Electronic Supplementary Information for

Dipole-driven self-assembly of redox-active mesogenic tetracyanoanthraquinodimethanes

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Materials and Syntheses. All reagents and solvents were purchased from Aldrich, Tokyo Kasei, Kanto Chemical, or Wako, and used as received. Benzoic acids (**8–10**) having various number of alkoxy chains were prepared by the procedures of the literature.[1] All reactions were performed under an Ar atmosphere in dry solvents, unless otherwise noted.

2,6-Bis(3,4-didodecyloxybenzoyloxy)-11,11,12,12-tetracyanoanthraquinodimethane (2a). This compound was prepared from **5a** (0.83 g, 0.7 mmol), malononitrile (0.69 g, 10.5 mmol), $TiCl_4$ (0.4 mL), and pyridine (1.1 mL) in dry CH_2Cl_2 (30 mL) by adopting the procedure used for **1a**. The product was purified by column chromatography (silica, $CHCl_3$/hexane = 1:6, v/v), recrystallized from $CHCl_3$/methanol, and dried under vacuum to afford **2a** as a bright orange solid (0.27 g, 30%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.8 Hz, 2H), 8.16 (d, *J* = 2.0 Hz, 2H), 7.83 (dd, *J* = 8.4 and 2.0 Hz, 2H), 7.64 (d, *J* = 2.0 Hz, 2H), 7.60 (dd, *J* = 8.8 and 2.0 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 4.12-4.04 (m, 8H), 1.92-1.80 (m, 8H), 1.57-1.43 (m, 8H), 1.42-0.90 (m, 64H), 0.89-0.85 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.98, 158.92, 154.57, 154.03, 148.80, 131.83, 129.27, 127.06, 125.99, 124.96, 121.51, 119.81, 114.55, 112.87, 112.65, 111.86, 83.40, 69.40, 69.10, 31.92, 29.69, 29.65, 29.62, 29.60, 29.40, 29.36, 29.13, 28.98, 25.99, 25.94, 22.69, 14.13. Anal. Calcd for $C_{82}H_{112}N_4O_8$: C, 76.84; H, 8.81; N, 4.37%. Found: C, 76.65; H, 9.03; N, 4.07%.

2,6-Bis(3,4-ditetradecyloxybenzoyloxy)-11,11,12,12-tetracyanoanthraquinodimethane (2b). This compound was prepared from **5b** (0.65 g, 0.5 mmol), malononitrile (0.50 g, 7.5 mmol), $TiCl_4$ (0.7 mL), and pyridine (0.8 mL) in dry CH_2Cl_2 (30 mL) by adopting the procedure used for **1a**. The product was purified by column chromatography (silica, $CHCl_3$/hexane = 1:6, v/v), recrystallized from $CHCl_3$/methanol, and dried under vacuum to afford **2b** as a bright orange solid (0.51 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 8.8 Hz, 2H), 8.16 (d, *J* = 2.4 Hz, 2H), 7.83 (dd, *J* = 8.4 and 2.4 Hz, 2H), 7.64 (d, *J* = 2.0 Hz, 2H), 7.60 (dd, *J* = 8.8 and 2.4 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 4.12-4.04 (m, 8H), 1.90-1.80 (m, 8H), 1.54-1.43 (m, 8H), 1.42-0.90 (m, 80H), 0.89-0.85 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.98, 158.94, 154.57, 154.04, 148.81, 131.83, 129.28, 127.07, 125.99, 124.96, 121.51, 119.82, 114.55, 112.87, 112.65, 111.86, 83.40, 69.41, 69.11, 31.92, 29.71, 29.67, 29.63, 29.61, 29.41, 29.36, 29.14, 28.99, 26.00, 25.95, 22.69, 14.13. Anal. Calcd for $C_{90}H_{128}N_4O_8$: C, 77.54; H, 9.26; N, 4.02%. Found: C, 77.32; H, 9.41; N, 3.88%.

2,6-Bis(4-dodecyloxybenzoyloxy)-11,11,12,12-tetracyanoanthraquinodimethane (3a). This compound was prepared from **6a** (0.80 g, 9.8 mmol), malononitrile (0.97 g, 14.7 mmol), $TiCl_4$ (0.54 mL), and pyridine (1.6 mL) in dry CH_2Cl_2 (80 mL) by adopting the procedure used for **1a**. The product was purified by column chromatography (silica, $CHCl_3$/ethyl acetate = 5:1, v/v), recrystallized from $CHCl_3$/methanol, and dried under vacuum to afford **3a** as a bright yellow solid (0.26 g, 29%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 8.8 Hz, 2H), 8.16 (d, *J* = 2.0 Hz, 2H), 8.14 (d, *J* = 9.2 Hz, 4H), 7.61 (dd, *J* = 8.8 and 2.0 Hz, 2H), 6.99 (d, *J* = 9.2 Hz, 4H), 4.06 (t, *J* = 6.8 Hz, 4H), 1.83 (quint, *J* = 6.8 Hz, 4H), 1.56-1.43 (m, 4H), 1.40-0.95 (m, 32H), 0.89 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.25, 163.83, 158.91, 153.99, 132.72, 131.83, 129.27, 127.04, 125.95, 121.46, 119.85, 114.56, 112.88, 112.66, 83.39, 68.46, 31.91, 29.65, 29.63, 29.58, 29.54, 29.35, 29.03, 25.93, 22.69, 14.13. Anal. Calcd for $C_{58}H_{64}N_4O_6$: C, 76.29; H, 7.06; N, 6.14%. Found: C, 76.24; H, 7.30; N, 5.99%.

2,6-Bis(4-tetradecyloxybenzoyloxy)-11,11,12,12-tetracyanoanthraquinodimethane (3b). This compound was prepared from **6b** (2.00 g, 2.3 mmol), malononitrile (2.27 g, 34.4 mmol), $TiCl_4$ (1.3 mL), and pyridine (3.6 mL) in dry CH_2Cl_2 (80 mL) by adopting the procedure used for **1a**. The product was purified by column chromatography (silica, $CHCl_3$/ethyl acetate = 5:1, v/v), recrystallized from $CHCl_3$/methanol, and dried under vacuum to afford **3b** as a bright yellow solid (1.35 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.8 Hz, 2H), 8.16 (d, *J* = 2.4 Hz, 2H), 8.14 (d, *J* = 8.8 Hz, 4H), 7.61 (dd, *J* = 8.8 and 2.4 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 4H), 4.06 (t, *J* = 6.4 Hz, 4H), 1.83 (quint, *J* = 6.4 Hz, 4H), 1.56-1.43 (m, 4H), 1.40-0.95 (m, 40H), 0.88 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.26, 163.83, 158.90, 154.00, 132.73, 132.54, 131.85, 129.28, 127.05, 125.94, 121.46, 119.88, 114.58, 112.88, 83.39, 68.48, 31.92, 29.68, 29.67, 29.65, 29.59, 29.54, 29.36, 29.05, 25.96, 22.69, 14.12. Anal. Calcd for $C_{62}H_{72}N_4O_6$: C, 76.83; H, 7.49; N, 5.78%. Found: C, 76.68; H, 7.54; N, 5.53%.

2,6-Bis(3,4,5-tridodecyloxybenzoyloxy)-9,10-anthraquinone (4a). This compound was prepared from **7** (0.50 g, 2.1 mmol), **8a** (2.97 g, 4.4 mmol), 4-dimethylaminopyridine (DMAP, 0.26 g, 2.1 mmol), and 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC, 1.19 g, 6.2 mmol) in dry CH_2Cl_2 (20 mL) by adopting the procedure used for **6a**. The product was purified by column chromatography (silica, $CHCl_3$), recrystallized from $CHCl_3$/methanol, and dried under vacuum to give **4a** as a light-yellow solid (2.79 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, *J* = 8.4 Hz, 2H), 8.15 (d, *J* = 2.4 Hz, 2H), 7.67 (dd, *J* = 8.4 and 2.4 Hz, 2H), 7.43 (s, 4H), 4.10-4.04 (m, 12H), 1.90-1.72 (m, 12H), 1.58-1.15 (m, 108H), 0.90-0.86 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.45, 164.23, 155.96, 153.08, 143.54, 135.23, 131.05, 129.50, 127.73, 122.88, 120.47, 108.73, 73.65, 69.33, 31.92, 30.36, 29.73, 29.70, 29.66, 29.63, 29.57, 29.40, 29.36, 29.30, 26.07, 22.69, 14.11. Anal. Calcd for $C_{100}H_{160}O_{12}$: C, 77.27; H, 10.38%. Found: C, 77.09; H, 10.60%.

2,6-Bis(3,4,5-tritetradecyloxybenzoyloxy)-9,10-anthraquinone (4b). This compound was prepared from **7** (0.36 g, 1.5 mmol), **8b** (2.28 g, 3.0 mmol), DMAP (0.18 g, 1.5 mmol), and EDC (0.86 g, 4.5 mmol) in dry CH_2Cl_2 (50 mL) by adopting the procedure used for **6a**. The product was purified by column chromatography (silica, $CHCl_3$), recrystallized from $CHCl_3$/methanol, and dried under vacuum to give **4b** as a light-yellow solid (2.29 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, J = 8.4 Hz, 2H), 8.15 (d, J = 2.4 Hz, 2H), 7.67 (dd, J = 8.4 and 2.4 Hz, 2H), 7.43 (s, 4H), 4.10-4.05 (m, 12H), 1.89-1.70 (m, 12H), 1.56-1.15 (m, 132H), 0.89-0.85 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.41, 164.21, 155.91, 153.04, 143.43, 135.18, 131.01, 129.43, 127.67, 122.85, 120.38, 108.67, 73.64, 69.33, 31.92, 30.35, 29.74, 29.70, 29.66, 29.63, 29.56, 29.38, 29.36, 29.29, 26.08, 22.68, 14.11. Anal. Calcd for $C_{112}H_{184}O_{12}$: C, 78.09; H, 10.77%. Found: C, 77.95; H, 10.91%.

2,6-Bis(3,4-didodecyloxybenzoyloxy)-9,10-anthraquinone (5a). This compound was prepared from **7** (0.48 g, 2.0 mmol), **9a** (1.96 g, 4.0 mmol), DMAP (0.24 g, 2.0 mmol), and EDC (1.15 g, 6.0 mmol) in dry CH_2Cl_2 (30 mL) by adopting the procedure used for **6a**. The product was recrystallized from THF and dried under vacuum to give **5a** as a light-yellow solid (1.30 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, J = 8.8 Hz, 2H), 8.15 (d, J = 2.8 Hz, 2H), 7.85 (dd, J = 8.4 and 2.0 Hz, 2H), 7.69-7.66 (m, 4H), 6.96 (d, J = 8.4 Hz, 2H), 4.13-4.04 (m, 8H), 1.93-1.83 (m, 8H), 1.53-1.45 (m, 8H), 1.40-0.90 (m, 64H), 0.89-0.85 (m, 12H). Anal. Calcd for $C_{76}H_{112}O_{10}$: C, 76.99; H, 9.52%. Found: C, 76.73; H, 9.73%.

2,6-Bis(3,4-ditetradecyloxybenzoyloxy)-9,10-anthraquinone (5b). This compound was prepared from **7** (0.24 g, 1.0 mmol), **9b** (1.09 g, 2.0 mmol), DMAP (0.12 g, 1.0 mmol), and EDC (0.58 g, 3.0 mmol) in dry CH_2Cl_2 (20 mL) by adopting the procedure used for **6a**. The product was recrystallized from THF and dried under vacuum to give **5b** as a light-yellow solid (0.87 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$):

δ 8.41 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 2.0 Hz, 2H), 7.85 (dd, *J* = 8.8 and 1.6 Hz, 2H), 7.69-7.66 (m, 4H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.13-4.05 (m, 8H), 1.95-1.83 (m, 8H), 1.58-1.45 (m, 8H), 1.40-0.90 (m, 80H), 0.89-0.85 (m, 12H). Anal. Calcd for $C_{84}H_{128}O_{10}$: C, 77.73; H, 9.94%. Found: C, 77.59; H, 9.76%.

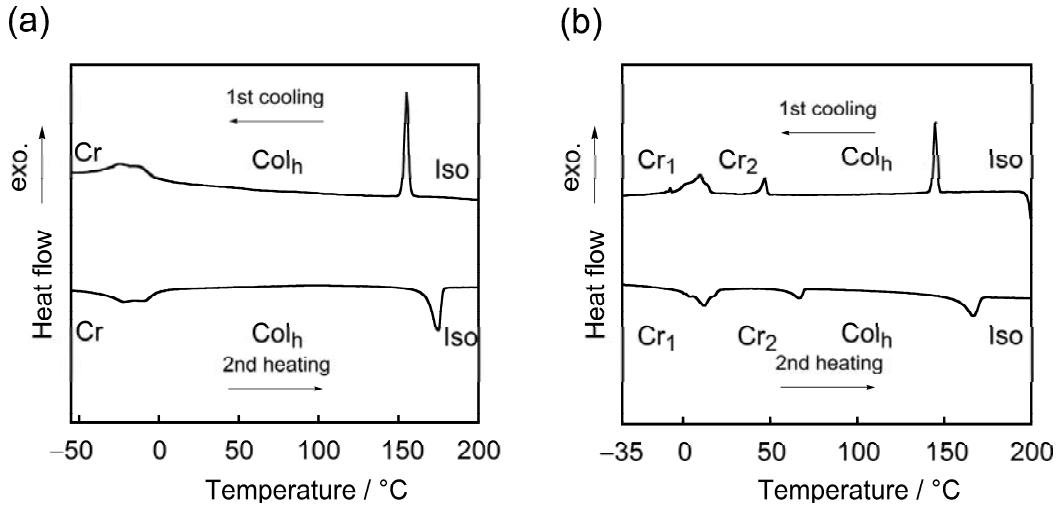

Figure S1. DSC thermograms of (a) **1a** and (b) **1b** at a scanning rate of 5 °C min^{-1}. Cr: crystalline; Col_h: hexagonal columnar; Iso: isotropic.

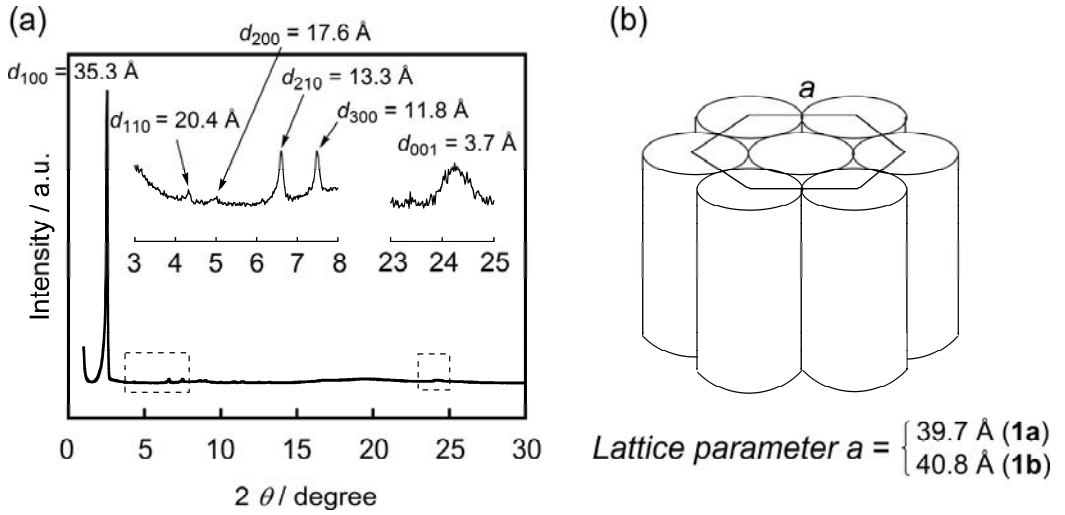

Figure S2. (a) XRD pattern of **1b** in the Col_h phase at 100 °C. The insets show the magnified views. (b) Schematic illustration of a hexagonal columnar structure. The intercolumnar distance (a) was calculated according to the equation : $a = d_{100} \times 2/\sqrt{3}$.

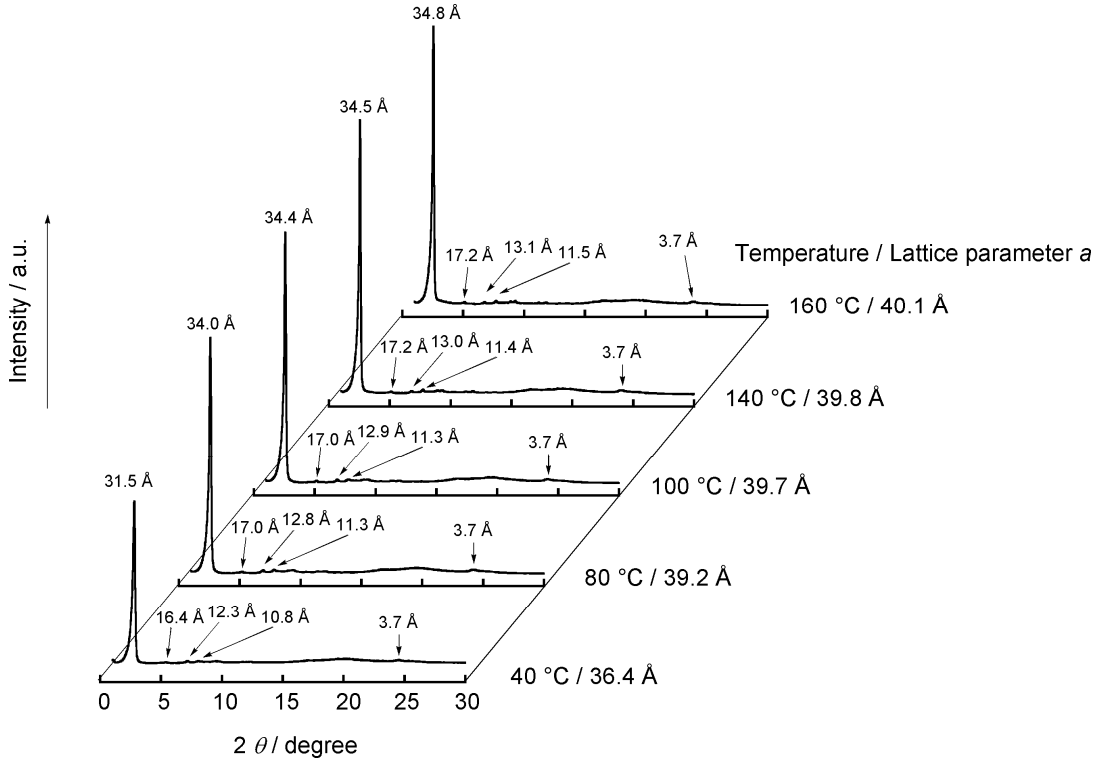

Figure S3. Temperature dependence of the XRD pattern and the intermolecular distance in the Col_h phase of **1a**.

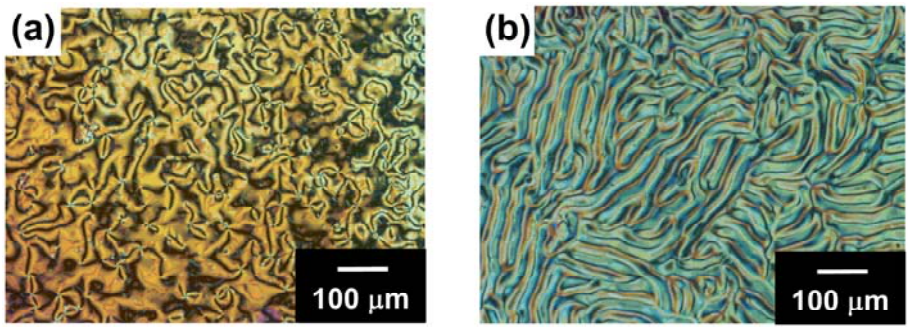

Figure S4. Polarized optical micrographs of **6b** (a) in the nematic phase at 210 °C and (b) in the smectic C phase at 195 °C on cooling.

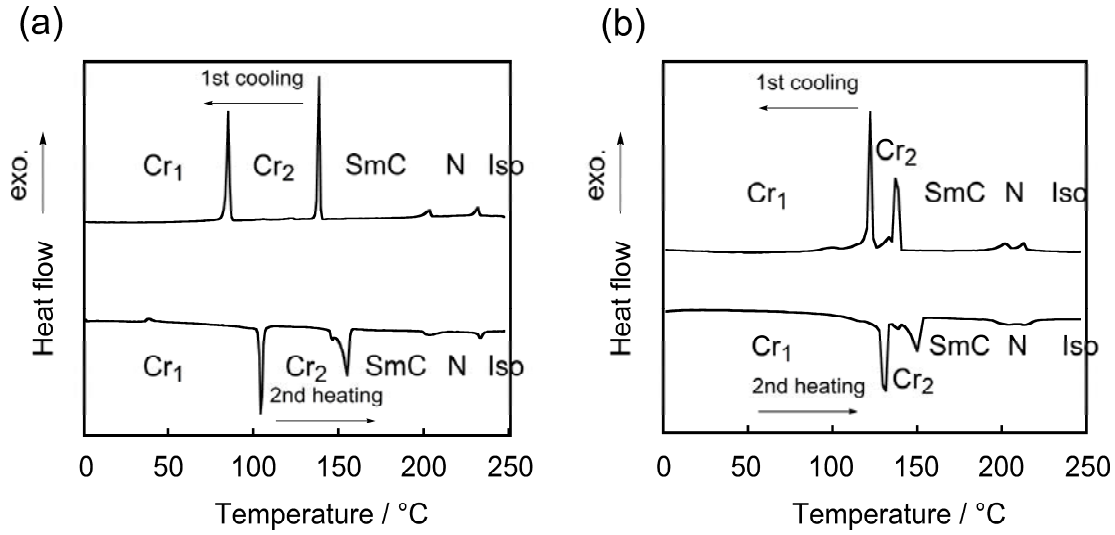

Figure S5. DSC thermograms of (a) **6a** and (b) **6b** at a scanning rate of 5 °C min^{-1}. Cr: crystalline; SmC: smectic C; N: nematic; Iso: isotropic.

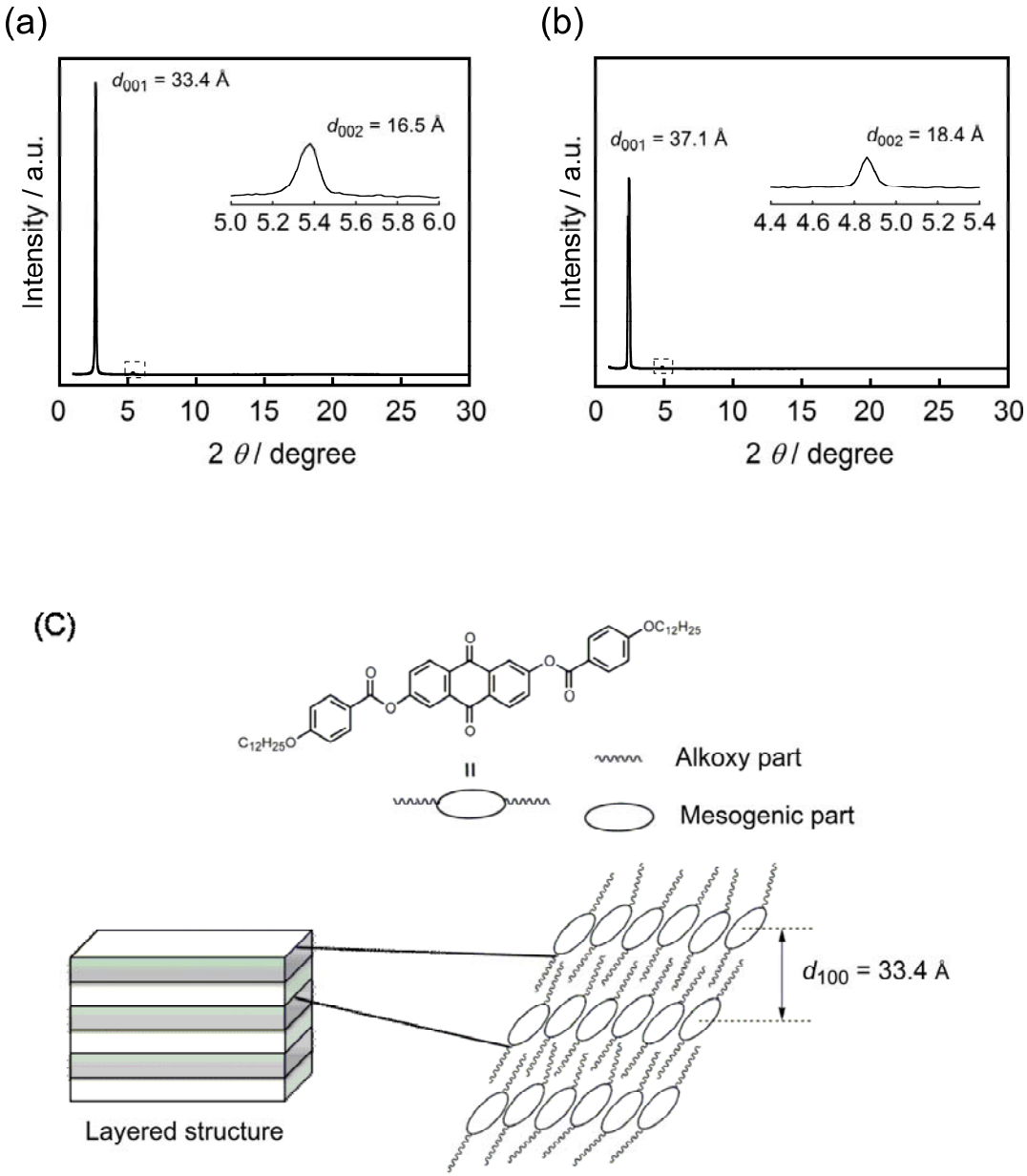

Figure S6. XRD patterns of (a) **6a** and (b) **6b** in the SmC phase at 140 °C. The insets show the magnified views. (c) Schematic illustration of a layered SmC structure.

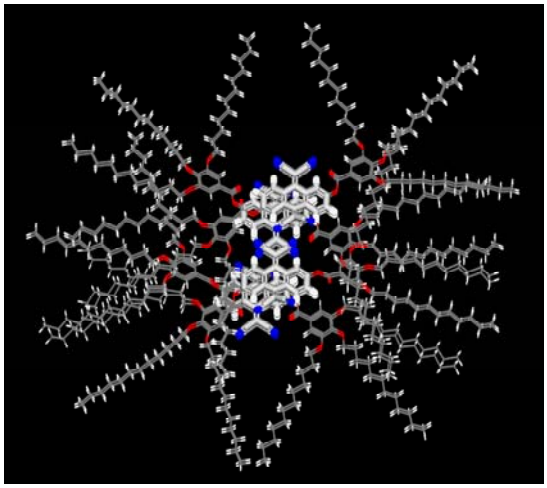

Figure S7. Top view of the columnar structure formed by **1a**.

Table S1. Gelation properties of **1–6**[a]

Solvent	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**	**6a**	**6b**
Dodecane	G	G	P	S	I	I	S	P	I	I	I	I
Hexane	S	S	S	S	I	I	P	P	I	I	I	I
Cyclohexane	S	S	S	S	I	I	S	S	I	I	I	I
Dodecyl benzene	S	S	P	P	I	P	S	S	I	I	I	I
1-Dodecanol	G	G	P	I	I	I	P	P	I	I	I	I
THF	S	S	S	S	S	S	S	S	P	P	P	P
$CHCl_3$	S	S	S	S	S	S	S	S	P	P	S	S
Ethyl acetate	S	S	P	P	S	S	P	P	I	I	I	I
Toluene	S	S	S	S	S	S	S	S	P	P	P	P
Acetone	P	P	P	P	S	S	I	I	I	I	I	I
CH_3OH	I	I	I	I	I	I	I	I	I	I	I	I
DMF	P	P	P	P	P	P	I	I	I	I	I	I

[a]The following abbreviations are used: G, gel; P, precipitation; S, solution; I, insoluble when heated. Tests were performed at 10 g L^{-1} for organic solvents.

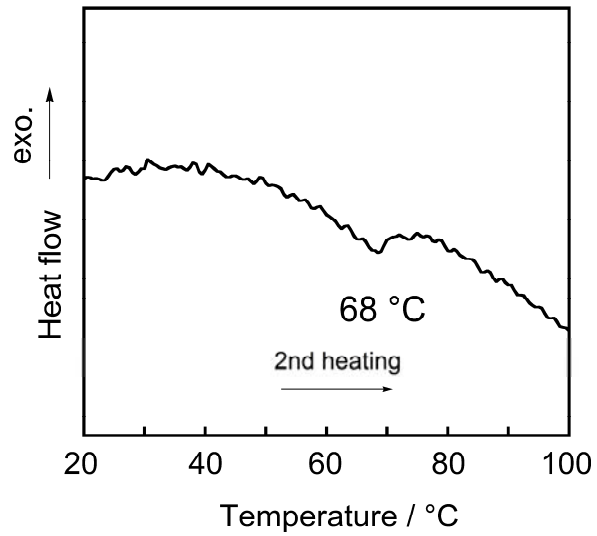

Figure S8. DSC thermogram of the dodecan gel of **1a** at a scanning rate of 5 °C min^{-1}.

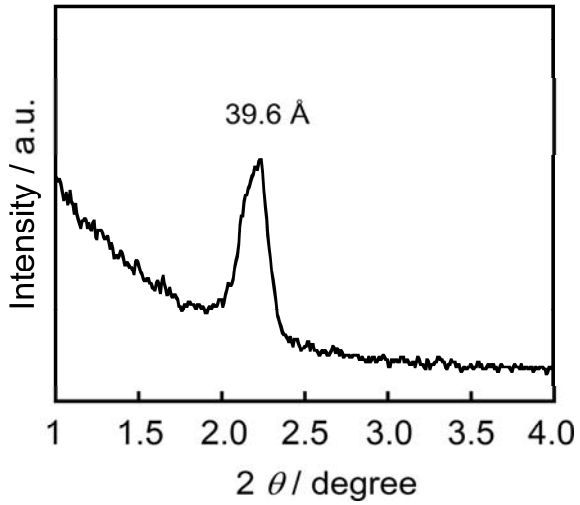

Figure S9. SAXS pattern of the dodecane gel of **1a** at room temperature.

Table S2. Electrochemical data of **1–6**

Compound	Redox potential[a] (V vs Ag^+/Ag)	
	$E_{1/2}{}^1$	$E_{1/2}{}^2$
1a	−0.46	
1b	−0.41	
2a	−0.42	
2b	−0.47	
3a	−0.44	
3b	−0.45	
4a	−1.10	−1.63
4b	−1.10	−1.60
5a	*b*	*b*
5b	*b*	*b*
6a	−0.99	−1.54
6b	−1.02	−1.65

[a]Measured by cyclic voltammetry in a CH_2Cl_2 solution of Bu_4NClO_4 (0.10 M). [b]Not determined due to poor solubility.

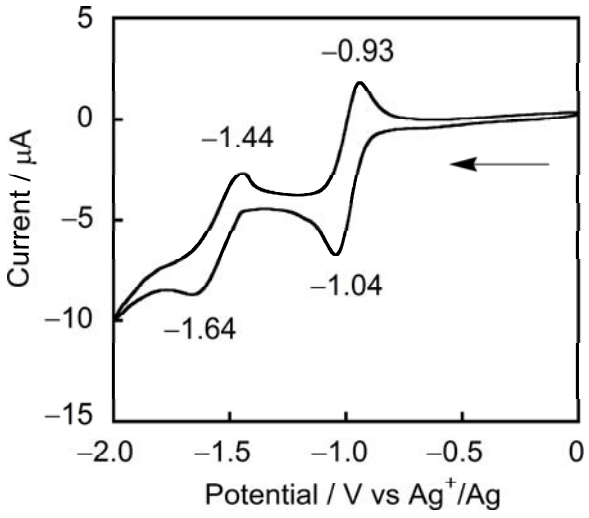

Figure S10. Cyclic voltammogram of **6a** (2.0 mM) recorded in a CH_2Cl_2 solution of Bu_4NClO_4 (0.10 M). Sweep rate is 50 mVs^{-1}.

References.

1. (a) V. Percec, D. Schlueter, J. C. Ronda, G. Johansson, G. Ungar and J. P. Zhou, *Macromolecules,* 1996, **29**, 1464; (b) G. S. Lim, B. M. Jung, S. J. Lee, H. H. Song, C. Kim, and J. Y. Chang, *Chem. Mater.,* 2007, **19**, 460; (c) J. Ropponen, S. Nummelin and K. Rissanen, *Org. Lett.,* 2004, **6**, 2495; (d) V. Percec, J. G. Rudick, M. Peterca, M. Wagner, M. Obata, C. M. Mitchell, W. D. Cho, V. S. K. Balagurusamy and P. A. Heiney, *J. Am. Chem. Soc.,* 2005, **127**, 15257; (e) J. Barberá, L. Puig, P. Romero, J. L. Serrano and T. Sierra, *J. Am. Chem. Soc.,* 2006, **128**, 4487.