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Spontaneous chiral resolution directed by symmetry restriction and π - π interaction

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COORDINATION CHEMISTRY

CHEMICAL BONDING

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Received
14 May 2013Accepted
26 September 2013Published
15 October 2013Correspondence and
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In order to understand and rationally construct homochiral self-assembled structures from racemic molecules, two novel crystalline metal-organic frameworks with chiral cavities were developed. The homochirality of the layers in both MOFs was achieved by forming strong coordinate bonds between the C_3 -symmetric cyclotrimeratrylene and $Zn_4O(CO_2)_6$ cluster. By changing weak π - π interactions between organic building blocks, the achiral assembly of ZnCTV-1 was successfully transformed into a chiral assembly in ZnCTV-2. This study demonstrated a possible route for designing the synthesis of chiral MOF through weak interactions.

Chirality is a common phenomenon in nature, and represents the evolution of matters towards more complicated cases. Many chiral systems achieve their functions through the interaction with other chiral molecules or the environment (chiral recognition or chiral assembly)¹⁻³. However, the rules controlling (a)chiral interactions, such as chiral symmetry breaking, self-resolution, supramolecular chirality formed by achiral molecular aggregation, etc. remain relatively poorly understood. Therefore, the understanding and rational construction of chiral structures from achiral or racemic molecules are still challenging^{4,5}.

Metal-organic frameworks (MOFs), an important class of self-assembled materials, built by organic linkers and metal ions or clusters have attracted great attention over the past decades due to the structural diversity and outstanding properties⁶⁻²⁰. Chiral MOFs are more attractive because of their additional properties for asymmetric catalysis, enantiomorphous selectivity, chiral molecular imaging, etc¹⁴⁻¹⁸. To prepare homochiral MOF materials, three complimentary approaches have been widely used¹⁹: direct synthesis from enantiopure ligands or *via* self-resolution process, chiral-templated synthetic procedures and post-synthetic modification approaches. Among these, spontaneous resolution during crystallization is of higher interest.

Cyclotrimeratrylene (CTV) is a rigid cyclic macromolecule with a shallow electron-rich cavity²⁰⁻²². New progress in the domain of macrocyclic CTV-based hosts includes applications in material science, sensing and separations²³⁻²⁸. Owing to a pyramidal shape and convergent binding modes, CTV itself and CTV-based ligands are capable of forming coordination complexes with group one elements and transition metals²⁹⁻⁴⁴. Hardie *et al.* conducted excellent works on pyridyl decorated CTV derivatives that form discrete or infinite metallo-supramolecular assemblies³³⁻³⁸. When it comes to carboxylic acid decorated CTV ligands, only a few structures have been reported³⁹⁻⁴⁴, and their transition metal complexes are even rarer⁴²⁻⁴⁴. We recently reported the first CTV based 1D ternary independent nanotubular framework with permanent porosity⁴⁴. In this work, C_3 -symmetric tritopic corner ligands tri-(4-carboxyl)-trimethoxycyclobenzylebe (H_3L_1) and tri-(4-carboxy-phenyl)-trimethoxy-cyclobenzylebe (H_3L_2) were used for the construction of chiral MOFs (Fig. 1a). As far as we know, there is no CTV-based infinite coordination polymer with chiral cavities reported until now.

Here, six-coordinated octahedral $Zn_4O(CO_2)_6$ clusters were selected as inorganic nodes due to a relative easy formation as well as good thermal stability. According to the principles of reticular chemistry, (6,3)-coordinated networks are expected. Yaghi *et al.* have reported two kinds of 3D (6,3)-coordinated networks (known as **pyr**⁴⁵ and **qom**⁴⁶ topology) with flat three-connected organic linkers and $Zn_4O(CO_2)_6$ clusters, which show ultrahigh porosity than most MOFs. While, due to the concave and bowl-shape structure of CTV type ligands, different topologies are formed as we will discuss below.

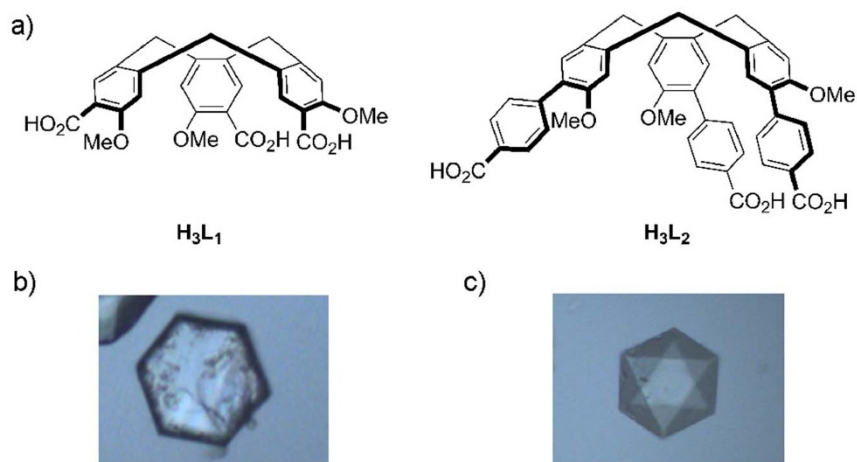


Figure 1 | Ligands and crystal images. (a), Chemical structures of the two ligands based on C_3 -symmetrical CTV, H_3L_1 and H_3L_2 . (b), Crystal image of ZnCTV-1. (c), Crystal images of ZnCTV-2.

Results

Synthesis and crystal structure of ZnCTV-1. A preliminary experiment resulted in the formation of ZnCTV-1, which is synthesized from the solvothermal reaction of $Zn(NO_3)_2 \cdot 6H_2O$ and H_3L_1 in N,N' -dimethylformamide (DMF) at $95^\circ C$ (Fig. 1b). The colourless hexagonal plate crystals of ZnCTV-1 are insoluble in water and common organic solvents (DMF, alcohol, THF, etc), elemental analysis gave a formula of $[Zn_4O(L_1)_2] \cdot DMF \cdot EtOH \cdot H_2O$. Single crystal X-ray diffraction analysis showed that ZnCTV-1 is a stacking of 2D (6,3)-coordinated layers in the space group of $P31c$. Each layer can be considered as a fused honeycomb bilayer in eclipsed mode shown in Fig. 2a & 2b. In each layer, face-to-face arranged ligands of the same enantiomer link to $Zn_4O(CO_2)_6$ clusters through their carboxylates, forming rigid chiral capsules with C_3 symmetry and a cavity volume of 167 \AA^3 . The homochirality in each bilayer is

due to symmetry restriction and the chirality was transferred from one ligand to another through the rigid $Zn_4O(CO_2)_6$ cluster. Unfortunately, the adjacent bilayers are symmetrically related by the c -glide and contain the opposite enantiomers (Fig. 2c).

Based on the analysis of ZnCTV-1, we could devise two possible ways to obtain a chiral MOF. The first consists in using a homochiral CTV ligand to exclude the formation of the layers with the opposite chirality. However, with the present solvothermal synthetic conditions, ligand molecules could easily flip to their enantiomers during the reaction process⁴⁷. A new synthetic route with milder conditions is under investigation. The alternative route is to keep the homochiral layer but modify the interaction between layers to assemble the homochiral layers selectively. In ZnCTV-1, the main interaction between layers is the π - π interaction in a parallel-displaced mode with a plane distance of about 3.2 \AA (Supplementary Fig. S2). In order

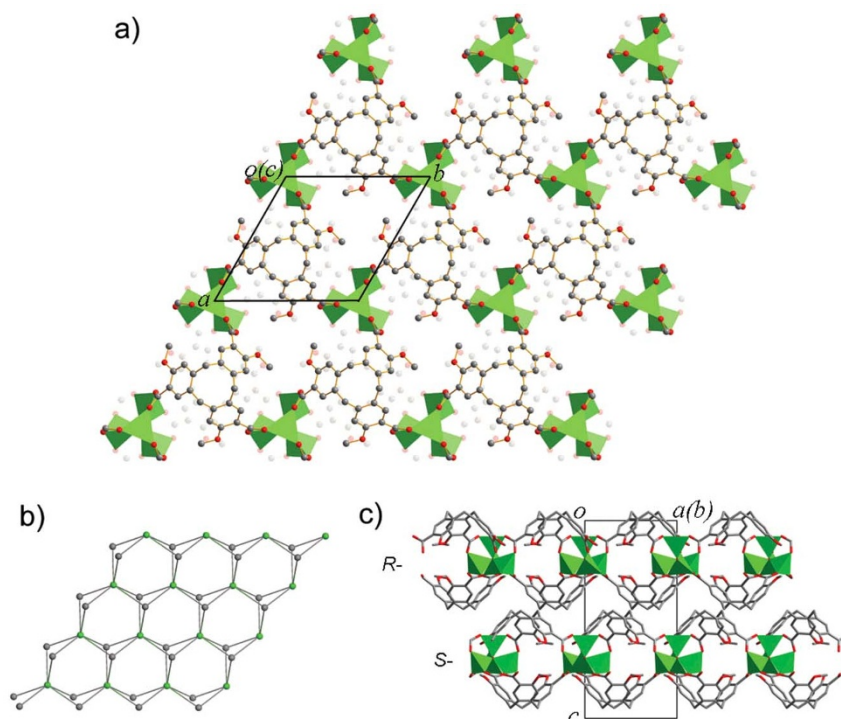


Figure 2 | Layered crystal structure of ZnCTV-1. (a), One 2D (6,3)-coordinated bilayer of real structure (top view). (b), Topology of eclipsed 2D structure. (c), Two adjacent bilayers with opposite enantiomers (side view). (Zn, green tetrahedron; O, red; C, gray; H atoms were omitted for clarity.)

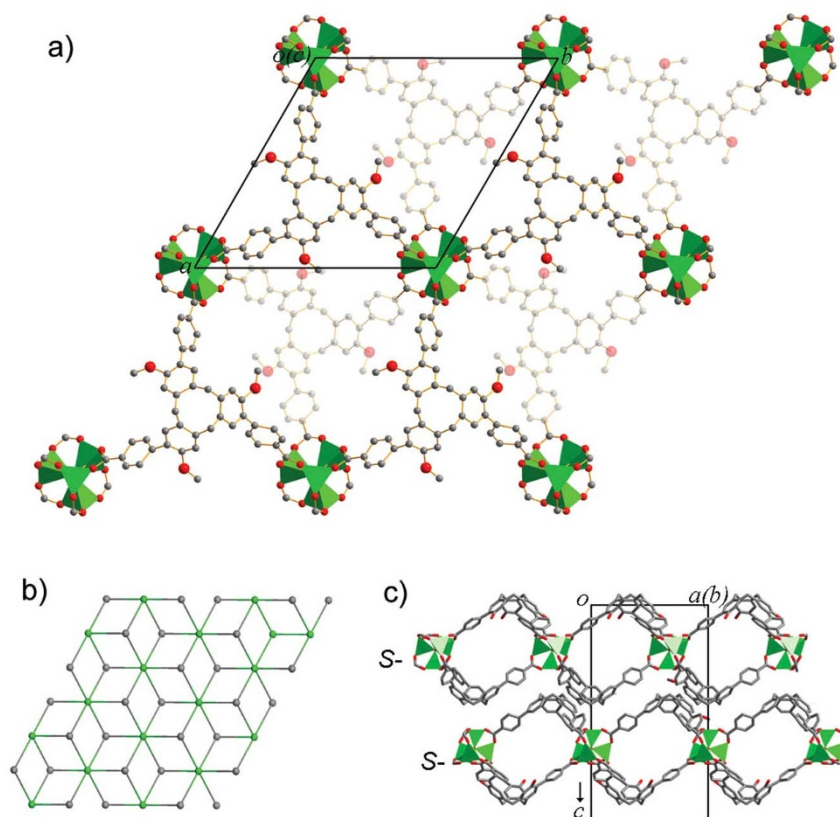


Figure 3 | Crystal structure of ZnCTV-2. (a), One 2D (6,3)-coordinated bilayer of real structure (top view). (b), Topology of 2D structure. (c), Two adjacent bilayers with the same enantiomers (side view). (Zn, green tetrahedron; O, red; C, gray; H atoms were omitted for clarity.)

to modify the possible π - π interaction, our strategy is to insert a phenyl group between the CTV-skeleton and the carboxylate group with the H_3L_2 shown in Fig. 1.

Synthesis and crystal structure of ZnCTV-2. Similar solvothermal reactions of $ZnCl_2$ and H_3L_2 in N,N' -diethylformamide (DEF) produced beautiful octahedral crystals, ZnCTV-2 (Fig. 1c), with a yield of 86%. The product was formulated as $Zn_4O(L_2)_2 \cdot 13DEF \cdot 3H_2O$ on the basis of elemental analysis. Single crystal X-ray diffraction revealed also a layered (6,3)-connected framework but with the topology shown in Fig. 3b with space group $R32$. This layer can also be considered as a fused honeycomb bilayer but in a staggered mode (Fig. 3a & 3b). Although the geometry restriction here is weaker than that in ZnCTV-1 structure due to the longer CTV arms, all CTV molecules in each layer still have the same chirality as those in ZnCTV-1. However, in stark contrast with ZnCTV-1, the ligands of

adjacent layers in ZnCTV-2 have the same chirality and the whole structure is in a chiral space group (Fig. 3c). Note that due to the racemic nature of the reactant, the whole batch of materials are considered as a mixture of homochiral left and right-handed crystals.

Weak interactions in ZnCTV-2. To understand the formation of homochiral ZnCTV-2, the interaction between the honeycomb bilayers were examined carefully. There are two types of bilayer interfaces. At $z = 0$, two CTV molecules are symmetry related by the 2-fold rotation, and their two pairs of phenyl groups have a plane distance about 3.4 Å, showing typical π - π interactions in a parallel-displaced mode (Fig. 4a & Supplementary Fig. S3). At $z = 0.5$, two CTV molecules are also symmetry related by the 2-fold rotation, while the two pairs of phenyl groups have a typical π - π interaction in a T-shaped mode⁴⁸ with a C-Centroid distance of about 3.9 Å (Supplementary Fig. S3). Thus, in both cases, the interactions are

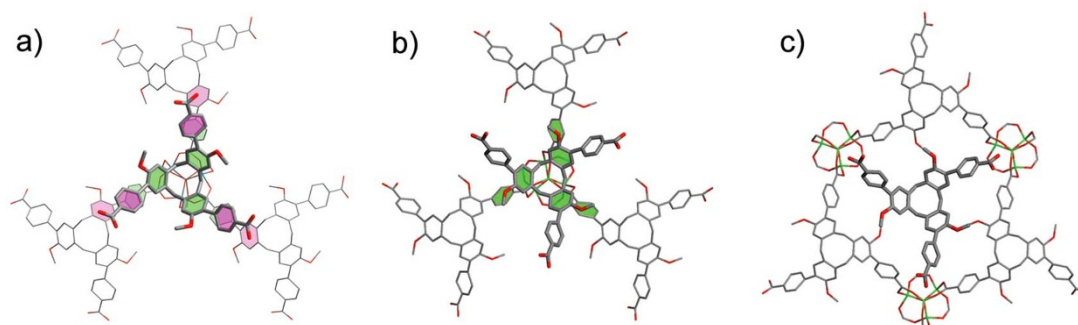


Figure 4 | The π - π interactions of two CTV ligands from adjacent layers. (a), The π - π interactions of two homochiral ligands from adjacent layers in a parallel-displaced mode in the real structure of ZnCTV-2. (b) and (c), Two possible models with racemic organic linkers. Homochiral ZnCTV-2 contains more π - π interaction sites than the racemic models. Two adjacent interacting phenyls are shown in same color.

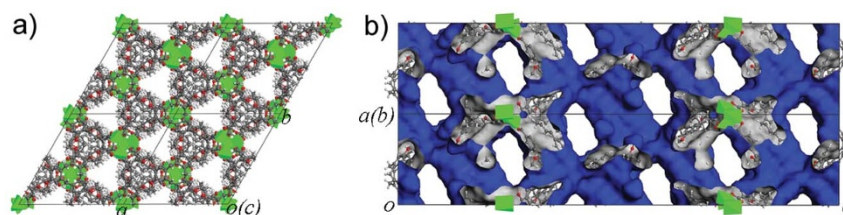


Figure 5 | Cavity display of ZnCTV-2. (a) top and (b) side view indicating the van der Walls surface. (Zn, green tetrahedron; O, red; C, gray).

about twice as strong as those in ZnCTV-1 (only one pair of π - π interaction). This may explain why the ZnCTV-2 crystals are much thicker than ZnCTV-1 along the c -axis. Moreover, as we expected, the stronger interaction between the bilayers in ZnCTV-2 may increase the chiral recognition and result in a spontaneous self-sorting process of CTV molecules during the crystallization. To confirm this, two structure models were built with racemic CTVs in adjacent bilayers and it turns out that due to the long CTV arms, the π - π interaction between layers becomes much weaker than that of ZnCTV-2 as shown in Fig. 4 (see also Supplementary Fig. S4–S7 for all possible models). A structure model with layers the same as ZnCTV-1 was also built (see Supplementary Fig. S6 & S7) but no efficient π - π interaction or other hydrophobic interactions between layers were found. Thus, we can conclude that by elongation of the CTV arms with a phenyl group, the inter layer π - π interactions became more selective and finally resulted in the chiral structure of ZnCTV-2.

Stability and porosity. The stability and porosity were studied by thermal gravimetric analysis (TGA) and N_2 gas adsorption. Although ZnCTV-1 has a solvent void volume of about 577 \AA^3 (20% of the cell volume) from the SQUEEZE calculation in PLATON, the void is not accessible since the framework decomposed as soon as the guest molecule started releasing at *ca.* 340°C (Supplementary Fig. S9 & S11), similar to other previously observed layered frameworks without permanent porosity⁴⁹. Solvent exchange process and evacuation also failed in emptying the pores because of the small windows of the capsule. The total solvent accessible void volume of ZnCTV-2 is 15573 \AA^3 (63% of the cell volume) (Fig. 5), where guest molecules are highly disordered, and cannot be located by X-ray diffraction. According to TGA, the weight loss of 44% below 270°C corresponds to the release of 13 DEF molecules together with three water molecules and the framework is stable up to 410°C . The PXRD pattern of the desolvated sample reveals that, upon guests exchange and evacuation, the desolvated materials have much lower crystallinity and its structure cannot be obtained (Supplementary Fig. S10 & S12). N_2 gas adsorption isotherms of desolvated ZnCTV-2 at 77K shows a reversible type I behaviour without hysteresis upon desorption, indicating an open framework with accessible microporosity (Supplementary Fig. S13–S16).

Discussion

CTV analogues are a type of macrocyclic molecule with convergent binding modes, which can be easily functionalized to construct amazing structures. By using reticular chemistry, we prepared two novel crystalline MOFs with chiral cavities based on C_3 -symmetric macrocyclic CTV ligands and the octahedral $Zn_4O(CO_2)_6$ clusters. We showed our strategy to understand and to construct homochiral MOFs from racemic C_3 -symmetrical linkers. In the layer, the rigid $Zn_4O(CO_2)_6$ cluster guides the selection of enantiomers through strong coordination bonds, while between layers, the relatively weak π - π interaction plays a great role in directing the formation of chiral MOFs. This approach contributes a new guidance in the construction of chiral functional materials.

Methods

Materials. All reagents and solvents used in synthetic studies were commercially available and used as supplied without further purification unless stated otherwise. Ligand H_3L_1 and H_3L_2 were synthesized according to the method as shown in Supplementary or according to the literature procedure^{32,44}.

Synthesis of ZnCTV-1. A mixture of H_3L_1 (9 mg, 0.018 mmol), and $Zn(NO_3)_2 \cdot 6H_2O$ (19 mg, 0.064 mmol) was dissolved in a 20 mL Teflon vial containing 1 mL DMF, 1 mL ethanol, and 0.5 mL H_2O . The vial was sealed and heated at 95°C for 48 h. The resulting colorless hexagonal plate crystals were collected and washed with DMF and ethanol, dried in air overnight (10 mg, 77%). Elemental analysis (%): calcd. for $[Zn_4O(L_1)_2] \cdot DMF \cdot EtOH \cdot H_2O$ ($C_{59}H_{57}NO_{22}Zn_4$): C, 50.84; H 4.12; N 1.00; found: C, 50.84; H, 4.14; N 1.06.

Synthesis of ZnCTV-2. A mixture of H_3L_2 (10 mg, 0.014 mmol), and $ZnCl_2$ (11.5 mg, 0.084 mmol) was dissolved in a 20 mL Teflon vial containing 1 mL DEF, 1 mL ethanol, and 0.2 mL H_2O . The vial was sealed and heated at 105°C for 48 h. The resulting small colorless octahedron like crystals were collected, washed with DEF dried in air overnight (18 mg, 86%). Elemental analysis (%): calcd. for Anal. Calcd. for $[Zn_4O(L_2)_2] \cdot 13DEF \cdot 3H_2O$ ($C_{155}H_{215}N_{13}O_{35}Zn_4$): C, 60.40; H, 7.03; N, 5.91; found: C, 60.16; H, 6.48; N, 6.08.

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Acknowledgments

This work was supported by the National Natural Science Foundation of China (20932004), the Major State Basic Research Development Program of China (2011CB932501 & 2013CB933402) and the Chinese Academy of Sciences.

Author contributions


J.-T.Y., J.S., J.L., Z.-T.H. and Q.-Y.Z. designed the study, analyzed the data and wrote the paper. Y.-Y.S. conducted part of the synthetic work. J.S. and Q.-Y.Z. performed the crystal-structure analyses and constructed the models. J.-T.Y. performed the sorption measurements. All authors discussed the results and commented on the manuscript.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Yu, J.-T. *et al.* Spontaneous chiral resolution directed by symmetry restriction and π - π interaction. *Sci. Rep.* **3**, 2947; DOI:10.1038/srep02947 (2013).

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