Supporting Information

Charge Transport in Liquid Crystal Network of Terthiophene-Siloxane Block Molecules

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1. Materials, instruments and protocols

All chemicals were purchased from commercial sources and used without further purification. Dry solvents were obtained with an MBRAUN solvent purification system (MB-SPS). Ovendried glassware (120 °C) was used for all reactions carried out under argon atmosphere. Reactions were followed by thin-layer chromatography (TLC) using 60-F254 silica gel plates from Merck and visualized by UV light at 254 nm.

Thin films preparation: Glass slides were cleaned by sonication with ethyl alcohol for 10 min. These glass slides were then etched in a UV-ozone photoreactor (PR-100) for 20 min. To prepare a spin-cast thin film, a solution of the mixture in heptane (1 mg.mL⁻¹) was spin-coated on the etched glass slides (5000 rpm, 40 s, 500 rpm acceleration). The film thicknesses were about 40 or 750 nm, respectively. To prepare the LCN, cells were made by gluing together two glass plates. Glass beads with a diameter of 2-20 μ m were used to precisely control the gap of the cell. The cells were filled at the isotropic temperature of the mixture and polymerized in their LC phase with UV light source (EXFO Omincure-S2000) for 20 minutes. The light intensity during the polymerization was about 50 ± 15 mW.cm⁻². The photopolymerization was carried out under normal air because the monomers are isolated from oxygen in the LC cell. All thin films were stored in the dark and protected by aluminum foil.

Spectroscopy: NMR spectra were recorded on a Varian Mercury Vx 400 MHz (100 MHz for ¹³C) spectrometer. Chemical shifts are expressed in ppm and are referred to the residual peak of the solvent. Peak multiplicity is abbreviated as s: singlet; d: doublet, q: quartet; p: pentet; hept: heptet; m: multiplet; dd: double doublet; dt: double triplet; ddt: double doublet of triplets. Matrix assisted laser absorption/ionization-time of flight mass spectra (MALDI-TOF) were obtained on a PerSeptive Biosystems Voyager DE-PRO spectrometer using α -cyano-4-hydroxycinnamic acid (CHCA) or trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-

malononitrile (DCBT) as matrix. UV-Vis spectra were recorded on a PerkinElmer Lambda 750 spectrometer. A scanning rate of 200 nm.min⁻¹, a bandwidth of 1 nm, a response time of 0.24 s, a data pitch of 1 nm, a data interval of 1 nm, and single accumulation were employed. IR spectra were recorded on a Perkin–Elmer spectrum two FTIR spectrometer.

Polarized Optical Microscopy: POM was carried out using Nikon Eclipse Ci POL equipped with a Linkam LTS 420 heating stage.

Small-Angle X-Ray Scattering: SAXS of thin films were performed on an instrument from Ganesha Lab. The flight tube and sample holder were all under vacuum in a single housing, with a GeniX-Cu ultra-low divergence X-ray generator. The source produces X-rays with a wavelength (λ) of 0.154 nm and a flux of 1 × 108 ph s⁻¹. Scattered X-rays were captured on a 2-dimensional Pilatus 300K detector with 487 × 619 pixel resolution. The sample-to-detector distance was 0.084 m (WAXS mode) or 0.48 m (MAXS mode), and the instrument was calibrated with diffraction patterns from silver behenate.

2. Synthesis and molecular characterization of RM-TTPSi3



Figure S1. Synthesis scheme of terthiophene-siloxane reactive mesogen **RM-TTPSi3**. Reaction conditions: (i) Karstedt's catalyst, DCM, RT; (ii) K₂CO₃, KI, DMF, 60 °C; (iii) Karstedt's catalyst, DCM, RT; (iv) PdCl₂(PPh₃)₂, Na₂CO₃, DME/H₂O; (v) TEA, DCM, from 0 °C to RT.

Synthesis of 6-(1,1,3,3,5,5-hexamethyltrisiloxaneyl)hexan-1-ol (3):

A 250 mL dried two-neck round-bottom flask equipped with a magnetic stirring bar under a positive pressure of argon was charged with 1,1,3,3,5,5-hexamethyltrisiloxane (2.70 g, 27.0 mmol) (1), 5-hexen-1-ol (2) (11.3 g, 54.0 mmol) and dichloromethane (27 mL, dehydrated). The solution was stirred at room temperature and xylene solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Pt ~2 %, 135 μ L, ~0.27 mmol) was added. After stirring for 30 min at room temperature, the solvent was removed under vacuum and the resulting mixture were purified by silica gel column chromatography (R_f = 0.4, heptane/ethyl acetate=5/1). After drying in vacuo, the pure product was obtained as a colorless oil (2.39 g, 29 %). ¹H-NMR (400 MHz, chloroform-*d*): δ = 4.69 (hept, *J* = 2.5 Hz, 1H), 3.63 (td, *J* = 6.7, 1.4 Hz, 2H), 1.60 – 1.51 (m, 2H), 1.34 (s, 6H), 0.57 – 0.48 (m, 2H), 0.18 (t, *J* = 2.0 Hz, 6H), 0.06 (d, *J* = 1.4 Hz, 12H) ppm; ¹³C-NMR (100 MHz, chloroform-*d*): δ = 63.18, 33.30, 32.87, 25.60, 23.31, 18.32, 1.11 ppm.

Synthesis of 4,4,5,5-tetramethyl-2-(4-(pent-4-en-1-yloxy)phenyl)-1,3,2-dioxaborolane (6):

A 250 mL dried two-neck round-bottom flask equipped with a magnetic stirring bar under a positive pressure of argon was charged with 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (4.40 g, 20.0 mmol) (4), 5-bromo-1-pentene (5) (2.98 g, 20.0 mmol), potassium carbonate (6.91 g, 50.0 mmol), potassium iodide (664 mg, 4.0 mmol) and N,N-dimethylformamide (40 mL, dehydrated). The solution was stirred at 80 °C for 18 h. After cooling to room temperature, the resulting suspension was filtered with a filter paper to remove the precipitates. Next, the resulting solution was extracted with ethyl acetate (200 mL) and the organic layer was washed with water (100 mL × 2). After drying with sodium sulfate, the solvent was removed under vacuum and the resulting mixture were purified by silica gel column chromatography (R_f = 0.4, heptane/ethyl acetate=10/1). After drying in vacuo, the pure product was obtained as a colorless oil (4.51 g, 78 %). ¹H-NMR (400 MHz, chloroform-*d*): δ = 7.79 – 7.70 (m, 2H), 6.93 – 6.85 (m, 2H), 5.85 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.11 – 4.96 (m, 2H), 4.00 (t, *J* = 6.4 Hz, 2H), 2.30 – 2.18 (m, 2H), 1.90 (dt, *J* = 8.1, 6.6 Hz, 2H), 1.33 (s, 12H) ppm. ;¹³C-NMR (100 MHz, chloroform-*d*): δ = 161.79, 137.91, 136.62, 115.35, 114.00, 83.65, 67.07, 30.23, 28.52, 25.01 ppm.

Synthesis of 6-(1,1,3,3,5,5-hexamethyl-5-(5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)pentyl)trisiloxaneyl)hexan-1-ol (7):

A 50 mL dried two-neck round-bottom flask equipped with a magnetic stirring bar under a positive pressure of argon was charged with compound **3** (2.06 g, 6.69 mmol), compound **6** (1.93 g, 6.69 mmol) and dichloromethane (13 mL, dehydrated). The solution was stirred at room temperature and xylene solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Pt ~2 %, 130 µL, ~0.26 mmol) was added. After stirring for 30 min at room temperature, the solvent was removed under vacuum and the resulting mixture were purified by silica gel column chromatography ($R_f = 0.2$, heptane/ethyl acetate=4/1). After drying in vacuo, the pure product was obtained as a colorless oil (2.69 g, 68 %). ¹H-NMR (400 MHz, chloroform-*d*): $\delta = 7.78 - 7.69$ (m, 2H), 6.93 - 6.84 (m, 2H), 3.97 (t, J = 6.6 Hz, 2H), 3.63 (t, J = 6.6 Hz, 2H), 1.85 - 1.73 (m, 2H), 1.60 - 1.21 (m, 25H), 0.61 - 0.49 (m, 4H), 0.06 (d, J = 3.8 Hz, 18H) ppm; ¹³C NMR (101 MHz, chloroform-*d*) δ 160.88, 135.62, 113.00, 82.66, 66.92, 62.24, 32.35, 31.91, 28.87, 28.12, 24.63, 24.01, 22.36, 22.24, 17.39 ppm.

Synthesis of HO-TTPSi3:

A 50 mL dried two-neck round-bottom flask equipped with a magnetic stirring bar under a positive pressure of argon was charged with 5,5"-dibromo-2,2':5',2"-terthiophene (406 mg, 1.00 mmol), compound 7 (1.31 g, 2.20 mmol), bis(triphenylphosphine)palladium(II) dichloride (28 mg, 2 mol%), 2 M sodium carbonate aq. (2 mL) and 1,2-dimethoxyethane (5 mL). The solution was stirred under reflux for 14 h. After cooling to room temperature, the resulting mixture was extracted with chloroform (50 mL × 3) and the organic layer was dried with sodium sulfate. After filtration, the solvent was removed under vacuum and the resulting mixture were purified by silica gel column chromatography ($R_f = 0.2$, heptane/ethyl acetate=2/1). After drying in vacuo, the pure product was obtained as an orange solid (795 mg, 67 %). ¹H-NMR (400 MHz, chloroform-*d*): $\delta = 7.55 - 7.48$ (m, 4H), 7.10 (d, J = 14.0 Hz, 6H), 6.95 - 6.87 (m, 4H), 3.98 (t, J = 6.5 Hz, 4H), 3.64 (t, J = 6.6 Hz, 4H), 1.82 (q, J = 7.1 Hz, 4H), 1.58 - 1.22 (m, 26H), 0.56 (dt, J = 16.1, 8.1 Hz, 8H), 0.07 (dd, J = 5.5, 1.6 Hz, 36H) ppm; ¹³C-NMR (100 MHz, chloroform-*d*): $\delta = 159.07$, 143.50, 136.25, 135.47, 127.02, 126.77, 124.62, 124.08, 122.80, 115.06, 68.28, 63.26, 33.35, 32.91, 29.90, 29.16, 25.63, 23.36, 23.25, 18.39, 1.48 ppm; MALDI-TOF MS (m/z): [M]+ calc. for C₅₈H₉₆O₈S₃Si₆ 1184.49, found 1184.55.

Synthesis of **RM-AzoSi**₃:

A 25 mL dried three-neck round-bottom flask equipped with a magnetic stirring bar under a positive pressure of argon was charged with **HO-TTPSi3** (593 mg, 0.50 mmol), dichloromethane (15 mL, dehydrated), and triethylamine (177 mg, 1.75 mmol). The solution was stirred at 0 °C and acryloyl chloride (127 mg, 1.40 mmol) was added. After stirring for 18 h at room temperature, the solvent was removed under vacuum and the resulting mixture were purified by silica gel column chromatography ($R_f = 0.5$, heptane/ethyl acetate = 4/1). After drying in vacuo, the pure product was obtained as a waxy orange solid (621 mg, 96 %). ¹H-NMR (400 MHz, chloroform-*d*): $\delta = 7.55 - 7.48$ (m, 4H), 7.10 (d, J = 13.3 Hz, 6H), 6.94 – 6.87 (m, 4H), 6.40 (d, J = 17.3 Hz, 2H), 6.12 (dd, J = 17.4, 10.4 Hz, 2H), 5.81 (d, J = 10.4 Hz, 2H), 4.15 (t, J = 6.7 Hz, 4H), 3.98 (t, J = 6.6 Hz, 4H), 1.81 (p, J = 6.9 Hz, 4H), 1.66 (p, J = 6.8 Hz, 4H), 1.52 – 1.29 (m, 20H), 0.56 (dt, J = 16.8, 7.8 Hz, 8H), 0.07 (d, J = 4.7 Hz, 36H) ppm; ¹³C-NMR (100 MHz, chloroform-*d*): $\delta = 166.49$, 159.08, 143.51, 136.26, 135.47, 130.57, 128.79, 127.02, 126.77, 124.62, 124.08, 122.80, 115.06, 68.26, 64.88, 33.18, 29.90, 29.16, 28.72, 25.82, 23.29, 23.26, 18.40, 18.36, 1.48 ppm; MALDI-TOF MS (m/z): [M]+ calc. for C₆₄H₁₀₀O₁₀S₃Si₆ 1292.51, found 1293.57.



Figure S2. ¹H-NMR spectrum (400 MHz, CDCl₃) of **3**.



Figure S3. ¹³C-NMR spectrum (100 MHz, CDCl₃) of 3.



Figure S4. ¹H-NMR spectrum (400 MHz, CDCl₃) of 6.



Figure S5. ¹³C-NMR spectrum (100 MHz, CDCl₃) of 6.



Figure S6. ¹H-NMR spectrum (400 MHz, CDCl₃) of 7.



Figure S7. ¹³C-NMR spectrum (100 MHz, CDCl₃) of 7.



Figure S8. ¹H-NMR spectrum (400 MHz, CDCl₃) of HO-TTPSi₃.



Figure S9. ¹³C-NMR spectrum (100 MHz, CDCl₃) of HO-TTPSi₃.



Figure S10. MALDI-TOF Mass spectrum of HO-TTPSi3 with DCTB matrix.



Figure S11. ¹H-NMR spectrum (400 MHz, CDCl₃) of RM-TTPSi₃.



Figure S12. ¹³C-NMR spectrum (100 MHz, CDCl₃) of RM-TTPSi₃.



Figure S13. MALDI-TOF Mass spectrum of RM-TTPSi3 with DCTB matrix.



Figure S14. Bulk POM images of HO-TTPSi₃. The images were captured around (a) 100 °C and (b) 120 °C after cooling from 180 °C. The study was carried out with casted thin films. Scale bars: $20 \mu m$.



Figure S15. Bulk POM images of RM-TTPSi₃. The images were captured around (a) 30 °C and (b) 100 °C after cooling from 180 °C. The study was carried out with casted thin films. Scale bars: $20 \mu m$.



Figure S16. Bulk POM images of **HO-TTPSi3**. The images were captured around 40 °C after cooling from 180 °C. The study was carried out with glass cells of 10 μ m thickness (a) coated with a homeotropic alignment layer (Polyimide Sunever grade 5300) and (b) coated with a planar alignment layer (Polyimide Optimer Al 1501, JSR corporation, Japan). Scale bars: 50 μ m.



Figure S17. Bulk POM images of **HO-TTPSi3**. The images were captured around 130 °C after cooling from 180 °C. The study was carried out with glass cells of 10 μ m thickness (a) coated with a homeotropic alignment layer (Polyimide Sunever grade 5300) and (b) coated with a planar alignment layer (Polyimide Optimer Al 1501, JSR corporation, Japan). Scale bars: 50 μ m.



Figure S18. Bulk POM image of **RM-ATTPSi3**. The image was captured around 40 °C after cooling from 180 °C. The study was carried out with a glass cell of 10 μ m thickness coated with a homeotropic alignment layer (Polyimide Sunever grade 5300). Scale bar: 50 μ m.



Figure S19. Bulk POM images of **RM-TTPSi3**. The images were captured around 100 °C after cooling from 180 °C. The study was carried out with glass cells of 10 μ m thickness (a) coated with a homeotropic alignment layer (Polyimide Sunever grade 5300) and (b) coated with a planar alignment layer (Polyimide Optimer Al 1501, JSR corporation, Japan). Scale bars: 50 μ m.



Figure S20. Normalized UV-vis absorption spectra of dichloromethane (DCM) solution ($\sim 1.0 \times 10^{-5}$ mol L⁻¹) and a spin-casted thin film of **RM-TTPSi3**. All the spectra were recorded at 20 °C.



Figure S21. Bulk POM image of RM-TTPSi₃ after polymerization. The polymerization was carried out with UV light source for 20 min at 90 °C. The study was carried out with a glass cell of 6 μ m thickness. Image was captured at 20 °C. Scale bar: 20 μ m.



Figure S22. IR spectra of thin films of RM-TTPSi₃. Black and red lines indicate unpolymerized and polymerized films, respectively. The polymerization was carried out with UV light source for 20 min at 90 °C using a glass cell of 6 μ m thickness. All the spectra were recorded at 20 °C.