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PAPER

A 3D chiral porous In(III) coordination polymer with PtS topological net†

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The solvothermal reaction of In(III) and 1,2,4,5-benzeneteracarboxylic acid with the presence of piperazine leads to the generation of a novel 3D chiral porous coordination polymer with PtS topological net. Interestingly, the resulting crystals were not a racemic mixture but enantiomeric excess, which was confirmed by the measurement of optical rotation of bulk samples using solid vibrational circular dichroism (VCD) spectra and the solid circular dichroism (CD) spectra based on large crystals from one crystallization. High-pressure CO_2 and CH_4 adsorption measurement at 298 K reveals that activated **1** can absorb 45.8 cm^3 (STP)/g CO_2 at 22 atm and 22.5 cm^3 (STP)/g CH_4 at 25 atm.

Introduction

The design and synthesis of metal–organic frameworks (MOFs) has attracted much attention not only because of their intriguing variety of architectures and topologies but also owing to their potential applications in gas adsorption and separation, catalysis and magnetic materials.[1–5] Among them, the stable porous MOFs is the most foreground research field, and many porous coordination networks with extremely large surface areas have been constructed, based on the secondary building unit (SBU) concept that has been extensively used in the synthesis of MOFs.[6] Another important section of MOFs can be designed to possess porous functionalities and chirality, which may be exploited in size-dependent asymmetric catalysis and enantioselective separation.[7] The predictable syntheses of chiral coordination frameworks have been accomplished in the following two ways: (1) use of chiral organic building blocks as linkers to connect the adjacent metal centres or metal clusters or using chiral agents as chiral directing agent to induce the generation of chiral compounds;[8] (2) use of achiral starting materials without any chiral sources *via* spontaneous resolution, which yield chiral compounds.[9] Among them, the main synthetic approach to generate chiral materials is to use chiral multifunctional ligands, because spontaneous resolution from achiral starting materials rarely occurred due to the lack of homochiral intermolecular interactions.[10] and the products are normally a racemic mixture of chiral crystals, although each

crystal is a single enantiomer. Chirality in these frameworks is obtained from the presence of helices within noncentral space groups rather than through a chirally enriched component in the reaction mixture.[11] To date, many chiral porous metal–organic frameworks have been synthesized, while there are only limited examples of spontaneous resolution, in which the chiral information in the building units can be transmitted into higher dimensionality to generate chiral coordination polymers.[12]

1,2,4,5-Benzenetetracarboxylic acid (H_4btec) is an interesting multidentate rigid ligand employed in the assembly of coordination frameworks.[13] As compared to the number of coordination polymers assembled by transition metal ions and organic ligands, the coordination complexes formed by In(III) and organic ligands are less documented.[14] In this paper, we will report on the synthesis and structural characterization of a novel 3D chiral porous In(III) framework [H_3O][In(btec)]·0.8H_2O(**1**) with In-btec-In helical chains. To our surprise, the crystals of **1** were not a racemic mixture but enantiomeric excess, which was confirmed by the measurement of optical rotation of bulk samples using the solid VCD spectra and the solid CD spectra.

Experimental section

Materials and methods

All reagents and solvents employed were commercially available and used without further purification. The C, H and N microanalyses were carried out with Perkin–Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet 5DX spectrometer. X-ray powder diffraction (XPRD) data were recorded with a Bruker D8 diffractometer with Cu-Kα radiation (λ = 1.5418 Å). VCD spectra were measured with the Bruker PMA 37 spectrometer (resolution: 4 cm^{-1}; zero filling factor: 2; scan time: 3 h). CD spectra were measured using a JASCO J-810 spectropolarimeter. Spectra were collected on powder samples of a crystal embedded in KBr pellets between 190 and 400 nm at a speed of 100 nm min^{-1}.

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Thermogravimetric analysis (TGA) was taken on a Perkin–Elmer Pyrisl (25–600 °C, 5 °C min^{-1}, flowing $N_2(g)$).

Solvothermal synthesis

$[H_3O][In(btec)]\cdot 0.8H_2O$ (**1**). The mixture of $InCl_3\cdot 4H_2O$ (0.2 mmol, 0.059 g), H_4btec (0.3 mmol, 0.076 g), DMA (3 mL) (DMA = N,N′-dimethyl acetamide), C_2H_5OH (2 mL), piperazine (0.1 mL, 0.9 mol L^{-1} in DMF) and HNO_3 (0.28 mL, 0.7 mol L^{-1} in DMF) was added to a 23 mL teflon reactor and stirred for 20 min in air. Then the reaction system was heated at 358 K for 21 h and warmed up to 378 K for 36 h, followed by cooling to room temperature at a rate of 5 K h^{-1}. The resulting red block crystals of **1** were obtained. (30% yield, based on $InCl_3$). Elemental analysis (%) calcd. for $C_{10}H_{6.6}InO_{9.8}$ **1**: C, 30.15; H, 1.67. Found: C, 30.38; H, 1.78. Selected FTIR data (KBr, cm^{-1}): 3467(s), 1629(s), 1512(s), 1389(s), 1336(m), 1258(s), 1138(s), 1021(s), 891(s), 849(s), 827(s).

X-ray crystallography

Crystallographic data of **1** were collected at room temperature with an Apex II diffractometer with Mo-Kα radiation (λ = 0.71073 Å) and graphite monochromator using the ω-scan mode. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL.[15] The H atoms were placed at calculated positions in the riding model approximation (C–H 0.93, O–H 0.85 Å) with their temperature factors set to 1.2 times those of the equivalent isotropic temperature factors of the parent atoms. The lattice water molecules located and refined with the occupancy was fixed as exactly 0.45 according to the TGA results. Crystallographic data and experimental details for structural analyses are summarized in Table 1. The selected bond lengths and bond angles are listed in Table 2. The CCDC reference number is 821438 for **1**. †

Results and discussion

Crystal structure

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the hexagonal system, chiral space group $P6_222$ (No. 180).

Table 1 Crystallographic data and structural refinement summary for **1**

Compound	**1**
Chem. form.	$C_{10}H_{6.6}InO_{9.8}$
Form. wt	398.37
Cryst. syst.	Hexagonal
Space group	$P6_222$
a/Å	9.038(2)
c/Å	18.975(10)
V/Å^3	1342.2(9)
T/K	173(2)
D_c/g cm^{-1}	1.479
Z	3
μ(Mo-Kα)/mm^{-1}	1.356
No. unique data (R_{int})	893 (0.0669)
No. total refns	11174
Final R indices [$I > 2\sigma(I)$]^a	R_1 = 0.0615
wR_2 = 0.2140	
R indices (all data)	R_1 = 0.0767, wR_2 = 0.2285

^{a} $R_1 = \sum \|F_o| - |F_c\| / \sum |F_o|$; w$R_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$.

Table 2 Selected bond distances (Å) and angles (deg) for **1**

Bond length (Å)			
In(1)–O(1)	2.187(6)	In(1)–O(2)	2.342(6)
Bond angle (°)			
O(1A)–In(1)–O(1)	80.5(4)	O(1B)–In(1)–O(1)	115.8(5)
O(1)–In(1)–O(1C)	136.9(3)	O(1)–In(1)–O(2)	55.3(2)
O(1)–In(1)–O(2A)	131.7(2)	O(1)–In(1)–O(2B)	84.3(3)
O(2A)–In(1)–O(2)	172.6(3)	O(2)–In(1)–O(2C)	78.3(5)

Symmetry transformations used to generate equivalent atoms: A = −x+2, −x+y+1, −z+1/3, B = x, x−y−1, −z+1/3, C = −x+2, −y, z.

In this structure, there are 0.25 crystallographically independent In(III) centre, 0.25 btec ligand and 0.45 lattice water molecules in the asymmetrical unit. In consideration of charge balance, one water molecule per formula unit is protonated. As shown in Fig. 1, each In(III) centre is eight-coordinate and surrounded by eight oxygen atoms from four individual btec ligands *via* bidentate chelating coordination with the bond lengths and the bond angles in the normal range.[16] The coordination polyhedron around In(III) centre can be described as a slightly distorted square-based antiprism.[17] Four carboxylate oxygen atoms of the btec ligands are all deprotonated and adopt the same bidentate chelating coordination modes. The adjacent In(III) centres are connected by the bridging btec ligands to form 1D In-btec-In helical chain along the *c*-axis (Fig. 2a). Comparing with the previously reported compound constructed by btec ligand and In^{3+}, $[HL][In_3(btec)_2(OH)_2]$(**2**) (L = 2-picoline).[18] **2** is a 3D achiral framework, in which the In(III) atom is seven-coordinate and the four carboxylate groups of btec ligand adopt chelating bidentate, bidentate, and monodentate modes. In addition, there exists $\mu 3$-OH group in **2**.
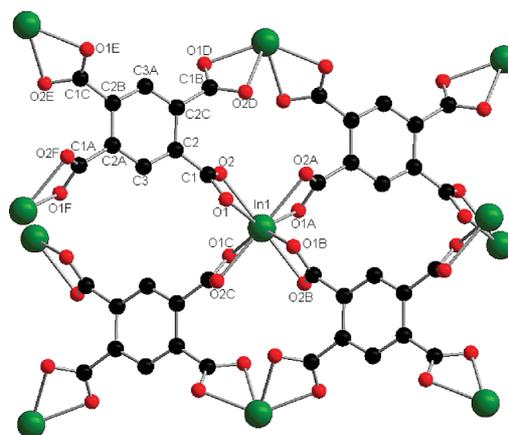
Fig. 1 The coordination environment of In(III) centres in **1**. Symmetry code: (A) −x+2, −y, −z; (B) −x+2, −x+y+1, 1/3−z; (C) +x, +x−y−1, 1/3−z; (D) −x+1, −y, +z; (E) −x+y+1, +y, −z. (F) +x−y, −y, −z.

There exist 6_1 rotation axes which contribute to the chirality of the compounds in **1** (Fig. 2b). In addition to the helical chains, the extraordinary structural feature of **1** is that there exist two types of open channels with dimensions 4.92 × 4.26 Å^2 and 9.31 × 8.47 Å^2, respectively (Fig. 3a). The micropores are occupied by lattice water molecules, and the solvent-accessible volume of the unit cell was estimated (PLATON program[19]) to be 684.4 Å^3, which is approximately 51.0% of the unit-cell volume. Hydrogen
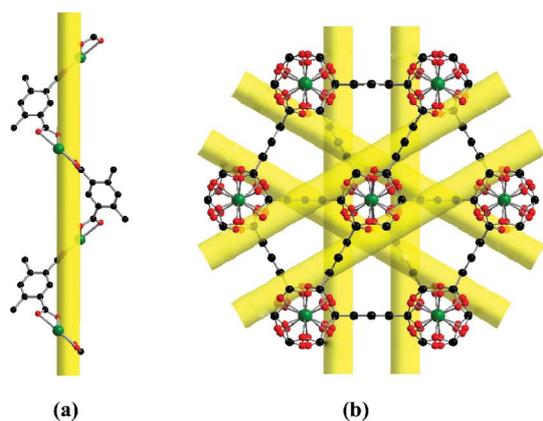
Fig. 2 (a) The fragment of In-btec-In helical chain viewed along the *c*-axis. (b) The 3D chiral framework of **1** possesses 6_1 screw axis viewed along the *c* axis.
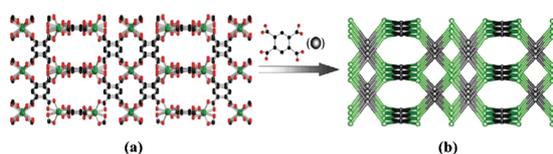
Fig. 3 (a) The 3D framework of **1** viewed along the *a*-axis. The lattice water molecules and hydrogen atoms were omitted for clarity. (b) The perspective view of the framework of **1**, oriented to show the PtS topology. (In, green circles; btec, grey circles).

bonding interactions exist between the lattice water molecules and the carboxylate oxygen atoms of btec ligands. The typical hydrogen bonds are O2W···O1W(*x*, *y*−1, *z*) 2.679(2) Å, O2W···O2(−*x*+1, −*y*−1, *z*) 3.358(2) Å.

The topological analysis of the network has been performed using OLEX[20] by considering both the metal ion and the ligand as topological nodes. The individual 3D motif can be reduced as a 4-connected network (Schläfli symbol is $(4^2)_2(8^4)$ if the btec ligand can be considered as square planar vertices and In(III) ions are simplified as tetrahedral nodes (Fig. 3b). Equal numbers of tetrahedral nodes and square planar vertices exist. This is the feature of PtS (cooperite) topology in which Pt forms PtS_4 rectangles and S forms SPt_4 tetrahedra.[21–22]

The most attractive structural feature of **1** is that the 3D framework possesses chirality. Fig. 4 shows the experimental IR and VCD spectra of the crystals, which are assigned as follows: the
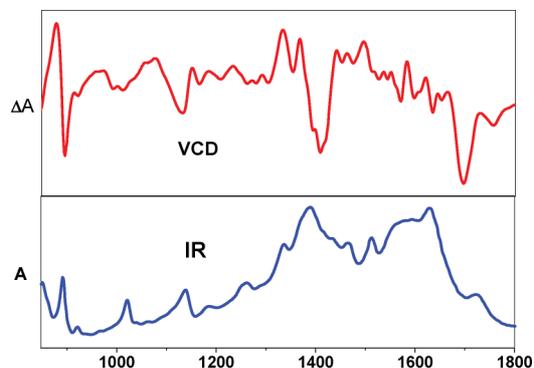
Fig. 4 The IR absorption spectra (top) and VCD (bottom) of **1** in the solid state at room temperature.

bands at 1258, 1336, 1389, 1468 and 1629 cm^{-1} are attributed to C–O stretch vibrations, and the bands at 1512 cm^{-1} are assigned to skeleton vibrations of the aromatic ring. The experimental VCD bands at 1246–1275, 1323–1344, 1388–1422, 1451–1472 and 1625–1644 cm^{-1} correspond to C–O stretch vibrations, and the bands at 1508–1540 cm^{-1} correspond to skeleton vibrations of the aromatic rings. The carboxyl group and the aromatic ring construct one type of In-btec-In helical chain. There is good agreement between the IR and VCD spectra. Each infrared absorption peak corresponded to a VCD feature, which could be either positive or negative. The relative intensities of the VCD bands could be greater or less than the relative intensities of their absorption bands. The vibrational modes were identified and conformational information can also be observed in VCD spectra. The strong VCD signals show that the crystals of $[H_3O][In(btec)]\cdot 0.8H_2O$ were not racemic.

To further investigate the absolute configurations of the two enantiomers, solid CD spectra of crystals synthesized in the same crystallization were measured.[23] As shown in Fig. 5, A and B are mirror images of one another and show different cotton effects in the wavelength range of 190–400 nm, demonstrating the formation of either left-handed or right-handed enantiomers in a crystal, which confirms the spontaneous resolution during the course of crystallization. Furthermore, based on the CD measurement of 20 crystals from one crystallization (Fig. S1†), the enantiomeric excess ee value (ee = $100 \times (A-B)/(A+B)$) for the crystallization is calculated to be *ca.* 60,[24] also confirming that there exists enantiomeric excess of the whole crystallization.
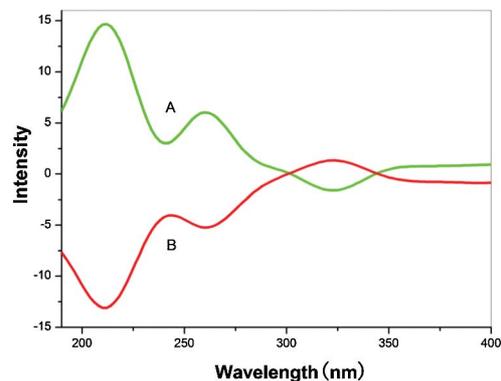
Fig. 5 Solid-state CD spectra of crystals of **1** showing the contrasting cotton effects.

In order to investigate the reason for the observed enantiomeric excess in the $[H_3O][In(btec)]\cdot 0.8H_2O$ product, we have checked all the reagents and solvents, and confirmed that we did not introduce any chiral stimulant during the synthetic procedure. The enantiomeric excess is unusual in spontaneous resolution and the reason may be explained by the fact that the initial crystals formed may seed the handedness of the bulk product in crystal growth, and thus the particular handedness of the bulk depends on which random hand is formed, which is similar to the previous reported results.[25]

XRPD patterns, thermogravimetric analysis and solid state electronic spectra

The simulated and experimental XRPD pattern of **1** is shown in Fig. S2. Its peak positions are in good agreement with each other,

indicating the phase purity of the products. The differences in intensity may be due to the preferred orientation of the powder samples. The thermal stability of **1** was examined by TGA in a dry nitrogen atmosphere from 25 to 600 °C. The first step from 25–135 °C with *ca.* 8.23% loss may be attributed to the loss of guest water molecules (the weight *ca.* 8.13%), and then began to decompose upon further heating (Fig. S3†). The diffuse reflectance UV-vis spectra for **1** show absorption bands at 248, 288 and 422 nm (Fig. 6), corresponding to the intraligand π–π^* transitions of ligands.[26] On the other hand, the longer wavelength band in the UV region shifts toward lower energy upon coordination, which may arise from the n-π^* transition perturbed by the In^{3+} ions.
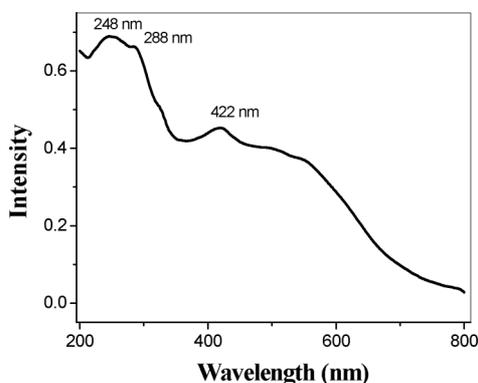
Fig. 6 The solid UV-vis Spectra of **1** in the solid state at room temperature.

Photoluminescent property

The excitation and emission spectra of **1** are depicted in Fig. 7. In the solid state, strong fluorescent emission bands at 467 nm (λ_{ex} = 316 nm) are observed at room temperature. Because the H_4btec has weak emission at 340 nm under the same experimental conditions,[27] the fluorescent emission of **1** may be attributed the charge transition of btec ligands to In(III) centres (LMCT).[28] Although the photoluminescence of some d^{10} metal coordination polymers with aromatic carboxylate ligands have been widely documented, the photoluminescent properties of In(III) coordination polymers are rarely reported.[25a,28]
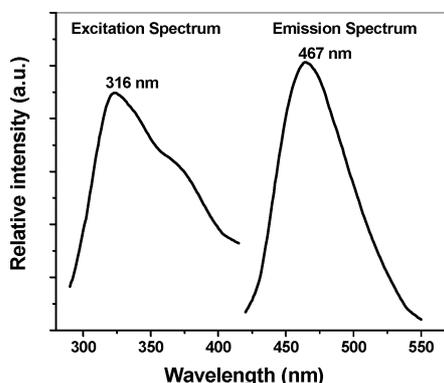
Fig. 7 The luminescent spectra of **1** in the solid state at room temperature.

Gas sorption properties

The porosity of **1** is confirmed by their CO_2 and CH_4 sorption at 298 K. Before the measurements, the samples of **1** were soaked in methanol and evacuated at room temperature for 24 h to obtain the activated samples. Fig. 8 displays the adsorption isotherms of CO_2/CH_4 gases in **1** at 298 K. The results show that **1** possesses a maximum uptake of 45.8 cm³ (STP)/g (22.0 atm) for CO_2 and 22.5 cm³ (STP)/g (25 atm) for CH_4, respectively. CO_2 is more strongly adsorbed than CH_4, which is expected because CO_2 has a significant quadrupole moment, whereas CH_4 is essentially nonpolar.[29] The CO_2 sorption isotherms of **1** exhibit the typical type I behaviors and CH_4 sorption isotherms of **1** exhibit sigmoidal shape with increasing uptake. The CO_2/CH_4 adsorption isotherms are irreversible and the presence of a hysteresis suggests that **1** has uniformed microporsity,[30] which is consistent with the results of single-crystal X-ray diffraction analysis.
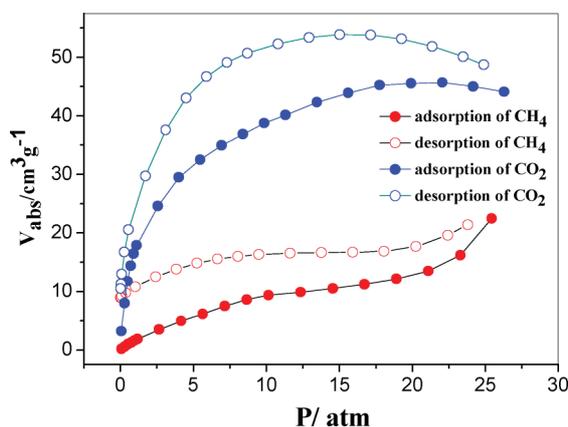
Fig. 8 Gas adsorption isotherms of the activated **1**: CO_2 and CH_4 at room temperature.

Conclusions

In summary, we have developed a synthetic strategy toward 3D chiral porous PtS-type coordination framework with In(III)-btec-In(III) helical chains by using btec ligand and In(III) ion with the presence of piperazine. CD and VCD spectra confirm that the bulk samples were not a racemic mixture but enantiomeric excess. This work provides a good route for further exploration of preparing optical coordination polymer and other aesthetic structural motifs.

Acknowledgements

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