

Incorporation of N-Heterocyclic Carbenes and Their Precursors into Metal-Organic Frameworks



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Declaration

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Patrick Capon, 31st of October, 2016

Abstract

Metal-organic Frameworks (MOFs) are a class of porous materials with excellent potential for application in catalysis, gas storage or molecular separations. MOFs are synthesised by combination of an organic linker unit and metal node precursor to yield an overall network structure that typically extends in two or three dimensions. Often the network contains void space, which is the origin of the large surface areas and high porosity observed for many MOFs.

N-Heterocyclic Carbenes (NHCs) were originally applied as ligands for metal complexes, and are commonly used as supporting ligands for organometallic catalysis. For example, an NHC is incorporated into Grubbs' second generation catalyst. NHC precursors have been incorporated into MOFs, leading to properties that make them applicable to catalysis and gas sorption. Metalation of the NHC precursor to yield a MOF bound NHC-metal complex provides an opportunity to further enhance a MOF's capacity for gas sorption or to provide a site for catalysis to be performed.

The main aim of this thesis was to incorporate NHCs into MOFs to yield materials with applications in catalysis (via NHC metalation) or gas sorption. In Chapter 2 five new azolium or NHC containing 1-D MOFs are presented (**1-Cu**, **2**, **3**, **4**, and **5**), with **1-Cu** and **2** showing strong enthalpy of adsorption values for H₂ gas. An NHC-Cu(I) complex was generated concomitantly with MOF synthesis to yield **1-Cu**, however this metal site was not viable for catalysis due to the low porosity of **1-Cu**.

These studies were extended to the highly stable DUT-5 MOF in Chapter 3 with two new DUT-5 analogues and two new mixed linker DUT-5 analogues generated. All four materials showed improved porosity compared to the MOFs in Chapter 2. In Chapter 4, the DUT-5 analogues were investigated for CO₂ and CH₄ gas sorption properties at high pressure in order to provide increased industrial relevance. Furthermore, ionic liquids (ILs) were included within the DUT-5 analogues in an attempt to improve CO₂ uptake. However, excessive loading of the IL resulted in a loss of MOF porosity and minimal uptake of CO₂ or CH₄. Finally, early metalation outcomes of the NHC precursor containing DUT-5 analogues are discussed in Chapter 4, with an aim toward NHC-metal based catalysis in further experiments.

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Abbreviations

1-D – One Dimensional

2-D – Two Dimensional

3-D – Three Dimensional

AIBN – 1,1'-azobisisobutyronitrile

ABCN - 1,1'-azobis(cyclohexanecarbonitrile)

BET – Brunauer-Emmet-Teller

bpdc – 4,4' biphenyl dicarboxylic acid

bpdc-Im – 3-((4,4'-dicarboxy-[1,1'-biphenyl]-2-yl)methyl)-1-methyl-1H-imidazol-3-ium bromide

bpdc-ImPF₆ – 3-((4,4'-dicarboxy-[1,1'-biphenyl]-2-yl)methyl)-1-methyl-1H-imidazol-3-ium hexafluorophosphate

bpdc-Me – 2-methyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid

bpy – 4,4' bipyridine

bpydc – 2,2' bipyridyl dicarboxylic acid

cod - cyclooctadiene

Cp – Cyclopentadiene

Cy - Cyclohexyl

DCM – Dichloromethane

DMF – *N, N'* Dimethyl formamide

DUT – Dresden University of Technology

EDX – Energy Dispersive X-ray analysis

EMIM-ES – 1-ethyl-3-methylimidazolium ethyl sulfate

EXAFS – Extended X-ray Absorption Fine Structure

FTIR – Fourier Transform Infrared

ICP-MS – Inductively Coupled Plasma Mass Spectrometry

IL – Ionic Liquid

IR-MOF – Isorecticular Metal-organic Framework

H₃L1 – 1,3-Bis(3-carboxyphenyl)-1H-imidazol-3-ium bromide

H₃L2 – 3,3'-methylenebis(1-(4-carboxyphenyl)-1H-imidazol-3-ium) chloride

H₄L3 – 1,3-bis(4-carboxyphenyl)-1H-imidazol-3-ium chloride

H₂L4 – 4,4'-(1,1'-methylenebis(3,5-dimethyl-1H-pyrazole-4,1-diyl))dibenzoic acid

MIL – Materials Institute Lavoisier

ML-MOF – Mixed Linker Metal-Organic Framework

MOF – Metal-Organic Framework
MTVMOF – Multivariate Metal-Organic Framework
NHC – N-Heterocyclic Carbene
NMR – Nuclear Magnetic Resonance
NU – Northwestern University
PCN – Porous Coordination Network
PSA – Pressure Swing Adsorption
PSM – Post Synthetic Modification
PSMet – Post Synthetic Metalation
PXRD – Powder X-ray Diffraction
SALE – Solvent Assisted Linker Exchange
SBU – Secondary Building Unit
SCXRD – Single Crystal X-ray Diffraction
TGA – Thermo-Gravimetric Analysis
THF - Tetrahydrofuran
TSA – Temperature Swing Adsorption
UiO – University of Oslo
XRD – X-ray Diffraction
ZIF – Zeolitic Imidazolate Framework

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