

Supramolecular Tubule from Seesaw Shaped Amphiphile and Its Hierarchical Evolution into Sheet

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Abstract: Although supramolecular one-dimensional (1D) and two-dimensional (2D) structures with various unique properties have been extensively studied, the reversible switching between tubules and sheets via lateral association remains challenging. Here, we report the unique structures of a supramolecular tubular bamboo culm in which the hollow-tubular interior is separated, at intervals, by nodes per 1.3 nm. Interestingly, the discrete tubules are able to hierarchically assemble into a flat sheet in response to an aromatic guest. The addition of *trans*-azobenzene, as a guest, enables the tubules to form a hierarchical sheet assembly via the lateral interaction. The hierarchical sheet structures are disassembled into their constituent tubules upon UV irradiation due to trans-cis isomerization. The recovery from cis-azobenzene to trans-form induces repeatedly the hierarchical sheet assembly, indicative of a reversible switching behavior between tubules and sheets triggered by an external stimulus.

The construction of functional materials through molecular selfassembly, facilitated by non-covalent interactions, is a challenging research topic in the field of supramolecular chemistry.^[1,2] The reversibility of such non-covalent interactions enables the formation of dynamic architectures with responsive functions.^[3] Various switchable supramolecular structures in response to external stimuli can be formed by the self-assembly of synthetic aromatic amphiphiles, consisting of hydrophobic aromatic and hydrophilic coil segments.^[4] Among the supramolecular architectures, a one-dimensional (1D) fibrillar assembly and a twodimensional (2D) sheet structure have been proven to be particularly interesting for applications because of the precise control of their morphologies with their well-defined shapes and sizes.^[5,6] For example, bent-shaped aromatic amphiphiles can self-assemble into non-covalent hexameric macrocycles in an aqueous solution, and the resulting macrocycles can subsequently stack on top of each other to afford tubular structures as a 1D assembly.^[7] The well-defined supramolecular tubules exhibit responsive and controllable functions, such as chirality inversions, guest encapsulations, and catalytic regulations.^[8] Recent examples for 2D structures are provided by aromatic macrocyclic amphiphiles with oligoether dendron, at the center of the aromatic plane, which can self-assemble into porous 2D structures. The supramolecular 2D sheets exhibit highly efficient guest-capturing functions, with regard to their uptake capacity and selectivity because of their well-defined porosity and extremely high surface area, coupled with many unique chemical and physical properties.^[9]

Although supramolecular 1D and 2D structures have been extensively studied, there are limited reports on the supramolecular switching between tubules and sheets through the reversible lateral association, triggered by external stimuli.^[10] Here, we report unique supramolecular tubular bamboo-culm structures, formed by the self-assembly of a seesaw-shaped aromatic amphiphile in which the hollow tubular interior was separated, at intervals, by nodes per 1.3 nm (Figure 1). The encapsulation of *trans*-azobenzene enabled the tubular culm to interconnect toward achieving a hierarchical sheet assembly via the lateral interaction of the tubules. When isomerization, from *trans*-azobenzene and its *cis*-isomer, was induced via UV irradiation, the hierarchical sheet structures were disassembled

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Figure 1. Molecule 1 and the schematic of the reversible switching between the supramolecular tubular culm and a hierarchical sheet-assembly, based on a seesaw-shaped amphiphile.

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into their constituent tubules because of the weakened lateral association caused by *cis*-azobenzene. The transformation, from *cis*-isomer to *trans*-azobenzene, in the absence of light, induced the formation of a hierarchical sheet assembly again, which was indicative of a reversible switching behavior between tubules and sheets.

The self-assembling amphiphile 1 was composed of a naphthalene-based hydrophobic segment and hydrophilic oligoether chains. The amphiphile was synthesized, beginning with the acid-catalyzed condensation reaction of 3,6-dibromo-2,7-dihydroxynaphthalene 2 and formaldehyde (Scheme 1). The C1-position of the two naphthalenes was connected via a single methylene unit to afford a molecule 3 without any noticeable traces of the product with two methylene linkers in the C1 and C8 positions of naphthalenes. This result implied that the C8 position in molecule 3 was far off because of the steric hindrance between the neighboring hydroxyl groups, suggesting a unique and rigid molecular conformation. Thereafter, four hydroxyl groups of molecule 3 were subjected to etherification reaction with tosylated penta(ethylene glycol) monomethyl ether, to produce another molecule 4. The final compound, possessing four aromatic rods, was successfully synthesized via the Suzuki coupling reaction between four bromo groups of molecule 4 and 4-biphenylboronic acid. The target amphiphilic molecule, 1, was characterized by proton and carbon-13 (¹H and ¹³C) nuclear magnetic resonance (NMR) spectroscopies and matrix-assisted laser desorption/ionization-time-of-flight (MAL-DI-TOF) mass spectroscopy (MS) to confirm the structure presented herein (Figures S1-S4).

When dissolved in a solvent that was suitable for the oligoether chains, molecule 1 could self-assemble into an aggregation structure because of its amphiphilic characteristics. The aggregation behavior of 1 under different solvent conditions was studied by absorption spectroscopy (Figures 2a and S5a). The solution of 1 in MeOH (53 µM) exhibited an almost similar absorption spectrum with that of a chloroform solution in which the molecules were considered to be fully dissolved. This result indicates that the MeOH solution of 1 could not induce an aggregation structure (Figure S5a). To induce the aggregation of 1, different volume of H₂O and MeOH was added to the dried film of molecule 1 to be 53 μ M concentration, and the solution was sonicated for 30 min in ice bath. Upon the addition of water, as an inappropriate solvent for aromatic segments, the absorbance at 286 nm was reduced, and the fluorescence near 385 nm was guenched (Figures 2a and 2b), indicating that the π - π stacking interactions between



(a) 10.0

Absorbance (a.u.)

(c)

8.0

6.0

4.0

20

0.0

200



Figure 2. (a) Absorption spectra and (b) emission spectra (excitation wavelength: 290 nm) of molecule 1 (53 μ M) in MeOH–H₂O (v/v). (c) Negatively stained TEM of molecule 1 (53 μ M) in MeOH–H₂O (40/60, v/v). The inset image shows the separated hollow-tubular interior by nodes per 1.3 nm. (d) AFM images of molecule 1 (53 μ M) in MeOH–H₂O (40/60, v/v) and cross-sectional profile denoted by the white line. (e) Calculated dimensions of the tetrameric macrocycle.

the aromatic segments were enhanced because of the increased solvophobic interaction.^[10] In the pure water solution, the absorbance and fluorescent intensity were very weak because of poor solubility, which was evidenced by noticeable precipitations.

To investigate the aggregation behavior of 1, we performed negatively stained transmission electron microscopy (TEM) experiments. The TEM images exhibited irregular aggregates in 0, 20, and 40% water solution in MeOH (Figure S6). However, we could observe the discrete tubular structures with a uniform diameter of 7.0 nm in a 60% water in MeOH (Figure 2c, S7, and S8) and tubular aggregates in a 80% water in MeOH (Figure S6). The appearance of the discrete tubules, as observed in the TEM



Scheme 1. Synthetic method for a seesaw-shaped amphiphile 1.

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image, consisted of a white periphery separated by a dark interior, which is characteristic of projection images of hollow tubules. Interestingly, the magnified TEM image of the tubules revealed that the tubular cavities with the dark interior were separated periodically by white nodes per 1.3 nm, suggesting that the assembled structure adopted a unique morphology, similar to a bamboo-culm in shape. Atomic force microscopy (AFM) experiment was performed with the prepared samples prepared by drop-casting the 53 μ M solution on a hydrophilic mica surface as a substrate. The AFM measurement demonstrated the existence of closely packed fiber-like aggregates, with a height of 7.2 nm (Figure 2d).

Computer simulation was conducted to understand the formation of the tubular structure through the self-assembly of molecule 1. To reduce the calculation time, a truncated structure with shortened oligoether chains was simulated to explore the molecular conformations. A total of 384 conformers was found and among them, 50 stable conformers, within the energy range of 7.0 kJ/mol of the global minimum, were merged and utilized for further analysis. The merged fifty conformers demonstrated that the molecule 1 adopted a seesaw geometry (disphenoidal geometry) in which the molecule possessed two types of aromatic rods, namely the axial and equatorial positions (Figure S9). The axial pair was placed along a common axis, at an average angle of 182°, across the methylene linkage (Figure 1 and S7). The equatorial pair of rods was positioned in a plane, which was orthogonal to the axis of the axial pair. Considering the angle (88°) between the two equatorial rods, four molecules of 1 were arranged in a tetrameric macrocycle by non-covalent aromatic interactions of the equatorial rods and subjected to energy minimization.^[7] The calculated diameter of the minimized tetrameric macrocycle, formed by the equatorial rods, was 3.4 nm (Figure 2e), implying that the calculated diameter of the tubules is ~7.4 nm by the tetrameric macrocycle, surrounded by a hydrophilic oligoether with a length of 2.0 nm. The calculated tubular dimension corresponded to the diameters obtained from the TEM and AFM experiments. The resulting tetrameric macrocycles could be stacked on top of each other to form tubular structures through the aromatic interactions between the axial rods on macrocycles. Moreover, based on 2.5 nm of the calculated height of the tetrameric macrocycle, the observed distance between the nodes in the TEM measurement (1.3 nm) could imply the stacking of the tetrameric macrocycles via overlapped packings of the axial aromatic segments. Inclusively, we could propose supramolecular bamboo-culm structures, obtained by the self-assembly of the seesaw-shaped aromatic amphiphiles in which the hollow tubular cavity was separated and exposed to a solvent environment periodically, by nodes per 1.3 nm.

The formation of the supramolecular tubular culm structures inspired us to investigate whether the tubular culm could encapsulate a guest molecule, such as azobenzene, into the exposed tubular cavity in the sides of the tubules. Indeed, upon the addition of azobenzene, the tubule solution readily solubilized azobenzene in the MeOH–water solution, and the absorbance near 287 nm increased up to two equivalents of azobenzene (Figure 3a). The absorbance, with the further





Figure 3. (a) Absorption spectra and (b) emission spectra (excitation wavelength: 290 nm) of 1 (53 μ M) with different equivalents of azobenzene in MeOH–H₂O (40/60, *v/v*), respectively. (c) Negatively stained TEM, cryo-TEM image (inset), and (d) AFM images of 1 (53 μ M) with two equivalents of azobenzene in MeOH–H₂O (40/60, *v/v*) solution.

addition of azobenzene, decreased significantly with noticeable precipitation due to its poor solubility. Therefore, the equivalent ratio of azobenzene and 1 (2:1) was selected as an optimal condition in further experiments. The fluorescence near 385 nm also decreased, indicating that the aromatic interaction between the tubular culms and azobenzenes was enhanced (Figure 3b). We investigated the influence of azobenzene intercalation on the tubular culm by cryogenic TEM (cryo-TEM) and negatively-stained TEM experiments of a solution of 1, in the presence of two equivalents of azobenzene (Figure 3c). The resulting image exhibited large planar sheets with straight edges, indicative of the morphological transformation, from tubular culms to sheets, which was triggered by the addition of azobenzene in the bulk solution. This transformation was also confirmed by TEM taken at intermediate stages which showed lateral association of the tubular objects to form flat sheets (Figure S10 and S11). Additional structural information of the sheets was obtained by fluorescence optical microscopy (Figure S12) and a AFM measurement. The AFM result revealed the closely packed sheet-like aggregates with a height of 7.2 nm (Figure 3d), which is consistent with the diameter of the tubules.

The *trans-cis* isomerization of azobenzene by UV irradiation is well-known as a molecular switch in sensors and photosensitive materials. The structural transformation of azobenzene from 9.0 Å (*trans*) to 5.5 Å (*cis*) led us to investigate whether the lateral interactions of the tubules facilitated by *trans*-azobenzene would be changed or not. In the sheet solution, the absorption spectrum showed an absorption maximum peak near 287 nm which is attributed to the π - π * absorption band of the *trans*- azobenzene moiety. When the sheet solution was irradiated by 365 nm UV light, the 287 nm absorption band decreased with concomitant increases in n- π * bands of *cis*- azobenzene around 432 nm as shown in Figure 4a, and the fluorescence emission was also quenched (Figure 4b).^[11] The spectral changes over time demonstrated that the *trans* to *cis* transition of azobenzene was completed with 8 h of 365 nm UV irradiation.

The sample solution with *cis*-azobenzene by UV irradiation was subjected to TEM experiments to investigate the morphological transformation in the self-assembled structures. The TEM image revealed that the sheet structures were disassembled into discrete tubules with the diameters of 7.1 nm (Figure 4c). This result indicates that the cis-isomer, with a shorter dimension (5.5 Å) than that of the trans-isomer (9.0 Å), might weaken the lateral associations in the sheet assembly, to afford the structural change from sheets to tubules. When the sample solution with the discrete tubules by cis-azobenzene was kept in a dark room for one week, we observed the restoration of trans-azobenzene through the absorption spectrum (Figure S13) and the fully recovered sheet structure, shown in the negatively stained TEM image (Figure 4d). The result indicated the reversible switching behavior between the tubules and sheets by an altered lateral association via the trans-cis isomerization of azobenzene by UV irradiation.

We demonstrated unique supramolecular tubular bambooculm structures, obtained by the self-assembly of a seesawshaped aromatic amphiphile in which the hollow tubular interior was separated, by nodes per 1.3 nm, at intervals. The periodic tubular cavity was exposed to the solvent environment and could capture a hydrophobic guest. The addition of *trans*azobenzene, as a guest, enabled the interconnectivity of the tubular culm to form a hierarchical sheet assembly via the enhanced lateral interaction in the tubules. When an isomerization, from *trans*-azobenzene to its *cis*-isomer, was induced by 365 nm UV irradiation for 8 h, the hierarchical sheet structures



Figure 4. (a) Absorption spectra and (b) emission spectra (excitation wavelength: 290 nm) of 1 (53 μ M) with two equivalents of azobenzene in MeOH–H₂O (40/60, *v/v*) by UV irradiation, at 0, 2, 4, 6, 8, and 10 h. Negatively stained TEM images, obtained (c) after 8 h irradiation and (d) aging in a dark room for 1 week of 1 (53 μ M) with two equivalents of azobenzene in MeOH–H₂O (40/60, *v/v*) solution.

were disassembled into their constituent discrete tubules through the weakening of their lateral association because of the shorter length of *cis*-azobenzene. The re-transformation of the sheet structures from the tubules was fully achieved by aging, in a dark environment as evidenced by the restored *trans*-azobenzene, indicating the reversible switching between tubules and sheets via *trans*-*cis* isomerization of azobenzene, and triggered by UV irradiation. Such a unique switch motion between 1D and 2D structures with photoresponsive characteristics affords a new possibility of fabricating the functional materials in nano-optics and dynamic membrane systems.

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Conflict of Interest

The authors declare no conflict of interest.

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