

Branched quaternary ammonium amphiphiles: nematic ionic liquid crystals near room temperature

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Supplementary Information

1. Materials

Ethyl 2,4-hydroxybenzoate (97 %) was purchased from Sigma. 1,6-dibromohexane (96 %) was obtained from Aldrich. N, N'-dicyclohexylcarbodiimide (DCC, 99 %) and 4-dimethylaminopyridine (DMAP, 99 %) were the product of Fluka. All the starting compounds for synthesis were used without further purification. 4-((4-butoxyphenyl)diazenyl)phenol was synthesized previously.^[1] Solvents applied in the preparation were analytical grade and obtained from local chemical reagent company. Doubly distilled water was used in the experiments. Silica gel (200-300 mesh) was employed for the purification of column chromatography.

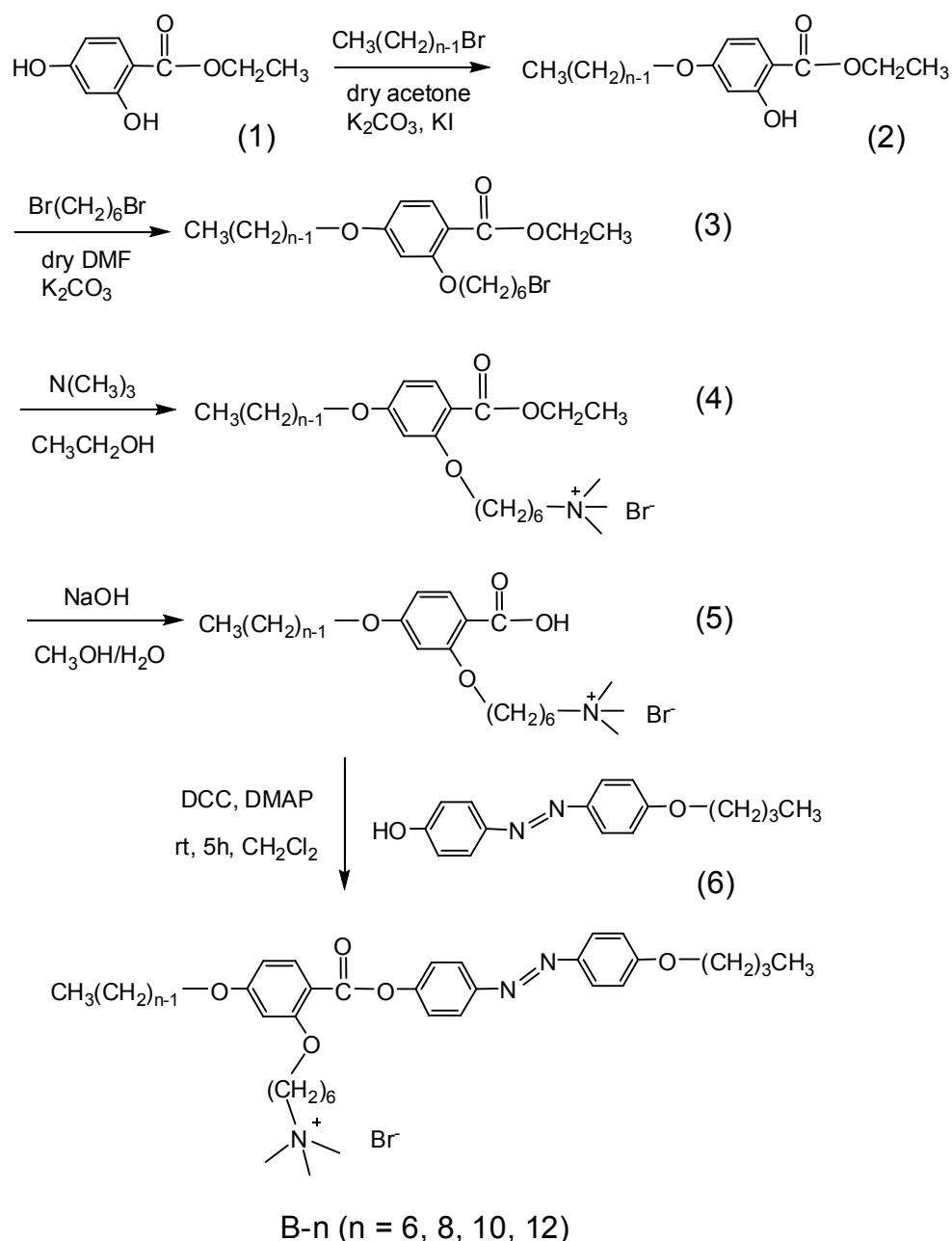
2. Measurements

¹H NMR spectra were recorded using standard pulse sequences on a Bruker Avance 500 spectrometer operating at 500.13 MHz. The spectra were measured in CDCl₃ or DMSO-*d*₆ solvent at room temperature. Chemical shifts are given in ppm relative to SiMe₄ (TMS) as internal standard (0.00 ppm). Elemental analysis (C, H, N) were performed on a Flash EA1112 from ThermoQuest Italia S.P.A. The MALDI-TOF mass spectra were obtained from autoflex TOF/TOF (Bruker, Germany) mass spectrometer, equipped with a nitrogen laser (337 nm, 3 ns pulse). The mass spectrometer was operated in the positive ion reflector mode with a detector potential of -4.75 kV. The chloroform solution of amphiphiles B-n was used directly for measurement without the matrix because the sample is ammonium salt. The mass range for data acquisition is from *m/z*

0 to 1500 Da. FT-IR spectra were obtained on a Bruker IFS66V equipped with a DTGS detector for the solid-state samples (KBr, 32 scans). The spectra were recorded with a resolution of 4 cm^{-1} . Thermogravimetric analysis (TGA) was conducted with a Perkin-Elmer TG/DTA-7 instrument and the heating rate is $10\text{ }^{\circ}\text{C min}^{-1}$. The optical textures of the mesophases were studied with a Zeiss Axioskop 40 polarizing microscope equipped with a Linkam THMSE 600 hot stage, a central processor, and a DF1 cooling system. The transition temperatures and enthalpies were performed by differential scanning calorimetry with a Netzsch DSC 204. The samples were examined at a scanning rate of $5\text{ }^{\circ}\text{C min}^{-1}$ for several heating and cooling cycles. The temperatures were read at the maximum of the transition peaks, and the glass transition temperature was read at the midpoint of the heat capacity increase. Variable-temperature X-ray diffraction (XRD) experiments were performed on a Philips PW 1700 X-ray diffractometer (using $\text{Cu K}\alpha_1$ radiation of a wavelength of 1.54 \AA) with a TTK-HC temperature controller. The calculation of molecular length along the long axis of ammonium was obtained using the program of ChemDraw combining energy minimized MM2 calculations.

3. Synthesis of branched quaternary ammonium amphiphiles B-n

The synthesis of branched amphiphiles **B-n** was carried out according to the following route shown in Scheme S1, and as a representative example, the detailed procedures of B-8 are described below:



Scheme S1. Synthetic path for branched quaternary ammonium amphiphiles B-n.

Ethyl 2-hydroxy-4-(octyloxy)benzoate (2). 1-bromooctane (2.48 g, 12.86 mmol) was added to a mixture of ethyl 2,4-dihydroxybenzoate (2 g, 11 mmol), K_2CO_3 (2.28 g, 16 mmol) and dry acetone (150 mL), and the resulting mixture was stirred for 24 h under refluxing. The solvent was evaporated under the reduced pressure, and the residue was redissolved in chloroform and then filtered. After removing the solvent, the residue was purified by chromatography (1:5 of chloroform/petroleum ether in volume ratio as the eluent), giving the product **2** in yield of 63%. $^1\text{H NMR}$ (CDCl_3 , 500 MHz): $\delta = 0.84\text{-}0.87$ (t, 3 H), $\delta = 1.17\text{-}1.42$ (m, 13 H), $\delta = 1.67\text{-}1.72$ (m, 2

H), δ = 3.99-4.02 (t, 2 H), δ = 4.30-4.35 (m, 2 H), δ = 6.48-6.49 (d, 1 H), δ = 6.51-6.53 (m, 1H), δ = 7.69-7.71 (d, 1 H), δ = 10.84 (s, 1 H).

Ethyl 2-(6-bromohexyloxy)-4-(octyloxy)benzoate (3). Compound **(2)** (2 g, 6.8 mmol), 1,6-dibromohexane (3.32 g, 13.6 mmol) and potassium carbonate (1.4 g, 10.2 mmol) were added into 50 ml of dry N,N-dimethylformamide (DMF). The resulting solution was stirred at room temperature for 36 hours. The reaction mixture was poured into ice water and filtered. The precipitate was dried and treated with dichloromethane. The insoluble solid was filtered off and the filtrate was evaporated under the reduced pressure. The residue was purified by column chromatography using silica gel (100-200 mesh) with chloroform/petroleum ether (1:2, v/v) as eluent to give the product **3**. Yield: 65%. ^1H NMR (CDCl_3 , 500MHz): δ = 0.87-0.90 (t, 3 H), δ = 1.25-1.37 (m, 11 H), δ = 1.40-1.50 (m, 6 H), δ = 1.75-1.80 (m, 2 H), δ = 1.80-1.87 (m, 4 H), δ = 3.39-3.42 (t, 2 H), δ = 3.96-3.99 (m, 4 H), δ = 4.29-4.33 (m, 2 H), δ = 6.44-6.48 (m, 2 H), δ = 7.81-7.83 (d, 1 H).

6-(2-(ethoxycarbonyl)-5-(octyloxy)phenoxy)-N,N,N-trimethylhexan-1-aminium bromide (4). A 33 % trimethylamine aqueous solution (2.48 g, 10 mmol) was added to a solution of **(3)** (2.02 g, 4.42 mmol) in 150 mL of ethanol. The mixture was stirred for 24 h under refluxing. The solvent was evaporated; the resulting reaction mixture was treated with chloroform, washed with water; and then dried over anhydrous MgSO_4 . After removing the solvent, the crude product was purified through column chromatography on silica gel using 15/1 of chloroform/methanol (v/v) as eluent, giving product **4** in yield of 90 %. ^1H NMR (CDCl_3 , 500MHz): δ = 0.87-0.90 (t, 3 H), δ = 1.11-1.49 (m, 17 H), δ = 1.75-1.84 (m, 6 H), δ = 3.46 (s, 9 H), δ = 3.55-3.57 (t, 2 H), δ = 3.96-3.99 (m, 4 H), δ = 4.28-4.32 (m, 2 H), δ = 6.44-6.46 (m, 2 H), δ = 7.80-7.82 (d, 1 H).

6-(2-carboxy-5-(octyloxy)phenoxy)-N,N,N-trimethyldecan-1-ammonium bromide (5). Compound **(4)** was dissolved in a mixture of methanol (22 ml), water (3 ml), and sodium hydroxide pellets (0.5 g), and heated under refluxing for 3 h. The mixture was diluted with water (75 ml), and then concentrated hydrobromic acid was added to adjust pH to 2. The yielded white precipitate was then filtered off and washed with water. The dried crude product was recrystallized from 2:1 of chloroform and ether to give a white product **5**. Yield: 83%. ^1H NMR (CDCl_3 , 500 MHz): δ = 0.92-0.95 (t, 3 H), δ = 1.31-1.42 (m, 9 H), δ = 1.47-1.53 (m, 4 H), δ = 1.63-1.69 (m, 2 H), δ = 1.78-1.94 (m, 6 H), δ = 3.45 (s, 9 H), δ = 3.66-3.70 (t, 2 H), δ = 3.97-4.03 (t, 2 H), δ =

4.18-4.24 (t, 2 H), δ = 6.50 (s, 1 H), δ = 6.58-6.62 (m, 1 H), δ = 8.03-8.08 (d, J = 10 Hz, 1 H), δ = 10.80 (s, 1 H).

6-(2-((4-((4-butoxyphenyl)diazenyl)phenoxy)carbonyl)-5-(octyloxy)phenoxy)-N,N,N-trimethylhexan-1-ammonium bromide (B-8). A mixture of compound **(5)** (1.84 g, 3.77 mmol) and 4-((4-butoxyphenyl)diazenyl)phenol **(6)** (2.04 g, 7.54 mmol), DCC (0.85 g, 4.17 mmol), DMAP, dry dichloromethane was stirred overnight with the exclusion of moisture at room temperature. The resulting mixture was filtered and the filter pad was washed with dichloromethane and the solvent was then evaporated under the reduce pressure. The crude product was then added to dichloromethane, giving some white precipitate. The precipitate was filtered and the filtrate was concentrated through evaporation of solvent. This process was repeated 2 to 3 times until no more precipitate appeared. The solvent was removed, and then the residue was purified by column chromatography (10/1 of chloroform/methanol in volume ratio), giving B-8 in yield of 48 %. ^1H NMR (CDCl_3 , 500 MHz): δ = 0.87-0.92 (m, 3 H), δ = 0.96-1.10 (m, 3 H), δ = 1.24-1.39 (m, 10 H), δ = 1.45-1.53 (m, 6 H), δ = 1.59-1.63 (m, 2 H), δ = 1.78-1.86 (m, 6 H), δ = 3.08 (s, 9 H), δ = 3.42-3.44 (s, 2 H), δ = 4.03-4.05 (m, 6 H), δ = 6.48 (s, 1 H), δ = 6.53-6.55 (d, J = 10 Hz, 1 H), δ = 7.00-7.02 (d, J = 10 Hz, 2 H), δ = 7.27-7.29 (d, J = 10 Hz, 2 H). δ = 7.89-7.94 (m, 4 H), δ = 8.07-8.09 (d, J = 10 Hz, 1 H). Anal. Calc for amphiphile B-8 ($\text{C}_{40}\text{H}_{58}\text{N}_3\text{O}_5\text{Br}\cdot\text{H}_2\text{O}$): C, 63.31; H, 7.97; N, 5.54. Found: C, 63.53; H, 7.63; N, 5.41. MALDI-TOF MS: m/z : 660.36, which corresponds to the $[\text{C}_{40}\text{H}_{58}\text{N}_3\text{O}_5]^+$ ion.

6-(2-((4-((4-butoxyphenyl)diazenyl)phenoxy)carbonyl)-5-(hexyloxy)phenoxy)-N,N,N-trimethylhexan-1-ammonium bromide (B-6). Amphiphile B-6 was synthesized similarly to B-8, by using 1-bromohexane instead of 1-bromooctane. ^1H NMR (CDCl_3 , 500 MHz): δ = 0.90-0.94 (m, 3 H), δ = 0.98-1.01 (m, 3 H), δ = 1.34-1.38 (m, 4 H), δ = 1.45-1.56 (m, 6 H), δ = 1.60-1.66 (m, 2 H), δ = 1.69-1.75 (m, 2 H), δ = 1.78-1.84 (m, 6 H), δ = 3.11 (s, 9 H), δ = 3.50-3.54 (m, 2 H), δ = 4.02-4.07 (m, 6 H), δ = 6.49 (d, 1 H), δ = 6.54-6.56 (m, 1 H), δ = 7.00-7.02 (d, J = 10 Hz, 2 H), δ = 7.26-7.28 (d, 2 H). δ = 7.90-7.94 (m, 4 H), δ = 8.09-8.11 (d, J = 10 Hz, 1 H). Anal. Calc for amphiphile B-6 ($\text{C}_{38}\text{H}_{54}\text{N}_3\text{O}_5\text{Br}\cdot\text{H}_2\text{O}$): C, 62.46; H, 8.72; N, 5.75. Found: C, 62.87; H, 8.51; N, 5.47. MALDI-TOF MS: m/z : 632.35, which corresponds to the $[\text{C}_{38}\text{H}_{54}\text{N}_3\text{O}_5]^+$ ion.

6-(2-((4-((4-butoxyphenyl)diazenyl)phenoxy)carbonyl)-5-(decyloxy)phenoxy)-N,N,N-trimethylhexan-1-ammonium bromide (B-10). Amphiphile B-10 was synthesized similarly to B-8, by using

1-bromodecane instead of 1-bromooctane. ^1H NMR (CDCl_3 , 500 MHz): $\delta = 0.87\text{-}0.90$ (m, 3 H), $\delta = 0.98\text{-}1.01$ (m, 3 H), $\delta = 1.23\text{-}1.38$ (m, 14 H), $\delta = 1.44\text{-}1.56$ (m, 6 H), $\delta = 1.60\text{-}1.66$ (m, 2 H), $\delta = 1.79\text{-}1.85$ (m, 6 H), $\delta = 3.10$ (s, 9 H), $\delta = 3.51\text{-}3.54$ (m, 2 H), $\delta = 4.03\text{-}4.07$ (m, 6 H), $\delta = 6.48$ (s, 1 H), $\delta = 6.54\text{-}6.56$ (m, 1 H), $\delta = 7.00\text{-}7.02$ (d, $J = 10$ Hz, 2 H), $\delta = 7.26\text{-}7.28$ (d, 2 H). $\delta = 7.90\text{-}7.94$ (m, 4 H), $\delta = 8.09\text{-}8.11$ (d, $J = 10$ Hz, 1 H). Anal. Calc for amphiphile B-10 ($\text{C}_{42}\text{H}_{62}\text{N}_3\text{O}_5\text{Br}\cdot 2\text{H}_2\text{O}$): C, 62.67; H, 8.26; N, 5.22. Found: C, 62.44; H, 8.51; N, 4.97. MALDI-TOF MS: m/z : 688.41, which corresponds to the $[\text{C}_{42}\text{H}_{62}\text{N}_3\text{O}_5]^+$ ion.

6-(2-((4-((4-butoxyphenyl)diazenyl)phenoxy)carbonyl)-5-(dodecyloxy)phenoxy)-N,N,N-trimethylhexan-1-ammonium (B-12). Amphiphile B-12 was synthesized similarly to B-8, by using 1-bromododecane instead of 1-bromooctane. ^1H NMR (CDCl_3 , 500 MHz): $\delta = 0.87\text{-}0.93$ (m, 6 H), $\delta = 1.23\text{-}1.38$ (m, 20 H), $\delta = 1.43\text{-}1.53$ (m, 6 H), $\delta = 1.79\text{-}1.87$ (m, 6 H), $\delta = 3.32$ (s, 9 H), $\delta = 3.37\text{-}3.40$ (m, 2 H), $\delta = 4.03\text{-}4.06$ (m, 6 H), $\delta = 6.50$ (d, 1 H), $\delta = 6.53\text{-}6.55$ (m, 1 H), $\delta = 7.00\text{-}7.02$ (d, $J = 10$ Hz, 2 H), $\delta = 7.31\text{-}7.33$ (d, 2 H), $\delta = 7.90\text{-}7.95$ (m, 4 H), $\delta = 8.02\text{-}8.04$ (d, $J = 10$ Hz, 1 H). Anal. Calc for amphiphile B-12 ($\text{C}_{44}\text{H}_{66}\text{N}_3\text{O}_5\text{Br}\cdot \text{H}_2\text{O}$): C, 64.85; H, 8.41; N, 5.16. Found: C, 64.64; H, 8.71; N, 5.03. MALDI-TOF MS: m/z : 716.46, which corresponds to the $[\text{C}_{44}\text{H}_{66}\text{N}_3\text{O}_5]^+$ ion.

References:

- (1) R. A. Lewthwaite, J. W. Goodby, K. J. Toyne, *J. Mater. Chem.* 1993, **3**, 241-245.
- (2) W. Li, W. F. Bu, H. L. Li, L. X. Wu, M. Li, *Chem. Commun.* 2005, 3785-3787.

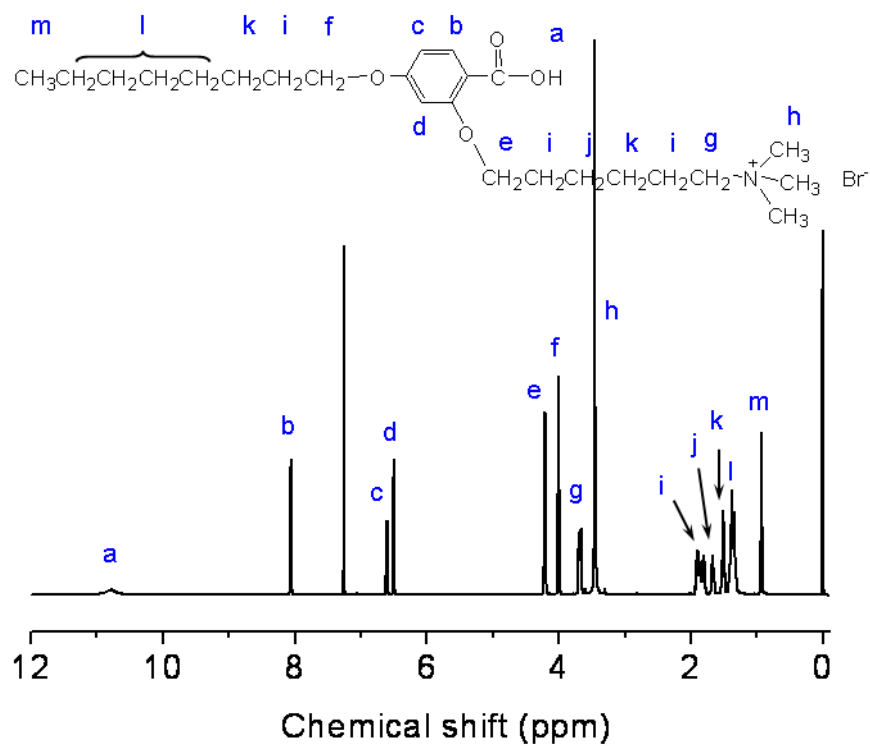


Figure S1. ¹H NMR spectrum of compound (5) in CDCl₃.

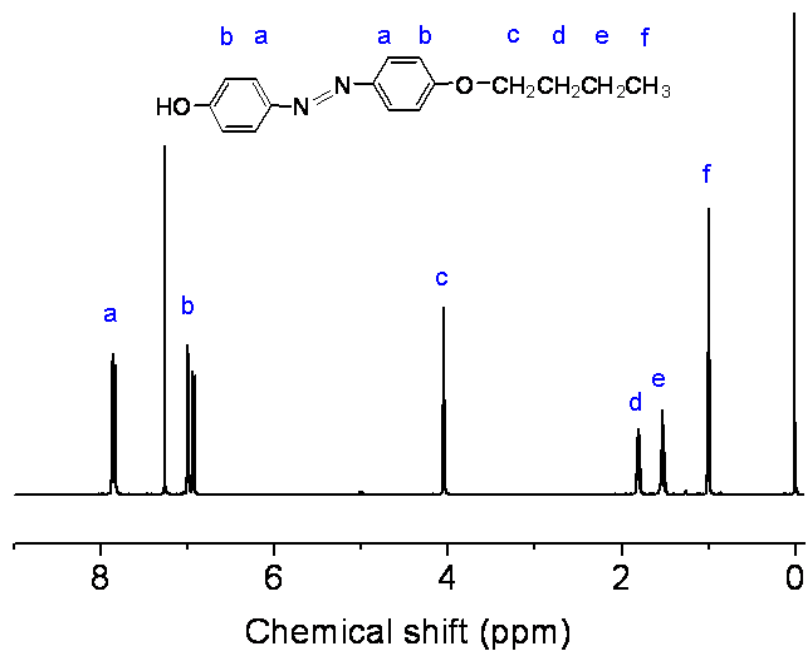


Figure S2. ¹H NMR spectrum of compound (6) in CDCl₃.

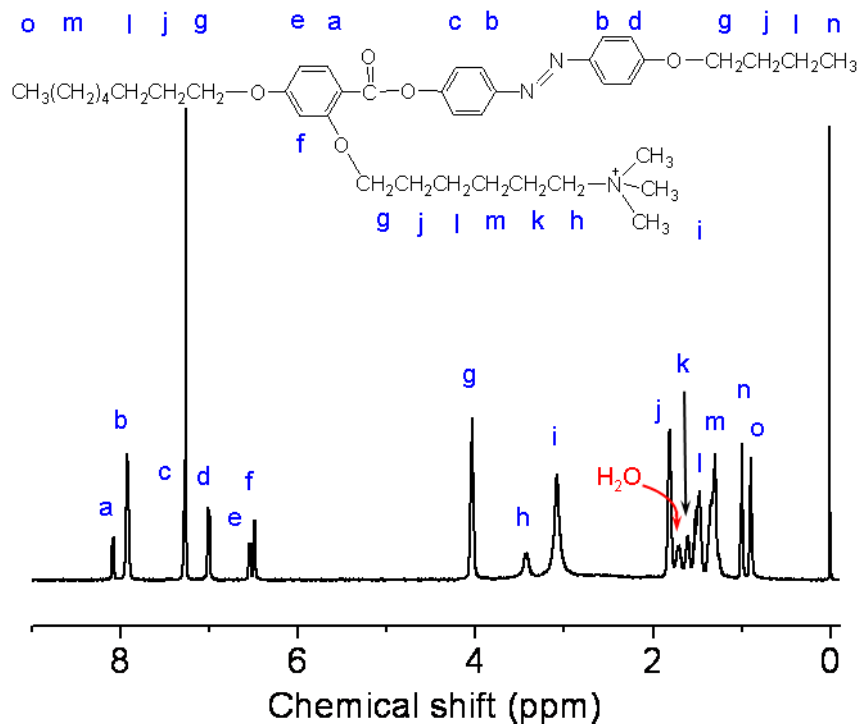


Figure S3. ¹H NMR spectrum of amphiphile **B-8** in CDCl₃.

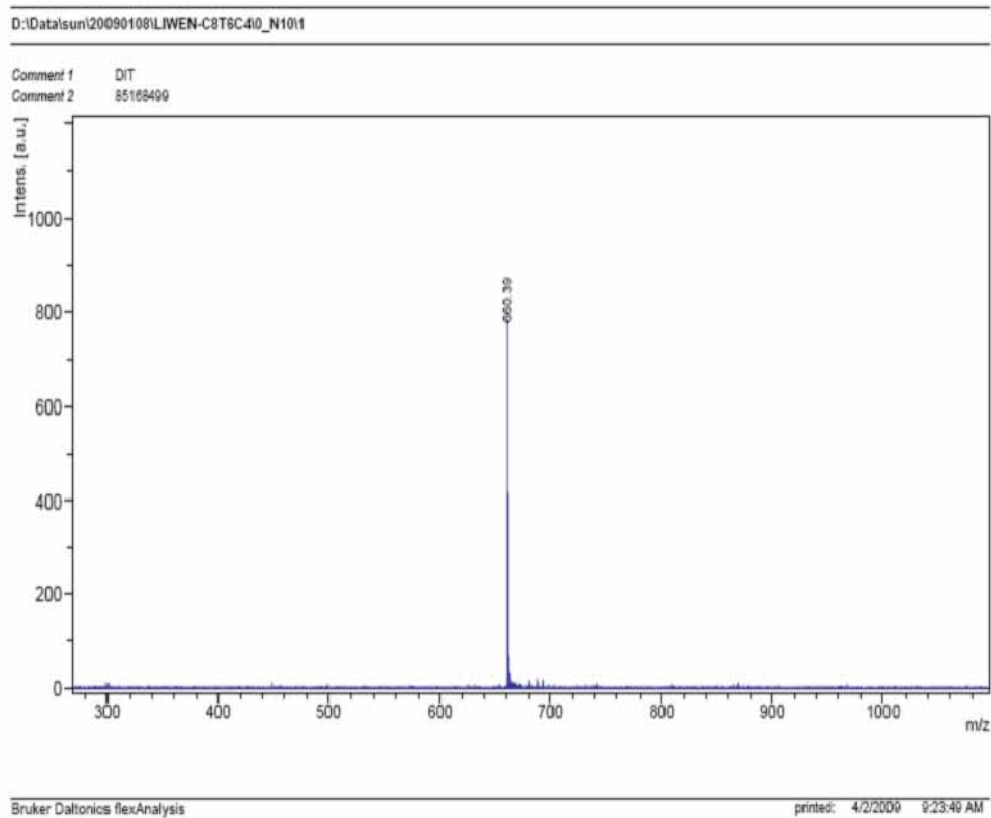


Figure S4. MALDI-TOF Mass spectrum of amphiphiles **B-8**. Peak is observed corresponding to

$[C_{40}H_{58}N_3O_5]^+$ ion.

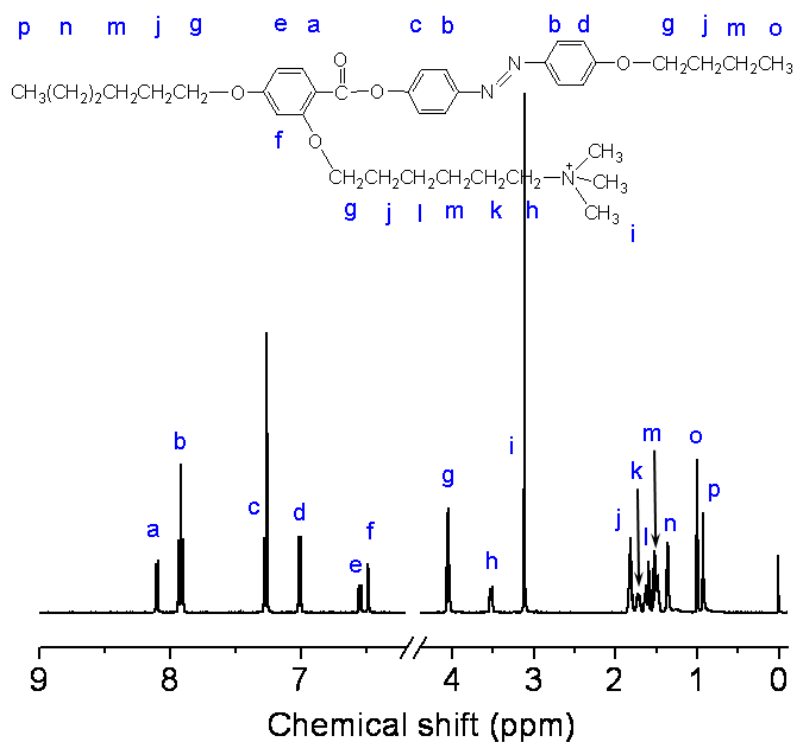


Figure S5. 1H NMR spectrum of amphiphile **B-6** in $CDCl_3$.

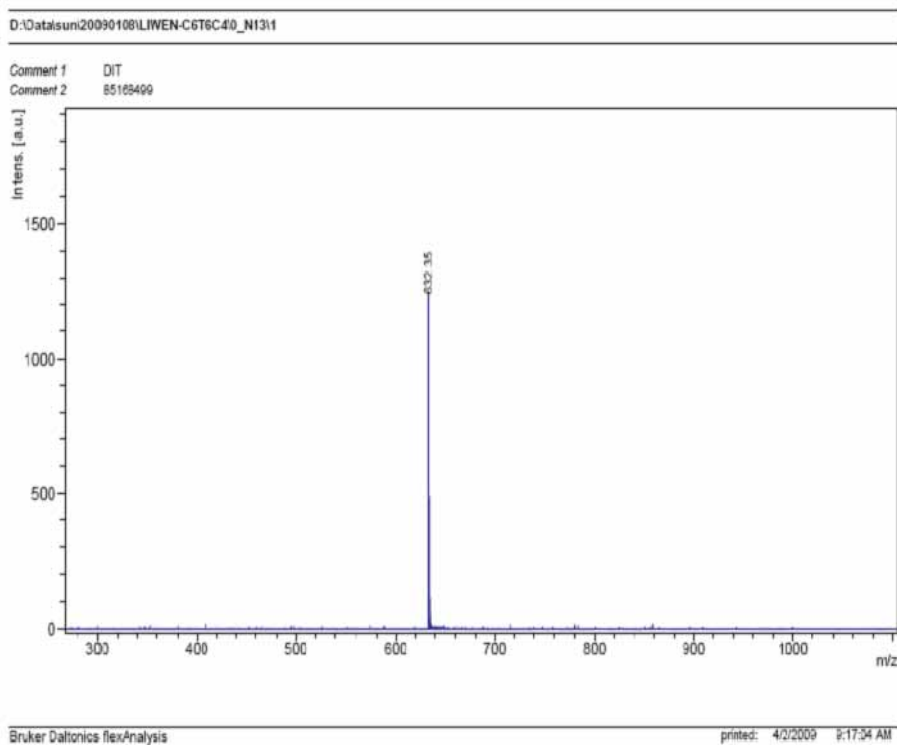


Figure S6. MALDI-TOF Mass spectrum of amphiphiles **B-6**. Peak is observed corresponding to

$[C_{38}H_{54}N_3O_5]^+$ ion.

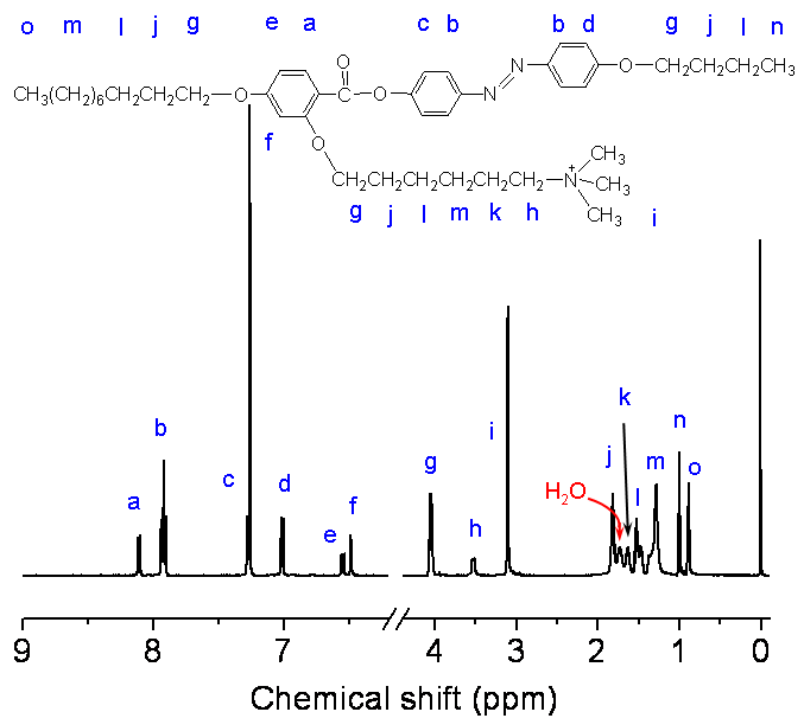


Figure S7. ^1H NMR spectrum of amphiphile **B-10** in CDCl_3 .

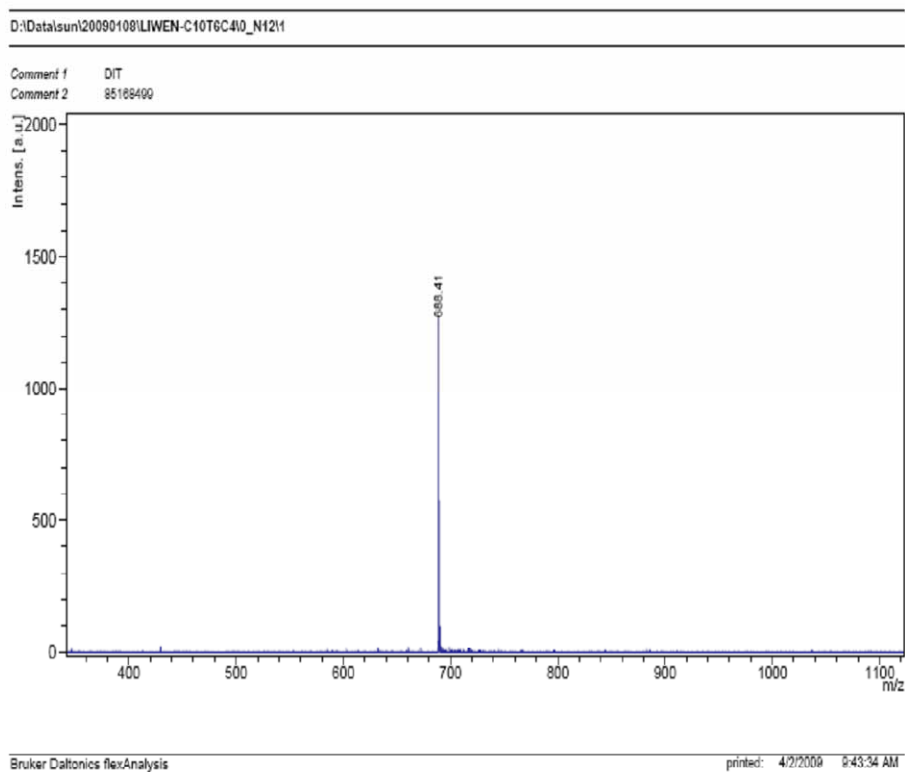


Figure S8. MALDI-TOF Mass spectrum of amphiphiles **B-10**. Peak is observed corresponding to

$[\text{C}_{42}\text{H}_{62}\text{N}_3\text{O}_5]^+$ ion.

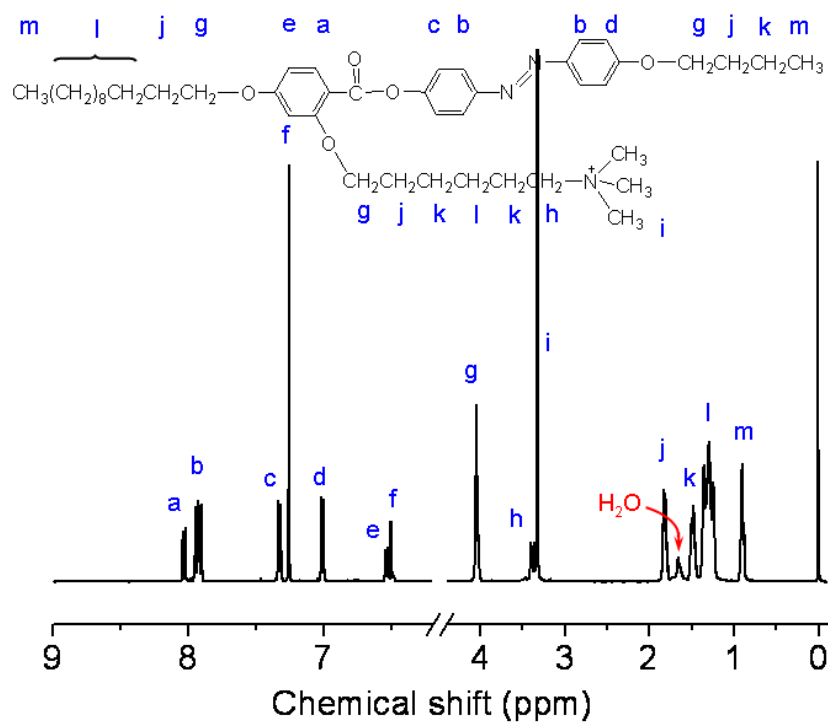


Figure S9. ^1H NMR spectrum of amphiphile **B-12** in CDCl_3 .

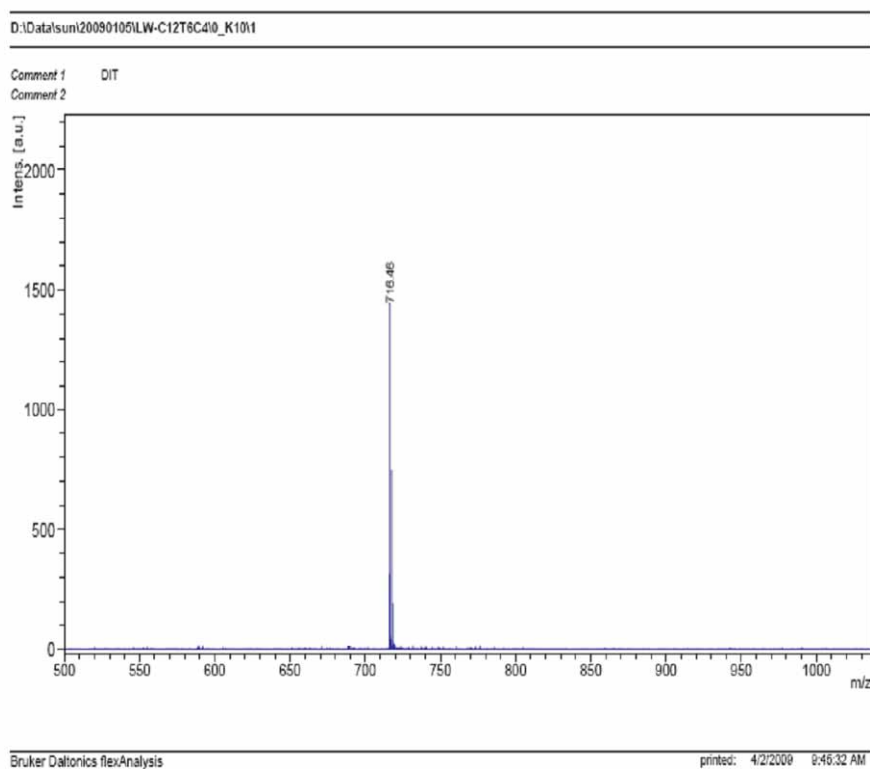


Figure S10 MALDI-TOF Mass spectrum of amphiphiles **B-12**. Peak is observed corresponding to

$[C_{44}H_{66}N_3O_5]^+$ ion..

4. Thermal behaviors of branched amphiphiles B-n.

Thermal behaviors of amphiphiles **B-n** were examined by TGA and DSC. TGA curve of amphiphile B-8 under a nitrogen atmosphere is showed in Figure S11. 2 % weight of B-8 loses at 170 °C, indicating that B-8 keeps it's weight at 170 °C, a significantly high temperature than the clearing point. Figure S12 depicted the DSC curves of amphiphile B-8 for four heating and cooling runs. No significant change appears at the transition temperatures for the glassy-to-mesophase transition and for the mesophase-to-isotropic transition during the subsequent heating-cooling cycles, indicating it's stable thermotropic phase transition property.

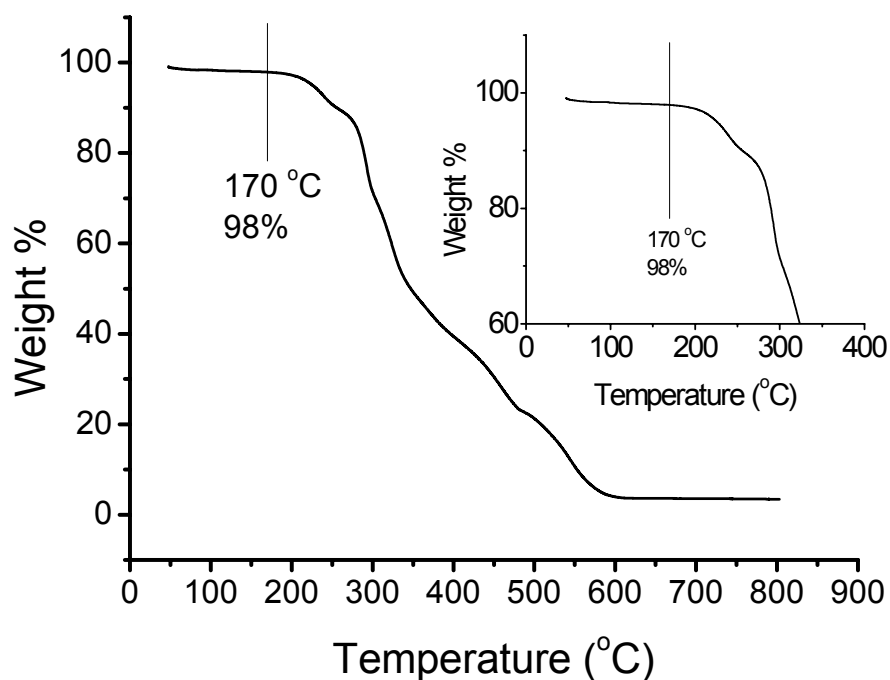


Figure S11. TGA curve of amphiphile **B-8** in the temperature range between 0 and 900 °C. (heating rate: 10 °C min⁻¹). (Inset: Enlargement of TGA curve between 0 and 400 °C)

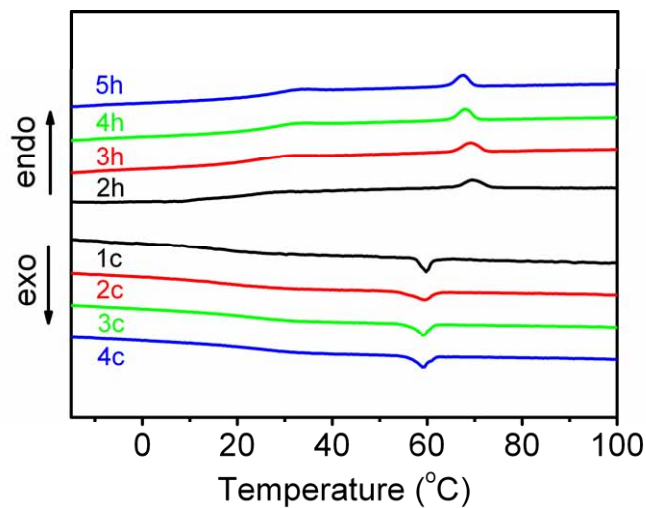
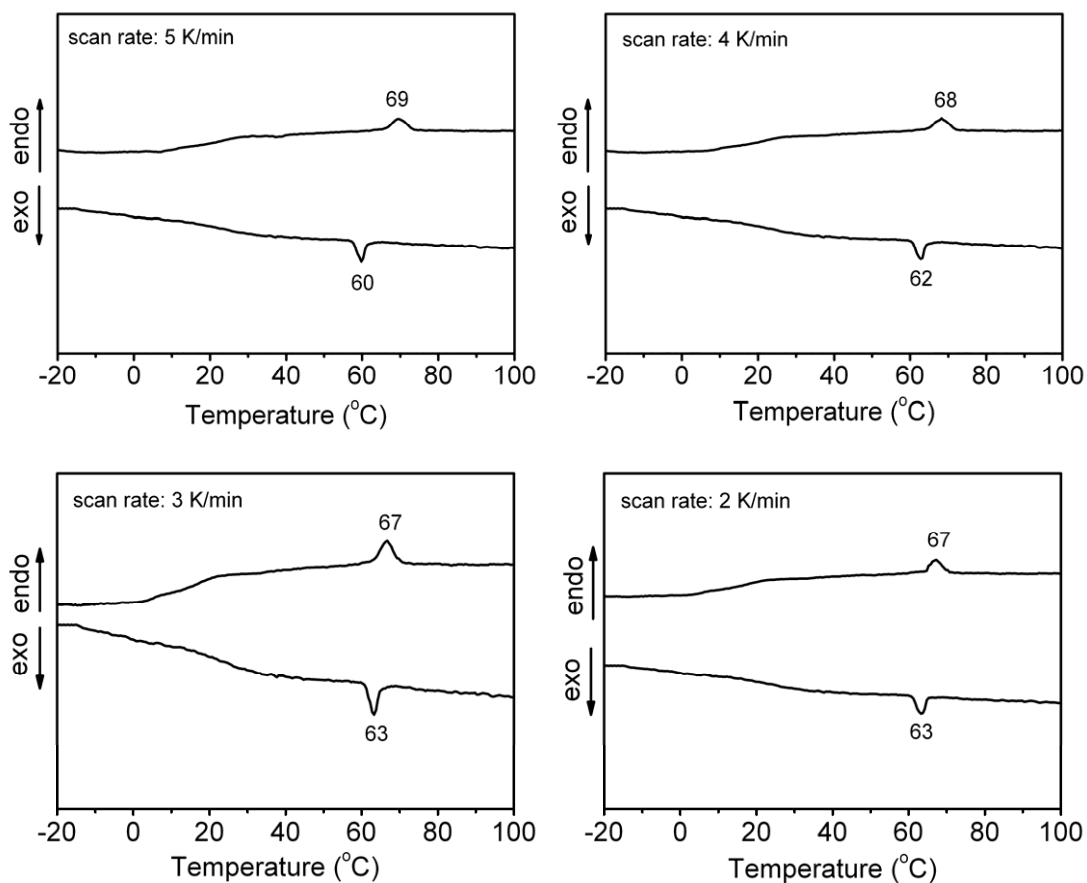


Figure S12. DSC curves of amphiphile **B-8** running four heating and cooling cycles with a rate of 5 °C/min



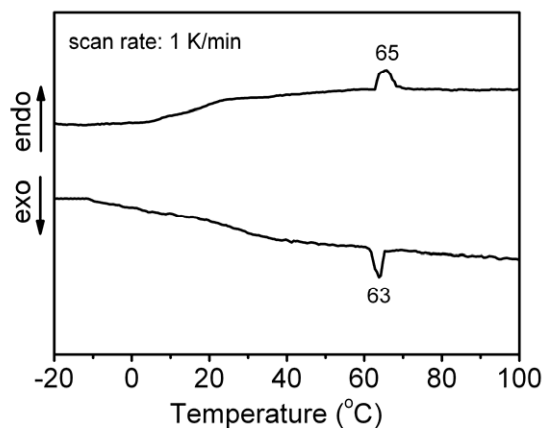


Figure S13. DSC curves of ammonium B-8 with different scan rate.

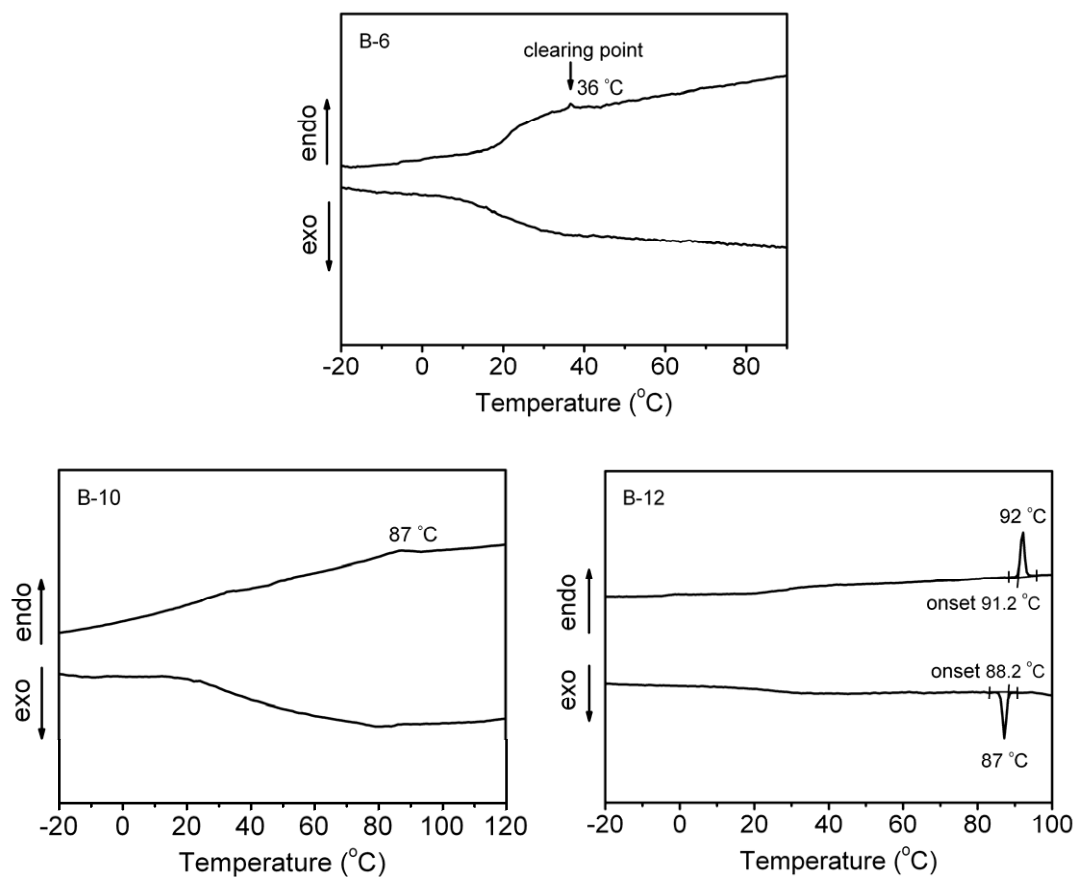


Figure S14. DSC curves of amphiphiles **B-6**, **B-10** and **B-12** on their first cooling and second heating process with a rate of 5 °C/min.

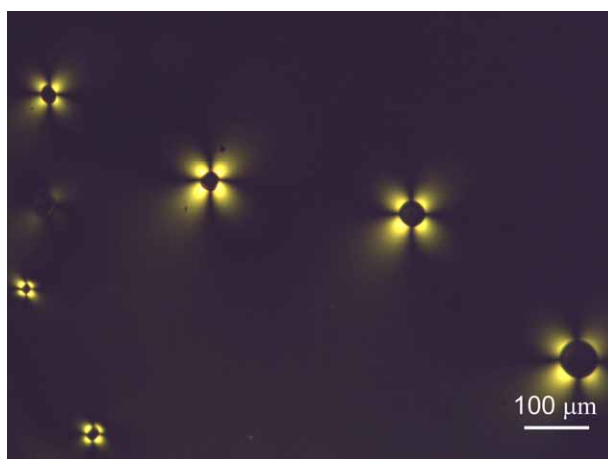


Figure S15. POM image of the amphiphile **B-12**.

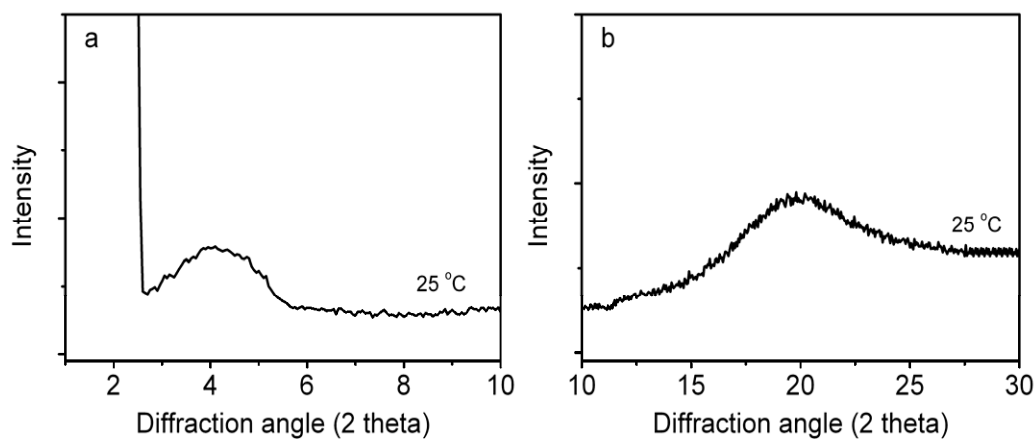


Figure S16. X-ray diffractions of amphiphiles **B-6** at room temperature: (a) in low-angle region, (b) in wide-angle region.

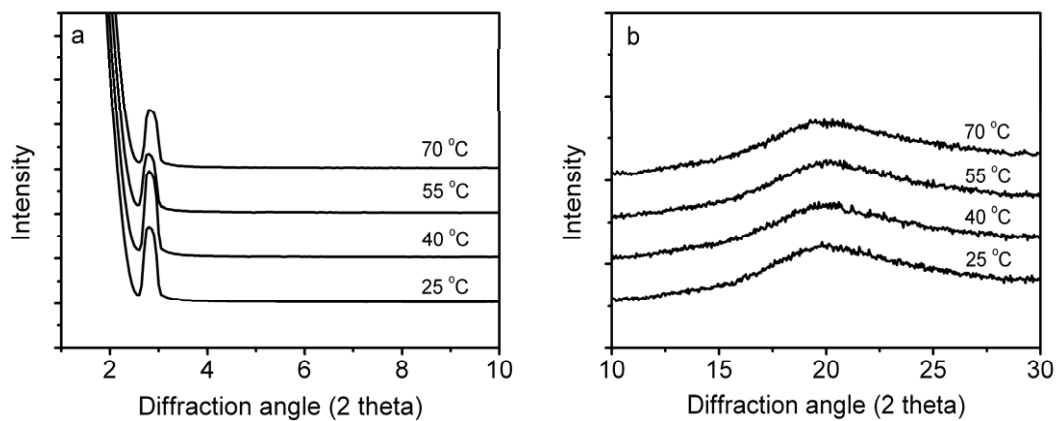


Figure S17. Variable-temperature X-ray diffractions of amphiphiles **B-10**: (a) in low-angle region, (b) in wide-angle region.

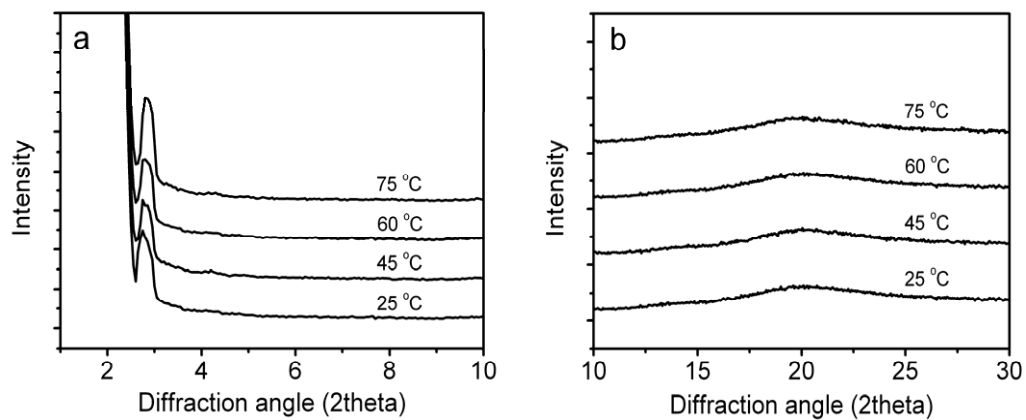


Figure S18. Variable-temperature X-ray diffractions of amphiphiles **B-12**: (a) in low-angle region, (b) in wide-angle region.