Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information for

Photobleaching Dynamics in Small Molecule *vs.* Polymer Organic Photovoltaic Blends with 1,7-Bis-Trifluoromethylfullerene

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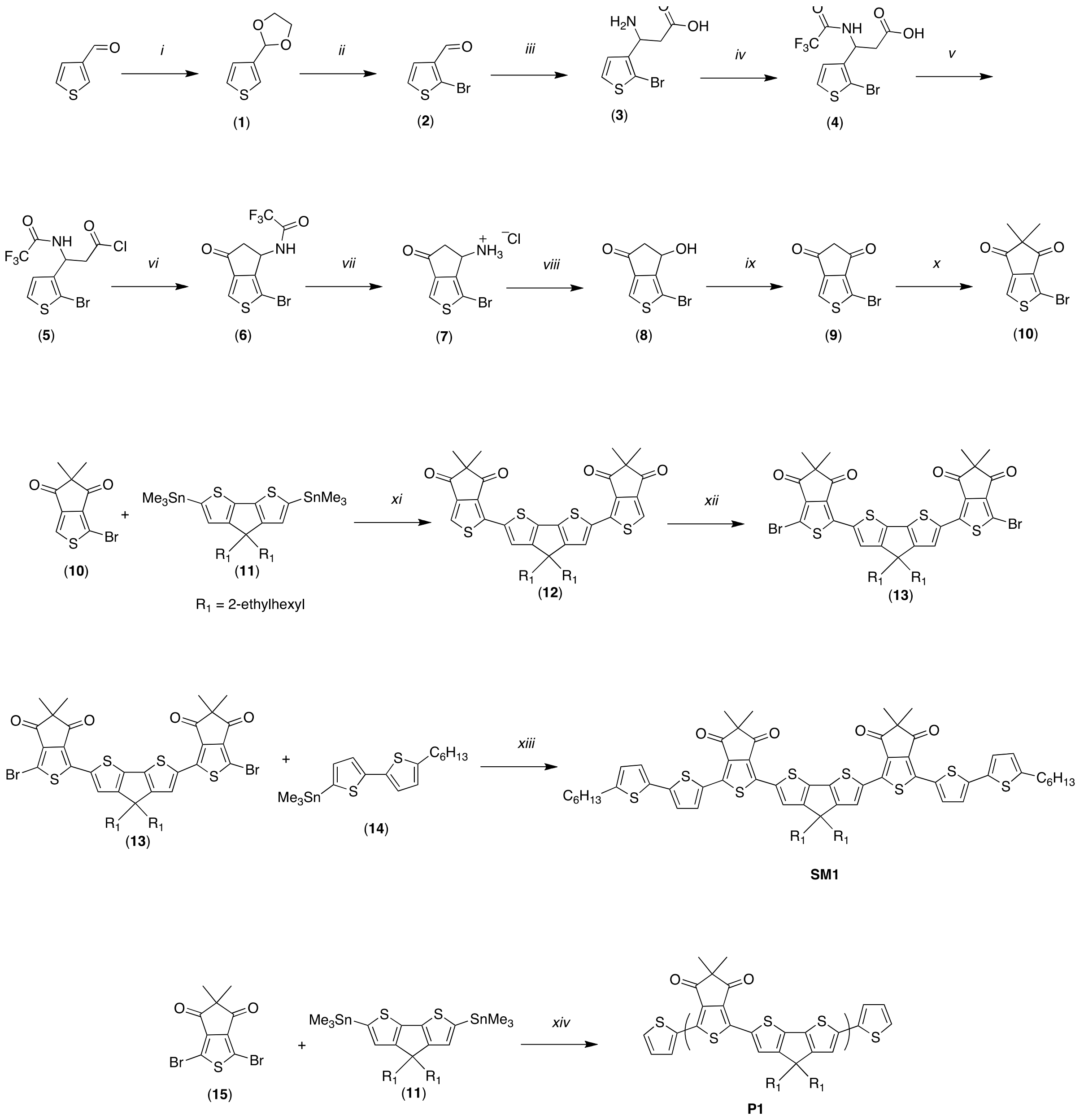
I. General and Synthetic Procedures



Scheme S1. Reaction conditions: *(i)* ethylene glycol, *p*-toluenesulfonic acid, dry benzene, Dean-Stark apparatus, reflux, 80 °C, 48 hours. *(ii)* 1. n-BuLi, dry THF, -78 °C to 0 °C over 45 min then cool to -78 °C; 2. CBr_4, -78 °C to RT, overnight; 3. THF, 5 M HCl (Aq.), RT, 1 hour. *(iii)* malonic acid, ammonium acetate, EtOH, reflux, 12 hours. *(iv)* trifluoroacetic anhydride, dry Et_2O, 0 °C to RT, 4 hours. *(v)* $SOCl_2$, dry 1,2-dichloroethane, DMF (cat.), 80 °C, 2 hours. *(vi)* $AlCl_3$, dry CH_2Cl_2, 45 °C, 4 hours. *(vii)* 5 M HCl (Aq.), reflux. *(viii)* 10% AcOH (aq., by vol.), $NaNO_2$, 0 °C to RT, overnight. *(ix)* CrO_3, H_2SO_4, trace H_2O, acetone. *(x)* 1. Bu_4NF, THF, 10 min; 2. MeI, RT, overnight. *(xi)* $Pd_2(dba)_2$, P(*o*-tol)$_3$, chlorobenzene, 80 °C, overnight. *(xii)* NBS, $CHCl_3$/AcOH, 75 °C, 4 hours. *(xiii)* $Pd_2(dba)_2$, P(*o*-tol)$_3$, chlorobenzene, 80 °C, overnight. *(xiv)* $Pd_2(dba)_2$, P(*o*-tol)$_3$, chlorobenzene, 100 °C, 48 hours.

General. All reagents employed in this study were obtained from commercial sources at the highest available purity and used without further purification, unless otherwise noted. All reactions were performed under dry N_2. Methylene chloride, toluene, and THF were purified by passing through alumina in an MBraun solvent purification system. Column chromatography was performed with Fluka Silica Gel 60 (220-440 mesh). Small molecules were characterized by ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz), where appropriate, on a Bruker Avance III HD NanoBay NMR Spectrometer. $PC_{70}BM$ was purchased from Nano-C, Inc., was >99% pure, and was used without further purification.

Compounds **11**,[1] **14**,[2] and **15**[3] were prepared according to literature procedures. $C_{60}(CF_3)_2$ was synthesized in the high-temperature reaction between C_{60} and CF_3I, as previously described,[4] and isolated[5], with 98+% purity, according to ^{19}F NMR, HPLC and ESI mass spectrometry.

Preparation of 1. A round bottom flask was charged with 3-thiophenecarboxaldehyde (1 eq., 138 mmol, 15.5 g), *p*-toluenesulfonic acid monohydrate (0.021 eq., 2.86 mmol, 0.544 g), ethylene glycol (2 eq., 276 mmol, 17.13 g, 15.39 mL) and dry benzene (150 mL). The round bottom reaction flask was then equipped with a Dean-Stark apparatus interfaced with a reflux condenser; the top of the reflux condenser was connected via Tygon tubing to a drying tube containing anhydrous calcium chloride. The reaction solution was stirred at 80 °C (note: in our hands reaction temperatures in excess of 80 °C resulted in little or no conversion) for 48 hrs. The reaction solution was then poured into 5% $NaHCO_3$ (aq.). The resulting solution was extracted with ethyl acetate (2X), the organic layers isolated and dried over $MgSO_4$, and solvent removed to afford **1** as a light brown oil in 90% yield. This material was of sufficient purity to be used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (m, 1H), 7.31 (m, 1H), 7.16 (m, 1H), 5.91 (s, 1H), 4.12-3.98 (m's, 4H).

Preparation of 2. A 250 mL Schlenk flask was charged with **1** (1 eq., 113.4 mmol, 17.707 g), sealed via septum, interfaced with s Schlenk manifold, and placed under inert atmosphere. Dry THF (~50 mL) was added via cannula and the resulting solution was cooled to -78 °C via dry ice acetone bath. Upon completion of cooling *n*-butyllithium (1.05 eq., 119 mmol, 47.61 mL of 2.5 M in hexanes; note: for safety reasons this reagent was added sequentially with 10 mL syringes to avoid handling of entire volume in a single large syringe) was added dropwise and the resulting solution was stirred for 30 min at -78 °C and then allowed to warm to ~ 0 °C over the course of 15-30 min before being re-cooled back to -78 °C. Following *n*-butyllithium addition and during the 45-60 min stirring of the solution in the 250 mL Schlenk reaction flask a separate 100 mL Schlenk flask was charged with CBr_4 (1.5 eq., 170.1 mmol, 56.41 g), sealed via septum, interfaced with a Schlenk manifold and placed under inert atmosphere. Dry THF (~50 mL) was added to the Schlenk flask containing the CBr_4 via cannula and stirred until all solids were dissolved. Upon completion of the allotted reaction time following *n*-butyllithium addition and re-cooling of the reaction solution within the 250 mL Schlenk flask the CBr_4 solution in THF was transferred slowly into the 250 mL Schlenk flask via cannula. The resulting solution was stirred overnight at room temperature before being poured into 5% $NaHCO_3$ (aq.). The resulting solution was extracted with CH_2Cl_2 (2X), the organic layers isolated and dried over $MgSO_4$, and solvent removed to afford the intermediate compound in with aldehyde group still protect in the form of the cyclic acetal. NMR of crude acetal intermediate before deprotection: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (dd, J_1 = 5.68 Hz, J_2 = 0.4 Hz, 1H), 7.01 (d, J = 5.68 Hz, 1H), 5.85 (s, 1H), 4.16-3.95 (m's, 4H)

A 500 mL round bottom flask was charged with the crude acetal intermediate, THF (200 mL), and 5 M HCl (100 mL) and the resulting solution was stirred for 1 hour. The solution was then extracted with CH_2Cl_2 (2X), the organic layers isolated and dried over $MgSO_4$, and solvent removed to afford crude **2**. Purification via silica gel chromatography using 1:4 hexanes: CH_2Cl_2 eluent afforded pure **2** in 51% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.92 (s, 1H), 7.34 (d, J = 5.76 Hz, 1H), 7.28 (dd, J_1 = 5.76 Hz, J_2 = 0.9 Hz, 1H).

Preparation of 3. A round bottom flask was charged with **2** (1 eq., 51.93 mmol, 9.92 g), malonic acid (1 eq., 51.93 mmol, 5.40 g), ammonium acetate (2.5 eq., 130 mmol, 10.01 g), and ethanol (150 mL). The flask was interfaced with a reflux condenser and the solution was heated at reflux with stirring for 12 hours. The solution was then allowed to cool to room temperature. The reaction flask was then placed in the refrigerator and the reaction solution was further cooled to ~5 °C. The target product, **3**, precipitates out of solution during the reaction and upon cooling and was collected via filtration, washed with ethanol, and dried under vacuum affording **16** in 21% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.61 (d, J = 5.72 Hz, 1H), 7.19 (d, J = 5.76 Hz, 1H), 4.25 (q, 1H), 2.43-2.29 (m's, 2H).

Preparation of 4. A Schlenk flask was charged with **3** (1 eq., 10.96 mmol, 2.74 g), sealed via septum, interfaced with a Schlenk manifold, and placed under inert atmosphere. Dry diethyl ether (200 mL) was added to the flask via cannula and the solution containing the undissolved **3** was cooled to 0 °C via ice bath. Once the solution had cooled trifluoroacetic anhydride (2 eq., 21.91 mmol, 4.602 g, 3.05 mL) was added via syringe. The solution was then allowed to warm to room temperature with stirring and allowed to react for 4 hours. As the reaction proceeds the solution becomes homogeneous. The reaction solution was then poured into ice water and stirred under a purging stream of nitrogen until all diethyl ether has evaporated and the product has precipitated. Collection of the precipitate, washing with water, and drying under vacuum afforded **4** in 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (broad doublet, 1H), 7.29 (d, $J = 5.6$ Hz, 1H), 6.93 (d, $J = 5.7$ Hz, 1H), 5.51 (m, 1H), 3.12-2.95 (m's, 2H). ^{19}F NMR (400 MHz, $CDCl_3$): δ -75.88 (s, 3F).

Preparation of 6 (through intermediate 5). A two-neck Schlenk flask was charged with **4** (1 eq., 10.78 mmol, 3.73 g), interfaced with a reflux condenser (one neck sealed via septum), interfaced with a Schlenk manifold, and placed under inert atmosphere. Dry 1,2-dichloroethane (150 mL) was added via cannula, thionyl chloride (1.3 eq., 14.01 mmol, 1.67 g, 1.022 mL) and a catalytic amount of dimethylformamide (1-2 drops) were added via syringe and the solution was stirred at 45 °C for 1 hour. The reaction temperature was then increased and the solution stirred at 80 °C for 1.5 hrs. The reaction solution was then cooled to 40 °C and the solvent was removed via nitrogen purge to afford **5**; which was immediately used without being removed from the reaction apparatus. Upon removal of the 1,2-dichloroethane solvent dry CH_2Cl_2 (275 mL; note: dilute conditions favor the desired intramolecular interaction) was added to the reaction flask containing **5** and stirred until the solution was homogeneous. The septum was removed, with the apparatus under positive dynamic nitrogen pressure, long enough to add $AlCl_3$ (3 eq., 32.43 mmol, 4.32 g) before being replaced. The reaction solution was stirred at 40 °C for 4 hours before being poured into ice water. The ice water solution was stirred until all ice melted. The solution was then poured into a separation funnel and extracted with diethyl ether (3X), the organic layers were combined, washed with brine, dried over $MgSO_4$, and solvent was removed to afford crude **6** as a brown solid. Purification via silica gel chromatography using 1:1 hexanes:ethyl acetate afforded **6** and a small amount of side product (that elutes from column with **6**) in 48% yield. ^{1}H NMR (400 MHz,

$CDCl_3$): δ 7.8 (s, 1H), 7.1 (broad doublet, 1H), 5.5 (m, 1H), 5.5 (m, 1H), 3.58-3.51 (dd, 1H), 2.95-2.89 (dd, 1H). ^{19}F NMR (400 MHz, $CDCl_3$): δ -75.69 (s, 3F).

Preparation of 7. A round bottom flask was charged with **6** (1 eq., 4.66 mmol, 1.53 g) and 45 mL of 5 M HCl (aq.) and interfaced with a reflux condenser. The solution was heated at reflux with stirring for 3 hours (when reaction is complete the solution is homogeneous). The solution was then cooled to 50 °C and the reflux condenser was replaced with a septum that pierced with two rigid pieces of Teflon tubing. One of the Teflon tubes was interfaced with the Schlenk manifold to serve as the nitrogen purge 'in' port and the other Teflon tube was interfaced with a length of Tygon tubing that was run into an Erlenmeyer flask containing 10 M KOH (aq.). The tubing run into the Erlenmeyer flask was secured so that the end of the tubing remained submerged in the KOH solution. The aq. HCl solution in the reaction flask was slowly removed via nitrogen purge with the purge exhaust being bubbled though the KOH solution to quench gas phase HCl. Upon completion of drying **7** was afforded in 92% yield. ^1H NMR (400 MHz, DMSO-d_6): δ 8.83 (broad singlet, 3H), 8.28 (s, 1H), 4.77 (dd, 1H), 3.51-3.44 (dd, 1H), 3.03-2.97 (dd, 1H).

Preparation of 8. A round bottom flask was charged with **7** (1 eq., 3.06 mmol, 0.822 g) and 40 mL of 10% acetic acid (aq.) and the solution cooled to 0 °C. Once the solution had cooled $NaNO_2$ (3 eq., 8.07 mmol, 0.557 g; dissolved in 1 mL water and added as solution) was added slowly over 15 minutes (safety note: this reaction evolves N_2 and should be done in a reaction vessel ~10X the volume of the reaction solution and should always be vented to avoid buildup of pressure). The solution was stirred overnight at room temperature before being diluted with water (25 mL). The diluted solution was extracted with CH_2Cl_2 (2X), the organic layers isolated and dried over $MgSO_4$, and solvent removed to afford **8** in 91% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (s, 1H), 5.3 (dd, 1H), 3.42-3.35 (dd, 1H), 2.97-2.91 (dd, 1H).

Preparation of 9. A round bottom flask was charged with **8** (1 eq., 1.95 mmol, 0.454 g) and 7 mL acetone and the solution was cooled to 0 °C. Once solution was cooled an aq. solution composed of 1 mL water, CrO_3 (1.35 eq., 2.273 mmol, 0.2273 g), and H_2SO_4 (1.2 eq. 0.1 mL of 18 M) was added to the reaction flask. The resulting solution was stirred at for 1-2 hrs while being allowed to slowly warm to room temperature. The reaction solution was then diluted with water, extracted with CH_2Cl_2 (2X), the organic layers isolated and dried over $MgSO_4$, and solvent removed to afford **9** in 72% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1H), 3.52 (s, 2H).

Preparation of 10. A 25 mL round bottom flask was charged with **9** (1 eq., 0.733 mmol, 0.1693 g) and 15 mL of THF and stirred until all solids were dissolved. At which time Bu_4NF (2.2 eq., 1.39 mmol, 1.39 mL of 1 M solution in THF) was added and the resulting solution was allowed to stir at room temperature for 5-10 minutes. After stirring for the allotted time methyl iodide (4 eq., 2.532 mmol, 0.359 g, 0.158 mL) was added to the reaction solution. The resulting solution was stirred over night at room temperature. The reaction solution was poured into water, extracted with CH_2Cl_2 (2X), the organic layer isolated and dried over $MgSO_4$, and solvent removed to afford crude **10**. Purification via silica gel chromatography using 3:1 hexanes: ethyl acetate eluent afforded pure **10** as a yellow-orange solid in 60% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 1H), 1.31 (s, 6H).

Preparation of 12. A glass pressure flask was charged with **10** (2 eq., 0.206 mmol, 0.0531 g), **11** (1 eq., 0.103 mmol, 0.07514 g), tris(dibenzylidineacetone)dipalladium(0)-chloroform adduct (0.15 eq., 1.54×10^{-5} mol, 16 mg), tri-*ortho*-tolylphosphine (0.6 eq., 6.18×10^{-5} mol, 19 mg), and 5 mL of dry chlorobenzene. The resulting solution was bubbled with nitrogen to remove oxygen and purge the headspace. Once sufficiently purged the Teflon cap was quickly installed to ensure inert atmosphere within the reaction vessel. The solution was heated overnight at 80 °C with stirring. The reaction solution was allowed to cool, poured into a separation funnel containing water, was extracted with CH_2Cl_2 (3X), the organic layer isolated and dried over $MgSO_4$, and solvent removed to afford crude **12**. Purification via silica gel chromatography using 1:4 hexanes: CH_2Cl_2 eluent afforded pure **12** in 30% yield as a bright red solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.13-8.05 (m, 2H), 7.71 (s, 2H), 2.0 (m, 4H), 1.36 (d, 12H), 1.01-0.93 (m's, 18H), 0.68 (t, 6H), 0.63 (t, 6H).

Preparation of 13. A glass pressure flask was charged with **12** (1 eq., 1.97×10^{-5} mol, 15.0 mg) and 5 mL of $CHCl_3$:acetic acid (1:1). Once all solid was dissolved *N*-bromosuccinimide (3 eq., 5.91×10^{-5} mol, 10.5 mg) was added and the reaction flask was sealed. The reaction solution was heated with stirring at 70 °C for 24 hours. The reaction solution was allowed to cool, was poured into a separation funnel containing water, was extracted with CH_2Cl_2 (3X), the organic layer isolated and dried over $MgSO_4$, and solvent removed to afford crude **13**. Purification via silica gel chromatography using 1:4 hexanes: CH_2Cl_2 eluent afforded pure **13** in 87% yield in the form of a bright red solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.10-03 (m, 2H), 1.97 (m, 4H), 1.35 (d, 12H), 1.01-0.89 (m's, 18H), 0.69 (t, 6H), 0.62 (t, 6H).

Preparation of SM1. A glass pressure flask was charged with **13** (1 eq., 9.27×10^{-5} mol, 85 mg), **14** (2 eq., 1.85×10^{-4} mol, 76.6 mg), tris(dibenzylidineacetone)dipalladium(0)-chloroform adduct (0.25 eq., 2.32×10^{-5} mol, 24 mg), tri-*ortho*-tolylphosphine (1 eq., 9.27×10^{-5} mol, 28.2 mg), and 5 mL of dry chlorobenzene. The resulting solution was bubbled with nitrogen to remove oxygen and purge the headspace. Once sufficiently purged the Teflon cap was quickly installed to ensure inert atmosphere within the reaction vessel. The solution was heated overnight at 80 °C with stirring. The reaction solution was allowed to cool, poured into a separation funnel containing water, was extracted with CH_2Cl_2 (3X), the organic layer isolated and dried over $MgSO_4$, and solvent removed to afford crude **SM1**. Purification via silica gel chromatography using 1:4 hexanes:CH_2Cl_2 eluent afforded **SM1** with a small aromatic impurity that co-eluted with the product. The impurity was removed by stirring the solid in a slurry of acetone to yield pure **SM1** in 53% yield as very dark blue-black solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.17-8.01 (m, 2H), 8.03 (d, $J = 3.6$ Hz, 2H), 7.11 (d, $J = 3.6$ Hz, 4H), 6.73 (d, $J = 3.6$ Hz, 2H), 2.82 (t, $J = 7.6$ Hz, 4H), 2.00 (m, 4H), 1.70 (quintet, 4H), 1.39-1.27 (m's, 24H), 1.08-0.91 (m's, 24H), 0.72 (t, $J = 6.8$ Hz, 6H), 0.65 (t, $J = 7.6$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 196.9, 161.4, 147.7, 142.2, 141.1, 141.0, 138.5, 138.2, 137.9, 136.7, 135.4, 134.3, 131.5, 131.4, 125.7, 125.4, 125.2, 124.6, 60.1, 55.0, 43.5, 36.0, 34.7, 32.1, 32.0, 30.8, 29.3, 29.0, 20.0, 28.1, 23.4, 23.1, 21.9, 21.8, 21.7, 14.6, 11.2. HRMS m/z: $[M + H]^+$ calcd. for $C_{71}H_{82}O_4S_8$ 1254.3979; found 1254.3950.

Preparation of P1. A glass pressure flask was charged with **11** (1 eq., 0.1 mmol, 72.8 mg), **15** (1 eq., 0.1 mmol, 33.8 mg), tris(dibenzylidineacetone)dipalladium(0)-chloroform adduct (2.1 mg), tri-*ortho*-tolylphosphine (3.7 mg), and 6 mL of dry chlorobenzene. The resulting solution was bubbled with nitrogen to remove oxygen and purge the headspace. Once sufficiently purged the Teflon cap was quickly installed to ensure inert atmosphere within the reaction vessel. The solution was heated for 48 hours at 110 °C with stirring. The polymer was precipitated into methanol, re-dissolved in 2 mL of chloroform along with a 20 mg of a palladium scavenger (diazenecarbothiamide,N,N- diethyl-2-phenyl). This solution was then purged with nitrogen for 30 minutes and stirred at 60 °C for 3 h. The polymer was again precipitated in methanol, filtered, and dried under vacuum overnight.

The polymer samples were then 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 performed on a PL-Gel 300 × 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. The polymer M_n was determined to be ~10 kg/mol, with $M_w/M_n = 1.8$.

Film Preparation. Stock solutions of SM1, P1, $PC_{70}BM$, and $C_{60}(CF_3)_2$ were prepared in chlorobenzene at concentrations of 24 mg/mL. Neat films were cast directly from SM1 and P1 stock solutions. Blend forming solutions were prepared by combining equal volumes of donor and acceptor solution to achieve 50:50 blend ratios, 12 mg/mL of each component. Films were spin cast inside a glove box under inert atmosphere onto 1 cm x 2cm quartz substrates from ~70 μL of 90 °C solution using a spin speed of 800 rpm, a ramp rate of 800 rpm/sec, and a spin time of 60 sec.

II. NMR Spectra

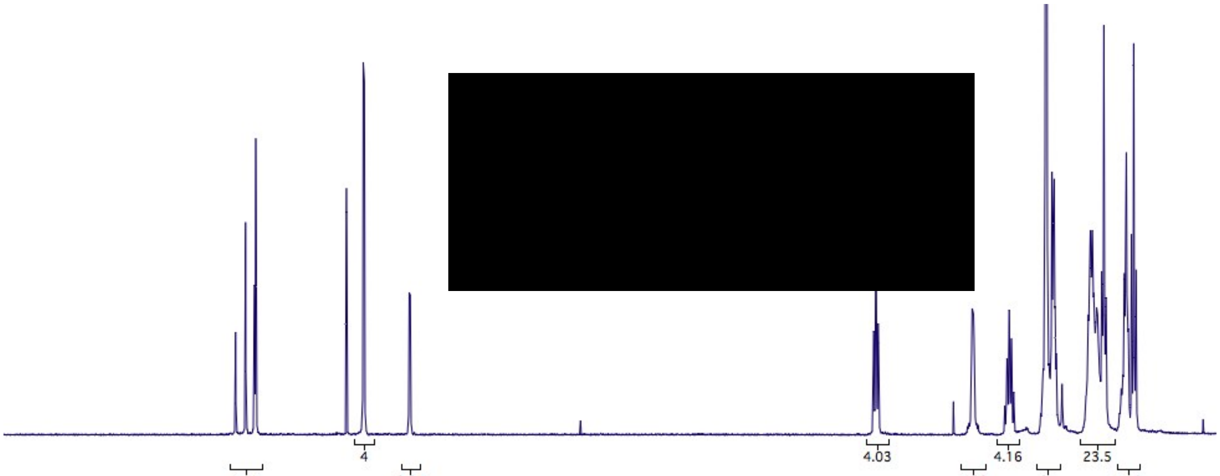

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Figure S1. ^{1}H NMR spectrum of **SM1** in CDCl$_3$.

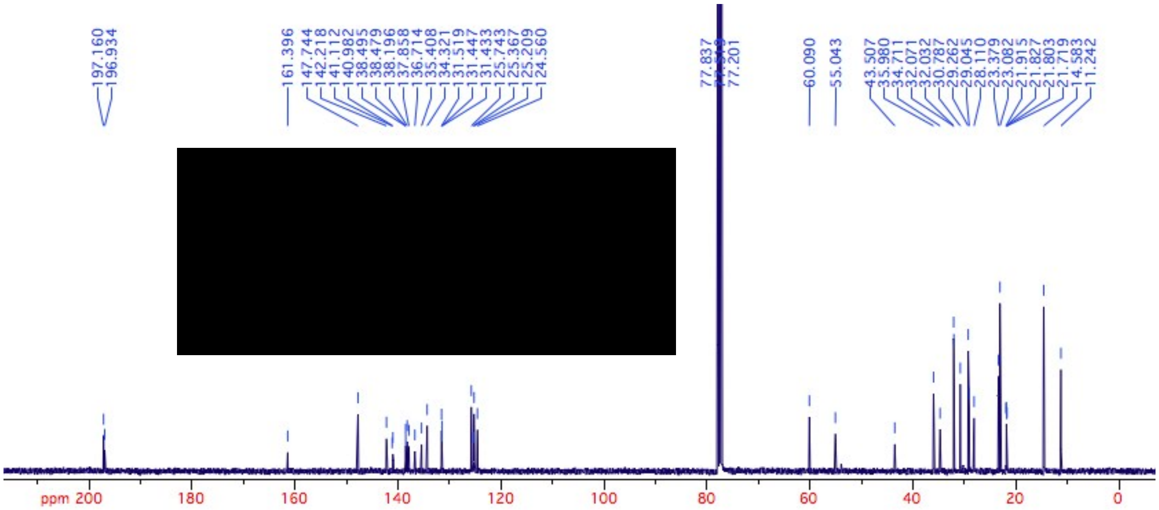
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Figure S2. ^{13}C NMR spectrum of **SM1** in CDCl$_3$.

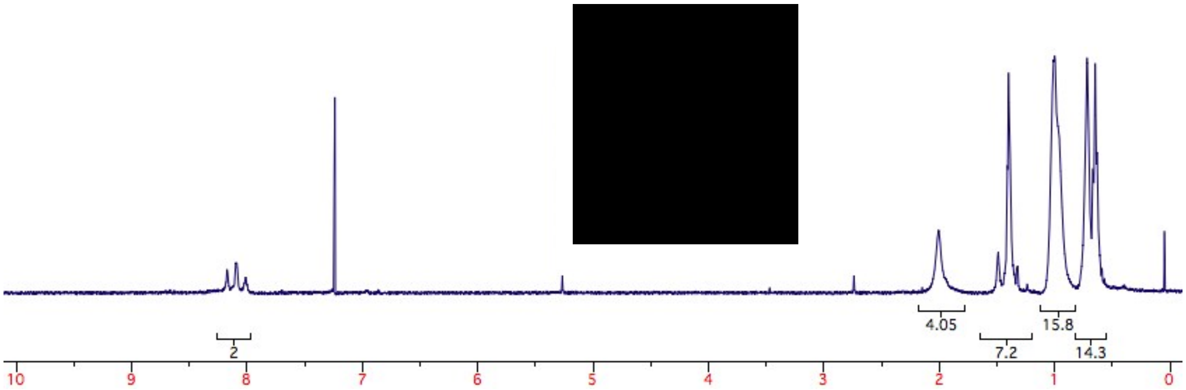
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Figure S3. ^{1}H NMR spectrum of **SM1** in CDCl$_3$.

III. Laser Desorption Ionization Mass Spectrometry

Data for laser desorption ionization mass spectrometry analysis were collected on a 7T Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS, SolariX XR, Bruker, Bremen, Germany). The mass resolving power (m/Δm 50%) was at least 100,000 at m/z 400 during calibration. The sample dissolved in organic solvent (DCM) at approximately 0.1 wt% concentration was spotted at 2 uL on a ground stainless steel MTP 384 MALDI target plate (#8280784, Bruker). Laser ionization was initiated with a Nd:YAG laster, 355 nm, set at between 12 and 60% relative laser power and < 50 um beam diameter. Because these products are naturally light absorbing, no matrix was needed to obtain a highly sensitive signal. Mass spectra were collected in positive ion mode and 50 time domain transient scans were co-added for each sample prior to fast Fourier transformation and frequency to m/z conversion. The mass spectrometer was internally calibrated to achieve sub-part-per-million mass measurement accuracy on NaTFA in positive ion mode (-0.086 ppm at m/z 702.863262 m/z; 0.138 ppm at m/z 1246.762494) and tuned for m/z 100-1500 detection, at 0.7 ms ion time of flight in transfer optics.

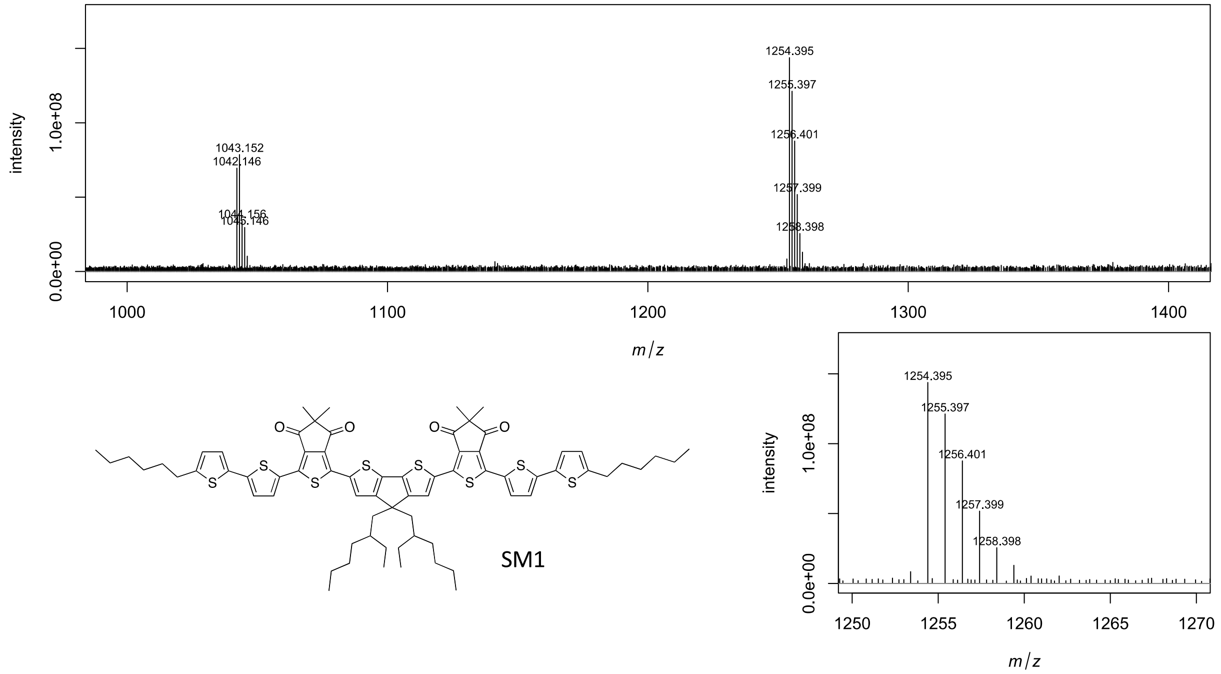


Figure S4. Laser Desorption Ionization mass spectrometry analysis of SM1.

IV. Photobleaching

Samples were exposed to a four bulb DC halogen lamp (Sylvania 58321) array outputting 120 mW/cm^2 at the surface of the samples. Radiative heating from the lamps kept the samples at a temperature of 65 °C which was spot-checked throughout the experiments using a contact thermocouple. Fraction of light Absorbed (FA) spectra were calculated using Eq. S1 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.

$$FA = 1 - FT - FR \tag{S1}$$

A first surface aluminum mirror was used as the reflectance reference. Accumulated photon dose was calculated using Eq. S2 where $I_{L_{photon}}$ is the spectral photon flux of the degradation lamp array.

$$Accumulated\ Photon\ Dose\ (t_i) = \int_{t=t_0}^{t=t_i} \int_{\lambda_1}^{\lambda_2} FA(\lambda, t) \cdot I_{L_{photon}}(\lambda)\, d\lambda\, dt \tag{S2}$$

Spectral irradiance data of the photobleaching light source was gathered using a six-inch integrating sphere (Optronic Labs OL IS-670) fitted with silicon (Soma S-2441C) and InGaAs (Spectral evolution LF1250) diode arrays. The spectral irradiance data was then converted to photon flux using Eq. S3.

$$I_{Lphoton}(\lambda) = \frac{Spectral\ irradiance(\lambda) * \lambda}{hc} \tag{S3}$$

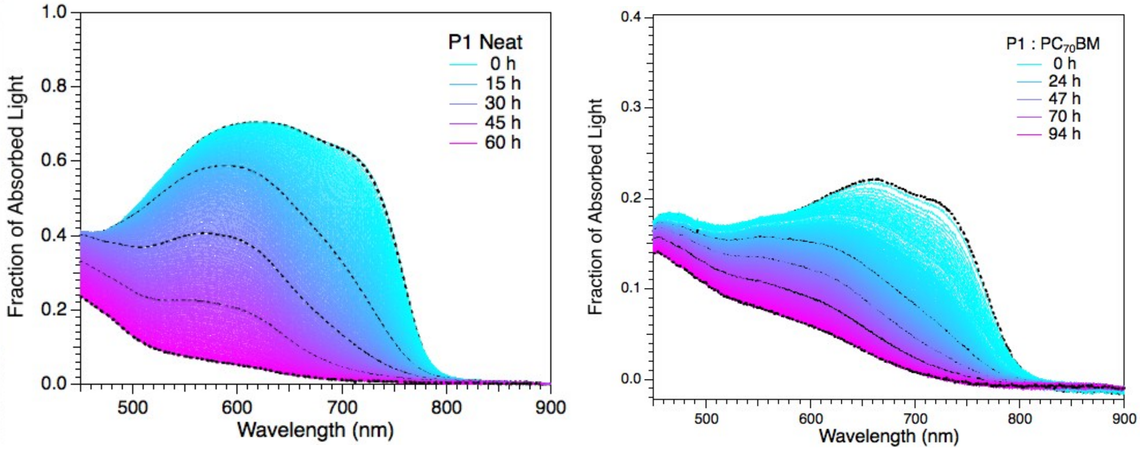


Figure S5. Approximately 360 spectra of neat P1 (left) and 560 spectra of P1:PC$_{70}$BM (right) were auto-recorded every 10 minutes during continuous illumination at 120 mW/cm^2 in air. Dashed lines correspond to spectra taken at 0, 15, 30, 45, and 60 h for neat P1, and 0, 24, 47, 70, and 94 h for P1:PC$_{70}$BM.

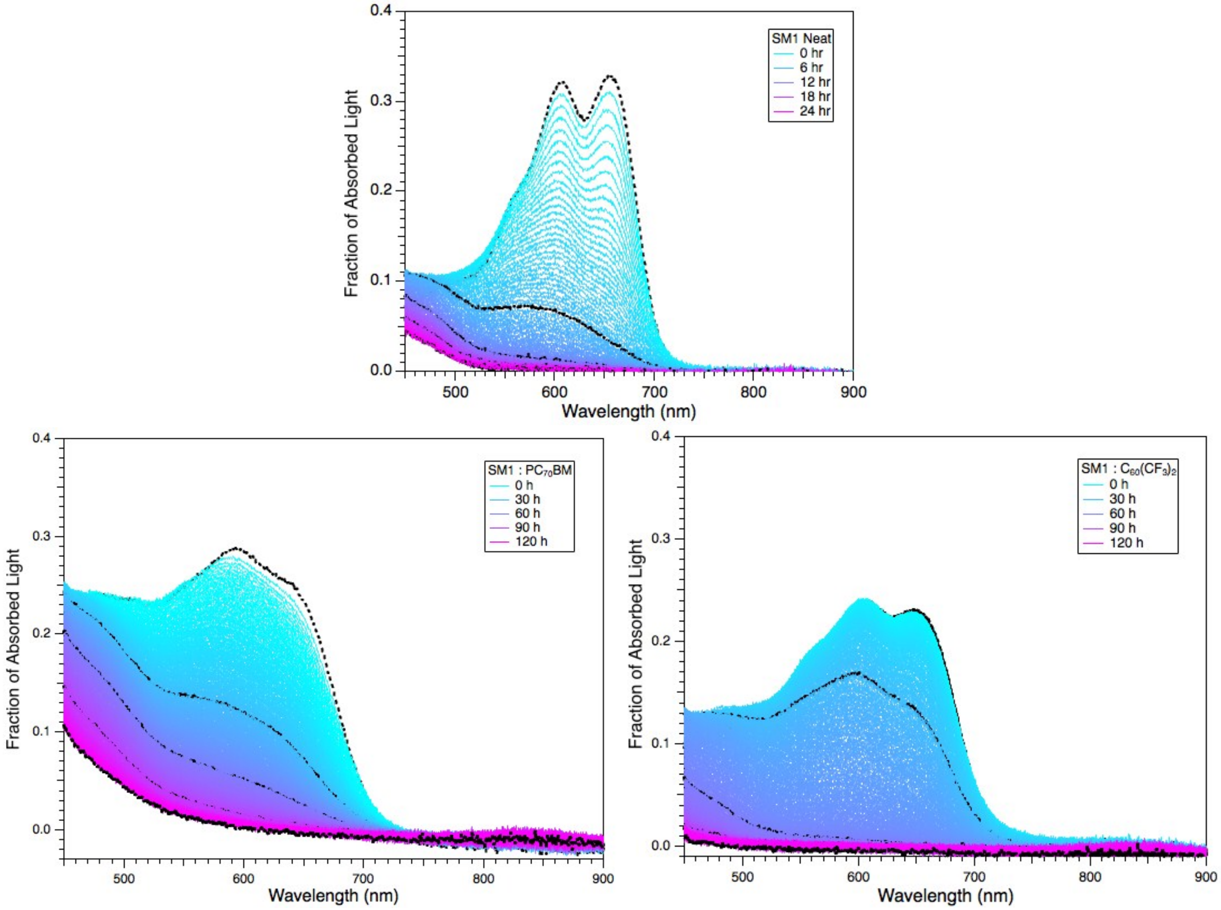


Figure S6. Approximately 140 spectra of neat SM1 (top) and 720 spectra of SM1:PC$_{70}$BM (bottom left) and SM1:C$_{60}$(CF$_3$)$_2$ (bottom right) were auto-recorded every 10 minutes over 24 hours and 120 hours, respectively, during continuous illumination at 120 mW/cm^2 in air. Dashed lines correspond to spectra taken at times in the respective legends.

V. Time-Resolved Photoluminescence

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 excitation wavelength used was 600 nm and the pulse energy was approximately 1 nJ. 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.

A representative contour plot of the TRPL data is illustrated in Figure S7 for the neat SM1 film. From this data, PL decays (like those in Figure 5 of the main text and Figure S8 below) were plotted by first normalizing for the number of scans and the fraction of absorbed light at the excitation wavelength (600 nm) in each sample and then by integrating the intensity (counts) between 675 and 805 nm, where the signal was most intense. Quenching efficiencies among the different samples were calculated by integrating the latter data between 0.2 and 0.3 ns. TRPL was measured at 3 points on each sample, and each quenching efficiency reported in the main text is an average of these 3 measurements.

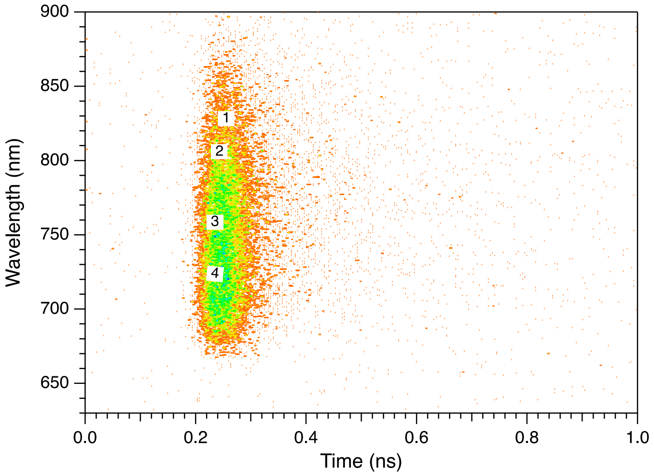


Figure S7. Representative contour plot of TRPL data for neat SM1, excited at 600 nm. The green, yellow, orange and red points are associated with 4, 3, 2, and 1 PL counts for a given coordinate.

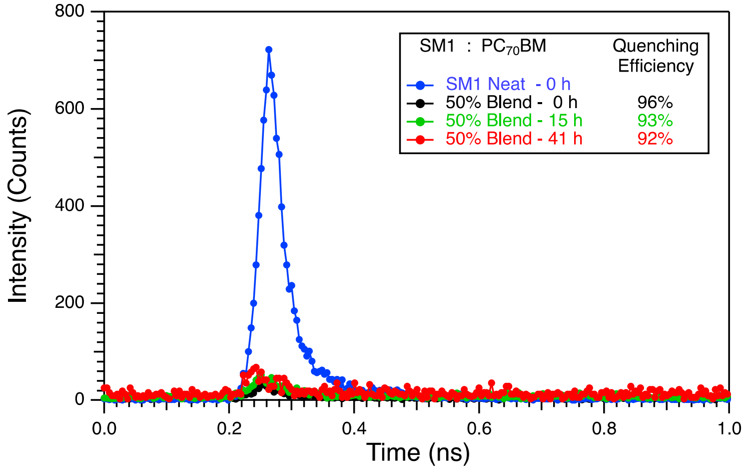


Figure S8. Photoluminescence decays for un-aged neat SM1 film (blue) as well as 1:1 blends of SM1: $PC_{70}BM$ aged for 0, 15, and 41 h (black, green, and red, respectively) in air at ~1.2 suns.

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 abrorption 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 as[7]

$$\Delta G = \beta q_e F_A I_0 (\phi \cdot \Sigma\mu) \qquad \textbf{(S4)}$$

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. S4 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 under identical conditions as used for the photobleaching studies.

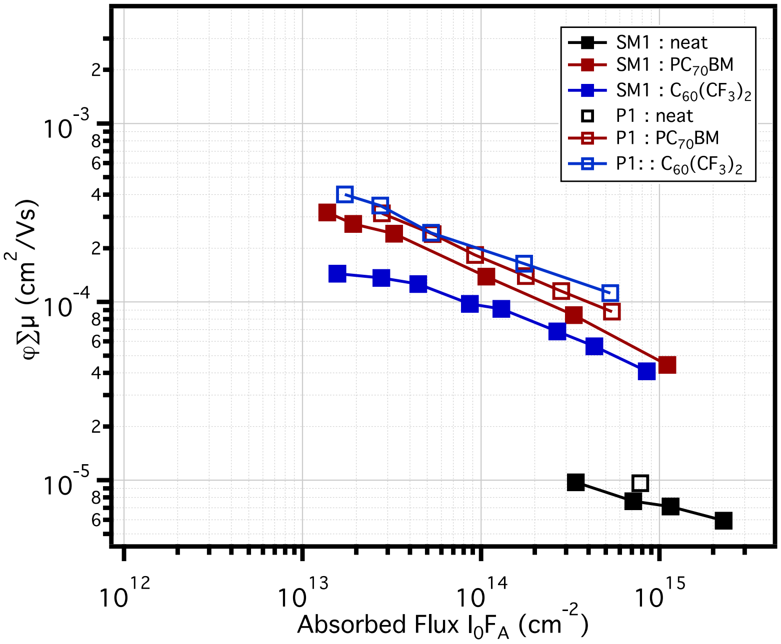
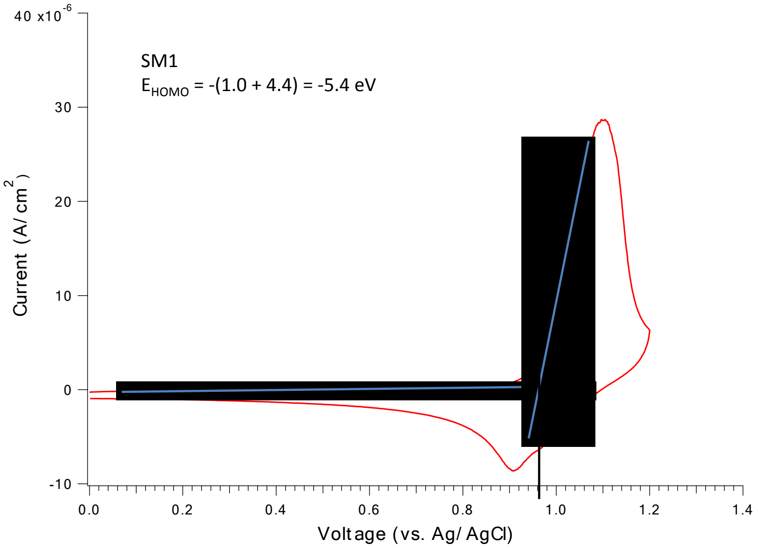


Figure S9. The product of charge carrier yield (ϕ) and sum of hole and electron mobilities ($\Sigma\mu$) is illustrated over a range of intensities spanning two orders of magnitude at a laser excitation wavelength of 620 nm for P1 samples (open squares) and 640 nm for SM1 samples (closed squares).

VII. Cyclic Voltammograms.

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^{-1} 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.[9] Polymer films were drop cast onto a platinum disk working electrode from a 1 mg/mL chloroform solution and dried under a stream of nitrogen prior to measurement in a 0.1 M Bu_4NBF_4 acetonitrile solution.



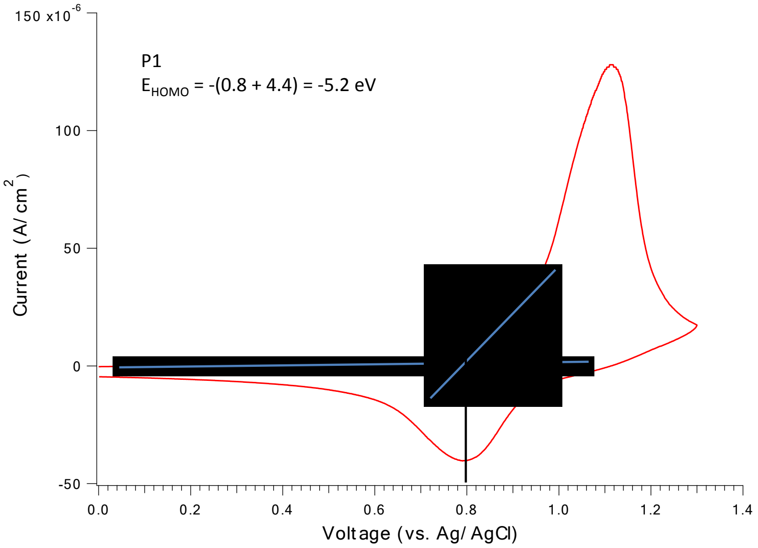


Figure S10. Cyclic voltammograms of **SM1** (top) and **P1** (bottom).

VIII. XRD Data

X-ray diffraction measurements were performed with a Rigaku D/MAX-2500H goniometer (185 mm Bragg−Brentano geometry) equipped with a rotating anode X-ray generator (40 kV, 200 mA) using Cu Kα radiation with a wavelength of 0.154 nm anddetected with a scintillation counter filtered with a single-bounce graphite monochromator. The scan rate was 1° min^{-1} in the 2θ range of 2° to 10° using 0.02° steps.

Analyses conducted on small molecule films prepared on quartz substrates immediately after spin casting and prior to photobleaching suggested the films were amorphous. Similarly, analyses conducted on the samples that were photobleached for 15 and 41 h revealed no crystalline peaks. However, if samples were prepared and stored for 2 months in the dark in an inert environment of nitrogen gas, distinct peaks in the XRD spectra of both the neat and blend samples began to emerge (Figure S10). The results provide some evidence that the degree of order in SM1 films is prone to changing with time.

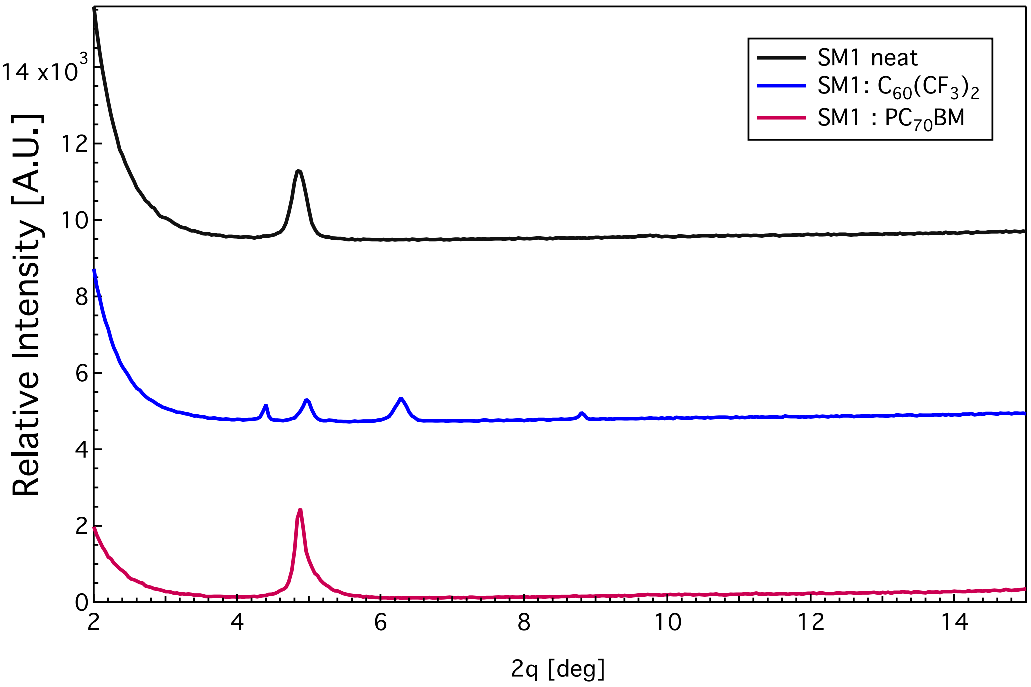


Figure S11. X-ray diffraction patterns of neat films of SM1 (black) and 1:1 blends by weight of SM1 with $C_{60}(CF_3)_2$ (blue) and $PC_{70}BM$ (red), all aged for 2 months in the dark.

IX. References

1. C. Dou, Z. Ding, Z. Zhang, Z. Xie, J. Liu and L. Wang, *Angew. Chem., Int. Ed.*, 2015, 54, 3648-3652.
2. S. D. Oosterhout, V. Savikhin, J. Zhang, Y. Zhang, M. A. Burgers, S. R. Marder, G. C. Bazan and M. F. Toney, *Chem. Mater.*, 2017, 29, 3062-3069.
3. M. Endou, Y. Ie and Y. Aso, *Chem. Commun.*, 2012, 48, 540-542.
4. I. V. Kuvychko, J. B. Whitaker, B. W. Larson, R. S. Raguindin, K. J. Suhr, S. H. Strauss and O. V. Boltalina, *J. Fluorine Chem.*, 2011, 132, 679-685.
5. W. A. Braunecker, S. D. Oosterhout, Z. R. Owczarczyk, R. E. Larsen, B. W. Larson, D. S. Ginley, O. V. Boltalina, S. H. Strauss, N. Kopidakis and D. C. Olson, *Macromolecules*, 2013, 46, 3367-3375.
6. J. E. Kroeze, T. J. Savenije, M. J. W. Vermeulen and J. M. Warman, *J. Phys. Chem. B*, 2003, 107, 7696-7705.
7. A. J. Ferguson, N. Kopidakis, S. E. Shaheen and G. Rumbles, *J. Phys. Chem. C* 2011, 115, 23134–23148.
8. S. Dayal, N. Kopidakis and G. Rumbles, *Faraday Discuss*, 2012, 155, 323-337.
9. J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bassler, M. Porsch and J. Daub, *Adv. Mater.*, 1995, 7, 551-554.