Chapter 1
Introduction

1.1 Crystal engineering

Crystal engineering is a branch of crystallography that entails the rational design of functional materials at the molecular level (Desiraju, 2003). It is able to achieve this by controlling the various molecular interactions such as non-covalent interactions and coordination complexes, which occur during the nucleation process (Hollingsworth, 2002). This allows researchers to tailor-make solids with desirable chemical and physical properties in both the molecular and bulk forms, thus making this field of prime interest to researchers (Zheng *et al*., 2005).

The utilisation of these intermolecular interactions may vary between organic and inorganic systems. Organic systems primarily utilise non-covalent interactions, whereas inorganic systems are mainly made up of metal coordination complexes. The bonding interaction within these systems may vary from metal to ligand bonding to non-covalent interactions in the form of hydrogen bonding, electrostatic interactions, and van der Waals forces which include $\pi\cdots\pi$ interactions (Oshovsky *et al*., 2007, Lehn, 1988). The approach of using non-covalent interactions to create new materials, make up a part of chemistry known as supramolecular chemistry.

Supramolecular chemistry deals with the formation of superstructures through the design and utilisation of non-covalent interactions, by making use of small molecular building blocks (Ghosh *et al*., 2005). These non-covalent interactions are far weaker than covalent bonding and have been demonstrated in important concepts such as host-guest chemistry, molecular recognition, molecular self-assembly and folding (foldamers) (Oshovsky *et al*., 2007). Molecular self-assembly and molecular recognition allow for the formation of host guest complexes through non-covalent interactions and are studied extensively in supramolecular chemistry (Oshovsky *et al*., 2007, Lehn, 1988).

Their use in chemistry has been greatly exploited in crystal engineering due to the fact that they form supramolecular networks that can self assemble by directional molecular recognition between the molecules or ions (Bis *et al.*, 2005). Interactions between molecules are often conservatively maintained in different supramolecular structures, as a consequence these molecular combinations may be referred to as supramolecular synthons (Desiraju, 1995). Supramolecular synthons can be classed into two different groups namely, homosynthons and heterosynthons (Walsh *et al.*, 2003, Etter, 1982). Homosynthons refers to interaction between the self complimentary functional groups e.g. carboxylic acids (Walsh *et al.*, 2003, Etter, 1982), whereas heterosynthons refer to interactions between different but complimentary functional groups e.g. acid-pyridines interactions (Vishweshwar, 2003). Detailed knowledge of these non-covalent interactions is useful as they provide information for constructing supramolecular structures. Thereby allowing researchers to expand and exploit solid-state chemical research and engineering (Bis *et al.*, 2005, Zaworotko, 2000).

Homosynthon Heterosynthon

Figure 1.1: Schematic representation of homosynthon (Bis *et al.*, 2005) and heterosynthon (Walsh *et al.*, 2003).

1.2 Porous materials

Industry and academia has provided particular interest into porous materials (Kitagwa *et al.*, 2004), which was fuelled by the formation of highly rigid structures that are permeable (Barbour, 2006). Permeability plays an important role in the formation of porous materials as the removal of guest molecules should lead to the formation of a cavities, which form a network on interconnected channels within a rigid structure (Barbour, 2006). These vacant channels and cavities allow porous materials to be utilised in areas such as gas storage, drug delivery, sensor technologies and catalysis (Hermes *et al*., 2006, Férey, 2008, Kitagwa *et al*., 2004, Volkringer *et al*, 2009). There are currently three known types of porous materials, namely zeolites, activated carbons and metal organic frameworks (MOFs) (Kitagwa *et al*., 2004), and each class has problems associated with them. The problems faced by zeolites and activated carbon materials is that they either have low porosity (zeolites) or broad pores (carbons), thus hindering gaseous uptake and storage (Kitagwa *et al*., 2004). In addition to these problems, exhisiting synthetic methods do not allow for the design ablity, and tailoring of these structures (Kitagwa *et al*., 2004). However, the last and most recent form of porous materials MOFs (coordination polymers), has attracted a lot of attention recently amongst material scientists. This is due to current synthetic methods allowing for the creation and modification of regular repeating nano-sized pores within the framework (Eddaoudi *et al*., 2001, Kitagwa *et al*., 2004). Figure 1.2 outlines the possible modification of these materials in terms of size, shape, surface functionality and dimensionality by altering their fundamental components.

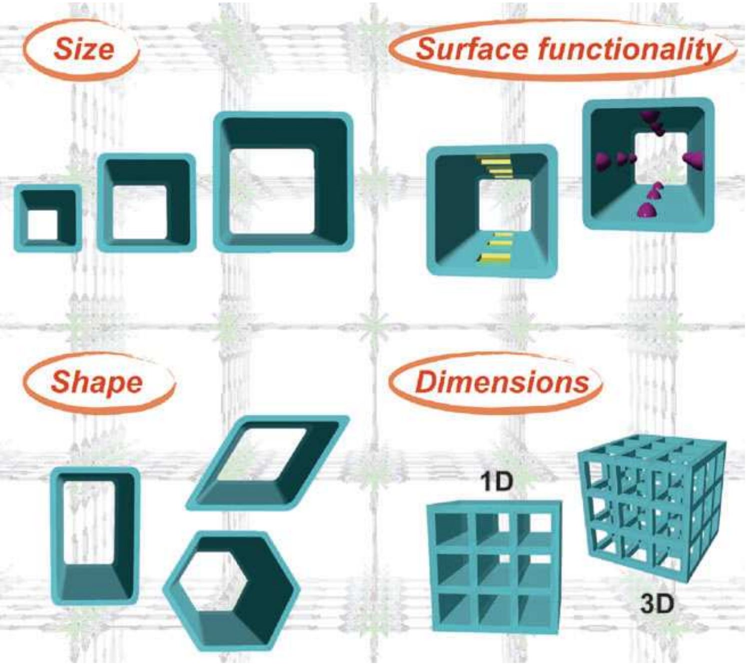


Figure 1.2: Possible alterations of MOF materials via current synthethic methods (Uemura *et al*., 2009).

1.3 Metal Organic Frameworks (MOFs)

The design, synthesis and characterisation of MOFs have shown exponential growth over the recent years (Kitagwa *et al*., 2004, Long *et al*., 2009). As a result there are close to 4000 fully characterised MOFs structures found in the CSD, with roughly a 1000 journal articles being published every year since 2002 (Kitagwa *et al*., 2004, Long *et al*., 2009, Mueller *et al*., 2006).

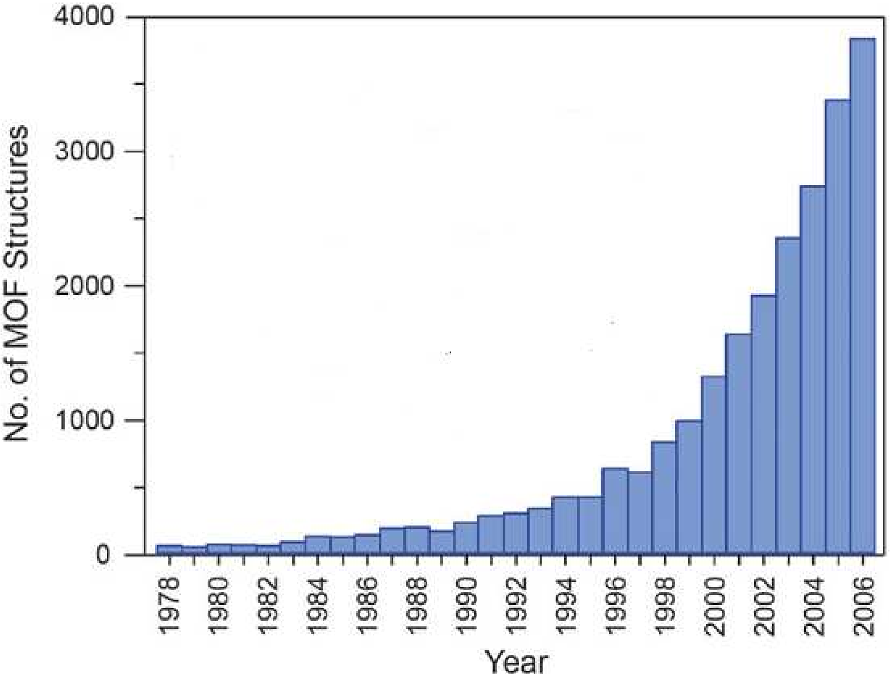


Figure 1.3: Exponential growth in MOF research over the past three decades (Long *et al*., 2009).

The reason for this immense growth is due to the possibility of altering these materials in a systematic manner (Roswell *et al*., 2004). Thus allows researchers, molecular control of structural details by utilising concepts from both classic organic and inorganic solid-state structural chemistry (Ohashi, 1993). As a consequence it is possible to design materials that are able to self-assemble into 1D, 2D and 3D extended network structures (figure 1.4) (Roswell *et al*., 2005, Janiak, 2003).

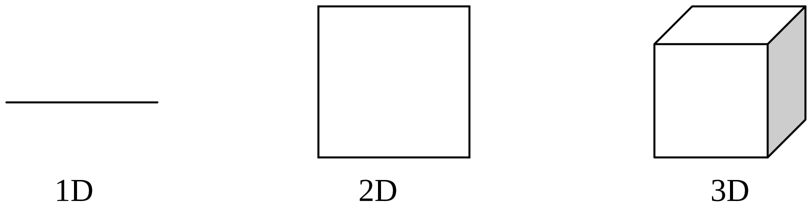


Figure 1.4: Representation of 1D, 2D and 3D network structures in MOFs.

1.4 MOF components

MOFs are hybrid materials that are mainly based on organic ligands (linkers) and cationic transition metal ions (connectors) (Kitagwa *et al*., 2004, Mueller *et al*., 2006). Metals are used as they readily self assemble and directly influence the framework topologies formed by a MOF material (Czaja *et al*., 2009, Volkringer *et al*., 2009). The two main linker components that are extensively used for MOF production are usually based on a pyridyl and/or carboxylate functionality, which occurs at the both terminal positions of the organic molecule (Mueller *et al*., 2006, Hao *et al*., 2004). These functional groups are essential as they coordinate onto a metal thereby forming a metal cluster (figure 1.5 (b)), these clusters are then usually linked together by the organic molecule (linker), thereby forming the MOF framework.

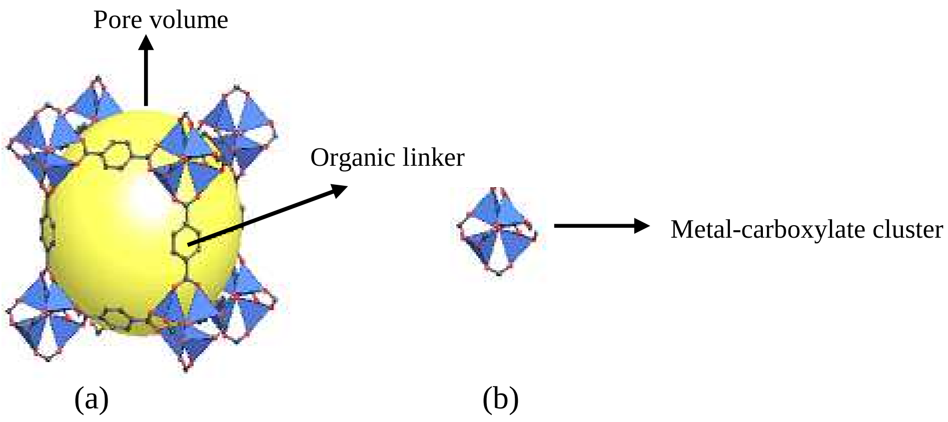


Figure 1.5: Diagram of MOF-5 (Mueller *et al*., 2006), indicating (a) organic linker and pore volume and (b) metal-carboxylate cluster.

1.4.1 Linkers

Currently pyridyl and carboxylate groups are the two main functional groups used in linker components for MOF synthesis. Each linker provides its own unique structural characteristics to the MOF. The use of monodentate dipyridyl linkers leads to the formations of cationic frameworks with the addition of counterions (Eddaoudi *et al*., 2001). Pyridyl linker components often form nonporous structures as the counterions tend to inhibit pore formation (Kim *et al*., 2001, Montney *et al*., 2007). Topology prediction is made extremely difficult due to the flexible nature of these linkers coupled with the presence of counterions (Kim *et al*., 2001).

Carboxylate linkers in the form of dianionic dicarboxylates have been shown to be essential in the formation of neutral porous MOF materials without the incorporation of counterions (Montney *et al*., 2007, Kitagawa *et al*., 2004, Eddaoudi *et al*., 2001). It has also been noted by Eddaoudi and co-workers (2001), that the use of carboxylate groups (known to be essential in chelating metal ions) actually locks the metal into a respective position, thereby forming a secondary building unit (SBU) (figure 1.5 (b)) (Kitagawa *et al*., 2004). It does this by forming an M-O-C cluster, which has the ability to aggregate (Eddaoudi *et al*., 2001). These SBU's are very rigid and as a result tend to be structurally stable and robust. Figure 1.6 indicates various pyridyl and carboxylate linker components.

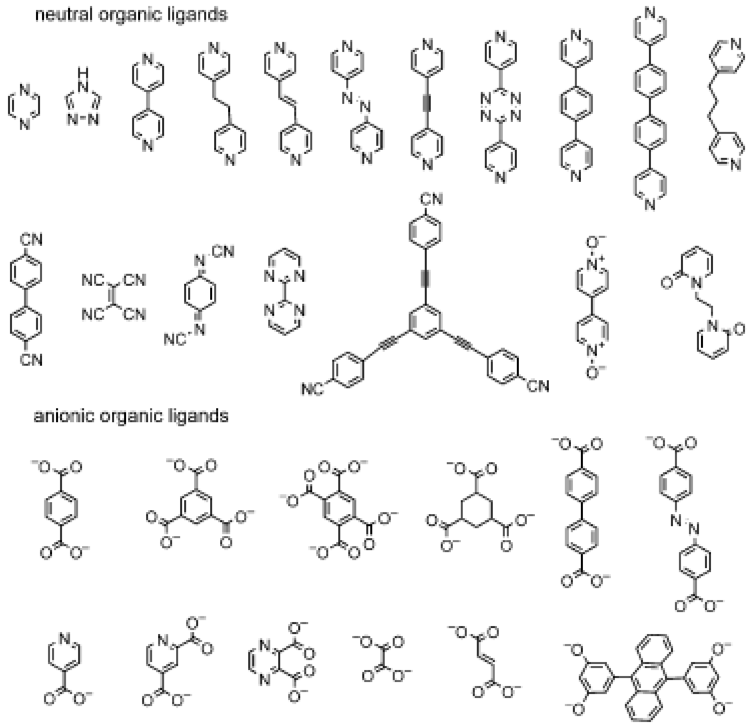


Figure 1.6: Various pyridyl and carboxylate linker components used in MOF formation.

1.4.2 Connectors

The use of transitional metal-ions plays a large role in the formation of MOF materials as they are able to self assemble and act as coordination sites for a wide range of polyatomic bridging ligands (Czaja *et al*., 2009). The oxidation state of the metal also influences the overall topology of MOFs by altering the coordination site, which could range from linear to octahedral (Kitagwa *et al*., 2004). This is illustrated by figure 1.7, whereby a linear linker component is utilised with metals of various oxidation states. The use of metals also enhances the physical properties by forming robust materials that have increased thermal and mechanical stability (Czaja *et al*., 2009).

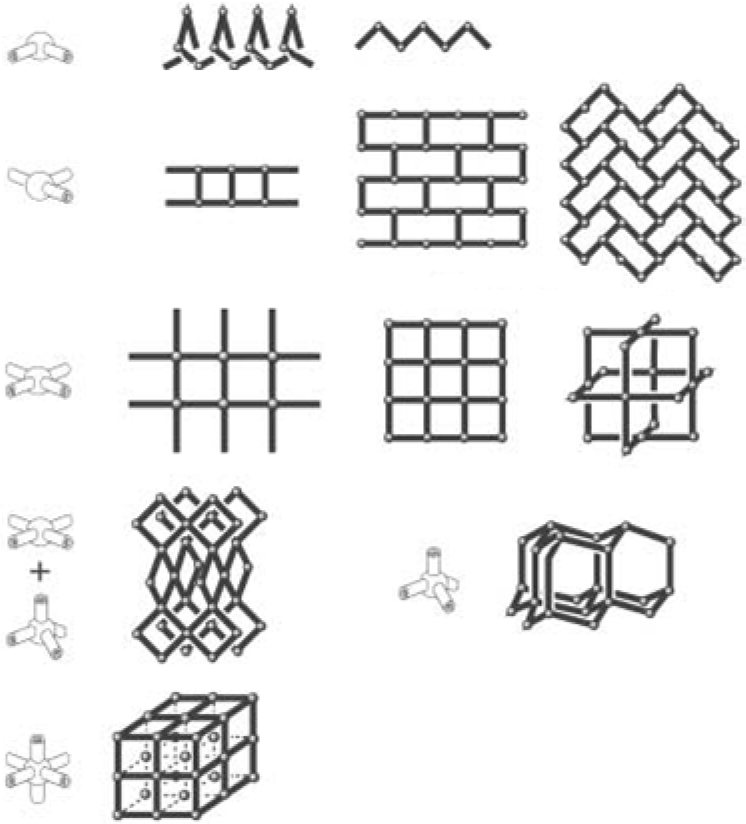


Figure 1.7: Framework alteration with varying metal geometries using a linear linker (Kitagwa *et al*., 2004).

1.5 Bonding interactions

There are a large number of different framework structures possible due to the relative abundance of different metals and organic linkers. These frameworks are able to extend infinitely in all dimensions due to bonding interactions between the clusters (Janiak, 2003). Bonding interactions may vary from coordination bonding (CB), hydrogen bonding (HB), $\pi \cdots \pi$ interactions and other van der Waals interactions (Nattinen *et al*., 2003). The use of weak interactions in conjuction with coordination bonding (CB) results in the formation of flexible and robust MOF structures (Kitagwa *et al*., 2004).

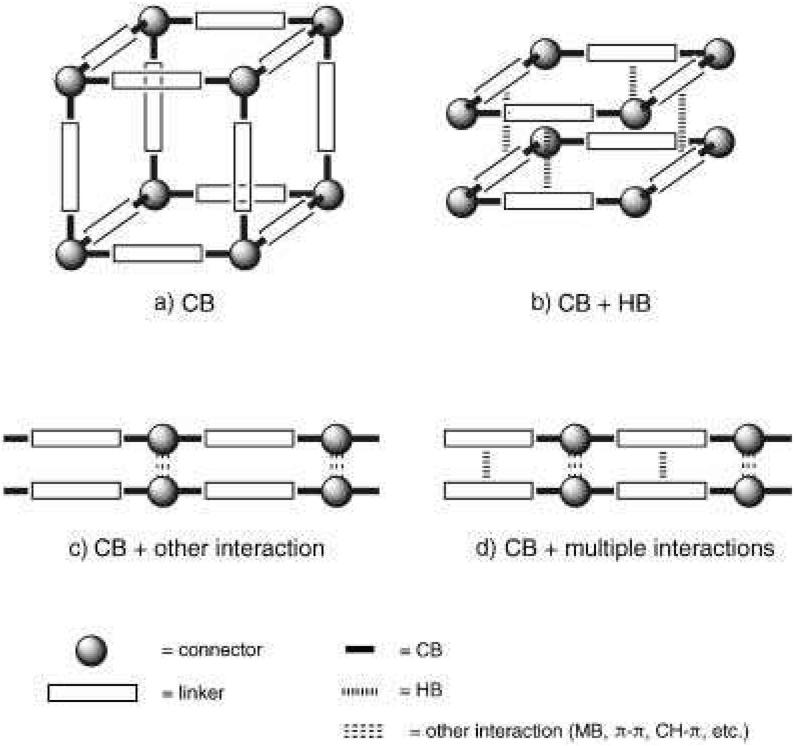


Figure 1.8: Interactions resulting in overall extension of MOF structures (Kitagwa *et al*., 2004).

1.6 Alterations

The alteration of these crystalline porous materials enables researchers to develop materials with specific chemical functionality (Long *et al*., 2009, Hao *et al*., 2004). As a result, careful selection of linker and connector components makes it possible to tune the physical characteristics of the MOFs to suite specific applications (Janiak, 2003). The large variety of ligand and metal ions results in large diversity in topologies in the metal building unit within the MOF (Janiak, 2003), thereby allowing for the design of very novel materials.

Void formation and functionality (Roswell *et al*., 2004) within the framework is dependant on the size, length, and the functionality of the organic unit, as shown in figure 1.8 and table 1.1. Hence understanding the bonding interactions between the linker and connector components is essential, as it aids in understanding how these materials (MOF) come into existence, and so providing material designers with predictive capabilities (Yaghi *et al.*, 2003).

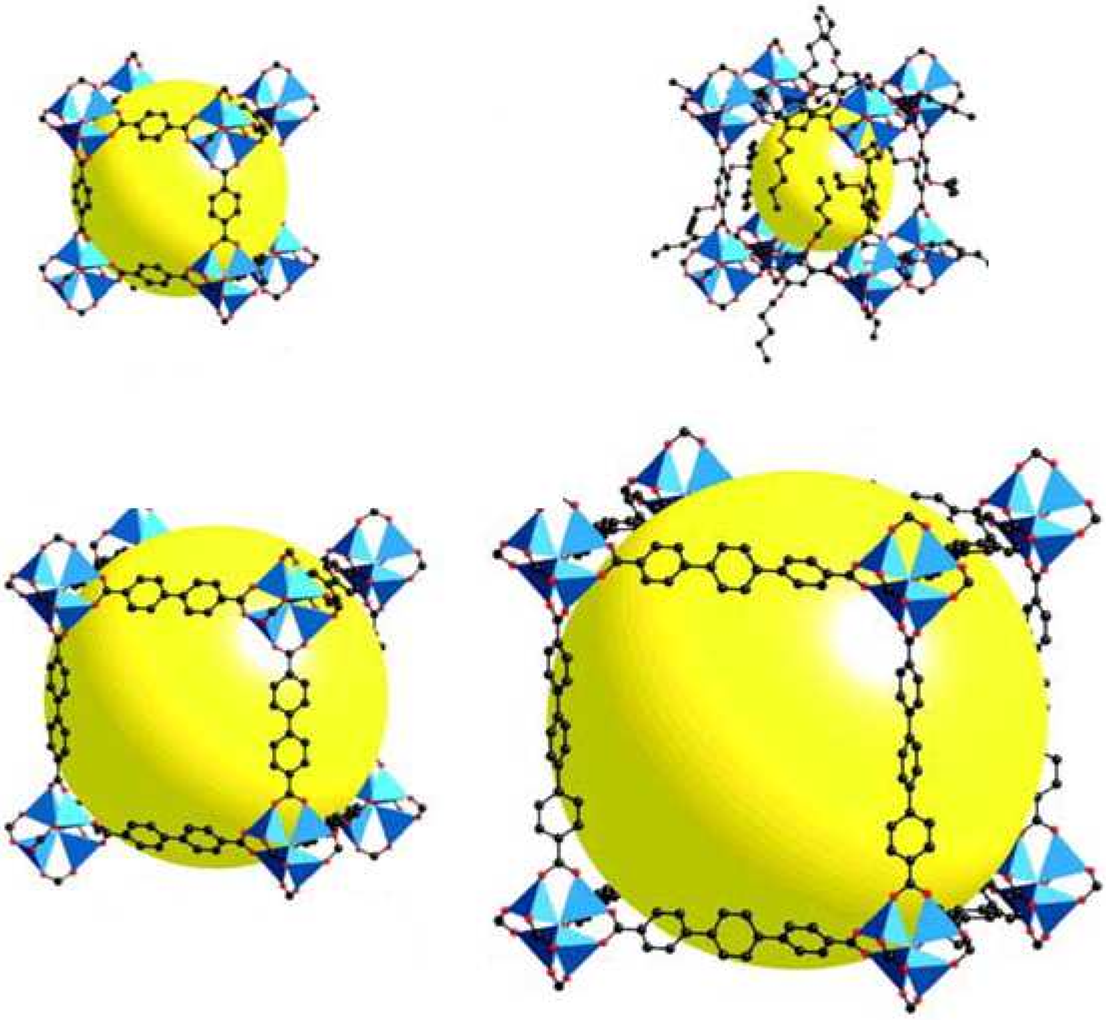
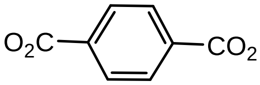
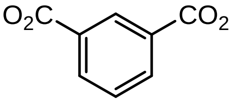
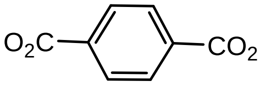
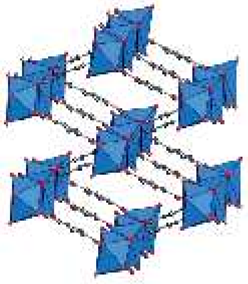
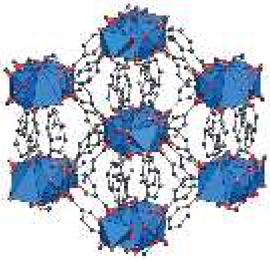
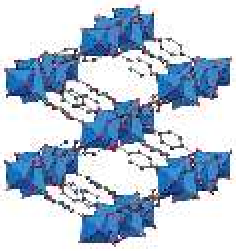


Figure 1.9: Effect of ligand size on the pore volume of MOFs with the same metal cluster (Kesanli *et al*., 2003).

Table 1.1: Effect of linkers and joiners on the unit cell dimensions of MOF materials. (Rosi *et al.*, 2005).

	MOF-70	MOF-72	MOF-73
Linker			
Metal	Pb	Cd	Mn
Unit cell:			
a(Å)	8.36	13.69	24.78
b(Å)	17.99	18.25	10.58
c(Å)	9.96	14.91	17.42
α(°)	90.00	90.00	90.00
β(°)	102.687	101.01	129.93
γ(°)	90.00	90.00	90.00
Volume (Å^3)	1462.40	3654.52	3504.1
Z	4	8	8
Space group	*P*2$_1$/*n*	*C*2/*c*	*C*2/*c*
Structure			

From table 1.1 and figure 1.8, it can clearly be seen that MOFs can be altered by simply changing the metal ion and/or linkers, thereby altering the MOFs chemical and physical (pore size) properties (Clausen *et al.*, 2005).

MOF networks provide attractive properties such as regioselectivity, stereoselectivity, shape selectivity and precise binding (Nattinen *et al*., 2003), and can be used in a number of applications, which are listed below:

Current applications where MOFs have been used or considered:

- Gas purification (Mueller *et al*., 2006).
- Gas separation (Mueller *et al*., 2006).
- Magnetic properties (Clausen *et al*., 2005).
- Production of optically pure compounds (Lin, 2005).
- Gas storage (Hydrogen and Hydrocarbons) (Hermes *et al*., 2006).
- Zeolite type catalysts (Hermes *et al*., 2006).
- Conductivity applications (Kepert, 2006).
- Gas sensor applications (Achmann *et al*, 2009).

1.7 Formation of MOF materials

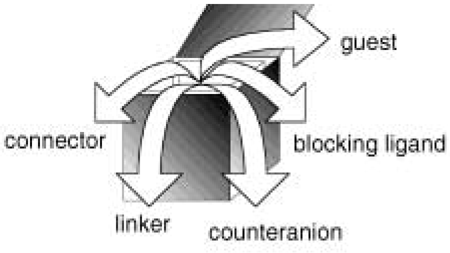


Figure 1.10: Vital components in MOF formation (Kitagwa *et al*., 2004).

MOF synthesis usually requires the use of a metal salt and an anionic/neutral linker, with the relevant stoichiometry. In addition to this, various other auxiliary components can be used, in the form of blocking agents, counteranions and guest molecules (Kitagwa *et al*., 2004). Each of these components play a role in the eventual formation of the MOF material (Kitagwa *et al*., 2004). Blocking agents actually help in the formation of the SBU's (Roswell *et al*., 2004), whereas counterions are used in the formation of cationic frameworks when pyridyl linkers are used (Eddaoudi *et al*., 2001). The use of non-bonding guests (such as solvents) aid in the formation of porous structures, by facilitating the formation of extended structures (Kitagwa *et al*., 2004). These guests can be displaced by various methods such as irradiation wherein more reactive species can be incorporated within the pore, provided that it is volatile enough and can fit into the cavity (Hermes *et al*., 2006).

1.8 Problems affecting MOFs

The predictive capability associated with MOFs allows control of certain crystal properties to be achieved, by controlling the orientation of building blocks in the solid state (Kim *et al*., 2001). Unfortunately crystal engineering still faces immense problems over the control of overall topology, stability and reproducibility of a framework (Huang *et al*., 2006, Nattinen *et al*., 2003). This has been noted by Yaghi and Wright, who synthesised MOF-2, in different labs that yielded different gas absorption properties (Nattinen *et al*., 2003).

Synthesis still remains a key obstacle in the formation of these materials (Eddaoudi *et al*., 2001), as they are synthesised under relatively mild conditions (Zheng *et al*., 2002). These mild conditions do not allow crystallisation to be greatly effected, hence making it difficult for crystalline materials to be obtained (Eddaoudi *et al*., 2001).

The prediction of the resulting structure remains a great challenge, and when obtained are often difficult to reproduce (Kim *et al*., 2001). However, MOFs are more attractive than more conventional porous materials as their basic molecular building blocks are retained in the final assembled network (Clausen *et al*., 2005).

1.9 Solid State Gas Sensors

Solid state gas sensor technologies have become of increasing importance over the past decade (Capone *et al*., 2003). This is due to the need for improved monitoring devices for safety and environmental protection purposes. It is believed that solids state gas sensors are currently the best sensor technology available. The main reason for this is due to these sensors being able to provide real-time chemical analysis for a wide range of gaseous chemical compounds (Capone *et al*., 2003). These sensors are also typically of a compact design, portable, highly sensitive and most important inexpensive, all of which are highly desirable properties (Capone *et al*., 2003, Allendorf *et al*., 2009). This current technology provides numerous advantages over the more conventional analytical techniques, as real time data analysis is possible, sample preparation is not required and there is no investment in costly and bulky instruments (Capone *et al*., 2003).

As with all new technology, current solid state gas sensors do suffer from a few problems, especially with regard to long term thermal and chemical stability (Capone *et al*., 2003, Achmann *et al*., 2009). However, these problems are being overcome through advances in nanotechnology. Nanotechnology looks at controlling and manipulating the material on a nanometer scale, and these alterations greatly affect the materials properties and characteristics (Capone *et al*., 2003). A material which is prone to manipulation on the nanometer scale is MOFs.

MOFs are highly ordered nanoporous materials that contain extremely high surface areas (Achmann *et al*., 2009, Allendorf *et al*., 2009). These desirable properties have attracted a great deal of attention particularly with regard to gas separation and storage, thus making MOFs ideal candidates for gas sensor applications (Park *et al*., 2008, Allendorf *et al*., 2009). They have also shown superior adsorption-desorption properties over the more conventional inorganic materials, as gases are not covalently bonded to the framework (Achmann *et al*., 2009). This allows the gas to be easily desorbed at relatively low partial pressures (Achmann *et al*., 2009).

Current research by Allendorf and Hesketh (2009) has shown that this reversible process can be both selective and sensitive to a specific gas (Achmann *et al*., 2009, Allendorf *et al*., 2009). These include, testing for chemical weapons and being utilised as breathalysers that could determine pre-symptomatic infections due to exposure to environmental toxins (Capone *et al*., 2003, Allendorf *et al*., 2009). The possibilities are endless.

1.10 Charge Transfer Complexes / Host-guest complexes

Charge transfer (CT) complexes are electron-donor-acceptor based structures. They can either be formed intra-molecularly or inter-molecularly. The host-guest framework is made up of weak interactions (Lehn, 1990), which allows for flexibility. This enables it to accommodate for a large variety of electron rich systems (donor) (Kishikawa *et al*., 1999). A key feature of CT complexes is that they can be formed in gas, liquid and solid states of matter, and can emit a range of colors depending on the size and shape of the donor molecules. These colors occur in the visible range and so can be clearly seen with the naked eye.

The formation of CT complexes is due to an electrostatic interaction between the donor (electron rich) and the acceptor (electron poor) aromatic molecules. This interaction (stabilising force) allows the aromatic rings to overlap such that there is a $\pi \cdots \pi$ interaction between them (Hunter *et al*., 1990). The strength of these non-covalent interactions between the donor-acceptor molecules are usually strong and of a short range order, and depends on the stacking arrangements (orbital overlap for donor to acceptor charge transfer) between the donor-acceptor molecules, (Hunter *et al*., 1990., Gabriel *et al*., 2002., Zheng *et al*., 2005)

1.10.1 Host molecules

The availability of host molecules for the purpose of studying CT interactions is currently very scarce due to lack of new acceptor molecules (Park *et al*., 2003). Acceptor molecules need to have an aromatic ring which is made electron deficient due to electron withdrawing groups close by. An example of such a molecule is 2-(2-hydroxyethyl)isoindoline-1,3-dione (figure 1.11), a derivative of phthalimide. It is an interesting acceptor molecule, as it rapidly self assembles to form host-guest complexes. A reason for this rapid formation of host guest complexes is mainly due to the molecule being relatively flat as well as containing polar carbonyl groups and π acceptor sites (Barooah *et al*., 2003). These carbonyl and π acceptor sites are able to stabilise host-guest framework by CH···π and CH···O, hydrogen bonding interactions (Barooah *et al*., 2003).

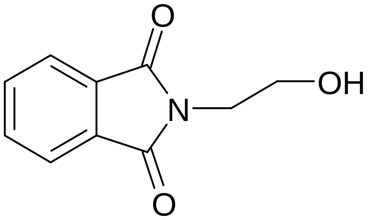


Figure 1.11: Diagrammatic representation of 2-(2-hydroxyethyl)isoindoline-1,3-dione (Barooah *et al*., 2003).

The acceptor molecule of choice to form host guest complexes in this study is *N,N'*-bis(glycinyl) pyromellitic diimide (figure 1.12). This molecule was chosen as it is a derivative of phthalimide, with the addition of an imide and terminal polar carbonyl groups (Barooah *et al*., 2006). The addition of these groups makes the ring highly electron deficient as it pulls electron density away from the carbon backbone. According to Barros and co-workers (1997), the addition of the second imide group lowers the first transition energy, $S_0 \rightarrow S_1$ which is due to the π,π*. This indicates that the addition of the second imide helps to stabilise the π,π* transition state and illustrates a strong π conjugation between the carbonyl groups and the electron rich aromatic rings (Barros *et al*., 1997). The pyromellitic diimide molecule, just like phthalimide, is also relatively planar in shape and as a result should be able to readily accommodate donor molecules to form host guest complexes.

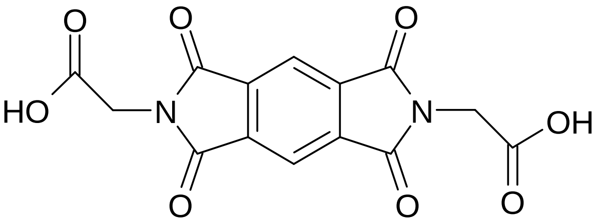
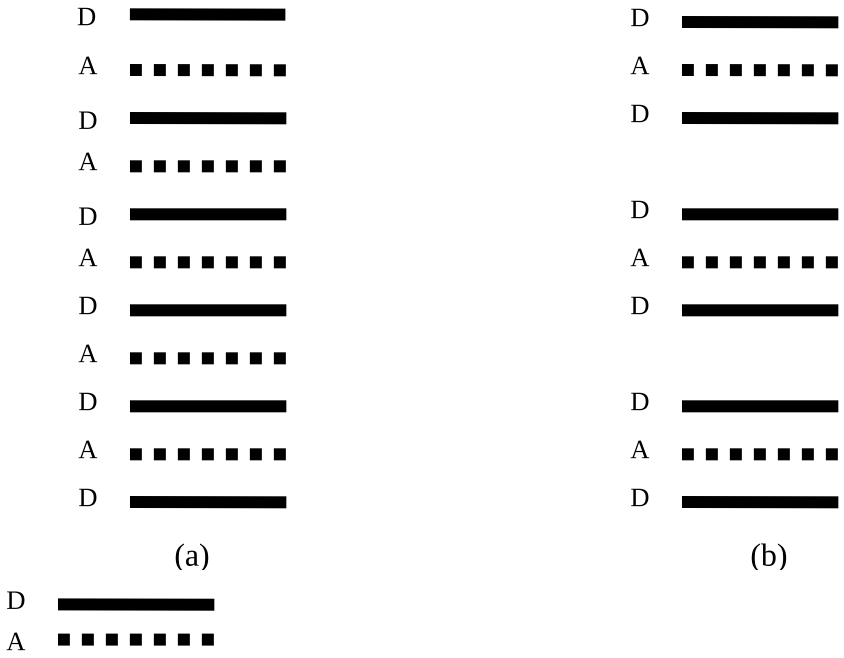


Figure 1.12: *N,N'*-bis(glycinyl)-pyromellitic diimide.

These host molecules also allow for the formation of complexes with different donor acceptor ratios (D:A). The ratio between the D:A molecules may vary from 1:1, which leads to a D-A-D-A-D-A structure being stacked up in an alternating fashion as well as a 2:1 ratio which results in a sandwich type structure D-A-D D-A-D (Kishikawa *et al*., 1999) as illustrated in the figure below:



(a) (b)

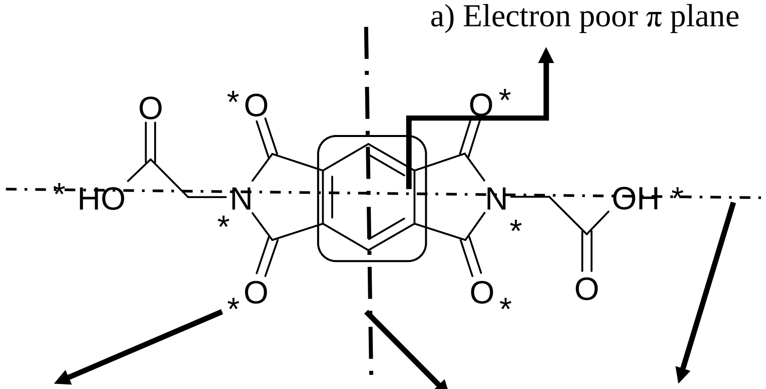
Figure 1.13: Diagram illustrating different stacking arrangements between donor and acceptor molecules, (a) alternating stacking 1:1 ratio of donor and acceptors and (b) sandwich stacking 2:1 ratio of donor and acceptors.

Thus in this work, a number of guests were used in the formation of host guest networks with the pyromellitic diimide ligand. A variation of this ligand was used extensively by Kishikawa and his co-workers (1999), where they showed that in order for host-guest complexes to form in a stacking formation the following criterion has to be met:

1.) The host molecules must contain an electron poor π-plane at the centre of the molecule, and the guest molecules must be an electron rich aromatic compound.

2.) The π plane on the host molecule must have the identical environment on each side to successfully undergo 1:2 complexations.
3.) The formation of the stacking conformation requires the host molecule to contain four hydrogen bond acceptors, and the guest molecule to contain two hydrogen bond donors, so as to stabilise to host-guest framework.
4.) The host-host interaction should be weaker than the host-guest interactions.

a) Electron poor π plane



c) * - Hydrogen bond acceptors

b) Lines of symmetry

Figure 1.14: Diagrammatic representation of *N*,*N*'-bis(glycinyl)-pyromellitic diimide indicating a) electron poor π plane, b) lines of symmetry and c) hydrogen bond acceptors.

From the above figure, it can be seen that the *N*,*N'*-bis(pyridyl)-pyromellitic diimide ligand of choice meets the above criteria set out by Kishikawa and co-workers (1999). Hence it is likely that the pyromellitic diimide molecule will readily self-assemble with various electron rich aromatic systems to form host-guest complexes.

Recent work by Barooah and co-workers (2006) has successfully shown the formation of colour when using various aromatic systems with their respective diimide host molecule. They also illustrated that the production of color is possible when non aromatic molecules are incorporated into the host-guest complexes. An example of this was the formation of red crystals when nitromethane (a clear liquid) incorporated itself into the CT complex formed between *N*,*N'*-bis(glycinyl)-

pyromellitic diimide (colourless) and 4,4’-dihydroxybiphenyl (beige). This expression of colour change in the form of CT complexes could have tremendous applications in the gas sensor applications, especially once incorporated into a MOF.

1.11 Non-covalent network interactions.

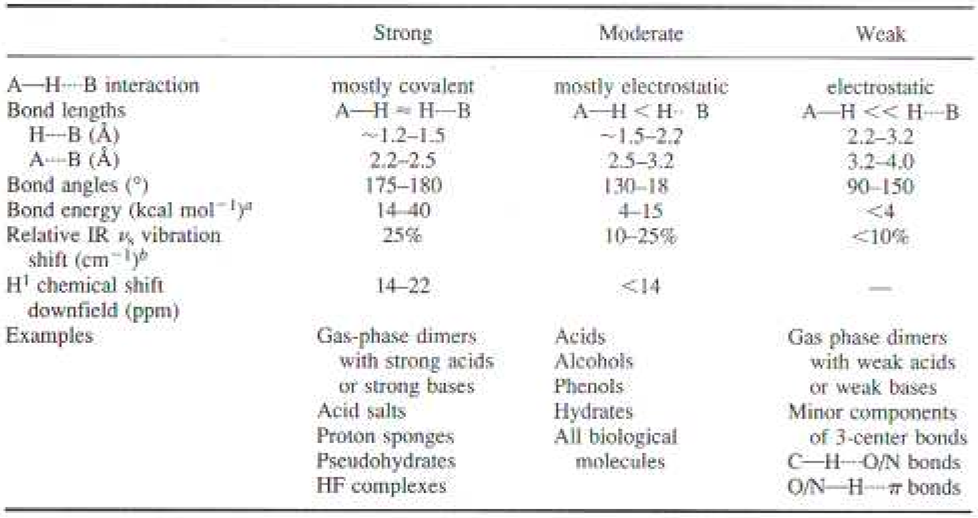
Interactions between host-guest complexes are usually made up of non-covalent bonds. These non-covalent bonding between the host and guest molecules allow for the formation of rather flexible networks to be produced (Kishikawa *et al*., 1999), due to the flexible nature of non-covalent bonds. Flexible networks have an advantage over more rigid networks as they can accommodate a variety of guest molecules and adjust the crystal lattice to form single crystals (Kishikawa *et al*., 1999).

The weak non-covalent bonding interaction are primarily made up of hydrogen bonding and intermolecular forces, dipole-dipole and ion-dipole forces, hydrogen bonding and π···π interactions

1.11.1 Hydrogen bonding

Hydrogen bonding plays a vital role in chemistry, nature and in all biological systems (Jeffrey, 1997). They are essential as they help in the stabilisation of protein structures within the skin, muscles and other animal tissues (Brown *et al*., 2003). Hydrogen bond properties differ relative to the groups of atoms surrounding them (Jeffrey, 1997), and these can be characterised into three types; namely strong, moderate and weak interactions (table 1.2):

Table 1.2: Characteristics of strong, moderate and weak hydrogen bonds (Jeffrey, 1997).



	Strong	Moderate	Weak
A—H···B interaction	mostly covalent	mostly electrostatic	electrostatic
Bond lengths	A—H ≈ H—B	A—H < H···B	A—H << H···B
H···B (Å)	~1.2–1.5	~1.5–2.2	2.2–3.2
A···B (Å)	2.2–2.5	2.5–3.2	3.2–4.0
Bond angles (°)	175–180	130–18	90–150
Bond energy (kcal mol^{-1})^{a}	14–40	4–15	<4
Relative IR ν_s vibration shift (cm^{-1})^{b}	25%	10–25%	<10%
H^{1} chemical shift downfield (ppm)	14–22	<14	—
Examples	Gas-phase dimers with strong acids or strong bases Acid salts Proton sponges Pseudohydrates HF complexes	Acids Alcohols Phenols Hydrates All biological molecules	Gas phase dimers with weak acids or weak bases Minor components of 3-center bonds C—H···O/N bonds O/N—H···π bonds

Due to the large number of different types of hydrogen bonding interactions occurring amongst molecules, a methodology in the form of graph set notation was proposed by Etter (1990). This methodology takes into account the formation of certain hydrogen bonding patterns without considering the chemical nature of the compounds involved (Bernstein *et* al., 1995, Jeffrey, 1997). This methodology allows all hydrogen bonding patterns to be broken down and indentified in terms of chains (C), rings (R), finite complexes (D) and intramolecular interactions (S), as indicated by fig. 1.15 (Bernstein *et* al., 1995, Jeffrey, 1997). In addition to this the number of hydrogen bond acceptor (a) and donor (d) sites can be described along with the number of symmetry independent hydrogen bonds (n) (Jeffrey, 1997), hence leading to the formation of a graph-set designation $G^{a}_{d}(n)$ (Jeffrey, 1997).

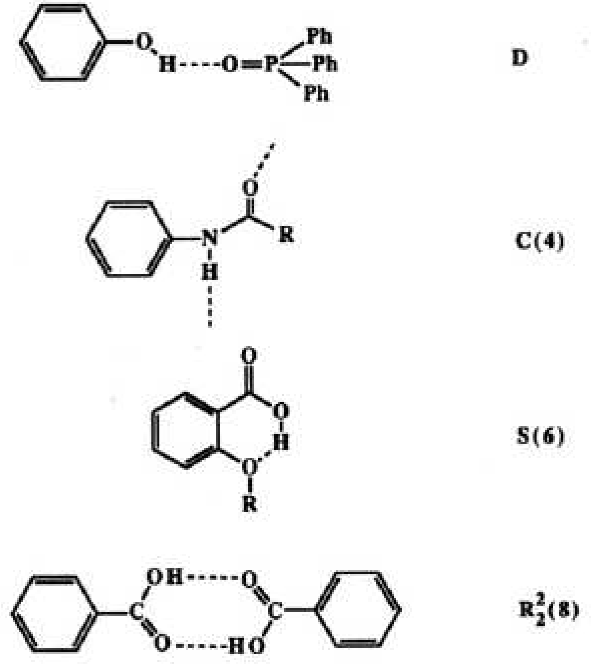


Figure 1.15: Graph set notation of various hydrogen bonding molecules (Etter, 1991).

1.11.2 π···π interactions

π···π interactions allows for the partial overlapping of aromatic rings (Hunter *et al*., 1990). This formation is possible due to these organic molecules being planar (Barooah *et al*., 2003), hence allowing for overlapping of p-orbitals in π-conjugated systems to occur. These systems do not directly overlap each other due to repulsion interactions between the rings and are aligned in an offset orientation relative to each other. The strength of these interactions are usually strong and of a short range order, and depends on the stacking arrangements of the molecules (Hunter *et al*., 1990., Gabriel *et al*., 2002., Zheng *et al*., 2005).

1.12 Project Aims

Development of MOFs materials has grown exponentially over the past decade due to the ease with which these materials can undergo physical and chemical change. The ability customise components with these materials has allowed them to be utilised for a number of applications. One application of current importance is with regard to solid state sensors technologies. A key feature of this technology is that it provides real time analysis for chemical compounds that occur in all different states of matter, i.e. solid, liquid and gas. With this in mind, the diimide linker component was chosen as it contained the correct terminal functionality to form MOF materials as well as having the ability to formed coloured materials. These features allow this type of linker to be incorporated within an MOF framework and undergo colour formation through CT complex formation. Therefore, the aims of this project can be summed up in the following points:

- To design diimide linker components with the appropriate chemical functionality to be incorporated into a MOF framework as well as undergo colour formation for sensor technologies.
- To develop methods for the synthesis and modification diimide linker components.
- To determine the effect of diimide modification on color formation.
- To form porous MOF materials using synthesised and modified linker components.
- To incorporate various aromatic rings into porous frameworks.
- To study the effect of CT complex formation within the MOF framework, and to determine the possibility of colour formation needed for sensor applications.
- To fully characterise and compare all obtained structures through various experimental techniques.

1.13 References

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