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Scrolled Nanosheet with Thermo-Responsive Unrolling in Self-Assembly of Aromatic Amphiphile

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Rod-coil molecules comprising rigid rod segments and flexible hydrophilic chains have gained attention for generating highly defined nanostructures in solution. In this work, we report the fabrication of scrolled sheet and planar sheet structures from the self-assembly of laterally grafted rod-coil molecules. The mono-grafted rod-coil self-assembles into a scrolled sheet through the spontaneous rolling-up of the planar sheet perpendicular to the fiber long axis, interestingly, the scrolled structures undergo unrolling at higher temperature, exhibiting a thermal-responsive behavior. In contrast, the symmetrically grafted rod-coil molecules form planar sheet structures that do not exhibit the rolling-up behavior.

1. Introduction

The construction of novel nanostructures via the molecular self-assembly of amphiphilic molecules has garnered significant interest due to their well-defined dimensions, structural complexity, as well as promising functions and potential applications.[1–3] A well-designed of the molecular structure and the precise control of the relative volume fraction between the hydrophilic and hydrophobic segments in amphiphilic molecules enable the formation of highly ordered supramolecular structures.[4–6] In particular, rod-coil block molecules which consisting of aromatic units and poly(ethylene oxide) (PEO) coils are promising candidates for creating a well-defined self-assembled structures though modulating the interplay among multiple noncovalent interactions by the rational design of molecular modules. Significant research has been conducted on the characteristic features of these rigid-flexible block molecules. One characteristic is the lower critical solution temperature (LCST) property of the ethylene oxide chain, which exhibit a reversible hydration-dehydration switching in response to a thermal signal.[7] The other feature is the ability of rigid aromatic segments to generate π-π interaction, which plays an important role in controlling the architecture of the self-assembled structures. Owing to these fascinating structural characteristics, pioneering studies have shown that the aggregation of the rigid-flexible block molecules can easily provide various of self-assembled structures, such as sheets, nanofibers, nanodishes, vesicles, tubes, and scrolls in aqueous solutions, owing to the pronounced stiffness contrast between rigid hydrophobic segments and flexible hydrophilic coil domains.[8–12]

Among the various self-assembled structures, scrolled structures with hollow interiors which can be further transformed from flat structures, are particularly interesting,[13,14] because their cavities exhibit diverse functions.[15,16] For example, multicompartment drug delivery vehicles or virosomes formed from the spontaneous curving of thin sheets can be used for drug delivery and biomedical engineering.[17] Previously, we reported flat structures that could roll up to scroll structures formed from the selective self-assembly of macrocyclic amphiphilic molecules. These scrolls structures showed thermally responsive behaviors.[13] This prompted us to systematically explore the switchable self-assembly behavior of aromatic amphiphilic molecules. Herein, we report the dynamic and static nanosheet structures formed by the self-assembly of rod-coil aromatic amphiphiles with two penta(oxyethylene) chains and four tri(oxyethylene) chains, **1** and **2**, respectively (Figure 1). Molecules **1** and **2** self-assemble into 2D sheets through the lateral association of primary nanofibers in a H_2O:THF solution (the volume ratio of H_2O and THF is 4:1). However, molecules **1** self-assemble into a dynamic rolled sheet structure with thermally responsive behavior, whereas molecules **2** self-assemble into static planar sheet structures with a lack of thermo-responsive rolling up behavior.

2. Results and Discussion

The aggregation behavior of the molecules **1** and **2** was investigated in a H_2O:THF solution performed by transmission electron microscopy (TEM). Molecule **1** was not dissolved in water, nevertheless, the addition of THF induced the self-assembly of the nanostructures. To investigate the self-aggregation behavior of **1**,

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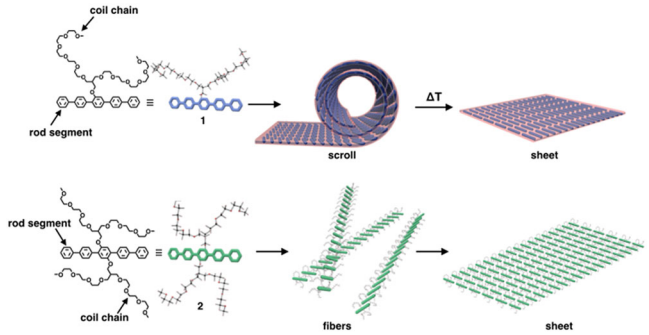

Figure 1. Molecular structures of **1** and **2** and a representation of dynamic scrolled sheets and static planar sheets.

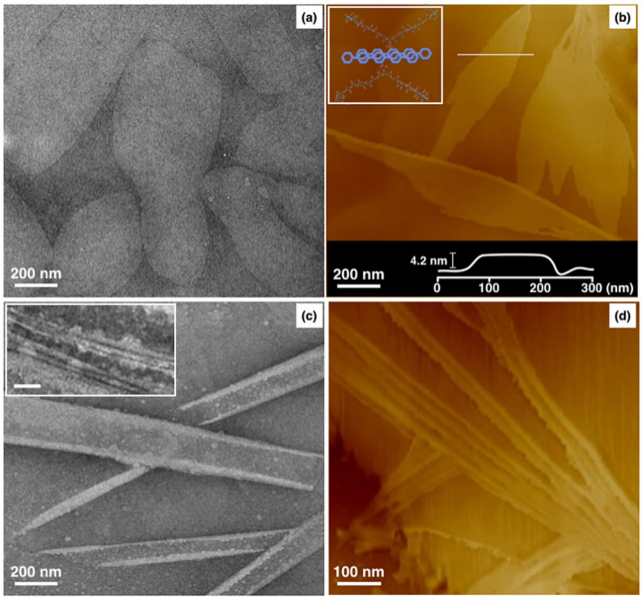

Figure 2. (a) TEM image and (b) AFM image of **1** (0.105 mM) from a mixed solution (H_2O:THF = 4:1 v/v) during the initial stages of self-assembly (3h). The inset image is the schematic representation of bimolecular packing to a single layer. (c) TEM image and (d) AFM image of **1** (0.105 mM) from a mixed solution (H_2O:THF = 4:1 *v/v*) at 20h. The inset image is the extended image of the tubular scroll. Inset scale bar: 20 nm.

we performed ultraviolet-visible (UV-vis) and fluorescence measurements on a H_2O:THF solution (H_2O:THF = 4:1 v/v, 0.105 mM) of **1** (Figure S5). The absorption maximum of **1** in a H_2O:THF solution was red-shifted relative to that examined in THF, and the fluorescence was decreased, indicating aggregation of the rod-shaped aromatic segments.[18] TEM measurements were performed to investigate the packing arrangement of the rod segments within the aromatic domains. Figure 2a shows a micrograph achieved from a 0.105 mM mixed solution (H_2O:THF = 4:1 v/v) of **1** drop casting onto a TEM grid. The TEM image of the sample subjected to negatively stained using uranyl acetate, showed the formation of planar sheet structures during the initial stages of self-assembly (3h). To confirm the planar sheet nanostructures, atomic force microscopy (AFM) measurements were carried on a hydrophilic mica substrate in a completely dried state (Figure 2b). The AFM image of **1** demonstrated the planar sheets exhibiting a thickness of 4.2 nm. Considering the molecular elongation along the lateral axis (2.0 nm by the molecular dynamics simulations, Figure S7a), a width of 4.2 nm is corresponding to twice the MD-calculated lateral molecular extension which is corroborate with the predicted thickness of the single layers (Figure 2b inset). This result demonstrates that the rod-like motifs within the domains are aligned parallel to both the layer planes and to each other to form an inplane pseudo-nematic architectures.[19] Subsequently, the sheets spontaneously rolled up, as shown in the intermediate stages in Figure 2b, and eventually assembled into closely packed scrolls after 20 hours (Figure 2c). By extending the tubular surface, a fiber-like line is observed (Figure 2c inset), which suggests that the sheets scroll perpendicular to the fiber long axis into hexagonally close-packed nanotubes. The nanotubes consist of a bright outer rim separated by a dark interior, which is indication of the projection images of hollow tubules with single- or multi-walled structures. To further confirm the tubular structures, AFM experiments were performed (Figure 2d), and the results were consistent with the TEM results. As previously reported, rod-coil molecules consisted of lateral chains undergo spontaneous self-assembly into layered structures, in which the rod-like motifs are inplane alignment parallel to the layer planes.[20,21] Taken together, these results suggest that the rod segments exhibit parallel alignment with respect to the layer planes and that the rods are organized parallel with each other to self-assemble into sublayers within the layers, which are separated by the amorphous layers originating from lateral coils.[19,22] Because of the asymmetric surfaces between the top and bottom of the aromatic planar structure, the planar sheet spontaneously curved to form rolled tubules. This special arrangement of the rod-like motifs into asymmetric 2D layers can be attributed to the 2D self-assembly of the laterally grafted single dendrimer of **1**.[23–25]

In great contrast to the scrolled structures of **1**, **2** with symmetrically disubstituted dendrimers forms only planar sheet structures in 0.085 mM mixed solution (H_2O:THF = 4:1 v/v) with a lack of a rolling up behavior (Figure 3a). The formation of planar nanostructures was also validated by AFM on a hydrophilic mica substrate in the anhydrous state, which showed 2D sheet-like assemblies with straight edges (Figure 3b), demonstrating that the sheets exhibited robust and free-standing configurations in the bulk solution. The AFM image of **2** reveals the presence of planar sheets exhibiting an average thickness of 3.1 nm, which is approximately equal to the molecular length (3.0 nm for **2**, from the molecular dynamics simulations, Figure S7b), consistent with the predicted thickness of a monolayer. To investigate the aggregation behavior of **2**, we performed UV-vis and fluorescence spectroscopic analyses on a H_2O:THF solution (0.085 mM) of **2** (Figure 3c). The UV-vis absorption profile of **2** in the H_2O:THF solution exhibited a red-shift, which was attributed to the conjugated rod block. Notably, the fluorescence spectrum of the H_2O:THF solution showed slightly decreased emission compared with that of the THF solution. Both the red-shifted absorption and the decreased fluorescence intensity conclusively indicated the π-π stacking-driven aggregation of aromatic moieties. To elucidate the formation mechanism of the planar structures of **2**, we systematically conducted TEM investigations under highly diluted condition (0.017 mM) in a H_2O:THF solution. The solution

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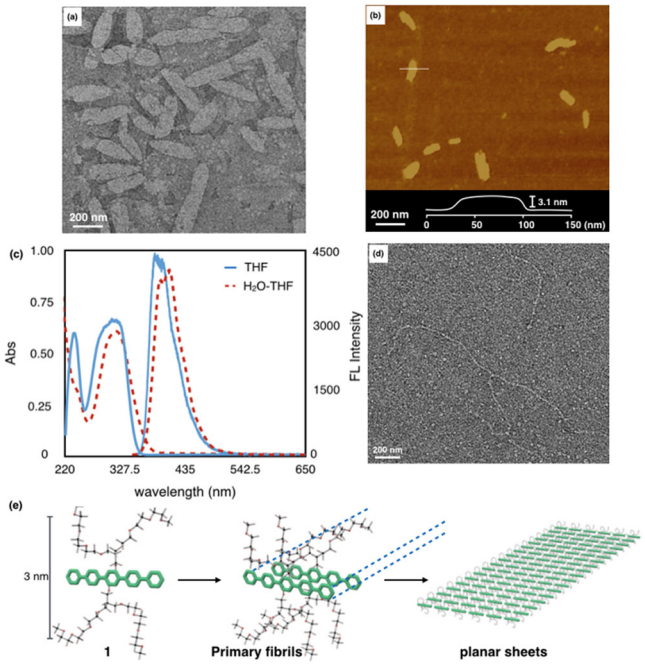

Figure 3. (a) TEM image and (b) AFM image of **2** (0.085 mM) from a mixed solution (H_2O:THF = 4:1 *v/v*). (c) Absorption and emission spectra of **2** in THF (blue and solid line) and a H_2O:THF solution (red and dashed line, H_2O:THF = 4:1 *v/v*). (d) TEM image of **2** (0.017 mM) from a mixed solution (H_2O:THF = 4:1 *v/v*). (e) Schematic representation of the formation of 2D sheet structures through the lateral association of elementary fibrils.

of **2** revealed monodisperse nanofiber structures with uniform diameter of 3 nm (Figure 3d). The fiber-like aggregates suggested that the planar structure of **2** originated from the lateral alignment of nanofibers.[26,27] A diameter of 3 nm corresponds to the length of the single molecular packing of **2**, demonstrating that the aromatic segments face each other to form thin nanofibers. With increasing concentration, the primary nanofibers further assembled through lateral interactions to minimize the contact between the adjacent aromatic cores of the fibers and water molecules and generate 2D sheet structures (Figures 1 and 3e).[28]

The formation of oligoether-coated scrolls suggests that the structures have thermo-responsive characteristics in aqueous solutions arising from the thermal dehydration propensity of the oligoether chains.[29,30] Interestingly, the scrolls of **1** undergo unfolding at 42 °C, the temperature at which the oligo(oxyethylene) chains undergo dehydration. Upon heating to 42 °C, the tightly packed scrolls gradually loosened and subsequently transformed into open sheets (Figure 4a). Scanning electron microscopy experiment (SEM) (Figure 4b) and AFM experiments (Figure S8) at 42 °C exhibited flexible sheets, demonstrating that the scrolls undergo thermo-responsive unrolling into flat sheets upon thermal activation (Figure 4b). This thermo-responsive behavior can be rationalized by the entropy-driven dehydration of the oligoether chains upon heating the solution.[31] However, we did not observe recovery of the original scrolls after 24 hours of resting at room temperature, indicating that the scrolls of **1** could not undergo reversible switching between the folding and unfolding states. Indeed, the inability to recover from UV-vis and fluorescence also indicates that the scrolls of **1** lack reversibility (Figure S9). In contrast to **1**, **2** did not show stable thermal-responsive behavior. Upon heating to 42 °C, the planar structure of **2** was disassembled (Figure S10). Indeed, this is further supported by the red-shifted absorption maximum (Figure S11a) and fluorescence quenching at the temperature above 45 °C (Figure S11b). The disassembly of the planar sheet upon heating was attributed to the thermally induced dehydration of the dendritic oligoether chains in aqueous media. At room temperature, the aromatic side faces of the primary fibers are incompletely surrounded by hydrophilic chains. To reduce the contact between the aromatic segments and water molecules, the nanofibers were laterally assembled into planar structures. However, upon heating, the shrunken oligoether chains with a globular shape arising from dehydration would make the planar sheet unstable, as a result of steric hindrance between the dehydrated dendritic globules with a larger intersecting surface on the 2D flat surfaces.

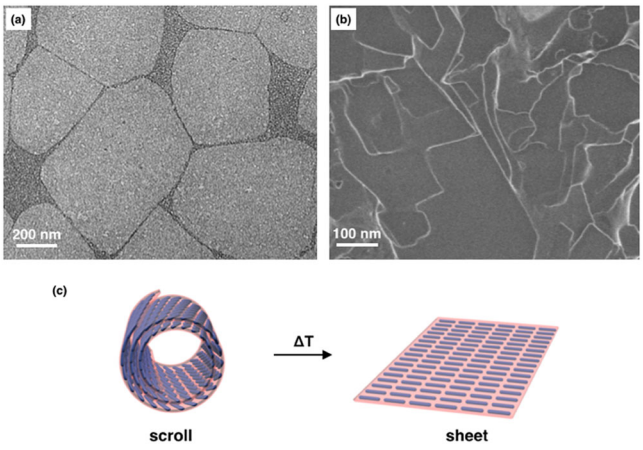

Figure 4. (a) TEM image and (b) SEM image of **1** (0.105 mM) from a mixed solution at 42 °C (H_2O:THF = 4:1 *v/v*). (c) Schematic representation of the structural change between scrolls and sheets.

3. Conclusion

We rationally designed and synthesized rod-coil aromatic amphiphiles with laterally grafted hydrophilic dendrimer chains that self-assembled into sheet structures in a H_2O:THF solution. Molecule **1** is based on mono-grafted self-assembly into a dynamic scrolled structure with thermally responsive behavior, the scrolled structure spontaneously opens to a planar sheet structure upon heating. In contrast to molecule **1**, molecule **2** based on symmetrically grafted dendrons self-assembles into static planar sheet structures without thermo-responsive rolling up behavior. The most distinctive feature of the rod-coil molecules explored herein is their ability to self-assemble into scrolled sheets with thermo-responsive unrolling behavior. We anticipate that this unrolling behavior of the scrolls provides access to intelligent 2D materials with precisely controlled functions in applications from energy storage device with abundant active sites and fast ion diffusion channels to drug delivery vehicles for controlled catch and release.[32–34]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in [NAME] at [DOI], reference number [REF].

Keywords: planar sheet · responsive unrolling · self-assembly · scrolled sheet

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