Journal of Materials Chemistry C



View Article Online

View Journal | View Issue

PAPER



Cite this: J. Mater. Chem. C, 2015, **3**, 1982

Ferroelectric liquid-crystalline semiconductors based on a phenylterthiophene skeleton: effect of the introduction of oligosiloxane moieties and photovoltaic effect[†]

Yusuke Funatsu,^a Akinari Sonoda^b and Masahiro Funahashi*^a

Ferroelectric liquid-crystalline phenylterthiophene derivatives bearing a decenyl group, disiloxane chain, and cyclotetrasiloxane ring were synthesized. These compounds exhibited a chiral smectic C (SmC*) phase. The spontaneous polarizations of the compounds exceeded 50 nC cm⁻². The hole mobilities determined by the time-of-flight method were in the order of 1×10^{-4} cm² V⁻¹ s⁻¹. The compound with a decenyl group exhibited an anomalous photovoltaic effect in the SmC* phase although the conversion efficiency was lower than 0.01%. Notably, even the compound bearing a bulky cyclotetrasiloxane ring exhibited an enantiotropic SmC* phase.

Received 31st July 2014 Accepted 14th December 2014

DOI: 10.1039/c4tc01690d

www.rsc.org/MaterialsC

Introduction

Liquid-crystalline (LC) semiconductors exhibit high carrier mobilities exceeding 0.1 cm² V⁻¹ s⁻¹.¹ The close and ordered molecular packing structures in LC phases enhance the electronic charge carrier transport in columnar² and smectic phases.³ Solution-processable LC oligothiophene and fluorene derivatives have been applied in field-effect transistors (FETs)⁴ and polarized electroluminescence devices,⁵ respectively. Solar cells based on LC phthalocyanine and LC diketopyrrolopyrrole have also been reported.⁶ LC semiconductors are soft and consequently more suitable for flexible devices than crystalline semiconductors.^{4e}

Moreover, the introduction of proper side chains and functional groups into the π -conjugated cores of LC semiconductors promotes nanosegregation.^{7a,b} Three-dimensional network structures are formed in the bicontinuous cubic phase of oligothiophene, which has a polycatenar structure.^{7e} LC phenylterthiophene derivatives bearing imidazolium moieties exhibit electrochromism in the smectic phase.^{7d,e} Perylene tetracarboxylic bisimide derivatives bearing oligosiloxane moieties exhibit nanosegregated columnar and lamellar phases at room temperature.⁸

Some chiral LC molecules exhibit a ferroelectric chiral smectic C (SmC*) phase.^{9a,b} In the SmC* phase, the LC

molecules tilt from the layer normal and form a helical structure without an electric field. Under a DC bias, the helical structure disappears and the molecular dipoles orient in the direction of the electric field, resulting in spontaneous polarization. By reversing the polarity of the electric field, the director of the LC molecules can be rapidly changed.^{9c} LC applications in displays have been studied extensively.^{9d}

LC semiconductors exhibiting a SmC* phase are expected to facilitate novel electronic functions based on coupling between electronic charge carrier transport and internal electric fields, based on their ferroelectricity. The first example of a ferroelectric LC semiconductor was reported by Hanna and Funahashi.¹⁰ However, the spontaneous polarization was lower than 1 nC cm⁻². No phenomena brought on by the synergism between carrier transport and ferroelectricity have been observed in ferroelectric LCs.

In this study, we synthesized LC phenylterthiophene derivatives exhibiting SmC* phases, with spontaneous polarization exceeding 100 nC cm⁻² and an effective hole mobility in the order of 10^{-4} cm² V⁻¹ s⁻¹. An LC phenylterthiophene derivative bearing a 1,3,3,5,5,7,7-heptamethylcyclotetrasiloxane ring also exhibited an enantiotropic SmC* phase. We observed an anomalous photovoltaic effect based on the coupling of hole transport and ferroelectricity in the SmC* phase.

Anomalous photovoltaic effects are exhibited by semiconductors showing ferroelectricity.^{11a} In the presence of internal electric fields, which are formed by spontaneous polarization, excitons generated by illumination dissociate to produce holes and electrons. They are transported to the electrodes by the internal electric field, resulting in photovoltaic effects without the application of any external voltage.

^aDepartment of Advanced Materials Science, Faculty of Engineering, Kagawa University, 2217-20 Hayashi-cho, Takamatsu, Kagawa 761-0396, Japan. E-mail: m-funa@eng.kagawa-u.ac.jp; Fax: +81-87-864-2411; Tel: +81-87-864-2411

^bHealth Research Institute, National Institute of Advanced Industrial Science and Technology, 2217-14 Hayashi-cho, Takamatsu, Kagawa 761-0395, Japan

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c4tc01690d

Anomalous photovoltaic effects have been observed in ferroelectric ceramics and their applications in solar cells have been proposed because solar cells can produce higher voltages than their band gaps.^{11a-c} However, reports regarding these effects in organic materials have been quite limited. Sasabe and co-workers studied the photovoltaic effect of dye-doped poly-vinylidene fluoride, which is a typical ferroelectric polymer.^{11d} The density of the dye was very low and the resulting photo-current was very small.^{12a} Tasaka and co-workers observed an anomalous photovoltaic effect in the ferroelectric crystals of a triphenylene derivative.^{12b} In this study, the sample was composed of vacuum-deposited crystalline thin films.

In addition to conventional ferroelectric LC phases consisting of chiral rod-like molecules, achiral bent-cores^{13*a*-*c*} and columnar LC compounds^{13*d*-*f*} exhibit ferroelectricity in soft mesophases. Ferroelectric switching currents based on polarization inversion and second harmonic generation have been observed. However, anomalous photovoltaic effects have not been confirmed in ferroelectric LC phases.

Experimental section

Characterization of LC phases

The mesomorphic properties of the phenylterthiophene derivatives were studied by differential scanning calorimetry (DSC), polarizing optical microscopy, and X-ray diffraction (XRD). A polarizing optical microscope (Olympus DP70) equipped with a hand-made hot stage was used for the visual observation of optical textures. DSC measurements were conducted on a NETZSCH DSC 204 Phoenix. XRD measurements were carried out on a Rigaku Rapid II diffractometer using Ni-filtered CuKα radiation.

Characterization of carrier transport and spontaneous polarization

Electron mobilities were measured by the time-of-flight (TOF) method.14 A liquid crystal cell was fabricated by combining two ITO-coated glass plates. The cell was placed on a hot stage and heated at 125 °C. LC samples were melted and filled into the cell via a capillary. The cells were cooled at a rate of 0.1 degree min⁻¹. The liquid crystal cell was placed on the hot stage of the TOF setup, a DC voltage was applied to the cell using an electrometer (ADC R8252) and a pulse laser was illuminated on the cell. The excitation source was the third harmonic generation of an Nd:YAG laser (Continuum MiniLite II, wavelength = 356 nm, pulse duration = 2 ns) and the induced displacement currents were recorded using a digital oscilloscope (Tektronics TDS 3044B) through a serial resistor. In order to obtain nondispersive transient photocurrent curves, the penetration depth of the laser light has to be sufficiently thinner than the sample thickness. The penetration depths for the three compounds were estimated to be less than 500 nm from the absorption spectra (Fig. S1 in ESI[†]).

Spontaneous polarization was measured by the triangular wave and Sawyer Tower methods. Triangular waves generated by a function generator (NF WF1973) were applied to the LC cells. Induced currents were recorded using a digital oscilloscope (Tektronics TDS 3044B) through a serial resistor or a serial capacitor.

Synthesis of materials

All the ¹H and ¹³C NMR spectra were recorded on a Varian UNITY INOVA400NB spectrometer. FTIR measurements were conducted on a JASCO FT/IR-660 Plus spectrometer. 4-Bromo-2-fluorophenol and (*S*)-2-octanol were purchased from Tokyo Chemical Industry. 5-Bromobithiophene was available from Aldrich-Sigma Inc. 1,1,1,3,3-Pentamethyl-1,3-disiloxane, 1,3,3,5,5,7,7-heptamethyl-1,3,5,7-cyclotetrasiloxane, and the Karstedt catalyst were purchased from Gelest Inc. Tetrahydrofuran, toluene, and dimethoxyethane were obtained from Wako Pure Chemical Industries and were used without purification. Silica gel was purchased from Kanto Chemicals.

LC phenylterthiophene bearing linear alkyl chains exhibit ordered smectic phases at room temperature. Homogenous thin films can be produced by spin-coating and they can be applied in field-effect transistors.^{4b} TOF measurements revealed band-like hole transport in the ordered smectic phase.^{3h}

Ferroelectric phenylterthiophene derivative **1** bearing a chiral alkyl chain was designed. A fluorine atom substituted on the phenyl ring increases spontaneous polarization. Another functional group can be introduced *via* the double bond at the terminus of the alkyl chain.

Compound **1** was synthesized as shown in Scheme 1. Phenyl ether **4** was obtained from 4-bromo-2-fluorophenol by Mitsunobu reaction.^{15a} Compound **4** was converted to phenyl boric acid ether **5** using Grignard reagent. Boric acid **5** was reacted with 5-bromobithiophene *via* Suzuki coupling^{15b} to produce the chiral phenylbithiophene derivative **6**. Compound **6** was brominated *via* the reaction with *N*-bromosuccinimide to afford compound **7**, which was coupled with a



2-decenylthienyl boric acid derivative *via* Suzuki coupling catalyzed by a palladium(0) complex to afford the chiral phenylterthiophene derivative **1**.

Conventional liquid crystals bear alkyl side chains of which thermal motion moderately weakens the strong intermolecular interaction between the aromatic cores. A few liquid crystals bearing oligosiloxane moieties have been investigated.¹⁶ Silsesquioxane derivatives bearing rod-like mesogens exhibit smectic phases.^{16a,b} Smectic liquid crystals bearing trisiloxane and disiloxane chains at the ends of their alkyl side chains have been synthesized.^{16c,d} They exhibit smectic phases stabilized by the nanosegregation of the oligosiloxane chains. This effect is also seen in bent-core ferroelectric LCs.^{16e} Recently, perylene tetracarboxylic bisimide (PTCBI) derivatives bearing oligosiloxane chains that exhibit columnar phases have been reported.⁸ PTCBI derivatives bearing tetracyclosiloxane rings also exhibit columnar phases. Nanosegregation of oligosiloxane moieties is a significant factor in the formation of columnar phases.^{8d}

In addition to compound **1**, we synthesized chiral phenylterthiophene derivatives **2** and **3** bearing a 1,1,1,3,3-pentamethyl-1,3-disiloxane chain and a 1,3,3,5,5,7,7-heptamethyl-1,3,5,7-cyclotetrasiloxane ring, respectively. The introduction of the oligosiloxane moieties onto the termini of the alkyl side chains was carried out by hydrosilylation using the Karstedt catalyst,¹⁷ as shown in Scheme 2.

2-(R)-(4-Bromo-2-fluorophenyloxy)octane (4)

4-Bromo-2-fluorophenol (5.83 g, 30 mmol), (*S*)-2-octanol (3.90 g, 30 mmol), and triphenylphosphine (7.88 g, 30 mmol) were dissolved in toluene (50 mL). A solution of diethylazodicarboxylate (2.2 mol L⁻¹, 15 mL) in toluene was added to the mixture for over 30 min at 0 °C. The solution was stirred at room temperature for 3 h. Then, *n*-hexane (50 mL) was added to the reaction mixture, and the produced white precipitates were filtered. The solvent was evaporated under reduced pressure, and the residual oil was purified by silica gel column chromatography (eluent: *n*-hexane). A pale yellow oil (8.32 g, 27 mmol) was obtained in 90% yield.





Me₃SiOSiMe₂H

Scheme 2 Synthetic route of chiral phenylterthiophene derivatives bearing oligosiloxane moieties.

¹H NMR (400 MHz, CDCl₃): δ = 7.21 (dd, 1H, *J* = 10.8, 2.4 Hz), 7.14 (ddd, 1H, *J* = 8.8, 2.4, 1.2 Hz), 6.82 (t, 1H, *J* = 8.8 Hz), 4.28 (sext, 1H, *J* = 6.0 Hz), 1.71–1.80 (m, 1H), 1.52–1.60 (m 1H), 1.45–1.21 (m, 8H), 1.27 (3H, d, *J* = 6.0 Hz), 0.86 (t, 3H, *J* = 7.2 Hz); IR (ATR): ν = 2927, 2855, 1581, 1491, 1467, 1409, 1378, 1302, 1263, 1206, 1130, 1115, 1035, 973, 939, 854, 800, 724, 638, 573, 452, 401 cm⁻¹; elemental analysis calcd (%) for C₁₄H₂₀BrFO: C, 55.46; H, 6.65; Br, 26.35; F, 6.27; O, 5.28; found: C, 55.7; H, 6.7. Exact mass: 302.07; molecular weight: 303.21, *m*/ *z*: 302.05, 304.05.

4-(2-(*R*)-Octyloxy)-3-fluorophenylboric acid 2,2-dimethyl-1,3propanediyl ester (5)

Turnings of magnesium (0.84 g, 35 mmol) were dispersed in tetrahydrofuran (30 mL). Compound 4 (7.38 g, 24 mmol) was added to the dispersion and the solvent was gently refluxed. After the formation of the Grignard reagent, the reaction mixture was cooled to -78 °C and a solution (5 mL) of trimethyl borate (2.7 g, 25 mmol) in tetrahydrofuran was added. After the reaction mixture was stirred for 3 h, the temperature was increased to room temperature. 2,2-Dimethylpropanediol (3.64 g, 35 mmol) was added to the mixture, which was stirred for 3 h. Water was added to the mixture, and the product was extracted with *n*-hexane. The extract was dried over sodium sulfate. After the solvent was evaporated, the residual mixture was purified by silica gel column chromatography (eluent: *n*-hexane–ethyl acetate = 10/1 v/v). Colorless crystals (3.77 g, 11 mmol) were obtained in 45% yield.

¹H NMR (400 MHz, CDCl₃): δ = 7.47 (d, 1H, *J* = 2.4 Hz), 7.44 (d, 1H, *J* = 2.4 Hz), 6.91 (t, 1H, *J* = 8 Hz), 4.38 (sext, 1H, *J* = 6 Hz), 3.72 (s 4H), 1.72–1.81 (m, 1H), 1.52–1.61 (m, 1H), 1.35–1.48 (m, 2H), 1.24–1.31 (m, 6H), 1.31 (d, 3H, *J* = 6.0 Hz), 0.99 (s, 6H), 0.86 (t, 3H, *J* = 7.2 Hz); IR (ATR): ν = 2958, 2931, 2859, 1612, 1509, 1478, 1424, 1408, 1377, 1339, 1316, 1306, 1267, 1250, 1217, 1195, 1134, 1116, 1038, 991, 937, 892, 853, 813, 775, 748, 726, 703, 692, 675, 642, 564, 537, 496, 453, 401 cm⁻¹; elemental analysis calcd (%) for C₁₉H₃₀BFO₃: C, 67.87; H, 8.99; B, 3.22; F, 5.65; O, 14.27; found: C, 67.8; H, 9.1. Exact mass: 336.23; molecular weight: 336.25, *m/z*: 336.23, 335.23, 337.23, 338.23.

5-{4-(2-(R)-Octyloxy)-3-fluorophenyl}bithiophene (6)

Compound 5 (5.46 g, 16 mmol), 5-bromo-2,2'-bithiophene (4.02 g, 16 mmol), and tetrakistriphenylphosphine palladium(0) (50 mg, 0.043 mmol) were dissolved in dimethoxyethane (150 mL). An aqueous solution of sodium carbonate (10 wt%, 100 mL) was added to the solution, and the resulting reaction mixture was refluxed for 6 h. Dimethoxyethane was removed from the reaction mixture under reduced pressure. The produced precipitates were filtered and purified by silica gel column chromatography (eluent: *n*-hexane-ethyl acetate = 10/1 v/v). Colorless crystals (5.75 g, 15 mmol) were obtained in 90% yield.

¹H NMR (400 MHz, CDCl₃): δ = 7.30 (dd, 1H, *J* = 12.0, 2.4 Hz), 7.25 (ddd, 1H, *J* = 8.8, 2.0, 1.2 Hz), 7.20 (dd, 1H, *J* = 4.8, 0.8 Hz), 7.17 (dd, 1H, *J* = 3.6, 1.2 Hz), 7.10 (d, 1H, *J* = 3.6 Hz), 7.09 (d, 1H, *J* = 3.6 Hz), 7.01 (dd, 1H, *J* = 5.6, 3.6 Hz), 6.95 (t, 1H, *J* = 8.8 Hz), 4.36 (sextet, 1H, *J* = 6.0 Hz), 1.83–1.73 (m 1H), 1.64–1.53

(m, 1H), 1.31 (d, 3H, J = 6.0 Hz), 1.30–1.27 (m, 7H), 0.87 (t, 3H, J = 6.8 Hz); IR (ATR): $\nu = 2951$, 2919, 2854, 1611, 1577, 1521, 1504, 1466, 1428, 1375, 1300, 1266, 1245, 1226, 1205, 1123, 1064, 1028, 995, 967, 940, 888, 858, 848, 834, 800, 781, 729, 716, 696, 647, 616, 534, 473, 448, 420 cm⁻¹; Elemental analysis calcd (%) for C₂₂H₂₅FOS₂: C, 68.00; H, 6.49; F, 4.89; O, 4.12; S, 16.50; found: C, 68.5; H, 6.8. Exact mass: 388.13; molecular weight: 388.56, *m/z*: 388.13, 389.14, 390.13, 390.14.

5-Bromo-5'-{4-(2-(R)-octyloxy)-3-fluorophenyl} bithiophene (7)

Compound **6** (5.75 g, 15 mmol) was dissolved in tetrahydrofuran (200 mL). *N*-Bromosuccinimide (3.2 g, 18 mmol) was added to the solution over a period of 30 min. An aqueous solution of sodium carbonate (10 wt%) was then added to the reaction mixture, and the product was extracted with ethyl acetate. The extract was dried over sodium carbonate and the solvent was evaporated under reduced pressure. The residual material was purified by silica gel column chromatography (eluent: *n*-hexane–ethyl acetate = 10/1 v/v). The product was recrystallized from *n*-hexane. Yellow crystals of compound 7 (5.3 g, 11 mmol) were obtained in 76% yield.

¹H NMR (400 MHz, CDCl₃): δ = 7.28 (dd, 1H, *J* = 12.0, 2.0 Hz), 7.23 (dd, 1H, *J* = 8.0, 2.0 Hz), 7.07 (d, 1H, *J* = 4.0 Hz), 7.03 (d, 1H, *J* = 4.0 Hz), 6.96 (d, 1H, *J* = 4.0 Hz), 6.94 (t, 1H, *J* = 8.4 Hz), 6.90 (d, 1H, *J* = 4.0 Hz), 4.36 (sextet, 1H, *J* = 6.0 Hz), 1.73–1.83 (m, 1H), 1.56–1.63 (m, 1H), 1.35–1.51 (m, 2H), 1.31, (d, 3H, *J* = 6.0 Hz), 1.23–1.35 (m, 6H), 0.86 (t, 3H, *J* = 6.8 Hz); IR (ATR): ν = 2927, 2855, 1615, 1575, 1556, 1524, 1498, 1460, 1427, 1377, 1350, 1299, 1268, 1238, 1174, 1126, 1057, 999, 969, 937, 864, 788, 724, 688, 610, 577, 532, 477, 448 cm⁻¹; Elemental analysis calcd (%) for C₂₂H₂₄BrFOS₂: C, 56.53; H, 5.17; Br, 17.09; F, 4.06; O, 3.42; S, 13.72; found: C, 56.8; H, 5.1. Exact mass: 466.04; molecular weight: 467.46, *m/z*: 468.04, 466.04, 469.04.

2-(9-Decenyl)thienylboric acid 2,2-dimethyl-1,3-propanediyl ester (8)

Reagent 2-(9-decenyl)thiophene (30.0 g, 0.13 mol) was dissolved in tetrahydrofuran (20 mL). The solution was cooled to 0 °C and *n*-butyllithium (99.7 mL, 1.6 M/*n*-hexane solution) was added over a 2 h period. The reaction mixture was cooled to -78 °C and a solution (20 mL) of trimethyl borate (13.8 g, 0.13 mol) in tetrahydrofuran was added. While stirring for 6 h, the temperature of the reaction mixture increased to room temperature. To the mixture, 2,2-dimethyl-1,3-propanediol (13.8 g, 0.13 mol) was added. After 4 h, water was added to the mixture. The product was extracted with ethyl acetate and the extract was dried over sodium sulfate. The crude product was purified by silica gel chromatography (eluent: *n*-hexane). The white solid (20.4 g, 60 mmol) was obtained in 45% yield.

¹H NMR (400 MHz, CDCl₃): δ = 7.38 (d, 1H, *J* = 4.0 Hz), 6.81 (d, 1H, *J* = 4.0 Hz), 5.77 (ddt, 1H, *J* = 16.8, 10.4, 6.4 Hz), 4.96 (dd, 1H, *J* = 16.8, 3.6 Hz), 4.88 (dd, 1H, *J* = 10.4, 3.6 Hz), 3.73 (s, 4H), 2.80 (t, 2H, *J* = 8.0 Hz), 2.02 (quartet, 2H, *J* = 6.4 Hz), 1.68 (quintet, 2H, *J* = 8.0 Hz), 1.24–1.39 (m, 10H), 1.00 (s, 6H); IR (ATR): ν = 2924, 2850, 1643, 1537, 1480, 1465, 1434, 1415, 1378, 1326, 1286, 1252, 1206, 1108, 1043, 993, 905, 848, 811, 779, 722,

696, 680, 658, 571, 497, 483 cm⁻¹; Elemental analysis calcd (%) for C₁₉H₃₁BO₂S: C, 68.26; H, 9.35; B, 3.23; O, 9.57; S, 9.59; found: C, 68.4; H, 9.4. Exact mass: 334.21; molecular weight: 334.32, *m*/*z*: 334.21.

5-(9-Decenyl)-5''-{4-(2-(*R*)-octyloxy)}-3-fluorophenyl}-2,2'-5',2''terthiophene (1)

Compound 7 (2.7 g, 5.8 mmol), compound 8 (2.89 g, 8.7 mmol), and tetrakistriphenylphosphine palladium(0) (50 mg, 0.043 mmol) were dissolved in dimethoxyethane (150 mL). An aqueous solution of sodium carbonate (10 wt%, 100 mL) was added, and the mixture was refluxed for 6 h. Dimethoxyethane was removed from the reaction mixture under reduced pressure. The produced precipitate was filtered and purified by silica gel column chromatography (eluent: *n*-hexane–ethyl acetate = 10/1 v/v). Pale yellow crystals (1.56 g, 2.6 mmol) were obtained in 44% yield.

¹H NMR (400 MHz, CDCl₃): δ = 7.29 (dd, 1H, J = 12.0, 2.4 Hz), 7.25 (ddd, 1H, J = 8.4, 2.0, 1.2 Hz), 7.09 (d, 1H, J = 3.6 Hz), 7.07 (d, 1H, J = 3.6 Hz), 7.04 (d, 1H, J = 4.0 Hz), 6.98 (d, 1H, J = 3.6 Hz), 6.97 (d, 1H, J = 3.6 Hz), 6.94 (t, 1H, J = 6.3 Hz), 6.67 (d, 1H, *J* = 3.6 Hz), 5.80 (ddt, 1H, *J* = 16.8, 10.4, 6.8 Hz), 5.00 (ddd, 1H, J = 16.8, 3.6, 1.2 Hz, 4.92 (ddt, 1H, J = 10.4, 3.6, 1.2 Hz), 4.36 (sextet, 1H, J = 6.0 Hz), 2.78 (2H, t = J = 7.6 Hz), 2.03 (quintet, 2H, J = 6.8 Hz), 1.82–1.73 (m, 1H), 1.67 (quintet, 2H, J = 7.2 Hz), 1.64–1.56 (m, 1H), 1.40–1.25 (m, 18H), 1.31 (d, 3H, J = 6.4 Hz), 0.87 (t, 3H, J = 6.4 Hz); ¹³C NMR (100 MHz CDCl₃): $\delta =$ 145.9, 139.4, 137.0, 136.4, 135.6, 134.6, 125.0, 124.5, 124.3, 123.7, 123.6, 121.6, 121.5, 118.0, 114.3, 114.0, 113.8, 113.5, 76.8, 36.7, 34.0, 32.0, 31.8, 30.4, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 25.6, 22.8, 20.0, 14.3, 14.2; IR (ATR): *v* = 3072, 2919, 2848, 1640, 1616, 1576, 1546, 1524, 1506, 1464, 1427, 1379, 1303, 1268, 1234, 1209, 1123, 1069, 996, 942, 911, 894, 857, 810, 799, 790, 726, 661, 630, 594, 549, 474, 447 cm⁻¹; Elemental analysis calcd (%) for C₃₆H₄₅FOS₃: C, 71.01; H, 7.45; F, 3.12; O, 2.63; S, 15.80; found: C, 71.4; H, 7.6. Exact mass: 608.26; molecular weight: 608.94, m/z: 608.26, 609.27.

5-{10-(1,1,1,3,3-Pentamethyl-1,3-disiloxanyl)decan-1-yl}-5''-{4-(2-(*R*)-octyloxy)}-3-fluorophenyl}-2,2'-5',2''-terthiophene (2)

Compound 1 (0.50 g, 0.82 mmol) and 1,1,1,3,3-pentamethyl-1,3disiloxane were dissolved in toluene (30 mL). The Karstedt catalyst (1,3-divinyl-1,1,3,3-tetramethyldisiloxane platinum(0), 10 μ L, 3.4 atom% in xylene) was added, and the solution was stirred for 12 h at room temperature. The solvent was evaporated and the resulting crude product was purified by silica gel column chromatography (eluent: *n*-hexane–ethyl acetate = 10/1 v/v). The yellow waxy product (0.21 g, 0.27 mmol) was obtained in 34% yield.

¹H NMR (400 MHz, CDCl₃): δ = 7.30 (dd, 1H, *J* = 12.0, 2.0 Hz), 7.25 (dd, 1H, *J* = 8.4, 2.0 Hz), 7.10 (d, 1H, *J* = 4.0 Hz), 7.08 (d, 1H, *J* = 4.0 Hz), 7.05 (d, 1H, *J* = 4.0 Hz), 6.99 (d, 1H, *J* = 3.6 Hz), 6.97 (d, 1H, *J* = 3.6 Hz), 6.95 (t, 1H, *J* = 6.3 Hz), 6.67 (d, 1H, *J* = 3.6 Hz), 4.36 (sextet, 1H, *J* = 6.0 Hz), 2.78 (t, 2H, *J* = 3.6 Hz), 1.84–1.75 (s, 1H), 1.69 (quintet, 2H, *J* = 7.2 Hz), 1.65–1.57 (m, 1H), 1.42–1.25 (m, 18H), 1.32 (d, 3H, *J* = 6.4 Hz), 0.87 (t, 3H, *J* =

6.8 Hz), 0.49 (t, 2H, J = 7.2 Hz), 0.05 (s, 9H), 0.02 (6H, s); ¹³C NMR (100 MHz CDCl₃): $\delta = 0.6$, 2.2, 14.3, 18.6, 20.0, 22.8, 23.5, 25.6, 29.3, 29.4, 29.6, 29.8, 30.4, 31.8, 32.0, 33.6, 36.7, 76.8, 113.8, 114.0, 118.0, 121.5, 121.6, 122.5, 123.6, 123.7, 124.3, 124.5, 125.0, 134.6, 135.6, 136.5, 137.1, 145.9; IR (ATR): $\nu = 2957$, 2922, 2853, 1575, 1545, 1523, 1505, 1445, 1378, 1300, 1252, 1233, 1125, 1052, 942, 840, 789, 753, 625, 477, 447 cm⁻¹; Elemental analysis calcd (%) for C₄₁H₆₁FO₂S₃Si₂: C, 65.03; H, 8.12; F, 2.51; O, 4.23; S, 12.70; Si, 7.42; found: C, 65.40; H, 8.1. Exact mass: 756.34; molecular weight: 757.29, *m/z*: 756.34, 757.34, 758.33, 758.34, 759.33.

$5-\{10-(1,3,3,5,5,7,7-\text{Heptamethyl}-1,3,5,7-\text{cyclotetrasiloxan}-1-yl\}$ decan-1-yl}-5''-{4-(2-(*R*)-octyloxy)}-3-fluorophenyl}-2,2'-5',2''terthiophene (3)

Compound 1 (0.75 g, 1.24 mmol) and 1,3,3,5,5,7,7-heptamethyl-1,3,5,7-cyclotetrasiloxane (0.52 g, 1.86 mmol) were dissolved in toluene (30 mL). The Karstedt catalyst (1,3-divinyl-1,1,3,3-tetramethyldisiloxane platinum(0), 10 μ L, 3.4 atom% in xylene) was added, and the solution was stirred for 12 h at room temperature. The solvent was evaporated and the resulting crude product was purified by silica gel column chromatography (eluent: *n*-hexane–ethyl acetate = 10/1 v/v). The yellow waxy product (0.21 g, 0.27 mmol) was obtained in 34% yield.

¹H NMR (400 MHz, CDCl₃): $\delta = 7.31$ (dd, 1H, J = 12.4, 2.4Hz), 7.26 (ddd, 1H, J = 8.4, 2.4, 1.2 Hz), 7.10 (d, 1H, J = 3.6 Hz), 7.09 (d, 1H, J = 3.6 Hz), 7.06 (d, 1H, J = 4.0 Hz), 7.00 (d, 1H, J = 4.0 Hz), 6.98 (d, 1H, J = 4.0 Hz), 6.96 (t, 1H, J = 8.4 Hz), 6.68 (d, 1H, J = 4.0 Hz), 4.37 (sextet, 1H, J = 6.0 Hz), 2.79 (t, 2H, J = 3.6Hz), 1.84–1.75 (m, 1H), 1.68 (quintet, 2H, J = 7.2 Hz), 1.65–1.57 (m, 1H), 1.42-1.25 (m, 18H), 1.33 (d, 3H, J = 6.8 Hz), 0.89 (t, 3H, J = 6.8 Hz), 0.50 (dd, 2H, J = 9.2, 6.0 Hz), 0.09 (s, 18H), 0.07 (s, 3H); ¹³C NMR (100 MHz CDCl₃): $\delta = 145.9$, 136.4, 135.5, 135.4, 134.6, 125.0, 124.5, 124.3, 123.7, 123.6, 121.6, 121.5, 118.0, 117.9, 114.0, 113.8, 113.7, 76.7, 36.6, 33.3, 33.2, 31.9, 31.8, 30.4, 30.3, 29.8, 29.7, 29.5, 29.4, 29.3, 25.6, 25.5, 23.1, 22.8, 20.0, 17.3, 14.2, 0.96, 0.93; IR (ATR): $\nu = 2961, 2923, 2853, 1545, 1524, 1507$, 1445, 1378, 1300, 1259, 1234, 1060, 941, 854, 789, 696, 553, 477 cm⁻¹; Elemental analysis calcd (%) for C₄₃H₆₇FO₅S₃Si₄: C, 57.93; H, 7.57; F, 2.13; O, 8.97; S, 10.79; Si, 12.60; found: C, 57.8; H, 7.6. Exact mass: 890.32; molecular weight: 891.52, m/z: 890.52, 891.52, 892.52.

Results and discussion

Characterization of mesophases of compounds 1-3

Compounds 1–3 exhibited an enantiotropic SmC* phase, as well as more ordered smectic G (SmG) and smectic F (SmF) phases. Fig. 1 shows the DSC thermograms of compounds 1–3. Compound 1 formed crystals *via* recrystallization from *n*-hexane. The crystals changed to the SmG phase at 58 °C. Upon cooling, they did not crystallize and the SmG phase was retained. Compounds 2–3 formed waxy mesomorphic precipitates during recrystallization from *n*-hexane and did not crystallize upon cooling to -100 °C. Compounds 1 and 2 exhibited an SmC* phase between 124 and 140 °C and between 116 and



Fig. 1 DSC thermograms of (a) compound 1, (b) compound 2, and (c) compound 3. The heating and cooling rates are 10 K min⁻¹. The green curves exhibit the thermograms of materials formed *via* recrystallization from *n*-hexane.

129 °C, respectively. The SmF phases were observed below the SmC* phase. As reported previously for LC molecules bearing disiloxane chains at the end of their alkyl side chain, $^{16c-e}$ the temperature range of the SmC* phase for compound **2** was slightly lower than that of compound **1**.

Surprisingly, compound 3 with a bulky cyclotetrasiloxane ring also exhibited a SmC* phase between 110 and 122 $^{\circ}$ C. Below 110 $^{\circ}$ C, a SmF phase appeared and a glass transition associated with the thermal motion of the cyclotetrasiloxane moiety was observed at -70 $^{\circ}$ C.

Fig. 2(a) shows the XRD patterns of compound **1**. In the hightemperature phase, peaks derived from the (001), (002), and (003) diffraction planes were observed at $2\theta = 2.97^{\circ}$, 6.35° , and 9.47° in the low-angle region. A broad halo associated with the



Fig. 2 X-ray diffraction patterns in the smectic phases of (a) compound 1, (b) compound 2, and (c) compound 3.

liquid-like packing of the alkyl chains appeared around $2\theta = 16^{\circ}$. The layer spacing estimated from the (001) diffraction was 29.6 Å, which was shorter than the extended molecular length of 37 Å. Therefore, this phase was assigned to the SmC* phase. In the low-temperature phase, wide-angle peaks derived from the (200), (010), (110), and (210) diffraction planes were observed, indicating the long-range rectangular order of the molecular position within the layers. The layer spacing was shorter than the extended molecular length, indicating that the low-temperature phase was an SmG phase.¹⁸

Fig. 2(b) displays the XRD patterns of compound 2. In the high-temperature phase, the ratio of the lattice constants determined by the low angle peaks at $2\theta = 2.61^{\circ}$, 4.04° , 4.83° , and 9.23° was 1/2 : 1/3 : 1/4 : 1/7. This result suggested

dimeric aggregation in the low-temperature phase, and these peaks were indexed to the (002), (003), (004), and (007) diffraction planes. The diffraction peak derived from the (001) plane was not observed because it was shielded by a stopper. In the wide-angle region, two halos around 12° and 18° were attributed to the liquid-like orders of disiloxane and the alkyl chains, respectively. The lattice constant derived from the (002) diffraction was 33.5 Å, which was shorter than the fully extended length of compound 2 (42 Å), indicating that the LC molecules tilt from the normal of the layers or the disiloxane chains interdigitate. Thus, the high-temperature phase was identified as the SmC* phase. In the low-temperature phase, a broad peak around 18° was observed in addition to the lowangle peaks associated with the lamellar organization of the LC molecules. This broad peak suggested a hexatic bond order within the layers. The low-temperature phase should be a SmF phase. From the low-angle peaks, the dimeric structure was retained in the low-temperature phase. The interaction between the disiloxane chains promoted the formation of the dimeric layer structure.

Fig. 2(c) shows the XRD patterns of compound 3 bearing a bulky cyclotetrasiloxane ring. In the high-temperature phase, three low angle peaks derived from the (001), (002), (003), and (004) diffraction planes were observed. In the high-angle region, two halos appeared. The halo around 18° was attributed to the liquid-like packing of alkyl chains, and the other halo around 12° was ascribed to the disordered aggregation of the cyclotetrasiloxane rings. No diffraction peaks indicating the long-range order of the molecular position within the smectic layers were observed. The layer spacing of 36.2 Å was shorter than the extended molecular length, indicating the tilted orientation of the molecules in the smectic layers. Therefore, the high-temperature phase was assigned to the SmC* phase.

The XRD patterns revealed that the low-temperature phase should be an SmF phase. The low-angle peaks were assigned to the (001), (002), (003), and (004) diffraction planes. Similar to compound **2**, the positional order within the smectic layers was ambiguous in the low-temperature phase. The layer spacing was also shorter than the extended molecular length. Two broad halos were observed around 12° and 18°, which were derived from the liquid-like aggregation of the cyclotetrasiloxane rings and alkyl chains, respectively. Compared to the SmG phase of compound **1**, the diffraction peaks associated with the positional order within the smectic layers were broad, indicating a more disordered structure in the SmF phase¹⁸ for compound **3**.

In contrast to compounds 1 and 3, compound 2 exhibited a dimeric SmC* phase. In compound 2, the interaction between the disiloxane chains and their interdigitation should promote the formation of a dimeric layer structure. In compound 3, the same interaction between the cyclotetrasiloxane rings should be plausible. However, the interdigitation between the cyclotetrasiloxane rings of compound 3 is difficult because of their bulkiness as compared to the disiloxane rings of compound 2. Therefore, a monomeric



Fig. 3 Polarizing optical micrographs without the application of a DC bias in the SmC* phase of (a) compound 1 at 130 °C, (b) compound 2 at 125 °C, and (c) compound 3 at 120 °C.

layer structure should be favorable in compound 3 in spite of the presence of oligosiloxane moieties.

Polarizing optical micrographic textures of compounds 1-3

In the SmC* phases of compounds 1 and 3, broken fan-like domains with stripe patterns were observed without an electric field under a polarizing optical microscope (Fig. 3). The stripe patterns were derived from the helical structures of the SmC* phases of the compounds. The helical pitches were about 2 μ m for compound 1, 3 μ m for compound 2, and 10 μ m for compound 3.

As observed in conventional ferroelectric SmC* phases, the stripe patterns disappeared when a DC voltage was applied to the LC cells. As shown in Fig. 4, the transmittances of the domains changed with the crossed polarizers when the polarity of the DC voltage was inverted. This behavior is typical of a ferroelectric SmC* phase. The transmittance switching of the optical textures was based on the change in the molecular orientation caused by the inversion of the spontaneous polarization.



Fig. 4 Polarizing optical micrographs of the SmC* phases for compound 1 under the application of a (a) positive and (b) negative bias (\pm 1.5 V for 4 µm thick sample) as well as for compound 2 ((c) positive and (d) negative bias (\pm 5 V for 9 µm thick sample)) and compound 3 ((e) positive and (f) negative bias (\pm 5 V for 9 µm thick sample)).

Characterization of the spontaneous polarization in the SmC* phases of compounds 1–3

Spontaneous polarizations in the SmC* phases of compounds 1–3 were determined by the triangular wave method. Fig. 5(a) shows the polarization inversion current curves in the SmC* phases of compounds 1–3 when triangular voltages were applied to the LC cells. As observed in the SmC* phase of conventional ferroelectric LCs, current peaks caused by polarization inversion were obtained in the current response curves.

In the SmC* phase of compound **1**, the polarization inversion occurred in several microseconds. This rate was slower than that of conventional ferroelectric LCs. The higher viscosity attributed to stronger π - π interactions in the SmC* phase of compound **1** should result in this slow inversion. The spontaneous polarization was determined to be 151 nC cm⁻². This value was considerably higher than those of classical ferroelectric LCs such as DOBANBC^{9b} and ferroelectric phenylnaphthalene derivatives.¹⁰

In the SmC^{*} phase of compound **2**, the spontaneous polarization was 120 nC cm⁻². The bulky disiloxane moiety should slightly inhibit close molecular aggregation in the SmC^{*} phase



Fig. 5 (a) Polarization inversion current measured by the triangular wave method in the SmC* phase of compound 1 at 130 °C, compound 2 at 125 °C, and compound 3 at 120 °C. The sample thickness was 2 μ m. (b) Hysteresis loops in the SmC* phase of compounds 1 (130 °C), 2 (125 °C), and 3 (120 °C). The frequency was 100 Hz and the capacitance of serial capacitor was 33 nF.

of compound 2 and decrease the macroscopic polarization. The more disordered structure of the SmC* phase of compound 2 than that of compound 1 should decrease the viscosity of the SmC* phase of compound 2. The polarization inversion was more rapid than that of compound 1.

In the SmC* phase of compound 3, the disorder of the molecular aggregation structure is more remarkable, compared to compounds 1 and 2. The measurement revealed a spontaneous polarization of 62 nC cm⁻² in the SmC* phase of compound 3. This value was lower than that of compound 1 by a factor of 2.5. Compound 3 bears a very bulky cyclotetrasiloxane ring, which perturbs close molecular aggregation in its SmC* phase. This disordered structure inhibits macroscopic ordering of molecular dipole moments. The response time in the SmC* phase of compound 3 was two times slower than that of compound 1. This slower response in the polarization current for compound 3 should also be attributed to the higher viscosity in its SmC* phase. The temperature range of the SmC* phase of compound 3 was 10 degrees lower than that of compound 1 and thermal fluctuation was smaller in the SmC* phase of compound 3 than the case of compound 1. The larger molecular weight of compound 3 than that of compound 1 should also contribute to the higher viscosity in the SmC* phase of compound 3.

Fig. 5(b) exhibits hysteresis *D–V* loops in the SmC* phase of compounds **1–3**, which were measured by the Sawyer–Tower method. For the SmC* phase of all the compounds, ferroelectric hysteresis loops were obtained. The values of the obtained spontaneous polarizations for compounds **1–3** were 83 nC cm⁻², 58 nC cm⁻², and 38 nC cm⁻², which are about half of those determined by the triangular method. The hysteresis loop indicates that the coercive voltage and electric field in the SmC* phase of compound **1** are around 1 V and 5 × 10³ V cm⁻¹, respectively.

Carrier transport properties in the SmC* phase of compounds 1–3

The carrier mobilities in the SmC* phases of compounds 1–3 were determined by the TOF method. In the SmC* phases of compounds 1–3, non-dispersive transient photocurrent signals originating from hole transport were observed. The transient photocurrent signals for electrons were too weak for the determination of electron mobilities.

Fig. 6(a) shows the transient photocurrent curves for holes in the SmC* phase of compound **1** at 130 °C. Non-dispersive transient photocurrent curves with initial spikes were obtained and transit times were determined by the linear plots of the curves. The hole mobility calculated from the transit times was 3×10^{-4} cm² V⁻¹ s⁻¹, and was independent of the electric field and temperature.

Fig. 6(b) shows the transient photocurrent curves for holes in the SmC^{*} phase of compound 2 at 125 °C. Non-dispersive transient curves were obtained and the hole mobility was determined to be 2×10^{-4} cm² V⁻¹ s⁻¹. The hole mobility was independent of the electric field and temperature in the SmC^{*} phase.



Fig. 6 Transient photocurrent curves for holes in the SmC* phases of (a) compound 1 at 130 °C (sample thickness = 15 μ m), (b) compound 2 at 125 °C (sample thickness = 9 μ m), and (c) compound 3 at 120 °C (sample thickness = 9 μ m).

Fig. 6(c) shows the transient photocurrent curves for the holes in the SmC* phase of compound 3 at 120 °C. Nondispersive transient photocurrent curves with delays in the rise of the curves were observed. The transit times were determined from the linear plots of the transient photocurrent curves. The hole mobility was 1×10^{-4} cm² V⁻¹ s⁻¹. The hole mobility was also independent of the electric field and temperature.

In the smectic phases of LC semiconductors above room temperature, temperature- and field-independent mobilities are typically observed.^{3a,b} These temperature- and field-

independent mobilities are explained based on Gaussian disorder¹⁹ or small polaron hopping models.²⁰ In contrast to amorphous organic semiconductors in which carrier mobilities are strongly dependent on the electric field and the temperature, smaller energetic and positional disorders result in a smaller dependency of the carrier mobilities in the liquid crystal phases.^{2g,3g} In addition, the positive temperature-dependence of the carrier mobility is cancelled by the negative temperature-dependence, which is derived from the thermal fluctuation of the mesomorphic structures.^{8e}

In amorphous organic semiconductors, the dipole moments of semiconductor molecules increase the energetic disorder because local electric fields produced by randomly oriented molecular dipoles increase the dispersion width of the energy levels of semiconductor molecules.²¹ In the columnar phase of a nitrotriphenylene derivative, increased energetic disorder was reported.^{21c} However, molecular dipoles are oriented in one direction in the SmC* phase under the application of electric fields. Therefore, the temperatureand field-dependencies in the SmC* phases of compounds 1–3 should not be remarkable.

Anomalous photovoltaic effect in the SmC* phase of compounds 1 and 3

Conventional photovoltaic effects are caused by an internal electric field, which is produced at the p–n junction or Schottky barrier formed at the interface between a semiconductor layer and an electrode. In contrast, anomalous photovoltaic effects are observed in ferroelectrics and they originate from the electric field generated by spontaneous polarization. The polarity of the photovoltaic effect is determined by the polarity of the internal electric field. After the application of a DC voltage pulse, light illumination under zero bias produces a photocurrent with a reversed polarity to the DC bias prior to the light illumination. The inversion of the DC bias direction changes the polarity of the photovoltaic effect under zero bias.^{12b}

Fig. 7(a) shows the steady state photocurrent response under zero bias. In the initial state, in which the sample was cooled from the isotropic phase to the SmC* phase, the photocurrent response was quite ambiguous. In this state, the dipole moments of the molecules did not orient macroscopically because of the helical structure of the SmC* phase. However, after the application of the DC voltage, a clear photocurrent response was observed. It should be emphasized that the polarities of the photocurrents were opposite to those of the DC biases applied prior to light illumination. In these states after the application of the positive and negative biases, the helical structures disappeared and macroscopic spontaneous polarizations and internal electric fields were produced. The internal fields are opposite to the polarities of the DC biases applied prior to the light illumination.

When the illuminated electrode was negatively biased, the photocurrent response under zero bias was stronger than that observed after the application of the positive DC voltage. In the case of the stronger photocurrent response, the photocurrent was attributed to the hole transport. Compared to electrons, the



Fig. 7 (a) Steady state photocurrent response in the SmC* phase of compound 1 at 127 °C under zero bias. The sample thickness was 2 μ m and the electrode area was 0.16 cm². (b) Current–voltage characteristics in the same sample. The wavelength and intensity of the illuminated light were 360 nm and 3 mW cm⁻², respectively.

holes are generated and efficiently transported in the SmC* phase as verified in the TOF experiments.

Fig. 7(b) exhibits the current-voltage characteristic of the same sample of compound **1**. The open circuit voltage was 0.35 V and the short circuit current was 200 nA. In the SmC* phase of compound **1**, the coercive electric field and voltage are 1×10^4 V cm⁻¹ and 2 V at 100 Hz, respectively, as shown in Fig. 5(b). This result indicates that the spontaneous polarization is retained for several ms. However, the spontaneous polarization should be partially relaxed on the time scale (several seconds) of the experiment of the steady-state photocurrent measurement.

The transient photovoltaic effect was also studied. Fig. 8(a) shows the photocurrents under zero bias after pulse laser illumination in the SmC* phase of compound 1 at 130 °C. Prior to the photocurrent measurement, DC biases of 0 V, +20 V, and -20 V were applied to the sample for 1 min. When the DC bias was 0 V prior to illumination, the photocurrent under zero bias was almost zero. Immediately after the light illumination, a non-zero photocurrent was generated, but it was very low. A strong spike should be caused by the local electric field formed on the electrode surface, due to local molecular alignment. When the DC bias was +20 V prior to the light illumination, a photocurrent of approximately 10 nA was generated. The



Fig. 8 (a) Photocurrent under zero bias after laser pulse (wavelength = 356 nm, pulse duration = 2 ns) illumination in the SmC* phase of compound 1 at 130 °C. Before the laser illumination, DC voltages of 0, 20, and -20 V were applied to the sample (thickness of 2 μ m) for 1 min. (b) Transient photocurrent curves under DC biases of 0.5 and -0.5 V in the SmC* phase of compound 1.

polarity of the photocurrent was reversed to that of the DC bias prior to the illumination. In the case of the DC bias of -20 V before the illumination, a photocurrent of over 10 nA was generated and the polarity was reversed. In the isotropic phase, the generated photocurrents under zero bias were considerably smaller than those in the SmC* phase. In the SmG phase, a nonzero photocurrent was observed, but such a change in the photocurrent polarity did not occur.

Fig. 8(b) shows the photocurrent curves in the SmC* phase of compound 1 at 130 °C under the DC bias of +0.5 and -0.5 V, which corresponds to the electric field of $\pm 2.5 \times 10^3$ V cm⁻¹. In the electric field region, the diffusion of the charge carrier was dominant over the drift movement of the carriers resulting in a featureless current decay without clear kink points.

The strengths and shapes of the transient photocurrents were similar to those of the zero-field photocurrents after the DC bias application shown in Fig. 8(a). This indicated that an internal electric field in the order of 10^3 V cm^{-1} was formed by spontaneous polarization in the ferroelectric SmC* phase.

The estimated value of the internal electric field was in the same order of that determined by the steady-state photocurrent measurement as shown in Fig. 7(b). These internal electric field values determined by the steady and transient photocurrent

measurements were smaller than the coercive electric field determined at 100 Hz by the Sawyer–Tower method, as shown in Fig. 5(b). The partial relaxation of the spontaneous polarization should decrease the internal electric field.

The value of spontaneous polarization (145 nC cm⁻²) should lead to the production of an electric field in the order of 5×10^5 V cm⁻¹. In this experiment, the induced internal field was in the order of 10^3 V cm⁻¹, which was considerably smaller than the theoretically expected value. In this case, the sample thickness was 2 µm. Near the electrode–LC interface, ferroelectric polarization should be retained although it should be relaxed in the bulk under the zero-field because of the reconstruction of the helical structure.

This zero-field photocurrent was not observed in the isotropic phase without spontaneous polarization. In the SmG phase, the inversion of the sign of the zero-field photocurrent did not occur when the polarity of the DC voltage was changed prior to the laser illumination.

For compounds 2 and 3, zero-field photocurrents were observed in the SmC* phase and the polarities were changed according to the sign of the DC bias prior to laser illumination. However, the value of the photocurrent was weaker than that of compound 1. Such photovoltaic effects can be caused by the formation of an electrical double layer at the interface between the electrode and the LC layer. In the samples containing ionic impurities such as sodium and halogen ions, which are contaminated in the synthetic processes, additional peaks other than the peak originating from the ferroelectric polarization inversion are observed in the triangular wave measurements. However, no additional peaks associated with ionic transport were observed in the SmC* or isotropic phases. The detection limit of the current peaks in the triangular wave experiment was about 1 nC cm $^{-2}$. The charge formed by ionic impurities on the electrodes should be lower than 1 nC cm⁻², which is two orders of magnitude lower than the spontaneous polarization in the SmC* phase of compound 1.

The anomalous photovoltaic effect can produce a higher voltage than the band gap of the semiconductors. The production of thin films of the ferroelectric phenylterthiophene derivatives and measurements of the photovoltaic effect in the thin film states are in progress.

Conclusions

Phenylterthiophene derivatives bearing a decenyl group, disiloxane chain, and cyclotetrasiloxane ring were synthesized. They exhibited hole mobilities in the order of 10^{-4} cm² V⁻¹ s⁻¹ in the SmC* phase. Even the compound bearing a bulky cyclotetrasiloxane ring exhibited an enantiotropic SmC* phase. The spontaneous polarization in the SmC* phases exceed 100 nC cm⁻². Compound 1 exhibited a photovoltaic effect based on the internal electric field produced by spontaneous polarization.

Acknowledgements

This study was financially supported by the Japan Security Scholarship Foundation, the Ogasawara Foundation, a GrantJournal of Materials Chemistry C

in-Aid for Scientific Research on Innovative Areas (Coordination Programming, no. 24108729 and Element-Block Polymers, no. 25102533) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), a Grant-in-Aid for Scientific Research (B) (no. 22350080) from the Japan Society for the Promotion of Science (JSPS), the Iwatani Naoji Foundation, the Asahi Glass Foundation, and the Murata Science Foundation. The authors thank T. Kusunose at Kagawa University for help with the DSC measurements. We also thank Prof. N. Tamaoki of Hokkaido University, Prof. T. Kato of the University of Tokyo, and Dr Emi Uchida of the National Institute of Advanced Materials Science and Technology for fruitful discussions.

Notes and references

- 1 (a) W. Pisula, M. Zorn, J. Y. Chang, K. Müllen and R. Zentel, Macromol. Rapid Commun., 2009, 30, 1179–1202; (b)
 Y. Shimizu, K. Oikawa, K. Nakayama and D. Guillon, J. Mater. Chem., 2007, 17, 4223–4229; (c) M. O'Neill and
 S. M. Kelly, Adv. Mater., 2011, 23, 566–584; (d)
 M. Funahashi, H. Shimura, M. Yoshio and T. Kato, Struct. Bonding, 2008, 128, 151–179; (e) M. Funahashi, T. Yasuda and T. Kato, Handbook of Liquid Crystals, Wiley-VCH, 2nd edn, 2014, vol. 8, pp. 675–708.
- 2 (a) D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher and K. Siemensmeyer, Phys. Rev. Lett., 1993, 70, 457-460; (b) N. Boden, R. J. Bushby, J. Clements, B. Movaghar, K. J. Donovan and T. Kreouzis, Phys. Rev. B: Condens. Matter Mater. Phys., 1995, 52, 13274-13280; (c) A. M. van de Craats, J. M. Warman, A. Fechtenkötter, J. D. Brand, M. A. Harbison and Müllen, Adv. Mater., 1999, 11, 1469–1472; (d) Κ. M. Ichihara, A. Suzuki, K. Hatsusaka and K. Ohta, Liq. Cryst., 2007, 34, 555-567; (e) K. Ban, K. Nishikawa, K. Ohta, A. M. van de Craats, J. M. Warman, I. Yamamoto and H. Shirai, J. Mater. Chem., 2001, 11, 321-331; (f) A. Demenev, S. H. Eichhorn, T. Taerum, D. Perepichka, S. Patwardhan, F. C. Grozema and L. D. A. Siebbeles, Chem. Mater., 2010, 22, 1420-1428; (g) I. Bleyl, C. Erdelen, H.-W. Schmidt and D. Haarer, Philos. Mag. B, 1999, 79, 463-475; (h) J. Simmerer, B. Glüsen, W. Paulus, A. Kettner, Ρ. Schuhmacher, D. Adam, К.-Н. Etzbach, K. Siemensmeyer, J. H. Wendorf, H. Ringsdorf and D. Haarer, Adv. Mater., 1996, 8, 815-819.
- 3 (a) M. Funahashi and J. Hanna, Phys. Rev. Lett., 1997, 78, 2184–2187; (b) M. Funahashi and J. Hanna, Appl. Phys. Lett., 2000, 76, 2574–2576; (c) M. Funahashi and J. Hanna, Adv. Mater., 2005, 17, 594–598; (d) K. Oikawa, H. Monobe, J. Takahashi, K. Tsuchiya, B. Heinrich, D. Guillon and Y. Shimizu, Chem. Commun., 2005, 5337–5339; (e) A. Matsui, M. Funahashi, T. Tsuji and T. Kato, Chem.-Eur. J., 2010, 16, 13465–13472; (f) H. Aboubakr, M.-G. Tamba, A. K. Diallo, C. Videlot-Ackermann, L. Belec, O. Siri, J.-M. Raimundo, G. H. Mehl and H. Brisset, J. Mater. Chem., 2012, 22, 23159–23168; (g) M. Funahashi, F. Zhang, N. Tamaoki and J. Hanna, ChemPhysChem, 2008, 9, 1465–

1473; (*h*) M. Funahashi, T. Ishii and A. Sonoda, *ChemPhysChem*, 2013, **14**, 2750–2758.

- 4 (a) A. J. J. M. van Breemen, P. T. Herwig, C. H. T. Chlon, J. Sweelssen, H. F. M. Schoo, S. Setayesh, W. M. Hardeman, C. A. Martin, D. M. de Leeuw, J. J. P. Valeton, C. W. M. Bastiaansen, D. J. Broer, A. R. Popa-Merticaru and S. C. J. Meskers, J. Am. Chem. Soc., 2006, 128, 2336–2345; (b) M. Funahashi, F. Zhang and N. Tamaoki, Adv. Mater., 2007, 19, 353–358; (c) W. Pisula, A. Menon, M. Stepputat, I. Lieberwirth, U. Kolb, A. Tracz, H. Sirringhaus, T. Pakula and K. Müllen, Adv. Mater., 2005, 17, 684–689; (d) M. Funahashi, Polym. J., 2009, 41, 459–469; (e) F. Zhang, M. Funahashi and N. Tamaoki, Org. Electrochem., 2010, 11, 363–368.
- 5 (a) T. Hassheider, S. A. Benning, H.-S. Kitzerow, M.-F. Achard and H. Bock, *Angew. Chem., Int. Ed.*, 2001, 40, 2060–2063; (b)
 M. P. Aldred, A. E. A. Contoret, S. R. Farrar, S. M. Kelly, D. Mathieson, M. O'Neill, W. C. Tsoi and P. Vla-chos, *Adv. Mater.*, 2005, 17, 1368–1372; (c) S. A. Benning,
 R. Oesterhaus and H.-S. Kitzerow, *Liq. Cryst.*, 2004, 31, 201–205; (d) M. W. Lauhof, S. A. Benning, H.-S. Kitzerow,
 V. Vill, F. Scheliga and E. Thorn-Csányi, *Synth. Met.*, 2007, 157, 222–227.
- 6 (a) T. Hori, Y. Miyake, N. Yamasaki, H. Yoshida, A. Fujii,
 Y. Shimizu and M. Ozaki, *Appl. Phys. Express*, 2010, 3, 101602; (b) W. Shin, T. Yasuda, G. Watanabe, Y. S. Yang and C. Adachi, *Chem. Mater.*, 2013, 25, 2549–2556.
- 7 (a) T. Kato, T. Yasuda, Y. Kamikawa and M. Yoshio, Chem. Commun., 2009, 729–739; (b) M. Funahashi, J. Mater. Chem. C, 2014, 2, 7451–7459; (c) T. Yasuda, H. Ooi, J. Morita, Y. Akama, K. Minoura, M. Funahashi, T. Shimomura and T. Kato, Adv. Funct. Mater., 2009, 19, 411–419; (d) S. Yazaki, M. Funahashi and T. Kato, J. Am. Chem. Soc., 2008, 130, 13206–13207; (e) S. Yazaki, M. Funahashi, J. Kagimoto, H. Ohno and T. Kato, J. Am. Chem. Soc., 2010, 132, 7702– 7708; (f) M. Yoneya, Chem. Rec., 2011, 11, 66–76.
- 8 (a) M. Funahashi and A. Sonoda, Org. Electrochem., 2012, 13, 1633–1640; (b) M. Funahashi and A. Sonoda, J. Mater. Chem., 2012, 22, 25190–25197; (c) M. Funahashi and A. Sonoda, Dalton Trans., 2013, 42, 15987–15994; (d) M. Funahashi, M. Yamaoka, K. Takenami and A. Sonoda, J. Mater. Chem. C, 2013, 1, 7872–7878; (e) M. Funahashi, T. Ishii and A. Sonoda, Phys. Chem. Chem. Phys., 2014, 16, 7754–7763.
- 9 (a) C. Y. Young, R. Pindak, N. A. Clark and R. B. Meyer, *Phys. Rev. Lett.*, 1978, 40, 773-776; (b) N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, 1980, 36, 899-901; (c) S. T. Lagerwall and I. Dahl, *Mol. Cryst. Liq. Cryst.*, 1984, 114, 151-187; (d) W. J. A. M. Hartmann, *Ferroelectrics*, 1991, 122, 1-26.
- 10 K. Kogo, H. Maeda, H. Kato, M. Funahashi and J. Hanna, *Appl. Phys. Lett.*, 1999, **75**, 3348–3350.
- 11 (a) Y. Zhang, Y. Liu and Z. L. Wang, Adv. Mater., 2011, 23, 3004–3013; (b) T. Choi, S. Lee, Y. J. Choi, V. Kiryukhin and S.-W. Cheong, Science, 2009, 324, 63–66; (c) I. Grinberg, D. V. West, M. Torres, G. Gou, D. M. Stein, L. Wu, G. Chen and E. M. Gallo, Nature, 2013, 503, 509–517; (d) T. Furukawa, Phase Transitions, 1989, 18, 143–211.

- 12 (a) H. Sasabe, T. Nakayama, K. Kumazawa, S. Miyata and E. Fukuda, *Polym. J.*, 1981, 13, 967–973; (b) A. Sugita, K. Suzuki and S. Tasaka, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2004, 69, 212201.
- 13 (a) J. Watanabe, Y. Nakata and K. Simizu, J. Phys. II, 1994, 4, 581–588; (b) T. Niori, T. Sekine, J. Watanabe, T. Furukawa and H. Takezoe, J. Mater. Chem., 1996, 6, 1231–1233; (c) G. Pelzl, S. Diels and W. Weissflog, Adv. Mater., 1999, 11, 707–724; (d) C. F. C. Fitié, W. S. C. Roelofs, M. Kemerink and R. P. Sijbesma, J. Am. Chem. Soc., 2010, 132, 6892–6893; (e) D. Miyajima, F. Araoka, H. Takezoe, J. Kim, K. Kato, M. Takata and T. Aida, J. Am. Chem. Soc., 2010, 132, 8530–8531; (f) D. Miyajima, F. Araoka, H. Takezoe, K. Kato, M. Takata and T. Aida, Science, 2012, 336, 209–213.
- 14 (a) R. G. Kepler, *Phys. Rev.*, 1960, **119**, 1226–1229; (b)
 W. E. Spear, *J. Non-Cryst. Solids*, 1968, **1**, 197–214.
- 15 (a) D. L. Hughes, Org. Prep. Proced. Int., 1996, 28, 127–164; (b)
 N. Miyaura and A. Suzuki, Chem. Rev., 1995, 95, 2457–2483.
- 16 (a) G. H. Mehl and J. Goodby, Angew. Chem., Int. Ed. Engl., 1996, 35, 2641–2643; (b) I. M. Saez, J. W. Goodby and R. M. Richardson, Chem.–Eur. J., 2001, 7, 2758–2764; (c) J. Newton, H. Coles, P. Hodge and J. Hannington, J. Mater. Chem., 1994, 4, 869–874; (d) J. C. Roberts, N. Kapernaum, F. Giesselmann and R. P. Lemieux, J. Am. Chem. Soc., 2008, 130, 13842–13843; (e) D. Apreutesei and G. Mehl, J. Mater. Chem., 2007, 17, 4711–4715.
- 17 B. D. Karstedt, US Patent 3,775,452, 1973.

- 18 (a) A. de Vries, *Mol. Cryst. Liq. Cryst.*, 1985, 131, 125–145; (b)
 S. Diele, D. Jaeckel, D. Demus and H. Sackmann, *Cryst. Res. Technol.*, 1982, 17, 1591–1598; (c) P. A. C. Gane and
 A. J. Leadbetter, *J. Phys. C: Solid State Phys.*, 1983, 16, 2059–2068.
- 19 (a) H. Bässler, Phys. Status Solidi B, 1993, 175, 15–56; (b)
 M. van der Auweraer, F. C. Schryver, P. M. Borsenberger and H. Bässler, Adv. Mater., 1994, 6, 199–213; (c) A. Köhler and H. Bässler, Top. Curr. Chem., 2012, 312, 1–66; (d)
 R. Goehoorn and P. A. Bobbert, Phys. Status Solidi A, 2012, 209, 2354–2377; (e) T. Nagase, K. Kishimoto and H. Naito, J. Appl. Phys., 1999, 86, 5026–5035.
- 20 (a) M. A. Palenberg, R. J. Silbey, M. Malagoli and J.-L. Brédas, J. Chem. Phys., 2000, 112, 1541-1546; (b) V. Duzhko, A. Semvonov, R. J. Twieg and K. D. Singer, Phys. Rev. B: Condens. Matter Mater. Phys., 2006, 73, 064201; (c) I. Shiyanovskaya, K. D. Singer, R. I. Twieg. L. Sukhomlimova and V. Gettwert, Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys., 2002, 65, 041715; (d) T. Kreouzis, K. J. Donovan, N. Boden, R. J. Bushby, O. R. Lozman and Q. Liu, J. Chem. Phys., 2001, 114, 1797-1802.
- 21 (a) A. Hirao and H. Nishizawa, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, 54, 4755–4761; (b) T. Nagase and H. Naito, *J. Appl. Phys.*, 2000, 88, 252–259; (c) H. Iino, J. Hanna, R. J. Bushby, B. Movaghar and B. J. Whitaker, *J. Appl. Phys.*, 2006, 100, 043716.