

## Supporting Information

# Molecular Orientation within Thin Films of Isomorphous Molecular Semiconductors

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## Materials and Methods

**Solvents and Synthetic Intermediates.** Toluene was degassed and dried through a standard solvent system. Chloroform was purchased from Sigma-Aldrich and stored inside a N<sub>2</sub>-filled glovebox before use. Chloroform and hexanes used for silica gel column chromatography were analytical grade and used without further purification. Compounds *4-(4,4-Bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophen-2-yl)-7-bromobenzo[c][1,2,5]thiadiazole (1)*<sup>S1</sup> and *5'-hexyl-2,2'-bithiophene-5-trimethylstannane (2)*<sup>S2</sup> were prepared using the reported procedures. Stille coupling reaction was conducted on a Biotage® Microwave Initiator.

**<sup>1</sup>H, and <sup>13</sup>C Nuclear Magnetic Resonance (NMR)** spectra were recorded on a Bruker Avance 500 MHz spectrometer by using either CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub> or C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>. Chemical shifts ( $\delta$ ) were expressed as parts per million (ppm), and calibrated using residual solvent signals by referring tetramethylsilane (TMS) as 0 ppm. Coupling constants ( $J$ ) were reported in Hertz (Hz).

**Field Desorption Time-of-Flight (FD-TOF) Mass Spectra** were measured on a VG70 Magnetic Sector instrument at the Mass Spectrometry Facility of UCSB Department of Chemistry and Biochemistry. Samples were prepared by dissolving each molecule into chloroform with a final concentration of ~1 mg/mL.

**Solution and Thin-film Ultraviolet/Visible (UV/vis) Absorption** measurement were performed by using a Beckman Coulter DU 800 series UV-vis spectrophotometer. Solution samples were measured in dry chloroform with a solid concentration of 0.02 mg/mL at room temperature. Thin films were casted from chloroform solutions (10 mg/mL) on pre-cleaned glass substrates at a spin speed of 1500 rpm for 60 s. The thicknesses of all films were calculated between 50 to 65 nm from X-ray reflectivity measurements, which were used to calculate absorption coefficient ( $\alpha$ ) in the solid state.

**Density Functional Theory (DFT)** calculations were done using the Gaussian 09 software suite.<sup>S3</sup> The hybrid long range corrected CAM-B3LYP functional<sup>S4</sup> with the basis set 6-31G(d,p) were used for both the optimization of the geometry as well as the time-dependent and natural transition orbital analysis.<sup>S5</sup>

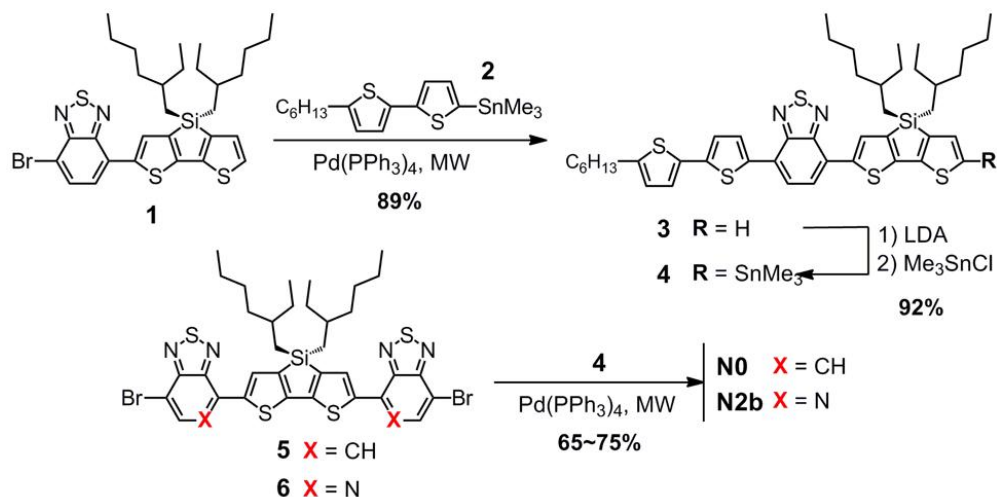
**Ultraviolet Photoelectron Spectroscopy (UPS)** analysis was done on a Kratos Axis Ultra equipped with a hemispherical electron energy analyzer and was held at a constant pressure of  $1.35 \times 10^{-7}$  Torr. Neat films of **N0**, **N2a**, **N2b**, and **N4** were spun cast on cleaned and UV/ozone-treated Corning 1737 glass patterned with 140 nm of ITO from solutions with concentrations ~2 mg/mL at 2000 RPM for 60 seconds yielding films with an approximate thickness of 10-15 nm. Films were cast in a glovebox with an N<sub>2</sub> atmosphere and were transferred using an air-free sample holder to minimize exposure to Air. UPS spectra were then obtained using a He I ( $h\nu = 21.21$  eV) and the electron energy analyzer was held at a constant pass energy of 5 eV.

**Differential Scanning Calorimetry (DSC)** was performed on a TA Instruments DSC (Model Q-20 with a RCS90 cooling system) with 3~4 mg of each sample with a heating/cooling ramp of 10 °C/min under an N<sub>2</sub> atmosphere. The data from the second cycle of each measurement was collected in order to eliminate thermal history of materials.

**Grazing-Incidence Wide Angle X-ray Scattering (GIWAXS)** measurements were performed at beamline

7.3.3 of the Advanced Light Source with an incidence angle of  $\sim 0.13^\circ$  under a helium environment to minimize beam damage and reduce scattering from the air. Thin film samples were prepared by spin-casting 10 mg/mL chloroform solution of each material on top of silicon (100) substrates.

## Synthesis and Characterization of Molecules N0 and N2b



**Scheme S1.** Synthetic Procedures for Molecules **N0** and **N2b**.

*Synthesis of 5-{4-(7-hexylthiophen-2-yl)thiophen-2-yl-benzo[*c*][1,2,5]thiadiazole}-3,3'-bis (2-ethylhexyl)silylene-2,2'-bithiophene (**3**).* Inside a nitrogen-filled glovebox, compound **1** (400 mg, 0.71 mmol, 1.0 eq), **2** (293 mg, 0.71 mmol, 1.0 eq), Pd(PPh<sub>3</sub>)<sub>4</sub> (49 mg, 0.04 mmol, 0.06 eq), and dry toluene (4 mL) were combined in a 5 mL Biotage® reaction vial and sealed. The solid suspension was subsequently subjected to microwave irradiation with a heating program as 70 °C for 2 min, 100 °C for 2 min, 130 °C for 5 min, and 160 °C for 40 min. The resulting mixture was purified by using silica gel column chromatography (hexane:chloroform = 10:3 as eluent). Compound **3** (506 mg, 89%) was obtained as a deep red oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ: 8.15–8.12 (m, 1H), 8.02–8.00 (d, *J* = 4.0 Hz, 1H), 7.83–7.79 (m, 2H), 7.27–7.25 (d, *J* = 3.5 Hz, 1H), 7.18–7.17 (d, *J* = 4.0 Hz, 1H), 7.10–7.08 (m, 1H), 6.73–6.71 (d, *J* = 3.5 Hz, 1H), 2.84–2.80 (t, *J* = 7.5 Hz, 2H), 1.74–1.67 (m, 2H), 1.53–1.14 (m, 24H), 1.08–0.96 (m, 4H), 0.93–0.78 (m, 15H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ: 152.9, 152.8, 150.8, 149.2, 146.3, 144.3, 143.8, 143.7, 140.3, 139.5, 137.9, 135.0, 130.8, 130.3, 128.4, 126.6, 126.3, 125.6, 125.3, 125.0,

124.1, 124.0, 36.3, 36.1, 31.9, 30.6, 29.3, 29.2, 29.1, 23.4, 23.3, 22.9, 18.2, 18.1, 18.0, 14.5, 14.4, 11.2.

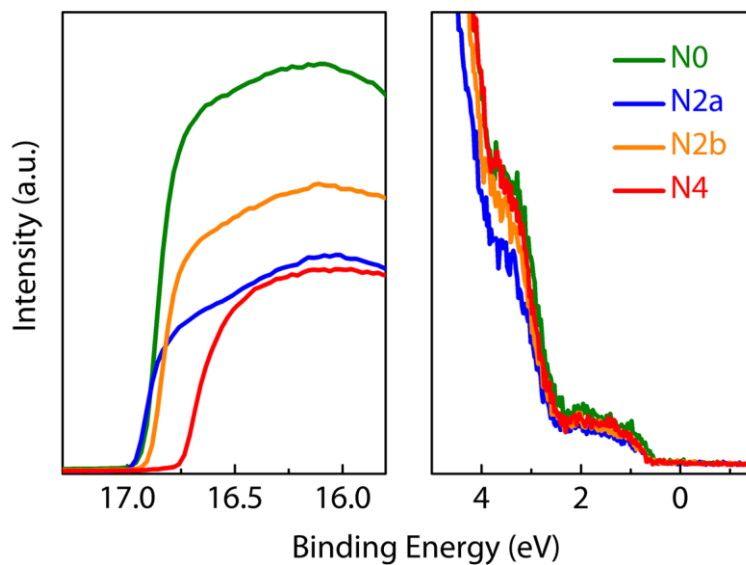
*Synthesis of 5-{4-(7-hexylthiophen-2-yl)thiophen-2-yl-benzo[*c*][1,2,5]thiadiazole}-5'-{trimethylstannyl}-3,3'-bis(2-ethylhexyl)silylene-2,2'-bithiophene (4).* A solution of compound **3** (460 mg, 0.57 mmol, 1.0 eq) in dry THF (13 mL) was cooled to  $-35\text{ }^{\circ}\text{C}$  under  $\text{N}_2$  and then LDA (0.6 M in THF/hexane, 1.4 mL, 0.86 mmol, 1.5 eq) was added dropwise. The mixture was stirred for 10 min at  $-35\text{ }^{\circ}\text{C}$ . Trimethyltin chloride ( $\text{Me}_3\text{SnCl}$ , 193 mg, 0.97 mmol, 1.7 eq) in THF (0.6 mL) was added subsequently and the resulting mixture was stirred for 1 hour while warming up to room temperature. The solution was then quenched in water and diluted with ether (200 mL), followed by washing with brine ( $2 \times 100\text{ mL}$ ) and water ( $2 \times 100\text{ mL}$ ). Compound **4** (506 mg, 92%) was afforded as a purple oil after the solvents were evaporated off.  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ , 500 MHz)  $\delta$ : 8.21–8.19 (m, 1H), 8.06–8.04 (d,  $J = 4.0\text{ Hz}$ , 1H), 7.88–7.87 (m, 2H), 7.23–7.21 (d,  $J = 4.0\text{ Hz}$ , 1H), 9.20–7.19 (s, 1H), 7.14–7.13 (d,  $J = 4.0\text{ Hz}$ , 1H), 6.77–6.75 (d,  $J = 3.5\text{ Hz}$ , 1H), 2.86–2.82 (t,  $J = 8.0\text{ Hz}$ , 2H), 1.75–1.69 (m, 2H), 1.52–1.14 (m, 24H), 1.10–0.97 (m, 4H), 0.94–0.78 (m, 15H), 0.48–0.35 (s, 9H).

*Synthesis of N0 and N2b.* Molecules **N0** and **N2b** were prepared according to the same reaction and purification procedures that were previously described in the synthesis of **3** by only varying reactants as follows. The amount and yield obtained for each molecule are shown in parenthesis. **N0** (130 mg, 75%): **4** (150 mg, 0.16 mmol, 2.1 eq), **5** (64 mg, 0.08 mmol, 1.0 eq), and  $\text{Pd}(\text{PPh}_3)_4$  (7 mg, 0.006 mmol, 0.08 eq); **N2b** (113 mg, 65%): **4** (150 mg, 0.16 mmol, 2.1 eq), **6** (64 mg, 0.08 mmol, 1.0 eq), and  $\text{Pd}(\text{PPh}_3)_4$  (7 mg, 0.006 mmol, 0.08 eq).

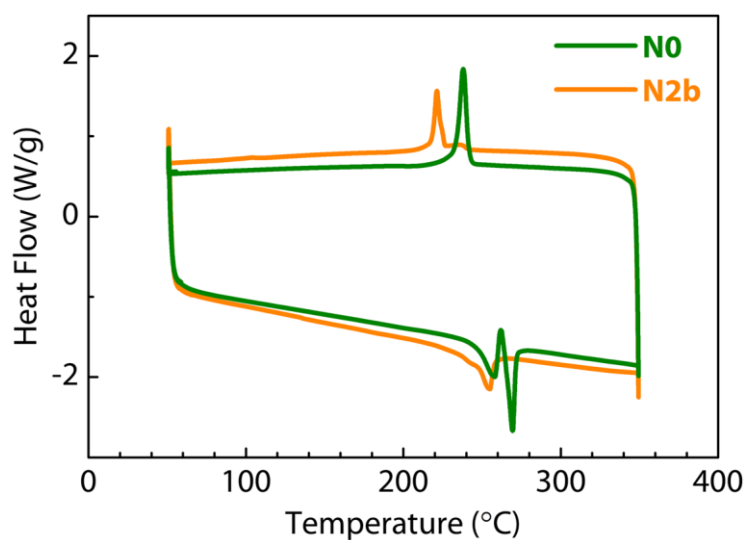
**N0**:  $^1\text{H NMR}$  ( $\text{C}_2\text{D}_2\text{Cl}_4$ , 373 K, 500 MHz)  $\delta$ : 8.29–8.25 (m, 6H), 8.12–8.10 (d,  $J = 4.0\text{ Hz}$ , 2H), 7.94–7.87 (m, 8H), 7.30–7.28 (d,  $J = 3.5\text{ Hz}$ , 2H), 7.22–7.20 (d,  $J = 3.5\text{ Hz}$ , 2H), 6.84–6.82 (d,  $J = 3.5\text{ Hz}$ , 2H), 2.96–2.91 (t,  $J = 8.0\text{ Hz}$ , 4H), 1.87–1.80 (m, 4H), 1.75–1.67 (m, 4H), 1.57–1.20 (m, 74H), 1.05–0.93 (m, 42H). FD-TOF MS: Calculated for  $\text{C}_{124}\text{H}_{150}\text{N}_8\text{S}_{14}\text{Si}_3$ : 2282.7. Found: 2282.6 ( $\text{M}^+$ ), 1141.3 ( $\text{M}^{2+}$ ), 760.9 ( $\text{M}^{3+}$ ).

**N2b**:  $^1\text{H NMR}$  ( $\text{C}_2\text{D}_2\text{Cl}_4$ , 373 K, 500 MHz)  $\delta$ : 8.98–8.96 (s, 2H), 8.85–8.82 (m, 2H), 8.29–8.25 (m, 4H), 8.15–8.13 (d,  $J = 4.0\text{ Hz}$ , 2H), 7.98–7.92 (m, 4H), 7.31–7.29 (d,  $J = 3.5\text{ Hz}$ , 2H), 7.22–7.20 (d,  $J = 3.5\text{ Hz}$ , 2H), 6.85–6.83 (d,  $J = 3.5\text{ Hz}$ , 2H), 2.96–2.91 (t,  $J = 8.0\text{ Hz}$ , 4H), 1.88–1.80 (m, 4H), 1.74–1.64 (m,

4H), 1.58–1.19 (m, 74H), 1.05–0.90 (m, 42H). FD-TOF MS: Calculated for  $C_{122}H_{148}N_{10}S_{14}Si_3$ : 2284.7.  
Found: 2284.6 ( $M^+$ ), 1142.3 ( $M^{2+}$ ), 761.6 ( $M^{3+}$ ).



**Figure S1.** UPS spectra of **N0**, **N2a**, **N2b**, and **N4**.



**Figure S2.** DSC traces of **N0** and **N2b**.

## References

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