Temperature-Controlled, Reversible, Nanofiber Assembly from an Amphiphilic Macrocycle

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S Supporting Information

ABSTRACT: One-dimensional nanostructures are self-assembled from an amphiphilic arylene-ethynylene macrocycle (AEM) in solution phase. The morphology and size of the nanostructures are controlled by simply changing the temperature, reversibly switching between monomolecular cross-sectioned nanofibers and large bundles. At elevated temperature in aqueous solutions, the tri(ethylene glycol) (Tg) side chains of the AEM become effectively more hydrophobic, thus facilitating intermolecular association through side chain interactions. The enhanced intermolecular association causes the ultrathin nanofibers to be bundled, forming an opaque dispersion in solution. The reported observation provides a simple molecular design rule that may be applicable to other macrocycle molecules for use in temperature-controlled assembly regarding both size and morphology.
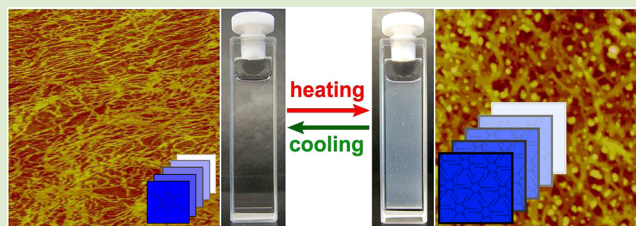
Self-assembly is a versatile and powerful method to construct well-defined nanostructures, for which the building block molecules are arranged in three dimensions through various types of intermolecular interactions. Due to their inherent shape-persistent structure and large-area delocalized π-electron system, arylene-ethynylene macrocycle (AEM) molecules are usually conducive to promoting intermolecular π−π stacking, and thus enhancing the intermolecular electronic coupling.[1−5] This in turn leads to long-range exciton diffusion and charge carrier transport.[6] For the advantages mentioned above, AEMs have been employed as building blocks in the construction of a broad range of functional materials and structures, such as porous solids,[2,7,8] sensors,[9,10] fullerene complexes,[11,12] and optoelectronic devices.[13,14] Specifically, under appropriate fabrication conditions, AEMs can self-assemble into one-dimensional (1D) nanostructures, typically nanofibers, which are well-suited for fabrication into optoelectronic nanodevices.[6,15,16]

Previously, we have studied the influence of side chains on the intermolecular stacking of AEM molecules during self-assembly,[6,15,17] for which the dimensional control of molecular arrangement may lead to formation of different shapes of nanostructures such as nanoparticles and nanofibers. However, less attention has been paid to the size control of the corresponding nanostructures; such size control is challenging through common solution based self-assembly processing. Herein, we demonstrate a simple approach to the size control of self-assembly through reversible hydrophilic and hydrophobic transition of the side chains of the AEM molecule. The building block molecule, named TgHC (as shown in Chart 1), is a hexacyclic (HC) AEM modified with six Tg side chains.

Chart 1. Molecular Structure of TgHC
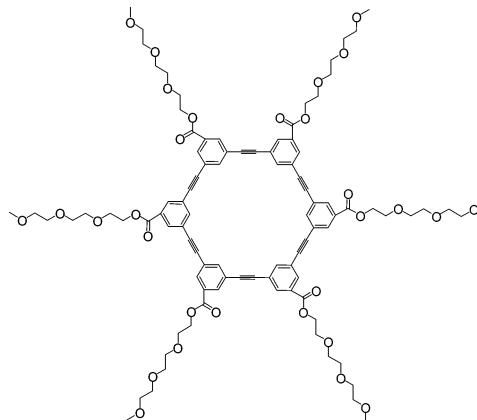
The molecule is amphiphilic with a hydrophobic central core and peripheral hydrophilic side chains. Interestingly, TgHC is highly soluble in almost all organic solvents. The high solubility makes it difficult to find an appropriate "poor" solvent to process self-assembly of this molecule. Indeed, the only solvent we have found that enables the assembly of TgHC is water. Because the hydrophilicity of Tg is highly sensitive to temperature, exhibiting hydration−dehydration transition (i.e., lower critical solution temperature behavior) in response to even a small change of temperature,[18,19] we may adjust the

intermolecular hydrophobic interactions by changing the solution temperature as evidenced in the investigations below.

The large HC skeleton in coplanar geometry with the six Tg side chains is favorable for TgHC to stack to form columnar structure via intermolecular $\pi-\pi$ interaction as evidenced previously in the surface-assisted self-assembly.[20] Upon injection from a concentrated acetone solution into water at room temperature, spontaneous self-assembly of TgHC occurs, leading to the formation of ultrafine, well-defined, nanofibril structures with lengths ranging from tens of nanometers to micrometers. Because of the small size, the water dispersion of these nanofibers looks clear and transparent, similar to molecularly dissolved solution. By fast spin-casting this clear solution on a silicon substrate, homogenously distributed nanofibers can be imaged and analyzed by the AFM, as shown in Figure 1a and Figure S1. Measurement of a large number of
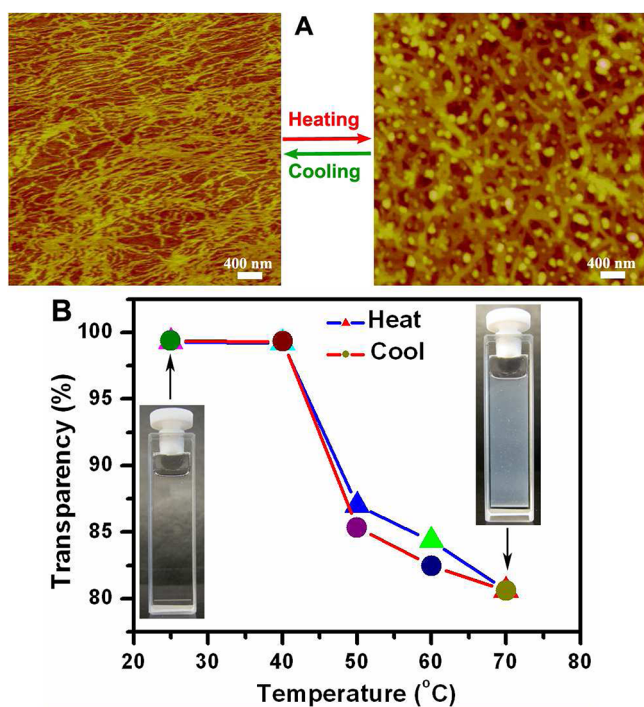

Figure 1. (A) AFM images showing the morphology of TgHC in water obtained at room temperature (left) and 70 °C (right); (B) plot showing the transparency (measured at 600 nm wavelength) of TgHC nanofibril dispersion changing with temperature, where the insets are the photographs taken over the nanofibril dispersions at room temperature and 70 °C, respectively.

nanofibers gives an average cross-sectioned height of 2.5 nm; one such line scan profile is presented in Figure S3. This size corresponds to the central skeleton size of TgHC (ca. 2.0 nm) surrounded by the six side chains collapsed into folded configuration.[20] The nanofibers thus assembled are monomolecular cross-sectioned. This assembly is presumably a consequence of the strong cofacial $\pi-\pi$ intermolecular stacking along the long axis.[20]

When gradually heating up the aqueous solution of nanofibers as prepared at room temperature, the solution remained clear and transparent up to 40 °C (Figure 1b). However, when the temperature was increased above 40 °C, the transparency was dramatically decreased and the solution became opaque, turning into a milky dispersion (right inset in Figure 1b). Further heating of the dispersion to higher

temperature eventually led to complete evaporation of the small amount of acetone solvent, resulting in a decrease in the transparency of dispersion. After an extended time at 70 °C, larger white aggregates formed, as viewed by the naked eyes. By spin coating the opaque dispersion at 70 °C onto a silicon substrate at high speed (3000 rpm), the morphology of TgHC aggregates are preserved as revealed by AFM imaging. As shown in Figure 1a (right part), the large chunks of TgHC formed at high temperature are composed of fibril bundles entangled with individual agglomerates formed during the fast ripening under high temperature. The cross sectional size of the bundles is between 40 and 140 nm.

To confirm that the temperature-induced aggregation of TgHC is a reversible process, the milky dispersion was cooled slowly from 70 °C to room temperature. As shown in Figure 1b, at the beginning of the cooling process, the transparency of the dispersion gradually increased. When it was cooled to near 40 °C, the transparency dramatically increased and the whole dispersion became clear and transparent again (left inset in Figure 1b). The transparency versus temperature profile is nearly identical to the initial heating and cooling cycle. This observation indicates that upon cooling down to room temperature the large TgHC bundles formed at high temperature are converted back into monomolecular crosssectioned nanofibers, as evidenced by the AFM imaging shown in the left part in Figure 1a. Further heating−cooling cycles gave similar results, implying that the association and dissociation process of the nanofibers is completely reversible. It should be pointed out that the nanofibril dispersion is very stable at room temperature, remaining clear and transparent after several months.

The reversible morphology transformation of nanofibers was also observed with in situ dynamic light scattering (DLS) measurements performed in aqueous dispersion under heating−cooling cycle as shown in Figure 2. At room
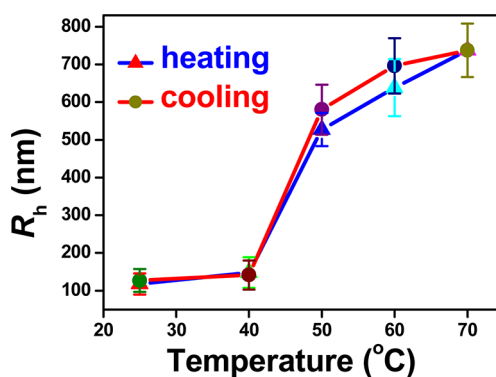

Figure 2. Temperature-dependent R_h of TgHC nanofibers measured in aqueous dispersion. The concentration of TgHC is 1.0×10^{-4} M.

temperature, the hydrodynamic radius (R_h) of TgHC fiber was measured to be about 100 nm, which is much larger than the size of individual TgHC molecules, about 3 nm, as measured by DLS in acetone solution (Figure S2). Considering the fact that TgHC nanofibers dispersed under roomtemperature are monomolecular cross-sectioned as evidenced by the AFM imaging (Figure 1a and Figure S1), we speculate that the larger R_h value measured by DLS under the same condition represents the size of random coils formed by the soft nanofibers, rather than the cross-section of individual nanofibers. When the dispersion was heated up to 40 °C, the value
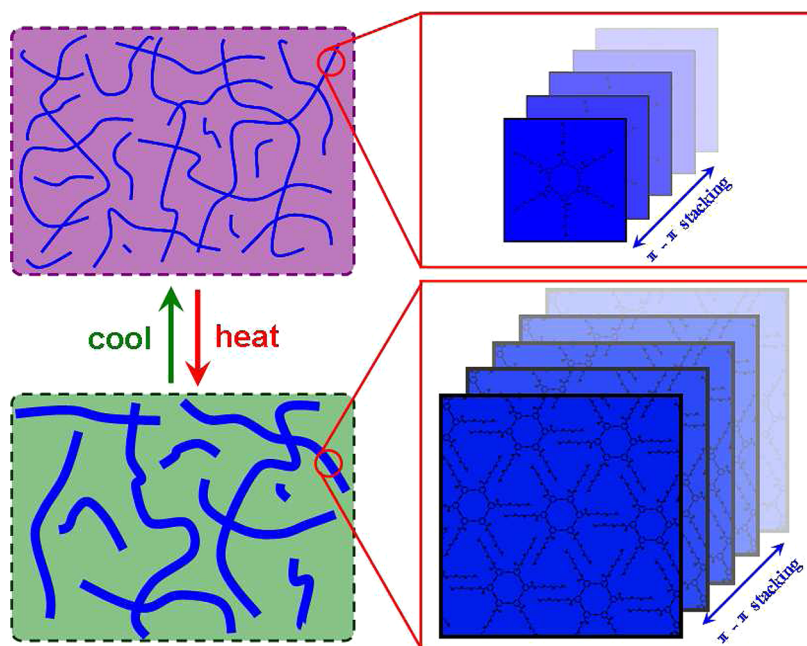
Figure 3. Schematic illustration showing the columnar molecular stacking of TgHC within the nanofibers and the temperature-controlled transformation between monomolecular cross-sectioned nanofibers (top half) and large bundles (bottom half) in water solution.

of R_h was only slightly increased likely due to the expansion of nanofibril coils. Upon further increasing the temperature above 40 °C, the averaged R_h was substantially increased, reaching about 700 nm at 70 °C, characteristic of formation of large aggregates. When cooling down the dispersion, the change of R_h follows nearly the same trend as the heating process, further confirming the reversible transformation controlled by temperature.

The above observed temperature-dependent self-assembling behavior of TgHC is mostly due to the amphiphilic property of Tg side chains.[21] It is well-known that the ethylene glycol oligomer chain is hydrophilic at room temperature, forming a hydrogen bond with water molecules.[18,22−24] Therefore, at room temperature the lateral association or interdigitation between TgHC molecules will be diminished. The central skeleton of TgHC always remains hydrophobic and the solvophobic interaction will facilitate the strong $\pi-\pi$ stacking interaction between the HC aromatic core, forming the well-defined nanofibers composed of single molecular columnar stacks (top half in Figure 3). Such solvophobic enhancement has widely been observed for the one-dimensional self-assembly of surfactants and other amphiphilic molecules,[18,25,26] including those containing the similar rigid planar π-conjugated structure as central backbone.[27] When heated significantly above room temperature, for example, higher than 40 °C, as we examined above, the hydrophilicity of Tg chain decreases. The otherwise increased hydrophobicity of the Tg chains then enable and facilitate the interdigitation between the side chains through the common hydrophobic van der Waals interactions. We suggest that this lateral intermolecular association causes bundling of the nanofibers (bottom half in Figure 3), as observed in the experiments above. Upon cooling back to room temperature, the Tg side chain returns to be hydrophilic, forming a hydrogen bond with water molecules. The strong association with solvent will thus dissociate the bundles back to individual nanofibers as presented in the left part in Figure 1a.

In an attempt to further verify the role played by the Tg side chains during the temperature change, we synthesized an analogue of TgHC by changing the Tg side chain to a dodecyl chain ($-C_{12}H_{25}$) while still maintaining the same HC core. We refer this molecule as $C_{12}HC$, the structure of which is shown in Figure S4. Comparative investigations were performed using $C_{12}HC$. As expected, after injecting a THF solution of $C_{12}HC$ into water, large white aggregates formed immediately, and the whole solution became opaque (Figure S4). Heating up such a dispersion caused the aggregates to grow even larger. When cooled to room temperature, the large aggregates remained precipitated (insoluble) in the aqueous medium, and the dispersion remained unclear. One AFM image of such large aggregates is shown in Figure S5. This result supports that the above observed reversible transformation between monomolecular cross-sectioned nanofibers and large bundles of TgHC is indeed the result of temperature induced hydrophilic and hydrophobic transition of Tg side chains in water.

In summary, ultrafine nanofibers have been fabricated from an amphiphilic π-conjugated macrocycle molecule modified with hydrophilic side chains of ethylene glycol oligomer through self-assembly under room temperature. High-resolution AFM imaging reveals that the nanofiber is composed of a single molecule columnar stack. Upon heating in aqueous solution, the monomolecular cross-sectioned nanofibers are reversibly transformed to large bundles, which in turn can be dispersed into individual nanofibers upon cooling back to room temperature. Such a reversible morphology transformation is due to the fact that the hydrophilicity of ethylene glycol oligomer side chain is strongly dependent on temperature. The finding presented represents a simple way to control the morphology and size of nanostructural self-assembly and may be extended to other macrocycle molecules with a similar amphiphilic property.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, molecular structure of $C_{12}HC$, AFM images, and UV−vis absorption spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

Notes. The authors declare no competing financial interest. The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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