

Dynamic Extension–Contraction Motion in Supramolecular Springs

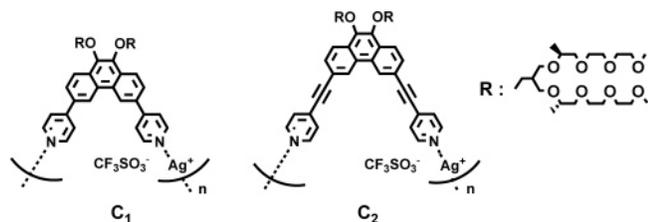
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One of the most significant recent highlights in the field of supramolecular polymer chemistry is the development of folded helical structures which are important modules in the engineering of functional nanoobjects such as nanotubes, nanowires, and nanomachines.¹ In particular, helical architecture that undergoes conformational changes triggered by external stimuli has received attractive attention during recent years.^{2,3} Although DNA and proteins are well-known to exhibit molecular motions in response to external stimuli,⁴ synthetic helical systems to mimic the molecular motions of complicated biological systems remain challenging. With this in mind, we have become interested in the preparation of stimuli-responsive helical chains by using supramolecular coordination polymers with bent conformations.⁵

In this Communication, we present the formation of supramolecular springs with switchable pitch, from the aqueous self-assembly of supramolecular coordination polymers (Figure 1). We have synthesized the coordination polymers based on Ag(I) ion complexed with pyridine ligands with a bent conformation and investigated their dynamic self-assembling behavior in aqueous solution. The ditopic bridging ligands based on phenanthrene and pyridine units were selected as helical building blocks and were synthesized according to previously reported similar methods.⁵ The resulting pyridine ligands were complexed with AgOTf to afford the coordination chains, **C**₁ and **C**₂.



The aggregation behavior of the coordination polymers in aqueous solution was subsequently investigated by using fluorescence and circular dichroism (CD) spectroscopies. The fluorescence spectra showed that the emission maxima of the coordination polymers were red shifted (~ 15 nm) with respect to those of the ligands, and the fluorescences are significantly quenched, indicative of aggregation of the aromatic units (Figure S3).⁵ The CD spectra of the polymers showed strong CD signals over the absorption ranges (Figure 2a), indicating the formation of a helical structure with a preferred handedness.^{2,6} Dynamic light scattering (DLS) experiments showed that both **C**₁ and **C**₂ self-assemble into cylindrical aggregates (Figures S4 and S5).^{7,8} The evidence for the formation of helical structures was also provided by transmission electron microscopy (TEM) experiments. As shown in Figure 2b, the TEM image of **C**₂ with a negative stained sample shows elementary cylindrical fibers with a uniform diameter of about 6.5 ± 0.4 nm and lengths of several micrometers.⁹

Remarkably, the aqueous solutions of the coordination polymers were shown to reversibly transform from transparent to translucent

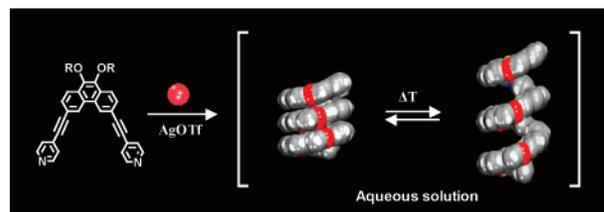


Figure 1. Schematic representation of a reversible helical spring.

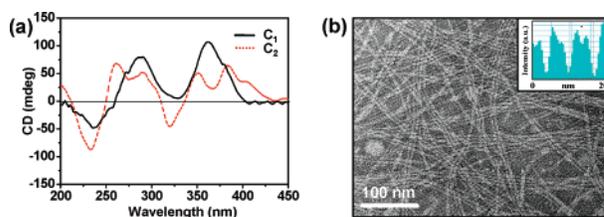


Figure 2. (a) CD spectra for **C**₁ and **C**₂ in aqueous solution (0.1 wt %) at 25 °C. (b) TEM image of **C**₂ with density profile inset.

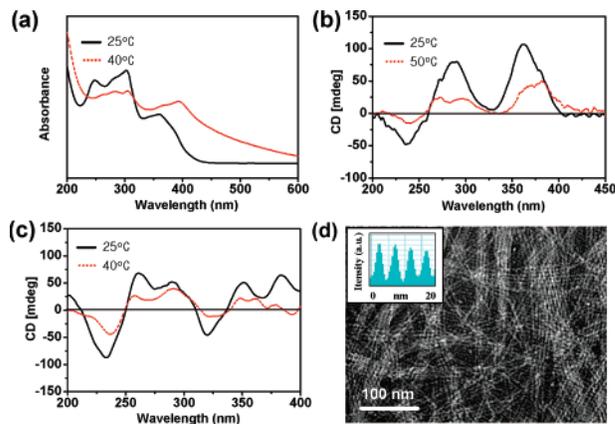


Figure 3. (a) UV/vis spectra of **C**₂ and CD spectra of (b) **C**₁ and (c) **C**₂ (0.1 wt % aqueous solutions) with temperature variation. (d) TEM image of **C**₂ with density profile inset (prepared at 50 °C).

states above certain temperatures. Accordingly, the transition temperatures of **C**₁ and **C**₂ were determined by turbidity measurements by using UV–vis transmittance to be 48 and 38 °C, respectively (Figure S6). Interestingly, the absorption spectra sharply changed above the transition temperatures, accompanied by notable changes in the CD patterns (Figure 3). At high temperatures, absorption spectra of **C**₁ and **C**₂ were significantly red shifted (10 and 20 nm, respectively) with respect to those at low temperatures, indicating that the coordination polymers adopt longer conjugation length.^{2,10} The CD spectra, upon heating, showed red-shifted signals and significant decreases in intensity, which are attributed to the diminished exciton coupling between aromatic stackings due to elongated conjugation length. To corroborate the aggregation structure above the transition temperatures, TEM experiments were performed with both samples prepared at 50 °C. The TEM images

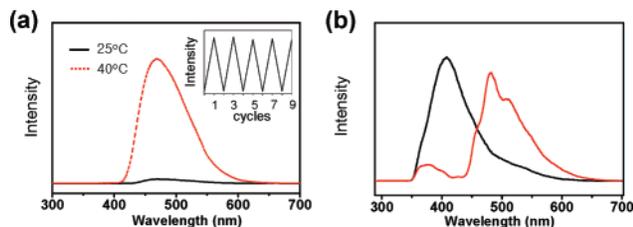


Figure 4. (a) Fluorescence spectra and reversible switching cycles of emission intensity in aqueous solution of C_2 (0.1 wt %, excited at 280 nm) with temperature variation. (b) Fluorescence spectra of C_3 (1 wt % aqueous solution) in the absence (black, solid line) and in the presence (red, dashed line) of 5 equiv of perylene at 40 °C (excited at 280 nm).

of both coordination polymers revealed bundles of the elementary cylindrical objects aligned in a parallel fashion, indicating that the 1-D structure in shape remains unchanged upon heating. However, there is a significant decrease in the cross-sectional dimensions of the cylindrical objects upon heating. The density profile of C_2 taken perpendicular to the long axis of the bundle showed the diameter to be about 5.5 ± 0.4 nm (Figure 3d), indicative of 15% reduction in cylindrical width compared to that taken at room temperature.¹¹ Similarly, C_1 also showed 14% reduction in cylindrical width upon heating (Figure S9). These results suggest that the helical strands are elongated accompanied by a decrease in the cross-sectional width. The fluorescence spectra of C_2 , upon heating, showed a significant increase in the emission intensity (Figure 4a), indicative of separation between the adjacent aromatic units within the helical fiber due to breakup of π - π stacking interactions.¹² To provide further evidence of the helical spring motion, fluorescence resonance energy transfer (FRET) and 2-D NMR experiments were performed with model complex C_3 .¹³ The FRET experiments with C_3 and perylene dye showed efficient energy transfer to occur only above lower critical solution temperature (LCST), clearly indicating that the π -stacked helical chains are extended upon heating (Figure 4b). This extension of the helical chains was further evidenced by preliminary 2-D NMR experiments with C_3 , showing the extended π -stacking NOE correlations above LCST, again demonstrating the extension of the helical chains.

These results can be explained by considering a LCST behavior of the ethylene oxide chains in aqueous medium.¹⁴ At room temperature, the ethylene oxide chains are fully hydrated and thus adopt a random coil conformation. Above the LCST, however, the ethylene oxide chains would be dehydrated to collapse into a molecular globule due to the loss of the hydrogen bonding between ether oxygens and water molecules. This dehydration of the ethylene oxide dendritic chains was confirmed by ^1H NMR measurements. Upon heating above the LCST, the resonances associated with the ethylene oxide segments were shifted upfield (Figure S8), clearly demonstrating the loss of hydrogen-bonding interactions between ether oxygens and water. Consequently, the conformational transformation of the side ethylene oxide dendritic chains into a dehydrated molecular globule drives the π -stacked helical structure to be unstable due to steric crowdings between the globules with greater cross-sectional area. To relieve the steric crowdings at the interface, the helical strands would be extended to allow a larger interfacial area, thus lowering total free energy, as evidence by TEM.

The unique feature of the coordination polymers investigated here is their ability to adopt a helical structure that displays

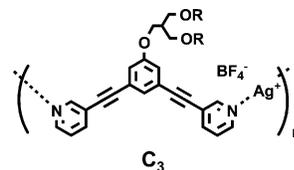
reversible extension–contraction motions, triggered by temperature. It is also notable that this dynamic conformational change leads to a fluorescence switching between the fluorescent stretched and nonfluorescent compressed states of the supramolecular springs (Figure 4a, inset). Such mechanical motions of the supramolecular spring may offer intriguing potentials for dynamic nanodevices, optical modulators, and fluorescent thermometers.

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Supporting Information Available: Synthetic procedures, characterization, SLS, DLS, TEM, NMR, and calculated helical conformation of C_2 . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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