Supporting Information for Physical Chemistry Chemical Physics

Electron transport characteristics in nano-segregated columnar phases of perylene tetracaroboxylic bisimide derivatives bearing oligosiloxane chains

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Synthesis of materials

General

All ¹H NMR spectra were recorded on a Varian UNITY INOVA400NB spectrometer. FT-IR measurements were conducted on a JASCO FT/IR-660 Plus spectrometer. The synthetic procedure and spectral data of compounds **1** and **3** were already reported previously.^{1,2} Compound **2** was synthesized as shown in Scheme S1. Perylene tetracarboxylic acid anhydride was treated with 6-amino-1,10-undecadiene in the presence of zinc acetate in quinoline. Hydrosilylation reaction between the PTCBI derivative **6** and 1,1,1,3,3-pentamethyldisiloxane in the presence of the Karstedt catalyst produced compound **2**.



Scheme S1

N,N'-Bis(1,10-undeccen-6-yl)-perylene-3,4:9,10-tetracarboxylic bisimide (6)

Perylene tetracarboxylic anhydride (4) (2.49 g, 6.3 mmol), 5-amino-1,10-undecadiene (5) (2.42 g, 14.5 mmol), and zinc acetate (1.43 g, 7.8 mmol) were dissolved in quinoline (30 ml) and heated at $150 \,^{\circ}$ C for 2 hours. To the reaction mixture was added dilute hydrochloric acid, and the produced red precipitates were filtered. The red precipitates were washed with dilute hydrochloric acid and methanol. The crude crystals were purified by a silicagel column chromatography (elutant:

dichloromethane). The red fibrous crystals are dissolved in dichloromethane and poured into methanol. The red precipitates were filtered. Red fibrous crystals (2.54 g, 3.7 mmol) were obtained in the yield of 59 %. ¹H NMR (400 MHz, CDCl₃): $\delta = 8.66$ (d, 4H, br), 8.59 (dd, 4H, J = 7.2, 4.0 Hz), 5.74 (ddt, 4H, J = 16.8, 10.4, 6.4 Hz), 5.20 (tt, 2H, J = 10.0, 5.2 Hz), 4.96 (dd, 4H, J = 16.8, 1.6 Hz) , 4.88 (dd, 4H, J = 10.4, 1.6 Hz), 2.27 (ddt, 4H, J = 14.1, 9.2 5.6 Hz), 2.06 (quart, 8H, d = 6.4 Hz), 1.83-1.92 (m, 4H), 1.38-1.49 (m, 8H), 1.28-1.38 (m, 4H); ¹³C NMR (100 MHz CDCl₃): $\delta = 26.4$, 32.0, 54.5, 114.9, 123.2, 126.6, 129.8, 131.4, 132.1, 134.7, 138.8; IR (ATR) : v = 3077, 2972, 1692, 1650, 1593, 1405, 1385, 1247, 1173, 908, 809, 746, 619, 430, 395 cm⁻¹; elemental analysis calcd (%) for C₄₆H₄₆N₂O₄: C, 79.97; H, 6.71; N, 4.05; O, 9.26; found: C, 79.80; H, 6.78; N, 4.04; Exact Mass: 690.35; Molecular Weight: 690.87, m/z: 689.98, 691.00, 692.00, 693.00.

N-N'-Bis(1,11-di(1,1,1,3,3-pentamethyl-1,3-disiloxanenyl)undecan-6-yl)perylene-3,4,9,10-tetracarboxylic bisimide (2)

N,*N*[°]-Bis(1,10-undeccen-6-yl)-perylene-3,4:9,10-tetracarboxylic bisimide (**6**) 0.52 g (0.75 mmol) and 1,1,1,3,3-pentamethyldisiloxane 0.71 g (4.8 mmol) were dissolved in toluene (30 ml) and 5 µl of Karstedt catalyst (1,3-divinyl-1,1,3,3-tetramethyldisiloxane platinum (0), 2.1 At%, 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 (0.67 g, 0.52 mmol) was obtained in the yield of 69 %. ¹H NMR (400 MHz, CDCl₃): δ = 8.68 (d, br, 4H, J = 8.0 Hz), 8.61 (d, 4H, J = 8.0 Hz), 5.17 (tt, 2H, J = 9.2, 5.6 Hz), 2.18-2.29 (m, 4H), 1.79-1.89 (m, 4H), 1.19-1.37 (m, 24H), 0.43 (dd, 8H, J = 10.0, 6.4 Hz), -0.01 ppm (s, 36H), -0.04 ppm (s, 24H); ¹³C NMR (100 MHz CDCl₃): δ = 0.5, 2.1, 18.5, 23.4, 26.9, 32.5, 33.6, 55.0, 123.2, 124.2, 126.7, 129.8, 131.4, 132.1, 134.7; IR (ATR) : v = 2958, 1697, 1651, 1594, 1338, 1254, 1044, 837, cm⁻¹; Elemental Analysis (%) calculated for C₆₆H₁₁₀N₂O₈Si₈: C, 61.72; H, 8.63; N, 2.18; O, 9.97; Si, 17.50; found: C, 61.70; H, 9.09; N, 2.19; Exact Mass: 1282.64; Molecular Weight: 1284.27; m/z [M⁺]: 1283.20, 1282.21, 1284.20, 1285.20, 1284.2, 1286.22, 1287.24.

Thermal properties of compounds 1-3

Differential scanning calorimetry (DSC) measurements were conducted with a NETZSCH DSC 204 Phoenix. DSC thermograms of compounds **1-3** are shown in Figure S1.



Figure S1 DSC thermograms of (a) compound **1**, (b) compound **2**, and (c) compound **3**. The heating and cooling rates are 10 K/min.

Structures of the columnar phases of compounds 1-3

X-ray diffraction (XRD) measurements were carried out on a Rigaku Rapid II diffractometer with the use of Ni-filtered CuKa radiation. Structural analyses of the columnar phases of compound **1** and **3** were already reported in previous papers.^{1,2} Figure S2 exhibits X-ray diffraction pattern of compound **2** at room temperature. The peaks at $2\theta = 3.84$, 6.71, 7.59, 9.10, 12.00, and 13.94 are assigned to (100), (110), (200), (210), (300), and (220) diffraction planes. The ratio of the estimated lattice constants is $1:1/\sqrt{3}:1/2:1/\sqrt{7}: 1/3:1/12}$, indicating a hexagonal columnar arrangement. Halos around 15 degrees and 20 degrees are assigned to liquid-like packing of disiloxane and alkyl chains, respectively. At $2\theta = 25.22$ degrees, a diffraction peak indexed to (001) is observed. This peak indicates the existence of π - π stacking in the columnar aggregates in this columnar phase. Therefore this columnar phase is identified to be a hexagonal disordered columnar phase.



Figure S2 X-ray diffraction patterns of (a) compound 1 at 100 °C, (b) compound 1 at 30 °C, (c) compound 2 at 30 °C, and (d) compound 3 at 30 °C

References

- 1. M. Funahashi, A. Sonoda, Org. Electr., 2012, 13, 1633-1640.
- 2. M. Funahashi, A. Sonoda, J. Mater. Chem., 2012, 22, 25190-25197.