

Conglomerate with Periodic Enantiomer Inclusion: A Mechanism for Homochirality Erosion

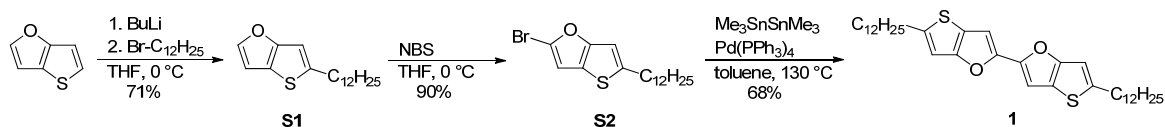
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Scheme S1. Synthetic route to oligomer **1**.

1. Synthesis of compound 1

General. Thieno[3,2-*b*]furan¹ was prepared according to literature procedures. THF was dried by passage through a column packed with activated alumina. Infrared absorption spectra were collected on a Nicolet AVATAR 360 FT-IR instrument. Melting point determination was performed using a TA DSC Q10 instrument. Samples were prepared in hermetic aluminum pans and cycled from 0 °C to 225 °C (5 °C/min) under a nitrogen purge.

5-dodecylthieno[3,2-*b*]furan (S1):

In a dry flask, 1.6 M butyllithium in hexanes (5.63 mL, 9.00 mmol) was added dropwise to a stirring solution of thieno[3,2-*b*]furan¹ (1.24 g, 10.0 mmol) in THF (200 mL) at 0 °C under a N₂ atmosphere. After 1 h at 0 °C, 1-bromododecane (2.49 g, 10.0 mmol) was added dropwise and the reaction mixture was allowed to warm to r.t. and stir for an additional 10 h. The reaction mixture was then diluted with hexanes and washed with H₂O and brine. The organic layer was separated and dried over anhydrous Na₂SO₄ and the solvent was removed in vacuo. The crude material was placed under vacuum (15 mTorr) at r.t. for 1 h to remove residual thieno[3,2-*b*]furan. Purification by column chromatography on silica gel eluting with hexanes yielded **S1** (1.90 g, 6.50 mmol, 72%). Note: Careful attention to column chromatography is required in order to isolate the desired product from its isomer 2-dodecylthieno[3,2-*b*]furan (crude mixture contains ~4% of undesired isomer). ¹H NMR (500 MHz, 23 °C, CDCl₃, δ): 7.45 (d, *J* = 2.1 Hz, 1H), 6.78 (dt, *J* = 0.6, 0.8 Hz, 1H), 6.66 (dd, *J* = 0.6, 2.1 Hz, 1H), 2.82 (dt, *J* = 0.8, 7.5 Hz, 2H), 1.69 (tt, *J* = 7.3, 7.5 Hz, 2H), 1.41-1.20 (br, 18H), 0.88 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃, δ): 157.1, 146.8, 144.2, 120.3, 108.3, 106.0, 31.9, 31.6, 31.5, 29.65, 29.63, 29.55, 29.354, 29.347, 29.0, 22.7, 14.1. IR (KBr): 3147 (w), 3124 (w), 2955 (s), 2924 (vs), 1547 (w), 1498 (m), 1487 (w), 1466 (m), 1437 (m), 1419 (w), 1377 (w), 1346 (m), 1134 (s), 1047 (w), 1005 (w), 897 (m), 800 (w), 717 (s) cm⁻¹. MS (EI, 70eV) *m/z* (relative intensity): 293.2 (1.1), 292.2 (14.8, M⁺), 138.3 (2.6), 136.3 (100). Anal. Calcd. for C₁₈H₂₈OS: C, 73.92; H, 9.65. Found: C, 73.62; H, 9.77.

2-bromo-5-dodecylthieno[3,2-*b*]furan (S2):

N-bromosuccinimide (488 mg, 2.74 mmol) was dissolved in THF (5 mL) and added dropwise to stirring solution of 5-dodecylthieno[3,2-*b*]furan (**S1**) (800 mg, 2.74 mmol) in THF (25 mL) at 0 °C in the absence of light. After 1 h at this temperature the reaction mixture was allowed to warm to r.t. and stir for an additional 10 h. The solution was then diluted with hexanes and washed with H₂O and brine, dried over anhydrous Na₂SO₄ and the solvent was removed in vacuo. The residue was then passed through a silica plug eluting with hexanes to yield **S2** (922 mg, 2.49 mmol, 90%). Note: This neat compound should be stored in the absence of light at -10 °C as it appears to be unstable upon exposure ambient conditions for more than 8 h. ¹H NMR (500 MHz, 23 °C, CDCl₃, δ): 6.74 (dt, *J* = 0.6, 0.8 Hz, 1H), 6.59 (d, *J* = 0.6 Hz, 1H), 2.80 (dt, *J* = 0.8, 7.5 Hz, 2H), 1.67 (tt, *J* = 7.3, 7.5 Hz, 2H), 1.41-1.20 (br, 18H), 0.88 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃, δ): 157.0, 146.1, 123.0, 121.4, 108.1, 107.6, 31.9, 31.5, 31.2, 29.64, 29.62, 29.61, 29.5, 29.34, 29.32, 29.0, 22.7, 14.1. IR (KBr): 3138 (w), 3097 (w), 2953 (s), 2924 (vs), 2852 (vs), 2729 (w), 2673 (w), 1498 (s), 1466 (s), 1437 (m), 1398 (s), 1335 (m), 1176 (s), 1030 (s), 918 (s), 785 (s), 721 (w) cm⁻¹. MS (EI, 70eV) *m/z* (relative intensity): 372.1 (16.3, M⁺), 371.1 (5.0), 370.1 (20.4), 216.8 (85.9), 215.8 (6.9), 214.8 (100), 108.0 (18.1).

5,5'-didodecyl-2,2'-bithieno[3,2-*b*]furan (**1**):

In a pressure vessel, 1,1,1,2,2,2-hexamethyldistannane (47.0 mg, 0.143 mmol) and 2-bromo-5-dodecylthieno[3,2-*b*]furan (**S2**) (106 mg, 0.287 mmol) were combined in toluene (3 mL) and the solution was sparged with N₂ gas. Pd(PPh₃)₄ (7.0 mg, 5.7 μmol) was added to the mixture all at once and the vessel was quickly sealed. The solution was then stirred for 12 h at 130 °C. Upon removing the solvent in vacuo, the residue was redissolved in CH₂Cl₂ and passed through a celite plug. The filtrate was evaporated and the resulting material was recrystallized (dissolved in acetone at r.t. and then cooled to -80 °C) to yield **1** (57.0 mg, 97.7 μmol, 68%). mp 101 °C. ¹H NMR (500 MHz, 23 °C, CDCl₃, δ): 6.85 (d, *J* = 0.6 Hz, 2H), 6.79 (dt, *J* = 0.6, 0.8 Hz, 2H), 2.84 (dt, *J* = 0.8, 7.5 Hz, 4H), 1.70 (tt, *J* = 7.3, 7.5 Hz, 4H), 1.41-1.20 (br, 36H), 0.88 (t, *J* = 6.9 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃, δ): 156.5, 148.1, 147.3, 122.3, 108.2, 101.2, 31.9, 31.6, 29.65, 29.63, 29.55, 29.3, 29.0, 22.7, 14.1. IR (KBr): 3122 (w), 3091 (w), 2955 (w), 2916 (vs), 2874 (m), 2848 (s), 1533 (w), 1470 (m), 1383 (w), 1169 (m), 1105 (w), 1032 (w), 893 (m), 822 (w), 797 (m), 871 (m), 719 (w) cm⁻¹. MS (EI, 70eV) *m/z* (relative intensity): 585.4 (6.4), 584.4 (19.8), 583.4 (43.1), 582.4 (100, M⁺), 581.4 (6.0), 580.4 (5.0), 429.2 (4.4), 428.2 (8.4), 427.2 (24.4), 274.0 (2.0), 273.0 (3.5), 272.0 (13.6), 68.0 (17.1), 84.0 (25.2). Anal. Calcd. for C₃₆H₅₄O₂S₂: C, 74.17; H, 9.34. Found: C, 73.93; H, 9.36.

2. STM experiments

A Nanoscope E STM (Digital Instruments) was used for all imaging. Highly oriented pyrolytic graphite (HOPG) (SPI-1 grade, Structure Probe Inc.) was used as a substrate for monolayer formation. A phenyloctane solution of **1** was made, of which 1 μL was placed on freshly cleaved HOPG to obtain a self-assembled monolayer. The tips were made from Pt/Ir wire (20% Ir, 0.010 inch diameter, California Fine Wire) by mechanical cutting. STM imaging was performed using quasi-constant height mode under ambient conditions and typical STM settings include 300 pA of current and 700-900 mV of bias voltage (sample positive). All images are unfiltered. The concentrations for STM experiments were varied from 0.10 to 20.0 mM.

3. Computational Modeling

The packing structure of **1** apparent from the metrics and symmetry of the STM images was modeled and energy minimized from Materials Studio version 4.3 (Accelrys Software Inc.) using a COMPASS forcefield. However, non-periodic 2D crystal can not be modeled in this way. Using high resolution STM images and the energy minimized periodic model of **1**, the one-dimensionally periodic assembly was modeled. This model was overlaid on a fixed graphite slab and energy minimized to get the optimized packing structure on HOPG using a COMPASS forcefield.

4. STM images of interfaces at pure L1 and R1 domains

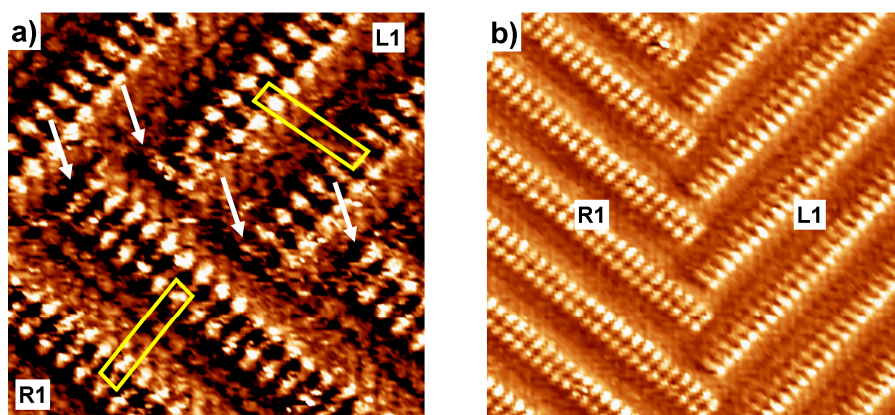


Figure S1. STM images of interfaces at pure L1 and R1 domains showing (a) defects indicated by white arrows and (b) close packed structure at interfaces. The unit cell parameters were $7.0 \pm 0.3 \text{ \AA} \times 35.5 \pm 2.0 \text{ \AA}$ with $\gamma = 87 \pm 2^\circ$ for L1 and $6.9 \pm 0.2 \text{ \AA} \times 36.4 \pm 2.2 \text{ \AA}$ with $\gamma = 87 \pm 2^\circ$ for R1.

5. Large scale STM images showing concentration dependence

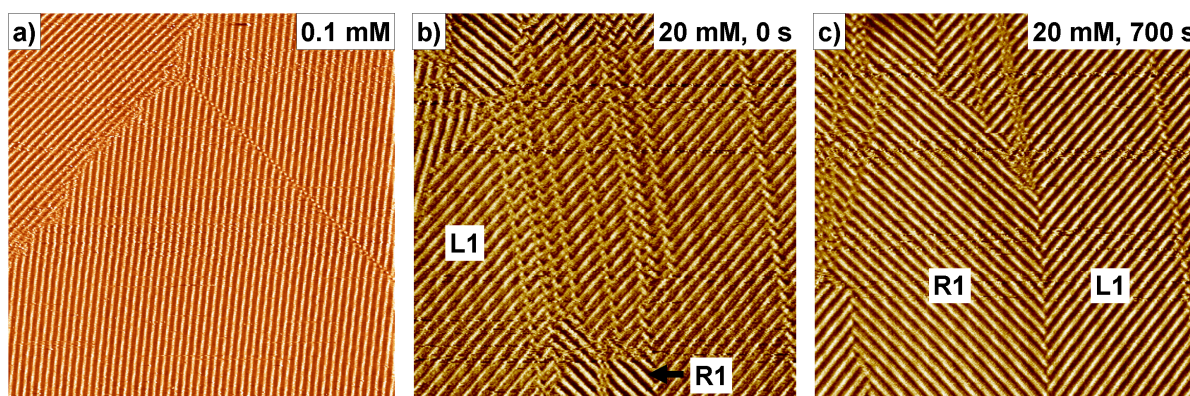


Figure S2. Large scale STM images showing concentration dependence: (a) $200 \times 200 \text{ nm}^2$, 0.10 mM, (b) $150 \times 150 \text{ nm}^2$, 20.0 mM, and (c) after 700s, $150 \times 150 \text{ nm}^2$, 20.0 mM

No free surface has been observed at the lowest concentration (0.10 mM) and multilayers from the 20 mM solution have not been observed in the present study.

6. Reference

- (1) Henssler, J. T.; Matzger, A. J. *Org. Lett.* **2009**, *11*, 3144-3147.