Supplementary Information

Bisphenylsulfone-based molecular assemblies: polar columnar liquid crystals aligned in electric fields and fibrous aggregates in organic solvents

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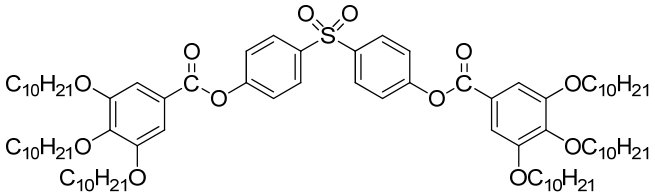
Synthesis of bisphenylsulfone ester 2a.



A solution of bis(4-hydroxyphenyl)sulfone (0.18 g, 0.72 mmol), 3,4,5-tris(decyloxy)benzoic acid (0.89 g, 1.5 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (0.35 g, 1.8 mmol), 4-(*N,N*-dimethylamino)pyridine (10 mg, 0.082 mmol) in dichloromethane (40 mL) was stirred for 12h at room temperature. The reaction mixture was washed by a NH_4Cl aqueous solution and the organic phase was separated and dried with $MgSO_4$. After filtration and concentration, the residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 10/1) to allow 0.69 g (69 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.04 (d, *J* = 8.8 Hz, 4H), 7.38 (d, *J* = 8.0 Hz, 4H), 7.37 (s, 4H), 4.08-4.02 (m, 12H), 1.86-1.72 (m, 12H), 1.47-1.27 (m, 84H), 0.88 (t, *J* = 6.8 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 164.17, 154.82, 153.00, 143.42, 138.59, 129.45, 122.89, 122.86, 108.62, 73.61, 69.27, 31.91, 31.88, 30.31, 29.70, 29.64, 29.59, 29.55, 29.53, 29.37, 29.36, 29.32, 29.24, 26.04, 26.01, 22.68, 22.66, 14.09.

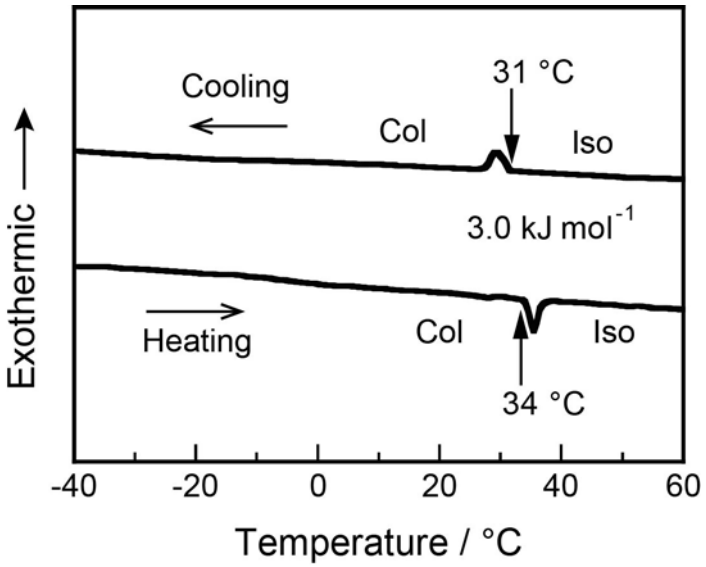


***Figure S1*.** DSC thermograms of **1a** (*n* = 10). Transition temperatures were taken at the onset points of the transition peaks. Col: columnar, Iso: isotropic liquid.

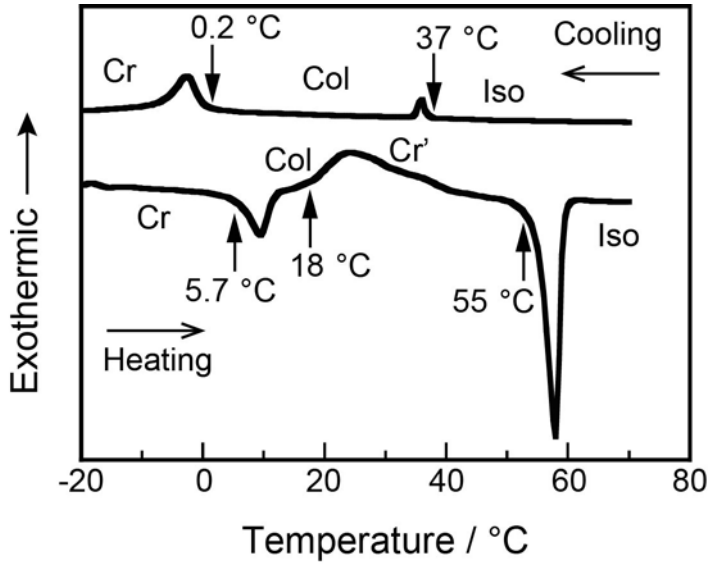


Figure S2. DSC thermograms of **1b** (*n* = 12). Transition temperatures were taken at the onset points of the transition peaks. Cr, Cr‘: crystalline, Col: columnar, Iso: isotropic liquid. The values of isotropic-columnar and columnar-crystalline (Col-Cr) transition enthalpies on cooling are 3.0 and 15 kJ mol^{-1}, respectively. On the heating scan, the crystalline-columnar (Cr-Col) transition takes place at 5.7 °C (19 kJ mol^{-1}). A further heating of sample induces the cold crystallization between 18 and 41 °C (53 kJ mol^{-1}) and the crystalline (Cr’) phase becomes the isotropic liquid phase at 55 °C (82 kJ mol^{-1}).

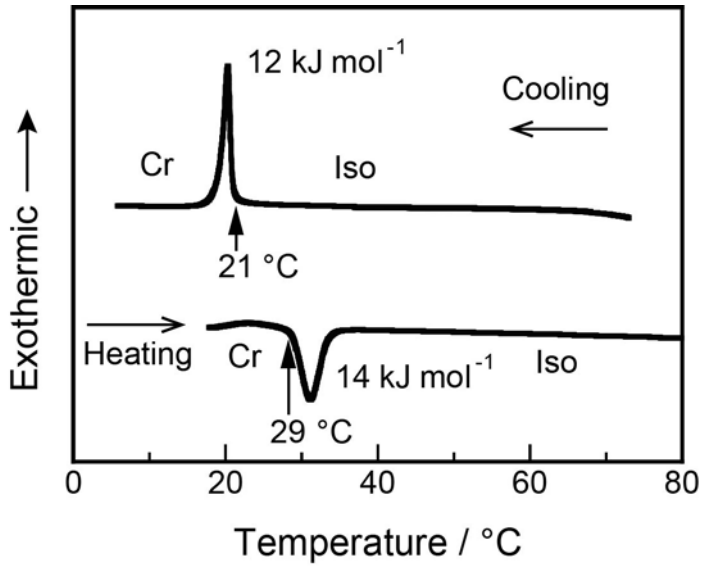


Figure S3. DSC thermograms of **2a** (*n* = 10). Transition temperatures were taken at the onset points of the transition peaks. Cr: crystalline, Iso: isotropic liquid.

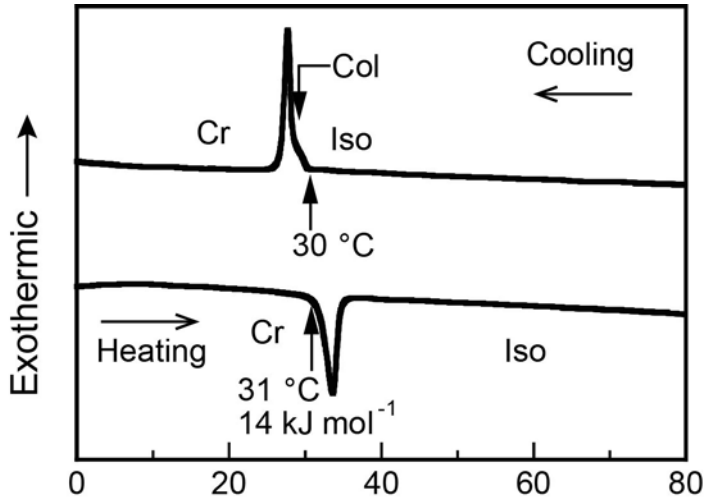


Figure S4. DSC thermograms of **2b** (*n* = 12). Transition temperatures were taken at the onset points of the transition peaks. Cr: crystalline, Col: columnar; Iso: isotropic liquid. The columnar phase is formed from 30 to 28 °C only on a cooling process.

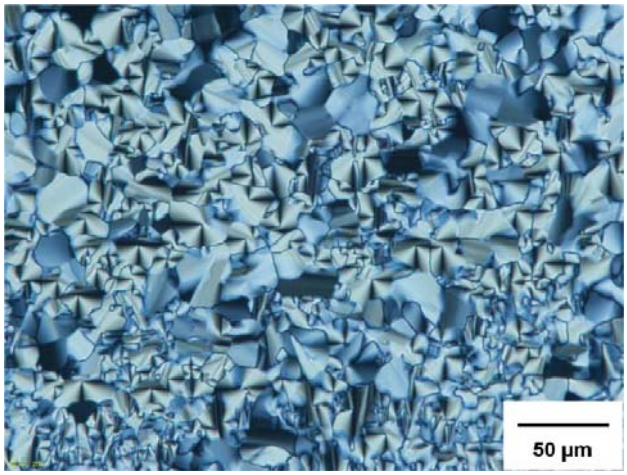


Figure S5. Polarized optical microscopic image of **2b** (*n* = 12) in the columnar phase at 30 °C.

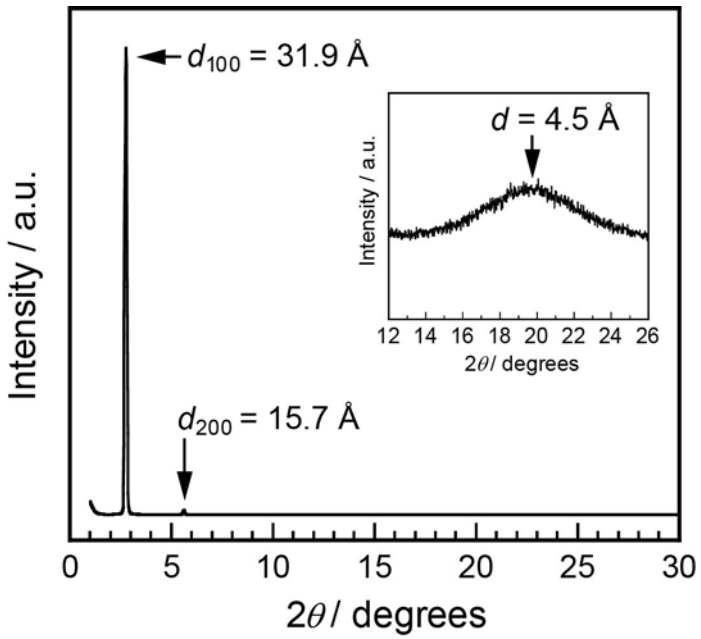


Figure S6. X-ray diffraction pattern of **1a** (*n* = 10) at 30 °C. The inset shows a magnified image of the wide-angle region, indicating a halo.

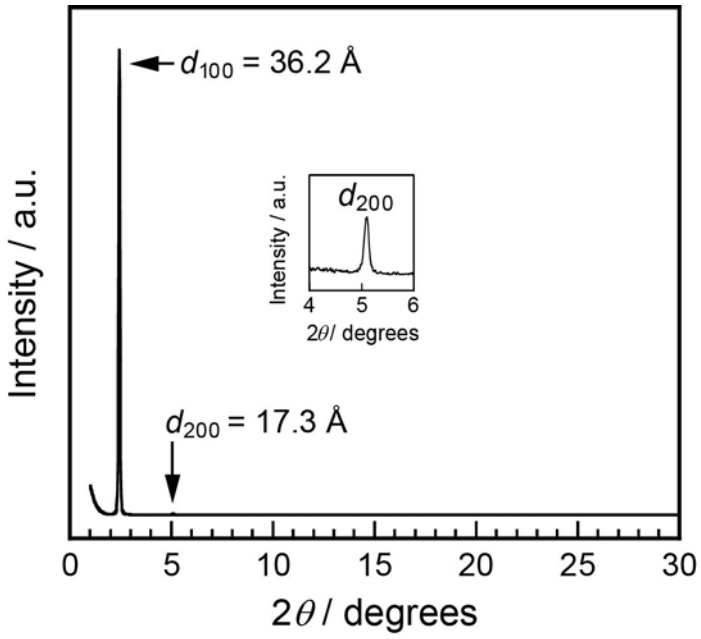


Figure S7. X-ray diffraction pattern of **1b** (*n* = 12) at 28 °C. The inset shows a magnified image of the small-angle region.

Estimation of the number of molecules per unit cell in the column for 1a.

Assuming a hexagonal columnar structure in the columnar liquid-crystalline phase for **1a**, the number (n) of molecules per unit cell in a hexagonal lattice is estimated to be 2 from $n = \sqrt{3}N_A a^2 h\rho/2M$,[1] where N_A is Avogadro's number (6.02×10^{23} mol^{-1}), a is intercolumnar distance (37 Å) roughly calculated from the equation: $a = 2d_{100}/\sqrt{3}$, (d_{100} = 31.9 Å), h is the layer thickness (4.5 Å), and M is molecular weight (1368.11 g mol^{-1}). The density (ρ) of the material is approximated to be 1.0 g cm^{-3}. The value of h has been taken from the halo of X-ray shown in Figure S6.

[1] (a) V. Percec, W.-D. Cho, G. Ungar, D. J. P. Yeardley, *J. Am. Chem. Soc*. **2001**, *123*, 1302-1315; (b) A. Schaz, E. Valaityte; G. Lattermann, *Liq. Cryst*. **2005**, *32*, 513-525.

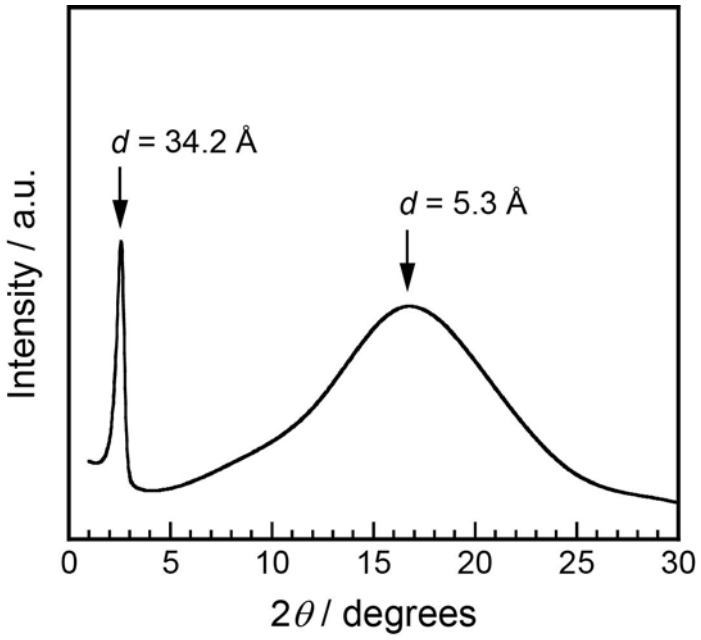


Figure S8. X-ray diffraction pattern of the dodecylbenzene gel of **1b** (n = 12) at room temperature.

Determination of the Sol-Gel transition temperature of the dodecylbenzene gel of 1b (5 wt%).

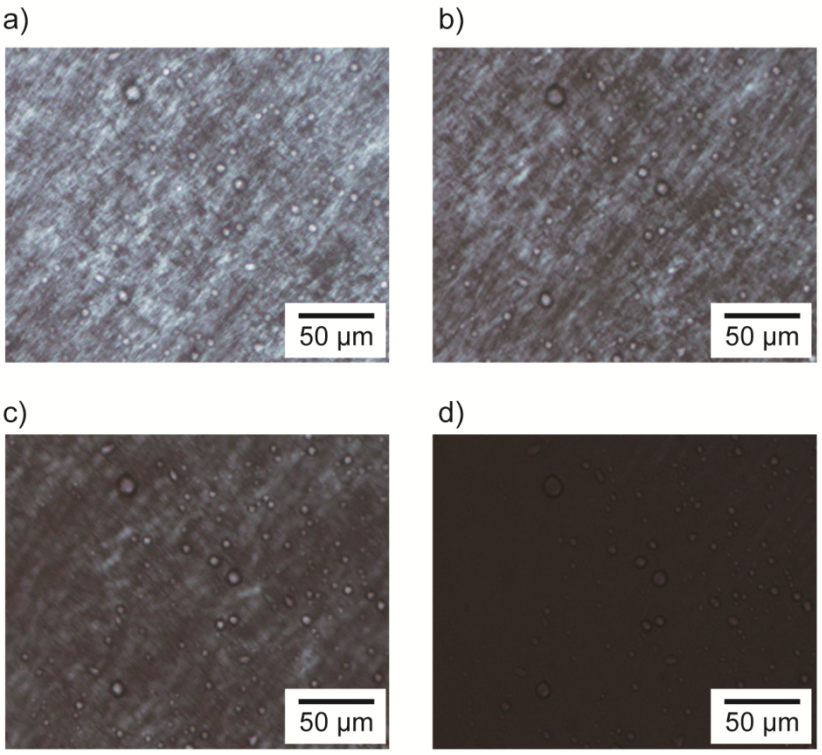


Figure S9. Polarizing optical microscopic images of the dodecylbenzene gel of **1b** (*n* = 12) at a) 20 °C; b) 23 °C; c) 24 °C; d) 25 °C during heating process (heating rate: 1 °C min^{-1}).

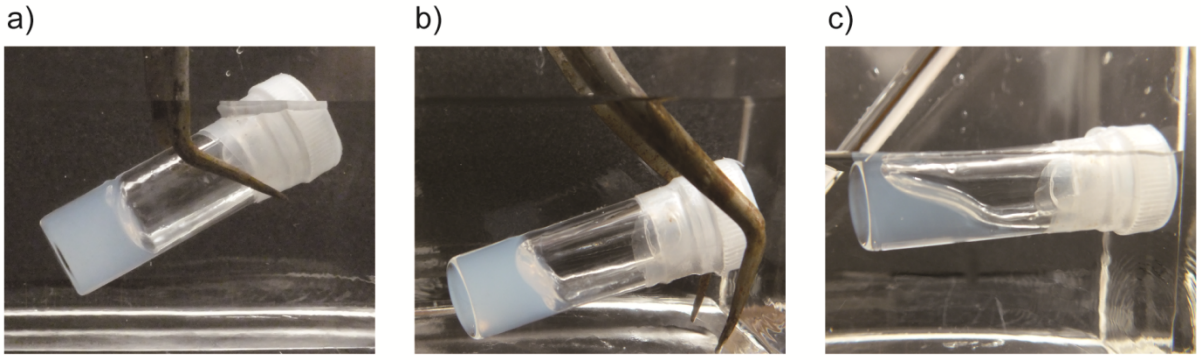


Figure S10. Photographs of the dodecylbenzene gel of **1b** (*n* = 12) in a glass tube soaked in a water bath at a) 20 °C; b) 23 °C; c) 25 °C.