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Enantioselective Recognition and Separation of Racemic 1-Phenylethanol by a Pair of 2D Chiral Coordination Polymers

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Supporting Information

ABSTRACT: A pair of 2D chiral coordination polymers were constructed through the self-assembly of a chiral metal-camphor-10-sulfonate salt and a bidentate linker, which show selective inclusion of *S* and *R* enantiomers of 1-phenylethanol respectively with an enantioselectivity of 9:1.

Chiral coordination polymers (CCPs) have been attracting unprecedented attention because of their potential applications in enantioselective separation, heterogeneous asymmetric catalysis, and nonlinear optics.[1−3] Recently, CCPs have been used for chromatography and membrane-based separation, exhibiting a new generation of chiral separation materials.[4] To date, the most effective strategy to construct CCPs is to directly utilize the chiral ligand as the starting material;[1] for instance, Rosseinsky and co-workers used chiral nickel aspartate [Ni(L-asp)] and 4,4′-bipyridine as building units to construct a neutral chiral 3D framework with 1D open chiral channels, which exhibits the ability for enantioselective separation of diols.[2c] The advantage of using chiral metal salts as starting materials to construct CCPs is that CCPs are neutral, preventing open-channel blockage by counteranions.

Despite much progress in the chemistry of chiral porous materials,[5] the mechanism for enantioselective separation of chiral guest molecules by CCPs has not been fully understood. Single-crystal structural analysis can offer a straightforward explanation to understand the enantioselective discrimination of CCPs toward chiral guest molecules, which can further help to design new CCPs effectively. However, up to now, there are only a few examples that show the intermolecular interactions between the chiral porous frameworks and chiral guest molecules through X-ray crystal structural analysis[3] and quantum-mechanical simulation.[6] In most cases, the guest molecules are disordered, and it is hard to see such host−guest interactions.

On the other hand, during the synthesis of porous CCPs using chiral ligands as starting materials, undesirable achiral crystalline solids are often obtained owing to racemization of chiral ligands.[2c,7] Chiral camphor derivatives feature two chiral carbon atoms in their rigid skeleton and thus are unlikely to undergo racemization, which could become an appropriate chiral building unit to construct CCPs.[8] Although chiral CCPs based on camphor-10-sulfonic acid (cpsH) have been reported[9] and cpsH has been also widely used as a chiral resolution reagent,[10] enantioselective separation by CCPs constructed by cpsH still remains unexplored.[9a]

Herein, we present the synthesis and structures of a pair of 2D CCPs, $\{[Cd_2(L\text{-cps})_4(bix)_4]\cdot(CH_2Cl_2)_2(EtOH)(H_2O)\}_n$ (L-**1**) and $\{[Cd_2(D\text{-cps})_4(bix)_4]\cdot(CH_2Cl_2)_2(EtOH)(H_2O)\}_n$ (D-**1**), which were constructed by the self-assembly of a bix ligand with $Cd(L\text{-cps})_2\cdot(H_2O)_6$ and $Cd(D\text{-cps})_2\cdot(H_2O)_6$, respectively [bix = 1,4-bis(imidazol-1-yl-methyl)benzene; see Figure 1].

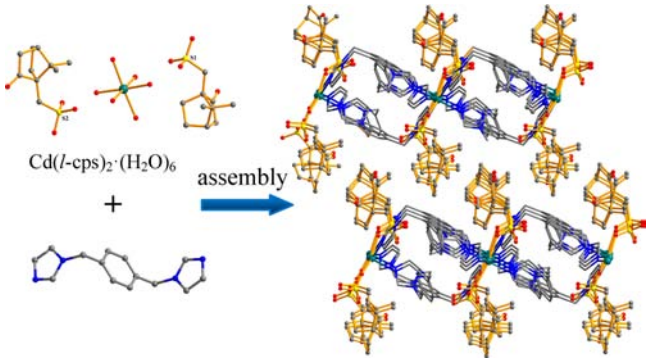

Figure 1. Construction of L-**1** through the self-assembly of $Cd(L\text{-cps})_2\cdot(H_2O)_6$ with the bix ligand. The included guest molecules within the interlayer are omitted for clarity.

Dissolving L-**1** and D-**1** in racemic 1-phenylethanol (PEA) and $CHCl_3$ (1:1) generated $\{[Cd_2(L\text{-cps})_4(bix)_4]\cdot(PEA)_4\}_n$ (L-**2**) and $\{[Cd_2(D\text{-cps})_4(bix)_4]\cdot(PEA)_4\}_n$ (D-**2**), respectively. The results of structural analysis reveal that L-**2** and L-**2** show a selective inclusion of (*R*)-PEA and (*S*)-PEA, respectively, with an enantioselectivity of 9:1.

The reaction of chiral L-cpsH with CdO in water produced $Cd(L\text{-cps})_2\cdot(H_2O)_6$, which was confirmed by single-crystal X-ray diffraction analysis. Single crystals of L-**1** were obtained by diffusing an ethanol solution of $Cd(L\text{-cps})_2\cdot(H_2O)_6$ into the CH_2Cl_2 solution of bix (see the Supporting Information, SI). The result of X-ray crystal structural analysis reveals that L-**1** crystallizes in chiral space group *P*1. The asymmetric unit consists of two crystallographic independent Cd^{II} ions (Figure S1 in the SI), in which each Cd^{II} is six-coordinated to four nitrogen atoms from four bix ligands and two sulfonate oxygen atoms from two individual L-cps^- anions, forming a slightly distorted N_4O_2 octahedral geometry. The Cd−O and Cd−N distances are in the normal range.[11] In L-**1**, Cd^{II} ions are connected by bix ligands to generate a layered structure, with a 4,4 network in the

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ac plane (Figure S2 in the SI), and the monocoordinated L-cps$^-$ anions locate on and below the layer to induce a homochiral layer. The adjacent chiral layers are connected via interdigitation of L-cps$^-$ groups along the *b* axis to generate the 3D chiral framework of L-**1** (Figure S3 in the SI), and the guest molecules locate within the interlayer.

The results of solid circular dichroism (CD) spectroscopy measurements demonstrate that the chirality of L-**1** comes from the starting material of L-cps$^-$ anions (Figure S4 in the SI). The result of thermogravimetric analysis (TGA) indicates that the guest molecules in L-**1** can be removed below 160 °C (Figure S5 in the SI), and the framework can be stable up to 300 °C. Variable-temperature powder X-ray diffraction (PXRD) of L-**1** was performed from room temperature to 300 °C, showing that the position of the peak at 6.7° gradually moved to higher angles upon heating (Figure S6 in the SI), demonstrating that the framework of L-**1** shrinks after the loss of guest molecules within the interlayer.

To see if chiral L-**1** has the ability for enantioselective separation of racemic guest molecules, the crystals of L-**1** were immersed in a mixture of racemic PEA and $CHCl_3$. However, the quality of the generated crystals is not good enough for X-ray crystal structural analysis. Thus, the crystals of L-**1** were dissolved in a mixture of racemic PEA and $CHCl_3$ under heating and evaporated slowly at room temperature, and single crystals of L-**2** were obtained. L-**2** also crystallizes in the chiral space group *P*1 and shows a chiral layered structure similar to that of L-**1**. In contrast to L-**1**, one of the imidazole rings of the bix ligand bonded to Cd2 is disordered in L-**2**, with an occupancy of 0.6:0.4 for two different positions (Figure 2), and this leads to one L-cps$^-$

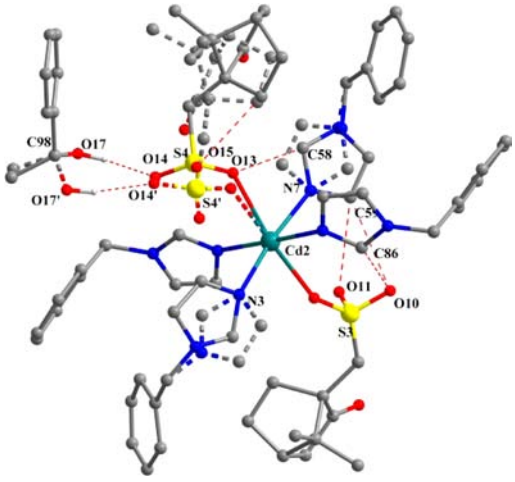

Figure 2. Structure of the disordered L-cps$^-$ anion and PEA molecule around Cd2 in L-**2** (the part of the occupancy of 0.4 is drawn as dotted lines).

anion bonded to Cd2 being disordered with the same occupancy of 0.6:0.4 (Figure 2). The other three L-cps$^-$ anions bonded to Cd1 and Cd2 are ordered, and their positions are fixed by forming weak O···H−C hydrogen bonds between the uncoordinated sulfonate oxygen atoms of L-cps$^-$ and the carbon atoms of ordered imidazole rings of bix ligands (Figures 2 and S7 in the SI), with O···H−C distances of 2.25−2.53 Å. Interestingly, each L-cps$^-$ anion connects one PEA molecule within the interlayer through O···H−O hydrogen bonding between the uncoordinated sulfonate oxygen atom of L-cps$^-$ and the oxygen atom of the PEA molecule, with O···H−O distances of 1.95−2.09 Å (Figure 3). After bonding of the PEA molecules within the interlayer, the distance between the adjacent layers extends from

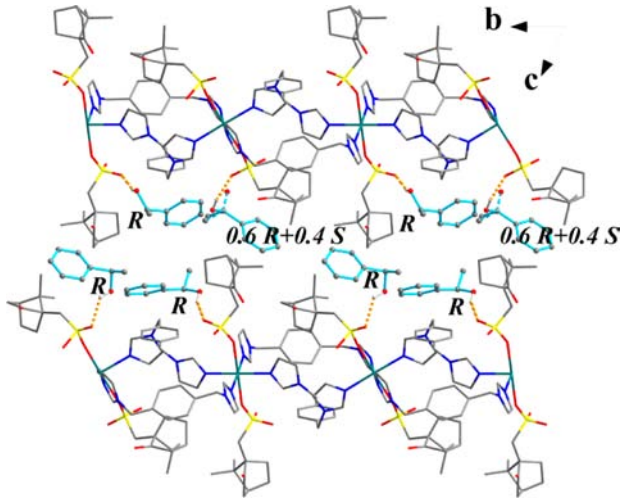

Figure 3. Structure of L-**2** showing hydrogen-bonding interactions between the L-cps$^-$ anions and chiral PEA molecules [3.62(*R*)-PEA + 0.38(*S*)-PEA in one asymmetric unit].

13.50 Å in L-**1** to 16.55 Å in L-**2** (Figure S8 in the SI). Owing to the chiral environment induced by L-cps$^-$ anions, the three ordered L-cps$^-$ anions in L-**2** selectively bond three (*R*)-PEA rather than (*S*)-PEA, while the fourth disordered L-cps$^-$ bonds both (*R*)- and (*S*)-PEA enantiomers (Figure 2), with a ratio of (*R*)-PEA/(*S*)-PEA equal to 0.6:0.4. Also, this ratio is the same as that of the positional occupancy of 0.6:0.4 for the disordered L-cps$^-$ anion. Obviously, it is the disorder of the L-cps$^-$ anion that leads the selectivity of (*R*)-PEA over (*S*)-PEA to decrease from 1:0 to 0.6:0.4. The above results demonstrate that the 2D CCP of L-**1** has the ability for enantioselective separation of racemic PEA molecules within its interlayer, with an *ee* value of 80% and a selectivity of 9:1 for (*R*)-PEA over (*S*)-PEA.

Similarly, the reaction of $Cd(d\text{-cps})_2\cdot(H_2O)_6$ with the bix ligand led to the formation of D-**1**, and dissolving D-**1** in racemic PEA and $CHCl_3$ (1:1) generated D-**2**. The results of X-ray crystal structural analysis demonstrate that the structures of D-**1** and D-**2** (Figure S9 in the SI) are similar to those of L-**1** and L-**2**, respectively. One of the imidazole rings of the bix ligand and one L-cps$^-$ bonded to Cd2 in D-**2** are also disordered, with a close positional occupancy of 0.6:0.4. In contrast to L-**2**, D-**2** shows a selective inclusion of the (*S*)-PEA enantiomer over the (*R*)-PEA enantiomer, with the same *ee* value of 80% and a selectivity of 9:1 for (*S*)-PEA over (*R*)-PEA.

Once L-**2**/D-**2** was immersed in $CHCl_3$, the included PEA guest molecules can be readily released, allowing its potential application for enantioselective separation of racemic PEA. The experiment for enantioselective separation of racemic PEA was performed by suspending the crystalline solid sample of L-**1**/D-**1** in a mixture of racemic PEA and $CHCl_3$ (1:1) at −18 °C for 1 week; the resulting solid was filtered with filter paper and dried in air. The solid was then extracted with $CHCl_3$, and the contents of the (*R*)- and (*S*)-PEA enantiomers were analyzed by chiral high-performance liquid chromatography (HPLC). The *ee* value for (*R*)-PEA over (*S*)-PEA for L-**2** is 28.2%, and the *ee* value for (*S*)-PEA over (*R*)-PEA for D-**2** is 27.3% (see the SI). The lower *ee* value is attributed to the residual of racemic PEA on the surface of the crystalline solid of L-**2**/D-**2**. Similar enantioselective

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separation was also observed for racemic 1-phenylpropan-1-ol (PPA), and L-**1** exhibits an *ee* value of 17.9% for (*R*)-PPA over (*S*)-PPA (see the SI).

In summary, a pair of 2D CCPs of L-**2** and D-**2** were constructed by the self-assembly of a bix ligand with a pair of chiral $Cd(L\text{-cps})_2\cdot(H_2O)_6$ and $Cd(D\text{-cps})_2\cdot(H_2O)_6$, respectively. The results of X-ray structural analysis demonstrate that L-**2** and D-**2** can recognize the (*R*)-PEA and (*S*)-PEA enantiomers, respectively, through the O···H−O hydrogen-bonding interactions between the uncoordinated sulfonate oxygen atom of L-cps$^-$/D-cps$^-$ and the oxygen atom of the (*R*)-PEA/(*S*)-PEA molecule, with an *ee* value of 80% and an enantioselectivity of 9:1. The disorder of L-cps$^-$/D-cps$^-$ in the 2D chiral framework causes the selectivity of (*R*)-PEA/(*S*)-PEA to decrease from 1:0 to 0.6:0.4. From the above results, it can be concluded that it is important to avoid disorder of the chiral groups in the host framework to increase its enantioselecivity toward one enantiomer over the other.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format (CCDC 952244−952248), experimental details, single-crystal data, IR, CD, TGA, PXRD patterns, HPLC graphs, and fragments of structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Li, J.-R.; Sculley, J.; Zhou, H.-C. *Chem. Rev.* **2012**, *112*, 869−932. (b) Yutkin, M. P.; Dybtsev, D. N.; Vdladimir, P. F. *Russ. Chem. Rev.* **2011**, *80*, 1009−1034. (c) Liu, Y.; Xuan, W.; Cui, Y. *Adv. Mater.* **2010**, *22*, 4112−4135. (d) Ma, L.; Abney, C.; Lin, W. *Chem. Soc. Rev.* **2009**, *38*, 1248−1256. (e) Lin, W. *J. Solid State Chem.* **2005**, *178*, 2486−2490. (f) Ye, Q.; Wang, X.-S.; Zhao, H.; Xiong, R.-G. *Chem. Soc. Rev.* **2005**, *34*, 208−225.

(2) (a) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982−986. (b) Dybtsev, D. N.; Nuzhdin, A. L.; Chun, H.; Bryliakov, K. P.; Talsi, E. P.; Fedin, V. P.; Kim, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 916−920. (c) Vaidhyanathan, R.; Bradshaw, D.; Rebilly, J.-N.; Barrio, J. P.; Gould, J. A.; Berry, N. G.; Rosseinsky, M. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 6495−6499. (d) Wu, C.-D.; Hu, A.; Zhang, L.; Lin, W. *J. Am. Chem. Soc.* **2005**, *127*, 8940−8941. (e) Banerjee, M.; Das, S.; Yoon, M.; Choi, H. J.; Hyun, M. H.; Park, S. M.; Seo, G.; Kim, K. *J. Am. Chem. Soc.* **2009**, *131*, 7524−7525. (f) Ou, G.-C.; Wang, Z.-Z.; Yang, L.-Z.; Zhao, C.-Y.; Lu, T.-B. *Dalton Trans.* **2010**, *39*, 4274−4279. (g) Song, F.; Wang, C.; Falkowski, J. M.; Ma, L.; Lin, W. *J. Am. Chem. Soc.* **2010**, *132*, 15390−15398.

(3) (a) Xiong, R.-G.; You, X.-Z.; Abrahams, B. F.; Xue, Z.; Che, C.-M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4422−4425. (b) Yuan, G.; Zhu, C.; Xuan, W.; Cui, Y. *Chem.—Eur. J.* **2009**, *15*, 6428−6434. (c) Xiang, S.-C.; Zhang, Z.; Zhao, C.-G.; Hong, K.; Zhao, X.; Ding, D.-R.; Xie, M.-H.; Wu, C.-D.; Das, M. C.; Gill, R.; Thomas, K. M.; Chen, B. *Nat. Commun.* **2011**, *2*, 204−210. (d) Suh, K.; Yutkin, M. P.; Dybtsev, D. N.; Fedin, V. P.; Kim, K. *Chem. Commun.* **2012**, *48*, 513−515.

(4) (a) Nuzhdin, A. L.; Dybtsev, D. N.; Bryliakov, K. P.; Talsi, E. P.; Fedin, V. P. *J. Am. Chem. Soc.* **2007**, *129*, 12958−12959. (b) Padmanaban, M.; Muller, P.; Lieder, C.; Gedrich, K.; Grunker, R.; Bon, V.; Senkovska, I.; Baumgartner, S.; Opelt, S.; Paasch, S.; Brunner, E.; Glorius, F.; Klemm, E.; Kaskel, S. *Chem. Commun.* **2011**, *47*, 12089−12091. (c) Xie, S.-M.; Zhang, Z.-J.; Wang, Z.-Y.; Yuan, L.-M. *J. Am. Chem. Soc.* **2011**, *133*, 11892−11895. (d) Tanaka, K.; Muraoka, T.; Hirayama, D.; Ohnish, A. *Chem. Commun.* **2012**, *48*, 8577−8579. (e) Wang, W.; Dong, X.; Nan, J.; Jin, W.; Hu, Z.; Chen, Y.; Jiang, J. *Chem. Commun.* **2012**, *48*, 7022−7024. (f) Zhang, M.; Pu, Z.-J.; Chen, X.-L.; Gong, X.-L.; Zhu, A.-X.; Yuan, L.-M. *Chem. Commun.* **2013**, *49*, 5201−5203.

(5) (a) Xuan, W.; Zhang, M.; Liu, Y.; Chen, Z.; Cui, Y. *J. Am. Chem. Soc.* **2012**, *134*, 6904−6907. (b) Liu, T.; Liu, Y.; Xuan, W.; Cui, Y. *Angew. Chem., Int. Ed.* **2010**, *49*, 4121−4124. (c) Li, G.; Yu, W.; Cui, Y. *J. Am. Chem. Soc.* **2008**, *130*, 4582−4583. (d) Kaczorowski, T.; Justyniak, I.; Lipińska, T.; Lipkowski, J.; Lewiński, J. *J. Am. Chem. Soc.* **2009**, *131*, 5393−5395. (e) Yang, H.; Wang, F.; Kang, Y.; Li, T.-H.; Zhang, J. *Chem. Commun.* **2012**, *48*, 9424−9426. (f) Zhang, J.; Liu, R.; Feng, P.; Bu, X. *Angew. Chem., Int. Ed.* **2007**, *46*, 8388−8391. (g) Zhang, J.; Chen, S.; Valle, H.; Wong, M.; Austria, C.; Cruz, M.; Bu, X. *J. Am. Chem. Soc.* **2007**, *129*, 14168−14169. (h) Das, M. C.; Guo, Q.; He, Y.; Kim, J.; Zhao, C.-G.; Hong, K.; Xiang, S.; Zhang, Z.; Thomas, K. M.; Krishna, R.; Chen, B. *J. Am. Chem. Soc.* **2012**, *134*, 8703−8710.

(6) (a) Zhang, L.; Jiang, J. *J. Membr. Sci.* **2011**, *367*, 63−70. (b) Jiang, J.; Babarao, R.; Hu, Z. *Chem. Soc. Rev.* **2011**, *40*, 3599−3612. (c) Dybtsev, D. N.; Yutkin, M. P.; Samsonenko, D. G.; Fedin, V. P.; Nuzhdin, A. L.; Bezrukov, A. A.; Bryliakov, K. P.; Talsi, E. P.; Belosludov, R. V.; Mizuseki, H.; Kawazoe, Y.; Subbotin, O. S.; Belosludov, V. R. *Chem.—Eur. J.* **2010**, *16*, 10348−10356. (d) Bao, X.; Broadbelt, L. J.; Snurr, R. Q. *Phys. Chem. Chem. Phys.* **2010**, *12*, 6466−6473. (e) Bao, X.; Broadbelt, L. J.; Snurr, R. Q. *Mol. Simul.* **2009**, *35*, 50−59. (f) Zhang, H.-X.; Wang, F.; Tan, Y.-X.; Kang, Y.; Zhang, J. *J. Mater. Chem.* **2012**, *22*, 16288−16292.

(7) (a) Chen, L.; Bu, X. *Chem. Mater.* **2006**, *18*, 1857−1860. (b) Liang, X.-Q.; Li, D.-P.; Li, C.-H.; Zhou, X.-H.; Li, Y.-Z.; Zuo, J.-L.; You, X.-Z. *Cryst. Growth Des.* **2010**, *10*, 2596−2605.

(8) (a) Zhang, J.; Bu, X. *Angew. Chem., Int. Ed.* **2007**, *46*, 6115−6118. (b) Zhang, J.; Chen, S.; Zingiryan, A.; Bu, X. *J. Am. Chem. Soc.* **2008**, *130*, 17246−17247.

(9) (a) Guo, P. *Dalton Trans.* **2011**, *40*, 1716−1721. (b) Guo, P.; Wang, L.; Pan, D.; Xu, G. *Solid State Sci.* **2010**, *12*, 2091−2095.

(10) (a) Shaw, S. A.; Aleman, P.; Vedejs, E. *J. Am. Chem. Soc.* **2003**, *125*, 13368−13369. (b) Xu, Q.; Appella, D. H. *J. Org. Chem.* **2006**, *71*, 8655−8657. (c) Luzzio, F. A.; Chen, J. *J. Org. Chem.* **2009**, *74*, 5629−5632. (d) Aggarwal, V. K.; Ford, J. G.; Fonquerna, S.; Adams, H.; Jones, R. V. H.; Fieldhouse, R. *J. Am. Chem. Soc.* **1998**, *120*, 8328−8339. (e) Liu, C.; Zhu, Q.; Huang, K.-W.; Lu, Y. *Org. Lett.* **2011**, *13*, 2638−2641.

(11) (a) Wen, L.; Li, Y.; Lu, Z.; Lin, J.; Duan, C.; Meng, Q. *Cryst. Growth Des.* **2006**, *6*, 530−537. (b) Wang, Q.; Zhang, J.; Zhuang, C.-F.; Tang, Y.; Su, C.-Y. *Inorg. Chem.* **2008**, *48*, 287−295. (c) Jin, S.; Chen, W.; Qiu, H. *Cryst. Growth Des.* **2007**, *7*, 2071−2079.