

# Stereoselective and hierarchical self-assembly from nanotubular homochiral helical coordination polymers to supramolecular gels†

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**A new binaphthylbisbipyridine-based ligand underwent diastereoselective self-assembly with silver(I) ions to form nanotubular homochiral helical coordination polymers, which further hierarchically self-assemble into nanofibers, capable of immobilizing organic solvents.**

The self-assembly of metallohelical supramolecular architectures continues to attract considerable interest due to their aesthetic appeal and potential applications in areas such as molecular recognition and catalysis.<sup>1</sup> Bisbipyridines have been widely used to form helical complexes with a range of transition metal ions.<sup>2</sup> Furthermore, a number of related studies have demonstrated that the introduction of asymmetric carbon centers or axially-chiral atropisomerism in the spacer or at the termini of the bisbipyridine ligands is an effective method to achieve homochiral metallohelicates.<sup>3</sup> Most of them are discrete polynuclear complexes with helical arrangements. For example, Lützen *et al.* previously and recently described the enantiomerically pure dinuclear double- and triple-stranded helicates by diastereoselective self-assembly of chiral binaphthyl-bisbipyridine ligands and metal ions.<sup>4</sup> However, very few nanotubular homochiral helical coordination polymers are reported.<sup>5</sup>

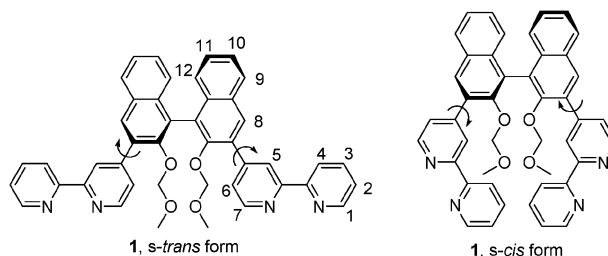
In addition, studies on metallogels have received much interest from chemists because the presence of the metal ions may endow the gel unusual functionalities.<sup>6</sup> The reported metallogels are mainly focused on the discrete metal complexes and 3D cross-linked coordination polymers.<sup>7</sup> To date, only a few examples of metallogels based on 1D coordination polymers have been reported. For instance, the Lee group has designed stimuli-responsive hydrogels from silver-bent bipyridine coordination polymers.<sup>8</sup> You *et al.* have reported helical nonracemic tubular coordination polymer gelators from silver-bisimidazole systems.<sup>9</sup> Vittal *et al.* have described coordination polymer hydrogels from Zn<sup>2+</sup>/Mg<sup>2+</sup> and coumarin-derivatized amino acid ligands.<sup>10</sup>

We previously reported coordination polymer gels built from chiral binaphthylbisbipyridine ligands and Cu(I) ions being used as catalysts in the Huisgen 1,3-dipolar cycloaddition reaction.<sup>11</sup> In order to extend this work and establish the

robustness of the approach based on the concept of 1D coordination polymers toward supramolecular gels, we designed structurally similar bisbidentate *exo*-ligand (*S*)-**1** to avoid the formation of discrete cyclic polynuclear species (Scheme 1). Herein, we presented stereoselective self-assembly of (*S*)-**1** and silver(I) ions into nanotubular homochiral helical coordination polymers, which can hierarchically self-assemble into nanofibers capable of gelating organic solvents.

The coordination reaction of (*S*)-**1** and AgPF<sub>6</sub> in a 1 : 1 stoichiometry was studied by ESI mass spectrometry and NMR spectroscopy. The MS spectrum showed a peak at *m/z* 789.16 for a singly charged complex [**1**·Ag]<sup>+</sup>, which was mixed with the doubly charged complex [**1**<sub>2</sub>·Ag<sub>2</sub>]<sup>2+</sup> and triply charged complex [**1**<sub>3</sub>·Ag<sub>3</sub>]<sup>3+</sup> judged by the isotope distribution (Fig. S1†). The complex (*S*)-**1**·AgPF<sub>6</sub> gave rise to significantly shifted NMR signals with respect to the free ligand (*S*)-**1** (Fig. 1), indicative of the formation of metal coordination bonds. In addition, the NMR spectrum of (*S*)-**1**·AgPF<sub>6</sub> showed the same number of protons as the free ligand (*S*)-**1**, indicating the ligand retains its C<sub>2</sub>-symmetry in solution upon complexation. 2D NOESY spectrum revealed dipole-dipole interactions between H8 and H5, H4 (Fig. S2†), thus suggesting the (*S*)-**1** molecules render *s-trans* form in solution upon coordination to silver(I) ions. The preservation of C<sub>2</sub>-symmetry for the ligand in the complex on the NMR time scale, combined with the observation of oligomeric species in mass spectrum, suggests a very dynamic exchange behavior in solution, which was further supported by NMR experiments both at variable temperature (Fig. S3†) and with different metal/ligand ratios (Fig. S4†). Complexation studies of (*S*)-**1** with other silver salts AgX (X = BF<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>, NO<sub>3</sub>) also provided similar results.

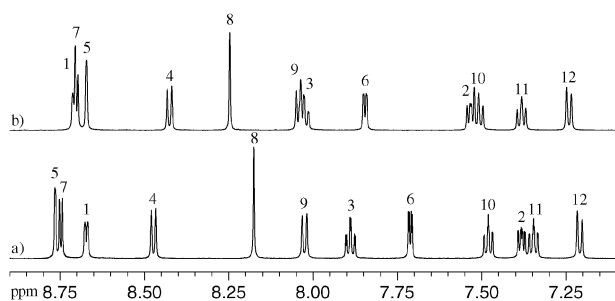
Fortunately, a colorless rodlike single crystal was obtained by slow evaporation of a CH<sub>3</sub>CN solution containing equimolar AgBF<sub>4</sub> and (*S*)-**1**.† (*S*)-**1**·AgBF<sub>4</sub> crystallizes in the chiral orthorhombic P222<sub>1</sub> space group with a silver(I) ion, a (*S*)-**1** molecule and a BF<sub>4</sub><sup>-</sup> ion in the asymmetric unit (Fig. 2a). The silver center coordinates to two bipyridyl groups of two different ligands (*S*)-**1** in a strongly distorted tetrahedral



**Scheme 1** The molecular structure of compound (*S*)-**1**.

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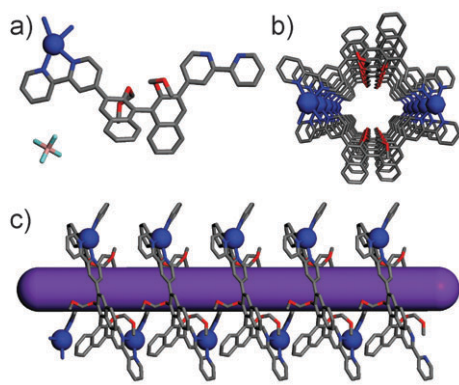
† Electronic supplementary information (ESI) available: Synthetic procedures and characterization of **1**, gel tests, MS, NMR, FTIR, UV, CD, SEM, TEM. CCDC 774704 and 774706. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc01433h



**Fig. 1**  $^1\text{H}$  NMR spectra (600.1 MHz, 298 K,  $\text{CD}_3\text{CN}$ ) of (a) (*S*)-**1** and (b) (*S*)-**1** + 1.0 equiv.  $\text{AgPF}_6$ .  $c = 5.3$  mM.

geometry. Adjacent silver centers are thus bridged by (*S*)-**1** along the *a*-axis to form an infinite coordination polymer. The dihedral angle between the two naphthyl rings in the 1,1'-binaphthyl subunit of (*S*)-**1** is  $71.08^\circ$ . All the silver centers adopt the same  $\Lambda$  configuration, indicating the chirality of silver(I) ions is predetermined by the binaphthyl axial chirality in the ligands. Thus, this leads to an overall nanotubular single-stranded *P*-helical coordination polymer (Fig. 2b–c). The helical pitch, given by the distance between equivalent silver atoms, is  $8.23 \text{ \AA}$ , and the diameter of the cavity is about  $9 \text{ \AA}$ . When (*R*)-**1** was used, a nanotubular coordination polymer (*R*)-**1**· $\text{AgBF}_4$  with the opposite helicity was obtained, $\ddagger$  further demonstrating that the configuration of the BINOL group can stereoselectively control the chirality of the newly formed stereogenic silver centers and therewith the helicity of the whole coordination polymers. $^{12}$

Very interestingly, complexes (*S*)-**1**· $\text{AgX}$  ( $\text{X} = \text{PF}_6, \text{BF}_4, \text{CF}_3\text{SO}_3, \text{NO}_3$ ) can successfully gelate  $\text{CH}_3\text{CN}$  after screening common solvents. The formation of the gel is dependent on the stoichiometry and the cooling rate. The use of less than one equivalent of  $\text{Ag}^+$  resulted in the formation of a solution. In the case of complexes (*S*)-**1**· $\text{AgX}$  ( $\text{X} = \text{CF}_3\text{SO}_3, \text{NO}_3$ ), cooling naturally to room temperature led to precipitation, while keeping in the refrigerator (*ca.*  $-20^\circ\text{C}$ ) led to gel formation. The stability of gels depends on the counterions. Gel (*S*)-**1**· $\text{AgPF}_6$  was stable for at least one year without visible changes, while gels (*S*)-**1**· $\text{AgX}$  turned into precipitates after several days ( $\text{X} = \text{CF}_3\text{SO}_3, \text{NO}_3$ ) or crystals after three



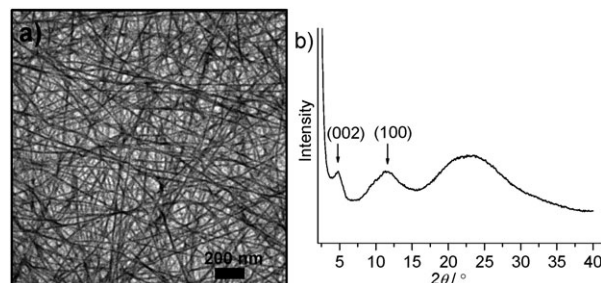
**Fig. 2** The repeating unit of the complex (*S*)-**1**· $\text{AgBF}_4$  (a), and perspective (b) and side (c) views of the nanotubular *P*-helical coordination polymer (*S*)-**1**· $\text{AgBF}_4$ . Hydrogen atoms are omitted for clarity.

months ( $\text{X} = \text{BF}_4$ ) (Fig. S5 $\dagger$ ). To the best of our knowledge, there are no reports on gel-single crystal transition from coordination polymer gel systems so far. $^{13}$  The single crystal thus obtained is the same as the one by slow evaporation.

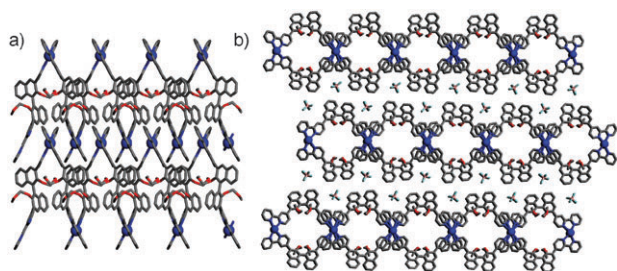
The gel (*S*)-**1**· $\text{AgPF}_6$  was characterized by various analytical techniques. The characteristic C–N stretching peaks of the bipyridine in ligand (*S*)-**1**, observed at  $1584, 1462 \text{ cm}^{-1}$  in the IR spectrum, shifted to  $1605, 1479 \text{ cm}^{-1}$  in the xerogel (*S*)-**1**· $\text{AgPF}_6$  (Fig. S6 $\dagger$ ), suggesting the coordination of the bipyridines. $^{14}$  The absorption spectrum of gel (*S*)-**1**· $\text{AgPF}_6$  exhibited a much broadened and red-shifted band when compared with dilute solution (Fig. S7 $\dagger$ ), indicating that  $\pi$ – $\pi$  stacking interactions between 1D polymeric chains could play an important role in the formation of gel fibers. The negative CD effect at around  $395 \text{ nm}$  corresponding to MLCT band decreased with a rise in the temperature, suggesting a gradual destruction of chiral supramolecular structures (Fig. S8 $\dagger$ ).

The micromorphologies of the gels were obtained through scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images reveal the xerogels (*S*)-**1**· $\text{AgX}$  ( $\text{X} = \text{PF}_6, \text{BF}_4, \text{CF}_3\text{SO}_3, \text{NO}_3$ ) consist of 3D entangled fiber-like aggregates (Fig. S9 $\dagger$ ), responsive for the observed gelation. Moreover, TEM provides clearer images (Fig. S10 $\dagger$ ). Straight nanofibers were observed in gels (*S*)-**1**· $\text{AgPF}_6$  and (*S*)-**1**· $\text{AgBF}_4$ . As compared to the latter, the former consisted of higher-aspect-ratio nanofibers, in which the length is more than several micrometres and the diameter is  $10$ – $20 \text{ nm}$  (Fig. 3a). When the counterions were replaced by  $\text{CF}_3\text{SO}_3/\text{NO}_3$ , bent nanofibers were observed. These results indicate that the counterions could change the superstructures of the assemblies, thus resulting in different morphologies. Additionally, in contrast with other gels, gel (*S*)-**1**· $\text{AgPF}_6$  has denser fibers, which is in accordance with the better gelation ability of (*S*)-**1**· $\text{AgPF}_6$ .

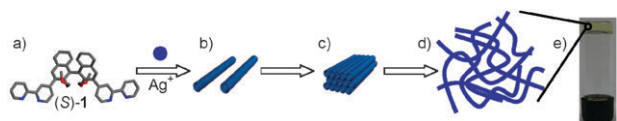
Deep insights into the gel structures were derived from single-crystal structure and X-ray diffraction (XRD) analysis. In crystalline (*S*)-**1**· $\text{AgBF}_4$ , almost perfect  $\pi$ – $\pi$  stacking interactions involving bipyridine moieties between two neighboring helices afford a 2D layer. Further interconnection of these adjacent 2D layers through electrostatic attraction as well as weak C–H···F hydrogen bonding between the cationic polymers and the  $\text{BF}_4^-$  anions results in the formation of a 3D structure (Fig. 4). The single crystal structure analysis could provide us useful information about the packing structure in the gel phase. The XRD pattern of xerogel (*S*)-**1**· $\text{AgPF}_6$  gave three peaks at *d*-spacings of  $1.86 \text{ nm}$ ,  $0.78 \text{ nm}$  and  $0.38 \text{ nm}$  (Fig. 3b).



**Fig. 3** TEM image of gel (*S*)-**1**· $\text{AgPF}_6$  ( $23.7 \text{ mM}$ ) (a) and XRD pattern of xerogel (*S*)-**1**· $\text{AgPF}_6$  (b).



**Fig. 4** The  $\pi$ - $\pi$  stacking interaction involving bipyridine moieties between two neighboring helices (a) and the lamellar structure formed by electrostatic attraction as well as C-H...F hydrogen bonding between the cationic polymers and the  $\text{BF}_4^-$  anions (b) in crystalline (S)-1-AgBF<sub>4</sub>.



**Fig. 5** Schematic representation of the hierarchical self-assembly of (S)-1-AgPF<sub>6</sub> into gel nanofibers. (a) Molecule (S)-1, (b) nanotubular P-helical polymers, (c) multilayers, (d) gel nanofibers, (e) gel formed by (S)-1-AgPF<sub>6</sub>.

The former two peaks were ascribed to the diffraction from (002) plane constructed from 2D layers corresponding to a layer thickness of 3.72 nm, and the diffraction from (100) plane corresponding to a helical pitch, respectively. The diffraction signal at  $d$ -spacing of 0.38 nm was ascribable to  $\pi$ - $\pi$  interactions between the bipyridine moieties. Interestingly, the XRD patterns of other xerogels exhibited different interlayer distances and helical pitches (Fig. S11†), which were evidently affected by the counterions. These results supported the fact that the tubular helical coordination polymers were preserved in the gels. Thereby, the stereoselective and hierarchical self-organization processes of these supramolecular gels could be reasonably deduced. The tubular homochiral helical coordination polymer by chiral binaphthylbisbipyridine ligands and silver(I) ions, the 2D layer by  $\pi$ - $\pi$  interactions between polymeric chains, and the nanofibers with the lamellar structure by 2D layers, were formed step by step (Fig. 5).

In summary, we have successfully demonstrated the stereoselective and hierarchical self-assembly behaviors of a new binaphthylbisbipyridine-based ligand and silver(I) ions from nanotubular homochiral helical coordination polymers to supramolecular gels. The counterions could change the superstructures of the assemblies, such as the interlayer distance and helical pitch. Incorporation of functional groups into such nanotubular helical coordination polymers and their application in *enantio*-selective recognition and separation are currently underway.

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## Notes and references

† Crystal data for (S)-1-AgBF<sub>4</sub>: C<sub>44</sub>H<sub>34</sub>AgBF<sub>4</sub>N<sub>4</sub>O<sub>4</sub>,  $M = 877.43$ , orthorhombic, space group  $P222_1$ ,  $a = 8.2318(3)$ ,  $b = 13.8544(5)$ ,  $c = 41.7301(16)$  Å,  $U = 4759.2(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.225$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.480$  mm<sup>-1</sup>,  $F(000) = 1784$ , final  $R_1 = 0.0747$  for

$I > 2\sigma(I)$ ,  $wR_2 = 0.2390$  for all data, GoF = 1.040, Flack parameter =  $-0.07(6)$ . CCDC 774704. Crystal data for (R)-1-AgBF<sub>4</sub>: C<sub>44</sub>H<sub>34</sub>AgBF<sub>4</sub>N<sub>4</sub>O<sub>4</sub>,  $M = 877.43$ , orthorhombic, space group  $P222_1$ ,  $a = 8.2140(5)$ ,  $b = 13.8169(7)$ ,  $c = 41.563(2)$  Å,  $U = 4717.1(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.236$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.484$  mm<sup>-1</sup>,  $F(000) = 1784$ , final  $R_1 = 0.0728$  for  $I > 2\sigma(I)$ ,  $wR_2 = 0.2215$  for all data, GoF = 1.083, Flack parameter = 0.08(6).

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