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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. <sup>1</sup>H and <sup>13</sup>C 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.<sup>1</sup>

#### **Characterization of mesophases**

The mesophase structures were characterized by polarizing optical microscopy and X-ray diffraction (Rigaku Rapid II, Cu K $\alpha$ 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)<sub>2</sub> (0.102 g, 0.44 mmol), and K<sub>3</sub>PO<sub>4</sub> (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 NH<sub>4</sub>Cl 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 Na<sub>2</sub>SO<sub>4</sub> 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%.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) :  $\delta$  = 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<sup>-1</sup>. Chemical Formula: C<sub>37</sub>H<sub>46</sub>O<sub>4</sub>; Exact Mass: 554.34; Molecular Weight: 554.77; [M<sup>+</sup>]: 554.26.



Figure S1<sup>1</sup>H 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%.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) :  $\delta$  = 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<sup>-1</sup>. Chemical Formula: C<sub>38</sub>H<sub>48</sub>O<sub>3</sub>; Exact Mass: 552.36; Molecular Weight: 552.80; [M<sup>+</sup>]: 552.28.



Figure S2<sup>1</sup>H 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)<sub>2</sub> (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 NH<sub>4</sub>Cl solution (50 ml) and water (50 ml) and extracted with dichloromethane a few times. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. 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%.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) :  $\delta$  = 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<sup>-1</sup>. Chemical Formula: C<sub>91</sub>H<sub>108</sub>O<sub>8</sub>; Exact Mass: 1328.80; Molecular Weight: 1329.86; [M<sup>+</sup>]: 1329.06. Elemental Analysis (%) calculated for C<sub>91</sub>H<sub>108</sub>O<sub>8</sub>: C, 82.19; H, 8.19; O, 9.62; found: C, 82.51; H, 8.21.



Figure S3 <sup>1</sup>H 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)<sub>2</sub> (0.006 g, 0.028mmol) and K<sub>3</sub>PO<sub>4</sub> (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 Na<sub>2</sub>SO<sub>4</sub>. 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%.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) :  $\delta$  = 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<sup>-1</sup>. Elemental Analysis (%) calculated for C<sub>93</sub>H<sub>106</sub>F<sub>6</sub>O<sub>8</sub>: C, 76.20; H, 7.29; F, 7.78; O, 8.73; found: C, 76.58; H, 7.17.



Figure S3 <sup>1</sup>H 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).