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Supplementary Information:

## Mechanoresponsive liquid crystals exhibiting reversible luminescent color changes at ambient temperature

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## Synthesis:

3,7,11,-Trimethyldodecyl bromide <sup>S1</sup> and 5,5''-diethynyl-2,2':5',2''-terthiophene <sup>S2</sup> were obtained according to the reported procedures.



**Methyl 3,4,5-tris(3,7,11-trimethyldodecyloxy)benzoate (4)**. A mixture of methyl 3,4,5-trihydroxybenzoate (877 mg, 4.76 mmol), 3,7,11,-trimethyldodecyl bromide (5.00 g, 17.16 mmol), and K<sub>2</sub>CO<sub>3</sub> (3.95 g, 28.60 mmol) in DMF (30 mL) was stirred for 8 h at 70 °C. After the resulting mixture was cooled to room temperature, the mixture was poured into ethyl acetate and a saturated NH<sub>4</sub>Cl aqueous solution. The organic layer was washed with H<sub>2</sub>O and brine and dried over anhydrous MgSO<sub>4</sub>. After filtration and evaporation, the residue was purified by silica gel flash column chromatography (eluent: gradient from hexane/ethyl acetate = 1:0 to hexane/ethyl acetate = 9:1), and dried under vacuum to afford **4** as colorless liquid (3.00 g, 77%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.26 (s, 2H), 4.10–3.99 (m, 6H), 3.89 (s, 3H), 1.92–1.77 (m, 3H), 1.77–1.45 (m, 9H), 1.45–1.00 (m, 39H), 0.96–0.91 (m, 9H), 0.88–0.83 (m, 27H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  166.97, 152.84, 142.30, 124.66, 107.88, 71.69, 67.45, 52.12, 39.37, 37.58, 37.39, 37.29, 36.36, 36.27, 32.82, 29.85, 29.65, 27.98, 24.82, 24.43, 22.73, 22.63, 19.73, 19.65, 19.61, 19.57, 19.54. MS (MALDI-TOF): *m/z* 837.47 [M + Na]<sup>+</sup>; calcd. 837.73. Anal. Calcd for C<sub>53</sub>H<sub>98</sub>O<sub>5</sub>: C, 78.07; H, 12.11%; found: C, 78.04; H, 12.20%.

**3,4,5-Tris(3,7,11-trimethyldodecyloxy)benzoic acid (5)**. A mixture of **4** (2.00 g, 2,45 mmol) and KOH (412 mg, 7.35 mmol) in THF (20 mL), ethanol (10 mL), and water (1 mL) was stirred for 3 h under reflux. After removing the solvent, the residue was poured into a mixture of 5% hydrochloric acid/ethyl acetate. The organic phase was washed with water and brine, dried over anhydrous MgSO<sub>4</sub>, filtered, and evaporated to afford **5** as colorless liquid (1.84 g, 94%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.34 (s, 2H), 4.13 (m, 6H), 1.92–1.78 (m, 3H), 1.77–1.45 (m, 9H), 1.45–1.00 (m, 39H), 0.96–0.92 (m, 9H), 0.87–0.84 (m, 27H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  171.79, 152.86, 143.12, 123.61, 108.47, 71.77, 67.48, 39.37, 37.57, 37.39, 37.33, 37.29, 36.32, 36.23, 32.82, 29.86, 29.65, 27.98, 24.82, 24.44, 22.73, 22.63, 19.74, 19.66, 19.61, 19.54. MS (MALDI-TOF): *m/z* 823.46 [M + Na]<sup>+</sup>; calcd. 823.72. Anal. Calcd for C<sub>52</sub>H<sub>96</sub>O<sub>5</sub>: C, 77.94; H, 12.08%; found: C, 78.12; H, 12.27%.

**N-(4-Ethynylphenyl)-3,4,5-tris(3,7,11-trimethyldodecyloxy)benzamide (6)**. A mixture of **5** (800 mg, 1.00 mmol), 4-ethynylaniline (140 mg, 1.20 mmol), EDC (383 mg, 2.00 mmol), and DMAP (24 mg, 0.20 mmol) in dry  $CH_2Cl_2$  (20 mL) was stirred for 16 h at room temperature. The reaction mixture was washed with 5% hydrochloric acid, a saturated NaHCO<sub>3</sub> aqueous solution and brine. The organic phase was dried over anhydrous MgSO<sub>4</sub>, filtered, and evaporated. The residue was purified by flash column chromatography on silica gel (eluent: chloroform/hexane = 5/2) to afford **6** as colorless liquid (704 mg, 78%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.79 (s, 1H), 7.61 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.04 (s, 2H), 4.10–3.99 (m, 6H), 3.06 (s, 1H), 1.92–1.77 (m, 3H), 1.77–1.45 (m, 9H), 1.45–0.99 (m, 39H), 0.95–0.92 (m, 9H), 0.87–0.84 (m, 27H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  165.62, 153.31, 141.72, 138.46, 133.02, 129.60, 119.66, 117.86, 105.81, 83.36, 76.91, 71.82, 67.83, 39.38, 37.62, 37.41, 37.31, 36.42, 36.34, 32.84, 29.87, 29.69, 27.98, 24.83, 24.45, 22.73, 22.63, 19.74, 19.66, 19.62, 19.56. MS (MALDI-TOF): *m/z* 900.57 [M + H]<sup>+</sup>; calcd. 900.78. Anal. Calcd for C<sub>60</sub>H<sub>101</sub>NO<sub>4</sub>: C, 80.03; H, 11.31; N, 1.56%; found: C, 80.26; H, 11.36; N, 1.60%.

**5,5'-Bis[p-(3,4,5-tris{3,7,11-trimethyldodecyloxy}benzamido)phenylethynyl]-2,2'-bithiophene** (1). Pd(PPh<sub>3</sub>)<sub>4</sub> (21.4 mg, 0.0185 mmol) and CuI (3.5 mg, 0.0185 mmol) were added to a mixture of 5,5'-dibromo-2,2'-bithiophene (60.0 mg, 0.185 mmol) and **6** (400 mg, 0.444 mmol) in toluene (30 mL) and Et<sub>3</sub>N (6 mL). After stirring for 12 h at 80 °C, the mixture was dissolved in chloroform and the organic phase was washed with H<sub>2</sub>O and brine, then was dried over anhydrous MgSO<sub>4</sub>. After filtration and evaporation, the resulting residue was purified by flash column chromatography on silica gel (eluent: chloroform) to afford **1** as yellow solid (197 mg, 54%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.80 (s, 2H), 7.66 (d, J = 8.4 Hz, 4H), 7.52 (d, J = 8.8 Hz, 4H), 7.17 (d, J = 4.0 Hz, 7.09 (d, J = 4.0 Hz, 2H), 7.05 (s, 4H), 4.11–4.00 (m, 12H), 1.92–1.78 (m, 6H), 1.78–1.45 (m, 18H), 1.45–1.00 (m, 78H), 0.96–0.93 (m, 18H), 0.87–0.84 (m, 54H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  165.60, 153.33, 141.74, 138.30, 138.01, 132.72, 132.32, 129.62, 124.00, 122.68, 119.75, 118.50, 105.81, 94.38, 82.39, 71.83, 67.84, 39.38, 37.62, 37.41, 37.31, 36.42, 36.35, 32.84, 29.88, 29.70, 27.98, 24.83, 24.46, 22.73, 22.64, 19.74, 19.66, 19.57. MS (MALDI-TOF): *m/z* 1963.56 [M + H]<sup>+</sup>; calcd. 1963.52. Anal. Calcd for C<sub>128</sub>H<sub>204</sub>N<sub>2</sub>O<sub>8</sub>S<sub>2</sub>: C, 78.31; H, 10.47; N, 1.43%; found: C, 78.36; H, 10.65; N, 1.47%.

**N-(4-iodophenyl)-3,4,5-tris(3,7,11-trimethyldodecyloxy)benzamide (7)**. A mixture of **5** (1500 mg, 1.87 mmol), 4iodoaniline (451 mg, 2.06 mmol), EDC (718 mg, 3.74 mmol), and DMAP (46 mg, 0.37 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was stirred for 15 h at room temperature. The reaction mixture was washed with 5% hydrochloric acid, a saturated NaHCO<sub>3</sub> aqueous solution and brine. The organic phase was dried over anhydrous MgSO<sub>4</sub>, filtered, and evaporated. The residue was purified by flash column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 1:0 to hexane/ethyl acetate = 9:1) to afford 7 as colorless liquid (1370 mg, 73%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.72 (s, 1H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 2.05, 9.2 Hz), 7.03 (s, 2H), 4.10–3.99 (m, 6H), 1.92–1.78 (m, 3H), 1.77–1.45 (m, 9H), 1.45–1.00 (m, 39H), 0.96–0.92 (m, 9H), 0.87–0.84 (m, 27H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  165.62, 153.30, 141.67, 138.00, 137.78, 129.55, 121.94, 105.74, 87.64, 71.80, 67.80, 39.37, 37.61, 37.40, 37.33, 37.30, 36.41, 36.33, 32.83, 29.86, 29.67, 27.98, 24.83, 24.45, 22.73, 22.64, 19.74, 19.66, 19.60, 19.55. MS (MALDI-TOF): *m/z* 1002.56 [M + H]<sup>+</sup>; calcd. 1002.68. Anal. Calcd for C<sub>58</sub>H<sub>100</sub>INO<sub>4</sub>: C, 69.50; H, 10.06; N, 1.44%.

**5,5''-Bis[p-(3,4,5-tris{3,7,11-trimethyldodecyloxy}benzamido)phenylethynyl]-2,2':5',2''-terthiophene** (2). Pd(PPh<sub>3</sub>)<sub>4</sub> (48.3 mg, 0.0418 mmol) and CuI (8.0 mg, 0.0418 mmol) were added to a mixture of 5,5''-diethynyl-2,2':5',2''-terthiophene (124 mg, 0.418 mmol) and 7 (964 mg, 0.962 mmol) in toluene (60 mL) and Et<sub>3</sub>N (15 mL). After stirring for 20 h at 50 °C, the mixture was dissolved in chloroform and the organic phase was washed with H<sub>2</sub>O and brine, then was dried over anhydrous MgSO<sub>4</sub>. After filtration and evaporation, the resulting residue was purified by flash column chromatography on silica gel (eluent: gradient from hexane/chloroform = 1:3 to hexane/chloroform = 1:6) and GPC (eluent: chloroform) to afford **2** as orange solid (325 mg, 38%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.79 (s, 2H), 7.66 (d, J = 8.8 Hz, 4H), 7.53 (d, J = 8.8 Hz, 4H), 7.18 (d, J = 4.0 Hz, 2H), 7.11 (s, 2H), 7.08 (d, J = 4.0 Hz, 2H), 7.05 (s, 4H), 4.12–4.00 (m, 12H), 1.92–1.78 (m, 6H), 1.78–1.46 (m, 18H), 1.46–1.00 (m, 78H), 0.96–0.93 (m, 18H), 0.87–0.84 (m, 54H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  165.59, 153.32, 141.70, 138.25, 138.21, 136.09, 132.75, 132.30, 129.62, 124.88, 123.70, 122.37, 119.74, 118.52, 105.77, 94.32, 82.44, 71.82, 67.82, 39.37, 37.61, 37.40, 37.30, 36.42, 36.33, 32.83, 29.87, 29.68, 27.98, 24.83, 24.45, 22.73, 22.63, 19.74, 19.66, 19.56. MS (MALDI-TOF): *m/z* 2045.11 [M + H]<sup>+</sup>; calcd. 2045.50. Anal. Calcd for C<sub>132</sub>H<sub>206</sub>N<sub>2</sub>O<sub>8</sub>S<sub>3</sub>: C, 77.52; H, 10.15; N, 1.37%; found: C, 77.65; H, 9.89; N, 1.37%.

**5-Bromo-5'-(4-aminophenylethynyl)-2,2'-bithiophene (8)**.  $PdCl_2(PPh_3)_2$  (77.9 mg, 0.111 mmol) and CuI (21.1 mg, 0.111 mmol) were added to a mixture of 5,5'-dibromo-2,2'-bithiophene (857 mg, 2.66 mmol) and 4-ethynylaniline (260 mg, 0.444 mmol) in dry THF (10 mL) and Et<sub>3</sub>N (5 mL). After stirring for 6 h at 60 °C, the mixture was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and the organic phase was washed with H<sub>2</sub>O and brine, then was dried over anhydrous MgSO<sub>4</sub>. After filtration and evaporation, the resulting residue was purified by flash column chromatography on silica gel (eluent: chloroform/hexane = 2/1) to afford **8** as yellow solid (340 mg, 43%), then used for the next reaction without further purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.31(d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 4.4 Hz, 1H), 6.97–6.94 (m, 2H), 6.90 (d, *J* = 3.6 Hz), 6.62 (d, *J* = 8.8 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  147.05, 138.49, 136.89, 132.97, 131.94, 130.79, 124.09, 123.82, 123.46, 114.81, 112.01, 111.42, 95.39, 80.41.

**5-Bromo-5'-[p-(3,4,5-tris{3,7,11-trimethyldodecyloxy}benzamido)phenylethynyl]-2,2'-bithiophene** (9). A mixture of **5** (687 mg, 0.86 mmol), **8** (340 mg, 0.94 mmol), EDC (329 mg, 1.72 mmol), and DMAP (21 mg, 0.17

mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (25 mL) was stirred for 36 h at room temperature. The reaction mixture was washed with 5% hydrochloric acid, a saturated NaHCO<sub>3</sub> aqueous solution and brine. The organic phase was dried over anhydrous MgSO<sub>4</sub>, filtered, and evaporated. The residue was purified by flash column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 1:0 to hexane/ethyl acetate = 17:3) to afford **9** as green solid (920 mg, 94%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.77 (s, 1H), 7.65 (d, J = 9.2 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 3.6 Hz, 1H), 7.05 (s, 2H), 7.00 (d, J = 4.0 Hz, 1H), 6.98 (d, J = 4.0 Hz, 1H), 6.93 (d, J = 4.0 Hz, 1H), 4.12–4.00 (m, 6H), 1.92–1.78 (m, 3H), 1.78–1.46 (m, 9H), 1.46–1.00 (m, 39H), 0.96–0.93 (m, 9H), 0.87–0.84 (m, 27H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  165.58, 153.34, 141.76, 138.30, 138.23, 137.60, 132.61, 132.32, 130.77, 129.61, 124.25, 123.80, 122.57, 119.74, 118.47, 111.66, 105.82, 94.24, 82.25, 71.83, 67.86, 39.38, 37.62, 37.41, 37.31, 36.42, 36.35, 32.84, 29.88, 29.70, 27.98, 24.83, 24.45, 22.73, 22.64, 19.74, 19.66, 19.57. MS (MALDI-TOF): *m/z* 1144.53 [M + H]<sup>+</sup>; calcd. 1144.66. Anal. Calcd for C<sub>68</sub>H<sub>104</sub>BrNO<sub>4</sub>S<sub>2</sub>: C, 71.42; H, 9.17; N, 1.22%; found: C, 71.56; H, 8.98; N, 1.13%.

## 5,5""-Bis[p-(3,4,5-tris{3,7,11-trimethyldodecyloxy}benzamido)phenylethynyl]-2,2":5",2""-

**quaterthiophene (3)**. A mixture of Pd(PPh<sub>3</sub>)<sub>4</sub> (26.3 mg, 0.0227 mmol), **9** (1300 mg, 1.14 mmol), and hexa*n*-butylditin (396 mg, 0.682 mmol) in toluene (60 mL) was stirred for 24 h at 110 °C. After the resulting mixture was cooled to room temperature, the mixture was poured into chloroform and H<sub>2</sub>O. The organic layer was washed with 5% hydrochloric acid, a saturated NaHCO<sub>3</sub> aqueous solution and brine. The organic phase was dried over anhydrous MgSO<sub>4</sub>, filtered, and evaporated. The residue was purified by flash column chromatography on silica gel (eluent: chloroform) and GPC (eluent: chloroform) to afford **3** as red solid (352 mg, 29%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.75 (s, 2H), 7.66 (d, J = 8.8 Hz, 4H), 7.53 (d, J = 8.8 Hz, 4H), 7.18 (d, J = 3.6 Hz, 2H), 7.12–7.10 (m, 4H), 7.08 (d, J = 4.0 Hz, 2H), 7.05 (s, 4H), 4.13–4.00 (m, 12H), 1.92–1.78 (m, 6H), 1.78–1.46 (m, 18H), 1.46–1.00 (m, 78H), 0.96–0.93 (m, 18H), 0.87–0.84 (m, 54H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  165.56, 153.33, 141.70, 138.28, 138.23, 136.26, 135.81, 132.76, 132.30, 129.63, 124.90, 124.57, 123.62, 122.26, 119.71, 118.53, 105.74, 94.29, 71.80, 67.81, 39.37, 37.61, 37.40, 37.29, 36.41, 36.32, 32.83, 29.86, 29.67, 27.98, 24.83, 24.45, 22.73, 22.63, 19.74, 19.66, 19.60, 19.56. MS (MALDI-TOF): *m/z* 2127.06 [M + H]<sup>+</sup>; calcd. 2127.49. Anal. Calcd for C<sub>136</sub>H<sub>208</sub>N<sub>2</sub>O<sub>8</sub>S<sub>4</sub>: C, 76.78; H, 9.85; N, 1.32%; found: C, 76.92; H, 9.99; N, 1.36%.



Fig. S1 (a) A luminescence image of compound 1 in the crystalline phase under UV irradiation ( $\lambda_{ex} = 365$  nm). (b) A polarizing optical microscopic image of compound 1 in the crystalline phase at 25 °C. Scale bar: 200 µm. Arrows indicate the directions of polarizer and analyzer axes. (c) A XRD pattern of compound 1 in the crystalline phase at 25 °C.



**Fig. S2** Luminescence images of compound **2** under UV irradiation ( $\lambda_{ex} = 365$  nm): (a) in the OI phase (OY-form); (b) in the crystalline phase. Polarizing optical microscopic images of compound **2**: (c) in the OI phase (OY-form) at 25 °C; (d) in the crystalline phase at 25 °C. Arrows indicate the directions of polarizer and analyzer axes.



Fig. S3 DSC traces on 1st cooling at the rate of 5 K min<sup>-1</sup>: (a) compound 1; (b) compound 2; and (c) compound 3.



**Fig. S4** DSC traces of compound **1** starting from the OI phase (G-form) at different scanning rates: (a) 2 K min<sup>-1</sup>; (b) 5 K min<sup>-1</sup>; and (c) 10 K min<sup>-1</sup>.



**Fig. S5** DSC traces of compound **2** on 1st heating at the rate of 5 K min<sup>-1</sup>: (a) starting from the OI phase (OY-form) obtained by rapid cooling the isotropic liquid; (b) starting from the recovered OI phase (OY-form) obtained by aging the shear-induced M phase (YG-form) for three hours at room temperature.



**Fig. S6** DSC traces of compound **3** on 1st heating at the rate of 5 K min<sup>-1</sup>: (a) starting from the Col<sub>r</sub> phase obtained by cooling the isotropic liquid at the rate of 5 K min<sup>-1</sup>; (b) starting from the recovered M phase (RO-form) obtained by aging the shear-induced M phase (Y-form) for three hours at room temperature. M, M<sub>2</sub>: unidentified mesophase.



Fig. S7 Emission spectra of compound 1 ( $\lambda_{ex} = 380$  nm): the initial OI phase (G-form) (green solid line, the same spectrum which is shown in Fig. 7a); after mechanical shearing and subsequent aging at room temperature for three hours (black dashed line); and after mechanical shearing and subsequent aging at room temperature for two days (black dotted line).



**Fig. S8** Luminescence decay profiles of compound 1 ( $\lambda_{ex} = 365 \text{ nm}$ ): (blue) in the chloroform solution ( $c = 1 \times 10^{-5}$  M,  $\lambda_{mon} = 454 \text{ nm}$ ); (green) in the OI phase (G-form,  $\lambda_{mon} = 540 \text{ nm}$ ); (red) in the M phase (BG-form,  $\lambda_{mon} = 492 \text{ nm}$ ).



**Fig. S9** Luminescence decay profiles of compounds 1–3 in the chloroform solution ( $c = 1 \times 10^{-5}$  M,  $\lambda_{ex} = 365$  nm): (blue) compound 1 ( $\lambda_{mon} = 454$  nm); (green) compound 2 ( $\lambda_{mon} = 487$  nm); (red) compound 3 ( $\lambda_{mon} = 512$  nm).



**Fig. S10** Luminescence decay profiles of (a) compound **2** in the OI phase (OY-form,  $\lambda_{ex} = 365$  nm,  $\lambda_{mon} = 598$  nm) and (b) compound **3** in the Col<sub>r</sub> phase ( $\lambda_{ex} = 405$  nm,  $\lambda_{mon} = 624$  nm).



Fig. S11 Emission spectra of compound 2 ( $\lambda_{ex} = 380$  nm): the initial OI phase (OY-form) (orange solid line, the same spectrum which is shown in Fig. 7b); after mechanical shearing and subsequent aging at room temperature for three hours (black dashed line); and after mechanical shearing and subsequent aging at room temperature for two days (black dotted line).



Fig. S12 Emission spectra of compound 3 ( $\lambda_{ex} = 430$  nm): the Col<sub>r</sub> phase (red solid line, the same spectrum which is shown in Fig. 7c); after mechanical shearing and subsequent aging at room temperature for three hours (black dashed line); and after mechanical shearing and subsequent aging at room temperature for two days (black dotted line).



**Fig. S13** FT-IR spectra of compound **2** at 25 °C: (a) in chloroform solution  $(1 \times 10^{-3} \text{ M})$ ; (b) in the OI phase (OY-form); (c) in the crystalline phase.



**Fig. S14** FT-IR spectra of compound **3**: (a) in chloroform solution  $(1 \times 10^{-3} \text{ M})$ ; (b) in the Col<sub>r</sub> phase at 25 °C; (c) in the Col<sub>tet</sub> phase at 131 °C.

## **Supporting references**

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