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Supporting Information

Carrier transport characteristics of glass-forming chiral liquid crystalline dimers based on oligo(phenylenevinylene) units

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Synthesis of Materials

General

All reactions were performed under nitrogen atmosphere in a well-dried three-necked flask equipped with a magnetic stirring bar. Organic solvents and other chemicals were commercially available from Sigma-Aldrich, Tokyo Chemical Industry, Kanto Chemicals, and Fujifilm Wako Chemicals. Silica gel was purchased from Kanto Chemicals. All purchased materials were used as received. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Varian UNITY INOVA 400NB spectrometer. Fourier transform infrared (FT/IR) spectra were determined using Perkin-Elmer Spectrum 3 FTIR. Compound **6** was synthesized by the procedure reported previously.¹

Characterization of mesophases

The mesophase structures were characterized by polarizing optical microscopy and X-ray diffraction (Rigaku Rapid II, Cu K α 1). An optical texture of a N* phase was studied using a polarized light microscope (Olympus DP70) equipped with a hand-made hot stage. The phase transition temperature and the transition enthalpy were determined with differential scanning calorimetry (DSC) using NETZSCH Maia DSC 200 F3.

Synthetic procedures and spectral data



Scheme S1 Synthetic route of compounds 1 and 2

4-[((E)-4"-decyloxyphenylethenyl)-(E)-(2',5'-diethoxyphenyl)]-1-benzaldehyde (7) :

In a round-bottomed flask, 4-bromobenzaldehyde (2.06 g, 11.1 mmol), (*E*)-4-decyloxy-2',5'diethoxy-4'-vinyl-stilbene (**6**) (6.0 g, 13.3 mmol), Pd(OAc)₂ (0.102 g, 0.44 mmol), and K₃PO₄ (2.735 g, 12.9 mmol) ware dissolved in dry DMF. The solution was stirred at 90 °C for overnight under nitrogen. The precipitate was filtered through Celite and washed with ethyl acetate. The filtrate was poured into aqueous NH₄Cl solution (150 mL) the solvent was removed on a rotary evaporator. The blown precipitate was filtered and washed with a large amount of water to reduce the remaining DMF. The residue was dissolved in dichloromethane, and dried over Na₂SO₄ and filtered, and the solvent was removed on a rotary evaporator. The brown precipitate was purified by silica gel column chromatography (eluent: dichloromethane/hexane = 2/1; v/v). The yellow solid was suspended with methanol, filtered, and washed with methanol. A yellow solid (4.6 g) was obtained in the yield of 75%.

¹H-NMR (400 MHz, CDCl₃) : δ = 9.98 (s, 1H), 7.86 (d, 2H, *J* = 8.4 Hz), 7.66 (d, 2H, *J* = 8.4 Hz), 7.63 (d, 1H, *J* = 16.4 Hz), 7.47 (d, 2H, *J* = 8.8 Hz), 7.34 (d, 1H, *J* = 16.4 Hz), 7.15 (d, 1H, *J* = 16.4 Hz), 7.12 (s, 2H), 7.10 (d, 1H, *J* = 16.4 Hz), 6.89 (d, 2H, *J* = 8.8 Hz), 4.15 (q, 2H, *J* = 6.93 Hz), 4.12 (q, 2H, *J* = 6.93Hz), 3.96 (t, 2H, *J* = 6.8Hz), 1.79 (quin, 2H, *J* = 7.1Hz), 1.54-1.21 (m, 20H), 0.89 (t, 3H, *J* = 7.0 Hz) ppm. FT-IR (ATR): v = 2923, 2853, 1694, 1590, 1509, 1474, 1421, 1391, 1346, 1305, 1291, 1241, 1202, 1165, 1110, 1048, 1018, 962, 850, 811, 722 cm⁻¹. Chemical Formula: C₃₇H₄₆O₄; Exact Mass: 554.34; Molecular Weight: 554.77; [M⁺]: 554.26.



Figure S1¹H NMR spectrum of compound 7

1-ethenyl-[4-[(*E*)-2-(2',5'-diethoxyphenyl)ethenyl]-4'-[(*E*)-2-[4"-(decyloxyphenyl)]ethenyl] benzene (8) :

In the round-bottomed flask, 4-[((*E*)-4"-decyloxyphenylethenyl)-(*E*)-(2',5"-diethoxyphenyl)]-1benzaldehyde (3.85 g, 6.93 mmol), methyltriphenylphosphonium bromide (3.07 g, 8.6 mmol), *t*-BuOK (0.96 g, 8.6 mmol) ware dissolved in dry THF(50 ml). The solution was stirred at 80 °C for 6 hours under nitrogen. The yellow solution was concentrated and poured into ethyl acetate (10 % v/v) in *n*-hexane. Triphenylphosphine oxide was filtered off and washed with *n*-hexane. The filtrate was concentrated. The residue was purified by silica gel column chromatography (eluent: dichloromethane/hexane = 1/3; v/v). A yellow solid (2.7 g) was obtained in the yield of 70%.

¹H-NMR (400 MHz, CDCl₃) : δ = 7.51-7.45 (ddd, 5H, *J* = 8.4, 16.8, 8.4 Hz), 7.40 (d, 2H, *J* = 8.0 Hz), 7.33 (d, 1H, *J* = 16.4 Hz), 7.11 (s, 1H), 7.10 (d, 2H, *J* = 17.6 Hz), 7.07 (d, 2H, *J* = 16.4 Hz), 6.89 (d, 2H, *J* = 8.8 Hz), 6.72 (dd, 1H, *J* = 10.8, 17.6 Hz), 5.76 (dd, 1H, *J* = 0.8, 17.6 Hz), 5.24 (dd, 1H, *J* = 0.8, 10.8 Hz), 4.13 (q, 2H, *J* = 6.93 Hz), 4.12 (q, 2H, *J* = 6.93Hz), 3.97 (t, 2H, *J* = 10.8 Hz), 1.79 (quin, 2H, *J* = 7.1 Hz), 1.51-1.23 (m, 20H), 0.89 (t, 3H, *J* = 6.8 Hz) ppm. FT-IR (ATR): *v* = 2919, 2851, 1606, 1511, 1470, 1421, 1392, 1344, 1290, 1241, 1199, 1178, 1109, 1044, 965, 911, 854, 821 cm⁻¹. Chemical Formula: C₃₈H₄₈O₃; Exact Mass: 552.36; Molecular Weight: 552.80; [M⁺]: 552.28.



Figure S2¹H NMR Spectrum of compound 8

5,5'-((1E,1'E)-(((1E,1'E)-((((S)-propane-1,2-diyl)bis(oxy))bis(4,1-phenylene))bis(ethene-2,1-diyl))bis(4,1-phenylene))bis(ethene-2,1-diyl))bis(2-((E)-4-(decyloxy)styryl)-1,4-diethoxybenzene)(1):

In a round-bottomed flask, (*R*)-1,2-bis(4-bromophenoxy)-propane (0.278 g, 0.72 mmol), 1-ethenyl-[4-[(*E*)-2-(2',5'-diethoxyphenyl)ethenyl]-4'-[(*E*)-2-[4''-(dethoxyphenyl)]ethenyl]benzene (0.78 g, 1.6 mmol), Pd(OAc)₂ (0.0135 g, 0.058mmol) \cdot tri-(*o*-tolyl)phosphine (0.054 g, 0.17mmol) ware dissolved in triethylamine (15ml) and dry THF (35 ml). The solution was refluxed for 3 days under nitrogen and then allowed to room temperature. The resulting solution was poured into NH₄Cl solution (50 ml) and water (50 ml) and extracted with dichloromethane a few times. The organic phase was dried over Na₂SO₄. After sodium sulfate was filtered off, the solvent was removed on a rotary evaporator. The residue was purified by silica gel column chromatography (eluent: dichloromethane/hexane = 3/7; v/v). A yellow solid (0.12 g) was obtained in the yield of 12%.

¹H-NMR (400 MHz, CDCl₃) : δ = 7.51 (d, 4H, J = 8.8 Hz), 7.49 (d, 2H, J = 16.4 Hz), 7.47 (d, 4H, J = 16.4 Hz), 7.47 (d, 4H,

8.8 Hz), 7.46 (d, 4H, J = 8.8 Hz), 7.42-7.43 (m, 4H),7.34 (d, 2H, J = 16.0 Hz), 7.10 (d, 2H, J = 15.2 Hz), 7.113 (s, 4H), 7.07 (d, 2H, J = 16.4 Hz), 6.98 (d, 2H, J = 16.4 Hz), 6.97 (d, 2H, J = 16.4 Hz), 6.95 (d, 2H, J = 8.8 Hz), 6.91 (d, 2H, J = 8.8 Hz), 6.89 (d, 4H, J = 8.8 Hz), 4.76 (ddt, 1H, J = 2.4, 5.2, 6.6 Hz), 4.19 (dd, 1H, J = 2.4, 6.9 Hz), 4.13 (q, 4H, J = 6.9 Hz), 4.12 (q, 4H, J = 7.1 Hz), 4.04 (dd, 1H, J = 5.2, 6.9 Hz), 3.96 (t, 4H, J = 6.6 Hz), 1.79 (quin, 4H, J = 7.1 Hz), 1.52-1.23 (m, 43H), 0.89 (t, 6H, J = 6.8 Hz) ppm. FT-IR (ATR): v = 2920, 2851, 1605, 1511, 1471, 1421, 1392, 1291, 1239, 1200, 1109, 1045, 959, 851, 819 cm⁻¹. Chemical Formula: C₉₁H₁₀₈O₈; Exact Mass: 1328.80; Molecular Weight: 1329.86; [M⁺]: 1329.06. Elemental Analysis (%) calculated for C₉₁H₁₀₈O₈: C, 82.19; H, 8.19; O, 9.62; found: C, 82.51; H, 8.21.



Figure S3 ¹H NMR spectrum of compound 1.

5,5'-((1E,1'E)-(((1E,1'E)-((((S)-propane-1,2-diyl)bis(oxy))bis(3-(trifluoromethyl)-4,1-phenyl ene))bis(ethene-2,1-diyl))bis(4,1-phenylene))bis(ethene-2,1-diyl))bis(2-((E)-4-(decyloxy)styryl)-1,4-diethoxybenzene) (2) :

In a round-bottomed flask, (*S*)-1,2-bis(4-bromo-2-trifluoromethylphenoxy)-propane (0.43 g, 0.823 mmol), 1-ethenyl-[4-[(*E*)-2-(2',5'-diethoxyphenyl)ethenyl]-4'-[(*E*)-2-[4"-(dethoxyphenyl)]ethenyl] benzene (1.02 g, 1.8 mmol), Pd(OAc)₂ (0.006 g, 0.028mmol) and K₃PO₄ (g, 12.9 mmol) ware dissolved in dry DMF (100ml). The solution was refluxed for 3 days under nitrogen and then allowed to room temperature. The resulting solution was poured into water (50 ml) and extracted with dichloromethane a few times. The organic phase was dried over Na₂SO₄. After sodium sulfate was filtered off, the solvent was removed on a rotary evaporator. The residue was purified by silica gel column chromatography (eluent: dichloromethane/hexane = 3/7; v/v). A yellow solid (0.055 g) was obtained in the yield of 4.9%.

¹H-NMR (400 MHz, CDCl₃) : δ = 7.72 (m, 2H), 7.61 (m, 2H), 7.55-7.43 (m, 14H), 7.33 (d, 2H, *J* = 16.3 Hz), 7.16-6.97 (m, 14H), 6.88 (d,4H, *J* = 8.8 Hz), 4.92 (dt, 1H, *J* = 2.4, 6.5 Hz), 4.19 (dd, 1H, *J* = 5.9 Hz), 4.18-4.05 (m, 9H), 3.97 (t, 4H, *J* = 6.68 Hz), 1.78 (quin, 4H, *J* = 7.78 Hz), 1.52-1.19 (m,

43H), 0.89 (t, 6H, J = 6.9 Hz) ppm. FT-IR (ATR): v = 2995, 2923, 1609, 1511, 1246, 1130, 1050, 958, 817, 523 cm⁻¹. Elemental Analysis (%) calculated for C₉₃H₁₀₆F₆O₈: C, 76.20; H, 7.29; F, 7.78; O, 8.73; found: C, 76.58; H, 7.17.



Figure S3 ¹H NMR Spectrum of compound **2**.





Figure S4 Polarizing optical micrographs in the N* phase of (a) compound **1** at 175 °C, (b) compound **2** at 180 °C, and (c) compound **3** at 130 °C.



Figure S5 Polarizing optical micrographs of the mixture of compounds 1-3 (molar ratio of 1:2:3 = 4:2:3) (a) at 170 °C and (b) at 27 °C.

Reference

1) E. Shimaoka, M. Kunihiro, M. Funahashi, ACS Appl. Polym. Mater., 4, 565-574 (2022).