COMMUNICATION

Dalton
www.rsc.org/dalton

Homochiral crystallization of helical coordination chains bridged by achiral ligands: can it be controlled by the ligand structure?†

Yong-Tao Wang,[a] Ming-Liang Tong,[a] Hai-Hua Fan,[b] He-Zhou Wang[b] and Xiao-Ming Chen*[a,b]

[a] *School of Chemistry & Chemical Engineering, Sun Yat-Sen University, Guangzhou, 510275, China. E-mail: cescxm@zsu.edu.cn; Fax: (+86)20-8411-2245; Tel: (+86)20-8411-2074*

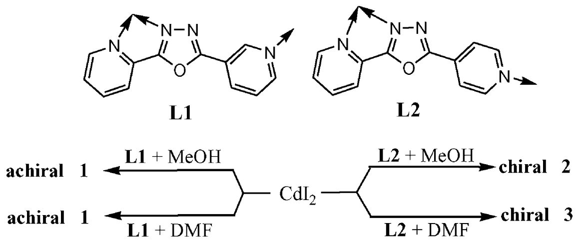
[b] *State Key Laboratory of Optoelectronic Materials and Technologies, Sun Yat-Sen University, Guangzhou, 510275, China*

Received 27th October 2004, Accepted 14th December 2004
First published as an Advance Article on the web 4th January 2005

DOI: 10.1039/b416412a

Homochiral/heterochiral crystallizations of helical chiral polymer chains bridged by achiral poly-pyridyl ligands dependent on the structures of the bridging ligands and independent on the solvent are described, implying a possible strategy to design achiral crystals of helical chains using chiral bridging ligands.

Chiral coordination polymers with different networks,[1–3] which have potential functions, such as enantioselective separations[4] and catalysis,[5] could be obtained by using chiral ligands,[1a,6] and achiral ligands.[7] The use of achiral ligands is more attractive since usually such ligands are easier to generate. Unfortunately, the construction of chiral coordination polymers using achiral ligands is currently a challenging research field, especially that of helical chains.[8] So far our understanding of chiral coordination polymer chains constructed by achiral bridging ligands is very limited,[9] only several asymmetric and achiral pyridyl-bridged polymers[10] and chiral coordination chains constructed by some other asymmetric bridging ligands were recently reported.[11] In fact, the construction of non-centrosymmetrical solids based on 1D chains is a formidable task owing to the lack of control in the two other dimensions.[8] On the other hand, it should be anticipated that the structures of asymmetric bridging ligands have significant effect on recognition and crystallization of the chiral chains into solids. Therefore, we synthesized two new poly-pyridyl ligands, 2-[5-(pyridin-3-yl)-1,3,4-oxadiazol-2-yl]pyridine (**L1**) and 2-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]pyridine (**L2**) (Scheme 1).† Both **L1** and **L2** have two sites (chelate and monodentate) for metal ligation and may extend into polymeric structures with different bridging geometries.



Scheme 1 The asymmetrical bridging ligands and the synthesis of their Cd(II) complexes.

To generate polymer chains, **L1** and **L2** were used to react with CdI_2 (ratio 1 : 1) in MeOH, furnishing $[CdI_2(\mathbf{L1})]_\infty$ (**1**) and $[CdI_2(\mathbf{L2})]_\infty$ (**2**), respectively (Scheme 1). Solvent effect on the crystallization was also evaluated by reactions of CdI_2 with **L1** and **L2** in *N*,*N*-dimethylformamide (DMF), which led to **1** and $\{[CdI_2(\mathbf{L2})(H_2O)]\cdot 2DMF\}_\infty$ (**3**), respectively. Interestingly, **1**, **2** and **3** crystallize in the space groups $C2/c$, $P2_1$, and $P2_12_12_1$, respectively.‡

Single-crystal X-ray analysis reveals that centrosymmetrical **1** consists of one Cd(II) atom and one **L1** ligand in an asymmetric unit (Fig. 1a), and the metal atom is coordinated in square-pyramidal geometry [Cd–N 2.424(4)–2.434(4) Å, Cd–I 2.706(1)–2.738(1) Å, N–Cd–N 68.4(1)–151.8(1)°, N–Cd–I 92.5(1)–130.6(1)°, I–Cd–I 123.64(2)°]. Such chains helically extended along the 2_1 axis in the *b* direction have the both left- and right-handedness, having a pitch of 7.412(1) Å. A left-handed helix is represented in Fig. 2a. Adjacent right- and left-handed chains (1 : 1) are packed in the lattice (see Fig. S1†), exhibiting significant π–π stacking interactions (offset face-to-face distance 3.64 Å) between 3-pyridyl rings from neighbour

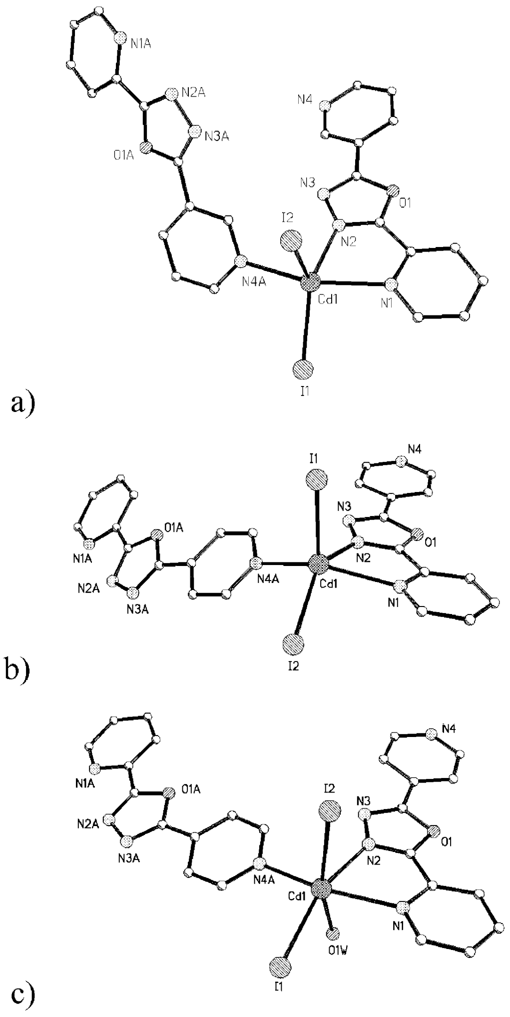


Fig. 1 The coordination arrangements of the Cd(II) atoms in **1** (a), **2** (b) and **3** (c).

---

† Electronic supplementary information (ESI) available: Synthesis for **L1**, **L2**, **1**–**3**, and additional plots for **1**–**3**. See http://www.rsc.org/suppdata/dt/b4/b416412a/

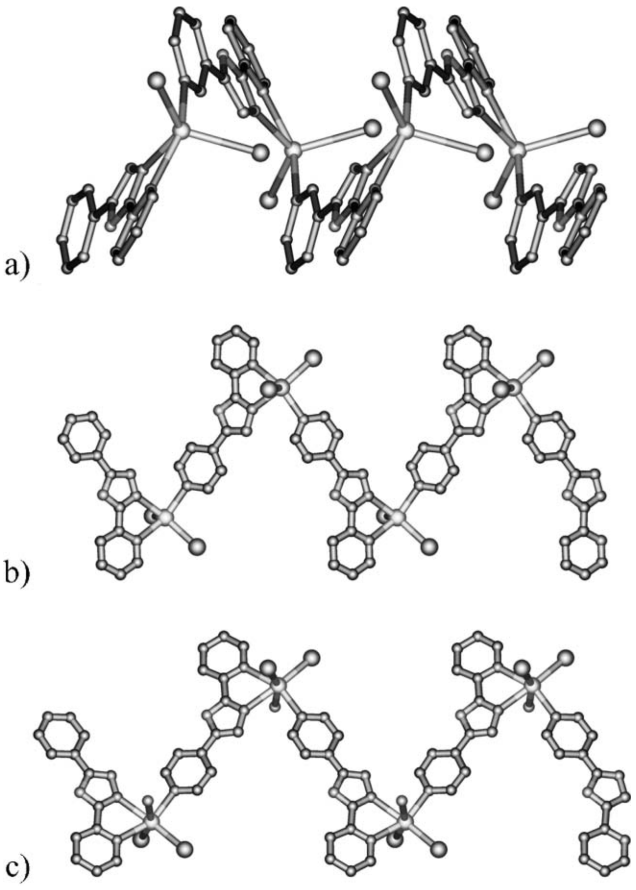


Fig. 2 Perspective views of the *chiral* chains in **1** (a), **2** (b) and **3** (c).

chains in a zipper-like fashion. It is notable that **1** could be isolated in both MeOH and DMF solutions, which implies **1** has the optimized molecular packing fashion.

Each metal atom in **2** is coordinated in a square-pyramidal geometry [Cd–N 2.398(11)–2.469(11) Å, Cd–I 2.717(3)–2.745(2) Å, N–Cd–N 68.4(4)–143.5(4)°, N–Cd–I 90.6(3)–140.8(2)°, I–Cd–I 118.63(6)°] (Fig. 1b), very similar to that in **1**. Interestingly, **2** crystallizes in the chiral space group with each (*P*) right-handed helical chain related by a 2_1-screw axis in the *b* direction, as shown in Fig. 2b. The pitch of the helix in **2** (14.116(1) Å) is almost twice than that of **1**, attributable to the structural difference between **L1** and **L2**. Consequently, the packing mode of **2** is different, neighbouring chains in **2** do not have significant π–π stacking interaction, and they are homochiral (Fig. S2†).

In **3**, the metal atom exhibits a distorted octahedral geometry [Cd–N 2.360(5)–2.474(5) Å, Cd–I 2.790(1)–2.878(1) Å, Cd–O 2.463(5) Å, N–Cd–N 68.9(2)–155.5(2)°, N–Cd–I 86.4(1)–160.9(1)°, I–Cd–I 109.15(2)°, N–Cd–O 75.0(2)–83.1(2)°, O–Cd–I 88.7(1)–161.2(1)°], being additionally ligated by one aqua ligand (Fig. 1c). Although the coordination geometry has been drastically changed, similar to those in **2**, homochiral, (*P*) right-handed helices exist in **3** (Fig. 2c) and are related by the 2_1-screw axes in the *b* direction. The pitch of **3** is only longer by 0.608 Å than that of **2**, which is attributed to the increase of coordination number in **3**. Different from those in **2**, neighbouring chains in **3** have interchain π–π stacking interactions (offset face-to-face, distances between 2-pyridyl and 4-pyridyl rings 3.64 Å), being different from that in **1** (Fig. S3†). Also interestingly, two unusual C–H · · · I hydrogen bonds (C–H · · · I 4.03 and 4.08 Å, C–H · · · I 168 and 165°) (Fig. S4†) between chains are found in **3**, which dominate the molecular packing of **3**. Therefore, we may be able to conclude that the structure of the bridging ligand is critically important, compared to the solvent and coordination geometry. This observation represents a new strategy different from the literature reports that the existence of solvent, change of solvent or temperature can alter heterochiral/homochiral crystallization.[7d,10c,12,13]

Quasi-Kurtz powder second harmonic generation (SHG) measurements[14] show that **2** and **3** display modest powder SHG efficiencies approximately 0.4 and 0.5 times than that potassium dihydrogen phosphate (KDP), respectively. Unfortunately, we were unable to clarify whether the bulk materials were homochiral.

In summary, this work represents a successful example of ligand-controlled homochiral crystallization of coordination polymer chains *via* structural variation of achiral, asymmetric bridging ligands. This implies that upon appropriate design of analogous asymmetric bridging ligands, homochiral crystallizations could be achieved and may lead to potential applications. Further study on the related coordination polymers is in progress.

This work was supported by the National Natural Science Foundation of China (No. 20131020) and the Scientific and Technological Bureau of Guangdong Province (No. 04205405).

Notes and references

‡ *Crystal data* for **1** ($C_{12}H_8CdI_2N_4O$): monoclinic, space group $C2/c$, $M = 590.42$, $a = 33.006(7)$, $b = 7.412(3)$, $c = 13.816(3)$ Å, $\beta = 111.460(3)°$, $V = 3146(1)$ Å^3, $Z = 8$, $\mu = 5.314$ mm^{-1}, $R_1 = 0.0360$, $wR_2 = 0.0947$. *Crystal data* for **2** ($C_{12}H_8CdI_2N_4O$): monoclinic, space group $P2_1$, $M = 590.42$, $a = 7.057(7)$, $b = 14.116(1)$, $c = 8.743(9)$ Å, $\beta = 112.36(2)°$, $V = 805.5(14)$ Å^3, $Z = 2$, $\mu = 5.188$ mm^{-1}, $R_1 = 0.0342$, $wR_2 = 0.0890$, Flack $x = -0.03(6)$. *Crystal data* for **3** ($C_{18}H_{24}CdI_2N_6O_4$): orthorhombic, space group $P2_12_12_1$, $M = 754.63$, $a = 8.295(1)$, $b = 14.724(2)$, $c = 21.236(2)$ Å, $V = 2593.8(5)$ Å^3, $Z = 4$, $\mu = 3.26$ mm^{-1}, $R_1 = 0.0453$, $wR_2 = 0.0983$, Flack $x = 0.02(3)$. CCDC reference numbers 253093–253095. See http://www.rsc.org/suppdata/dt/b4/b416412a/ for crystallographic data in CIF or other electronic format.

1 (*a*) B. Kesanli and W. Lin, *Coord. Chem. Rev.*, 2003, **246**, 305; (*b*) N. G. Pschirer, D. M. Ciurtin, M. D. Smith, U. H. F. Bunz and H.-C. zur Loye, *Angew. Chem., Int. Ed.*, 2002, **41**, 583; (*c*) Z.-R. Qu, H. Zhao, Y.-P. Wang, X.-S. Wang, Q. Ye, Y.-H. Li, R.-G. Xiong, B. F. Abrahams, Z.-G. Liu, Z.-L. Xue and X.-Z. You, *Chem.–Eur. J.*, 2004, **10**, 53.

2 (*a*) C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005; (*b*) M. Albrecht, *Chem. Rev.*, 2001, **101**, 3457; (*c*) P. A. Maggard, C. L. Stern and K. R. Poeppelmeier, *J. Am. Chem. Soc.*, 2001, **123**, 7742; (*d*) A. D. Cutland-Van Noord, J. W. Kampf and V. L. Pecoraro, *Angew. Chem., Int. Ed.*, 2002, **41**, 4667.

3 (*a*) B. Moulton and M. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (*b*) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (*c*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1461.

4 R.-G. Xiong, X.-Z. You, B. F. Abrahams, Z.-L. Xue and C.-M. Che, *Angew. Chem., Int. Ed.*, 2001, **40**, 4422.

5 J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kimoon, *Nature*, 2000, **404**, 982.

6 (*a*) A. Akasaka, K. Biradha, S. Sakamoto, K. Yamaguchi and M. Fujita, *Angew. Chem., Int. Ed.*, 2002, **41**, 3269; (*b*) E. V. Anokhina and A. J. Jacobson, *J. Am. Chem. Soc.*, 2004, **126**, 3044.

7 (*a*) E. Q. Gao, S. Q. Bai, Z. M. Wang and C. H. Yan, *J. Am. Chem. Soc.*, 2003, **125**, 4984; (*b*) L. Han, M. C. Hong, R. H. Wang, J. H. Luo, Z. Z. Lin and D. Q. Yuan, *Chem. Commun.*, 2003, 2580; (*c*) U. Siemeling, I. Scheppelmann, B. Neumann, A. Stammler, H.-G. Stammler and J. Frelek, *Chem. Commun.*, 2003, 2236; (*d*) T. Ezuhara, K. Endo and Y. Aoyama, *J. Am. Chem. Soc.*, 1999, **121**, 3279.

8 O. R. Evans and W. B. Lin, *Acc. Chem. Res.*, 2002, **35**, 511.

9 X.-M. Chen and G.-F. Liu, *Chem.–Eur. J.*, 2002, **8**, 4811.

10 (*a*) M.-L. Tong, X.-M. Chen, B.-H. Ye and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 5278; (*b*) K. Uemura, S. Kitagawa, K. Fukui and K. Saito, *J. Am. Chem. Soc.*, 2004, **126**, 3817; (*c*) A. N. Khlobystov, M. T. Brett, A. J. Blake, N. R. Champness, P. M. W. Gill, D. P. O'Neill, S. J. Teat, C. Wilson and M. Schröder, *J. Am. Chem. Soc.*, 2003, **125**, 6753; (*d*) I. S. Lee, D. M. Shin and Y. K. Chung, *Chem.–Eur. J.*, 2004, **10**, 3158; (*e*) D. A. Beauchamp and S. J. Loeb, *Chem. Commun.*, 2002, 2484.

11 (*a*) Y. Cui, H. L. Ngo and W. Lin, *Chem. Commun.*, 2003, 1388; (*b*) A. Jouaiti, M. W. Hosseini and N. Kyritsakas, *Chem. Commun.*, 2002,

1898; (*c*) M. Kondo, M. Miyazawa, Y. Irie, R. Shinagawa, T. Horiba, A. Nakamura, T. Naito, K. Maeda, S. Utsuno and F. Uchidac, *Chem. Commun.*, 2002, 2156; (*d*) R.-H. Wang, L.-J. Xu, X.-S. Li, Y.-M. Li, Q. Shi, Z.-Y. Zhou, M.-C. Hong and A. S. C. Chan, *Eur. J. Inorg. Chem.*, 2004, 1595.

12 J. Jacques, A. Collet and S. H. Wilen, *Enantiomers, Racemates and Resolutions*, Krieger Publishing Company, Malabar, FL, 1994.

13 L. Pérez-García and D. B. Amabilino, *Chem. Soc. Rev.*, 2002, **31**, 342.

14 S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, 1968, **39**, 3798.