Metal–Organic Frameworks Containing Dihydroxy Motifs: Control of Phase Formation and Pore Environments

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Table of Contents

List of Abbreviations

2D	Two-Dimensional
3D	Three-Dimensional
Ac	Acetyl
BDC	1,4-Benzenedicarboxylic acid
BET	Brunauer-Emmett-Teller
bipy	1,1'-Bipyridine
bpdc	Biphenyl-4,4-dicarboxylic acid
$CDCl_3$	Deuterated chloroform
DABCO	Diazobicyclo[2.2.2]octane
DEF	N,N'-Diethylformamide
DHTA	Dihydroxyterephthalic acid
DMF	N,N'-Dimethylformamide
DMSO	Dimethylsulfoxide
dobpdc	Dioxobiphenyldicarboxylic acid
EDTA	Ethylenediamine tetraacetic acid
eq	equivalents
ESI-MS	Electrospray Ionisation-mass Spectrometry
EtOAc	Ethyl Acetate
EtOH	Ethanol
FT-IR	Fourier-Transform Infrared Spectroscopy
MeCN	Acetonitrile
MeOH	Methanol
mmen	methylethylenediamine
MOF	Metal-Organic Framework
NaOH	Sodium Hydroxide
Oh	Octahedral
phen	Phenanthroline
PSM	Post-Synthetic Modification
PSMet	Post-Synthetic Metalation
PTE	Positive thermal expansion
PXRD	Powder X-ray Diffraction
SCXRD	Single-Crystal X-ray Diffraction
SP	Square Planar
t-BOC	*tertiary*-butoxycarbonyl
Td	Tetrahedral
XANES	X-ray Absorption Near Edge Spectroscopy
XRD	X-ray Diffraction

Thesis Overview

This thesis is comprised of 4 manuscripts that form the results chapters 2 to 5. All manuscripts were completed during candidature and have been published in international, peer-reviewed journals. The connections between these publications will be briefly presented here, tying in the content of each chapter with the overarching theme of this thesis.

Herein, the use of ligand-bound hydroxyl groups, specifically potentially chelating dihydroxyl motifs, in support of carboxylate donors for the formation of novel Metal-organic Frameworks (MOFs) was explored using a rational design and modification approach. The multi-dentate ligand 2,2'-dihydroxy-1,1'-biphenyl-4,4'-dicarboxylic acid, that was used throughout this work, was utilised in both an ester protected form (Chapter 2) or with free phenol groups (Chapters 3-5). Careful control of synthetic conditions (e.g. choice of starting metal salt, co-ligand or reaction conditions) to dictate the desirable MOF phase and tailor final MOF characteristics was a major theme of investigation, along with the use of post-synthetic processing methods to access enhanced functionality within the pore structures of the resultant materials. A further focus was placed on establishing new synthetic, or post-synthetic, protocols for efficient synthesis of functional MOF materials.

Chapter 1 serves to introduce the broad field of coordination polymers and inform the reader of seminal developments in the sub-field of metal-organic framework (MOF) chemistry, focussing on methods for controlling both the structure and internal pore environment of MOFs. A short review of pertinent literature concludes this chapter, highlighting the use of hydroxyl groups in the formation and application of MOFs. Influential examples of MOFs that incorporate hydroxyl groups into their structures and onto the backbone of the ligand moiety are discussed to highlight the potential of, and the opportunities, in this area.

Chapter 2 presents a fundamental study into the incorporation of a biphenyl carboxylate ligand (2,2'-dihydroxy-1,1'-biphenyl-4,4'-dicarboxylic acid), with protected hydroxyl groups, into metal-organic frameworks. Predicable inclusion of such functional groups had previously proven difficult in cases where these groups can also function as donors for the MOF nodes and adopt a structural role. This manuscript describes an in *situ* method for MOF synthesis and deprotection of ester–protected hydroxyl functional groups with retention of crystallinity, eliminating the need for potentially degradative post–synthetic deprotection strategies. Reliable access to non-interpenetrated structures was realised with this method, as well as the post–synthetic incorporation of Cu(II) at the free diol moieties. Modification of the pore environment

with dihydroxyl moieties, and subsequently with Cu(II) ions, resulted in increased pore size and improved enthalpy of CO_2 adsorption at low pressures.

Chapter 3 describes the direct use of 2,2'-dihydroxy-1,1'-biphenyl-4,4'-dicarboxylic acid in the synthesis of Ni(II) MOFs with kagome-like topology. Relatively unusual solvent-dependent porosity was observed, related to free rotation of coordinated solvent molecules in an activated form of the material. Upon removal of this coordination solvent, a transition in metal coordination environment is observed from O_h to a distorted-square planar (d-SP) geometry, clearly observable by a stark colour change from green to yellow. Significant changes in the unit cell of the structure indicated structural contraction along the crystallographic *c*-axis, resulting in drastic modification to the accessible pore volume and internal pore environment. Re-solvation of the MOF was observed to be solvent size dependent, with MeOH successfully able to penetrate the contracted framework structure, re-forming the O_h coordination environment and pore dimensions, and occupying the axial coordination sites. Due to differences in magnetic moment between O_h and d-SP Ni(II), time-dependant magnetic susceptibility measurements were used to monitor the progress of structural modification. These structural changes were further confirmed by X-ray absorption near-edge spectroscopy (XANES), computational modelling and variable-temperature powder X-ray diffraction (PXRD), which incidentally uncovered marked positive thermal expansion along the crystallographic *c*-axis of the material.

Chapter 4 examined the impact of increasing the ionic radii of alkali earth metals, Mg(II), Ca(II) and Sr(II), in the synthesis of MOFs using 2,2'-dihydroxy-1,1'-biphenyl-4,4'-dicarboxylic acid and common bidentate co-ligand 1,4-diazabicyclo[2.2.2]octane (DABCO). Three distinct MOF structures were formed with different alkali earth metal salts, showing observable differences in ligand-derived fluorescence emission. Reaction with Mg(II) yielded a MOF isostructural with the Ni(II) kagome structure described in Chapter 3. DABCO was not incorporated into this structure, despite being present during synthesis, and as the ligand dihydroxy moiety was involved in structural coordination, fluorescence quenching was observed. In contrast, the use of Ca(II) or Sr(II) formed novel MOFs containing both ligands, in which the dihydroxy ligand moiety is not involved in structural coordination. This was attributed to the limited ability of the chelate bite angle of the ligand to accommodate metal ions of particular ionic radii. As a result, large metal ions, such as Sr(II) and Ca(II) are unable to chelate the diol and preferentially form alternative topologies. Solid-state fluorescence emission (λ = 435 nm) is observed when MOFs are solvated with polar aprotic solvents, such as DMF or DMSO. Judicious selection of metal ion has been shown to selectively influence

coordinating mode of 2,2'-dihydroxy-1,1'-biphenyl-4,4'-dicarboxylic acid and tailor the physical and spectroscopic properties of the resulting MOFs.

Chapter 5 describes how the control of synthetic conditions and choice of metal ion utilised during synthesis could be used to form a novel MOF containing trimeric nodal clusters from 2,2'-dihydroxy-1,1'-biphenyl-4,4'-dicarboxylic acid. Using Co(II) salts, two structurally distinct MOF phases are formed at high and low temperatures, with a mixture forming at intermediate temperatures, indicating thermodynamic and kinetic control over MOF formation. By doping the Co(II) reaction solution with small amounts of a Zn(II) salt, which only forms the one MOF phase, the kinetic conditions were able to be 're-programmed' to generate only the thermodynamically-favoured phase with a mixed Zn(II)/Co(II) composition. Additionally, preferential incorporation of Co(II) over Zn(II) was evident at higher temperatures, with fluorescence emission spectroscopy and pore size distributions indicating coordination of metal ions to the 'free' ligand dihydroxyl groups present within the thermodynamically favoured MOF material. The extent of metal incorporation at the 'free' diol sites was further able to be controlled by post-synthetic metalation (PSMet) with Co(II), which allows the internal pore dimensions to be fine-tuned and the MOF to exhibit an increased enthalpy of adsorption for CO_2. The combination of specific synthetic protocols and post-synthetic metalation in this study allow precise control over both phase formation and internal pore environments. While not examined there is a possibility that this 'reprogramming' approach can be further applied in other MOF systems that exhibit competing phases.

Finally, conclusions and future prospects are presented in Chapter 6, followed by general appendices in Chapter 7, which include statements of authorship and copies of additional publications that this author has contributed to during the course of this candidature, but are not central to this thesis research.