**Supporting Information**

**Highly polarized luminescence from ordered guest-host systems**E:\研\成果\论文\2\文章图\Scheme 1-1.tif

SchemeS1. Synthetic route of **T1**, **T2**, **T3**and **T4**.

**1.1 Synthesis of 4,7-bis (4- methoxyphenyl) benzo-2,1,3-thiadizole** **(1)**

Dibrombenzothidiazole (11.76g, 40mmol), 4-methoxyphenylboronic acid (15.19g, 100mmol) and Pd(PPh3)4 (3.48g, 3mmol) were added to a 500mL two-neck flask equipped with septum. The flask was evacuated and back filled with nitrogen. 1,4-dioxane (210mL) and K2CO3 (2M, 60mL, 120mmol) was added via a syringe at room temperature. The reaction mixture was heated at 110 °C for 24h. The precipitation was collected by filtration and the crude product was performed silica gel column to give a yellow green powder (9.53g) with a yield of 68.4%.

1H-NMR ( CDCl3, 600 MHz, δ= ppm ): 7.92 ( d, 4 H, *J* = 9.0 Hz ), 7.71 ( s, 2 H ), 7.08 ( d, 4 H, *J* = 9.0 Hz ), 3.89 ( s, 6 H ).

13C-NMR ( CDCl3, 150 MHz, δ= ppm ): 162.39, 156.85, 134.98, 133.04, 132.65, 130.09, 116.75, 58.08.

**1.2 Synthesis of 4,7-bis(4-hydroxyphenyl) benzo-2,1,3-thiadizole (2)**

4,7-bis(4-methoxyphenyl)benzo-2,1,3-thiadizole (1) (4.65g, 13mmol) and tetrabutylammoni-um bromide (4.62g, 13mmol) were added to a 250mL flask. Then, HBr (33% in HOAc, 100mL) was added. The mixture was heated for 24h at 100 °C, then cooled to room temperature, and 300mL water was added. The precipitation was collected by filtration and washed with methanol to give a yellow powder (3.05g) with a yield of 72.2%.

1H-NMR ( DMSO, 600 MHz, δ= ppm ): 9.74 ( s, 2 H ) , 7.86 ( d, 4 H, *J* = 6.0Hz ) , 7.80 ( s, 2 H ) , 6.92 ( d, 4 H, *J* = 6.0Hz).

13C-NMR ( DMSO, 150 MHz, δ= ppm ): 160.79, 156.59, 133.40, 130.25, 118.48, 109.99.

**1.3 Synthesis of 6-bromohexyloxy acrylate (3)**

Triethylamine (2.62g, 26mmol) was added to a cold solution (0 °C) of 6-bromohexyloxy (3.60g, 20mmol) in 50mL of CH2Cl2.Then, acryloyl chloride (1.98 g, 22 mmol) was added dropwise to the solution at 0 °C. The solution was allowed to stir for 24h at 25 °C and 30 mL water was added. The solution was extracted with CH2Cl2 for three times and the organic solution was collected, dried with NaSO4 and evaporated with a rotary evaporator to give the brown liquid monomer (3.62g) with a yield of 77.0%.

1H-NMR ( CDCl3, 600 MHz, δ= ppm ): 6.37 ( d, 1 H, *J* = 12.0 Hz ) , 6.09 ( q, 1 H , *J* = 10.0 Hz ) , 5.79 ( d, 1 H, *J* = 12.0 Hz ) , 4.13 ( t, 2 H, *J* = 6.0 Hz ) , 3.38 ( t, 2 H, *J* = 6.0 Hz ) , 1.84 ( m, 2 H, *J* = 6.0 Hz ) , 1.66 ( m, 2 H, *J* = 6.0 Hz ) , 1.45 ( m, 2 H, *J* = 6.0 Hz ) , 1.38 ( m, 2 H, *J* = 6.0 Hz ).

13C-NMR ( CDCl3, 150 MHz, δ= ppm ): 168.96, 133.30, 131.15, 67.07, 36.43, 35.25, 31.09, 30.44, 27.82.

**1.4 Synthesis of 9-bromononyloxy acrylate (4)**

Triethylamine (2.62 g, 26 mmol) was added to a cold solution (0 °C) of 9-bromononylox**y** (4.46 g, 20 mmol) in 50 mL of CH2Cl2. Then, acryloyl chloride (1.98 g, 22 mmol) was added dropwise to the solution at 0 °C. The solution was allowed to stir for 24 h at 25 °C and 30 mL water was added. The solution was extracted with CH2Cl2 for three times and the organic solution was collected, dried with NaSO4 and evaporated with a rotary evaporator to give the brown liquid monomer (4.34 g) with a yield of 78.3%.

1H-NMR ( CDCl3, 600 MHz, δ= ppm ): 6.36 ( d, 1 H, *J* = 12.0 Hz ) , 6.08 ( q, 1 H , *J* = 10.0 Hz ) , 5.78 ( d, 1 H, *J* = 12.0 Hz ) , 4.12 ( t, 2 H, *J* = 6.0 Hz ) , 3.37 ( t, 2 H, *J* = 6.0 Hz ) , 1.83 ( m, 2 H, *J* = 6.0 Hz ) , 1.64 ( m, 2 H, *J* = 6.0 Hz ) , 1.42 ( m, 2 H, *J* = 6.0 Hz ) , 1.35 ( m, 8 H, *J* = 6.0 Hz ).

13C-NMR ( CDCl3, 150 MHz, δ= ppm ): 168.87, 133.26, 131.22, 67.13, 36.67, 35.23, 32.25, 32.09, 31.57, 31.25, 30.54, 28.17.

**1.5 Synthesis of 11-bromoundecyloxy acrylate (5)**

Triethylamine (2.62 g, 26 mmol) was added to a cold solution (0 °C) of 11-bromoundecyloxy (5.07 g, 20 mmol) in 50 mL of CH2Cl2. Then, acryloyl chloride (1.98 g, 22 mmol) was added dropwise to the solution at 0 °C. The solution was allowed to stir for 24 h at 25 °C and 30 mL water was added. The solution was extracted with CH2Cl2 for three times and the organic solution was collected, dried with NaSO4 and evaporated with a rotary evaporator to give the brown liquid monomer (4.54 g) with a yield of 74.5%.

1H-NMR ( CDCl3, 600 MHz, δ= ppm ): 6.36 ( d, 1 H, *J* = 12.0 Hz ) , 6.09 ( q, 1 H , *J* = 10.0 Hz ) , 5.78 ( d, 1 H, *J* = 12.0 Hz ) , 4.11 ( t, 2 H, *J* = 6.0 Hz ) , 3.37 ( t, 2 H, *J* = 6.0 Hz ) , 1.82 ( m, 2 H, *J* = 6.0 Hz ) , 1.63 ( m, 2 H, *J* = 6.0 Hz ) , 1.39 ( m, 2 H, *J* = 6.0 Hz ) , 1.31 ( m, 12 H, *J* = 6.0 Hz ).

13C-NMR ( CDCl3, 150 MHz, δ= ppm ): 168.99, 133.14, 131.25, 67.35, 36.75, 35.46, 32.10, 32.08, 32.05, 31.87, 31.40, 31.23, 30.81, 28.55.

**1.6 Synthesis of 4,7-Bis(4-hexyloxy acrylate)phenyl)benzo-2,1,3-thiadizole (T1)**

4,7-bis(4-hydroxyphenyl) benzo-2,1,3-thiadizole (2) (1.28 g, 4 mmol), K2CO3 (1.38 g, 10 mmol), 6-bromohexyloxy acrylate (3) (2.08 g, 8.8 mmol) and 25mLDMF were added to a 100mL two-neck flask. The reaction mixture was heated at 90 °C for 24 h, then cooled to room temperature, and 200 mL water was added. The solution was extracted with CH2Cl2 for three times and the organic solution was collected, dried with NaSO4 and evaporated with a rotary evaporator. The crude product was performed silica gel column to give a yellow green powder (1.71 g) with a yield of 68.2%.

1H-NMR ( CDCl3, 600 MHz, δ= ppm ): 7.91 ( d, 4 H, *J* = 12.0 Hz ) , 7.72 ( s, 2 H ) , 7.07 ( d, 4 H, *J* = 6.0 Hz ) , 6.42 ( d, 2 H, *J* = 12.0 Hz ) , 6.14 ( q, 2 H, *J* = 10.0 Hz ) , 5.83 ( d, 2 H, *J* = 12.0 Hz ) , 4.19 ( t, 4 H, *J* = 6.0 Hz ) , 4.05 ( t, 4 H, *J* = 6.0 Hz ) , 1.85 ( m, 4 H, *J* = 6.0 Hz ) , 1.73 ( m, 4 H, *J* = 6.0 Hz) , 1.53 ( m, 8 H, *J* = 12.0 Hz ).

13C-NMR ( CDCl3, 150 MHz, δ= ppm ): 169.03, 161.90, 156.85, 134.98, 133.29, 133.01, 132.49, 131.22, 130.05, 117.27, 70.52, 67.22, 31.82, 31.24, 28.44.

FT-IR ( KBr, cm−1 ): 2931 (vs), 1723 (vs), 1604 (s), 1512 (s), 1470 (vs), 1408 (vs), 1249 (vs), 1179 (vs), 1070 (vs), 1003 (vs), 891 (vs), 815 (vs).

HRMS (MALDI-TOF) m/z: Found: [M+H]+ 628.2582; molecular formula C36H40N2O6S requires [M+H]+ 628.2607.

**1.7 Synthesis of 4,7-Bis(4-nonyloxy acrylate)phenyl)benzo-2,1,3-thiadizole (T2)**

4,7-bis(4-hydroxyphenyl) benzo-2,1,3-thiadizole (2) (1.28 g, 4 mmol), K2CO3 (1.38 g, 10 mmol),9-bromononyloxy acrylate (4) (2.43 g, 8.8 mmol) and 25mLDMF were added to a 100mL two-neck flask. The reaction mixture was heated at 90 °C for 24 h, then cooled to room temperature, and 200 mL water was added. The solution was extracted with CH2Cl2 for three times and the organic solution was collected, dried with NaSO4 and evaporated with a rotary evaporator. The crude product was performed silica gel column to give a yellow green powder (1.93 g) with a yield of 67.7%.

1H-NMR ( CDCl3, 600 MHz, δ= ppm ): 7.91 ( d, 4 H, *J* = 6.0 Hz ) , 7.72 ( s, 2 H ) , 7.07 ( d, 4 H, *J* = 6.0 Hz ) , 6.40 ( d, 2 H, *J* = 12.0 Hz ) , 6.12 ( q, 2 H, *J* = 10.0 Hz ) , 5.82 ( d, 2 H, *J* = 12.0 Hz ) , 4.16 ( t, 4 H, *J* = 6.0 Hz ) , 4.05 ( t, 4 H, *J* = 6.0 Hz ) , 1.83 ( m, 4 H, *J* = 6.0 Hz ) , 1.68 ( m, 4 H, *J* = 6.0 Hz) , 1.49 ( m, 4 H, *J* = 6.0 Hz ) , 1.38 ( m, 16 H, *J* = 12.0 Hz ).

13C-NMR ( CDCl3, 150 MHz, δ= ppm ): 168.98, 161.99, 156.87, 134.99, 133.05, 132.97, 132.44, 131.29, 130.00, 117.30, 70.73, 67.33, 32.07, 31.93, 31.90 31.83, 31.25, 28.68, 28.56.

FT-IR ( KBr, cm−1 ): 2927 (vs), 1721 (s), 1603 (vs), 1512 (s), 1471 (s), 1406 (s), 1248 (vs), 1183 (vs), 1062 (vs), 887 (m), 816 (vs).

HRMS (MALDI-TOF) m/z: Found: [M+H]+ 712.3527; molecular formula C42H52N2O6S requires [M+H]+ 712.3546.

**1.8 Synthesis of 4,7-Bis(4-undecyloxy acrylate)phenyl)benzo-2,1,3-thiadizole (T3)**

4,7-bis(4-hydroxyphenyl) benzo-2,1,3-thiadizole (2) (1.28 g, 4 mmol), K2CO3 (1.38 g, 10 mmol),11-bromoundecyloxy acrylate(5) (2.67 g, 8.8 mmol) and 25mLDMF were added to a 100mL two-neck flask. The reaction mixture was heated at 90 °C for 24 h, then cooled to room temperature, and 200 mL water was added. The solution was extracted with CH2Cl2 for three times and the organic solution was collected, dried with NaSO4 and evaporated with a rotary evaporator. The crude product was performed silica gel column to give a yellow green powder (1.91 g) with a yield of 62.2%.

1H-NMR ( CDCl3, 600 MHz, δ= ppm ): 7.91 ( d, 4 H, *J* = 6.0 Hz ) , 7.71 ( s, 2 H ) , 7.07 ( d, 4 H, *J* = 6.0 Hz ) , 6.40 ( d, 2 H, *J* = 12.0 Hz ) , 6.12 ( q, 2 H, *J* = 10.0 Hz ) , 5.82 ( d, 2 H, *J* = 12.0 Hz ) , 4.15 ( t, 4 H, *J* = 6.0 Hz ) , 4.04 ( t, 4 H, *J* = 6.0 Hz ) , 1.83 ( m, 4 H, *J* = 7.5 Hz ) , 1.67 ( m, 4 H, *J* = 6.0 Hz) , 1.48 ( m, 4 H, *J* = 6.0 Hz ) , 1.31 ( m, 24 H, *J* = 12.0 Hz ).

13C-NMR ( CDCl3, 150 MHz, δ= ppm ): 169.05, 161.98, 156.86, 134.98, 133.18, 132.98, 132.41, 131.27, 130.04, 117.28, 70.75, 67.41, 32.22, 32.17, 32.05, 31.92, 31.26, 28.73, 28.59.

FT-IR ( KBr, cm−1 ): 2920 (vs), 1723 (s), 1604 (vs), 1512 (s), 1470 (s), 1408 (s), 1249 (vs), 1198 (vs), 1042 (vs), 974 (s), 887 (m), 818 (vs).

HRMS (MALDI-TOF) m/z: Found: [M+H]+ 768.4172; molecular formula C46H60N2O6S requires [M+H]+ 768.4153.

**1.9 Synthesis of 4,7-Bis(4-nonylalkoxy)phenyl)benzo-2,1,3-thiadizole (T4)**

4,7-bis(4-hydroxyphenyl) benzo-2,1,3-thiadizole (2) (1.28 g, 4 mmol), K2CO3 (1.38 g, 10 mmol),1-Bromononane(1.82 g, 8.8 mmol) and 25mLDMF were added to a 100mL two-neck flask. The reaction mixture was heated at 90 °C for 24 h, then cooled to room temperature, and 200 mL water was added. The solution was extracted with CH2Cl2 for three times and the organic solution was collected, dried with NaSO4 and evaporated with a rotary evaporator. The crude product was performed silica gel column to give a yellow green powder (1.65 g) with a yield of 72.3%.

1H-NMR ( CDCl3, 600 MHz, δ= ppm ): 7.91 ( d, 4 H, *J* = 6.0 Hz ) , 7.91 ( d, 4 H, *J* = 12.0 Hz ) , 7.72 ( s, 2 H ) , 7.07 ( d, 4 H, *J* = 12.0 Hz ) , 4.04 ( t, 4 H, *J* = 6.0 Hz ) , 1.83 ( m, 4 H, *J* = 6.0 Hz ) , 1.49 ( m, 4 H, *J* = 6.0 Hz) , 1.33 ( m, 20 H, *J* = 6.0 Hz ) , 0.89 ( t, 6 H, *J* = 6.0 Hz ).

13C-NMR ( CDCl3, 150 MHz, δ= ppm ): 162.02, 156.88, 135.01, 132.97, 132.43, 130.00, 117.32, 70.80, 34.54, 32.21, 32.06, 31.93, 31.25, 28.72, 25.33, 16.76.

FT-IR ( KBr, cm−1 ): 2922 (vs), 1719 (s), 1603 (vs), 1517 (s), 1471 (s), 1402 (s), 1237 (vs), 1183 (vs), 1062 (vs), 887 (m), 816 (vs).

HRMS (MALDI-TOF) m/z: Found: [M+H]+572.3418; molecular formula C36H48N2O2S requires [M+H]+572.3436.

E:\研\成果\论文\2\文章图\Scheme 2-2.tif

SchemeS2. Synthetic route of LC monomer **P**.

**2.1 Synthesis of (4- hydroxyhexoxy) ethylbenzoate (6)**

Ethyl 4-hydroxybenzoate (9.96 g, 60 mmol), K2CO3 (9.98 g, 60 mmol) and 80 mL DMF were added to a 250 mL two-neck flask. The reaction mixture was heated at 90 °C for 24 h, then cooled to room temperature, and 500 mL water was added. The solution was extracted with ethyl acetate for three times and the organic solution was collected, dried with NaSO4 and evaporated with a rotary evaporator to give the pale yellow liquid monomer (13.24 g) with a yield of 82.9%.

1H-NMR ( CDCl3, 600 MHz, δ= ppm ): 7.91 ( d, 2 H, *J* = 6.0 Hz ) , 6.82 ( d, 2 H, *J* = 6.0Hz ) , 4.27 ( q, 2 H, *J* = 9.0 Hz ) , 3.93 ( t, 2 H, *J* = 6.0 Hz ) , 3.58 ( t, 2 H, *J* = 6.0 Hz ) , 2.43 ( s, 1 H ) , 1.74 ( m, 2 H, *J* = 4.5 Hz ) , 1.53 ( m, 2 H, *J* = 6.0 Hz ) , 1.40 ( m, 4 H, *J* = 7.5 Hz ) , 1.30 ( t, 3 H, *J* = 8.0 Hz ).

13C-NMR ( CDCl3, 150 MHz, δ= ppm ): 169.09, 165.45, 134.14, 125.34, 116.64, 70.66, 65.45, 63.25, 35.24, 31.73, 28.47, 28.17, 17.02.

**2.2 Synthesis of (4- hydroxyhexoxy)benzoicacid (7)**

(4- hydroxyhexoxy) ethylbenzoate (6) (10.64 g, 40 mmol) and 100mL THF were added to a 250 mL two-neck flask. Then, KOH (6.72 g, 120mmol) in aqueous solutions 50mL was added. The reaction mixture was heated at 90 °C for 24 h, then cooled to room temperature. The precipitation was collected by filtration and dissolved in 400mL H2O. The product was separated outafter regulate pH = 1 and collected by filtration to give the white powder (8.76 g) with a yield of 92.0%.

1H-NMR ( DMSO, 600 MHz, δ= ppm ): 12.57 ( s, 1 H ) , 7.87 ( t, 2 H, *J* = 6.0Hz ) , 6.99 ( t, 2 H, *J* = 9.0 Hz ) , 4.34 ( s, 1 H ), 4.03 ( t, 2 H, *J* = 6.0 Hz ) , 3.39 ( t, 2 H, *J* = 6.0 Hz ) , 1.72 ( m, 2 H, J = 7.5 Hz ) , 1.42 ( m, 4 H, *J* = 7.0 Hz ) , 1.35 ( m, 2 H, *J* = 6.0 Hz ).

13C-NMR ( DMSO, 150 MHz, δ= ppm ): 170.09, 165.40, 134.43, 125.87, 117.31, 70.85, 63.73, 35.57, 31.70, 28.47, 28.36.

**2.3 Synthesis of 4-(6-acryloyloxyhexyloxy) benzoic acid (8)**

Triethylamine (2.62 g, 26 mmol) was added to a cold solution (0 °C) of (4- hydroxyhexoxy)benzoic acid (7) (4.76 g, 20 mmol) in 300 mL of THF. Then, acryloyl chloride (1.98 g, 22 mmol) was added dropwise to the solution at 0 °C. The solution was allowed to stir for 24 h at 25 °C and 30 mL water was added. The solution was extracted with CH2Cl2 for three times and the organic solution was collected, dried with NaSO4 and evaporated with a rotary evaporator. The crude product was performed silica gel column to give a white solid (4.18 g) with a yield of 71.6%.

1H-NMR ( DMSO, 600 MHz, δ= ppm ): 12.57 ( s, 1 H ) , 7.85 ( d, 2 H, *J* = 12.0 Hz ) , 6.98 ( d, 2 H, *J* = 12.0 Hz ) , 6.30 ( d, 1 H, *J* = 12.0 Hz ) , 6.15 ( q, 1 H, *J* = 6.0 Hz ) , 5.91 ( d, 1 H, *J* = 12.0 Hz ) , 4.09 ( t, 2 H, *J* = 6.0 Hz ) , 4.02 ( t, 2 H, *J* = 6.0 Hz ) , 1.72 ( m, 2 H, *J* = 6.0 Hz ) , 1.62 ( m, 2 H, *J* = 6.0 Hz ) , 1.43 ( m, 2 H, *J* = 6.0 Hz ) , 1.37 ( m, 2 H, *J* = 6.0 Hz ).

13C-NMR ( DMSO, 150 MHz, δ= ppm ): 170.10, 168.64, 165.37, 134.50, 134.43, 131.51, 125.87, 117.31, 70.77, 67.14, 31.51, 31.14, 28.23, 28.22.

**2.4 Synthesis of 1,2-bis(4-hydroxyphenyl)ethane (9)**

To a solution of 4,4'-ethylenedianiline (10.61 g, 50 mmol) in 75 mL concentrated hydrochloric acid and 400 mL water, cooled to 0 °C, a solution of sodium nitrite (7.59 g, 110 mmol) in 50mL water was added dropwise with stirring. After the addition was complete, the solution mas stirred for 20 minutes and then the excess nitrous acid was destroyed with urea. The resulting mixture was heated to boiling. cooled and filtered with suction. The residue was washed with water and taken up in a solution of sodium hydroxide (12.05 g, 300 mmol) in 500mL water, decolorized with activated carbon. The solution was extracted with ethyl acetate for three times and the organic solution was collected, dried with NaSO4 and evaporated with a rotary evaporator to give a brown-yellow solid (8.57 g) with a yield of 80.1%.

1H-NMR ( DMSO, 600 MHz, δ= ppm ): 9.1 ( s, 2 H ) , 6.97 ( d, 4 H, *J* = 12.0Hz ) , 6.94 ( d, 4 H, *J* = 12.0 Hz ) , 2,68 ( s, 4 H ).

13C-NMR ( DMSO, 150 MHz, δ= ppm ): 158.38, 134.88, 132.25, 118.03, 39.83.

**2.5 Synthesis of 6-(4-(2-(4-hydroxyphenyl)ethyl)phenoxy)hexanol(10)**

1,2-bis(4-hydroxyphenyl)ethane(9) (6.42 g, 30 mmol), K2CO3 (4.14 g, 30 mmol) and 80 mL DMF were added to a 250 mL two-neck flask. The reaction mixture was heated at 90 °C for 24 h, then cooled to room temperature, and 500 mL water was added. The solution was extracted with ethyl acetate for three times and the organic solution was collected, dried with NaSO4 and evaporated with a rotary evaporator to give the pale yellow liquid monomer (7.43 g) with a yield of 67.3%.

1H-NMR ( DMSO, 600 MHz, δ= ppm ): 9.08 ( s, 1 H ) , 7.06 ( q, 2 H, *J* = 4.2 Hz ) , 6.96 ( q, 2 H, *J* = 4.2 Hz ) , 6.78 ( d, 2 H, *J* = 12.0 Hz ) , 6.62 ( d, 2 H, *J* = 6.0 Hz ) , 4.22 ( t, 1 H, *J* = 6.0 Hz ) , 3.88 ( t, 2 H, *J* = 6.0 Hz ) , 3.62 ( d, 2 H, *J* = 6.0 Hz ) , 3.36 ( q, 2 H, *J* = 6.0 Hz ) , 2.69 ( m, 4 H, *J* = 10.3 Hz ) , 1.66 ( m, 2 H, *J* = 6.0 Hz ) , 1.39 ( m, 4 H, *J* = 7.7 Hz ) , 1.31 ( m, 2 H, *J* = 6.0 Hz ).

13C-NMR ( DMSO, 150 MHz, δ= ppm ): 159.90, 158.38, 136.55, 134.88, 132.25, 118.03, 117.22, 70.37, 63.75, 39.83, 39.70, 35.60, 31.92, 28.57, 28.41.

**2.6 Synthesis of 6-(4-(2-(4-hydroxyphenyl) ethyl) phenoxy) hexyl acrylate (11)**

Triethylamine (2.62 g, 26 mmol) was added to a cold solution (0 °C) of 6-(4-(2-(4-hydroxyphenyl)ethyl)phenoxy)hexanol (10) (6.28 g, 20 mmol) in 80 mL of THF. Then, acryloyl chloride (1.98 g, 22 mmol) was added dropwise to the solution at 0 °C. The solution was allowed to stir for 24 h at 25 °C and 30 mL water was added. The solution was extracted with CH2Cl2 for three times and the organic solution was collected, dried with NaSO4 and evaporated with a rotary evaporator. The crude product was performed silica gel column to give a white solid (5.47 g) with a yield of 74.4%.

1H-NMR ( DMSO, 600 MHz, δ= ppm ): 9.09 ( s, 1 H ) , 7.06 ( d, 2 H, *J* = 12.0 Hz ) , 6.96 ( d, 2 H, *J* = 12.0 Hz ) , 6.78 ( d, 2 H, *J* = 12.0 Hz ) , 6.62 ( d, 2 H, *J* = 12.0 Hz ) , 6.30 ( d, 1 H, *J* = 12.0 Hz ) , 6.15 ( q, 1 H, J = 6.0 Hz ) , 5.91 ( d, 1 H, *J* = 12.0 Hz ) , 4.10 ( t, 2 H, *J* = 6.0 Hz ) , 3.88 ( t, 2 H, *J* = 6.0 Hz ) , 2.69 ( m, 4 H, *J* = 6.0 Hz ) , 1.67 ( m, 2 H, *J* = 6.0 Hz ) , 1.61 ( m, 2 H, *J* = 6.0 Hz ) , 1.39 ( m, 4 H, *J* = 6.0 Hz ).

13C-NMR ( DMSO, 150 MHz, δ= ppm ): 168.64, 159.87, 158.40, 136.56, 134.75, 134.47, 132.35, 132.27, 131.51, 118.04, 117.21, 70.29, 67.15, 39.71, 31.73, 31.16, 28.32, 28.28.

**2.7 Synthesis of 4-(4-(6-(Acryloyloxy)hexyloxy)phenethyl) phenyl-4-(6-(Acryloyloxy)hexyloxy) benzoate (P)**

To a solution of 6-(4-(2-(4-hydroxyphenyl) ethyl) phenoxy) hexyl acrylate (11)(3.68 g, 10 mmol) in 50 mL of dichloromethane, 4-(6-acryloyloxyhexyloxy) benzoic acid (8) (2.93 g, 10 mmol) and *N,N*-dimethylaminopyridine (0.12 g, 1mmol) and few crystals of 2,6,-ditert-butyl-4-methylphenol (radical inhibitor) were added under argon atmosphere. The solution was cooled into an ice-water bath and, after 15 minutes, dicylohexylcarbodiimide (2.06 g, 10 mmol) were added. The mixture was stirred at 0ºC during 15 minutes and then stirred overnight at room temperature. Afterwards, it was filtered through a pad of silica gel and the solvent evaporated to yield the crude product. Compound was recrystallised from ethanol to give a white powder (4.19 g) with a yield of 65.2%.

1H-NMR ( CDCl3, 600 MHz, δ= ppm ): 8.13 ( d, 2 H, *J* = 6.0 Hz ) , 7.20 ( d, 2 H, *J* = 12.0 Hz ) , 7.09 ( t, 4 H, *J* = 6.0 Hz ) , 6.96 ( d, 2 H, *J* = 12.0 Hz ) , 6.81 ( d, 2 H, *J* = 6.0 Hz ) , 6.41 ( d, 2 H, *J* = 6.0 Hz ) , 6.12 ( m, 2 H, *J* = 6.0 Hz ) , 5.82 ( m, 2 H, *J* = 6.0 Hz ) , 4.17 ( m, 4 H, *J* = 6.0 Hz ) , 4.05( t, 2 H, *J* = 6.0 Hz ) , 3.94 ( t, 2 H, *J* = 6.0 Hz ) , 2.89 ( m, 4 H, *J* = 6.0 Hz ) , 1.84 ( m, 2 H, *J* = 6.0 Hz ) , 1.79 ( m, 2 H, *J* = 6.0 Hz ) , 1.72 ( m, 4 H, *J* = 6.0 Hz ) , 1.50 ( m, 8 H, *J* = 6.0 Hz ).

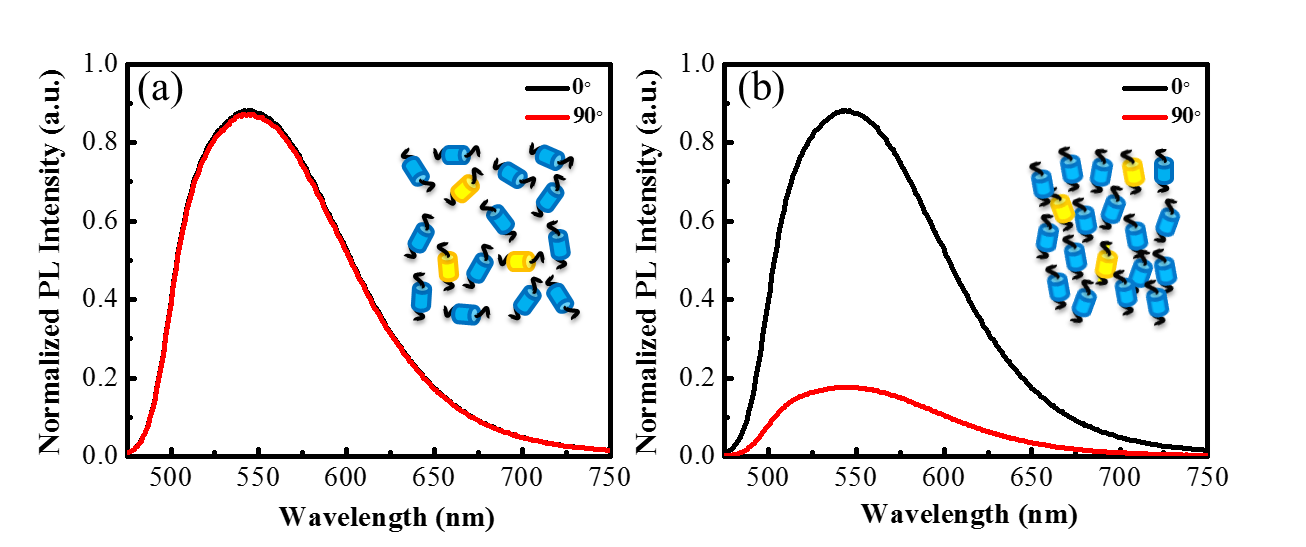
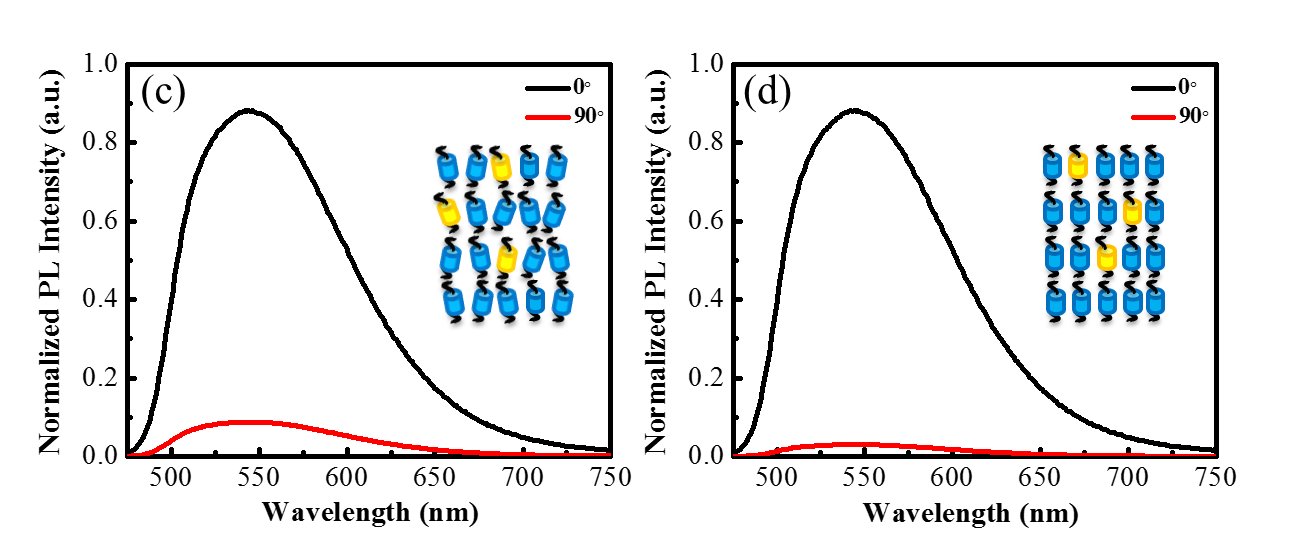
13C-NMR ( CDCl3, 150 MHz, δ= ppm ): 168.97, 167.72, 166.01, 159.99, 151.81, 141.91, 136.22, 134.88, 133.20, 133.14, 132.03, 131.98, 131.24, 131.21, 124.42, 124.15, 117.03, 116.89, 70.72, 70.43, 67.20, 67.12, 40.24, 39.66, 31.87, 31.64, 31.22, 31.20, 28.44, 28.42, 28.38, 28.35.

FT-IR ( KBr, cm−1 ): 2937 (vs), 2858 (s), 1716 (vs), 1602(vs), 1514 (vs), 1409 (s), 1260(vs), 1190(vs), 1075 (vs), 978 (vs), 812 (s).

HRMS (MALDI-TOF) m/z: Found: [M+H]+ 643.3172; molecular formula C46H60O6N2S requires [M+H]+ 643.3193.

E:\研\成果\论文\2\初稿\Fig. 1.tif

Fig. S1 The optimized molecular structure of the (a) **T1**, (b) **T2**, (c) **T3**, (d) **T4**. µ indicate the molecular transition dipole moment, l indicate the molecular long axis.

Fig.S2 Polarized PL spectra of **M2** (a) in the isotropic liquid *DR* = 1 and *S* = 0; (b) in the Nematic phase at 104 oC, *DR* = 5, *ρ* = 0.66, *S* = 0.57; (c) in the SmA phase at 100 oC, *DR* = 10, *ρ* = 0.83, *S* = 0.77; (d) in the SmB phase at 30 oC, *DR* = 37, *ρ* = 0.95, *S* = 0.92. The black line represents absorbance in the parallel direction, red line represents absorbance in the perpendicular direction. Blue cylinders represent the LC molecules, Yellow cylinders represent dichroic dye molecules.

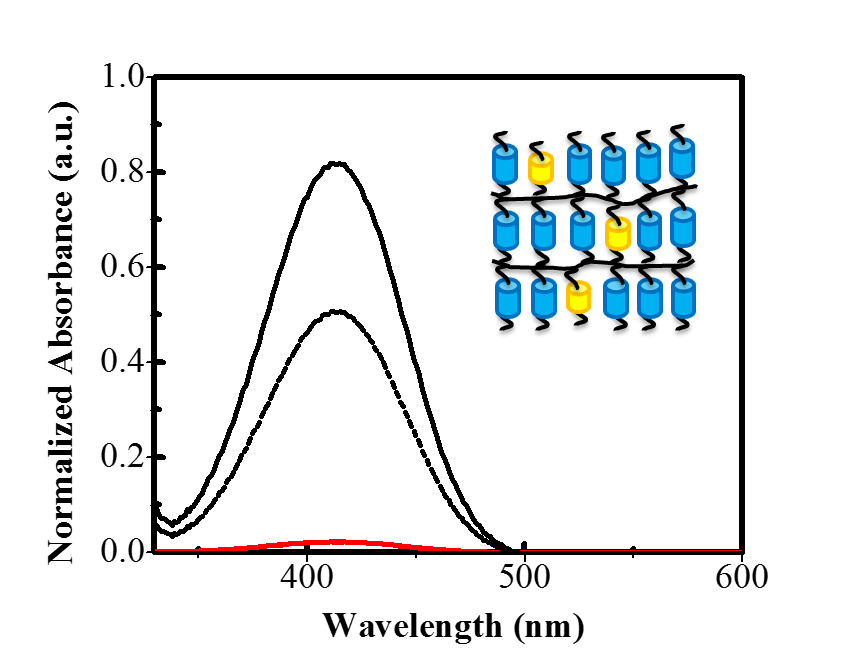


Fig. S3 Polarized UV/vis spectra of **M1** in the SmB phase before polymerization (solid line) at 45 oC, DR=43, ρ=0.95, S=0.93. and after polymerization (dotted line) at RT, DR =25, ρ=0.92, S=0.89. The black line represents absorbance in the parallel direction, red line represents absorbance in the perpendicular direction. Blue cylinders represent the LC molecules, Yellow cylinders represent dichroic dye molecules.

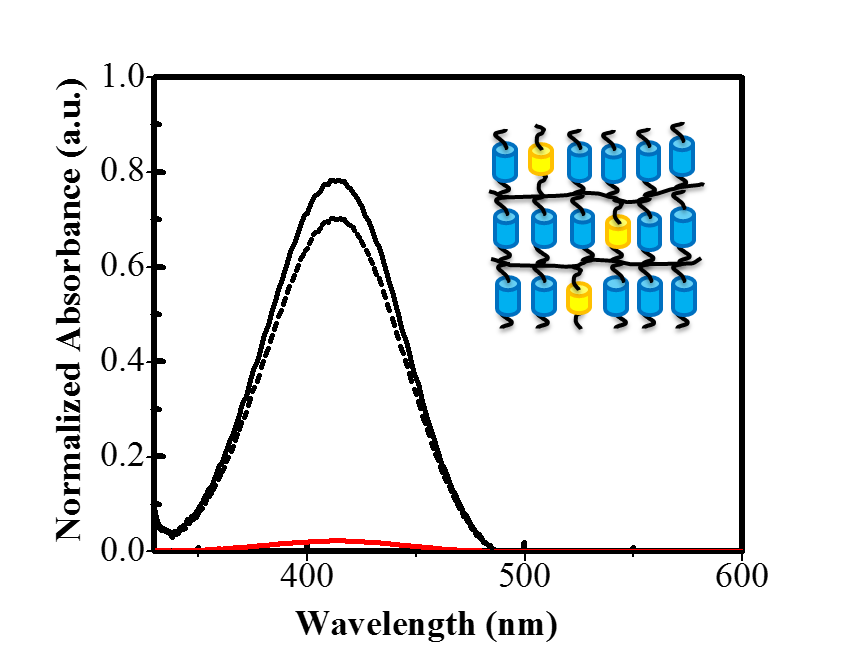


Fig. S4 Polarized UV/vis spectra of **M3** in the SmB phase before polymerization (solid line) at 45 oC, *DR* = 31, *ρ* = 0.94, *S* = 0.91. and after polymerization (dotted line) at RT, *DR* = 27, *ρ* = 0.93, *S* = 0.90. The black line represents absorbance in the parallel direction, red line represents absorbance in the perpendicular direction. Blue cylinders represent the LC molecules, Yellow cylinders represent dichroic dye molecules.

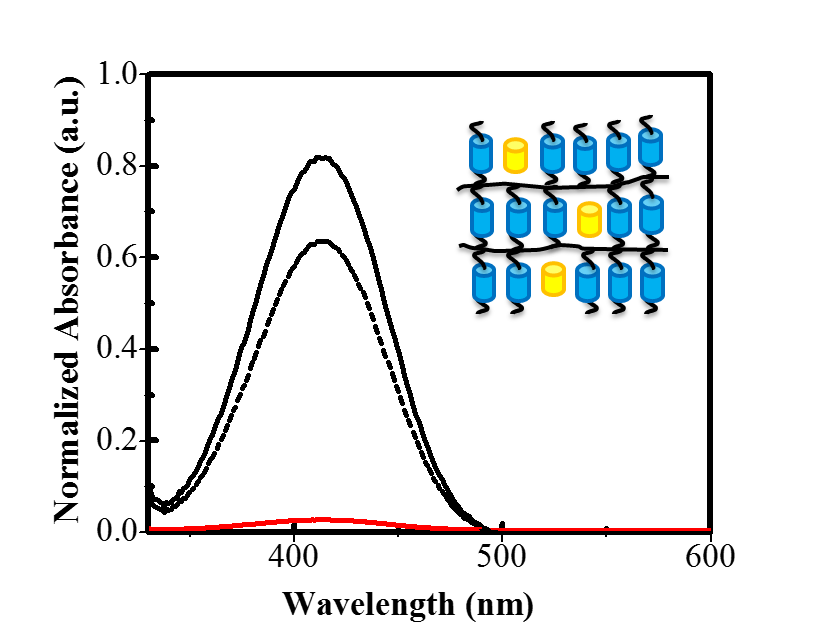


Fig. S5 Polarized UV/vis spectra of **M4** in the SmB phase before polymerization (solid line) at 45 oC, *DR* = 44, *ρ* = 0.96, *S* = 0.93. and after polymerization (dotted line) at RT, *DR* = 33, *ρ* = 0.94, *S* = 0.91. The black line represents absorbance in the parallel direction, red line represents absorbance in the perpendicular direction. Blue cylinders represent the LC molecules, Yellow cylinders represent dichroic dye molecules.

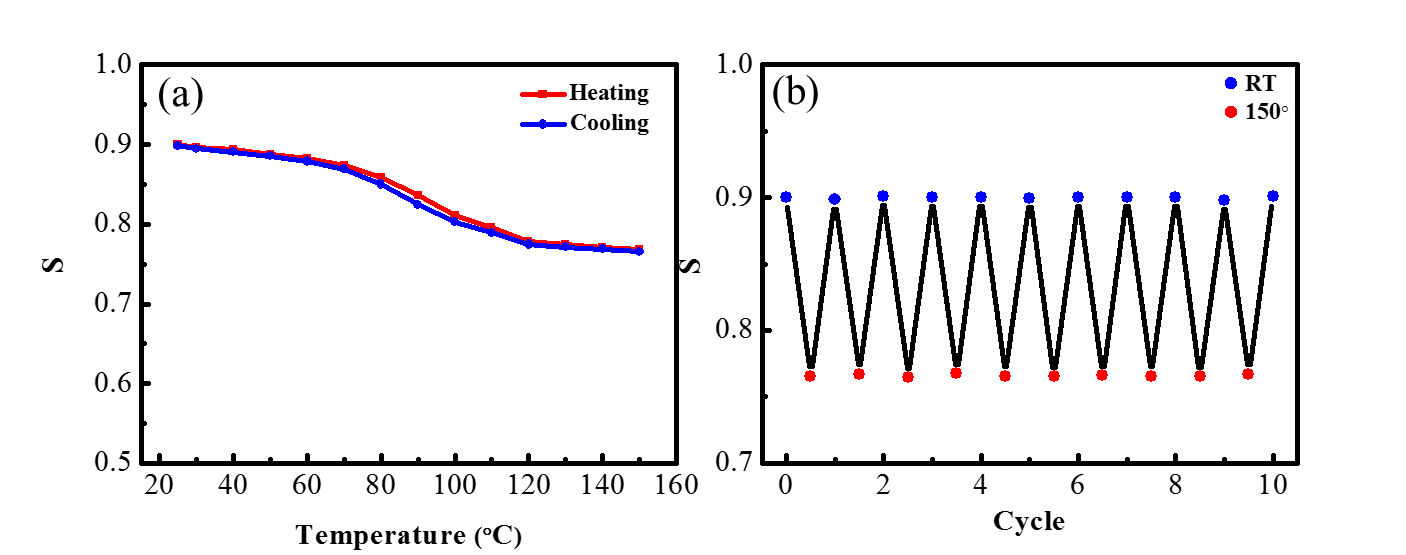


Fig. S6 Thermal stability for the film prepared from **M2**. S data measured for the film (a) on the heating and cooling process, (b) for repeated switching on the heating and cooling process.