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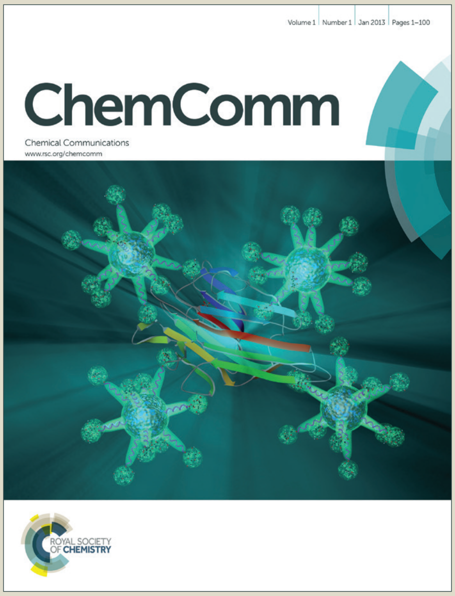

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ARTICLE TYPE

Integration of Rigid and Flexible Organic Parts for the Construction of Homochiral Metal-Organic Framework with High Porosity

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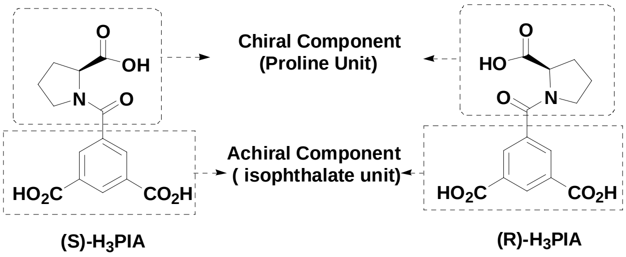
Presented is a pair of homochiral metal-organic frameworks built from mixed ligands integreting rigid and flexible organic parts, and each compound shows high porosity and can be used for enantioselective separation of racemic 1-phenethylalcohol and methyl lactate.

Homochiral metal-organic frameworks (HMOFs) have attracted more attentions for their promising application in enantioselective separation, asymmetry catalysis, and so on.[1-3] Although great progresses have made in the past ten years, the design and synthesis of HMOFs with high porosity is still a huge challenge. Self-assembly of enantiopure organic ligands with metal ions is the most effective synthesis method to construct HMOFs.[3] However, an ideal enantiopure ligand should have easy availability, low price, coordination variety and rigidity or semi-rigidity. Therefore, rational design and selection of chiral ligands has become a key factor to get multifunctional HMOFs.[4]

Nature amino acids, which are inexpensive, nontoxic and readily available, may be the ideal enantiopure linkers for the formation of HMOFs. However, for the flexible nature of amino acids, HMOFs from amino acids that possess 3D architecture as well as permanent porosity are always limited.[5] In order to overcome this limitation, we have modified the -NH_2 group of proline with 1,3,5-benzenetricarboxylic acid (H_3BTC) and synthesized a pair of proline derivatives ((*S*)-H_3PIA and (*R*)-H_3PIA) (Scheme 1). Containing proline and isophthalate units, the (*S*)-H_3PIA and (*R*)-H_3PIA are semi-rigid chiral ligands and have provided a new approach to design and construct 3D HMOFs with large porosity.[6] Furthermore, adding rigid auxiliary ligands (e.g. 4,4'-bipyridine) to support the porous structures of such HMOFs is also an effective approach.[7] So we believe the combination of semi-rigid links ((*S*)-H_3PIA or (*R*)-H_3PIA) and a rigid auxiliary ligand can synthesize HMOFs with larger porosity and specific functions.



Scheme 1. The enantiopure linkers: (*S*)-H_3PIA and (*R*)-H_3PIA.

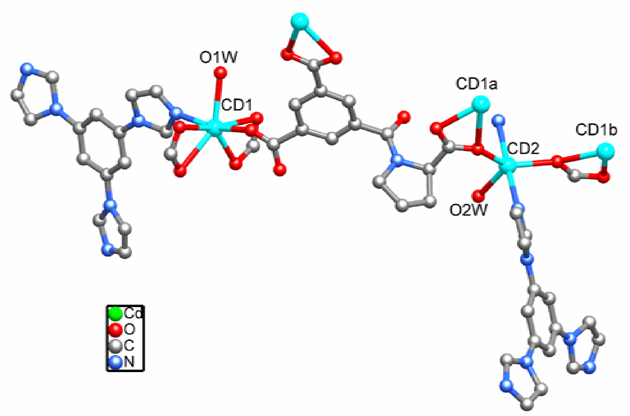


Figure 1. The coordination environment in **1-D**.

According to the above mentioned synthetic strategy, we chose a C_3 symmetric rigid ligand, 1,3,5-tri(1H-imidazol-1-yl) benzene (TIB), to help (*S*)-H_3PIA or (*R*)-H_3PIA to build HMOFs. In this contribution, a pair of Cd-based HMOFs has been gained by using mixed DMF and H_2O solvents, namely $[Cd_9((R)\text{-}PIA)_6(TIB)_4(H_2O)_{12}]\cdot 3H_2O$ (**1-D**) and $[Cd_9((S)\text{-}PIA)_6(TIB)_4(H_2O)_{12}]\cdot 3H_2O$ (**1-L**).† Compound **1-D** (**1-L**) exhibits three-dimensional porous structure with unique nanocages and trigonal helical channels.

Because compounds **1-D** and **1-L** are enantiomers, we mainly focused on the structural details of **1-D**. X-ray crystallography reveals that compound **1-D** crystallizes in the chiral space group $P4_332$ with a Flack parameter of -0.001(14).‡ There are two independent Cd(II) ions in the asymmetric unit of **1-D** (Figure 1). Cd1 has distorted pentagonal bipyramid geometry, which is coordinated by five carboxylate O atoms from three (*R*)-PIA ligands, one N atom from TIB ligand and a water O atom. Cd2 shows distorted trigonal bipyramid geometry, and it is coordinated by two carboxylate O atoms, two N atoms from two TIB ligands and a water O atom. The (*R*)-PIA ligand acts as a μ_4-linker and has two types of carboxylate groups with different coordination modes: (a) the carboxylate group from proline unit acts in bidentate bridging mode to link Cd1 and Cd2; (b) the carboxylate group of isophthalate unit only links a separate Cd ion (Cd1 or Cd2). Due to the unique coordination modes of (*R*)-H_3PIA ligand, a trigonal trinuclear Cd (Cd2, Cd1, Cd2) unit $Cd_3(CO_2)_6$ is formed (Figure S1). In this $Cd_3(CO_2)_6$ unit, the Cd1···Cd2 distance is 4.425 Å. Some guests in the pores are

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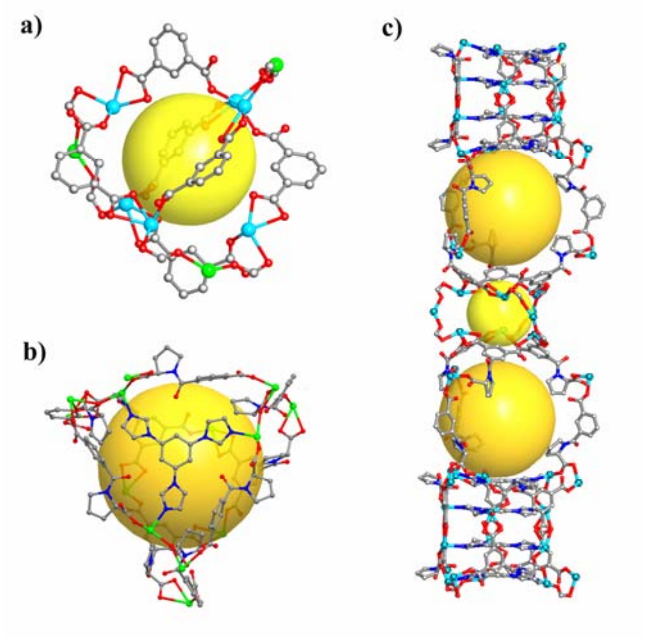

Figure 2. a) The A-cage- in **1-D**; b) the B-cage substructure in **1-D**; c) the cages in **1-D**.

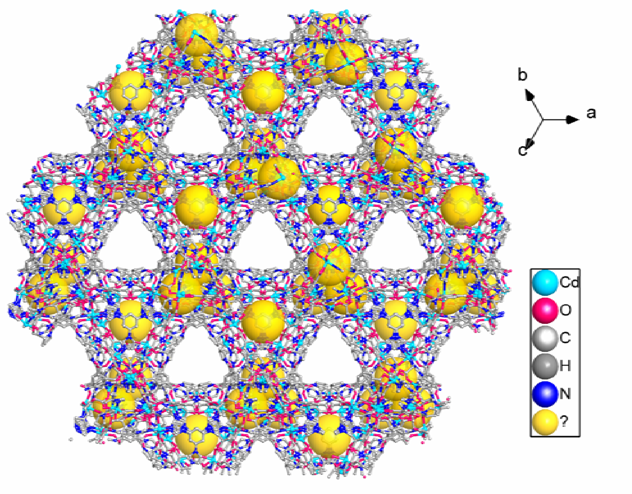

Figure 3. The 3D framework of **1-D** (The yellow balls represent the cages.).

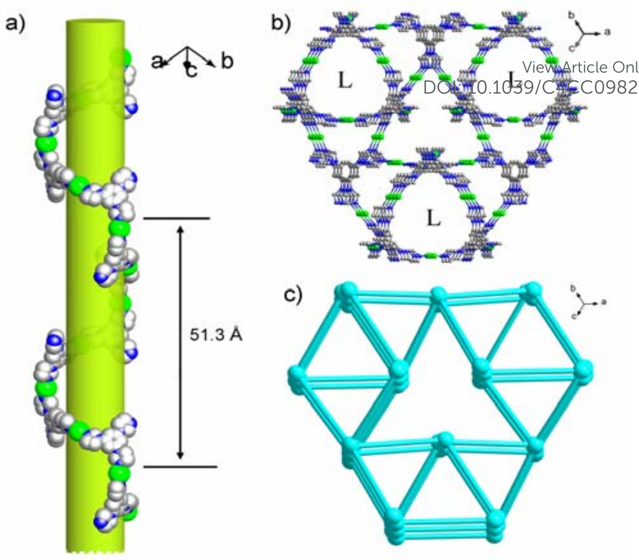

Figure 4. a) The left-handed helical channel in **1-D**; b) the 3D Cd-TIB framework in **1-D**; c) the *srs* net of Cd-TIB framework in 1-D.

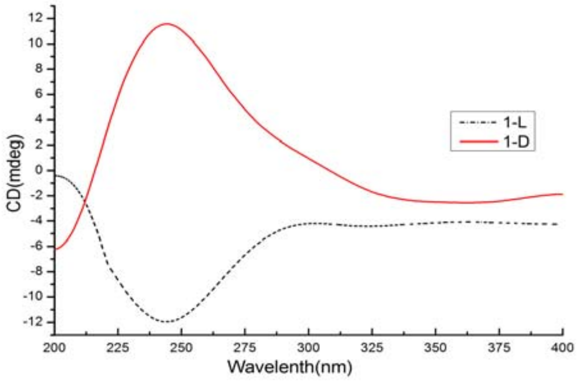

Figure 5. The solid-state CD spectra of bulk samples of **1-D** and **1-L**.

disorder and cannot be identified. The contribution of the disordered guests was subtracted from the reflection data by the SQUEEZE method.

The first outstanding structural feature of **1-D** is the presence of two types of cages in the structure (A-cage and B-cage; Figure 2). Each A-cage with inner diameter of 8 Å consists of three $Cd_3(CO_2)_6$ units and six (*R*)-PIA fragments (Figure 2a). It is interesting to note that all these (*R*)-PIA fragments are only rigid isophthalate units of (*R*)-PIA ligands and do not involve chiral proline units. However, the A-cage is still a chiral cage, because we can't find any necessary symmetry operations in it. The B-cage with inner diameter of 16 Å consists of ten Cd1, three Cd2, a TIB ligand, three (*R*)-PIA ligands and six (*R*)-PIA fragments (Figure 2b). The (*R*)-PIA fragments with proline units in B-cage are different from those in A-cage. Each A-cage links two B-cages by sharing of two triangular windows formed from three isophthalate units and three Cd1 centers (Figure 2c). Such cage-by-cage mode leads to the generation of the 3D framework of **1-D** (Figure 3).

Since the structure of **1-D** contains two distinct ligands (TIB and (*R*)-PIA), it is easy to divide the whole structure into two parts and further simplify this complicated topological net. If only the connectivity between TIB and Cd2 centers is considered, a 3D Cd-TIB framework with helical channels is generated (Figure 4a-b). The existence of trigonal helical channels is the second remarkable structural feature of **1-D**. In this Cd-TIB framework, the Cd2 ions are linked by the TIB ligands to form an infinite left-handed helical chain running along the [111] direction in **1-D**. Such a helical chain just has a trigonal channel with inner diameter of 11 Å and pitch lengths of 51.3 Å (Figure 4a). Finally, this Cd-TIB framework can be reduce into a 3-connected *srs* net with point (Schläfli) symbol of $(10^5 \cdot 10^5 \cdot 10^5)$ (Figure 4c). If the whole framework of **1-D** is considered, both (R)-PIA and TIB ligands are 3-connected nodes, and each $Cd_3(CO_2)_6$ unit is a 10-connected node. The whole framework of **1-D** can be topologically represented as a (3,3,10)-connected net with point (Schläfli) symbol of $(4^{14}.6^{10}.8^{12}.10^9)_3\,(4^3)_{10}$.

The solid-state circular dichroism (CD) measurements with

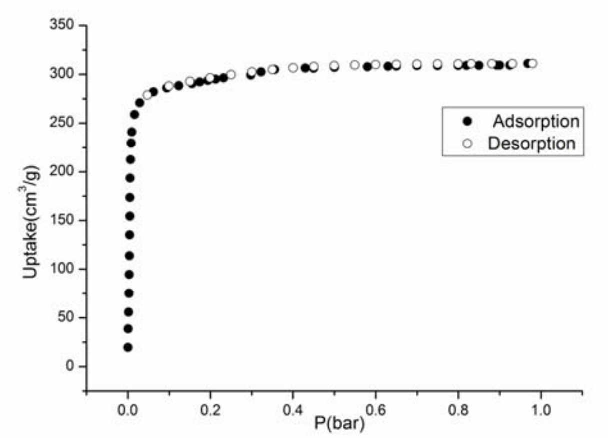

Figure 6. The N_2 sorption isotherms of **1-D** at 77k.

KCl plates between 200 and 600 nm are performed to further demonstrate the homochirality of **1-D** and **1-L** (Figure 5). The CD spectrum for the bulk sample of **1-D** exhibits an obvious positive CD signal at 243 nm, revealing its homochiral nature. A mirror image is observed for **1-L**, confirming that compounds **1-D** and **1-L** are enantiomers.

The co-existenc of cages and helical channels in the structure of **1-D** makes it a porous framework with solvent accessible volume of about 49.2% per unit cell as calculated by PLATON. The permanent porosity of **1-D** was further demonstrated by the N_2 gas sorption at 77K. The desolvated sample of **1-D** shows type-I sorption isotherms (Figure 6), and the Langmuir and Brunauer-Emmett-Teller (BET) surface areas for **1-D** are 1327.9 m^2/g and 955.8 m^2/g, respectively. To the best of our knowledge, HMOFs with such high surface area are rarely reported.

The presence of high porosity in **1-D** (**1-L**) prompts us to explore their application on enantioselective separation of racemic compounds. After screening some racemic alcohols, our studies identified that **1-D** (**1-L**) can enantioselectively separate 1-phenethylalcohol and methyl lactate (Table 1, Figures S6-7). It is obvious that **1-D** has high affinity to (*R*)-phenethylalcohol or (*R*)-methyl lactate and **1-L** is good for (*S*)-phenethylalcohol or (*S*)-methyl lactate. Such enantioselective adsorption should be attributed to hydrogen-bonding interactions between the framework and racemic agents that make the corresponding chiral molecules orderly dock in the chiral channels.[8]

In summary, by employment of a pair of predesigned proline derivative ligands ((*R*)-PIA and (*S*)-PIA) to assemble with TIB and Cd^{2+} ion, a pair of HMOFs with permanent porosity were successfully synthesized. It is unusual that the cages and helical channels are presented in the homochiral framework together. Both HMOFs have promising application on enantioselective separation of racemic alcohols. The results reveal a successful strategy on the construction of stable HMOFs with high porosity via organic ligands integreting rigid and flexible parts.

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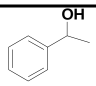
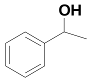
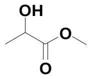
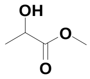
Notes and references

Table 1 Enantioselective sorption of **1-D** (**1-L**) toward racemic 1-phenethylalcohol and methyl lactate [a]

Entry	Substrate	Adsorbent	ee[b] (%)
1		**1-L**	20.3 (***S***)
2		**1-D**	21.2 (***R***)
3		**1-L**	33.0 (***S***)
4		**1-D**	34.8 (***R***)

[a] For details, see the Experimental section in ESI. [b] Determined by GC (letters in brackets specify the preferable isomer), and the deviations for the ee values are less than 5%.

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[b]*Department of Chemistry, Zunyi Normal College, Zunyi, Guizhou 563002, P. R. China.*

† Synthesis of $[Cd_9((R)\text{-PIA})_6(TIB)_4(H_2O)_{12}]\cdot 3H_2O$ (**1-D**) : the mixture of $Cd(CH_3COO)_2\cdot 2H_2O$ (0.2 mmol, 0.053 g), (*R*)-H_3PIA (0.032 g, 0.1 mmol), TIB (0.2 mmol, 0.055 g), DMF (3 ml) and H_2O (1 ml) was sealed in a 20 ml vial and heated to 100 °C for 3 days. After cooling to room-temperature, the colourless polyhedral crystals **1-D** were separated from the mixture by filtration (Yield: 42%). Similar procedure was used to synthesis compound **1-L** (Yield: 45%).

‡ Crystal data for **1-D**: $C_{48}H_{36}Cd_3N_{10}O_{18}$, $M = 1378.10$, Cubic, $a = b = c = 29.59550(10)$ Å, $V = 25922.51(15)$ Å^3, $T = 100(2)$ K, space group $P4_332$, $Z = 12$, 12945 reflections measured, 4716 independent reflections ($R_{int} = 0.0354$). The final R_1 value was 0.0557 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.1518 ($I > 2\sigma(I)$).The final R_1 value was 0.0816 (all data). The final $wR(F^2)$ value was 0.1663 (all data). The goodness of fit on F^2 was 0.982 and the Flack parameter was 0.001(14).

§ Electronic Supplementary Information (ESI) available: [Experimental details, IR spectra, TGA, powder X-ray diffraction patterns, and CIF file (CCDC-1031194 (**1-D**)]. See DOI: 10.1039/b000000x/

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