Communications

Reversible Conformational Change

Cationic coordination polymers adopt two distinct conformations in response to the nature of the anions bound. Therefore, a simple exchange of anion type results in a reversible change in the bulk properties of the solution, from liquid to gel and back. M. Lee and co-workers describe the characterization of these polymers in their Communication on the following pages.

Supramolecular Chemistry

Stimuli-Responsive Gels from Reversible Coordination Polymers**

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The design of supramolecular helices that mimic the macromolecular organization observed in biological systems is a topic of great interest.[1] Therefore, considerable effort has been made to introduce helicity into artificial systems.[2] The most widely used strategy for generating supramolecular helices requires a noncovalent motif, which can provide the desired connectivity of the building blocks in a predictable manner.[3] For example, relatively strong directional interactions, such as complexation between bent ligands and transition-metal atoms that adopt a linear coordination geometry can give rise to extended polymeric chains with a helical secondary structure.[4,5] Especially for conformationally flexible ligands, one can envisage the formation of linear coordination chains that can adopt folded or unfolded secondary structures as a function of counteranion binding to cationic polymeric backbones through electrostatic interactions.[6,7] Indeed, a folded helical conformation has been reported to transform directly into an unfolded state in response to external stimuli.[8] These observations led us to investigate whether the secondary structure of cationic coordination chains can interconvert in aqueous solution from a folded helical conformation into an unfolded zigzag conformation in response to a counteranion guest to exhibit a reversible sol–gel transition.[9]

Herein, we report reversible sol–gel interconversion of coordination polymers in aqueous media, from folded helical chains into an unfolded zigzag conformation with counteranion exchange; the process is driven by depolymerization or conformational change (Figure 1). The synthesis of the bent ligands (**1**–**3**) containing hydrophilic dendritic side groups was per-
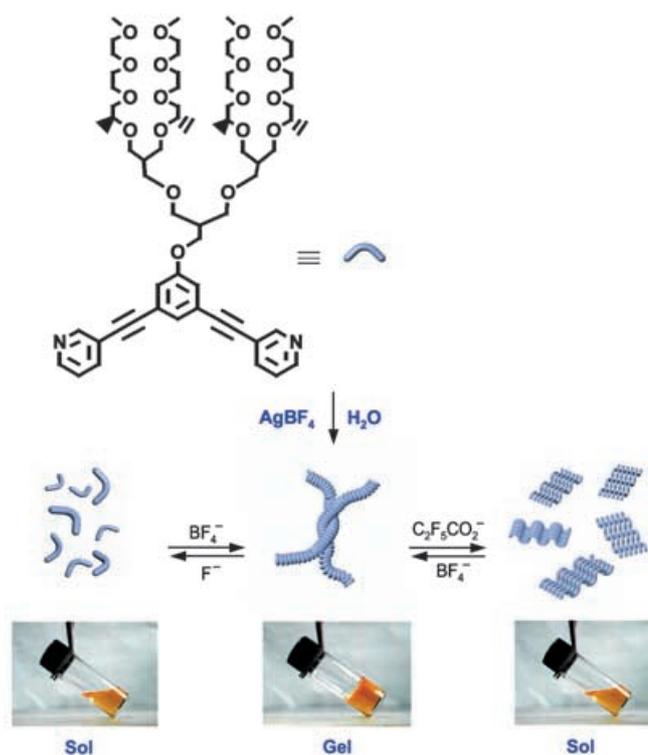
Figure 1. Schematic representation of reversible polymerization and reversible conversion between folded and unfolded conformations of a coordination chain upon counteranion exchange.

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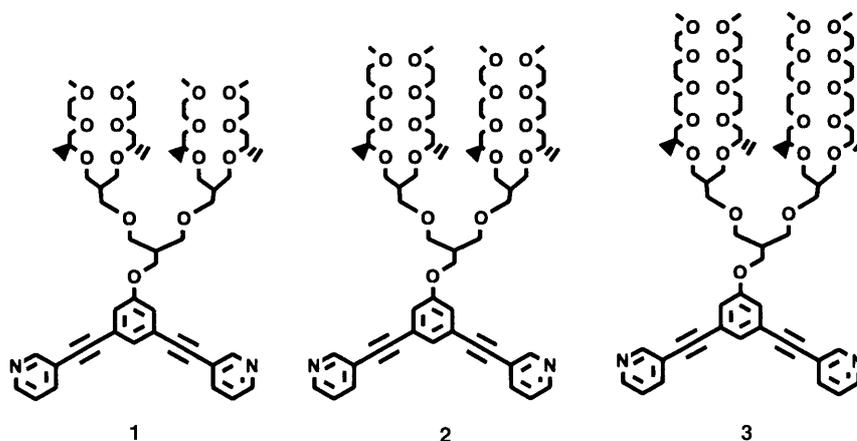
formed stepwise according to previously reported methods.[10,11] The resulting pyridine ligands were complexed with silver tetrafluoroborate to afford the coordination chains, [Ag-**n**]BF$_4$, in which **n** is one of the ligands, **1**–**3**. All of the analytical data are in full agreement with the chemical structures presented. In the solid state, all of the coordination polymers self-assembled into a hexagonal columnar structure (see Supporting Information), which suggests that the size of the BF$_4^-$ ion is compatible with the internal cavity of the helical columns.

In contrast to [Ag-**1**]BF$_4$, which precipitates in water, [Ag-**2**]BF$_4$ and [Ag-**3**]BF$_4$ form dilute aqueous solutions that undergo spontaneous gelation at concentrations above

2.5 wt %. Upon addition of 1.2 equivalents of tetra-*n*-butyl-ammonium fluoride $Bu_4N^+F^-$ to the gels, which drives the coordination polymers to depolymerize through a strong electrostatic interaction between the Ag^+ and F^- ions, the gels rapidly become a fluid solution. After the addition of 1.2 equivalents of F^- ions, the signals corresponding to aromatic protons in the ^1H NMR spectrum of $[Ag\text{-}2]BF_4$ show an upfield shift relative to those of the coordination polymer solution (1 wt % in CD_3OD), which indicates that the addition of F^- ions leads to decomplexation of the coordination polymer to give free ligands (Figure 2a). Upon addition of 1.2 equivalents of $Bu_4N^+BF_4^-$, the solution returns to the gel state; thus the polymerization is reversible.
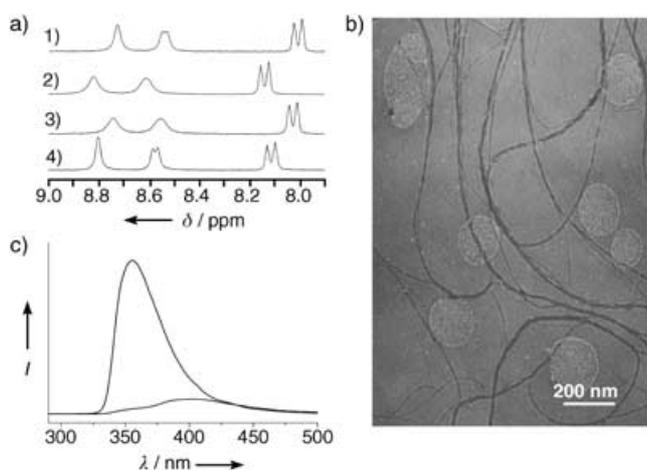
Figure 2. a) ^1H NMR spectra (250 MHz, 298 K) in CD_3OD (1 wt %) of 1) **2**; 2) $[Ag\text{-}2]BF_4$; 3) $[Ag\text{-}2]BF_4$ and 1.2 equiv $Bu_4N^+F^-$; 4) same as (3) after the addition of 1.2 equiv $Bu_4N^+BF_4^-$. b) TEM image of dried gel from $[Ag\text{-}2]BF_4$ in H_2O (0.3 wt %) stained with RuO_4. c) Fluorescence spectra of **2** and gel of $[Ag\text{-}2]BF_4$ (5 wt % in H_2O; $\lambda_{ex}=275$ nm).

TEM analysis of the gels revealed right-handed helical bundles of elongated fibers with diameters of 6–30 nm, which in turn form an entangled fibrillar network (Figure 2b). The gels reveal a significant Cotton effect in the chromophore of the aromatic unit, which supports the presence of elongated helical aggregates in aqueous solution.[12, 13] These results demonstrate that the complexes self-assemble into a helical secondary structure that forms a coiled-coil superstructure, and the fibrous aggregates entangle to form gels. This aggregation of the coordination chains is further supported by fluorescence measurements, which showed a strong red-shift of the emission maximum[14] and a significant decrease in the emission intensity of the gel state relative to that of the ligand (Figure 2c).[15] The formation of the helical secondary structure in aqueous solution can be rationalized by considering supramolecular polymerization through coordination bonding and subsequent binding of counteranions through the *cis*-like conformation of the monomeric units. Molecular models indicate that the size of the BF_4^- ion is compatible with the internal cavity formed by the *cis*-like conformation of the ligands. To maximize electrostatic interactions of the cationic chains with the counteranions, the coordination

chains adopt a folded helical conformation, which is responsible for the formation of the entangled fibrillar network.

More importantly, the gels reversibly transform into a fluid solution with counteranion exchange of BF_4^- with a larger ion, $C_2F_5CO_2^-$. Upon addition of 1 equivalent of $Bu_4N^+C_2F_5CO_2^-$ to the $[Ag\text{-}2]BF_4$ gel, it transforms rapidly into a fluid solution (Figure 1).[16] CD spectra of the $[Ag\text{-}2]BF_4/C_2F_5CO_2$ solution shows no Cotton effect (Figure 3a), thus demonstrating the absence of helical aggregation in this condition. The fluorescence spectrum of the gel of $[Ag\text{-}2]BF_4$ exhibits an emission maximum at 400 nm, which is indicative of a helical aggregation as described above. However, upon addition of up to 0.8 equivalent of $C_2F_5CO_2^-$ ions, the emission maximum gradually red-shifts (20 nm) with respect
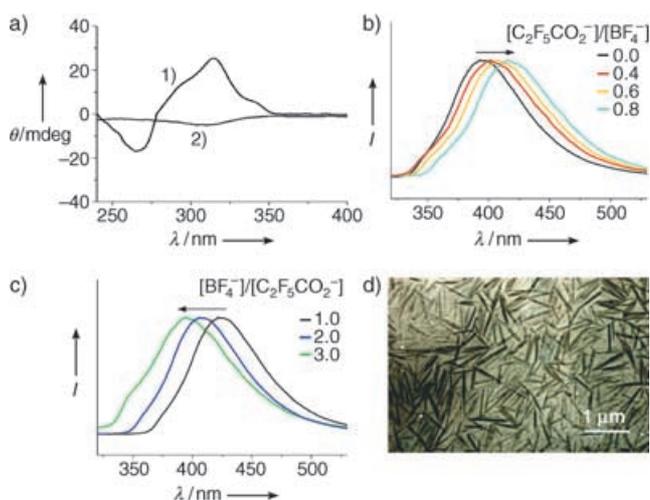
Figure 3. a) Circular dichroism (CD) spectra of: 1) $[Ag\text{-}2]BF_4$ (5 wt %); 2) $[Ag\text{-}2]BF_4$ (5 wt %) after the addition of 1 equiv $Bu_4N^+C_2F_5CO_2^-$. b) Fluorescence spectra of $[Ag\text{-}2]BF_4$ (5 wt %) with increasing amounts of $Bu_4N^+C_2F_5CO_2^-$. c) Fluorescence spectra of a mixture of $[Ag\text{-}2]BF_4$ (5 wt %) and $Bu_4N^+C_2F_5CO_2^-$ (1:1) with increasing amounts of $Bu_4N^+BF_4^-$. d) TEM image of $[Ag\text{-}2]C_2F_5CO_2$ in H_2O (0.3 wt %) stained with RuO_4.

to that observed in the gel state (Figure 3b), thus demonstrating that the chain conformation transforms into a *trans*-like state.[10] It should be noted that the addition of more $C_2F_5CO_2^-$ ions (up to 2 equivalents) did not further change the spectrum. This process was reversed by the addition of BF_4^- ions to give a gel (Figure 3c). Remarkably, TEM images indicate that there is a dramatic change in morphology on replacing BF_4^- with $C_2F_5CO_2^-$ ions. In contrast to that of the gel of $[Ag\text{-}2]BF_4$, the TEM image of the homologous complex, $[Ag\text{-}2]C_2F_5CO_2$, shows discrete ribbonlike aggregates with lengths of 0.7–1.3 μm and widths of 20–40 nm (Figure 3d), which indicates that the size of counteranion has a profound effect on the nanoscale structure and macroscopic properties of the complex. In light of the *trans*-like conformation of the coordination chains as confirmed by fluorescence spectroscopy, we consider these ribbonlike aggregates to be based on a discrete layered structure in which the coordination chains adopt an unfolded zigzag conformation. An inspection of the molecular models indi-

cates that the $C_2F_5CO_2^-$ ion is too large for the cavity formed by the *cis*-like conformation of the polymer chains and thus the chain conformation is likely to adopt an unfolded *trans*-like state for efficient binding of the larger counteranion while maintaining close packing of the rigid segments.

We performed ^{19}F NMR spectroscopic experiments to further investigate the role of added $C_2F_5CO_2^-$ ions in the structural change. The ^{19}F NMR spectrum of a D_2O gel of complex [Ag-**2**]BF_4 shows a resonance at $\delta = -151.85$ ppm along with a resonance from a minor isotope at $\delta = -151.80$ ppm, which is downfield with respect to those of free BF_4^- ion (Figure 4). This result suggests that BF_4^- ions
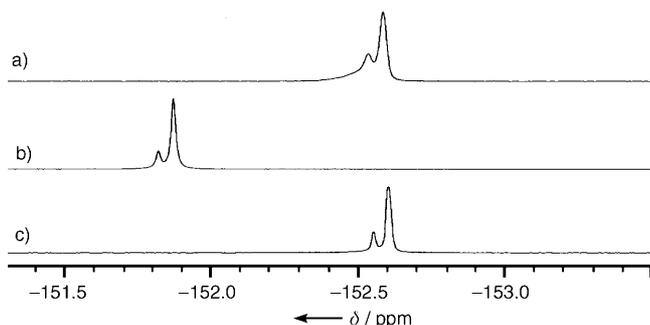
Figure 4. Comparison of ^{19}F NMR spectra in D_2O (470 MHz, 298 K): a) free AgBF$_4$; b) [Ag-**2**]BF$_4$ (5 wt%); c) [Ag-**2**]BF$_4$ (5 wt%) after the addition of 1 equiv of Bu$_4$N$^+$C$_2$F$_5$CO$_2^-$. The chemical shifts were measured as upfield shifts relative to that of CFCl$_3$ as an external standard.

are entrapped within the helical chains.[17] The downfield shift observed for the entrapped anions is due to their coordination to Ag$^+$ ions. Upon addition of 1 equivalent of Bu$_4$N$^+$C$_2$F$_5$CO$_2^-$ to the gel of [Ag-**2**]BF$_4$, however, the signal at $\delta = -151.85$ ppm shifts to -152.60 and the signal from the minor isotope, $\delta = -151.80$ ppm, shifts to -152.55 ppm. These shifts indicate the release of entrapped BF$_4^-$ ions through the modification of the helical conformation. Together with fluorescence spectra, these results demonstrate that this anion exchange triggers release of the entrapped BF$_4^-$ ions with concomitant transformation of the folded helical structure into an unfolded zigzag conformation. Consequently, this conformational change of the coordination chains gives rise to a significant structural change from elongated fibers into discrete ribbonlike aggregates thereby sol–gel interconversion. Therefore, the helical conformation of the coordination chain is most probably the principal driving force for the gelation of the complexes in water.

The results described herein demonstrate that the reversible coordination polymers self-assemble into a helical structure which, in turn, forms an entangled fibrillar network thereby immobilizing the solvent. Remarkably, the aqueous gels were observed to transform rapidly into fluid solutions with counteranion exchange of BF$_4^-$ with F$^-$ or C$_2$F$_5$CO$_2^-$, which can be used to trigger reversible sol–gel phase transition. This sol–gel interconversion in response to external stimuli is attributed to depolymerization or transformation of the folded helical conformation into an unfolded zigzag conformation of the coordination chains; there is

subsequent structural change from elongated fibers to discrete ribbons with counteranion exchange. These results are a significant example of changing the size of an entrapped guest in a self-assembling system providing a useful strategy to create stimuli-responsive smart nanoscale materials with functions that can be produced at any time on demand.

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[16] Dynamic light scattering (DLS) experiments performed with this solution (1 wt%) indicated the presence of aggregates of a narrow size distribution with an average hydrodynamic radius of about 1.1 μm (Supporting Information).

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