

Electronic Supplementary Information for

Construction of gyroid-structured matrices through the design of geminized amphiphilic zwitterions and their self-organization

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1. General Procedures

¹H NMR spectra were obtained using a JNM-ECA500 (JEOL) spectrometer. Chemical shifts of ¹H signals were referenced to (CH₃)₄Si ($\delta = 0.00$) as an internal standard. Elemental analysis was performed with an Elementar Analytical vario EL3 instrument. Thermal properties of the materials were examined with a DSC-6220 (Seiko Instruments) differential scanning calorimeter at a heating and cooling rate of 5 °C min⁻¹. The textures of liquid-crystalline (LC) materials were obtained with an Olympus BX51 polarizing optical microscope equipped with a Lincam hot-stage. Powder X-ray diffraction measurement was performed using a Rigaku RINT-2500 diffractometer with CuK α radiation. Ionic conductivity was measured with an impedance analyzer Solartron 1260 (Schlumberger) at a heating rate of 2 °C min⁻¹.

2. Materials

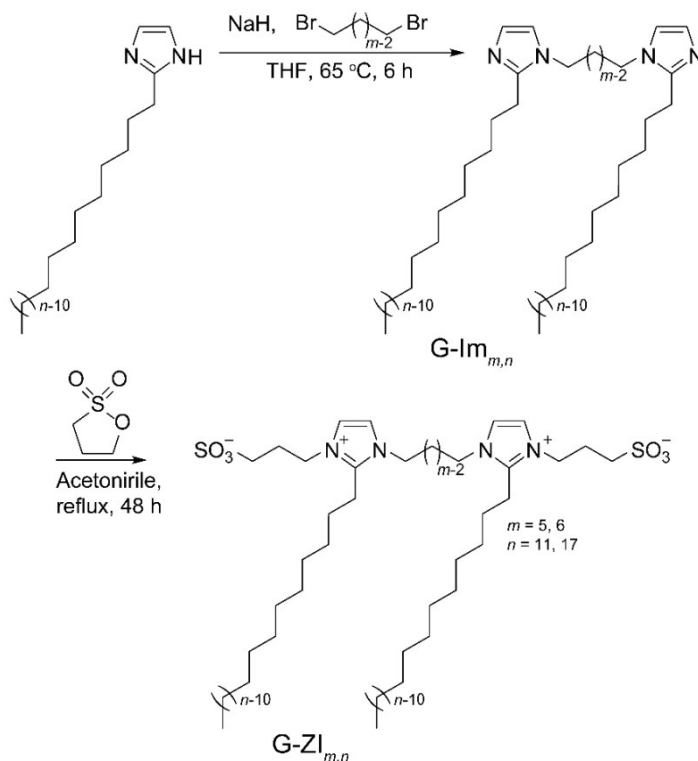
All chemical reagents and solvents were commercially obtained and used as received. All reactions were performed in anhydrous solvents under argon atmosphere.

3. Synthesis

3-1. Synthesis of gemini amphiphilic zwitterion **G-ZI_{m,n}**

Gemini amphiphilic zwitterions **G-ZI_{m,n}** were synthesized according to the literature.¹ The synthetic pathway is depicted in Scheme S1.

Scheme S1. Synthesis of gemini amphiphilic zwitterions (**G-ZI_{m,n}**).



G-Im_{6,17}

2-Heptadecylimidazole (22.2 g, 72.5 mmol) was added slowly into the suspension of sodium hydride (60 wt%, dispersion in paraffin liquid, 3.34 g, 83.5 mmol) in THF (250 ml) at room temperature. The mixture was stirred at 40 °C for an hour. 1,6-Dibromohexane (7.23 g, 29.6 mmol) was added dropwise and stirred at 65 °C for 6 h. Then methanol and water were added successively to quench the reaction mixture, and the resulting solution was concentrated by rotary evaporation. The mixture was extracted by chloroform and washed with water. The organic phase was dried over anhydrous MgSO₄ and the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography (silica, chloroform/MeOH = 10/1 (v/v) as an eluent). The crude product was further purified by recrystallization from acetone to give **G-Im_{6,17}** (4.81 g, 6.91 mmol; 23.3 %) as a white solid.

¹H NMR (500 MHz, CDCl₃): δ = 6.94 (d, *J* = 1.50 Hz, 2H), 6.78 (d, *J* = 1.00 Hz, 2H), 3.81 (t, *J* = 7.50 Hz, 4H), 2.61 (t, *J* = 8.00 Hz, 4H), 1.78-1.70 (m, 8H), 1.39-1.25 (m, 60H), 0.88 (t, *J* = 6.75 Hz, 6H).

G-ZI_{6,17}

1,3-Propanesultone (3.17 g, 26.0 mmol) was added to a solution of **G-Im_{6,17}** (3.01 g, 4.32 mmol) in acetonitrile (40 mL) and heated at reflux for 48 h. The crude product was purified by recrystallization from isopropanol to give **G-ZI_{6,17}** (3.00 g, 3.19 mmol; 73.8 %) as a white solid.

¹H NMR (500 MHz, CDCl₃): δ = 7.87 (d, *J* = 2.00 Hz, 2H), 7.72 (d, *J* = 1.50 Hz, 2H), 4.43 (t, *J* = 6.50 Hz, 4H), 4.16 (t, *J* = 7.25 Hz, 4H), 3.07 (t, *J* = 7.50 Hz, 4H), 2.75 (t, *J* = 6.50 Hz, 4H), 2.34-2.30 (m, 4H), 1.92 (m, 8H), 1.58-1.25 (m, 60H), 0.88 (t, *J* = 7.00 Hz, 6H). Elemental analysis. Calcd. for C₅₂H₉₈N₄O₆S₂ 1.0H₂O: C, 65.23; H, 10.53; N, 5.85. Found: C, 64.96; H, 10.14; N, 5.94.

G-ZI_{6,11}

Compound **G-ZI_{6,11}** was prepared by a procedure similar to that reported for **G-ZI_{6,17}**.

¹H NMR (500 MHz, CDCl₃): δ = 7.87 (d, *J* = 1.50 Hz, 2H), 7.73 (d, *J* = 1.00 Hz, 2H), 4.41 (t, *J* = 6.25 Hz, 4H), 4.16 (d, *J* = 7.00 Hz, 4H), 3.07 (t, *J* = 7.75 Hz, 4H), 2.76 (t, *J* = 6.25 Hz, 4H), 2.35-2.31 (m, 8H), 1.94 (m, 4H), 1.58-1.25 (m, 36 H), 0.88 (t, *J* = 7.00 Hz, 6H). Elemental analysis. Calcd. for C₄₀H₇₄N₄O₆S₂ 1.5H₂O: C, 60.19; H, 9.72; N, 7.02. Found: C, 60.31; H, 9.47; N, 6.72.

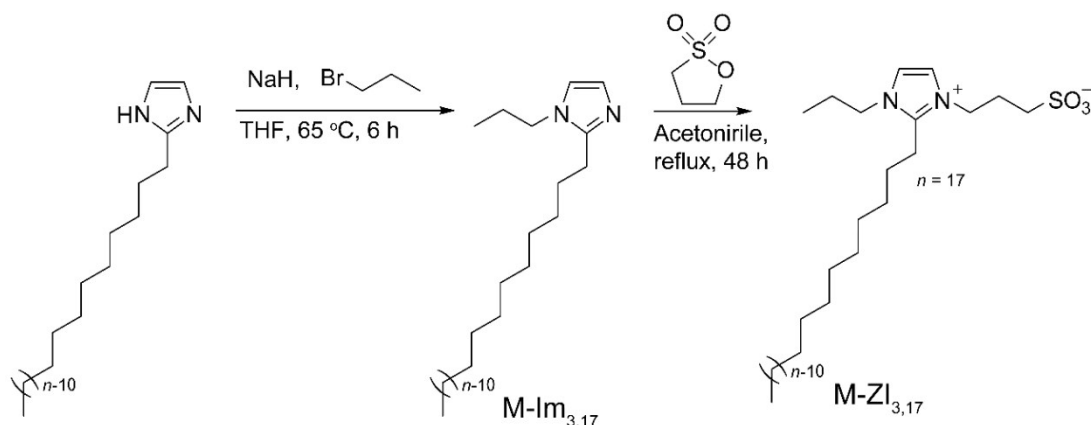
G-ZI_{5,17}

¹H NMR (500 MHz, CDCl₃): δ = 7.87 (s, 2H), 7.72 (s, 2H), 4.36 (m, 4H), 4.16 (m, 4H), 3.06 (m, 6H), 2.76 (m, 4H), 2.36-2.30 (m, 4H), 1.96 (m, 4H), 1.59-1.25 (m, 60 H), 0.88 (t, *J* = 7.00 Hz, 6H). Elemental analysis. Calcd for C₅₁H₉₆N₄O₆S₂ 3.0H₂O: C, 62.54; H, 10.50; N, 5.72. Found: C, 62.80; H, 10.43; N, 5.37.

3-2. Synthesis of monomeric amphiphilic zwitterion M-ZI_{3,17}

Monomeric amphiphilic zwitterion **M-ZI_{3,17}** was synthesized according to a similar procedure. The synthetic pathway is depicted in Scheme S2.

Scheme S2. Synthesis of monomeric amphiphilic zwitterion (**M-ZI_{3,17}**).



M-Im_{3,17}

2-Heptadecylimidazole (20.1 g, 65.5 mmol) was added slowly into the suspension of sodium hydride (60 wt%, dispersion in paraffin liquid, 3.06 g, 76.5 mmol) in THF (250 mL) at room temperature. The mixture was stirred at 40 °C for an hour. 1-bromopropane (7.81 g, 63.5 mmol) was added dropwise and stirred at 65 °C for 6 h. Then methanol and water were added successively to quench the reaction mixture, and the resulting solution was concentrated by rotary evaporation. The mixture was extracted by chloroform and washed with water. The organic phase was dried over anhydrous MgSO₄, and the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography (silica, chloroform/MeOH = 20/1 (v/v) as the eluent). The crude product was further purified by recrystallization from ethyl acetate to give **M-Im_{3,17}** (1.46 g; 4.19 mmol; 6.59 %) as a white solid.

¹H NMR (500 MHz, CDCl₃): δ = 6.94 (d, *J* = 1.50 Hz, 1H), 6.81 (d, *J* = 1.50 Hz, 1H), 3.79 (t, *J* = 7.25 Hz, 2H), 2.63 (t, *J* = 7.75 Hz, 2H), 1.80-1.72 (m, 4H), 1.41-1.25 (m, 28H), 0.94 (t, *J* = 7.50 Hz, 3H) 0.88 (t, *J* = 6.75 Hz, 3H).

M-ZI_{3,17}

1,3-Propanesultone (1.28 g, 10.5 mmol) was added to a solution of **M-Im_{3,17}** (1.05 g, 3.00 mmol) in acetonitrile (30 mL) and heated at reflux for 48 h. The crude product was purified by recrystallization from an acetone/methanol solvent mixture to give **M-ZI_{3,17}** (1.15 g, 2.43 mmol; 81.1 %) as a white solid.

¹H NMR (500 MHz, CDCl₃): δ = 7.79 (d, *J* = 2.00 Hz, 1H), 7.38 (d, *J* = 2.50 Hz, 1H), 4.50 (t, *J* = 7.00 Hz, 2H), 4.07 (d, *J* = 7.50 Hz, 2H), 3.08 (t, *J* = 8.00 Hz, 2H), 2.79 (t, *J* = 6.25 Hz, 2H), 2.37-2.32 (m, 2H), 1.95-1.88 (m, 2H), 1.64-1.58 (m, 2H), 1.45-1.25 (m, 28H), 1.03 (t, *J* = 7.25 Hz, 3H), 0.88 (t, *J* = 6.75 Hz, 3H). Elemental analysis. Calcd. for C₂₆H₅₀N₂O₃S 1.0H₂O: C, 63.89; H, 10.72; N, 5.73. Found: C, 64.14; H, 10.48; N, 5.37.

4. Characterization

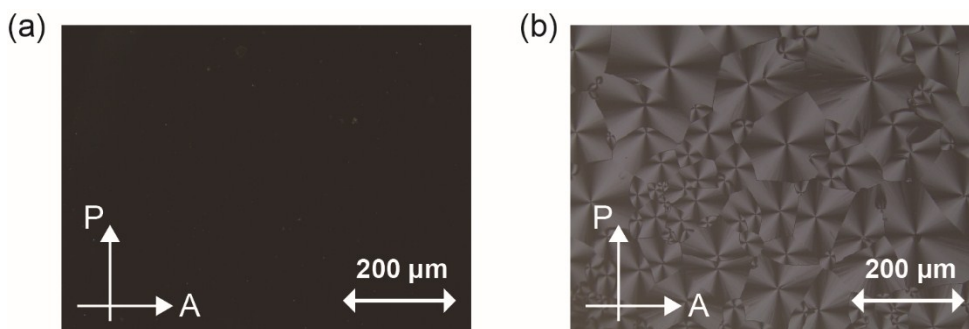


Figure S1. POM images of: (a) **G-ZI_{5,17}** in the Cub_{bi} phase at 180 °C, (b) **G-ZI_{5,17}/HTf₂N** in the molar ratio of 1:2 in the Col_h phase at 100 °C.

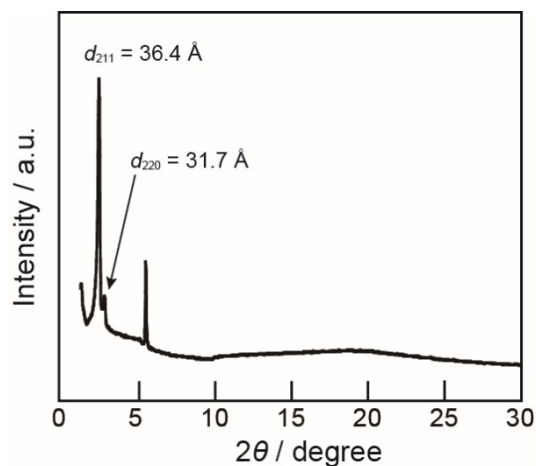


Figure S2. XRD pattern of **G-Zl_{5,17}** in the **Cub_{bi}** phase at 180 °C.

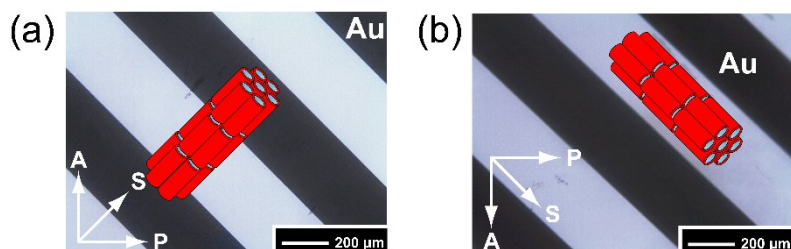


Figure S3. POM image of the 1:2 (mol/mol) **G-Zl_{6,17}/HTf₂N** mixture forming a hexagonal columnar phase aligned (a) parallel and (b) perpendicular to an applied electric field. The orientation of the columns were achieved by the mechanical shearing for ion conduction measurement. A, analyzer; P, polarizer; S, shearing.

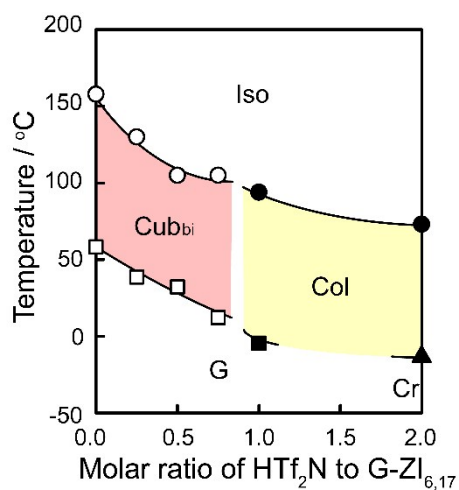


Figure S4. Phase diagram of **G-Zl_{6,17}/HTf₂N** mixtures on cooling.

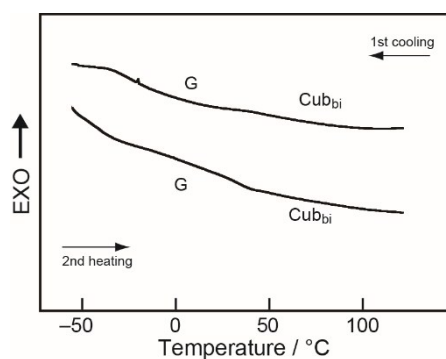


Figure S5. DSC thermograms of a 4:1 (mol/mol) **G-Zl_{6,17}/HTf₂N** mixture.

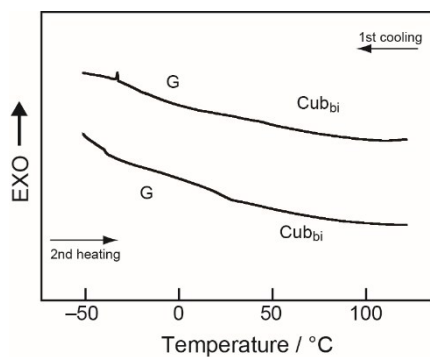


Figure S6. DSC thermograms of a 2:1 (mol/mol) **G-Zl_{6,17}/HTf₂N** mixture.

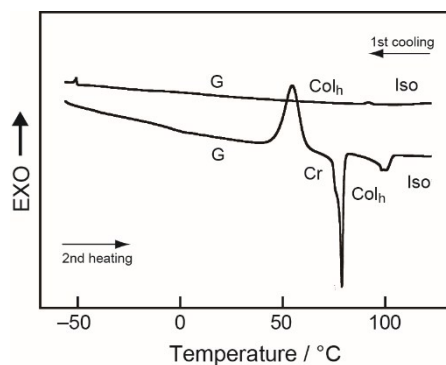


Figure S7. DSC thermograms of a 1:1 (mol/mol) **G-Zl_{6,17}/HTf₂N** mixture.

5. Reference

1. J. E. Bara, E. S. Hatakeyama, B. R. Wiesenauer, X. Zeng, R. D. Noble and D. L. Gin, *Liq. Cryst.*, 2010, **37**, 1587.