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Metal-Organic Frameworks Based on Main Group Metals

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Chemistry

by

Xiang Zhao

December 2011

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Dedication

To my parents, my wife Wei Huo and my daughter Iris
ABSTRACT OF THE DISSERTATION

Metal-Organic Frameworks Based on Main Group Metals

by

Xiang Zhao

Doctor of Philosophy, Graduate Program in Chemistry
University of California, Riverside, December 2011
Dr. Pingyun Feng, Chairperson

Metal-organic frameworks (MOFs) represent a large family of crystalline porous materials which have been extensively studied during the past decade. Due to their great porosity, precise and uniform pore size and functional organic linkers, they have found applications in the area of gas storage, separation, ion-exchange, catalysis and sensors. While previous studies in this area emphasize more on transition metal based MOFs, the main group metal based MOFs have been relatively less explored, which, however, may bring improved properties and novel structures. This dissertation focuses on two categories of metal-organic frameworks based on the s-block metal Li and p-block metal In, respectively. The design, synthesis, structure and properties will be discussed.

Lithium is the lightest metallic element and is therefore desired for construction of ultralight MOFs with the expectation of improved gas sorption properties. In addition, the appropriate binding energy between lithium and H\textsubscript{2} make it an ideal candidate for H\textsubscript{2} storage. Nonetheless, almost all Li-MOFs to date have shown quite dense structures. There is no effective strategy for construction of lithium based open frameworks. In this
work, we have intentionally introduced lithium cubane cluster into framework design as a versatile secondary building unit (SBU). Through this method, a series of open-framework materials were obtained, among which even a highly symmetric zeolitic framework was achieved. Surprisingly, except the coordination compounds, a series of H-bonded frameworks have also been observed in this system. In addition, a mixed multivalent ligand route has also been successfully applied for construction of 4-connected lithium imidazolate frameworks. \( \text{H}_2 \) and \( \text{CO}_2 \) sorption properties have been studied upon these compounds.

In-MOF represents another area that has recently attracted researcher’s attention due to its higher charge and bigger coordination sphere that differs from the traditional divalent transition metals. In this work, we have developed a series of indium based charged frameworks in two opposite categories, indium trimer based cationic frameworks (ITCs) and indium monomer based anionic frameworks (IMAs). Especially, it is found that the introduction of intrinsically positively charged indium trimer SBUs can be an effective way for systematical synthesis of cationic frameworks, which are less common in the MOFs study. The ion-exchange of a series of organic dyes upon the nanogated cationic frameworks has been studied in detail. The size and charge dependent behaviors make the reported MOF a promising candidate for the stationary phase materials of ion-exchange based separation process.
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Chapter 1
Overview of Metal-Organic Frameworks

1.1 Introduction

1.1.1 General Description

Metal-organic frameworks (MOFs) represent a large family of crystalline compounds that are composed of metal ions or clusters and organic linkers through coordination interactions.\(^1\)\(^-\)\(^8\) Some of the reported MOFs have shown great porosity and therefore they can find potential applications in gas storage (especially for H\(_2\) and CO\(_2\)),\(^9\) separation,\(^10,11\) catalysis\(^12,13\) and sensors.\(^14\) Metal-organic frameworks originate from the zeolite chemistry, but are distinguished from it by replacing the oxo ligands with organic linkers such as bipyridine, dicarboxylates and azoles. By design and synthesis of various types of organic ligands, MOFs have shown greater structural diversity than zeolites. Furthermore, the longer distances between structural nodes caused by the larger linkers lead to greater porosity. Another major difference between MOFs and zeolites lies in the types of metal nodes used. Unlike the zeolite synthesis, in which Si\(^{4+}\), Al\(^{3+}\), P, Ga\(^{3+}\), Ge\(^{4+}\) play essential roles, in MOFs, the first row transition metals such as Zn\(^{2+}\), Cu\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Fe\(^{3+}\), Cr\(^{3+}\), Mn\(^{2+}\) are widely used. In contrast, the examples of main group metals as structural nodes are relatively less studied in MOFs. Despite the above difference, MOFs actually have inherited many important concepts (such as SBUs), structure theories and synthetic methods from zeolite chemistry.
Figure 1.1 Illustration of three classical examples of MOFs, namely MOF-5, MIL-101 and HKUST-1, which feature the $\text{Zn}_4\text{O}(\text{CO}_2)_6$, $\text{Cr}_3\text{O}(\text{CO}_2)_6$ and $\text{Cu}_2(\text{CO}_2)_4$ SBUs respectively.
During the past decade, hundreds of metal-organic compounds have been reported. Some of them have shown beautiful structural features and interesting properties. Figure 1.1 illustrates several famous examples of MOFs. Each of the above MOFs contains a highly symmetric SBU, which is a metal carboxylate cluster (Zn_4O(O_2C)_6 in MOF-5, Cr_3O(O_2C)_6 in MIL-101, Cu_2(O_2C)_4 in HKUST-1). These clusters were previously found in discrete forms with mono-carboxylate ligands. When ditopic or multitopic carboxylate ligands were used instead, these clusters can be linked into continuous frameworks. Depending on the coordination features, different metal ions tend to form their characteristic SBUs. The geometry of SBUs, together with the geometry of ligands will determine the final structure. Thus the concept of structure design becomes more realistic in MOFs synthesis by intentionally choosing the appropriate metal and choosing or even synthesizing the appropriate ligands to achieve the desired structure. In this chapter, we are going to introduce several aspects that are only related to this work.

1.1.2 Light-weight MOFs

In the effort to improve hydrogen uptake capacities of MOFs, several strategies have been proposed such as creation of open metal sites, catenation, doping and etc. Among these strategies, one straightforward way is through substitution of the metallic elements. By replacing the heavy weight metal centers (such as Zn^{2+}, Cu^{2+}, etc.) with light weight elements (such as Li^{+}, Be^{2+}, B^{3+}, Mg^{2+}, Al^{3+}), the framework density will decrease and therefore the gravimetric gas sorption capacity will be improved.

Beryllium is interesting for its light weight and known as the possibility to form discrete cluster in the formula of Be_4O(CO_2)_6, which is the analogue of Zn_4O(CO_2)_6.
cluster in the famous MOF-5. It has been illustrated that the replacement of zinc atoms in the framework of MOF-5 by beryllium atoms may result in a roughly 40% increase in its surface area and gravimetric hydrogen storage capacity. Unfortunately, no single crystal data has been reported so far for MOFs containing this cluster. Instead, a structure features \([\text{Be}_{12}(\text{OH})_{12}]^{12+}\) rings has been reported by applying the tritopic btb ligand, which has shown the BET surface area of 4030 m\(^2\)/g (Figure 1.2). However, due to its
high toxicity, the beryllium system is less studied. Meanwhile, MOFs based on Mg$^{2+}$ and Al$^{3+}$ have been occasionally reported. One interesting example is CPO-27-Mg (also denoted as Mg-MOF-74), which is based on a series of isoreticular structures built from 2,5-dioxido-1,4-benzenedi-carboxylate ligand (DOBDC) that feature a 1D cylindrical channel. The Mg based structure has shown improved CO$_2$ sorption properties compared to its transition metal alternatives. Actually, this material has shown the highest CO$_2$ uptake capacity to date. Other materials like Mg$_3$(ndc)$_3$ has also shown interesting gas sorption properties. Compared to the Mg and Al MOFs, the Li MOF is even less reported, which will be described later in this chapter.

1.1.3 Zeolitic Imidazolate Frameworks (ZIFs)

Zeolitic imidazolate frameworks (ZIFs) represent a large family of metal organic frameworks that are usually constructed from divalent transition metal ions (such as Zn$^{2+}$, Co$^{2+}$, Cd$^{2+}$, Cu$^{2+}$) and imidazolate and its derivatives. ZIFs mimic the structures of traditional zeolites by adopting the 4-connection nodes and similar T-O-T angle from imidazole type ligands. By incorporating the larger organic ligands, ZIFs have shown much higher porosity than traditional zeolites. It is found that the substitution groups on the imidazolate backbone have a strong structure directing role. By using one type of imidazolate ligand alone or combine two different ligands, different framework structures can be obtained. Till now, above ten zeolitic topology types have been achieved for ZIFs (Figure 1.3). Although sometimes different ligand combinations can lead to the same framework connectivity or say isostructures, the size of different functionality and their spatial configuration in the framework will lead to varied porosity.
Figure 1.3 Building scheme and structure illustration of selected ZIFs.
Since zeolite chemistry is the origin of MOFs, it provides many important guidelines of MOFs synthesis. Thus, in addition to ZIFs, some other structures that adopt similar structural principle but different contents have been developed, such as boron imidazolate frameworks (BIFs) initiated by our group and other zeolitic metal organic frameworks (ZMOFs), which will be depicted in detail later.

1.1.4 Novel Synthetic Methods

The synthesis and crystallization of MOFs is highly related to the solvent, starting materials, pH level and temperature. It’s very commonly seen that one structure can be only obtained in a specific solvent, and as well different structures will often emerge by using different solvent but same starting materials. While the earlier studies on MOF

![Scheme 1.1](image-url) Regular and novel methods for MOF synthesis and solvents used.
synthesis are relatively limited to the traditional solvents used in zeolite synthesis, nowadays, there is much more abundant database for our choice and even some novel types of synthetic medium have been developed. In addition to the traditional hydrothermal and solvothermal synthesis, two novel methods named ionothermal and urothermal synthesis, respectively, have been developed. For example, a series of imidazolium based ionic liquids have been adopted for both zeolite and MOF synthesis (Scheme 1.1). Deep eutectic solvent (DES) represents another class of ionic liquids that typically uses a 1:2 mixture of choline chloride and urea, which has been proved to be effective for MOF synthesis. Amide type solvents like DMF and DEF are very useful for MOF synthesis due to the great solubility for organic linkers, the basicity lead by their possible dissociation and even sometimes the dissociation product will act as the template in the MOFs. Thus recently many of its derivatives and chemically close species like pyrrolidinones and ureas are also adopted in MOF synthesis. The new solvents are great extensions for traditional ones in terms of the solubility, polarity, basicity and the range of synthetic temperature.

1.1.5 MOFs Used as Separation Medium

MOFs have been extensively studied as a platform for gas separation due to their precise and uniform pore size, also known as one category of molecular sieves. Currently, most studies have focused on the separation of small gas molecules such as O₂/N₂, CO₂/CH₄, CO₂/CO, and etc. Dynamic separations based on MOF membranes have also been frequently reported recently. Meanwhile, examples of separation of bigger sized molecules such as alkanes, olefins and small aromatic compounds have been
An impressive work by Prof. Chen reported the separation of alkane mixtures by a zinc based MOF with one dimensional pores, which has been packed into a column for gas chromatography (Figure 1.4). The separation of larger molecules with molecular weight of several hundred daltons has not been seen until very recently. In 2010, Prof. Xu reported the liquid chromatography (LC) separation of Rhodamine 6G and Brilliant Blue R-250. However the above separations are based on neutral hosts, which show relative weak interaction with the guests.

1.2 Lithium Based Metal-Organic Frameworks

Lithium is the third lightest element and the lightest metal in nature. Thus it is a good alternative to heavier transition metals. In addition, the binding energy of Li$^+$ with H$_2$ in gas phase is about 27 kJ/mol, which is very close to the desired binding energy with H$_2$ of ca. 15~20 kJ/mol from theoretical calculation for room temperature H$_2$ storage. Such binding energy is very important for the near room temperature adsorption of hydrogen gas. Till now, the lithium based MOFs has not been extensively explored and only very limited amount of Li MOFs are known, partly because of the challenge in the

**Figure 1.4** Schematic representation of the GC separation of alkanes with MOF-508.
synthesis due to quite different coordination chemistry in the lithium system and the easy occurrence of solvation. Furthermore, among the reported Li MOFs, compounds with open structures are rare.

1.2.1 Lithium Carboxylates

The carboxylate type ligands such as terephthalic acid (or 1,4-BDC) are the most commonly used linkers in the synthesis of metal-organic frameworks. They have also been applied in the synthesis of lithium based compounds.\textsuperscript{16-19} While carboxylates can form many highly symmetric SBUs with transition metal ions, it appears quite differently in the lithium system. Although a lithium carboxylate tetramer cluster of moderate symmetry was previously reported in the discrete form, no examples have been found by incorporating this cluster into framework construction.

Recently, Prof. Parise has reported a series of lithium dicarboxylate compounds, which have shown the same 2-D Li-O dense layers pillared by high density array of linear shaped dicarboxylates.\textsuperscript{16-17} The existence of such dense Li-O layer leads to high thermal stability but poor porosity (Figure 1.5a-d). To avoid the dense layer structure, they have also introduced the pyridine functionality by using pyridine-dicarboxylic acid type ligands.\textsuperscript{18} Through this strategy, they have obtained three different topologies (Figure 1.5e-g). Although the 2D layer is no longer formed by this route, however, 1D chains, tetramers and trimers are formed instead, respectively in these structures. While these lower dimension building units can generate more open structures, the porosity is still quite low.

An interesting progress was reported by Prof. Robson and co-workers, who used
Figure 1.5 Structure illustrations of lithium carboxylate compounds with (a-d) linear dicarboxylic acid; (e-g) pyridinedicarboxylic acid; (h) isonicotinic acid and (i-k) amino acids.
the isonicotinic acid to obtain a neat structure with one dimensional channel. Figure 1.5h shows the hierarchical assembly process. First the lithium will form 1D chain with the carboxylates by using its three coordination sites, the forth coordination site is left to bind with pyridine group and thus all the parallel chains are connected together to form 3D framework with rectangle-shaped channels. The gas sorption properties have been systematically studied upon this compound and it is found that the binding energy in this case is about 9.9 kJ/mol, which is a relatively high value among MOFs.

Another interesting work reported very recently by Prof. Zaworotko is based on a series of 4-connected frameworks built by amino acids zwitterions and lithium (Figure 1.5i-k). Different from the above ligands, the amino acids used here are traditionally considered monotopic ligands with only one carboxylate. Such ligands are unlikely to form MOFs with transition metals, however in the lithium system, the two carboxylate oxygens can act as a bridge to connect two lithium atoms and thus the formation of 3D network becomes possible. Through this method, a square planar, a diamond network and even ABW zeolitic frameworks were obtained. Surprisingly, these compounds were crystallized from water and thus they are water-stable, which is very rare for lithium compounds. Furthermore, homochiral crystallization was observed by using amino acid with certain chirality. Nonetheless, due to the bulky pendent groups located toward the pore channels and the short bridge length of carboxylate, the void space in these compounds seems to be limited.

A detailed structure analysis has been performed upon these lithium carboxylate compounds (Figure 1.6). It is found that, the carboxylate oxygen has been frequently seen
in the $\mu_3$-O and $\mu_4$-O form. In contrast, $\mu_2$-O is the dominating form in the first row transition metal carboxylates while $\mu_3$-O and $\mu_4$-O is less often and usually located at the center position of clusters. This difference may come from the high affinity between lithium and oxygen. Such high density of three or four connected oxygen tends to draw lithium atoms from the environment and form various aggregates. As illustrated in Figure 1.3, the first row has shown six coordination modes between lithium and carboxylate at the bottom level. These units often combine with each other to form 1D to 3D higher
level architectures as in the illustrated examples. The above features make the lithium carboxylate structures extremely complicated and difficult to predict. In addition, the aggregates usually lead to quite dense structures.

1.2.2 Lithium Boron Imidazolate Frameworks (BIFs)

Boronic imidazolate frameworks (BIFs) indicate a family of open-frameworks composed of pre-synthesized tritopic or tetratopic boron imidazolate ligands. Especially, when monovalent metal ion such as Li$^+$ or Cu$^+$ is used as metal nodes with tetrahedral shaped boron imidazolate ligands, a series of neutral zeolitic frameworks were obtained. These framework topologies include RHO, SOD, dia, zni (Figure 1.7). BIFs origins from the zeolitic imidazolate frameworks (ZIFs), but represent a big progress in two aspects. The first aspect is about the charge redistribution of the metallic elements. The traditional ZIFs in common sense indicate a series of divalent metal imidazolates, such as Zn$^{2+}$ or (Co$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$). In BIFs, it uses a trivalent B$^{3+}$ together with a monovalent Li$^+$ (or Cu$^+$) in a 1:1 ratio to replace the divalent metal nodes, while keeps its tetrahedral coordination nature with imidazolates. Thus the whole frameworks remain neutral. Such evolution is extremely similar to the zeolite research about one and half decade ago, when scientists used Al$^{3+}$ and P$^{3+}$ to replace the Si$^{4+}$. The second aspect is about the framework density. By replacing the heavy weight transition metals with the ultralight weight lithium and boron, the framework density has been largely reduced. Actually, the Li BIFs only contains the lightest elements (H, Li, B, C, N) in the periodic table. However, although BIFs exhibit elegant structure design, the improvement for the gas sorption properties has not achieved the expectation. Part of the reason may lie in the
much shorter covalent bond length between B and N (~ 1.5 Å) than Zn-N bond (~ 2.0 Å) will result in the shrinkage of the cages and reduce the pore volume.

Compared to lithium carboxylates, the coordination of lithium with such azole (or pyridine) type ligand is much simpler, which is usually a monomeric lithium ion tetrahedrally coordinated by four ligands. Such tetrahedral coordination feature mimics
the zeolite structures and is more promising to generate open structures. Also the simpler coordination makes it easier for structural design. However, the synthetic challenge arises with azole type ligands. As is known, the affinity between Li and O is much larger than that between Li and N. Thus to synthesize a structure that only contains Li-N bonds, the synthetic condition will become very harsh in the aspect of lithium source and the solvent to overcome the competition from the oxygen containing species.

1.2.3 Lithium Aryloxide Clusters

In lithium chemistry, it is well known that lithium can form various clusters with aryloxides (Figure 1.8). In most cases, the lithium in these clusters is tetrahedrally coordinated. However, in some rare cases especially when strong steric hindrance exists, it can be three coordinated. The formation of different clusters is highly related to the solvent, size and shape of the aryloxides, as well as the crystallization temperature. While the dimer, tetramer and hexamer are relatively easy to obtain, the octamer and dodecamer

![Figure 1.8 The lithium aryloxide clusters reported in the literature.](image)
are rarely seen. Interestingly, due to the four coordination nature of both lithium and oxygen in this system, some of these clusters can be considered the analogues of SBUs in zeolites. In specific, the tetramer can be considered a double four ring (D4R) analogue, similarly, the hexamer, octamer and dodecamer can be also considered the analogues of double six ring (D6R), AWW cage (AWW), and sodalite cage (SOD), respectively. Among these clusters, the tetramer, known as the lithium cubane, is the most studied one and can be controllably synthesized.

While all the previous studies on lithium aryloxides have focused on their discrete cluster forms, one initial attempt to introduce lithium cubane cluster into framework design as a secondary building unit (SBU) has been reported by Prof. Henderson in 2005. In this study, the lithium cubane clusters have been connected by 1,4-dioxane to form 1D to 3D structures (Figure 1.9). The different structures were obtained by

**Figure 1.9** Polymeric structures containing 2, 3 and 4 connected lithium cubane clusters, showing zig-zag chain, the (6,3) honeycomb and diamond network.
changing the aromatic part (Ar = Ph, 4-Et-C₆H₄ and 1-naphth) in the Li₄(OAr)₄ cluster. Although the use of bulky naphthol can lead to the formation of 3D diamond structure, the big pendant group seems to take up a lot of void space and also brings extra weight to the framework. Thus no gas sorption study has been performed on these compounds. It’s important to point out that the above compounds were crystallized out from the dioxane solvent, which also went into the final structure acting as the linker. Such dual role has limited the range of synthetic conditions.

1.3 Indium Based Metal-Organic Frameworks

1.3.1 Indium Trimer Based Structures

As well as many transition metal ions, indium can form trimer cluster with carboxylate in the formula of In₃O(CO₂)₆L₃, in which indium is always six coordinated and L is the ligand in the axial position. However, the examples of MOFs containing such trimer clusters are rare. In 2007, Eddaoudi and co-workers reported the first example of indium trimer based structures. These two structures are constructed with 1,3-benzene-dicarboxylic acid (compound 1) and 3,3′,5,5′-azobenzenetetracarboxylic acid (compound 2), respectively (Figure 1.10a), both of which features a 120° angle. Although indium trimers are six connected in both structures, the charge of two compounds are different. In compound 1, one axial position of the three indium is coordinated with imidazolate, making the cluster neutral with the formula In₃O(CO₂)₆(Im)(H₂O)₂, whereas in compound 2, all the three axial position is capped by water so the entire cluster in the formula of In₃O(CO₂)₆(H₂O)₃ is with +1 charge.
Furthermore, the hydrogen adsorption of 2.61% (at 78 K, 1.2 atm) for compound 2 is quite impressive.

Figure 1.10 Three examples of indium trimer based metal organic frameworks.
Another interesting structure reported by Prof. Xu is synthesized through a mixed ligand method (Figure 1.10b).\textsuperscript{46} By combining a long 4,4’-azodicarboxylic acid ligand and short isonicotinic acid ligand in a 1:1 ratio, a 3D framework with mesopore structure in the formula of (In\(_3\)O)(OH)(adc\(_2\))(ina\(_2\))\(\cdot\)4.67H\(_2\)O has been obtained. Distinct from the six connected trimer cluster mentioned above, in this structure, the indium trimer adopt an eight fold connection. With two axial positions connected by isonicotinic acid, the third one is terminated by a hydroxyl group. Such coordination feature makes the cluster neutral. This compound also exhibit high H\(_2\) adsorption (2.08 wt\% at 1 atm, 77 K).

Interestingly, with the introduction of amino group substituted isonicotinic acid, the same structure was obtained but with an improved H\(_2\) uptake capacity of 2.31 wt\%.

Interestingly, such eight connected trimer was also observed recently by our group in the form of trimer chains with formate linkage.

Recently, Prof. Bu has reported a compound named CPM-5 (& CPM-6) which is made of indium and 1,3,5-tribenzoate, which exhibits an interesting cage in cage structure (denoted as In\(_{12}\)@In\(_{24}\)).\textsuperscript{47} The unique feature of this structure is it contains two types of indium nodes simultaneously, the six connected indium trimer cluster and four connected monomeric In\(^{3+}\) ion (Figure 1.10c). In each repeating structural unit, four trimer clusters (with 12 indium atoms) connecte to each other in a tetrahedral shape, which form the inner cage and 24 monomeric indium atoms form the outer cage. The inner and outer cage is connected by the btc ligand. To be mentioned, although the water capped indium trimer [In\(_3\)O(CO\(_2\))\(_6\)(H\(_2\)O)\(_3\)]\(^+\) has a positive charge, the entire framework is still anionic due to the higher amount of negative monomeric In(CO\(_2\))\(_4\)\(^-\) centers. Despite
the interesting structure, the mentioned compounds have shown high CO$_2$ uptake capacity. With smaller templating organic cations, CPM-6 has a CO$_2$ adsorption of 106.7 cm$^3$/g at 1 atm, 273 K.

1.3.2 Indium Monomer Based Structures

Despite indium trimers, indium is more commonly seen in the monomer form in MOFs studies (Table 1.1), in which it usually adopts eight (or occasionally six or seven) coordination and four connected.$^{48-55}$ This four connection nature is desired for the formation of zeolitic structures. While early examples use linear shaped bdc and ndc to form quartz and GIS type networks. Prof. Bu has reported a series of indium monomer based 4-connected homochiral and achiral frameworks in ionic liquids, by applying dicarboxylate ligands (such as thiophenedicarboxylic acid, camphoric acid and 4,4’-oxybis(benzoic acid) that mimic the T-O-T angle in zeolites. Through this method, the diamond (dia), quartz (qtz), CdSO$_4$ (cds) and ThSi$_2$ (ths) topologies have been obtained. With the use of tritopic ligand such as btc, a (3,4)-connected C$_3$N$_4$ framework has been obtained. Actually, the use of tritopic ligand such as btc and btb can also lead to other structural topologies. Prof. Schröder has reported several indium compounds constructed with tetratopic ligands, which lead to PtS and double interpenetrated diamond topologies.

Mixed ligand route is one important strategy to generate novel structures with sophisticated architectures. An interesting progress by using mixed ligands in indium system was reported by our group recently. A 120$^\circ$ geometry ligand can lead to the formation of characteristic three rings, which are further connected by another linear type
With such combination, a zeolitic framework with NPO topology and a Johnson-type metal organic polyhedron (MOP) have been obtained.

In contrast to the above carboxylate type ligands, another class of indium monomer based structures is by using of bis(bidentate) bridging ligands such as imidazoledicarboxylic acid reported by Prof. Eddaoudi (Figure 1.11). Compared to carboxylic acid, although this ligand is also bonded with indium in a chelating feature and form 8-coordinated and 4-connected nodes, the geometry about indium is different. The carboxylates tend to form a compact 4-member ring while the imidazoledicarboxylic acid will form a 5-member ring, which is more relaxed. The different local geometry has essentially led to different framework topologies. In fact, several zeolitic metal-organic frameworks (ZMOFs) have been obtained by using imidazoledicarboxylic acid, with connectivity of quite symmetric SOD, RHO and a new topology type USF. Interestingly,
these structures can be also considered another version for ZIFs, but with metals in higher valence and higher coordination number and with higher charged ligands.
Table 1.1  A summary of monomeric indium based MOFs and their network topologies.

<table>
<thead>
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<tr>
<td>ALF-1 (2)</td>
<td>(EMIm)[In(D-cam)₂]</td>
<td>D-cam</td>
<td>dia</td>
<td>48a</td>
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<tr>
<td>ALF-3</td>
<td>(EMIm)₃[In(obb)₂]·(Es)₂·(H₂O)</td>
<td>obb</td>
<td>cds</td>
<td>48a</td>
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<td>(EMIm)₂[In₂(D-cam)₃(D-Hcam)₂]</td>
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<td>dia</td>
<td>48b</td>
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<td>(TMA)[In(D-cam)₂]·2H₂O</td>
<td>D-cam</td>
<td>qtz</td>
<td>48c</td>
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<td>(choline)₃[In₃(btc)₄]·2DMF</td>
<td>btc</td>
<td>C₃N₄</td>
<td>48e, 49</td>
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<td>[In(bdc)(Hbdc)]·solvent</td>
<td>bdc</td>
<td>qtz</td>
<td>50</td>
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<td>---</td>
<td>(Et₂NH₂)[In(ndc)₂·2(H₂O)·(DEF)]</td>
<td>ndc</td>
<td>GIS</td>
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<td>---</td>
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<td>PtS</td>
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<td>NOTT-200</td>
<td>[H₂ppz][In₂(ppz)₂]·3.5(DMF)·5(H₂O)</td>
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<td>dia</td>
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<td>ppz</td>
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<td>aip + bpdc</td>
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<td>53</td>
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<td>rho-ZMOF</td>
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<td>RHO</td>
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To be continued
Table 1.1 continued

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<th>SOD</th>
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<td>USF</td>
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<td>pmdc</td>
<td>SOD</td>
<td>54c</td>
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<td><a href="DMF">In$<em>8$(Himdc)$</em>{12}$</a>$_{6.8}$</td>
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<td>H-AST</td>
<td>54d</td>
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<td>ZSA-2</td>
<td>[K$_3$(NO$_3$)$_3$(H$<em>2$O)$</em>{2.5}$(MeCN)$_3$][In$_4$(tzdc)$_4$(H$_2$dach)$_4$]</td>
<td>Imdc,</td>
<td>H-RHO</td>
<td>55</td>
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</table>

[a] Structures with the same network topology but different template or ligand in different chirality are omitted for clarity.

[b] EMim = 1-ethyl-3-methylimidazolium; Es = ethylsulfonate; D-cam = D-camphoric acid; obb = 4,4’-oxybis(benzoic acid); thb = 2,5-thiophendicarboxylic acid; btc = 1,3,5-benzenetricarboxylic acid; bdc = 1,4-benzenedicarboxylic acid; ndc = 2,6-naphthalendicarboxylic acid; bptc = biphenyl-3,3’,5,5’-tetracarboxylic acid; ppz = 1,1’,4’,1’’,4’’’,1’’’-quaterphenyl-3,5,3’’,5’’’-tetracarboxylate; bpdc = 4,4’-biphenyldicarboxylic acid; hip = 5-hydroxyisophthalic acid; aip = 5-amino-isophthalic acid; ipa = 1,3-benzenedicarboxylic acid; sdc = 4,4’-stilbenedicarboxylic acid; pdc = pyridine-2,5-dicarboxylic acid; imdc = 4,5-imidazoledicarboxylic acid; im = imidazole; hpp = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine; dach = 1,2-diaminocyclohexane; pmdc = 4,6-pyrimidinedicarboxylic acid.
1.3.3 Indium 1D Chain Based Structures

Except the above mentioned two basic forms of indium SBUs, indium can also form 1D infinite chains in the formula of In(OH)(CO$_2$)$_2$, which is neutral. Such structure was first reported in 2005 by Prof. Jacobson, in which the chains are parallel to each other and linked by bdc and lives a rhombic shaped 1D channel.$^{56}$ Similar work was also reported by Prof. Férey and Prof. Rosseinsky, but with different connection between the chains, which resulted in different shaped 1D channels.$^{57,58}$ The 1D chain can be also arranged perpendicular to one another with a bent obb linker, which resulted in 1D channels in two different orientations.$^{35}$ Prof. Bu also has reported several interesting chain structures with different configurations.$^{47}$

![Figure 1.12](image)

**Figure 1.12** (a) The In(OH)(CO$_2$)$_2$ 1D chain structure and (b-d) different connectivity in three examples.

1.4 Contribution from This Work

At the current stage of MOFs study, researchers have put more emphasis on developing novel strategies to improve the gas sorption properties (especially on H$_2$ and
CO$_2$), design and synthesis of novel materials with special structures and compositions for specific applications (such as separation, catalysis), discovering novel properties of MOFs which can potentially lead to new applications. The latest trend on this area requires highly targeted and fully designed research rather than randomly growing new crystals.

Since our group started the research on MOFs area, we have focused on the chirality of MOFs, developing novel synthetic methodologies, synthesis of low-connected frameworks mimicking zeolitic structures and improving gas sorption properties by developing light weight MOFs. In contrast to most research groups that focused on transition metal MOFs, which have been extensively studied, we have particular emphasis on MOFs based on main group metal ions such as Li$^+$, Mg$^{2+}$, In$^{3+}$ and etc. In this work, we have mainly focused on the structure design, synthesis, and properties of MOFs based on two metals, lithium and indium, which has been less studied so far.

Lithium is one of the best choices to construct light weight MOFs and therefore reduce the gravimetric density of frameworks, which can be a good strategy for improvement of gas storage capacities. However, the synthetic difficulty and structural complexity impeded the study on Li MOFs. In Chapter 2-4, we have developed several strategies to successfully make lithium based open frameworks.

In Chapter 2, we have introduced the lithium cubane cluster into framework design as a robust SBU. By applying different synthetic strategies and ligands of varied configurations, seven structures have been synthesized in four distinct connection modes.
Before this work, the phenol type ligands are rarely used in the synthesis of MOFs. However, we found that the phenol containing linkers are effective in the lithium system and better than the traditionally used carboxylates to generate porous structure. A representative material LIF-5 has shown not only interesting structural features but also quite high thermal stability.\textsuperscript{59} The H\textsubscript{2} sorption properties is also impressive, which is the highest among lithium based MOFs. In addition, the 4-pyridinolate ligand used in this compound combines the phenolate and pyridine functionality into one ligand, which is seen for the first time in MOFs for this type of ligands. The novel ligand type has enriched the database for MOF synthesis and provided a family of ligands that can be used in the synthesis of Li MOFs in the future.

Chapter 3 has illustrated a family of supramolecular assemblies build from the lithium cubane clusters, which represent a novel strategy to make supramolecular assemblies and another pathway to make lithium based crystalline porous materials.\textsuperscript{60} The idea of using inorganic clusters as novel tectonics to replace conventional molecular tectonics has been proposed. The advantages of the former are embedded in its high symmetry, ease in synthesis and structural diversity. By using a quite different solvent system, these hydrogen bonded frameworks were obtained with similar starting materials as those used in previous chapter.

Chapter 4 represents a distinct strategy to make lithium based MOFs. This strategy is derived from zeolitic imidazolate frameworks (ZIFs) and has close relationship with it. The goal is to synthesize a series of all lithium based 4-connected networks that exhibit zeolitic topologies. The targeted materials can be considered the
lithium version of ZIFs. A mixed multivalent ligand route was developed to compensate the reduced charge resulted from the substitution of Zn\(^{2+}\) by Li\(^+\).\(^{61}\) The synthetic challenge has been overcome by applying appropriate lithium source and solvent. Two initial examples have been realized that exhibit 3D 4-connected topologies and exactly match the structural design. In addition, the two compounds have shown mild H\(_2\) sorption properties.

Compared to the most commonly used metals in MOFs such as Zn\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), indium has a higher valence state and higher coordination number (Cr\(^{3+}\) and Fe\(^{3+}\) are in the same charge but difficult to form single crystals). These unique features of indium make it possible to generate novel interesting structures. Also different from the transition metal MOFs, which in most case is neutral, it is very easy for indium to form charged frameworks, in both directions, anionic frameworks or cationic frameworks. In Chapter 5 and 6 we have described the studies in the two aspects.

In Chapter 5, we have reported a series of indium trimer based cationic frameworks of isoreticular structures in two topology types.\(^{62}\) The resulting structures are quite symmetric and exhibit interesting cage structures. The 9-connected indium trimer has been first observed in this study. These frameworks are highly porous and have shown high surface area and H\(_2\) uptake capacity. More importantly, based on the cationic feature, a systematic study of ion exchange of anionic organic dyes has been performed upon this platform. The results have revealed that the ion exchange dynamic on the MOF platform is highly size and charge dependent. For certain host guest combination, the size exclusive ion exchange has been observed, which is difficult to achieve for traditional
ion-exchange resins. All the above results indicate that these cationic frameworks can be further applied for separation (in the forms of ion exchange chromatography or solid phase extraction) of charged species of molecular weight below 1000 Da. This work for the first time has proved the feasibility of ion-exchange based separation by using the charged metal-organic frameworks.

In the last chapter, we described the synthesis of a series of anionic frameworks containing indium monomer tetrahedral nodes. While there are a number of such examples in the previous studies either by others or by our group, there is some shortage in two aspects. On one hand, by using of a single dicarboxylate ligand, it is very easy to form simple net as well as interpenetration, which will largely reduce the pore volume. On the other hand, by using of a single bis-bendentate type ligand, zeolitic frameworks can be often obtained, however, the short linkage length of such ligand limit the pore and window size. With the aim to overcome these shortages and improve the porosity, we think of a trade-off method by using a mixed ligand method. By using the imdc type ligand and the dicarboxylate ligand, a GIS net with large 1D channels and extremely low density have been obtained. Furthermore, reticular chemistry can even help enlarge the pore size by substitution of the dicarboxylate ligand by a longer one. The successful synthesis of such zeolitic frameworks has proved the effectiveness of the proposed strategy, which can be further applied to synthesize a series of novel zeotype structures.

1.5 References


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(60) Zhao, X.; Wu, T.; Bu, X.; Feng, P. Dalton Trans. 2012, ASAP.


(62) Unpublished results.
Chapter 2

Design and Synthesis of 4-Connected Coordination Polymers

Based on Lithium Cubane Clusters

2.1 Introduction

Porous metal-organic frameworks (MOFs) have been extensively studied for potential applications in gas storage.\textsuperscript{1-20} Compared to other gas storage materials such as carbon nanotubes,\textsuperscript{21} activated carbons,\textsuperscript{22} and microporous polymers,\textsuperscript{23,24} MOFs have some unique advantages including modular synthesis, abundant choice of metal ions and clusters, numerous organic ligands, and great structural diversity. Very recently, some efforts have been made on increasing the gravimetric uptake capacity by introducing lightweight main group ions such as Li\textsuperscript{+}, Be\textsuperscript{2+}, Mg\textsuperscript{2+}, B\textsuperscript{3+} and Al\textsuperscript{3+}, instead of heavier transition metal ions.\textsuperscript{25-33} Most of these frameworks, including recently discovered Li-containing porous materials (e.g., Lithium isonicotinate, BIFs with Li and B) were built by using carboxylates and azole type ligands.\textsuperscript{25,31-33}

Secondary building units act an extremely important role in the construction of open-framework materials in the aspects of dictating the framework geometry and increasing thermal stability compared to mono-cation based structural nodes. So far, tens of metal-oxo clusters were used for SBU in the construction of porous coordination polymers, including the well known Zn\textsubscript{4}O(CO\textsubscript{2})\textsubscript{6} in MOF-5 and Cr\textsubscript{3}O(CO\textsubscript{2})\textsubscript{3} in MIL-101.
Nonetheless, most of these building blocks are based on transition metals and reports on main group metal cluster containing SBUs are rare.

Meanwhile, it has long been known that lithium, together with aryloxide can form various types of metal clusters in which lithium and oxygen atoms are both four coordinated. Among many lithium aryloxides, Li$_4$O$_4$ cubane cluster is the most stable one and has been extensively studied as discrete molecule in lithium chemistry. A typical cubane cluster is formed from four monovalent lithium cations and four phenolates. In this structure, the phenolate oxygens contribute to the four corners of cubane clusters. The lithium and oxygen atoms are usually tetrahedrally coordinated, with lithium atoms capped by exterior Lewis bases. The following features make the Li$_4$O$_4$ a perfect building block for open framework construction. i) The lithium cubanes are usually the more stable phase compared to other possible lithium phenolate derivatives such as Li$_6$O$_6$, etc. and easy to be obtained in a homogeneous solution. ii) The cubane cluster is thermally stable. iii) The cubane cluster is highly symmetric, making it feasible to generate open structures. iv) The total charge of the cluster is neutral, which is perfect for construction of a neutral framework similar to Zn$_4$O(CO$_2$)$_6$. v) Lithium is the lightest possible element that can serve as a structural node and the extremely light weight of Li$_4$O$_4$ (91.76 Da in contrast to its transition metal analogues, e.g. 541.58 Da for Zn$_4$O(CO$_2$)$_6$ and 488.04 Da for Cr$_3$O(CO$_2$)$_6$) can be used for constructing ultralight open frameworks, which is highly desired for high guest/host weight ratio demanded applications. Unfortunately, so far only one three-dimensional framework topology (dia net) containing this SBU has been obtained with no gas sorption property reported. In addition, the linker used in that
work is more like a solvent and not typically used in construction of coordination polymers.

In this chapter, we report the design and synthesis of a series of lithium cubane based coordination polymers, by using the phenolate containing ligands. In the synthesis, a two-step strategy with mixed ligand and a one batch strategy have been used, respectively. All of these synthetic methods lead to the formation of cubane based core, but in different connectivity. The structures have been analyzed and also the thermal stability and gas sorption properties of selected compounds have been studied.

2.2 Experimental Section

2.2.1 Solvothermal Synthesis

All reagent and solvent were commercially available and used as supplied without further purification. Scheme 2.1 shows the synthetic procedures used in this study. In general, two synthetic strategies have been applied. LIF-1 to LIF-4 were synthesized by the first strategy which is a two step procedure. First, a phenol type ligand was reacted with the lithium source and form cubane clusters in the solution. Then a ditopic or tritopic pyridine type ligand was introduced to form the polymer. Compared to the first strategy, LIF-5 to LIF-7 were synthesized in a one step method by using a pyridine-phenolate type ditopic ligand. Depending on the configuration of ligand, different framework topology can be obtained.

The lithium source can be either $t$-BuLi or $t$-BuOLi (both used as a toluene solution) for most of the cases. Both of them can easily deprotonate the phenol functionality and won’t react with the solvent. Although $t$-BuLi and $t$-BuOLi are very
sensitive to the moisture in the atmosphere, the synthesis could be performed in the air when small amount of reagent was used. Compared to the t-BuLi, the reactivity of t-BuOLi is a lot gentler and easier to handle so it is preferred in most cases. Usually a syringe was used to transfer the lithium source to the reaction vials.

Most of the above compounds were crystallized from the acetonitrile solution. Other solvents such as alcohols or DMF won’t lead to the formation of these compounds. In addition, this system is very sensitive to the moisture so anhydrous acetonitrile was used to eliminate the amount of water. LIF-5 is an exception which was obtained from the methanol solution.

Scheme 2.1 The ligands used in this study and the schematic illustration of the synthetic procedure for LIF-n.
Synthesis of Li$_4$(OPh)$_4$(4,4'-bpy)$_2$ (LIF-1): 94 mg of phenol was weighed to a 20 ml vial and 0.521 g acetonitrile and 2.430 g toluene was added. The mixture was stirred until phenol completely dissolved. Then 1.0 ml $t$-BuOLi (1.0 M solution in hexane) was added and the solution was stirred for 30 minutes, 78 mg 4,4'-bipyridine was added. After stirring the mixture for another 30 minutes, the solution was heated in a 90 °C oven. Large amount of yellow crystals were obtained after 2 days.

Synthesis of Li$_4$(OPh)$_4$[CH$_2$(mim)$_2$]$_2$ (LIF-2): 94 mg of phenol was weighed to a 20 ml vial and 0.532 g acetonitrile and 2.489 g toluene was added. The mixture was stirred until phenol completely dissolved. Then 1.0 ml $t$-BuOLi (1.0 M solution in hexane) was added and the solution was stirred for 30 minutes, 88 mg of CH$_2$(mim)$_2$ was added. After stirring the mixture for another 30 minutes, the solution was heated in a 90 °C oven. Large amount of yellow crystals were obtained after 2 days.

Synthesis of Li$_4$(OPh)$_4$(tpt)$_2$ (LIF-3): 85 mg of phenol was weighed to a 20 ml vial and 1.002 g acetonitrile and 1.238 g toluene was added. The mixture was stirred until phenol completely dissolved. Then 0.9 ml $t$-BuOLi (1.0 M solution in hexane) was added and the solution was stirred for 30 minutes, 95 mg of 2,4,6-tri(4-pyridyl)-1,3,5-triazine was added. After stirring the mixture for another 30 minutes, the solution was heated in a 90 °C oven. Large amount of yellow crystals were obtained after 2 days.

Synthesis of Li$_4$(OPhEt)$_4$(tpt)$_2$ (LIF-4): 110 mg of 4-ethylphenol was weighed to a 20 ml vial and 1.010 g acetonitrile and 1.235 g toluene was added. The mixture was stirred until the solid was completely dissolved. Then 0.9 ml $t$-BuOLi (1.0 M solution in hexane) was added and the solution was stirred for 30 minutes, 97 mg of
2,4,6-tri(4-pyridyl)-1,3,5-triazine was added. After stirring the mixture for another 30 minutes, the solution was heated in a 90 °C oven. Large amount of yellow crystals were obtained after 2 days.

**Synthesis of Li$_4$(OPy)$_4$ (LIF-5):** 0.5 ml of t-BuOLi (1.0 M solution in hexane) was added to a 20 ml glass vial containing well stirred methanol (5.0 g) solution of 4-hydroxypyridine (48.2 mg, 0.5 mmol). After stirring for 15 min, the glass vial was loosely sealed and placed in a 120 °C oven for about 24 hours, when the solvent was almost evaporated out and pure colorless crystals were obtained at the bottom of the vial. The yield was above 95% based on the metal. This compound was also synthesized in the 2-propanol solution and t-BuLi could be also adopted as the lithium source.

**Synthesis of Li$_4$(OPhPy)$_4$ (LIF-6):** In a 20 ml glass vial, 33 mg (~0.2 mmol) of 4-(4-pyridyl)phenol was dissolved in about 3.6 g acetonitrile, after stirring for 10 minutes, 0.2 ml of t-BuOLi (1.0 M solution in hexane) was added and stirred for another 20 minutes. The solution was sealed and placed in the 70 °C oven. Colorless crystals were obtained after 7 days.

**Synthesis of Li$_4$(OPhIm)$_4$ (LIF-7):** 0.5 ml of t-BuOLi (1.0 M solution in hexane) was added to a 20 ml glass vial containing 4-hydroxypyridine (80 mg, 0.5 mmol) in a mixed solution of methanol (1.0 g) and toluene (2.5 g). After stirring for 10 min, the glass vial was sealed and placed in a 70 °C oven. Pure colorless crystals were obtained after about 72 hours heating. The yield was above 90% based on the metal.

**Synthesis of Li$_2$(OPy)$_2$(DMF)$_2$ (LIF-8):** 38.8 mg of 4-hydroxypyridine was added to a 20 ml glass vial and dissolved in a mixed solvent containing 5.018 g DMF and
1.012 g THF. After stirring for a while, 0.8 ml of \( t\)-BuOLi (1.0 M solution in hexane) was added and stirred for another 20 minutes, the glass vial was sealed and placed in a 120 °C oven for about 96 hours. Large amount of colorless crystals were obtained.

2.2.2 Powder X-ray Diffraction

Powder X-ray diffraction experiments were performed on a Bruker D8 Advance X-ray powder diffractometer operating at 30kV and 30mA (Cu K\( \alpha \) radiation, \( \lambda = 1.5418 \AA \)). The data collection was performed with a step size of 0.03° and counting time of 1s per step. The 2-theta angular range is from 5 to 40°. The simulated XRD pattern was calculated from the structure data using the CSD Mercury 2.4 software.

2.2.3 Thermal Analysis

The simultaneous DSC-TGA thermal analysis was performed on TA Instruments SDT Q600 under the flowing nitrogen atmosphere. The flow rate of the nitrogen gas was controlled at about 100 milliliters per minute. The thermal treated samples were prepared by heating up the samples to the desired temperature at 20 °C/min under nitrogen flow. After holding the temperature for 30 minutes, the samples were allowed to slowly cool down to room temperature.

2.2.4 Gas Sorption Measurements

\( N_2 \) gas sorption experiments were carried out on a Micromeritics ASAP 2010 surface area and pore size analyzer. Prior to the measurement, powder samples of LIF-5 and LIF-8 were dried by using the “degas” function of the surface area analyzer for 10 hours at 180 °C and 120 °C, respectively. The \( N_2, H_2 \) and \( CO_2 \) adsorption measurement were performed at 77K, 77K, and 273K, respectively.
2.2.5 Single-Crystal Crystallography

Single-crystal X-ray analysis was performed on a Bruker Smart APEX II CCD area diffractometer with nitrogen-flow temperature controller using graphite-monochromated Mo Kα radiation (λ=0.71073 Å), operating in the ω and φ scan mode. Raw data collection and refinement were done using SMART. Data reduction was performed using SAINT+ and corrected for Lorentz and polarization effects. The SADABS program was used for absorption correction. The structure was solved by direct methods, and the structure refinements were based on |F²| with anisotropic displacement using SHELX-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions. All crystallographic calculations were conducted with the SHELXTL software suites. The crystallographic data and the structural refinement parameters were summarized in Table 2.1.
Table 2.1 A summary of crystallographic data and refinement results for the structures covered in chapter 2

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>LIF-1</td>
<td>Li$_4$(OPh)$_4$(4,4’-bpy)$_2$</td>
<td>I$_4$/acd</td>
<td>22.678(2)</td>
<td>22.678(2)</td>
<td>104.34(6)</td>
<td>90</td>
<td>90/90</td>
<td>0.1277</td>
<td>dia</td>
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<tr>
<td>LIF-2</td>
<td>Li$_4$(OPh)$_4$[CH$_2$(mim)$_2$]$_2$</td>
<td>C2/c</td>
<td>41.268(2)</td>
<td>10.739(9)</td>
<td>20.627(4)</td>
<td>114.16(0)</td>
<td>90/90</td>
<td>0.0484</td>
<td>hcb</td>
</tr>
<tr>
<td>LIF-3</td>
<td>Li$_4$(OPh)$_4$(tpt)$_2$</td>
<td>P4$_2$/n</td>
<td>20.121(4)</td>
<td>20.121(4)</td>
<td>28.606(1)</td>
<td>90</td>
<td>90/90</td>
<td>0.0637</td>
<td>1D</td>
</tr>
<tr>
<td>LIF-4</td>
<td>Li$_4$(OPhEt)$_4$(tpt)$_2$</td>
<td>P-1</td>
<td>10.949(4)</td>
<td>11.113(4)</td>
<td>27.863(1)</td>
<td>84.82(1)</td>
<td>79.25(1)/84.30(1)</td>
<td>0.1383</td>
<td>1D</td>
</tr>
<tr>
<td>LIF-5</td>
<td>Li$_4$(OPy)$_4$·(MeOH)$_x$</td>
<td>P-42c</td>
<td>10.990(9)</td>
<td>10.990(9)</td>
<td>10.991</td>
<td>90</td>
<td>90/90</td>
<td>0.0942</td>
<td>bcu</td>
</tr>
<tr>
<td>LIF-6</td>
<td>Li$_4$(OPhPy)$_4$</td>
<td>I$_4$/a</td>
<td>17.147(6)</td>
<td>17.147(6)</td>
<td>12.471(0)</td>
<td>90</td>
<td>90/90</td>
<td>0.0513</td>
<td>dia</td>
</tr>
<tr>
<td>LIF-7</td>
<td>Li$_4$(OPhIm)$_4$</td>
<td>P-1</td>
<td>8.974(3)</td>
<td>15.356(4)</td>
<td>17.107(5)</td>
<td>75.148(3)</td>
<td>81.191(4)/83.820(3)</td>
<td>0.0973</td>
<td>sql</td>
</tr>
<tr>
<td>LIF-8</td>
<td>Li$_2$(OPy)$_2$(DMF)$_2$</td>
<td>P2$_1$</td>
<td>9.431(3)</td>
<td>10.673(3)</td>
<td>9.431(3)</td>
<td>98.70</td>
<td>90/90</td>
<td>0.0618</td>
<td>sql</td>
</tr>
</tbody>
</table>

[a] Crystal structures were solved from single-crystal data collected at 150 K on a SMART CCD diffractometer with MoKα.

\[ R(F) = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \] with \( F_o > 4.0 \sigma(F) \).

[b] LIF = hydrogen bonded lithium frameworks.
[c] 4,4′-bpy = 4,4′-bipyridine; \( \text{CH}_2(\text{mim})_2 \) = bis(methylimidazolyl)methane; OPh = phenolate; OPhEt = 4-ethylphenolate; OPy = 4-pyridinolate; OPhPy = 4-(4-pyridinyl)-phenolate; OPhIm = 4-(1-imidazolyl)-phenolate; tpt = 2,4,6-tri(4-pyridyl)-1,3,5-triazine; DMF = N,N-dimethylformamide.

[d] For definitions of three-letter abbreviations, see Reticular Chemistry Resource (http://rcsr.anu.edu.au). dia = diamond, hcm = honeycomb, bcu = body centered cubic, sql = square planar. All the net descriptions in this table take \( \text{Li}_4\text{O}_4 \) as a whole as structure nodes. However, LIF-5 can be considered an ACO net when using Li and O as 4-connected nodes.
2.3 Results and Discussion

2.3.1 General Description and Connection Modes

Based on the structural features of the cubane cluster, two different synthetic strategies have been designed. (Scheme 2.1) In the first strategy, phenolate is first introduced to build discrete clusters with lithium atoms and then an exterior neutral linker such as bipyridine needs to be applied to bridge different clusters to form coordination polymers. By this method, only four lithium atoms act as connection nodes, thereafter the cubane cluster can be considered as simple as a tetrahedron. In contrast to the previous mixed ligand strategy, the later one utilizes all the eight lithium and oxygen atoms as

![Figure 2.1](image) The same Li$_4$O$_4$N$_4$C$_4$ core leads to four different connection modes.
connection nodes. To achieve this goal, several ditopic ligands are chosen, which combine both phenolate and pyridine functional groups into one molecule. Thus clusters and frameworks can be formed in one batch, with both functional groups embedded in the ligands. Through the two strategies described above, in total seven different structures have been obtained (denoted as LIF-n).

Interestingly, all the seven structures have exactly the same core composition formulated as Li$_4$O$_4$N$_4$C$_4$ (Figure 2.1). The Li$_4$O$_4$ is the core of the cubane clusters, the N atoms are always from pyridine groups and the O atoms are always from phenol groups. Surprisingly, within the seven structures, four different connection modes are found, which will be depicted in detail later. This result has revealed the structural variability by using the Li$_4$O$_4$ SBUs.

### 2.3.2 Connection Mode I

LIF-1 to LIF-4 represents the first strategy of building 4-connected frameworks. In such strategy, two distinct types of ligands for separate functional purposes were used, a phenol type cluster forming ligand and a pyridine type linker. Since the phenolate is a terminal ligand, the connection only occurs at four corners of lithium atoms though Li-N bonding. The SBU can be thought as a tetrahedron with 4 lithium vertexes (Figure 2.2a). Since Li$_4$(OPh)$_4$ cluster is neutral, charge free bipyridine or tripyridine type ligands were used as the linker to construct a neutral framework. From LIF-1 to LIF-3, we used three different linkers as representatives, a linear ditopic linker 4,4′-bipyridine (4,4′-bpy), a nonlinear ditopic linker bis(2-methylimidazolyl)-methane (CH$_2$-(mim)$_2$) and a tritopic linker 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt). In LIF-4, we used the same linker as in
Figure 2.2 (a) The tetrahedral secondary building unit (SBU) based on cubane cluster (b) the diamonoid cage in LIF-1 (c) the two dimensional structure of LIF-2 and (d) the one dimensional structure of LIF-3 (purple: Li; red: O; blue: N; grey: C red tetrahedron: Li$_4$(OPh)$_4$).
LIF-3 but replace the phenol with 4-ethylphenol to test the steric effect of the cluster forming ligand.

In LIF-1, the linear linker 4,4'-bpy connects adjacent Li₄(OPh)₄ clusters to form a diamond structure. Figure 2.2b illustrates a typical dianonoid cage in this structure. The large void space within the diamond cage induces the appearance of 4-fold interpenetration. LIF-2 was obtained by using a bent imidazole-type ligand, namely bis(2-methylimidazolyl)-methane. Different from the linear 4,4'-bipyridine, the bent angle of bis(2-methylimidazolyl)-methane helps to generate a double linkage between two adjacent clusters, leading to the edge-sharing between two large tetrahedra. The connectivity of the final structure adopts the 2D hcb net (also called honeycomb or 63 net).

When a tritopic linker, 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt) ligand is used, LIF-3 with a one-dimensional chain structure was obtained. This 1D structure also features the doubly connected clusters with edge-sharing lithium tetrahedron. When the phenol group in the cubane cluster is replaced with 4-ethylphenol, LIF-4 which possesses the similar chain structure to LIF-3, was obtained, even though the packing of chains is very different from that in LIF-3, due to the steric effect of the ethyl group.

2.3.3 Connection Mode II

In the first strategy, two types of functional ligands were used for cluster formation and framework connectivity, respectively. Such strategy exclusively leads to connection mode I. The other strategy differs from the previous strategy by combining the roles of two ligands into one and results in the later three coordination modes.
LIF-5 is the first example of this type, which has shown a quite interesting structure. In LIF-5, by using of the 4-pyridinol ligand, which integrates the phenol functional group and pyridine functional group into one ligand, both $\text{Li}_4\text{O}_4$ cluster formation and linkage between clusters can be achieved in one batch. The assembly can be regarded as a two-step process (Figure 2.3), first the phenolate functional group will react with lithium atoms and form the cubane clusters, and then the cubane clusters further connect with each other through the Li-N bonding. In this structure, the cubane cluster is 8-connected through the pyridinol linkers using its all eight corners. In

**Figure 2.3**  Schematic illustration of the self-assembly process from molecular species to cubane clusters to polycubanes and finally to 3D framework. (purple: Li; red: O; blue: N; grey: C)
comparison, the previous connection mode only uses four corners of the lithium cubane cluster for connection and therefore it is 4-connected. Although the coordination environment around the Li$_4$O$_4$ cluster (including the nearest neighboring C and N atoms) is exactly the same as the first strategy, the C and N atoms belong to the same 4-pyridinol ligand in LIF-5 instead of two different ligands in LIF-1 to 4.

**Figure 2.4** Representation of the (top left) 3D channels viewed along the c-axis, (top right) the tiling diagram and (bottom) the space filling diagram from (001), (010), (100) directions, respectively. (purple: Li; red: O; blue: N; grey: C)
Through the above connection method, a highly symmetric and open 3D network was finally obtained. Figure 2.4 illustrates the framework structure viewed along the (001) direction and shows the 8-ring channels. Due to the highly symmetrical structure, similar pore channels can also be observed from the (100) and (010) directions. The tiling diagram shows that this framework is simply composed by two types of tiles. The purple tiles represent the cubane cluster while the yellow tiles represent the void space in between. The free volume accessible to solvents in this compound is 34.1% as calculated with the PLATON program,\(^{41}\) which is very high for framework structures with only lithium as the framework nodes.

Compared to the previous synthetic strategy, the current strategy has shown a more optimal way to make open-frameworks. In the aforementioned structures, the phenol group only acts as a cluster-forming ligand using its -OH group and does not have an additional functional group for crosslinking with adjacent clusters. Even if Li\(_4\)(OAr)\(_4\) clusters can be further linked into a polymeric framework with a different ligand, the resulting structure may not be porous because the large dangling phenyl groups can severely block the pore access and reduce or totally eliminate the pore space. However, the 4-pyridinolate ligand here has been efficiently utilized by acting dual roles simultaneously and minimizes the extra weight brought to the framework.

The topology of this framework is quite interesting. If each Li\(_4\)O\(_4\) cubane as a whole is treated as a secondary building unit (an 8-connected node), the resulting topology can be understood as a \textit{bcu} type net topology.\(^{42}\) Alternatively, since all lithium and oxygen atoms are tetrahedrally coordinated in this structure, they can be all
Figure 2.5 The topology of LIF-5 can be described in two ways: a bcu net (Left) or an ACO net (Right), depending on the node used. The purple nodes represent Li₄O₄ clusters (Left) and Li (or O) atoms (Right), respectively.

considered as tetrahedral sites similar to those in zeolites. The resulting framework topology adopts the ACO zeotype (Figure 2.5), originally found in an aluminum cobalt phosphate.\textsuperscript{43}

In zeolite chemistry, double four ring (D4R) is a very interesting SBU and is present in a number of zeolite topologies such as ACO, AFY, and commercially important LTA.\textsuperscript{44} In MOF chemistry, these cluster units are also highly desirable because not only do they help to generate highly open framework architecture, they also contribute to the high framework stability. Actually Li₄O₄ cubane cluster can be considered as an example of the double four ring (D4R). With this in mind, it is highly possible to design and synthesize other zeolitic frameworks based on such cubane cluster, with proper ligands with the same functionalities but different configurations.

2.3.4 Connection Mode III & IV
Following the guide from the above thoughts, we have explored a series of such pyridine-phenolate type ditopic ligands other than 4-pyridinolate used in LIF-5. Unexpectedly, two novel connection modes have been discovered.

In LIF-5, the adjacent Li₄O₄ clusters are connected by one ligand from one corner to another, which can be considered as vertex-vertex connection topologically. However, the experimental results have revealed quite different cases in LIF-6 and LIF-7, in which the 4-(4-pyridinyl)-phenolate ligand and the 4-(1-imidazoly1)-phenolate ligand were adopted, respectively (Figure 2.6). In contrast to LIF-5, the adjacent cubane clusters in both LIF-6 and LIF-7 were connected by two ligands and this doubly bridged feature can

Figure 2.6 Connection between adjacent cubane clusters in LIF-5 to LIF-7.
be considered as edge-edge connection in topology. Therefore although in all three structures, all eight corners of the cubane clusters are used for connection, LIF-5 is 8-connected while LIF-6 and LIF-7 are 4-connected since the ligands are always paired. Moreover, the connection mode in LIF-6 and LIF-7 differs with each other by the different combination of edges for connection. In LIF-6, two edges are approximately perpendicular to the other two and thus form a tetrahedral SBU, while in LIF-7, all the four edges are approximately parallel to each other and form a pinwheel-like SBU.

![The diamondoid cage in LIF-6 and the square planar net in LIF-7.](image)

**Figure 2.7** The diamondoid cage in LIF-6 and the square planar net in LIF-7.

Directly affected by the geometry of their SBUs, LIF-6 exhibits a three dimensional diamond type framework, while LIF-7 exhibits a two dimensional 4⁴ net (Figure 2.7). Similar to LIF-1, due to the large void space within the diamondoid cage in LIF-6, interpenetration is favored to stabilize the structure, which makes the framework structure less open. In LIF-7, the packing geometry between two adjacent layers through van der Waals interaction is found to be optimal to expose a one dimensional square shaped channel, which allows the adsorption of small guest molecules.
2.3.5 Thermal Stability

Surprisingly, LIF-5 exhibits very high thermal stability under the N$_2$ atmosphere. Thermogravimetric analysis of the compound indicates that solvent loss (~13%) occurs in

![Figure 2.8](image)

**Figure 2.8** (top) Thermogravimetric analysis (TGA) plot of LIF-5 and (bottom) simulated and experimental X-ray diffraction patterns for as-synthesized sample and samples after thermal treatment at different temperatures.
the range 60-120 °C (Figure 2.8 top), which is mainly due to the weight loss of guest solvents such as MeOH, toluene and t-BuOH. No further weight loss is observed until approximately 540 °C, after which the compound starts to lose more weight. To further examine the thermal stability of the framework, the sample was heated at different temperatures under N\textsubscript{2} gas flow, after which powder X-ray diffraction patterns were recorded. The XRD patterns reveal that the structure remains unchanged until at least 520 °C (Figure 2.8 bottom). Such a thermal stability is very high among metal organic frameworks. To our knowledge, it is in fact the highest among porous MOFs containing monovalent cations as framework nodes. The high thermal stability may be attributed to the cluster feature of the building block and the eightfold connection of each cluster to its adjacent clusters, which leads to a very rigid framework.

2.3.6 Gas Sorption Properties

LIF-5 was selected to study the gas sorption properties. The sample was degassed at 180 °C overnight prior to the measurement. The N\textsubscript{2} adsorption/desorption curves obtained at 77 K exhibit type-I isotherm characteristics, which proves the permanent porosity of the compound (Figure 2.9a). The isotherm also shows a significant H4 hysteresis loop between 0.4~1.0 P/P\textsubscript{o} range. The Brunauer–Emmett–Teller and Langmuir surface areas are 440.3 m\textsuperscript{2}/g and 632.5 m\textsuperscript{2}/g, respectively. The pore size analysis obtained by the Horvath-Kawazoe method showed a uniform and narrow pore size distribution around 11 Å when the cylinder pore geometry was used for calculation.

Hydrogen adsorption studies gave a gravimetric uptake of 108.7 cm\textsuperscript{3}/g (or 0.96 wt\%) and a volumetric uptake of 9.83 g/L (calculated crystal density: 1.013 g/cm\textsuperscript{3}) at 760
Torr and 77 K (Figure 2.9b). To our knowledge, the best hydrogen uptake capacity for an all lithium based framework is CO$_2$ adsorption isotherms were also investigated. At 760 Torr and 273 K, the volume of CO$_2$ adsorbed by the compound reached 35.9 cm$^3$/g (1.61 mmol/g).

![Gas sorption isotherms of LIF-5 for (a) N$_2$ at 77 K, P/Po is the ratio of gas pressure (P) to saturated pressure (Po), with Po = 772 Torr, and for (b) H$_2$ at 77 K and CO$_2$ at 273 K.](image)

**Figure 2.9** Gas sorption isotherms of LIF-5 for (a) N$_2$ at 77 K, P/Po is the ratio of gas pressure (P) to saturated pressure (Po), with Po = 772 Torr, and for (b) H$_2$ at 77 K and CO$_2$ at 273 K.

2.4 Conclusion

In conclusion, the light weight lithium cubane clusters were introduced to the design and synthesis of coordination polymers. Two synthetic strategies have lead to seven types of frameworks, which share the same core structure but can be classified into four different connection modes. The successful synthesis of these compounds has revealed the structural variability in this system. More importantly, it indicates that the introduction of Li$_4$O$_4$ cubane cluster as SBUs is a very effective way to construct lithium based open-frameworks. Since Li$_4$O$_4$ can be considered as a double four ring (D4R)
analogue, which is a very important SBU in zeolite chemistry, it is possible to obtain a series of zeolitic structures by adopting proper ligand and synthetic conditions. In this work, an initial example of zeolitic framework has been obtained, which has the ACO topology.

For the first time, the dual functional ditopic ligand containing phenolate and pyridine functionalities were introduced into the construction of coordination polymers. Such phenolate containing ligand is extremely rare in the area of MOFs, probably due to the weak interaction between phenolate and transition metal ions. However, for the metals with high oxygen affinity, such as lithium in this study, the use of phenolate containing ligands has been proved to be very effective. It’s even better than traditional carboxylate type ligands to construct open-frameworks. In addition, their stability can be quite high, depending on the structure characteristics. For example, LIF-5 has a quite high thermal stability up to 520 °C.

Finally, some compounds can reversibly adsorb N₂, H₂ and CO₂. Although the uptake capacity for H₂ and CO₂ is moderate when considering all microporous materials, it is impressive considering few lithium based porous materials are currently known. In addition to the cubane-type clusters, lithium and aryloxides can form other clusters such as hexamer and octamer, which are analogues of SBUs in zeolites such as double six-ring (D6R) and aww cage. Therefore our work reported here demonstrates a great potential to synthesize porous frameworks with various zeolitic topologies based on lithium aryloxides clusters, which will hopefully lead to further improvement of the gas sorption properties and possible applications such as gas storage and separation.
2.5 References


(40) G. M. Sheldrick, *SHELX97—Programs for Crystal Structure Analysis*, release 97–2; Institut für Anorganische Chemie der Universität Göttingen, Göttingen, Germany, **1998**.


(44) W. M. Meier, D. H. Olson, *Atlas of Zeolite Structure Types*;
    Butterworth-Heinemann: Boston, **1992**.
Chapter 3

Supramolecular Assemblies Using Lithium Cubane Clusters as Novel Tectonics

3.1 Introduction

The designed synthesis of crystalline porous materials (CPMs) have attracted great interest due to their significance in understanding host-guest chemistry, as well as their potential use in gas storage, separation and catalysis, etc. In general, CPMs can be assembled through two major chemical processes, coordination chemistry and supramolecular chemistry that are characterized by the type of fundamental interactions at molecular level. Recently developed metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) represent a large variety of the former category and the major interaction between building blocks is coordination bonds. In the latter category, the relatively weak interactions such as hydrogen bond (H-bond) and Van der Waals interaction are widely utilized to guide the self-assembly of molecular species. One well-known example is a series of pillared compounds with guanidinium sulfonate layers. By replacing the sulfonate anion with borate anion, a more symmetric 3D network has been achieved.

The building blocks within most H-bonded networks are organic molecules that are dominated by covalent bonds. These molecules usually exhibit a configuration with lower symmetry (Scheme S2). Although more symmetric organic molecules have been
studied for building supramolecular assemblies, the synthesis of those molecules can be quite challenging.\textsuperscript{12,13} Distinct from the above strategy, recently, some H-bonded frameworks involving metal complexes have been reported.\textsuperscript{14-19} Among these reports, an interesting example is metal-organic cubes constructed from indium ion and imidazoledicarboxylate ligand, which are further used as building blocks for 3D H-bonded frameworks.\textsuperscript{18,19} Such building blocks are obtained in-situ and are also highly symmetric. They are quite useful for building 3D porous structures.

Lithium aryloxide cubane clusters are well known in lithium chemistry and they can be easily formed in-situ. Henderson and co-workers first reported that lithium cubane cluster can be used in the construction of 3D frameworks.\textsuperscript{20,21} Recently, we have synthesized a lithium-cubane-cluster based porous zeolitic framework by careful design of a ditopic pyridinolate ligand.\textsuperscript{22} All the above materials can be thought as purely coordination compounds.

Herein we report that under appropriate conditions, the lithium cubane clusters can act as novel building blocks in supramolecular assemblies. In general, to generate such a system, a ditopic ligand that contains a phenol functionality and a pyridine (or its derivatives such as quinoline and isoquinoline) functionality is needed. The phenol group plays the essential role in the formation of cubane clusters, while the pyridine group acts as the H-bond acceptor. In addition, the methanol is needed to occupy the fourth coordination site of lithium atom (other three are occupied by the phenol oxygens) and importantly, it acts as the H-bond donor. In each cluster, the eight corners are occupied
by four methanol molecules and four pyridine functional groups, which correspond to
four H-bond donors and four H-bond acceptors respectively.

3.2  Experimental Section

3.2.1  Solvothermal Synthesis

All reagent and solvent were commercially available and used as supplied without
further purification. Scheme 3.1 shows all the ditopic ligand use in this work. In general,
the ditopic ligand requires a pyridine functional group and a phenolate functional group.
Different ligand is distinguished from each other by the relative position of the two
functional groups. The lithium source can be either t-BuLi or t-BuOLi (both used as a
toluene solution) for most of the cases. Both of them can easily deprotonate the phenol
functionality and only form a relatively inert side product such as t-butane and t-butanol.
However, t-BuOLi is more often adopted since the reactivity of t-BuOLi is much less
than t-BuLi and also less sensitive to the moisture in the air. Methanol is used as the
major solvent in all systems and it is also part of the structure. Aromatic solvents like
benzene, toluene and xylene are also very important solvents in this system since lithium
interact very weakly with these solvents compared to methanol. They can be used to
adjust the polarity of the solvent to help crystallization. Sometimes, the volume ratio
between the polar and nonpolar solvent is important for the crystallization. But too much
nonpolar solvent will lead to the difficulty in crystallization.

\[ \text{Li}_4(\text{PyO})_4(\text{MeOH})_4 \text{ (HLIF-0)} \]. In a 20 mL vial, 25 mg of 4-pyridinol was
dissolved in 5.018 g methanol and stirred for 10 minutes, then 0.3 mL of t-BuOLi (1.0 M
solution in hexane) was added and stirred for another 10 minutes. The final clear solution
was sealed and heated in a 100 °C oven for about 48 hours. Large amount of colorless crystals were obtained.

**Li₄(6-iQIO)₄(MeOH)₄ (HLIF-1).** In a 20 mL vial, 73 mg of 6-isoquinolinol was dissolved in 4.024 g methanol and stirred for 10 minutes, then 0.5 mL of t-BuOLi (1.0 M solution in hexane) was added and stirred for another 10 minutes. The final clear solution was sealed and heated in a 90 °C oven for about 24 hours. Large amount of colorless crystals were obtained.

**Li₄(6-QIO)₄(MeOH)₄ (HLIF-2).** In a 20 mL vial, 73 mg of 6-quinolinol was dissolved in a mixture of 0.525 g methanol and 2.525 g toluene to form a dark brown solution, after stirring for 10 minutes, 0.5 mL of t-BuOLi (1.0 M solution in hexane) was

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**Scheme 3.1**  Ditopic ligands used for the synthesis of HLIFs in this study.

![Diagram of ligands](image-url)
added, the turbid solution was stirred for another 10 minutes. The final solution was sealed and placed in a 70 °C oven for about 48 hours. Large amount of colorless crystals were obtained.

\( \text{Li}_4(4\text{-QlO})_4(\text{MeOH})_4 \) (HLIF-3). In a 20 mL vial, 72 mg of 4-quinolinol was dissolved in a mixture of 0.523 g methanol and 2.531 g toluene to form a clear solution, after stirring for 10 minutes, 0.5 mL of \( t\)-BuOLi (1.0 M solution in hexane) was added, the turbid solution was stirred for another 10 minutes. The final solution was sealed and placed in a 90 °C oven for about 48 hours. Large amount of colorless crystals were obtained.

\( \text{Li}_4(5\text{-QlO})_4(\text{MeOH})_4 \) (HLIF-4). In a 20 mL vial, 73 mg of 5-quinolinol was dissolved in 5.024 g methanol to form a clear solution, after stirring for 10 minutes, 0.5 mL of \( t\)-BuOLi (1.0 M solution in hexane) was added. After stirring for another 10 minutes, the final solution was sealed and heated in a 120 °C oven for about 24 hours. Large amount of colorless crystals were obtained.

\( \text{Li}_4(6\text{-QlO})_4(\text{MeOH})_4 \) (HLIF-5). In a 20 mL vial, 73 mg of 6-quinolinol was dissolved in a mixture of 0.514 g methanol and 2.516 g toluene to form a dark brown solution, after stirring for 10 minutes, 0.5 mL of \( t\)-BuOLi (1.0 M solution in hexane) was added, the turbid solution was stirred for another 10 minutes. The final solution was sealed and placed in a 70 °C oven for about 48 hours. Large amount of colorless crystals were obtained.

\( \text{Li}_4(7\text{-Qlo})_4(\text{MeOH})_4 \) (HLIF-6). In a 20 mL vial, 71 mg of 7-isoquinolinol was dissolved in a mixture of 1.045 g methanol and 1.609 g toluene to form a dark brown
solution, after stirring for 10 minutes, 0.5 mL of \( t\)-BuOLi (1.0 M solution in hexane) was added, the turbid solution was stirred for another 10 minutes. The final solution was sealed and placed in a 70 °C oven for about 48 hours. Large amount of colorless crystals were obtained.

\[ \text{Li}_4(7-iQlo)_4(\text{MeOH})_4 \text{(HLIF-7).} \] In a 20 mL vial, 73 mg of 7-isoquinolinol was dissolved in 4.027 g methanol and stirred for 10 minutes, 0.5 mL of \( t\)-BuOLi (1.0 M solution in hexane) was then added and stirred for another 10 minutes. The final solution was sealed and placed in a 90 °C oven for about 24 hours. Large amount of colorless crystals were obtained.

\[ \text{Li}_4(\text{PyPhO})_4(\text{MeOH})_4 \text{(HLIF-8).} \] In a 20 mL vial, 42 mg of 4-(4-pyridyl)phenol was dissolved in 1.502 g methanol and 1.042 g toluene and stirred for 10 minutes, 0.1 mL of \( t\)-BuLi (2.5 M solution in hexane) was then added and stirred for another 10 minutes. The final solution was sealed and placed in a 70 °C oven for about 72 hours. Large amount of colorless crystals were obtained.

3.2.2 Powder X-ray Diffraction

X-ray powder diffraction experiments were performed on a Bruker D8 Advance powder diffractometer, equipped with a Sol-X detector using Cu K\( \alpha_1 \) radiation (\( \lambda = 1.5406 \) Å). The simulated XRD pattern was calculated from the structure data using the CSD Mercury 2.4 software.

3.2.3 Thermal Analysis

Thermogravimetric (TGA) analysis was carried out on a TA-Q500 thermal analyzer by TA instrument under nitrogen flow. The flow rate of the nitrogen gas was
controlled at about 60 milliliters per minute. The heating rate is 10°C/min from 30 °C to 900 °C.

3.2.4 Gas Sorption Measurements

HLIF-3, HLIF-4 and HLIF-5 were picked up for gas sorption study. As-synthesized samples were dried under vacuum and then evacuated (10⁻³ torr) at 40 °C for 12h. Gas sorption experiments were carried out on a Micromeritics ASAP 2020 surface area and pore size analyzer. N₂ sorption was performed under 77 K and CO₂ sorption was performed under 273 K.

3.2.5 Single Crystal Crystallography

Single-crystal X-ray analysis was performed on a Bruker Smart APEX II CCD area diffractometer with nitrogen-flow temperature controller using graphite-monochromated Mo Kα radiation (λ=0.71073 Å), operating in the ω and φ scan mode. Raw data collection and refinement were done using SMART. Data reduction was performed using SAINT⁺ and corrected for Lorentz and polarization effects. The SADABS program was used for absorption correction. The structure was solved by direct methods, and the structure refinements were based on |F²| with anisotropic displacement using SHELX-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions. All crystallographic calculations were conducted with the SHELXTL software suites. The crystallographic data and the structural refinement parameters were summarized in Table 3.1.
Table 3.1  A summary of crystallographic data and refinement results for the structures covered in chapter 3[^a]

<table>
<thead>
<tr>
<th>Code[^b]</th>
<th>Formula[^c]</th>
<th>sp. gr.</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
<th>α (°)/γ (°)</th>
<th>R(F)</th>
<th>Net[^d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HLIF-0</td>
<td>Li$_4$(4-PyO)$_4$(MeOH)$_4$</td>
<td>Pcca</td>
<td>17.7886(4)</td>
<td>8.5114(2)</td>
<td>19.2578(5)</td>
<td>90</td>
<td>90/90</td>
<td>0.0769</td>
<td>0D</td>
</tr>
<tr>
<td>HLIF-1</td>
<td>Li$_4$(6-ìQlO)$_4$(MeOH)$_4$</td>
<td>I4$_1$/a</td>
<td>18.261(2)</td>
<td>18.261(2)</td>
<td>11.857(3)</td>
<td>90</td>
<td>90/90</td>
<td>0.0842</td>
<td>T. D.</td>
</tr>
<tr>
<td>HLIF-2</td>
<td>Li$_4$(6-QlO)$_4$(MeOH)$_4$</td>
<td>C2/c</td>
<td>24.4815(2)</td>
<td>24.8772(2)</td>
<td>17.9408(2)</td>
<td>133.02</td>
<td>90/90</td>
<td>0.0763</td>
<td>D. D.</td>
</tr>
<tr>
<td>HLIF-3</td>
<td>Li$_4$(4-QlO)$_4$(MeOH)$_4$</td>
<td>P4$_2$/n</td>
<td>11.4137(5)</td>
<td>11.4137(5)</td>
<td>14.4242(1)</td>
<td>90</td>
<td>90/90</td>
<td>0.0425</td>
<td>D. D.</td>
</tr>
<tr>
<td>HLIF-4</td>
<td>Li$_4$(5-QlO)$_4$(MeOH)$_4$</td>
<td>P-1</td>
<td>11.836(2)</td>
<td>13.981(3)</td>
<td>15.105(3)</td>
<td>108.956(13)</td>
<td>102.449(13)/102.803(13)</td>
<td>0.0774</td>
<td>sql</td>
</tr>
<tr>
<td>HLIF-5</td>
<td>Li$_4$(5-QlO)$_4$(MeOH)$_4$</td>
<td>P2/n</td>
<td>15.9156(5)</td>
<td>17.0505(7)</td>
<td>16.1674(5)</td>
<td>90.00</td>
<td>90/90</td>
<td>0.0615</td>
<td>sql</td>
</tr>
<tr>
<td>HLIF-6</td>
<td>Li$_4$(7-ìQlO)$_4$(MeOH)$_4$</td>
<td>P-1</td>
<td>10.3245(13)</td>
<td>11.0182(12)</td>
<td>17.927(3)</td>
<td>98.510(9)</td>
<td>93.664(8)/97.060(8)</td>
<td>0.0689</td>
<td>linear</td>
</tr>
<tr>
<td>HLIF-7</td>
<td>Li$_4$(7-QlO)$_4$(MeOH)$_4$</td>
<td>P-1</td>
<td>11.051(4)</td>
<td>13.239(5)</td>
<td>14.003(5)</td>
<td>82.428(4)</td>
<td>88.476(5)/79.801(5)</td>
<td>0.0684</td>
<td>linear</td>
</tr>
<tr>
<td>HLIF-8</td>
<td>Li$_4$(PyPhO)$_4$(MeOH)$_4$</td>
<td>I4$_1$/a</td>
<td>16.813(7)</td>
<td>16.813(7)</td>
<td>16.561(19)</td>
<td>90</td>
<td>90/90</td>
<td>0.0972</td>
<td>T. D.</td>
</tr>
</tbody>
</table>

[^a]: Crystal structures were solved from single-crystal data collected at 150 K on a SMART CCD diffractometer with MoKα.

\[ R(F) = \Sigma ||F_o|-|F_c||/ \Sigma |F_o| \text{ with } F_o > 4.0\sigma(F). \]

[^b]: HLIF = hydrogen bonded lithium frameworks
[c] 4-PyO = 4-pyridinolate; 6-iQlO = 6-isoquinolinolate; 6-QlO = 6-quinolinolate; 4-QlO = 4-quinolinolate; 5-QlO = 5-quinolinolate; 7-iQlO = 7-isoquinolinolate; PyPhO = 4-(4-pyridyl)phenolate.

[d] T. D. = triple diamond, D. D. = double diamond, sql = square planar
3.3 Results and Discussion

3.3.1 Formation of Lithium Cubane Cluster

The basis for this series of structures is the methanol capped lithium cubane clusters. As was described in Chapter 2, in general, a lithium cubane cluster was formed by reaction between equimolar organometallic lithium salt and aryloxide. Previous report has shown that the pyridine functionality won’t affect the formation of cubane cluster due to the strong affinity between lithium and oxygen. In this specific case, the phenolate part of the ditopic ligand contributes to the formation of lithium cubane and the pyridine part is exposed toward the environment, which will act as the hydrogen bond acceptor later. The methanol is on the fourth coordination site of the lithium and make lithium tetrahedrally coordinated, which is the most common and stable coordination environment for lithium. The hydroxyl group of methanol will act as the hydrogen bonding donor.

Interestingly, it is not necessary for all such structure to form hydrogen bond with each other to further self-assemble into a polymer based materials. Fortunately we have obtained one such isolated cluster that is closely packed by Van der Waals interaction only (Figure 3.1(a)). The successful isolation of this cluster suggests that the formation of supramolecular assemblies in such system might be a multi-step process. The discrete methanol-capped cluster is likely formed first, which is then followed by the self-assembly of such in-situ formed clusters into higher level architectures. During the process, the first step is dominated by coordination chemistry, while the second step is dominated by supramolecular chemistry.
3.3.2 Hydrogen Bond Formation

Figure 3.1 Illustration of (a) the isolated methanol capped lithium pyridinolate cubane cluster and (b) two adjacent lithium 4-quinolinolate cubane clusters within the supramolecular assembly showing double H-bonding modes (purple: Li; red: O; blue: N; grey: C; yellow: H, only two hydrogen atoms are shown, others are omitted for clarity).

3.3.2 Hydrogen Bond Formation

Figure 3.1(b) gives a typical example showing how two adjacent clusters interact with each other through supramolecular interactions. In HLIF-3, a methanol and a 4-quinolinolate from the same edge of one lithium cubane cluster form two H-bonds with a 4-quinolinolate and a methanol from the same edge of an adjacent cluster. The direction
Figure 3.2 The connection between adjacent lithium cubane clusters in HLIFs that feature the double hydrogen bonding. H-bonding distance and $\pi-\pi$ distances are given. (purple: Li; red: O; blue: N; grey: C; yellow: H, only part of the hydrogen atoms are shown, others are omitted for clarity).
of H-bond donation is opposite to each other. The O-H…N type H-bond has a typical enthalpy of 29 kJ/mol, which is a relatively strong H-bond. Depending on the spatial configuration of ligand adopted, two adjacent clusters can form double hydrogen bonds (Figure 3.2) or even quadruple hydrogen bonds (Figure 3.3).

Interestingly, in addition to the H-bonds, it is found that the π systems in two quinoline ligands are arranged parallel to each other and the distance between two rings is approximately 3.91 Å, which indicates a π-π interaction between two ligands. This π-π

![Figure 3.3](image_url) The connection between adjacent lithium cubane clusters in HLIF-6 and HLIF-7 that feature the quadruple hydrogen bonding. H-bonding distance and π-π distances are given. (purple: Li; red: O; blue: N; grey: C; yellow: H, only part of the hydrogen atoms are shown, others are omitted for clarity).
Table 3.2  A summary of the hydrogen bond distances and $\pi-\pi$ stacking distances in HLIFs.

<table>
<thead>
<tr>
<th>Code</th>
<th>O-H…N distance (Å) (H…N distance)$^{[a]}$</th>
<th>$\pi-\pi$ stacking distance (Å)$^{[b]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HLIF-1</td>
<td>2.717 (1.937)</td>
<td>3.93</td>
</tr>
<tr>
<td>HLIF-2</td>
<td>2.700 (2.164)</td>
<td>N/A$^{[c]}$</td>
</tr>
<tr>
<td>HLIF-3</td>
<td>2.746 (2.005)</td>
<td>3.91</td>
</tr>
<tr>
<td>HLIF-4</td>
<td>2.685 (1.892)</td>
<td>4.00</td>
</tr>
<tr>
<td>HLIF-5</td>
<td>2.713 (1.897)</td>
<td>4.06</td>
</tr>
<tr>
<td>HLIF-6</td>
<td>2.675 (1.856), 2.691 (1.791), 2.696 (1.890), 2.714 (1.986)</td>
<td>N/A</td>
</tr>
<tr>
<td>HLIF-7</td>
<td>2.717 (1.930), 2.689 (1.943), 2.746 (2.014), 2.644 (2.048)</td>
<td>N/A</td>
</tr>
<tr>
<td>HLIF-8</td>
<td>2.754 (1.891)</td>
<td>4.11</td>
</tr>
</tbody>
</table>

[a] The hydrogen atoms are not directly observed and determined by the constrain method.

[b] The $\pi-\pi$ stacking distance reported here were measured based on the distance between the centers of corresponding aromatic rings.

[c] In HLIF-2, although the two quinoline rings are parallel to each other, the $\pi-\pi$ distance is about 5.18 Å. The $\pi-\pi$ interaction is usually very weak at such distance and can be ignored.

Stacking is not only found in HLIF-3, but also found in other compounds reported here except for 1D HLIF-6 and HLIF-7 structures in which quadruple H-bond exists between
adjacent clusters, eliminating the need or possibility for the π-π interaction. The H-bond lengths and π-π distances of all relevant compounds are listed in Table 3.2. Compared to the charge assisted H-bonding, the interaction between neutral clusters here lacks electronstatic interaction. However, such dual-connected (also quadruply connected, see below) H-bond feature plus π-π stacking interaction between the ligands provide extra stablization of these compounds.

3.3.3 Connectivity in Supramolecular Assemblies

The connectivity of these compounds is also interesting. As mentioned above, in each lithium cubane cluster, there are four H-bond donors and H-bond acceptors. It is found that when these donors and acceptors take part in the assembly process, they are usually paired on the same edge of lithium cubane clusters except for HLIF-6 and HLIF-7 in which the adjacent cubane cluster are quadruply connected. Thus, three types of connection modes (i.e., tetrahedral, square planar, and linear) have been discovered (Figure 3.4). They can be considered as edge-edge connection and depending on which set of edges are used, these connection modes guide the formation of the final net topology from 1D through 3D.

Specifically, HLIF-1, HLIF-2, HLIF-3 and HLIF-8 contain clusters with the tetrahedral configuration, and exhibit the diamonoid topology (Figure 3.5a & b). In principle, diamonoid net is not the nesassary result when a tetrahedral building unit is used. There is possibility to obtain zeolitic frameworks other than diamond net under suitable synthetic conditions and with suitable ligand configuration (which affects the dihedral angle between two adjacent building units). However, from the results of
Figure 3.4 Three types of connection modes in the supramolecular assemblies: (a) tetrahedral; (b) square planar (windmill-like); (c) linear. (A represents hydrogen bond acceptor and D represents hydrogen bond donor)
previous research in supramolecular assembly, the diamond net does occur frequently when the tetrahedral building block is quite symmetric. Interpenetration is a common phenomenon in diamonoid topology and it is also observed here. Interpenetration occurs in all four diamonoid nets in this work. However, the degree of interpenetration is

**Figure 3.5** (a) The connection between adjacent clusters in HLIF-3; (b) a single diamonoid network; (c) double diamond net in HLIF-2 and HLIF-3; (d) triple diamond net in HLIF-1 and HLIF-8.
different. HLIF-2 and HLIF-3 have the 2-fold interpenetrated nets, while HLIF-1 and HLIF-8 have the 3-fold interpenetrated nets (Figure 3.5c & d). The above difference seems reasonable since the distance between neighboring lithium cubane clusters increases due to the more straight and longer 6-isoquinolinolate and 4-(4-pyridyl)-phenolate ligands and the extra void space within the diamond cage needs to be filled and stabilized by an additional network.

In contrast to the above tetrahedron shaped building blocks, HLIF-4 and HLIF-5 contain building blocks with a square planar configuration. Such geometry leads to the formation of square planar net or $4^4$ net (Figure 3.6). Furthermore, two adjacent layers are packed by weak Van der Waals interaction. The mode of the packing leads to porous 1-D channels through the layers.

In HLIF-6 and HLIF-7, the adjacent cubane clusters are connected by four pairs

![Figure 3.6 Illustration of square planar net in (a) HLIF-4 and (b) HLIF-5.](image)
of H-bond donors and acceptors. Different from the above compounds, in which the two π systems are parallel to each other, the four quinonline rings in these two compounds have no such π-π stacking.

Interestingly, the different connection modes are likely to be induced by the configuration of ligands (the relative position of phenol and pyridine functionalities). For example, the 5-quinolinol only leads to the formation of square planar type connection whereas 7-isoquinolinol only leads to the formation of linear type connection. Other ligands are only found in the diamonoid type assemblies.

3.3.4 Molecular Tectonics vs Cluster Tectonics

Scheme 3.2 Comparison of traditional molecular tectonics (left) and the novel lithium cubane cluster tectonics reported in this work (right).
In the supramolecular area, the fundamental building units are usually called synthons or tectonics and they are exclusively organic molecules. While the organic molecules can provide many different hydrogen bonding modes, the examples of highly symmetric structures based on hydrogen bonds are less reported. The reason is largely related to the low symmetry of these molecular building blocks (Scheme 3.2 left). Although some attempt has been made to use more symmetric tectonics as building blocks such as tetratopic ligands in the $T_d$ symmetry, the synthesis is usually complex and costly.

In contrast, the cluster based tectonic first proposed here represents a novel strategy in supramolecular chemistry. The cluster is formed in-situ and the synthesis is easy and can be precisely controlled due to the highly reliable synthetic procedure of Li$_4$O$_4$. In addition, the cluster is in high symmetry and multiple connection modes exist. Furthermore, based on the same Li$_4$O$_4$ core, various ligands of different configuration can be applied to generate different structures (Scheme 3.2 right). They can even work together with traditional molecular tectonics to form higher level assemblies. The above features make cluster tectonics a great alternative to the molecular tectonics.

### 3.3.5 Gas Sorption Properties

HLIF-3, HLIF-4 and HLIF-5 are selected to examine the CO$_2$ adsorption properties. Under 1 atm and 273 K, HLIF-4 shows CO$_2$ uptake up to 38.1 cm$^3$/g (Figure 3.7). This value is quite high among lithium based porous materials and even higher than that for previously reported RHO and SOD type boron imidazolate framework.$^{24,25}$ In contrast, the uptake capacities for HLIF-3 and HLIF-5 are 16.80 cm$^3$/g and 19.5 cm$^3$/g
under the same condition, respectively. Surprisingly, the 2D structure of HLIF-4 has a much larger CO$_2$ sorption ability than the 3D framework of HLIF-3, which may be related to their structural features. The 2D layers of HLIF-4 are packed in a fashion to leave a one dimensional channel in the middle. Interestingly, MOF-74, which has the largest CO$_2$ uptake capacity among current MOFs, also exhibits such a one dimensional channel, although it is much larger. In contrast, in HLIF-3, two independent diamondoid net interpenetrate with each other and the accessible void space is thus largely reduced.

3.4 Conclusion

In conclusion, lithium cubane clusters with various binding geometry have been found to be effective in the construction of a family of supramolecular assemblies.
Compared to molecular building blocks, this lithium cubane cluster is formed in-situ and only needs simple chemical sources and mild reaction conditions to form. Also these tectonics can provide variable connection modes, which are less common in molecular tectonics. Through these connection modes, 1D to 3D assemblies can be obtained. Furthermore, the phenol-pyridyl bifunctional ligands used in this work can be extended by appropriate ligand design, which may lead to 3D H-bonded frameworks with new topology and greater porosity.

3.5 References


Chapter 4

A Mixed Ligand Route for Construction of Tetrahedrally Coordinated Porous Lithium Imidazolate Frameworks

4.1 Introduction

The synthesis of crystalline porous frameworks has long been of great interest because of their many possible applications.\textsuperscript{1-12} Materials based on imidazolates, such as zeolitic imidazolate frameworks (ZIFs) which are a family of 3D porous crystalline materials, have caught the attention of many researchers in recent years.\textsuperscript{13-31} Typically, ZIFs are simply built by using divalent metal cations (such as Zn\textsuperscript{2+}, Co\textsuperscript{2+}, or Cd\textsuperscript{2+}) with imidazolate bridges. In these materials, all the cations are tetrahedrally coordinated and the final 3D frameworks are neutral. The topology can be controlled by applying different substitution groups on the imidazolate module. In this way, about ten zeolitic topologies have been obtained and their gas sorption studies have showed some exciting results.

Introducing lightweight elements into the construction of metal-organic frameworks is one strategy to enhance the gas sorption properties by directly reducing the framework density.\textsuperscript{32-45} Recently, a method based on the mixed tetrahedral nodes has been developed by utilizing tetrahedrally coordinated B\textsuperscript{3+} and Li\textsuperscript{+}.\textsuperscript{44,45} Since the total charge of B\textsuperscript{3+} and Li\textsuperscript{+} equals that of two Zn\textsuperscript{2+} ions, the resulting frameworks (known as boron imidazolate framework or BIF) are still neutral. These BIFs exhibit similar zeolitic
topologies as ZIFs, however, the framework boron and lithium ions are much lighter than zinc.

The short B-N bond (≈ 1.5Å) in BIFs, however, leads to a closer contact and stronger steric repulsion between imidazolate bridges, making it challenging to tune the framework topology by introducing imidazolates with various substituent groups (e.g., benzimidazole). In this work, we aim to develop imidazolate frameworks with only 4-connected lithium nodes (Li-N bond ≈ 2.0Å). However, we noticed that the total charge of the resulting 4-connected framework will become negative if B$^{3+}$/Li$^+$ is replaced with Li$^+$/Li$^{2+}$ and no change is made on the imidazolate ligands.

Thus, we have developed the mixed ligand route to balance the charge of the framework (Scheme 4.1). By replacing half of the negatively charged imidazolate ligands with neutral ligands, the resulting 3D framework will be neutral. To execute this strategy, any neutral ditopic ligands can be examined. However, we are particularly interested in

\[
\text{Zn}^{2+} + 2L_1^- \quad \rightarrow \quad \text{Li}^+ + L_1^- + L_2^0
\]

\(L_1 = \text{imidazole} \quad L_2 = \text{neutral ditopic ligand}\)

**Scheme 4.1** Schematic illustration of the mixed valent ligand strategy to build tetrahedrally coordinated lithium framework.
neutral ligands whose coordination geometry and bonding features closely mimic the imidazolate in a way similar to those in ZIFs and BIFs. In this work, we used bis(imidazoly)-methane type ligand which contains an imidazole-like ring on each side, but is neutral in charge.

Here, we report the synthesis and structures of two 3D networks in LiL₁L₂ type (L₁ is a negatively charged imidazole type ligand and L₂ is a neutral bis(imidazolyl)-methane type ligand) denoted as MVLIF-1 and MVLIF-2 with formula Li(bim)[CH₂(im)₂] and Li(im)[CH₂(mim)₂], respectively (MVLIF = Mixed Valent ligand Lithium Imidazolate Framework). In contrast to the inability to prepare 3D BIFs from benzimidazole, the 3D framework of benzimidazole-containing MVLIF-1 demonstrates the effect of the longer Li-N distance (as compared to the B-N distance).

4.2 Experimental Section

4.2.1 Synthesis of the Bis(imidazolyl)methane Type Ligands

All reagent and solvent were commercially available and used as supplied without further purification. In general, bis(imidazolyl)methane ligands were synthesized through a liquid-liquid phase transfer reaction according to the literature report with minor modifications (Scheme 4.2). In brief, a mixture of sodium hydroxide, tetraethyl-ammonium bromide (TEAB), and imidazole in a mixed solvent of methylene chloride and water was reacted under reflux condition. After about 24 hours, the final white powder product was obtained by extraction of the reaction mixture with methylene chloride, followed by rotating evaporation. To examine the structure-directing role of substitution groups on the ligands, the bis(2-methyl-imidazolyl)methane and bis-
Synthesis of bis(imidazolyl)methane:
In a 250 ml flask, 17.984 g NaOH, 4.752 g imidazole and 441 mg tetraethylammonium bromide (TEAB) were dissolved in a mixed solution of 25 g H₂O and 100 ml methylene chloride. The solution was stirred and heated under reflux condition for about 24 hours and white precipitate forms. Extraction was performed thereafter by adding extra methylene chloride and water. The product was obtained by rotating evaporation of the extract.

Synthesis of bis(2-methylimidazolyl)methane: The synthesis of bis(2-methylimidazolyl)methane is very similar to its imidazolyl analogue. However, the
imidazole was replaced by 5.743 g 2-methylimidazole and the reaction time became approximate 72 hours.

**Synthesis of bis(benzimidazolyl)methane:** The synthesis of bis(2-methylimidazolyl)methane is very similar to its imidazolyl analogue. However, the imidazole was replaced by 5.743 g 2-methylimidazole and the reaction time became approximate 72 hours.

4.2.2 Solvothermal Synthesis
Synthesis of Li(bim)[CH₂(im)]₂ (MVLIF-1): 88 mg Li₂S, 91 mg CH₂(im)₂ and 73 mg benzimidazole was loaded in a 20 ml Teflon-lined vial and 5.158 g of anhydrous acetonitrile solvent was added. After stirring for 4 hours, the resulted turbid solution was placed in a 90 °C oven. In about 72 hours, the vial was allowed to cool at room temperature and large amount of colorless crystals were obtained.

Synthesis of Li(im)[CH₂(mim)]₂ (MVLIF-2): 48.5 mg Li₂S, 55.3 mg CH₂(mim)₂ and 22.3 mg imidazole was loaded in a 20 ml Teflon-lined vial and 5.121 g of anhydrous acetonitrile solvent was added. After stirring for 4 hours, the resulted turbid solution was placed in a 120 °C oven. In about 48 hours, the vial was allowed to cool at room temperature and large amount of colorless crystals were obtained.

4.2.3 Powder X-ray Diffraction

X-ray powder diffraction experiments were performed on a Bruker D8 Advance powder diffractometer, equipped with a Sol-X detector using Cu Kα₁ radiation (λ = 1.5406 Å). The simulated XRD pattern was calculated from the structure data using the CSD Mercury 2.4 software.

4.2.4 Thermal Analysis

Thermogravimetric (TGA) analysis were carried out on a TA-Q500 thermal analyzer by TA instrument with a heating rate of 10°C/min. Nitrogen (60 ml/min) flow was applied during the analyses.

4.2.5 Gas Sorption Measurements

H₂ gas sorption experiments were carried out on a Micromeritics ASAP 2010 surface area and pore size analyzer. Prior to the measurement, powder samples of
MVLIF-1 and MVLIF-2 were dried by using the “degas” function of the surface area analyzer for 20 hours at 160 °C and 140 °C, respectively. The H₂ sorption measurements were performed at 77K.

4.2.6 Single-Crystal Crystallography

Single-crystal X-ray analysis was performed on a Bruker Smart APEX II CCD area diffractometer with nitrogen-flow temperature controller using graphite-monochromated Mo Kα radiation (λ=0.71073 Å), operating in the ω and φ scan mode. Raw data collection and refinement were done using SMART. Data reduction was performed using SAINT⁺ and corrected for Lorentz and polarization effects. The SADABS program was used for absorption correction. The structure was solved by direct methods, and the structure refinements were based on \(|F^2|\) with anisotropic displacement parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions. All crystallographic calculations were conducted with the SHELXTL software suites. The crystallographic data and the structural refinement parameters were summarized in Table 4.1.
Table 4.1  A summary of crystal data and structural refinement results of MVLIF-n.

<table>
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<tr>
<th></th>
<th>MVLIF-1</th>
<th>MVLIF-2</th>
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<tr>
<td>formula</td>
<td>Li(bim)[CH₂(im)₂]</td>
<td>Li(im)[CH₂(mim)₂]</td>
</tr>
<tr>
<td>FW</td>
<td>272.24</td>
<td>250.24</td>
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<td>P2₁2₁2₁</td>
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<td>9.23(4)</td>
</tr>
<tr>
<td>b, Å</td>
<td>8.9721(8)</td>
<td>9.46(4)</td>
</tr>
<tr>
<td>c, Å</td>
<td>15.304(3)</td>
<td>14.73(6)</td>
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<td>90</td>
</tr>
<tr>
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<td>90</td>
</tr>
<tr>
<td>V, Å³</td>
<td>1066.9(2)</td>
<td>1287(10)</td>
</tr>
<tr>
<td>Z</td>
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<td>4</td>
</tr>
<tr>
<td>d_calcd, g cm⁻³</td>
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<td>0.778</td>
</tr>
<tr>
<td>R₁, wR₂</td>
<td>0.0300, 0.0680</td>
<td>0.0540, 0.1312</td>
</tr>
<tr>
<td>net</td>
<td>qzd</td>
<td>dia</td>
</tr>
</tbody>
</table>

[a]  bim = benzimidazolyl; im = imidazolyl; mim = 2-methylimidazolyl.

[b]  Crystal structures were solved from single-crystal data collected at 150 K on a SMART CCD diffractometer with MoKα. R₁ = \( \sum ||F_o|| - |F_c|| / \sum |F_o| \) and \( wR₂ = (\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2)^{1/2} \) with \( F_o > 4.0\sigma(F) \)

[c]  For definitions of three-letter abbreviation, see Reticular Chemistry Structure Resource (http://rcsr.anu.edu.au/).
4.3 Results and Discussion

4.3.1 Structure

The crystal structures of both compounds have been solved by single-crystal X-ray diffraction (Table 4.1). In both compounds, lithium sites are tetrahedrally coordinated with four N atoms from different imidazole rings (Figure 4.2). Specifically, the lithium ion is connected to two negatively charged benzimidazole ligands and two neutral bis(imidazolyl)methane ligands in MVLIF-1, while the lithium ion is connected by two negatively charged imidazole ligands and two neutral bis(2-methyl-imidazolyl)methane ligands in MVLIF-2. Such a bonding mode by mixed charge-complementary ligands follows exactly our original synthetic strategy. However, an obvious difference between the two structures is that, in MVLIF-1, two neutral ligands attached to the same Li site are oriented away from each other, while in MVLIF-2, the two neutral ligands are oriented towards each other (Figure 4.2). In addition, unlike the typical case in which the

![Figure 4.2 Coordination environment of Li$^+$ in (a) MVLIF-1 and (b) MVLIF-2. (purple: Li; blue: N; black: C)](image-url)
M-N bond between the metal ion and imidazole is located within the imidazole plane, in MVLIF-1, the structure is slightly distorted with one of the Li-N bonds located off the benzimidazole plane.

Figure 4.3 Framework structures of (a) MVLIF-1 and (b) MVLIF-2. (purple tetrahedron: LiN4; blue: N; black: C)
Similar to ZIFs and BIFs, the steric effects of substituent groups exhibit strong structure-directing effects. Through two unique combinations between neutral and charged ligands (bim and CH$_2$(im)$_2$ in MVLIF-1 vs. im and CH$_2$(mim)$_2$ in MVLIF-2), two totally different chiral frameworks (Figure 4.3) were obtained. The topological analysis shows that MVLIF-1 adopts the quartz dual (qzd) topology (Figure 4.4a), which is an intrinsically chiral net. In comparison, MVLIF-2 adopts the single diamond (dia) topology (Figure 4.4b), also with a chiral symmetry.

**Figure 4.4** Illustration of the framework topologies: (a) qzd net in MVLIF-1 and (b) dia net in MVLIF-2 (The green sticks represent the neutral L1 ligands and red sticks represent the negatively charged L2 ligands).

The structure of MVLIF-1 can be understood as parallel helical chains of Li(bim) inter-connected by the neutral bis(imidazolyl)methane (Figure 4.5). In MVLIF-2, zig-zag
chains of Li(im) are further bridged by the neutral bis(2-methyl-imidazolyl)methane ligand into the 3D framework.

4.3.2 Synthesis

The typical synthesis of the LiL₁L₂ compounds was performed by solvothermal reactions of excess Li₂S and equal molar amount of both types of ligands (HIm type and CH₂(Im)₂ type) in acetonitrile. Keeping the reaction mixture at 120 °C for 48 hours leads to the formation of high quality colorless crystals for single-crystal X-ray diffraction measurement. The purity of the compounds was confirmed by the powder XRD patterns. In fact, the synthesis of such lithium compounds has proven to be challenging, mainly in two aspects: (1) the choice of the solvent and (2) the choice of the lithium source. As is well known, lithium has a strong affinity with oxygen-containing species. However, there are only Li-N bonds in our target structures, whose affinity is weaker than that between lithium and oxygen. Thus we chose acetonitrile as the solvent to eliminate the strong...
solvation effect that is likely with oxygen-containing solvents such as amides, alcohols, or water. Similarly, we used Li$_2$S as the metal source to exclude possible affect from oxygen-containing anions. In addition, it is essential to maintain the basic environment by using excess Li$_2$S to fully deprotonate the imidazole ligand during the synthesis. Other salts such as LiNO$_3$ have been found ineffective.

4.3.3 Gas Sorption Properties

The gas sorption properties of both compounds have also been studied, and both compounds showed the ability to reversibly adsorb hydrogen gas (Figure 4.6). The volumetric uptake capacity is 31.4 cm$^3$/cm$^3$ and 39.4 cm$^3$/cm$^3$ at 1 atm and 77 K for MVLIF-1 and MVLIF-2, respectively. No significant N$_2$ adsorption was observed, likely

![Figure 4.6](image.png)

**Figure 4.6** H$_2$ uptake of MVLIF-1 and MVLIF-2 at 1 atm and 77 K.
due to the limitation of the pore size. To further enhance the gas sorption properties, the creation of porous materials with larger pore size and greater pore volume would be beneficial. The successful synthesis of MVLIF-1 and MVLIF-2 certainly demonstrates the feasibility for the synthesis of other members of the MVLIF family through the judicious choice of L1 and L2 ligands.

4.4 Conclusion

In conclusion, two types of 3D imidazolate frameworks containing uninodal tetrahedrally coordinated lithium ions have been successfully realized by applying a mixed valent ligand synthetic route. The framework densities of MVLIF-1 and MVLIF-2 reach as low as 0.766 g/cm$^3$ and 0.778 g/cm$^3$, respectively, which is a direct result of extremely lightweight elements (Li, C and N) used in the synthesis strategy. Both compounds can reversibly adsorb H$_2$. This work demonstrates a general method for constructing the mixed valent ligand lithium imidazolate frameworks. Further optimization in the ligand design could result in a family of more open architectures that could lead to promising gas sorption properties.

4.5 References


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Chapter 5

Selective Ion Exchange of Organic Anions upon a Series of Nanogated Isoreticular Cationic Metal-Organic Frameworks

5.1 Introduction

Metal organic frameworks have been recognized as a perfect platform for host-guest chemistry, which includes gas storage, ion exchange, and separation. The pore size of metal organic frameworks varies from one angstrom to a few nanometers, making it available as a host to incorporate species ranging from small gas molecules to small organic molecules, metal complexes or even large organic species or inorganic polyanions. While the adsorption and separation of gas molecules and small organic molecules (limited to one benzene ring, Mw < 100 Da) has been extensively studied, the incorporation of more bulky molecules (Mw up to 1000 Da) has been rarely reported and is even less for separation. Separation of organic species at this level has special significance in biotechnology and pharmaceutical industries, for example the separation of nucleotides.

However, most of the reported separation processes are based on the interaction between neutral framework and neutral guests. Although some cationic or anionic dye molecules have been reported to be separated by neutral frameworks, the interaction between the host and guests has not been discussed thoroughly, though it seems more
likely to be intermolecular van der waals interaction. None of the separation process is based on coulomb interaction between charged species.

Ion exchange chromatography and ion exchange solid phase extraction based on ion exchange resins have been proved to be a powerful tool for the separation of proteins, nucleotides and amino acids. The stronger coulomb interaction between the stationary phase and mobile phase gave additional speed and sensitivity to the separation process, compared to the hydrophobic, hydrophilic interaction used in conventional HPLC. Therefore, there is no doubt that the ion exchange based separation will also work properly on the charged MOF platform in principle. In addition, the structural characteristics of MOFs such as the nanosized pore structure, precisely defined pore and window sizes (nonetheless tunable with variable functionality) can result in some interesting properties such as size exclusive effect that can’t be achieved by regular ion exchange resins. Thus for some special applications, MOFs may provide extra opportunity and can possibly make the separation process more efficient and easier.

There are a lot of examples of the synthesis of charged metal organic frameworks (MOFs). However, it’s quite surprising that there is no report so far on the ion exchanged based separation upon these charged MOFs. Although ion exchange performed upon charged metal organic frameworks has been reported for many times, however, most of the studies have focused on the capture of special metal ions or for improved gas sorption capability.

In the ion exchange based separation, both anionic and cationic stationary phases are desired for different analytes. In specific, the separation of organic anions is specially
interesting because they are related to nucleotides and amino acids, whose backbones are usually anionic under some pH range. However, we noticed that among the many reported charged MOFs, the amount of cationic frameworks is far less than the amount of anionic frameworks, which has been also observed for crystalline porous materials other than MOFs such as zeollites. Although some cationic MOFs have been reported occasionally, most of the structures are relatively dense and only able to exchange small inorganic anions such as $\text{Mn}_2\text{O}_7$.\textsuperscript{13} A good strategy is needed for construction of cationic frameworks.

To realize the separation of organic anions, cationic mofs that has considerable void space and suitable window size are required, plus stability is another important consideration. One of the best strategies to achieve this goal is to introduce an intrinsic positively charged SBU into framework design. $\text{In}_3\text{O(CO}_2\text{)}_6$ trimer cluster is one of the rare examples in metal organic frameworks that are intrinsic positive (in comparison to the neutral SBU such as $\text{Zn}_4\text{O(CO}_2\text{)}_6$, $\text{Cu}_2\text{(CO}_2\text{)}_4$, $\text{Ni}_3$(OH)(CO\textsuperscript{2})\textsubscript{6}). Many interesting structures based on metal trimer clusters have been reported,\textsuperscript{15} however, indium trimer based cationic structure is rare and only reported once by Eddaoudi in 2007.\textsuperscript{16} Although several other structures also contain indium trimer unit, they are not cationic for the whole frameworks.\textsuperscript{17-18} Recently a high connected structure prototype synthesized through mixed ligand route that contains Ni trimer units was initialed by Xiaoming Chen group and later an isostructure was reported by us.\textsuperscript{19,20} This structure has large void space yet quite stable, partially due to the triangle containing topology. While the original Ni based structure is neutral, the In trimer based alternatives could be positively charged.
With the above thought in mind, we aim to synthesize a series of indium trimer based cationic MOFs.

Here we reported a series of isoreticular indium trimer based MOFs, and ion exchange of dye molecules has been systematically studied upon this platform, which unveil the potential of such materials as an excellent candidate for separation of organic molecules below 1000 Da.

5.2 Experimental Section

5.2.1 Solvothermal Synthesis

All reagent and solvent were commercially available and used as supplied without further purification. The In MOFs were synthesized via traditional solvothermal methods by combining two different types of ditopic ligands, the isonicotinic acid type ligand ($\text{L}_1$, including ina and pba) and the 1,4-bdc type ligand ($\text{L}_2$, including bdc, NH$_2$-bdc, Br-bdc, ndc, bpdc) in a 2:1 molar ratio, which reflects the molar ratio of the two ligands in the final structure. By applying different $\text{L}_1$ and $\text{L}_2$ ligands, six isostructured ITCs have been obtained. In a typical synthesis, 0.2 mmol In(NO$_3$)$_3$·H$_2$O, 0.2 mmol pba and 0.1 mmol bpdc was dissolved and mixed in 2.0 g of dimethylacetamide (DMA) solvent, and heated under 90 °C after stirring. After 3 days, colorless truncated cube like crystals were obtained in high yield and purity. Compared to the synthetic condition of Ni based structures reported previously, the solvothermal temperature of the In MOF is much lower. Actually, in this work, we found that the Ni based structures can be also synthesized under 120 °C in good yield.
Synthesis of $[\text{In}_3\text{O}(\text{ina})_3(\text{bdc})_{1.5}](\text{NO}_3)$: In a 20 ml glass vial, 65.4 mg (0.1 mmol) of $\text{In(NO}_3)_3\cdot\text{H}_2\text{O}$, 23.0 mg isonicotinic acid (ina, 0.2 mmol) and 18.0 mg 1,4-benzenedicarboxylic acid (bdc, 0.1 mmol) was dissolved in 2.0 g of DMF solution. After the mixture was stirred for 20 minutes, the vial was sealed and placed in a 120 °C oven for 4 days. Pure colorless truncated cube like crystals was obtained after cooling to room temperature. The yield was about 81% based on the metal. The phase purity was identified by the powder X-ray diffraction.

Synthesis of $[\text{In}_3\text{O}(\text{pba})_3(\text{bdc})_{1.5}](\text{NO}_3)$: In a 20 ml glass vial, 33.4 mg (0.1 mmol) of $\text{In(NO}_3)_3\cdot\text{H}_2\text{O}$, 20.0 mg 4-(4-pyridyl)benzoic acid (pba, 0.1 mmol) and 8.0 mg 1,4-benzenedicarboxylic acid (bdc, 0.05 mmol) was dissolved in 2.0 g of DMA solution. After the mixture was stirred for 20 minutes, the vial was sealed and placed in a 90 °C oven for 4 days. Pure colorless truncated cube like crystals was obtained after cooling to room temperature. The yield was about 90% based on the metal.

Synthesis of $[\text{In}_3\text{O}(\text{pba})_3(\text{NH}_2\text{-bdc})_{1.5}](\text{NO}_3)$: The synthesis is similar to the synthesis of ITC-2 except the 1,4-benzenedicarboxylic acid (bdc) is replaced by 2-amino-1,4-benzenedicarboxylic acid (NH$_2$-bdc).

Synthesis of $[\text{In}_3\text{O}(\text{pba})_3(\text{Br-bdc})_{1.5}](\text{NO}_3)$: The synthesis is similar to the synthesis of ITC-2 except the 1,4-benzenedicarboxylic acid (bdc) is replaced by 2-bromo-1,4-benzenedicarboxylic acid (Br-bdc).

Synthesis of $[\text{In}_3\text{O}(\text{pba})_3(\text{ndc})_{1.5}](\text{NO}_3)$: In a 20 ml glass vial, 32.1 mg (0.1 mmol) of $\text{In(NO}_3)_3\cdot\text{H}_2\text{O}$, 20.0 mg 4-(4-pyridyl)benzoic acid (pba, 0.1 mmol) and 11.0 mg 2,6-naphthalenedicarboxylic acid (ndc, 0.05 mmol) was dissolved in 2.0 g of DMA solution.
solution. After the mixture was stirred for 20 minutes, the vial was sealed and placed in a 120 °C oven for 4 days. Pure colorless truncated cube like crystals was obtained after cooling to room temperature. The yield was about 83% based on the metal.

**Synthesis of [In₃O(pba)₃(bpdc)₁.₅](NO₃):** In a 20 ml glass vial, 31.8 mg (0.1 mmol) of In(NO₃)₃·H₂O, 20.0 mg 4-(4-pyridyl)benzoic acid (pba, 0.1 mmol) and 14.0 mg biphenyldicarboxylic acid (bpdc, 0.05 mmol) was dissolved in 1.0 g of DMA solution. After the mixture was stirred for 20 minutes, the vial was sealed and placed in a 90 °C oven for 5 days. Pure colorless truncated cube like crystals was obtained after cooling to room temperature. The yield was about 86% based on the metal.

**Synthesis of [In₃O(bpdc)₃(H₂O)₃](NO₃):** In a 20 ml glass vial, 71 mg of In(NO₃)₃·H₂O and 34.0 mg 4,4’-biphenyldicarboxylic acid was dissolved in 1.5 g of DMA solution. After the mixture was stirred for 20 minutes, the vial was sealed and placed in a 120 °C oven for one week. Pure colorless prism like crystals was obtained after cooling to room temperature. The yield was about 90% based on the metal.

**Synthesis of [In₃O(bdc)₃(H₂O)₃](NO₃):** The synthesis is similar to the synthesis of ITC-5 except the 4,4’-biphenyldicarboxylic acid (bpdc) is replaced by 1,4-benzene-dicarboxylic acid (bdc).

**Synthesis of [Ni²⁺Ni³⁺(µ₃-OH)(pba)₃(ndc)₁.₅]⁺(solvent):** Small modification was made compared to the previously reported procedure. In a 20 ml glass vial, 30 mg Ni(NO₃)₂·6H₂O was dissolved in 4.0 g of DMA and 1.0 g of methanol, then 20 mg of 4-(4-pyridyl)benzoic acid (pba, 0.1 mmol) and 11 mg of 2,6-naphthalenedicarboxylic acid (ndc, 0.05 mmol) was added and the mixture was stirred under room temperature for
20 minutes. Then the vial was sealed and heated under 120 °C for 4 days. Pure green cube like crystals were obtained.

**Synthesis of [Ni\textsuperscript{II}2Ni\textsuperscript{III}(µ\textsubscript{3}-OH)(pba)\textsubscript{3}(bdc)\textsubscript{1.5}]\textsuperscript{-}(solvent):** In a 20 ml glass vial, 30 mg Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O was dissolved in 4.0 g of DMA and 1.0 g of methanol, then 20 mg of 4-(4-pyridyl)benzoic acid (pba, 0.1 mmol) and 8 mg of 1,4-benzenedicarboxylic acid (bdc, 0.05 mmol) was added and the mixture was stirred under room temperature for 20 minutes. Then the vial was sealed and heated under 120 °C for 4 days. Pure green cube like crystals were obtained.

5.2.2 Powder X-ray Diffraction

X-ray powder diffraction experiments were performed on a Bruker D8 Advance powder diffractometer, equipped with a Sol-X detector using Cu K\textsubscript{α1} radiation (\(\lambda = 1.5406 \text{ Å}\)). The simulated XRD pattern was calculated from the structure data using the CSD Mercury 2.4 software.

5.2.3 Thermal Analysis

Thermogravimetric (TGA) analysis were carried out on a TA-Q500 thermal analyzer by TA instrument with a heating rate of 10°C/min. Nitrogen (60 ml/min) flow was applied during the analyses.

5.2.4 Gas Sorption Measurements

ITC-3 and ITC-4 were picked up for gas sorption study. The as-synthesized samples were filtered and washed by DMA and soaked in methylene chloride for about 1 week. Then the powder was filtered again then evacuated (10\textsuperscript{-3} torr) at 60 °C for 10 hours. Gas sorption experiments were carried out on a Micromeritics ASAP 2020 surface area
and pore size analyzer. N\textsubscript{2} and H\textsubscript{2} sorption was performed under 77K and CO\textsubscript{2} sorption was performed under 273K. For the sample after loading of dye through ion exchange, the same procedure for treatment was performed.

### 5.2.5 Single-Crystal Crystallography

Single-crystal X-ray analysis was performed on a Bruker Smart APEX II CCD area diffractometer with nitrogen-flow temperature controller using graphite-monochromated Mo K\alpha radiation (\( \lambda = 0.71073 \, \text{Å} \)), operating in the \( \omega \) and \( \varphi \) scan mode. Raw data collection and refinement were done using SMART. Data reduction was performed using SAINT\textsuperscript{+} and corrected for Lorentz and polarization effects. The SADABS program was used for absorption correction. The structure was solved by direct methods, and the structure refinements were based on \(|F^2|\) with anisotropic displacement parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions. All crystallographic calculations were conducted with the SHELXTL software suites. The crystallographic data and the structural refinement parameters were summarized in Table 5.1.

### 5.2.6 Ion Exchange Experiments

ITC-1 to ITC-4 were picked up for ion exchange study. DMF are used as the solvent of anionic dyes for all the ion exchange experiments. In most studies, the MOF:dye molar ratio is kept 20:1. For the capacity experiments, the MOF:dye ratio is kept 2:1. All ion exchange experiments were performed in a closed vial by keeping the system still. The upper clear solution is picked up for absorbance measurements. For the recycle experiments, the ion exchange process can be accelerated by stirring.
Table 5.1 A summary of crystal data and structural refinement results of ITCs[^a].

<table>
<thead>
<tr>
<th>Code</th>
<th>Formula[^b][^c]</th>
<th>sp. gr.</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
<th>R(F)[^d]</th>
<th>Mw (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITC-1</td>
<td><a href="NO%E2%82%83">In₃O(ina)₃(bdc)₁₅</a></td>
<td>I-43m</td>
<td>22.1436(5)</td>
<td>22.1436(5)</td>
<td>10857.87(4)</td>
<td>0.0359</td>
<td>1034.95</td>
</tr>
<tr>
<td>ITC-2</td>
<td><a href="NO%E2%82%83">In₃O(pba)₃(bdc)₁₅</a></td>
<td>I23</td>
<td>27.7223(4)</td>
<td>27.7223(4)</td>
<td>21305.30(5)</td>
<td>0.0925</td>
<td>1263.24</td>
</tr>
<tr>
<td>ITC-2NH₂</td>
<td><a href="NO%E2%82%83">In₃O(pba)₃(NH₂-bdc)₁₅</a></td>
<td>I-43m</td>
<td>27.7889(6)</td>
<td>27.7889(6)</td>
<td>21346.14(80)</td>
<td>0.0641</td>
<td>1285.77</td>
</tr>
<tr>
<td>ITC-2Br</td>
<td><a href="NO%E2%82%83">In₃O(pba)₃(Br-bdc)₁₅</a></td>
<td>I-43m</td>
<td>27.66(3)</td>
<td>27.66(3)</td>
<td>21161.99(12)</td>
<td>N/A[^e]</td>
<td>1381.58</td>
</tr>
<tr>
<td>ITC-3</td>
<td><a href="NO%E2%82%83">In₃O(pba)₃(ndc)₁₅</a></td>
<td>I-4</td>
<td>29.0505(1)</td>
<td>28.7967(1)</td>
<td>24302.45(2)</td>
<td>0.1250</td>
<td>1338.33</td>
</tr>
<tr>
<td>ITC-4</td>
<td><a href="NO%E2%82%83">In₃O(pba)₃(bpdc)₁₅</a></td>
<td>I-43m</td>
<td>30.0772(5)</td>
<td>30.0772(5)</td>
<td>27208.98(8)</td>
<td>0.0551</td>
<td>1377.39</td>
</tr>
<tr>
<td>ITC-5</td>
<td><a href="NO%E2%82%83">In₃O(bpdc)₃(H₂O)₃</a></td>
<td>P6₃/mmc</td>
<td>18.1359(4)</td>
<td>25.3442(1)</td>
<td>7219.17(39)</td>
<td>0.1320</td>
<td>1135.15</td>
</tr>
<tr>
<td>ITC-6</td>
<td><a href="NO%E2%82%83">In₃O(bdc)₃(H₂O)₃</a></td>
<td>P6₃/mmc</td>
<td>15.99(2)</td>
<td>16.70(6)</td>
<td>3697.80(12)</td>
<td>N/A[^e]</td>
<td>906.86</td>
</tr>
</tbody>
</table>

[^a]: ITCs = indium trimer based cationic frameworks
[^b]: ina = isonicotinic acid
[^c]: pba = 4-(pyridyl)benzoic acid
[^d]: bdc = 1,4-bezenedicarboxylic acid (or terephthalic acid)
[^e]: NH₂-bdc = 2-amino-1,4-bezenedicarboxylic acid (or 2-aminiterephthalic acid)
Br-bdc = 2-bromo-1,4-bezenedicarboxylic acid (or 2-bromoterephthalic acid)

ndc = 2,6-naphthalenedicarboxylic acid

bpdc = 4,4'-biphenyldicarboxylic acid.

[c] The nitrate counter anions in all structures are disordered from the structure refinement data and are arbitrarily added according to the charge calculation.

d] Crystal structures were solved from single-crystal data collected at 150 K on a SMART CCD diffractometer with MoKα.

\[ R(F) = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \] with \( F_o > 4.0\sigma(F) \)

[e] The structure of ITC-2Br and ITC-6 are obtained by comparing the powder XRD with the simulation data. Single crystal data have not been collected for these structures.
5.3 Results and Discussion

5.3.1 Structures of ITC-1 to ITC-4

The structures of ITCs have been determined by single crystal X-ray diffraction. All the ITCs contain only one type of SBU, which is a classical indium trimer cluster. However, depending on the connectivity of the trimer SBU and the topology of the entire framework, the eight structures can be divided into two categories. The first six structures from ITC-1 to ITC-4 belong to the first category. Interestingly, although the organic contents and unit cell parameters varies, the six structures are isoreticular which have the same framework connectivity. Except for ITC-3, all the other five structures have cubic lattices, but the unit cell and space group differs with different ligand combinations.

5.3.1.1 Nine Connected Indium Trimer SBU

The general formula for the ITC-1 to ITC-4 series can be written as [In$_3$O(L$_1$)$_3$(L$_2$)$_{1.5}$](NO$_3$). For each trimer cluster, half of the six carboxyl groups are from L$_1$ and the other half are from L$_2$ ligand and the same ligands are arranged on one side of the plane of indium trimer. In addition, the axial position for the indium metal is capped by the pyridyl group from L$_1$, making the trimer cluster nine connected. Interestingly, such a nine connection is rarely seen among all trimer clusters and has never been observed for indium based frameworks. While there are a lot of examples for six connected trimer based frameworks, higher connected (7-, 8- and 9-connected) trimer cluster are relatively less reported. Recently, a mesoporous framework with eight connected indium trimers was reported by Prof. Xu. However, structures based on the nine connected indium trimer has never been seen prior to this work. Interestingly, the
above mentioned eight connected framework is also constructed with the combination of \( L_1 \) and \( L_2 \) type ligand, yet in a 1:1 molar ratio. The different connection number of the node eventually led to a totally different structure. The reason for the structural difference may lie in the way of ligand combination. In their case, it features a short \( L_1 \) ligand (isonicotinic acid) and a long \( L_2 \) ligand (4,4’-azodibenzoic acid), while in our case, the lengths of \( L_1 \) and \( L_2 \) ligands are much closer, although there is considerable flexibility in the length range for \( L_2 \) when pba was used for \( L_1 \).

It’s quite important to point out that in this structure the center of the indium trimer is a \( \mu_3-O \), which is the same to some previously reported trivalent metal trimers. Thus the total charge for this trimer cluster is +1. Therefore the whole framework is
cationic and the positive charge is balanced by the nitrate anion guests located inside the channel, making the whole materials neutral. Since each unit cell contains eight trimer clusters, the charge density is +8 per cell for all six structures but the volumetric charge density varies due to the different unit cell parameter. In comparison, a previously reported nine connected framework based on Ni trimer (Ni^{II}$_2$Ni^{III}(μ$_3$-OH)) is neutral because it contains a mixed valent Ni and a μ$_3$-OH in the center instead of the μ$_3$-O. The oxidation state of Ni was calculated from the bond valence method.

**Figure 5.1** Topology illustration of the nine connected ncb net in ITC-1 to ITC-4 and a comparison of their projections on [001] plane.
5.3.1.2 Framework Topology

The geometry feature of the nine connected trimer cluster leads to the formation of the ncb net, which is the simplest (uninodal, two kinds of edges, high symmetry $I-43m$) nine connected topology type and has been reported only in Ni based MOFs. As is illustrated in Figure 5.1, the unique gold dots represent the indium trimers, the purple sticks represent the $L_1$ ligand which contains a carboxylate and a pyridine functional groups, the yellow sticks represent the dicarboxylate type $L_2$ ligands. Interestingly, although the ITC-1 to ITC-4 have the same network connectivity, their shapes are a little different. With the length ratio between $L_1$ and $L_2$ decreasing, the square shaped windows of the channel get more twisted viewed from the [001] projection.

The structure constitutes of three types of cages, as illustrated by Figure 5.2, which were named cage I, II and III. Cage I is a distorted cube like cage constructed from

![Figure 5.2 Three types of cages in the structure and their compositions.](image-url)
eight trimers, twelve $L_1$ and four $L_2$, cage II is an equilateral tetrahedron constructed from four trimers and six $L_2$, while cage III is an irregular tetrahedron constructed from four trimers, three $L_1$ and three $L_2$, respectively. Obviously, type I cage has the largest void space among all three. The numbers of three types of cages are in a 3:1:4 ratio throughout the whole framework. Cage I is interconnected with each other and form a

![Image](image.png)

**Figure 5.3** The tiling diagram of ITC-n, the yellow tiles represent the NbO channel constructed from type I cage, green and purple tiles represent cage II and cage III, respectively. The right diagram is a picture after removal of the NbO channel.

NbO type 3D channel system, which is responsible for the largest portion of the void space within the framework. Each type II cage is surrounded by four type III cages and the 5-tetrahedron assemblies are arranged in a body center cubic feature and only connected with each other by sharing the corner.

Accordingly, the structure also contains three types of windows, which were named window I, II and III. As is illustrated in Figure 5.4, Type I window is in a square
like shape built by four trimer clusters and four $L_1$ ligand, type II window is a triangle built by three trimer clusters and three $L_2$ ligand and type III is also a triangle shaped window which contains three trimer clusters, two $L_1$ ligands and one $L_2$ ligand.

5.3.1.3 Pore Analysis

To evaluate the accessibility of organic molecules into the voids of the frameworks, both window size and pore size are important parameters. The window size brings the gate effect and directly determines whether or not a guest can diffuse into the framework and the pore size represents the volume available for the guest and finally affects the capacity. Therefore, we have analyzed and summarized the dimensional information for both pores and windows for all six structures. The pore and window size listed in Table 5.2 are estimated from structural data by using the diamond structure.
Table 5.2  A summary of pore properties in ITCs.

<table>
<thead>
<tr>
<th>Code</th>
<th>Void Space</th>
<th>$d_{pI}$ (Å)</th>
<th>$d_{pII}$ (Å)</th>
<th>$d_{pIII}$ (Å)</th>
<th>$d_{wI}$ (Å)</th>
<th>$d_{wII}$ (Å)</th>
<th>$d_{wIII}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITC-1</td>
<td>53.7%</td>
<td>9.8</td>
<td>7.6</td>
<td>5.6</td>
<td>4.6</td>
<td>4.2</td>
<td>3.2</td>
</tr>
<tr>
<td>ITC-2</td>
<td>68.9%</td>
<td>13.7</td>
<td>7.6</td>
<td>6.6</td>
<td>8.5</td>
<td>4.4</td>
<td>4.2</td>
</tr>
<tr>
<td>ITC-2NH$_2$</td>
<td>66.2%</td>
<td>13.7</td>
<td>7.6</td>
<td>5.8</td>
<td>8.5</td>
<td>3.0</td>
<td>4.0</td>
</tr>
<tr>
<td>ITC-2Br</td>
<td>65.1%</td>
<td>13.7</td>
<td>7.6</td>
<td>5.8</td>
<td>8.5</td>
<td>2.8</td>
<td>4.1</td>
</tr>
<tr>
<td>ITC-3</td>
<td>68.5%</td>
<td>12.4</td>
<td>10.0</td>
<td>7.0</td>
<td>7.6</td>
<td>4.7</td>
<td>4.2</td>
</tr>
<tr>
<td>ITC-4</td>
<td>72.2%</td>
<td>15.4</td>
<td>11.4</td>
<td>9.0</td>
<td>8.5</td>
<td>7.4</td>
<td>5.4</td>
</tr>
</tbody>
</table>
Figure 5.5 The dimension of type I windows in a square shaped model.
software using a standard method. When the Van der Waals radius of all the atoms (including hydrogen) of the frameworks are considered, the diameters of the largest sphere (colored balls in Figure 5.2 & Figure 5.4) that can fit in the voids or windows are picked up as a measure of the pore and window size. Obviously, such isotropic model has not considered the shape of the cages and windows. For example, the largest dimension in the square shaped window in this structure should be comparable to the diagonal length, which is actually much longer than the diameter of the sphere. Thus, a more accurate method that takes the shape into consideration is also used to estimate the maximum dimension for window I.

From the table, we can see that the length of $L_1$ will largely affect the size of type I cage and type I window. Due to the shorter isonicotinic acid, the sizes of cage I and window I are obviously smaller than those for the other five. However, minor difference still exists between the other five structures, although in which the same $L_1$ ligand is used. The above difference may come from the different degree of distortion of cage I due to the different symmetry and length of the $L_2$ ligand. Similarly, the length of $L_2$ will contribute to the size for cage II and window II. The above relationship can be easily understood from the compositions of cages and windows.

The void volume was calculated from the refined structural data by using the Platon routine. The percentage of voids ranges from 53.7% to 72.2% for ITC-n, which indicates that these structures are quite open and have great potential to incorporate considerable amount of guests from the environment.

### 5.3.2 Structures of ITC-5 and ITC-6
Figure 5.6 The connection between adjacent clusters in ITC-6 (a) and ITC-5 (b); the (001) and (100) view of the structure and 1D channel in ITC-6 (c, e) and ITC-5 (d, f). The H₂O molecules capped on axial positions of indium trimers have been omitted.
Although ITC-5 and ITC-6 also feature the same indium trimer SBU, the trimer clusters in these two structures are six connected, different from the nine connected structure mentioned above (Figure 5.6). The three axial positions are terminated by water molecules, which can be potentially removed under appropriate treatment. Also both structures make use of a single dicarboxylate ligand instead of combining two different ligands into one compound. ITC-5 and ITC-6 are isostructures which exhibit a hexagonal symmetry. The framework topology is coded acs in the RCSR database, which is a structure analogue of MIL-88, which are a series of chromium trimer based structures. The general formula for the two isostructures can be written as \([\text{In}_3\text{O}(\text{L})_3(\text{H}_2\text{O})_3](\text{NO}_3)\). Thus the two structures are also cationic frameworks with nitrate counter ion in the channel. Both two structures have large void space, especially ITC-5 has achieved 79.4% calculated from the Platon program, which is even larger than the ITC-4 mentioned before. These two structures have shown cylinder shaped 1D channel with diameter of 12.4 Å and 10.0 Å, respectively, which are also possible to allow the access of many large sized molecules. In addition, such MIL-88 type structures have been found to have solvent depending large swelling effect. These effects may be applicable to ITC-5 and ITC-6 too.

### 5.3.3 Synthesis

ITC-1 to ITC-4 were synthesized via traditional solvothermal methods by combining two different types of ditopic ligands, the isonicotinic acid type ligand (L1, including ina and pba) and the 1,4-bdc type ligand (L2, including bdc, NH2-bdc, Br-bdc, ndc, bpdc) in a 2:1 molar ratio, which reflects the molar ratio of the two ligands in the
final structure. By applying different \textbf{L1} and \textbf{L2} ligands, six isostructured ITCs have been obtained (scheme 1). In a typical synthesis, 0.2 mmol In(NO$_3$)$_3$·H$_2$O, 0.2 mmol pba and 0.1 mmol bpdc was dissolved and mixed in 2.0 g of dimethylacetamide (DMA) solvent, and heated under 90 °C after stirring. After 3 days, colorless truncated cube like crystals were obtained in high yield and purity. Compared to the synthetic condition of Ni based structures reported previously, the solvothermal temperature of the In MOF is much lower. Actually, in this work, we found that the Ni based structures can be also synthesized under 120 °C in good yield.

\textbf{5.3.4 Gas Sorption Properties}

The N$_2$ gas sorption properties of the ITC-4 have been studied (Figure 5.7). The Langmuir and BET surface area for ICF-4 have achieved 1697.50 and 1078.13 cm$^3$/g.

\begin{center}
\textbf{Figure 5.7} N$_2$ sorption isotherms for ITC-3 and ITC-4 at 1 atm and 77 K.
\end{center}
respectively, which is quite high. Importantly, it is found that the adsorbed amount for N\textsubscript{2} gas is quite related to the treatment of the compounds. The original DMA solvent adsorbed in the as-synthesized sample is nonvolatile and very difficult to remove under vacuum. Thus it is necessary to replace the DMA guests by treatment with a more volatile solvent. The best result is obtained by soaking the materials in methylene chloride for about one week prior to degas.

The ICFs have also shown the ability to reversibly adsorb H\textsubscript{2} and CO\textsubscript{2} (Figure 5.8). Under 1 atm and 77 K, the hydrogen uptake capacity for ITC-4 and ITC-3 is 137.3 cm\textsuperscript{3}/g and 77.8 cm\textsuperscript{3}/g, respectively. The carbon dioxide uptake capacity is about 60.0 cm\textsuperscript{3}/g and 40.8 cm\textsuperscript{3}/g under 1 atm and 273 K.

![Figure 5.8](image)

**Figure 5.8** The H\textsubscript{2} and CO\textsubscript{2} sorption isotherms of ITC-3 and ITC-4 under 77 K, 1 atm and 273 K, 1 atm, respectively.

### 5.3.5 Ion Exchange Study

#### 5.3.5.1 Experimental Design

Ion exchange is a process that is intrinsically dominated by the interactions
Table 5.3  A summary of charge and dimensions for organic guests.

<table>
<thead>
<tr>
<th>Abbr.</th>
<th>MLB</th>
<th>SDI</th>
<th>AO7</th>
<th>SY</th>
<th>NC</th>
<th>AR88</th>
<th>TOO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z^{[b]}$</td>
<td>+1</td>
<td>0</td>
<td>-1</td>
<td>-2</td>
<td>-3</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$M_w^{[c]}$</td>
<td>284.40</td>
<td>248.28</td>
<td>327.33</td>
<td>406.38</td>
<td>535.49</td>
<td>377.39</td>
<td>352.39</td>
</tr>
<tr>
<td>$x$ (Å)</td>
<td>4.00</td>
<td>3.68</td>
<td>5.44</td>
<td>5.44</td>
<td>5.44</td>
<td>5.44</td>
<td>6.48</td>
</tr>
<tr>
<td>$y$ (Å)</td>
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[a] The names listed in the table are abbreviations: MLB = Methylene Blue, SDI = Sudan I, TOO = Tropaeolin OO, AR88 = Acid Red 88, AO7 = Acid Orange 7, OG = Orange G, SY = Sunset Yellow FCF, P6R = Ponceau 6R, CS3B = Crosciein Scarlet
3B, CS7B = Crocein Scarlet 7B, AB1 = Acid Black 1, NC = New Coccine, MB = Methyl Blue.

[b] All the R-OH in the experimental conditions are considered in a deprotonated form.

c] Molecular weights only count the ionized form (for example, only R-SO$_3^-$ is calculated in a R-SO$_3$Na salt).

d] All the guest molecules are treated as rectangular cuboids. X, y, z are arranged in increasing order. X is usually the dimension perpendicular to the conjugation plane and Y is the smallest dimension in-plane.

between hosts and guests. Previously ion chromatography studies based on ion exchange resins have revealed that charge and size are two major factors for such separation. But it has never been proved on a MOF platform. In this work, we are going to explore the ion exchange behavior of organic anions upon the previously mentioned ITCs series of cationic frameworks. Based on the structural feature of MOFs, we are going to study the possibility of charge and size exclusive ion exchange, the dynamic difference depending on the charge and size of guests, as well as the size control by choosing applying MOFs with appropriate pore size. In addition, for practical use, the recyclability, stability and capacity are of equal importance, which will also be studied. To study the size or charge effect alone, other factors need to be identical. Thus, we have carefully chosen a series of azo type anionic dyes with same charge but different size and also of similar size but different charge. (Table 5.3)
5.3.5.2 Charge Exclusive Ion-exchange (anionic vs cationic guests)

Coulomb interaction plays a determining role in the ion exchange process. In principle, only anionic species are favored by the cationic framework. Thus we have designed an experiment to support this hypothesis. A light-orange solution containing a single anionic dye of orange G (OG) and a light blue solution containing a single cationic dye of methylene blue (MLB) was mixed together to give a green colored solution. Then half of this solution was transferred to a vial containing the cationic framework materials ITC-2 and the other half was kept as a reference. The color of the solution gradually turned blue from green and the original colorless crystal become orange (Figure 5.9). After about 2 hours, the color of the solution became blue, indicating the successful exchange of ions.

Figure 5.9 UV-vis absorbance change with time by immersing ITC-4 in the equimolar mixture of cationic MLB\(^+\) and anionic OG\(^2-\) solution.
days, the color of the upper solution looked exactly the same as the pure MLB solution. All the observation from the naked eyes was proved by the UV-vis spectroscopy. MLB and OG were chosen because they are close in size but opposite in charge, so the size effect can be excluded. Actually MLB has a even smaller cross section than OG but still can’t be incorporated into the framework.

5.3.5.3 Charge Exclusive Ion-exchange (cationic vs neutral hosts)

To further figure out the charge effect on ion exchange, we aimed to test the response of the same anionic molecule to MOF materials with different charges. However, to make the experimental results comparable, other factors caused by structural difference need to be excluded. Thus, materials with exactly the same structure but only different in charge are highly desired. Thanks to the beauty of metal organic frameworks, sometimes it is possible to obtain two materials with the same structure but different content. The possibility becomes even larger with trimer based structures since trimer cluster is the most versatile SBU that can incorporate a number of different metals.

Fortunately, there is a Ni based isostructure of ITC-3 reported, which is the prototype of such ncb net and we were able to synthesize a new Ni based isostructure of ITC-2. The two structures are named ITC-2Ni and ITC-3Ni. While the indium trimer based ITC-2 and ITC-3 are positively charged, the Ni based structures are neutral because they adopt a slightly different trimer core configuration in the formula of Ni$^{II}_2$Ni$^{III}$(OH)(CO$_2$)$_6$, which makes it neutral.

Anion exchange experiments were conducted by soaking the selected MOF materials in the OG solution in the MOF/dye molar ratio of 20:1. Then the exchange
process was monitored by the UV-vis spectroscopy. After ion exchange for 24 hours, the results have shown that for the cationic ITC-2 and ITC-3 samples, the dye has been exchanged into the MOF materials in different extent, while for the neutral charged ITC-2Ni and ITC-3Ni samples, the dye content in both solutions doesn’t decrease at all, which indicates no ion exchange happened (Figure 5.10a). Interestingly, the above observation is obviously different from the results recently reported by Prof. Xu, in which the charged guest have been absorbed into the Zn based neutral frameworks. However, the reason is not known.

**Figure 5.10** Dynamic curves of dye conc. vs. time showing the ion exchange process of (a) OG upon two cationic frameworks and two neutral frameworks with isostructures. (b) Similar sized dyes of different charge upon ITC-4.
5.3.5.4 Charge Dependent Ion-exchange Dynamics

A separation system is usually built on dynamic difference resulted from the different strength of interaction between host and guests. For an ion exchange based system, charge should play the primary role on the exchange dynamics since such system is dominated by coulomb interaction. To perform a systematic study on the charge effect on exchange dynamics, a series of azo type anionic dye were chosen as samples. These molecules have very similar azo based backbones with similar size and shape. The charge of the dye selected ranges from 0 to -3, with the addition of the anionic sulfonyl group. With the charge getting more negative, the molecular weight will increase. Anion exchange experiments have been performed by soaking ITC-4 in the dye solution. To exclude the concentration effect on ion-exchange dynamics and make the experimental results comparable to each other, the MOF/dye molar ratio was again kept 20:1. The dynamic curves were obtained from the absorbance data for the remaining dye content in the solution (Figure 5.10b). From the plot, we can see obvious difference in the trend of exchange dynamics classified by charge. For the neutral SDI, no exchange happened, for the -1 charged AO7 and AR88, although ion exchange happened, the kinetic is relatively slow and not complete. Actually, the exchange process is not complete until four days and decreases no more after that. In comparison with the -1 charged species, the ion exchange process for the -2 and -3 charged dyes is much faster and is complete within about 40 hours. Although the -3 charged NC has a faster dynamic than -2 charged OG and SY, the difference between them is not that obvious, most probably due to the decreased diffusion rate of NC resulted from its much larger molecular weight.
5.3.5.5 Size Dependent Ion-exchange Dynamics

Except the charge, size is the other key factor that dominates the separation process. However, the precise definition of the size effect seems to be difficult since it is a comprehensive concept involving the meaning of dimension, shape and molecular weight. Unfortunately, it is almost impossible to study the effect of the above three factors independently since the change of one factor is usually accompanied with the change of another. Thus our expectation is to observe the dynamic difference for the guest molecules with adequate difference, which will be enough for the separation purpose.
We have carefully chosen a series of anionic species that is of the same charge but different size (Table 5.3). The charge of the molecules should be kept the same to eliminate the influence from coulomb interaction. From the left to the right in Table 1, the molecular weight is gradually increasing and also is the dimension. The dimension of the organic molecules is estimated using a previously reported method that was applied to analyze simple aromatic compounds. In this method, the most and second minimum dimensions for molecular orientations are important to determine whether or not a guest can enter the channel of the host materials.

Exchange experiment was performed using ITC-4 as the host also in a 20:1 MOF to dye molar ratio. The dynamic plot was obtained by recording the absorbance of dye solution at different time and compared with initial value. From the plot, we can see that no exchange has occurred for the largest sized MB, while all the other five dyes have been exchanged in different extent (Figure 5.11a). This result is reasonable since the two minimum dimensions for MB is 13.89 Å and 14.35 Å, which are both larger than the dimension of the quasi-square shaped window for the ITC-4 (the diagonal length is about 13.2 Å). In contrast, the dimensions of the other five dye molecules are small enough to travel through the channels of the host. However, they have also shown difference from each other in exchange dynamics. Actually, OG, P6R, CS3B and CS7B are very close to each other in the two minimum dimensions due to their similar backbone structure. The major difference is in their third dimension and also the molecular weight. The general trend reveals that with increasing molecular weight, the exchange rate will decrease. The rate difference is obvious comparing OG and P6R with CS3B and CS7B because there is
a relatively large gap in their lengths in the z direction. The exchange process for AB1 is even slower since it is longer in the y dimension (12.69 Å), which is comparable with the size of type I window in ITC-4. In fact, in addition to the above experiments, the exchange dynamic of several anionic species of -1 charge have also been studied, which have also shown size dependent exchange rates (Figure 5.11b). The above results indicate that for a certain host, the exchange dynamic is highly dependent on the size of the guest molecules. In addition, large sized guests will be blocked by the host materials due to the size exclusion effect.

5.3.5.6 Size Exclusive Ion-exchange on Selected Host

Figure 5.12 The ion exchange dynamics of OG upon different cationic frameworks.
The above study has illustrated the size dependent effect of guest exchanged into a certain host. In practice, however, the ability to separate analytes in various range of size is desired and thus a variable choice for the hosts is expected for different applications. In addition, for a certain guest, both size-compatible and size-exclusive hosts are desired for different purposes. Fortunately, thanks to the extensive study in MOFs during the last decade, there is a bunch of choice of different structures with various pore and window sizes. Furthermore, the concept of reticular chemistry can often guide us to synthesize isostructures with different pore properties. In this study, we are lucky to obtain six isostructures, which indeed have shown different pore properties (Table 5.2). Based on these six different host materials, ion-exchange experiments have been performed by using the same guest molecule OG. The dynamic curves have shown that except ITC-1, OG can be exchanged into the channels of all other five hosts, yet in different rate (Figure 5.12). It’s not difficult to understand the above phenomena because the maximum dimension of the largest type I window in ITC-1 is about 7.24 Å, which is too small to incorporate the OG molecule, which has a second minimum dimension of 10.41 Å.

5.3.5.7 Dye Release and Recycle

The reversibility, stability and capacity are of great importance in real application. In general, ion-exchange is a reversible process. When excess amount of the substitution ion is added to the system, the original equilibrium will be shifted due to the concentration gradient. Thus the original guest ions will be released. The release experiment was performed after a complete ion exchange of OG into ITC-4 (in a 20:1
MOF:dye ratio), after which the mixture was centrifuged and the upper colorless solution was replaced by the same amount of DMF solution containing excess NaNO₃ (200:1 NO₃⁻:dye ratio). With the new solution kept still, it was observed from naked eyes that a rapid release of the orange colored dye occurs immediately after the addition of NaNO₃ solution. The dynamic curve from the UV-vis absorbance reveals the release process in a more precise way. The release rate decreases with increasing dye concentration in the solution. After about 12 hours, the OG is almost released completely from the host. At final stage, the color of the solution is as the same as the original OG solution and the powder at the bottom of the vials became white again. The recyclability was proved by

![Graphs and images showing release dynamics and recyclability](image)

**Figure 5.13** (a) The release dynamic of a fully loaded OG@ITC-4 upon addition of NaNO₃; (b) Recyclability by performing ten ion exchange-release cycle in a row; (c) Powder XRD pattern showing ITC-4 before and after ten ion exchange-release cycles.
performing ten of such exchange-release cycles in a row. After each release cycle, the host material was collected by centrifuge and a new portion of OG solution was added. The result shows that the either dye-exchange or dye-release process can be complete after ten cycles. The powder XRD measurement has further proved the structural completeness of the host material after ten cycles. All the above data indicate that the host material can be repeatedly used for ion exchange without any loss of its exchange ability.

5.3.5.8 Capacity

To estimate the capacity of the host material to dye molecules, ion exchange was performed in a much higher dye concentration, compared to the 20:1 MOF:dye ratio adopted in the above mentioned experiments. Again ITC-4 and OG was picked up as an

![Graph](image_url)

**Figure 5.14** N$_2$ sorption isotherms at 77 K for ITC-4 before and after ion exchange in a 2:1 MOF:OG mixture.
example, however, in a molar ratio of 2:1. Consider the -2 charge on the OG, it actually gives a 1:1 molar ratio of NO$_3^-$ to RSO$_3^-$. After ion exchange for 4 days, there’s no more obvious decrease on the absorbance of the dye solution, which indicate the system has reached the equilibrium and the ion exchange process can be thought as completion. By comparing the absorbance of solution before and after ion exchange, the percentage of NO$_3^-$ replaced can be calculated. The calculation result has shown that about 47.2% of NO$_3^-$ in the host materials has been replaced by OG. This value is very close to the 50% of NO$_3^-$ among all anions in the solution. Such result indicates that despite the much greater size of OG, the degree of OG exchanged into the host material is mainly related to the given molar ratio (or concentration ratio) between new and original guests, between which a dynamic equilibrium will be built. Thus, it’s expected that most of the NO$_3^-$ will be replaced when excess OG is applied. In another word, the host materials have a high capacity for the organic guest.

N$_2$ gas sorption measurements have been performed upon ITC-4 before and after ion exchange of OG (Figure 5.14). The Brunauer-Emmett-Teller (BET) surface area has been decreased from 1078.13 cm$^2$/g to 505.13 cm$^2$/g. This is in accordance with the reduced pore volume with the incorporation of OG into the pore system.

5.4 Conclusion

In conclusion, we have developed a strategy to synthesize cationic metal organic frameworks by introducing the intrinsic positively charged indium trimer clusters. Through solvothermal synthesis, eight examples of two structural categories have been obtained. Two structure types feature the nine connected and six connected indium trimer
cluster, respectively, and thus exhibit different framework topologies. Especially the nine connected indium trimer is the first example among all indium based MOFs. By using these cationic frameworks as host, a systematic study has been performed on the ion exchange behavior of a series of organic molecules upon the MOF platforms. It is found that the synthesized cationic MOFs have shown charge and size dependent ion exchange dynamics and for certain combinations, the ion exchange can be exclusive for cationic and neutral guests as well as anionic species with large size. Also the process is reversible and the host materials have shown great stability and capacity. The above phenomena have proved the feasibility of charged MOFs being applied in the ion exchange based separation process (such as ion chromatography) in the future.

5.5 References


(20) Jiang, G.; Wu, T.; Zheng, S-T; Zhao, X.; Lin, Q.; Bu, X.; Feng, P. Crystal
Chapter 6

Anionic Metal-Organic Frameworks Based on 4-Connected Indium Monomers

6.1 Introduction

In contrast to the previous chapter, where the indium trimer SBUs are used to construct a series of cationic metal-organic frameworks, herein we will depict a series of indium monomer based anionic frameworks. Different from many first row transition metals such as Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, which usually show a maximum coordination number of six, the bigger coordination sphere make it very common for indium to form a 8-coordinated 4-connected monomeric structure with formula of [In(CO$_2$)$_4$]$^-$, which is intrinsically negative. This building unit will essentially lead to the formation of anionic frameworks.\textsuperscript{1-8} Furthermore, such a 4-connected building unit is always attracting due to its close relation with zeolitic structures.\textsuperscript{9} However, the 4-connected nodes alone can’t promise the formation of zeolitic structures, both the geometry of linkers and the coordination environment about the metal center can affect the final structures.

Our early works and previous research by others indicate that by using of a linear or bent dicarboxylate ligand, although 4-connected 3D frameworks can be obtained, it’s very easy to form relatively dense topologies such as diamond or quartz nets.\textsuperscript{1,10} The dicarboxylate type linkers are advantageous to other type linkers (such as azoles used in ZIFs) in its length, which can leave considerable space between two structural nodes and
thus promise larger voids. Furthermore the isoreticular chemistry in principle allows short linkers to be replaced by longer linkers with same geometry, which will potentially improve the gas sorption properties.\textsuperscript{11} However in practice, the adopting of longer dicarboxylate bridges will often result in increased interpenetration, especially in the monomer based diamond type structures, which on the contrary will reduce the potential pore volume.

To obtain more open and non-interpenetrated frameworks, the bis-bidentate type linkers like imidazoledicarboxylic acid and pyrimidinedicarboxylic acid have been successfully applied to synthesize a series of zeolitic structures including the highly symmetric SOD and RHO topologies.\textsuperscript{4} Such bis-bidentate ligands have also been proved to be effective in building zeolitic frameworks with other monomeric metal nodes such as Cd\textsuperscript{2+}.\textsuperscript{12} Nevertheless, both the short linkage length and the heavy weight of imdc or pmdc ligand have limited the gas sorption properties.

To achieve a compromise between the above two strategies, a third strategy is proposed here. In contrast to the above studies, in which only one type of organic linkers is used, we assume that by combing a bis-bidentate type linker with a dicarboxylate type linker, novel structures will be obtained with both zeolitic structures and enough distance between adjacent structure nodes. The two types of linkers embedded will play their own roles simultaneously. The bis-bidentate linker will change the coordination environment about indium dramatically to facilitate the formation of zeolitic topologies, while dicarboxylate ligands are used for creating considerable distance between structural nodes and for performing reticular chemistry.
6.2 Experimental Section

6.2.1 Solvothermal Synthesis

All reagent and solvent were commercially available and used as supplied without further purification. Most compounds were synthesized using amide or its derivatives as solvents, mixed solvent were used as well. IMA-11 is synthesized in an aqueous system. Quaternary ammonium salts are used for synthesis of IMA-1 to IMA-6 as a counter ion in the anionic frameworks. While the structure is very sensitive to the cation when 3,3’-adb was used, the structure with 4,4’-adb is quite inert to the cation. Five different cations finally lead to the same structure (Scheme 6.1). IMA-8 to IMA-11 were obtained through a mixed ligand route. They are generally obtained by solvothermal or urothermal methods. Although crystals can form in many solvent combinations, however, high quality crystals for single crystallography were only obtained in limited systems. Different from the synthesis of IMA-1 to IMA-6, in which a exterior counter ion is introduced, the counter ion in IMA-7 to IMA-10 are from the in-situ decomposition of amide solvents.

(Et$_4$N)[In(4,4’-adb)$_2$] (IMA-1). In a 20 mL glass vial, 15.4 mg of In(NO$_3$)$_3$·H$_2$O, 27.3 mg of 4,4’-azodibenzoic acid (4,4’-adb) and 26.0 mg of Et$_4$NI was dissolved in 10.0 g DMF and stirred for 1 hour. Then the vial is sealed and placed still in a 120 °C oven for 8 days. Pure orange colored crystals with octahedron shape were obtained. The yield is about 76% based on metal. IMA-1 can be also synthesized by using different ammonium salts or even amines under similar conditions (see Scheme 6.1).
Scheme 6.1  Procedures for the synthesis of IMA-1 to IMA-6 and the different organic cations used.

\((\text{Me}_4\text{N})[\text{In}(3,3'\text{-adb})_2]\) (IMA-2). In a 20 mL glass vial, 16.0 mg of \(\text{In(NO}_3)_3\cdot\text{H}_2\text{O}\), 27.5 mg of 3,3'-azodibenzoic acid (3,3'-adb) and 12.5 mg of \(\text{Me}_4\text{NCI}\) was dissolved in
10.0 g DMF and stirred for 1 hour. Then the vial is sealed and placed still in a 120 °C oven for 3 days. Large deep yellow colored crystals with diamond-like shape were obtained. The yield is about 85% based on metal.

(\text{Et}_4\text{N})\text{[In(3,3'-adb)\textsubscript{2}] (IMA-3).} In a 20 mL glass vial, 15.4 mg of In(NO\textsubscript{3})\textsubscript{3}·H\textsubscript{2}O, 27.3 mg of 3,3'-azodibenzoic acid (3,3'-adb) and 26.5 mg of Et\textsubscript{4}NI was dissolved in 10.0 g DMF and stirred for 1 hour. Then the vial is sealed and placed still in a 120 °C oven for 3 days. Yellow plate-like crystals were obtained. The yield is about 82% based on metal.

(\text{choline})\text{[In(3,3'-adb)\textsubscript{2}] (IMA-4).} The synthesis is similar to the above procedures, but choline chloride is used instead of the tetraethylammonium iodide.

(\text{Pr}_4\text{N})\text{[In(3,3'-adb)\textsubscript{2}] (IMA-5).} In a 20 mL glass vial, 16.2 mg of In(NO\textsubscript{3})\textsubscript{3}·H\textsubscript{2}O, 27.6 mg of 3,3'-azodibenzoic acid (3,3'-adb) and 31.1 mg of Pr\textsubscript{4}NBr was dissolved in 10.0 g DMF and stirred for 1 hour. Then the vial is sealed and placed still in a 120 °C oven for 6 days. Colorless block crystals were obtained. The yield is about 92% based on metal.

(\text{Ph}_4\text{P})\text{[In(3,3'-adb)\textsubscript{2}] (IMA-6).} In a 20 mL glass vial, 16.1 mg of In(NO\textsubscript{3})\textsubscript{3}·H\textsubscript{2}O, 27.9 mg of 3,3'-azodibenzoic acid (3,3'-adb) and 40.8 mg of Ph\textsubscript{4}PBr was dissolved in 10.0 g DMF and stirred for 1 hour. Then the vial is sealed and placed still in a 120 °C oven for 3 days. Yellow colored hexagonal shaped prism crystals were obtained.

(\text{Et}_4\text{NH})\text{[In(NH}_2\text{-bdc)\textsubscript{2}] (IMA-7).} In a 20 mL glass vial, 67.9 mg of In(NO\textsubscript{3})\textsubscript{3}·H\textsubscript{2}O and 63 mg of 2-amino-benzene-dicarboxylic acid (NH\textsubscript{2}-bdc) was dissolved in 2 g DEF and 2g DMA and stirred for 20 minutes. Then the vial is sealed and placed still in a 120 °C oven for 9 days. Deep yellow diamond-like crystals were obtained.
**6.2.2 Powder X-ray Diffraction**

X-ray powder diffraction experiments were performed on a Bruker D8 Advance powder diffractometer, equipped with a Sol-X detector using Cu Kα₁ radiation (λ=
1.5406 Å). The simulated XRD pattern was calculated from the structure data using the CSD Mercury 2.4 software.

6.2.3  Thermal Analysis

Thermogravimetric (TGA) analysis was carried out on a TA-Q500 thermal analyzer by TA instrument under nitrogen flow. The flow rate of the nitrogen gas was controlled at about 60 milliliters per minute. The heating rate is 10°C/min from 30 °C to 900 °C.

6.2.4  Gas Sorption Measurements

The gas sorption of IMA-9 and IMA-1 was performed. The as-synthesized IMA-9 samples were filtered and washed by DEF and soaked in methylene chloride for 5 days. IMA-1 was treated with methanol. Then the powder was filtered again then evacuated (10⁻³ torr) at 60 °C for 12 hours. Gas sorption experiments were carried out on a Micromeritics ASAP 2010 surface area and pore size analyzer. N₂ and H₂ sorption was performed under 77K.

6.2.5  Single-Crystal Crystallography

Single-crystal X-ray analysis was performed on a Bruker Smart APEX II CCD area diffractometer with nitrogen-flow temperature controller using graphite-monochromated Mo Kα radiation (λ=0.71073 Å), operating in the ω and φ scan mode. Raw data collection and refinement were done using SMART. Data reduction was performed using SAINT+ and corrected for Lorentz and polarization effects. The SADABS program was used for absorption correction. The structure was solved by direct methods, and the structure refinements were based on |F²| with anisotropic displacement
using SHELX-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions. All crystallographic calculations were conducted with the SHELXTL software suites. The crystallographic data and the structural refinement parameters were summarized in Table 6.1.
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<td>25.4925(6)</td>
<td>25.3326(11)</td>
<td>90</td>
<td>0.2126 GIS</td>
<td></td>
</tr>
<tr>
<td>IMA-9</td>
<td>(Et₂NH₂)[In(imdc)(tdc)]</td>
<td>I4₁/amd</td>
<td>25.111(3)</td>
<td>25.111(3)</td>
<td>25.364(4)</td>
<td>90</td>
<td>0.1404 GIS</td>
<td></td>
</tr>
<tr>
<td>IMA-10</td>
<td>(Et₂NH₂)[In(imdc)(ndc)]</td>
<td>I4₁/amd</td>
<td>29.487(3)</td>
<td>29.487(3)</td>
<td>25.287(4)</td>
<td>90</td>
<td>0.2453 GIS</td>
<td></td>
</tr>
<tr>
<td>IMA-11</td>
<td>(NH₄)[In(imdc)(ox)]</td>
<td>Fddd</td>
<td>17.2989(15)</td>
<td>18.1191(16)</td>
<td>31.676(3)</td>
<td>90</td>
<td>0.0238 sql</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1  A summary of crystallographic data and refinement results for the structures covered in this chapter[^{a}]

[^{a}]: The superscript 'a' is used to denote the footnote for the table.
[a] Crystal structures were solved from single-crystal data collected at 150 K on a SMART CCD diffractometer with MoKα.

\[ R(F) = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \text{ with } F_o > 4.0\sigma(F). \]

[b] IMA = indium monomer based anionic frameworks

c] \( \text{Et}_4\text{N}^+ = \text{tetraethylammonium; Me}_4\text{N}^+ = \text{tetramethylammonium; Pr}_4\text{N}^+ = \text{tetrapropylammonium; Ph}_4\text{P}^+ = \text{tetraphenylphosphine; } 4,4'\text{-adb} = 4,4'\text{-azodibenzoic acid; } 3,3'\text{-adb} = 3,3'\text{-azodibenzoic acid; } \text{NH}_2\text{-bdc} = 2\text{-amino-dibenzoic acid; } \text{tdc} = \text{thiophenedicarboxylic acid; ndc} = 2,6\text{-naphthalenedicarboxylic acid; ox} = \text{oxalic acid; imdc} = 4,5\text{-imidazoledicarboxylic acid.} \]

6.3 Results and Discussion

6.3.1 Structures with Single Ligands

All the structures reported in this study are based on four connected monomeric indium nodes. Among these structures, IMA-1 to IMA-7 are constructed from a single linear dicarboxylate ligand, while IMA-8 to IMA-11 are constructed by combining a dicarboxylate ligand with a imidazoledicarboxylate ligand into one structure.

Among these structures, IMA-1, IMA-2 and IMA-7 have the interpenetrated diamond structure. The diamond network is very commonly seen when linear ligand combines with 4-connected nodes. Interestingly, although both IMA-1 and IMA-2 exhibit 4-fold interpenetration, their interpenetration modes are different, possibly due to the different configuration of the two ligands. Although both ligands adopted the linear shape, the 3 position substituted carboxylate shows a large shift between the two carboxylate than its 4 position substituted alternative. In addition, from the refined structure it is found that the 3,3’-adb in this structure has shown partial destroy of the conjugation on the azo group since the two aromatic rings have some degree of distortion. The difference in interpenetration has resulted in a big difference on the accessible void space. From the Platon Calculation, the void space for IMA-1 reaches 63.0%, while it is only 17.6% for IMA-2. The above difference may also explain the different behaviors of quaternary ammonium for IMAs with the two different ligands (Scheme 6.1). The longer length 4,4’-ADB and the large void space of IMA-1 promise different types of organic cations can be included in the pores. So it appears on the synthesis that 4,4’-ADB is inert to the size of organic cations. In contrast, the shorter length of 3,3’-ADB and the small void
space can only allow small cations (Me₄N⁺) to go into the channel. When large cations are applied, it will tend to form other structures to keep the charge of the framework neutral. So that’s why the 3,3’-ADB based structures are quite sensitive to the counter ion present in the system.

Figure 6.1 A comparison between two 4-fold interpenetrated diamond networks of IMA-1 and IMA-2 showing their diamond cages (a & d), framework connectivity (b & e) and different interpenetration modes (c & f) (purple: In, red: O, blue: N, grey: C).
With the use of Et₄N⁺ and choline, 2D layer structures of IMA-3 and IMA-4 have appeared with the same connectivity. This layer structure features a double connection between part of the two adjacent indium nodes (Figure 6.2a&b). Two adjacent layers are packed together by weak Van der Waals interaction.

When even larger cations such as Pr₄N⁺ and Ph₄P⁺ are applied, one dimensional structures have been formed. IMA-5 and IMA-6 represent two such 1D chain structures (Figure 6.2c&d). In contrast to the above two layered compounds, in which single and double connection between adjacent indium nodes are simultaneously seen in the

**Figure 6.2** (a) The 2D structure in IMA-3 and IMA-4 and (b) its connectivity; (c) 1D structure of (c) IMA-5 and (d) IMA-6 (purple: In, red: O, blue: N, grey: C).
structure, in IMA-5 and IMA-6, all the indium nodes are doubly connected. Such connectivity fashion determines that only 1D structure can be formed. Interestingly, although IMA-5 and IMA-6 use the same ligand and same connectivity, their structures appears quite different. In IMA-6 it shows regular square shaped window while in IMA-5 the window become distorted. From a detailed look of the structures, we can find out that in IMA-5 the conjugation system between the two benzene rings in original structure no longer exist, which indicates that the azo group is almost completely destructed after the solvothermal reaction.

6.3.2 Structures with Mixed Ligands

IMA-8 to IMA-11 are obtained by applying the mixed ligand strategy. The crystal data has shown that IMA-8 indeed meet our original design exactly. In this structure, only one type of 4-connected nodes is found. However, different from any of

![Figure 6.3](image)

**Figure 6.3** The coordination environments about indium in (left) indium carboxylate (IMA-7), (middle) previously reported indium imidazoedicarboxylate and (right) this work by mixed ligand strategy (IMA-8) (purple: In, red: O, blue: N, grey: C)
the previous examples, this monomer is six coordinated from four ligands, two imidazolodiacarboxylate take up four coordination sites and two aminodibenzoate take up the rest two (Figure 6.3). The other oxygen on the carboxylate is far from the indium center (ca 3.00 Å). Due to the 1:1 ratio of two ligands in the structure, the final formula of IMA-8 can be written as \((\text{Et}_2\text{NH}_2)[\text{In(imdc)}(\text{NH}_2\text{-bdc})]\). It’s important to point out that, similar to the cases in the previously reported ZMOF structures, only two acidic hydrogens among all three in the imdc ligand are deprotonated.

The structure analysis indicates that the entire framework exhibits a gismondine (GIS) network, which is a zeolitic topology. Although there is only one type of structure node in IMA-8, however, there are two types of edges, which correspond to two types of ligands. As illustrated in Figure 6.4a, the blue sticks represent the imdc ligand and red sticks represent the diacarboxylate ligands. The structure can be thought as many infinite \(\text{In(imdc)}\) chains linked by dicarboxylate bridges. The structure can be also considered as dcc chains linked by imdc ligands, or a 3D tiling from the gis SBU.

Based on the structure of IMA-8, we have further used the 2,5-thiophen-dicarboxylic acid (tdc) and 2,6-naphthalenendicarboxylic acid (ndc) to replace the 2-amino-benzenedicarboxylic acid (NH\(_2\)-bdc) to prove the possibility for isoreticular chemistry. Indeed, two isostructures (IMA-9 and IMA-10) have been made, in the formula of \((\text{Et}_2\text{NH}_2)[\text{In(imdc)}(\text{tdc})]\) and \((\text{Et}_2\text{NH}_2)[\text{In(imdc)}(\text{ndc})]\), respectively. The yellow ball diagrams of these two structures illustrated in Figure 6.4b indicate that the maximum diameter of a sphere that can fit in is 12.4 Å and 15.4 Å. Obviously, the difference comes from the different lengths of dicarboxylate linkers. While there is
Figure 6.4  (a) Illustration of the simplified net for IMA-8 (gold ball: In$^{3+}$, blue sticks: imdc; red sticks: NH$_2$-bdc) together with the building units contained and the tiling diagram. (b) Illustration of the gis tiles showing the coordination between metal and ligands in IMA-9 and IMA-10. The yellow balls represent the maximum diameter of a sphere that is allowed to fit in. (gold: In; red: O; blue: N; grey: C; yellow: S, hydrogen atoms are omitted for clarity).
almost no change in the (001) direction due to the same In(imdc) chain, the distance between adjacent nodes has been extended with the substitution of tdc by longer ndc ligands in the (100) and (010) directions.

The window sizes are limited in the $ac$ and $bc$ planes since the large pendant carboxylate groups in imdc always point to the center of the windows. However, large square shaped windows are exposed in the $ab$ plane and leave large 1D channels throughout the entire structure (Figure 6.5). The size of the channel is controlled by the length of the dicarboxylate ligands.

By applying this mixed ligand strategy, the obtained compounds have a very low framework density. Table 6.2 has compared the framework density of IMA-8 and IMA-10 with some ZIF and ZMOF structures reported before, in terms of tetrahedral metal nodes per unit cell volume (T/V). It is found that, the both compounds illustrated

![Figure 6.5](image)

**Figure 6.5** The square-shaped window and 1D channels in IMA-9 and IMA-10 viewing from (001) direction.
here exhibit extremely low density of T atoms. The density of IMA-10 is less than one third the density of ZIF-75, which has a same topology type, but with only imidazole type ligands. In addition, the pore size is quite large, which is even comparable to the ZIF-20 with LTA topology, which is a very open topology type. Considering GIS is a relatively

Table 6.2  A comparison of framework densities and pore diameters among some zeolitic metal-organic framework materials$^{7,14,15}$

<table>
<thead>
<tr>
<th>Code</th>
<th>Topology$^a$</th>
<th>T/V (nm$^{-3}$)$^b$</th>
<th>d$_{p}$ (Å)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMA-8</td>
<td>GIS</td>
<td>0.97</td>
<td>12.4</td>
</tr>
<tr>
<td>IMA-10</td>
<td>GIS</td>
<td>0.71</td>
<td>15.4</td>
</tr>
<tr>
<td>ZIF-75</td>
<td>GIS</td>
<td>2.47</td>
<td>8.6</td>
</tr>
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<td>ZIF-20</td>
<td>LTA</td>
<td>2.04</td>
<td>15.4</td>
</tr>
<tr>
<td>ZIF-70</td>
<td>GME</td>
<td>2.10</td>
<td>15.9</td>
</tr>
<tr>
<td>ZIF-10</td>
<td>MER</td>
<td>2.25</td>
<td>12.2</td>
</tr>
<tr>
<td>ZIF-71</td>
<td>RHO</td>
<td>1.92</td>
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</tr>
<tr>
<td>ZIF-67</td>
<td>SOD</td>
<td>2.45</td>
<td>14.2</td>
</tr>
<tr>
<td>sod-ZMOF</td>
<td>SOD</td>
<td>2.05</td>
<td>8.1</td>
</tr>
<tr>
<td>rho-ZMOF</td>
<td>RHO</td>
<td>1.60</td>
<td>26.9</td>
</tr>
</tbody>
</table>

[a]  For definitions of three-letter abbreviations, see International Zeolite Association (www.iza-structure.org/databases/).

[b]  The definition of T/V is the number of T atoms per 1000 Å$^3$ cell volume.

[c]  The pore size is obtained through yellow ball diagram, which can’t represent the real pore volume.
dense topology type, this pore volume is impressive. These results indicate that such mixed ligand route has shown significant advantages to synthesize metal-organic frameworks with extremely low density.

In contrast to IMA-8 to IMA-10, when oxalic acid is applied together with imdc, the indium node is again 8-coordinated with two different bidentate ligands. Although it is also 4-connected, the IMA-11 shows a square planar type 2D layer structure (Figure 6.6). In this structure, there are three types of squares in the formula of $\text{In}_4(\text{imdc})_4$, $\text{In}_4(\text{oxa})_4$ and $\text{In}_4(\text{imdc})_2(\text{oxa})_2$, respectively.

![Figure 6.6 The square planar structure in IMA-11. (gold: In; red: O; blue: N; grey: C, hydrogen atoms and guest molecules are omitted for clarity)](image)
6.3.3 Gas Sorption Properties

IMA-1 and IMA-9 are selected for gas sorption studies. N\textsubscript{2} sorption of IMA-9 shows the BET and Langmuir surface area is 816.94 cm\textsuperscript{2}/g and 1190.26 cm\textsuperscript{2}/g, respectively. The H\textsubscript{2} uptake capacity of IMA-9 and IMA-1 at 77K and 1 atm is 176.51 cm\textsuperscript{3}/g and 40.44 cm\textsuperscript{3}/g. The H\textsubscript{2} uptake value for IMA-9 is quite high.

Figure 6.7 (a) N\textsubscript{2} sorption isotherm of IMA-9 and (b) H\textsubscript{2} sorption isotherms of IMA-1 and IMA-9 (at ~77 K).
6.4 Conclusion

In conclusion, a series of indium monomer based anionic metal-organic frameworks have been synthesized. By using linear shaped dicarboxylate ligands, 1D to 3D networks have been synthesized. The 3D diamond structures have shown different interpenetration modes. To avoid interpenetration and generate more porous zeolitic structures, a mixed ligand strategy involving a bis-bidentate ligand and a dicarboxylate ligand has been applied. Through this route, a novel GIS network has been achieved. Furthermore, guided by isoreticular chemistry, an isostructure with larger pore channels has been obtained. Both compounds have shown extremely low framework density. In addition, IMA-9 has shown quite high H$_2$ uptake capacity.

6.5 References


(10) Unpublished results.


Chapter 7

Outlook

7.1 Lithium Cubane Based Frameworks with Open Metal Sites

In previous work, we have proved the effective use of phenol-pyridine type bifunctional ligands in the construction of lithium cubane based coordination frameworks and supramolecular assemblies. However, in both case, the lithium atoms are always capped by organic linkers, which are indispensable for the framework formation. Such configuration make lithium fully coordinated and leaves no possibility for creation of the open lithium sites, which are highly desired for enhancing the interaction between metal and gas molecules in the application of gas storage (especially for $\text{H}_2$). Actually, a strategy has been designed by us to achieve this goal (Scheme 7.1). By using ditopic or multitopic all phenol type linkers, the formation of cubane clusters and the linkage between adjacent clusters can be simultaneously achieved. Only the oxygen atoms in cubane clusters act as structural nodes and lithium atoms are terminated by a volatile solvent molecule. When the materials are activated by removing the solvent (usually through heating under vacuum), high density of open metal sites will be exposed (4 open Li sites per cubane cluster). Such structure design integrates light weight elements, 4-connected network and open metal sites, thus is very interesting and worth exploring.

7.2 Synthesis of Lithium MOFs by Applying Superbase as Solvents
Although in zeolite chemistry, by using the d4R SBU only, several topology types can be obtained such as ACO, LTA, AFY, CLO and etc, so far we have only achieved the ACO topology. As well, the other types of lithium aryloxide clusters such as the d6R type hexamers, in principle can be also used as SBUs to construct zeolitic structures. The formation of the above mentioned structures requires diverse synthetic environment. However, the diversity of current synthesis is partially limited to the solvents. While many types of solvents have been attempted, only alcohol type solvents and acetonitrile have been proved to be effective for the formation of Li₄O₄ clusters. The large family of amide solvents most often leads to the formation of other structures.

Organic superbase has been recognized as an alternative system to traditional solvents, where strong base condition is required. Recently, some crystalline
chalcogenide clusters have been synthesized under organic superbase system reported by us. However, it has never been used for MOF synthesis. In fact, the \( t \)-BuLi and \( t \)-BuOLi used in the previously mentioned systems belong to another superbase category known as organometallic superbase. Therefore organic superbase may be a good candidate for the solvent used for the lithium system, in three aspects. First, similar to \( t \)-BuOLi, the strong basicity can ensure the deprotonation of aryloxides ligands. Second, the superbase type solvent avoids the strong interaction between lithium and oxygen containing protic and aprotic solvents. Third, it is possible for superbase to act as templates for the framework formation. Thus, in the future we are going to explore the possibility for Li MOFs synthesis in such systems.

### 7.3 Application of Charged Indium MOFs in Ion Chromatography

In chapter 5, we have studied the synthesis of a series of indium trimer based cationic frameworks as well as the ion exchange of organic anions based on the cationic In MOFs platforms. The results have shown size and charge exclusive exchange as well as the dynamic difference based on different size and charged organic anions. The above difference has provided the fundamental driving force for separation. In the next step, we are going to perform the dynamic separation of more complicated mixtures with greater application significance, such as nucleotides. To achieve the dynamic separation, the MOFs can act as the stationary phase in either of ion exchange chromatography (IEC) or ion exchange solid phased extraction (IE-SPE). The organic species in the mobile phase will be separated by different retention time depending on the different strength of host-guest interaction. Despite the cationic MOFs, anionic MOFs such as the ones
described in Chapter 6 should have similar ion exchange abilities, but for cationic species. In addition, MOFs have shown interesting properties such as large breathing effect, flexibility in the interwoven frameworks. All the above properties may lead to different ion-exchange behaviors, which could be interesting research topics in the future.

### 7.4 Synthesis of Novel Zeolitic Structures Based on Indium Monomer

We have described in chapter 6 the special role of bis-bidentate type ligand to create a coordination environment that will possibly lead to the formation of zeolitic structures. By using a mixed ligand strategy involving the imdc and dicarboxylates, we have obtained a GIS network. In fact, there are many other ligands that contain the bidentate structure, which will play a similar role as imdc did in this work. Some ligands even combine the bidentate functionality and carboxylate into one (Scheme 7.2). By using these new types of ligands with different T-L-T angles, it’s highly possible to obtain other zeolitic structures such as SOD, RHO and etc., which will show more interesting gas sorption properties.

[Scheme 7.2] Examples of some organic linkers with bidentate functionality.