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Controlled Helicity of the Rigid-Flexible Molecular Assembly Triggered by Water Addition: From Nanocrystal to Liquid Crystal Gel and Aqueous Nanofibers

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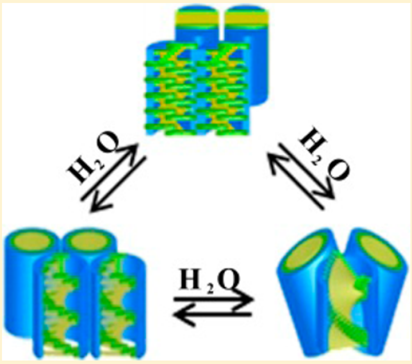
Supporting Information

ABSTRACT: Despite recent advances in synthetic nanometer-scale helical assembly, control of supramolecular chirality remains a challenge. Here, we describe the fine-tuning of the shape and morphology transitions of twisted and helical assembly from dumbbell-shaped rigid-flexible amphiphile triggered by concentration. The amphiphile **2** self-assembles into nonchiral 3D columnar crystals with alternative packing of aromatic segment in solid state. Remarkably, with the addition of water into the solid, the achiral crystal transforms into 2D hexagonally ordered liquid crystal gel with supramolecular chirality due to increased entropy of flexible coil in aqueous environment. Notably, the helical liquid crystal gel was observed to dissolve into optically active aqueous nanofibers caused by a conformational change of hydrophobic aromatic rods and enhanced hydro-volume of the ethylene oxide chains.



1. INTRODUCTION

The chiral induction from molecular level into well-defined supramolecular nanostructure has been the subject of intense study in recent years both for life and materials science.[1−6] In general, the chirality of supramolecular systems can be generated by the assembly of chiral molecules through $\pi-\pi$ stacking,[7−9] hydrogen bonding,[10−12] electrostatic interactions,[13,14] and coordination.[15,16] Among them, chirality control of the helical architectures is one of the highlighted topics in the applications of chiral and sensing materials.[17−19] The majority of these studies are reported in polymers,[20−23] liquid crystalline phases,[24] or host−guest complexes[25−28] systems by changing the external conditions such as solvent, temperature, light, pH, or by interaction with specific guests. Previously, we have reported that fibrillar aggregates with reversible chiral-nonchiral states could be obtained from a dumbbell-shaped rigid-flexible amphiphile triggered by lower critical solution temperature (LCST) of flexible oligoether dendritic chains in aqueous solution.[29,30] We have also found that the introduction of ethylene oxide segment into aromatic rod gave rise to morphological transformation from isotropic solution to rigid gel upon heating.[31,32] The senses of chirality in self-assembled systems are ascribed to a change of helical twisting power (HTP) or a conformational change of the molecular backbones due to supramolecular aggregations.[33−37] Although stimulus-responsive synthesized helix has been extensively studied, the mechanism for the morphological twisting and bending remains a challenge.[38,39]

Herein, we report the formation of concentration responsive helical assembly from the dumbbell-shaped rigid component as a stem segment connected with a chiral oligoether chains as a flexible part (Scheme 1) and investigate the chiral amplification in the bulk, gel, and aqueous solution. Because of hydrogen bonding and steric constraints, a new approach for the helicity control from morphological transformation could be found by dissolution of bulk solid.

2. EXPERIMENTAL SECTION

The synthesis of the rigid-flexible amphiphiles was performed with the preparation of chiral oligoether chains and 9-arylcarbazole aromatic scaffold according to the procedure described previously.[29,30] The resulting compounds were subjected to an etherification reaction, and thereafter, the final compound was successfully synthesized by Suzuki coupling with the biphenyl units. The analytical data from the resulting molecules are in full agreement with the expected chemical structures.

3. RESULTS AND DISCUSSION

The aggregation behavior of **1** and **2** in the bulk was investigated by means of differential scanning calorimetry (DSC), thermal optical polarized microscopy, and X-ray scatterings. All of the block molecules show an ordered structure, and the transition temperatures were determined from DSC scans (Figure 1A).

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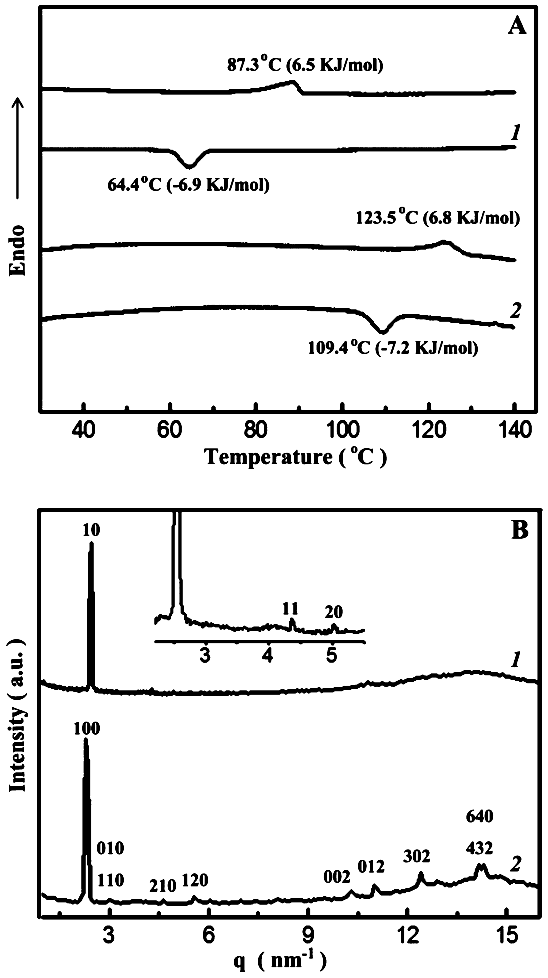


Figure 1. (A) DSC traces (10 °C/min) recorded during the heating and the cooling scan of **1** and **2**. (B) X-ray diffraction patterns of **1** and **2** against q ($q = 4\pi \sin 2\theta/\lambda$) at room temperature (the inset is a partial of SAXS of **1**).

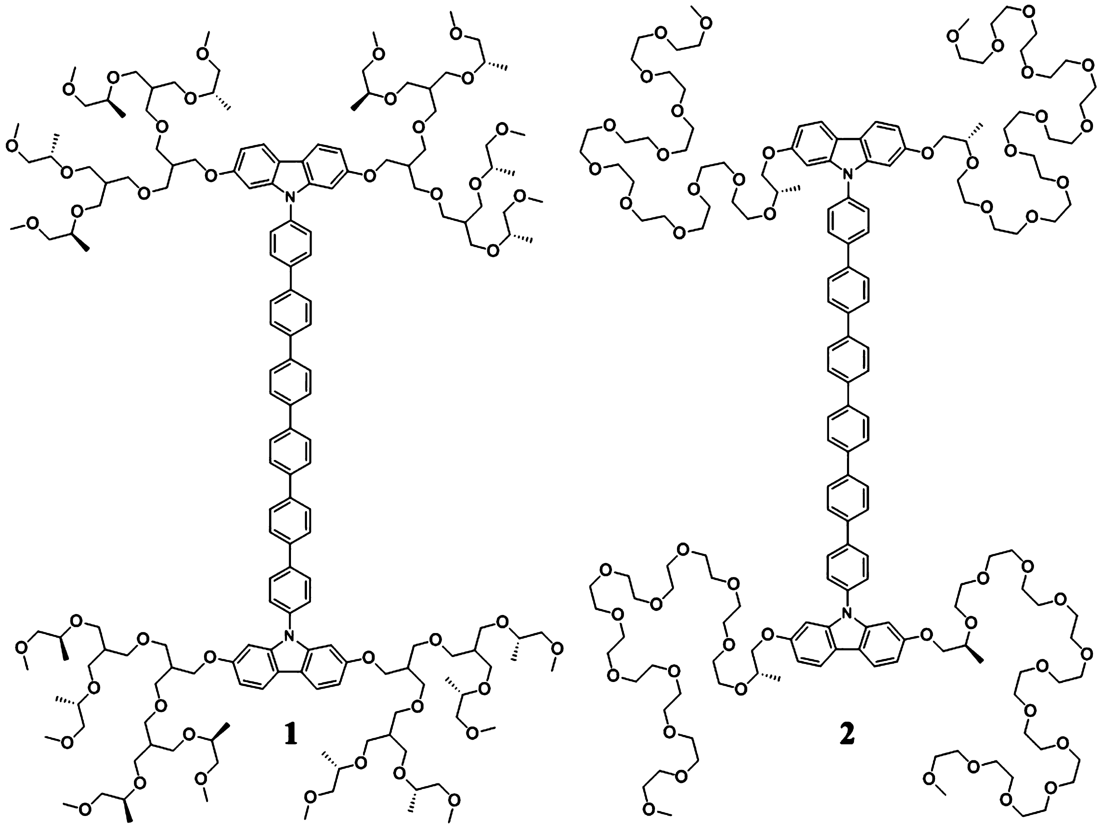
The DSC thermograms showed **1** melts into isotropic liquid at 87.3 °C. On slow cooling from the optically isotropic phase of **1**, the formation of unique domains that correspond to a hexagonal columnar texture could be observed between crossed polarizers (Figure S2A, Supporting Information). This aggregated structure of **1** was further confirmed by X-ray scattering experiments. The small-angle X-ray diffraction (SAXS) pattern of **1** displayed three sharp reflections with the ratio of $1{:}\sqrt{3}{:}2$ in the low-angle region that can be assigned as a 2D hexagonal columnar structure with a lattice constant of 2.8 nm. The wide-angle X-ray diffraction pattern only shows a diffused halo, which is due to liquid crystal packing of the rod segments (Figure 1B). To further understand the 2D structures, we performed circular dichroism (CD) measurements with thin film of **1**. As shown in Figure 2A, the liquid crystal of **1** gives positive Cotton effect in the spectral range of the aromatic units, indicating the helical stacks of the rod segments with a preferred handedness.[40,41] To prove that the CD signal was not from artifacts, linear dichroism (LD) experiments were performed. Figure S3, Supporting Information, shows the LD values appeared to be negligibly smaller than those arising from CD, demonstrating that the CD signal was from molecular assemblies. In order to better confirm the formation of helical structures, we calculated the number (n) of molecules in a unit cell of the column. From the lattice constants and measured density, the average number of molecules in a unit cell of the column was estimated to be one. On the basis of these results and extended aromatic length (3.3 nm by Corey−Pauling−Koltun (CPK) molecular model), we consider that the neighboring aromatic segments are stacked along the c axis with mutual rotation to minimize a steric repulsion between bulky dendritic segments to adopt helical arrangements.

We envisioned that a reduction of the cross-sectional area of the flexible dendritic chain would result in the formation of crystal aggregates.[42,43] Indeed, the SAXS of **2** based on linear coil shows a number of sharp reflections at room temperature with some new peaks at wide angle (Figure 1B), indicative of the existence of a highly ordered nanoscopic structure with three distinct lattice parameters. These reflections indeed can be indexed as an oblique columnar crystalline structure with lattice parameters a = 3.0 nm, b = 2.3 nm, c = 1.2 nm, and γ = 67°. Similar to that of **1** recorded at room temperature, the average number of molecules is calculated and showed each bundle consists of two molecules. However, in contrast to **1**, no CD signal could be detected from annealed sample **2**, indicating that the aggregated structure is optically slight even though **2** contains chiral side groups. On the basis of these results, a possible model is responsible for the generation of the nonchiral columnar structure. The rod of **2** based on linear branched coil has a strong tendency of anisotropic crystalline ordering to drive the rod segments to aggregate in one dimension with an ABAB arrangement through microphase separation between incompatible molecular components and π−π stacking interactions, thus, frustrating the chiral transfer from the side groups to the aromatic cores, leading to a nonchiral column.

This structural progression from chiral to nonchiral columnar formation suggests that the strongly packed crystal of **2** would exhibit water-responsive chiral behavior due to the hydrophilic ethylene oxide interacting with water molecules to increase the coil volume.[44] As shown in Figure 2C and S4, Supporting Information, upon the addition of water, the compound of **2** at high concentration (60−10 wt %) undergoes turbid gelation. The optical polarized micrograph of the gels showed a birefringent texture, which was typical of a liquid crystalline phase (Figure S2B, Supporting Information). Optical experiments reviewed the gel, which before and after evaporation shows similar aggregated structures (Figure S5, Supporting Information). As a further analysis, small-angle X-ray scattering experiments were performed with dried film of the gel. The small-angle X-ray scattering pattern from 35 wt % aqueous solution of **2** also displayed three broad reflections with the ratio of $1{:}\sqrt{3}{:}2$ in the low-angle region, which corresponds to hexagonal ordering with a lattice constant of 2.8 nm (Figure S2C, Supporting Information). Notably, the CD spectra of the gel showed strong CD signals over the absorption ranges (Figure 2B), indicating the formation of helical structure with a preferred handedness. The CD spectra did not change appreciably when the concentration diluted to 10 wt %, suggesting that the helical structure is stable within gel state.

As expected, the liquid crystal gel transforms into a fluid solution as the concentration decreased to 6 wt %. Interestingly, the absorption spectra sharply changed with further dilution from the gel, accompanied by notable changes in the CD patterns. In dissolved solution, absorption spectra of **2** was significantly blue-shifted 20 nm with respect to liquid crystal gel (Figure 2D), indicating that the effective conjugation within aromatic rod is reduced.[45] The CD spectra in aqueous solution of **2** showed that bisignate CD signal accompanied the absorption

Scheme 1. Molecular Structure of the Dumbbell-Shaped Aromatic Amphiphiles



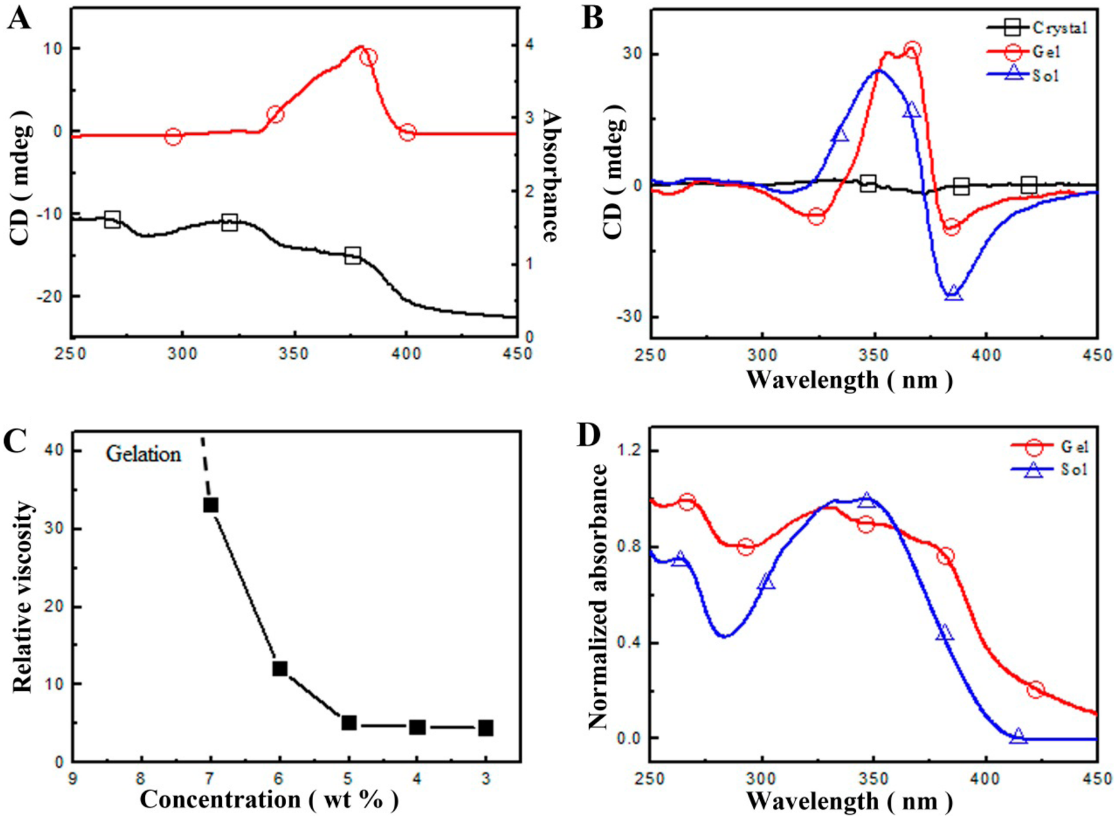


Figure 2. (A) Absorption (black and square) and CD (red and circle) spectra of thin films of **1**. (B) CD spectra of **2** in solid state (black and square), in gel state (red and circle), and in aqueous solution (blue and triangle, 0.003 wt %). (C) Relative viscosities of **2** in aqueous solution. (D) Normalized absorption of **2** in gel state (red and circle), and in aqueous solution (blue and triangle).

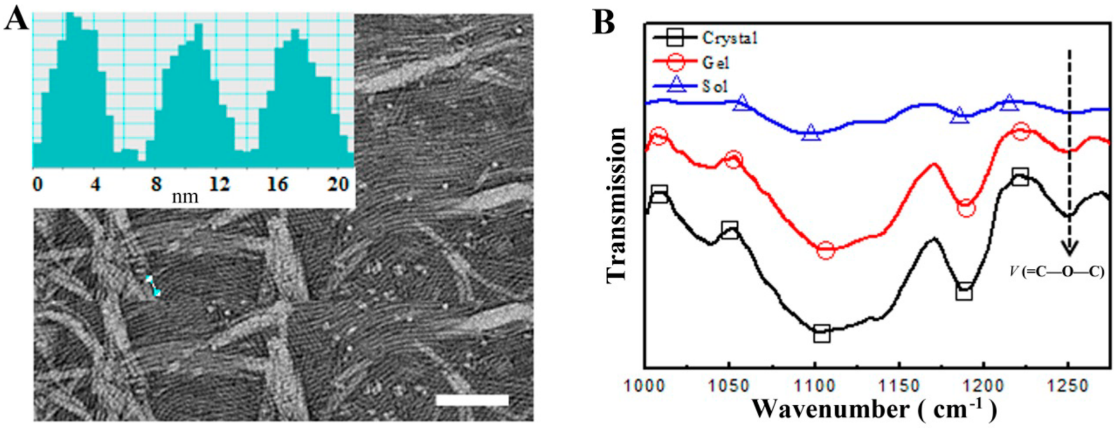


Figure 3. (A) TEM image of **2** from 0.01 wt % aqueous solution with density profile inset (scale bar, 100 nm). (B) FTIR spectra (1000−1275 cm^{-1}) of **2** in solid (black and square), gel (red and circle), and aqueous solution (blue and triangle).

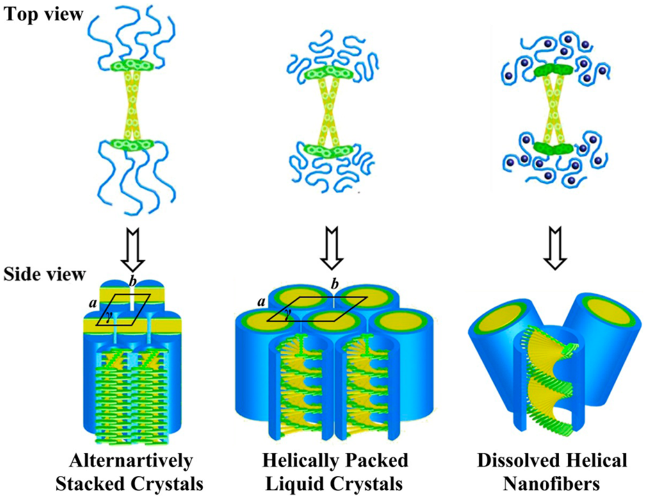


Figure 4. Schematic representation of water induced helical assembly from nonchiral crystal to chiral liquid crystal gel and chiral aqueous nanofibers.

band, which is attributed to the diminished excition coupling between aromatic stacking due to reduced conjugation length (Figure S5C, Supporting Information). To corroborate the dissolved aggregation, TEM experiments were performed. When the aqueous solution (0.01 wt %) is cast onto a TEM grid, then stained with uranyl acetate reveals one-dimensional cylindrical fibers with a uniform diameter of about 5.6 nm (Figure 3A). Considering the observed lattice of the hexagonal columnar structures from the liquid crystal gel of **2** is 2.8 nm, the increase of diameter may be caused by hydrogen bonding between ether oxygen and water molecules. The hydrated feature is reflected in FTIR spectroscopic experiments. The IR of **2** from crystal and gel states showed two characteristic bands at 1250 and 1105 cm^{-1}, which corresponds to phenyl ring-O and aliphatic C−O stretching, respectively. However, the band at 1105 cm^{-1} shifted to 1097 cm^{-1} in aqueous solution, indicating that the oligoether chains are hydrated through hydrogen bonding interaction (Figure 3B).[46]

This unique feature of induction of chirality can be explained by enhanced entropy of hydrophilic ethylene oxide coil and variation in hydrodynamic volumes. When amphiphilic crystal of **2** was exposed to aqueous solution, the coil wrapped up hydrophobic aromatic rods and increased the cross-sectional area of rigid-flexible segments to weaken anisotropic interaction leading to the molecular chirality amplified into a one-dimensionally stacked nanostructure. In diluted solution, the ethylene oxide chains would be fully hydrated to increase the effective volume fraction of oligoether chains, which requires a larger interfacial area. To avoid the hydrophobic aromatic rod confront in aqueous environment, the rod segments would be slightly twisted to generate bigger hydrophobic area, giving rise to a new helical arrangement (Figure 4).

4. CONCLUSIONS

In summary, we have demonstrated that dumbbell-shaped aromatic amphiphile self-assembles into columnar crystal, liquid crystal gel, and aqueous nanofibers consisting of aromatic cores surrounded by hydrophilic oligo(ethylene oxide) coil. In the solid state, the molecules were observed to self-assemble into nonchiral columnar crystals with alternative packing of aromatic segment. Notably, these crystals were shown to recognize water by inducing supramolecular chirality. When the crystal exposed to aqueous environment, the achiral crystal transforms into 2D hexagonally ordered liquid crystal gel with supramolecular chirality due to both entropy enhancement of hydrophilic ethylene oxide coils and variation of anisotropic interaction of rigid rods. Additionally, in further diluted solution, the ethylene oxide chains would be hydrated and the 2D ordered liquid crystalline gel dissolved into aqueous nanofibers, which results in enhanced hydro-volume to force each aromatic rod to be twisted, forming another helical structure. The unique feature in here is their ability to adopt a tunable helical conformation with reversibility in bulk, gel, and aqueous solution, triggered by concentration. These results represent a significant example in dynamic aggregated states triggered by external stimuli in the chiral self-assembling systems, thus providing a useful strategy to create supramolecular devices with chiroptical switching behavior.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials, methods, synthesis, detailed experimental procedures, and supporting figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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