Supporting Information for

Synthesis and Self-assembly of Amphiphilic Bent-Shaped Molecules Based on Dibenzo[a,c]Phenazine and Poly(ethylene oxide) Units

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Synthesis

Synthesis of compound 7

9,10-Phenanthrenequinone (10.40 g, 50.00 mmol) and BPO (0.80 g, 3.30 mmol) were added to nitrobenzol (90 mL). Liquid bromine (5.80 mL) was introduced with a syringe. The reaction mixture was stirred at 80 °C for 36 hours with an environment of high pressure mercury lamp. The resulting mixture was cooled to room temperature until solid separated out and then filtered the mixture. The solid was washed with absoluted ethanol. Absoluted ethanol (20 mL) was added into filtrate and then placed in 0 °C until solid separated out. Filtered the mixture and combined the solid. An earthy yellow powder was obtained after dried overnight under vacuum (12.52 g, 68.8%).

¹H NMR (300 MHz, CDCl₃, *δ*, ppm): 8.12 (d, *J* = 1.8 Hz, 2H), 8.07 (d, *J* = 8.3 Hz, 2H), 7.67 (dd, *J* = 8.4, 1.8 Hz, 2H)

Synthesis of compound 8

Compound 7 (2.42 g, 6.65 mmol) was dissolved in glacial acetic acid, *o*-Phenylenediamine (0.86 g, 7.96 mmol) were added to a 500 mL round bottom flask. The reaction mixture was heated to reflux for 7 hours. The resulting mixture was cooled to room temperature and then filtered. Filter cake was washed by glacial acetic acid, then a yellow solid was obtained (2.66 g, 91.4%).

¹H NMR (300 MHz, CDCl₃, δ, ppm): 9.30 (d, *J* = 9.0 Hz, 2H), 8.62 (s, 2H), 8.35-8.31 (m, 2H), 7.90-7.87 (m, 4H)

Synthesis of compound 12

The syntheis of (2S)-2-(tetrahydropyran-2-yloxy)propan-1-ol has been described previously.¹

Synthesis of compounds 13d and 13e

Compounds **13d** and **13e** were prepared according to the similar procedures reported previously.²

Compound 13d: yellow liquid (yield 57.2%). ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.79 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 4.14 (t, *J* = 4.8 Hz, 2H), 3.52-3.68 (m, 26H), 3.24 (s, 3H), 2.43 (s, 3H).

Compound 13e: yellow liquid (yield 68.3%). ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.80 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 4.14 (t, *J* = 4.8 Hz, 2H), 3.52-3.68 (m, 34H), 3.22 (s, 3H), 2.45 (s, 3H).

Synthesis of compounds 14d and 14e

Compounds **14d** and **14e** were prepared according to the similar procedures reported previously.³

Compound 14d: yellow liquid (yield 49.6%). ¹H NMR (300 MHz, CDCl₃, δ , ppm) 4.74-4.64 (m, 1H), 3.65-3.45 (m, 22H), 3.37 (s, 3H), 1.27 (d, J = 6.0 Hz, 3H).

Compound 14e: yellow liquid (yield 44.2%). ¹H NMR (300 MHz, CDCl₃, δ , ppm) 4.74-4.64 (m, 1H), 3.65-3.45 (m, 30H), 3.37 (s, 3H), 1.27 (d, J = 6.0 Hz, 3H).

Synthesis of compounds 11d and 11e

A representative example is described for **11d**. Compound **14d** (1.64 g, 5.28 mmol) and TsCl (2.01 g, 10.57 mmol) were dissolved in methylene chloride (35 mL) in a single-neck flask. Then pyridine (10 mL) was added to the solution. The reaction mixture was further stirred at room temperature for 12 hours. Then water (30 mL) was poured into the solution and stirred for 1 hour, the diluted hydrochloric acid was

added into the flask and acidified to PH<7 and stirred for 0.5 hour. The resulting solution was extracted with methylene dichloride, the combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated to dryness. The crude product was purified by column chromatography (silica gel) using ethyl acetate/ methylene dichloride (1:1 v/v) as eluent to yield a yellow liquid (1.17 g, 47.6%).

¹H NMR (300 MHz, CDCl₃, *δ*, ppm) 7.80 (d, *J* = 9.0 Hz, 2H), 7.32 (d, *J* = 6.0 Hz, 2H), 4.74-4.64 (m, 1H), 3.65-3.45 (m, 22H), 3.37 (s, 3H), 2.44 (s, 3H), 1.27 (d, *J* = 6.0 Hz, 3H).

Compound **11e**: yellow liquid (yield 50.3%).¹H NMR (300 MHz, CDCl₃, δ , ppm): 7.81(d, J = 8.3 Hz, 2H) , 7.33 (d, J = 8.2 Hz, 2H), 4.75-4.64 (m, 1H), 3.70-3.52 (m, 30H), 3.38 (s, 3H), 2.45 (s, 3H), 1.28 (d, J = 6.0 Hz, 3H).



Synthesis of compounds 11a-11c

Compounds **11a**, **11b** and **11c** were prepared according to the similar procedures reported previously.²

Compound **11a**: yellow liquid (yield 75.8%).¹H NMR (300 MHz, CDCl₃, δ , ppm): 7.79 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 4.17(t, J = 6.0 Hz, 2H), 3.64-3.37 (m, 22H), 3.30 (s, 3H), 2.45(s, 3H). Compound **11b**: yellow liquid (yield 79.7%). ¹H NMR (300 MHz, CDCl₃, δ , ppm) 7.78 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 4.08 (t, J = 6.0 Hz,2H), 3.69-3.40 (m, 30H), 3.37 (s, 3H), 2.43(s, 3H).

Compound **11c**: yellow liquid (yield 76.2%).¹H NMR (300 MHz, CDCl₃, δ , ppm) 7.79 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 4.15(t, J = 6.0 Hz, 2H), 3.70-3.31 (m, 46H), 3.30 (s, 3H), 2.43(s, 3H).

Synthesis of compounds 6a-6e

These compounds were synthesized using the same procedure. A representative example is described for **6a**. Compound **11a** (4.13 g, 8.30 mmol) and 4-iodophenol (2.64 g, 12 mmol) were dissolved in acetonitrile (50 mL) and then excess potassium carbonate (6.90 g, 50 mmol) was added to the solution. The mixture was heated at reflux overnight with vigorous stirring. The solvent was removed in a rotary evaporator and the resulting mixture was poured into water and extracted with ethyl acetate, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated to dryness. The crude product was purified by column chromatography (silica gel) using ethyl acetate as eluent to yield a slightly yellow liquid (4.02 g, 80.9%).

¹H NMR (300 MHz, CDCl₃, δ , ppm): 7.60 (d, J = 9.0 Hz, 2H),6.67 (d, J = 9.0 Hz, 2H), 4.31(t, J = 6.0 Hz, 2H), 3.79 (t, J = 6.0 Hz,2H) 3.74-3.69 (m, 22H), 3.30 (s, 3H). Compound **6b**: yellow liquid (yield 76.2%). ¹H NMR (300 MHz, CDCl₃, δ , ppm) 7.54 (d, J=9.0 Hz, 2H), 6.70 (d, J = 9.0 Hz, 2H), 4.08 (t, J = 6.0 Hz,2H), 3.83 (t, J = 6.0 Hz, 2H), 3.69-3.54 (m, 28H), 3.37 (s, 3H).

Compound **6c**: yellow liquid (yield 66.4%).¹H NMR (300 MHz, CDCl₃, δ , ppm) 7.56 (d, J = 9.0 Hz, 2H),6.67 (d, J = 9.0 Hz, 2H), 4.31(t, J = 6.0 Hz, 2H), 3.79 (t, J = 6.0 Hz, 2H) 3.70-3.54 (m, 44H), 3.30 (s, 3H).

Compound **6d**: yellow liquid (yield 60.7%).¹H NMR (300 MHz, CDCl₃, δ , ppm) 7.53 (d,*J* = 9.0 Hz, 2H), 6.71 (d,*J* = 9.0 Hz, 2H), 4.55-4.45 (m, 1H), 3.98-3.49(m, 22H), 3.38 (s, 3H), 1.28 (d, *J* = 9.0 Hz, 3H).

Compound **6e**: yellow liquid (yield 77.0%). ¹H NMR (300 MHz, CDCl₃, δ , ppm) 7.53 (d, J = 9.0 Hz, 2H), 6.71 (d, J = 9.0 Hz, 2H), 4.53-4.48 (m, 1H), 4.10-3.51(m, 30H), 3.38 (s, 3H), 1.29 (d, J = 9.0 Hz, 3H).

Eq. (1)

$$n = \frac{abc\rho\sin\gamma N_A}{M}$$

M is the molecular weight and N_A is Avogadro's number. Calculation based on the lattice constants and the density (ρ =1.02) of 1-4.

Table S1: Small-angle X-ray diffraction data for oblique columnar structure for mediatule 1 (measured at 25° C)

for molecule 1 (measured at 2)	5°C).
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.467
.780
.588

 q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections ($\lambda = 0.154$ nm).

Table S2: Small-angle X-ray diffraction data for oblique columnar structurefor molecule 2 (measured at 80°C).

h	k	1	$q_{obsd}(nm^{-1})$	$q_{calcd}(nm^{-1})$
1	0	0	1.100	1.097
0	1	0	1.452	1.453
2	2	0	2.963	2.962

 q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections ($\lambda = 0.154$ nm).

h	k	1	q _{obsd} (nm ⁻¹)	$q_{calcd}(nm^{-1})$
1	0	0	1.079	1.082
0	1	0	1.383	1.381
2	0	0	2.151	2.150

Table S3: Small-angle X-ray diffraction data for oblique columnar structurefor molecule 3 (measured at 25° C).

 q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections ($\lambda = 0.154$ nm).

Table S4: Small-angle X-ray diffraction data for oblique columnar structurefor molecule 4 (measured at 25° C).

h	k	1	$q_{obsd}(nm^{-1})$	$q_{calcd}(nm^{-1})$
1	0	0	1.535	1.538
0	1	0	2.146	2.150
2	1	0	3.090	3.088

 q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections ($\lambda=0.154$ nm).

Figure S1. Absorption and emission spectra of (a) **2**, (b) **3** and (c) **5** $(2 \times 10^{-5} \text{ M})$ in dichloromethane and aqueous solution.



Figure S2. Size distribution graphs of aqueous solutions of 1-5 (2×10⁻⁵ M) from DLS measurements: (a) 1, (b) 2, (c) 3, (d) 4, (e) 5.



Figure S3. TEM image of negatively stained aggregates obtained from **5** (0.005 wt% in aqueous solution).



Figure S4. AFM images of helical aggregates obtained from 5 (0.01 wt% in aqueous solution).

References for Supporting Information

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