

Supplementary files

Enhancement of Spontaneous Polarization and Acid Vapor-Induced Polymerization in the Thin-Film States of Phenylterthiophene Derivative Bearing a Cyclotetrasiloxane Ring

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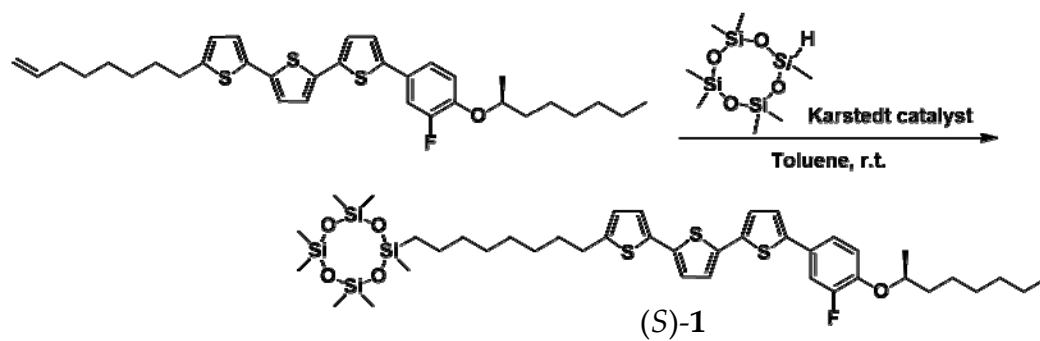
S-3. Evaluation of ferroelectric properties of (S)-1

S-1. Synthetic procedure and spectral data

5-{8-(1,3,3,5,5,7,7-Heptamethyl-1,3,5,7-cyclotetrasiloxan-1-yl)octane-1-yl}-5''-{4-(2-(S)-octyloxy)}-3-fluorophenyl}-2,2'-5',2''-terthiophene: (S)-1

A total of 0.50 g of 5-(7-Octenyl)-5''-{4-(2-(S)-octyloxy)}-3-fluorophenyl}-2,2'-5',2''-terthiophene (0.86 mmol) and 0.32 g of 1,3,3,5,5,7,7-heptamethyl-1,3,5,7-cyclotetrasiloxane (1.12 mmol) were dissolved in toluene (30 mL) and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane platinum(0) (xylene solution (2.1 mol%), 10 μ L) was added to the solution. The reaction mixture was stirred overnight at room temperature. After the solvent was evaporated under reduced pressure, the resultant residue was purified by a silica gel column chromatography (eluent: *n*-hexane/toluene = 5/1; v/v). Recrystallization from *n*-hexane afforded yellow solid weighing 0.54 g (0.63 mmol) in the yield of 73%.

¹H-NMR (400 MHz, CDCl₃) : δ (ppm) = 7.31 (dd, 1H, *J* = 12.0, 2.4 Hz), 7.26 (ddd, 1H, *J* = 8.5, 2.3, 0.9 Hz), 7.09 (quintet, 2H, *J* = 3.2 Hz), 7.06 (d, 1H, *J* = 4.0 Hz), 6.99 (dd, 2H, *J* = 6.0, 3.6 Hz), 6.95 (d, 1H, *J* = 8.4 Hz), 6.68 (d, 1H, *J* = 3.6 Hz), 4.37 (sext, 1H, *J* = 5.1 Hz), 2.79 (t, 2H, *J* = 7.6 Hz), 1.75-1.84 (m, 1H), 1.56-1.72 (m, 5H), 1.25-1.53 (m, 19H), 0.89 (t, 3H, *J* = 6.8 Hz), 0.53 (br-t, 2H, *J* = 7.8 Hz), 0.09 (s, 18H), and 0.07 (s, 3H); IR (ATR) (cm⁻¹): ν = 2961, 2923, 2854, 1545, 1523, 1507, 1444, 1378, 1300, 1258, 1056, 941, 854, 790, 696, 533, and 477. Elemental analysis calcd (%) for C₄₁H₆₃FO₅Si₄: C 57.03, H 7.35; found: C 57.31 and H 7.25.



Scheme S1. Synthetic route of compound (S)-1.

S-2. Characterization of mesomorphism of (S)-1

S-2.1. DSC thermogram of (S)-1

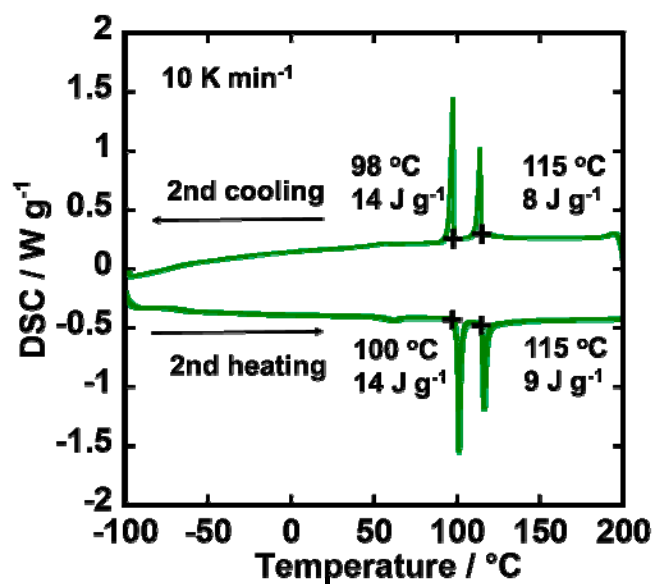


Figure S1. DSC thermogram of compound (S)-1 at scanning rates of 10 K/min.

S-2.2. X-Ray Diffraction Patterns of (S)-1

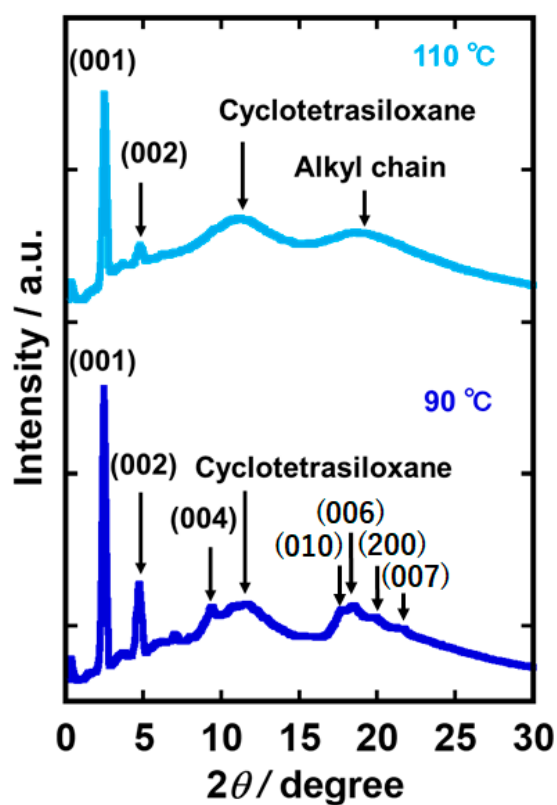


Figure S2. X-ray diffraction patterns of compound (S)-1 in the (a) SmC* phase at 110 °C, and (b) SmG* phase at 90 °C.

S-2.3. Polarizing Optical Micrographs of (S)-1

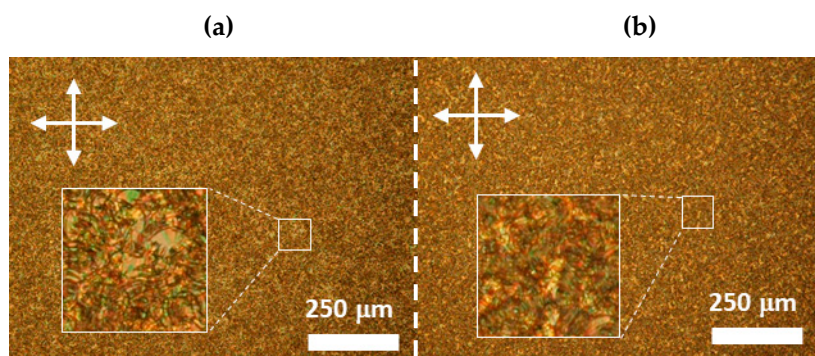


Figure S3. Polarizing optical micrographs of compound (S)-1 in the (a) SmC* phase at 110 °C, and (b) SmG* phase at 90 °C. The liquid crystal (LC) samples were filled in an indium tin oxide (ITO) sandwich cell with the gap of 2 μm.

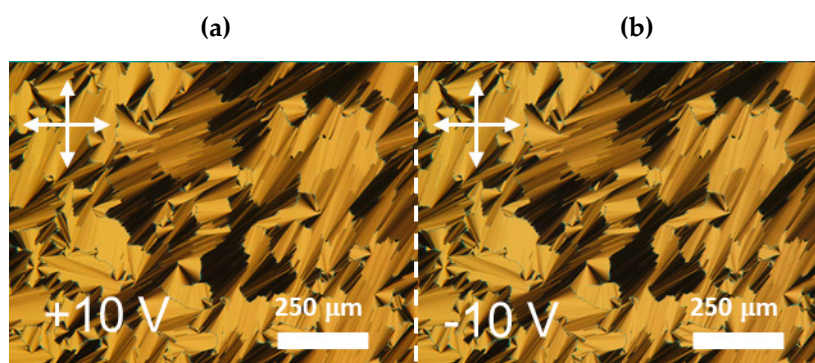


Figure S4. Polarizing optical micrographs of compound (S)-1 in the SmC* phase at 110 °C under the application of DC bias. The DC voltage was applied (a) to backward direction (+10 V) and (b) to forward direction (−10 V). The LC samples were filled in an ITO sandwich cell with the gap of 2 μm.

The stripes in the SmC* domains disappeared when a DC bias was applied to the LC cell. Clear broken fan-like textures were observed (Figure S4a,b). The obtained broken fan-like textures were similar to that in an achiral SmC phase. The texture change supported the reorientation of the LC molecules to form the polarized state.

S-3. Evaluation of Ferroelectric Properties of (S)-1

S-3.1. Determination of Spontaneous Polarization in the Polarization Inversion Current Method for (S)-1

We mathematically estimated the value of spontaneous polarization (P_s) according to following equations, where t_{on} is the time of peak onset, t_{off} is the time of peak offset, and $i(t)$ is a current as a function of time (t).

$$P_s = \frac{1}{2} \int_{t_{on}}^{t_{off}} i(t) dt \quad (\text{Equation. S1})$$



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