

Controlled generation of heterochiral or homochiral coordination polymer: helical conformational polymorphs and argentophilicity-induced spontaneous resolution†

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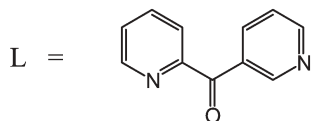
Received (in Cambridge, UK) 25th May 2005, Accepted 14th July 2005

First published as an Advance Article on the web 9th August 2005

DOI: 10.1039/b507363d

In the pair of helical conformational polymorphs of the coordination polymer $\{[\text{AgL}](\text{CF}_3\text{SO}_3)\}_\infty$ ($\text{L} = 2\text{-pyridinyl-3-pyridinylmethanone}$), the 2_1 helices of opposite chirality in one supramolecular isomer are stacked alternately to form a racemate, while the 4_1 helices in the other are assembled homochirally by inter-chain argentophilic interaction to generate a conglomerate.

Both chirality¹ and polymorphism² are central issues in the domains of chemistry, life sciences, and materials research. The design of chiral coordination polymers, especially by the use of achiral components without any chiral auxiliary, has been spurred by potential applications in connection with their promising catalytical, nonlinear optical and magnetic properties.^{3,4} However, there are only a few examples of spontaneous resolution in which the chiral information in enantiomeric forms of the building blocks can be transmitted into higher dimensionality to generate chiral coordination polymers.³⁻⁵ Conformational polymorphism, the occurrence of distinct conformers in different polymorphic structural modifications, is a widely observed phenomenon in molecular crystals² and biological polymers,⁶ but this rarely occurs in coordination compounds.⁷ To date, the decisive physical principles governing either spontaneous resolution or conformational polymorphism remain poorly understood.



Functioning as a flexible bridging ligand, 2-pyridinyl-3-pyridinylmethanone (L) readily forms single helical chains with various metal cations, such as Ag^+ , Cu^{2+} , Co^{2+} and Zn^{2+} .⁸ To facilitate the occurrence of conformational polymorphism, we devoted our effort to the solvent-controlled reaction,⁹ aiming to exploit the subtle tuning effect of the solvent on the bridging mode and conformation of ligand L in the generation of silver(I) coordination polymers. To our pleasant surprise, variation of the reaction and crystallization medium not only led to an

occurrence of spontaneous chiral resolution, but also afforded the first pair of helical metal-organic conformational polymorphs. Here we report two coordination polymers of the same structural formula, in which the 2_1 helical chains in one [Fig. 1(a) and (b)] are stacked in a heterochiral manner to form a racemate, whereas the 4_1 helical chains in the other [Fig. 1(c) and (d)] are assembled into a homochiral crystal.

The reaction of L with AgCF_3SO_3 in an organic solvent (methanol, ethanol, acetone or THF) gave a pale-white powder of $\{[\text{AgL}](\text{CF}_3\text{SO}_3)\}_\infty$ (**1**, m.p. 254.3–254.5 °C) in 60–70% yield, which was re-crystallized in space group $P2_1/c$.¹⁰ X-Ray analysis revealed that the infinite 2_1 *P*- and *M*-helical $[\text{AgL}^+]_\infty$ chains are assembled alternately into a heterochiral layer, and such layers are further stacked to form a racemic crystal [Fig. 2(a)]. Reaction of L with AgCF_3SO_3 in water afforded conglomerate $\{[\text{AgL}](\text{CF}_3\text{SO}_3)\}_\infty$ (**2**, m.p. 253.0–253.2 °C) in 69% yield,¹¹ which is a supramolecular isomer of **1**. The crystal structure of **2** comprises infinite 4_1 helical $[\text{AgL}^+]_\infty$ chains, and spontaneous resolution induced by argentophilic interaction¹² occurs to assemble the helical chains in a homochiral fashion [Fig. 2(b)]. Single-crystal X-ray analyses† of both enantiomers of **2** revealed that *P*-helical chains are packed in space group $P4_12_12$ (**2a**) while *M*-helical chains assemble in space group $P4_32_12$ (**2b**).¹³ Though crystals in two apparently differentiable habits¹⁴ are obtained for **2**, they belong randomly to either enantiomorphic space group according to X-ray structure analyses of three pieces of single crystals for each habit. The structures of **1** and **2** in the bulk were further confirmed by the perfect match of their powder X-ray diffraction spectra with simulated patterns. Our persistent attempt to carry out interconversion of **1** and **2** showed that it could only be partially achieved (see Supplementary Information for

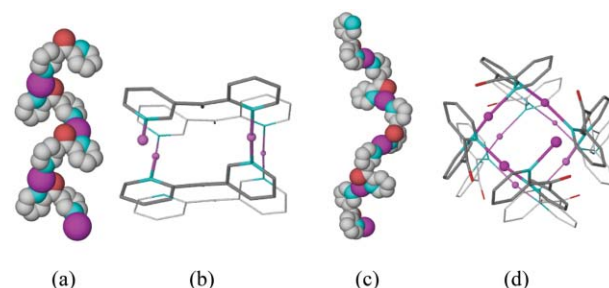


Fig. 1 Infinite 2_1 $[\text{AgL}^+]_\infty$ chain in **1**: (a) lateral view of space-filling model; (b) view along the 2_1 helical axis. Infinite 4_1 $[\text{AgL}^+]_\infty$ chain in **2**: (c) lateral view of space-filling model; (d) view along the 4_1 helical axis. Color code: C: light gray, N: turquoise, O: red, Ag: purple.

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† Electronic supplementary information (ESI) available: experimental and further structural description. See <http://dx.doi.org/10.1039/b507363d>

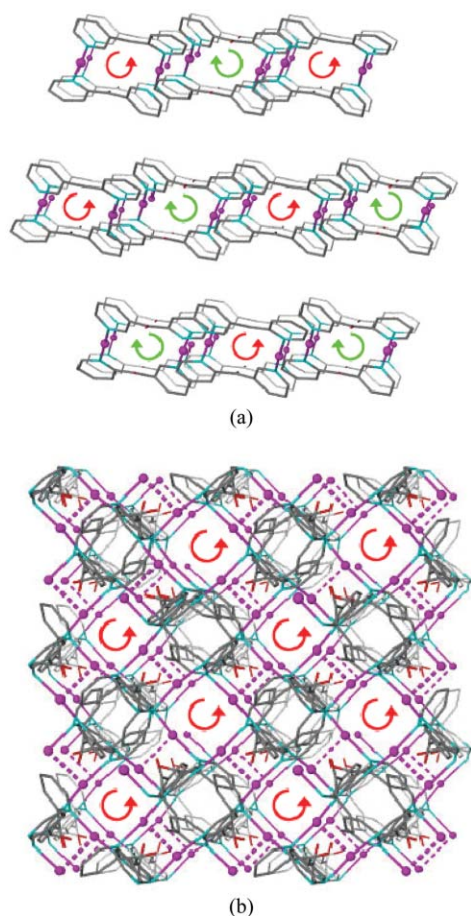


Fig. 2 (a) Heterochiral assembly of the 2_1 helical chains in **1**. (b) Homochiral assembly of the 4_1 helical chains in **2**. Triflate anions and hydrogen atoms are omitted for clarity. Color code: C: light and deep gray, N: turquoise, O: red, Ag: purple. Red and green curved arrows indicate *P*- and *M*-helicities, respectively. Argentophilic interactions are represented by broken lines.

experimental details[†]). The IR (KBr) spectra, as well as ^1H NMR and ^{13}C NMR spectra in DMSO-d_6 show minor differences between **1** and **2**.

To the best of our knowledge, **1** and **2** together constitute the first example of conformational polymorphism observed for helical coordination polymers. Ligand L takes the *anti*-configuration, bridging the silver(I) atoms to form an infinite chain, which winds around a 2_1 axis in **1** and a 4_1 axis in **2**. The dihedral angle between the pyridyl rings in an individual L molecule is 65.8° for **1** and 69.6° for **2**. The Ag–N bond distances are 2.176(4)/2.163(4) Å for **1** and 2.183(6)/2.162(6) Å for **2**, and the corresponding N–Ag–N angles are $176.4(2)^\circ$ and $158.0(2)^\circ$. In accordance with the normally small free energy difference between polymorphs (1–2 kcal mol $^{-1}$),^{2d} the thermal stabilities of **1** and **2** are similar according to TGA analysis, implying that bending of the N–Ag–N angle in **2** is compensated by contribution from weak interactions. Different orientations of bridging ligand L lead to the generation of the pair of helical conformational polymorphs. The angle between the helical axis and the intramolecular vector joining the N atoms (which approximately represents the longest dimension of L) is 117.1° for **1** and 6.2° for **2**; accordingly, L can be considered

as winding latitudinally round the 2_1 axis and longitudinally round the 4_1 axis. X-Ray photoelectron spectroscopy showed that the two supramolecular isomers have a similar metal–organic coordination environment around the silver atom. Similar fluorescence spectra observed for **1**, **2** and ligand L both in CH_3CN solution and in the solid state from room temperature to 77 K indicate that they originate exclusively from intra-ligand transitions (Fig. 3).

To generate a chiral coordination polymer from an achiral ligand without any chiral auxiliary, two key factors come into consideration: (i) generation of chiral units from achiral components; (ii) assembly of the chiral units homochirally into three-dimensional chiral aggregates.⁵ The bottleneck of this strategy hinges on how to extend the chirality of the building units by chirally discriminative interactions to realize homochiral assembly. Application of an unsymmetric bidentate bridging ligand has already proven to be efficient for the generation of helical chains,^{5a–5d,8,15} which however normally assemble into a racemic crystal due to the lack of chirality-inducing interactions. Such is the case with the use of L in **1**. On the other hand, spontaneous resolution yielding homochiral crystals occurs in **2** through inter-chain argentophilic interactions that assemble the *P*- and *M*-helices separately. The silver atoms in a 4_1 helix are more exposed as compared to the case of a 2_1 helix, leading to favored manifestation of argentophilicity that provides the impetus for spontaneous chiral resolution of **2**. The argentophilic Ag \cdots Ag distance is 2.998 Å in **2**, in contrast to the shortest interchain Ag \cdots Ag separation of 4.646 Å in **1**.

Another notable structural feature of **2** is that it comprises intercrossed chiral channels along all three axial directions, which accommodate the trifluoromethanesulfonate anions (Fig. 4). Our unsuccessful attempt to prepare an analogous 4_1 helical polymer by the reaction of L with AgCF_3CO_2 , in contrast to the ready formation of the 2_1 helical polymer $\{[\text{AgL}](\text{CF}_3\text{CO}_2)\}_\infty$ (**3**),¹⁶ suggests that the triflate anion plays a crucial role in templating the homochiral assembly of 4_1 helical chains in **2**.

In summary, conformational polymorphism in a helical coordination polymeric system has been observed for the first time. Argentophilicity accounts for the homochiral assembly of 4_1 helical chains that leads to spontaneous resolution of **2**, demonstrating that helical chirality in a metal–organic fragment

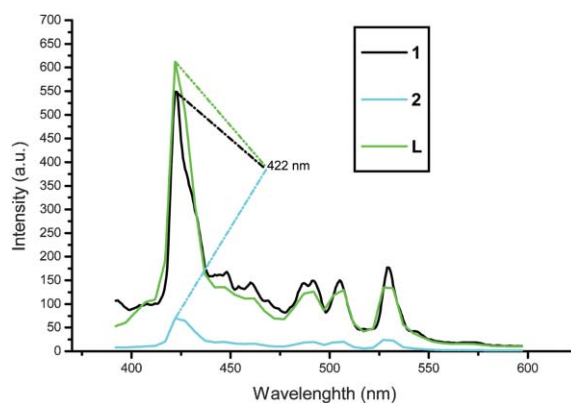


Fig. 3 The luminescent properties of the ligand (L) and compounds **1** and **2** in solid state.

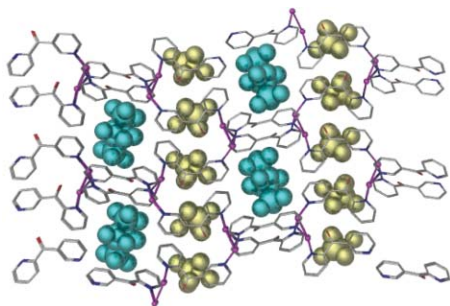


Fig. 4 Channels in different directions that accommodate the trifluoromethanesulfonate anions in **2**. The balls in turquoise represent anions located in channels along [100], the balls in yellow represent anions located in channels along [010], and the small balls in purple represent silver atoms. Color code: C: light gray, N: blue, O: red.

can be extended to higher dimensionality by metallophilic interaction.†

This work is dedicated to the memory of Prof. J. Monteath Robertson. Financial support from the Hong Kong Research Grants Council Earmarked Grant (CUHK 402003) is gratefully acknowledged.

Notes and references

† CCDC 271230–271232 for **1**, **2a** and **2b**. See <http://dx.doi.org/10.1039/b507363d> for crystallographic data in CIF or other electronic format.

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- To be published. See Supplementary Information for unit cell parameters.
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- Single crystals of **1** were obtained by diffusion of diethyl ether into the methanol solution obtained from the reaction of L with AgCF₃SO₃. Structure of the powder was confirmed by powder X-ray diffraction. See Supplementary Information for further details. Crystal data for **1**: C₁₂H₈F₃N₂O₄SAg, 293 K, *M* = 441.13, monoclinic, *P*₂₁/*c*, *a* = 9.5431(6), *b* = 12.4438(8), *c* = 13.3198(9) Å, β = 105.165(1)°, *V* = 1526.7(2) Å³, *Z* = 4, 3927 unique MoKα reflections (*R*_{int} = 0.0338), *R*₁ = 0.0536, *wR*₂ = 0.1669 for 2687 observed reflections [*I* > 2σ(*I*)].
- Single crystals of **2** were obtained by slow cooling of a hot aqueous solution. Its identity was confirmed by powder X-ray diffraction.
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- Crystal data for **2a**: C₁₂H₈F₃N₂O₄SAg, 293 K, *M* = 441.13, tetragonal, *P*₄₁2, *a* = 10.2355(4), *c* = 28.105(2) Å, *V* = 2944.4(3) Å³, *Z* = 8, 2596 unique MoKα reflections (*R*_{int} = 0.0193), *R*₁ = 0.0229, *wR*₂ = 0.0582 for 2490 observed reflections [*I* > 2σ(*I*)], Flack parameter 0.00(3); refinement in space group *P*₄₃2₁2 gave *R*₁ = 0.0277 and Flack parameter 1.01(4). Crystal data for **2b**: C₁₂H₈F₃N₂O₄SAg, 293 K, *M* = 441.13, tetragonal, *P*₄₃2₁2, *a* = 10.2364(4), *c* = 28.109(2) Å, *V* = 2945.4(3) Å³, *Z* = 8, 2596 unique MoKα reflections (*R*_{int} = 0.0194), *R*₁ = 0.0227, *wR*₂ = 0.0576 for 2486 observed reflections [*I* > 2σ(*I*)], Flack parameter 0.00(3); refinement in space group *P*₄₂2₁2 gave *R*₁ = 0.0277 and Flack parameter 1.02(4). See Supplementary Information for details.
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- Reactions of L with AgCF₃CO₂ in water, methanol, or acetonitrile at both room temperature and 60 °C afforded crystals of **3** in 23–49% yield: C₁₃H₈F₃N₂O₃Ag, 293 K, *M* = 405.08, monoclinic, *P*₂₁/*c*, *a* = 7.7407(5), *b* = 13.6362(8), *c* = 13.5921(9) Å, β = 109.424(1)°, *V* = 1353.0(2) Å³, *Z* = 4, 2388 unique MoKα reflections (*R*_{int} = 0.0284), *R*₁ = 0.0350, *wR*₂ = 0.0934 for 1974 observed reflections [*I* > 2σ(*I*)].