Inorg. Chem. **2006**, *45*, 174–180

Inorganic Chemistry
Article

Assemblies of a New Flexible Multicarboxylate Ligand and d^{10} Metal Centers toward the Construction of Homochiral Helical Coordination Polymers: Structures, Luminescence, and NLO-Active Properties

Shuangquan Zang, Yang Su, Yizhi Li, Zhaoping Ni, and Qingjin Meng*

*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry,
Nanjing University, Nanjing 210093, China*

Received September 2, 2005

Hydro(solvo)thermal reactions between a new flexible multicarboxylate ligand of 2,2′,3,3′-oxydiphthalic acid (2,2′,3,3′-H_4ODPA) and $M(NO_3)_2 \cdot xH_2O$ (M = Zn, $x = 6$; M = Cd, $x = 4$) in the presence of 4,4′-bipyridine (bpy) afford two novel homochiral helical coordination polymers {$[Zn_2$(2,2′,3,3′-ODPA)(bpy)$(H_2O)_3] \cdot (H_2O)_2$ for **1** and $[Cd_2$(2,2′,3,3′-ODPA)(bpy)$(H_2O)_3] \cdot (H_2O)_2$ for **2**}. Though having almost the same chemical formula, they have different space groups ($P2_12_12_1$ for **1** and $P2_1$ for **2**) and different bridging modes of the 2,2′,3,3′-ODPA ligand. Two kinds of homochiral helices (right-handed) are found in both **1** and **2**, each of which discriminates only one kind of crystallographical nonequivalent metal atom. **1** has a 2D metal–organic framework and can be seen as the unity of two parallel homochiral Zn1 and Zn2 helices, in which the nodes are etheric oxygen atoms. In contrast, **2** has a 3D metal–organic framework and consists of two partially overlapped homochiral Cd1 and Cd2 helices in the two dimensions. Moreover, metal–ODPA helices give a 2D chiral herringbone structural motif in both **1** and **2** in the two dimensions, which are further strengthened by the second ligand of bpy. Bulk materials for **1** and **2** all have good second-harmonic generation activity, approximately 1 and 0.8 times that of urea.

Introduction

The construction of novel coordination polymers is the current interest in the field of supramolecular chemistry and crystal engineering, not only for their interesting molecular topologies and crystal packing motifs[1] but also for their potential applications as functional materials.[2,3] Among them, noncentrosymmetric metal−organic frameworks (MOFs) have attracted much attention because of their charming prospect in second-order nonlinear (NLO) materials.[4−9] Noncentrosymmetric MOFs with desired topologies can be rationally designed by taking advantage of well-defined metal coordination geometries in combination with carefully chosen suitable achiral bridging ligands.[5b] In general, structural motifs of these hybrid compounds are closely related to the geometry and the number of coordination sites provided by organic ligands.[5,10]

---

* To whom correspondence shoulld be addressed. E-mail: Mengqj@nju.edu.cn.

(1) (a) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474. (b) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W. S.; Withersby, M. A.; Schroer, M. *Coord. Chem. Rev.* **1999**, *183*, 117. (c) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (d) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483. (e) Pérez-García, L.; Amabilino, D. B. *Chem. Soc. Rev.* **2002**, *31*, 342. (f) Bradshaw, D.; Claridge, J. B.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J. *Acc. Chem. Res.* **2005**, *38*, 273. (g) Chou, J.-H.; Kosal, M. E.; Nakagaki, S.; Smithenry, D. W.; Wilson, S. R. *Acc. Chem. Res.* **2005**, *38*, 283. (h) Ockwig, N. W.; Delgado-Friedrichs, O.; O'Keefee, M.; Yaghi, O. M. *Acc. Chem. Res.* **2005**, *38*, 176. (i) Hill, R. J.; Long, D. L.; Champness, N. R.; Hubberstey, P.; Schroöder, M. *Acc. Chem. Res.* **2005**, *38*, 377.

(2) (a) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *271*, 49. (b) Kahn, O.; Martinez, C. *Science* **1998**, *279*, 44. (c) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2003**, 2781. (d) James, S. L. *Chem. Soc. Rev.* **2003**, *32*, 276. (e) Maspoch, D.; Ruiz-Molina, D.; Veciana, J. *J. Mater. Chem.* **2004**, *14*, 2713.

(3) (a) Eddaoudi, M.; Moler, D. B.; Li, H. L.; Chen, B. L.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319. (b) Pan, L.; Sander, M. B.; Huang, X.; Li, J.; Smith, M.; Bittner, E.; Bockrath, B.; Johnson, J. K. *J. Am. Chem. Soc.* **2004**, *126*, 1308. (c) Dybtsev, D. N.; Chun, H.; Yoon, S. H.; Kim, D.; Kim, K. *J. Am. Chem. Soc.* **2004**, *126*, 32. (d) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (f) Kitaura, R.; Onoyama, G.; Sakamoto, H.; Matsuda, R.; Noro, S. I.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2684.

(4) (a) Albrecht, M. *Chem. Rev.* **2001**, *101*, 3574. (b) Moulton, B.; Zaworoko, M. J. *Chem. Rev.* **2001**, *101*, 1629B.

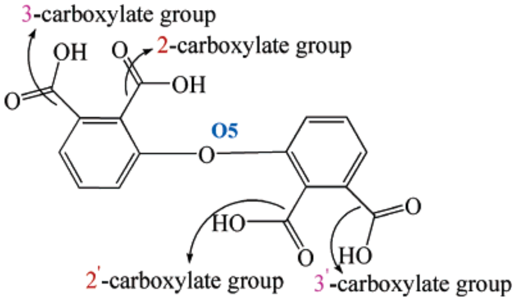
(5) (a) Evans, O. R.; Xiong, R.; Wang, Z.; Wong, G. K.; Lin, W. *Angew. Chem., Int. Ed.* **1999**, *38*, 536. (b) Evans, O. R.; Lin, W. *Acc. Chem. Res.* **2002**, *35*, 511. (c) Kesanli, B.; Lin, W. *Coord. Chem. Rev.* **2003**, *246*, 305. (d) Lin, W.; Evans, O. R.; Xiong, R. G.; Wang, Z. *J. Am. Chem. Soc.* **1998**, *120*, 13272. (e) Lin, W.; Evans, O. R. *Chem. Mater.* **2001**, *13*, 2705. (f) Evans, O. R.; Lin, W. *Chem. Mater.* **2001**, *13*, 3009.

10.1021/ic051502m CCC: $33.50

As an important family of multidentate O-donor ligands, organic aromatic polycarboxylate ligands, including 1,2-benzenedicarboxylate, 1,4-benzenetricarboxylate, 1,3,5-benzenetricarboxylate, etc., have been extensively employed in the preparation of such metal−organic complexes with multidimensional networks and interesting properties.[11] Being widely found in nature, helical structural motifs exhibit axial chirality, and their solids can crystallize in a noncentrosymmetrical space group. Thus, using achiral ligands to generate chiral networks (chiral networks are all noncentrosymmetrical) with helices has aroused great interest, and the facility makes it more and more attractive.[2e,12−14] It also has been noted that the employment of flexible or the V-shaped exo-multidentate organic bridges can improve the helicity of the polymeric chains.[15]

2,2′,3,3′-Oxydiphthalic acid[16] (2,2′,3,3′-H$_4$ODPA; Chart 1) is just the ligand that combined the structural characters referred to above: (1) It has eight potential donor carboxylate oxygen atoms to coordinate to metal ions with different coordination modes. (2) The skew coordination orientation of the carboxy groups, the hindrances between the 2,2′-, 2,3-, and 2′,3′-positioned carboxylate groups, and the nonliner flexility around the etheric oxygen atom make it quite a versatile ligand for constructing novel metal−organic hybrid compounds with helical chains (upon coordination as a bridge, the freedom of the ligand to rotate around the etheric oxygen atom is restrained and the ligand can be locked in a twisted chiral conformation). However, to the best of our knowledge, 2,2′,3,3′-H$_4$ODPA d^{10} metal complexes have not been studied so far. With the aim of understanding the coordination chemistry of 2,2′,3,3′-H$_4$ODPA and preparing new materials with interesting structural topology and excellent physical properties, we have recently engaged in the research of these kinds of polymer complexes with this and related ligands. Herein, we present two new acentric MOFs based on the 2,2′,3,3′-H$_4$ODPA ligand. As is our understanding of MOFs, both **1** and **2** have the chiral unprecedented fortified herringbone motif with homochiral helices in the two dimensions.

Chart 1. Structure of the 2,2′,3,3′-H$_4$ODPA Acid



Experimental Section

2,2′,3,3′-Oxydiphthalic dianhydride (2,2′,3,3′-ODPA) was synthesized according to the literature.[16] 2,2′,3,3′-H$_4$ODPA was obtained through the hydrolysis of 2,2′,3,3′-ODPA in the presence of HCl at reflux temperature in water. All other starting materials were of reagent quality and were obtained from commercial sources without further purification.

Colorless needle crystals of compounds **1** and **2** were synthesized hydro(solvo)thermally in a 23-mL Teflon-lined autoclave by heating a mixture of 0.1 mM 2,2′,3,3′-H$_4$ODPA, 0.1 mmol of bpy, 0.2 mM M(NO$_3$)$_2$·xH$_2$O (M = Zn, x = 6; M = Cd, x = 4), and 0.4 mM NaOH at 120 °C in 8 mL of water and 2 mL of ethanol for 2 days. Yield: 83% for **1**; 67% for **2**. Reproducibility of the hydrothermal syntheses for both compounds is good. Both **1** and **2** are insoluble in water and common organic solvents. Anal. Found (calcd for **1**): C, 43.36 (43.42); H, 3.42 (3.36); N, 3.80 (3.89). IR (KBr, cm^{-1}): 3404 (s), 3086 (w), 2917 (w), 1612 (s), 1607 (s), 1560 (vs), 1372 (s), 1241 (vs), 1072 (m), 818 (m), 768 (m), 640 (m), 508 (w). Anal. Found (calcd for **2**): C, 38.26 (38.40); H, 2.83 (2.97); N, 3.58 (3.45). IR (KBr, cm^{-1}): 3470 (s), 3092 (w), 2924 (w), 1608 (vs), 1562 (vs), 1391 (s), 1239 (vs), 1066 (m), 817 (m), 770 (m), 633 (m), 486 (w).

Physical Measurements

Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were obtained as KBr pellets on a VECTOR 22 spectrometer. Thermal analyses were performed

---

(6) Maggard, P. A.; Stern, C. L.; Poeppelmeier, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 7742.

(7) Znang, H.; Wang, X.; Zhang, K.; Teo, B. K. *Coord. Chem. Rev.* **1999**, *183*, 157.

(8) (a) Abrahams, B. F.; Jackson, P. A.; Roboson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 2656. (b) Zhang, J.; Lin, W.; Chen, Z.-F.; Xiong, R.-G.; Abrahams, B.-F.; Fun, H.-K. *J. Chem. Soc., Dalton. Trans.* **2001**, 1804. (c) Xiong, R.-G.; Xue, X.; Zhao, H.; Abrahams, B. F.; You, X.-Z.; Xue, Z. *Angew. Chem., Int. Ed.* **2002**, *41*, 3800. (d) Wang, L.-Z.; Qu, Z.-R.; Zhao, H.; Wang, X.-S.; Xiong, R.-G.; Xue, Z.-L. *Inorg. Chem.* **2003**, *42*, 3969. (e) Qu, Z.-R.; Zhao, H.; Wang, Y.-P.; Wang, X.-S.; Ye, Q.; Li, Y.-H.; Xiong, R.-G.; Abrahams, B. F.; Liu, Z.-G.; Xue, Z.-L.; You, X.-Z. *Chem.*—*Eur. J.* **2004**, *10*, 53.

(9) Zhou, Y.-F.; Yuan, D.-Q.; Wu, B.-L.; Wang, R.-H.; Hong, M.-C. *New. J. Chem.* **2004**, *28*, 1590.

(10) Zhang, J.; Li, Z. J.; Kang, Y.; Cheng, J. K.; Yao, Y. G. *Inorg. Chem.* **2004**, *43*, 8085.

(11) (a) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276. (b) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148. (c) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keefe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469. (d) Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705. (e) Chae1, H. K.; Siberio-Përez, D. Y.; Kim, J.; Go, Y. B.; Eddaoudi1, M.; Matzger1, A. J.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2004**, *427*, 523. (f) Rao, C. N. R.; Natarajan, S.; Vaidhyanathan, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1466. (g) Lin, Z.-H.; Jiang, F.-L.; Chen, L.; Yuan, D. Q.; Hong, M. C. *Inorg. Chem.* **2005**, *44*, 73. (h) Ye, B.-H.; Tong, M.-L.; Chen, X.-M. *Coord. Chem. Rev.* **2005**, *249*, 545.

(12) (a) Keppert, C.; Prior, T.; Rosseinsky, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 5158. (b) Prior, T.; Rosseinsky, M. J. *Inorg. Chem.* **2003**, *42*, 1546. (c) Cussen, E. J.; Claridge, J. B.; Kepert, C. J.; Rosseinsky, M. J. *J. Am. Chem. Soc.* **2002**, *124*, 9574. (d) Bradshaw, D.; Prior, T. J.; Cussen, E. J.; Claridge, J. B.; Rosseinsky, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 6106.

(13) (a) Han, L.; Hong, M.-C. *Inorg. Chem. Commun.* **2005**, *8*, 406. (b) Carlucci, L.; Ciani, G.; Prosperpio, D. M.; Sironi, A. *Inorg. Chem.* **1998**, *37*, 5914. (c) Wang, M.; Li, J. Y.; Yu, J. H.; Pan, Q. H.; Song, X. W.; Xu, R. R. *Inorg. Chem.* **2005**, *44*, 4604. (d) Gao, E.-Q.; Bai, S.-Q.; Wang, Z.-M.; Yan, C.-H. *J. Am. Chem. Soc.* **2003**, *125*, 4984. (e) Gao, E.-Q.; Yue, Y.-F.; Bai, S.-Q.; He, Z.; Yan, C.-H. *J. Am. Chem. Soc.* **2004**, *126*, 1419.

(14) (a) Zhang, J.-P.; Yong, Y.; Huang, X.-C.; Chen, X.-M. *Chem. Commun.* **2005**, 1258. (b) Tian, G.; Zhu, G.-S.; Yang, X.-Y.; Fang, Q.-R.; Xue, M.; Sun, J.-Y.; Wei, Y.; Qiu, S.-L. *Chem. Commun.* **2005**, 1396.

(15) (a) Tong, M.-L.; Cheng, X.-M.; Ye, B.-H.; Ng, S. W. *Inorg. Chem.* **1998**, *37*, 5278. (b) Carlucci, L.; Ciani, A.; Gramaccioli, Proserpio, D. M.; Rizzato, S. *CrystEngCommun* **2000**, 29. (c) Chen, X. M.; Liu, G. F. *Chem.*—*Eur. J.* **2002**, *8*, 4811. (d) Wang, R.-J.; Xu, L.-J.; Li, X.-S.; Li, Y.-M.; Shi, Q.; Zhou, Z.-Y.; Hong, M.-C.; Chan, A. S. C. *Eur. J. Inorg. Chem.* **2004**, 1595.

(16) Li, Q.-X.; Fang, X.-Z.; Wang, Z.; Gao, L.-X.; Ding, M.-X. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3249.

Table 1. Crystallographic Data and Refinement Parameters for **1** and **2**

compound	**1**	**2**
empirical formula	$C_{26}H_{24}N_2O_{14}Zn_2$	$C_{26}H_{24}N_2O_{14}Cd_2$
fw	719.21	813.27
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1$
a (Å)	10.091(5)	7.133(2)
b (Å)	14.828(7)	20.059(4)
c (Å)	19.711(9)	10.117(2)
α (deg)	90.0	90.0
β (deg)	90.0	110.642(3)
γ (deg)	90.0	90.0
V (Å^3)	2949(2)	1354.6(5)
Z	4	2
ρ (g cm^{-1})	1.620	1.994
F(000)	1464	804
GOF on F^2	1.072	1.077
R1, wR2[a] [$I > 2\sigma(I)$]	0.0538, 0.1178	0.0465, 0.0890
R1, wR2[a] [all data]	0.0648, 0.1210	0.0571, 0.0908
flack	0.07(2)	0.03(4)

[a] $R1 = \sum||F_o| - |F_c||/|F_o|$, $wR2 = [\sum w(\sum F_o^2\text{-}\ F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

on a TGA V5.1A Dupont 2100 instrument from room temperature to 500 °C with a heating rate of 10°C/min in air. Powder X-ray diffraction (XRD) patterns were recorded on a RigakuD/max-RA rotating-anode X-ray diffractometer with graphite-monochromatized Cu Kα ($\lambda = 1.542$ Å) radiation at room temperature. The circular dichroism (CD) spectra of **1** and **2** were recorded at room temperature with a Jasco J-810(S) spectropolarimeter (KBr pellets).[17] Luminescence spectra for the solid samples were recorded with a Hitachi 850 fluorescence spectrophotometer.

Measurement of the Second-Harmonic Generation (SHG) Response.[8c] The second-order nonlinear optical intensity was approximately estimated by measuring a powder sample of 80−150-μm diameter in the form of a pellet relative to urea. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate a SHG signal from powder samples. The backscattered SHG light was collected by a spherical concave mirror and passed through a filter that transmits only 532-nm radiation.

X-ray Crystallographic Studies

Single crystals of dimensions 0.3 × 0.2 × 0.1 mm for **1** and 0.4 × 0.2 × 0.1 mm for **2** were used for structural determinations on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\ 73$ Å) at room temperature using the ω-scan technique. Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods and refined with the full-matrix least-squares technique using the *SHELXS-97* and *SHELXL-97* programs.[18] Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The crystallographic data and selected bond lengths for **1** and **2** are listed in Tables 1 and 2. CCDC 274122 (**1**) and 274123 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, U.K., fax (+44) 1223-336033, or deposit@ccdc.cam.ac.uk).

Table 2. Selected Bond Lengths [Å] and Angles [deg] for **1** and **2**

Compound **1**[a]			
Zn1−O3#1	1.995(4)	Zn1−O2	2.005(4)
Zn1−O10	2.012(4)	Zn1−N1#2	2.059(6)
Zn1−O1	2.356(4)	Zn1−O4#1	2.757(8)
Zn2−O7	2.067(4)	Zn2−N2	2.093(5)
Zn2−O11	2.098(4)	Zn2−O12	2.136(4)
Zn2−O6	2.401(4)	Zn2−O9#3	2.023(4)
O3#1−Zn1−O2	138.6(2)	O3#1−Zn1−O10	104.7(2)
O3#1−Zn1−N1#2	105.0(2)	O2−Zn1−N1#2	95.2(2)
O10−Zn1−N1#2	93.0(2)	O3#1−Zn1−O1	103.0(1)
O2−Zn1−O1	59.3(2)	O10−Zn1−O1	85.4(2)
N1#2−Zn1−O1	151.5(2)	O9#3−Zn2−O7	120.0(2)
O9#3−Zn2−N2	97.6(2)	O7−Zn2−N2	93.0(2)
O9#3−Zn2−O11	93.1(2)	O7−Zn2−O11	145.7(2)
N2−Zn2−O11	91.1(2)	O9−Zn2−O12	83.5(2)
O7−Zn2−O12	83.1(2)	N2−Zn2−O12	175.9(2)
O11−Zn2−O12	92.8(2)	O9#3−Zn2−O6	169.6(2)
O7−Zn2−O6	57.2(2)	N2−Zn2−O6	92.7(2)
O11−Zn2−O6	88.6(2)	O12−Zn2−O6	86.2(1)
Compound **2**[b]			
Cd1−N1#1	2.272(7)	Cd1−O9#2	2.283(6)
Cd1−O4#3	2.297(7)	Cd1−O12	2.389(6)
Cd1−O1	2.409(6)	Cd1−O8#2	2.476(6)
Cd1−O3#3	2.604(6)	Cd2−N2	2.291(7)
Cd2−O10	2.340(5)	Cd2−O11	2.381(6)
Cd2−O6#4	2.382(7)	Cd2−O7#4	2.418(6)
Cd2−O1	2.510(6)	Cd2−O2	2.323(6)
N1#1−Cd1−O9#2	146.0(3)	N1#1−Cd1−O4#3	90.4(2)
O9#2−Cd1−O4#3	117.0(2)	N1#1−Cd1−O12	78.4(2)
O9#2−Cd1−O12	86.8(2)	O4#3−Cd1−O12	147.1(2)
N1#1−Cd1−O1	125.1(2)	O9−Cd1−O1	81.6(2)
O4#3−Cd1−O1	80.4(2)	O12−Cd1−O1	81.3(2)
N1#1−Cd1−O8#2	92.2(2)	O9B−Cd1−O8#2	54.8(2)
O4#3−Cd1−O8#2	131.7(2)	O12−Cd1−O8#2	80.0(2)
O1−Cd1−O8#2	133.1(2)	N1#1−Cd1−O3#3	88.0(2)
O9−Cd1−O3#3	93.3(2)	O4−Cd1−O3#3	52.2(2)
O12−Cd1−O3#3	155.0(2)	O1−Cd1−O3	123.6(2)
O8#2−Cd1−O3#3	79.7(2)	N2−Cd2−O2	98.3(2)
N2−Cd2−O10	89.2(2)	O2−Cd2−O10	131.4(2)
N2−Cd2-O11	176.9(3)	O2−Cd2−O11	83.5(2)
O10−Cd2−O11	91.4(2)	N2−Cd2−O6#4	98.2(3)
O2−Cd2−O6#4	142.3(2)	O10−Cd2−O6#4	82.5(2)
O11−Cd2−O6#4	78.9(2)	N2−Cd2−O7#4	85.2(2)
O2−Cd2−O7#4	93.6(2)	O10−Cd2−O7#4	135.0(2)
O11−Cd2−O7#4	92.2(2)	O6#4−Cd2−O7#4	54.4(2)
N2−Cd2−O1	98.5(2)	O2−Cd2−O1	53.8(2)
O10−Cd2−O1	77.6(2)	O6#4−Cd2−O1	153.7(2)
O11−Cd2−O1	84.5(2)	O7#4−Cd2−O1	147.4(2)

[a] Symmetry codes: #1, $x + {}^1/_2, -y + {}^3/_2, -z + 1$; #2, $x - {}^1/_2, -y + {}^3/_2, -z + 1$; #3, $x + {}^1/_2, -y + {}^3/_2, -z + 2$. [b] Symmetry codes: #1, $-x + 1, y - {}^1/_2, -z + 2$; #2, $-x + 1, y + {}^1/_2, -z + 2$; #3, $x + 1, y, z$; #4 $-x, y + {}^1/_2, -z + 1$.

Results and Discussion

Syntheses. To obtain acentric metal−ODPA networks, we carried out the hydrothermal reaction of two different d^{10} metal salts with 2,2′,3,3′-H_4ODPA. It is observed that the direct reaction of a M(II) (M = Zn or Cd) ion with 2,2′,3,3′-H_4ODPA gave a white precipitate without any SHG effect. When the “second” ligand of bpy was added to the reaction system, both **1** and **2** in their crystalline forms with a SHG effect were successfully isolated in good yield. Although detailed studies are still required to better understand this phenomenon, we propose that the rate of polymerization of M(II) (M = Zn or Cd) ions with 2,2′,3,3′-$ODPA^{4-}$ is too fast to obtain crystalline products. In addition, the “second”

---

(17) Siemeling, U.; Scheppilmann, I.; Neumann, B.; Stammler, A.; Stammler, H.-G.; Frelek, J. *Chem. Commun.* **2003**, 2236.

(18) (a) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 457. (b) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

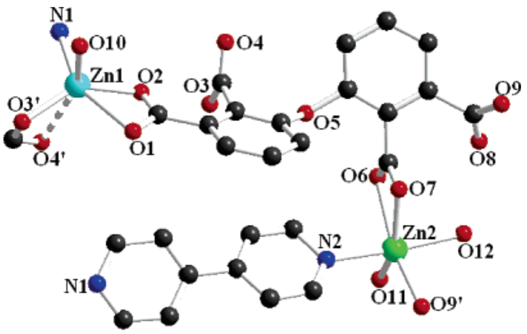


Figure 1. Coordination arrangements of the Zn(II) atoms in **1**. Hydrogen atoms and solvent water molecules are omitted for clarity.

ligand of bpy should play some role in the formation of acentric MOFs, just like the recent attention of the "mixed-ligand" method in the design of acentric MOFs.[19]

Crystal Structures

$Zn_2(2,2',3,3'$-ODPA)(bpy)$(H_2O)_3 \cdot (H_2O)_2$ (1). A single-crystal XRD study has revealed a lamellar framework structure of **1** that is built from interlinking of two different helices (see below) and crystallizes in the $P2_12_12_1$ space group. The asymmetric unit contains two crystallographically nonequivalent Zn atoms (Zn1 and Zn2), one 2,2′,3,3′-ODPA^{4-}, one bpy, and three coordinated and two solvated water molecules (Figures 1 and S1 in the Supporting Information). As to 2,2′,3,3′-ODPA^{4-}, the dihedral angle between two phenyl rings is 88.8°, the 2- and 2′-carboxylate groups are almost perpendicular to the plane of corresponding linking phenyl rings, with the dihedral angle between them being 89.0° and 78.2°, respectively. The 3- and 3′-carboxylate groups have 8.3° and 136.6° dihedral angles with the plane of corresponding linking phenyl rings, respectively. A dramatic twisting is also observed between two 2 (2′)- and 3 (3′)-carboxylate groups in ODPA, with the dihedral angles between them being 84.8° and 62.4°, respectively. The combination of these twists and the nonlinear flexibility around the O5 atom results in the formation of the metal−ODPA helical chains. Both Zn1 and Zn2 adopt a distorted octahedral configuration. At first glance, Zn1 should take a distorted square-pyramidal geometry: three oxygen atoms of one 3-COO$^-$ in bichelating fashion and one 2-COO$^-$ of the neighboring molecule in monochelating fashion, one nitrogen atom N1 of bpy, as well as one coordination water (O10). However, the distance of 2.757 Å between Zn1 and O4′ of a 2-COO$^-$ of the neighboring molecule suggests a nonnegligible interaction between them. Thus, the Zn1 center can be regarded as a distorted-octahedron geometry. In contrast, the Zn2 center coordinates to one 2′-COO$^-$ in bichelating fashion, one 3′-COO$^-$ of the neighboring molecule in monochelating fashion, one nitrogen atom of bpy, and two oxygen atoms of water.

Through spontaneous resolution, Zn1 and Zn2 are bridged by 2,3- and 2′,3′-carboxylate groups, respectively, to give two similar helices (Figure 2a). The winding axis corresponds

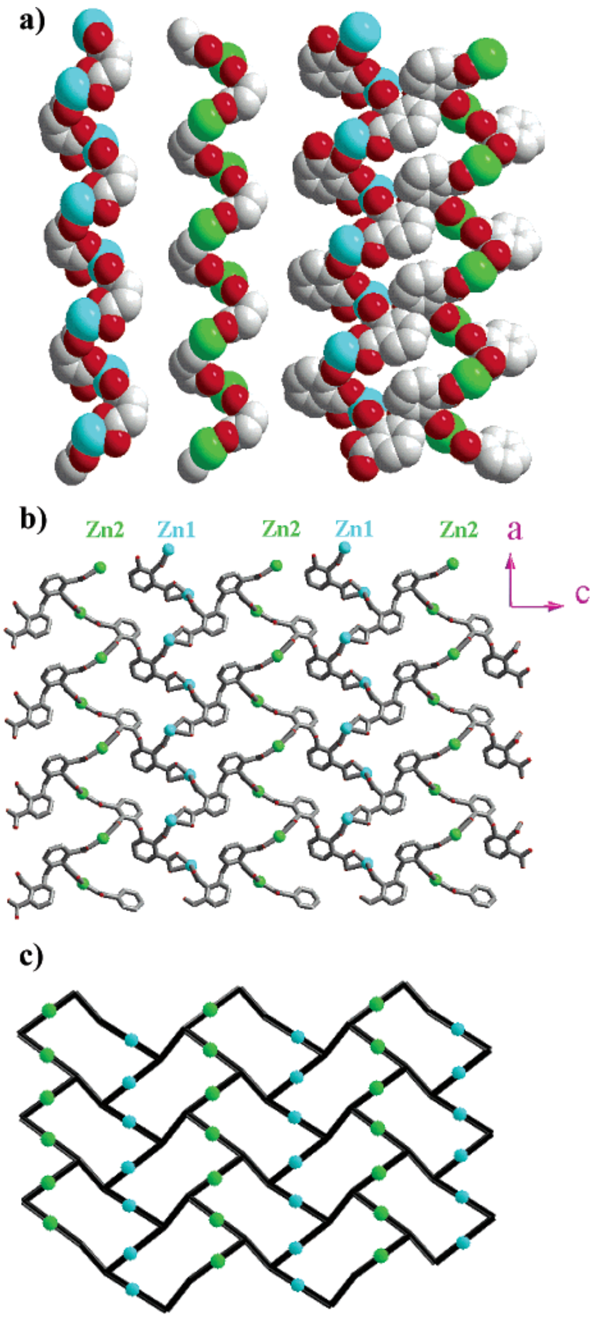


Figure 2. (a) Zn1 helix (left), Zn2 helix (middle), and the unity of Zn1 and Zn2 helices (right). (b) Herringbone motif formed by Zn1(cyan)−ODPA and Zn2(green)−ODPA helices. The two types are of all homochiral helices (*P* helix) in **1** along the [010] direction (water and bpy molecules are omitted for clarity). (c) Simple topology for **1**.

to the *a* axis and the pitch to the length of 10.091(5) Å. Each helix only discriminates one kind of Zn atom (Zn1 or Zn2). Interestingly, both Zn1 and Zn2 helices are of right-handed screws (*P* helix). Two kinds of parallel helices are connected by etheric oxygen atoms (O5) to give a chiral puckered-herringbone (or parquet) structural motif (Figure 2b,c). This herringbone structural motif is strengthened by the interlocked bpy (two terminal nitrogen atoms coordinate to Zn1 and Zn2, respectively) between neighboring helices (Figure 3a,b). It should to be noticed that the bpy and bridged ODPA ligands are linked together to give another kind of *pseudo*he-

---

(19) Wang, Y.-T.; Fan, H.-H.; Wang, H.-Z.; Chen, X.-M. *Inorg. Chem.* **2005**, *44*, 4128.

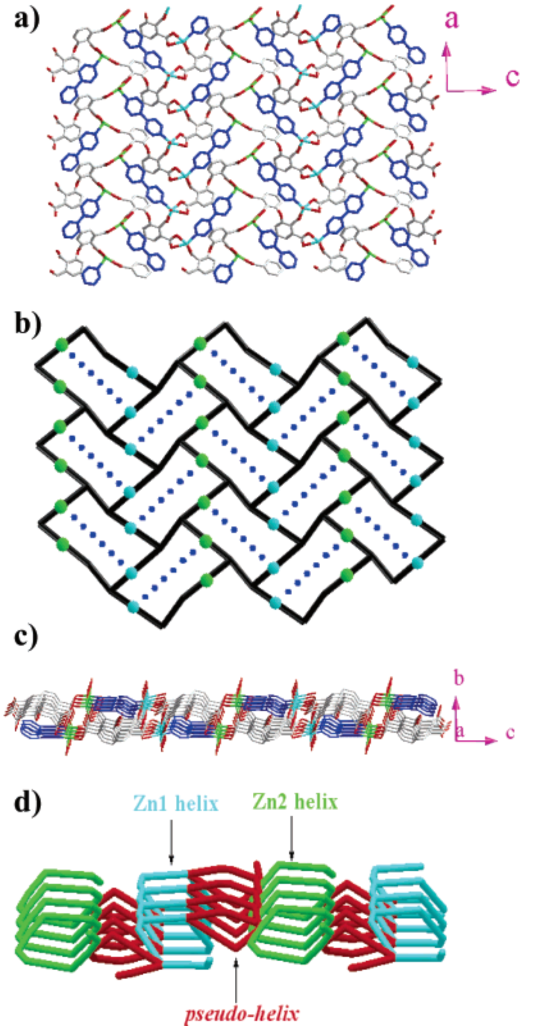


Figure 3. (a) Full layer showing the helices and second ligand of bpy molecules (blue). (b) Topology showing the fortified herringbone architecture in **1** (the blue broken lines are bridged bpy molecules). (c) Zn1, pseudo-, and Zn2 helices. (d) Illustration of two homochiral helices cross-linked together by the pseudohelix.

lix and cross-link the primary helices to afford a 2D network (Figure 3c,d).

Though individual 2D networks can be designed to be necessarily noncentrosymmetric, stacking along the third dimension is still dictated by weaker noncovalent interactions.[5a,f] In **1**, the chiral layers are parallel to the *ac* plane and are stacked along the *b* direction. Adjacent layers are related by the 2_1-screw axis and stacked in a slipped *AAAA* fashion (Figure 4) through hydrogen bonds (Table 3 and Figure S2 in the Supporting Information), resulting in a 3D chiral network (Figure S2 in the Supporting Information). The simultaneous crystallization of the chiral network suggests that a spontaneous resolution occurs.

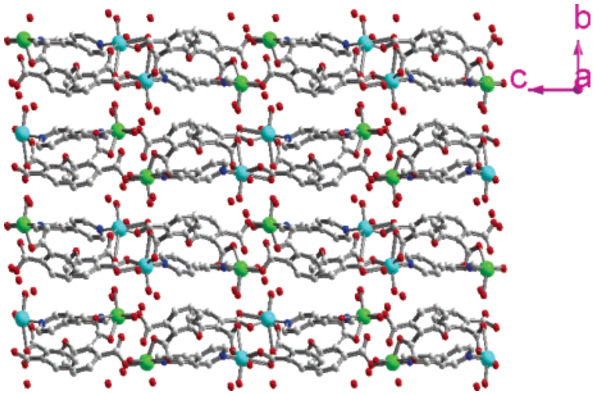


Figure 4. *AAAA* stacking fashion for **1**.

Table 3. Geometry Parameters for Hydrogen Bonds in **1**[a]

D−H	d(D−H)	d(H···A)	∠DHA	d(D···A)	A
O11−H11A	0.85	2.33	116.9	2.82	O1#1
O13−H13B	0.85	2.27	141.9	2.98	O4#1
O10−H10A	0.85	1.92	138.4	2.62	O9#2
O12−H12B	0.85	2.41	164.0	3.24	O13#3
O13−H13A	0.85	2.48	154.7	3.27	O6#4
O14−H14A	0.85	2.20	115.4	2.68	O12#5

[a] Symmetry codes: #1, $-x+1$, $y+{}^{1}/_{2}$, $-z+{}^{3}/_{2}$; #2, $-x+{}^{1}/_{2}$, $-y+1$, $z-{}^{1}/_{2}$; #3, $x-1$, y, z; #4, $x+1$, y, z; #5, $x+1$, y, $z-1$.

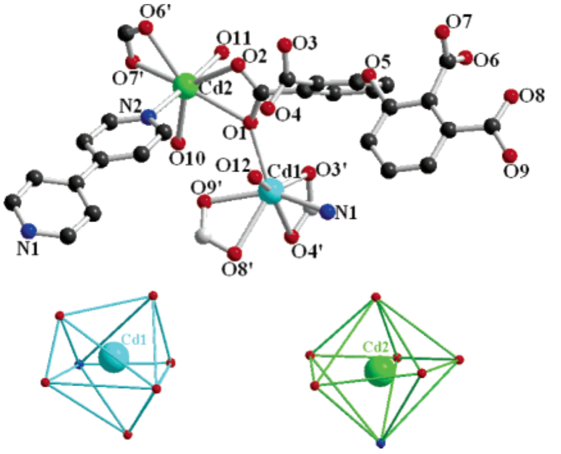


Figure 5. Coordination arrangements of the Cd(II) atoms in **2**. Solvent water molecules are omitted for clarity.

Cd_2(2,2′,3,3′-ODPA)(bpy)$(H_2O)_3\cdot(H_2O)_2$ (2). A single-crystal XRD study has revealed a 3D MOF structure of **2** that is built from the interlinking of lamellars that consist of homochiral helices and crystallizes in the $P2_1$ space group. Similar to that in **1**, there are also some twists for 2,2′,3,3′-ODPA in **2** (see the Supporting Information). The asymmetric unit contains two crystallographically nonequivalent Cd atoms, one 2,2′,3,3′-ODPA, one bpy, and three coordinated and two solvated water molecules (Figures 5 and S3 in the Supporting Information). Cd1 adopts a distorted capped-octahedral conformation, while Cd2 displays an uncommon pentagonal-bipyramidal geometry. The Cd1 center coordinates to 3-COO^- in a monochelating fashion, two other carboxylate groups (2′- and 3′-COO^- in the adjacent layer) in a bichelating fashion as a cis conformation, one nitrogen atom of bpy (N1), and one oxygen atom of water (O12). In contrast, the Cd2 center coordinates to two carboxylate groups in a bichelating fashion as a trans conformation, two oxygen atoms of solvated water (O11 and O12), and one nitrogen atom of bpy (N2).

2 has two similar kinds of helices (Cd1 and Cd2) along the *b* axis and the pitch to the length of 20.059(4) Å. These helices are also of homochiral and right-handed screws (*P* helix). Different from that in **1**, each kind of helix almost uses the whole ODPA ligand, and these two kinds of helices are overlapped together through the 2,2′,3,3′-ODPA ligand

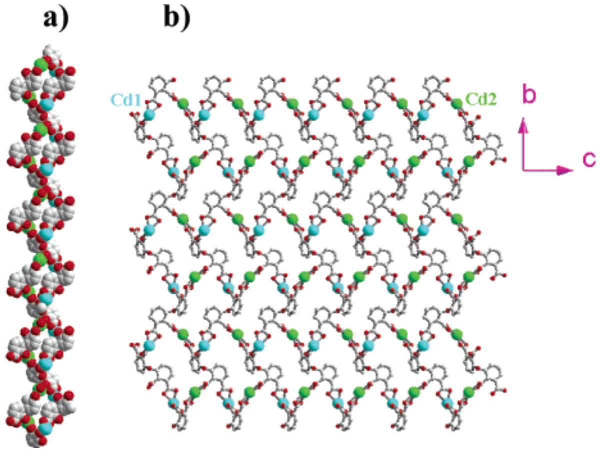


Figure 6. (a) Two partially overlapped homochiral helices including one Cd1−ODPA helix and one Cd2−ODPA helix. (b) Chiral herringbone architecture built from homochiral helices (solvated water and bpy molecules are omitted for clarity).

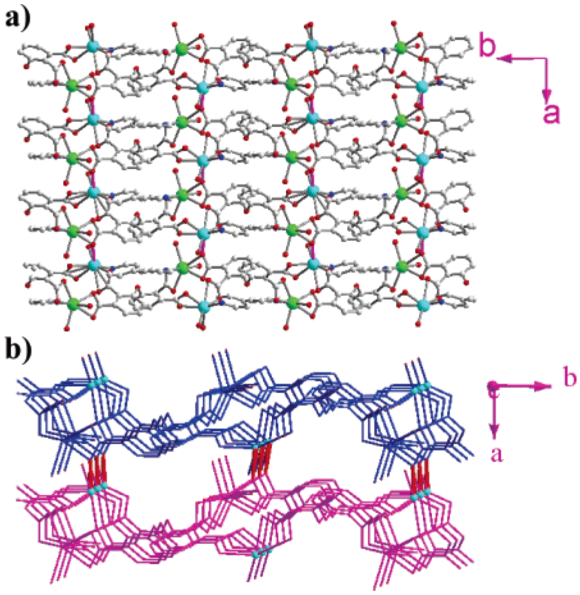


Figure 7. (a) 3D network for **2** (along the *c* axis). (b) Fragment enlargement to show adjacent layer coordination interactions (water and bpy molecules are omitted for clarity) in **2**.

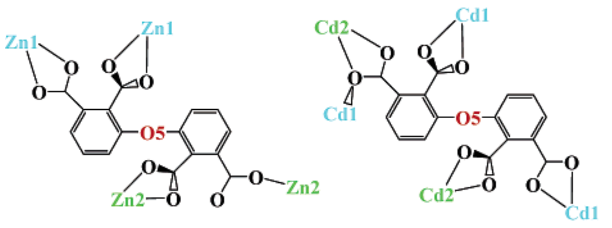
(Figure 6a) to give a chiral puckered-herringbone (or parquet) structural motif, such as that in **1** (Figure 6b). Similar to that in **1**, this herringbone structural motif in **2** is also strengthened by the interlocked rigid bpy molecules between neighboring helices (Figure S4 in the Supporting Information). The chiral layers are parallel to the *bc* plane and are stacked along the *a* direction. Different from that in **1**, interlayer interactions are directly accomplished through coordination bonds (Cd1−O1) in **2** (Figure 7) to give a 3D chiral network. In addition, many hydrogen bonds are also found in **2** between adjacent layers (Figure S5 in the Supporting Information and Table 4).

Table 4. Geometry Parameters for Hydrogen Bonds in **2**[a]

D−H	*d*(D−H)	*d*(H⋯A)	∠DHA	*d*(D⋯A)	A
O10−H10C	0.85	1.98	159.37	2.79	O13
O13−H13C	0.85	2.61	116.90	3.09	O1
O14−H14B	0.85	2.14	139.81	2.85	O7
O12−H12B	0.85	1.99	142.56	2.72	O3
O11−H11C	0.85	2.11	144.87	2.84	O13
O13−H13A	0.85	1.92	168.39	2.76	O2#1
O13−H13C	0.85	2.24	135.30	2.91	O4#1
O14−H14D	0.85	2.38	125.30	2.96	O6#1
O10−H10B	0.85	1.94	152.06	2.72	O9#2
O12−H12A	0.85	2.23	124.89	2.80	O14#2
O11−H11A	0.85	2.45	134.89	3.11	O14#3

[a] Symmetry codes: #1, $x + 1, y, z$; #2, $-x + 1, y + {}^{1}/_{2}, -z + 2$; #3, $-x + 1, y + {}^{1}/_{2}, -z + 1$.

Chart 2. Two Different Coordination Modes of 2,2′,3,3′-ODPA^{4-} in **1** and **2**



According to the above structural description of our example compounds, two kinds of bridging modes for the ODPA ligand and two different metal ion arrangements are found as shown in Chart 2. In fact, **1** can be seen as the unity of two parallel homochiral Zn−1,2-benzenedicarboxylate helices, and the nodes are etheric oxygen O5 atoms. The Zn(II) ions arrange in the two dimension, so **1** can only form a 2D MOF. In contrast, **2** is more complicated and can be seen as two glued Cd−2,3′- and 3,2′-oxybis(benzoate) homochiral helices. Through the interlayer Cd1−O1 bonds, **2** gives a 3D chiral network.

Thermal Analyses and XRD Patterns

For **1**, the weight loss of about 12.37% (calcd 12.52%) below 198 °C corresponds to the loss of two solvent and three coordinated water molecules per formula. Moreover, it begins to decompose until 298 °C. For **2**, the weight loss of about 10.84% (calcd 11.08%) below 150 °C is attributed to the release of two free and three coordinated water molecules. The decompose temperature for **2** is about 250 °C. Guest water molecules are removed by heating **1** and **2** at 150 °C for 1 h. Powder XRD studies of **1** and **2** before and after water expulsion show only minor changes in the diffraction patterns, which indicate that the MOFs of **1** and **2** are intact after removal of the water molecules.

Physical Properties

Excitation of solid samples at $\lambda = 350$ nm produces luminecescence peaks with a maximum at 416 nm for **1** and 438 nm for **2** (Figure 8). The two emission bands might be attributed to the intraligand emission from 2,2′,3,3′-ODPA. Free 2,2′,3,3′-ODPA exhibits a luminescence at 389 nm. Compared with **1**, a baseochromic shift of emission occurs in **2**, which is probably due to the differences of the metal ions and the coordination environment around them because the photoluminescence behavior is closely associated with the metal ions and the ligands coordinated around them.[20] Both **1** and **2** may be suitable as excellent candidates of blue-fluorescent materials. Each crystal may give a pronounced Cotton effect in their CD spectra (usually opposite at random) for materials derived from spontaneous resolution from

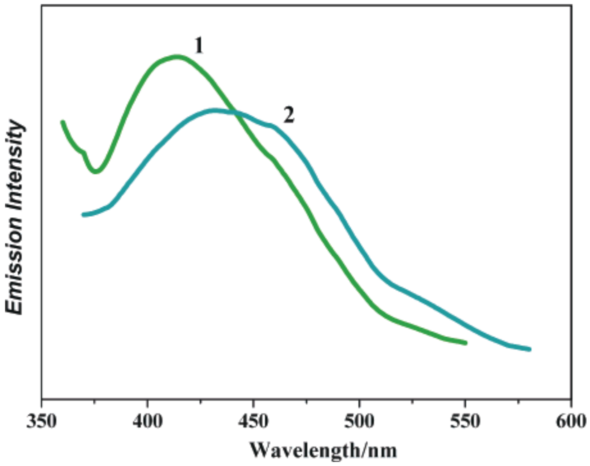


Figure 8. Fluorescent emission spectra of **1** and **2** in the solid state at room temperature.

achiral compounds. Bulk materials for **1** and **2** show no visible Cotton effect in their CD spectra. However, a chiral network is itself noncentrosymmetric, so our bulk materials are acentric materials that have the potential application as NLO-active materials. We have performed quasi-Kurtz SHG measurements on powder samples to confirm their acentricity as well as to evaluate their potential application in second-order NLO material.[21] Preliminary experimental results show that the bulk materials display modest powder SHG efficiencies of approximately 1 and 0.8 times that of urea. Both **1** and **2** exhibit remarkable thermal stability and are insoluble in common solvents because of their neutral 2D and 3D polymeric structures, which make them potential candidates for practical applications.

Conclusion

In this paper, a new versatile multicarboxylate ligand has been introduced to construct new acentric MOFs. Results indicate that this ligand has the potential of forming homochiral metal−ODPA helical chains when it reacts with metal ions. As is our understanding of helical coordination polymers, this is the first example of chiral fortified herringbone motifs. These 2D chiral layers are further united to give 3D chiral networks through hydrogen bonds in **1** and coordination bonds in **2**. More interestingly, both **1** and **2** are NLO-active materials. Further studies are directed toward the design of other homochiral helical solids with the help of other “second” ligands and homochiral porous crystal structures based on this and related ligands.

Acknowledgment. We are grateful for the financial support of the State Basic Research Project and the National Natural Science Foundation of China. The authors also thank Prof. Y.-J. Liu and R.-G. Xiong for their kind help.

Supporting Information Available: Thermogravimetric curves, XRD patterns, additional crystallographic figures, and X-ray crystallographic files in CIF format for the structure determination of compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051502M

---

(20) (a) Zhang, L.-Y.; Liu, G.-F.; Zheng, S. L.; Ye, B.-H.; Zhang, X.-M.; Chen, X.-M. *Eur. J. Inorg. Chem.* **2003**, 2965. (b) Dai, J. C.; Wu, X. T.; Fu, Z. Y.; Cui, C. P.; Wu, S. M.; Du, W. X.; Wu, L. M.; Zhang, H. H.; Sun, Q. *Inorg. Chem.* **2002**, *41*, 1391. (c) Wang, X.-L.; Qin, C.; Li, Y.-G.; Hao, N.; Hu, C. W.; Xu, L. *Inorg. Chem.* **2004**, *43*, 1850.

(21) Kurtz, S. K. *J. Appl. Phys.* **1968**, *39*, 3798.