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 NH₄Cl aqueous solution and the organic phase was separated and dried with MgSO₄. 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. ¹H NMR (400 MHz, CDCl₃): 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). ¹³C NMR (100 MHz, CDCl₃): 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 \( n = \sqrt{3}N_\text{A}a^2h\rho/2M,\) where \( N_\text{A} \) is Avogadro’s number \( (6.02 \times 10^{23} \text{ mol}^{-1}) \), \( a \) is intercolumnar distance \( (37 \text{ Å}) \) roughly calculated from the equation: \( a = 2d_{100}/\sqrt{3}, \) \( (d_{100} = 31.9 \text{ Å}) \), \( h \) is the layer thickness \( (4.5 \text{ Å}) \), and \( M \) is molecular weight \( (1368.11 \text{ g mol}^{-1}) \). The density \( \rho \) of the material is approximated to be \( 1.0 \text{ g cm}^{-3} \). The value of \( h \) has been taken from the halo of X-ray shown in Figure S6.


**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.