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General Characterization

Nuclear magnetic resonance (NMR) spectra were obtained with a Varian Gemini 400 MHz NMR spectrometer at room temperature. Mass spectra (LR-ESI and EI) were collected at the University of Illinois, Chicago. Elemental analyses were conducted by Atlantic Microlab, Inc. Optical properties of the molecules were obtained with Shimadzu UV-2600 UV-visible spectrophotometer and Horiba Fluorimeter using a xenon lamp excitation source for absorption and fluorescence emission, respectively. Electrochemistry measurements were performed using cyclic voltammetry (CV) on a CH instrument 660D with a three electrode configuration, with a cell equipped with a platinum plate as the counter electrode, a platinum disc as the working electrode (2 mm diameter), and a non aqueous Ag/Ag⁺ electrode (Ag in 10 mM AgNO₃ solution in anhydrous acetonitrile) as the reference electrode. Solution state CV measurements for all compounds were recorded in a methylene chloride solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. Thin film CV measurements were performed by coating the Pt working electrode with a concentrated solution of each compound, and were recorded in an acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. All solutions were purged with Ar for 20 - 30 min before each experiment, and a positive pressure of Ar was maintained over the sample solution during the experiments. The scan rate was $v = 100$ mV/s for all experiments. All potentials are reported versus the ferrocene/ferrocenium (Fc/Fc⁺) redox couple which was used as an internal standard. Thermal gravimetric analyses were performed under a nitrogen flow at a heating rate of 10°C/min using a TA instrument TGA-Q50. Differential Scanning Calorimetric (DSC) analyses were performed under a nitrogen flow at heating and cooling rates of 5°C/min using a TA instrument 2010 DSC. FE-SEM images were obtained using a JEOL field-emission SEM JSM-6700F with an operating voltage of 5.00kV. Samples were prepared on a gold/mica substrate followed by air drying, and were then coated with gold for 35 seconds. X-ray diffraction (XRD) patterns were collected on a Pananalytical X'Pert PRO X-ray diffractometer, for which a Cu-K α radiation ($\lambda = 1.54$ Å, 20 mA, 40 kV) was used.

Synthesis

All chemicals were purchased from commercial sources and used as received without further purification, unless otherwise noted below. Solvents used for Pd catalyzed Stille coupling were degassed with Argon for 30 minutes prior to use.

TH-P

1,4-Dibromo-7,8-bis(decyloxy)phenazine (929 mg, 1.43 mmol)¹ was added to a round bottom flask containing 5 mol% Pd(PPh₃)₄ (89.0 mg, 0.072mmol). [2,2']Bithiophenyl-5-yl-tributyl-stannane² (1.40 g, 3.00 mmol) was diluted in 2 mL toluene and added to the reaction flask via syringe. An additional 8mL of toluene was added to the reaction flask. The solution was stirred at 90°C overnight under positive nitrogen pressure. The resulting solution was allowed to cool to room temperature and methanol was added to precipitate the crude product. The precipitates were filtered, and washed with methanol and hexane. Silica gel column chromatography with CH₂Cl₂ as an eluent gave the pure product in 72%

yield. ^1H NMR (400MHz, CDCl_3 , ppm) δ 7.85 (2H, d, J = 4.0 Hz), 7.42 (2H, s), 7.34 (2H, dd, J = 3.6, 1.2 Hz), 7.28 (2H, overlapping with CHCl_3 peak at 7.26), 7.09 (2H, dd, J = 5.2, 3.6 Hz), 4.28 (4H, t, J = 6.6 Hz), 1.99 (4H, m), 1.59 (4H, m), 1.46-1.29 (24H, overlapping peaks), 0.89 (6H, t, J = 6.8 Hz). ^1H NMR (400 MHz, $\text{THF}-d_8$, ppm) 8.22 (2H, s), 7.94 (2H, d, J = 4.0 Hz), 7.51 (2H, s), 7.36-7.35 (4H, overlapping peaks), 7.27 (2H, d, J = 4.0 Hz), 7.06 (2H, dd, J = 5.0, 3.8 Hz), 4.31 (6H, t, J = 6.2 Hz), 1.96 (4H, m), 1.63 (4H, m), 1.70-1.31 (24H, overlapping peaks), 0.89 (6H, t, J = 7.0 Hz). ^{13}C (100 MHz, CDCl_3 , ppm): 154.80, 140.60, 139.91, 138.36, 138.29, 138.00, 130.80, 127.17, 127.04, 125.35, 123.74, 123.60, 105.53, 105.40, 69.39, 31.93, 29.64, 29.59, 29.42, 29.37, 26.08, 22.69, 14.08. LR-ESI $[\text{M}+\text{H}]^+$: Calcd: 821.32 Found: 821.3. Anal. Calcd for $\text{C}_{48}\text{H}_{56}\text{N}_2\text{O}_2\text{S}_4$: C, 70.20; H, 6.87; N, 3.41. Found: C, 70.40; H, 6.86; N, 3.46.

5,8-Dibromo-2,3-dimethylquinoxaline

3,6-Dibromo-benzene-1,2-diamine (2.15 g, 8.08 mmol) was added to a round bottom flask. Acetic Acid (70 mL) was added to the reaction flask followed by 2,3-butanedione (0.70 mL, 8.08 mmol). The solution was stirred under nitrogen at 70°C for 30 minutes. The solution was poured into water and the resulting precipitates were filtered and washed with water giving pure product in 93% yield. ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.84 (2H, s), 2.83 (6H, s). ^{13}C (100 MHz, CDCl_3 , ppm): 155.42, 139.56, 138.26, 122.93, 23.05.

TH-Q

5,8-Dibromo-2,3-dimethylquinoxaline (442 mg, 1.40 mmol) was added to a round bottom flask containing 5 mol% $\text{Pd}(\text{PPh}_3)_4$ (87.0 mg, 0.070 mmol). $[2,2']$ Bithiophenyl-5-yl-tributyl-stannane (1.40 g, 3.00 mmol) was diluted in 2 mL toluene and added to the reaction flask via syringe. An additional 8mL of toluene was added to the reaction flask. The solution was stirred at 90°C overnight under a positive nitrogen pressure. The resulting precipitates were filtered and washed with methanol. Two times of silica gel column chromatography (CH_2Cl_2) followed by refluxing in MeOH provided the pure compound in 26% yield. ^1H NMR (400 MHz, CDCl_3 , ppm) δ 8.05 (2H, s), 7.77 (2H, d, J = 4.4 Hz), 7.30 (2H, dd, J = 3.4, 1.0 Hz), 7.25 (4H, overlapping with CHCl_3 peak), 7.07 (2H, dd, J = 5.0, 3.8 Hz), 2.85 (6H, s). ^1H NMR (400 MHz, $\text{THF}-d_8$, ppm) 8.19 (2H, s), 7.87 (2H, d, J = 4.0 Hz), 7.35-7.32 (4H, overlapping peaks), 7.26 (2H, d, J = 4.0 Hz), 7.05 (2H, dd, J = 4.8, 3.6 Hz), 2.86 (6H, s). ^{13}C (100 MHz, CDCl_3 , ppm): 152.33, 140.18, 137.91, 137.88, 137.36, 130.53, 127.88, 126.89, 125.54, 124.41, 123.58, 123.44, 22.73. LR-EI $[\text{M}]^+$: Calcd: 486.04 Found: 486. Anal. Calcd for $\text{C}_{26}\text{H}_{18}\text{N}_2\text{S}_4$: C, 64.16; H, 3.73; N, 5.76. Found: C, 63.97; H, 3.65; N, 5.81.

Device fabrication and photovoltaic measurement:

All the photovoltaic cells were prepared on a commercial pre-patterned Indium tin oxide (ITO)-coated glass substrate. Prior to use, the ITO glass substrates were cleaned with deionized water, acetone, and isopropyl alcohol using by ultrasonication, followed by treatment with a UV-ozone cleaner for 15 minutes. After passing through 0.45 μm poly(tetrafluoroethylene) (PTFE) filter, a dispersion of PEDOT:PSS in water (CleviosTM P VP AI 4083) was spin coated on the ITO glass at 4000 rpm for 1min, generating a thin film with a thickness of about 40 nm and dried at 120°C for 15 min in the air. For BHJ device, the blends of **TH-Q** or **TH-P** with certain amount of PC₆₁BM (Nano-C, Inc.) were dissolved in DCM and spin coated on the PEDOT:PSS after passing through 1 μm PTFE filter. For PHJ device, **TH-Q** or **TH-P** was dissolved in chloroform and spin coated on PEDOT:PSS layer, then the solution of PC₆₁BM in DCM was spin coated on top of the previous layer. The devices were completed by the thermally deposition of a 0.5nm layer of LiF and a 100 nm layer of aluminium at a pressure of 2×10^{-6} mbar with a shadow mask. The active area of every device was 0.12 cm^2 . The current density–voltage (J–V) characteristics of the photovoltaic devices were measured with a Keithley 2400 source-measure unit under white light illumination at 100 mW/cm^2 AM 1.5G condition with a solar simulator

(Oriel 91160, 300 W), calibrated with a mono-crystalline silicon solar cell as standard PV reference (2×2 cm, calibrated at NREL, Colorado, USA). The incident photon-to-current conversion efficiency (IPCE) measurement was carried out under monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp), and the calibration of the incident light was performed with a monocrystalline silicon diode. The thicknesses of films were recorded by a profilometer (Alpha-Step 200, Tencor Instruments), and AFM images were taken using an Asylum Research MFP3D atomic force microscope on finished devices.

Hole mobility measurement:

The hole mobility was measured through space charge limited current (SCLC) method in the hole-only devices with a configuration of ITO/ PEDOT:PSS (40 nm)/ pure donor or donor:PC₆₁BM/ MoO₃ (10 nm)/Al(100 nm). Such devices were fabricated similarly as the devices for OPV characterization except that different electrodes were evaporated. The experimental dark current densities J of donor:PC₆₁BM blends were measured when applied with voltage from 0 to 5V. The applied voltage V was corrected from the voltage drop across the ITO/PEDOT:PSS due to series resistance and contact resistance, which were calculated from a reference device without the donor:PCBM layer. From the plots of $J^{0.5}$ vs V , hole mobilities can be deduced from the equation:

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_h \frac{V^2}{L^3}$$

where ε_0 is the permittivity of free space, ε_r is the dielectric constant of the active layer, which is assumed to be around 3 for the donors or donor:PC₆₁BM blends, μ_h is the hole mobility, V is the voltage drop across the device, and L is the film thickness of active layer.

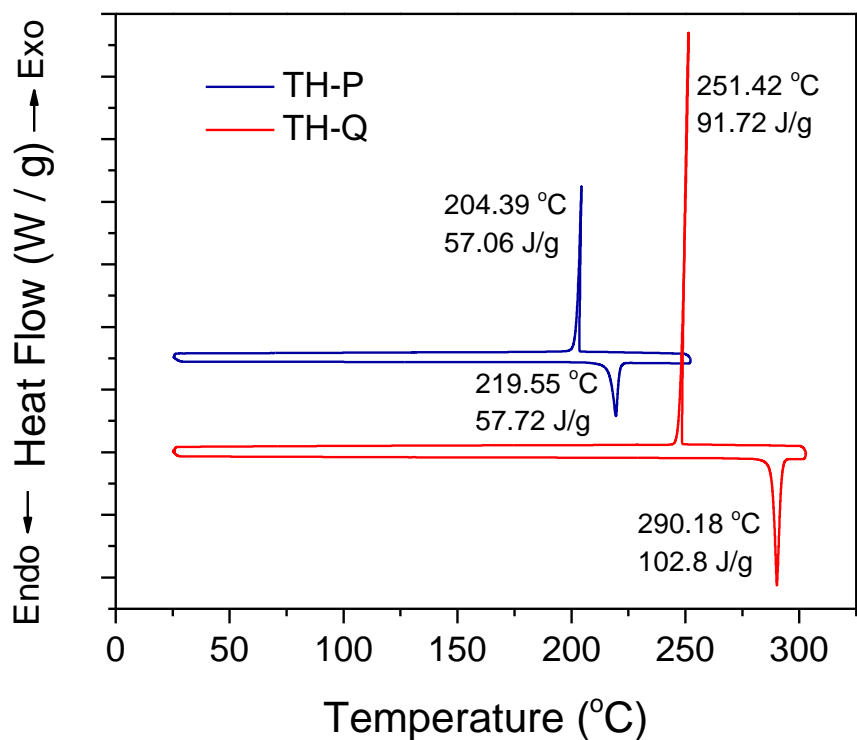


Figure S1. DSC heating and cooling scans of **TH-P** and **TH-Q**. Scan rate = 5 °C / min.

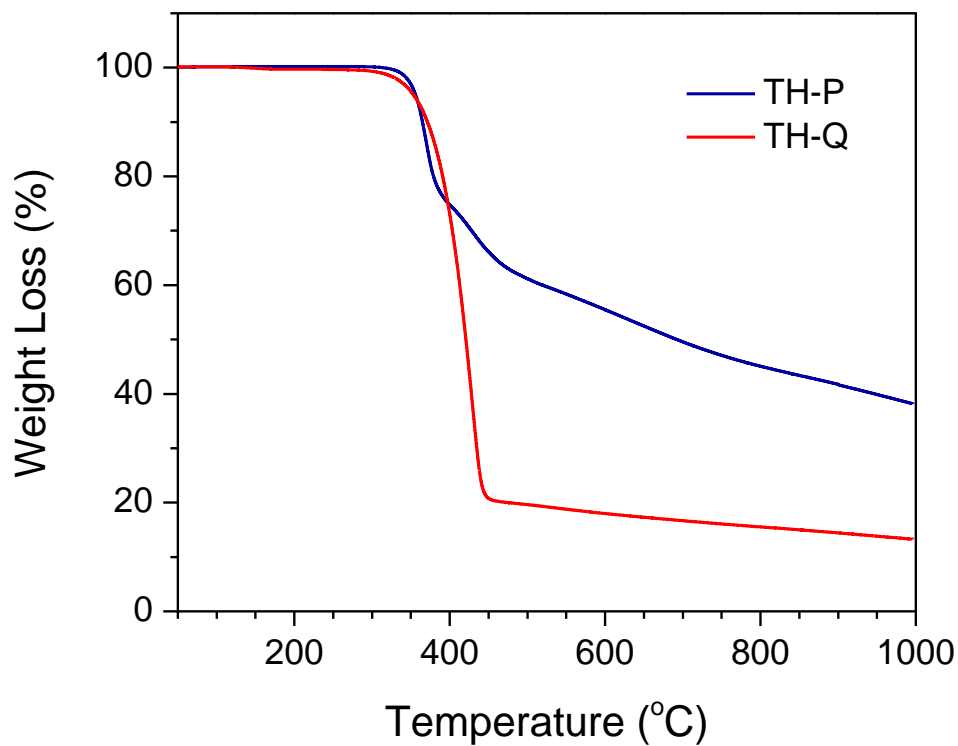


Figure S2. TGA thermograms of **TH-P** and **TH-Q**. Note: The decomposition behavior of **TH-Q** was not properly measured due to sublimation.

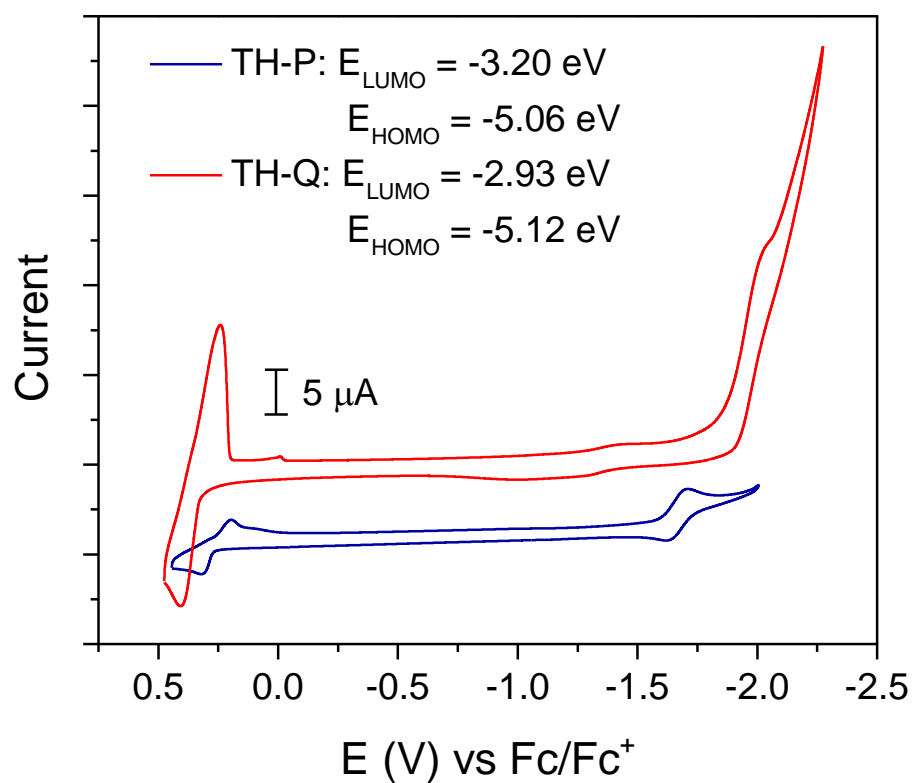


Figure S3. Cyclic voltammograms of **TH-P** and **TH-Q**. Scan rate = 100 mV/s.

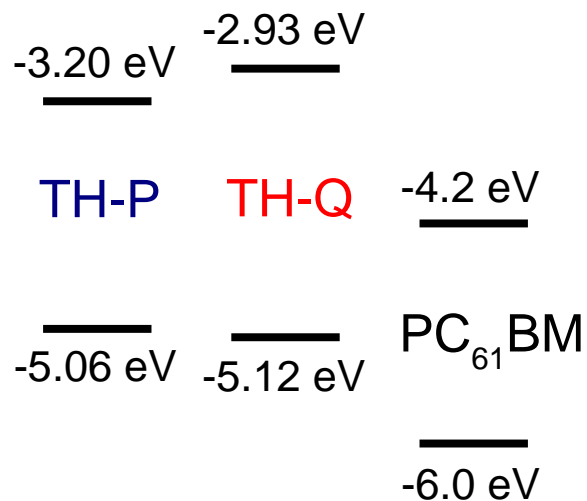


Figure S4. E_{HOMO} and E_{LUMO} levels of **TH-P** and **TH-Q** in comparison to E_{LUMO} of PC₆₁BM.

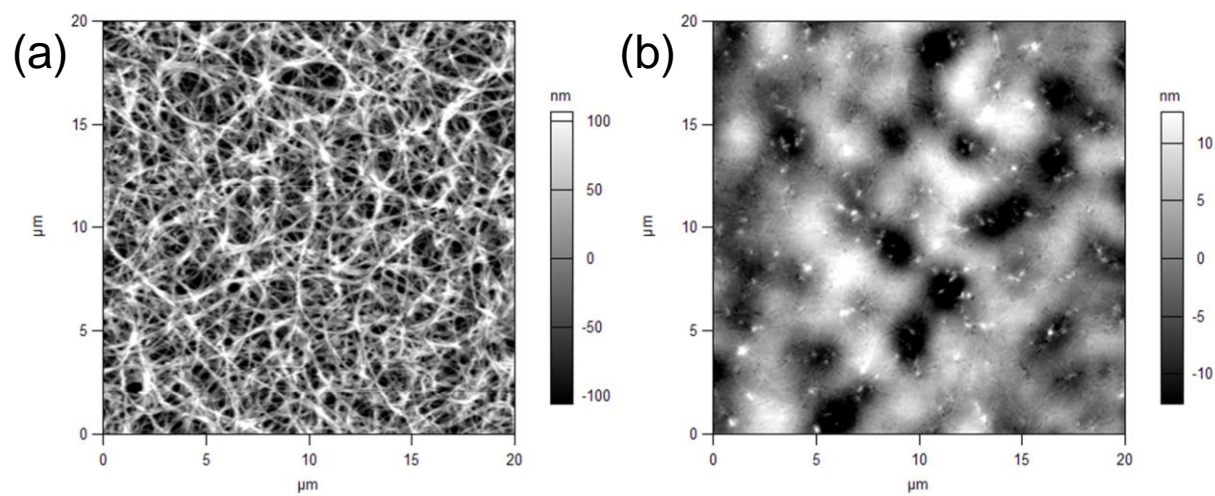


Figure S5. AFM images of (a) **TH-P** layer and (b) **TH-P** / PC₆₁BM layers.

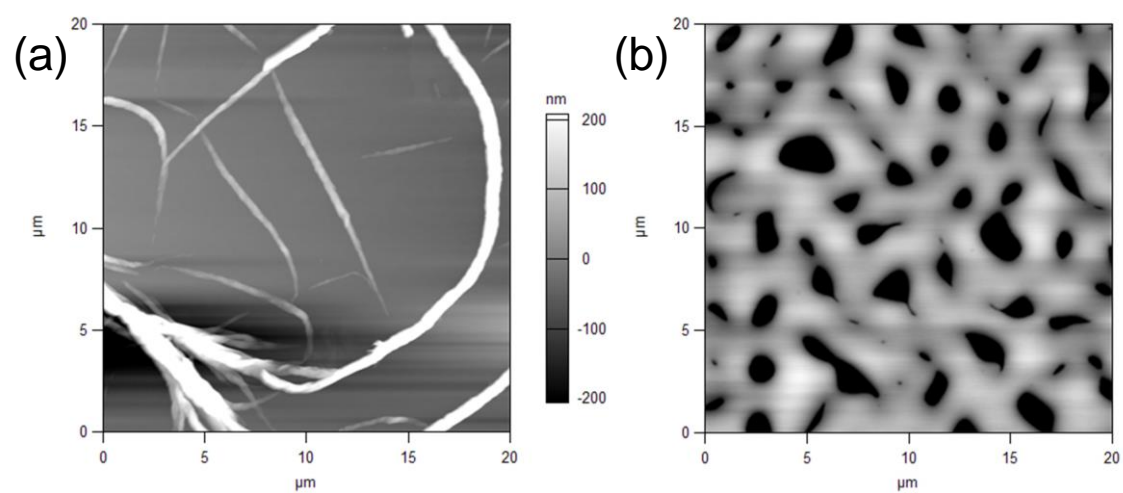


Figure S6. AFM images of (a) **TH-Q** layer and (b) **TH-Q** / PC₆₁BM layers.

Table S1. Photovoltaic performances of BHJ devices of **TH-P** & **TH-Q** at different compositions.

	Donor:PC ₆₁ BM (w/w)	Thickness (nm)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
TH-P	1:0.5	178	0.18±0.02	1.19±0.04	31±1	0.07±0.01
	1:1	107	0.21±0.02	1.26±0.08	31±1	0.08±0.01
	1:3	136	0.64±0.02	1.54±0.16	38±3	0.38±0.06
TH-Q	1:0.5	125	0.48±0.16	0.72±0.10	34±3	0.12±0.06
	1:1	61	0.74±0.04	1.63±0.21	30±2	0.36±0.04
	1:3	73	0.67±0.03	0.87±0.10	24±1	0.14±0.02

Table S2. Hole mobility of the donor molecules in neat and BHJ junction under the SCLC condition.

	Donor Only		Donor:PC ₆₁ BM ^a		
	Thickness (nm)	Mobility (cm ² /V ⁻¹ s ⁻¹)	Thickness (nm)	Mobility (cm ² /V ⁻¹ s ⁻¹) Pristine	Mobility (cm ² /V ⁻¹ s ⁻¹) Annealed
TH-P	165	3.51×10 ⁻³	150	1.06×10 ⁻⁵	1.41×10 ⁻⁵
TH-Q	91	1.74×10 ⁻³	134	4.42×10 ⁻⁵	9.60×10 ⁻⁵

^a Ratio of **TH-P**:PC₆₁BM = 1:3 and **TH-Q**:PC₆₁BM = 1:1.

References:

1. Lee, D.-C.; Cao, B.; Jang, K.; Forster, P. M. *J. Mater. Chem.* **2010**, *20*, 867-873.
2. Zhu, S. S.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 12568-12577.