Self-assembly of coordination polymers into multi-stranded nanofibers with tunable chirality†

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We have demonstrated that the formation of multi-stranded nanofibers with tunable chirality from coordination polymers and their hierarchical assembly into interconnected 3-D networks leading to thermoresponsive gelation.

The construction of elaborately prepared supramolecular nanostructures has received a great deal of attention due to their potential in the development of novel functional materials based on self-organizing systems.[1] Among the diverse morphologies that are expected in supramolecular systems, one-dimensional (1-D) structures like fibers, tubules and ribbons are one of the most important subjects in material and biological chemistry.[2] For example, 1-D architectures can be used for electro-active wires in nanodevices, scaffolding blocks for gel materials, and structure-directing agents for shape-specific mineralization, *etc.*[3] In particular, 1-D structures are proven to be excellent candidates for chiral objects, which are widely investigated for advanced functional materials such as bio-informative storages, chiral guest molecular receptors, and chiral synthesis.[4] We have shown that amphiphilic rigid-flexible macrocycles self-assemble into 1-D tubular organization with left-handed coiled ribbons.[5a] We have also shown that incorporation of a conjugated rod into an amphiphilic dumbbell-shaped molecular architecture gives rise to the formation of helical fibers.[5b]

Recently, we have shown that the formation of single-stranded helical nanofibers from self-assembly of coordination polymers through complexation of *meta*-linked bent-shaped ligands with Ag(I).[6] The coordination polymers adopt a helical structure *via* a cisoid conformation or a layer structure *via* a transoid conformation depending on the capability to wrap counterions.[6a,b] One can envision that the single-stranded organization of the coordination polymer chains would be unstable when their bent-shaped ligands are elongated due to space filling frustration. Instead, the polymer chains would self-assemble into unique multi-stranded organization to maximize electrostatic interactions. With this idea in mind, we have prepared coordination polymers based on elongated ligands (Fig. 1a).

We present herein the formation of multi-stranded nanofibers with tunable chirality from coordination polymers and their hierarchical assembly into interconnected 3-D networks leading to thermoresponsive gelation (Fig. 1). The bipyridine ligands based on bent-shaped aromatic segments with different lengths containing chiral oligo(ethylene oxide) dendritic segments have been synthesized in a stepwise fashion according to similar procedures described previously.[6]

The resulting ligands were complexed with silver triflate to prepare coordination polymers **1–2** (Fig. 1a).

The coordination polymers, when dissolved in a selective solvent for the oligoether segments, can self-assemble into an aggregate structure because of their amphiphilic characteristics. The aggregation behavior of the coordination polymers in aqueous solution was subsequently investigated by using optical spectroscopies, dynamic light scattering (DLS), and transmission electron microscopy (TEM) experiments. The minimum aggregation concentrations of both **1** and **2** in aqueous solutions were determined to be 0.02 wt%. Above this concentration, the emission maxima of the coordination polymers were red-shifted by about 10 nm and the fluorescences were significantly quenched, with respect to those at low concentrations, indicative of aggregation of the aromatic polymer backbones (Fig. S1 and 2†).[7]

To investigate the aggregation structures of the coordination polymers, TEM experiments were performed in aqueous solutions. As shown in Fig. 2a and b, the TEM images of **1** and **2** with negative stained samples show nanofibers with a uniform diameter of about 5 and 6.5 nm, respectively, and

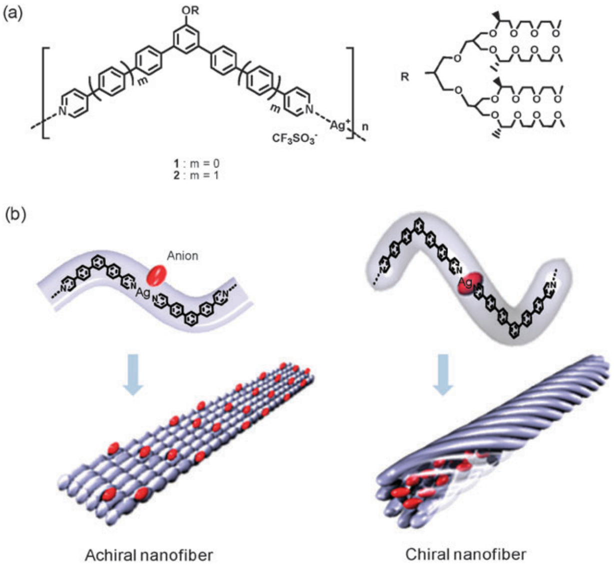

Fig. 1 (a) Molecular structures of coordination polymers **1** and **2**. (b) Schematic representation of formation of nanofibers from coordination polymers with tunable chirality.

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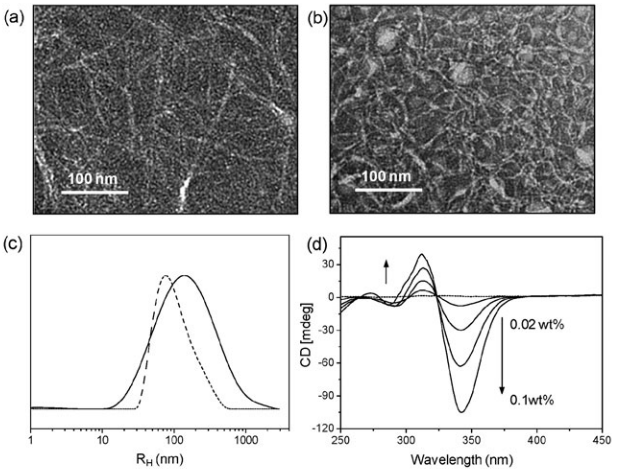

Fig. 2 TEM images of (a) **1** and (b) **2** prepared from evaporation of aqueous solution. (c) Size distribution graphs at an angle of 90° and (d) CD spectra of **1** (dashed line, 0.1 wt%) and **2** (solid line) in aqueous solutions (25 °C).

lengths with several micrometres. The formation of nanofibers in aqueous solution was further confirmed by DLS experiments. The CONTIN analysis of the autocorrelation function for both solutions showed a broad peak corresponding to average hydrodynamic radii (R_H) of approximately 75 and 110 nm for **1** and **2**, respectively (Fig. 2c). The slopes of angular dependence of **1** and **2** were observed to be 0.03 and 0.05, respectively, consistent with values predicted for cylindrical aggregates.[8] The formation of cylindrical aggregates was further confirmed by the Kratky plots that showed a linear angular dependence over the scattering light intensity of both polymers (see ESI†). On the basis of spectroscopic, DLS, and TEM results, we consider that these coordination polymers form the 1-D aggregates through aromatic stacking surrounded by hydrophilic dendritic segments that are exposed to the aqueous environment.

Interestingly, **1** shows no apparent circular dichroism (CD) signals even above the aggregation concentrations, indicative of the nanofibers with a lack of supramolecular chirality. In great contrast, **2** based on an elongated ligand exhibited strong CD signals over the absorption ranges (Fig. 2d), indicating the formation of a helical structure with a preferred handedness. The CD spectra of **2** are concentration-dependent with a clear isosbestic point at 322 nm, indicating that the formation of 1-D aggregates remains unaltered above aggregation concentration ranges.[9] These results suggest that the 1-D structure of **1** is based on an unfolded zigzag conformation, whereas **2** adopts a folded helical conformation. In spite of the same chiral moieties in dendritic chains of both **1** and **2**, such an extreme difference in chiroptical property within the same 1-D structures is very rare in supramolecular systems. Although there are few reports on nanostructures exhibiting a tunable chirality, the chirality change is accompanied by structural changes such as transformation from 1-D chiral helices to achiral vesicles or layers.[5*b*,10] This chiroptical contrast within the same 1-D architecture is believed to be attributed to the difference in the stacking arrangement of aromatic chains within the nanofibers.

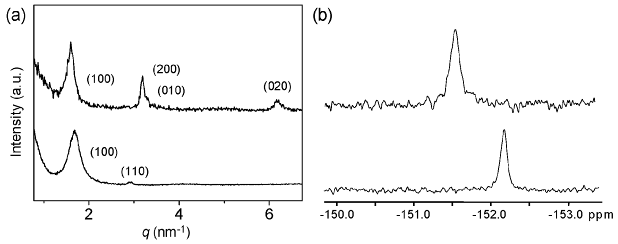

Fig. 3 (a) XRD patterns of **1** (top) and **2** (bottom) prepared from evaporation of aqueous solution. (b) Comparison of ^{19}F-NMR spectra in D_2O (470 MHz, 298 K) of **1** (top) and **2** (bottom).

To investigate stacking arrangements of the aromatic backbones within the fibers, X-ray diffraction (XRD) measurements were performed on the films prepared from fast evaporation of aqueous solution. The 1-D and 2-D XRD patterns of **1** showed several sharp reflections corresponding to a lamellar structure with a layer thickness of 3.95 nm with in-plane order (1.97 nm of Ag ordering) as shown in Fig. 3a and Fig. S9.† The lamellar structure with this indicates that the polymer backbones of **1** are laterally stacked with an unfolded zigzag conformation to form layers which are separated by dendritic chains with about 3.5 nm. This result suggests that the 1-D objects formed in dilute aqueous solution of **1** consist of ribbon-like layers with a width of 5 nm. The molecular modeling revealed that 6 polymer chains with a zigzag conformation stack laterally into long ribbons with a width of 5 nm, surrounded external flexible dendritic chains (Fig. 1b).

In contrast, the XRD patterns of **2** revealed a hexagonal columnar ordering with a lattice constant of a = 4.36 nm, suggesting that the nanofibers of **2** consist of multi-stranded helical aggregates. Considering the XRD results and density considerations, the number of polymer strands per cross-sectional area in a multi-stranded helix can be estimated to be approximately 18 (see ESI†).[11] Energy minimization revealed that the polymer backbones of **2** adopt a helical conformation with a pitch of 7.66 nm consisting of 3 ligands together with silver ions, and subsequently self-assemble into multiple-helical tubules through intertwining of 18 individual polymeric chains, in which the interior is occupied by triflate counterions (Fig. 1b). The optimized structure of the helix exhibits the aromatic core with a diameter of 3.2 nm and a tilted angle of 39° relative to the long axis, and an outer diameter of 4.5 nm including the fully extended aliphatic chains. This result is in excellent agreement with the lattice constant of the 2-D hexagonal structure obtained from the XRD (Fig. S11†).

The ability of multi-stranded nanofibers to display a tunable chirality can be rationalized by considering the space filling requirements in aromatic stacking as a function of length in *meta*-linked backbones. **1** based on a short aromatic ligand self-assembles into ribbon-like aggregates with laterally stacked polymer chains in which the aromatic building blocks are arranged with their long axes parallel to each other. The bulky flexible coils attached to the aromatic segments as side group would prohibit the 2-D growth of a self-assembled structure. Instead, the aromatic segments should be strongly driven to aggregate in one dimension based on laterally stacked 6 polymer strands. In contrast to achiral nanofiber

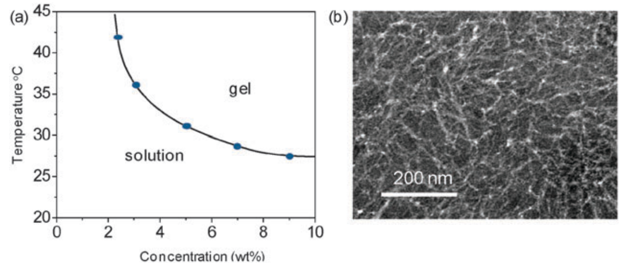

Fig. 4 (a) Phase diagram plotted in terms of the temperature *versus* the concentration of **1** in aqueous solution. (b) TEM image of **1** prepared at 50 °C.

of **1**, **2** based on an elongated aromatic ligand adopts a chiral helical arrangement due to an elongated transoid conformation with curvature. The conformational unstability for flat lateral stacking drives the polymeric backbones to adopt a helical curvature with a long pitch along a long axis of the fibers.[12] The vacant space between elongated pitches will be filled with other helical chains to form multi-stranded tubules, in which the interior is filled by anions.

To clarify the location of counterions in multi-stranded nanofibers, we have performed ^{19}F-NMR spectroscopic experiments on **2** based on BF_4^- which is sensitive to external environment.[13] The ^{19}F-NMR spectrum of a D_2O solution of **2** based on BF_4^- shows a resonance at $\delta = -152.18$ ppm, which is upfield with respect to those of BF_4^- ions of **1** at $\delta = -151.62$ ppm (Fig. 3b). The shielded NMR signals strongly suggest that the counterions of **2** are confined within the inner-space of helical organization whereas those of **1** are exposed to the external surface of hydrophilic dendritic shells.[14]

Another interesting point to be noted is that the fibrillar structures consist of a hydrophilic ethylene oxide dendritic exterior which is well-known to exhibit a lower critical solution temperature (LCST) behavior in aqueous solution.[15] Consequently, an increment in temperature can lead to hierarchical assembly of nanofibers into larger aggregates through hydrophobic interactions. Therefore, the thermo-responsive aggregation behavior of polymers in aqueous solutions was investigated as a function of concentration and temperature (Fig. 4a). Upon heating, the fluid solutions of the polymers spontaneously transform into stable hydrogels, as opposed to conventional gels that are dissolved upon heating. The TEM image of the gel dried on a carbon-coated copper grid revealed the formation of bundles of the fibrils at higher temperatures (Fig. 4b), which indicates that the gelation can be attributed to the interconnection of fibrillar aggregates through hydrophobic interactions caused by dehydrated polyether chains.

In summary, we have demonstrated that the coordination polymers based on *meta*-linked aromatic ligands self-assemble into multi-stranded nanofibers with tunable supramolecular chirality. The coordination polymers based on short ligands self-assemble into achiral nanofibers based on a flat zig-zag conformation, while elongated ligands induce chiral nanofibers based on a helical conformation. More important, the helical fibers consist of multi-stranded tubules, in which the internal cavity is occupied by counter anions. In addition, the multi-stranded nanofibers showed a reversible sol–gel interconversion triggered by temperature due to LCST behaviour of the polyether chains. We believe that this approach to construct elongated nanofibers with tunable chirality can provide a novel strategy for creating intelligent nanomaterials that can mimic the unique biological functions of natural multi-stranded fibrillar proteins.

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