attenuated Total Reflection
Atz	=	3-amino-1,2,4-triazole
BET	=	Brunauer Emmett Teller
BDC	=	benzene-1,4-dicarboxylate
BDP	=	1,4-benzenedipyrazolate
BPE	=	1,2-bis(4-pyridyl)-ethene
bpy	=	4,4'-Bipyridine
BTC	=	1,3,5-benzenetricarboxyalte
BTB	=	4,4',4''-benzene-1,3,5-triyl-tribenzoate
CSD	=	Cambridge Structural Database
CCD	=	Charge Coupled Device
CIF	=	Crystallographic Information File
CMOS	=	Complementary Metal-Oxide-Semiconductor
CP-MAS	=	Cross Polarization Magic Angle Spinning
CPL-1	=	Coordination polymer 1- [Cu(pzdc)(pyz)]
DABCO	=	1,4-diazabicyclo[2.2.2]octane
DUT-4	=	[Al(OH)(ndc)]
DMF	=	N,N-dimethylformamide
DMOF	=	Zn ₂ (BDC) ₂ (DABCO)
DMSO	=	dimethylsulphoxide
ESRF	=	European Synchrotron Radiation Facility
HKUST-1	=	[Cu ₃ (BTC) ₂]
HPLC	=	High-Performance Liquid Chromatography

IUPAC	=	International Union of Pure and Applied Chemistry
IR	=	Infra-Red
INS	=	Inelastic Neutron Scattering
IM19	=	[Ga(OH)(BDC)]
IPCC	=	Intergovernmental Panel on Climate Change
MAF-23	=	[Zn ₂ (BTM) ₂], H ₂ BTM = Bis(5-methyl-1 <i>H</i> -1,3,4-triazol-3-yl)methane
MAF-X7	=	(Me ₂ NH ₂)(H-DMF)[Co ₂ Cl ₄ (ppt) ₂], H ₂ ppt = 3-(2-phenol)-5-(4-pyridyl)-1,2,4-triazole
MCF-18	=	[M ₃ (μ-OH)(L) ₃], M = metal, L = 2,6-di- <i>p</i> -carboxyphenyl-4-4'-bipyridine
MEM	=	Maximum Entropy Method
MIL-53	=	M(OH)(BDC), M = Cr ³⁺ , Al ³⁺ , Fe ³⁺
MIL-69	=	[Al(OH)(ndc)], ndc = naphthalene-2,6-dicarboxylate
MIL-88	=	[Fe ^{III} ₃ O(CH ₃ OH) ₃ {O ₂ C-C ₂ H ₂ -CO ₂ }{O ₂ C-CH ₃ }]
MIL-101	=	[M ₃ F(H ₂ O) ₂ (μ ₃ -O)(BDC) ₃], M = metal
MOF	=	Metal-Organic Framework
MOF-5	=	[Zn ₄ O(BDC) ₃]
MOF-74	=	[Mg ₂ (dhtp)(OH ₂) ₂], dhtp = dihydroxyterephthalate
MOF-177	=	[Zn ₄ O(BTB) ₃], BTB = 4,4',4''-benzene-1,3,5-triyl-tribenzoate
NMR	=	Nuclear Magnetic Resonance
NOTT-300	=	[Al ₂ (OH) ₂ (L)], H ₄ L = biphenyl-3,3',5,5'-tetracarboxylic acid
obb	=	4,4'-oxybis(benzoate)
ox	=	Oxalate
ppm	=	Parts per million
PSD	=	Position Sensitive Detector
PSM	=	Post-synthetic modification
PXRD	=	Powder X-ray diffraction
pyz	=	Pyrazine

PZDC	=	2,3-pyrazinedicarboxylate
QMOF2	=	[InH(BDC) ₂]
RT	=	Room temperature
SBU	=	Secondary Building Unit
SC-SC	=	Single-crystal-to-single-crystal
SCXRD	=	Single Crystal X-ray Diffraction
Temp	=	Temperature
TGA	=	Thermogravimetric analysis
THF	=	Tetrahydrofuran
UiO-66	=	[Zr ₆ O ₄ (OH) ₄ (BDC) ₆]
ZIF	=	Zeolitic imidazole framework
ZIF-8	=	[Zn(MeIm) ₂], MeIm = 2-methylimidazolate

