

A structurally versatile coordination polymer: demonstrating spontaneous resolution, conformational polymorphism and gel formation†

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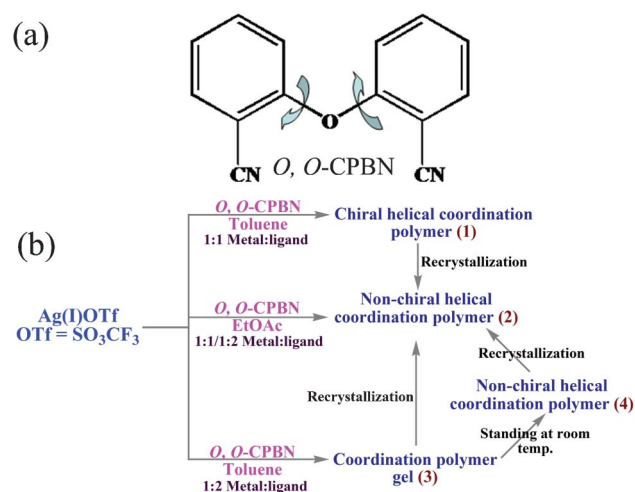
Savarimuthu Philip Anthony,^{ab} Longsheng Wang,^{ac} Sunil Varughese^a and Sylvia M. Draper^{*a}

Conformationally flexible C_2 -symmetric 2-(2'-cyanophenoxy) benzonitrile (O,O -CPBN) was self-assembled using silver ions into spontaneously resolved, helical and coordination polymer gel structures including unprecedented four different ligand conformation in a single polymer network structure.

Developing an understanding of molecular self-assembly is important to systematically unravelling the complexity of living organisms, biominerals, and functional molecular materials.¹ Hence the driving forces of self-assembly processes have been intensively explored for the past few decades. Self-assembly arising from the metal coordination of simple organic molecules has become a significant area of research in crystal engineering. It has resulted in a range of fascinating architectures including polymorphism,^{1–3} that have found application in catalysis,⁴ porous zeolite mimics,⁵ and chemical biology.⁶ Helical chiral structures lie at the heart of the genetic code⁷ and are ubiquitous in nature. They are interesting targets for metal-directed coordination self-assembly and find use in optical devices, sensors and asymmetric catalysis.⁸ Exploiting the plethora of metal-ion coordination geometries and rational ligand design, chemists have successfully introduced helicity into artificial systems based on coordination polymers.⁹ Coordination polymers that undergo changes in conformation on external stimuli are of particular interest. These have the potential to mimic biological polymers that exhibit conformational polymorphism with consequent changes in both physiochemical property and function.^{10–12} Conformationally flexible ligands are expected to exhibit polymorphism as well as supramolecular isomerism that would lead to coordination polymers with diverse topologies in the solid state.^{2,13} These are

influenced directly by subtle factors such as the type and presence of counterions,^{14,15} the metal-to-ligand ratio,¹⁶ and exposure to different solvents either during or post-synthesis.¹⁷ The flexible ligands in coordination polymers can exhibit multiple conformational modes but it is rare to find more than one conformation in any given polymer network.¹⁸ One recent example is that of a single helical polymorphic network structure in which the ligand displayed three different conformations.¹⁴

C_2 -symmetric bidendate ligands have been used extensively to generate metal ion-dependent 1-, 2- and 3-dimensional helical supramolecular structures.⁹ Here we investigate the self-assembly habits of a C_2 -symmetric and conformationally flexible (bis-cyanophenoxy)benzonitrile (O,O -CPBN) with Ag(I). The free rotation about each O–C bond and the consequent changes in CN directionality in O,O -CPBN (Scheme 1a) was expected to give rise to a degree of conformational diversity in the coordination polymers formed. The metal : ligand ratio, the reaction temperature and the solvent of crystallisation all contributed to the range of extended solid-state structures produced. The combination of O,O -CPBN



Scheme 1 (a) Molecular structure of O,O -CPBN and (b) schematic representation of the preparative routes to coordination polymers **1–4**.

^aSchool of Chemistry, Trinity College Dublin, Dublin 2, Ireland.

E-mail: smdraper@tcd.ie; Fax: +35316712826

^bSchool of Chemical & Biotechnology, SASTRA University, Tamil Nadu 613401, India

^cSchool of Chemical and Chemical Eng., Hubei Univ. of Technology, Wuhan City 430068, People's Republic of China

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and Ag(I) produced spontaneously resolved chiral helical, 1-D helical network structures and a supramolecular coordination polymer gel. Importantly *O,O*-CPBN displayed distinctly different molecular conformations in each structure and also showed four different conformations in one single, unprecedented polymeric network structure.

Single crystals of *O,O*-CPBN were grown from methanol and their structural analysis revealed a monoclinic $P2(1)/C$ space group (SI 3 and 4, ESI†). Mixing *O,O*-CPBN and silver trifluoromethanesulfonate (Ag(I)OTf) produced four different coordination polymeric structures including a coordination polymer gel (**1–4**, Scheme 1b) depending on the metal : ligand ratio and the reaction/crystallising conditions.

Mixing equimolar, toluene solutions of Ag(I)OTf and *O,O*-CPBN produced needle-shaped crystals of **1** after standing at room temperature for 12 h. Single crystal analysis revealed that these had grown in a chiral space group ($C222(1)$, SI 3, ESI†) giving rise to a chiral, 2_1 helical supramolecular structure (Fig. 1a). The helices are generated by distorted tetrahedrally coordinated Ag(I) centres (SI 5b, ESI†) which are bound by two cyano nitrogen atoms from different ligands along the *c*-axis and two disordered oxygen atoms from two OTf anions along the *a*-axis (SI 5c, ESI†). The helices all have the same handedness suggesting spontaneous resolution in the crystals. The formation of single, pure enantiomeric crystals in the whole batch was confirmed by measuring the solid state circular dichroism (CD) of the bulk sample (Fig. 1c). The reason for the spontaneous self-sorting into a single enantiomer in **1** is not known, however, the intermolecular H-bond interactions formed between the cyanophenyl hydrogens and the oxygen atoms of the OTf in the crystal lattice stabilises the twisted phenyl conformation and could be a contributory factor in the driving force for spontaneous resolution (SI 5c, ESI†). Non-covalent interactions are known to mediate the supramolecular formation of chirality in the self-assembly of achiral molecules.¹⁹ Either positive (P) or negative (M) cotton effects were observed for crystals of **1** obtained from different crystallization batches suggesting that either P or M enantiopure crystals form in each crystallization batch. Synthetic control over which enantiopure crystals (*i.e.* P or M) were formed could not be established. Achiral molecules crystallizing in chiral space groups with enantiopure helical supramolecular crystals as here, are a rare phenomenon.²⁰ Achiral molecules that spontaneously self-sort into a chiral space

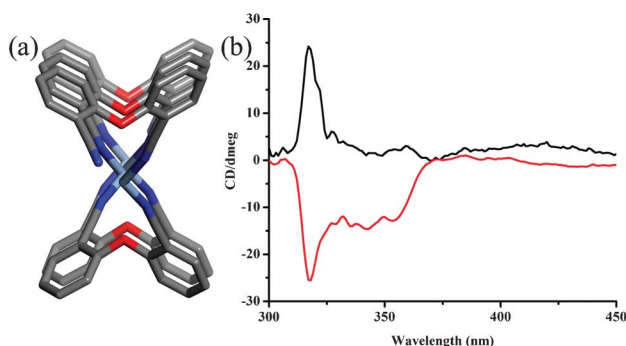


Fig. 1 (a) Chiral helical structure and (b) CD spectra of **1**.

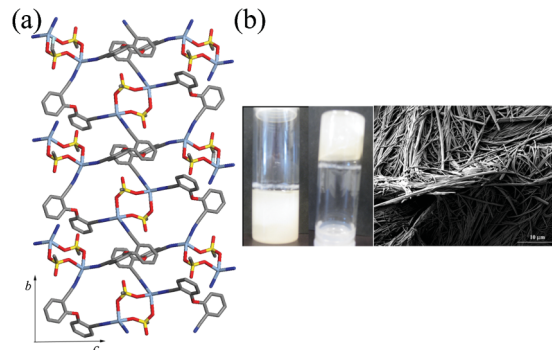


Fig. 2 (a) Helical structure of **2**, (b) digital images and FESEM images of **3**. C (gray), N (blue), O (red), H (white), S (yellow), Ag (pale blue).

group commonly exhibit both P and M enantiomeric single crystals in the batch.²¹

The crystallising conditions were very important to the formation of spontaneously resolved enantiopure crystals of **1**. Mixing equimolar toluene solutions of Ag(I)OTf and *O,O*-CPBN under hot conditions (75 °C) or recrystallising **1** from toluene (dissolving under hot conditions, but with crystal formation at room temperature) or using other solvents (ethyl acetate and DCM) for the preparation/crystallisation produced single crystals with a very different morphology (**2**, SI 1, ESI†).

2 also formed a 2_1 helical supramolecular structure in the crystal lattice (Fig. 2a), however, adjacent helix adopt the opposite handedness and this leads to the formation of a non-chiral helical structure overall. Similar to **1**, Ag(I) adopts a distorted trigonal pyramidal coordination geometry which is generated by two cyano nitrogens from two different *O,O*-CPBN and two oxygen atoms from two different OTf anions. In contrast to **1**, however the counterion acts as a bridging bidentate ligand by using two different oxygen atoms to coordinate to two Ag(I) centres. The combination of two OTf anions and two Ag(I) centres results in an 8-membered cyclic structure (SI 6, ESI†). Thermogravimetric analysis (TGA) shows higher thermal stability for **2** relative to **1** (SI 7, ESI†). Using toluene but changing the reaction conditions so as to increase the metal : ligand ratio (Ag(I) : *O,O*-CPBN, 1 : 2) produced a coordination polymer gel (**3**). Scanning electron microscopy showed this to have a nanowire (50 nm diameter and >10 mm long) morphology (Fig. 2b). The coordination of the cyanophenyl nitrogen to Ag(I) in **3** was confirmed by IR spectroscopy. The C≡N bond strength increased on coordination ($\nu_{\text{C}\equiv\text{N}(\text{stretch})}$) at 2248 cm^{-1} compared to 2234 cm^{-1} in the free ligand). The IR spectrum of **1** shows $\nu_{\text{C}\equiv\text{N}(\text{stretch})}$ bands at 2236 cm^{-1} and 2248 cm^{-1} , and 2247 cm^{-1} in **2** (SI 8, ESI†). It is noted that σ -donation of a cyano nitrogen shifts the $\nu_{\text{C}\equiv\text{N}(\text{stretch})}$ bands to higher wavenumbers, whereas π -back-bonding has the reverse effect.²² The coordination polymer gel was found to be stable for two weeks but slowly converts to another crystalline form on standing at room temperature for longer periods (**4**).

4 has a complex-network, supramolecular helical structure with the Ag(I) involved in three different coordination environments; two distorted trigonal pyramidal and one square pyramidal

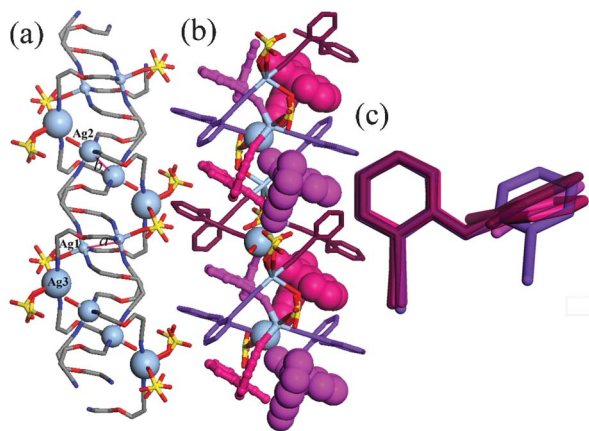


Fig. 3 (a) The three different Ag(I) coordination environments (balls) of **4** (only C and O involved in connecting both CN are shown), (b) the four different *O,O*-CPBN conformations (different colour) and the two independent helical networks (ball-stick and space filling) and their interconnecting networks and (c) the superposition of the four different conformations; C (gray), N (blue), O (red), H (white), F (cyan), S (yellow), Ag (pale blue). $d_{\text{Ag}\cdots\text{Ag}}$ distances (Å) are marked as *a* and *b* where $a = 3.352$ and $b = 3.323$. O atoms in the anions show disorder.

geometry with the *O,O*-CPBN displaying four different conformations (Fig. 3a and SI 9b, ESI†). One distorted trigonal pyramidal coordination geometry results from the coordination of three cyano nitrogen atoms from three different *O,O*-CPBN and an oxygen atom from an anion (Ag1 in SI 9b, ESI†) whereas the other distorted trigonal pyramidal geometry is formed by three cyano nitrogen atoms from three different *O,O*-CPBN and a water oxygen at an apical position (Ag2 in SI 9b, ESI†). The square pyramidal coordination geometry are filled by the almost linear coordination of two cyano nitrogen atoms from two different *O,O*-CPBN ($\text{N4-Ag3-N6} = 165.88^\circ$) and an oxygen atom from an anion (Ag3 in SI 9b, ESI†). The remaining two sites are filled by a weakly coordinated anion and the oxygen of a water molecule (SI 9b, ESI†). Along the *b*-axis, two independent 1-D supramolecular helical network structures are formed by the alternate involvement of the two trigonal pyramidal Ag(I) coordination centres and the *O,O*-CPBN in two different conformations (Fig. 3b). Both the helical structures adopt opposite helicity. These independent helical networks are interconnected *via* the Ag(3) coordination centre, the ligand showing a further two conformations, and an oxygen atom of a bidentate coordinated anion and water. The networks are further held together by argentophilic interactions involving the trigonal pyramidal Ag(I) centres of both helical networks.¹³ The result is that the *O,O*-CPBN in the complex are displaying four different conformations which is unprecedented in a single network structure (Fig. 3c and SI 10, ESI†). However, recrystallization of both **3** and **4** from toluene or ethyl acetate solutions produces single crystals of **2** suggesting that **2** is the more thermodynamically stable structure. TGA data supports the relative thermal stabilities as $2 > 3, 4$ (SI 7, ESI†).

The crystalline solids of **1–4** were ground and examined by powder X-ray diffraction to confirm the phase purity of the samples (SI 11 and SI 12, ESI†). The completely different PXRD patterns of **3** confirm that it is structurally different from other

three materials. The most exciting phenomena of these self-assembled coordination polymeric structures result from the conformational robustness displayed by the *O,O*-CPBN. In each coordination polymer, the cyanophenyl groups adopt different conformations none of which replicate the free ligand conformation (SI 10, ESI†).

In conclusion, the conformational flexibility of *O,O*-CPBN has been richly exploited to generate silver coordination polymer with spontaneously resolved, helical and polymer gel structures. The coordination polymeric network of **4** shows the unprecedented phenomenon of four different ligand conformations in a single polymeric structure, a feature which is more commonly the reserve of biopolymers. We hope that more such conformationally robust polymorphic structural investigation might provide greater understanding of conformationally dependent biopolymer functions.

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