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Toward Quartz and Cristobalite: Spontaneous Resolution, Structures, and Characterization of Chiral Silica–Mimetic Silver(I)–Organic Materials

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An α-quartz–mimetic chiral coordination network of $[Ag(L^1)(CF_3SO_3)]_n$ (L^1 = 5,5′-bipyrimidine), after treatment with PF_6^- anions, undergoes a solution-state structural transformation toward $[Ag(L^1)(PF_6)]_n$ with a cristobalite–mimetic chiral structures. This structural transformation is accompanied by substantial enhancement in the fluorescent intensity and in the second-harmonic-generation response. The results also demonstrate an effective design strategy based on the spontaneous resolution route for the preparation of chiral architectures.

Metal–organic framework (MOF) materials truly represent a remarkable advance in materials science,[1] owing to a wide array of applications, including gas storage, separation, catalysis, sensing, nonlinear optics, and drug delivery.[2] Thanks to efficient design strategies, preprogrammed frameworks can be prepared through the assembly of judiciously selected molecular building blocks.[3] Although it is still difficult to prepare MOFs with predictable architectures, one of the most appealing routes to fulfilling the targets is to mimic mineral structures, such as quartz, NbO, pyrite, rutile, sodalite, halite, fluorite, and CsCl.[4,5] Silica (SiO_2), with its several polymorphs, is one of the most impressive minerals from the earth's crust. Quartz, the most stable form of the silica group, possesses electrooptics, piezoelectricity, and luminescence properties. Cristobalite is a metastable polymorph of quartz. In nature, without any enantiopure chiral auxiliary, the quartz group can yield a conglomerate by spontaneous resolution.[4,6] Because of the chirality and noncentrosymmetry, the mimicking of physical properties of the quartz group, such as second-harmonic generation (SHG) and piezoelectricity, remains possible.[2f] Compared with other mineral-like structures, however, the development of silica–mimetic MOF materials, especially quartz, is still limited.[3j,4]

As part of our ongoing efforts in the design and synthesis of functional crystalline materials,[3l,5g] herein are reported two chiral MOFs, $[Ag(L^1)(OTf)]_n$ (**1**; L^1 = 5,5′-bipyrimidine, OTf = CF_3SO_3) and $[Ag(L^1)(PF_6)]_n$ (**2**). Compound **1** has an α-quartz–mimetic structure, and **2** is similar to a cristobalite

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(1) (a) Ward, M. D. *Science* **2003**, *300*, 1104. (b) Hupp, J. T.; Poeppelmeier, K. R. *Science* **2005**, *309*, 2008. (c) Zaworotko, M. J. *Nature* **1999**, *402*, 242.

(2) (a) Rowsell, J. L. C.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4670. (b) Pan, L.; Parker, B.; Huang, X.; Olson, D. H.; Lee, J. Y.; Li, J. *J. Am. Chem. Soc.* **2006**, *128*, 4180. (c) Heitbaum, M.; Glorius, F.; Escher, I. *Angew. Chem., Int. Ed.* **2006**, *45*, 4732. (d) Wong, K. L.; Law, G. L.; Yang, Y. Y.; Wong, W. T. *Adv. Mater.* **2006**, *18*, 1051. (e) Halder, G. J.; Kepert, C. J.; Moubaraki, B.; Murray, K. S.; Cashion, J. D. *Science* **2002**, *298*, 1762. (f) Evans, O. R.; Lin, W. *Acc. Chem. Res.* **2002**, *35*, 511. (g) Horcajada, P.; Serre, C.; Vallet-Regí, M.; Sebban, M.; Taulelle, F.; Férey, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 5974.

(3) (a) Ruben, M.; Rojo, J.; Romero-Salguero, F. J.; Uppadine, L. H.; Lehn, J. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 3644. (b) Bradshaw, D.; Claridge, J. B.; Cussen, E. J.; Prior. T. J.; Rosseinsky, M. J. *Acc. Chem. Res.* **2005**, *38*, 273. (c) Janiak, C. *Dalton Trans.* **2003**, 2781. (d) Rao, C. N. R.; Natarajan, S.; Vaidhyanathan, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1466. (e) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705. (f) Kesanli, B.; Lin, W. *Coord. Chem. Rev.* **2003**, *246*, 305. (g) Steel, P. J. *Acc. Chem. Res.* **2005**, *38*, 243. (h) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (i) Hosseini, M. W. *Chem. Commun.* **2005**, 5825. (j) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460. (k) Chen, X. M.; Tong, M. L. *Acc. Chem. Res.* **2007**, *40*, 162. (l) Luo, T. T.; Hsu, L. Y.; Su, C. C.; Ueng, C. H.; Tsai, T. C.; Lu, K. L. *Inorg. Chem.* **2007**, *46*, 1532.

(4) (a) Sun, J.; Weng, L.; Zhou, Y.; Chen, J.; Chen, Z.; Liu, Z.; Zhao, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 4471. (b) Chen, Z. F.; Zhang, S. F.; Luo, H. S.; Abrahams, B. F.; Liang, H. *CrystEngComm* **2007**, *9*, 27. (c) Tynan, E.; Jensen, P.; Kelly, N. R.; Kruger, P. E.; Lees, A. C.; Moubaraki, B.; Murray, K. S. *Dalton Trans.* **2004**, 3440.

(5) (a) Chen, B.; Ockwig, N. W.; Fronczek, F. R.; Contreras, D. S.; Yaghi, O. M. *Inorg. Chem.* **2005**, *44*, 181. (b) Chae, H. K.; Kim, J.; Friedrichs, O. D.; O'Keeffe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 3907. (c) Qin, C.; Wang, X. L.; Wang, E. B.; Su, Z. M. *Inorg. Chem.* **2005**, *44*, 7122. (d) Dincă, M.; Han, W. S.; Liu, Y.; Dailly, A.; Brown, C. M.; Long, J. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 1419. (e) Long, D. L.; Hill, R. J.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Wilson, C.; Schröder, M. *Chem.–Eur. J.* **2005**, *11*, 1384. (f) Chun, H.; Kim, D.; Dybtsev, D. N.; Kim, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 971. (g) Luo, T. T.; Tsai, H. L.; Yang, S. L.; Liu, Y. H.; Yadav, R. D.; Su, C. C.; Ueng, C. H.; Lin, L. G.; Lu, K. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 6063.

(6) Pérez-García, L.; Amabilino, D. B. *Chem. Soc. Rev.* **2002**, *31*, 342.

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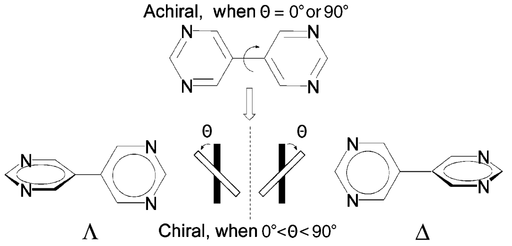
Chart 1. Flexible 5,5′-Bipyrimidine and Its Conformational Chirality



structure. 5,5′-Bipyrimidine, in spite of its simplicity, is a very versatile molecule and is suitable as a bridge ligand. As shown in Chart 1, two chiral conformations (Λ and Δ configurations) appear as a result of the free rotation and coordination of the pyrimidine rings. The strategy of this study was to focus on transmitting the chiral information in three dimensions, thereby allowing spontaneous resolution to be induced.[6,7] As early as in 1848, Louis Pasteur found spontaneous resolution, yet it remains to be unpredictable. However, it is still an effective method for using achiral molecular units to generate enantiopure crystalline materials.[7] Although pyrimidine and its simple derivatives have been applied in MOF systems, since their inception, usage of the L^1 ligand has not yet been fully explored.[8] Surprisingly, the results of the present study reveal that the bipyrimidine L^1 ligand has a strong tendency to yield 3D chiral-resolved structures.[9]

Compound **1** was prepared in high yield (92%) by a single-step self-assembly process from AgOTf and L^1 in a water/ethanol diffusion system at ambient temperature. A single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the chiral trigonal space group $P3_121$, the same as α-quartz, and forms a 3D non-interpenetrating cationic network, which is filled with OTf^- anions (Figure 1a).[9] Each Ag^I center is bound to four pyrimidine N atoms and adopts a distorted tetrahedral AgN_4 coordination geometry (Figure S1a in the Supporting Information). Each pyrimidine ring of the L^1 ligand serves as a two-connected node that links to two Ag atoms. In comparison to the α-quartz structure, the Ag^I center adopts the same crystallographic site as the Si atom, while the augmented pyrimidine ring can take the place of the O atom (Figure 2a). The overall network is almost equivalent to the α-quartz structure if the σ bond between the two pyrimidine rings of the L^1 ligand is ignored.[5b] As expected, the unit cell volume of **1** is about 8 times that of the α-quartz mineral. The Flack parameter is nearly zero, indicating that each individual crystal of **1** consists of a single enantiomer.[9] Just like the α-quartz, **1** has individually left- and right-handed crystals.[10]

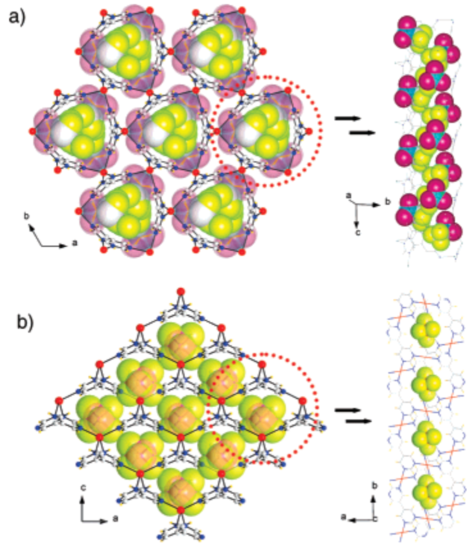


Figure 1. (a) Packing diagrams of **1** showing the α-quartz−mimetic network incorporating disordered OTf^- anions and the single-stranded OTf^- helix in the helical channel (only one site of the disordered OTf^- anions is shown). (b) Packing diagrams of **2** showing the cristobalite−mimetic network and the PF_6^- anions stacking inside the 1D channels (Ag = red, N = blue, C = gray, F = yellow-green, P = deep red, O = violet, S = cyan, H = orange).

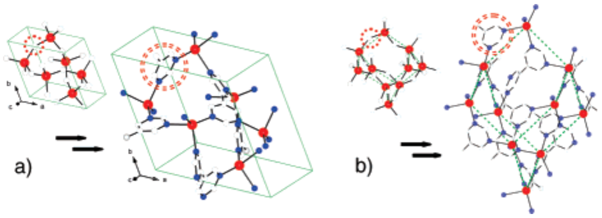


Figure 2. (a) Unit cell contents of the α-quartz (left) and **1** (right). (b) Adamantane units of the cristobalite (left) and **2** (right) showing their expanded structural relationships.

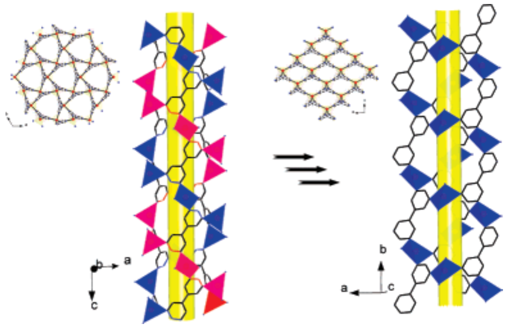


Figure 3. Schematic representation of the structural transformation from **1** (left) to **2** (right).

Analysis of the quartz structure is very interesting and helps explain many of its physical attributes.[4,10] The basic structure of **1** consists of pseudo-6_1 spiral chains of Ag tetrahedrons around the 3-fold screw axes (Figure 3). These helical chains with only the *M* configuration are double-stranded and run along the *c* axis to give 1D helical channels.

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(7) (a) Gao, E. Q.; Yue, Y. F.; Bai, S. Q.; He, Z.; Yan, C. H. *J. Am. Chem. Soc.* **2004**, *126*, 1419. (b) Sun, D.; Collins, D. J.; Ke, Y.; Zuo, J. L.; Zhou, H. C. *Chem.*—*Eur. J.* **2006**, *12*, 3768. (c) Sun, Q.; Bai, Y.; He, G.; Duan, C.; Lin, Z.; Meng, Q. *Chem. Commun.* **2006**, 2777.

(8) (a) Keller, S. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 247. (b) Navarro, J. A. R.; Barea, E.; Galindo, M. A.; Salas, J. M.; Romero, M. A.; Quirós, M.; Masciocchi, N.; Galli, S.; Sironi, A.; Lippert, B. *J. Solid State Chem.* **2005**, *178*, 2436.

(9) Crystal data for **1**: $C_9H_6N_4O_3F_3SAg$, $M_r = 415.11$, trigonal, $P3_121$, $a = 10.8161(1)$ Å, $c = 9.7482(1)$ Å, $V = 987.64(2)$ Å^3, $Z = 3$, $\rho_{calcd} = 2.094$ g cm^{-3}, R1 = 0.0399, wR2 = 0.0989, GOF = 1.05, Flack parameter = 0.03(6). The other mirrorlike structure of **1** had also been determined in the space group $P3_221$ with a randomly selected crystal. Crystal data for **2**: $C_8H_6N_4PF_6Ag$, $M_r = 411.01$, orthorhombic, $Fdd2$, $a = 17.236(2)$ Å, $b = 9.1835(9)$ Å, $c = 15.478(2)$ Å, $V = 2450.0(4)$ Å^3, $Z = 8$, $\rho_{calcd} = 2.229$ g cm^{-3}, R1 = 0.0240, wR2 = 0.0611, GOF = 1.119, Flack parameter = −0.04(4).

(10) Jung, J. H.; Ono, Y.; Shinkai, S. *Chem.*—*Eur. J.* **2000**, *6*, 4552.

The Ag−Ag translation is 19.50 Å per turn of the helix. The pseudohexagonal chiral channel has dimensions of 10.82 × 10.82 Å (based on diagonal Ag···Ag distances). The OTf^- anions are closely stacked inside the channels to give a *P*-configured single-stranded helix around a 3-fold screw axis (Figure 1a). The structure of a helix inside a helix is very interesting.[11] Because of the same type of charge, to our knowledge, a helical arrangement of closely packed anions inside a helical channel is rare.

Compound **2** was prepared under similar conditions, with the exception of using $AgPF_6$. It crystallizes in the chiral orthorhombic space group *Fdd*2 and is also a 3D non-interpenetrating cationic framework, which is filled with PF_6^- anions (Figure 1b).[9] The four-connected AgN_4 distorted tetrahedral node and the two-connected pyrimidine bridge are similar to those in **1** (Figure S1b in the Supporting Information). Further structural analysis reveals that **2** has a cristobalite−mimetic structure if the σ bond between two pyrimidine rings of the L^1 ligand is disregarded. As shown in Figure 2b, an expanded adamantane-like arrangement of the Ag atom is apparent. Unlike **1**, the basic structure of **2** consists of only single-stranded helices with *M* configuration of Ag tetrahedron spiral chains around a pseudo-4_1 screw axis, which runs along the *b* axis to give 1D chiral channels (Figure 3). The Ag−Ag translation is 9.18 Å per turn of the helix. The rhombic chiral channel has dimensions of 9.00 × 9.76 Å (based on diagonal Ag···Ag distances). The PF_6^- anions are incorporated inside the helical pores separately and aligned linearly (Figure 1b). The Flack parameter is nearly zero, indicating that **2** also contains distinct enantiopure single crystals.[9]

The structural transformation between natural quartz and cristobalite is reconstructive, requiring the breaking up and reforming of the frameworks.[12] In compounds **1** and **2**, the interactions between the Ag^I centers and the N-donor pyrimidine ligands are not strong. As a consequence, the structural transformation of **1** and **2** may occur, even if **1** and **2** possess 3D chiral frameworks.[13,14] After treatment with PF_6^- anion in aqueous solution at room temperature, **1** slowly transforms into **2**, as indicated by powder X-ray diffraction (PXRD), Fourier transform infrared (FTIR), and elemental analyses (see the Supporting Information). However, no significant reverse transformation happens, as revealed by PXRD analysis. The transformation of one network into the other is very interesting and probably has to do with the anion playing a templating effect,[15] while the structure transforms in solution through recrystallization.[14]

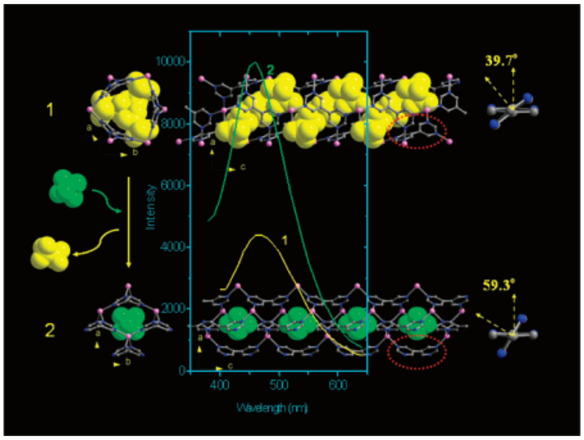

Figure 4. Anion-triggered structural transformation from **1** to **2** which produces a large enhancement of photoluminescence in the solid state.

Thermogravimetric analyses (TGA) of **1** and **2** show that no small molecules are eliminated from the networks when the temperature is increased from room temperature to about 300 °C, after which decomposition of the frameworks occurs. At room temperature, both **1** and **2** showed strong blue photoluminescence with emission maxima at 471 and 460 nm, respectively, upon excitation at 340 nm in the solid state. A large fluorescent intensity was observed in **2**. This phenomenon might be attributed to the ligand twisting tuned by the exchange of anion guests. As shown in Figure 4, the dihedral angle of the pyrimidine rings of L^1 had changed from 39.7° (in **1)** to 59.3° (in **2**) owing to the hingelike σ linkage between two pyrimidine rings of the L^1 ligand.[16] In addition, the metal−anion interactions [Ag1···F2 = 3.574(3) Å] also play a role in the emission enhancement of **2** in the solid state.[13e] Because both **1** and **2** crystallize in a noncentrosymmetric space group, their SHG responses are expected and were measured. Experimental results indicate that **2** has a better SHG response than **1**.

In conclusion, we have prepared two chiral MOFs that can mimic natural silica minerals. Compound **1** with its quartz−mimetic structure can undergo a reconstructive structural transformation upon anionic guest exchange toward **2** with the cristobalite−mimetic structure, and this chiral-net-to-chiral-net transformation is accompanied by substantial enhancement in the fluorescent intensity and in the SHG response. Because of the unique physical properties of the silica group materials, the expanded silica analogous MOFs represent a new family of chiral crystalline materials having great potential for practical application.

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Supporting Information Available: Crystallographic details in CIF format for **1** and **2**, experimental section, additional pictures, related crystal lattice data, and TGA, PXRD, IR, and SHG data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Sreenivasulu, B.; Vittal, J. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5769.

(12) Martoňák, R.; Donadio, D.; Oganov, A. R.; Parrinello, M. *Nat. Mater.* **2006**, *5*, 623.

(13) (a) Min, K. S.; Suh, M. P. *J. Am. Chem. Soc.* **2000**, *122*, 6834. (b) Oxtoby, N. S.; Blake, A. J.; Champness, N. R.; Wilson, C. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4905. (c) Dong, Y. B.; Xu, H. X.; Ma, J. P.; Huang, R. Q. *Inorg. Chem.* **2006**, *45*, 3325. (d) Diaz, P.; Benet-Buchholz, J.; Vilar, R.; White, A. J. P. *Inorg. Chem.* **2006**, *45*, 1617. (e) Chi, Y. N.; Huang, K. L.; Cui, F. Y.; Xu, Y. Q.; Hu, C. W. *Inorg. Chem.* **2006**, *45*, 10605.

(14) Khlobystov, A. N.; Champness, N. R.; Roberts, C. J.; Tendler, S. J. B.; Thompson, C.; Schröder, M. *CrystEngComm* **2002**, *4*, 426.

(15) Tynan, E.; Jensen, P.; Kruger, P. E.; Lees, A. C. *Chem. Commun.* **2004**, 776.

(16) Zhang, J. P.; Horike, S.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 889.