

Efficient Polymer Solar Cells Based On Copolymers of Dithieno[3,2-*b*:2',3'-*d*]silole and Thienopyrroledione

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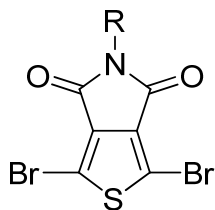
Experimental:

Materials and method.

All reagents and starting materials were purchased from commercial sources and used as received, unless otherwise noted. 1,3-dibromo-5-(2-ethylhexyl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (1),¹ 1,3-dibromo-5-dodecyl-4*H*-thieno[3,4,-*c*]pyrrole-4,6(5*H*)-dione (2),² and 4,4'-dioctyl-5,5'-bis(trimethylsilyl)-dithieno[3,2-*b*:2',3'-*d*]silole (3)³ were prepared according to reported procedures. ¹H NMR spectra were collected on a Bruker DPX 400 400 MHz spectrometer using CDCl₃ and chemical shifts were referenced with residual CHCl₃ in CDCl₃. Size Exclusion Chromatography (SEC) was performed using a Waters 2690 liquid chromatography system with a miniDAWN light scattering detector (Wyatt Technology) using two columns in series (Waters Styragel HR 4E and 5E columns). HPLC grade THF was used as

the mobile phase at a flow rate of 1.0 mL/min. The apparent molecular weights and polydispersities (M_w/M_n) were determined with a calibration based on narrow molecular weight poly(methyl methacrylate) standards using Empower software from Waters. All absorption spectra were collected using Shimadzu model 2501-PC. Differential scanning calorimetry (DSC) was carried out under nitrogen on a TA Instrument DSC 2920 (scanning rate of $10\text{ }^\circ\text{Cmin}^{-1}$). Thermogravimetric analysis (TGA) was carried out using a TA instrument TGA Q500 (heating rate of $10\text{ }^\circ\text{Cmin}^{-1}$). Cyclic voltammetry were performed using an Autolab potentiostat (model PGSTAT30) by Echochimie. Thin polymer films were dropcasted on a glassy carbon button electrode and a platinum and a silver wire were used as a counter and a pseudo-reference electrode respectively. All electrochemical measurements were performed in a nitrogen filled glove box using deaerated acetonitrile solution with 100 mM tetrabutylammonium hexafluorophosphate as a supporting electrolyte using the scan rate of 100 mV/s. Ferrocene/ferrocenium ion (Fc/Fc^+) was used as the internal standard and measured to be 524 mV under the same conditions. Tapping-mode Atomic Force Microscopy (TM-AFM) was performed on a Nanoscope V microscope (Veeco Inc.).

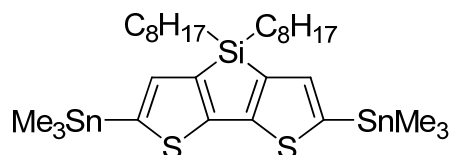
Synthesis.



1, R = 2-ethylhexyl
2, R = dodecyl

1,3-dibromo-5-(2-ethylhexyl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione 1. Prepared according to reported procedure starting from 3,4-dibromothiophene and commercially available 2-ethylhexylamine. The final product was further purified by recrystallization from hexane as white crystals. ¹H NMR (400 MHz, CDCl₃): δ ppm 3.48 (d, *J* = 7.14 Hz, 2H), 1.77 (m, 1H), 1.16 – 1.41 (m, 8H), 0.95 – 0.82 (m, 6H).

1,3-dibromo-5-dodecyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione 2. Prepared according to reported procedure starting from 3,4-dibromothiophene and *n*-dodecylamine. The final product was further purified by recrystallization from hexane as white crystals. ¹H NMR (400 MHz, CDCl₃): δ ppm 3.59 (t, 2H, *J* = 7.8 Hz); 1.63 (m, 2H); 1.37 – 1.20 (m, 18H); 0.87 (t, 3H, *J* = 7.8 Hz).



4,4'-dioctyl-5,5'-bis(trimethylsilyl)-dithieno[3,2-*b*:2',3'-*d*]silole 3. Prepared according to reported procedure and purified via flash column chromatography on neutral alumina column pretreated with triethylamine (hexane eluent) to give **3** as a light yellow oil. The monomer was used without further purification. ¹H NMR (400 MHz, CDCl₃): δ ppm 7.08 (s, 2H); 1.45-1.37 (m, 4H); 1.33-1.18 (m, 20H); 0.90 – 0.84 (m, 10H); 0.38 (s, 18H).

P1. To a 100 mL schlenk tube were introduced monomer **1** (192 mg, 0.45 mmol) and monomer **2** (338mg, 0.45 mmol). The tube was then pumped into a nitrogen filled glove box and tris(dibenzylideneacetone)dipalladium(0) (Pd₂(dba)₃) (16.6 mg 4 mol%), tri(*o*-tolyl)phosphine (P(*o*-tolyl)₃) (22.1 mg 16 mol%) , and 20 mL of chlorobenzene were added. The tube was sealed,

taken out of the glove box, and quickly degassed and filled with nitrogen three times. The tube was then placed in an oil bath and stirred at 120 °C for 3 days. After cooling to room temperature, the reaction mixture was precipitated into a mixture of methanol (200 mL) and conc. hydrochloric acid (5 mL) and stirred for 4 hours at room temperature. The precipitate was filtered through a Soxhlet thimble and washed in a Soxhlet apparatus with methanol and hexane sequentially for 2 days. Finally the polymer was extracted with chloroform, concentrated by evaporation, and reprecipitated in methanol (200 mL). The purified polymer was collected by filtration as a dark blue solid (224 mg, 72%) and dried under vacuum for 1 day. ¹H NMR (400 MHz, CDCl₃): δ ppm 8.02 (br, 2H); 3.60 (br, 2H); 2.05-0.62 (m, 49H). SEC analysis: Mn = 20 kDa, Mw = 52 kDa, PDI = 2.58.

P2. P2 was prepared analogous to P1 as a dark blue solid (186 mg, 81%). ¹H NMR (400 MHz, CDCl₃): δ ppm 8.06 (br, 2H); 3.71 (br, 2H); 2.04-0.66 (m, 57H). SEC analysis: Mn = 27 kDa, Mw = 70 kDa, PDI = 2.56.

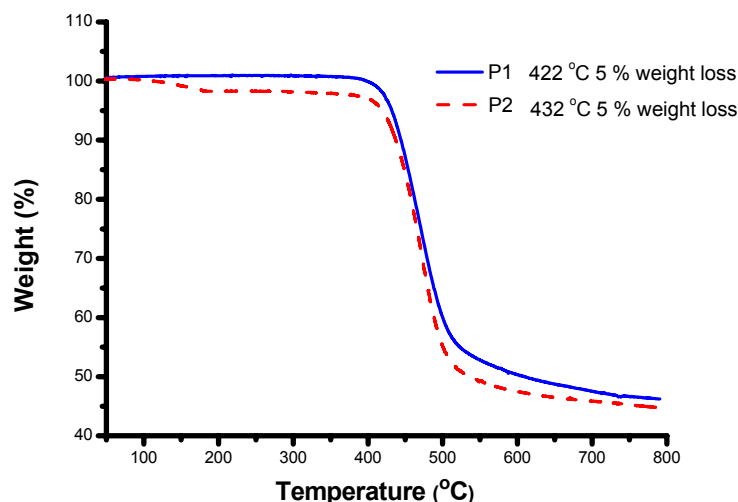


Figure S1. TGA thermograms of Polymer P1 and P2 at temperature ramp of 20 °C min⁻¹ under a N₂ atmosphere.

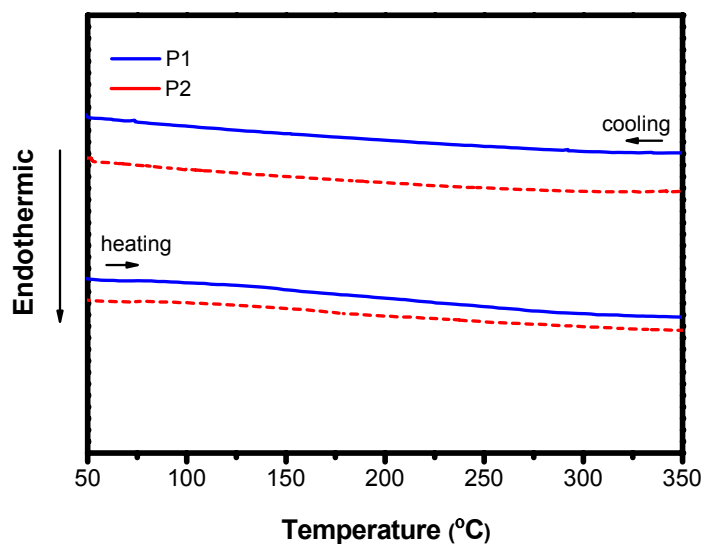


Figure S2. DSC thermograms of second heating and cooling scan of polymer P1 and P2 at temperature ramp of 10 °C/min.

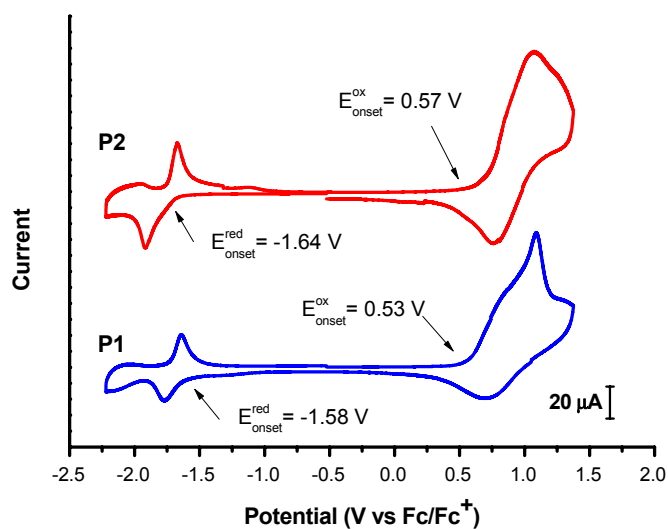


Figure S3. Cyclic voltammograms of P1 and P2 films casted on a glassy carbon electrode in deaerated acetonitrile solution with 100 mM tetrabutylammonium hexafluorophosphate as a supporting electrolyte, scan rate = 100 mV/s.

OTFT Device Fabrication and characterization

Top-contact, bottom-gate TFT test devices were prepared on silicon wafer in ambient conditions without taking any special precautions to exclude air, moisture and ambient light. A heavily n-doped silicon wafer <100> with a 200-nm thermal silicon dioxide (SiO₂) was used as the substrate/gate electrode, with the top SiO₂ layer serving as the gate dielectric. The SiO₂ surface was cleaned by sonication in acetone, and then immersed in piranha solution for 8 minutes at room temperature. The cleaned wafer was then immersed in a 0.1 M solution of octyltrichlorosilane (OTS-8) in toluene at 60 °C for 30 min, followed by rinsing with toluene and then N₂ blown dried. The semiconductor layer was deposited on top of OTS-8-modified SiO₂ surface by spin coating the solution in *o*-dichlorobenzene (4 mg/ml) at 1000 rpm for 120 seconds and vacuum annealed at 200 °C for 30 min to give about 30 nm-thick semiconductor layer. Subsequently, a series of gold source/drain electrode pairs were deposited by vacuum thermal evaporation through a shadow mask to create a series of TFTs with various channel length (L) and width (W) dimensions. Patterned transistors with channel length of 100 and 150 μm and channel width of 4 mm were used for I-V measurements. Silicon oxide at the backside of the silicon wafer of the TFT device was removed with sandpaper to provide a conductive gate contact. The TFT devices were then characterized using a Keithley SCS-4200 probe station under an ambient environment with relative humidity level of 65%. The FET mobility was extracted using the following equation in the saturation regime from the gate sweep:

$$I_{DS} = \mu C_i (V_{GS} - V_T)^2 (W/2L)$$

where I_{DS} is the drain current, μ is the field-effect mobility, C_i is the capacitance per unit area of the gate dielectric layer (SiO₂, 200 nm, $C_i = 17.25 \text{ nF cm}^{-2}$), and V_{GS} and V_T are respectively gate voltage and threshold voltage. V_T was derived from the relationship between the square root

of I_D at the saturated regime and V_G by extrapolating the measured data to $I_D = 0$. W and L are respectively channel width and length.

OPV Device Fabrication and characterization

The devices were fabricated with the structure ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al. The ITO patterned glass substrates were cleaned by sonication in a detergent (Hellmanex), de-ionized water, acetone, and finally in iso-propanol followed by N₂ blow dry. The substrates were then placed in an oven at 80 °C for at least an hour and subjected to an UV ozone treatment for 10 minutes before a PEDOT:PSS (CLEVIOS™ P VP Al 4083) layer of 40-45 nm thickness was spin-coated onto the ITO surface. The PEDOT:PSS-coated substrates were then annealed at 120 °C for 10 minutes. Both polymer and PC₇₁BM solution were dissolved separately in anhydrous *o*-dichlorobenzene (DCB). The polymer solution was stirred at 70 °C for 2 hours; while the PCBM solution was stirred at 40 °C for 2 hours. The two solutions were then mixed together. 1,8-Diiodooctane (DIO) or 1-chloronaphthalene (CN) was then added to the mixture as a processing additive. The final polymer concentration of the blend was 10 mg/ml. The solution blend was then stirred overnight at 40 °C. The active layer was spin-coated on the substrates in an inert glovebox (N₂ atmosphere) and allowed to dry slowly for 2 hours. The thickness of the active layer is approximately 70 nm. Lastly, 10 nm calcium and 100 nm silver were deposited by thermal deposition as the cathode. The active area of the device was 0.09 cm². Thickness of the film was. Solar cell efficiencies were characterized under simulated AM 1.5G irradiation with the intensity of 100 mW/cm² using a solar simulator (SAN-EI Electric XES-301S 300W Xe Lamp JIS Class AAA). All fabrication steps after depositing PEDOT:PSS layer onto ITO substrate, and device characterizations were performed in glovebox under a N₂ atmosphere.

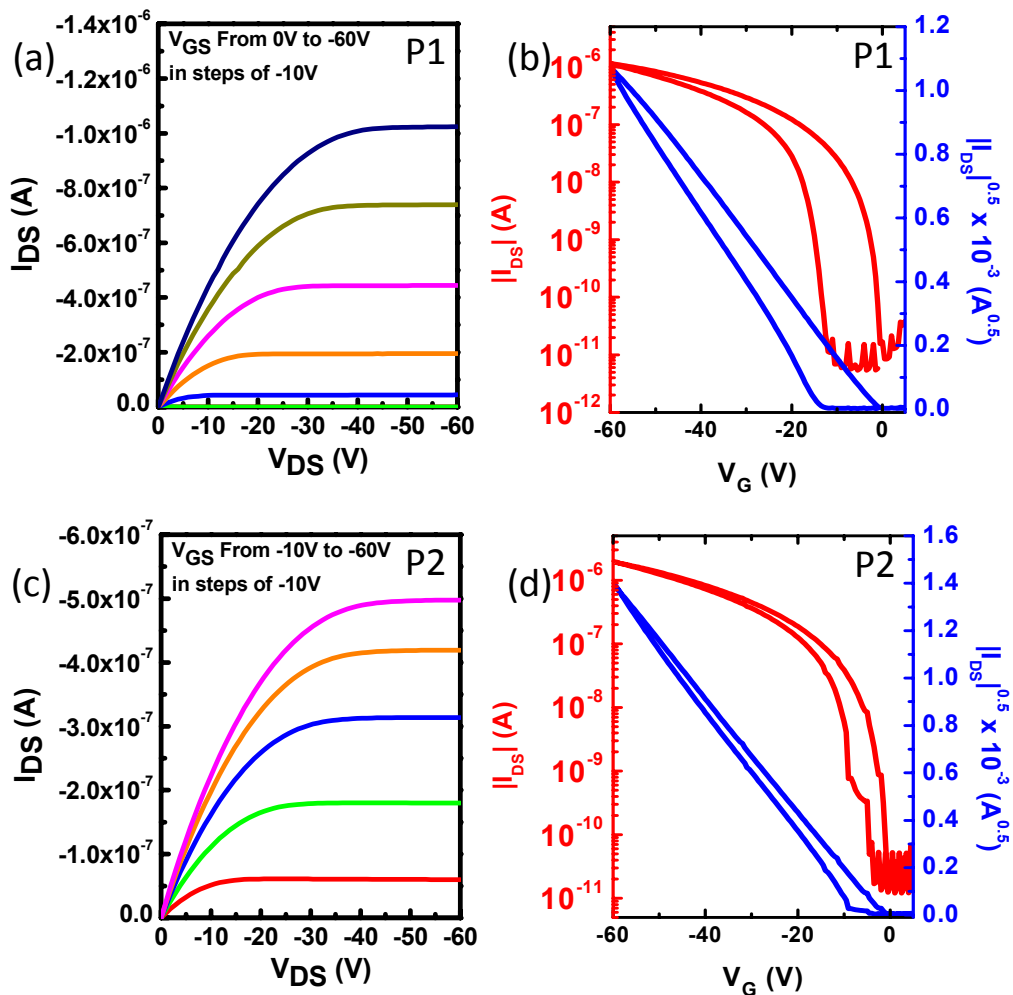


Figure S4. (a) , (c) Output Characteristics at different gate voltage and (b) , (d) Transfer characteristics in the saturated regime and plots of $|I_D|^{1/2}$ vs. V_G for P1 and P2 after annealing the films at 200 °C.

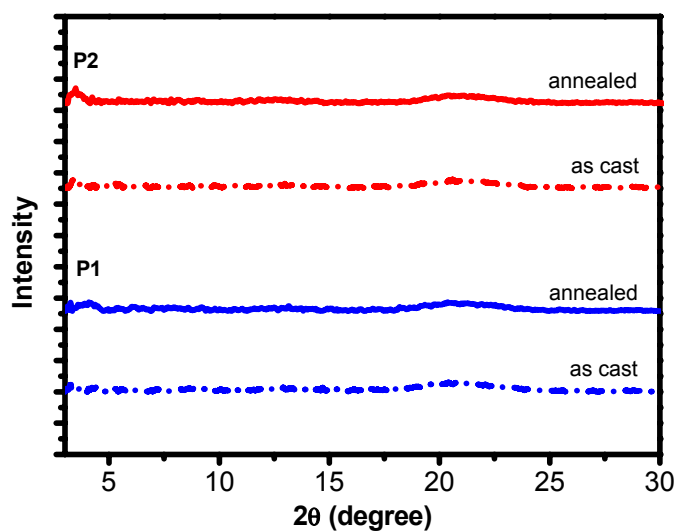


Figure S5. X-ray diffraction (XRD) scans of P1 and P2 films on octyltrichlorosilane (OTS) treated SiO₂/Si substrates after annealing at 200 °C. The broad peak at 2θ = 21 degree is originated from SiO₂/Si substrate.

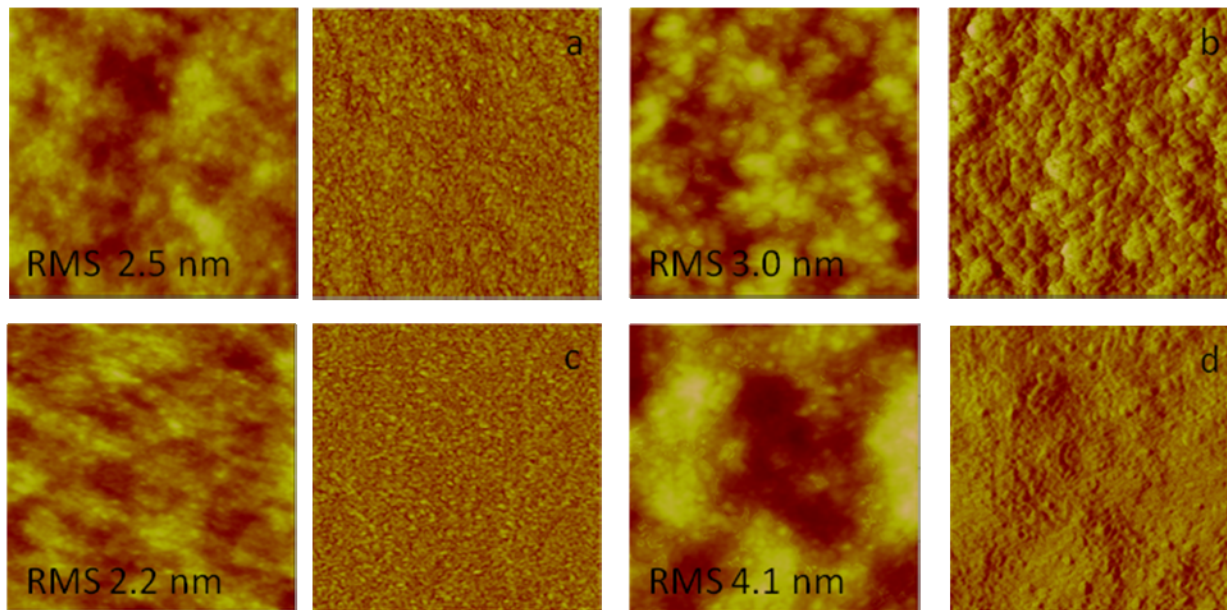


Figure S6. The AFM tapping mode height (left) and phase (right) images of optimized BHJ devices. a) P1:PC₇₁BM (1:1 wt:wt) b) P1:PC₇₁BM (1:1 wt:wt) with 1.5% DIO c) P1:PC₇₁BM (1:1 wt:wt) with 3% CN d) P2:PC₇₁BM 1:2. (1 x 1 μm scan area, the height scale is 30 nm, and the phase scale is 20 deg. for all images).

Reference

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