Supporting information for

Electric Field-Assisted Alignment of Self-Assembled Fibers Composed of Hydrogen-Bonded Molecules Having Laterally Fluorinated Mesogens

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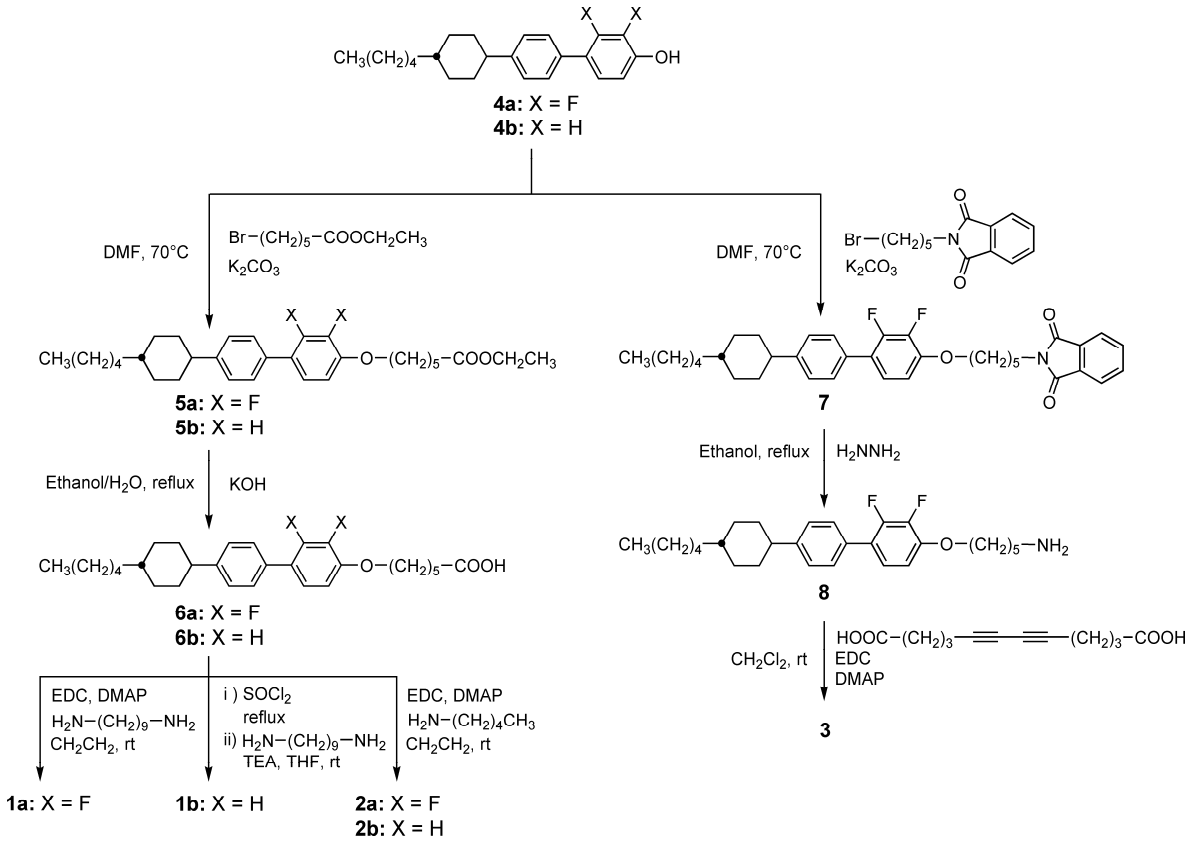
General Procedures. Reagents purchased from commercial suppliers were used without purification. All air and moisture sensitive reactions were performed under an Ar atmosphere in anhydrous solvents. Analytical thin-layer chromatography (TLC) was performed on silica gel plates of E. Merck (Silica Gel F_{254}). Silica gel column chromatography was carried out with silica gel 60 from Kanto (Silica Gel 60, spherical 40-50 μm). Recycling preparative GPC was performed using a Japan Analytical Industry LC-908 chromatograph. Infrared spectra were recorded on a JASCO FT/IR-660Plus spectrometer equipped with a JASCO Irtron IRT-30 microscope. ^{1}H and ^{13}C NMR spectra were obtained using a JEOL JNM-LA400 at 400 and 100 MHz, respectively. Chemical shifts of ^{1}H and ^{13}C NMR signals were expressed in ppm (δ) with TMS as the internal standard. Mass spectra (MALDI-TOF-MS) were recorded on a PerSeptive Biosystems Voyager-DE STR spectrometer. Elemental analyses were carried out on a Perkin-Elmer CHNS/O 2400 apparatus or a Yanako MT6-CHN autocorder. Self-assembled fibers were observed with an Olympus BH-2 optical polarizing microscope equipped with a Mettler FP82 HT hot-stage. Thermal properties were examined by differential scanning calorimetry using a Netzsch DSC204 *Phoenix*® at a scanning rate of 10 °C min^{-1}. Scanning electron microscopy (SEM) measurements of xerogels shielded by Pt were performed on a Hitachi S-900 at an accelerating voltage of 10 kV. X-ray diffraction patterns of fibers were obtained using a Rigaku RINT-2500 system with CuKα radiation. UV-vis absorption spectra of the dodecylbenzene gel of **2** were recorded on an Agilent (model 8453) UV/Vis spectrophotometer.

Materials. 6-Bromohexanoic acid ethyl ester, 1,5-dibromopentane, 4-(dimethylamino)pyridine (DMAP), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC), 1,9-nonanediamine, pentylamine, potassium phthalimide, thionyl chloride, triethylamine were obtained from TCI. 5,7-Dodecadiynedioic acid and hydrazine

monohydrate were purchased from Wako.

Synthesis. The synthetic routes used to obtain compounds **1–3** are shown in Scheme S1.



Scheme S1. Syntheses of amide derivatives having rod-shaped mesogenic moieties.

2,3-Difluoro-4-[4-(*trans*-4-pentylcyclohexyl)phenyl]phenol (4a). The laterally fluorinated rodlike mesogen used as the common part of compounds **1a, 2a,** and **3** was synthesized according to similar procedures reported in our previous paper.[1]

1-Iodo-4-[4-(*trans*-4-pentylcyclohexyl)]benzene (2.00 g, 5.61 mmol), 4-isopropoxy-2,3-difluorophenylboronic acid (1.34 g, 6.20 mmol), Na_2CO_3 (3.01 g, 28.4 mmol), and tetrakis(triphenylphosphine)palladium, $Pd(PPh_3)_4$ (0.65 g, 0.56 mmol) were added to a heterogeneous mixture of benzene (20 mL), ethanol (20 mL), and water (20 mL). The mixture was vigorously stirred and refluxed under an argon atmosphere for 3 h. After cooling to room temperature, the organic layer was separated and the aqueous solution was extracted with ethyl acetate (EtOAc). The combined organic solution was washed with a $NaHSO_3$ aqueous solution and brine. The resulting organic phase was dried over anhydrous $MgSO_4$ and filtered. Then, the solvent was removed under reduced pressure. The residue was

recrystallized from ethanol and purified by column chromatography (hexane : ethyl acetate = 10 : 1) to give 1-isopropoxy-2,3-difluoro-4-[4-(*trans*-4-pentylcyclohexyl)phenyl]benzene (2.23 g, 5.57 mmol) as a white solid in a yield of 99%. ^{1}H NMR ($CDCl_3$): δ = 7.43 (dd, J = 8.2, 2.0 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.05–7.10 (m, 1H), 6.77–6.82 (m, 1H), 4.56–4.62 (m, 1H), 2.47–2.52 (m, 1H), 1.01–1.95 (m, 23H), 0.90 (t, J = 7.1 Hz, 3H).

To the solution of the isopropyl ether derivative (2.23 g, 5.57 mmol) in CH_2Cl_2 (200 mL), 8.0 mL (8.0 mmol) of 1.0 M solution of BBr_3 in CH_2Cl_2 was slowly added at 0 °C. After stirring the reacting solution for 5 min, the solution was warmed to room temperature and stirred for additional 30 min. The solution was quenched with 2-propanol and water. The organic layer was separated and the aqueous solution was extracted with chloroform. The combined organic solution was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by using flash column chromatography (hexane : ethyl acetate = 5 : 1) and recrystallization from hexane to give **4a** (1.76 g, 4.91 mmol) as a white solid in a yield of 88%. ^{1}H NMR ($CDCl_3$): δ = 7.42 (dd, J = 8.2, 2.0 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.04–7.11 (m, 1H), 6.80–6.87 (m, 1H), 5.22 (d, J = 4.0 Hz, 1H), 2.45–2.56 (m, 1H), 1.86–1.95 (m, 4H), 1.04–1.45 (m, 13H), 0.90 (t, J = 7.1 Hz, 3H).

4-[4-(*trans*-4-Pentylcyclohexyl)phenyl]phenol (4b).
The coupling of 4-isopropoxyphenylboronic acid (1.57 g, 8.71 mmol) and 4-(*trans*-4-pentylcyclohexyl)phenyl-1,1,1-trifluoromethanesulfonate[2] (3.20 g, 8.46 mmol) using $Pd(PPh_3)_4$ (1.00 g, 0.87 mmol) and Na_2CO_3 (4.61 g, 43.5 mmol) gave 1-isopropoxy-4-[4-(*trans*-4-pentylcyclohexyl)phenyl]benzene (1.78 g, 4.87 mmol) as a white solid in a yield of 58%. Deprotection of the isopropyl ether derivative (1.22 g, 3.35 mmol) by BBr_3 (5.0 mmol) led to **4b** (0.922 g, 2.86 mmol) as a white solid in a yield of 85%. ^{1}H NMR ($CDCl_3$): δ = 7.45 (m, 4H), 7.25 (m, 2H), 6.80–6.87 (m, 2H), 5.10 (s, 1H), 2.50 (m, 1H), 1.86–1.95 (m, 4H), 1.04–1.45 (m, 13H), 0.90 (t, J = 7.1 Hz, 3H).

6-[2,3-Difluoro-4-[4-(*trans*-4-pentylcyclohexyl)phenyl]phenyloxy]hexanoic acid ethyl ester (5a). A mixture of **4a** (0.70 g, 2.0 mmol), 6-bromohexanoic acid ethyl ester (0.45 g, 2.0 mmol), and K_2CO_3 (0.81 g, 5.9 mmol) in DMF (15 mL) was vigorously stirred at 70 °C for 2.5 h. The mixture was poured into a mixture of EtOAc and a saturated NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic extract was washed with a saturated NH_4Cl aqueous solution and brine. The organic phase was dried over anhydrous $MgSO_4$, filtered through a pad of Celite, and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel (eluent: hexane : EtOAc = 5 : 1), followed by GPC to give **5a**

(0.90 g, 1.8 mmol, 90%) as a viscous liquid. ^{1}H NMR ($CDCl_3$): δ = 7.43 (d, J = 6.4 Hz, 2H), 7.31 (d, J = 7.6 Hz, 2H), 7.07-7.10 (m, 1H), 6.76-6.79 (m, 1H), 4.14 (q, J = 7.2, 2H), 4.07 (t, J = 6.4 Hz, 2H), 2.51 (m, 1H), 2.35 (t, J = 7.4 Hz, 2H), 0.90-1.94 (m, 29H).

6-[4-[4-(*trans*-4-Pentylcyclohexyl)phenyl]phenyloxy]hexanoic acid ethyl ester (5b). By following the synthetic procedure for **5a**, 0.39 g of compound **5b** (76%) as a viscous liquid was obtained by using **4b** (0.354 g, 1.10 mmol) and 6-bromohexanoic acid ethyl ester (0.269 g, 1.21 mmol). ^{1}H NMR ($CDCl_3$): δ = 7.43-7.50 (m, 4H), 7.25 (d, J = 6.8 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 4.14 (q, J = 7.2, 2H), 4.07 (t, J = 6.4 Hz, 2H), 2.51 (m, 1H), 2.35 (t, J = 7.4 Hz, 2H), 0.90-1.94 (m, 29H).

6-[2,3-Difluoro-4-[4-(*trans*-4-pentylcyclohexyl)phenyl]phenyloxy]hexanoic acid (6a). A solution of **5a** (0.894 g, 1.79 mmol) and KOH (1.47 g, 26.2 mmol) in ethanol (70 mL) and water (0.5 mL) was refluxed for 1 h. The solution was poured into water, acidified by a dilute HCl aq., and extracted with chloroform. The organic layer was washed with a saturated NH_4Cl aqueous solution and brine. The resulting organic layer was dried over anhydrous $MgSO_4$, filtered through a pad of Celite, and concentrated under reduced pressure. The residue was recrystallized from hexane and EtOAc to afford **6a** (0.786 g, 1.66 mmol, 93%) as a white solid. ^{1}H NMR (d^6-DMSO): δ = 7.41 (d, J = 6.8 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.23 (m, 1H), 7.07 (m, 1H), 4.10 (t, J = 6.2, 2H), 2.51 (m, 1H), 2.22 (t, J = 7.3 Hz, 2H), 0.86-1.82 (m, 26H).

6-[4-[4-(*trans*-4-Pentylcyclohexyl)phenyl]phenyloxy]hexanoic acid (6b). By following the synthetic procedure for **6a**, 0.37 g of compound **6b** (95%) as a white solid was obtained by using **5b** (0.39 g, 0.89 mmol) and KOH (0.68 g, 12 mmol). ^{1}H NMR (d^6-DMSO): δ = 7.45 (m, 4H), 7.25 (m, 2H), 6.80–6.87 (m, 2H), 4.10 (t, J = 6.2, 2H), 2.48 (m, 1H), 2.22 (t, J = 7.3 Hz, 2H), 0.86-1.82 (m, 26H).

***N*-[5-[2,3-Difluoro-4-[4-(*trans*-4-pentylcyclohexyl)phenyl]phenyloxy]pentyl]phthalimide (7).** A mixture of **4a** (1.20 g, 3.35 mmol), *N*-(5-bromopentyl)phthalimide (1.19 g, 4.02 mmol), and K_2CO_3 (1.39 g, 10.0 mmol) in DMF (20 mL) was vigorously stirred at 70 °C for 2 h. The mixture was poured into a mixture of EtOAc and a saturated NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic extract was washed with a saturated NH_4Cl aqueous solution and brine. The organic phase was dried over anhydrous $MgSO_4$, filtered through a pad of Celite, and concentrated under reduced pressure. The crude solid was purified by flash column

chromatography on a silica gel (eluent: $CHCl_3$), followed by GPC to give **7** (1.62 g, 2.82 mmol, 84%) as a white solid. ^{1}H NMR ($CDCl_3$): δ = 7.87-7.86 (m, 2H), 7.71-7.73 (m, 2H), 7.42-7.43 (m, 2H), 7.27-7.29 (m, 2H), 7.05-7.09 (m, 1H), 6.74-6.76 (m, 1H), 4.06 (t, J = 6.4, 2H), 3.74 (t, J = 7.2 Hz, 2H), 2.51 (m, 1H), 0.89-1.93 (m, 26H).

5-[2,3-Difluoro-4-[4-(*trans*-4-pentylcyclohexyl)phenyl]phenyloxy]pentylamine (8). Hydrazine monohydrate (0.54 mL, 11 mmol) was added dropwise to a solution of **7** (1.29 g, 2.25 mmol) in ethanol (50 mL) at room temperature. The solution was refluxed for 6 h. After removal of the solvent by a rotary evaporator, the resulting solid was dissolved in $CHCl_3$ and washed with water. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to afford **8** (0.800 g, 1.80 mmol, 80%) as a white solid. ^{1}H NMR ($CDCl_3$): δ = 7.43 (d, J = 6.8 Hz, 2H), 7.28 (d, J = 10 Hz, 2H), 7.07-7.09 (m, 1H), 6.76-6.80 (m, 1H), 4.08 (t, J = 6.4 Hz, 2H), 2.75 (br, 2H), 2.48-2.51 (m, 1H), 0.88-1.49 (m, 28H).

***N*,*N*'-Bis[6-[2,3-difluoro-4-[4-(*trans*-4-pentylcyclohexyl)phenyl]phenyloxy]hexanoyl]-1, 9-diaminononane (1a).** A mixture of **6a** (0.200 g, 0.423 mmol), 1,9-diaminononane (33.5 mg, 0.212 mmol), DMAP (5.2 mg, 0.043 mmol), EDC (0.122 g, 0.636 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 5 h. The reaction solvent was diluted with chloroform and washed with a sat. NH_4Cl aq. and sat. NaCl aq., successively. The organic layer was dried over anhydrous $MgSO_4$, filtered through a pad of Celite, and concentrated under reduced pressure. The crude solid was purified by flash column chromatography on a silica gel (eluent: $CHCl_3$: methanol = 10 : 1) and recrystallized from ethanol to give **1a** (0.209 g, 0.197 mmol, 93%) as a white solid. ^{1}H NMR ($CDCl_3$): δ = 7.42 (d, J = 6.7 Hz, 4H), 7.30 (d, J = 7.8 Hz, 4H), 7.04-7.11 (m, 2H), 6.73-6.80 (m, 2H), 5.50 (s, 2H), 4.07 (t, J = 6.3 Hz, 4H), 3.24 (dt, J = 6.2 Hz, 7.0 Hz, 4H), 2.50 (tt, J = 3.0, 12 Hz, 2H), 2.20 (t, J = 7.3 Hz, 2H), 0.90-1.95 (m, 68H). ^{13}C NMR ($CDCl_3$): δ = 172.5, 147.3, 132.2, 128.5 (d, J = 3 Hz), 126.9, 123.4 (dd, J = 4, 4 Hz), 123.2 (d, J = 3 Hz), 109.9, 69.8, 44.3, 39.4, 37.3, 37.2, 36.5, 34.2, 33.5, 32.1, 29.5, 29.1, 28.9, 28.8, 26.6, 26.5, 25.6, 25.3, 22.5, 13.9. Elemental analysis calcd. for $C_{67}H_{94}F_4N_2O_4$: C, 75.39; H, 8.88; N, 2.62 %. Found: C, 75.13; H, 8.61; N, 2.91 %. MS (MALDI-TOF): calcd. for $[M]^+$, 1066.71; found, 1066.30.

***N*,*N*'-Bis[6-[4-[4-(*trans*-4-pentylcyclohexyl)phenyl]phenyloxy]hexanoyl]-1,9-diaminono nane (1b).** A mixture of **6b** (0.320 g, 0.733 mmol) and thionyl chloride (10 mL, 0.14 mol) was refluxed with stirring for 3 h. The excess of thionyl chloride was removed under reduced pressure and the residue was dissolved in THF (10 mL). Then, 1,9-diaminononane (0.058 g,

0.366 mmol) and triethylamine (0.28 mL, 0.733 mmol) in THF (10 mL) were added dropwise to the THF solution of acid chloride at 0 °C. After the resulting mixture was stirred for 15 h at room temperatue, the solvent was evaporated. The residue was dissolved in chloroform and washed with a saturated NH_4Cl aqueous solution twice. The combined organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by silica gel chromatography (eluent: $CHCl_3$: methanol = 10 : 1) and washed with ethanol to give **1b** (0.216 g, 0.217 mmol) as a white solid in a yield of 62%. ^{1}H NMR ($CDCl_3$): δ = 7.43-7.50 (m, 8H), 7.25 (d, J = 6.8 Hz, 4H), 6.93 (d, J = 8.0 Hz, 4H), 5.44 (br, 2H), 3.98 (t, J = 6.3 Hz, 4H), 3.21-3.26 (m, 4H), 2.46-2.49 (m, 2H), 2.19 (t, J = 7.4 Hz, 4H), 0.88-1.93 (m, 66H). MS (MALDI-TOF): calcd. for $[M+H]^+$, 995.76; found, 995.32.

***N*-Pentyl-6-[2,3-difluoro-4-[4-(*trans*-4-pentylcyclohexyl)phenyl]phenyloxy]hexanamide (2a).** By following the synthetic procedure for **1a**, 0.20 g of compound **2a** (88%) as a white solid was prepared by using **6a** (0.20 g, 0.42 mmol) and pentylamine (37 mg, 0.42 mmol). ^{1}H NMR ($CDCl_3$): δ = 7.43 (d, J = 6.8 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.07-7.10 (m, 1H), 6.75-6.79 (m, 1H), 5.42 (s, 1H), 4.07 (t, J = 6.4 Hz, 2H), 3.22-3.27 (m, 2H), 2.51 (m, 1H), 2.21 (t, J = 7.2 Hz, 2H), 0.87-1.94 (m, 35H). ^{13}C NMR ($CDCl_3$): δ = 172.6, 147.4, 132.2, 128.5 (d, J = 3 Hz), 126.9, 123.4 (dd, J = 4, 4 Hz), 123.2 (d, J = 3 Hz), 109.4, 69.5, 44.3, 39.4, 37.3, 37.2, 36.6, 34.2, 33.5, 32.1, 29.3, 29.0, 28.8, 26.6, 26.5, 25.6, 25.3, 24.9, 22.5, 13.9. MS (MALDI-TOF): calcd. for $[M+H]^+$, 542.38; found, 542.19.

***N*-Pentyl-6-[4-[4-(*trans*-4-pentylcyclohexyl)phenyl]phenyloxy]hexanamide (2b).**
By following the synthetic procedure for **1a**, 0.23 g of compound **2b** (63%) as a white solid was prepared by using **6b** (0.31 g, 0.71 mmol) and pentylamine (0.12 g, 1.4 mmol). ^{1}H NMR ($CDCl_3$): δ = 7.43-7.50 (m, 4H), 7.25 (d, J = 6.8 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 5.44 (s, 1H), 3.98 (t, J = 6.4 Hz, 2H), 3.21-3.27 (m, 2H), 2.46-2.49 (m, 1H), 2.19 (t, J = 7.4 Hz, 2H), 0.87-1.94 (m, 35H). MS (MALDI-TOF): calcd. for $[M+H]^+$, 506.40; found, 506.49.

5,7-Dodecadiyne-1,12-dioyl bis[*N*-5-[2,3-difluoro-4-[4-(*trans*-4-pentylcyclohexyl)phenyl]phenyloxy]pentyl]amide (3). A mixture of **8** (0.444 g, 1.00 mmol), 5,7-dodecadiynedioic acid (0.145 g, 0.652 mmol), DMAP (24.2 mg, 0.198 mmol), EDC (0.587 g, 3.06 mmol) in CH_2Cl_2 (100 mL) was stirred at room temperature for 24 h. The solution was diluted with chloroform and washed with a saturated NH_4Cl aqueous solution. The organic layer was dried over anhydrous $MgSO_4$, filtered through a pad of Celite, and concentrated under reduced pressure in a light resistant container. The crude solid was purified by flash column chromatography on a silica gel

(eluent: chloroform : methanol = 10 : 1), followed by GPC to give **3** (70 mg, 0.065 mmol, 10%) as a white solid. ^{1}H NMR ($CDCl_3$): δ = 7.42 (d, J = 6.8 Hz, 4H), 7.30 (d, J = 6.8 Hz, 4H), 7.09 (m, 2H), 6.77 (m, 2H), 5.53 (br, 2H), 4.07 (t, J = 6.2 Hz, 4H), 3.29-3.30 (m, 4H), 2.50 (m, 2H), 2.28-2.33 (m, 8H), 0.90-1.90 (m, 58H). Elemental analysis calcd. for $C_{68}H_{88}F_4N_2O_4$: C, 76.09; H, 8.26; N, 2.61 %. Found: C, 75.84; H, 8.43; N, 2.64 %. MS (MALDI-TOF): calcd. for $[M]^+$, 1072.67; found, 1072.61.

FT-IR Studies. The IR spectra of the mixture of compound **1a** (47 mM) and dodecylbenzene in the gel state at room temperature (Figure S1a) and in the sol state at 175 °C (Figure S1b) were obtained to examine the hydrogen-bonded state of the amide groups of **1a**. The N-H stretching band of the amide groups at 3296 cm^{-1} for the gel state shifted to 3357 cm^{-1} for the sol state. The C=O stretching band changed from 1638 cm^{-1} for the gel state to 1682 cm^{-1} for the sol state. These results suggest that the amide N-H and C=O groups formed hydrogen bonds in the gel state.

Moreover, the IR spectra of the mixture of compound **2a** (8 mM) and dodecylbenzene were measured. The amide N-H stretching band seen at 3322 cm^{-1} for the gel state shifted to 3335 cm^{-1} for the sol state. The C=O stretching band shifted from 1644 cm^{-1} for the gel state to 1669 cm^{-1} for the sol state. Based on these results, it is assumed that the amide groups of **2a** were involved in hydrogen bonds in the gel state.

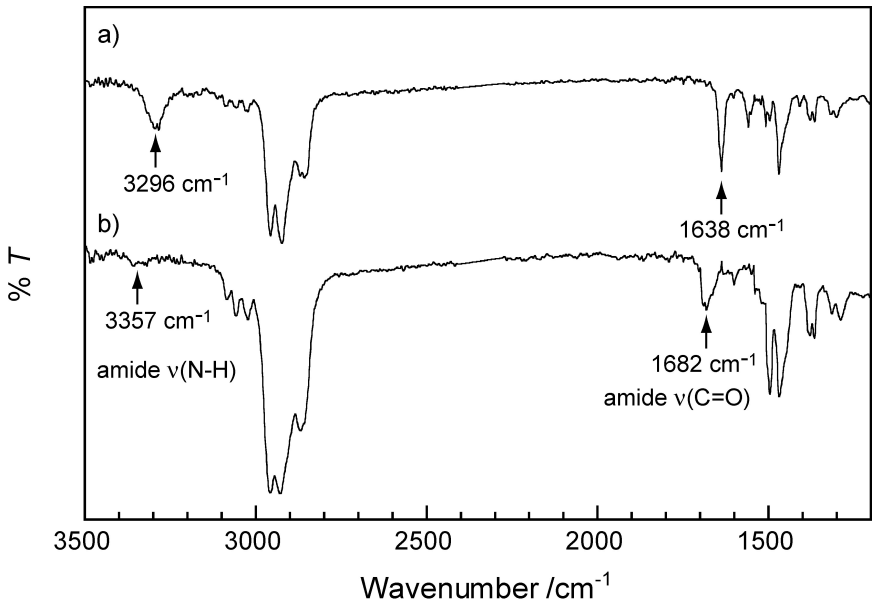


Figure S1. IR spectra of the mixture of **1a** and dodecylbenzene in the gel state at room temperature (a) and in the sol state at 175 °C (b).

Effects of the Concentration of 1a on the Electric Field-Alignment of Fibrous Aggregates. Aligned fibrous aggregates of **1a** in dodecylbenzene under an electric field (1.0 V/μm, 1 kHz) were obtained when the concentration of **1a** was in the range between 19 and 47 mM (Figure S2).

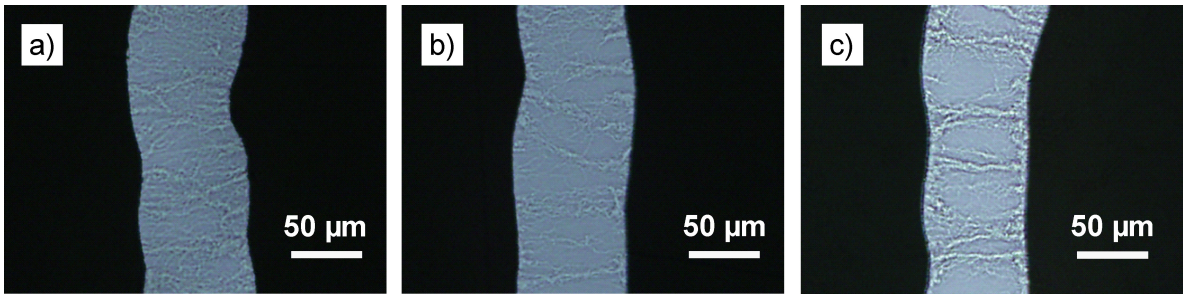


Figure S2. Optical microscopic images of the fibrous aggregates of **1a** in dodecylbenzene by applying an AC electric field (1.0 V/μm, 1 kHz). The concentration of **1a** in dodecylbenzene: (a) 19 mM; (b) 38 mM; (c) 47 mM.

Effects of Electric Fields on the Alignment of Molecular Aggregates for Compound 2a. Without electric fields, dispersed plate-like aggregates of **2a** were formed in dodecylbenzene when the sol solution of **2a** (32 mM) was cooled below 80 °C. The optical microscopic and SEM images are shown in Figure S3a and S3b, respectively. Upon application of AC electric fields, no oriented fibrous aggregates of **2a** were formed in dodecylbenzene (Figure S3c,d).

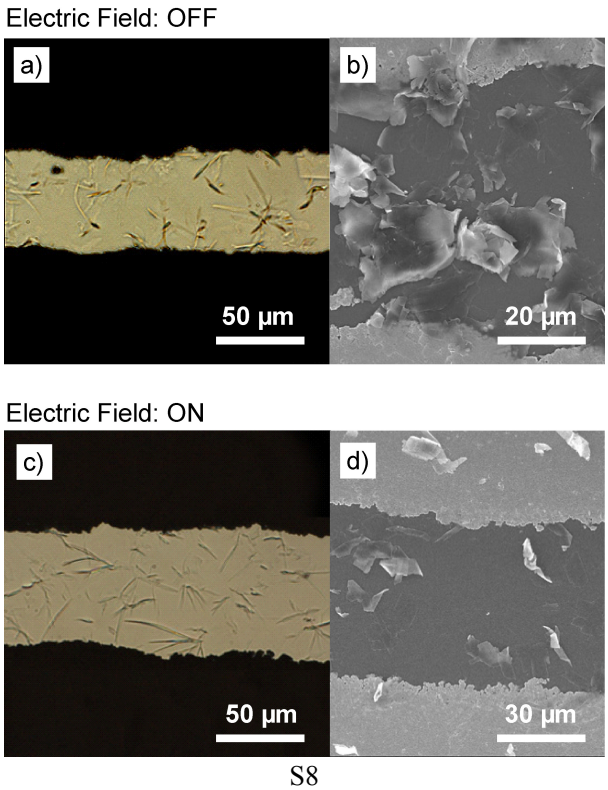


Figure S3. Optical microscopic images (a,c) and SEM images (b,d) of the plate-like aggregates of compound **2a** (32 mM) in dodecylbenzene: a,b) without electric fields, c,d) with an AC electric field (1.0 V/μm, 1 kHz).

Proposed Self-Assembled Structure of Compound 3 in the Fibrous Aggregates. The calculated extended molecular length of **3** is 6.4 nm (Figure S4). The X-ray diffraction pattern of the dodecylbenzene gel of **3** gave a weak peak at 2.9 nm (Figure S5). It is assumed that compound **3** also forms an interdigitated layered structure in the fibrous aggregates.

Figure S4. Molecular model of **3** with an extended conformation. The calculation was carried out using CS Chem3DPro employing MM2 energy minimization parameters.

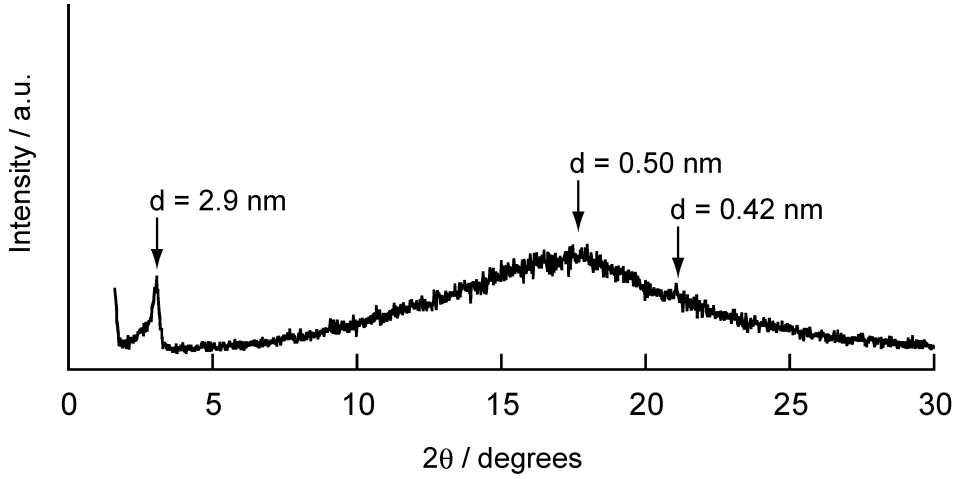


Figure S5. X-ray diffraction pattern of the dodecylbenzene gel of **3** (14 mM).

Photopolymerization of Fibrous Aggregates of 3. The UV-vis absorption spectra of the gel during UV irradiation are shown in Figure S6.

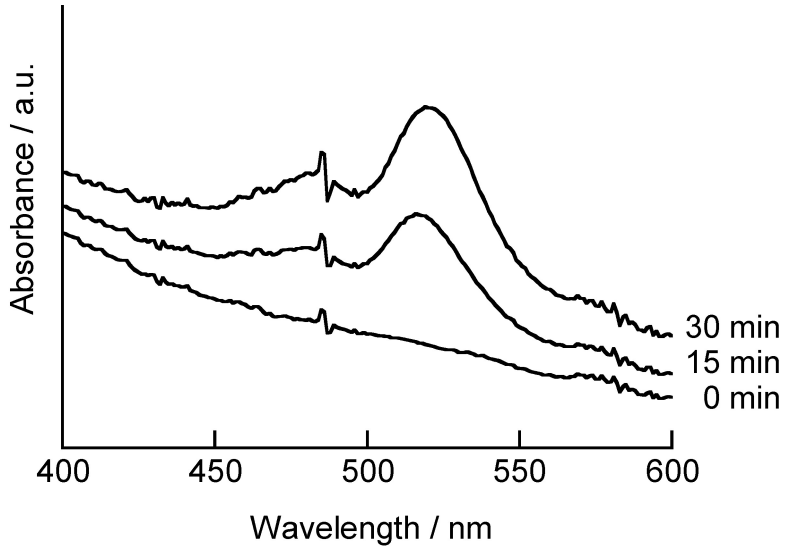


Figure S6. UV-vis absorption spectra of the dodecylbenzene gel of **3** (8 mM) during UV irradiation at room temperature.

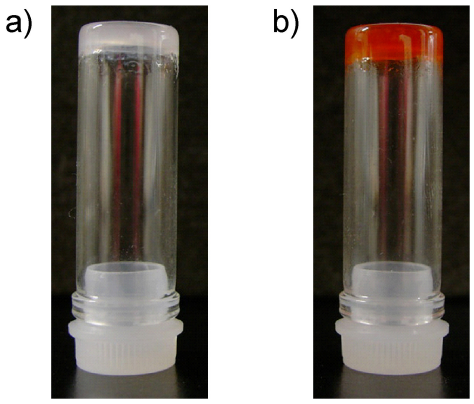


Figure S7. Photographs of the dodecylbenzene gels of **3** (8 mM): a) before UV irradiation; b) after UV irradiation.

Electric Field-Alignment of 2a and 2b in the Liquid-Crystalline States. In order to examine the effects of fluorine substituents on the electric field-alignment, we compared the alignment of liquid-crystalline compound **2a** with that of **2b** using a polarized optical microscope (Figures S8 and S9). The liquid-crystalline texture of **2a** in the SmA phase became dark when the sample in the isotropic state was cooled to the temperature at which the liquid-crystalline phase was formed under applying an AC electric field (1.0 V/μm, 1 kHz) (Figure S8a→b). The dark image in Figure S8b indicates that **2a** was oriented with its long axis perpendicular or parallel to the direction of applied electric field. The highest brightness was observed when the oriented sample of **2a** is in the angle of 45° (Figure S8c). On the other hand, the alignment of **2b** without fluorine substituents showed a smaller change compared to that of **2a** by the application of the AC electric field (Figure S9a→b). These results suggest that the fluorine substituents on the mesogen are effective for the electric field-alignment.

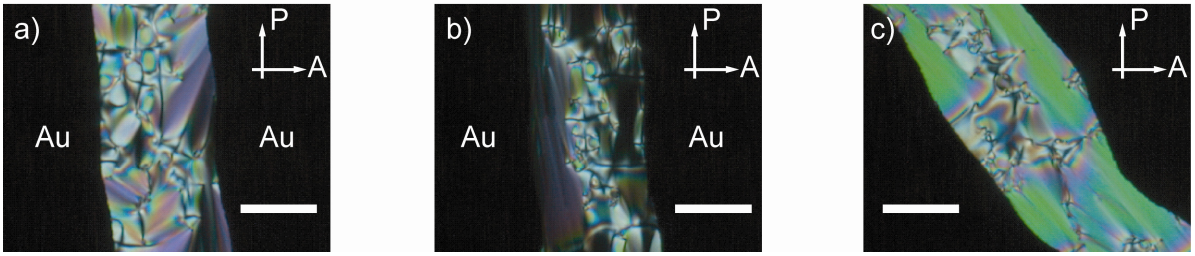


Figure S8. Polarized optical microscopic images of **2a** in the SmA phases at 140 °C: a) without applying an AC electric field; b) with applying an AC electric field (1.0 V/μm, 1 kHz); c) The sample was rotated by 45 degree from the position in the image of b). Scale bar indicates 50 μm. Directions of A: analyzer; P: polarizer.

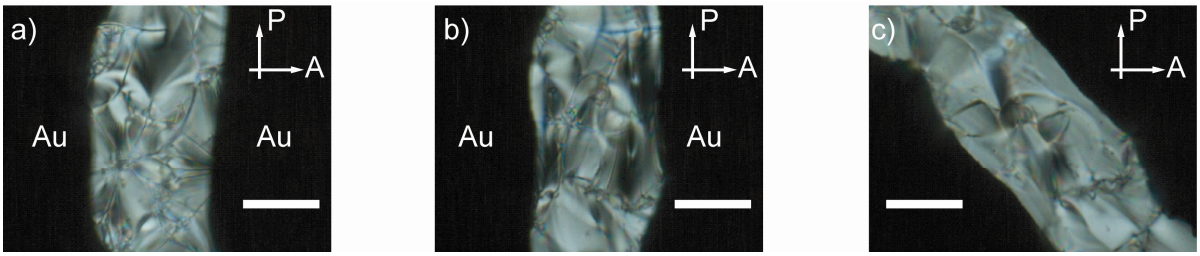


Figure S9. Polarized optical microscopic images of **2b** in the SmA phases at 170 °C: a) without applying an AC electric field; b) with applying an AC electric field (1.0 V/μm, 1 kHz); c) The sample was rotated by 45 degree from the position in the image of b). Scale bar indicates 50 μm. Directions of A: analyzer; P: polarizer.

References

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