Li et al. Homochiral zinc phosphite/phosphate networks with biofunctional amino acids

Holland Metal–dioxygen and metal–dinitrogen complexes: where are the electrons?
Two new homochiral inorganic–organic hybrid frameworks [Zn(HPO₃)(C₁₁N₂O₂H₁₂)] (denoted as ZnHPO-CJ56) and [Zn₆(H₂O)(PO₄)(HPO₄)(C₆H₉N₃O₂)₂(C₆H₈N₃O₂)] (ZnPO-CJ57) have been hydrothermally synthesized in the presence of chiral amino acids L-tryptophan and L-histidine. Both of their inorganic networks are featured by one-dimensional (1D) edge-sharing Zn₆P₃ ladder-like chains. The amino acid molecules as the ligands are grafted onto two sides of the chain. Extensive N–H◊◊◊O and O–H◊◊◊O hydrogen bonds of host–guest are formed to stabilize the chiral structures of ZnHPO-CJ56 and ZnPO-CJ57. It is noteworthy that the original chirality of the amino acid molecules is maintained in the structures of the as-synthesized compounds, and the resulting crystals have an enantiometric excess, which is confirmed by the solid state vibrational circular dichroism (VCD). Their syntheses, structures, and luminescence properties have been studied in detail. The formation of such chiral one-dimensional structures with multi-amino acids might be potentially applied in chiral catalysis, biochemistry processes or as functional materials.

**Introduction**

The increasing demand of materials for enantioselective separation and catalysis, and the importance of chirality in biological processes have stimulated extensive research in the synthesis of chiral open-framework materials. The control of chirality in the synthesis of open-framework materials is particularly difficult due to the unclear formation mechanism of the inorganic framework assembled around the organic templates. So far, several feasible synthetic approaches have been developed towards the synthesis of chiral framework materials. One effective synthetic approach is to use chiral templates to impart their chirality into the open frameworks. Our research group’s work further demonstrates that the use of chiral metal complex templates has greatly facilitated the formation of open-framework metal phosphates with chiral features. Another synthetic approach is to incorporate chiral groups into organic–inorganic hybrid frameworks to produce chiral structures by the utilization of the stereo effect of chiral groups. Such examples include a homochiral three-dimensional (3D) zinc phosphate Zn₆[(S)-O,PCH₁,NHC₄H₂O₂], by using an enantiomerically pure derivative of (S)-proline as a chiral building unit, and a 1D chain gallophosphate using enantiopure 1,2-R,R-diaminocyclohexane as the template. Recently, natural chiral amino acids as the attractive building blocks have been used for the synthesis of chiral framework structures. In the literature, a few successes have been achieved in the synthesis of inorganic open-framework structures by using chiral amino acid molecules as the templates or ligands. However, chiral amino acid used for this purpose tends to racemize under hydrothermal conditions. For example, chiral L-histidine and L-histidine molecules as the ligands were racemized in the synthesis of Zn(HPO₄)(C₆H₉N₃O₂), Zn(HPO₄)(O-1H-C₆H₅N₃O₂)(H₂O)₁/₂ and (C₆H₉N₃O₂)Zn(HPO₄)(PO₄)₂H₂O. One exceptional example is the chiral L-asparagine templated 1D zinc phosphate C₁₁N₂O₃H₂ZnHPO₃. More recently, Ken Yao and co-workers report the development of chiral layered spaces by grafting amino acids in layered CPAPhs, which exhibits the potential usefulness in chiral molecular recognition and selection processes.

Herein, we present two new zinc phosphate/phosphate compounds [Zn(HPO₄)(C₁₁N₂O₂H₁₂)] (ZnHPO-CJ56) and [Zn₆(H₂O)(PO₄)(HPO₄)(C₆H₉N₃O₂)₂(C₆H₈N₃O₂)] (ZnPO-CJ57) synthesized by using chiral L-tryptophan and L-histidine molecules as both the templates and the ligands. Significantly, the amino acid molecules retain their original chirality in the synthesis, and the resulting crystals have optical activity. This work will be helpful for the synthesis of crystalline inorganic–organic hybrid materials with chiral biofunctional ligands.
Experimental

Materials and methods

All reagents were obtained from commercial sources and used without further purification. X-Ray powder diffraction (XRD) data for the two compounds were collected on a Rigaku X-ray diffractometer using CuKα radiation (λ = 1.5418 Å). ICP analysis was carried out on a Perkin-Elmer Optima 3300 DV ICP instrument. Elemental analyses were conducted on a Perkin-Elmer 2400 elemental analyzer. Thermogravimetric (TG) analysis was performed on a Perkin-Elmer TG 2101 unit in the air with a heating rate of 10 °C min⁻¹. VCD spectra were measured with the Bruker Equinox 55 spectrometer (resolution: 4 cm⁻¹; scan time: 8 h). Photoluminescent spectra were measured on a RF-5301 PC spectrometer.

Synthesis of [Zn(HPO₃)(C₁₁N₂O₂H₁₂)] (ZnHPO-CJ56)

ZnHPO-CJ56 was prepared hydrothermally from a reaction mixture of ZnO, H₃PO₃, L-tryptophan (L-Trp) and H₂O with a molar ratio of 1.0 : 1.4 : 2.0 : 9.93 : 556.16 at 100 °C for 8 h. Photoluminescent spectra were measured on a RF-5301 PC spectrometer.

Characterization of ZnHPO-CJ56 and ZnPO-CJ57

X-Ray powder diffraction (XRD) data for the two compounds were collected on a Rigaku X-ray diffractometer using CuKα radiation (λ = 1.5418 Å). The experimental and simulated XRD patterns for ZnHPO-CJ56 and ZnPO-CJ57 were in good agreement, suggesting the phase purity of the as-synthesized products (ESI, Fig. S1). ICP analysis was carried out on a Perkin-Elmer Optima 3300 DV ICP instrument. Elemental analyses were conducted on a Perkin-Elmer 2400 elemental analyzer. Thermogravimetric (TG) analysis was performed on a Perkin-Elmer TG 2101 unit in the air with a heating rate of 10 °C min⁻¹. VCD spectra were measured with the Bruker Equinox 55 spectrometer (resolution: 4 cm⁻¹; scan time: 8 h). Photoluminescent spectra were measured on a RF-5301 PC spectrometer.

Synthesis of [Zn(H₂O)(PO₄)(HPO₄)(C₆H₉N₃O₂)₂(C₆H₈N₃O₂)] (ZnPO-CJ57)

ZnPO-CJ57 was synthesized by a hydrothermal reaction of ZnO, Na₂HPO₄, 12H₂O, L-histidine (L-His), HCl, and H₂O in a molar ratio of 1.0 : 1.4 : 2.0 : 9.93 : 556.16 at 100 °C for 8 h. The colourless rectangle shaped single crystals were separated from the remainder of the product by sonication, washed with distilled water, and then dried for characterization.

Results and discussion

Structures of ZnHPO-CJ56 and ZnPO-CJ57

Single-crystal structural analysis reveals that in the asymmetric unit of ZnHPO-CJ56 there are twenty non-hydrogen atoms, including one crystallographically distinct Zn atom, one crystallographically distinct P atom, and one L-tryptophan molecule (Fig. 1a). The zinc atom is tetrahedrally coordinated to three O atoms bridging P atoms, and a carboxylate O atom of the tryptophan molecule. The Zn–O bond lengths are in the range of 1.935(4)–1.993(3) Å and O–Zn–O bond angles vary from 103.02(15) to 117.46(15)°. The P atom shares three O atoms with adjacent Zn atoms, and the fourth tetrahedral vertex is occupied by an H atom. The existence of P–H bonds is confirmed by the characteristic band of the phosphate anion (ν(H–P), 2402 cm⁻¹) in the IR spectrum (ESI, Fig. S3). ICP analysis was carried out on a Perkin-Elmer Optima 3300 DV ICP instrument. Elemental analyses were conducted on a Perkin-Elmer 2400 elemental analyzer. Thermogravimetric (TG) analysis was performed on a Perkin-Elmer TG 2101 unit in the air with a heating rate of 10 °C min⁻¹. VCD spectra were measured with the Bruker Equinox 55 spectrometer (resolution: 4 cm⁻¹; scan time: 8 h). Photoluminescent spectra were measured on a RF-5301 PC spectrometer.

Various interchain N–H···O bonds are formed between L-tryptophan and the inorganic chains in ZnHPO-CJ56 (Fig. 3). The N(1) atom forms H-bonds with O(2), O(3), O(4) and O(5) atoms, and N···O distances are in the range of 2.792(6)–3.139(6) Å. These H-bonding interactions may help to stabilize the chiral structure of ZnHPO-CJ56.
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The framework of ZnPO-CJ57 is constructed by the alternating phosphate ZnPO-CJ57 also possesses 1D ladder-like chains. Its phosphates. Hydrogen bonding is an important factor in defining the molecular packing, and various intrachain and interchain N–

As with zinc phosphite ZnHPO-CJ56, the structure of zinc phosphate ZnPO-CJ57 also possesses 1D ladder-like chains. Its asymmetric unit contains three crystallographically distinct Zn atoms, two crystallographically distinct P atoms, three L-histidine molecules, and one water molecule (Fig. 1b). The Zn(1) and Zn(2) atoms are both coordinated to three O atoms bridging P atoms and an imidazole nitrogen atom of the protonated L-histidine. Zn(3) atom shares an oxygen atom with adjacent P atom, an oxygen atom of a water molecule and two nitrogen atoms within one histidine molecule to form ZnO2N2 tetrahedron. The Zn–O bond lengths are in the range of 1.904(4)–1.957(4) Å and O–Zn–O bond angles vary in the range of 107.33(18)–113.5(3)°. P(1) atom connects four O atoms to nearby Zn atoms, and P(2) atom shares three O atoms with adjacent Zn atoms, leaving one terminal -OH group (P–OH: 1.592(4) Å). The P–O_{\text{trigonal}} bond lengths (av. 1.522 Å), and O–P–O bond angles (105.7(2)–117.6(2)°) are typical for those observed in the metal phosphates.21

The framework of ZnPO-CJ57 is constructed by the alternating connection of ZnO2N2 and PO4/HPO4 tetrahedra to form edge-shared ladder-like Zn2P4 4-ring chains propagating along the c axis, and additional ZnO2N2 tetrahedra as pendants that are grafted onto the P atoms of one side of this chain (Fig. 4). L-histidine molecules as the ligands link to the Zn atoms of two sides of such chains, which exhibit two coordination modes: one is a monodentate ligand coordinating to Zn(1) and Zn(2) atoms, the other is a bidentate ligand coordinating to Zn(3) atom. The individual bond lengths and angles of histidine molecules are unexceptional.22 Interestingly, all the histidine molecules in the structure of ZnPO-CJ57 also have the same configuration as the initially added homochiral L-histidine molecules, resulting in the final structure crystallized in the chiral space group P21212 (no. 18), and the Flack absolute structure parameter of 0.028(16).

Hydrogen bonding is an important factor in defining the molecular packing, and various intrachain and interchain N–H···O and O–H···O bonds are present in ZnPO-CJ57 as seen in Fig. 5. The N(3) atom forms H-bonds with O(5), O(6) and O(9) atoms with the N···O distances in the range of 2.824(6)–2.878(6) Å. The N(4) atom forms H-bonds with O(2), O(4), O(13), O(14) atoms and the N···O distances are within 2.804(7)–3.036(6) Å. Each atom of N(1), N(6), N(7) and N(9) of histidine form a H-bond with framework O atoms with N··O separations between 2.67(8) and 2.93(8) Å. The water molecule also participates in hydrogen bonding with O(2), O(5) and O(13) atoms (O···O distance: 2.547(6)–2.940(6) Å). Thus, a pseudo-3D supramolecular structure is formed with extensive multipoint hydrogen bonds among the histidine molecules, water molecules and phosphate units. Such H-bonding interaction of host–guest plays an important role in stabilizing the chiral configuration of ZnPO-CJ57.

VCD spectra

The most interesting structural feature of ZnHPO-CJ56 and ZnPO-CJ57 is their chirality derived from the chiral amino acid molecules as both the templates and the ligands, which is studied by the solid state vibrational circular dichroism (VCD). The experimental IR and VCD spectra of ZnHPO-CJ56 (Fig. 6a) are assigned as follows: the IR bands at 1480 and 1633 cm\(^{-1}\) are attributed to the C–O stretching vibrations, and the band at 1557 cm\(^{-1}\) is assigned to skeleton vibrations of the aromatic
Fig. 1  (a) ORTEP diagrams of ZnHPO-CJ56. (b) ORTEP diagrams of ZnPO-CJ57.

Fig. 2  Chain structure of ZnHPO-CJ56 viewed along the $b$ axis.

The experimental VCD bands at 1632 cm$^{-1}$ and 1480 cm$^{-1}$ correspond to the C–O stretching vibrations, and the band at 1557 cm$^{-1}$ corresponds to skeleton vibrations of the aromatic rings. The good agreement between the VCD and the IR spectra identifies the vibrational modes and the chiral conformation of ZnHPO-CJ56. As for ZnPO-CJ57 (Fig. 6b), the IR bands at 1616 and 1432 cm$^{-1}$ are attributed to the C–O stretching vibrations. The band at 1315 cm$^{-1}$ is assigned to the stretching vibrations of the C= N and C–N bonds of the imidazole ring. The band at 1453 cm$^{-1}$ corresponds to the N–H bending vibrations of imidazole.

Fig. 3  Structure of ZnHPO-CJ56 viewed along the [010] direction. The dished lines represent hydrogen bonds (black = Zn, grey = P).

Fig. 4  Chain structure of ZnPO-CJ57 propagating along the $c$ axis (black = Zn, grey = P).
ring and the bending vibration of the CH₂ group. The bands at 1496 cm⁻¹ and 1262 cm⁻¹ are related to the breathing vibration of the imidazole ring. Every IR absorption peak corresponds to a VCD feature ($\nu$(C–O): 1604 and 1429 cm⁻¹; $\nu$(C=O) and $\nu$(C–N): 1325 cm⁻¹; $\nu$(N–H): 1446; $\nu$(imidazole ring): 1496 and 1262 cm⁻¹), which may be either positive or negative. The strong VCD signals indicate that the original chirality of the amino acids is maintained in the final structures of ZnHPO-CJ56 and ZnPO-CJ57, and the as-synthesized compounds have optical activity.

**Luminescent property**

The photoluminescent spectra of ZnHPO-CJ56 and ZnPO-CJ57, together with tryptophan and histidine molecules were measured in solid state at room temperature (Fig. 7). The emission spectrum of tryptophan exhibits one sharp peak at 326 nm excited at a wavelength of 290 nm (Fig. 7a). This can be assigned to the presence of chromophore indole group in the tryptphan molecules. A strong fluorescence emission band at 316 nm is observed for ZnHPO-56, slightly blue-shift compared to that of the
tryptophan, which may be caused by the ligand-to-metal charge transfer (LMCT).²⁶

As seen in Fig. 7b, the emission spectra of ZnPO-CJ57 and histidine molecules both show one sharp peak at 362 nm when excited at a wavelength of 220 nm. This emission is due to the presence of the imidazole moiety of the histidine molecules.²⁶

So far, several kinds of amino acids, such as asparagine, histidine and glycine, have been used as the templates and the ligands in the synthesis of open-framework structures. However, tryptophan amino acid, usually occurring in one or a few residues in most proteins and biologically active peptides, is firstly employed to synthesize metal phosphites or phosphates.²⁵ Although the use of chiral ligands is one of the main synthetic strategy to generate enantiopure materials, the chiral amino acid is easy to racemize under hydrothermal or solvothermal conditions. Beside zinc phosphate C₅N₂O₃H₈, ZnHPO₃, templated by L-asparagine, ZnHPO-CJ56 and ZnPO-CJ57 are the only known examples of chiral amino acids to the Zn atoms leaves free amino groups in ZnHPO-CJ56 and uncoordinated carboxyl oxygen atoms in ZnPO-CJ57, which are the active sites for asymmetric catalysis. These compounds can also be used for a number of organic reactions in the interchain spacing, including formation of peptide bonds and longer chains of different residues.²⁵ The related works are ongoing.

Conclusions

Chiral biological molecules, t-tryptophan and l-histidine, have been firstly successfully introduced into the hydrothermal reaction system to synthesize chiral inorganic networks [Zn(HPO₃)(C₅H₇NO₂)] (ZnHPO-CJ56) and [Zn₃(H₂O)(PO₄)₂(HPO₃)(C₅H₇NO₂)(C₅H₇NO₂)] (ZnPO-CJ57). ZnHPO-CJ56 possesses infinite edge-sharing ladder-like 4-ring chains built up from the alternation linkage of ZnO₄ tetrahedra and HPO₄ pseudo-pyramids; while ZnPO-CJ57 has similar ladder-like chains constructed by ZnO₄ and PO₄/HPO₄ tetrahedra, and additional ZnO₄ tetrahedra as pendants that are grafted onto one side of the chain. Both ZnHPO-CJ56 and ZnPO-CJ57 can emit strong light due to the existence of t-tryptophan and l-histidine molecules. The strong VCD signals indicate that the initially added chiral amino acid molecules are not racemic even through the hydrothermal reaction, and the as-synthesized compounds have optical activity. The temperature is a key factor in the keeping of the chirality of ZnHPO-CJ56 and ZnPO-CJ57. We believe that the successful preparation of the two amino-acid templated compounds would stimulate further studies on the syntheses of new chiral open-framework metal phosphites/phosphates materials, which have significant importance in the investigation of chiral molecular induction, selection, recognition, separation and self-assembly etc.

Acknowledgements

This work is supported by the National Natural Science Foundation of China, the State Basic Research Projects of China and Scientific and Technological Planning Project of Jilin Province (2006CB806103, 2007CB936402 and 20080504).

References


