

Supporting Information for:

**Molecular Insights into Photostability of Fluorinated
Organic Photovoltaic Blends: Role of Fullerene
Electron Affinity and Donor–Acceptor Miscibility**

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I. Materials

$C_{60}(CF_3)_2$ (also referred to as 60-2-1) was synthesized according to literature procedure¹ and purified to >99% purity as determined by HPLC, ^{19}F NMR, and APCI-MS. PC₆₀BM was purchased from Nano-C, Inc., was >99% pure, and was used without further purification. Poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-alt-(3,3'''-di(2-octyldodecyl)-2,2';5',2'';5'',2'''-quaterthiophen-5,5'''-diyl)], also known as PCE11 ($M_n = 74$ KDa, $M_w/M_n = 1.76$) was purchased from California Organic Semiconductors, Inc., as were the stannylated BDT monomer and brominated FBT units. The brominated BT unit was purchased from TCI. BT-BDT and FBT-BDT copolymers in Figure 1 were synthesized from these commercially available monomers according to literature procedures.² TPD-BDT ($M_n = 14$ KDa, $M_w/M_n = 2.74$) and TPD-BDT(EH) ($M_n = 12$ KDa, $M_w/M_n = 2.88$) were purchased from Ossila. TPD-CPDT was synthesized according to a literature procedure.³ All other reagents employed in this study were obtained from commercial sources at the highest available purity and used without further purification.

II. Polymer Characterization

Polymer Molecular Weight Determination. Polymer samples were dissolved in HPLC grade chloroform (~1 mg/mL), stirred at rt for 2 h, and then filtered through a 0.45 μm PVDF filter. Size exclusion chromatography was then performed on a PL-Gel 300 Å~ 7.5 mm (5 μm) mixed D column using an Agilent 1200 series autosampler, inline degasser, and diode array detector. The column and detector temperatures were 35 °C. HPLC grade chloroform was used as eluent (1 mL/min). Linear polystyrene standards were used for calibration to measure TPD-CPDT ($M_n = 10$ KDa, $M_w/M_n = 2.0$), BT-BDT ($M_n = 20$ KDa, $M_w/M_n = 2.7$), and FBT-BDT ($M_n = 22$ KDa, $M_w/M_n = 2.8$). Values for commercially available polymers are listed in the materials section above.

Cyclic Voltammetry. All voltammograms were recorded at 25 °C with a CH Instruments Model 600D potentiostat. Measurements were carried out under nitrogen at a scanning rate of 0.1 V/s using a platinum wire as the counter electrode and a glassy carbon disk as the working electrode. Potentials were measured vs. Ag/AgCl (and calibrated vs. Fc/Fc⁺, measured as 0.4 V vs. Ag/AgCl). The Fc/Fc⁺ energy level used in HOMO calculations was assumed to be -4.8 eV. Polymer films were drop cast onto a platinum disk working electrode from a 1 mg/mL chloroform solution and dried under an N₂ stream prior to measurement in 0.1 M Bu₄NBF₄ acetonitrile.

Polymer Film Absorbance. Fraction of light Absorbed (FA) spectra used for the TRPL measurements (*vide infra*) were calculated from fraction reflected (FR) and fraction transmitted

(FT) spectra collected by separate spectrometers (Ocean Optics HR2000) fitted with a ‘six around one’ reflectance probe (Ocean Optics R400-7-SR) and a collimating lens, respectively, according to the equation $FA = 1 - FT - FR$.

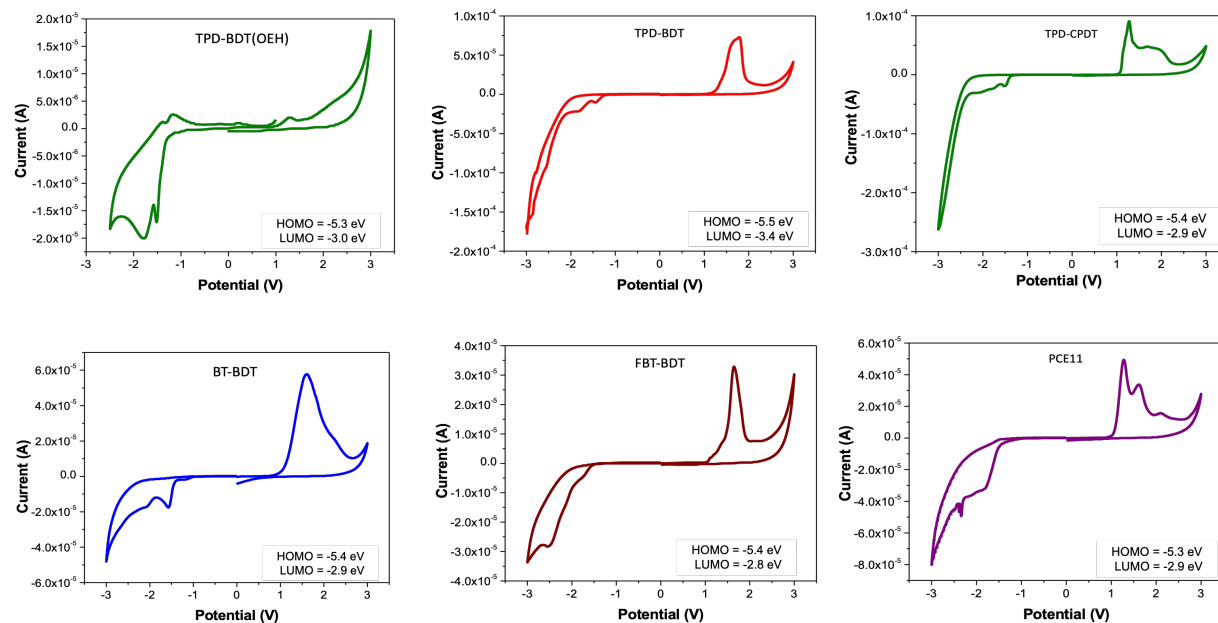


Figure S1. Cyclic voltammograms recorded vs. Ag/AgCl.

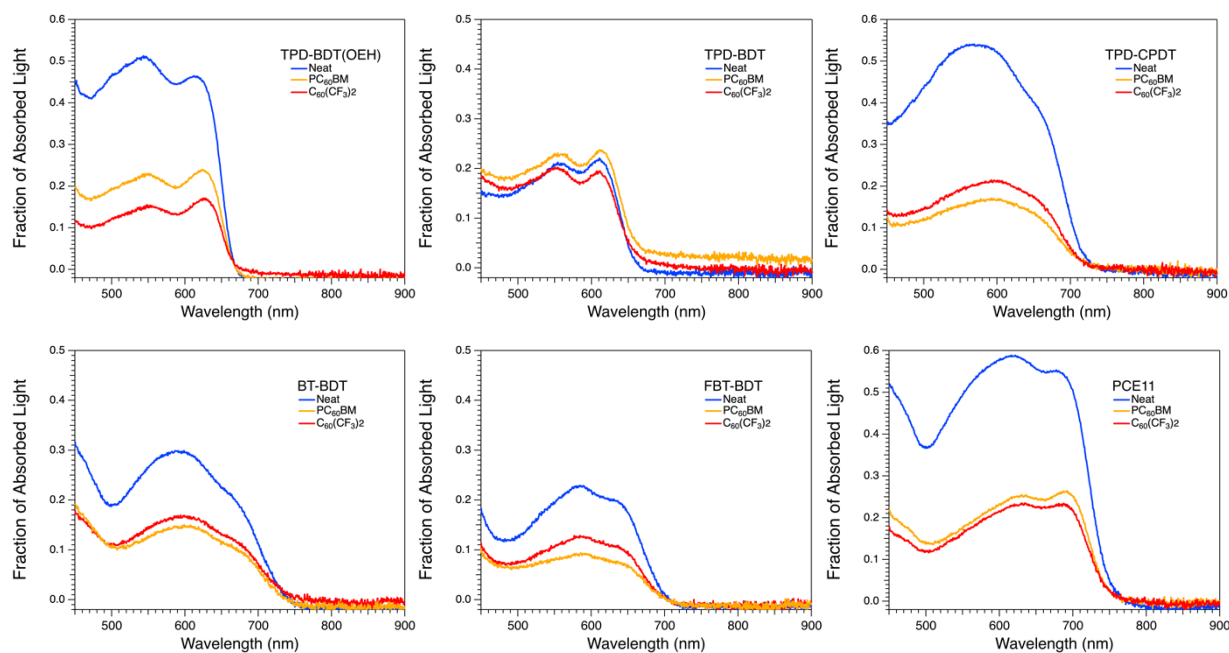


Figure S2. Normalized spectra illustrating fraction of absorbed light for 6 neat polymers and their respective blends used in this work.

III. Photobleaching

Sample preparation and ageing. Details of the photobleaching apparatus are provided elsewhere.⁴ All films were cast in air onto $1 \times 2 \text{ cm}^2$ quartz substrate, previously cleaned by brushing with detergent followed by sequential ultrasonication in acetone and isopropanol. Unless otherwise stated, films were cast from 70 μL solutions of 1:1 chlorobenzene:*o*-dichlorobenzene, at a spin rate of 600 RPM for 30 s followed by 2000 RPM for another 60 s. The films were then kept in the dark overnight to dry. Solutions containing 12 mg/mL were used to cast films of neat-polymer; this was also used to mix with equal amounts of fullerene solution of the same concentration (12 mg/mL in this case) for casting their respective film-blends. Each solution was heated and stirred for at least 1 h prior to casting to ensure all components were dissolved and well blended. Films containing the same polymer were prepared on the same day and photobleached together on a rotating spinner to account for differences in the lamp output, so each film is exposed to the same conditions and intensity of light throughout the aging process. Radiative heating from the lamps kept the samples at a temperature of 65 °C. Films were prepared to give an initial max absorbance of 0.2—0.3 for each film tested in this study. Alteration to the general procedure just described are listed below for the given polymer blend, the goal being to maintain a similar initial absorbance value between all films tested.

PCE11. A solution of PCE11 (6 mg/mL) was heated at 110 °C for 1 h with stirring prior to use. 100 μL of this was cast onto a hot substrate (also heated to 110 °C) at a spin rate of 1200 RPM for 60 s. To avoid the polymer from crashing out during the process of casting, the quartz substrate was heated using a hot plate set to 110 °C for 1 minute prior to transferring to onto the vacuum-chuck. The pipette tip used was warmed by wrapping in aluminum foil and placing on a hot plate (set to 110 °C) for 1 minute before use. The vacuum-chuck was heated by placing a hot metal block on it, which was previously heated on the same hot plate, onto the top of the chuck for 10 s and removed immediately prior to casting. *PCBM blends*; solutions were cast at a spin rate of 1000 RPM for 30 s followed by 2000 RPM for 60 s. *C₆₀(CF₃)₂ blends*; solutions were cast at a spin rate of 700 RPM for 30 s followed by 2000 RPM for 60 s.

TPD-BDT. A 50 μL solution of 6 mg/mL of polymer was cast at a spin rate of 500 RPM for 30 s, then increased to 2000 RPM 60 s. *C₆₀(CF₃)₂ blends*; solutions were cast at a spin rate of 500 RPM for 10 s followed by 2000 RPM for 60 s.

TPD-BDT(OEH) and TPD-CPDT. A solution of 7.5 mg/mL of polymer was heated at 110 °C for 1 h with stirring to fully dissolve, and cast while hot. Note the quartz substrate itself was not heated for these films.

BT-BDT films. Solutions of neat polymer were mixed while heated at 80 °C for 2 h to thoroughly dissolve, before cooling back to RT. Solutions (once cooled RT) were cast at a spin rate of 800 RPM for 60 s.

FBT-BDT films. A solution of FBT-BDT (6 mg/mL) was heated at 90 °C for 1 h with stirring prior use. 100 μ L of this was cast onto a RT substrate at a spin rate of 700 RPM for 10 s followed by 2000 RPM for 60 s. Note that both PCE11 and FBT-BDT films change color when heated in solution, from a greenish blue to a red magenta color, but revert when cooled down.

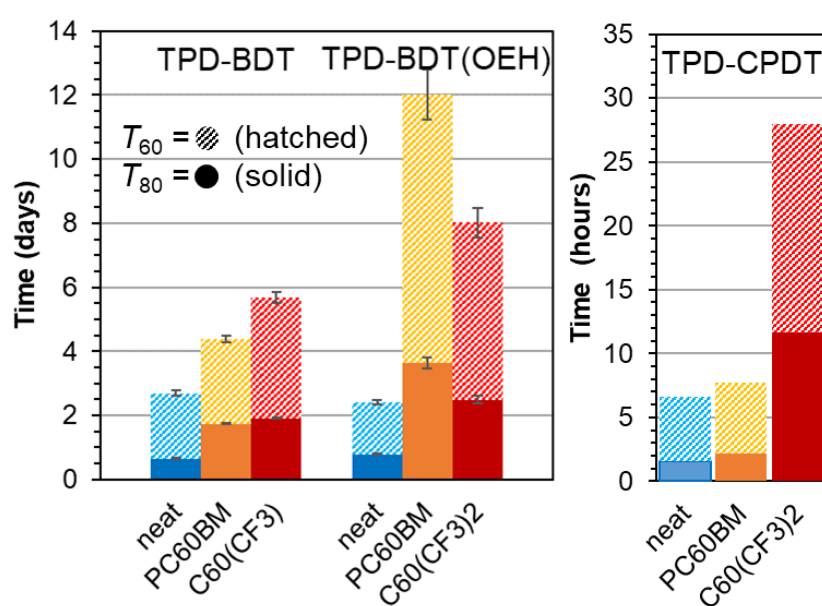


Figure S3. Comparison of T_{80} and T_{60} values for neat and blended films from Figure 3—using the same color key. Solid bars represent the average time it takes for a given film to irreversibly photobleach to 80% of the initial absorbance value (T_{80}), hatched bars represent the additional time to reach 60% of the initial absorbance value (T_{60}). (left) films of TPD-BDT and TPD-BDT(OEH) T_{80} and T_{60} values in units of days. (right): films of TPD-CPDT T_{80} and T_{60} values in units of hours.

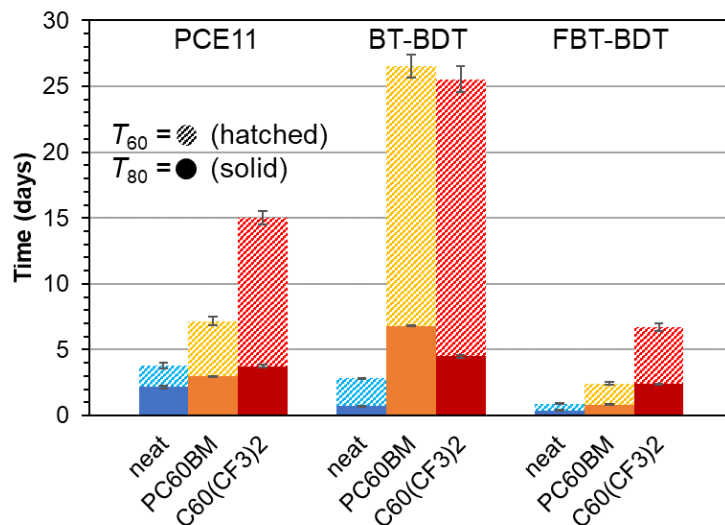


Figure S4. Comparison of T_{80} and T_{60} values for neat and blended films from Figure 3—using the same color key. Solid bars represent the average time it takes for a given film to irreversible photobleach to 80% of the initial absorbance value (T_{80}), hatched bars represent the additional time to reach 60% of the initial absorbance value (T_{60}).

IV. Time-resolved photoluminescence

TRPL was measured using a supercontinuum fiber laser (Fianium, SC-450-PP) operating at 0.2 MHz as the excitation source. The pulse energy was approximately 1 nJ, and the excitation wavelength used varied from polymer sample: TPD-BDT (560 nm), TPD-BDT(OEH) (550 nm), TPD-CPDT (600 nm), PCE11 (630 nm), BT-BDT (613 nm), FBT-BDT (590 nm). A streak camera for visible detection (Hamamatsu C10910-04) was used to collect time-resolved spectra over the range of 400-900 nm. The instrument response function (IRF) depends on the time window size, but at 1 ns range the IRF is approximately 80 ps, which was measured by collecting the scattered excitation beam from a roughened quartz slide. Representative contour plots of the TRPL data are illustrated elsewhere.⁵ From this data, PL decays were plotted by first normalizing for the number of scans and the fraction of absorbed light at the excitation wavelength in each sample and then by integrating the intensity (counts) over the full PL spectrum. Quenching efficiencies among the different samples were calculated by integrating that data between 0 and 2 ns.

V. STM/STS Analysis

STS measurements were performed at 80 K in an ultrahigh vacuum (2×10^{-10} Torr) condition. A RHK Pan style STM was used for this purpose in which both the tip and the film retained the same temperature. Tip-approach parameters were set to 2.0 V, 0.1 nA. Differential conductance measurements were performed through a standard lock-in technique with a modulation frequency of 971 Hz and rms voltage of 16 mV.

VI. Time-resolved microwave conductivity

TRMC is a pump-probe technique that can be used to measure the photoconductance of a film without the need for charge collection at electrical contacts.^{6,7} The details of the experimental methodology have been presented elsewhere.^{7,8} In brief, the sample is placed in a microwave cavity at the end of an X-band waveguide operating at ca. 9 GHz, and is photoexcited through a grid with a 5 ns laser pulse from an OPO pumped by the third harmonic of an Nd:YAG laser. The relative change of the microwave power, P , in the cavity, due to absorption of the microwaves by the photoinduced free electrons and holes, is related to the transient photoconductance, ΔG , by $\Delta P/P = -K\Delta G$, where the calibration factor K is experimentally determined individually for each sample. Taking into account that the electrons and holes are generated in pairs, the peak photoconductance during the laser pulse can be expressed as⁷

$$\Delta G = \beta q_e F_A I_0 (\phi \cdot \Sigma \mu) \quad (\text{S1})$$

where q_e is the elementary charge, $\beta = 2.2$ is the geometric factor for the X-band waveguide used, I_0 is the incident photon flux, F_A the fraction of light absorbed at the excitation wavelength, ϕ is the quantum efficiency of free carrier generation per photon absorbed and $\Sigma \mu$ the sum of the mobilities of electrons and holes.⁷ Eq. S1 is used to evaluate the quantum efficiency or free carrier generation per photon absorbed, multiplied by the local mobility of free carriers. These quantities can often be correlated with molecular structure to provide insight into the mechanisms for free carrier generation and transport in polymer-fullerene composites as a function of the microstructure. The photoconductance decay after the end of the laser pulse is also a useful tool for the characterization of free carrier decay mechanisms by recombination and trapping. Active

layer blend samples for this work were prepared on quartz substrates according to an optimized literature procedure.⁹

VII. OPV Device Work

BHJ devices were initially fabricated using PCE11-PC₆₀BM blends to understand the necessities and difficulties of processing PCE11. PCE11 has narrow temperature window for solution casting. It forms a viscous gel below 80°C and hence leads to bad films upon spin coating. ITO coated glass substrates were cleaned sequentially in soap solution, DI water, acetone and IPA and dried under a N₂ gas stream. They were then put in a UV Ozone cleaner for 60 min. ZnO was coated from Diethyl Zinc precursor following previously reported procedures. A solution with polymer concentration of 9.4 mg/mL was used with a donor/acceptor blend ratio of 1:1.5 (by mass). The solution, micropipette tips and substrates were maintained at 110°C before spin coating. The solution was spun at 500 rpm for 60s and subsequently annealed at 85°C for 5 min. MoO₃ (20 nm) and Al electrode (120nm) were deposited in a thermal evaporator. These processing conditions resulted in an active layer thickness of 300 nm. The JV characteristics and EQE for the best device are shown below in the top of Figure S5. Device efficiencies near 9% were achieved in our hands (Table S1), approaching the record literature efficiencies reported near 11% PCE for this polymer.¹⁰

The optimal processing conditions for PCE11:PC₆₀BM were then used for devices with C₆₀(CF₃)₂ as acceptor. Initial devices with C₆₀(CF₃)₂ and PCE11 gave a dismal 0.26% PCE, highlighting the need to develop a unique set of processing conditions for this blend. Inspired by some recent device work with C₆₀(CF₃)₂ and thiophene based small molecule donors which found that vacuum-deposition of these thermally stable fullerenes was efficient, with optimal device efficiencies > 3% achieved with just a 20 nm thick active layer,¹¹ we attempted to use thinner active layers by spinning a polymer concentration of 5 mg/mL at a rate of 2200 rpm. The resulting absorber thickness was 50-60 nm and hence resulted in low photocurrents. However, device efficiencies improved to 1.6% (Table S1). We attempted to spin coat PCE11 and C₆₀(CF₃)₂ blends to even thinner active layers by further increasing spin speeds and/or reducing the concentration of polymer and fullerene stock solutions; however, these attempts generally resulted in poor film quality that did not further improve device efficiency. The results ultimately suggest that the thickness dependent morphology of C₆₀(CF₃)₂ blends will be an important parameter to optimize

in future work when new polymers with deeper energy levels are designed and tailored for application with $C_{60}(CF_3)_2$.

Table S1. Device Characteristics of Photovoltaic Solar Cells of PCE11

Fullerene	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)	R_s (Ω cm ²)	R_{sh} (Ω cm ²)
PC ₆₀ BM	0.78	17.3	66	8.9	6.1	567
C ₆₀ (CF ₃) ₂	0.49	6.40	50	1.6	16	302

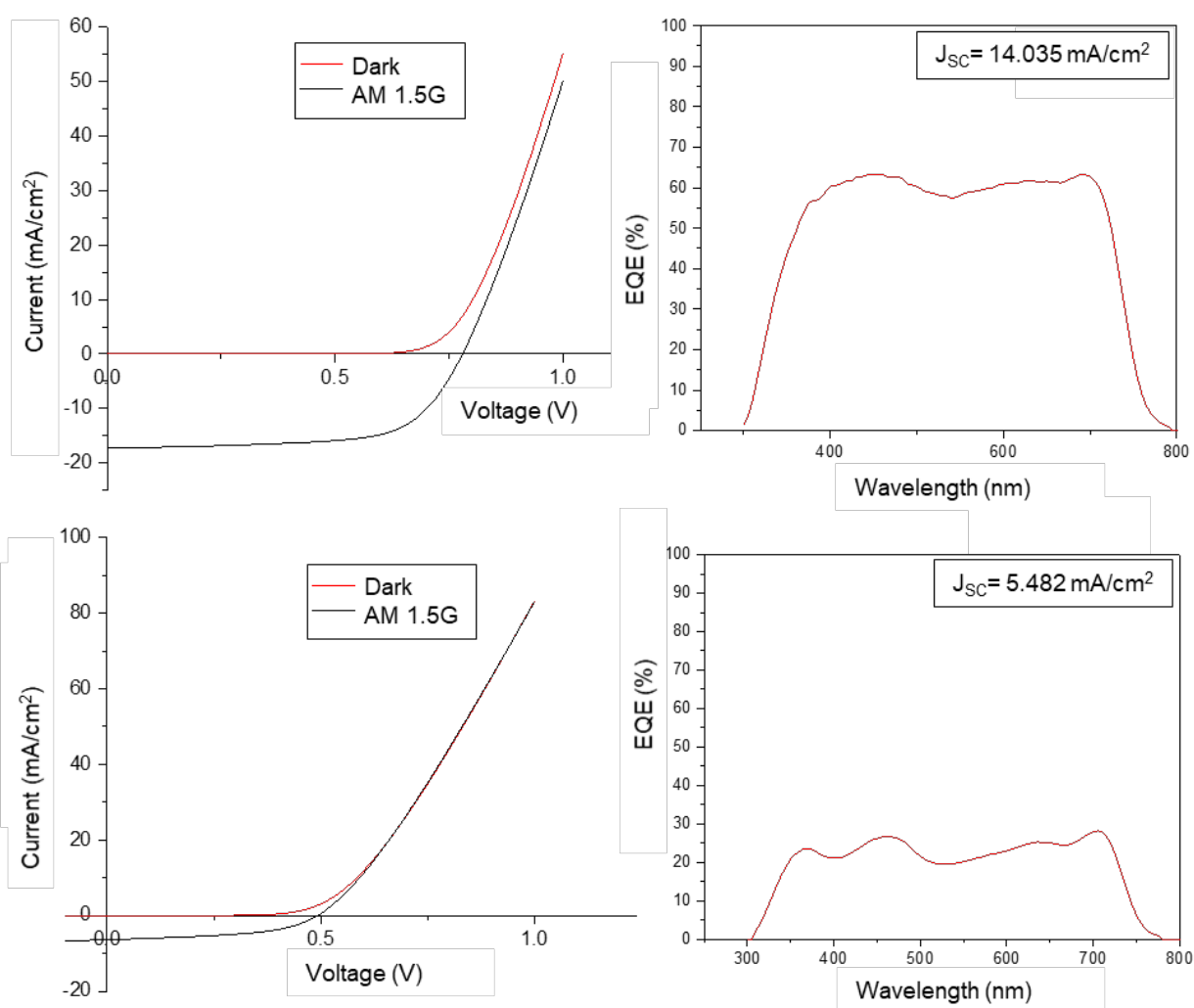


Figure S5. J - V plots (left) and EQE spectra (right) for the highest performing PCE11:PC₆₀BM device (8.9% PCE, top) and PCE11:C₆₀(CF₃)₂ device (1.6% PCE, bottom).

VIII. References

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