

Supporting Information

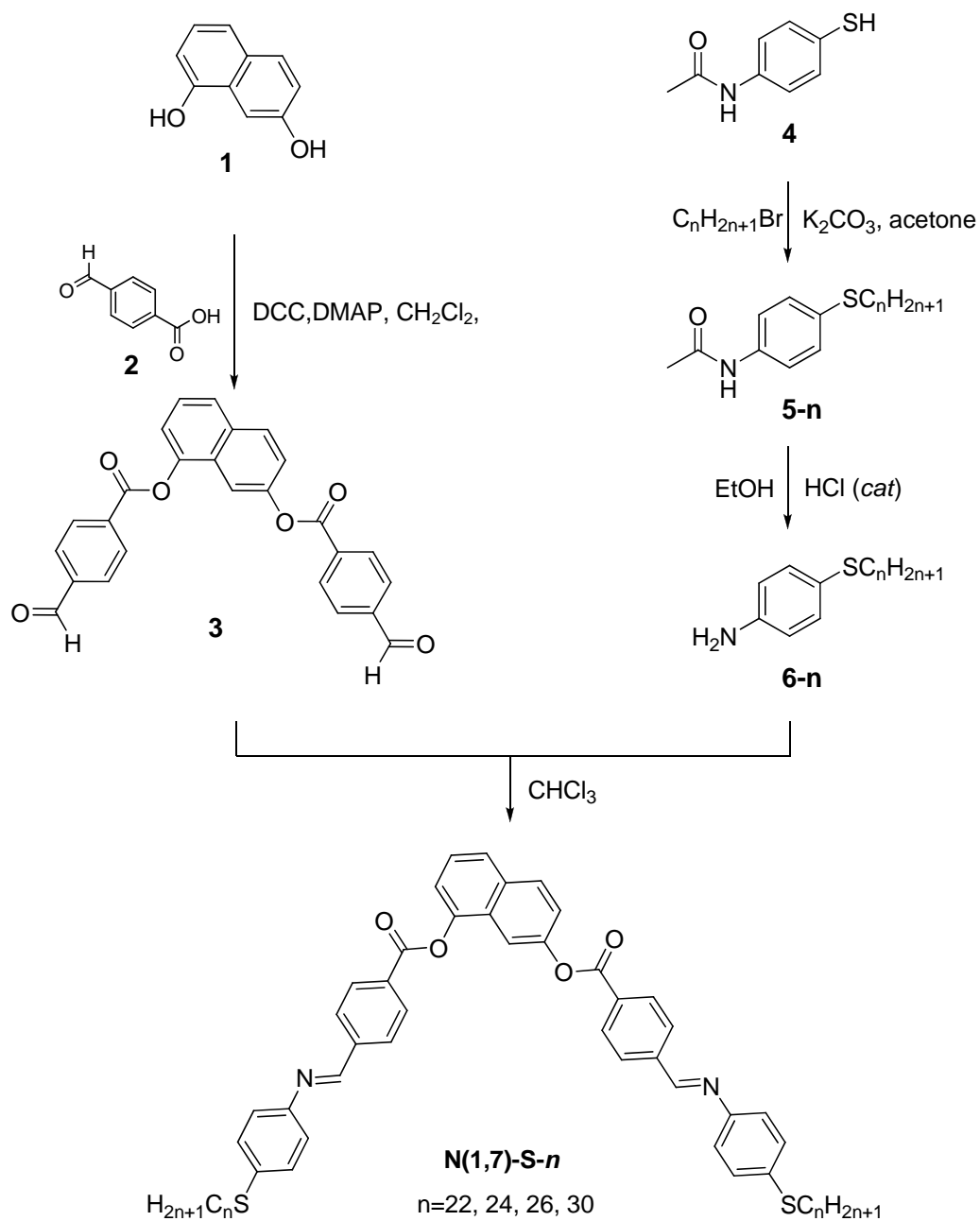
Notable Formation of a Cubic Phase from Small Bent-angle Molecules Based on the 1,7-Naphthalene Central Core and Alkylthio Tails

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Scheme S1 Synthesize route to N(1,7)-S-*n* compound

Synthesis and analytical data

The target bent-shaped molecules were synthesized by following the methods in our previous paper.¹² The synthetic routes were illustrated in Scheme S1. All reagents including bis(*p*-hydroxyphenyl)methane were purchased from TCI (Tokyo Kasei kogyo Co, Ltd) and used without further purification. Solvents were purified by normal procedures and handled under a moisture-free atmosphere. ¹H-NMR and ¹³C-NMR spectra were recorded on a JEOL FT-NMR AL400 (400 MHz) spectrometer using CDCl₃ as an internal standard. Elemental analysis was determined by CHN coder MT-6.

Synthesis of dialdehydes 3

To a solution of 1,7-dihydroxynaphthalene 1 (1.00 g, 6.24 mmol) in CH₂Cl₂ (100 ml) was added 1,3-dicyclohexylcarbodiimide (DCC) (3.22 g, 15.60 mmol), 4-dimethylaminopyridine (DMAP) (catalyst amount), and 4-formylbenzoic acid 2 (2.06 g, 13.72 mmol). The mixture was stirred at room temperature for three days. After filtration to remove precipitated materials, the filtrate was chromatographed on silica gel (CH₂Cl₂) and then recrystallized from dichloromethane/ethanol to isolate 3 (1.35 g, 51%) as a white solid. ¹H-NMR (400 MHz, CDCl₃) δ 7.42-8.07 (m, 6H), 8.37 (d, J=8.4 Hz, 4H), 8.48 (d, J=8.4 Hz, 4H), 10.14 (s, 1H), 10.16 (s, 1H).

Synthesis of N-(4-dodecylsulfanylphenyl)acetamide 5-22

A mixture of 4-acetamidobenzenethiol 4 (2.60 g, 15.5 mmol), 1-bromodocosane (7.32 g, 18.8 mmol) and potassium carbonate (6.41 g, 46.5 mmol) in acetone (100 ml) was heated under reflux 16h (For 1-Bromotetracosane, 1-Bromoheacosane and 1-Bromotriacosane, they were prepared by bromination of *n*-alcohol with hydrogen bromide). To this solution was added water (50 ml) and the produce was extracted with diethyl ether (30 ml × 3). The combined organic layers were dried (MgSO₄),

concentrated and recrystallized from ethanol to give 5-22 (4.4 g, 60%) as a white solid. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.88 (t, $J=6.6$ Hz, 3H), 1.25-1.61 (m, 40H), 2.17 (s, 3H), 2.86 (t, $J=7.4$ Hz, 2H), 7.05 (br s, NH), 7.30 (d, $J=8.4$ Hz, 2H), 7.42 (d, $J=8.3$ Hz, 2H).

For 5-24, $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.88 (t, $J=6.7$ Hz, 3H), 1.26-1.62 (m, 44H), 2.17 (s, 3H), 2.86 (t, $J=7.3$ Hz, 2H), 7.05 (br s, NH), 7.30 (d, $J=8.5$ Hz, 2H), 7.42 (d, $J=8.1$ Hz, 2H).

For 5-26, $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.88 (t, $J=6.7$ Hz, 3H), 1.25-1.61 (m, 48H), 2.18 (s, 3H), 2.86 (t, $J=7.4$ Hz, 2H), 7.06 (br s, NH), 7.30 (d, $J=8.5$ Hz, 2H), 7.42 (d, $J=8.3$ Hz, 2H).

For 5-30, $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.88 (t, $J=6.1$ Hz, 3H), 1.25-1.61 (m, 56H), 2.17 (s, 3H), 2.86 (t, $J=6.1$ Hz, 2H), 7.06 (br s, NH), 7.30 (d, $J=8.3$ Hz, 2H), 7.41 (d, $J=8.5$ Hz, 2H).

Synthesis of 4-dodecylsulfanylphenylamine 6-22

An ethanol (100 ml) solution of 5 (4.4 g, 9.30 mmol) and a catalytic amount of concentrated HCl was stirred at 70°C . After 1 day, the solvent was evaporated *in vacuo*; saturated NaHCO_3 (50 ml) was added to the residue. The mixture was filtered and dried, then give 6 (3.91 g, 97%). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.86 (t, $J=6.8$ Hz, 3H), 1.25-1.52 (m, 20 H), 2.72 (t, $J=7.2$ Hz, 2H), 3.20 (br s, NH_2), 6.63 (d, $J=8.5$ Hz, 2H), 7.10 (d, $J=8.3$ Hz, 2H).

For 6-24, $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.86 (t, $J=6.8$ Hz, 3H), 1.25-1.50 (m, 44 H), 2.68 (t, $J=7.1$ Hz, 2H), 3.01 (br s, NH_2), 6.53 (d, $J=8.5$ Hz, 2H), 7.06 (d, $J=8.8$ Hz, 2H).

For 6-26, $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.87 (t, $J=6.8$ Hz, 3H), 1.25-1.50 (m, 48 H), 2.75 (t, $J=7.3$ Hz, 2H), 3.10 (br s, NH_2), 6.60 (d, $J=8.8$ Hz, 2H), 7.10 (d, $J=8.8$ Hz, 2H).

For 6-30, $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.88 (t, $J=6.6$ Hz, 3H), 1.20-1.49 (m, 36 H), 2.70 (t, $J=7.3$ Hz, 2H), 4.88 (br s, NH_2), 6.54 (d, $J=8.8$ Hz, 2H), 7.06 (d, $J=8.3$ Hz, 2H).

Synthesis of 1,7-naphthalene bis[4-(4-dodecylsulfanylphenyliminomethyl)benzoate].

A solution of 6 (0.31 g, 1.08 mmol) and dialdehyde 3 (0.20 g, 0.47 mmol) in chloroform (25 ml) was heated under reflux for 3 hr. The reaction mixture was concentrated and recrystallized from chloroform/ethanol twice to give a yellow crystal of the target compound, N(1,7)-S-22 (0.33 g, 72%).

The NMR and Elemental analysis data are shown;

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.87 (t, $J=6.8$ Hz, 6H), 1.28-1.70 (m, 80H), 2.94 (t, $J=7.3$ Hz, 4H), 7.22-8.08 (m, 18H), 8.30 (d, $J=8.3$ Hz, 2H), 8.41 (d, $J=8.5$ Hz, 2H), 8.55 (s, 1H), 8.57 (s, 1H).

$^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ 15.36, 23.96, 30.13, 30.47, 30.49, 30.63, 30.79, 30.87, 30.89, 30.91, 30.92, 30.93, 30.95, 30.96, 30.97, 30.99, 31.10, 31.11, 31.13, 31.15, 33.20, 35.31, 120.37, 122.87, 122.89, 123.39, 126.79, 128.88, 130.03, 130.19, 131.13, 131.15, 131.17, 131.92, 132.05, 136.99, 146.35, 150.35, 150.64, 159.30, 159.33, 165.99.

Elemental analysis: calculated for $\text{C}_{82}\text{H}_{114}\text{N}_2\text{O}_4\text{S}_2$ C 78.42, H 9.15, N 2.23, O 5.10, S 5.11; found, C 78.37, H 9.17, N 2.25, O(+ S) 10.21.

Other target compounds, N(1,7)-S-24, N(1,7)-S-26 and N(1,7)-S-30 were similarly prepared in 52 %, 44 % and 42 % yields, respectively.

The NMR and Elemental analysis data are shown; For N(1,7)-S24, $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.88 (t, $J=7.0$ Hz, 6H), 1.25-1.66 (m, 88H), 2.94 (t, $J=7.1$ Hz, 4H), 7.20-8.09 (m, 18H), 8.30 (d, $J=8.3$ Hz, 2H), 8.42 (d, $J=8.5$ Hz, 2H), 8.55 (s, 1H), 8.58 (s, 1H).

$^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ 15.40, 24.03, 30.18, 30.45, 30.52, 30.70, 30.85, 30.88, 30.92, 30.94, 30.99, 31.03, 33.26, 35.21, 122.75, 122.94, 122.95, 124.06, 124.73, 130.08, 130.23, 131.04, 131.99, 132.11, 142.04, 150.26, 170.25

Elemental analysis: calculated for $\text{C}_{86}\text{H}_{122}\text{N}_2\text{O}_4\text{S}_2$ C 78.73, H 9.37, N 2.14, O 4.88, S 4.89; found, C 78.70, H 9.41, N 2.17, O(+ S) 9.72.

For N(1,7)-S26, ¹H-NMR 0.88 (t, J=6.6 Hz, 6H), 1.25-1.70 (m, 96H), 2.94 (t, J=7.4 Hz, 4H), 7.20-8.09 (m, 18H), 8.30 (d, J=8.3 Hz, 2H), 8.42 (d, J=8.5 Hz, 2H), 8.55 (s, 1H), 8.58 (s, 1H).

¹³C-NMR (400 MHz, CDCl₃) δ 15.46, 24.03, 30.18, 30.44, 30.52, 30.70, 30.85, 30.87, 30.93, 30.96, 31.00, 31.04, 33.26, 35.21, 122.94, 122.95, 128.87, 130.08, 130.23, 131.03, 131.24, 131.99, 132.11, 136.99, 147.86, 150.26, 159.44

Elemental analysis: calculated for C₉₀H₁₃₀N₂O₄S₂ C 79.01, H 9.58, N 2.05, O 4.68, S 4.69; found, C 78.95, H 9.62, N 2.10, O(+ S) 9.33.

For N(1,7)-S30, ¹H-NMR 0.88 (t, J=6.8 Hz, 6H), 1.25-1.70 (m, 112H), 2.94 (t, J=7.3 Hz, 4H), 7.20-8.09 (m, 18H), 8.30 (d, J=8.1 Hz, 2H), 8.42 (d, J=8.5 Hz, 2H), 8.55 (s, 1H), 8.58 (s, 1H).

¹³C-NMR (400 MHz, CDCl₃) δ 15.46, 30.17, 30.45, 30.85, 30.93, 31.00, 31.04, 31.07, 33.26, 35.21, 122.94, 128.25, 130.23, 131.03, 148.73

Elemental analysis: calculated for C₉₈H₁₄₆N₂O₄S₂ C 79.51, H 9.94, N 1.89, O 4.32, S 4.33; found, C 79.23, H 9.94, N 1.91, O(+ S) 8.92.

FIGURE CAPTION

Fig. S1 Polarization reversal current in the Col_h phase of N(1,7)-S-22 upon the application of the triangular wave (Temperature: 130 °C, Voltage: 120 V_{pp}, Frequency: 200 Hz, and Cell gap: 2.4 μm). A single reversal current peak can be clearly detected in the half period of the triangular wave field.

Fig. S2 Temperature dependence of the spontaneous polarization observed in N(1,7)-S-22 (Voltage: 120 V_{pp}, Frequency: 200 Hz, and Cell gap: 2.4 μm). The solid curve is calculated according to the equation of $P_s = P_{s0} (1 - T/T_{tr})^\beta$ with $P_{s0} = 628 \text{ nC} \cdot \text{cm}^{-2}$, $\beta = 0.37$, and $T_{tr} = 141 \text{ K}$

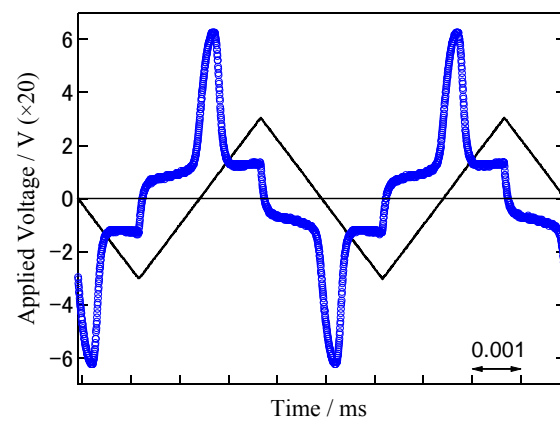


Figure S1

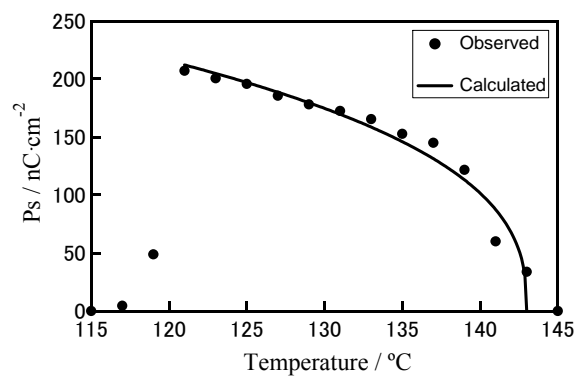


Figure S2