Helical nonracemic tubular coordination polymer gelators from simple achiral molecules†

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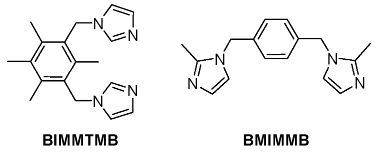
A novel class of helical nonracemic tubular coordination polymers, which can immobilize a wide range of solvents at very low concentrations, have been synthesized for the first time in the absence of chiral influences and appended groups.

Coordination chemistry as a rational design route toward gels is currently gaining intensive attention.[1] Surprisingly, among the examples describing metal coordination to assist molecular gelation, the direct use of the concept of coordination polymers, infinitely extending metal–ligand assemblies with bridging organic ligands, has been less explored and remains elusive despite its extensive application in crystal engineering.[2] In these limited reports with regard to coordination polymer gels,[3] the bridging organic units generally require appended moieties (*e.g.*, hydroxy, long hydrocarbons, ether chains, *etc.*) to stabilize aggregates in the gel state through extra noncovalent bonds such as hydrogen bonds and van der Waals forces. The main challenge in this area is maintaining the metal–organic polymeric structure in the gel rather than in the preferential crystalline state, especially in the absence of these auxiliary moieties.

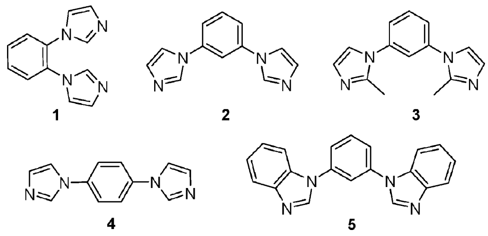
Helical and nonracemic architectures play a fundamental role in many natural systems, perhaps most prominently represented by biological macromolecular organizations. In recent years, coordination polymers have been frequently used to mimic these architectures.[4] One general approach to nonracemic helicity of coordination polymers depends on the coexistence of chiral influences (*e.g.*, chiral starting material, template, *etc.*) transferring their chirality to the helical sense of the polymers. In addition, there is also the possibility of the spontaneous formation of chiral helixes from achiral components (chiral symmetry breaking). However, only very few examples are known and the control or predetermination of chirality still remains a challenge.[5]

Imidazoles as building blocks are currently attracting special interest in the area of supramolecular chemistry due to their importance in biology and biochemistry.[6] Recent studies of self-assemblies of the conformationally flexible 1,3-bis-(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (BIMMTMB) with $CuCl_2{\cdot}2H_2O$ or 1,4-bis(2-methylimidazol-1-ylmethyl)-benzene (BMIMMB) with $AgBF_4$ have revealed the formation of discrete dinuclear metallocyclic complexes that are capable of stacking to form one-dimensional (1-D) nanosized channels in the crystalline solid state (Scheme 1).[7] Here we report a novel class of coordination polymer gelators which only stem from the coordination of Ag(I) and the imidazole derivative **2** or **5** (Scheme 2). The bridging organic ligands feature achiral, structural simplicity and a conformationally restricted bent shape. Our results demonstrate that the aggregates can be stabilized in the gel state, avoiding the bulky crystalline solids out of solution, even in the absence of side chain functionality fused together into the scaffold, which constitutes the structurally simplest coordination polymer gels in terms of the secondary building units (SBUs) reported so far. To our knowledge, the self-assemblies with helical, nonracemic and nanotubular architectures have been achieved for the first time from achiral components in the gel state (Fig. 1).



Scheme 1 Chemical structures of BIMMTMB and BMIMMB.

Initial results have shown that optically transparent gels are formed spontaneously upon simple addition of a methanol solution of the ditopic monomer **2** or **5** to an aqueous solution of silver nitrate at a 1 : 1 ratio of ligand : $AgNO_3$ at room temperature in a few minutes. In contrast, the mixture of Ag(I) and **1**, **3** or **4** could not undergo gelation but were immediately precipitated out of solution. To our surprise, further investigation demonstrated that the gelation driven by $\{[Ag\text{-}\mathbf{2}]NO_3\}_n$ could tolerate a wide scope of solvents involving dimethylformamide (DMF), glycol or mixtures of water and organic



Scheme 2 Chemical structures of ligands **1–5**.

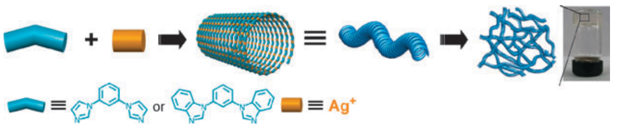


Fig. 1 A schematic representation of the self-assembly processes of the coordination polymer gels.

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solvents (*e.g.*, methanol, ethanol, *i*-propanol, acetonitrile, even chloroform, dichloromethane and toluene) (see ESI†, Table S1). It is noteworthy that the critical gel concentration (CGC) is as low as 0.3 wt% of the $\{[Ag\text{-}\mathbf{2}]NO_3\}_n$ gelator in CH_3OH and H_2O (3 : 2 wt/wt, see Fig. S1† for optimization of the mixed solvents' ratio). These gel materials maintained stability for a period of several months at ambient temperature. Interestingly, the gels could survive in a broad range of acidic conditions (pH = 1–7) although the 3-N position of the imidazolyl unit is protonated easily. More interestingly, the coordination polymer $\{[Ag\text{-}\mathbf{2}]NO_3\}_n$ gelator could even gelatinize the mixture of CH_3COOH and H_2O. In addition, we found that the counter-anions of Ag(I) would influence the gelation. For instance, $AgOSO_2CF_3$ drives the formation of the gel whereas $AgBF_4$ and $AgSbF_6$ immediately afford the precipitates, which are assumed to arise from rapid polymerization to hinder trapping of solvent molecules into the networks' interstitial spaces.[3j]

Transmission electron microscopy (TEM) was first conducted to investigate the supramolecular structures derived from $AgNO_3$ and **2**. A micrograph obtained in CH_3OH–H_2O shows the formation of cylindrical aggregates with a uniform diameter of *ca.* 9 nm and lengths up to several micrometres as the sample is negatively stained with an aqueous solution of uranyl acetate (Fig. 2a, also see Fig. S2 and S3† for the images unstained or negatively stained with phosphotungstic acid). The obvious contrast between the inner and periphery in the cylindrical structures is characteristic of the projection images of hollow tubular aggregates rather than tapes. Furthermore, from this image one can find that these tubules appear to feature a helical motif.

We further performed atomic force microscopy (AFM) experiments with a dried drop-cast solution of $\{[Ag\text{-}\mathbf{2}]NO_3\}_n$ in CH_3OH–H_2O on a freshly cleaved mica surface. The AFM image shows a well-developed network structure composed of fibrous aggregates (Fig. 2b). More interestingly, the zoomed-in image of individual objects unambiguously discloses the tubular structure with a well-grown helical arrangement along its 1-D aggregate (Fig. 2c), suggesting that thicker fibers consist of a bundle of helical tubes. Further analysis of these tubes reveals an average helical pitch of *ca.* 8.0 nm (Fig. S4†), and a width of *ca.* 9 nm after accounting for the tip-broadening factor,[8] which is consistent with the TEM images. In addition, a SEM image obtained from the freeze-dried $\{[Ag\text{-}\mathbf{2}]NO_3\}_n$ gel (xerogel) in CH_3OH–H_2O also demonstrates the formation of well-grown three-dimensional networks of fibrous assemblies, and these ribbon-like bundles must be formed during the drying process (Fig. 2d).

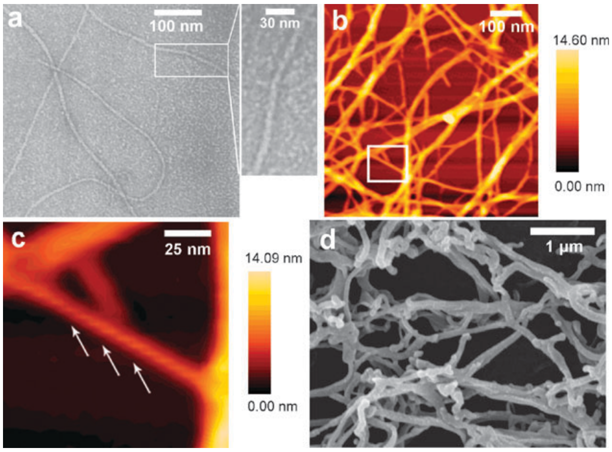

Fig. 2 The morphology of the $\{[Ag\text{-}\mathbf{2}]NO_3\}_n$ aggregates in CH_3OH–H_2O (3 : 2 wt/wt). (a) TEM image, 0.1 wt%, negatively stained with uranyl acetate aqueous solution. The inset shows a magnified picture of the area marked. (b) Tapping-mode AFM height image on drop-cast mica, 0.08 wt%. (c) A zoomed-in image of the area marked in (b). The arrows point to the helical structure. (d) A SEM image of xerogel, 0.8 wt%, Au shadowing at 45°.

The aggregation behavior observed by electron microscopy was further studied by circular dichroism (CD) spectra at the molecular level. In the absence of Ag(I), no CD Cotton effect for **2** was observed, as expected for an achiral molecule. As shown in Fig. 3a, in contrast, the CD spectra of the $\{[Ag\text{-}\mathbf{2}]NO_3\}_n$ gel exhibit a strong exciton-coupled split Cotton effect with the $\theta = 0$ crossing wavelength at 219 nm near the absorption maximum of the chromophore (214 nm, Fig. 3b). Possible contributions of linear dichroism (LD) and birefringence to the true CD signals have been excluded carefully using the method reported by Spitz *et al.*[9] These experiments are clearly indicative of the formation of a helical superstructure with a preferred handedness,[10] suggesting chiral symmetry breaking. Further repeating experiments show that each sample is CD active. However, the sign of the CD signals is undetermined for different batches [sometimes positive and sometimes negative, roughly giving a statistical (1 : 1) distribution]. These results indicate that the chirality is essentially governed by chance, and not by any external chiral impurities.[5,11–13] It is important to stress that the intensity of peaks of the gel phase was too strong to obtain reliable spectra using a conventional optical cell. Thus, the CD and UV-Vis spectra were measured with a gel sample sandwiched between two quartz glass plates. Under these conditions, the ordinate is expressed as an arbitrary unit because it is very difficult to control the thickness of the sample.[14] In this stage, therefore, we could not determine whether the symmetry breaking occurs throughout the whole sample or if there is always a significant bias, one way or the other, of say left-handed fibers in a certain case but with some contamination of right-handed fibers. It should be noted that the CD study for the gel formed by $\{[Ag\text{-}\mathbf{5}]NO_3\}_n$ afforded similar experimental

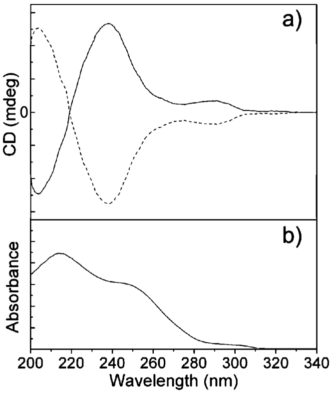

Fig. 3 Spectral analysis of the $\{[Ag\text{-}\mathbf{2}]NO_3\}_n$ gel (0.8 wt%) in CH_3OH–H_2O. (a) CD spectra obtained in different batches, positive (positive to negative on going from longer to shorter wavelengths, solid line) or negative (dash line). (b) UV-Vis spectrum.

results. Interestingly, Yuan and Liu recently reported chiral molecular assemblies from achiral amphiphilic imidazole-based ligand 2-(heptadecyl) naphtha[2,3]imidazole and $AgNO_3$, in which the chiral symmetry breaking occurred for the first time in the monolayer at the air–water interface and in LB films though interfacial coordination.[5b] As far as we know, we herein present the first example describing chiral symmetry breaking in the gel state.[11–13]

We rationalize that the helical architectures are generated from strong directional interactions derived from the complexation between the rigid bent bridging ligands and Ag(I) that adopts a linear coordination geometry. In the formation of the helical polymer, the occurrence of statistical fluctuations in the initial stage of metal–ligand coordination could lead to an accidental excess of one helical direction.[15] Once a certain helical sense excess exists, the new aggregates would follow to form a helical secondary structure with the same direction by chiral autocatalysis, while the competitive generation of the opposite helical sense is suppressed, thus leading to chiral amplification and eventual macroscopic chirality.

To further shed light on the possible formation mechanism of the helical tubular polymers, theoretical calculations have been carried out on the basis of the first principle density functional theory (DFT) (see ESI† for details).[16] The optimized result shows that the diameter of the helical tubule is *ca.* 9.1 nm and the helical pitch is *ca.* 7.1 nm, which is approximately in agreement with the experimental results from the TEM and AFM studies (Fig. S10†).

In summary, we have demonstrated that a simple achiral molecule could induce a helical nonracemic nanotubular structure when linked by a linear metal connecting point, which forms an entangled fibrillar network thereby immobilizing a wide range of solvents. In addition, the gels present another appealing feature in their extremely simple preparation at room temperature. Thus, the gel could be fabricated into various geometric morphologies in accordance with the vessel in which it was assembled.[17] We foresee that these findings will open a new avenue for the design of chiral functional soft materials from structurally simple achiral building blocks.

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