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From MOF-74-Zn to Triazolate-Directed Non-symmetric Assembly of Chiral Zn_6@Zn_6 Clusters

Huajun Yang, James Le, Andy Dinh, Xiang Zhao, Xitong Chen, Fang Peng, Pingyun Feng, and Xianhui Bu**

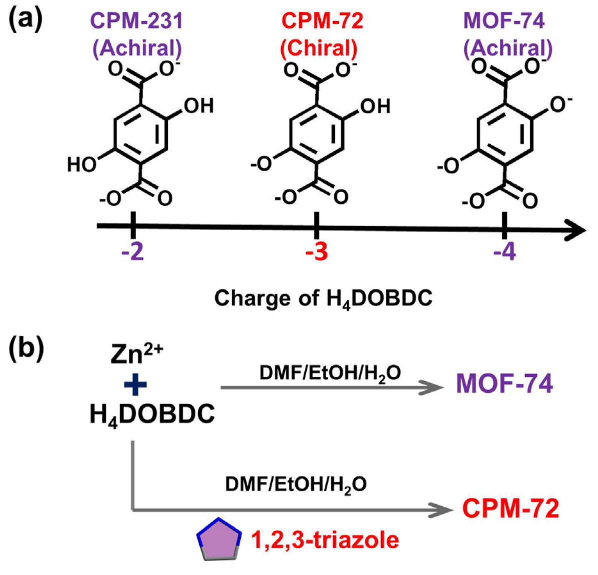
Abstract: *The creation of novel cluster building blocks, as well as new ligand coordination modes, are among the most effective ways to develop new framework materials. Yet, large and chiral clusters are both difficult to create and relatively few. Here, by studying the competing coordination of different azolates against carboxylate and combined carboxylate/phenolate, it is shown that the impact of azolates in the MOF-74 synthesis system differs dramatically, leading to the synthesis of MOF-74, UTSA-74, and CPM-72 for 2-methylimidazole, 1,2,4-triazole, and 1,2,3-triazole, respectively. New CPM-72 contains a novel chiral* Zn_{12} *triazolate cluster that features a trigonal-prismatic* Zn_6 *core inside an octahedral* Zn_6 *shell. In contrast with MOF-74 with fully deprotonated and symmetrically bonded 2,5-dihydroxyterephthalic acid (*H_4DOBDC*),* H_4DOBDC *adopts an unusual non-symmetric bonding mode in CPM-72 (carboxylate only at one end and carboxylate/phenolate at the other), resulting in a highly porous and intrinsically chiral 3-D framework. The non-symmetric bonding mode by* H_4DOBDC*, apparently dictated by the chiral* Zn_{12} *cluster, can be replicated with 2-hydroxyterephthalic acid (*H_3OBDC*), leading to the synthesis of porous isoreticular CPM-73.*

While metal-organic frameworks (MOFs) exhibit rich compositional and topological diversity, some particular structure types are of greater significance and impact.[1] Among important MOF building blocks, 2,5-dihydroxyterephthalic acid (H_4DOBDC or alternatively H_2DHBDC) is highly unique because its two -COOH and two -OH groups offer tunability in the charge of ligand, as well as its coordination modes. MOF-74 (or CPO-27) materials result from combined carboxylate/phenolate functionality and have outstanding properties for gas sorption.[2] The H_4DOBDC ligand in MOF-74 is fully deprotonated (-4) with a high charge density, and metal atoms are assembled into crosslinked high-density chains.

Impressively, in a different and lower-charged (-2) form, 2,5-dihydroxyterephthalic acid was also found to play an important role in a large family of trimer-based crystalline porous materials (e.g., pacs-CPM-231 with pore-partitioned *acs* topology).[3] Specifically, many of these isoreticular CPM materials exhibit a very high CO_2 uptake capacity comparable to the aforementioned record-setting MOF-74 family of materials. Moreover, the high CO_2 capacity can be achieved in the CPM family even though the heat of adsorption is only about half of that for corresponding best MOF-74 materials. In contrast with the ligand in MOF-74, 2,5-dihydroxyterephthalic acid is dianionic with two -OH groups intact in the CPM family.

The contrasting features and impressive properties of MOF-74 and CPM-231 demonstrate that 2,5-dihydroxyterephthalic acid is special in either -4 (DOBDC) or -2 (DHBDC) forms. We are thus intrigued by other phase possibilities, especially those beyond -2 or -4 forms.[4] For example, phases with -3 anions would be interesting (Scheme 1a). One difficulty working with H_4DOBDC is the unpredictable nature of the phenolate formation, which is a comparatively rare phenomenon, especially for metal ions of borderline hardness (e.g., Zn^{2+}). For this reason, the synthetic condition known to favor the phenolate formation (e.g., MOF-74) is a reasonable starting point. However, to develop new materials, it is necessary to identify new synthetic parameters to suppress the MOF-74 formation. It has been shown that competitive coordination by other ligands could suppress the MOF-74 formation and lead to other phases. For example, 2,4,6-tri(4-pyridinyl)-1,3,5-triazine (tpt) is instrumental in bringing about the change from MOF-74 to pacs-CPM-33, leading to the creation of an extraordinarily versatile platform for the engineering of high-performance gas-sorption CPM materials.[3a] However, the behavior of the MOF-74 system under the influence of negative azolate ligands remains largely unexplored.

Here, we explore the impact of azolate ligands in the MOF-74 synthesis system, leading to the creation of a novel material (CPM-72). One key step in the crystallization of CPM-72 appears to be the dominant formation of the core $[(Zn_3OH)_2(trz)_6]^{4+}$ cluster when three pairs of triazolate ligands brings together two $Zn_3(OH)$ trimers into the face-to-face configuration. 2,5-dihydroxyterephthalic acid adopts non-symmetrical bonding mode by using only one of two -OH groups for the framework formation. Recognizing the fundamental bonding features of CPM-72 has also allowed us to replicate such non-symmetrical bonding mode (by H_4DOBDC in CPM-72) with a related ligand H_3OBDC (H_3OBDC=2-hydroxyterephthalic acid), leading to the creation of isoreticular CPM-73. Prior to this study, we reported a number of highly unusual MOFs in which the symmetric ligand (1,3,5-benzenetricarboxylate) adopts various non-symmetric bonding modes, but in those instances we were unable to produce isoreticular structures by using a lower-symmetry ligand.[5] The CPM-72/CPM-73 pair is our first success in this regard.



Scheme 1. (a) Various deprotonated forms of H_4DOBDC ligand and the corresponding frameworks. (b) A comparison of synthetic routes between MOF-74 and CPM-72.

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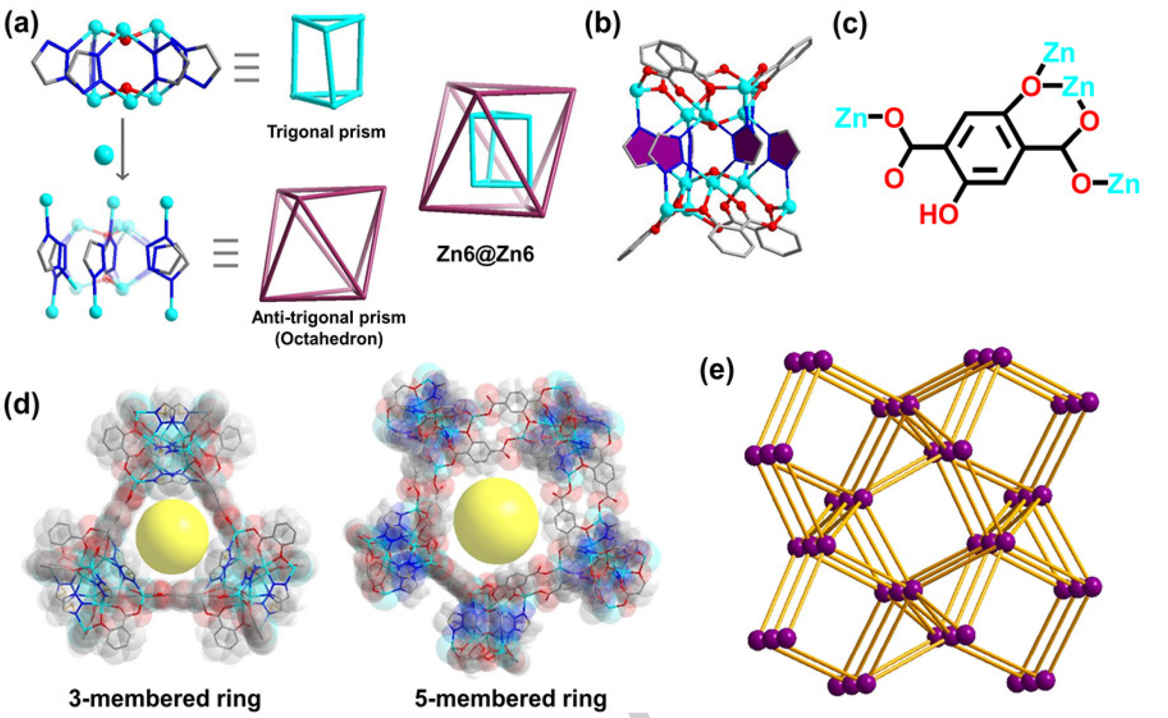

Figure 1. (a) The modualr construction of dodecameric Zn6@Zn6 cluster. (b) Zn12 cluster. (c) asymmetric bonding with O(OH)BDC ligand. (d) 3- and 5-membered rings with each cluster as the 6-connected node. (e) Chiral lcy net of CPM-72 & CPM-73 with Zn_{12}-cluster nodes.

CPM-72 was synthesized by adding 1,2,3-triazole into the synthetic system of MOF-74, without even changing the amount of the original reactants (Scheme 1b), or alternatively by starting from MOF-74 crystals in the same solvent medium (see details in SI). CPM-73 was made similarly with 2-hydroxyterephthalic acid. In CPM-72, one side of the ligand is fully deprotonated with the combined carboxylate/phenolate bonding similar to that found in MOF-74 (Figure S1).

In addition to CPM-72 and CPM-73, by systematically investigating the effect of various types of N-donor ligands in this MOF-74-related synthesis medium, we were also able to synthesize UTSA-74 using 1,2,4-triazole as the additive and under conditions similar to MOF-74 conditions, but different from that originally reported.[6] Compared with 1,2,3-triazolate, 1,2,4-triazolate is apparently less disruptive to the Zn-DOBDC interactions, likely due to the weaker chelating ability of 1,2,4-triazolate. When 2-methylimidazole with no chelating ability was used, MOF-74 phase was retained (Table S1).

The structure of CPM-72 was determined by single-crystal X-ray diffraction. It crystallizes in a cubic chiral space group $P4_132$ (or $P4_332$) with the formula $[(Zn_3OH)_2(trz)_6{\cdot}Zn_6(OHOBDC)_6]{\cdot}2NH_2(CH_3)_2$ (Table S2). The Flack parameter is near zero, indicating the spontaneous resolution of chiral crystals. While such samples are apparently racemic in the bulk form, they can potentially serve as the starting point for the application of chiral induction method to generate enantiopure or enatioenriched forms for chiral applications.[7]

The characteristic building unit of CPM-72 is a new Zn_{12} cluster, which can be described as a nested cage-within-cage (or cluster-within-cluster) structure (Figure 1a). The inside trigonal-prismatic Zn_6 cluster is unusual because it is formed from eclipsed face-to-face stacking of two zinc $[Zn_3(OH)]^{5+}$ trimers. The two core oxygen sites directly face each other with a short distance of only about 2.5 Å. Apparently, these two zinc trimers are brought into such an unusual contact by six triazolate ligands using two adjacent nitrogen atoms to capture a pair of Zn atoms.

Interestingly, these six triazolate ligands are arranged into an isolated hexagonal column sandwiched between two planes defined by Zn trimers. These six triazolates come in three pairs with two triazolates in each pair parralel to each other. The distance between two triazolate planes is around 3.3 Å, indicating a strong π-π interaction (Figure S2).

Upon the formation of the core $[(Zn_3OH)_2(trz)_6]^{4+}$ cluster, each of the six triazolate ligands has one remaining N site. These six N sites define the location of six Zn atoms that form the vertices of the octahedral Zn_6 shell (Figure 1a), reuslting in an overall Zn_{12} cluster with the unprecedented $Zn_6@Zn_6$ configuration with the formula $[(Zn_3OH)_2(trz)_6{\cdot}Zn_6]^{16+}$. It is likely that the Zn_{12} cluster is the largest one in Zn-triazolate materials (Figure S3) and also the largest in Zn-MOFs.[8] _ENREF_33_ENREF_39

With the $Zn_6@Zn_6$ configuration, the whole cluster exhibits the D_3 symmetry with the C_3 axis going through two trimer oxygen atoms. As a result, the cluster is chiral (Figure 1b). The establishement of a new chiral building block here is intriguing and may be of use for constructing other chiral framework materials. It is worth noting that chirality of chiral MOFs usually comes from ligands.[9]

The Zn_{12} cluster, $[(Zn_3OH)_2(trz)_6{\cdot}Zn_6]^{16+}$, assembled by triazolate clusters contains a large number of coordination sites that are not used for forming the $Zn_6@Zn_6$ cluster. These Zn coordination sites are used for bonding to six O(HO)BDC ligands (Figure 1c). One end of the ligand adopts fully deprotonated bonding mode (carboxylate/phenolate) similar to that in MOF-74, while the other end uses the carboxylate group with the monodentate coordination mode (-OH group not used, therefore the abbreviation OHOBDC). There are no apparent openmetal sites once clusters are linked into a 3D framework. The six core Zn sites exhibit the square-pyramidal coordination geometry (Zn-O/N distance from 1.98 to 2.13 Å) with the sixth oxygen site (from carboxylate) 2.70 Å away. In comparison, the six shell Zn sites are tetrahedrally coordinated.

Two adjacent Zn$_{12}$ clusters are doubly connected by two OHOBDC^{3-} or OBDC^{3-} ligands in CPM-72 and CPM-73, respectively (Figure S4). Such double briding mode contributes to the robustness of the framework. Through the double bridging mode, clusters were further connected to form 3-membered and 5-memerbered rings. The 5-membered ring has an aperture size around 10 Å × 14 Å (Figure 1d). In CPM-72 and CPM-73, a total of twelve dicarboxylate ligands were used to connect each cluster with six neighbouring clusters. Due to the double bridging, each cluster serves as the 6-connected node, and the topology can be simplified into chiral **lcy** net (Figure 1e). In fact, despite the complexity of its chemical composition, CPM-72 and CPM-73 possess the highest possible symmetry of this topological type ($P4_132$).[10] It is worth noting that the structure is not interpenetrated.

The negative charge of the framework leads to a different behavior towards exchange with organic dyes of opposite charges. The crystal of CPM-72 was found to change its color immediately after it was immersed in a cationic dye solution of methylene blue whereas no color change was observed in an anionic OG (Orange G) solution (Figure S5). CPM-72 was also found to exhibit a higher stability than CPM-73 and even after 1 day of immersion in water, it remains highly crystalline (Figure S11).

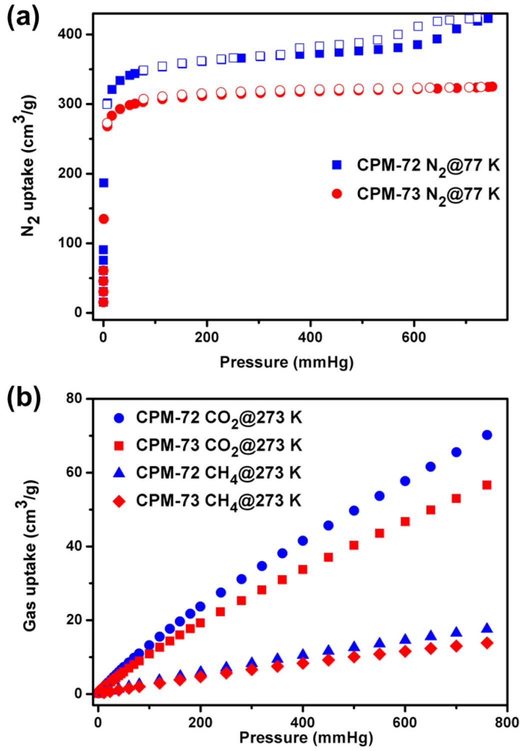

Figure 2. (a) N$_2$ adsorption at 77 K for CPM-72 and CPM-73. (b) CO$_2$ and CH$_4$ adsorption of CPM-72 and CPM-73 at 273K

As calculated by Platon program, CPM-72 and CPM-73 possess a large guest-accessiable volume of 67.5% and 68.9%, respectively. The high porosity of both samples was further demonstrated by gas adsorption experiments. Before degassing, CPM-72 was activated by solvent exchange in methanol for three day while the CPM-73 sample was refluxed in anhydrous CH$_3$CN for two days. Based on their N$_2$ adsorption at 77 K (Figure 2a), the Brunauer-Emmett-Teller surface area (P/P_0 < 0.3) and Langmuir surface area were determined to be 1143.7 m^2/g and 1590.4 m^2/g for CPM-72, 986.8 m^2/g and 1370.3 m^2/g for CPM-73, respectively. The micropore volumes of CPM-72 and CPM-73 were determined to be 0.539 and 0.476 cm^3/g. The smaller surface area for CPM-73 could be ascribed to the less-than-optimum activation due to the high boiling point of DBF molecules, even though a harsher activation was employed.

CPM-72 and CPM-73 can adsorb 142.1 and 124.0 cm^3/g of H$_2$ at 1 atm and 77 K, corresponding to 1.3 and 1.1 wt % (Figure S12). They can also both selectively adsorb CO$_2$ over CH$_4$ (Figure 2b). At 273 K and 1 atm, CPM-72 adsorbs 70 cm^3/g (3.13 mmol/g) of CO$_2$ and only 17.6 cm^3/g of CH$_4$ (0.79 mmol/g). The corresponding values for CPM-73 are 56.6 cm^3/g (2.52 mmol/g) and 13.9 cm^3/g (0.62 mmol/g).

In conclusion, through the mediation of triaolate in MOF-74's synthetic condition, a highly novel and chiral Zn$_{12}$ cluster with Zn$_6$@Zn$_6$ configuration has been made, through the structural tranformation from MOF-74 into chiral 3-D CPM-72. Under the influence of such chiral clusters whose formation is primarilly driven by triazolate, the normally symmetric H$_4$DOBDC ligand was found to adopt the unusal -3 form with aymmetric bonding mode. The whole crystallization process seems to be driven by triaozlate-cluster formation and the impact of its symmetry. The intrinsically chiral net of CPM-72 and CPM-73, toghter with their high porosity, is worth noting, and the exploration of coordination-driven re-assembly of archetypal MOF phases is seemingly a fruitful approach in the new materials synthesis and discovery process.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: metal-organic frameworks • zinc triazolate cluster • 2,5-dihydroxyterephthalic acid • chiral • MOF-74

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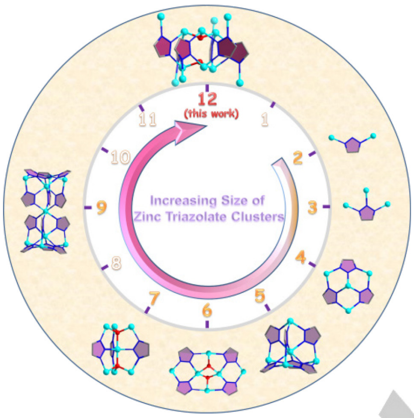
Text for Table of Contents

Asymmetry born out of symmetry: Mediated by triazolate, the achiral MOF-74 structure turns into a chiral framework built on large and chiral core-shell-type $Zn_6@Zn_6$ cluster with unusual low-symmetric bonding mode by H_4DOBDC ligand.



Huajun Yang, James Le, Andy Dinh, Xiang Zhao, Xitong Chen, Fang Peng, Pingyun Feng, and Xianhui Bu**

Page No. – Page No.

From MOF-74-Zn to Triazolate-Directed Non-symmetric Assembly of Chiral $Zn_6@Zn_6$ Clusters