

Supporting Information

Tubular Stacking of Water-Soluble Toroids Triggered by Guest

Encapsulation

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Materials and Methods

Materials

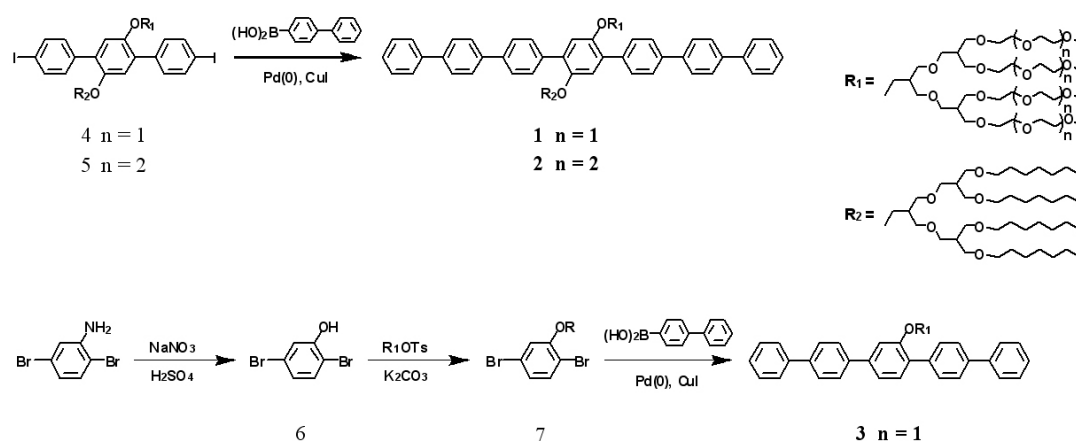
3-Chloro-2-chloromethyl-1-propene (96 %) from Acros and NaH (60 %), *p*-toluene-sulfonyl chloride (98 %) from Tokyo kansei and 1,4-dibromo-2,5-dimethoxybenzene (98 %) from Alfa Aesar and fullerene (C₆₀, 99.5 %), tetrakis(triphenylphosphine) palladium(0) (99 %), boron tribromide (1.0 M solution in dichloromethane) from TCI were used as received. Triethylene glycol monomethyl ether (95 %), di(ethylene glycol) methyl ether (99 %), 2,5-dibromoaniline (98 %), urea (98 %), borane-THF complex (1.0 M solution in THF), 4-(trimethylsilyl)phenylboronic acid (98 %), triisopropyl borate (98 %), 4-biphenylboronic acid, iodine monochloride (1.0 M solution in dichloromethane) from Aldrich and the conventional reagents were used as received. All atmosphere sensitive reactions were done under nitrogen. Flash chromatography was carried out with Silica Gel 60 (230-400 mesh) from EM Science. Visualization was accomplished with UV light and iodine vapor.

Techniques

¹H and ¹³C NMR spectra were recorded from CDCl₃ and DMSO-d solutions on a Bruker AM 250 spectrometer. The purity of the products was checked by thin layer chromatography (TLC; Merck, silica gel 60). Microanalysis was performed with a

Perkin Elmer 240 elemental analyzer at Organic Chemistry Research Center, Sogang University, Korea. MALDI-TOF-MS was performed on a Perseptive Biosystems Voyager-DE STR using a 2,5-dihydroxy benzoic acid matrix. Preparative high performance liquid chromatography (HPLC) was performed at room temperature using a 20 mm $\times$ 600 mm poly styrene column on a Japan Analytical Industry Model LC-908 recycling preparative HPLC system, equipped with UV detector 310 and RI detector RI-5. Dynamic light scattering measurements (DLS) were performed with an ALV/CGS-3 Compact Goniometer System. The steady-state fluorescence spectra were measured in a Hitachi F-4500 fluorescence spectrophotometer. The transmission electron microscopy (TEM) was performed at 120 kV using JEM-2010.

Synthesis



Scheme S1. Synthesis of laterally-grafted amphiphilic rod molecules **1-3**.

Synthesis of laterally-grafted amphiphilic molecules **1** and **2**

The synthesis laterally-grafted amphiphilic molecules **1** and **2** were synthesized according to the procedures described previously.^{S1}

Compounds were synthesized using the same procedure. A representative example is described for **1**. Compound **4** (0.50 g, 0.27 mmol) and 4-biphenylboronic acid (0.16 g, 0.80 mmol) were dissolved in degassed tetrahydrofuran (60 mL). Degassed 2M aqueous Na₂CO₃ (30 mL) was added to the solution and then tetrakis(triphenylphosphine) palladium(0) (0.02 g, 0.02 mmol) was added. The mixture was heated at reflux for 48h with vigorous stirring under nitrogen. Cooled to room temperature, aqueous layer was

washed twice with ethyl acetate. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, the crude products was purified by column chromatography (silica gel) using ethyl acetate / methanol and the product was further purified by recycling preparative HPLC to yield 0.37 mg (72 %) of a white waxy solid.

1 ; $^1\text{H-NMR}$ (250 MHz, CDCl_3 , ppm) : δ = 7.78-7.34 (m, 26H; Ar-*H*), 7.08 (s, 2H; Ar*H*; *o* to $-\text{CH}_2\text{OAr}$), 4.04 (s, 4H; $-\text{CH}_2\text{OAr}$), 3.58-3.30 (m, 84H; $-\text{CH}_2\text{O}$), 2.12-2.05 (m, 6H; $\text{CH}(\text{OCH}_2)_2$), 1.50-1.47 (m, 8H; $-\text{OCH}_2\text{CH}_2$), 1.25 (s, 32H; $-\text{CH}_2\text{CH}_2$), 0.85 (t, 12H; $-\text{CH}_2\text{CH}_3$) ; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , ppm) : δ = 150.43, 140.82, 140.22, 139.87, 139.26, 137.58, 130.50, 130.13, 128.94, 127.63, 127.49, 127.13, 126.60, 72.10, 71.40, 70.65, 69.84, 69.47, 69.27, 59.20, 40.44, 40.26, 31.95, 29.80, 29.28, 26.25, 22.73, 14.20; Anal. Calcd for: $\text{C}_{114}\text{H}_{174}\text{O}_{22}$: C, 72.19; H, 9.25 Found C, 72.15; H, 9.27 ; MALDI-TOF-MS m/z 1918.39 ($[\text{M}+\text{Na}]^+$), Calcd 1918.59.

2 ; $^1\text{H-NMR}$ (250 MHz, CDCl_3 , ppm) : δ = 7.78-7.35 (m, 26H; Ar-*H*), 7.08 (s, 2H; Ar*H*; *o* to $-\text{CH}_2\text{OAr}$), 4.04 (s, 4H; $-\text{CH}_2\text{OAr}$), 3.58-3.30 (m, 100H; $-\text{CH}_2\text{O}$), 2.12-2.05 (m, 6H; $\text{CH}(\text{OCH}_2)_2$), 1.50-1.47 (m, 8H; $-\text{OCH}_2\text{CH}_2$), 1.25 (s, 32H; $-\text{CH}_2\text{CH}_2$), 0.84 (t, 12H; $-\text{CH}_2\text{CH}_3$) ; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , ppm) : δ = 150.43, 140.82, 140.22, 139.87, 139.26, 137.58, 130.50, 130.13, 128.94, 127.63, 127.49, 127.13, 126.60, 72.10, 71.40, 70.65, 69.84, 69.47, 69.27, 59.20, 40.44, 40.26, 31.95, 29.80, 29.28, 26.25, 22.73, 14.20; Anal. Calcd for: $\text{C}_{122}\text{H}_{190}\text{O}_{26}$: C, 70.69; H, 9.24 Found C, 70.88; H, 9.20 ; MALDI-TOF-MS m/z 2095.97 ($[\text{M}+\text{Na}]^+$), Calcd 2095.80.

Synthesis of laterally-grafted amphiphilic molecules 3

The second-generation dendritic diethylene glycol coils (**R**₁) were prepared according to the similar procedures as described previously.^{S1}

Synthesis of compound 6 A three-necked round bottom flask equipped and 2,5-dibromoaniline (1.50 g, 6.0 mmol) was dissolved in the hot diluted acid obtained by adding concentrated sulfuric acid (15 mL) into water (5 mL). The clear solution was stirred and cooled to room temperature. Then ice (5 g) was added. As soon as the temperature had dropped below 5 °C, a solution of sodium nitrite (0.5 g, 7.2 mmol) in water (5 mL) was added from a syringe, the needle of which extended below the surface of the liquid. Then urea (0.05 g, 0.83 mmol) and cracked ice (5 g) of were added successively. The solution was kept in an ice water bath for further use. To another three-necked round bottom flask equipped with a condenser, a magnetic stir bar,

anhydrous sodium sulfate (2.3 g, 7.0 mmol), concentrated sulfuric acid (15 mL) and water (7.5 mL) were added. The mixture was boiled, then the diazonium solution was added in portions. The mixture was refluxed for 3 hours. After the reaction mixture cooled to room temperature, product was extracted by ether, and the combined extracts were washed successively with water and 10% sodium bicarbonate solution. The phenol was then extracted from the ether layer by 10% NaOH solution. The alkaline solution was neutralized, by the addition of concentrated hydrochloric acid. The phenol was then extracted with ether. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using hexane as eluent to yield 0.49 g (33%) of the product as a white solid.

$^1\text{H-NMR}$ (250 MHz, CDCl_3 , ppm) : δ = 7.29 (d, 1H; ArH, *p* to ArOH, J = 8.46 Hz), 7.19 (s, 1H; ArH, *o* to ArO), 6.94 (d, 1H; ArH, *m* to ArOH, J = 8.30 Hz), 5.63 (s, 1H; ArOH); Anal. Calcd for : $\text{C}_6\text{H}_4\text{Br}_2\text{O}_2$: C, 28.61; H, 1.60, Found C, 28.58; H, 1.56.

Synthesis of compound 7 Compound **6** (0.49 g, 1.9 mmol), R_1OTs (1.50 g, 1.8 mmol) and excess K_2CO_3 were dissolved in distilled acetonitrile (100 mL). The mixture was heated at reflux for 48 hours and then cooled to room temperature. The solvent was removed in a rotary evaporator, and the resulting mixture was poured into water and extracted with dichloromethane. The dichloromethane solution was washed with water, dried over anhydrous magnesium sulfate, and filtered. After the solvent was removed in a rotary evaporator, the crude products were purified by column chromatography (silical gel) using ethyl acetate / methanol as eluent to yield 0.85 g (47 %) of colorless waxy liquid.

$^1\text{H-NMR}$ (250 MHz, CDCl_3 , ppm) : δ = 7.30 (d, 1H; ArH, *p* to ArO, J = 8.35 Hz), 6.99 (d, 1H; ArH, *o* to ArO, J = 2.10 Hz), 6.89 (dd, 1H; ArH, *m* to ArO, J = 8.36, 2.10 Hz), 4.05 (d, 2H; CH_2OAr , J = 5.2 Hz), 3.58-3.40 (m, 48H; CH_2O), 3.31 (s, 12H; CH_3O), 2.15-2.09 (m, 3H; $\text{CH}(\text{OCH}_2)_2$); Anal. Calcd for : $\text{C}_{38}\text{H}_{68}\text{Br}_2\text{O}_{15}$: C, 49.35; H, 7.41 Found C, 49.41 ; H, 7.40.

Synthesis of compound 3 Compound **7** (0.85 g, 0.92 mmol) and 4-biphenlyboronic acid (0.45 g, 2.3 mmol) were dissolved in degassed tetrahydrofuran (60 mL). Degassed 2M aqueous Na_2CO_3 (30 mL) was added to the solution and then tetrakis(triphenylphosphine) palladium(0) (0.05 g, 0.05 mmol) was added. The mixture was heated at reflux for 48h with vigorous stirring under nitrogen. Cooled to room temperature, aqueous layer was washed twice with ethyl acetate. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was

removed in a rotary evaporator, the crude products was purified by column chromatography (silica gel) using ethyl acetate / methanol and the product was further purified by recycling preparative HPLC to yield 0.48 g (49 %) of a waxy liquid.

^1H -NMR (250 MHz, CDCl_3 , ppm) : δ = 7.72-7.43 (m, 21H; ArH), 4.14 (d, 4H; CH_2OAr , J = 5.3 Hz), 3.62-3.38 (m, 48H; CH_2O), 3.34 (s, 12H; CH_3O), 2.16-2.13 (m, 3H; $\text{CH}(\text{OCH}_2)_2$); ^{13}C -NMR (100 MHz, CDCl_3 , ppm) : δ = 156.464, 140.243, 140.071, 139.861, 139.744, 139.477, 137.393, 131.107, 130.114, 129.439, 128.901, 127.603, 127.400, 127.050, 126.446, 119.631, 111.073, 100.029, 71.976, 70.579, 70.528, 69.717, 69.553, 66.616, 59.038, 40.208, 40.006; Anal. Calcd for: $\text{C}_{62}\text{H}_{86}\text{O}_{15}$: C, 69.51; H, 8.09 Found C, 69.56 ; H, 8.07 ; MALDI-TOF-MS m/z 1093.75 ($[\text{M}+\text{Na}]^+$), Calcd 1093.34.

Solution Preparation

Self-organized samples were prepared by dissolving amphiphilic molecules in deionized water. For mixed samples, amphiphilic molecules were dissolved in THF, and dried in a vacuum oven at 60 °C for about 5 min. The dried mixtures were then dissolved in deionized water. The samples were sealed with para film at room temperature. Before using in each experiment they were stirred 3 days and stabilized more than a week.

Co-assembly of the mixed molecules (1+3 or 2+3) with C_{60} The molecules were mixed in toluene followed by evaporation of toluene and addition of a small amount of THF. After addition of water, THF was evaporated at 80°C for about 1 min.

DLS spectroscopy Dynamic light scattering measurements were performed using UNIPHASE He-Ne laser operating at 632.8 nm. The scattering was kept at 90° during the whole experiment. The maximum operating power of the laser was 30 mW. The detector optics employed optical fibers coupled to an ALV/SOSIPD/DUAL detection unit, which employed an EMI PM-28B power supply and ALV/PM-PD preamplifier/discriminator. The Signal analyzer was an ALV5000/E/WIN multiple tau digital correlator with 288 exponentially spaced channels. The hydrodynamic radius (R_H) was determined from the DLS autocorrelation functions by the cumulants and the CONTIN methods using the software provided by the manufacturer.

TEM Transmission electron microscopy observation was carried out with a JEOL JEM-2010 operated at 120 kV. For study of structure of laterally-grafted amphiphilic molecules in aqueous solution, a drop of aqueous solution (0.005 %) was placed on a carbon-coated copper grid and allowing the solution to evaporate under ambient conditions.

The cryogenic transmission electron microscopy experiments (cryo-TEM) were performed with a thin film of aqueous solution of molecule (5 μL) transferred to a lacey supported grid. The thin aqueous films were prepared under controlled temperature and humidity conditions (97-99 %) within a custom-built environmental chamber in order to prevent evaporation of water from sample solution. The excess liquid was blotted with filter paper for 2-3 seconds, and the thin aqueous films were rapidly vitrified by plunging them into liquid ethane (cooled by liquid nitrogen) at its freezing point. The grid was transferred, on a Gatan 626 cryoholder, using a cryo-transfer device. After that they were transferred to a JEM-2010 TEM. Direct imaging was carried out at a temperature of approximately $-175\text{ }^{\circ}\text{C}$ and with a 120 kV accelerating voltage, using the images acquired with a Dual vision 300W and SC 1000 CCD camera (Gatan, Inc.; Warrendale, PA).

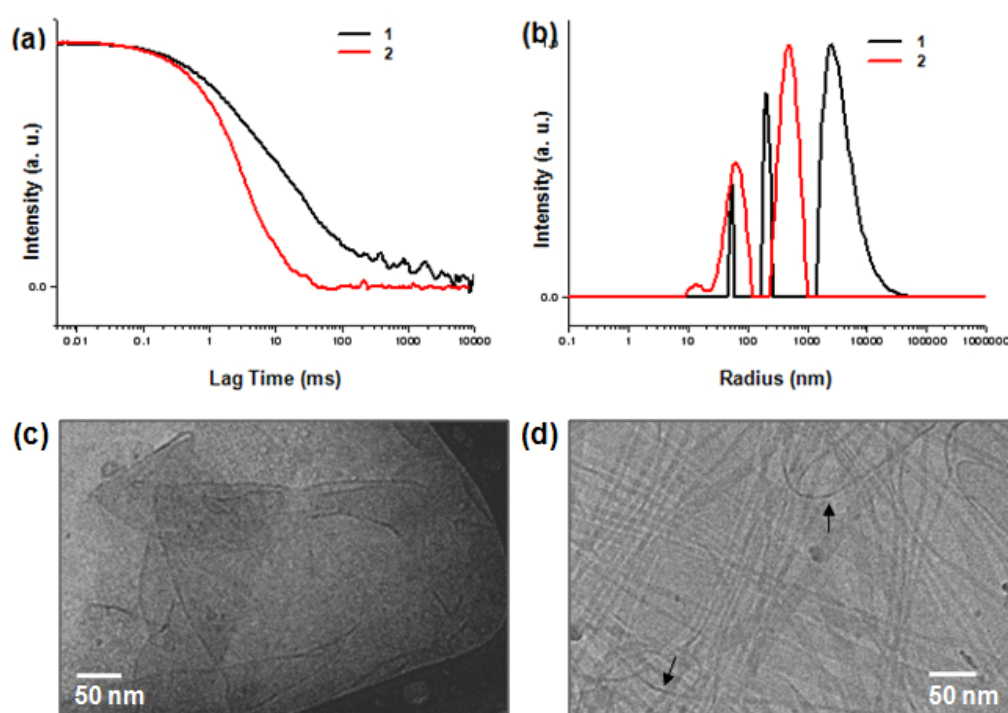


Figure S1. (a) Autocorrelation functions and (b) size distribution graphs at scattering angle 90° from CONTIN analysis of the autocorrelation function of laser light scattering of aqueous solutions **1** and **2** (0.005 wt %). Cryo-TEM images showing (c) the crumpled sheets of **1** and (b) the flat ribbons of **2** (arrows indicate folded edge of ribbons) in aqueous solution (0.005 wt %).

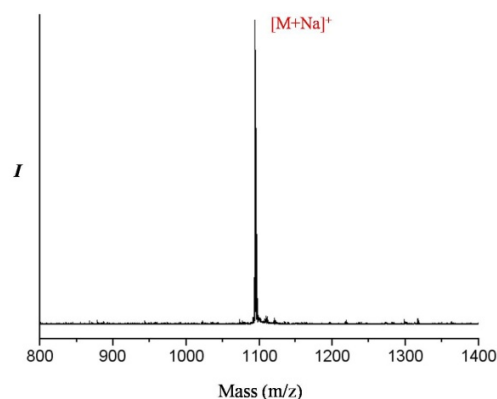


Figure S2. MALDI-TOF mass spectra of **3**.

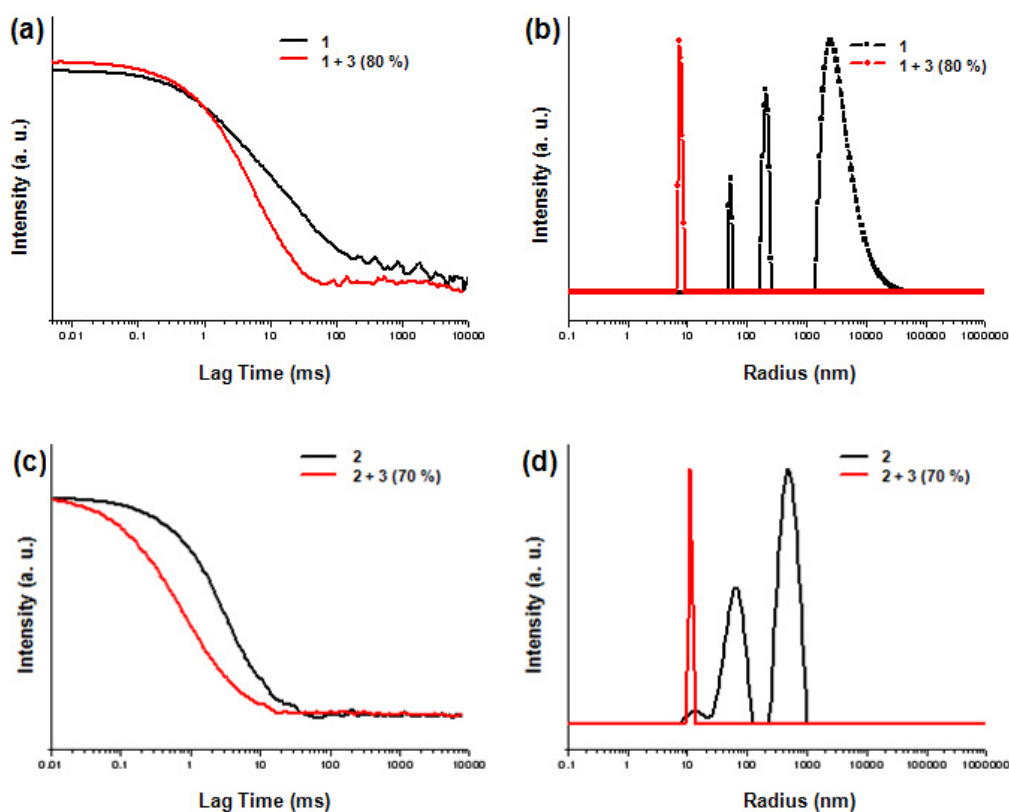


Figure S3. (a,c) Representative correlation functions of laser light scattering of aqueous solutions of (a) **1** and **1** containing **3** (80 mol % relative to **1**), and (c) **2** and **2** containing **3** (70 mol % relative to **1**). (b,d) Size distribution graphs at a scattering angle 90° from CONTIN analysis of the autocorrelations of (b) **1** and **1** containing **3** (80 mol % relative to **1**), and (d) **2** and **2** containing **3** (70 mol % relative to **1**).

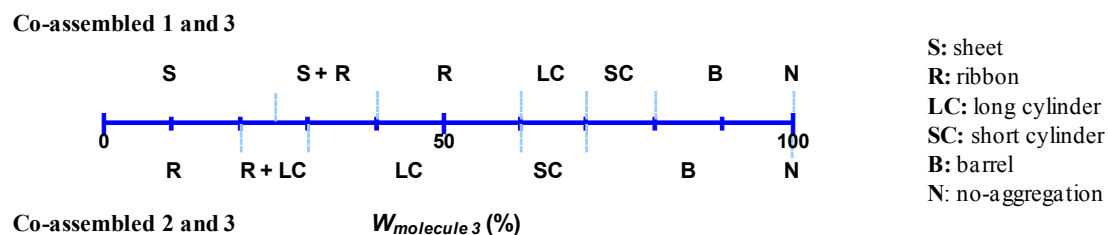


Figure S4. Morphology diagram correlating co-assembled system of **1** and **3**, and **2** and **3** in aqueous medium (0.005 wt %).

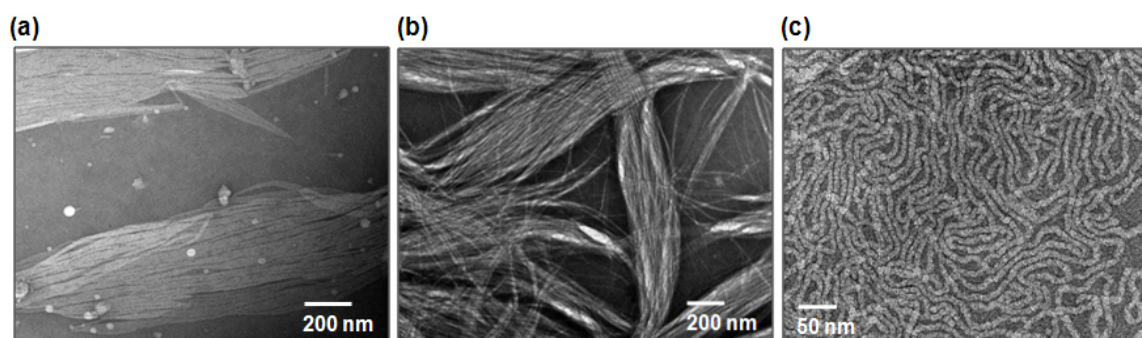


Figure S5. TEM images of premixed samples of **1** and **3** with different molar ratios: (a) 6:4, (b) 4:6 and (c) 3:7.

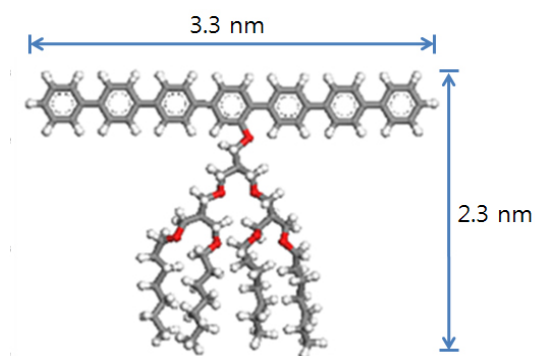


Figure S6. The CPK modeling of laterally-grafted amphiles **1** and **2**. It showed the only hydrophobic segment including the aromatic segment and alkyl chains.

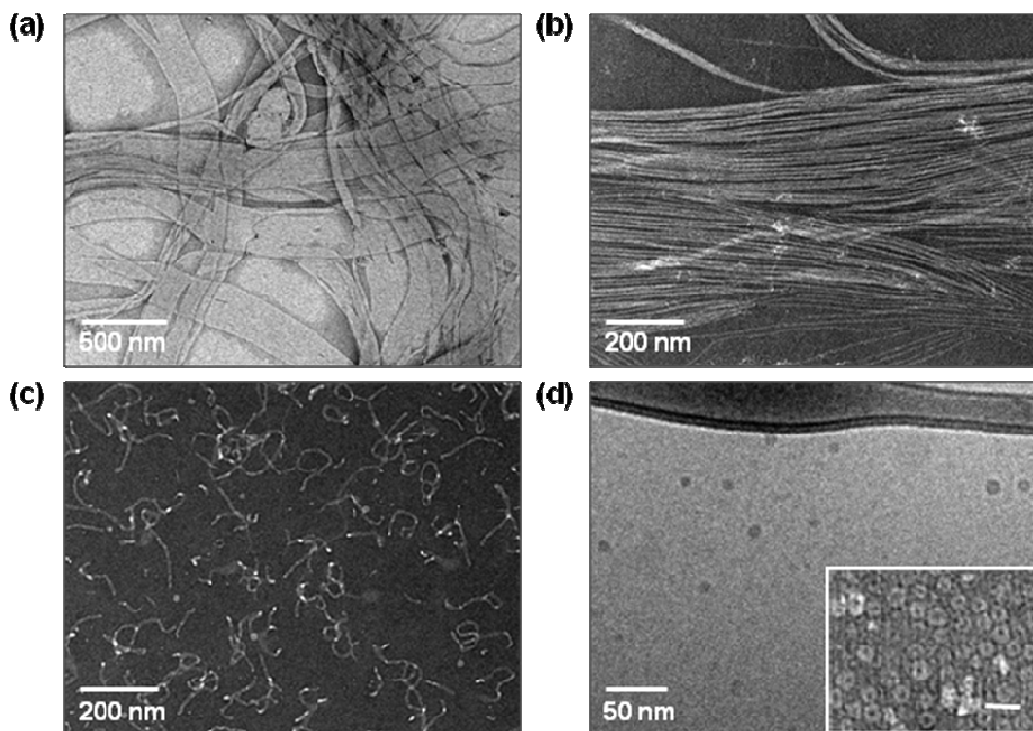


Figure S7. (a-c) TEM images and (d) cryo-TEM image of premixed samples of **2** and **3** with different molar ratios: (a) 9:1, (b) 6:4, (c) 4:6, (d) 2:8.

This structural progression from long ribbons, short cylinders to rings could be rationalized by considering steric repulsions between the bulky dendritic chains and a parallel arrangement of the rod segments. The tendency of the rod segments to pack into a parallel arrangement accompanies a strong repulsion of the dendritic chains, as the content of the flexible chains is increased through the addition of diblock molecule **3**. To reduce energetic penalty associated with steric repulsion, long ribbons would break up into short cylinders that allow more volume for dendritic chains to be explored. Eventually, short cylinders with hydrophobic ends would be transformed into highly curved barrels to reduce unfavorable contact between the hydrophobic ends of the short cylinders and water molecules.

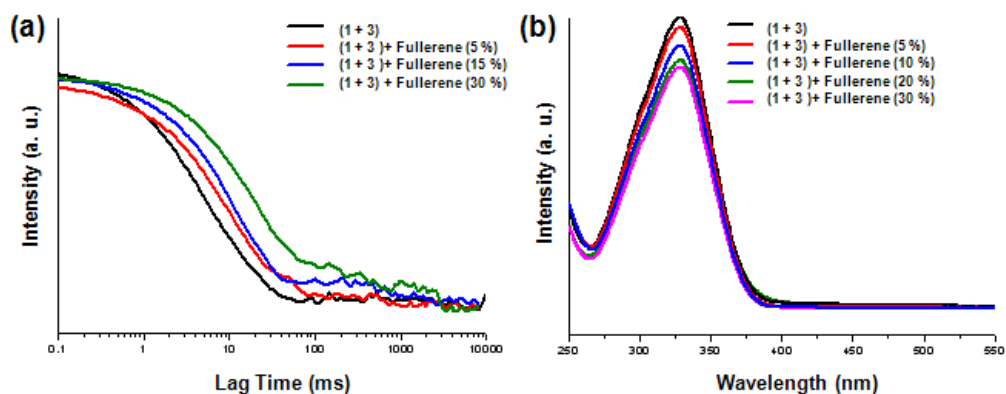


Figure S8. (a) Representative correlation functions of laser light scattering and (b) absorption spectra of aqueous solutions (0.005 wt %) of **1+3** without C_{60} fullerene and with C_{60} fullerene (5-30 mol %).

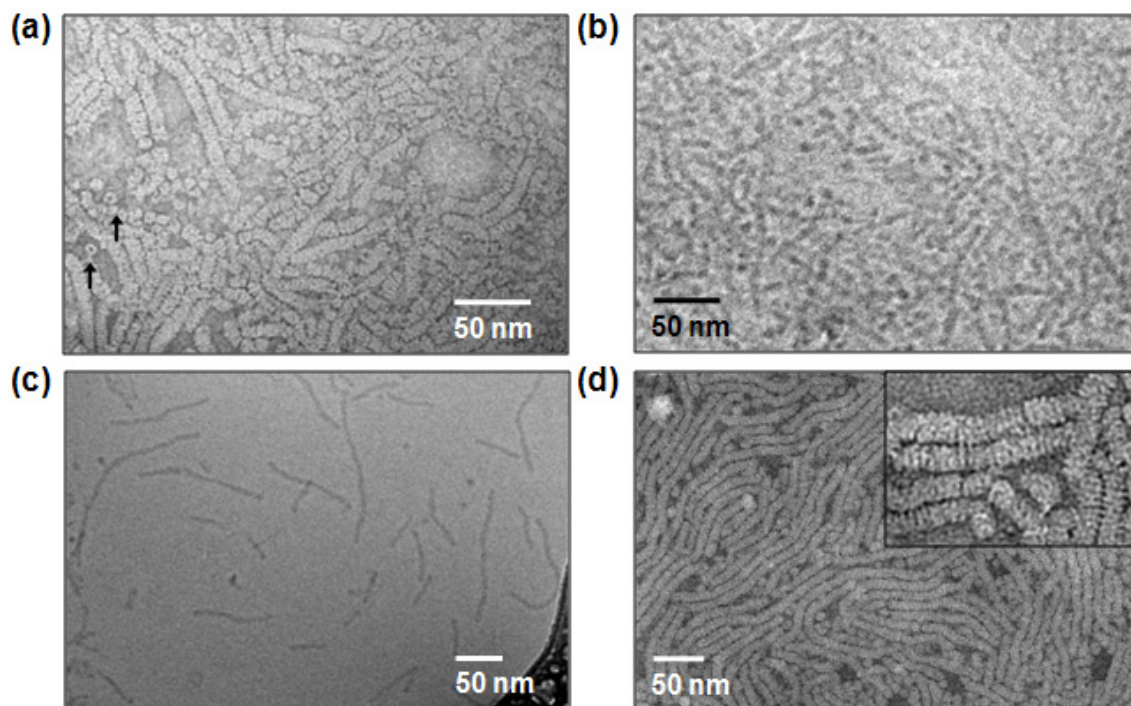


Figure S9. (a,d) TEM images and (b,c) cryo-TEM images of premixed samples of **1+3** containing C_{60} (a and b, 10 mol %; c, 20 mol %; d, 30 mol %).

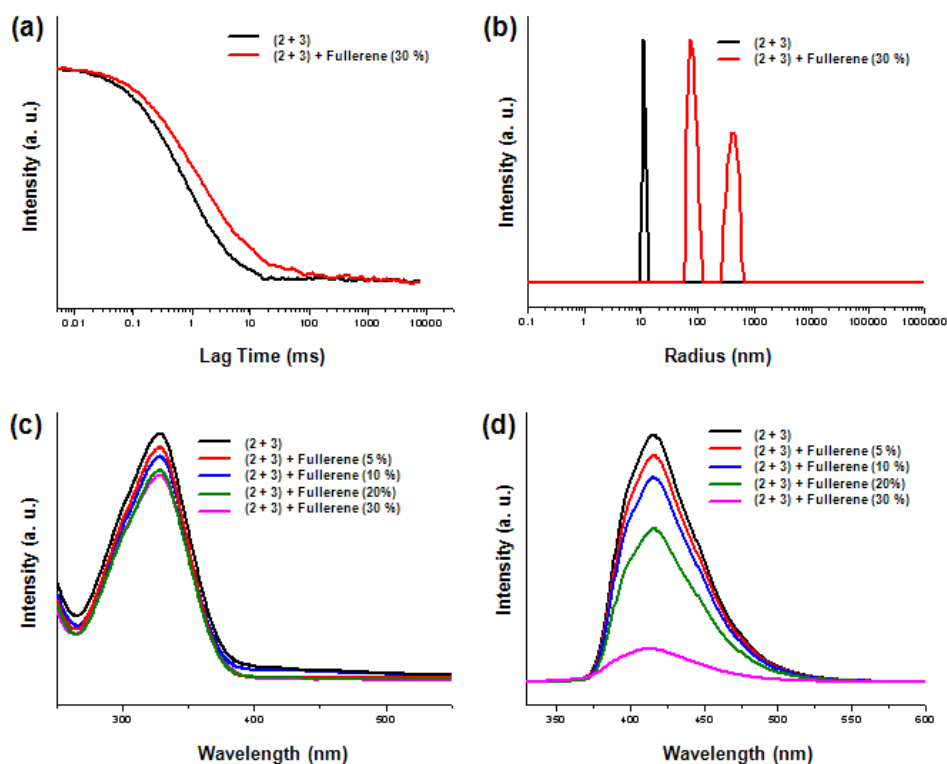


Figure S10. (a) Representative correlation functions of laser light scattering, (b) size distribution graphs at a scattering angle 90° from CONTIN analysis of the autocorrelation, (c) absorption spectra and d) fluorescence spectra ($\lambda_{\text{ex}} = 316 \text{ nm}$) of aqueous solutions (0.005 wt %) of **2+3** without C₆₀ and with C₆₀ (30 mol %).

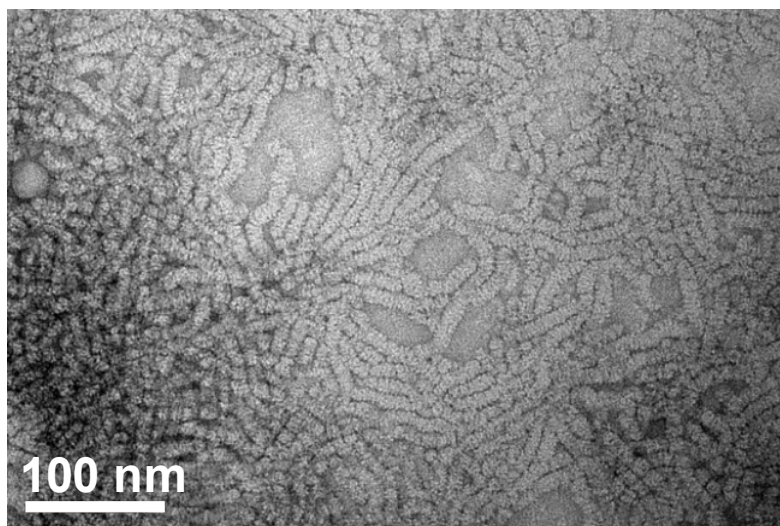


Figure S11. TEM image of one-dimensionally assembled **2+3** after mixing with C₆₀ (30 mol %).

References for Supporting Information

S1. Lee, E.; Kim, J.-K.; Lee, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 3657-3660.