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Aqueous nanofibers with switchable chirality formed of self-assembled dumbbell-shaped rod amphiphiles†

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We have demonstrated that fibrillar aggregates formed from the self-assembly of a dumbbell-shaped rod amphiphile undergo a reversible chiral–non-chiral transition triggered by temperature.

The construction of helical nanostructures is of growing interest in interdisciplinary areas combining chemistry, biology and materials science, because they are ideally suited for the design of intelligent materials.[1,2] Supramolecular helices can be generated through the intermolecular assembly of chiral building blocks.[3] Transfer of chiral information through the molecular assembly provides another strategy to construct elongated helical aggregates.[4] One of the most important strategies available to form these aggregates arises from twist stacking of rigid aromatic segments containing chiral side chains.[5] Although the introduction of helicity into one-dimensional fibrillar aggregates has been extensively studied through grafting chiral side groups, their switching behavior in response to external stimuli remains a challenge.[6]

In this Communication, we present the formation of aqueous nanofibers with switchable supramolecular chirality from the self-assembly of dumbbell-shaped molecules (Fig. 1). Notably, the helicity of the non-chiral nanofibers is induced in a reversible way upon heating. The self-assembling dumbbell-shaped molecules consist of a carbazole end-capped phenanthrene as a rigid stem and chiral oligoether segments laterally attached to the carbazole units as flexible chains, and were synthesized according to previously reported similar methods (Scheme 1).[7]

The dumbbell-shaped molecules can self-assemble into an aggregate structure in an aqueous solution because of their amphiphilic characteristics. The aggregation behavior of the molecules was subsequently studied in aqueous solution by using dynamic light scattering (DLS), transmission electron microscopy (TEM), and absorption and emission spectroscopies. The CONTIN analysis of the autocorrelation function of **1** shows a broad peak that corresponds to a hydrodynamic radius (R_H) of ∼250 nm (ESI, Fig. S2†). To confirm the aggregation structures, TEM experiments were performed. As shown in Fig. 2a, the image of **1** with a negatively stained sample shows elongated fibers with a uniform diameter of about 5 nm and lengths of several micrometres. Considering the extended molecular length (5.3 nm by CPK modeling), this image indicates that the diameter of the elementary cylindrical objects corresponds to one molecular length. This result suggests that molecule **1** self-assembles into fibrillar aggregates consisting of hydrophobic aromatic segments surrounded by hydrophilic oligoether segments that are exposed to the aqueous environment (Fig. 1). Within the core, the rod segments stack on top of each other with mutual rotations to reduce steric repulsions between the bulky dibranched oligoether chains. Interestingly, when the aqueous solution was subjected to circular dichroism (CD) measurements at room temperature, no CD signals could be detected even though **1** contains chiral side groups. This indicates that the fibrillar objects are non-chiral, even though the rods contain chiral side chains.

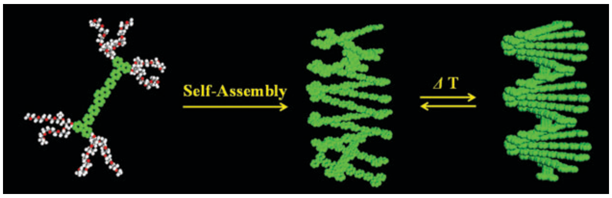
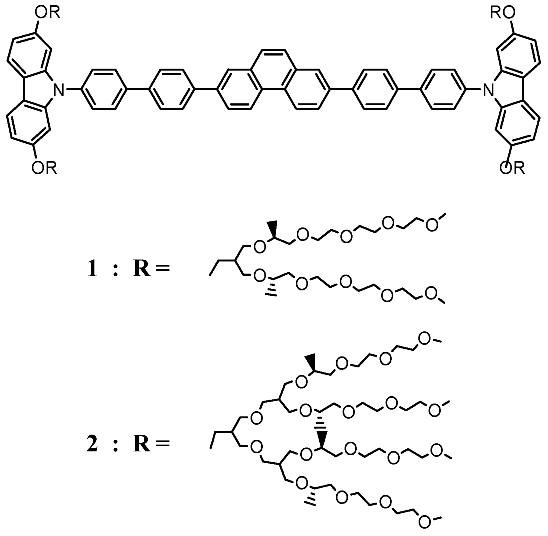


Fig. 1 Schematic representation of the reversible transformation from achiral extended to chiral compressed states of the cylindrical stack.

The formation of long nanofibers with a hydrophilic oligoether exterior suggests that they may lead to temperature-dependent solution behavior due to the lower critical solution



Scheme 1 Molecular structure of the dumbbell-shaped aromatic amphiphiles

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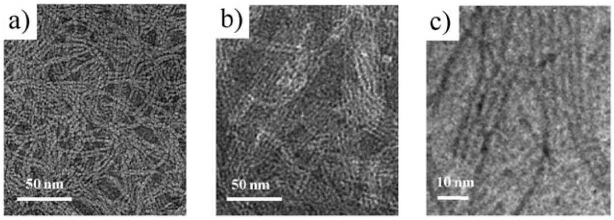

Fig. 2 TEM images (negatively stained with uranyl acetate) of aqueous solutions of **1** prepared (a) at 30 °C and (b) at 60 °C. (c) A cryo-TEM image of an aqueous solution of **1** prepared at 60 °C.

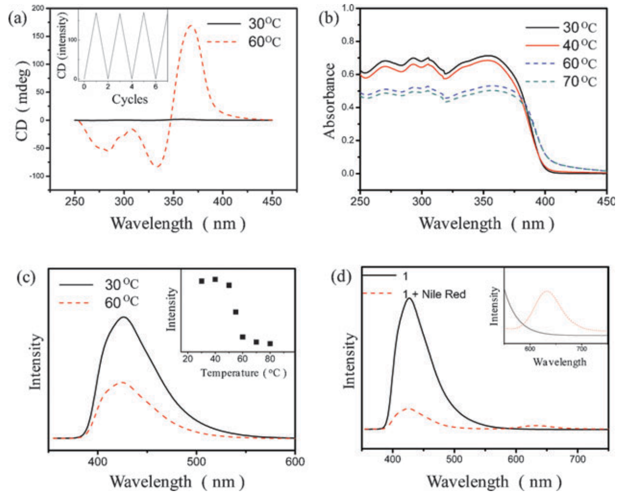

Fig. 3 (a) CD spectra and reversible switching cycles of the intensity at 370 nm in an aqueous solution of **1** (0.01 wt%); (b) UV-vis, and (c) fluorescence spectra of **1** (0.01 wt%) with temperature variation (inset: 425 nm intensity of **1** upon cooling from 80 to 30 °C); (d) fluorescence spectra of **1** (0.01 wt% aqueous solution) in the absence and in the presence of 1 equiv. of Nile Red at 30 °C (excited at 355 nm, inset: magnification between 550 and 750 nm).

temperature (LCST) behavior of the oligoether chains.[8] The transition temperature was subsequently determined to be 55 °C by turbidity measurements using UV-vis transmittance (ESI, Fig. S1†). TEM images at higher temperatures than the LCST also revealed elementary fibrillar objects with a diameter of ~5 nm (Fig. 2b), indicating that the elongated nanofibers remained unchanged in shape upon heating. The existence of the fibrillar aggregates at higher temperatures was further confirmed by cryo-TEM and DLS measurements at 60 °C (Fig. 2c and ESI, Fig. S2†). However, the CD spectra showed a strong Cotton effect above the transition temperature accompanied by notable changes in the absorption and emission spectra (Fig. 3a), indicating the formation of helical stacks of the rod segments with a preferred handedness.[5*b*] To prove that the CD signal was not from artifacts, linear dichroism (LD) experiments were performed at different temperatures (ESI, Fig. S4†).[9] The LD values appeared to be negligibly smaller than those arising from CD, demonstrating that the CD signal was from molecular assemblies.[10] Upon heating, the intensity of the absorption spectra is significantly reduced and the fluorescence is quenched (Fig. 3b and c), indicating that the π–π stacking interactions between the aromatic rods are enhanced.[11] These results suggest that the helicity induction of the nanofibers upon heating arises from closer packing between the adjacent aromatic units within the core. The strengthened π-stacking interactions would lead to a more planar conformation of the rod segment. This is reflected in the bathochromic shift of an absorption maximum in UV, which is attributed to the transformation into longer effective conjugation length.

To gain more insight into the π–π stacking interactions with temperature variation, fluorescence resonance energy transfer (FRET) experiments were performed with a hydrophobic dye, Nile Red. When the aqueous solution of **1** containing Nile Red is excited at 355 nm at higher temperatures, the fluorescence shows only a strong emission maximum at 425 nm corresponding to aggregated aromatic segments of **1** (ESI, Fig. S5†). However, on cooling to room temperature, the emission intensity at 425 nm sharply decreases with the concomitant formation of an emission at 620 nm, demonstrating that energy transfer occurs only below the LCST, indicative of separation between the adjacent rods within the fibers (Fig. 3d).[12] This result suggests that the nanofibers are somewhat lengthened through loose packing of the aromatic segments on cooling.

Based on these results, the rod segments within the cylindrical fibers at lower temperatures can be considered to be loosely stacked with each other to reduce steric repulsions between the bulky oligoether chains. This packing frustration would allow the rod segments to rotate in a random way within the cores to block the chiral transfer from the side groups to the aromatic cores, leading to non-chiral fibers. Above the LCST, however, the ethylene oxide chains would be dehydrated and collapse into molecular globules with reduced effective volume, leading to a decrease in steric repulsions between the oligoether chains.[8] This shrinkage, together with enhanced hydrophobic environment, leads to the increased strength of the π-stacking interactions with restricted rotational freedom, and helical stacks are formed with a reduced angle between the rod axis. Consequently, the non-chiral fibers, upon heating above the LCST, are reversibly transformed into one-handed helical fibers through enhanced π–π stacking interactions (Fig. 1).

To corroborate the role of the cross-sectional area of the oligoether chains in the helicity induction, molecule **2**, based on a tetrabranched oligo(ethylene oxide) chain, was investigated. Similar to **1**, molecule **2** is also self-assembled into fibrillar aggregates, as confirmed by TEM and DLS experiments (see the ESI†). However, **2** shows the absence of the Cotton effect at room temperature, and remains unchanged even above the LCST transition (ESI, Fig. S6†), indicating that the disordered packing of **2** is retained even above the LCST due to steric crowding between bulky tetrabranched chains. These results strongly support the idea that the cross-sectional area of the oligoether chain plays a crucial role in the reversible chiral switching behavior of the fibrillar aggregates.

In summary, the results described herein demonstrate that non-chiral nanofibers can be reversibly switched to a chiral state, triggered by external stimuli. The helicity induction of the nanofibers takes place through molecular reorganization within the aromatic core on heating. It is worth noting that, upon heating, the helicity induction in the non-chiral nanofibers represents a remarkable contrast to other supramolecular nanofibers that dissolve into molecular components and/or smaller non-chiral aggregates.[5a,6b,13] Such fibrillar aggregates with dynamic structural changes may provide a new strategy for the construction of supramolecular device with chiroptical switching behavior.

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