

Supporting information

**In-situ polymerization of liquid-crystalline thin films of electron-transporting perylene tetracarboxylic bisimide bearing cyclotetrasiloxane rings**

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**Synthesis of Materials**

All <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian UNITY INOVA400NB spectrometer. FT-IR measurements were conducted on a JASCO FT/IR-660 Plus spectrometer. Perylene tetracarboxylic acid anhydride and Karstedt catalyst were purchased from Tokyo Chemical Industry and Gelest inc., respectively. Zinc acetate, quinoline, and toluene which were commercially available from Wako Pure Chemical Industries were used without purification. Silicagel was purchased from Kanto Chemicals.

***N,N'*-BIS(1,11-DI(1,3,3,5,5,7,7-HEPTAMETHYL-1,3,5,7-CYCLOTETRASILOXAN-1-YL)UNDECAN-6-YL)PERYLENE-3,4,9,10-TETRACARBOXYLIC BISIMIDE (1)**

*N,N'*-bis(1,11-undecan-6-yl)perylene-3,4,9,10-tetracarboxylic acid bisimide (**3**) 0.98 g (1.53 mmol) and 1,3,3,5,5,7,7-heptamethyl-1,3,5,7-cyclotetrasiloxane 1.84 g (6.5 mmol) were dissolved in toluene (40 ml) and 10 μl of Karstedt catalyst (1,3-divinyl-1,1,3,3-tetramethyldisiloxane platinum (0), 2.1 atom%, xylene solution) was added to the reaction mixture. The solution was refluxed for two hours, and cooled to room temperature. The solvent was evaporated and the obtained red residue was purified by a column chromatography (elutant: *n*-hexane and ethyl acetate (5:1)). The crude product was dissolved in dichloromethane and the solution was poured into methanol. The red precipitates were filtered. Red powder (1.77 g, 1.00 mmol) was obtained in the yield of 65.6 %.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.60–8.72 (m, 8H), 5.17 (tt, 2H, J = 9.2, 6.0 Hz), 2.17–2.31 (m, 4H), 1.78–1.91 (m, 4H), 1.16–1.40 (m, 24H), 0.46 (dd, 8H, J = 6, 9.2 Hz), 0.01–0.05 (m, 70H), -0.003 ppm (s, 12H), -0.02–0.015 ppm (m, 2H); IR (ATR): ν = 2962, 2924, 2858, 1697, 1659, 1596, 1406, 1339, 1257, 1050, 851, 800, 746, 694, 548 cm<sup>-1</sup>; exact mass: 1818.58; molecular weight: 1821.23 m/z [M<sup>-</sup>]: 1820.73, 1821.73, 1822.73, 1823.74, 1824.74; elemental analysis (%) calculated for C<sub>74</sub>H<sub>134</sub>N<sub>2</sub>O<sub>20</sub>Si<sub>16</sub>: C, 48.80, H, 7.42, N, 1.54, O, 17.57, Si, 24.67; found: C, 48.26; H, 7.47; N, 1.56.

***N-N'*-BIS(1,13-DI(1,3,3,5,5,7,7-HEPTAMETHYL-1,3,5,7-CYCLOTETRASILOXAN-1-YL)TRIDECANE-7-YL)PERYLENE-3,4,9,10-TETRACARBOXYLIC BISIMIDE (2)**

*N-N'*-bis(1,12-tridecadien-7-yl)perylene-3,4,9,10-tetracarboxylic acid bisimide (**4**) 0.74 g (0.99 mmol) and 1,3,3,5,5,7,7-heptamethyl-1,3,5,7-cyclotetrasiloxane 1.76 g (5.9 mmol) were dissolved in toluene (50 ml) and 10  $\mu$ l of Karstedt catalyst (1,3-divinyl-1,1,3,3-tetramethyldisiloxane platinum (0), 2.1 atom%, xylene solution) was added to the reaction mixture. The solution was refluxed for two hours, and cooled to room temperature. The solvent was evaporated and the obtained red residue was purified by a column chromatography (elutant: *n*-hexane and ethyl acetate (10:1)). The crude product was dissolved in dichloromethane and the solution was poured into methanol. The red precipitates were filtered. Red powder (1.29 g, 1.05 mmol) was obtained in the yield of 74 %.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.60–8.72 (m, 8H), 5.17 (tt, 2H,  $J$  = 20, 4.0 Hz), 2.20–2.33 (m, 4H), 1.88–1.95 (m, 4H), 1.16–1.38 (m, 32H), 0.45 (t, 8H,  $J$  = 7.4 Hz), 0.01–0.05 (m, 71H), -0.004 ppm (s, 11H), -0.02 ppm (m, 4H); IR (ATR):  $\nu$  = 2967, 2925, 2856, 1696, 1650, 1594, 1405, 1339, 1258, 1054, 850, 800, 746, 696, 553  $\text{cm}^{-1}$ ; exact mass: 1874.65; molecular weight: 1877.33  $m/z$  [M $^-$ ]: 1876.85, 1877.86, 1878.86, 1879.87, 1880.87, 1881.88; elemental analysis (%) calculated for  $\text{C}_{78}\text{H}_{142}\text{N}_2\text{O}_{20}\text{Si}_{16}$ : C, 49.90, H, 7.62, N, 1.49, O, 17.04, Si, 23.94; found: C, 49.75; H, 7.61; N, 1.56.

### Polarizing optical micrographs of the columnar rectangular phase of compound 2

Figure S1 shows polarizing optical micrographs of the columnar rectangular phase of compound 2 rotating the sample. Birefringent domains and dark domains with low birefringence were observed. Character 'A' indicates a low-birefringent domain. The transmittance of the domain does not change so remarkably when the sample is rotated. Character 'B' indicates a high birefringent domain, whose transmittance changes remarkably when the sample is rotated.

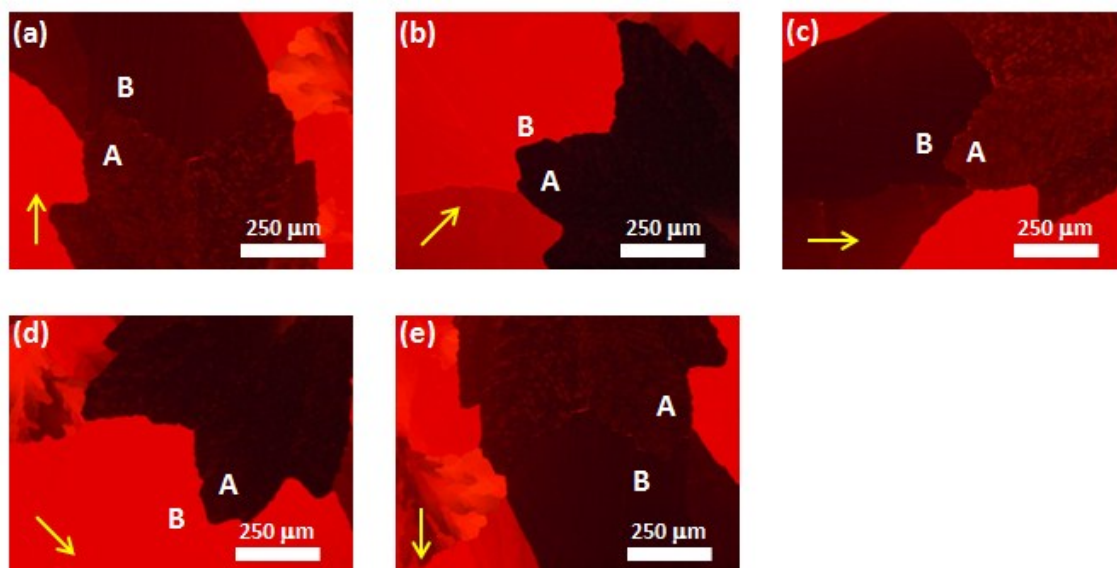


Figure S1 Polarizing optical micrographs of the columnar rectangular phase of compound 2 at room temperature. Yellow arrows indicate the sample direction to the optical axis of the polarizer. The angle between the sample direction and the polarizer axis is (a) 0 deg., (b) 45 deg., (c) 90 deg. (d) 135 deg., and (e) 180 deg. 'A' and 'B' indicate low-birefringent and high birefringent domains, respectively.

### Ring-opening polymerization of the thin films of compound 2

Polymerization of the thin films of compound 2 proceeds via acid-catalyzed ring-opening polymerization mechanism as shown in Figure S2.

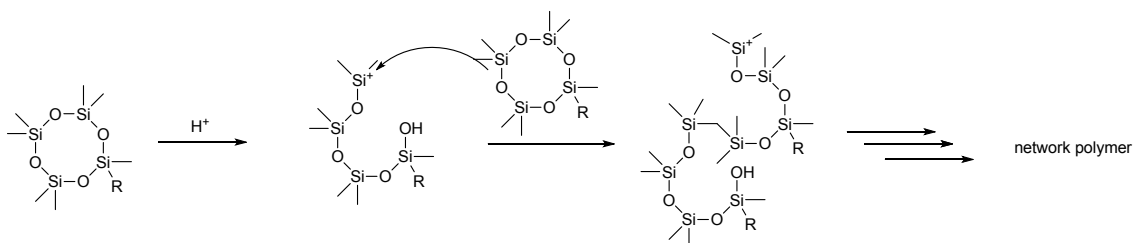


Figure S2 Ring-opening polymerization of the cyclotetrasiloxane rings

### **Determination of the lattice constant of the columnar phases**

In a two-dimensional rectangular lattice, the diffraction spacing  $d_{hko}$ , and lattice constants  $a$  and  $b$  have a relationship,

$$\frac{1}{d_{hko}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} \quad (1)$$

where  $h$ ,  $k$ , and  $l$  are Miller indexes.