Regioregular Pyridyl[2,1,3]thiadiazole-co-Indacenodithiophene Conjugated Polymers

Wen Wen,‡ Lei Ying,‡ Ben B. Y. Hsu, Yuan Zhang, Thuc-Quyen Nguyen, Guillermo C. Bazan*

Center for Polymers and Organic Solids, Department of Chemistry and Biochemistry and Materials, University of California, Santa Barbara, California 93106-7150, USA
‡ Both authors contributed equally to this work.
E-mail: bazan@chem.ucsb.edu

Supporting Information

Experimental

Instruments

Nuclear magnetic resonance (NMR) spectra were obtained on Bruker Avance DMX500 MHz spectrometer. Gel permeation chromatography (GPC, 135 °C in 1,2,4-trichlorobenzene) was performed on a Polymer Laboratories PL220 Chromatograph. Differential scanning calorimetry (DSC) was determined by a TA Instruments DSC (Model Q-20) with about 5 mg polymers samples at a rate of 10 °C / min in the temperature range of –20 to 300 °C. Cyclic voltammetry (CV) measurements were conducted using a standard three-electrode configuration under an argon atmosphere. A three-electrode cell equipped with a glassy carbon working electrode, a Ag wire reference electrode, and a Pt wire counterelectrode was employed. The measurements were performed in absolute acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte at a scan rate of 50-100 mV/s. Polymer films for CV test were drop-casted onto the glassy carbon working electrode from a 2 mg/mL chloroform solution. The absolute energy level of ferrocene/ferrocenium (Fc/Fc^+) to be 4.8 eV below vacuum. Ultraviolet-Visible (UV-Vis) absorption spectra were recorded on a Shimadzu UV-2401 diode array spectrometer. Atomic force microscopy (AFM) images were measured using a Innova scanning probe microscope (Veeco). Silicon probes with resonant frequencies of 75 KHz (Budget Sensors) were used for tapping mode AFM measurements.

Synthesis of monomers

(4,4,9,9-Tetrakis(4-hexylphenyl)-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b′*]dithiophene-2,7-diyl)bis(trimethylstannane) (M1)

A dry three-neck round bottom flask was equipped with a Schlenk adapter, dropping funnel, and rubber septum. Under nitrogen, 2,7-dibromo-4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-*b*:5,6-*b′*]dithiophene (1.06 g, 1 mmol) was dissolved in dry THF (20 mL) and cooled –78 °C using a dry ice/acetone cold bath. Under nitrogen, a solution of *n*-butyllithium (1.6 M in hexane, 1.50 mL, 2.4 mmol) was added dropwise over 15 minutes to the reaction vessel. The reaction was stirred at –78 °C under nitrogen for one hour. Then trimethyltin chloride (0.60 g, 3.0 mmol) was added dropwise over 5 minutes to the reaction vessel via syringe at –78 °C. The reaction was stirred at –78 °C under nitrogen for 1 hour and subsequently warmed to room temperature and stirred overnight. The mixture was then poured into deionized water (3 × 100 mL) and the organic phase was extracted with hexanes (3 × 100 mL). The organic phases were collected and washed with deionized water (5 × 100 mL), dried over sodium sulphate, filtered, and concentrated. The crude product was recrystallized from hexane/ethanol (10/90) and dried under high vacuum to give final product as white needles (1.07 g), yield 87%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.48 (s, 2H), 7.21 (d, 8H), 7.13 (d, 8H), 2.63 (t, *J* = 7.75 Hz, 8H), 1.66-1.57 (m, 8H), 1.42-1.30 (m, 24H), 0.89 (m, 12H), 0.41 (s, 18H). **^{13}C NMR** (125 MHz, CD_2Cl_2) δ (ppm): 157.64, 153.75, 147.14, 142.31, 141.90, 141.54, 134.71, 130.44, 128.35, 128.28, 127.81, 127.75, 117.65, 62.19, 35.48, 31.76, 31.66, 29.16, 22.64, 13.89, -8.39. **MS (FD)** m/z, calcd for Chemical Formula: $C_{70}H_{90}S_2Sn_2$ (M^+): 1232.45; found: 1232.5.

4,4'-(4,4,9,9-Tetrakis(4-hexylphenyl)-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b′*]dithiophene-2,7-diyl)bis(7-bromo-[1,2,5]thiadiazolo[3,4-*c*]pyridine) (M2)

To a 10-20 mL microwave tube was added **M1** (0.616 g, 0.5 mmol), 4,7-dibromo-[1,2,5]thiadiazolo[3,4-*c*]pyridine (0.295 g, 1 mmol), tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$, 57.8 mg, 0.05 mmol) and freshly distilled toluene (10 mL) under the protection of nitrogen, then the microwave tube was sealed. The microwave assisted Stille coupling was performed in the following procedure: 120 °C for 10 min, 140 °C for 10 min, 160 °C for 10 min and

170 °C for 40 min. The reaction was cooled down to room temperature, extracted with chloroform (100 mL × 3), washed with deionized water (100 mL × 3) and dried over with anhydrous magnesium sulfate. After removing solvent under reduced pressure, the mixture was separated by silica column with hexane/chloroform (form 100/0 to 0/100 in v/v) to give dark-red solid (0.553 g), yield of 83%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.64 (s, 2H), 8.60 (s, 2H), 7.65 (s, 2H), 7.31 (s, 8H), 7.16 (s, 8H), 2.61 (s, 8H), 1.63 (s, 8H), 1.45-1.26 (m, 24H), 0.90 (s, 12H). **^{13}C NMR** (125 MHz, CD_2Cl_2) δ (ppm): 158.11, 156.29, 154.63, 147.74, 147.54, 147.38, 145.91, 143.86, 141.84, 141.37, 136.01, 128.69, 128.55, 127.95, 127.95, 118.61, 107.54, 63.27, 35.60, 31.73, 31.35, 29.17, 22.61, 14.11. **MS (FD)** m/z, calcd for $C_{74}H_{74}Br_2N_6S_4$ (M^+): 1334.32; found: 1334.3.

Polymerization of PIPT-RG

M1 (123.3 mg, 0.1 mmol), **M2** (133.4 mg, 0.1 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) and freshly distilled xylenes (3 mL) were added to a 2-5 mL microwave tube under nitrogen. The tube was sealed and subjected to the following reaction conditions in a microwave reactor: 80 °C for 2 min, 130 °C for 2 min, 170 °C for 2 min and 200 °C for 40 min. The reaction was allowed to cool to room temperature, then freshly distilled xylenes (2 mL) and tributyl(thiophen-2-yl)stannane (20 μl) was added and the reaction was subjected to the following reaction conditions in a microwave reactor: 80 °C for 2 min, 130 °C for 2 min, 170 °C for 2 min and 200 °C for 20 min. After the reaction was cooled to room temperature, 2-bromothiophene (20 μl) was added and the reaction was subjected to the following reaction conditions in a microwave reactor: 80 °C for 2 min, 130 °C for 2 min, 170 °C for 2 min and 200 °C for 20 min. The mixture was precipitated in methanol, collected via centrifugation, then re-dissolved in hot 1,2-dichlorobenzene and re-precipitated in methanol and collected via centrifugation. The collected solid fibers were loaded into a cellulose extraction thimble and washed successively with methanol (12 hours), acetone (12 hours) and hexanes (12 hours), and then chloroform (2 hours) to collect the copolymer. The solid residue in the thimble was collected and dried followed by re-dissolved in hot 1,2-dichlorobenzene, filtrated and re-precipitated in methanol. Then the resulted dark-green fibers were collected via centrifugation, dried over high vacuum line to give 156 mg of polymers, yield 75%. **^{1}H NMR** (500 MHz, 1,2-dichlorobenzene-d_4, 110 °C) δ (ppm): 8.90 (s, 1H), 8.84 (s, 1H), 8.40 (s, 1H), 8.12 (s, 1H), 8.04 (s, 1H), 7.80-7.50 (br s, 8H), 7.30-7.15 (br s, 8H), 2.70 (br s, 8H), 1.71 (s, 8H), 1.55-1.32 (m, 24H), 0.98 (s, 12H). **^{13}C NMR** (125 MHz, 1,2-dichlorobenzene-*d₄*, 110 ^{o}C) δ (ppm): 180.06, 169.02, 163.49, 157.70, 141.59, 132.15, 130.04, 129.84, 129.71, 129.63, 129.42, 127.32, 127.22, 127.12, 127.05, 126.95, 126.85, 126.75, 126.65, 126.40, 102.74, 63.62, 35.38, 31.49, 30.98, 30.79, 28.88, 22.31, 13.61. M_n = 68 kDa, M_w = 163 kDa, PDI = 2.4.

Polymerization of PIPT-RA

The polymerization was performed following the procedure for **PIPT-RG** in a microwave reactor. The monomer **M1** (246.6 mg, 0.2 mmol), and replacing monomer **M2** by 4,7-dibromo-[1,2,5]thiadiazolo-[3,4-*c*]pyridine (59.0 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 0.01mmol) and xylenes (3 mL). The resulted dark-green solid was dried over high vacuum line to give 168.5 mg of polymer, yield 81%. **^{1}H NMR** (500 MHz, 1,2-dichlorobenzene-d_4, 110 ^{o}C) δ (ppm): 8.86 (s, 1H), 8.81 (s, 1H), 8.35 (s, 1H), 8.12 (s, 1H), 8.03 (s, 1H), 7.82-7.49 (br s, 8H), 7.36-7.18 (br s, 8H), 2.66 (br s, 8H), 1.70 (s, 8H), 1.52-1.38 (m, 24H), 0.92 (s, 12H). **^{13}C NMR** (125 MHz, 1,2-dichlorobenzene-d_4, 110 ^{o}C) δ (ppm): 180.07, 169.03, 163.50, 157.99, 141.56, 132.19, 130.24, 129.94, 129.81, 129.80, 129.58, 127.45, 127.32, 127.22, 127.18, 127.06, 126.97, 126.86, 126.72, 126.51, 102.83, 63.84, 35.39, 32.38, 31.50, 29.10, 22.47, 13.74. M_n = 60 kDa, M_w = 151 kDa, PDI = 2.5.

Preparation of molybdenum oxide (MoO_3) solution

The aqueous MoO_3 solution was prepared by hydration method according to the reported procedure.[1] Ammonium molybdate ($(NH_4)_6Mo_7O_{24}$) was dissolved in water to form 0.01 mol/L solution, marked as solution A. Hydrochloric acid (2 mol/L) aqueous solution was marked as solution B. Solution B was dropped into solution A until the pH value of the mixed solution was adjusted between 1.5 and 2.0. This mixed solution was marked as solution C, which is aqueous MoO_3 solution.

Preparation of ZnO solution

ZnO thin films coated on the top of ITO glass were obtained from ZnO precursor solution by sol-gel method.[2] The ZnO precursor was prepared by dissolving zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, 1 g) and ethanolamine (0.28 g) in 2-methoxyethanol (10 ml) under vigorous stirring for 12 h for the hydrolysis reaction in air.

Fabrication of polymer solar cells with conventional structure

Conventional polymer solar cells with architecture of ITO/solution-processed MoO_3/active layer/Al were fabricated as testing platforms. The ITO-coated glass substrates were firstly cleaned by ultrasonic treatment in detergent, deionized water, acetone and isopropyl alcohol for 30 minutes each, and subsequently dried in an oven overnight. After treated with UV/ozone for 20 min, MoO_3 (filtered at 0.45μm) was spin-coated from aqueous solution at 5000 rpm for 40 s to form a film of ~ 10 nm thickness. The substrates were then barked at 160°C for 25 min in air, and moved into a glovebox for spin-casting the active layer. Two kind of solutions containing with **PIPT-RA**:$PC_{71}BM$ (1:3, 1:4 in wt:wt) and **PIPT-RG**:$PC_{71}BM$ (1:1, 1:2, 1:3, 1:4 in wt:wt) in 1,2-dichlorobenzene with a concentration of 10 mg/ml were spin-casted on top of MoO_3 layer, respectively. The film thickness of ~90 nm was optimized by controlling the spin-casting speed at 2500 rpm for 40 seconds for **PIPT-RA**:$PC_{71}BM$ (1:4) blend film, and 3000 rpm for 40 seconds for **PIPT-RG**:$PC_{71}BM$ (1:4) blend film. In order to make a better aggregation, the BHJ films were annealing at 100°C for 10 min. After that, the cathode (Al, ~100 nm) was deposited through a shadow mask by thermal evaporation in a vacuum of about 3×10^{-6} Torr. The active area of device was 0.106 cm^2. The thickness of the active layer and MoO_3 was measured with an Ambios XP-100 stylus profilometer and AFM, respectively.

Fabrication of polymer solar cells with inverted structure

Inverted polymer solar cells with architecture of ITO/ZnO/polymer: $PC_{71}BM/MoO_3/Ag$ was fabricated according to the following procedure. The ITO-coated glass substrates were pre-cleaned as described before. The ZnO precursor solution was spin-cast on top of the clean ITO layer, and then the films (~30 nm) were annealed at 150 °C for 1 h in air. The ZnO-coated substrates were transferred into a glove box. The **PIPT-RA**:$PC_{71}BM$ and **PIPT-RG**:$PC_{71}BM$ (1:4) solutions were spin-casted on top of ZnO film, respectively. The BHJ film was heated at 100 °C for 10 min. Then, a thin layer of MoO_3 film (~6 nm) was evaporated on top of the BHJ layer. Finally, the anode (Ag, ~60 nm) was deposited through a shadow mask by thermal evaporation in a vacuum of about 3×10^{-6} Torr. The active area of device was 0.05 cm^2.

PSCs Characterization

Device characteristics were measured under illumination by a simulated 100 mW/cm^2 AM 1.5 G light source using a 300 W Xe arc lamp with an AM 1.5 global filter. Solar-simulator irradiance was calibrated using a standard silicon photovoltaic with a protective KG1 filter by the National renewable Energy Laboratory. External quantum efficiencies were determined using a 75W Xe source, monochromator, optical chopper, lock-in amplifier, and a National institute of Standards and technology calibrated silicon photodiode was used for power-density calibration.

UPS Characterization

75-nm-thick Au films were thermally deposited on precleaned Si substrates with a thin native oxide. **PIPT-RA** (or **PIPT-RG**):PC$_{71}$BM (1:4) solutions were then spin coated at spin speed of 2 000 rpm and concentration of 0.2 %. Films were prepared inside a nitrogen atmosphere glovebox and were transferred via an airtight sample holder to the UPS analysis chamber. Samples were also kept in a high vacuum chamber overnight to remove solvent residues. The UPS analysis chamber was equipped with a hemispherical electron-energy analyzer (Kratos Ultra spectrometer), and was maintained at 1.33×10^{-7} Pa. The UPS was measured using the He I ($h\nu$ = 21.2 eV) source, and the electron energy analyzer was operated at constant pass energy of 10 eV. During the measurements, a sample bias of -9 V was used in order to separate the sample and the secondary edge for the analyzer. In order to confirm reproducibility of UPS spectra, we repeated these measurements twice on two sets of samples.

FET device fabrication

0.4% (wt/v) **PIPT-RA** and **PIPT-RG** were dissolved in 1,2-dichlorobenzene, respectively. The copolymers were stirring under 110 ^{o}C before usage. Heavily doped n-type silicon substrates with 200 nm thermally grown SiO$_2$ were prepared as bottom gate electrode. After SiO$_2$ dielectric was passivated by (decyl)trichlorosilane (DTS). Coated substrates were sequentially heated under 80 ^{o}C for 10 min. Thermal evaporator was applied to deposit 100 nm metal contacts on polymer layer through a silicon shadow mask. Defined channel was 20 μm long and 1 mm wide. The copolymers were spun onto substrates by 2000 rpm/ 1 min. Devices were tested on a Signatone probe station inside a nitrogen glovebox with atmosphere < 1 ppm oxygen concentration. Data were all collected by a Keithley 4200 system. Mobility was extracted from saturation regime based on the following equation,

$$I_D = \frac{1}{2}\mu C \frac{W}{L}\left(V_G - V_T\right)^2$$

where, W is the channel width (1 mm), L is the channel length (20 μm), μ is the carrier mobility, V_G is the gate voltage, and V_T is the threshold voltage. The capacitance (C) of the SiO_2 is 14 nF/cm^2.

Hole/Electron-only diode fabrication

Hole only diodes were fabricated using ITO-coated glass substrates with an architecture of TO/MoO_3/polymer:$PC_{71}BM$/Au. A layer of MoO_3 was thermally evaporated atop ITO, then polymer:$PC_{71}BM$ layer were spin coated from 1% wt/v 1,2-dichlorobenzene solutions in nitrogen atmosphere with thickness about 130 nm. About 100 nm thick gold cathode was then deposited by thermal evaporation (chamber pressure ~ 10^{-6} torr). Electron only diodes were fabricated with an architecture of ITO/Al/polymer:$PC_{71}BM$/Al, where aluminum was used both as the cathode and anode. All devices were characterized in nitrogen atmosphere using a Keithley 4200 semiconductor characterization system. To obtain the zero-field hole or electron mobility, current density-voltage (*J*-*V*) curves were fitted using the Mott-Gurney law[3]

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_{h,e}\frac{(V - V_{bi})^2}{L^3}$$

In which $\varepsilon_0\varepsilon_r$ is the dielectric constant of the polymer, $\mu_{h,e}$ is the zero-field hole or electron mobility, L is the thickness of the polymer layer, V is the applied voltage, and V_{bi} is the built-in voltage.

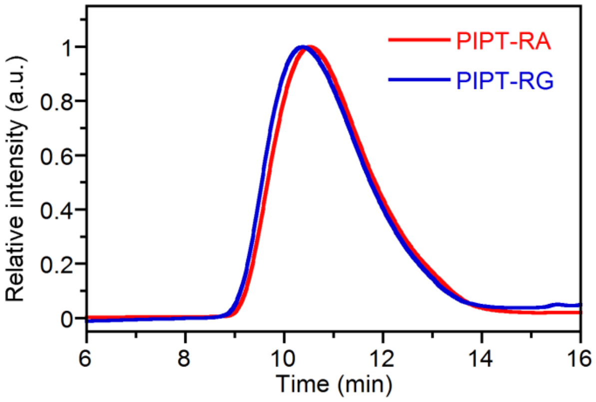

Figure 1S GPC profiles of polymers

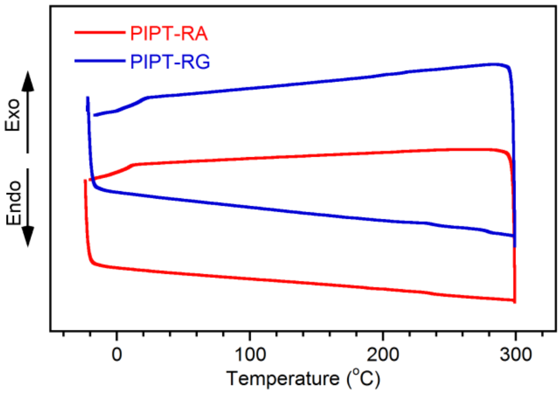

Figure 2S DSC characteristics of polymers.

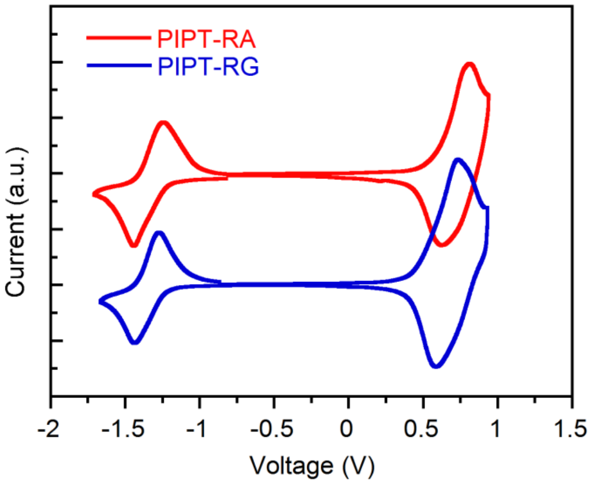

Fig. 3S CV characteristics of polymers

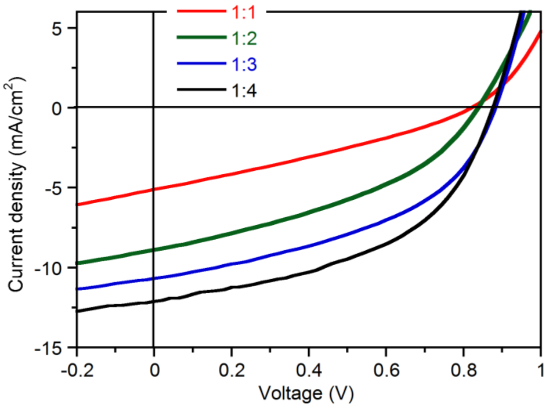

Figure 4S *J*-*V* characteristics of solar cells based on ITO/ solution-processed MoO_3/ **PIPT-RG**:$PC_{71}BM$/Al. The blend films were cast from 1 % (wt/v) solution with various ratios.

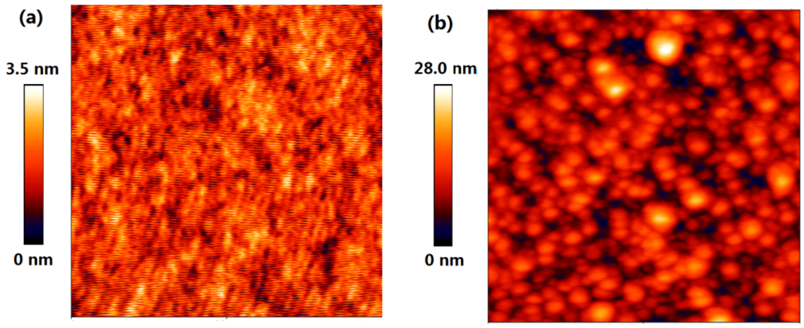

Figure 5S Topographic AFM images (2 μm × 2 μm) of blends containing (a) **PIPT-RG**:$PC_{71}BM$ (1:4) and (b) **PIPT-RA**:$PC_{71}BM$ (1:4). Images were taken after thermal annealing.

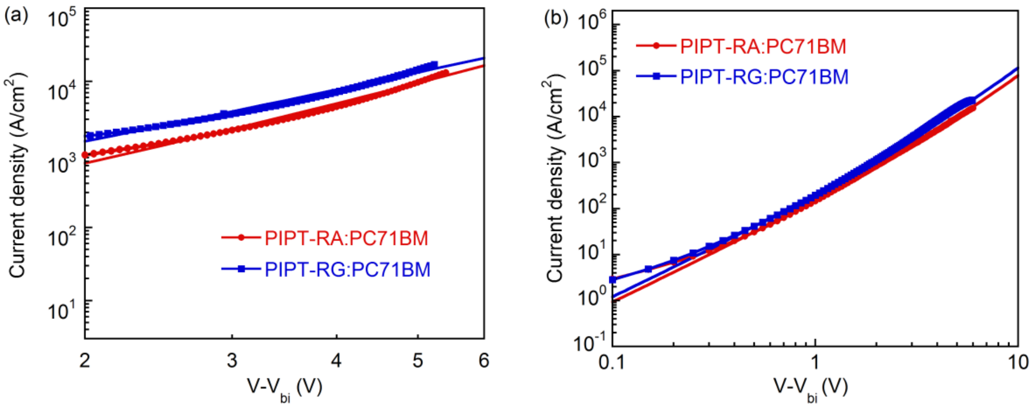

Figure 6S *J*-*V* curves of (a) hole-only device and (b) electron-only device.

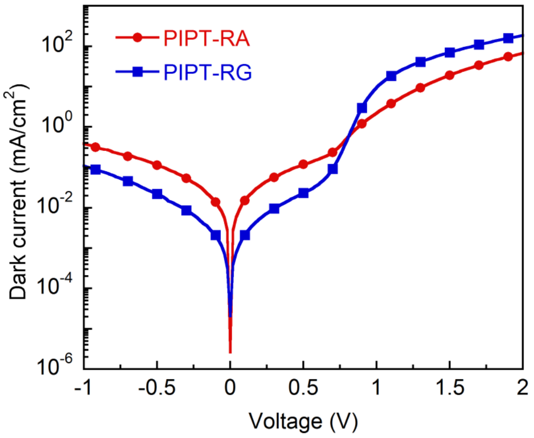

Figure 7S Dark current characteristics of devices after thermal annealing.

Table 1S Summary of device properties based on a testing platform

Polymer:PC$_{71}$BM (wt:wt)		J_{sc} (mA/cm^2)	V$_{oc}$ (V)	FF (%)	PCE (%)
PIPT-RG	1:1	5.3	0.82	30	1.3
PIPT-RG	1:2	8.9	0.84	39	2.9
PIPT-RG	1:3	10.7	0.88	45	4.2
PIPT-RG	1:4	12.1	0.88	48	5.1
PIPT-RA	1:3	8.4	0.74	37	2.3
PIPT-RA	1:4	10.5	0.82	40	3.4

* Devices based on solution processed MoO$_3$, and blend films cast from 1% wt/v solution, with thermal annealing at 100 ^{o}C for 10 min.

---

[1] F. M. Liu, S. Y. Shao, X. Y. Guo, Y. Zhao and Z. Y. Xie, *Sol Energ Mat Sol C*, 2010, **94**, 842-845.

[2] (a) T. B. Yang, W. Z. Cai, D. H. Qin, E. G. Wang, L. F. Lan, X. Gong, J. B. Peng and Y. Cao, *J Phys Chem C*, 2010, **114**, 6849-6853; (b) Y. M. Sun, J. H. Seo, C. J. Takacs, J. Seifter and A. J. Heeger, *Adv Mater*, 2011, **23**, 1679-1683.

[3] Mott, N. F.; Gurney, R. W. *Electronic Processes in Ionic Crystals*, Dover Publications, New York, 1940.