

## Polymorphism in Homochiral Zinc Phosphonates

Xun-Gao Liu, Song-Song Bao, Yi-Zhi Li, and Li-Min Zheng\*

State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China

Received January 11, 2008

This paper reports four homochiral zinc phosphonates,  $\alpha$ -(*S*)-[Zn<sub>2</sub>(pemp)(pempH)Cl] (**1**),  $\alpha$ -(*R*)-[Zn<sub>2</sub>(pemp)(pempH)Cl] (**2**),  $\beta$ -(*S*)-[Zn<sub>2</sub>(pemp)(pempH)Cl] (**3**), and  $\beta$ -(*R*)-[Zn<sub>2</sub>(pemp)(pempH)Cl] (**4**) [pempH<sub>2</sub> = (1-phenylethyl)amino]methylphosphonic acid]. Both **1** and **2** are enantiomers, crystallizing in an orthorhombic *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> space group, while **3** and **4** are polymorphic phases of **1** and **2**, respectively, crystallizing in a monoclinic *P*2<sub>1</sub> space group. The polymorphism is induced by temperature or additional organic molecules.

Chiral coordination polymers have been of intense current interest mainly because of their potential applications in the areas of enantioselective catalysis and separation.<sup>1</sup> Among the different approaches to introducing chirality, the main synthetic strategy is to use optically pure chiral multidentate ligands.<sup>2</sup> By employment of enantiomerically pure phosphonic acids, a few chiral metal phosphonates have been prepared and crystallographically characterized. These include layer compounds (*R*)- $\alpha$ -Zn(O<sub>3</sub>PCH<sub>2</sub>P(O)(C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)), (*R*)- $\alpha$ -Zn(O<sub>3</sub>PCH<sub>2</sub>P(O)(C<sub>6</sub>H<sub>5</sub>)(C<sub>2</sub>H<sub>5</sub>))·H<sub>2</sub>O, and (*R*)- $\beta$ -Zn(O<sub>3</sub>PCH<sub>2</sub>P(O)(C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>))·H<sub>2</sub>O,<sup>3</sup> chain compounds Ln[(*S*)-HO<sub>3</sub>PCH<sub>2</sub>NHC<sub>4</sub>H<sub>7</sub>CO<sub>2</sub>]<sub>3</sub>·2H<sub>2</sub>O (Ln = Tb, Dy, Eu, Gd),<sup>4</sup> three-dimensional compound Zn<sub>2</sub>[(*S*)-O<sub>3</sub>PCH<sub>2</sub>NHC<sub>4</sub>H<sub>7</sub>CO<sub>2</sub>]<sub>2</sub>,<sup>5</sup> and lamellar or pillared layered lanthanide diphosphonates based

on derivatives of 1,1'-binaphthalene-6,6'-bisphosphonic acid.<sup>6,7</sup> Some chiral porous zirconium phosphonates have also been reported that show promising heterogeneous asymmetric catalytic properties.<sup>8–10</sup> In this paper, we use an enantiopure organic phosphonic acid, (*S*)- or (*R*)-[(1-phenylethyl)amino]methylphosphonic acid (pempH<sub>2</sub>), to react with zinc salts under hydrothermal conditions. Homochiral zinc phosphonates  $\alpha$ -(*S*)-[Zn<sub>2</sub>(pemp)(pempH)Cl] (**1**) and  $\alpha$ -(*R*)-[Zn<sub>2</sub>(pemp)(pempH)Cl] (**2**) are obtained successfully. More interestingly, the presence of organic molecules in the reaction mixture or a higher reaction temperature can lead to new phases,  $\beta$ -(*S*)-[Zn<sub>2</sub>(pemp)(pempH)Cl] (**3**) and  $\beta$ -(*R*)-[Zn<sub>2</sub>(pemp)(pempH)Cl] (**4**), which are polymorphic to compounds **1** and **2**, respectively.

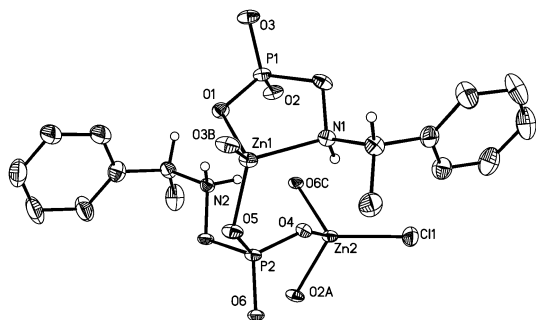
It is well-known that controlling polymorphism is of great interest in the fields of materials science and pharmacology because the various polymorphs of the same substance may have significantly different physical properties.<sup>11</sup> The crystallization of polymorphs could be affected by such factors as temperature, additives, solvents, cooling rate, interface, etc.<sup>12</sup> Polymorphism in metal phosphonates has been rare. As far as we are aware, the only example is a nanotubular uranyl phenylphosphonate (UO<sub>2</sub>)<sub>3</sub>(HO<sub>3</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(O<sub>3</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>·H<sub>2</sub>O, which shows  $\delta$ - and  $\epsilon$ -polymorphs, both crystallizing in orthorhombic space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. In the higher temperature  $\epsilon$  phase, a tilting of the organic groups to accommodate the nanotubes more efficiently is observed.<sup>13,14</sup> Polymorphism of homochiral metal phosphonates has never been reported.

Hydrothermal reactions of (*S*)-pempH<sub>2</sub> or (*R*)-pempH<sub>2</sub> with ZnSO<sub>4</sub>·7H<sub>2</sub>O and NaCl in a 1:1:0.5 molar ratio, adjusted to

\* To whom correspondence should be addressed. E-mail: lmzheng@netra.nju.edu.cn.

- (1) (a) Song, C. E.; Lee, S. G. *Chem. Rev.* **2002**, *102*, 3495. (b) Ngo, H. L.; Lin, W. *Top. Catal.* **2005**, *34*, 85. (c) Anokhina, E. V.; Jacobson, A. J. *J. Am. Chem. Soc.* **2004**, *126*, 3044. (d) Janiak, C. *Dalton Trans.* **2003**, 2781, and references cited therein.
- (2) (a) Zhang, J.; Chen, S.; Valle, H.; Wong, M.; Austria, C.; Cruz, M.; Bu, X. *J. Am. Chem. Soc.* **2007**, *129*, 14168. (b) Nuzhdin, A. L.; Dybtsev, D. N.; Bryliakov, K. P.; Talsi, E. P.; Fedin, V. P. *J. Am. Chem. Soc.* **2007**, *129*, 12958. (c) Lin, Z.; Slawin, A. M. Z.; Morris, R. E. *J. Am. Chem. Soc.* **2007**, *129*, 4880. (d) Wu, S.-T.; Wu, Y.-R.; Kang, Q.-Q.; Zhang, H.; Long, L.-S.; Zheng, Z.; Huang, R.-B.; Zheng, L.-S. *Angew. Chem., Int. Ed.* **2007**, *46*, 8475.
- (3) Fredoueil, F.; Evain, M.; Massiot, D.; Bujoli-Doeuff, M.; Bujoli, B. *J. Mater. Chem.* **2001**, *11*, 1106.
- (4) Yue, Q.; Yang, J.; Li, G.-H.; Li, G.-D.; Chen, J.-S. *Inorg. Chem.* **2006**, *45*, 4431.
- (5) Shi, X.; Zhu, G.; Qiu, S.; Huang, K.; Yu, J.; Xu, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6482.

- (6) Evans, O. R.; Ngo, H. L.; Lin, W.-B. *J. Am. Chem. Soc.* **2001**, *123*, 10395.
- (7) Ngo, H. L.; Lin, W.-B. *J. Am. Chem. Soc.* **2002**, *124*, 14298.
- (8) Shi, X.; Liu, J.; Li, C.; Yang, Q. *Inorg. Chem.* **2007**, *46*, 7944.
- (9) Costantino, U.; Fringuelli, F.; Nocchetti, M.; Piermatti, O. *Appl. Catal. A* **2007**, *326*, 100–105.
- (10) Ngo, H. L.; Hu, A.; Lin, W. *J. Mol. Catal. A: Chem.* **2004**, *215*, 177.
- (11) (a) Vippagunta, S. R.; Brittain, H. G.; Grant, D. J. W. *Adv. Drug Delivery Rev.* **2001**, *48*, 3–26. (b) Di Profio, G.; Tucci, S.; Curcio, E.; Drioli, E. *Chem. Mater.* **2007**, *19*, 2386.
- (12) Kobayashi, K.; Sato, A.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **2003**, *125*, 3035.
- (13) Aranda, M. A. G.; Cabeza, A.; Bruque, S.; Poojary, D. M.; Clearfield, A. *Inorg. Chem.* **1998**, *37*, 1827.
- (14) Poojary, D. M.; Cabeza, A.; Aranda, M. A. G.; Bruque, S.; Clearfield, A. *Inorg. Chem.* **1996**, *35*, 1468.

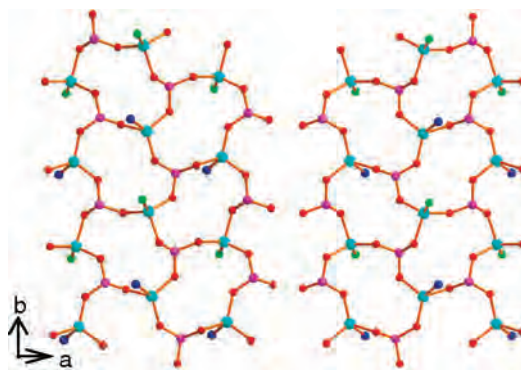


**Figure 1.** Coordination geometries of Zn in **1** with an atomic labeling scheme. Thermal ellipsoids are at the 30% probability level. All H atoms except those attached to N and chiral C atoms are omitted for clarity.

pH = 5.7 by NaOH at 140 °C, afforded colorless platelike crystals of **1** and **2**, respectively. Complexes **3** and **4** were obtained by following a similar procedure except at 160 °C or using additional organic molecules such as racemic 3-hydroxypiperidine, ethanolamine, (CH<sub>3</sub>)<sub>4</sub>NOH, and (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NOH.<sup>15</sup> The same compounds can be obtained without NaCl by using ZnCl<sub>2</sub> instead of ZnSO<sub>4</sub> as the starting material.

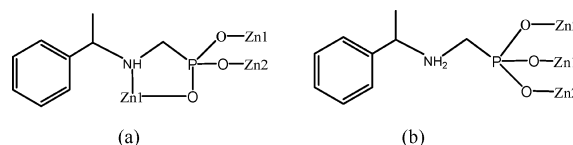
Single-crystal structural analyses reveal that complexes **1** and **2** are enantiomers crystallizing in the orthorhombic system, chiral space group  $P2_12_12_1$  (No. 19).<sup>16</sup> Take compound **1** as an example. The asymmetric unit of **1** contains two independent Zn atoms, two phosphonate ligands, and one Cl<sup>-</sup> anion (Figure 1). Both Zn1 and Zn2 atoms adopt slightly distorted tetrahedral coordination geometries. Zn1 is coordinated to three phosphonate O atoms (O1, O5, and O3B) and one N atom (N1) from three phosphonate ligands, with Zn1–O and Zn1–N bond lengths being 1.872(3)–1.983(3) and 2.044(3) Å, respectively. The four coordination sites around Zn2 are provided by three phosphonate O atoms (O2A, O4, and O6C) and one Cl<sup>-</sup> anion. The Zn2–O and Zn2–Cl bond lengths are 1.948(3)–1.997(3) and 2.201(1) Å, respectively.

There are two crystallographically different phosphonate ligands (pemp<sup>2-</sup> and pempH<sup>-</sup>). pemp<sup>2-</sup> behaves as a tet-



**Figure 2.** Inorganic enantiomorphous layer structures of **1** (*S* isomer, left) and **2** (*R* isomer, right). Color code: Zn, cyan; P, purple; O, red; N, blue; Cl, green.

#### Scheme 1



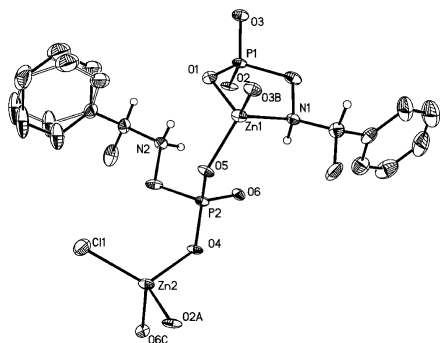
radentate ligand. It chelates to Zn1 through O1 and N1 atoms and coordinates to the equivalent Zn1 and Zn2 via O3 and O2 atoms, respectively (Scheme 1a). pempH<sup>-</sup> serves as a tridentate ligand, with each of its three phosphonate O atoms binding to one Zn1 and two equivalent Zn2, respectively (Scheme 1b). Consequently, each {ZnO<sub>3</sub>N} or {ZnO<sub>3</sub>Cl} tetrahedron is corner-shared with three {CPO<sub>3</sub>} tetrahedra and vice versa, leading to a two-dimensional inorganic layer in the *ab* plane where helical chains of –Zn1–O–P–O– and –Zn2–O–P–O– are running along the *a* axis and are alternatively arranged along the *b* axis (Figure 2). Hydrogen-bond interactions are found between the amino N and phosphonate O atoms within the layer. The N1⋯O4, N2⋯O1, N2⋯O6<sup>i</sup>, and N2⋯O2 distances are 3.073(5), 2.981(4), 2.868(5), and 3.051(4) Å, respectively (symmetry code: *i*,  $x - 1/2$ ,  $-y + 3/2$ ,  $-z + 1$ ). The organic groups are grafted onto the two sides of the inorganic layer. van der Waals interactions dominate between the layers.

Complexes **3** and **4** are enantiomers and crystallize in the monoclinic system, chiral space group  $P2_1$  (No. 4).<sup>17</sup> Both contain the same composition as those of **1** and **2** and show layer structures similar to those of **1** and **2**, respectively. Hence, **3** is selected to compare with **1**. The Zn–O, Zn–N, and Zn–Cl bond lengths of **3** are 1.845(5)–1.988(9), 2.033(7) and 2.196(3) Å, respectively, slightly different from those of **1** (Figure 3). Hydrogen-bond interactions are again observed within the layer, with the N1⋯O6, N2⋯O1, N2⋯O2, and N2⋯O4<sup>ii</sup> distances being 3.075(8), 2.964(8), 3.038(1), and 2.873(8) Å, respectively (symmetry code: *ii*,  $2 - x$ ,  $1/2 + y$ ,  $2 - z$ ). A significant structural difference between **3** and **1** lies in the packing modes of the layers. In

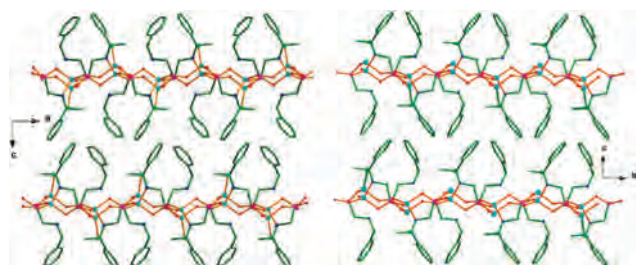
(15) Elem anal. Calcd (%) for C<sub>18</sub>H<sub>25</sub>ClN<sub>2</sub>O<sub>6</sub>P<sub>2</sub>Zn<sub>2</sub> (**1**): C, 36.42; H, 4.24; N, 4.72. Found: C, 36.33; H, 4.19; N, 4.62. IR (KBr, cm<sup>-1</sup>): 3429 (w), 3232 (w), 2981 (w), 1603 (w), 1456 (w), 1441 (w), 1272 (w), 1236 (m), 1199 (w), 1136 (s), 1095 (s), 1014 (s), 863 (w), 761 (m), 739 (w), 701 (m), 646 (w), 577 (m), 547 (w), 495 (w). Anal. Calcd for C<sub>18</sub>H<sub>25</sub>ClN<sub>2</sub>O<sub>6</sub>P<sub>2</sub>Zn<sub>2</sub> (**2**): C, 36.42; H, 4.24; N, 4.72. Found: C, 36.21; H, 4.33; N, 4.77. IR (KBr, cm<sup>-1</sup>): 3421 (w), 3231 (w), 2981 (w), 1602 (w), 1456 (w), 1441 (w), 1272 (w), 1236 (m), 1199 (w), 1136 (s), 1095 (s), 1004 (s), 862 (w), 761 (m), 739 (w), 701 (m), 636 (w), 577 (m), 547 (w), 495 (w). Anal. Calcd for C<sub>18</sub>H<sub>25</sub>ClN<sub>2</sub>O<sub>6</sub>P<sub>2</sub>Zn<sub>2</sub> (**3**): C, 36.42; H, 4.24; N, 4.72. Found: C, 36.31; H, 4.30; N, 4.61. IR (KBr, cm<sup>-1</sup>): 3446 (w), 3213 (w), 3031 (w), 2875 (w), 2360 (w), 1589 (w), 1454 (w), 1383 (w), 1275 (w), 1168 (s), 1133 (s), 1103 (s), 1052 (s), 1007 (s), 814 (w), 763 (m), 739 (w), 700 (m), 634 (w), 612 (m), 572 (w). Anal. Calcd for C<sub>18</sub>H<sub>25</sub>ClN<sub>2</sub>O<sub>6</sub>P<sub>2</sub>Zn<sub>2</sub> (**4**): C, 36.42; H, 4.24; N, 4.72. Found: C, 36.29; H, 4.21; N, 4.76. IR (KBr, cm<sup>-1</sup>): 3440 (w), 3212 (w), 3031 (w), 2852 (w), 2394 (w), 1588 (w), 1454 (w), 1383 (w), 1275 (w), 1168 (m), 1133 (s), 1104 (s), 1079 (s), 1054 (s), 1007 (s), 815 (w), 763 (m), 740 (w), 701 (m), 633 (w), 613 (m), 572 (w).

(16) Crystal data for **1**: orthorhombic,  $P2_12_12_1$ ,  $a = 8.979(1)$  Å,  $b = 10.000(1)$  Å,  $c = 26.840(1)$  Å,  $V = 2410.1(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.636$  g/cm<sup>3</sup>,  $\mu = 2.270$  mm<sup>-1</sup>,  $R1 = 0.0367$ ,  $wR2 = 0.0524$ ,  $GOF = 0.90$ . Crystal data for **2**: orthorhombic,  $P2_12_12_1$ ,  $a = 8.9611(10)$  Å,  $b = 9.9772(12)$  Å,  $c = 26.791(3)$  Å,  $V = 2395.3(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.646$  g/cm<sup>3</sup>,  $\mu = 2.284$  mm<sup>-1</sup>,  $R1 = 0.0589$ ,  $wR2 = 0.1150$ ,  $GOF = 1.02$ .

(17) Crystal data for **3**: monoclinic,  $P2_1$ ,  $a = 9.9477(16)$  Å,  $b = 8.9814(14)$  Å,  $c = 13.969(2)$  Å,  $\beta = 107.544(3)^\circ$ ,  $V = 1190.0(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.657$  g/cm<sup>3</sup>,  $\mu = 2.298$  mm<sup>-1</sup>,  $R1 = 0.0435$ ,  $wR2 = 0.0904$ ,  $GOF = 0.93$ . Crystal data for **4**: monoclinic,  $P2_1$ ,  $a = 9.981(1)$  Å,  $b = 8.961(2)$  Å,  $c = 13.903(14)$  Å,  $\beta = 107.504(2)^\circ$ ,  $V = 1185.9(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.662$  g/cm<sup>3</sup>,  $\mu = 2.306$  mm<sup>-1</sup>,  $R1 = 0.0623$ ,  $wR2 = 0.1414$ ,  $GOF = 1.09$ .



**Figure 3.** Coordination geometries of Zn in compound **3** with an atomic labeling scheme. Thermal ellipsoids are at the 30% probability level. All H atoms except those attached to N and chiral C atoms are omitted for clarity.

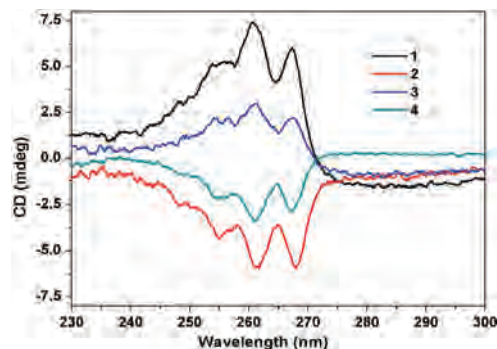


**Figure 4.** Packing diagrams of **1** along the *b* axis (left) and **3** along the *a* axis (right). All H atoms are omitted for clarity.

compound **1**, neighboring layers are stacked along the *c* axis and repeat in an  $\cdots ABAB \cdots$  sequence, while in compound **3**, they are stacked in the sequence of  $\cdots AA \cdots$  (Figure 4). The layer-to-layer separations are 13.420 Å for **1** and 13.969 Å for **3**.

The structural and composition similarity of compound **3** to **1** suggests that the two compounds are polymorphic isomers. Considering that the other experimental conditions are almost the same in preparing the two compounds, the polymorphism could be induced by temperature or by the presence of the additional organic molecules. The cell volume of **3** is 1.2% smaller than that of **1**, indicating that **3** could be thermodynamically more stable.<sup>18</sup> This is supported by the experiments; e.g., higher reaction temperature favors the formation of **3** instead of **1**. The same conclusion is held for **2** and **4**.

Solid-state circular dichroism (CD) spectra were measured on KBr pellets for compounds **1–4** (Figure 5). Clearly, compounds **1** and **3** exhibit positive Cotton effects while **2** and **4** show negative Cotton effects at the same wavelengths



**Figure 5.** CD spectra of **1** (black line), **2** (red line), **3** (blue line), and **4** (cyan line) in KBr pellets.

(254, 261, and 268 nm), reflecting that the optical activities of these compounds originate from the chiral organic phosphonate ligands.<sup>19</sup> For compounds **1** and **2**, the opposite sign of Cotton effects confirms that they are a pair of enantiomers. Similarly, compounds **3** and **4** are also a pair of enantiomers. The second harmonic generation (SHG) properties of powder samples **1–4** were also studied. The results indicate that both **1** and **2** exhibit SHG responses about 0.4 times that of urea, while **3** and **4** exhibit SHG responses about 0.5 times that of urea.

In summary, we report four novel enantiopure zinc phosphonates synthesized by hydrothermal reactions of (*S*)- or (*R*)-[(1-phenylethyl)amino]methylphosphonic acid and zinc sulfate under hydrothermal conditions, namely,  $\alpha$ -(*S*)-[Zn<sub>2</sub>(pemp)(pempH)Cl] (**1**),  $\alpha$ -(*R*)-[Zn<sub>2</sub>(pemp)(pempH)Cl] (**2**),  $\beta$ -(*S*)-[Zn<sub>2</sub>(pemp)(pempH)Cl] (**3**), and  $\beta$ -(*R*)-[Zn<sub>2</sub>(pemp)(pempH)Cl] (**4**). The results demonstrate that polymorphism of chiral zinc phosphonates can be induced by temperature or by additional organic molecules. Further work is in progress to prepare novel homochiral materials based on phosphonates with interesting chemical and physical properties.

**Acknowledgment.** We thank the NSFC (Grants 20325103, 20631030, and 20721002), the National Basic Research Program of China (Grant 2007CB925102), and 111 Project under Grant B07026 for financial support.

**Supporting Information Available:** Crystallographic files in CIF format, the experimental procedure, and five figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC800663T

(18) Zhang, J.; Bu, X. *Angew. Chem., Int. Ed.* **2007**, *46*, 6115.

(19) Kaneko, W.; Kitagawa, S.; Ohba, M. *J. Am. Chem. Soc.* **2007**, *129*, 248.