

Siloxane-Terminated Solubilizing SideChains: Bringing Conjugated Polymer Backbones Closer and Boosting Hole Mobilities in Thin-Film Transistors

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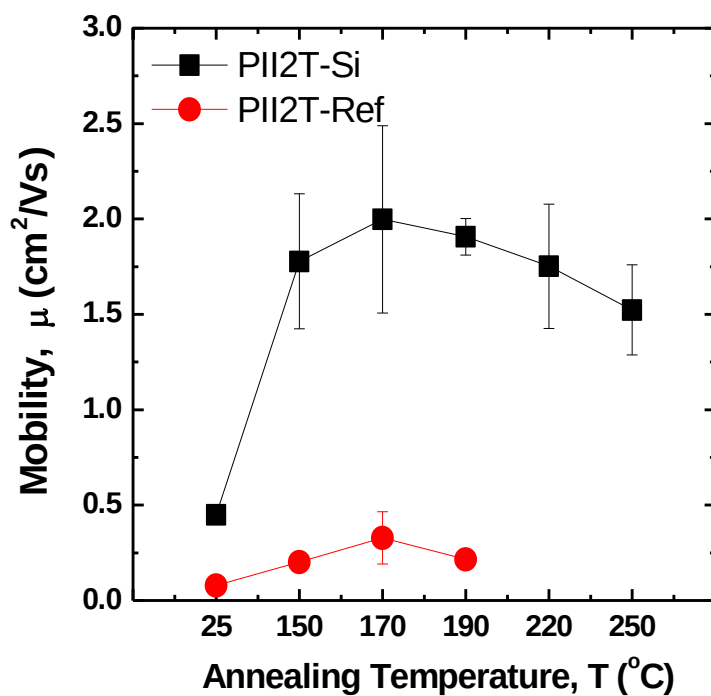


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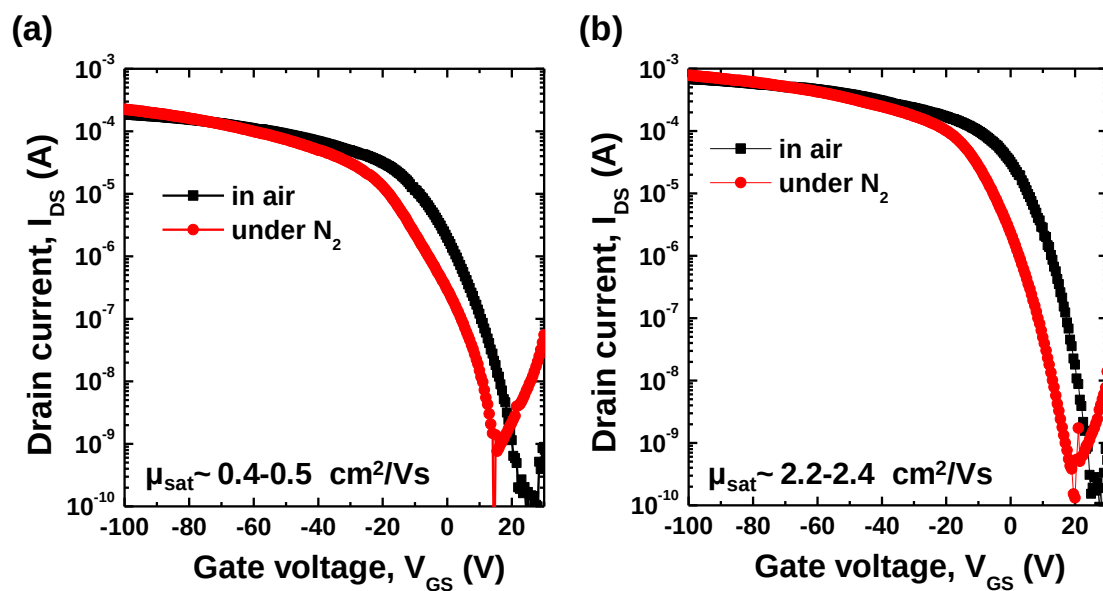


Figure S2. Effect of measurement condition (in air and under N₂) of (a) **PII2T-Ref** and (b) **PII2T-Si** OFETs.

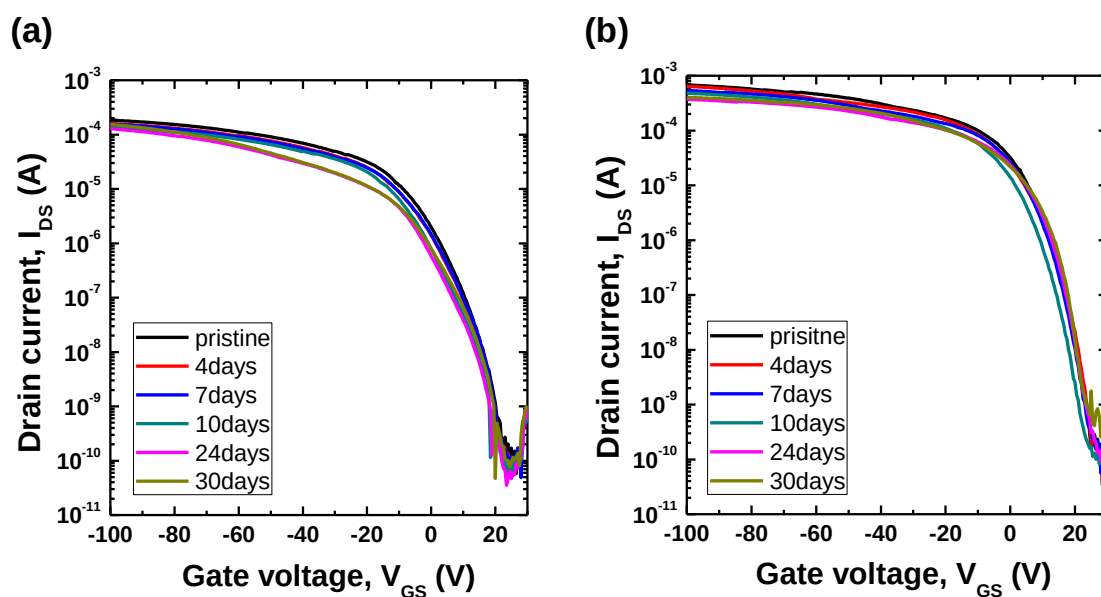


Figure S3. Air stability of (a) PII2T-Ref and (b) PII2T-Si OFETs. The devices were stored under ambient conditions ($R_H = 40\sim 45\%$).

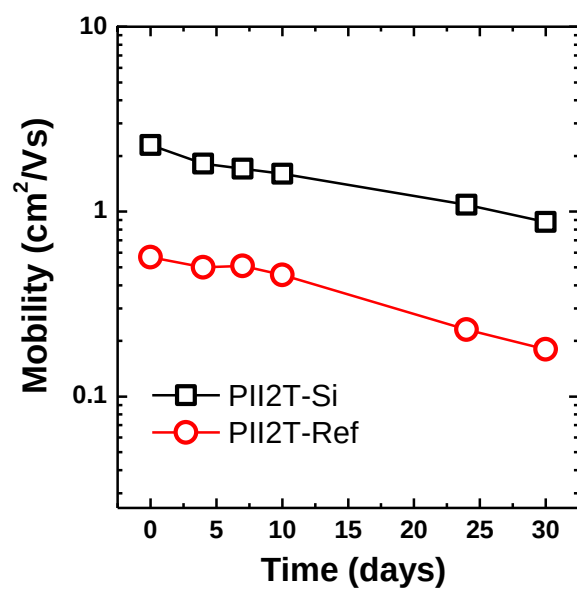


Figure S4. Mobility change in OFET devices as a function of time (day).

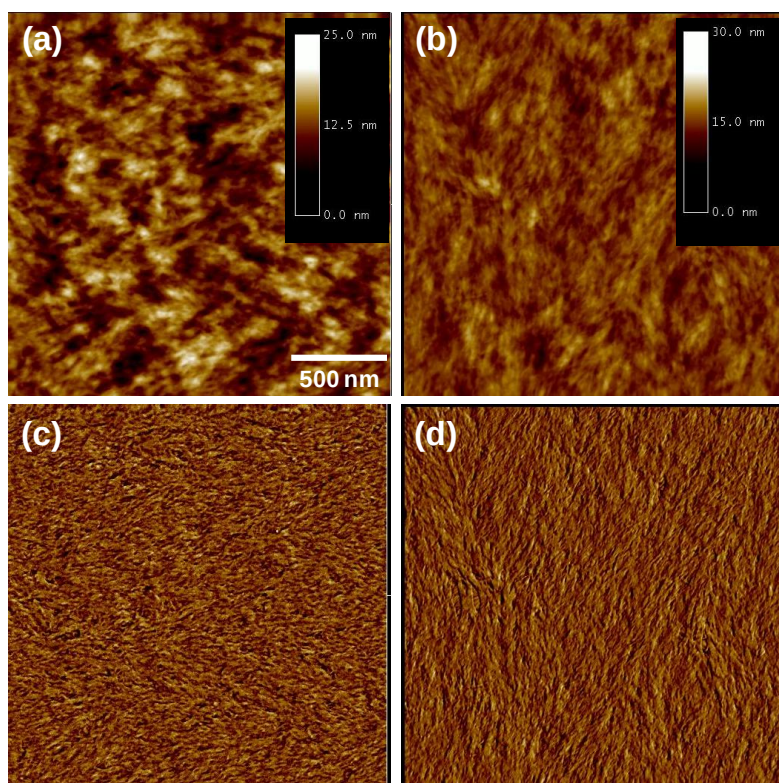


Figure S5. Tapping-mode AFM height and phase images of (a, c) **PII2T-Si** and (b,d) **PII2T-Ref** films annealed at 170°C on OTMS substrates

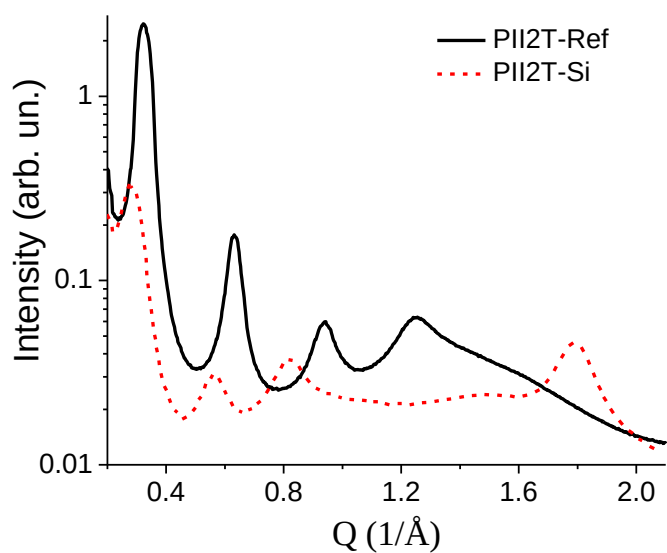
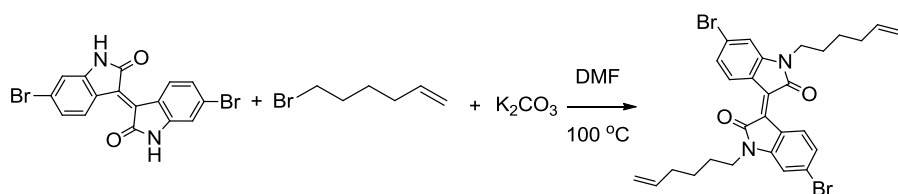


Figure S6. Out-of-plane line profiles for **PII2T-Ref** (solid black curve) and **PII2T-Si** (dashed red curve). The curves were generated by integrating the peaks over a cake slice

about Q_z from the 2-D GIXD images. Figure S6 shows the out-of-plane line profiles for the two polymer films. The (h00) peak progression characteristic of lamellar polymer ordering is clearly visible for both films. In addition, **PII2T-Si** shows the out-of-plane π -stacking peak at large Q that is absent in the **PII2T-Ref** film, as discussed in the main text. The out-of-plane reciprocal lattice vector $\mathbf{a}^*$ is smaller for **PII2T-Si** than that of **PII2T-Ref**, giving a lamellar spacing for the Si-containing polymer that is 2.5 Å larger.

Materials and characterizations: All reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted. ^1H and ^{13}C NMR spectra were recorded using Varian Inova 500 in deuterated chloroform at 293 K. Mass spectrograms were recorded on either a Finnigan MAT95Q Hybrid Sector (EI, HRMS) or a Bruker Reflex II (MALDI-TOF) mass spectrometer operated in linear mode with delayed Extraction at University of Florida. Elemental analyses were carried out by [Robertson Microlit](#). Size exclusion chromatography (SEC) was performed in THF solution and the molecular weights calculated using a calibration curve based on polystyrene standards. Thermal gravimetric analyses (TGA) were performed using a Mettler TOLEDO TGA/SDTA 851e at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under a nitrogen flow (20 mL/min).

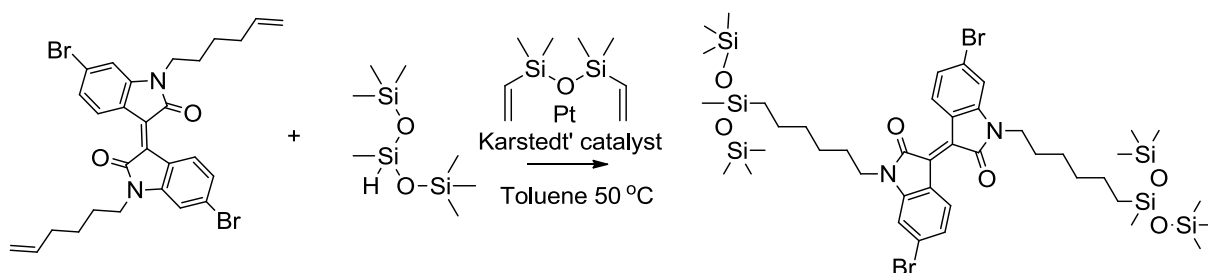
(E)-6,6'-dibromo-1,1'-di(hex-5-en-1-yl)-[3,3'-biindolinylidene]-2,2'-dione (1)



To a suspension of 6,6'-dibromoisindigo (1.47 g, 3.5 mmol) and potassium carbonate (1.93 g, 14.0 mmol) in dimethylformaldehyde (DMF) (30 mL), 1-bromo-hexene (1.37 g, 8.4 mmol) was injected through a septum under nitrogen. The mixture was stirred for 15 h at $100\text{ }^\circ\text{C}$ and then poured into water (200 mL). The organic phase was extracted by CH_2Cl_2 , washed with

brine and dried over MgSO_4 . After removal of the solvent under reduced pressure, the deep-red solids were purified by silica chromatography, eluting with (CH_2Cl_2 : Hexane = 1:1) to give (E)-6,6'-dibromo-1,1'-di(hex-5-en-1-yl)-[3,3'-biindolinylidene]-2,2'-dione (1.54 g, 75%). $^1\text{H-NMR}$ (CDCl_3 , 500 Hz) δ : 9.06 (d, J = 8.7 Hz, 2H), 7.17 (dd, J_1 = 8.7 Hz, J_2 = 1.5 Hz, 2H), 6.91 (d, J = 1.5 Hz, 2H), 5.81-5.75 (m, 2H), 5.05-5.00 (m, 4H), 3.74 (t, J = 7 Hz, 4H) 3.14-2.10 (m, 4H), 1.72-1.66 (m, 4H), 1.52-1.47 (m, 4H). $^{13}\text{C-NMR}$ (CDCl_3 , 500 Hz) δ : 168.0, 145.9, 138.4, 132.9, 131.5, 127.0, 125.4, 120.6, 115.4, 111.6, 40.3, 33.6, 27.0, 26.4. HRMS (ESI-TOF) Calculated for $\text{C}_{28}\text{H}_{28}\text{Br}_2\text{N}_2\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 585.0572, found: m/z 585.0576. Anal. Calcd for $\text{C}_{28}\text{H}_{28}\text{Br}_2\text{N}_2\text{O}_2$: C, 57.55; H, 4.83; N, 4.79; Found: C, 58.04; H, 4.54; N, 4.79.

(E)-6,6'-dibromo-1,1'-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-[3,3'-biindolinylidene]-2,2'-dione



Compound **1** (1.17 g, 2 mmol) was dissolved in anhydrous toluene (15 ml) under an argon atmosphere. 1,1,1,3,3,5,5,5-heptamethyltrisiloxane (1.02 g, 4.6 mmol) was injected through a septum, followed by the addition of a drop (20 μL) of Karstedt's catalyst (platinum-divinyltetramethyl-siloxane complex in xylene, 3 wt%). The resulting mixture was stirred at 50 $^\circ\text{C}$ under argon till complete consumption of compound **1**, which was monitored by TLC. The solution was directly subjected to silica gel chromatography using CH_2Cl_2 /Hexane (2:3) as an eluent, yielding dark red oil which was solidified over the time (500 mg, 40%).

$^1\text{H-NMR}$ (CDCl_3 , 500 Hz) δ : 9.03 (d, J = 8.5 Hz, 2H), 7.12 (dd, J_1 = 8.5 Hz, J_2 = 2 Hz, 2H), 6.85 (d, J = 2 Hz, 2H), 3.67 (t, J = 7 Hz, 4H), 1.68-1.60 (m, 4H), 1.40-1.28 (m, 12H), 0.45 (t,

J=6 Hz, 4H), 0.08 (bs, 36H), 0.01 (s, 6H). ^{13}C -NMR (CDCl_3 , 500 Hz) δ : 167.6, 145.7, 132.5, 131.2, 126.7, 125.1, 120.4, 111.2, 40.3, 32.9, 27.4, 26.8, 23.1, 17.6, 1.95, -0.23. HRMS (ESI-TOF) Calculated for $\text{C}_{42}\text{H}_{72}\text{Br}_2\text{N}_2\text{O}_6\text{Si}_6$ ($\text{M}+\text{Na}$) $^+$: 1051.2251, found: m/z 1051.2212. Anal. Calcd for $\text{C}_{42}\text{H}_{72}\text{Br}_2\text{N}_2\text{O}_6\text{Si}_6$: C, 49.01; H, 7.05; N, 2.72; Found: C, 49.33; H, 6.89; N, 2.61.

General procedure for polymerization: To a microwave vessel (8 mL) charged with a string bar, 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (123.0 mg, 0.25 mmol) and (E)-6,6'-dibromo-1,1'-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-[3,3'-biindolinylidene]-2,2'-dione (257.3 mg, 0.25 mmol) were added, followed by the addition of degassed toluene (6 mL). The resulting solution was bubbled with argon for 15 min. $\text{Pd}_2(\text{dba})_3$ (8 mg) and $\text{P}(\text{o-tyl})_3$ (4 mg) were quickly added under argon. The vessel was then sealed with a snap cap, purged with argon for 5 min and subjected to the following reaction conditions in a microwave reactor (Microwave Setups: CEM Discover Automatic Microwave Reactor; Power Cycling; Power, 300 W; Power Cycles, 200; Temperature, 110-135 $^\circ\text{C}$; Heating, 150s; Cooling, 30s; Pressure, 150 psi; Stirring, high.). After the completion, the reaction was cooled to room temperature and the obtained solids were suspended into acetone. The solids were collected by filtration through a high quality glass thimble. The thimble was left inside a Soxhlet extractor and the solids were successively extracted with acetone, hexane and chloroform. The chloroform fraction was concentrated and precipitated into acetone, yielding fiber-like precipitates. The polymer was filtered and dried *in vacuo* at 60 $^\circ\text{C}$ overnight. **PII2T-Si** gives M_n of 138 kDa with a PDI of 3.3. Anal. Calcd for **PII2T-Si**: C, 57.70; H, 7.33; N, 2.75; Found: C57.58; H, 7.45; N, 2.77.

PII2T-Ref and its isoindigo monomer: The monomer for PII2T-Ref was prepared according to the literature procedure.¹ The polymerization conditions were identical to **PII2T-Si**. **PII2T-Si** gives M_n of 135 kDa with a PDI of 5.5.

Device fabrication: The electrical properties (field-effect mobility and air-stability) of **PII2T-Ref** and **PII2T-Si** based OTFT devices were measured by using bottom-gate/top-contact geometry. A 300nm thick silicon oxide gate dielectric (capacitance $C_i=11.3 \text{ nFcm}^{-2}$) was thermally grown on a highly doped silicon wafer. Heavily n-doped thermally oxidized silicon substrates were cleaned in a piranha solution (70% vol H_2SO_4 + 30% vol H_2O_2) for 30 min, and then washed with copious amounts of distilled water. The SiO_2 dielectric surface was modified with a dense crystalline octadecyltrimethoxysilane (OTMS) self-assembled monolayer to enhance the electrical performance using a procedure reported previously.² **PII2T-Ref** and **PII2T-Si** thin films were prepared by spin-coating from 4mg/ml solution at 1000 rpm in chloroform, and annealed at 130°C, 150°C, 170°C, and 190°C for 1 hr under N_2 . Finally, source-drain electrodes (Au: thickness~40nm) were evaporated through shadow masks. The standard channel length (L) and width (W) are 50 μm and 1000 μm , respectively. A Keithley 4200-SCS semiconductor parameter analyzer was used to conduct all of the measurements for the current-voltage characteristics under ambient condition and N_2 . We compared the environmental stability of all devices under the same condition.

GIXD experiment: 2D-GIXD images were collected in reflection mode with a planar area detector in a He atmosphere at beamline 11-3 of the Stanford Synchrotron Radiation Lightsource. The sample-detector distance was nominally set to 400 mm, and the incidence angle was 0.12 degrees; the X-ray wavelength was 0.9758 Angstroms. Slits were set to 150 μm and 50 μm in the horizontal and vertical directions, respectively. GIXD images were calibrated and analyzed using WxDiff software provided by Stefan Mannsfeld (Adv. Mater. 2011, 23, 127–131). For details about the sample chamber, please see (Adv. Funct. Mater. 2010, 20, 3519).

Full citation for Reference 7: Bronstein, H.; Chen, Z.; Ashraf, R. S.; Zhang, W.; Du, J.; Durrant, J. R.; Shakya Tuladhar, P.; Song, K.; Watkins, S. E.; Geerts, Y.; Wienk, M. M.; Janssen, R. A. J.; Anthopoulos, T.; Sirringhaus, H.; Heeney, M.; McCulloch, I. J. *Am. Chem. Soc.* **2011**, 133, 3272-3275.

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