

Electronic Supplementary Information

The Relationship between Molecular Structure and Supramolecular Morphology in the Self-Assembly of Rod-Coil Molecules with Oligoether Chains

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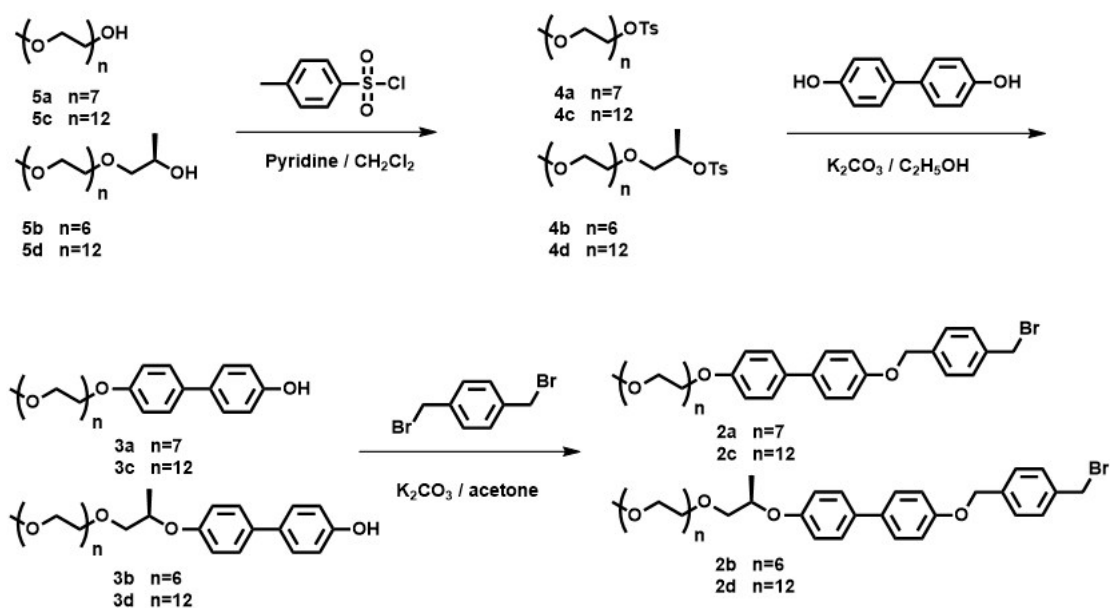
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Synthesis



Scheme S1. Synthetic route of rod-coil molecules **1a-1d**.

Compound 4a-4d: Compounds **4a**, **4b**, **4c** and **4d** were all synthesized using the same procedure. A representative example is described for **4a**. The compound poly (ethylene glycol) methyl ether (Mw = 350) (12 g, 34.2 mmol), toluene-p-sulfonyl chloride (13 g, 68.5 mmol) and pyridine (25 mL) were put into 250 mL one-neck flask dissolved in dry CH₂Cl₂ (60 mL). Room temperature for 12h, add distilled water to the reaction solution (60 mL), stirring 2h. Then add concentrated hydrochloric acid, significant acidity stirring 2h. The resulting solution was dried (MgSO₄) and filtered. The solvent was removed in a rotary evaporator and the crude product was purified by column chromatography on silica gel using CH₂Cl₂, CH₂Cl₂:MeOH (20:1 v/v) as eluent to yield 12.5 g of colorless liquid (73.0%). ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.80 (d, *J* = 9.0 Hz, 2H), 7.34 (d, *J* = 6.0 Hz, 2H), 4.16 (t, *J* = 6.0 Hz, 2H), 3.53-3.70 (m, 26H), 3.38 (s, 3H), 2.45 (s, 3H).

Compound 4b: Yellow liquid, yield 72.5%. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.80 (d, *J* = 9.0 Hz, 2H), 7.34 (d, *J* = 6.0 Hz, 2H), 4.67-4.73 (m,

1H), 3.52-3.66 (m, 26H), 3.38 (s, 3H), 2.45 (s, 3H), 1.28 (d, $J = 6.0$ Hz, 3H).

Compound 4c: Colorless liquid, yield 74.5%. ^1H NMR (300 MHz, CDCl_3 , δ , ppm): 7.80 (d, $J = 9.0$ Hz, 2H), 7.34 (d, $J = 6.0$ Hz, 2H), 4.16 (t, $J = 6.0$ Hz, 2H), 3.53-3.70 (m, 46H), 3.38 (s, 3H), 2.45 (s, 3H).

Compound 4d: Yellow liquid, yield 73.3%. ^1H NMR (300 MHz, CDCl_3 , δ , ppm): 7.80 (d, $J = 9.0$ Hz, 2H), 7.34 (d, $J = 6.0$ Hz, 2H), 4.67-4.73 (m, 1H), 3.52-3.66 (m, 50H), 3.38 (s, 3H), 2.45 (s, 3H), 1.28 (d, $J = 6.0$ Hz, 3H).

Compound 3a-3d: Compounds **3a**, **3b**, **3c** and **3d** were all synthesized using the same procedure. A representative example is described for **3a**. Excess K_2CO_3 (7.62 g, 53.5 mmol) and 4,4'-biphenol (7.71 g, 40.6 mmol) were dissolved in absolute ethyl alcohol (100 mL). Compound **4a** (6.8 g, 13.1 mmol) dissolved in absolute EtOH (30 mL) was added by drops into the above mixture for 5 h under reflux condition. The mixture was further refluxed for 24 h. The solvent was removed in a rotary evaporator. Water, a small amount of dilute H_2SO_4 were added into the resulting mixture, extracted with ethyl acetate. The ethyl acetate solution was neutralized with Na_2CO_3 , dried over anhydrous magnesium sulfate and filtered. After the solvent was removed in a rotary evaporator, the crude product was purified by silica gel chromatography to yield 4.2 g of a white solid (68.5%). ^1H NMR (300 MHz, CDCl_3 , δ , ppm): 7.37-7.43 (m, 4H), 6.87-6.94 (m, 4H), 6.65 (s, 1H), 4.13 (t, $J = 6.0$ Hz, 2H), 3.86 (t, $J = 6.0$ Hz, 2H), 3.54-3.74 (m, 24H), 3.38 (s, 3H).

Compound 3b: White solid, yield 64.3%. ^1H NMR (300 MHz, CDCl_3 , δ , ppm): 7.37-7.43 (m, 4H), 6.87-6.94 (m, 4H), 6.65 (s, 1H), 4.55-4.61 (m, 1H), 3.54-3.74 (m, 26H), 3.38 (s, 3H), 1.33 (d, $J = 6.0$ Hz, 3H).

Compound 3c: White solid, yield 66.5%. ¹H NMR (300 MHz, CDCl₃, δ, ppm) 7.37-7.43 (m, 4H), 6.87- 6.94 (m, 4H), 6.65 (s, 1H), 4.13 (t, *J* = 6.0 Hz, 2H), 3.86 (t, *J* = 6.0 Hz, 2H), 3.54-3.74 (m, 44H), 3.38 (s, 3H).

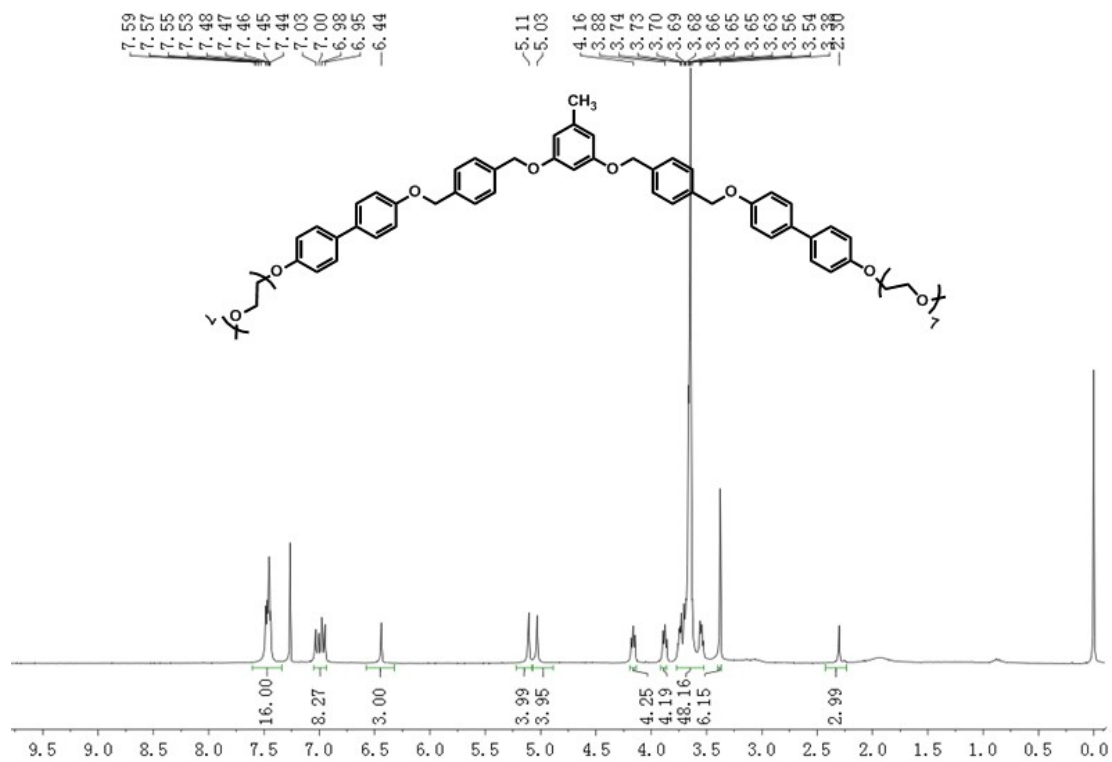
Compound 3d: White solid, yield 63.2%. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.37-7.43 (m, 4H), 6.87-6.94 (m, 4H), 6.65 (s, 1H), 4.55-4.61 (m, 1H), 3.54-3.74 (m, 50H), 3.38 (s, 3H), 1.33 (d, *J* = 6.0 Hz, 3H).

Compound 2a-2d: Compounds **2a**, **2b**, **2c** and **2d** were all synthesized using the same procedure. A representative example is described for **2a**. Excess K₂CO₃ (1.68 g, 12.1 mmol) and α,α'-dibromo-p-xylene (2.348 g, 8.7 mmol) were dissolved in acetone (80 mL). Compound **3a** (1.4 g, 2.6 mmol) was added by drops into the above mixture for 2 h under reflux condition. The mixture was further refluxed for 22 h, filtered and concentrated by evaporation, then separated by chromatography on silica gel (CH₂Cl₂, EA, CH₂Cl₂:CH₃OH = 20:1 as eluent). The desired compound was separated as the most polar fraction to yield 1.91 g of a wax-like white solid (85.6%). ¹H NMR (300 MHz, CDCl₃, δ, ppm) 7.43-7.48 (m, 8H), 6.95-7.02 (m, 4H), 5.09 (s, 2H), 4.51 (s, 2H), 4.16 (t, *J* = 6.0 Hz, 2H), 3.87 (t, *J* = 6.0 Hz, 2H), 3.54-3.74 (m, 24H), 3.38 (s, 3H).

Compound 2b: White solid, yield 83.2%. ¹H NMR (300 MHz, CDCl₃, δ, ppm) 7.43-7.48 (m, 8H), 6.95-7.02 (m, 4H), 5.09 (s, 2H), 4.55-4.61 (m, 1H), 4.51 (s, 2H), 3.54-3.74 (m, 26H), 3.38 (s, 3H), 1.33 (d, *J* = 6 Hz, 3H).

Compound 2c: White solid, yield 80.0%. ¹H NMR (300 MHz, CDCl₃, δ, ppm) 7.43-7.48 (m, 8H), 6.95-7.02 (m, 4H), 5.09 (s, 2H), 4.51 (s, 2H), 4.16 (t, *J* = 6.0 Hz, 2H), 3.87 (t, *J* = 6.0 Hz, 2H), 3.54-3.74 (m, 44H), 3.38 (s, 3H).

Compound 2d: White solid, yield 76.2%. ^1H NMR (300 MHz, CDCl_3 , δ , ppm) 7.43-7.48 (m, 8H), 6.95-7.02 (m, 4H), 5.09 (s, 2H), 4.55-4.61 (m, 1H), 4.51 (s, 2H), 3.54-3.74 (m, 50H), 3.38 (s, 3H), 1.33 (d, $J = 6.0$ Hz, 3H).



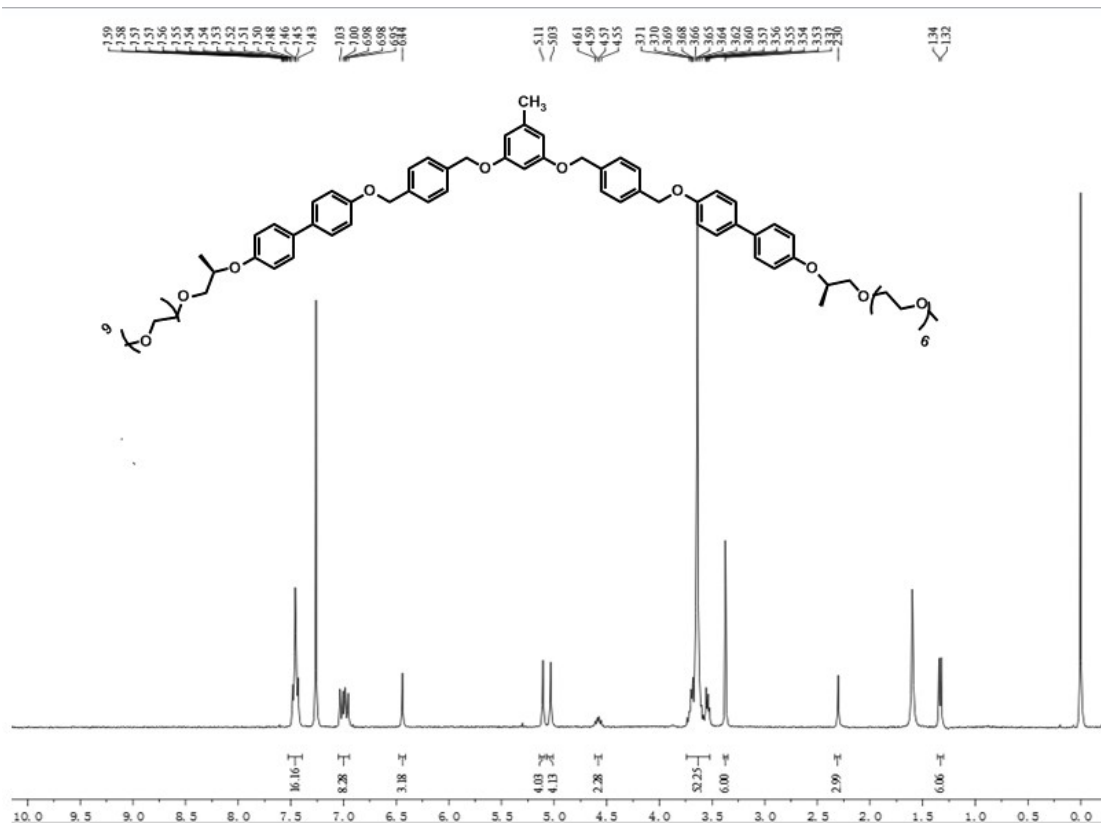


Figure S2. ^1H NMR spectrum of molecule **1b** in CDCl_3 .

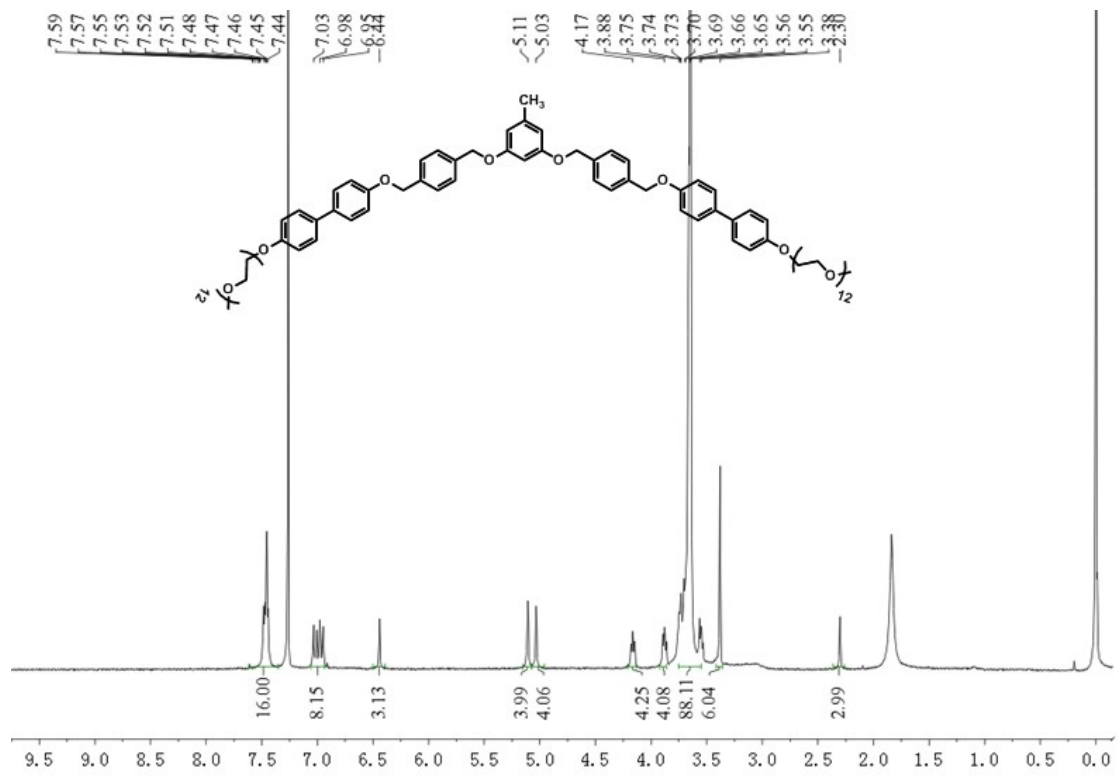


Figure S3. ^1H NMR spectrum of molecule **1c** in CDCl_3 .

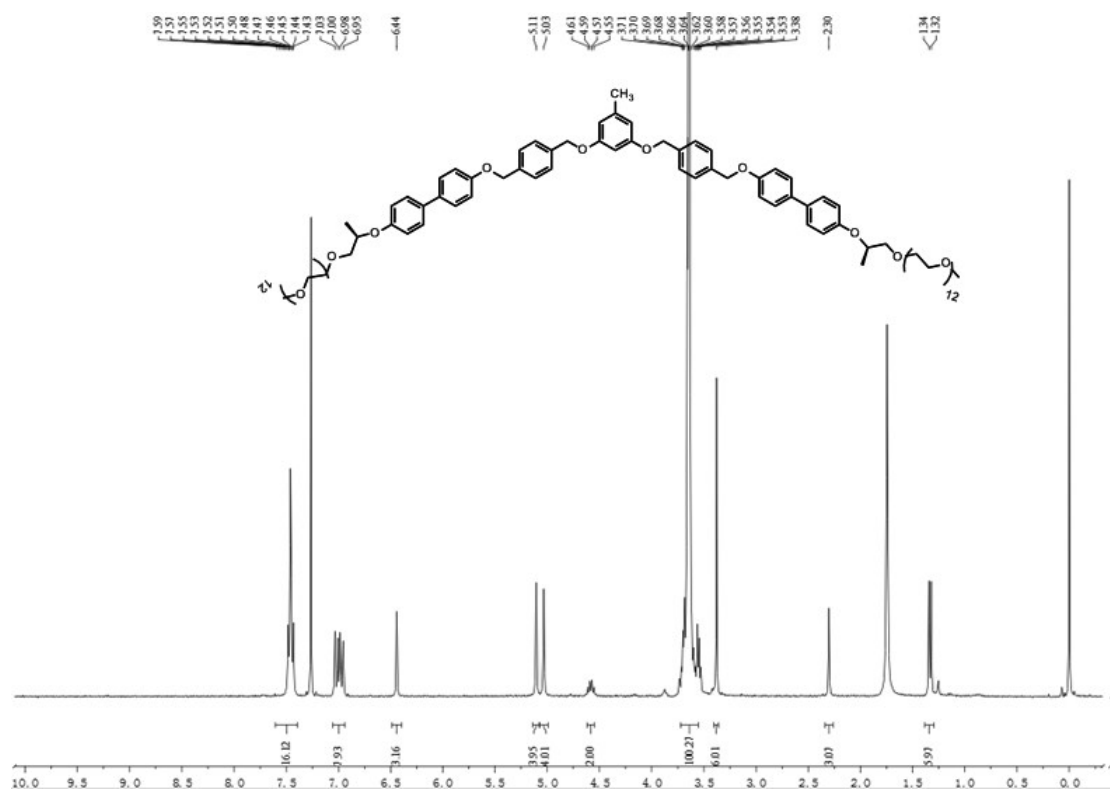


Figure S4. ^1H NMR spectrum of molecule **1d** in CDCl_3 .

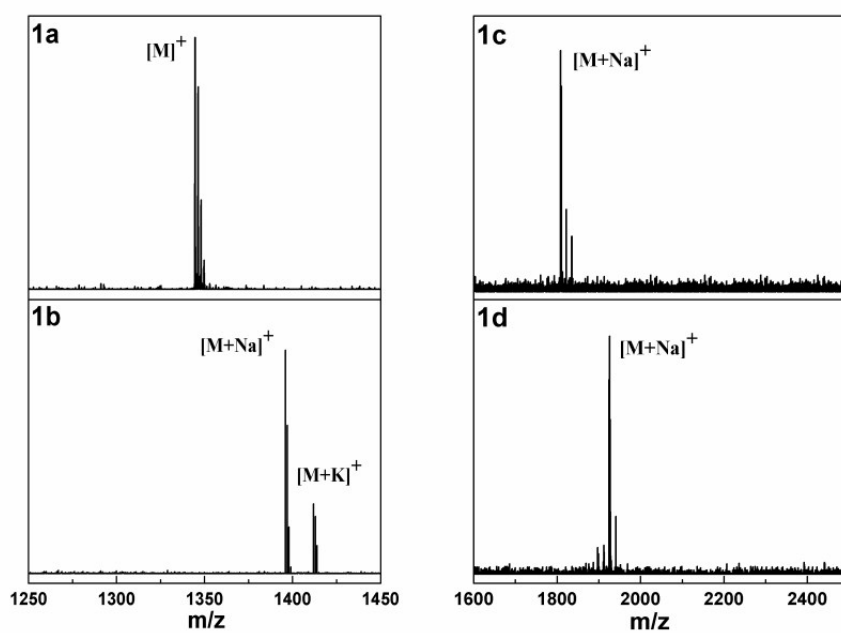


Figure S5. MALDI-TOF-MS spectra of **1a-1d** (matrix: CHCA)

Table S1. Thermal transitions of 1a-1d (data are from the second heating and the first cooling scans).

Molecule	Phase transition (°C)		
	$f_{\text{coil}}^{[a]}$	Heating	Cooling
1a	0.504	Col _o 96 i	i 85 Col _o
1b	0.515	Col _o 88 i	i 78 Col _o
1c	0.627	Col _h 78 i	i 70 Col _h
1d	0.650	k 64 i	i 51 k

[a] f_{coil} : volume fraction of the coil-rod-coil molecule. Col_o: oblique columnar phase. Col_h: hexagonal columnar. i: isotropic phase. k: crystalline

Table S2. Small-angle X-ray diffraction data for oblique columnar structure for molecule **1a**.

Mesophase (lattice constants)	Reflections		Miller indices
	$Q_{\text{obsd}}(\text{nm}^{-1})$	$q_{\text{calcd}}(\text{nm}^{-1})$	
	0.89806	0.89722	100
Col _o at 65 °C	1.39375	1.39563	010
a=7.56 nm;	1.82281	1.82070	210
b=4.82 nm;	2.53464	2.53646	310
$\gamma = 69^\circ$.			

Table S3. Small-angle X-ray diffraction data for oblique columnar structure for molecule **1b**.

Mesophase (lattice constants)	Reflections		Miller indices
	$Q_{\text{obsd}}(\text{nm}^{-1})$	$q_{\text{calcd}}(\text{nm}^{-1})$	
	0.93572	0.93994	100
Col _o at 50 °C	1.36024	1.36715	010
a=7.06 nm;	1.95618	1.95059	210
b=4.85 nm;	2.72385	2.71969	310
$\gamma = 72^\circ$.			

Table S4. Small-angle X-ray diffraction data for oblique columnar structure for molecule **1c**.

Mesophase (lattice constants)	Reflections		Miller indices
	$Q_{\text{obsd}}(\text{nm}^{-1})$	$q_{\text{calcd}}(\text{nm}^{-1})$	
	0.65560	0.65512	100
Col _h at 45 °C	1.13493	1.13931	110
a=11.06 nm;	1.31805	1.31019	210

Table S5. Summary of SAXS data for **1a-1d** in the bulk state.

Molecule	Crystalline phase			
	<u>Col_h</u>	<u>Col₀</u>		
	<i>a</i> (nm)	<i>a</i> (nm)	<i>b</i> (nm)	γ (°)
1a	—	7.6	4.8	69
1b	—	7.1	4.9	72
1c	11.1	—	—	—
1d	—	—	—	—

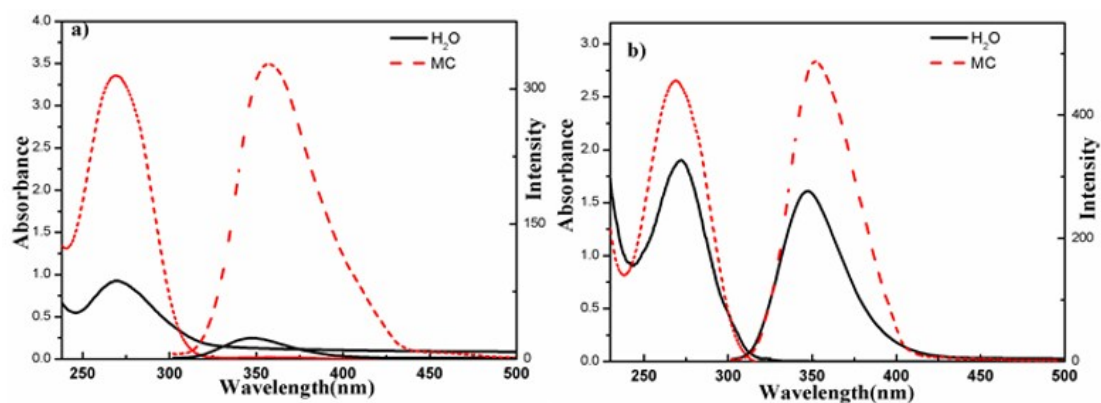


Figure S6. Absorption and emission spectra of a) **1b**; b) **1d** in methylene chloride and aqueous solution (0.01 wt%).

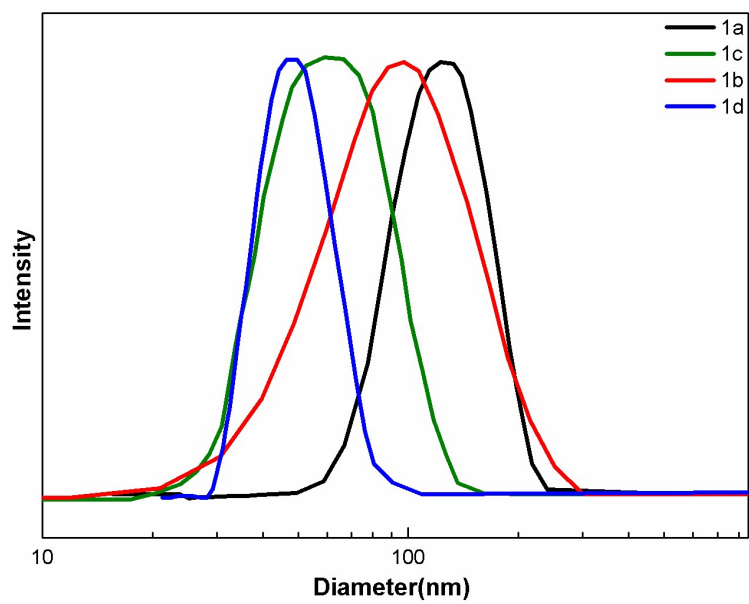


Figure S7. Size distribution graphs of aqueous solutions of **1a-1d** (0.01 wt%) from DLS measurements.