Electronic Supplementary Information (ESI)

Tuning the open circuit voltage by incorporating low cost diflurophenyl unit into polymer backbone to achieve high efficiency polymer solar cells

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Materials: The monomers of 2-Ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-b]thiophene-2-carboxylate **(R1) (Price=750 USD/g)** and 1,1'-[4,8-Bis[5-(2-ethylhexyl)-2-thienyl]benzo[1,2-b:4,5 b']dithiophene-2,6-diyl]bis[1,1,1-trimethylstannane] **(R2)** and $PC_{71}BM$ were purchased from Lumtec and 1,4-dibromo-2,5-difluorobenzene **(R3) (Price=7 USD/g)** and $Pd(PPh_3)_4$ were bought from Sigma Aldrich**.** The hole transporting material (HTM) Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, PVP AI 4083) was received from Clevios.

Instruments: ^1H NMR spectra of the polymers were recorded on a Bruker 400 MHz (at 298 K) spectrometers. Absorbance spectra of synthesized polymers film (spin coated from chlorobenzene on a pre cleaned glass slide and vacuum dried) were recorded using a Perkin–Elmer Lambda-35 UV-visible spectrophotometer. Gel permeation chromatography (GPC) measurements were performed on a Waters 515 chromatograph with tetrahydrofuran as eluent and polystyrene as standard. Thermal stabilities of all polymers under nitrogen atmosphere have been analyzed by thermogravimetric analysis (TGA) in a Netzch (STA 449, Jupiter) instrument at a heating rate of 10^oC/minute. To determine oxidation potential of polymers three electrode was used and polymer film was coated on a glassy carbon electrode. The thin film of PEDOT:PSS and the active layer blend were deposited on ITO-coated glass substrate by spin coating technique using a Laurell and Spin 150 spin. A JEOL 2100F FETEM was used for FETEM analysis of Blend film. A Veeco Dektak 150 Surface Profilometer was used to measure thicknesses of the thin films. AFM images of the thin active layer films were recorded by Agilent 5500-STM instrument. All the electrical parameters were characterized by Keithley-2400 digital source meter. Newport, Oriel Sol 3A solar simulator with an Oriel 500 W xenon lamp, connected to AM 1.5 Globe filter,

was used as solar cell characterization. Newport Oriel IQE-200 instrument was used for external quantum efficiency (EQE) measurement.

General Synthesis Procedure

To synthesize these polymers we have followed previously reported Stille polycondensation based methods.[1,2] R1, R2 and R3 were weighed into a dry 50-mL Schlenk tube equipped with a magnetic stirrer. After that $Pd(PPh_3)_4$ was added, the mixture was degassed three times, and then toluene and DMF (4:1) were added. The reaction mixture was stirred for 15 hours under argon at 110^0C - 115^oC. After cooling down to room temperature, the dense black gel was precipitated in to 300 mL of MeOH and then stirred for few minutes. By filtration the resulting polymer was collected and washed with MeOH. Further purification was done via Soxhlet extraction sequentially with MeOH, acetone, n-Hexane and $CHCl_3$. Then the $CHCl_3$ part was concentrated. Then it was again precipitated and used for device fabrication and other photo-physical studies.

Synthesis of PTB7-Th: The polymer, PTB7-Th was synthesized under the same reaction conditions with ratio of R1 (188.8mg, 0.4mmol) and R2 (361.82 mg, 0.4mmol) and Yield: 240mg (74%), ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.38-8.20 (br, 4 H), 6.40-7.20 (br, 2 H), 4.00-4.50 (br, 2 H), 2.50-3.55 (br, 4H), 0.45-1.95 (br, 45 H), M_w =149 kDa, M_n= 50 kDa, PDI=3.01.

Synthesis of m_1PTB7-Th: The polymer, m_1PTB7-Th was synthesized under the same reaction conditions with ratio of R1 (179.45mg, 0.38 mmol), R2 (361.82 mg, 0.4 mmol) and R3 (5.43mg, 0.02mmol) and Yield: 256mg (79%), ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.38-8.20 (br, 4 H), 6.40-7.20 (br, 2 H), 4.00-4.50 (br, 2.0 H), 2.50-3.55 (br, 4.0 H), 0.45-1.95 (br, 45 H), M_w = 261 kDa, M_n= 103 kDa, PDI=2.52.

Synthesis of m_2PTB7-Th: The polymer, m_2PTB7-Th was synthesized under the same conditions with ratio of R1 (170mg, 0.36mmol), R2 (361.82 mg, 0.4mmol) and R3 (10.87mg, 0.04mmol) and Yield: 256mg (79%), ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.38-8.20 (br, 4 H), 6.40-7.20 (br, 2 H), 4.00-4.50 (br, 2 H), 2.50-3.55 (br, 4 H), 0.45-1.95 (br, 45 H), M_w =122 kDa, M_n=46 kDa PDI=2.68.

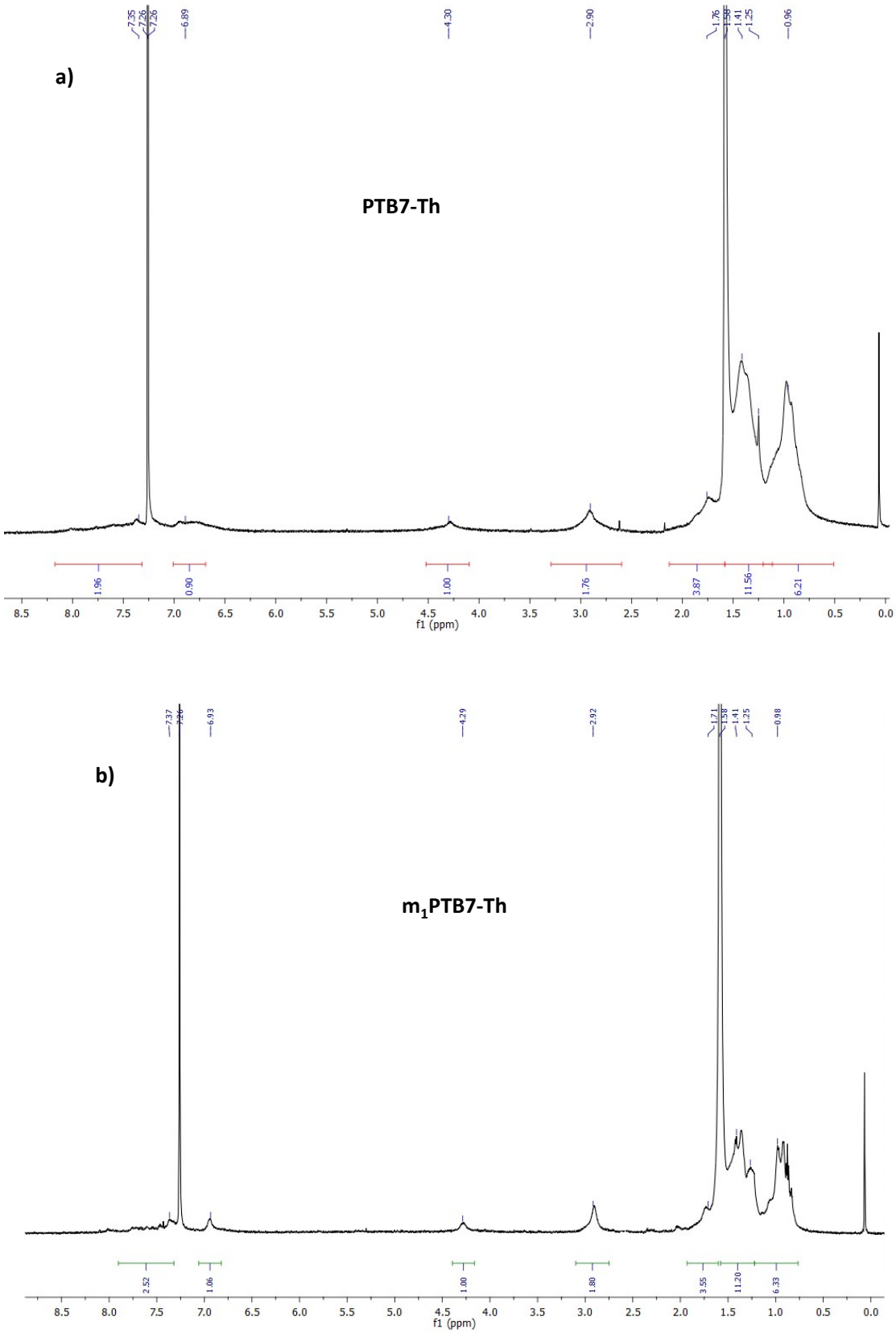

Figure S1. ^{1}**H** NMR spectra of a) PTB7-Th and b) m_1PTB7-Th in $CDCl_3$.

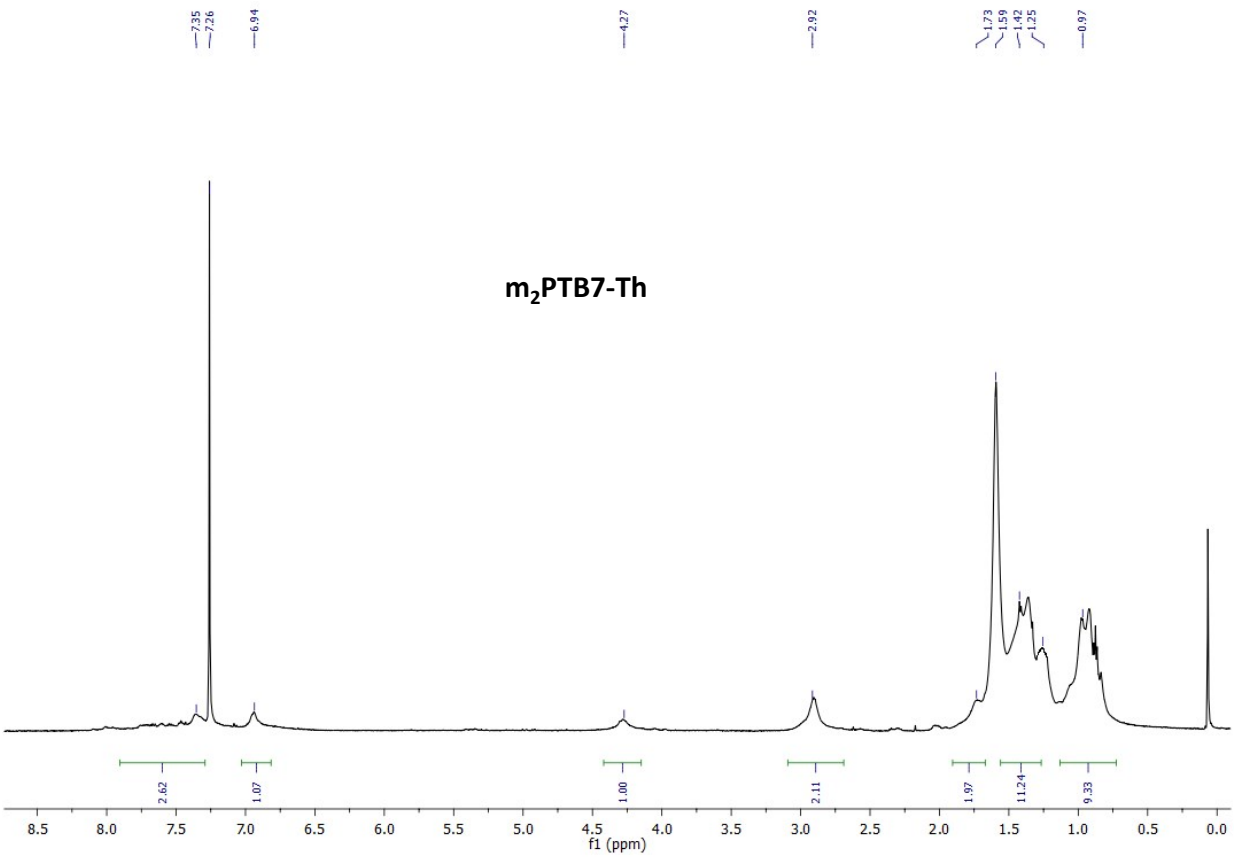

Figure S2. **^{1}H** NMR spectra of m_2PTB7-Th in $CDCl_3$.

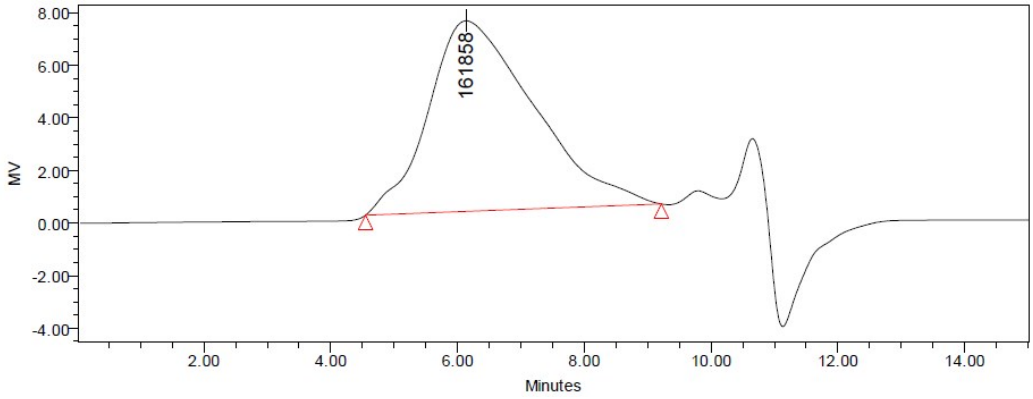

Figure S3. GPC of PTB7-Th.

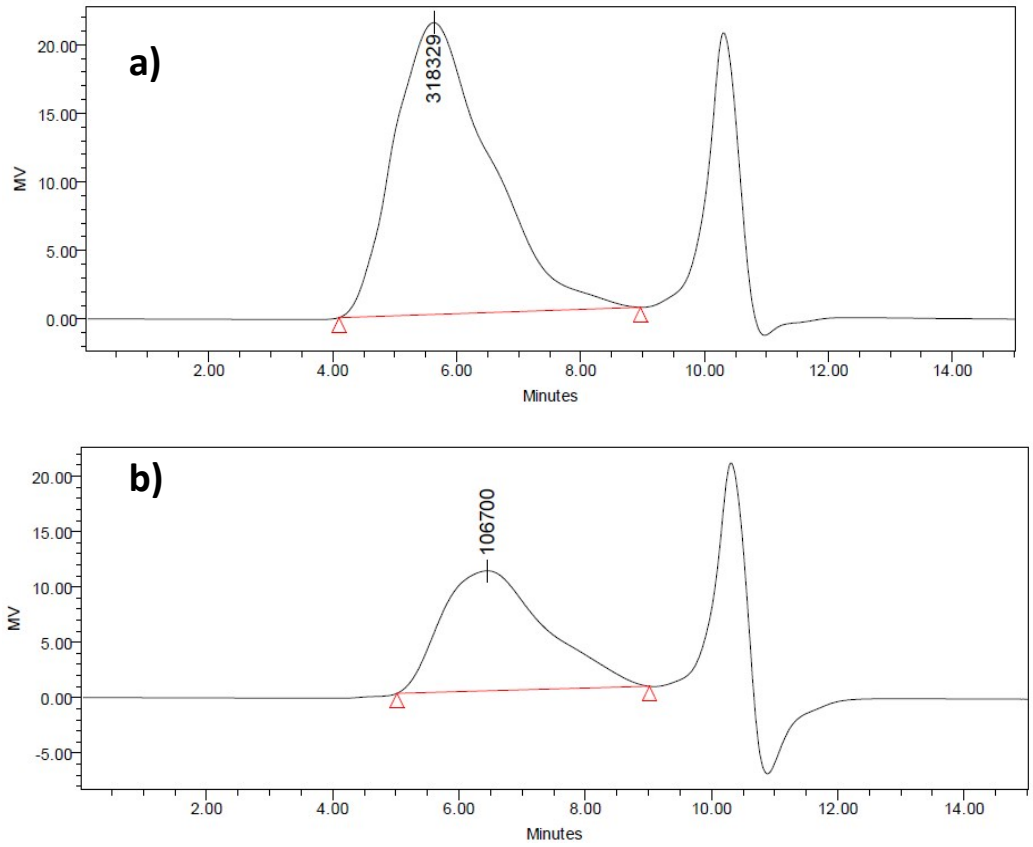

Figure S4. GPC of a) m_1PTB7-Th and b) m_2PTB7-Th.

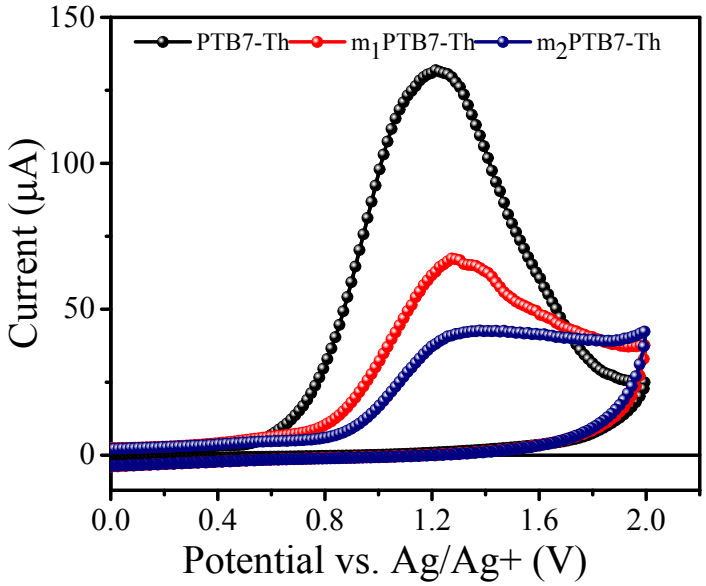

Figure S5. Cyclic voltammetry plots of polymer films using three-electrode system.

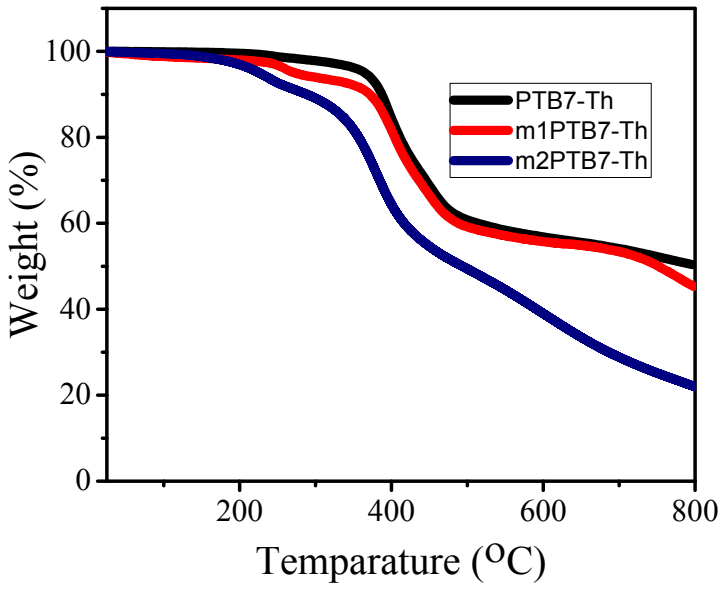

Figure S6. TGA plots of polymers with a heating rate of 10 °C/min under argon atmosphere.

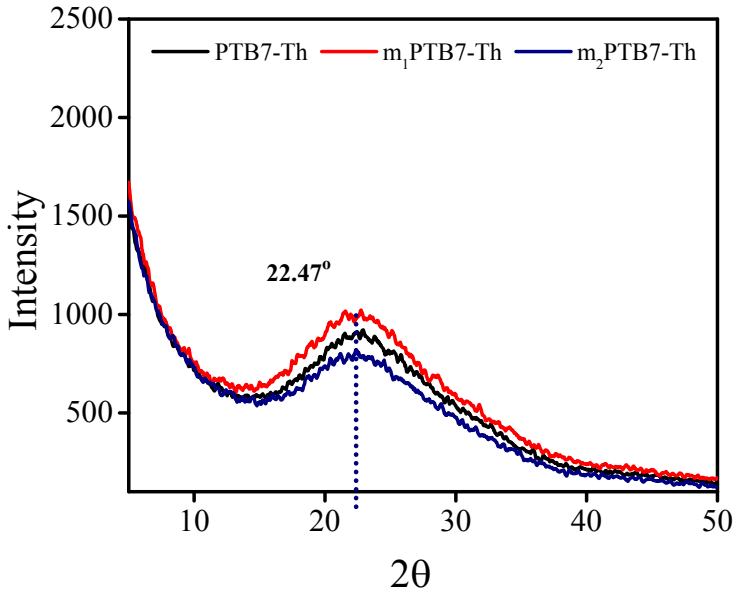

Figure S7. Thin film X-ray diffraction patterns of Polymers on glass.

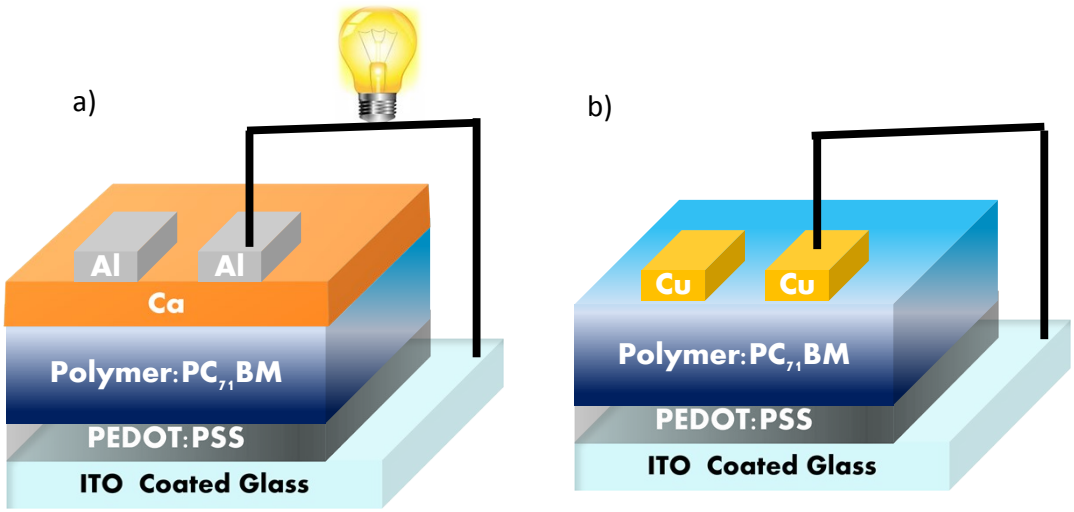

Figure S8. Device Architecture used for a) *J-V* and EQE characterization b) SCLC Characterization (hole only device)

Device Fabrication

Device architecture (**ITO/PEDOT: PSS/Active Layer blend/Ca/Al)** is shown in Fig. S6a where thin layer of PEDOT: PSS was Spin coated on pre-cleaned ITO-coated glass with a PEDOT:PSS aqueous solution at 4000 rpm and dried subsequently at 150^{o}C for 15 min in air, then the device was moved to a argon glove box. The Donor polymers and PCBM blend was prepared in 1:1.5 ratio with a concentration of 35mg/ml in chlorobenzene and stirrer for 12 hours and 15 mins before spin coating of active layer DIO was added to the solution. After that the donor polymer and PCBM blend was spin coated on PEDOT:PSS thin layer at rpm of 3000. Next sequentially Ca (~20nm) and Al (~70nm) was deposited in through a shadow mask on top of the active layer by thermal deposition under high vacuum (5×10^{-6} Torr). Same devices were used for EQE analysis. Hole mobility of the polymers was determined by fitting the dark current to the model of a single carrier SCLC using the device structure **ITO/PEDOT: PSS/Active Layer blend/Cu (**Fig. S6b).[3]

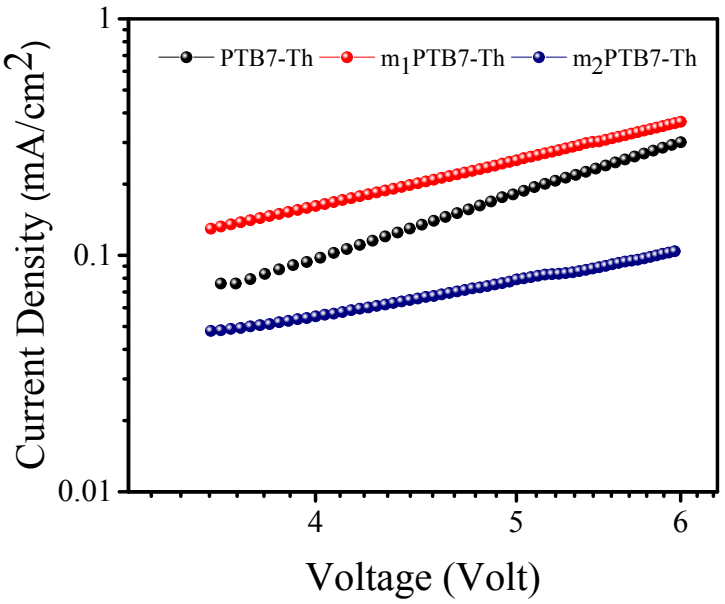

Figure S9. Plots obtained from the hole-only devices based on polymer: $PC_{71}BM$ blend films

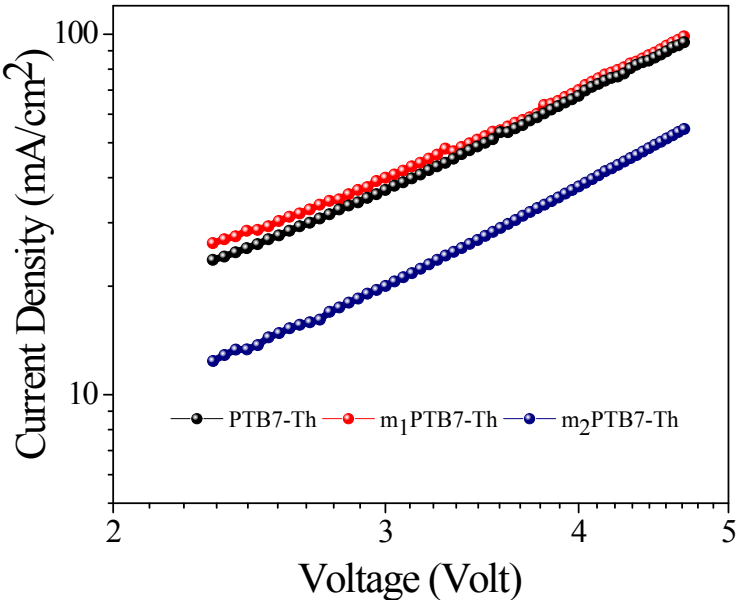

Figure S10. Plots obtained from the electron-only devices based on polymer: $PC_{71}BM$ blend films

References

1. J. Gao, W. Wang, S. Zhang, S. Xiao, C. Zhan, M. Yang, X. Lu and W. You, *J. Mater. Chem. A, 2018*, **6**, 179-188.
2. R. Garai, M. A. Afroz, R. K. Gupta, A. Choudhury and P. K. Iyer, *ACS Omega* 2020, 5, **6**, 2747-2754.
3. S. W. Qu, H. Wang, D. Z. Mo, P. J. Chao, Z. Yang, L. J. Li, L. L. Tian, W. Chen and F. He, *Macromolecules* 2017, **50**, 4962-4971.