

Tubular Stacking of Water-Soluble Toroids Triggered by Guest Encapsulation

Eunji Lee, Jung-Keun Kim, and Myongsoo Lee*

Center for Supramolecular Nano-Assembly and Department of Chemistry, Seoul National University,
599 Gwanak-ro, Seoul 151-742, Republic of Korea

Received November 1, 2009; E-mail: myongslee@snu.ac.kr

Construction of one-dimensional (1D) tubular structures by self-assembly of designed molecules has attracted considerable attention because of the potential applications and practical implications of such structures.¹ Supramolecular tubules can be constructed by rolling-up of elementary ribbons,² scrolling of 2D structures,³ and stacking of flat macrocyclic molecules.⁴ It can be speculated that 1D stacking of supramolecular rings through solvophobic interactions would provide a novel strategy for fabricating tubular structures.⁵

Herein we present the formation of water-soluble toroids with a hydrophobic cavity by coassembly of laterally grafted rod amphiphiles and their tubular stacking triggered by guest (C_{60}) encapsulation (Figure 1). The synthesis of laterally grafted amphiphilic molecules **1** and **2** was performed according to procedures described previously.³ Cryogenic transmission electron microscopy (cryo-TEM) revealed that **1** based on a bis(ethylene oxide) chain self-organizes into planar sheets, whereas **2** with a longer tris(ethylene oxide) chain forms a ribbonlike assembly (Figure S1 in the Supporting Information).

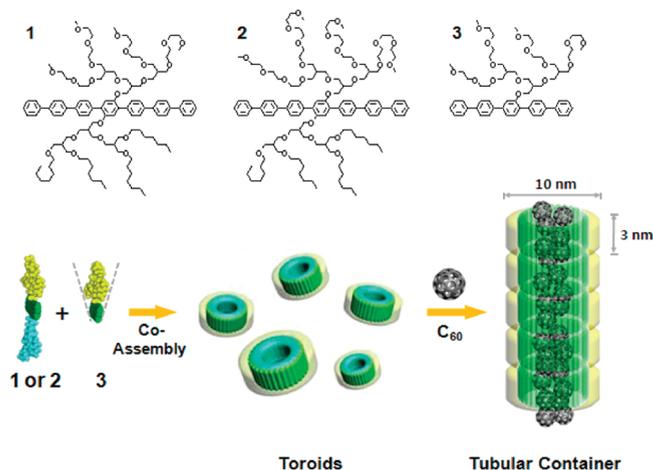


Figure 1. Chemical structures of **1–3** and schematic illustration of the stacking of toroids in a 1D manner upon addition of C_{60} guest molecules.

This structural behavior stimulated us to investigate whether increasing the volume fraction of hydrophilic chains would induce highly curved nanostructures to relieve steric crowding at the flat rod–coil interfaces of the sheets and the ribbons. With this in mind, **1** or **2** was mixed with **3** consisting of an aromatic rod and a hydrophilic branched chain for coassembly.⁶ Notably, the average hydrodynamic radii (R_H) of both mixture solutions decreased with increasing content of **3** (Figure S3), as confirmed by dynamic light scattering (DLS) experiments.^{7,8} These observations reflect a decrease in the size of the aggregates upon addition of **3**.

To corroborate the structural change upon addition of **3**, TEM experiments were carried out on 0.005 wt % solutions of **1**

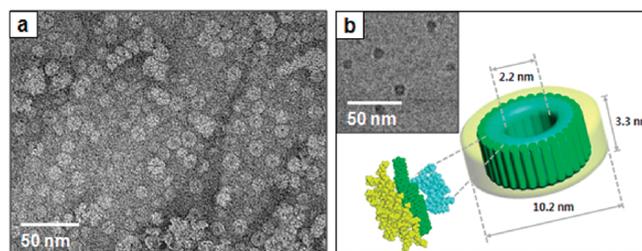


Figure 2. (a) TEM image and (b) model and (inset) cryo-TEM image of the ring structure of **1** containing **3** (90 mol % relative to **1**) in aqueous solution.

containing different amounts of **3** (Figure S4). Interestingly, at a **3** content of 40 mol %, the sheets were shown to split into a ribbonlike structure (Figure S5). Eventually, the ribbons with a parallel arrangement were gradually isolated into cylindrical fibers with a uniform diameter of 8 nm at a **3** content of >70 mol % (Figure S5). This dimension is in reasonable agreement with twice the fully extended molecular length (~ 4.1 nm by CPK modeling), thus indicating bilayer packing with the alkyl chains inside.

More importantly, a further increase in the **3** content forced the ribbon structure to transform into discrete nanostructures. The TEM image in Figure 2a reveals the formation of highly curved discrete rings at a **3** content of 80 mol %. The cross-sectional diameter of the ring is highly uniform (~ 4 nm). The diameter of the ring exterior and the internal pore were measured to be ~ 10 and 1.5–2 nm, respectively. The cryo-TEM image in Figure 2b shows dark ringlike objects against the vitrified solution background, demonstrating that the rings are not formed during the solvent evaporation process (0.005 wt % in aqueous solution). These dimensions together with the extended molecular length (see Figure S6) indicate that the rings are composed of a single layer of the molecules in which the rod segments are oriented perpendicular to the plane of the rings and arranged into highly curved barrel-like toroids.⁹ On the basis of these results, the mixed solution above a certain **3** content can be considered to coassemble into toroids that are composed of a hydrophobic interior with a diameter of ~ 2 nm and hydrophilic exterior with a diameter of ~ 10 nm (Figure 2b). Similar to **1**, the ribbon structure of **2** transforms into discrete toroids with a uniform size upon addition of 70 mol % **3** (Figures S4 and S7).

This structural transformation from planar sheets to elongated cylinders to discrete toroids upon addition of **3** can be explained by the increasing volume fraction of hydrophilic segments through coassembly. With increasing content of **3**, which contains only a hydrophilic flexible chain, the 2D sheets dissociate into smaller aggregates with larger volume, allowing the increased number of oligoether chains to be less confined without sacrificing the anisotropic packing of the rod segments.¹⁰ Since in most cases of ring structures the internal cavities have the same surface as the exterior,¹¹ it is remarkable that our rings consist of a hydrophobic interior and hydrophilic exterior.

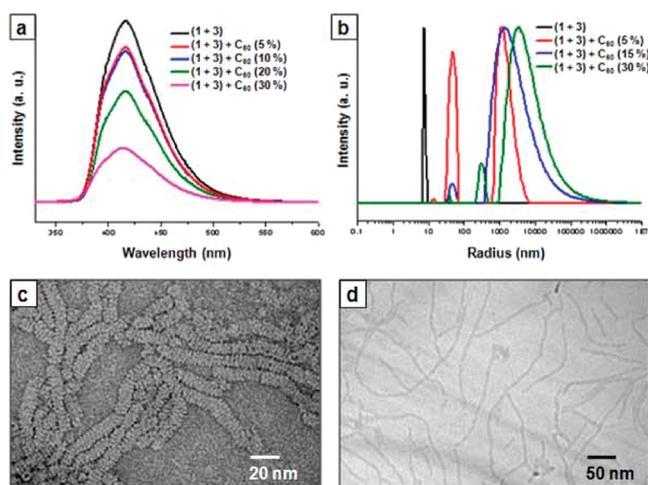


Figure 3. (a) Fluorescence spectra ($\lambda_{\text{ex}} = 316$ nm) and (b) size distribution graphs of aqueous solutions (0.005 wt %) of **1** and **3** (1/3 molar ratio = 1:9) without C_{60} and with 5–30 mol % C_{60} . (c) TEM and (d) cryo-TEM images of the cylinders of **1** and **3** after mixing with 30 mol % C_{60} .

The formation of barrel-like toroids with a hydrophobic cavity led us to investigate whether the supramolecular nanostructures would solubilize fullerenes (C_{60}) in aqueous solution through hydrophobic interactions. We therefore investigated the possibility of encapsulating C_{60} into a coassembled solution of **1** and **3** (1/3 molar ratio = 1:9). The emission spectrum of the coassembled solution in the absence of C_{60} displayed a strong fluorescence with a maximum at 415 nm (Figure 3a). In sharp contrast, upon addition of C_{60} to the solution,¹² the fluorescence intensity was significantly suppressed, indicating that C_{60} was effectively encapsulated within the hydrophobic interior of the rings.¹³ The fluorescence intensity decreased with an increase in the fullerene content to a certain point (30%) beyond which the fluorescence did not change with further increment of fullerene (Figure 3a). Therefore, the maximum mole percent of C_{60} loading per molecule can be considered to be ~30%.

Remarkably, R_{H} of the mixed solution of **1** and **3** increased upon addition of C_{60} up to 30 mol % (Figure 3b). These results indicate that the size of the aggregates increased with increasing C_{60} content.^{7,14} When a sample was cast from an aqueous solution (0.005 wt %) and then negatively stained with uranyl acetate, the TEM image of the mixed solution containing 30 mol % C_{60} revealed cylindrical aggregates with a diameter of 10 nm (Figure S9d). Closer examination of the samples showed that the cylinders are composed of lateral stripes with a regular spacing of 3.3 nm along the cylinder axis (Figure 3c). The formation of cylindrical objects in bulk solution was also confirmed by cryo-TEM (Figure 3d). The diameter and lateral spacing of the cylinders are in good agreement with the dimensional features of the individual toroids. This finding demonstrates that fullerene drives the supramolecular rings to stack on top of one another to form a tubular structure in which the fullerenes are encapsulated within the internal cavity (Figure 1). Encapsulation

of C_{60} within the cavities would force the rings to be more hydrophobic up and down. To reduce the exposure of the hydrophobic parts of the rings to a water environment, the rings self-associate in a 1D manner to form elongated tubules with C_{60} inside. As a result, the fullerene array can be attained within the 1D spatial confinement of the hollow tubules (Figure 1).¹⁵

In conclusion, the results described here demonstrate that the coassembly of laterally grafted amphiphilic analogues leads to the formation of water-soluble toroids with a hydrophobic interior. Notably, the toroids can efficiently encapsulate fullerene within their internal cavities, which forces the toroids to stack on top of each other to form a tubular container. This unique assembly could be successfully utilized to spatially order the fullerene, which might further broaden the application scope of fullerenes.

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Supporting Information Available: Synthetic and other experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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