Supporting Information

Bulk Heterojunction Solar Cells Using Thieno[3,4-*c*]pyrrole-4,6-dione and Dithieno[3,2-*b*:2',3'-*d*]silole Copolymer With a Power Conversion Efficiency of 7.3%

Ta-Ya Chu,[†] Jianping Lu,[†,*] Serge Beaupré,[‡] Yanguang Zhang,[†] Jean-Rémi Pouliot,[‡] Salem Wakim,[†] Jiayun Zhou,[†] Mario Leclerc,[‡,*] Zhao Li,[⊥] Jianfu Ding,[⊥] and Ye Tao[†,*]

[†] *Institute for Microstructural Sciences (IMS), National Research Council of Canada (NRC), Ottawa, ON, K1A 0R6,* [‡] *Département de Chimie, Université Laval, Quebec City, QC, Canada G1V 0A6, and* [⊥] *Institute for Chemical Process and Environmental Technology (ICPET), National Research Council of Canada, Ottawa, ON, K1A 0R6*

Table of contents

---

[*] To whom all correspondences should be addressed: email Jianping.Lu@nrc.ca, Mario.Leclerc@chm.ulaval.ca, Ye.Tao@nrc.ca.

Materials and Instrumentation

All starting materials, unless otherwise specified, were purchased from Aldrich Co. and used without further purification. THF used in the reactions was freshly distilled over sodium under argon. Column chromatography was carried out on silica gel (Size 40 - 63 µm, Pore size 60 Å, Silicycle). 4,4-Bis(2-ethylhexyl)-2,6-bis(trimethyltin)-dithieno[3,2-*b*:2',3'-*d*]silole[1] and 1,3-dibromo-5-octylthieno[3,4-*c*]pyrrole-4,6-dione[2] were synthesized according to the literature procedures. ^{1}H NMR spectra were recorded on a 400 MHz Varian Unity Inova spectrometer. UV-visible absorption spectra were recorded on a Varian Cary 50 UV-Vis spectrophotometer. The differential scanning calorimetry (DSC) analysis was performed on a TA Instruments DSC 2920 at a scan rate of 10 °C/min under nitrogen. Cyclic voltammograms (CV) were recorded on a Solartron 1287 potentiostat using platinum wires as working electrode and counter-electrode at a scan rate of 50 mV/s. The reference electrode was Ag/Ag^+ (0.1 M of $AgNO_3$ in acetonitrile) and the electrolyte was a solution of 0.1 M tetrabutylammonium tetrafluoborate (Bu_4NBF_4) in dry acetonitrile. Under these conditions, the half wave potential of oxidation of ferrocene was 0.09 V versus Ag/Ag^+, whereas the half wave of oxidation potential of ferrocene was 0.41 V versus SCE. The HOMO and LUMO energy levels were determined from the oxidation and reduction onsets from the cyclic voltammograms assuming that SCE electrode is 4.7 eV below vacuum.The molecular weight and polydispersity index (PDI) of the polymer were determined by gel permeation chromatography (GPC) using Waters Breeze HPLC system with 1525 binary HPLC pump and 2414 differential refractometer. Chlorobenzene was used as eluent and commercial polystyrenes were used as standards.

Synthesis of polymer PDTSTPD. In a 50 mL oven-dried one-necked flask, 397.5 mg (0.534 mmol) of 4,4-bis(2-ethylhexyl)-2,6-bis(trimethyltin)-dithieno[3,2-*b*:2',3'-*d*]silole and 214.7 mg (0.507 mmol) of ,3-dibromo-5-octylthieno[3,4-*c*]pyrrole-4,6-dione were added. The flask was purged 3 times with argon, and then 40 mg (0.035 mmol) of $Pd(PPh_3)_4$ was added in a nitrogen-filled glove-box. 8 mL of degassed toluene/DMF (10:1, v/v) was added under argon atmosphere, and the resulting solution was stirred at 115 °C under argon. After 42 h of polymerization, 19 mg of trimethylphenyltin (0.08

mmol) in 0.75 mL of degassed toluene/DMF (10:1, v/v) was added to the reaction flask and the reaction was kept at 115 °C for an additional 5 hours. 50 mg of bromobenzene (0.32 mmol) in 0.75 mL of degassed toluene/DMF (10:1, v/v) was then added to the reaction flask, and the reaction was kept at 110 °C for an additional 8 hours to complete the end-capping reaction. The dark blue polymerization solution was cooled to room temperature and precipitate into methanol. The resultant polymer was collected by filtration, dried, and extracted successively with hexanes and dichloromethane using a soxhlet extraction apparatus. The remaining solid was extracted with 200 mL of chloroform. After evaporation of the chloroform under reduced pressure, methanol was added and 130 mg of the polymer was collected by filtration (38 % yield). Molecular weight (by GPC using chlorobenzene as eluent and monodispersed polystyrene as standard): Mn = 28 kDa and PDI = 1.6. ^{1}H NMR (400 MHz, 1,2-dichlorobenzene-d_4, 50 °C, ppm) 8.59 (s, 1H), 7.52 (s, 1H), 3.64 (br, 2H), 2.10-0.60 (m, 49H). Elemeatal analysis. Calcd for $C_{38}H_{53}NO_2S_3Si$: C, 67.11; H, 7.86; N, 2.06, O, 4.70; S, 14.14; Si, 4.13. Found: C, 66.65; H, 7.85; N, 2.39; S, 13.97.

Devices fabrication and testing

The hole mobility of PDTSTPD was measured on organic field-effect transistors (OFETs) with a bottom-contact structure. Gold source and drain electrodes were sputtered on the SiO_2/Si substrate prior to the deposition of the polymer film. The channel width and length of the transistors are 10 mm and 20 µm, respectively. The polymer thin films were spin-coated on the SiO_2/Si substrates from the chlorobenzene solution to cover the source and drain electrodes. The OFETs were characterized inside a dark box at room temperature and under nitrogen with an Agilent (4155c) semiconductor parameter analyser. The hole mobilities were calculated in the saturation regime using the following equation $I_{DS} = (W/2L)\mu C_i(V_G - V_T)^2$, where V_{DS} is the source-drain voltage, I_{DS} is the source-drain current, W and L are, respectively, the channel width and length, μ is the field-effect mobility, C_i is the capacitance per unit area of the SiO_2 layer, and V_G and V_T are, respectively, the gate voltage and threshold voltage.

The BHJ solar cells were prepared on commercial glass slides coated with patterned ITO. The thickness and sheet resistance of the ITO are 80 nm and 18 Ω/square, respectively. The active area of each solar cell device was 1.0 cm^2 with a length:width ratio of 4:1. The substrates were sonicated sequentially in detergent, DI water, acetone, and isopropanol. Immediately prior to device fabrication, the substrates were treated in a UV-ozone oven for 15 min. First, a poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS) thin film (30 nm) was spin-coated and then baked at 140 °C for 15 min. Secondly, an active layer was spin-coated on top of the PEDOT-PSS from the solutions of the polymer:PC$_{71}$BM blends with different weight ratios. In the case of the devices using a processing additive, 1,8-diiodooctane (3% by volume) was added to the solutions before use. Finally, 5 nm of BCP and 80 nm of Al were deposited on the top of the active layer in a vacuum of 8×10^{-7} Torr to complete the PV device fabrication. The solar cells (with no protective encapsulation) were then tested in air under AM 1.5G illumination of 100 mW/cm^2 (ScienceTech Inc., SS 500W solar simulator), which was calibrated with a KG5 filter covered silicon photovoltaic solar cell traceable to the National Renewable Energy Laboratory (NREL). Current-voltage (*I-V*) characteristics were recorded using a computer-controlled Keithley 2400 source meter. The external quantum efficiency (EQE) was performed using a Jobin-Yvon Triax spectrometer, a Jobin-Yvon xenon light source, a Merlin lock-in amplifier, a calibrated Si UV detector, and an SR570 low noise current amplifier.

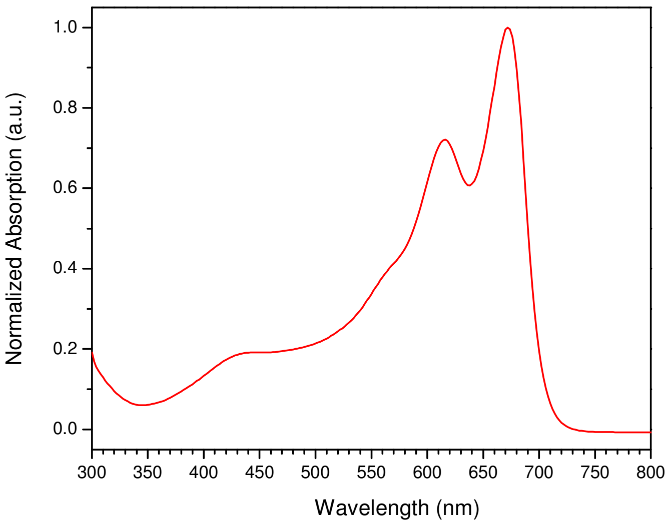

Figure S1. The absorption spectrum of PDTSTPD in 1,2-dichlorobenzene.

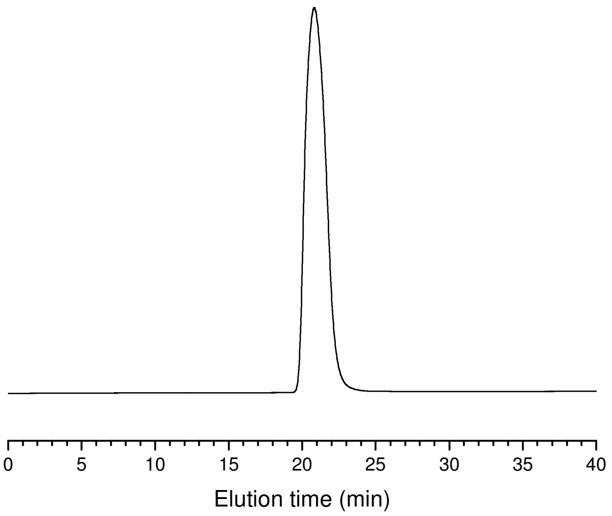

Figure S2. GPC curve of polymer PDTSTPD after purification.

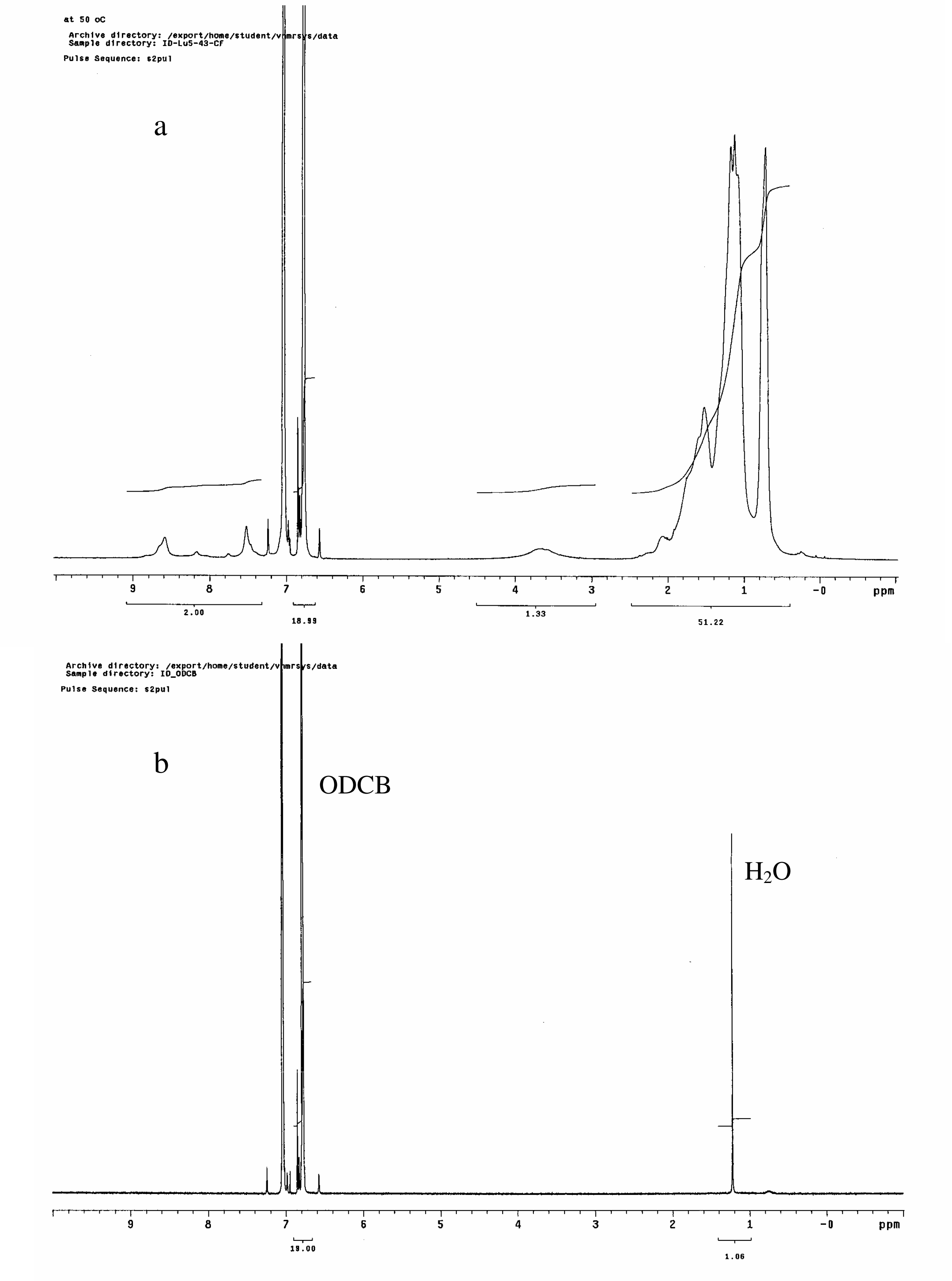

Figure S3. Proton NMR spectra of (a) PDTSTPD in 1,2-DCB-d_4 and (b) 1,2-DCB-d_4 NMR Solvent.

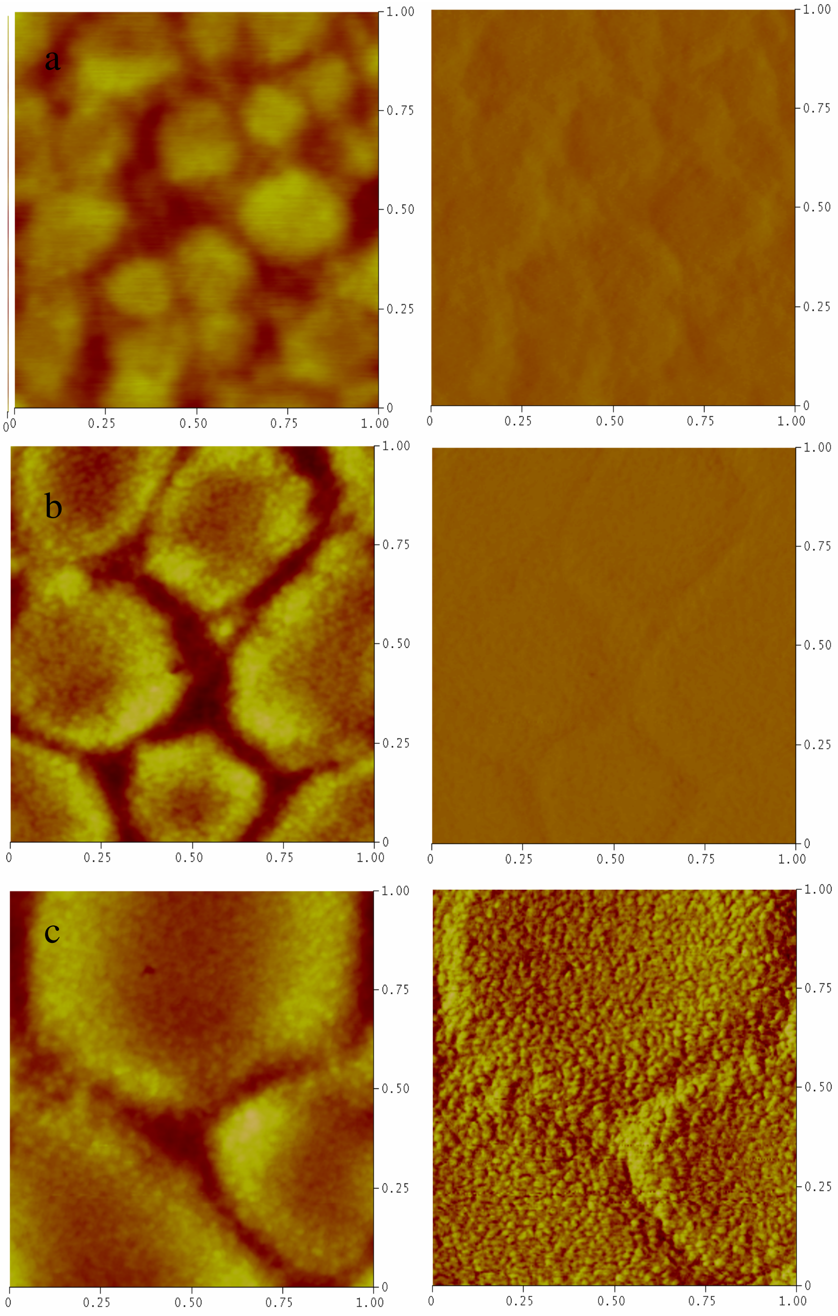

Figure S4. Height (left side, same scale bar) and phase (right side, same scale bar) AFM images of the PDTSTPD/PC$_{71}$BM BHJ films spin-cast from DCB solutions. (a) 1:1, (b) 1:2, (c) 1:3.

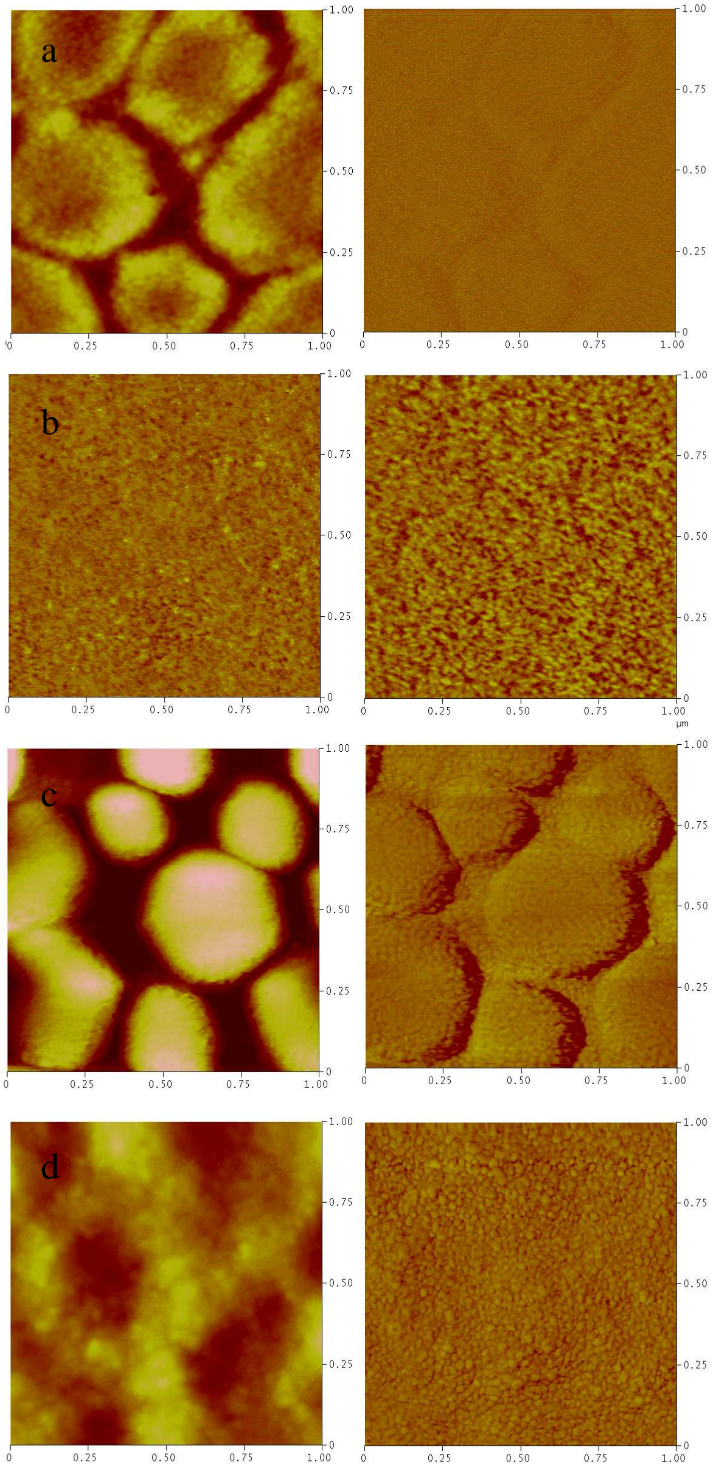

Figure S5. Height (left side) and phase (right side) AFM images of the 1:2 PDTSTPD/PC$_{71}$BM BHJ films spin-cast from different solutions. (a) dichlorobenzene, (b) dichlorobenzene + 3% DIO, (c) chlorobenzene, (d) chlorobenzene + 3% DIO.

References

1. (a) Liao, L.; Dai, L.; Smith, A.; Durstock, M.; Lu, J.; Ding, J.; Tao, Y. *Macromolecules* **2007**, *40*, 9406-9412. (b) Hou, J.; Chen, H.; Zhang, S.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16144-16145.
2. Zou, Y.; Najari, A.; Berrouard, P.; Beaupré, S.; Aïch, B. R.; Tao, Y.; Leclerc, M. *J. Am. Chem. Soc.* **2010**, *132*, 5330–5331.