

Supplementary Information

Supramolecular Polymerization of Spherical Micelles Triggered by Donor-Acceptor Interaction

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Materials and Methods

Generals. 3,5-dibromoanisole, 1,4-dibromobenzene, 1,3-dibromobenzene, pyrene-1-boronic acid, and iodine monochloride (1.0 M solution in dichloromethane) from Aldrich, 1-ethynyl pyrene, ethyl L-(-)-lactate, tetrakis (triphenylphosphine) palladium (0) (99 %), boron tribromide (1.0 M solution in methylene chloride) from TCI, 3-chloro-2-chloromethyl-1-propene (96 %) from Acros were used as received. Unless otherwise indicated, all starting materials were obtained from commercial suppliers (Aldrich, TCI, Acros, etc.) and were used without purification. Hexane, dichloromethane, and ethyl acetate were distilled before use. Visualization was accomplished with UV light, iodine vapor. Flash chromatography was carried out with Silica Gel 60 (230-400 mesh) from EM Science. Dry THF was obtained by vacuum transfer from sodium and benzophenone.

Techniques. ^1H NMR and ^{13}C NMR spectra were recorded from CDCl_3 or DMSO solutions on a Bruker AM 300 spectrometer. The purity of the products was checked by thin-layer chromatography (TLC; Merck, silica gel 60). Recycling preparative high-pressure chromatography (HPLC) was performed for further purification by using HITACHI model pump L-7110, JAI model UV detector 310 and JAI model RI detector RI-7S. MALDI TOF-MS spectroscopy (MALDI-TOF-MS) was performed on a Bruker Microflex LRF20 using α -cyano-4-hydroxy cinnamic acid (CHCA) as matrix. The dynamic light scattering experiment was performed by DLS-8000 from Otsuka Electronics with a 632.8 nm He-Ne laser. The UV/vis spectra was obtained from a Hitachi U-2900 Spectrophotometer. The fluorescence spectra were obtained from a

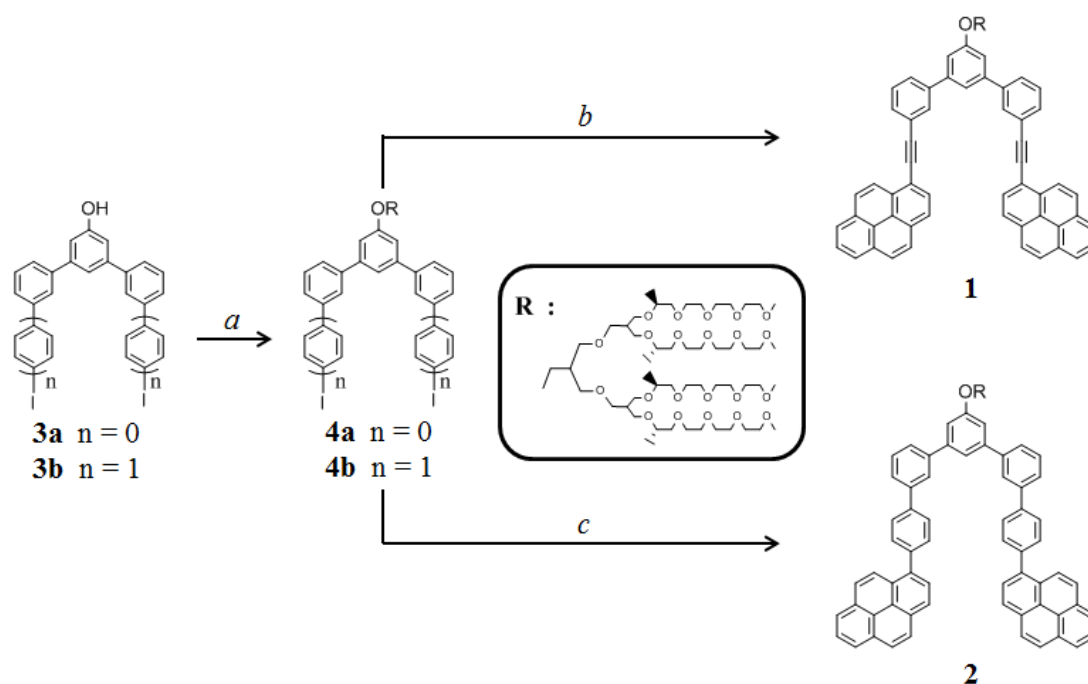
Hitachi F-7000 Fluorescence Spectrophotometer. The transmission electron microscopy (TEM) was performed at 120 kV using JEOL-JEM 2100.

TEM experiment. For the study of the self-assembled structures of **1** and **2** in solution, a drop of solution of amphiphilic molecules was placed on a carbon-coated copper grid and the solution was allowed to evaporate under ambient conditions. The samples were stained by depositing a drop of uranyl acetate onto the surface of the sample-loaded grid. The dried specimen was observed by using a JEOL-JEM 2100 instrument operating at 120 kV. The data were analyzed using Digital Micrograph software.

DLS spectroscopy. Dynamic light scattering measurements were performed using He-Ne laser operating at 632.8 nm. The scattering was kept at 90° during the whole experiment at 25 °C. The hydrophobic diameter (D_H) was determined from the autocorrelation functions by the time interval method of photon correlation and the CONTIN methods using the software provided by the manufacturer. In order to avoid contamination of dust, all solutions were filtered through a 0.45 μm membrane filter.

Synthesis of compounds 1 - 2

Second-generation chiral dendritic tetraethylene glycol coil(*S1*), aromatic scaffolds **3a** and **3b** (*S2*) were prepared according to the same procedures as described previously.



Reagents and conditions : (a) K_2CO_3 , CH_3CN , reflux; (b) triethylamine, copper iodide, tetrakis-triphenylphosphine palladium(0); (c) 4-biphenylboronic acid, 2M K_2CO_3 , tetrakis-triphenylphosphine palladium(0), THF, reflux.

Scheme 1. Synthesis of compounds 1-2.

Compound 4a and 4b. Compound were synthesized the same procedure. A representative example is described for **4a**. Compound **3a** (0.5 g, 1 mmol), ROTs(1.25 g, 1 mmol) and K_2CO_3 (1.1g, 7.0 mmol) were dissolved in 20 mL of anhydrous acetonitrile. The mixture was refluxed overnight 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 ethyl acetate. The ethyl acetate solution was dried over anhydrous magnesium sulfate and filtered. After the solvent was removed in a rotary evaporator, the crude products were purified by column chromatography (silica gel) using methanol : ethyl acetate (1:20 v/v) as eluent to yield 85 % (1.34 g) of colorless liquid.

Compound 4a. $^1\text{H-NMR}$ (300MHz, CDCl_3 , δ , ppm): 7.95 (s, 2H), 7.69 (d, $J = 7.8$ Hz, 2H), 7.57 (d, $J = 7.8$ Hz, 2H), 7.24 (s, 1H), 7.18 (t, $J = 7.8$ Hz, 2H), 7.06 (s, 2H), 4.11 (d, $J = 4.8$ Hz, 2H), 3.70-3.35 (m, 88H), 2.34-2.30 (m, 1H), 2.08-2.04 (m, 2H), 1.11 (d, 12H).

Compound 4b. $^1\text{H-NMR}$ (300MHz, CDCl_3 , δ , ppm): 7.78 (m, 6H), 7.64 (d, $J = 7.8$ Hz, 2H), 7.56 (s, 1H), 7.53 (d, $J = 7.8$ Hz, 2H), 7.40 (m, 6H), 7.16 (s, 2H), 4.14 (d, $J = 4.8$ Hz, 2H), 3.66-3.35 (m, 88H), 2.34-2.30 (m, 1H), 2.08-2.04 (m, 2H), 1.09 (d, 12H).

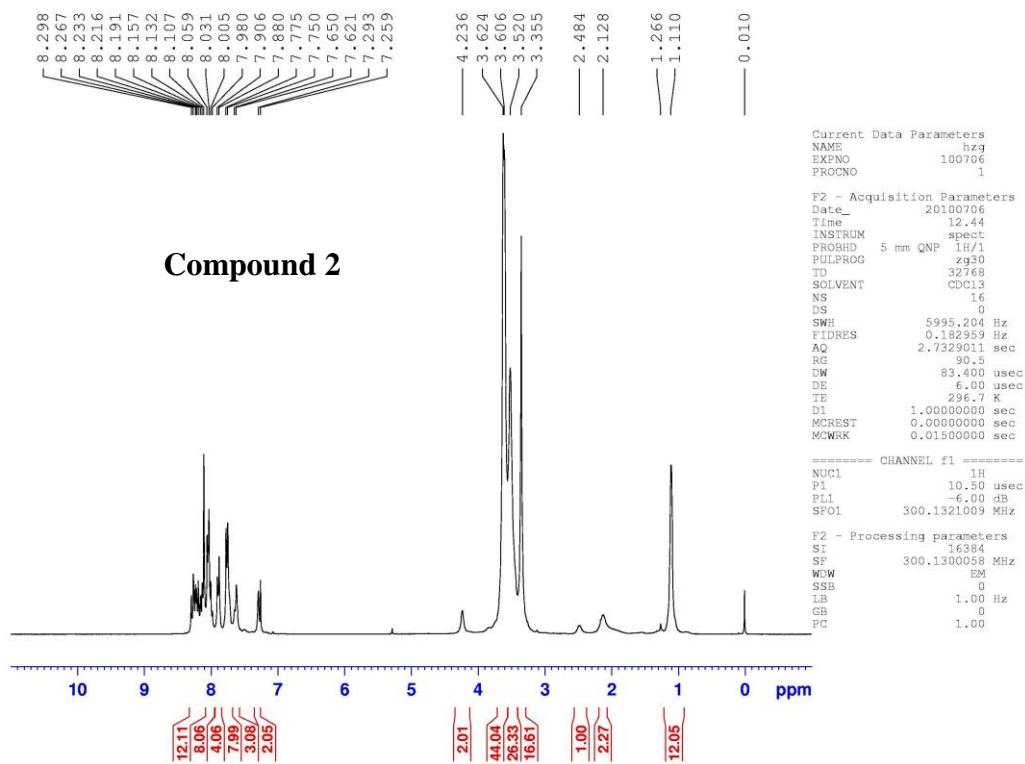
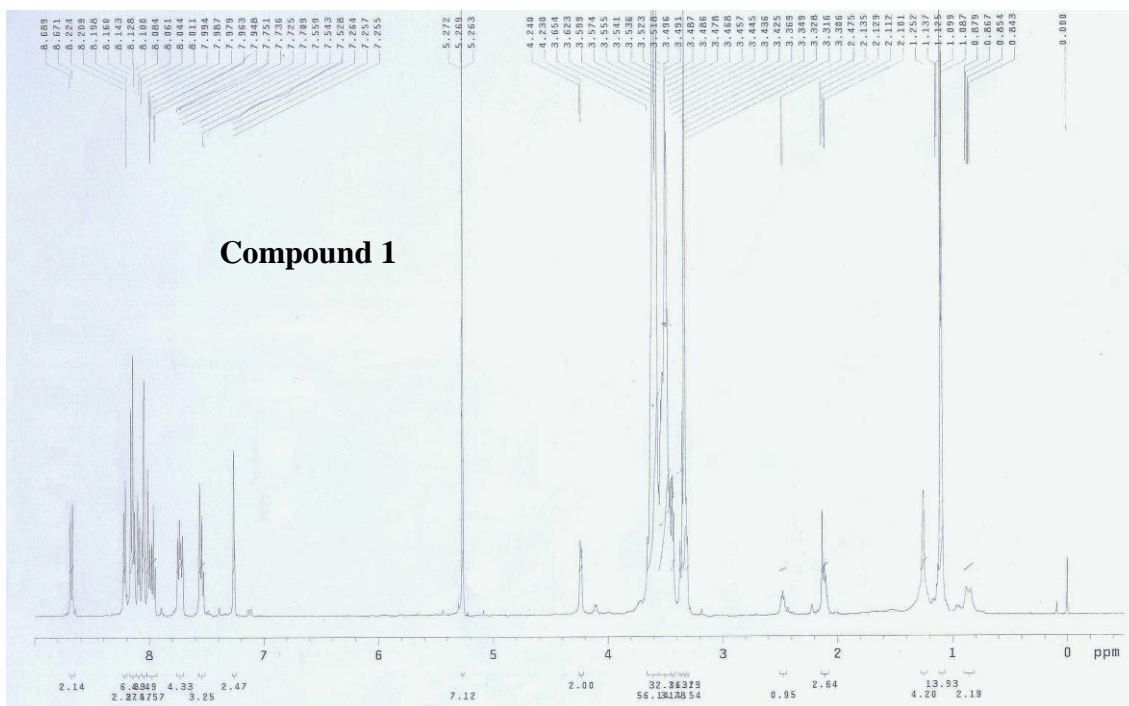
Compounds 1. Compound **3a** (0.43 g, 0.27 mmol), 1-ethynyl pyrene (0.14 g, 0.6 mmol), and copper(I) iodide (0.6 mg, 0.003 mmol) were added to a suspension of tetrakis(triphenylphosphine) palladium(0) (5.9 mg, 0.005 mmol) in 50mL of dry triethylamine. The mixture was degassed and then heated at 70 °C for 24 h. After evaporation, the resulting liquid was extracted with dichloromethane, and dried over anhydrous magnesium sulfate. The crude product was then purified by column chromatography using methanol : ethyl acetate (1:15 v/v) as eluent to yield 70 % (0.34 g) of yellow liquid.

Compound 1. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 8.68 (d, $J = 9$ Hz, 2H), 8.22-7.98 (m, 18H), 7.74 (m, 4H), 7.53 (m, 3H), 7.25 (s, 2H), 4.23 (d, $J = 4.8$ Hz, 2H), 3.70-3.35 (m, 88H), 2.34-2.30 (m, 1H), 2.08-2.04 (m, 2H), 1.10 (d, 12H).; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ , ppm): 160.1, 142.4, 141.4, 131.9, 131.3, 131.2, 131.0, 130.9, 130.5, 129.7, 129.1, 128.4, 128.2, 127.5, 127.2, 126.2, 125.7, 125.6, 125.5, 124.6, 124.4, 124.3, 124.1, 117.6, 112.7, 95.0, 88.9, 74.8, 72.0, 71.9, 70.7, 69.6, 69.3, 67.4, 59.0, 40.8, 17.2. MALDI-TOF mass: m/z calcd. For $\text{C}_{58}\text{H}_{108}\text{Br}_2\text{O}_{23}$ $[\text{M}+\text{H}]^+$, 1775.9; found: $[\text{M}+\text{H}]^+$, 1776.6.

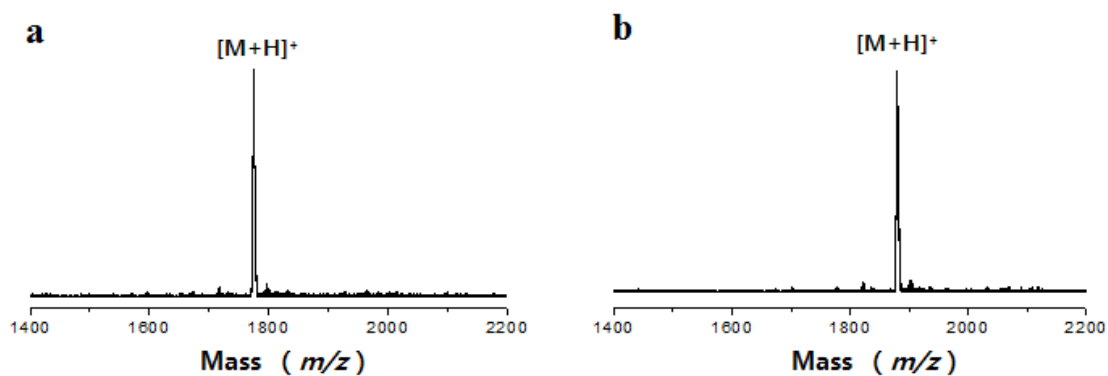
Compound 2. Compound **3b** (1.3 g, 0.74 mmol) and pyrene-1- boronic acid (0.55 g, 2.22 mmol, 3 eq.) were dissolved in degassed THF (30 mL). Degassed 2M aqueous K_2CO_3 (30 mL) was added to the solution and then tetrakis(triphenyl-phosphine) palladium (0) (0.06 g, 0.05 mmol) was added. The mixture was refluxed for 48 hours with vigorous stirring under argon. Cooled to room temperature, the layers were separated, and the aqueous layer was then washed twice with methylene chloride. The combined organic layers were 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 : methanol (15:1 v/v) as eluent to yield 1.0 g (74 %) of yellow liquid.

Compound 2. 1H -NMR (300MHz, $CDCl_3$, δ , ppm): 8.28-8.00 (m, 20H), 7.89 (m, 4H), 7.76 (m, 8H), 7.66 (d, $J = 7.8$ Hz, 2H), 7.62 (s, 1H), 7.29 (s, 2H), 4.23 (d, $J = 4.8$ Hz, 2H), 3.65-3.35 (m, 88H), 2.34-2.30 (m, 1H), 2.08-2.04 (m, 2H), 1.10 (d, 12H); ^{13}C -NMR (100 MHz, $CDCl_3$, δ , ppm): 157.3, 143.4, 142.7, 133.6, 131.8, 131.2, 131.0, 130.9, 130.5, 129.7, 129.1, 128.7, 128.1, 127.6, 127.2, 126.2, 125.7, 125.6, 125.5, 124.6, 124.4, 124.3, 124.1, 117.6, 112.7, 74.8, 72.0, 71.9, 70.7, 69.6, 69.3, 67.4, 59.0, 40.8, 17.2. MALDI-TOF mass: m/z calcd. For $C_{58}H_{108}Br_2O_{23}$ $[M+H]^+$, 1879.9; found: $[M+H]^+$, 1880.6.

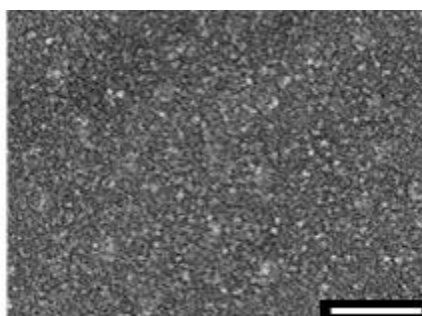
¹H-NMR spectra



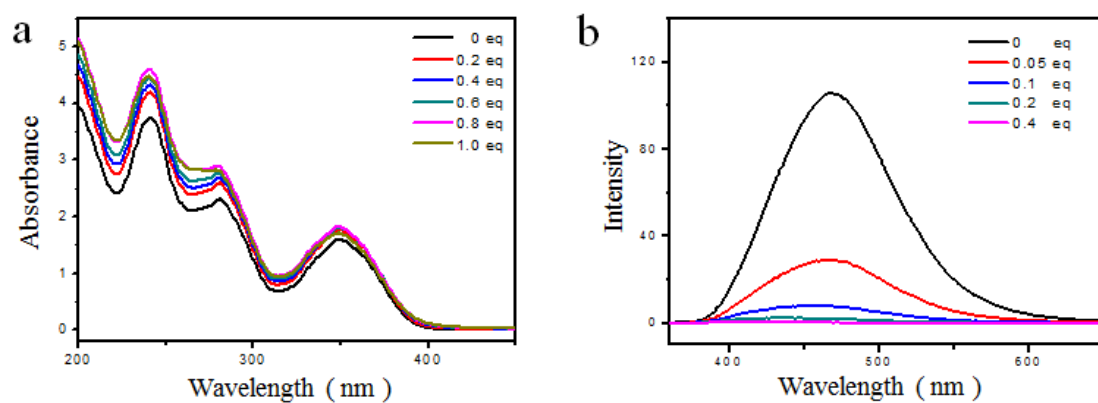
Supplementary Figures and Legends



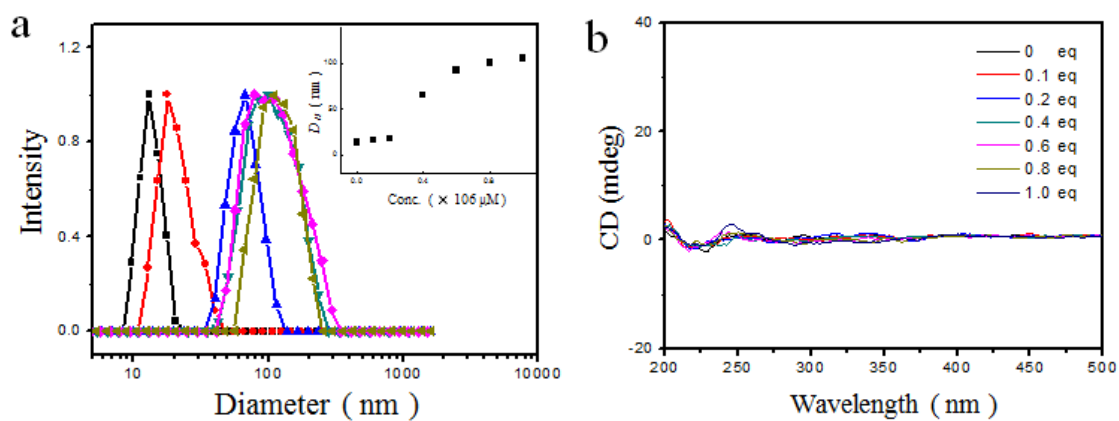
Supplementary Figure S1. MALDI-TOF mass spectra of molecule **1** (a), molecule **2** (b).



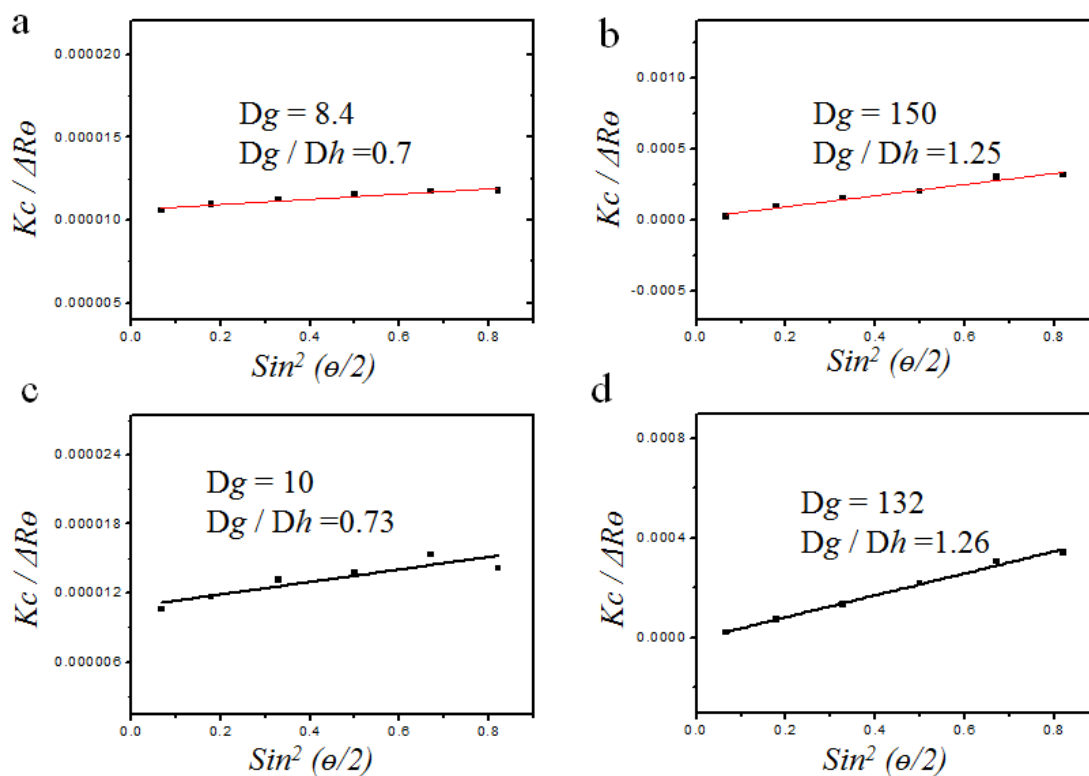
Supplementary Figure S2. A TEM image of **2** from 106 μM aqueous solution (scale bar, 200 nm).



Supplementary Figure S3. (a) Absorption spectra of **2** (53 μM) in the presence of TNF. (b) Fluorescence spectra of **2** (106 μM) in the presence of TNF.



Supplementary Figure S4. (a) Size distribution graphs of 106 μM of **2** in the presence of TNF. (b) CD spectra of **2** (106 μM) in the presence of TNF.



Supplementary Figure S5. Partial Zimm plot for the spherical micelles from 112 μM aqueous solution of **1** (a) and from 106 μM aqueous solution of **2** (c). Partial Zimm plot for the cylindrical micelles in the presence of 1.0 eq TNF from 112 μM aqueous solution of **1** (b) and from 106 μM aqueous solution of **2** (d).

Reference

- S1. H.-J. Kim, J.-H. Lee, M. Lee, *Angew. Chem. Int. Ed.* **44**, 5810 (2005).
- S2. J.-K. Kim, E. Lee, M.-C. Kim, E. Sim, M. Lee, *J. Am. Chem. Soc.* **2009**, *131*, 17768.