Supplementary Information

S1. Experimental Section

S1.1. Synthesis of the Coil Segment

Figure S1. Synthetic route of Coil Segment 3.

S1.1.1. Synthesis of Compounds 8

To a solution of Ethyl L-(−)-lactate (36.5 g, 0.308 mol), and 3,4-dihydro-2H-pyran (42.1 g, 0.5 mol) were slowly added 10 drops of concentrated HCl at 0 °C. The solution was stirred for 10 h while it reached room temperature. Na₂CO₃ (3 g) was added, and stirring was continued for 10 h. The reaction mixture was then filtered, concentrated to small volume, and distilled to give 8 (51.9 g, yield 83%).

S1.1.2. Synthesis of Compounds 9

To a suspension of LiAlH (12.0 g, 0.316 mol) in dry diethyl ether (80 mL) was added a solution of 15 (51.9 g, 0.257 mol) in diethyl ether (40 mL) at 0 °C under nitrogen atmosphere over 8 h. After 12 h at room temperature, the reaction mixture was refluxed for 5 h. Methyl acetate (5 g), 10% NaOH (20 mL), and water (80 mL) were then added in that order to the mixture cooled at room temperature. The precipitate was filtered off, and the solution was concentrated, dried over K₂CO₃ and finally distilled to give 9 (35.2 g, yield 86%).

S1.1.3. Synthesis of Compounds 11a–11c

These compounds were synthesized according to the same procedure; a representative example is described for 11a. To a 250 mL two-neck flask compound 9 (5 g, 31.2 mmol), dry THF (100 mL) was added. After stirring for several min at 0 °C, NaH (3.37 g, 84 mmol) was added slowly. And then 10a (10.98 g, 15.6 mmol) was added dropwise for 1.5 h at 0 °C. The reaction was refluxed for 24 h. The reaction was concentrated by evaporation and extracted with dichloromethane. The combined organic portions were dried over MgSO₄ and filtered. The residue was purified by flash column chromatography with EA/CH₃OH = 4/1 as eluent to give product 11a (9 g, 83%) as a colourless liquid.

S1.1.4. Synthesis of Compounds 3a–3c

These compounds were synthesized according to the same procedure, a representative example is described for 3a. To a 250 mL round bottom flask 11a (4 g, 6.46 mmol), p-Toluenesulfonyl chloride (2.46 g, 12.9 mmol), pyridine (20 mL), and dry Dichloromethane (100 mL) were added. After being
stirred at room temperature for 18 h, 30 mL water was added into the reaction mixture, the aqueous phase was slowly acidified with cold 3 N HCl to pH = 2–3 and extracted with dichloromethane (3 × 50 mL). Then the organic fractions were dried over MgSO₄. The residue was purified by flash column chromatography with EA/CH₃OH = 10/1 (v/v) as eluent to give product 3a (3.5 g, 70%) as colourless liquid.

**Figure S2.** ¹H-NMR spectra of molecules 1a in CDCl₃.

**Figure S3.** MALDI-TOF-Mass spectrum of 1a, 1b, 1c (matrix: CHCA).
Figure S4. $^1$H-NMR spectra of molecules 1b in CDCl$_3$.

Figure S5. $^1$H-NMR spectra of molecules 1c in CDCl$_3$. 
S2. Results and Discussion

**Figure S6.** DSC traces (10 °C/min) recorded during the second heating scan and the first cooling scan of the series of molecules (a) 1a; (b) 1b; (c) 1c.

**Table S1.** Thermal transitions and corresponding enthalpy changes of 2b and 2c.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Phase transitions (°C) and corresponding enthalpy changes (in brackets) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Heating</strong></td>
</tr>
<tr>
<td>2b</td>
<td>HPL 98.5 (2.0) Coli 236.4 (0.9)</td>
</tr>
<tr>
<td></td>
<td>Coli, 288.5 (0.4) i</td>
</tr>
<tr>
<td>2c</td>
<td>HPL 92.1 (1.6) Coli 235.4 (1.4) i</td>
</tr>
</tbody>
</table>

HPL: hexagonal perforated layer; Coli: rectangular column; Coli, oblique column; i: isotropic.

It is obvious that increasing the flexible chain length or incorporating side groups at the surface of rod and coil domains lead to reduce phase transition temperatures. This trend is believed to be attributed to a reduction in the extent of packing constraints of rod segments as a result of increasing the flexible chain length or incorporating side groups, subsequently reducing the driving force of pi-pi stacking.

**Figure S7.** Representative optical polarized micrograph (×100) of the texture exhibited by (a) hexagonal column structure of 1c in the crystal phase; (b) Body-centered tetragonal structure of 1c at the transition from the anisotropic liquid crystal phase.
Aggregation Behavior of Molecule 1a–1c in Aqueous Solution

Molecules 1a–1c can be considered as a novel class of amphiphiles due to the fact that these molecules consist of hydrophilic poly(ethylene oxide) flexible chains and hydrophobic conjugated rod segment. Aggregation behavior of molecules 1a–1c was subsequently studied in aqueous solution using UV–vis and fluorescence spectra. The absorption spectra of 1a–1c in aqueous solution (0.02 wt %) exhibit a blue-shifted absorption maxima compared to those of chloroform solutions. This is maybe caused by the cooperative effect between the hydrophilic and hydrophobic interactions and the π–π stacking interactions between the aromatic segments. The fluorescence spectra of 1a–1c in chloroform solution (0.02 wt %) exhibit a strong emission maximum at 430 and 455 nm respectively. However, the emission maximum in aqueous solution is significantly quenched, strongly indicative of aggregation of the conjugated rod segments.

Figure S8. (a) Absorption and emission spectra of 1a in chloroform and aqueous solution (0.002 wt %); (b) Absorption and emission spectra of 1b in chloroform and aqueous solution (0.002 wt %); (c) Absorption and emission spectra of 1c in chloroform and aqueous solution (0.002 wt %).