Supplementary Information

The dichotomous role of exciting the donor or the acceptor on charge generation in organic solar cells

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Synthesis

Commercial solvents and reactants were used without further purification unless stated otherwise. NMR spectra were recorded on a Varian Mercury (^{1}H 400 MHz, ^{13}C 100 MHz) spectrometer. Chemical shifts are given in ppm with respect to tetramethylsilane as internal standard. MALDI-TOF mass spectroscopy was performed on a Bruker Autoflex Speed spectrometer. UV/vis/NIR spectroscopy was conducted on a Perkin Elmer Lambda 1050 spectrophotometer. Molecular weight distributions of the polymers were estimated by GPC at 140 °C on a PL-GPC 220 system using a PL-GEL 10µm MIXED-C column with *o*-DCB as the eluent and using polystyrene internal standards. TEM was performed on a Tecnai G^2 Sphera TEM (FEI) operated at 20 kV. 4-(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole was purchased from SunaTech. 3,6-bis(5-bromopyridin-2-yl)-2,5-bis(2-hexyldecyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**1**) and 3,6-bis(5-bromopyridin-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**2**) were synthesized according to literature procedure.[S1,S2] Monomer **3** and the polymers were synthesized according to Figure S1 and the details given below.

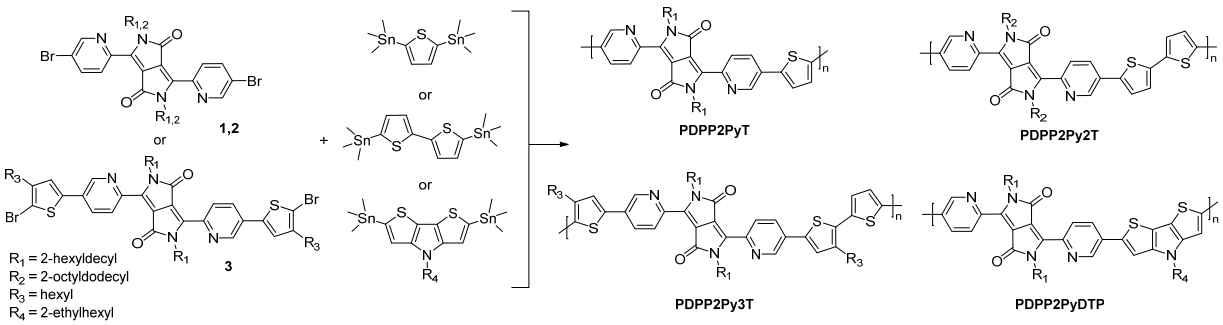


Figure S1. Synthesis of 2-pyridyl-DPP polymers.

3,6-bis(5-(4-hexylthiophen-2-yl)pyridin-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione. A Schlenk tube equipped with screw cap was loaded with **1** (400 mg, 0.446 mmol), 2-(4-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (328 mg, 1.12 mmol), triphenylphosphine (7.0 mg, 27 μmol), tris(dibenzylideneacetone)dipalladium (6.1 mg, 6.7 μmol), 8 mL toluene and 1 drop of Aliquat 336. The mixture was degassed with argon for 15 minutes after which a freshly prepared, degassed, potassium phosphate solution (2 M, 1.12 mL) was added. The mixture was degassed for an additional 10 min. after which the flask was sealed and heated to 115 °C for 45 min. The reaction mixture was diluted with 50 mL diethyl ether and washed with water (2 × 100 mL) and brine (100 mL). The organic phase was dried with $MgSO_4$, filtered and reduced. The residue was purified by silica gel chromatography using 1:1 dichloromethane/n-heptane as eluent and subsequently recrystallized from 200 mL ethanol to obtain the desired compound as a dark pink solid (420 mg, 88% yield). ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 9.02 (d, *J* = 8.4 Hz, 2H), 8.93 (d, *J* = 2.3 Hz, 2H), 8.02 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.32 (s, 2H), 7.03 (s, 2H), 4.37 (d, *J* = 7.2 Hz, 4H), 2.65 (t, *J* = 7.7 Hz, 4H), 1.71 – 1.61 (m, 6H), 1.42 – 1.10 (m, 60H), 0.90 (m, 6H), 0.83 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 162.75, 146.02, 145.59, 145.15, 145.01, 139.53, 132.78, 131.28, 127.46, 126.48, 121.98, 111.26, 46.30, 38.16, 31.92, 31.87, 31.67, 31.49, 30.53, 30.43, 30.05, 29.71, 29.62, 29.35, 28.99, 26.39, 22.67, 22.62, 14.12, 14.10 (some signals overlap). MALDI-TOF-MS: [M^+] calc: 1070.74, found: 1070.74.

3,6-bis(5-(5-bromo-4-hexylthiophen-2-yl)pyridin-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (3). A solution of 3,6-bis(5-(4-hexylthiophen-2-yl)pyridin-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (400 mg, 0.373 mmol) in 10 mL chloroform and 1 mL DMF was cooled to 0 °C and degassed with argon. *N*-bromosuccinimide (180 mg, 1.01 mmol) was added in portions after which the solution was left to warm to room temperature while stirring. After 2 hours, the mixture was diluted with dichloromethane and washed with water (2 × 100 mL) and brine (100 mL). The organic phase was dried with $MgSO_4$, filtered and reduced. The residue was purified by silica gel chromatography using 4:6 dichloromethane/n-heptane as eluent and subsequently recrystallized from 200 mL 9:1 ethanol/toluene to obtain **3** as a dark purple solid (206 mg, 45% yield). ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 9.03 (d, *J* = 8.5 Hz, 2H), 8.85 (s, 2H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.17 (s, 2H), 4.35 (d, *J* = 7.1 Hz, 4H), 2.61 (t, *J* = 7.7 Hz, 4H), 1.71 – 1.59 (m, 6H), 1.43 – 1.09 (m, 60H), 0.94 – 0.88 (m, 6H), 0.88 – 0.79 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 162.68, 146.31, 145.21, 145.05, 143.91, 139.21, 132.51, 130.42, 127.51, 126.00,

111.42, 111.14, 46.32, 38.19, 31.93, 31.87, 31.61, 31.49, 30.05, 29.70, 29.68, 29.65, 29.64, 29.37, 28.92, 26.40, 22.69, 22.67, 22.60, 14.13, 14.11, 14.09 (some signals overlap). MALDI-TOF-MS: [M^+] calc: 1228.56, found: 1228.56.

General polymerization procedure

A dry Schlenk tube equipped with screw cap was charged with 100.0 mg of pyridine DPP monomer **1**, **2**, or **3**, an equivalent molar amount of the corresponding freshly recrystallized bisstannyl compound, 6 mol% triphenylphosphine, and 1.5 mol% tris(dibenzylideneacetone)dipalladium. The tube was put under argon atmosphere and dry toluene (2 mL) and dry DMF (0.2 mL) were added. The resulting solution was degassed with argon for 15 minutes after which the tube was sealed and heated to 115 °C for 16 hours. The resulting gel was diluted with 15 mL hot 1,1,2,2-tetrachloroethane and precipitated in methanol. The solids were taken into chloroform and treated with EDTA (300 mg) and water, refluxing for 2 hours. The organic layer was separated and washed two times with water. The polymer solution was then concentrated and precipitated in methanol. The resulting solids were subjected to Soxhlet extraction with acetone and n-hexane. The residue in the thimble was dissolved in boiling chloroform, filtered hot and reduced in volume after which it was precipitated in acetone to afford the desired polymer after filtration and drying. (PDPP2PyT: 90 mg, 98% yield; PDPP2Py2T: 95 mg, 94% yield; PDPP2Py3T: 90 mg, 96% yield; PDPP2PyDTP: 110 mg, 96% yield).

Additional Figures and Tables

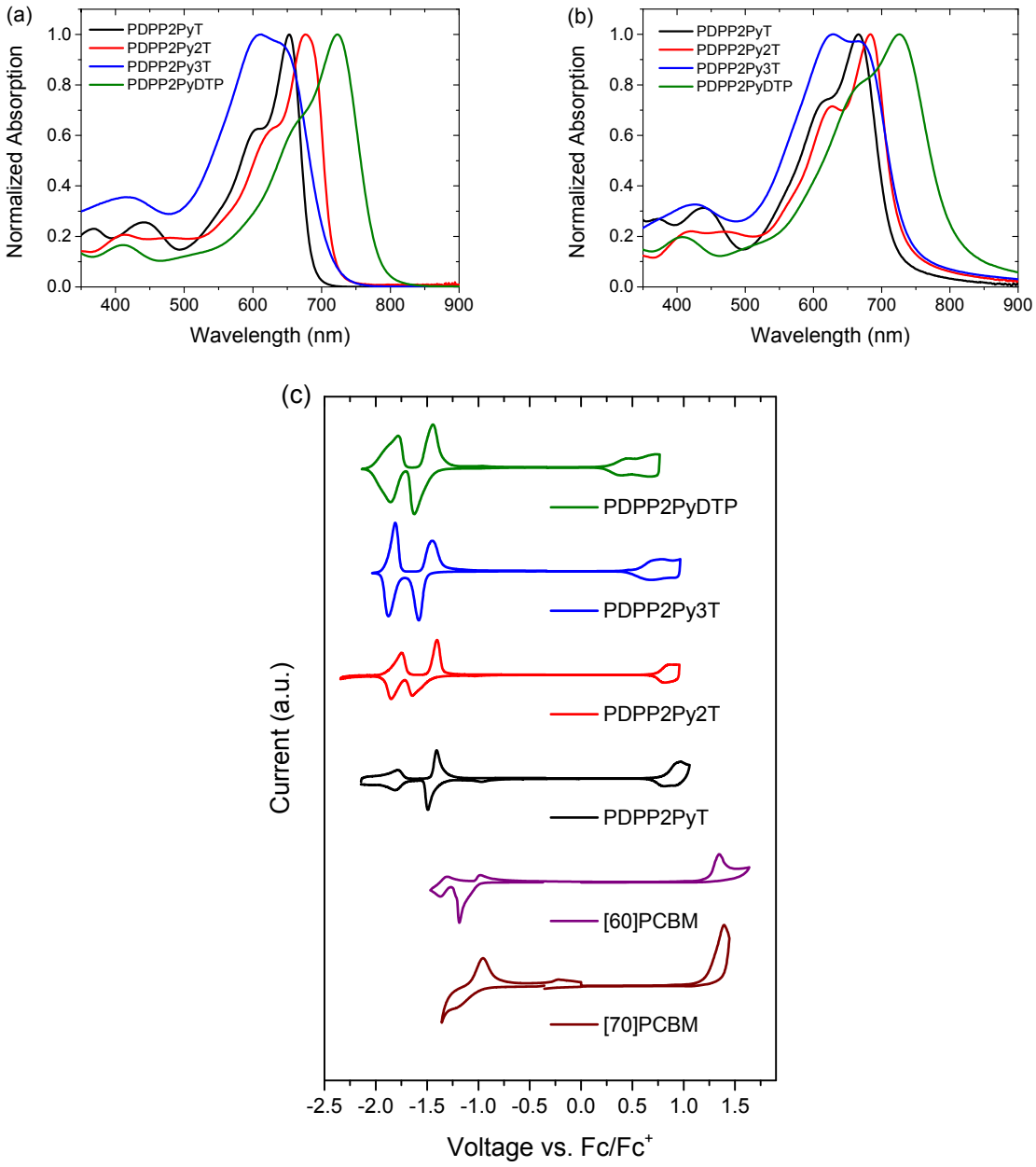


Figure S2. (a) Absorption spectra of pyridine DPP polymers in dilute chloroform solution. (b) Absorption spectra in thin films. Cyclic voltammograms vs. Fc/Fc^{+} of the polymers, [60]PCBM and [70]PCBM thin films (c). It was opted to measure all voltammograms from thin films, as CV of the polymers in solution proved difficult due to limited solubility, which is in contrast to PCBM. Therefore, it is noted that the thin film PCBM voltammogram does not show fully reversible peaks due to dissolution of oxidized and reduced species in the electrolyte. However, by using identical measuring technique for both the polymers and the PCBM, the resulting redox potentials are directly comparable.

Table S1. Molecular Weight, Optical Absorption, and Redox Potentials

	PDPP2PyT	*PDPP2Py2T*	*PDPP2Py3T*	*PDPP2PyDTP*
M_n (kg mol^{-1})	67.4	93.8	43.1	55.6
M_w (kg mol^{-1})	175.6	534.1	127.6	245.8
PDI	2.60	5.70	2.96	4.42
E_g^{sol} (eV)	1.81	1.73	1.74	1.58
E_g (eV)	1.73	1.70	1.68	1.54
E_{ox} (V) [a]	+0.82	+0.73	+0.54	+0.26
E_{red} (V) [a]	−1.40	−1.43	−1.51	−1.44
E(HOMO) (eV) [b]	−6.05	−5.96	−5.77	−5.49
E(LUMO) (eV) [b]	−3.83	−3.80	−3.72	−3.79
Δ_{LUMO} (eV) [c]	0.41	0.44	0.52	0.45
Δ_{HOMO} (eV) [c]	0.43	0.52	0.70	0.99

[a] Versus Fc/Fc$^+$. [d] Determined using a work-function value of −5.23 eV for Fc/Fc$^+$. [c] Energy offset to [60]PCBM HOMO/LUMO levels measured in identical fashion to the polymers (Figure S2c).

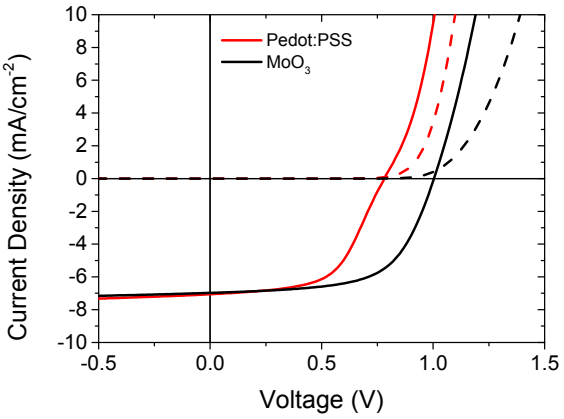


Figure S3. *J–V* curves of PDPP2PyT/[60]PCBM solar cells on PEDOT:PSS and MoO_3, showing an S-shape and reduced V_{oc} for the cell on PEDOT:PSS.

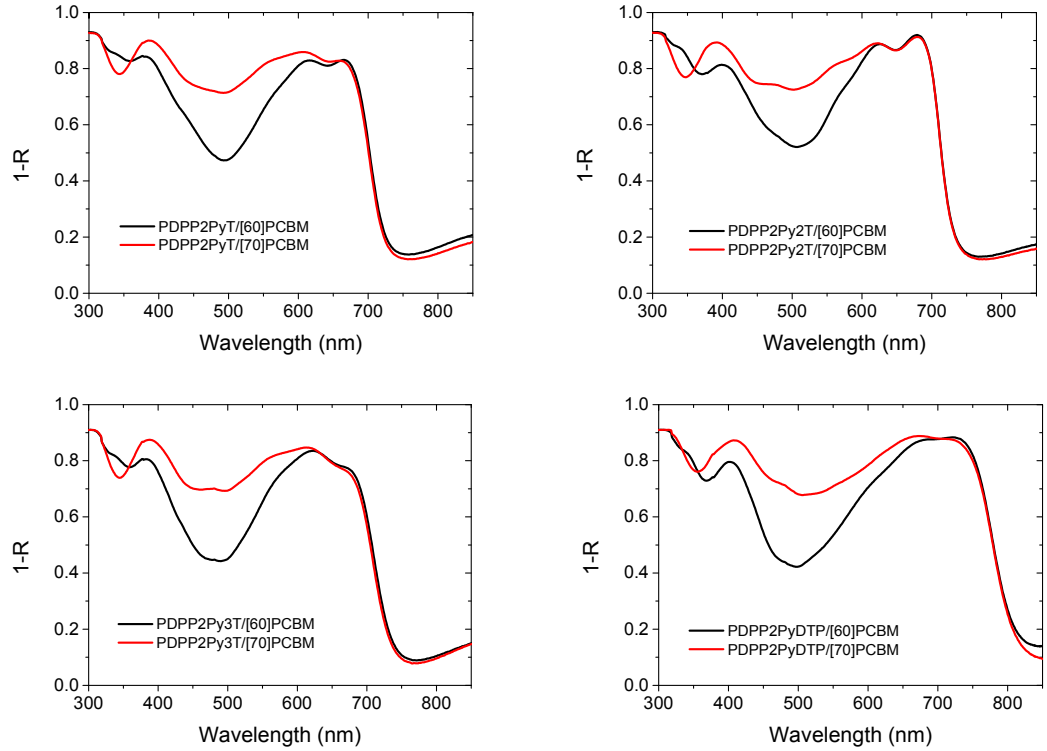


Figure S4. 1-Reflection spectra of pyridine DPP polymer solar cells with [60]PCBM and [70]PCBM showing a significant higher optical absorption for the [70]PCBM cells in the region of fullerene absorption, while the absorption in the polymer region is identical.

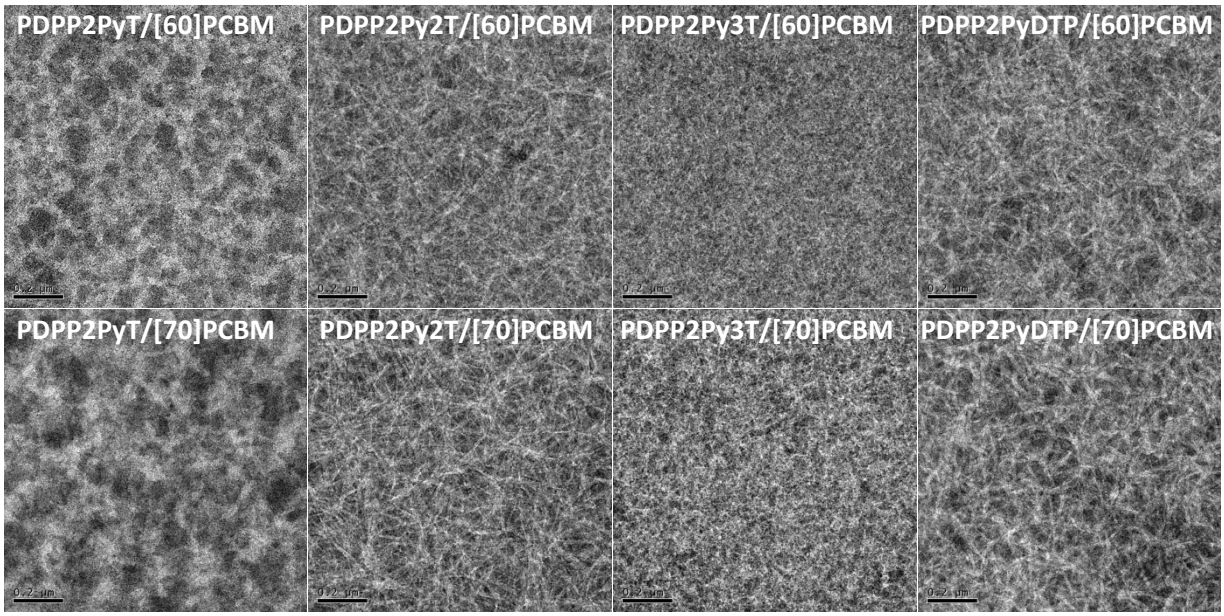
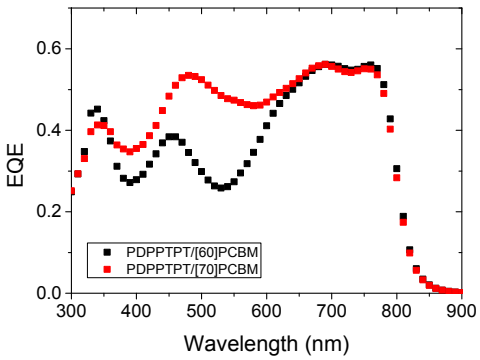
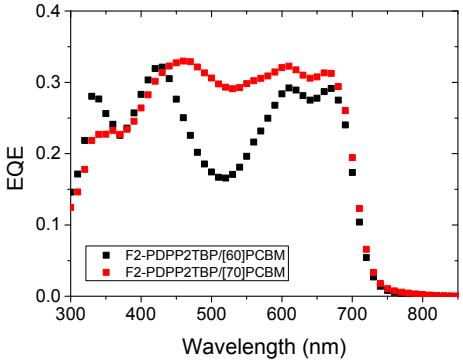
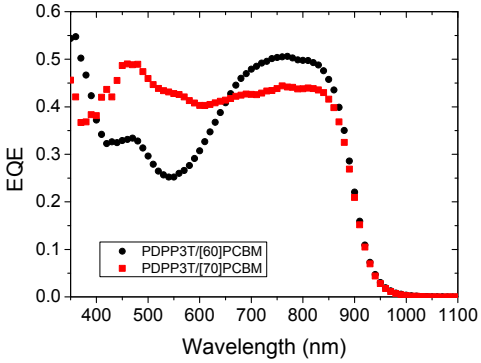
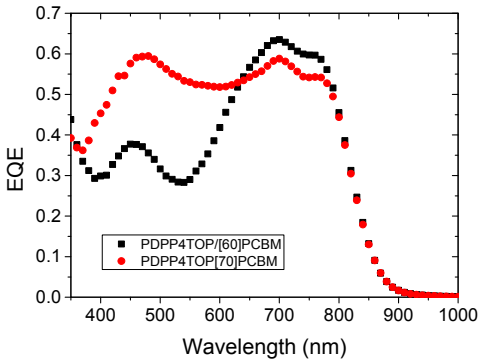


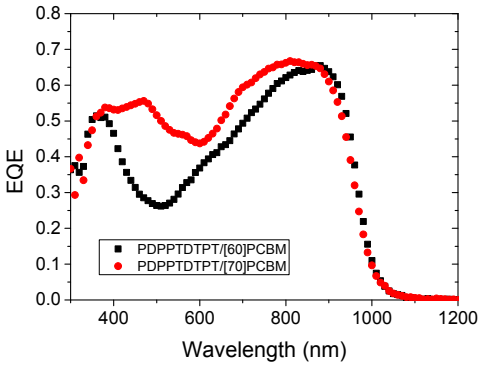
Figure S5. TEM images of active layers from the 2-pyridine DPP polymers with [60]PCBM (top) or [70]PCBM (bottom), the scale bar is 200 nm.

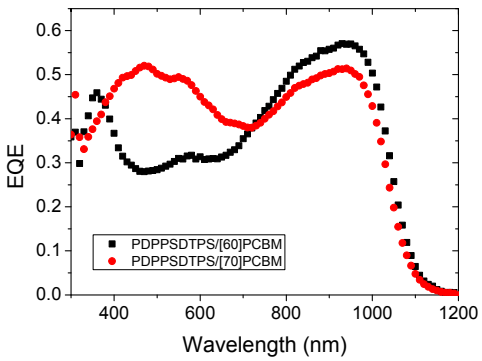

EQE
Wavelength (nm)
PDPPTPT/[60]PCBM
PDPPTPT/[70]PCBM

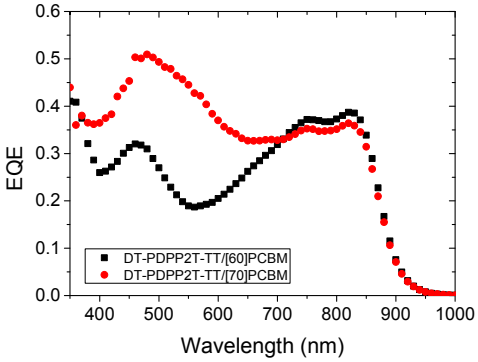

EQE
Wavelength (nm)
F2-PDPP2TBP/[60]PCBM
F2-PDPP2TBP/[70]PCBM

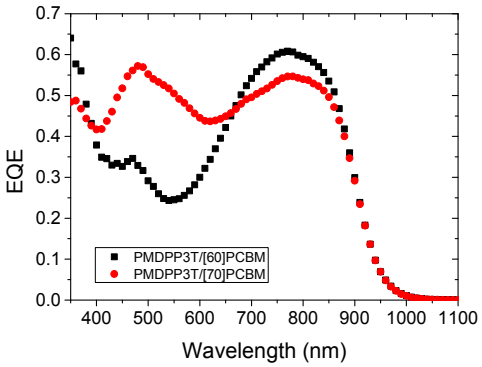

EQE
Wavelength (nm)
PDPP3T/[60]PCBM
PDPP3T/[70]PCBM


EQE
Wavelength (nm)
PDPP4TOP/[60]PCBM
PDPP4TOP[70]PCBM


EQE
Wavelength (nm)
PDPPTDTPT/[60]PCBM
PDPPTDTPT/[70]PCBM


EQE
Wavelength (nm)
PDPPSDTPS/[60]PCBM
PDPPSDTPS/[70]PCBM


EQE
Wavelength (nm)
DT-PDPP2T-TT/[60]PCBM
DT-PDPP2T-TT/[70]PCBM


EQE
Wavelength (nm)
PMDPP3T/[60]PCBM
PMDPP3T/[70]PCBM

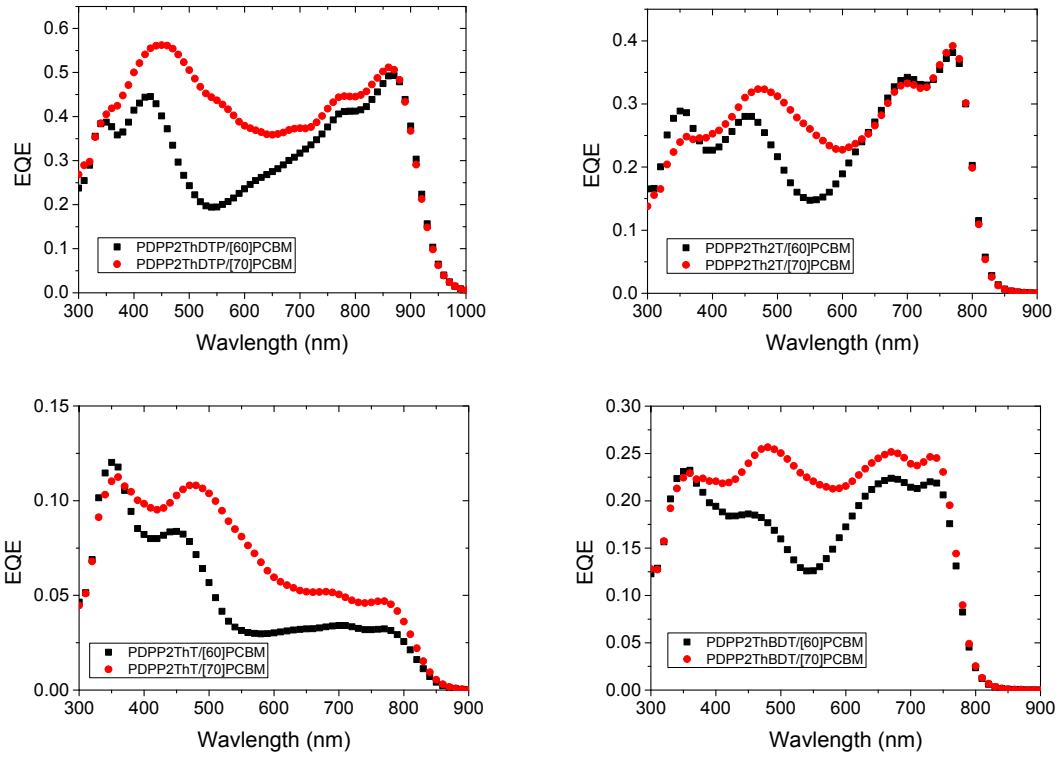


Figure 6. Comparison of reported and measured EQE spectra of various DPP polymer solar cells with [60]PCBM and [70]PCBM that were processed identically and have similar thickness. See references S3-9 for individual polymer and processing details.

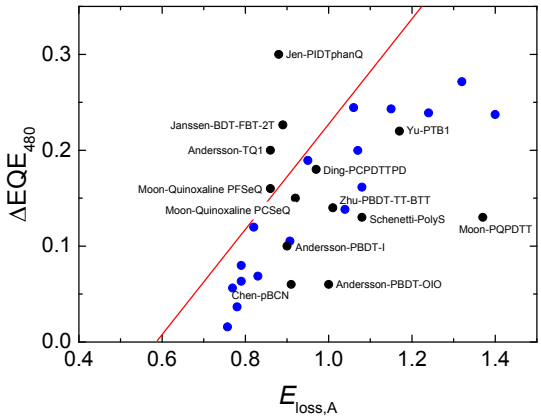


Figure S7. Energy loss acceptor versus ΔEQE_{480} for DPP polymers presented in Figure 4 (blue) and various other polymers reported in literature (black) from references S10-20. The red line is a guide to the eye and is the same as in Figure 4 of the main text.

References

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