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A Chiral Metal–Organic Framework Based on Heptanuclear Zinc Cores

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Two zinc(II) complexes, $[Zn_9(L1)_6(H_2O)_2]\cdot 13.5H_2O$ (**1**) and $[Zn_9(L2)_6(H_2O)_3]\cdot C_2H_5OH\cdot 8.5H_2O$ (**2**), were synthesized. Both **1** and **2** are constructed from molecular building units (MBUs) that contain heptanuclear zinc clusters as cores. By introducing an additional chiral site into the original ligand, we achieved the transformation of the MOF from a nonchiral to a chiral structure, which provides a new strategy for designing chiral compounds.

Introduction

Molecular building units (MBUs) facilitate the design and construction of functional materials, as exemplified by metal–organic frameworks (MOFs).[1] Such MOFs have attracted much attention on their considerable advantages, because of their unique structure, chemical and physical properties.[2] The MBUs approach represents an evolution of the "node-and-spacer" approach, which exploits the variety of architectures and topologies by metal connecting points and bridging ligands to generate 2D and 3D networks.[3] Thus, the size and the constructional mode of MBUs are crucial for the whole structure and functional properties of MOFs.[4] Of concurrent interest have been the construction of chiral systems: in recent years, most efforts have been made to generate chiral inorganic–organic materials for their numerous potential applications as enantioselective catalysts and chiral separators.[5] In order to exploit a new generation of functional materials, chemists have considered to introduce a chiral feature into such MOFs for wider applications.[6] However, the difficulties are obvious. On the one hand, the construction of MBUs often confine these complexes into highly ordered structures with high dimensionality.[7] On the other hand, the chiral features often disappear in the units and result in racemic structures,[8] so chiral complexes which are constructed from MBUs are rarely reported.

Results and Discussion

To construct such chiral MOFs, we first chose 1-phosphonomethylproline (H_3L1), as the chiral ligand and synthesized a novel 2D layered complex $[Zn_9(L1)_6(H_2O)_2]\cdot 13.5H_2O$ (**1**). Compound **1** crystallizes in the trigonal space group *P*31*c*. The asymmetric unit of **1** contains three coordination environments of Zn atoms, which are shown in Figure 1. Zn1 is octahedrally coordinated by six phosphonate oxygen atoms from tridentate chelating ligands, while both Zn2 and Zn3 are five-fold-coordinated by a chelate ligand (O6, N2, O8) and two phosphonate oxygen atoms (O4, O10) from two neighbouring ligands, exhibiting a distorted trigonal bipyramidal geometry. Unusually, Zn4 (Zn5) is four-coordinate, being coordinated by three carboxylate atoms (O2) from three ligands and one water molecule (O12) to form a distorted $[ZnO_4]$ tetrahedron. The crystal structure of **1** is assembled from previously unknown unit $\{[Zn_7(L1)_6][Zn_6(H_2O)_6]\}$ (MBU-**1**). One key feature of MBU-**1** is the presence of a $[Zn_7(L1)_6]^{4-}$ core, which is constructed from metal ions and chelate ligands. This octahedral core is surrounded by six outer ZnO_4 tetrahedra to form a novel structure with the heptanuclear zinc cluster as a core (Figure 1). Notably, the MBU-**1** in **1** contains three types of Zn atoms with the coordination numbers 6, 5 and 4, which are arranged in order from inside to outside (Figure 1). To the best of our knowledge, this is the first zinc complex that contains three kinds of coordination numbers in the Zn atoms.

In contrast to the chiral product by a similar reaction,[9] the whole structure of **1** is racemic, because the chiral groups in the original ligands are all coordinated. We wondered whether **1** could acquire the chiral feature if one more chiral site were introduced into the original ligand (H_3L1), and further whether it would transform the chiral feature to the whole structure. By using this idea, a new ligand, 1-phosphonomethyl-4-hydroxyproline (H_3L2), was adopted, and a chiral layered complex, $[Zn_9(L2)_6(H_2O)_3]\cdot C_2H_5OH\cdot 8.5H_2O$ (**2**), was synthesized under nearly the same conditions.

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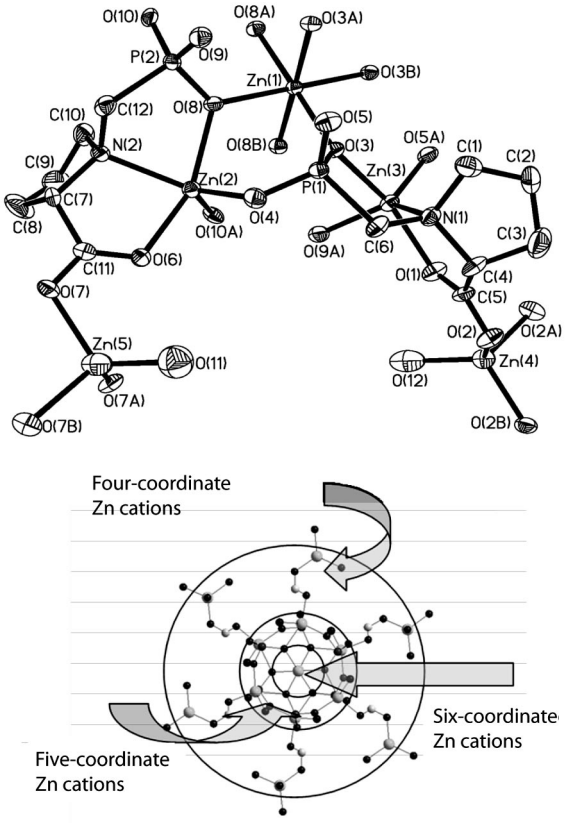
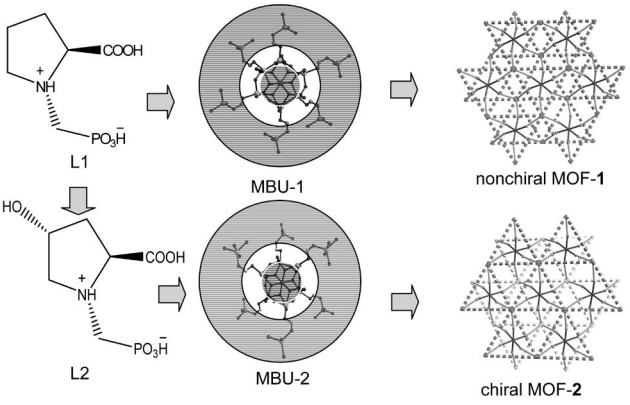


Figure 1. ORTEP drawing (at 50% probability) of the asymmetric unit for **1** and three types of Zn atoms of MBU-**1** with the coordination numbers 6, 5 and 4, which are arranged in order from inside to outside (Zn: big grey spheres; C: small grey spheres; O: black spheres).

Complex **2** crystallizes in the chiral space group *P*1. Seven zinc(II) cations in the heptanuclear $[Zn_7(L2)_6]^{4-}$ core form an unusual centred octahedron similar to the one in **1** (Figure S1). Similarly, **2** was constructed from $\{[Zn_7(L2)_6]$-$[Zn_3(H_2O)_3][Zn_3(H_2O)_6]\}$ units (MBU-**2**). Unlike MBU-**1**, MBU-**2** has the chiral –OH sites and further influences numbers of the coordination water molecules of the outer zinc atoms. One octahedral $[Zn_7(L2)_6]^{4-}$ core is surrounded by three ZnO_4 and three ZnO_5 polyhedra (Figure 2). The distance between two planes is about 12 Å (Figure S2). Both MBU-**1** and MBU-**2** are edge-sharing $[ZnO_n]$ (n = 4 or 5) polyhedra that construct infinite 2D layered structures, which exhibit an interesting geometry in the reported MOFs. Interestingly, the structures present intralayer channels of 4×5 Å^2 along the [010] direction (measuring the distances between the centres of opposite atoms, Figure S3).

In the structure of **2**, the coordination of H_3L2 to the zinc atoms through the phosphonate group, the bidentate carboxylate group and even the amine group leaves the hydroxy group free. Compared to **1**, the chiral site –OH of H_3L2 in **2** is uncoordinated, and the functionality of the material is retained. The free hydroxy groups with O–H bonds are active sites and are directed into the interlayers that provide the potential application for asymmetric catalysis and chiral separation (Scheme 1). Indeed, several chiral MOFs with active sites have been reported recently, but there are no polynuclear building units in their structures.[10]



Scheme 1. The constructions of MBU-**1** and MBU-**2** and the chiral transformation from MOF-**1** to MOF-**2**.

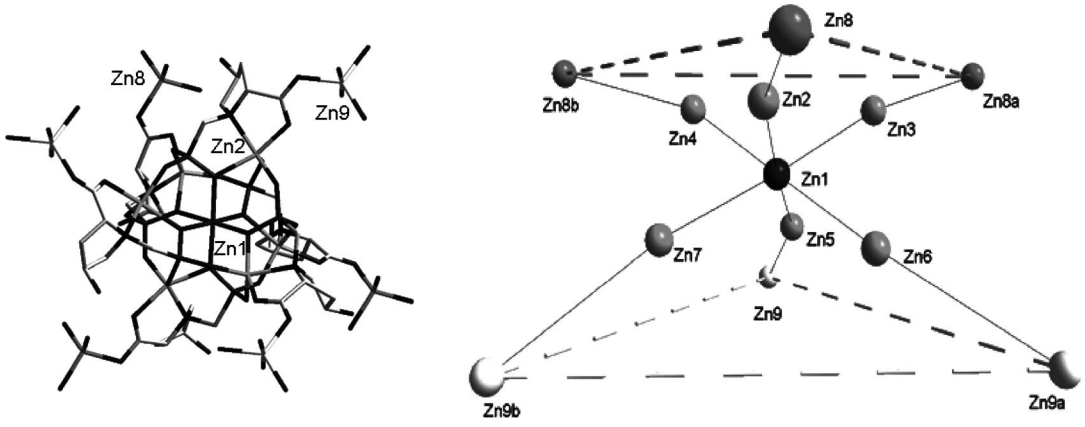


Figure 2. The wire (left) and representation (right) diagrams of MBU-**2** (Zn1: six-coordinate, Zn2: five-coordinate, Zn8: four-coordinate and Zn9: five-coordinate).

The thermal gravimetric analysis (TGA) curve for **1** shows one sharp weight loss of 12.7% in the range 313–443 K, which is equivalent to the loss of 15.5 water molecules per formula unit (calcd. 13.3%). For **2**, the curve shows a weight loss of 12.4% in the temperature range 298–473 K, which is equivalent to the loss of 11.5 water molecules and one ethanol molecule per formula unit (calcd. 11.6%) (Figure S4). The coordination networks have good thermal stability and begin to decompose at 673 K. The XRD spectra indicate that the structure remains compact after the coordinated and guess molecules are removed (Figure S5).

To examine the chiroptical activity of the enantiopure compound in solid state, solid CD spectra of **2** and ligand H_3L2 were investigated in the wavelength range 190–300 nm. The CD spectrum of H_3L2 exhibits a negative Cotton effect at 193 nm, while a positive Cotton effect is revealed at 212 nm. The CD spectrum of **2** displays strong Cotton effects with opposite signs at nearly the same wavelengths (Figure 3). The Flack parameter of **2** is 0.010 (10), which indicates that there is no racemization of the enantiopure ligand during the hydrothermal synthesis. The chiral feature transfers from the original chiral ligand to the MBUs through the metal–ligand–metal bridges, and it causes the units and even the whole structure to have a low symmetry.[11]

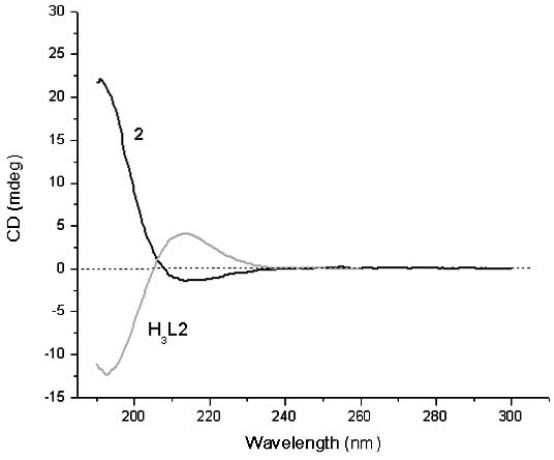


Figure 3. Solid CD spectra of **2** and ligand H_3L2.

The solid-state luminescence properties of ligands and compounds were investigated at room temperature. While the free ligands H_3L1 and H_3L2 display luminescence at 347 and 427 nm, **1** exhibits one emission at 352 nm and **2** has an emission at 431 nm (Figure 4). Thus, it can be presumed that these emissions originate from intraligand transitions, and the presence of Zn^{II} ions shows the electron-withdrawing effect owing to the +2 charge of the cations. The redshift of the emission peaks can be ascribed to metal–ligand coordinative interactions.

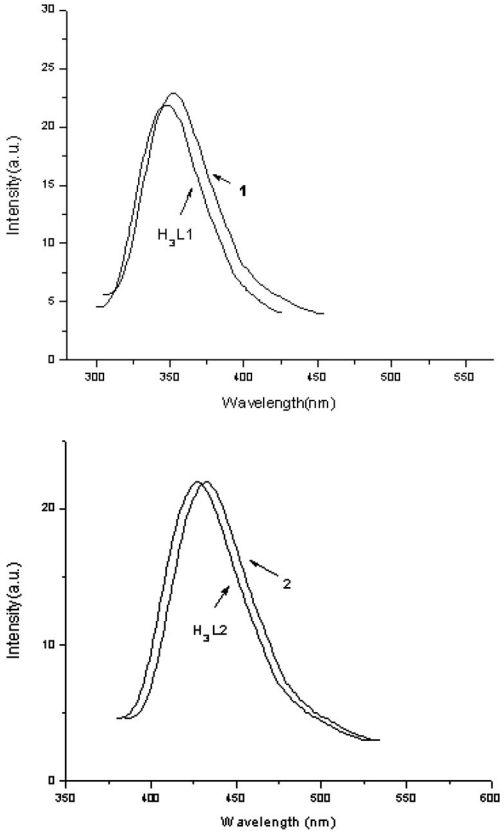


Figure 4. Photoinduced solid emission spectra of H_3L1 and **1** (excited at 280 nm) (top) and H_3L2 and **2** (excited at 362 nm) (bottom) at room temperature.

Conclusions

In summary, we have successfully synthesized two coordination compounds constructed from heptanuclear zinc cores linked by metal–ligand–metal bridges. Importantly, by introducing an additional chiral site to the original ligand (H_3L1), we achieved the transformation of the MOFs from a nonchiral to a chiral structure. The active chiral sites in **2** enable a wide range of potential applications in asymmetric catalysis and chiral separation. Further studies are in progress.

Experimental Section

H_3L1: HCHO (40 mmol, 36% in water) was added dropwise to a mixture of L-proline (10 mmol), H_3PO_3 (12 mmol) and HCl (30 mL of a 6.0 m aqueous solution) under reflux. The resultant solution was then heated at reflux for a further 12 h. A white solid was recovered after removal of water and recrystallized from EtOH. Yield: 1.88 g, 90% (based on L-proline). M.p. 256–257 °C. $C_6H_{12}NO_5P$ (209.14): calcd. C 34.44, N 6.69, H 5.74; found C 34.35, N 6.82, H 5.68.

H_3L2: HCHO (40 mmol, 36% in water) was added dropwise to a mixture of *trans*-4-hydro-L-proline (10 mmol), H_3PO_3 (12 mmol) and HCl (30 mL of a 6.0 m aqueous solution) under reflux. The resultant solution was then heated at reflux for a further 12 h. A white solid was recovered after removal of water and recrystallized

from EtOH. Yield: 1.82 g, 81% (based on *trans*-4-hydro-L-proline). M.p. 253–254 °C. $C_6H_{12}NO_6P$ (225.14): calcd. C 32.01, N 6.22, H 5.37; found C 32.11, N 6.31, H 5.28.

1: A mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (0.5 mmol, 0.149 g), H_3L1 (0.5 mmol, 0.105 g) and H_2O (10 mL), whose pH value was adjusted to 6.5 by addition of triethylamine, was heated at 160 °C in a Teflon-lined stainless steel autoclave for three days. Afterwards, the reaction system was slowly cooled to room temperature. After filtration, the ethanol was slowly diffused into the yellowish solution. After several days, colourless crystal plates were obtained. Yield: 0.028 g, 24% (based on metal). Inductively coupled plasma (ICP) analysis: calcd. Zn 27.97, P 8.83; found Zn 27.90, P 8.93. $C_{36}H_{85}N_6O_{45.5}P_6Zn_9$ (2104.60): calcd. C 20.54, H 4.07, N 3.99; found C 20.62, H 4.13, N 4.12.

2: A mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (0.5 mmol, 0.149 g), H_3L2 (0.5 mmol, 0.113 g) and H_2O (10 mL) whoshe pH value was adjusted to 6.5 by addition of triethylamine, was heated at 160 °C in a Teflon-lined stainless steel autoclave for three days. Afterwards, the reaction system was slowly cooled to room temperature. After filtration, the ethanol was slowly diffused into the yellowish solution. After several days, colourless crystal plates were obtained. Yield: 0.054 g, 45% (based on metal). $C_{38}H_{83}N_6O_{48.5}P_6Zn_9$ (2174.60): Inductively coupled plasma (ICP) analysis: calcd. Zn 27.07, P 8.55; found Zn 27.19, P 8.70. $C_{38}H_{83}N_6O_{48.5}P_6Zn_9$ (2174.60): calcd. C 20.99, H 3.85, N 3.86; found C 20.85, H 3.79, N 3.91.

Crystal Data for Compounds

Crystal Data for 1: $C_{36}H_{85}N_6O_{45.5}P_6Zn_9$, M_r = 2104.60, trigonal, space group $P31c$, a = 13.5658(10) Å, b = 13.5658(10) Å, c = 24.835(4) Å, γ = 120°, V = 3958.1(8) Å^3, Z = 2, μ = 2.888 mm^{-1}, ρ = 1.699 g cm^{-3}, T = 293(2) K, R_1 = 0.0413, wR_2 = 0.1102 ($I > 2\sigma$), GOF = 0.978.

Crystal Data for 2: $C_{38}H_{83}N_6O_{48.5}P_6Zn_9$, M_r = 2174.60, triclinic, space group $P1$, a = 13.329(3) Å, b = 13.566(3) Å, c = 13.580(3) Å, α = 60.67(3)°, β = 80.92(3)°, γ = 67.84(3)°, V = 1981.5(8) Å^3, Z = 1, μ = 2.897 mm^{-1}, ρ = 1.825 g cm^{-3}, T = 293(2) K, R_1 = 0.0538, wR_2 = 0.1397 ($I > 2\sigma$), GOF = 1.036.

CCDC-711334 (for **1**) and -711335 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): TGA curves and powder XRD patterns of **1** and **2** are available.

Acknowledgments

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