

A 3D chiral Zn(II) coordination polymer with triple Zn–oba–Zn helical chains (oba = 4,4'-oxybis(benzoate))[†]

Yi Ma,^a Zhengbo Han,^{*a} Yongke He^a and Liguo Yang^b

Received (in Cambridge, UK) 5th June 2007, Accepted 4th July 2007

First published as an Advance Article on the web 30th July 2007

DOI: 10.1039/b708479j

The solvothermal reaction of Zn(II) and 4,4'-oxybis(benzoic acid) in the presence of anhydrous ethanol leads to the generation of a novel 3D chiral coordination polymer with triple helical chains; the resulting crystals were not a racemic mixture but had an enantiomeric excess, which was confirmed by measuring the optical rotation of bulk samples using solid state vibrational circular dichroism (VCD).

Over the past decade, the rational design and synthesis of chiral metal–organic coordination polymers has attracted much attention in coordination chemistry, not only because of their intriguing variety of architectures and topologies, but also owing to their potential applications in non-linear optics and asymmetric catalysis.^{1,2} Consequently, many chiral coordination polymers have been generated by self-assembly processes.³ These chiral polymeric coordination frameworks have usually focused on three general synthetic strategies: (1) use of a chiral organic ligand as a spacer to connect adjacent metal centres,⁴ (2) use of achiral starting materials without any chiral sources *via* spontaneous resolution⁵ and (3) use of a homochiral ligand as a chiral auxiliary that does not directly participate in the formation of the framework backbone but forces the framework to adopt a specific chiral topology.⁶ Among them, the main synthetic strategy to generate enantiopure materials has been the use of chiral ligands, because spontaneous resolution from achiral starting materials occasionally occurs and the products are normally a racemic mixture of chiral crystals, although each crystal is a single enantiomer.⁷ Meanwhile, the use of enantiopure ligands leads to the generation of a single enantiomeric product. V-shaped dicarboxylates, for example, the 4,4'-oxybis(benzoate) ligand (in which the C–O–C angle is 121.8(4)° and thus the two benzene rings are not coplanar), have already proved to be efficient for the generation of helical coordination polymers.⁸

In this work, we employed achiral ligand 4,4'-oxybis(benzoic acid) (H₂oba) and synthesized a chiral 3D coordination polymer Zn₂(oba)₂ (**1**) containing three helical chains. The synthesis did not involve any chiral reactant, solvent or other auxiliary agent. To our surprise, the resulting crystals were not a racemic mixture, as evidenced by the observation of strong signals in vibrational circular dichroism (VCD) spectra. VCD spectroscopy is a powerful

technique for obtaining conformational information about chiral molecules.⁹ Compound **1** was solvothermally synthesized from a mixture of zinc nitrate and 4,4'-oxybis(benzoic acid) in a 1 : 1 stoichiometry in an anhydrous ethanol medium.[‡] Data collection on **1** was performed with Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker P4 diffractometer. FTIR spectra were obtained on a Bruker Vector 22 FTIR spectrometer using a KBr pellet. VCD spectra were measured with a Bruker PMA 37 spectrometer (resolution = 4 cm⁻¹, zero filling factor = 2, scan time = 3 h).

Single crystal X-ray analysis[§] revealed that **1**, which crystallizes in the chiral space group *P*3₂21, is an infinite 3D chiral coordination polymer without any solvent molecules in the structure. There are two crystallographically-independent Zn centres and two oba ligands in the asymmetric unit. To describe the complicated 3D structure of **1**, the two independent oba ligands are defined as oba(1) and oba(2), and the two Zn centres as Zn(1) and Zn(2). The coordination environment of the oba ligands is shown in Fig. 1.

In **1**, each Zn(1) and Zn(2) centre coordinates to four oxygen atoms from four different oba ligands, in which two are oba(1) while the other two are oba(2) (Zn(1)–O(1) = 1.991(7), Zn(1)–O(4A) = 1.928(5), Zn(1)–O(6B) = 1.960(8), Zn(1)–O(10) = 1.915(7), Zn(2)–O(2) = 1.922(7), Zn(2)–O(5C) = 1.924(6), Zn(2)–O(7B) = 1.919(6) and Zn(2)–O(9) = 1.935(7) Å). Thus, all the Zn centres display distorted tetrahedral coordination geometries, with O–Zn–O bond angles ranging from 97.4(4) to 130.3(3)°. Meanwhile, each oba(1) and oba(2) ligand coordinates to four Zn centres; two are Zn(1) centres, while the other two are Zn(2) centres exhibiting a bis(bidentate) bridging mode. As shown in

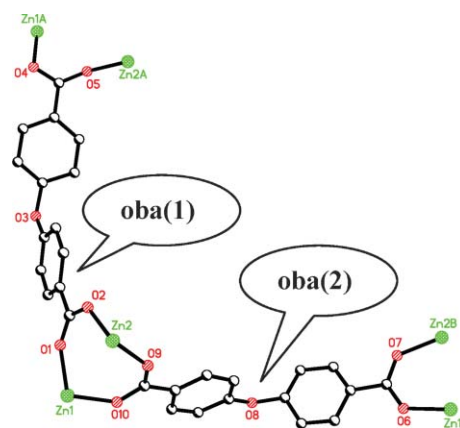


Fig. 1 Drawing showing the coordination environment of the oba ligands. Symmetry operations (A): $-x + y + 1, -x + 2, z + 1/3$ for Zn1, $-x + 1, -x + y + 1, -z + 2/3$ for Zn2; (B): $-x + y, -x, z + 1/3$.

^a College of Chemistry, Liaoning University, Shenyang 110036, P. R. China. E-mail: ceshzb@lnu.edu.cn

^b Alan G. MacDiarmid Institute, Jilin University, Changchun 130012, P. R. China

[†] Electronic supplementary information (ESI) available: Additional plots of the structures, TGA curve, photoluminescent spectra, additional VCD spectra, and simulated and experimental X-ray powder diffraction patterns. See DOI: 10.1039/b708479j

Fig. 1, the two carboxyl groups of oba(1) take different bridging patterns. One adopts a *syn-anti* and the other a *syn-syn* coordination mode to bridge two adjacent Zn centres, respectively. Unlike oba(1), the two carboxyl groups of oba(2) both adopt a *syn-syn* coordination pattern. The carboxyl oxygen atoms of the oba(1) ligands (O1, O4 and their equivalent atoms) interconnect the adjacent Zn(1) centres to form 1D helical chains along the *c*-axis (chain(1)). The carboxyl oxygen atoms of the oba(2) ligands (O6, O7, O9, O10 and their equivalent atoms) interconnect Zn(1) and Zn(2) centres to form another kind of 1D helical chains along the *c*-axis (chain(2)). Helical chains(1) are wrapped in helical chains(2) and are parallel to each other (Fig. 2a and Fig. 2b). The carboxyl oxygen atoms of the oba(1) ligands (O2, O5 and their equivalent atoms) interconnect the adjacent Zn(2) centres to form 1D helical chains propagating along the *b*-axis (chain(3)) (Fig. 2c). These distinct helical chains are all left-handed helices and their porous tunnel sizes are all different to each other. Chain(1) and chain(2) are intertwined together by chain(3), constructing a complicated 3D Zn-oba framework (Fig. S1, ESI†).

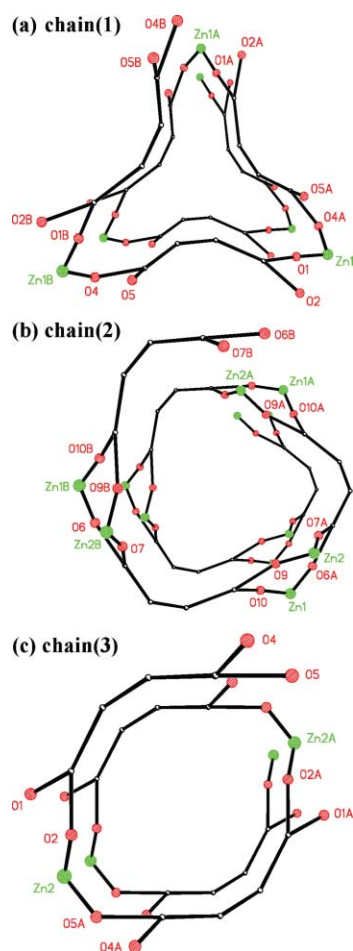


Fig. 2 Plots showing the triple helical chains in **1** constructed by (a) Zn(1) centres and oba(1) ligands viewed along the *c*-axis; symmetry operations (A): $-y + 2, x - y + 1, z - 1/3$; (B): $-x + y + 1, -x + 2, z + 1/3$; (b) Zn(1) and Zn(2) centres, and oba(2) ligands viewed along the *c*-axis; symmetry operations (A): $-y, x - y, z + 1/3$; (B): $-x + y, -x, z + 1/3$; (c) Zn(2) centres and oba(1) ligands viewed along the *b*-axis; symmetry operations (A): $x + 1, -x - y, -z + 2/3$.

The most attractive structural feature of **1** is the chirality of the 3D metal-organic framework. The value of Flack parameter $x = -0.01(3)$. Fig. 3 shows the experimental VCD and IR spectra of the $\text{Zn}_2(\text{oba})_2$ crystals. The IR and VCD spectra of **1** are assigned as follows: the bands at 1240, 1308, 1398, 1553 and 1633 cm^{-1} are attributed to C–O stretch vibrations, and the bands at 1527 and 1597 cm^{-1} are assigned to skeleton vibrations of the aromatic ring. The experimental VCD bands at 1254–1244, 1515–1497 and 1638–1626 cm^{-1} correspond to C–O stretch vibrations, and the bands at 1576–1515 cm^{-1} correspond to skeleton vibrations of the aromatic rings. The carboxyl group and aromatic ring construct the three types of Zn-oba-Zn helical chains. There is a good agreement between the VCD and IR spectra. Every IR absorption peak corresponds 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 could also be observed in the VCD spectra. The strong VCD signals showed that the crystals of $\text{Zn}_2(\text{oba})_2$ were not racemic. The experiment was repeated five times on compounds obtained from different independent syntheses.

The hydrothermal/solvothermal technique is widely used to prepare inorganic-organic hybrid compounds, and the mechanism is complex; any factor may influence the formation of target compounds. In fact, the V-shaped ligand plays a key role in the formation of helical chains, in which the chirality is transferred into the whole framework. Therefore, the design and selection of organic ligands is key in the course of preparing chiral coordination complexes from achiral starting materials.

In order to understand the reason for the observed enantiomeric excess in the $\text{Zn}_2(\text{oba})_2$ product, we have checked all the reagents and solvents, and confirmed that we did not introduce any chiral stimulant during the synthetic procedure. Five independent syntheses from different experiments have been made, and all crystals gave a similar VCD signal. 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 of subsequent crystal growth, and thus the particular handedness of the bulk depends on which random hand is initially formed, similarly to previous reported literature.^{9c}

Usually, V-shaped dicarboxylates and metal-ligand coordination can furnish 1D helical chains.¹⁰ Zn centres and oba ligands

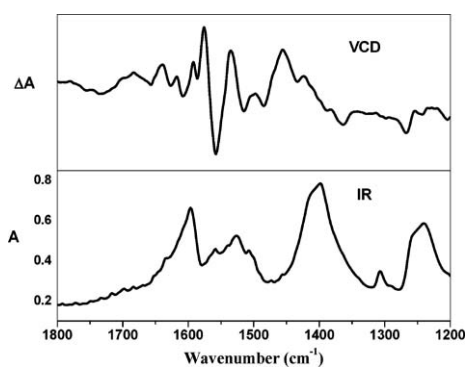


Fig. 3 The VCD (top) and IR absorption (bottom) spectra of **1** in the solid state at room temperature.

easily form 1D chains and 2D layers; 3D open frameworks can be formed through hydrogen bonding and π - π stacking interactions.¹¹ We undertook another control experiment using the same experimental conditions by using distilled water instead of anhydrous ethanol, and another colorless crystal $[\text{Zn}(\text{oba})(\text{H}_2\text{O})]_n$ (**2**) was isolated. Each Zn centre formed a distorted trigonal bipyramid with four carboxylate oxygen atoms from oba ligands and one water molecule, which has been previously been reported using a liquid diffusion method.^{11a}

The thermal stability of **1** was examined by TGA in a dry nitrogen atmosphere from 40 to 1000 °C. The 3D framework was stable up to ca. 400 °C and then began to decompose upon further heating (Fig. S2†).

The photoluminescent properties of **1** are shown in Fig. S3.† A strong fluorescent emission band at 358 nm (ex = 300 nm) is observed in the solid state at room temperature. We have confirmed that there is no obvious emission observed for the free oba ligand under the same experimental conditions. The fluorescent emissions of **1** may therefore be attributed to charge transition between oba ligands and zinc centres (LMCT).¹²

In summary, we have developed a synthetic strategy towards 3D homochiral coordination polymers with multiple helical chains by using a V-shaped ligand and a transition metal ion in organic solvents. This work provides a route for further exploration of the preparation of optical rotation coordination polymers. The investigation of other transition metal ion-V-shaped dicarboxylate systems in organic solvents is now under way.

This work was granted financial support from the Program for Liaoning Excellent Talents in University (RC-05-11).

Notes and references

† Synthesis of **1**: A reaction mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.148 g, 0.5 mmol), H_2oba (0.129 g, 0.5 mmol) and anhydrous ethanol (10 mL) was stirred for 20 min in air, then transferred to and sealed in an 18 mL Teflon-lined autoclave. This was heated in an oven to 383 K for 72 h, followed by slow cooling (5 K h⁻¹). The resulting dark yellow block crystals were washed with distilled water and dried in air (yield ca. 32%). Elemental analysis calc. for **1** ($\text{C}_{28}\text{H}_{16}\text{O}_{10}\text{Zn}_2$): C, 52.30; H, 2.56; found: C, 52.12; H, 2.68%. **1** is insoluble in water and common organic solvents such as DMF, DMSO, CH_3CN , benzene, toluene, methanol, ethanol, acetone and propanol.

§ Crystal data for **1**: Trigonal space group $P3_221$ (no. 154), $a = 13.298(2)$, $c = 29.544(5)$ Å, $V = 4524.5(12)$ Å³, $Z = 6$, $D_c = 1.416$ g cm⁻³, $F(000) = 1944$, $\mu = 1.641$ mm⁻¹; 8644 reflections measured, 6834 unique ($R_{\text{int}} = 0.0361$); final $R_1 = 0.0738$; $wR_2 = 0.1936$, $S = 1.041$ for all data, Flack parameter $x = -0.01(3)$. The structure was solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTL program.¹³ CCDC 649445.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b708479j

- (a) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705; (b) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334.
- (a) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982; (b) G. Cao, E. G. Maurie, A. Monica, F. B. Lora and E. M. Thomas, *J. Am. Chem. Soc.*, 1992, **114**, 7574; (c) S. J. Lee, A. G. Hu and W. B. Lin, *J. Am. Chem. Soc.*, 2002, **124**, 12948; (d) E. M. Thomas and A. G. Julia, *Acc. Chem. Res.*, 1998, **31**, 209.
- (a) L. Carlucci, G. Ciani, P. Macchi and D. M. Proserpio, *Chem. Commun.*, 1998, 1837; (b) C. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *Chem. Commun.*, 2000, 1319; (c) C. J. Kepert and M. J. Rosseinsky, *Chem. Commun.*, 1998, 31; (d) R. G. Xiong, J. L. Zuo, X. Z. You, B. F. Abrahams, Z. P. Bai, C. M. Che and H. K. Fun, *Chem. Commun.*, 2000, 2061; (e) A. J. Blake, N. R. Champness, P. A. Cooke and J. E. B. Nicolson, *Chem. Commun.*, 2000, 665.
- (a) C. D. Wu and W. B. Lin, *Angew. Chem., Int. Ed.*, 2005, **44**, 1958; (b) H. Y. An, E. B. Wang, D. R. Xiao, Y. G. Li, Z. M. Su and L. Xu, *Angew. Chem., Int. Ed.*, 2006, **45**, 904; (c) Y. G. Li, H. Zhang, E. B. Wang, N. Hao, C. W. Hu, Y. Xu and D. Hall, *New J. Chem.*, 2002, 1619.
- (a) Y. T. Wang, M. L. Tong, H. H. Fan, H. Z. Wang and X. M. Chen, *Dalton Trans.*, 2005, 424; (b) J. D. Ranford, J. J. Vittal, D. Wu and X. Yang, *Angew. Chem., Int. Ed.*, 1999, **38**, 3498; (c) T. Ezuhara, K. Endo and Y. Aoyama, *J. Am. Chem. Soc.*, 1999, **121**, 3279; (d) K. Biradha, C. Seward and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 1999, **38**, 492; (e) Y. Cui, H. L. Ngo and W. B. Lin, *Chem. Commun.*, 2003, 1388; (f) C. J. Kepert, T. J. Prior and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2000, **122**, 5158.
- (a) Z. H. Lin, A. M. Z. Slawin and R. E. Morris, *J. Am. Chem. Soc.*, 2007, **129**, 4880; (b) D. Bradshaw, T. J. Prior, E. J. Cussen, J. B. Claridge and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2004, **126**, 6106.
- (a) M. Kondo, M. Miyazawa, Y. Irie, R. Shinagawa, T. Horiba, A. Nakamura, T. Naito, K. Maeda, S. Utsuno and F. Uchida, *Chem. Commun.*, 2002, 2156; (b) E. Gao, Y. Yue, S. Bai, Z. He and C. Yan, *J. Am. Chem. Soc.*, 2004, **126**, 1419.
- E. Yang, J. Zhang, Z. J. Li, S. Gao, Y. Kang, Y. B. Chen, Y. H. Wen and Y. G. Yao, *Inorg. Chem.*, 2004, **43**, 6525.
- (a) H. Izumi, S. Yamagami, S. Futamura, L. A. Nafie and R. K. Dukor, *J. Am. Chem. Soc.*, 2004, **126**, 194; (b) T. B. Freedman, X. L. Cao, R. Dukor and L. A. Nafie, *Chirality*, 2003, **15**, 743; (c) G. Tian, G. S. Zhu, X. Y. Yang, Q. R. Fang, M. Xue, J. Y. Sun, Y. Wei and S. L. Qiu, *Chem. Commun.*, 2005, 1396; (d) H. Cao, T. Ben, Z. M. Su, M. Zhang, Y. H. Kan, X. Yan, W. J. Zhang and Y. Wei, *Macromol. Chem. Phys.*, 2005, **206**, 1140.
- X. M. Chen and G. F. Liu, *Chem.-Eur. J.*, 2002, **8**, 4811.
- (a) K. Mitsuru, I. Yasuhiko, S. Yusuke, M. Makoto, K. Hiroyuki, N. Akira, N. Tetsuyoshi, M. Kenji and U. Fumio, *Inorg. Chem.*, 2004, **43**, 6139; (b) J. Tao, M. L. Tong, J. X. Shi and X. M. Chen, *Inorg. Chem.*, 2001, **40**, 6328.
- (a) W. G. Lu, L. Jiang, X. L. Feng and T. B. Lu, *Cryst. Growth Des.*, 2006, **6**, 564; (b) Z. B. Han, Y. Ma, Z. G. Sun and W. S. You, *Inorg. Chem. Commun.*, 2006, **9**, 844.
- SHELXTL 6.10, Bruker Analytical Instrumentation, Madison, WI, USA, 2000.