

## Supporting Information

### Transformation of Isotropic Fluid to Nematic Gel Triggered by Dynamic Bridging of Supramolecular Nanocylinders

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#### Experimental section

**Materials.** *p*-Toluenesulfonyl chloride (98%), 4-hydroxy-4'-bromobiphenyl (99%) and tetrakis(triphenylphosphine) palladium (0) (99%) from TCI and Tokyo Kasei were used as received. Poly(ethylene glycol) monomethyl ether (MW 750 and MW 3400), *n*-butyllithium (1.6 M solution in *n*-hexane), borane-THF complex (1.0 M solution in THF) and triisopropyl borate (98+%) from Aldrich was used as received. Unless otherwise indicated, all starting materials were obtained from commercial suppliers (Aldrich, Lancaster, etc.) and were used without purification. 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. Biphenyl-boronic acid and molecule **1** were prepared according to the procedures described previously. The compounds were synthesized according to the procedure described scheme 1 and then purified by silica gel column chromatography and then prep-HPLC until transition temperature and

polydispersity index remained constant.

**Techniques.**  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded from  $\text{CDCl}_3$  solutions on a Bruker AM 250 spectrometer. The purity of the products was checked by thin layer chromatography (TLC; Merck, silica gel 60). A Perkin Elmer DSC-7 differential scanning calorimeter equipped with 1020 thermal analysis controller was used to determine the thermal transitions, which were reported as the maxima and minima of their endothermic or exothermic peaks. In all cases, the heating and cooling rates were  $10\text{ }^\circ\text{C min}^{-1}$ . A Nikon optical polarized microscopy (magnification:  $100\times$ ) equipped with a Mettler FP 82 hot-stage and a Mettler FP 90 central processor was used to observe the thermal transitions and to analyze anisotropic textures. Microanalyses were performed with a Perkin Elmer 240 elemental analyzer at Organic Chemistry Research Center. X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the 3C2 X-ray beam line at Pohang Accelerator Laboratory, Korea. In order to investigate structural changes on heating, the sample was held in an aluminum sample holder, which was sealed with the window of  $7\text{ }\mu\text{m}$  thick Kapton films on both sides. The sample was heated with two cartridge heaters and the temperature of the samples was monitored by thermocouple placed close to the sample. Subtracting the scatterings from the Kapton made background scattering correction. Molecular weight distributions ( $M_n/M_w$ ) were determined by gel permeation chromatography (GPC) with a Waters R401 instrument equipped with Stragel HR 3, 4 and 4E columns, M7725i manual injector, column heating chamber and 2010 Millennium data station. Measurements were made by using an UV detector,  $\text{CHCl}_3$  as solvent ( $1.0\text{ mL min}^{-1}$ ). Dynamic light scattering measurements were performed using

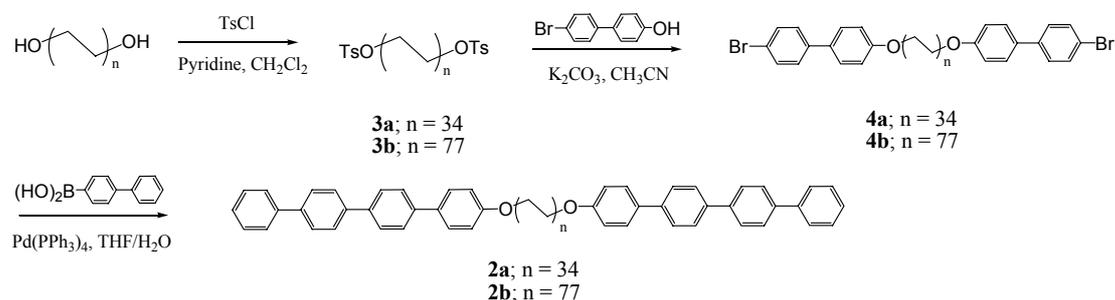
an ALV / CGS-3 Compact Goniometer System. The steady-state fluorescence spectra were obtained from a Hitachi F-4500 fluorescence spectrophotometer. The transmission electron microscope (TEM) was performed at 120kV using JEOL 1020. For study of gel structures in aqueous solution, a drop of aqueous solution of molecules (0.01 wt %) was placed on a carbon-coated copper grid, and dried at room temperature. Sample was stained by depositing a drop of 1 wt % uranyl acetate aqueous solution onto the surface of the sample-loaded grid. Solution viscosities were measured at 25 °C with a capillary viscometer to get reproducible results. The measurements were performed from concentrated to dilute solutions. The reduced viscosity was obtained from following equation.

$$\text{Reduced viscosity} = (\text{run time of solution} - \text{run time of water}) / (\text{run time of water}) / \text{concentration of molecules (g/L)}$$

**Gelation behavior:** Gelation concentration was measured by using the tube inversion method. In a test tube, molecule **1** and **2b** were mixed with appropriate amounts of water and the mixture was dissolved. To be equilibrium, the mixture was heated at 80 °C and slowly cooled for 12 h. When the test tube could be inverted without change of shape of its contents, it was identified as a gel, indicating that the bridging process takes several hours. To confirm the reversible bridging between nematic gel and isotropic fluid phase according to an amount of **2b**, the gelation behavior was investigated, at the fixed total concentration of solution at 3.0 wt%, with the concentration of **2b** relative to **1** changing from 5 to 10 wt%, by using POM. As shown in Figure 3a, 5 wt% **2b** solution is isotropic fluid. Upon addition of **2b** to 10wt%, the solution leads to the strong birefringence of nematic texture, indicating that the

gelation occurs, and then adding **1** to this birefringent gel to result in 5 wt% **2b** solution recovers isotropic fluid. These results mean that, depending on relative amount of **2b**, the transition between nematic gel and isotropic fluid phase shows to be reversible.

**Synthesis.** A general outline of the synthetic procedures is shown in Scheme 1.



**Scheme 1.** Synthesis of rod-coil-rod molecules **2a**, **2b**.

### Synthesis of compound **3a** and **3b**.

Compound **3a** and **3b** were synthesized using the same procedure. A representative example is described for **3b**. Poly (ethylene glycol) methyl ether ( $M_w = 3400$ ) (20.0 g, 5.9 mmol) and *p*-toluenesulfonyl chloride (4.7 g, 23.5 mmol) were dissolved in dry methylene chloride. Pyridine (4 ml, 40 mmol) was added under nitrogen. The reaction mixture was stirred at 25°C under nitrogen for 12 h. The resulting solution was extracted with methylene chloride and 1M HCl and water. The methylene chloride solution 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 methylene chloride : methanol (8:1 v/v) as eluent to yield 18 g (82.2%) of colorless liquid. <sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>, ppm): δ = 7.79 (d, 4Ar-H; *o* to SO<sub>3</sub>, *J* = 8.2 Hz), 7.34 (d, 4Ar-H; *m* to SO<sub>3</sub>, *J* = 8.0 Hz), 4.15 (t, 4H, -

$CH_2OS$ ,  $J = 5.1$  Hz), 3.51-3.68 (m, 304H,  $-CH_2O$ ), 2.43 (s, 6H,  $-CH_3$ phenyl).

Compound **3a**. yield 84%:  $^1H$ -NMR (250 MHz,  $CDCl_3$ , ppm):  $\delta = 7.79$  (d, 4Ar-*H*; *o* to  $SO_3$ ,  $J = 8.2$  Hz), 7.34 (d, 4Ar-*H*; *m* to  $SO_3$ ,  $J = 8.1$  Hz), 4.15 (t, 4H,  $-CH_2OS$ ,  $J = 5.0$  Hz), 3.51-3.68 (m, 132H,  $-CH_2O$ ), 2.43 (s, 6H,  $-CH_3$ phenyl).

### Synthesis of compound 4a and 4b.

Compound **4a** and **4b** were synthesized using the same procedure. A representative example is described for **4b**. Compound **3b** (5.5 g, 1.48 mmol), 4'-bromo-[1,1'-biphenyl]-4-ol (1.1 g, 4.43 mmol) and excess  $K_2CO_3$  (2.0g, 14.8 mmol) were dissolved in 100 mL of anhydrous acetonitrile. The mixture was heated at reflux for 12 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 methylene chloride : methanol (8:1 v/v) as eluent to yield 5.0 g (87.8 %) of a waxy solid.  $^1H$ -NMR (250 MHz,  $CDCl_3$ , ppm):  $\delta = 7.54$ -7.39 (m, 12Ar-*H*), 6.99 (d, 4Ar-*H* ; *o* to Br,  $J = 6.8$  Hz), 4.15 (t, 4H,  $CH_2OAr$ ,  $J = 5.1$  Hz), 3.51-3.68 (m, 304H,  $-CH_2O$ ).

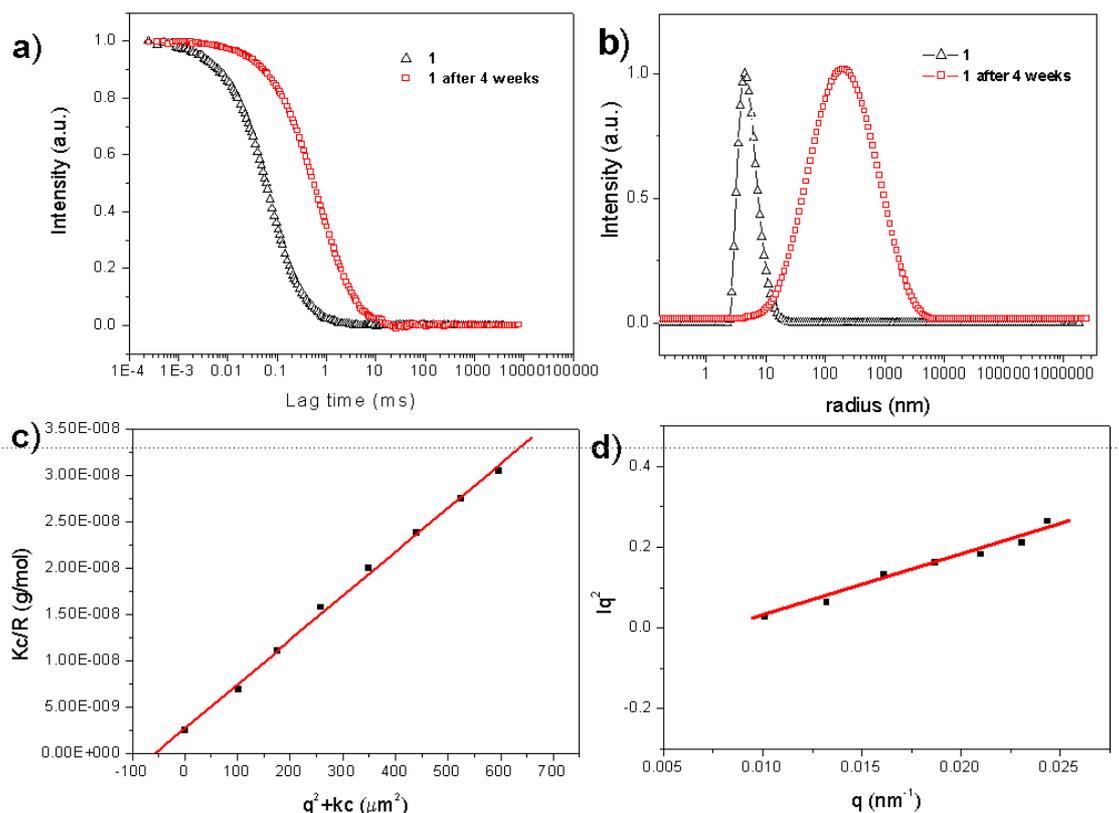
Compound **4a**. yield 84.5%:  $^1H$ -NMR (250 MHz,  $CDCl_3$ , ppm):  $\delta = 7.55$ -7.39 (m, 12Ar-*H*), 6.99 (d, 4Ar-*H* ; *o* to Br,  $J = 6.9$  Hz), 4.15 (t, 4H,  $CH_2OAr$ ,  $J = 5.2$  Hz), 3.51-3.68 (m, 132H,  $-CH_2O$ ).

### Synthesis of 2a and 2b.

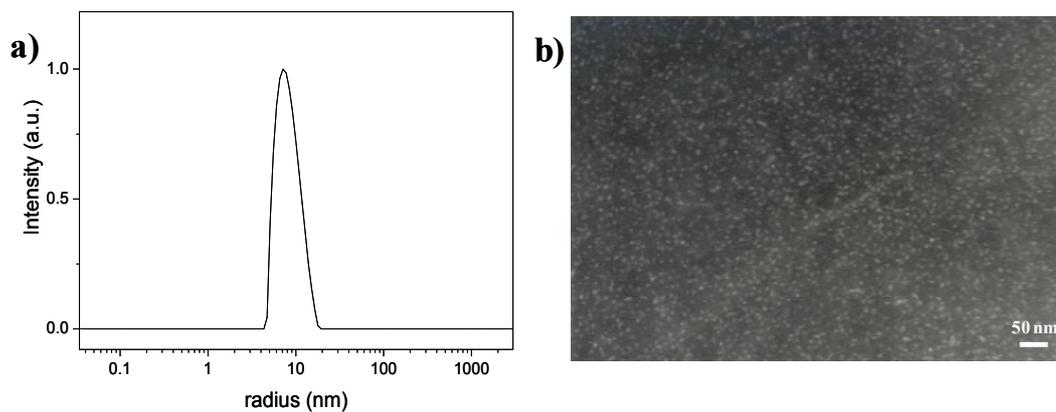
Compound **2a** and **2b** were synthesized using the same procedure. A representative example is described for **2b**. Compound **4b** (3.6 g, 0.93 mmol) and 4,4'-

biphenylboronic acid (0.37 g, 1.86 mmol) were dissolved in degassed THF (70 mL). Degassed 2M aqueous Na<sub>2</sub>CO<sub>3</sub> (70 mL) was added to the solution and then tetrakis(triphenylphosphine) palladium (0) (22 mg, 0.018 mmol) was added. The mixture was heated at reflux for 48 h 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. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using methylene chloride : methanol (8:1 v/v) as eluent and then prep-HPLC to yield 3.1 g (83.1 %) of a white solid. <sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>, ppm): δ = 7.34-7.71 (m, 30Ar-H), 7.00 (d, 4Ar-H; *o* to ArO, *J* = 8.7 Hz), 3.91 (t, 4H; Ar-OCH<sub>2</sub>, *J* = 4.9 Hz), 3.53-3.75(m, 304H; CH<sub>2</sub>O); <sup>13</sup>C-NMR (250 MHz, CDCl<sub>3</sub>, ppm): δ = 158.5, 139.8, 139.5, 128.0, 127.4, 127.3, 115.0, 77.6, 77.1, 76.6, 71.9, 70.8, 70.6, 69.7, 67.5;; M<sub>n</sub>/M<sub>w</sub> = 1.05 (GPC); Anal. Calcd. for C<sub>202</sub>H<sub>342</sub>O<sub>78</sub>: C, 60.37; H, 8.58. Found C, 60.32; H, 8.60.

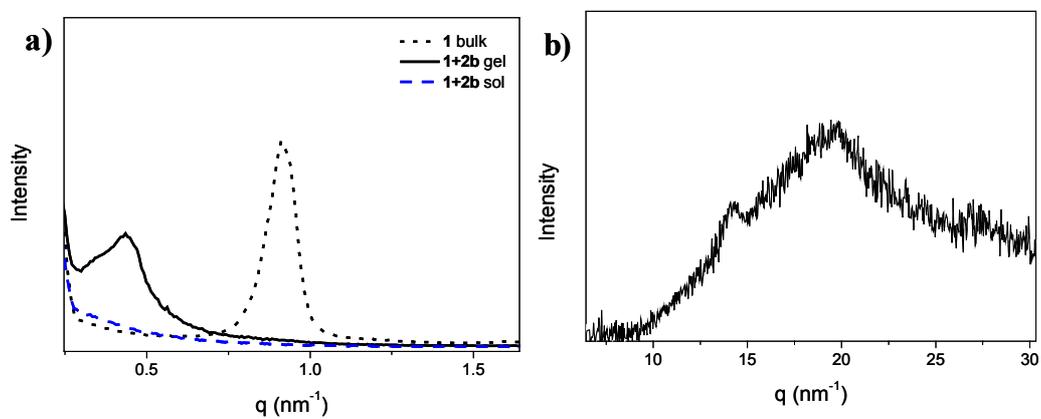
Compound **2a**. yield 80.5%: <sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>, ppm): δ = 7.34-7.72 (m, 30Ar-H), 7.00 (d, 4Ar-H; *o* to ArO, *J* = 8.6 Hz), 3.91 (t, 4H; Ar-OCH<sub>2</sub>, *J* = 5.0 Hz), 3.53-3.75 (m, 132H; CH<sub>2</sub>O); <sup>13</sup>C-NMR (250 MHz, CDCl<sub>3</sub>, ppm): δ = 158.3, 139.7, 139.4, 127.9, 127.3, 127.1, 114.9, 77.6, 77.1, 76.6, 71.9, 70.8, 70.6, 69.7, 67.4;; M<sub>n</sub>/M<sub>w</sub> = 1.04 (GPC); Anal. Calcd for C<sub>116</sub>H<sub>170</sub>O<sub>38</sub> : C, 64.13; H, 7.89. Found C, 64.06; H, 8.02.



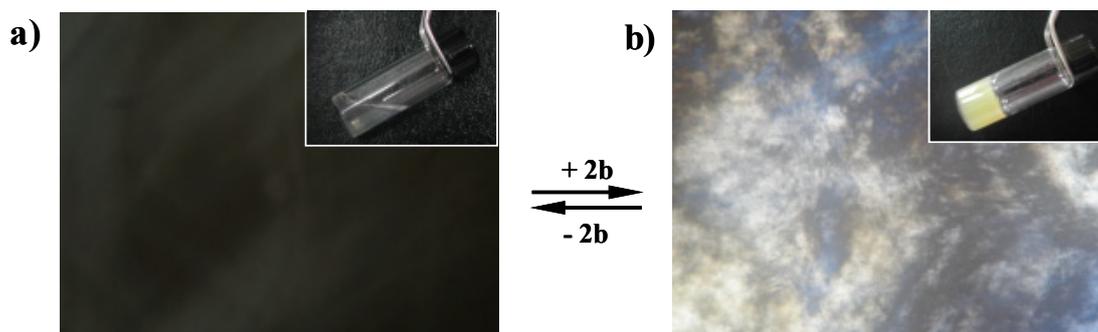
**Figure S1.** Laser light scattering of **1** (0.1 wt%) in H<sub>2</sub>O. (a) Autocorrelation functions and (b) size distribution graph at scattering angle of 90° (from CONTIN analysis of the autocorrelation function) from dynamic light scattering experiment. **1** shows a sharp peak corresponding to hydrodynamic radius ( $R_h$ ) of several nanometer micelles at once, however, after several weeks a broad peak corresponding to  $R_h = 158$  nm. (c) Zimm plot of **1** from static light scattering experiment. The radius of gyration ( $R_g$ ) was found to be 217 nm. Thus, the ratio of  $R_g$  to  $R_h$  is 1.37, suggesting the existence of cylindrical micelle. (d) Kratky plot(■) and linear fit was conformed the cylindrical micelle.



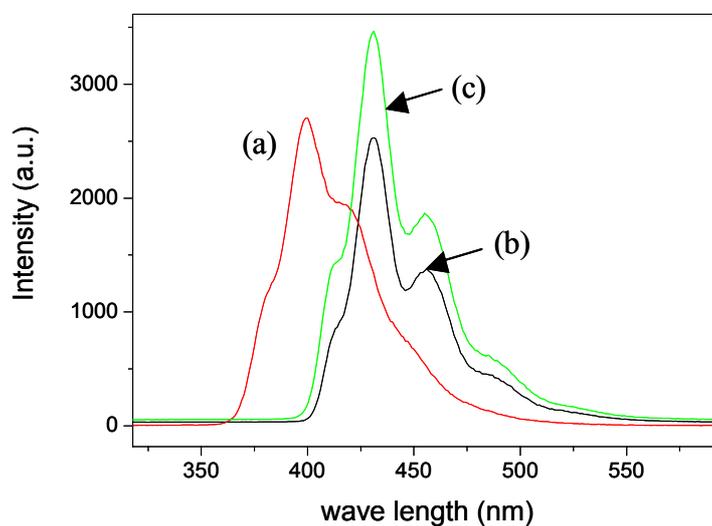
**Figure S2.** (a) Size distribution graph of **2b** (0.1 wt% in H<sub>2</sub>O) at scattering angle of 90° (from CONTIN analysis of the autocorrelation function) from dynamic light scattering experiment. (b) TEM image of **2b** with negative staining (0.01 wt%, scale bar = 50 nm)



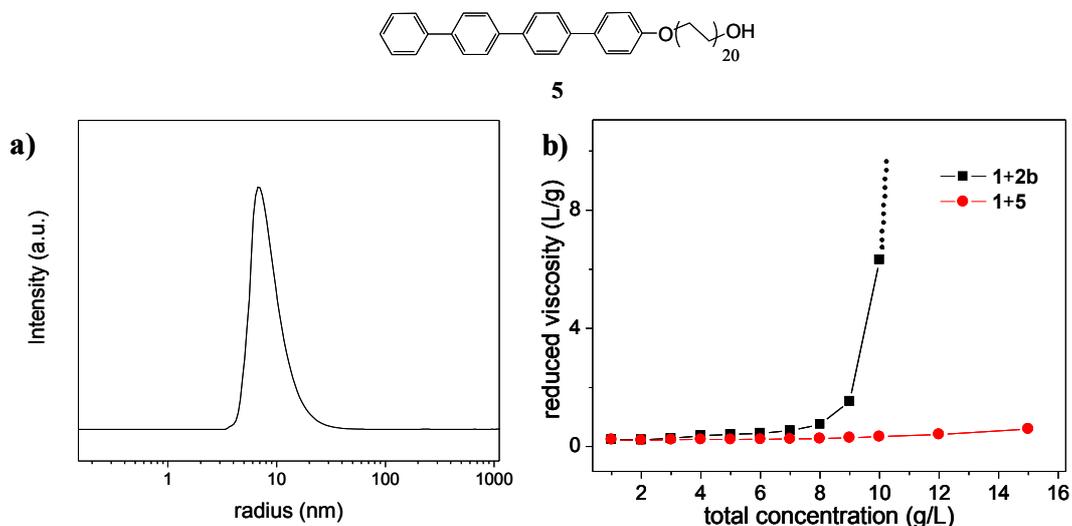
**Figure S3.** (a) Small angle X-ray scattering of **1** and **1·2b**, and (b) wide angle X-ray scattering of **1·2b** gel.



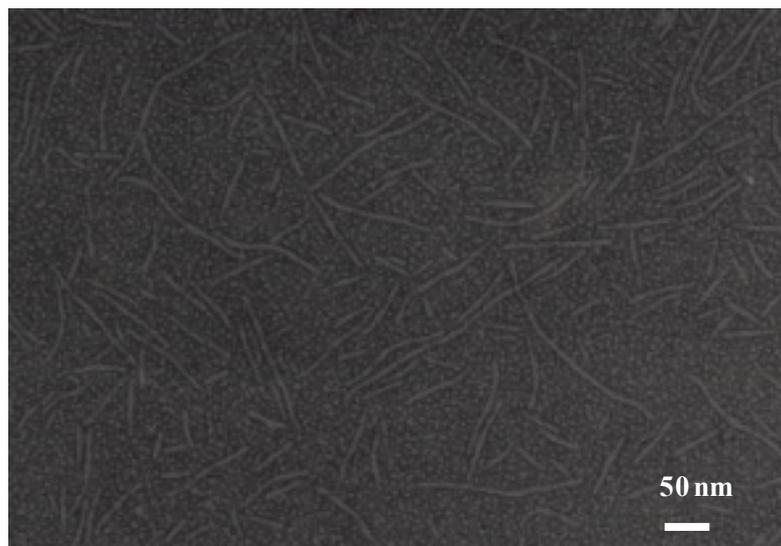
**Figure S4.** Polarized optical micrographs of (a) **1·2b** sol (5 wt% **2b** relative **1**) and (b) **1·2b** gel (10 wt% **2b** relative **1**). Insets show photographs for nematic gel and isotropic fluid phase. When the total concentration of solution fixed at 3.0 wt%, 5 wt% **2b** solution is isotropic fluid. In this solution, adding the **2b** to 10wt% leads to the strong birefringence of nematic texture, indicating that the gelation occurs, and then to reduce weight percent of **2b**, adding **1** solution to be 5 wt% **2b** give rise to disappearance of the birefringence again.



**Figure S5.** Fluorescence spectra of the aqueous solution of (a) **2b** and of (b) **1** and (c) **1·2b** aqueous solution (0.1wt %, excitation wavelength; 290 nm).



**Figure S6.** (a) Size distribution graph of **5** (0.1 wt% in H<sub>2</sub>O) at scattering angle of 90° (from CONTIN analysis of the autocorrelation function) from dynamic light scattering experiment. (b) Reduced viscosities of solution of 10 wt% **2b** and **5** relative to **1** versus concentration in water at 25 °C. The compound **5** forms spherical micelles in aqueous solution. The mixture where **5** was added 10 wt% relative to **1**, however, did not take place gelation in spite of increasing total concentration over 50 wt%. The viscosity of the mixture solution of concentrations up to 15 g/L was not observed essential change, indicating that the gelation behavior come from bridging of the cylinders, rather than depletion interactions.



**Figure S7.** TEM image of mixture of micelle and cylinder with 50 wt% **2b** relative to **1**. **2b** shows spherical micelles in aqueous solution. Upon addition of a small amount of **2b**, the cylinders of **1** are bridged each other. With increasing **2b** concentration the cylinders transform into micelles, most probably due to increasing the volume fraction of hydrophilic chains relative to rod segments. This is likely to be responsible for the re-entrant behavior in Figure 3a.