

Chapter 6

Conclusion

There are currently many uses for MOF materials, but research on MOF based on solid state sensor technologies is still relatively new and was adopted in this study. A few possible approaches were investigated for developing such MOF sensors, and a solution using CT complexes based on a diimide linker/host was attempted. CT complexes were thought to be interesting sensor components as incorporation in a MOF was expected to produce different colours depending on the nature of host-guest interaction. Interactions of different guest chemicals in the MOF voids were then expected to produce the variety of colours required of a sensor. A key feature of the diimide linker components is the ease with which they undergo modification as well as contain functionality needed for MOF formation. The existence of some reports on diimide modification and CT complex formation was also expected to ease research in this area. Therefore this work has focused on a diimide linker as a possible component for the formation of porous MOFs for sensor technologies.

The diimide linkers obtained in this study were all synthesised via a condensation reaction. This proved to be very useful as different linker components could be made by altering the size of the amino acid component. Two linker components were successfully synthesised namely *N,N'*-bis(glyciny)-pyromellitic diimide (gly-L) and *N,N'*-bis(γ -butyric)-pyromellitic diimide (but-L). The crystal structures of these linkers indicate that their molecular geometries are unique when compared to the more conventional organic linkers. The terminal carboxylate groups are arranged in a *trans* geometry, with both groups being out of the molecular plane. This *trans* geometry results in the formation of a step-like packing arrangement, which is predominant in all structures.

The SCXRD structures indicate that both gly-L and but-L crystallised in different crystal systems due to the variation in amino acids used. The 2D extension of these structures shows that the planar components associated with each molecule aligned up differently within the 2D layers. gly-L adopts a parallel orientation amongst adjacent 1D layers, whereas the adjacent 1D layers of but-L contain planar rings coupled with carboxylate bridges (figure 4.3). Both host molecules have an offset stacking arrangement of their respective planar components within the 2D layers.

Both diimide linkers are capable of incorporating aromatic donors to form CT complexes. CT complexes formed with both host molecules resulted in the formation of various coloured crystals, with their respective aromatic donors. The smaller gly-L molecule readily accommodated all four donor molecules used (naphthalene, anthracene, phenanthrene and perylene). Whereas the larger but-L showed a bias towards the bigger aromatic donor molecules (phenanthrene and perylene) while not forming complexes with naphthalene and anthracene. SCXRD indicated that all these CT complexes pack with a 1:1 stacking arrangement between the donor and host molecules within the 2D sheets. All CT structures extend similarly into the third dimension through various intermolecular hydrogen bonding interactions through host-host and host-guest interactions via the planar diimide and terminal glyciny carbonyls with the aromatic, and alkyl hydrogens. Thereby resulting in the formation of adjacent parallel sheets, with gly-ANT and but-PERY adopting a zigzag orientation amongst the adjacent 2D sheets.

Phenanthrene and perylene were the only two aromatic donors to form CT complexes with both host molecules. The but-L CT complexes crystals formed different (lighter) colours when compared to the equivalent gly-L complexes, due to them absorbing at much lower wavelengths, as confirmed by solid state UV-Vis. SCXRD showed that both phenanthrene complexes (gly-PHEN and but-PHEN) were isostructural as they crystallised within the same space group and had the same three dimensional packing arrangements, whereas the perylene complexes (gly-PERY and but-PERY) did not.

The increase in the alkyl chain of the but-L molecule did not allow for the formation of CH $\cdots\pi$ interactions as these are not present in the structures of both but-PHEN and but-PERY complexes.

Lattice energy calculations performed using the Oprop module of the OPIX suit indicated an increase in stabilisation energy as the size of a donor and/or acceptor increased. This trend was observed for all CT complexes except for gly-ANT, which contained the highest stabilisation energy due to the extra atoms associated with the solvent molecules (ANT+solvent > PERY > PHEN > NAP). The molecule-molecule arrangement associated with $\pi\cdots\pi$ interactions contained the single highest stabilising energy for all CT complexes.

The PXRD data observed for all CT complexes indicated that the calculated and observed patterns except for gly-ANT are in good agreement with each other. In the gly-ANT case the most likely reason for this deviation from the expected was the due to the loss of methanol upon grinding.

Thermal analysis in the form of TGA and DSC were carried out on all CT structures. Both techniques indicated that the thermal stability of CT complexes increased as the size of the donor molecules increased. These trends were consistent with the energy calculations obtained from Oprop. Again gly-ANT did not follow this trend as the solvent methanol solvent molecules were liberated at around 100°C, after which thermal stability was slightly lower than gly-PHEN. Despite having higher stabilisation energies, the but-L and but-L complexes had lower thermal stabilities due to lower crystal densities when compared to the equivalent gly-L structures.

The solid and liquid state UV-Vis differed when compared to each other indicating the effect of the crystal environment versus the liquid environment on such spectra. Both types of spectra indicated much higher wavelengths for the larger donor molecules. The most noticeable difference observed amongst spectra was for the

gly-ANT and gly-PERY CT complexes. With gly-ANT absorbing at lower energies within the solid state and gly-PERY absorbing with the lowest energy in the liquid state. All the IR spectra are consistent with the general structure of ligand and complexes.

MOF-Zn1 and 2 were obtained from one crystallisation, both optical microscopy and SCXRD indicated the formation of two different crystal structures with varying metal coordination. MOF-Cd1 and MOF-Co1 both produced the same octahedral metal coordination, with MOF-Co1 containing a water molecule coordinated to one of its equatorial positions. All MOF structures, except for MOF-Zn2, contained apical DMF molecules and formed 2D layers through a bridging linker, which lead to either a herringbone type arrangement (MOF-Zn1) or in a step-like arrangement (MOF-Cd1 and Co1). The offset stacking arrangement of the linker component was retained in all MOFs. Three dimensional extension of all MOF structures occurred mainly through weak intermolecular hydrogen bonding interactions. These hydrogen bonding interactions was seen in the linker (host) and CT complexes structures, and were retained in the framework structures. Only MOF-Zn2 and MOF-Cd1 formed 1D open network pores with pore diameters of $56\text{\AA}^3$ and $29\text{\AA}^3$ respectively, without the removal of solvent molecules.

The various divalent metals used in this study not only affected the overall topology (figure 1.6) of the MOF framework but also the overall crystal growth kinetics of the system as well. The use of divalent zinc and cadmium salts produced large MOF crystals at room temperature, while a solution containing cobalt (II) nitrate had to be cooled down to produce suitable crystals. Divalent cobalt was therefore more reactive towards the gly-L linker when compared to zinc and cadmium. However the use of a trivalent cobalt metal did not show any tendency to react with the gly-L linker.

The use of gly-L and but-L as organic linkers in MOF production seemed feasible as both contained terminal carboxylate functionality, which would produce neutrally

charged frameworks (Montney *et al.*, 2007). Unfortunately MOF crystals could only be obtained by utilising the gly-L linker. Many methods were employed to try and form MOF crystals with the but-L linker, but due to time constraints no solution could be obtained. It is believed that a solution to this problem could be obtained by substituting the alkyl chain for a more rigid aromatic system, as indicated by Cairns and co-worker (2008).

Assessing these materials for solid state sensors proved to be very difficult as all MOF materials were obtained in low yields coupled with poor stability when exposed to air. The lack of stability also made further characterisation on these materials unlikely. In addition, reproducibility of structures proved to be very difficult even under the same synthetic conditions, a phenomenon that has continually proven to be a nuisance in this field of research.

From the research undertaken it is evident that linker components with desired properties can be modified and be utilised in the way intended to suit the formation of novel MOF materials. However the formation of these porous materials is not easy as there are a number of variables affecting its formation. Things like linker functionality and geometry, metal oxidation and synthetic conditions. Each one plays a vital role in the overall structural formation and properties achieved from these materials. Only when each factor is successfully assessed and its contribution to the overall materials is noted can we engineer materials with relevant properties to suit specific applications.

6.2 References

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