Supporting Information

Smectic A–Hexagonal columnar–B7 phase Transition of Acute-angle Bent-core Molecules†

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**Fig. S1** POM micrographs of SmA (a and b) and B7 (c and d) phases for N(1,7)–EIE–S16. (a) and (c) without compensator, (b) retardation is enhanced along the layer normal (green-colored domain) with compensator (530 nm). (d) retardation is reduced in the same domain (orange colored) with compensator. Here, the axis of compensator (bar) was set to almost parallel to the layer normal direction which is 45° direction. The scale bar indicates 100 μm.
Fig. S2 (a) Transmittance spectrum observed for fan-shape domain in SmA phase for N(1,7)–EIE–S16 (black solid circle) and the fitted value (red open square) by determination of Cauchy’s coefficients. (b) Wavelength dispersion of obtained birefringence ($\Delta n'$).
Scheme S1 Synthetic route of N(1,7)-EIE-Sn. (n = 16, 18 and 20)
Experimental

Synthesis

1,7-naphthylene bis(4-(4-hydroxyphenyliminomethyl)benzoate)

A mixture of 1,7-naphthylene bis(4-formylbenzoate) (2 g, 4.7 mmol), 4-amino phenol (1.28 g, 11.78 mmol) and a few acetic acid catalyst was stirred in chloroform (50 ml) under nitrogen at 40 °C for 8 hr. The reaction mixture was filtered and a remind product was recrystallized from methanol to give a yellow crystal of the target compound. Yield: 2.46 g, 86.2 %; ¹H NMR (400MHz, DMSO, δ in ppm): 9.65 (s, 2H, -O\text{H}) 8.79 (s, H, N=CH), 8.75 (s, H, N=CH), 8.37 (d, J=7.92 Hz 2H, Ar–H), 8.25 (d, J=7.80 Hz 2H, Ar–H), 8.20 (d, J=8.90 Hz H, Ar–H), 8.14 (d, J=7.50 Hz 2H, Ar–H), 8.08 (d, J=7.92 Hz 2H, Ar–H), 8.03 (d, J=7.92 Hz H, Ar–H), 7.87 (s, 1H, Ar-H), 7.67-7.57 (m, 3H, Ar–H), 7.31-7.28 (m, 4H, Ar–H), 6.83 (d, J=8.48 Hz 4H, Ar-H).

1,7-naphthylene bis(4-(4-(4-(hexadecylthio)benzoyloxy)phenyliminomethyl)benzoate)

A mixture of 4-hexadecylthiobenzoic acid, (1.56 g, 4.12 mmol), N,N'-dicyclohexylcarbodiimide (DCC) (0.9 g, 4.2 mmol) a catalytic amount of 4-(N,N-dimethylamino)pyridine (DMAP) (0.05, 0.4 mmol), dichloromethane (40 ml) and 1,7-naphthylene bis(4-(4-hydroxyphenyliminomethyl)benzoate) (1.0 g, 1.64 mmol) was stirred for about 24h at room temperature. The precipitated N,N’dicyclohexylurea was filtered off and the filtered solution was washed with 5wt% aqueous acetic acid and water. Obtained solution was removed under reduced pressure. Obtained yellow material was washed by ethanol and was recrystallized from chloroform / ethyl acetate (1:4). Yield: 0.6 g 27.5%; ¹H NMR (400MHz, CDCl₃, δ in ppm): 8.59 (s, 2H, N=C\text{H}), 8.56 (s, 2H, N=C\text{H}), 8.44 (d, J=8.29 Hz 2H, Ar–H), 8.33 (d, J=8.23 Hz 2H, Ar–H), 8.11-7.99 (m, 9H, Ar–H), 7.87 (d, J=8.29 Hz 1H, Ar–H), 7.79 (s, 1H, Ar-H), 7.57 (t, J=7.99 Hz 4H, Ar-H) 7.48-7.44(m, 2H, Ar-H), 7.35-7.31(m, 8H, Ar–H),7.27-7.25(m, 4H, Ar–H), 3.01 (t, J=7.38 Hz 4H, O\text{CH}_2\text{-}), 1.73 (m, J=7.56 Hz 4H, OCH₂CH₂H₂), 1.46 (m, J=7.56 Hz 4H, OCH₂CH₂CH₂H₂), 1.26 (s, 48H, OCH₂CH₂CH₂CH₂(J=7.29 Hz), 0.88 (t, J=7.13 Hz 6H, OCH₂(CH₂)₄CH₂); ¹³C NMR (400MHz, CDCl₃, δ in ppm): 165.11, 164.89, 164.70, 159.06, 159.02, 153.01, 149.71, 149.37, 149.06, 146.62, 145.98, 140.85, 140.69, 131.61, 131.44, 130.92, 130.79, 130.60, 129.11, 128.96, 127.63, 126.25, 125.60, 122.64, 122.13, 32.06, 32.01, 29.83, 29.79, 29.71, 29.62, 29.51, 29.29, 29.05, 28.80, 22.84, 14.28 ; Anal. Calcd. for C₈₄H₉₈N₂O₈S₂ C 76.37, H 7.72, N 2.02. Found: C 76.12, H 7.58, N 2.04.

1,7-naphthylene bis(4-(4-(4-(octadecylthio)benzoyloxy)phenyliminomethyl)benzoate)

Yield: 0.38 g, 33.3 %; ¹H NMR (400MHz, CDCl₃, δ in ppm): 8.59 (s, 2H, N=CH), 8.56 (s, 2H, N=CH), 8.44 (d, J=8.29 Hz 2H, Ar–H), 8.33 (d, J=8.35 Hz 2H, Ar–H), 8.11-8.00 (m, 9H, Ar–H), 7.87 (d, J=8.23 Hz 1H, Ar–H), 7.80 (s, 1H, Ar-H), 7.57 (t, J=7.80 Hz 4H, Ar-H) 7.48-7.45(m, 2H, Ar-H), 7.35-7.31(m, 8H, Ar–H),7.27-7.24(m, 4H, Ar-H), 3.02 (t, J=7.38 Hz 4H, OCH₂H₂), 1.73 (m, J=7.56 Hz 4H, OCH₂CH₂H₂), 1.46 (m,
J=7.69 Hz 4H, OCH$_2$CH$_2$), 1.26 (s, 56H, OCH$_2$CH$_2$CH$_2$CH$_2$), 0.88 (t, J=7.02 Hz 6H, OCH$_2$(CH$_2$)$_{10}$CH$_3$); $^{13}$C NMR (400MHz, CDCl$_3$, δ in ppm): 165.08, 164.87, 164.69, 159.02, 158.97, 149.79, 149.78, 149.43, 149.10, 146.69, 145.99, 140.91, 140.76, 133.01, 131.68, 131.52, 130.92, 130.80, 130.60, 129.13, 127.69, 126.37, 125.72, 125.63, 122.12, 32.07, 29.84, 29.81, 29.78, 29.71, 29.63, 29.50, 29.30, 29.06, 28.85, 22.83, 14.26; Anal. Calcd. for C$_{88}$H$_{106}$N$_2$O$_8$S$_2$ C 76.37, H 7.72, N 2.02. Found: C 76.50, H 7.85, N 1.96.

1,7-naphthylene bis(4-(4-(4-((eicosylthio)benzoyloxy)phenyliminomethyl)benzoate)

Yield: 0.6 g, 63.2 %; $^1$H NMR (400MHz, CDCl$_3$, δ in ppm): 8.59 (s, 2H, N=CH), 8.57 (s, 2H, N=CH), 8.45 (d, J=8.42 Hz 2H, Ar–H), 8.33 (d, J=8.48 Hz 2H, Ar–H), 8.11-8.00 (m, 9H, Ar–H), 7.87 (d, J=8.29 Hz 1H, Ar–H), 7.79 (s, 1H, Ar–H), 7.57 (t, J=7.80 Hz 4H, Ar–H) 7.48-7.44(m, 2H, Ar–H), 7.36-7.32(m, 8H, Ar–H),7.28-7.25(m, 4H, Ar–H), 3.02 (t, J=7.38 Hz 4H, OCH$_2$), 1.72 (m, J=7.62 Hz 4H, OCH$_2$CH$_2$), 1.46 (m, J=7.62 Hz 4H, OCH$_2$CH$_2$), 1.25 (s, 56H, OCH$_2$CH$_2$CH$_2$CH$_2$), 0.88 (t, J=7.20 Hz 6H, OCH$_3$(CH$_2$)$_{20}$CH$_3$); $^{13}$C NMR (400MHz, CDCl$_3$, δ in ppm): 165.04, 164.87, 164.51, 160.55, 158.73, 149.81, 149.47, 149.08, 146.81, 146.01, 141.12, 140.48, 132.97, 131.60, 130.78, 130.67, 130.55, 130.51, 130.48, 130.45, 129.10, 128.89, 127.68, 126.63, 126.54, 125.94, 122.52, 32.29, 31.93, 29.69, 29.66, 29.63, 29.60, 29.58, 29.48, 29.34, 29.16, 28.92, 22.66 14.02; Anal. Calcd. for C$_{92}$H$_{114}$N$_2$O$_8$S$_2$ C 76.73 H 7.98, N 1.95. Found: C 77.95, H 8.17, N 2.01.