

Supporting Information

Carbohydrate-Coated Supramolecular Structures: Transformation of Nanofibers into Spherical Micelles Triggered by Guest Encapsulation

Ja-Hyoung Ryu, Eunji Lee, Yong-beom Lim, and Myongsoo Lee*

Center for Supramolecular Nano-Assembly and Department of Chemistry, Yonsei
University, Seoul 120-749, Korea

E-mail: mslee@yonsei.ac.kr

Experimental section

Materials

NaH (60%), *p*-toluene-sulfonyl chloride (98%) from Tokyo Kasei were used as received. D(+)-Mannose (99%), *tert*-butyldimethylsilyl chloride (97%), tetrabutylammonium fluoride (1.0 M solution in tetrahydrofuran), benzyl bromide (98%), sodium methoxide (95%), iodomethane (99%), 1-bromododecane (97%), palladium on carbon 5 wt%, ethylene glycol (95%), *n*-butyl lithium (1.6M solution in *n*-hexane), borane-THF complex (1.0M solution in THF), tetrakis (triphenylphosphine) palladium (0) (99%), triisopropyl borate (98+%), iodine monochloride (1.0M solution in dichloromethane), 3-chloro-2-chloromethyl-1-propene (99%) (all from Aldrich) and the conventional reagents were used as received. Unless otherwise indicated, all starting materials were obtained from commercial suppliers (Aldrich, Lancaster, TCI, etc.). All atmosphere sensitive reactions were done under nitrogen. Flash column chromatography was carried

out with Silica Gel 60 (230-400 mesh) from EM Science. Bromo-2,3,4,6-tetra-*O*-acetyl- α -D-mannopyranoside was prepared according to the procedures described previously.¹ For synthetic detail, see the Supporting Information. ¹H and ¹³C NMR spectra were recorded from CDCl₃ or DMSO 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. Dynamic light scattering measurements were performed using a UNIPHASE He-Ne laser operating at 632.8 nm. The maximum operating power of the laser was 30 mW. The detector optics employed optical fibers coupled to an ALV/SO-SIPD/DUAL detection unit, which employed an EMI PM-28B power supply and ALV/PM-PD preamplifier/discriminator. The signal analyzer was an ALV-5000/E/WIN multiple tau digital correlator with 288 exponentially spaced channels. MALDI-TOF mass was performed on a Perseptive Biosystems Voyager-DE STR using a 2,5-dihydroxy benzoic acid matrix. X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the 3C2 X-ray beam line at Pohang Accelerator Laboratory, Korea. For TEM measurements, 3 μ L of an aqueous solution of sample was placed onto a holey carbon-coated copper grid, and 3 μ L of 2 % (w/w) uranyl acetate solution was added for negative stain. The sample was deposited for 1 min, and excess solution was wicked off by filter paper. The dried specimen was observed with a JEOL-JEM 2010 instrument operating at 120 kV. The data were analyzed with Digital Micrograph software. In case of solid sample, the sample was microtomed at room temperature using a cyro-ultramicrotome without staining. Optical absorption spectra were obtained from a Shimadzu 1601 UV spectrophotometer. The steady-state fluorescence spectra were obtained from a Hitachi F-4500 fluorescence spectrophotometer.

Quantitative Con A precipitation: Fluorescein labeled Con A was obtained from Vector laboratories. The Con A was diluted into a concentration of 0.5 mg/mL with 10 mM Hepes, 0.15 M NaCl, 0.1 mM Ca^{2+} , 0.01 mM Mn^{2+} , 0.08% NaN_3 , pH 7.5. Twenty microliters of the Con A solution was mixed with an equal volume of the object solution in water. The mixture incubated for 10 min at room temperature, centrifuged for 3 min, and 20 μL of supernatant was taken. The fluorescence from non-precipitated Con A was measured at 495 nm (excitation) and 516 nm (emission).

***E. coli* motility inhibition assay:** Overnight culture of *E. coli* strain ORN178 was diluted into the concentration of 5×10^7 cells/mL with phosphate buffered saline (PBS). Two microliters of the *E. coli* solution was placed onto glass slide and 2 μL of serially diluted solutions of the objects in water were added. The sample was covered with a cover glass and a layer of rubber cement was placed around the edges. The *E. coli* was observed with Nikon Eclipse TE2000-U inverted fluorescence microscope equipped with DXM1200C digital camera. For the motility inhibition assay, time-lapse images were analyzed using Adobe Premiere software. The % motility was expressed as (number of mobile cells / number of total cells) $\times 100$.

UV-Vis spectroscope: To investigate the amount of dye encapsulation, the prepared Nile Red solution (1×10^{-3} M in methylene chloride) was added to aqueous solutions (1.0×10^{-4} M) of the carbohydrate conjugate aromatic molecules with different mole ratios, [Nile Red] / [molecule], from 0.05 to 1 and sonicated for a few hours at room temperature to allow for reaching equilibrium. The methylene chloride was removed via evaporation. After being filtered through 0.45 μm hydrophilic filter (0.45 μm pore PVDF membrane filter), UV/vis spectroscopy measurements were performed with the variation in Nile Red content at the fixed solution of molecule in

water (1.0×10^{-4} M).

Synthesis. The synthetic procedures used in the preparation of mannose-branched amphiphilic molecules is described in Scheme 1.

Synthesis of *tert*-butyldimethylsilyloxyethyl 2,3,4,6-tetra-*O*-acetyl- α -D-mannopyranoside (1).

To a solution of bromo 2,3,4,6-tetra-*O*-acetyl-mannopyranoside (25 g 63.7 mmol) in acetonitrile solution (200 mL) was added derierite (10 g), excess ethylene glycol (20 g, 322 mmol) and mercury(II) cyanide (24.0 g, 101 mmol). The mixture was stirred for overnight at room temperature and then filtered. The resulting residue was dissolved chloroform (200 mL) and washed with $\text{NaCl}_{(\text{sat})}$. The organic layer was dried over anhydrous magnesium sulfate and filtered and concentrated. The crude product was purified by a flash column chromatography (silica gel, EtOAc: hexane = 1: 1) to yield 12.3 g (60%). $^1\text{H-NMR}$ (250 MHz, CDCl_3 , ppm): δ = 5.22-5.12 (m, 3H; H-2, H-3, H-4), 4.78 (d, $J=1.5$ Hz, 1H; H-1), 4.18 (dd, $J=12.0, 5.5$ Hz, 1H; H-6a), 4.03-3.95 (m, 3H; H-6b, H-5), 3.68-3.53 (m, 4H; $\text{OCH}_2\text{CH}_2\text{OH}$), 2.05 2.00 1.94 1.91 (s, 12H; $\text{H}_3\text{CC=O}$).

The above compound (12.3 g, 31.3 mmol) was dissolved in CH_2Cl_2 (100 mL) and added *tert*-butyldimethylsilyl chloride (TBDMSCl) (7 g, 46.4 mmol) and imidazol (4.2 g, 61.5 mmol). The mixture was stirred for 2 hours at room temperature. Then the resulting solution was washed with 1M NaHCO_3 solution and the methylene chloride solution was dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by a flash column chromatography (silica gel, EtOAc: hexane = 1: 1) to yield 14.8 g (93%). $^1\text{H-NMR}$ (250

MHz, CDCl₃, ppm): δ = 5.22-5.12 (m, 3H; H-2, H-3, H-4), 4.78 (d, J =1.5 Hz, 1H; H-1), 4.18 (dd, J =12.0, 5.5 Hz, 1H; H-6a), 4.03-3.95 (m, 3H; H-6b, H-5), 3.68-3.53 (m, 4H; OCH₂CH₂OSi), 2.05 2.00 1.94 1.91 (s, 12H; H₃CC=O), 0.89(m, 12H; Si(CH₂)₂(C(CH₃)₃)), 0.08 (m, 6H; SiC(CH₃)₂(C(CH₃)₃)).

Synthesis of hydroxyethyl 2,3,4,6-tetra-*O*-benzyl- α -D-mannopyranoside (2).

Sodium methoxide (50 mg, 2.1 mmol) was added to a solution of **1** (14.8 g, 29.2 mmol) in methanol (100 mL). After the mixture had been stirred for 4 h at room temperature, was treated with ion-exchange resin and filtered and concentrated to yield hydroxyethyl- α -D-mannopyranoside (9.1 g, in 92% yield). ¹H-NMR (250 MHz, CDCl₃, ppm): δ 4.86 (d, J =1.5 Hz, 1H; H-1), 3.97-3.49 (m, 10H; H-2, H-3, H-4, H-5, H-6, OCH₂CH₂OSi), 0.89 (m, 12H; Si(CH₂)₂(C(CH₃)₃)), 0.08 (m, 6H; SiC(CH₃)₂(C(CH₃)₃)).

The solution of NaH (8.4 g, 350 mmol) in DMF (100 mL) was dropped the solution of the above compound (9.1 g, 26.9 mmol) in DMF (50 mL) in ice bath. Then benzyl bromide (41.46 mL, 350 mmol) was dropped slowly and stirred for 24 h at room temperature. The solution was quenched with MeOH and DMF was removed by vacuum distillation. The residue was extracted with methylene chloride and dried over anhydrous magnesium sulfate, and filtered and concentrated. The crude product was dissolved dried THF (100 mL) and added with 1M TBAF solution (34.3 mL). The mixture solution was stirred for 2 h at room temperature and the solvent was removed in a rotary evaporator, and the crude product by flash column chromatography (silica gel, ethyl acetate/hexane = 4:1) to yield 6.3 g (40.1%). ¹H-NMR (250 MHz, CDCl₃, ppm): δ 7.37-7.14 (m, 20Ar-H; OCH₂phenyl), 4.91 (d, J =1.5 Hz, 1H; H-1), 4.85-4.48 (m, 8H; OCH₂phenyl), 3.91-3.67 (m, 10H; H-2, H-3, H-4, H-5, H-6, OCH₂CH₂OH).

Synthesis of Compound 3.

Dry NaH (0.52 g, 21.7 mmol), 3-chloro-2-chloromethyl-1-propene (0.68 g, 5.5 mmol), and freshly distilled dry THF (50 mL) were placed in a dry round bottomed flask under N₂ gas. The compound **2** (6.3 g, 10.8 mmol) was added dropwise to this mixture at room temperature, and the mixture was stirred at 65 °C for 12 h. After cooling to room temperature, the reaction mixture was quenched with water and extracted with diethyl ether. The organic layer was dried over anhydrous MgSO₄, the solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) with ethyl acetate and hexane (2:1 v/v) as eluent to give a colorless liquid (6.6 g, in 96% yield). ¹H-NMR (250 MHz, CDCl₃, ppm): δ 7.37-7.14 (m, 40Ar-H; OCH₂phenyl), 5.13 (s, 2H; CH₂C), 4.91 (d, *J*=1.5 Hz, 2H; H-1), 4.85-4.48 (m, 16H; OCH₂phenyl), 3.98-3.50 (m, 24 H; H-2, H-3, H-4, H-5, H-6, OCH₂CH₂OCH₂, CH₂CCH₂O).

Freshly distilled dry THF (5 mL) and the above compound (6.6 g, 5.4 mmol) were placed in a dry round bottomed flask under N₂ and cooled to 0 °C in ice bath. A solution of BH₃ (1 M) in THF (11 mL) was added slowly to this mixture, which was then stirred at 0 °C for 2 h. The reaction mixture was quenched with a solution of NaOH in water (2 M, 4 mL) and allowed to stir for 15 min. This was followed by addition of an H₂O₂ aqueous solution of (30%, 4 mL), and the mixture was stirred at room temperature for 30 min. The reaction mixture was saturated with K₂CO₃ and extracted with diethyl ether. The organic layer was dried over anhydrous MgSO₄, the solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) with ethyl acetate and hexane (2:1 v/v) as eluent to afford a

colorless liquid (6.5 g, in 97% yield). $^1\text{H-NMR}$ (250 MHz, CDCl_3 , ppm): δ 7.37-7.14 (m, 40Ar-H; $\text{OCH}_2\text{phenyl}$), 4.91 (d, $J=1.5$ Hz, 2H; H-1), 4.88-4.50 (m, 16H; $\text{OCH}_2\text{phenyl}$), 3.98-3.50 (m, 26H; H-2, H-3, H-4, H-5, H-6, $\text{OCH}_2\text{CH}_2\text{OCH}_2$, $\text{CHCH}_2\text{OCH}_2$ and CHCH_2OH), 2.04 (m, 1H; $\text{CH}_2\text{CH}(\text{OCH}_2)_2$).

The above compound (6.5g, 5.2 mmol) were dissolved of dry dichloromethane (80 mL), pyridine (10 mL), and TsCl (1.5 g, 7.8 mmol) was then added under nitrogen. The reaction mixture was stirred at 25°C under nitrogen for 12 h. The resulting solution was washed with water, and the dichloromethane solution was dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) with ethyl acetate and hexane (2:1 v/v) as eluent to give a colorless liquid (5.5 g, in 75% yield). $^1\text{H-NMR}$ (250 MHz, CDCl_3 , ppm): δ 7.79 (d, $J=4.0$ Hz, 2Ar-H; *o* to SO_3), 7.37-7.14 (m, 42Ar-H; $\text{OCH}_2\text{phenyl}$, *m* to SO_3), 4.91 (d, $J=1.5$ Hz, 2H; H-1), 4.88-4.50 (m, 16H; $\text{OCH}_2\text{phenyl}$), 3.98-3.50 (m, 26H; H-2, H-3, H-4, H-5, H-6, $\text{OCH}_2\text{CH}_2\text{OCH}_2$, $\text{CHCH}_2\text{OCH}_2$, $\text{SO}_3\text{CH}_2\text{CH}$), 2.44 (s, 3H; $\text{SO}_3\text{phenylCH}_3$), 2.24 (m, 1H; $\text{CH}_2\text{CH}(\text{CH}_2\text{O})_2$).

Synthesis of Compound 4.

Compound 4 was synthesized using a similar procedure described previously.² $^1\text{H-NMR}$ (250 MHz, DMSO, ppm): δ = 9.59 (s, 2H; Ar-OH), 7.79-7.65 (m, 13Ar-H), 7.55(d, $J=8.5$ Hz, 2Ar-H; *o* to I), 6.87 (d, $J=8.6$ Hz, 4Ar-H; *o* to OH).

Synthesis of Compound 5.

Compound 4 (0.5 g, 0.93 mmol), compound 3 (2.7 g, 1.9 mmol) and excess K_2CO_3 were dissolved in 100 ml of anhydrous acetonitrile. The mixture was heated at

reflux for 48 h. The resulting solution was poured into water and extracted with methylene chloride. The methylene chloride solution was washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using ethyl acetate and hexane (1:1 v/v) as eluent to yield 2.6 g (94%) of a colorless liquid. $^1\text{H-NMR}$ (250 MHz, CDCl_3 , ppm): δ 7.79-7.51 (m, 15Ar-H), 7.37-7.14 (m, 80Ar-H; $\text{OCH}_2\text{phenyl}$), 7.01 (d, $J=8.6$ Hz, 4Ar-H; *o* to OCH_2CH), 4.95 (d, $J=1.5$ Hz, 4H; H-1), 4.88-4.50 (m, 32H; $\text{OCH}_2\text{phenyl}$), 4.00-3.50 (m, 52H; H-2, H-3, H-4, H-5, H-6, $\text{OCH}_2\text{CH}_2\text{OCH}_2$, $\text{CH}_2\text{CH}(\text{CH}_2)_2\text{O}$, $\text{phenylOCH}_2\text{CH}$), 2.42 (m, 2H; $\text{CH}_2\text{CH}(\text{CH}_2)_2\text{O}$).

Synthesis of Compound 6.

Compound **5** (2.6 g, 0.87 mmol) and 4-hydroxy-phenyl-boronic acid (0.44 g, 1.7 mmol) were dissolved in degassed THF (70 mL). Degassed 2M aqueous Na_2CO_3 solution (70 mL) was added to the solution and then tetrakis-(triphenylphosphine)palladium(0) (5 mg, 0.5 mol%) was added. The mixture was heated at reflux for 48h with vigorous stirring under nitrogen. Cooled to room temperature, the layers were separated, and the aqueous layer was then washed twice with methylene chloride. The combined organic layer was dried over anhydrous magnesium sulfate and filtered, and concentrated. The crude product was dissolved dried THF (100 mL) and added with 1M TBAF solution (1 mL). The mixture solution was stirred for 2 h at room temperature and the solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using ethyl acetate and hexane (1:1 v/v) to yield 2.1 g (79.6%) of a colorless liquid. $^1\text{H-NMR}$ (250 MHz, CDCl_3 , ppm): δ 7.79-7.51 (m, 17Ar-H), 7.37-7.14 (m, 80Ar-H; $\text{OCH}_2\text{phenyl}$), 7.01 (d, $J=8.6$ Hz, 4Ar-H;

o to OCH₂CH), 6.96 (d, *J*=8.5 Hz, 2Ar-H; *o* to OH), 4.95 (d, *J*=1.5 Hz, 4H; H-1), 4.88-4.50 (m, 32H; OCH₂phenyl), 4.00-3.50 (m, 52H; H-2, H-3, H-4, H-5, H-6, OCH₂CH₂OCH₂, CH₂CH(CH₂)₂O, phenylOCH₂CH), 2.42 (m, 2H; CH₂CH(CH₂)₂O).

Synthesis of Compounds 7 and 8.

Compounds were synthesized using the same procedure. A representative example is described for **8**. Compound **6** (0.9 g, 0.30 mmol), bromodocosane (1.16 g, 3.0 mmol) and excess K₂CO₃ were dissolved in 100 mL of anhydrous acetonitrile. The mixture was heated at reflux for 24 h. The resulting solution was poured into water and extracted with methylene chloride. The methylene chloride solution was washed with water, dried over anhydrous magnesium sulfate, and filtered, and concentrated. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using ethyl acetate and hexane (1:1 v/v) as eluent to yield 0.67 g (68%) of a waxy solid.

The above compound (0.5g, 0.15 mmol) was dissolved in methanol (20 mL) and added 5 wt% Pd-C (50 mg). The reaction mixture was stirred at r.t. under hydrogen atmosphere for 24 h until the disappearance of the starting material (TLC). The mixture was filtered through a pad of Celite, and concentrated to yield 0.27 g (96%) of a white solid.

7: mp >250 °C; ¹H-NMR (250 MHz, DMSO, ppm): δ 7.95 (d, *J*=3.8 Hz, 2Ar-H), 7.83-7.78 (m, 11Ar-H), 7.73 (d, *J*=5.5 Hz, 2Ar-H; *m* to OCH₂CH), 7.65 (d, *J*=4.0 Hz, 2Ar-H; *m* to OCH₂CH₂), 7.08 (d, *J*=4.0 Hz, 2Ar-H; *o* to OCH₂CH), 7.02 (d, *J*=4.1 Hz, 2Ar-H; *o* to OCH₂CH₂), 4.72 (d, *J*=1.5 Hz, 4H; H-1), 4.68, 4.65, 4.53, 4.42 (d, 20H; H-2, H-3, H-4, H-5) 4.05-3.98 (m, 4H; phenylOCH₂CH) 3.80 (s, 1H; phenylOCH₃), 3.66-3.45(m,

48H; H-6, $\text{OCH}_2\text{CH}_2\text{OCH}_2$, $\text{CH}_2\text{CH}(\text{CH}_2)_2\text{O}$), 2.30 (m, 2H; $\text{CH}_2\text{CH}(\text{CH}_2)_2\text{O}$). ^{13}C -NMR (250 MHz, DMSO, ppm) : δ 159.4, 142.2, 140.2, 139.9, 138.7 133.5, 132.8, 129.2 128.6, 128.0, 127.6, 124.0, 115.9, 100.8, 74.8, 71.9, 71.2, 70.6, 69.4, 68.4, 67.9, 67.0, 66.5, 62.2, 57.2, 40.0; Anal. Calcd for : $\text{C}_{98}\text{H}_{142}\text{O}_{31}$: C, 60.78; H, 6.62. Found C, 60.49; H, 6.65; MALDI-TOF-MS m/z (M+Na) $^+$ 1543.2, (M+K) $^+$ 1559.5.

8: mp >250 °C; ^1H -NMR (250 MHz, DMSO, ppm): δ 7.95 (d, $J=3.8$ Hz, 2Ar-H), 7.83-7.79 (m, 11Ar-H), 7.73 (d, $J=5.5$ Hz, 2Ar-H; *m* to OCH_2CH), 7.65 (d, $J=4.0$ Hz, 2Ar-H; *m* to OCH_2CH_2), 7.08 (d, $J=4.0$ Hz, 2Ar-H; *o* to OCH_2CH), 7.02 (d, $J=4.1$ Hz, 2Ar-H; *o* to OCH_2CH_2), 4.72 (d, $J=1.5$ Hz, 4H; H-1), 4.68, 4.65, 4.53, 4.42 (d, 20H; H-2, H-3, H-4, H-5) 4.05-3.98 (m, 6H; phenyl OCH_2CH , phenyl OCH_2CH_2), 3.65-3.45(m, 48H; H-6, $\text{OCH}_2\text{CH}_2\text{OCH}_2$, $\text{CH}_2\text{CH}(\text{CH}_2)_2\text{O}$), 2.30 (m, 2H; $\text{CH}_2\text{CH}(\text{CH}_2)_2\text{O}$), 1.72 (m, 2H; - $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.41-1.21 (m, 38H; - $\text{CH}_2(\text{CH}_2)_{19}\text{CH}_3$), 0.82 (t, $J=3.4$ Hz, 3H; - CH_2CH_3). ^{13}C -NMR (250 MHz, DMSO, ppm) : δ 159.4, 142.2, 140.2, 139.9, 138.7 133.5, 132.8, 129.2 128.6, 128.0, 127.6, 124.0, 115.9, 100.8, 74.8, 71.9, 71.2, 70.6, 69.4, 68.4, 67.9, 67.0, 66.5, 62.2, 40.0, 32.2, 29.9, 26.4 23.0, 14.5; Anal. Calcd for : $\text{C}_{98}\text{H}_{142}\text{O}_{31}$: C, 64.81; H, 7.88. Found C, 64.86; H, 7.85 ; MALDI-TOF-MS m/z M $^+$ 1815.1, (M+Na) $^+$ 1838.1, (M+K) $^+$ 1854.0.

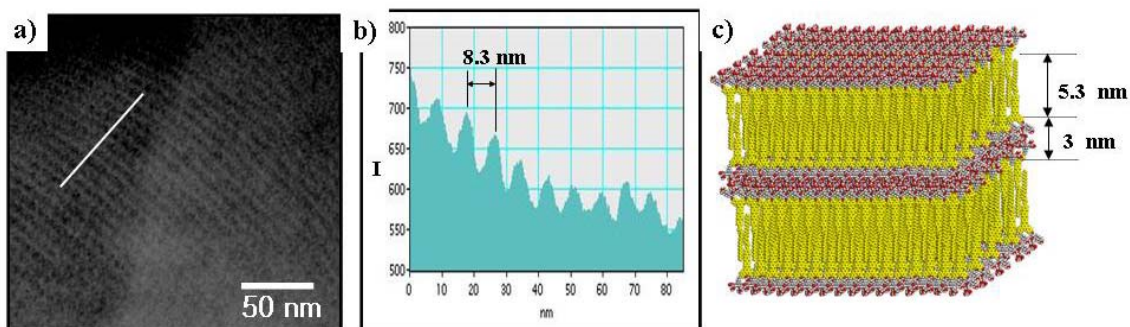


Figure S1. (a) TEM image of ultramicrotomed films of **8** stained with RuO₄ revealing layer array of alternating light hydrophilic, and dark hydrophobic layers and (b) the energy density profile. (c) Schematic representation of the layer structure. The TEM image stained with RuO₄ clearly showed a layered structure with a thickness of 8.3 nm, consistent with that obtained from X-ray diffraction pattern (Figure 2a). The layer consists of light hydrophilic part (~3 nm) and dark hydrophobic segments (~5.3 nm). Considering the molecular length of 5.4 nm and aromatic length (2 nm by Corey-Pauling-Koltun (CPK) molecular model), the dark domains with a thickness of 5.3 nm in the image suggest that the aromatic and docosyl segments are interdigitated. Considering light hydrophilic part of 3 nm in TEM image, the bulky hydrophilic segments can be considered to be packed with a bilayer fashion. Accordingly, we proposed the modified molecular packing of the layered structure.

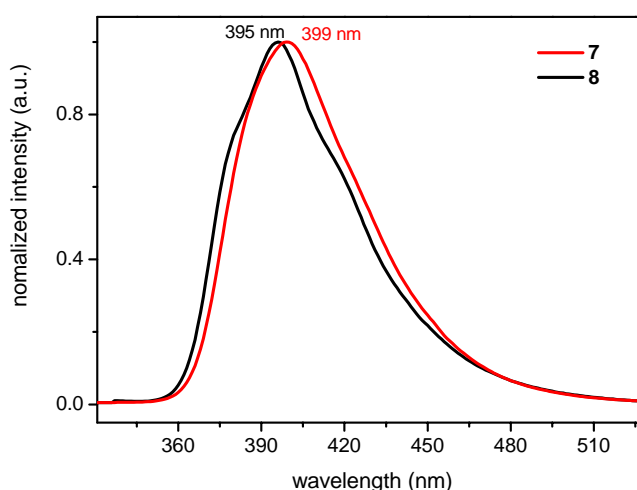


Figure S2. Emission spectra of **7** and **8** in the solid state (excitation wavelength; 300 nm). The emission maxima appear to be 395 and 399 nm for **8** and **7**, respectively and the shape of the emission curve of **7** is broader than that of **8**. These results suggest that aromatic and docosyl segments of **8** are interdigitated to an increase in the separation between aromatic segments.

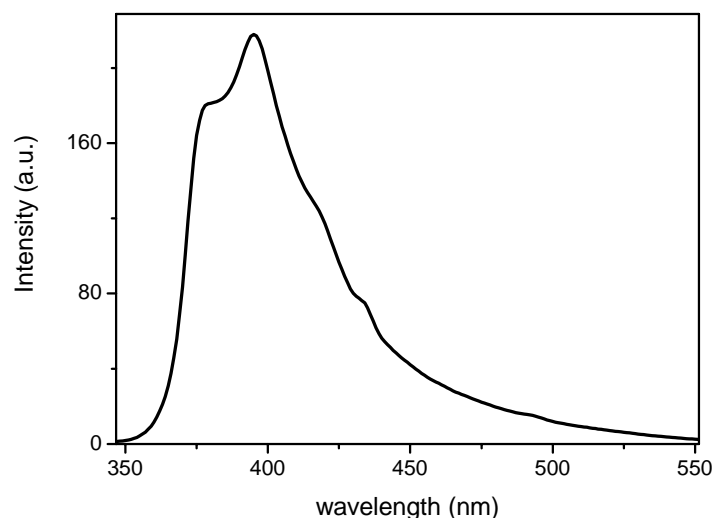


Figure S3. Encapsulation experiment. Fluorescence emission spectrum of **8** encapsulated with 10 mol percent of pyrene. The spectrum was gotten from the difference of **8** and **8** encapsulated with pyrene. Excitation wavelength was 336 nm. The ratio of the intensities of the first (371 nm) and the third (382 nm) peaks of the pyrene monomer, I_1/I_3 , can be used to determine the polarity of the pyrene environment.³ The measured I_1/I_3 ratio of 0.6 for the pyrene encapsulated in **8** indicates that the pyrene is located in the highly nonpolar microenvironment.

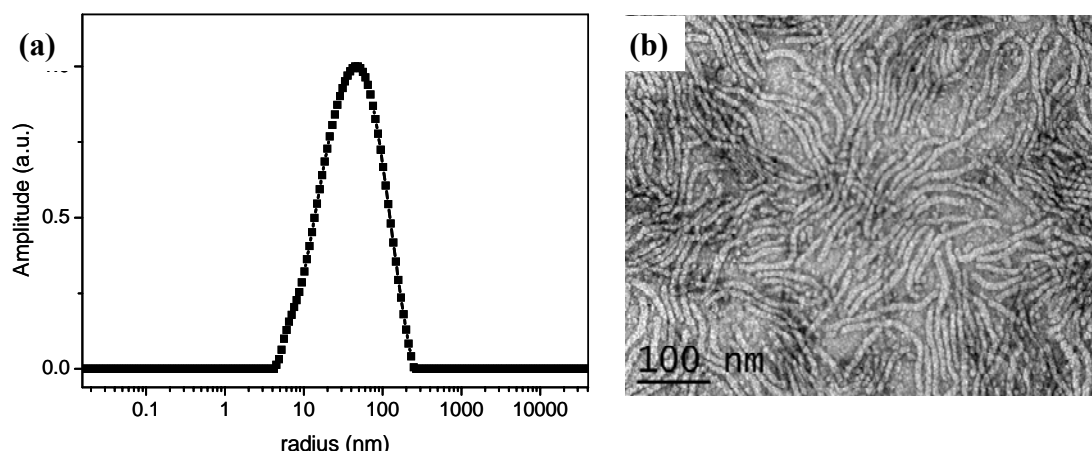


Figure S4. (a) The size distribution graph at scattering angle of 90° from CONTIN analysis of the autocorrelation function of laser light scattering of aqueous solution of **7** (0.1 wt%). (b) TEM image of **7** with negative staining.

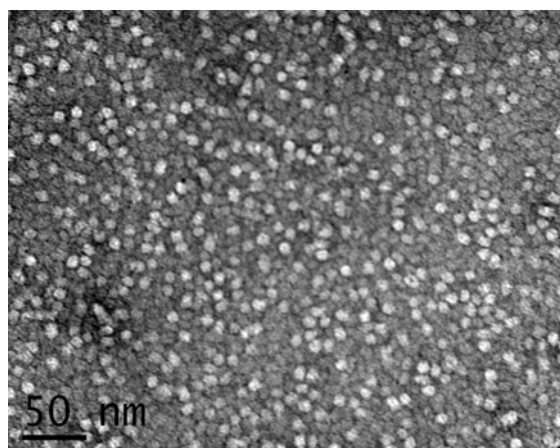


Figure S5. TEM image of mixture solution (0.01 wt%) of 7-Nile Red (5 mol% relative to 7) with negative staining shows the spherical shape.

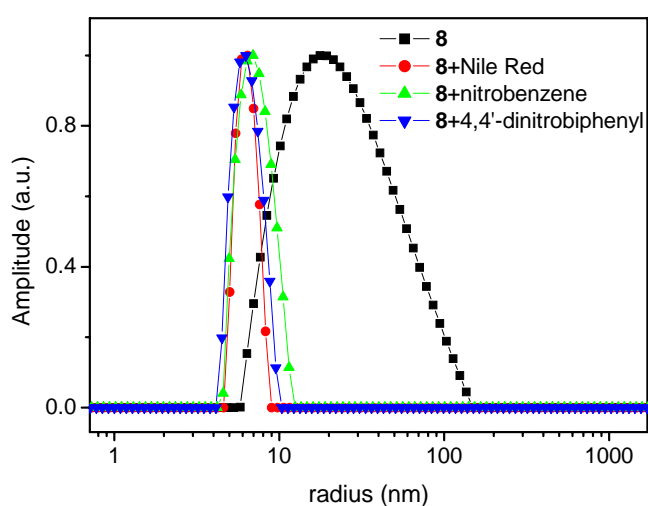


Figure S6. Size distribution graph at scattering angle of 90 ° from CONTIN analysis of the autocorrelation function of laser light scattering of aqueous solution of **8** (0.1 wt%), mixture solution (0.1 wt%) of **8** and Nile Red, nitrobenzene, and 4,4'-dinitrobiphenyl.

Reference

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