SUPPORTING INFORMATION (SI)

Fluorine Tuning of Morphology, Energy Loss, and Carrier Dynamics in Perylenediimide Polymer Solar Cells

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1. Material Synthesis

S1 and S2: Molecules S1 and S2 were synthesized according to reported literature procedures.^{1, 2} Pd(PPh₃)₄ was purchased from Strem Chemicals while all other reagents were purchased from Sigma-Aldrich. The photocyclization reaction was performed using a Cooper Lighting model number SQS505QD 500 W halogen lamp. Column chromatography was performed using silica gel from Sorbent Technologies. All solvents were spectrophotometric grade unless otherwise noted. NMR spectra were obtained on a Bruker Avance III (FT, ¹H, 600 MHz) spectrometer or Agilent DD MR-400 (FT, 400 MHz, ¹H; 101 MHz, ¹³C, 376 MHz, ¹⁹F) or Bruker Avance III (FT, DCH Cryoprobe, 500 MHz, ¹H; 125 MHz, ¹³C) spectrometers at ambient temperature unless otherwise noted. Chemical shifts for ¹H and ¹³C spectra are referenced to residual protio-solvent signals ($\delta^{1}H = 7.26$ for CDCl₃, 5.32 for CD₂Cl₂, 6.00 for C₂D₂Cl₄; $\delta^{13}C = 77.16$ for CDCl₃, 53.84 for CD₂Cl₂) and chemical shifts are reported in ppm.

Scheme S1. Synthesis of molecules **1** and **Ph(PDI)**₃. (a) Pd(PPh₃)₄, 2M Na₂CO₃, THF; (b) (1) I₂, CH₂Cl₂, *hv*, O₂ (2) I₂, Toluene, *hv*, O₂.



1: Compound 1 was synthesized following a literature procedure. Spectral data were consistent with previously reported data.³

Ph(PDI)₃: Compound 1 (200 mg, 0.092 mmol) was dissolved in CH_2Cl_2 (200 mL) along with I_2 (5 mg, 0.018 mmol). The deep red solution was bubbled with air and irradiated with a 500 W halogen lamp for 6 h, periodically refilling with CH_2Cl_2 . Then, the remaining CH_2Cl_2 was evaporated and the crude was re-dissolved in toluene (200 mL) with an additional 5 mg I_2 and irradiated while bubbling with air for an additional 24 h to result in an orange-red solution. The solvent was evaporated under reduced pressure and the crude material was purified by silica gel column chromatography (CH_2Cl_2), followed by further silica gel column chromatography (acetone:toluene 3.5:96.5) to give **Ph(PDI)**₃ as a bright red solid (88 mg, 44%). Spectral data were consistent with previously reported data.³



Figure S1. ¹H NMR (600 MHz) spectrum of $Ph(PDI)_3$ in $C_2D_2Cl_4$ at 373.5 K.

Synthesis of donor copolymers

The two copolymers were prepared by tin-free direct C-H arylation polymerization (DARP) according to the previously reported procedures,^{4, 5} and these batches were characterized by gel permeation chromatograph (GPC) yielding:

PBDTT-FTTE: $M_n = 25.5 \text{ kg/mol}$, D = 1.93. (batch no. P338)

PBDTTF-FTTE: $M_n = 25.6 \text{ kg/mol}$, D = 2.45. (batch no. P351)

2. Ultraviolet Photoelectron Spectroscopy (UPS)

Organic semiconductor films were spin-coated onto clean ITO/Au (80nm) substrates. ITO substrates (TFD Inc.) were first washed and cleaned (see the procedure in solar cell fabrication section), and the Au layer (80nm) was thermally deposited onto ITO substrates under vacuum ($< 4 \times 10^{-6}$ Torr, Denton Vacuum Explorer 14, 46368). Then, neat **PBDTT-FTTE** and **PBDTTF-FTTE** films were spin-coated from 11 mg/mL 1,2-dichlorobenzene (*o*-DCB) solution (1000 rpm, 120 s), and neat **Ph(PDI)**₃ films were spin-coated from 22 mg/mL *o*-DCB solution (1000 rpm, 120 s). Strips on the ITO side were made by cotton swabs for the clip contacts in the later UPS measurements.

Ultraviolet photoelectron spectroscopy (UPS) measurements were conducted on a Thermo Scientific Escalab 250Xi ultra photoelectron spectrometer (NUANCE) with an analysis pressure of 2×10^{-8} mbar. Measurements were made with He I photon source (hv = 21.22 eV) with a pass energy of 2.0 eV. Clips were used to electrically connect the ITO and the instrument station, a sample bias of -5.0 V was therefore applied to accurately acquire the high binding energy cutoff (E_{cutoff}). Gold (Au) was used for calibration of the instrument under the same bias of -5.0 V, and a shift value of 4.5 eV was therefore obtained to calibrate the gold that has a Fermi edge at 0.0 eV.⁶ This shift value was then applied to calibrate all the recorded UPS spectra from sample films.

Data analysis and export were performed in the Avantage Software (Version 5). The software can be downloaded on <u>www.surfsciftp.co.uk/avant5</u>. All the curves were plotted in Origin 9 software. The ionization potential (IP) is calculated, according to the equation widely used for organic semiconductor materials:⁶⁻⁸

$$IP = 21.22 - (E_{cutoff} - E_{onset})$$

where E_{onset} is the onset of the peak with a lowest binding energy.



Figure S2. Raw UPS spectra recorded from neat **PBDTT-FTTE**, **PBDTTF-FTTE**, and **Ph(PDI)**₃ films under a bias of -5 V.



Figure S3. The shifted UPS spectra of neat PBDTT-FTTE, PBDTTF-FTTE, and Ph(PDI)₃ films. The high binding energy cutoff (E_{cutoff}) and the onset of the peak with a lowest binding energy (E_{onset}) were extracted for the IP estimation.

Table S1. UPS-estimated HOMO energies (eV).

Material	IP (eV)	E _{HOMO} (eV)
PBDTT-FTTE	5.07	-5.07
PBDTTF-FTTE	5.32	-5.32
Ph(PDI) ₃	5.92	-5.92

3. UV-vis Absorption Spectroscopy

UV-vis spectra were recorded on a Varian Cary 100 Bio UV-vis spectrophotometer. The solution absorption spectra of **PBDTT-FTTE**, **PBDTTF-FTTE** copolymers were recorded on 0.0125 mg mL⁻¹ 1,2–dichlorobenzene (*o*-DCB) solutions at ambient temperature. The copolymer film optical absorption spectra were recorded from thin films cast from 5 mg mL⁻¹ *o*-DCB solutions (1700 rpm 20 s) onto glass slides (VWR). The solution absorption spectrum of **Ph(PDI)**₃ was recorded in chloroform (CHCl₃), and the film optical absorption spectrum of **Ph(PDI)**₃ was recorded from a film cast from 5 mg mL⁻¹ CHCl₃ solution (1700 rpm). **PBDTT-FTTE:Ph(PDI)**₃ and **PBDTTF-FTTE:Ph(PDI)**₃ blend films were spin-coated onto clear glass substrate (VWR), using the same conditions as optimized OPV devices (see the solar cell fabrication section for more details).



Figure S4. UV-vis absorption spectra of the donor and acceptor materials.

Table S2. Summary of the optical absorption properties of the donor and acceptor materials.

Material	Solution λ_{max} (nm)	Film λ _{max} (nm)	$E_{\rm g} \ ({ m eV})^{\#}$
Ph(PDI) ₃	516, 485 [‡] , 432 [‡] , 367 [‡]	523, 435 [‡] , 374 [‡]	2.07
PBDTT-FTTE	709, 641‡	708, 645‡	1.62
PBDTTF-FTTE	702, 634‡	696, 638 [‡]	1.65

[#] Optical bandgap E_{g} estimated from the absorption edge of the film.

[‡] Secondary absorbance peak or shoulder.

4. Cyclic Voltammetry (CV)

The electrochemical properties of the materials were investigated as **thin films** in deoxygenated anhydrous acetonitrile under nitrogen at a scan rate of 100 mV s⁻¹ using 0.1 M tetrakis(*n*-butyl)ammonium hexafluorophosphate $[(n-Bu)_4N^+PF_6^-]$ as the supporting electrolyte. Pt electrodes were used as both the working and counter electrodes, and with Ag/Ag⁺ (sat. NaCl) as the pseudoreference electrode. **Ph(PDI)**₃ films were drop-cast onto the Pt working electrode from a 5 mg mL⁻¹ CHCl₃ solution. A ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as internal standard and was assigned an absolute energy level of –4.88 eV vs vacuum.⁹ HOMO energies were then determined according to the equation:

$$E_{\rm HOMO} = -(E_{\rm ox}^{\rm onset} + 4.88)$$

where E_{ox}^{onset} is the onset of oxidation potential relative to the measured Fc/Fc⁺ redox couple. The LUMO energies were calculated according to the equation:

$$E_{\rm LUMO} = -(E_{\rm red}^{\rm onset} + 4.88)$$

where E_{red}^{onset} is the onset of reduction potential versus Fc/Fc⁺. The Fc/Fc⁺ redox couple was found at 0.443 V relative to the Ag/Ag⁺ electrode.



Figure S5. Cyclic voltammograms of a Ph(PDI)₃ film.

Material	E _{HOMO} ^{UPS} (eV)	$E_{ m g}^{\dagger}$ (eV)	<i>E</i> _{LUMO} [‡] (eV)	E _{LUMO} ^{CV} (eV)	E _{HOMO} ^{CV} (eV)	E _{HOMO} § (eV)
PBDTT-FTTE	-5.07	1.62	-3.45	/	/	/
PBDTTF-FTTE	-5.32	1.65	-3.67	/	/	/
Ph(PDI) ₃	-5.92	2.07	-3.85	-3.85	-6.27	-5.92

Table S3. Physicochemical properties of PBDTT-FTTE, PBDTTF-FTTE, and Ph(PDI)₃.

[†] Optical bandgap $E_{\rm g}$ was determined by the absorption edge of thin film;

[‡] Calculated from $E_{\text{LUMO}} = E_{\text{HOMO}}^{\text{UPS}} + E_{\text{g}}$, $E_{\text{HOMO}}^{\text{UPS}}$ is the HOMO estimated from UPS;

§ Calculated from $E_{\text{HOMO}} = E_{\text{LUMO}}^{\text{CV}} + E_{\text{g}}, E_{\text{LUMO}}^{\text{CV}}$ is the LUMO estimated from CV.

Table S4. Molecular orbital energy level offsets between polymers and Ph(PDI)₃.

Material	Δ _{HOMO} (eV)	Δ _{LUMO} (eV)
PBDTT-FTTE vs Ph(PDI) ₃	0.85	0.4
PBDTTF-FTTE vs Ph(PDI) ₃	0.6	0.18

5. Thermogravimetric Analysis (TGA)

The TGA measurements were performed on a SDT Q600 instrument (TA Instruments). The samples (weight range 1.0-2.0 mg) were heated with a rate of 10 °C/min under N₂. The thermal decomposition temperature (T_d) was measured at 5% mass loss of the samples.



Figure S6. TGA heating traces of PBDTT-FTTE, PBDTTF-FTTE, and Ph(PDI)₃.

6. Differential Scanning Calorimetry (DSC)

The DSC measurements were performed on a DSC 250 instrument (TA Instruments, Materials Characterization and Imaging Facility, MatCI). The samples were placed in lidded Al tzero pans (TA Instruments) and thermally cycled twice (heating-cooling-heating-cooling) under N_2 with a heating/cooling rate of 10 °C/min. All the data are reported using the second cycle and exotherm up.



Figure S7. DSC heating and cooling traces of PBDTT-FTTE, PBDTTF-FTTE, and Ph(PDI)₃.

7. Device. Solar Cell Device Fabrication and Measurements

Photovoltaic performance was studied using the "inverted" device structure: indium tin oxide (ITO)/zinc oxide (ZnO) (~22nm)/active layer/molybdenum oxide (MoO₃) (10nm)/Ag(100nm). ITO substrates were purchased from Thin Film Devices (TFD) Inc.. The dimensions are 14.8 mm \times 24.8 mm \pm 0.1 mm, and the thickness is 0.7 mm \pm 0.1 mm. The thickness of home-designed "Lshaped" ITO coating is 1450 Å \pm 100 Å, and the resistivity is 20 \pm 2 ohms/sq. The optical transmission parameter is 88% at 550 nm, and the work function of ITO is -4.8 eV to -5.0 eV. ITO substrates were sequentially sonicated by aqueous detergent solution, deionized water, methanol, isopropanol and acetone (each for 20 min), then dried by a N₂ gun, and treated by UV/ozone (Jelight Co. UVO Cleaner Model No. 42) for 15 min. The ZnO interfacial layer was spin-coated (7000 rpm, 30 s, ACL = 8000) on a Laurell WS-650MZ-23NPP spin coater from a filtered (0.45 um PVDF filter, Millipore Millex-HV) precursor solution, and then annealed at 170 °C for 10 min in air on a Wenesco hotplate. The ZnO precursor solution was 0.5 M zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, Sigma-Aldrich 379786-5G) and 0.5 M monoethanolamine (HO-(C₂H₄)-NH₂, Sigma-Aldrich 411000-100mL) in 2 mL 2-methoxyethanol (HO-(C₂H₄)-OCH₃, Sigma-Aldrich 284467-100mL), and stirred at room temperature overnight. The ZnO sol-gel reactions are:

> $2HO-(C_2H_4)-NH_2 + 2H_2O = 2H_2N^+-(C_2H_4) + 2OH^-$ Ionization: Zn(CH_3COO)_2 + OH^- = Zn(CH_3COO)(OH) + CH_3COO^-Zn(CH_3COO)(OH) + OH^- = Zn(OH)_2 + CH_3COO^-HO-Zn-OH + HO-Zn-OH = HO-Zn-O-Zn-OH + H_2O Zn(CH_3COO)_2 · 2H_2O = Zn(OH)_2 + 2CH_3COOH

The ITO/ZnO substrates were then transferred into an argon-filled glovebox (Mbraun Unilab-2000, project no. 2376, H₂O < 1 ppm, O₂ < 1 ppm) for spin-coating of organic active layer. The active layer solutions (200 μ L) were prepared by co-dissolving donor polymer and acceptor **Ph(PDI)**₃ (1:1 mass ratio) in 1,2-dichlorobenzene (*o*-DCB, anhydrous, 99%, Sigma-Aldrich, 240664-100mL) while stirring at 95 °C overnight on a Cimarec hot plate (make sure the materials were completely dissolved). The polymer concentration was fixed to 11 mg/mL. Active layer films were spin-coated on a Laurell Model WS-400B-6NPP/LITE spin coater (Laurell Technologies Corporation) in the glovebox using 1000 rpm 120 s ACL = 015 from the hot solutions kept at 95 °C, film thickness was found to be around 96 ~ 113 nm measured by Keck-II profilometer (NUANCE), and then allowed to dry for 1.5 hours inside fluoroware before loading into the deposition chamber. Finally, 10 nm MoO₃ (Alfa Aesar, 99.9995%) and 100 nm Ag (W. E. Mowrey Co.) were thermally evaporated (Midwest Tungsten Service boats) through home-designed shadow mask (made to match ITO's L shape) around 10⁻⁶ Torr (Cooke Vacuum Model FPS2-40). No device encapsulation was used.

All the solar cells were tested in ambient at room temperature by a Keithley 2400 source-measure unit under simulated AM1.5G irradiation (**100 mWcm**⁻²) using Xe arc lamp of a Spectra-Nova 300W Class-A solar simulator (Spectra-Solaris Inc.). As routine maintenance, the light intensity was calibrated by a National Renewable Energy Laboratory (NREL) certified monocrystalline Si

photodiode (Device ID: SNR004, $I_{max} = 51.907 \text{ mA}$) coupled to a KG3 filter to bring the spectral mismatch to unity. All the solar cells were put in custom designed contacting testing jig (Spectra-Solaris Inc. see **Figure S9**). The active area of all the solar cells was 6 mm² (3 mm × 2 mm). The solar cell testing and automation program used (Agilent VEE) was developed by Spectra-Solaris Inc. All the current density-voltage (*J-V*) plots were scanned in the reverse direction (from positive voltage to negative voltage).

Light intensity dependence measurements were conducted on the same home solar cell testing setup, using a series of density filters (New Focus, diameter ~ 2.5 cm) and a home-designed black box holder. In the experiments, different density filters were applied to AM 1.5G light (100 mWcm⁻²), and *J-V* curves were recorded. The dependence of J_{SC} on incident light intensity (I_{light}) can be described by:

$$J_{\rm SC} \propto (I_{\rm light})^{\alpha}$$

where α is an exponential factor related to device recombination losses. The dependence of V_{OC} on I_{light} is plotted as V_{OC} versus lg(I_{light}). Note that, the n k_{B} T/q values were fitted from:

$$V_{\rm OC} \propto nk_{\rm B}T/q \times \ln(I_{\rm light})$$

where $k_{\rm B}$ is Boltzmann's constant, T is the temperature, q is the elementary charge, and n is an ideality factor.

External quantum efficiency (EQE) spectra of solar cells were recorded in ambient at room temperature on a Newport QE-PV-SI setup. Incident light from Xe lamp (300 W) sequentially passing through motorized filter wheel, chopper wheel and monochromator (Newport Cornerstone 260) was focused on the active area of solar cells. The spot of output light was similar as the active area of sample cells. The incident light was perpendicular to (~90°) ITO/glass substrate. The frequency of chopper wheel was set as 30 Hz. The current was obtained using a current pre-amplifier (Newport, 70710QE) and a lock-in amplifier (Newport, 70105 Dual channel Merlin). Before scanning EQE spectra of solar cells, a Newport 70356_70316NS silicon diode was used as a standard reference (Present Signal Reading is ~ 4.5×10^{-1} at 555 nm). EQE J_{SC} values were calculated from the online Open Photovoltaics Analysis Platform (opvap.com) by submitting the obtained EQE spectra. The mismatch between J_{SC} and EQE is calculated by:

$$Mismatch = \frac{J_{sc} - EQE J_{sc}}{J_{sc}}$$



Figure S8. (a) Optical image of typical polymer: $Ph(PDI)_3$ solar cells (one substrate has four fingers, and each finger is corresponding to one solar cell device) in this lab, (b) relevant solar cell device structure and (c) energetics. MoO₃ changes to MoO_x when it is brought into air.



Figure S9. (a) Equivalent circuit diagram of solar cell, (b) optical image of contacting testing jig (Spectra-Solaris Inc.) and typical polymer-small molecule solar cells in this lab.

		Voc	$J_{ m SC}$	FF	PCE	Number
	Experimental details	(V)	(mA cm ⁻²)	(%)	(%)	of devices
	$1.1 \circ DCP = 10mg/mI$	1.055 ± 0.013	13.31 ± 0.64	56.96 ± 1.79	8.00 ± 0.37	0
	1.1, 0-DCB, 10ilig/iiiL	(1.074)	(14.00)	(57.77)	(8.68)	9
Polymer	1:1 o DCR 11mg/mI	1.058 ± 0.008	14.66 ± 0.45	56.36 ± 1.03	8.74 ± 0.19	13
concentration	1.1, 0-DCD, 11iig/iiiL	(1.058)	(15.31)	(56.18)	(9.10)	15
	$1.1 \circ DCR = 12mg/mI$	1.056 ± 0.008	14.43 ± 0.43	55.19 ± 1.06	8.41 ± 0.18	12
	1.1, 0-DCD, 12ing/iiiL	(1.049)	(15.19)	(54.57)	(8.70)	12
	1:1.25, <i>o</i> -DCB,	1.071 ± 0.005	13.53 ± 0.39	57.06 ± 0.88	8.26 ± 0.14	8
D:A	11mg/mL	(1.065)	(14.25)	(55.61)	(8.44)	0
mass ratio	1.25:1, <i>o</i> -DCB,	1.063 ± 0.005	11.52 ± 0.49	58.19 ± 0.99	7.12 ± 0.23	6
	11mg/mL	(1.063)	(12.32)	(57.43)	(7.52)	0
	1.1 CR 11mg/mI	1.056 ± 0.006	12.49 ± 0.32	47.03 ± 0.34	6.20 ± 0.16	10
	1.1, CD, 11iig/iiiL	(1.054)	(13.12)	(47.31)	(6.54)	10
Solvont	1:1 CE 7mg/mI	1.079 ± 0.005	13.56 ± 0.69	51.71 ± 1.42	7.57 ± 0.56	8
Solvent	1.1, CF, /ilig/iliL	(1.078)	(14.58)	(52.71)	(8.28)	0
	1:1 CE 11mg/mI	1.056 ± 0.006	10.25 ± 0.35	40.23 ± 1.13	4.35 ± 0.14	10
	1.1, CF, Thing/hill	(1.052)	(10.77)	(40.28)	(4.56)	10
	1:1, o-DCB, 11mg/mL,	1.065 ± 0.01	14.05 ± 0.56	56.97 ± 0.64	8.52 ± 0.19	5
	DIO 0.25%	(1.054)	(14.78)	(56.06)	(8.74)	5
Solvont	1:1, o-DCB, 11mg/mL,	1.056 ± 0.012	13.54 ± 1.14	52.35 ± 1.51	7.47 ± 0.48	7
Additivos	DIO 0.5%	(1.048)	(15.29)	(51.64)	(8.28)	/
(volume %)	1:1, o-DCB, 11mg/mL,	1.05 ± 0.007	11.83 ± 0.51	53.46 ± 1.86	6.64 ± 0.41	8
(volume 70)	DIO 1%	(1.037)	(12.75)	(54.88)	(7.26)	0
	1:1, o-DCB, 11mg/mL,	1.074 ± 0.007	14.10 ± 0.54	53.93 ± 1.20	8.16 ± 0.17	12
	CN 0.5%	(1.068)	(14.97)	(53.72)	(8.59)	12
	1:1, o-DCB, 11mg/mL,	1.076 ± 0.005	12.91 ± 0.41	57.57 ± 0.64	7.99 ± 0.16	8
	100°C, 5min	(1.072)	(13.52)	(56.80)	(8.23)	0
	1:1, o-DCB, 11mg/mL,	1.075 ± 0.005	11.91 ± 0.41	57.72 ± 1.16	7.39 ± 0.22	5
	150°C, 5min	(1.080)	(12.27)	(58.14)	(7.71)	5
Annealing	1:1, o-DCB, 11mg/mL,	1.066 ± 0.003	12.50 ± 0.67	57.19 ± 0.76	7.62 ± 0.34	6
Anneaning	200°C, 5min	(1.065)	(13.50)	(56.31)	(8.09)	0
	1:1, o-DCB, 11mg/mL,	1.061 ± 0.003	12.99 ± 0.71	57.20 ± 0.85	7.89 ± 0.34	6
	230°C, 5min	(1.059)	(14.01)	(56.33)	(8.36)	0
	1:1, o-DCB, 11mg/mL,	1.056 ± 0.003	12.66 ± 0.68	56.90 ± 0.77	7.60 ± 0.33	11
	250°C, 5min	(1.052)	(13.87)	(55.65)	(8.12)	11

Table S5. OPV optimization data for PBDTTF-FTTE:Ph(PDI)₃ blends.

The photovoltaic data are reported as averages taken over 5 or more separate devices \pm one standard deviation (1 σ). The device parameters in parenthesis are from the champion cells. The context in the "experimental details" column sequentially represent D:A mass ratio, solvent,

polymer concentration. Solvents: *o*-DCB is 1,2-dichlorobenzene (Sigma-Aldrich 240664-100mL, bp 180.2°C), CB is chlorobenzene (Sigma-Aldrich 284513-100mL, bp 131°C) and CF is chloroform (Sigma-Aldrich 288306-100mL, bp 61.2°C). Solvent additives: DIO is 1,8-diiodooctane (Sigma-Aldrich 250295-5G, bp 168°C) and CN is 1-chloronaphthalene (Sigma-Aldrich 185752-100G, bp 263°C). Thermal annealing of organic active layer/ZnO/ITO/glass was performed on a Wenesco hot plate inside of the Ar-filled glovebox after spin-coating and before the evaporation of MoO₃ and Ag.

	Experimental	Voc	$J_{ m SC}$	FF	РСЕ	Number of	EQE J _{SC}
BHJ Blend	details	(V)	(mA cm ⁻²)	(%)	(%)	devices	(mA cm ⁻²)
PBDTT-	1:1, <i>o</i> -DCB,	0.845 ± 0.006	13.85 ± 0.45	47.04 ± 1.73	5.50 ± 0.24	12	12.61
FTTE:Ph(PDI) ₃	11mg/mL	(0.853)	(14.31)	(48.59)	(5.93)	15	13.01
PBDTTF-	1:1, <i>o</i> -DCB,	1.058 ± 0.008	14.66 ± 0.45	56.36 ± 1.03	8.74 ± 0.19	12	14.06
FTTE:Ph(PDI) ₃	11mg/mL	(1.058)	(15.31)	(56.18)	(9.10)	13	14.00

Table S6. The fully optimized photovoltaic performance of polymer: Ph(PDI)₃ blends.

The photovoltaic data are reported as averages taken over 13 separate devices \pm one standard deviation (1 σ), and the numbers in parenthesis are from the champion cells. The mismatch between average J_{SC} and corresponding EQE is within or near 5%.

Table S7. Energy loss of the two BHJ polymer: Ph(PDI)₃ blend films.

DUI Dland	V _{oc}	$E_{ m g}$ of polymer film	$E_{\rm loss} = E_{\rm g} - eV_{\rm OC}$
DHJ DICHU	(V)	(eV)	(eV)
PBDTT-	PBDTT- 0.845 ± 0.006		1.62 - 0.845 = 0.78
FTTE:Ph(PDI) ₃	(0.8529)	1.02	(0.77)
PBDTTF-	1.058 ± 0.008	1.65	1.65-1.058 = 0.59
FTTE:Ph(PDI) ₃	(1.0804)	1.05	(0.57)

The V_{OC} s are reported as averages taken over 13 separate devices \pm one standard deviation (1 σ), and the numbers in parenthesis are maximal V_{OC} s and the corresponding minimal E_{loss} s.



Figure S10. (a) J_{SC} versus light intensity (I_{light}) and (b) V_{OC} versus I_{light} measurements of the polymer:**Ph(PDI)**₃ solar cell devices. Note that nk_BT/q values were extracted from the corresponding $V_{OC} \sim \ln(I_{light})$ plots. The detailed fitting parameters from the above curves are as follows: (a) $\alpha = 0.862$ for the **PBDTT-FTTE:Ph(PDI)**₃ blend; $\alpha = 0.959$ for the **PBDTTF-FTTE:Ph(PDI)**₃ blend; (b) n = 1.24 for the **PBDTT-FTTE:Ph(PDI)**₃ blend; n = 1.43 for the **PBDTTF-FTTE:Ph(PDI)**₃ blend; At lower light intensities ($I_{light} < 1 \text{ mW cm}^{-2}$), the **PBDTTF-FTTE:Ph(PDI)**₃-based devices exhibit a much stronger V_{OC} dependence on I_{light} .

8. Device. Space-charge-limited Current (SCLC) Measurement

Space-charge-limited current (SCLC) hole and electron mobilities were measured using ITO/MoO₃ (8nm)/Organics/MoO₃ (8nm)/Ag(100nm) and ITO/ZnO (~22nm)/Organics/LiF(1nm)/ Al(100nm) single carrier diode structure, respectively. ITO substrates (TFD Inc.) were sequentially sonicated by aqueous detergent solution, deionized water, methanol, isopropanol and acetone (each for 20 min), then dried by a N₂ gun, and treated by UV/ozone (Jelight Co.) for 15 min. **PBDTT-FTTE:Ph(PDI)**₃ and **PBDTTF-FTTE:Ph(PDI)**₃ blend films were spin-coated using the same conditions as the optimized OPV devices (see the solar cell fabrication section for more details). Neat **PBDTT-FTTE** and **PBDTTF-FTTE** films were spin-coated from 11 mg/mL *o*-DCB solution (1000 rpm, 120 s), and neat **Ph(PDI)**₃ films were spin-coated from 22 mg/mL *o*-DCB solution (1000 rpm, 120 s). ZnO layer was deposited by using the sol-gel method, while MoO₃ (Alfa Aesar, 99.9995%), Ag, LiF (Alfa Aesar, 99.99%), Al (Sigma-Aldrich, 433705-25G) were thermally evaporated under vacuum (around 10⁻⁶ Torr). The shadow mask size was 200 μ m × 200 μ m. No device encapsulation was used.

All the vertical diodes were measured in ambient at room temperature by a Signatone H100 series probe station (with assembled a Motic MLC-150C fiber optic illuminator and an Olympus SZ60 microscope) and an Agilent B1500A semiconductor device parameter analyzer. The tungsten probe tips (SE-20T, Signatone Corporation) were carefully cleaned by isopropanol or acetone before measurements, to insure we removed any contact resistance effects that could largely limit the current. In the hole-only diodes, ITO was the hole injection electrode, and MoO₃/Ag was the hole extraction electrode, while in the electron-only diodes, LiF/Al was the electron injection electrode, and ZnO/ITO was the electron extraction electrode (see **Figure S11**). The applied voltage scan (Power SMU) was from 0 V to + 3.5 V (too high applied voltage leads to the breakdown of vertical diodes, and linear current-voltage characterstics with large current were observed if we scanned the broken diodes for the second time), with another probe connected to the instrument ground (GNDU, potential of 0 V). The current-voltage curves of single carrier diodes were therefore obtained.

Data fitting was performed in Origin 9 software, using the protocol developed by this lab in a previous report.¹⁰ The zero-field mobility μ_0 and the field dependence coefficient γ (γ describes the strength of field-dependence effect), were fitted in the **SCLC regime** using the modified Mott-Gurney equation:¹¹⁻¹³

$$J = \frac{9 \epsilon_{\rm s}}{8 \rm L} E^2 \,\mu_0 e^{0.89 \,\gamma \sqrt{E}}$$

where ε_s is the semiconductor permittivity (here taken as $3\varepsilon_0$, ¹⁴ ε_0 is the permittivity of empty space, $\varepsilon_0 = 8.85 \times 10^{-12}$ F m⁻¹), *L* is the thickness of organic layer. The electric field *E* was corrected using the equation:

$$E = \frac{V_{app} - V_{bi} - JAR_{series}}{L}$$

where A is the device area (A = 4 × 10⁻⁸ m², 200 μ m × 200 μ m), R_{series} is the ITO resistivity (20 ± 2 ohms/sq), V_{app} is the applied voltage, V_{bi} is the built-in voltage resulting from the relative work function difference between the two electrodes (uesd the conducting band values for interfacial layers ZnO). In the hole-only diode, $V_{\text{bi}} = 0$ V from MoO₃ and MoO₃, while in the electron-only diode, $V_{\text{bi}} = 0.1$ V from ZnO and LiF/Al (see **Figure S11**). The SCLC zero-field mobilities of the holes (electrons) μ_{h} (μ_{e})s are reported as averages taken over 5 or more separate devices ± one standard deviation (1 σ) in **Table S8**.



Figure S11. Vertical single carrier diode structure and corresponding energetics of (a) hole-only and (b) electron-only diodes, respectively. The work function of ITO is from the manufacturer TFD Inc. The conducting band (CB) and valence band (VB) values of interfacial layer MoO₃ (MoO_x), ZnO are from references *Organic Electronics* **2012**, *13*, 2793, *Advanced Materials* **2011**, *23*, 1282, respectively.



Figure S12. Optical image of typical single carrier diodes ($200 \ \mu m \times 200 \ \mu m$).

Films	Experimental details	μ _h (10 ⁻⁴ cm ² /Vs)	Number of devices for µ _h	μ _e (10 ⁻⁴ cm ² /Vs)	Number of devices for µ _e	$\mu_{ m h}$ / $\mu_{ m e}$
Blend PBDTT-	1:1, <i>o</i> -DCB,	30.86 ± 8.80	10	2.16 ± 2.03	7	14 20
FTTE:Ph(PDI) ₃	11mg/mL	50.00 ± 0.00	19	2.10 ± 2.05	/	14.29
Blend PBDTTF-	1:1, <i>o</i> -DCB,	13 01 + 3 18	15	0 81 + 6 80	8	1.42
FTTE:Ph(PDI) ₃	11mg/mL	15.91 ± 5.10	15	9.01 - 0.09	0	1,72
Neat	o-DCB,	9.31 ± 2.17	7	/	/	/
PBDTT-FTTE	11mg/mL	9.91 - 2.17).51 - 2.17		1	/
Neat	o-DCB,	3.68 ± 3.17	5	/	/	/
PBDTTF-FTTE	11mg/mL	5.00 ± 5.17	5	1	1	1
Neat	o-DCB,	1	/	3.64 ± 1.41	5	/
Ph(PDI) ₃	22mg/mL	/	/	5.04 ± 1.41	5	/

 Table S8. SCLC zero-field mobilities of blend and neat films.

The SCLC zero-field mobilities of the holes (electrons) μ_h (μ_e)s are reported as averages taken over 5 or more separate devices \pm one standard deviation (1 σ). The μ_h / μ_e values were calculated from the average mobilities.



Figure S13. Average SCLC zero-field mobilities of blend and neat films.



Figure S14. Representative *J*-*E* curves of (a) hole-only and (b) electron-only diodes for blends. The detailed fitting parameters from above representative data are as follows: (a) $\mu_0 = 31.25 \times 10^{-4}$ cm²/Vs, $\gamma = 1.63 \times 10^{-4}$ m^{1/2} V^{-1/2}, L = 112 nm for the **PBDTT-FTTE:Ph(PDI)**₃ blend, while $\mu_0 = 13.98 \times 10^{-4}$ cm²/Vs, $\gamma = -2.40 \times 10^{-4}$ m^{1/2} V^{-1/2}, L = 98 nm for the **PBDTTF-FTTE:Ph(PDI)**₃ blend, while $\mu_0 = 1.95 \times 10^{-4}$ cm²/Vs, $\gamma = 5.41 \times 10^{-4}$ m^{1/2} V^{-1/2}, L = 113 nm for the **PBDTT-FTTE:Ph(PDI)**₃ blend, while $\mu_0 = 21.44 \times 10^{-4}$ cm²/Vs, $\gamma = -2.17 \times 10^{-4}$ m^{1/2} V^{-1/2}, L = 96 nm for the **PBDTTF-FTTE:Ph(PDI)**₃ blend. Average fitting parameters obtained from 7 or more separate devices are shown in **Table S8**.



Figure S15. Representative *J*-*E* curves of (a) hole-only and (b) electron-only diodes for neat films. The detailed fitting parameters from above representative data are as follows: (a) $\mu_0 = 9.93 \times 10^{-4}$ cm²/Vs, $\gamma = 2.38 \times 10^{-4}$ m^{1/2} V^{-1/2}, L = 87 nm for the neat **PBDTT-FTTE** film; $\mu_0 = 2.48 \times 10^{-4}$ cm²/Vs, $\gamma = 3.36 \times 10^{-4}$ m^{1/2} V^{-1/2}, L = 82 nm for the neat **PBDTTF-FTTE** film; (b) $\mu_0 = 3.15 \times 10^{-4}$ cm²/Vs, $\gamma = -3.824 \times 10^{-4}$ m^{1/2} V^{-1/2}, L = 75 nm for the neat **Ph(PDI)**₃ film. Average fitting parameters obtained from 5 or more separate devices are shown in **Table S8**.

9. Microscopy. Atomic Force Microscopy (AFM)

Sample **PBDTT-FTTE:Ph(PDI)**₃ and **PBDTTF-FTTE:Ph(PDI)**₃ BHJ blend films were spincoated as were the optimized OPV devices (see details in the solar cell fabrication section). All the neat films were spin-coated onto 2 cm \times 2 cm ZnO/Si substrates. Si substrates (WRS Materials) were firstly washed and cleaned using the same procedure as ITO substrates, and the ZnO layer was deposited in ambient using the sol-gel method. Neat **PBDTT-FTTE** and **PBDTTF-FTTE** films were spin-coated from 11 mg/mL *o*-DCB solution (1000 rpm, 120 s), and neat **Ph(PDI)**₃ films were spin-coated from 22 mg/mL *o*-DCB solution (1000 rpm, 120 s). All the blend and neat films were spin-coated in the Ar-filled glovebox.

Standard tapping-mode AFM measurements in ambient were performed on a Scanned Probe Imaging and Development (SPID) Bruker ICON using a TESPA probe (NU Atomic and Nanoscale Characterization Experimental Center, NUANCE). The AFM images were confirmed from different samples and scan areas. The root-mean-square roughness (Rq) values of height images were obtained from the whole scan area ($3 \mu m \times 3 \mu m$) in the NanoScope Analysis 1.9 software. All the AFM images were flattened and exported from the software.



Figure S16. AFM images of the **PBDTT-FTTE:Ph(PDI)**₃ and **PBDTTF-FTTE:Ph(PDI)**₃ BHJ blend films. The height images are also shown in main text.



Figure S17. AFM images of neat PBDTT-FTTE, PBDTTF-FTTE, and Ph(PDI)₃ films.



Figure S18. AFM images of ZnO/Si substrate.



Figure S19. AFM images of cleaned ITO surface.

10. Microscopy. Transmission Electron Microscopy (TEM)

A polystyrene sulfonate (PSS) layer was first deposited onto clean glass substrates (VWR, 25 mm \times 25 mm) from a filtered (NYLON 0.45 μ m) 18wt.% poly(4-styrenesulfonic acid) aqueous solution (Sigma-Aldrich 561223-500G), using 5000 rpm 30 s ACL = 6000, and annealed at 120 °C for 10 min in air on a Wenesco hotplate. **PBDTT-FTTE:Ph(PDI)**₃ and **PBDTTF-FTTE:Ph(PDI)**₃ BHJ blend films were then spin-coated onto the PSS covered glass substrates in the Argon-filled glovebox, using the same conditions as those of the optimized OPV devices (see details in the solar cell fabrication section). The organics/PSS/glass substrates were then immersed into deionized water at room temperature, and after several minutes, the BHJ blend films separated from the glass substrate. The floated single-layer organic blend films were transferred to transmission electron microscopy (TEM) copper grids with a lacey carbon coating (Ted Pella, Inc. PELCO No. I60). Carefully, one should make sure that the films are not folded, and there is only one layer transferred onto the copper grids. The films were then allowed to dry in air before TEM measurements.

TEM images were obtained on a Hitachi HT7700 microscope (Northwestern University Atomic and Nanoscale Characterization Experimental Center, Electron Probe Instrumentation Center, NUANCE EPIC) at an acceleration of 120 kV to gain sufficient transmission. TEM images were taken perpendicular to the plane of the films, and confirmed from different samples and areas, to make sure they are representative.



Figure S20. TEM images of PBDTT-FTTE:Ph(PDI)₃ and PBDTTF-FTTE:Ph(PDI)₃ BHJ blend films.



Figure S21. Typical TEM images of **PBDTT-FTTE:Ph(PDI)**₃ and **PBDTTF-FTTE:Ph(PDI)**₃ blend films with size of **Ph(PDI)**₃-rich domains (red circles ~ 3.5 nm).

11. X-ray. Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS)

GIWAXS samples were prepared on 2 cm \times 2 cm ZnO/Si substrates. Si substrates (WRS Materials) were firstly washed and cleaned using the same procedure as ITO substrates (see above), and ZnO layer was deposited using the sol-gel method. **PBDTT-FTTE:Ph(PDI)**₃ and **PBDTTF-FTTE:Ph(PDI)**₃ BHJ blend films were spin-coated applying the same conditions as the optimized OPV devices (see details in the solar cell fabrication section). Neat **PBDTT-FTTE** and **PBDTTF-FTTE** films were spin-coated from 11 mg/mL 1,2-dichlorobenzene solution (1000 rpm, 120 s), and neat **Ph(PDI)**₃ films were spin-coated from 22 mg/mL 1,2-dichlorobenzene solution (1000 rpm, 120 s).

Measurement and data processing:

GIWAXS measurements were performed using Beamline 8-ID-E at the Advanced Photon Source (APS) at Argonne National Laboratory.¹⁵ The photon energy is 10.92 keV ($\lambda = 1.13938$ Å). Samples were examined under vacuum, with a Pilatus 1M detector (Dectris) having a pixel size of 172 μ m × 172 μ m used to collect the two-dimensional (2D) scattering images. Two images with a vertical offset were used to avoid gaps in the detector, which consists of 10 modules. The sample-detector distance is 204 mm and the beam size is 200 μ m (h) × 20 μ m (v). Flat field, solid angle, and detector efficiency corrections were applied to the images and the images were combined and converted to q-space with the GIXSGUI package for Matlab.¹⁶ Further processing used local Origin software.

X-ray reflectivity was first performed to determine the critical angle of the film. At angles larger than the critical angle, the X-ray beam will penetrate the film and the higher the angle, the deeper the penetration. The X-ray beam angle of the incidence was chosen such that the beam would penetrate the entire active layer while minimizing scattering from the substrate. The films were illuminated at an incident angle of 0.14° .

The 2D GIXS images from the films can be analyzed according to the relationship between the scattering vector q and the *d*-spacing:

$$q = \frac{2\pi}{d}$$

Linecuts were taken along the horizontal and vertical axes of the 2D GIXS images and fit using a Gaussian procedure in Origin software. The crystalline correlation lengths (CCL) can be determined using the (100) and (010) peaks and Scherrer's equation:¹⁷

$$CCL = \frac{2\pi}{FWHM}$$

The full width at half maximum (FWHM) was extracted from the Gaussian fits described above.



Figure S22. GIWAXS linecuts of (a) pristine **PBDTT-FTTE**, (b) pristine **PBDTTF-FTTE**, (c) BHJ blend **PBDTT-FTTE:Ph(PDI)**₃, (d) BHJ blend **PBDTTF-FTTE:Ph(PDI)**₃, and (e) pristine **Ph(PDI)**₃ films showing in-plane (IP, q_{xy}) and out-of-plane (OoP, q_z) crystalline scattering peaks.

Film	<i>d</i> -space	d-spacing (Å)		Length (nm)
T IIII	IP (100)	OoP (010)	IP (100)	OoP (010)
Neat PBDTT-FTTE	25.76 ± (1.52)	3.91 ± (0.05)	$4.6 \pm (0.3)$	$1.78 \pm (0.03)$
Blend PBDTT- FTTE:Ph(PDI) ₃	-	$3.98 \pm (0.02)$	-	$1.49 \pm (0.08)$
Neat PBDTTF-FTTE	$26.32 \pm (2.23)$	$3.85 \pm (0.03)$	$4.0 \pm (0.7)$	1.83 ± (0.09)
Blend PBDTTF- FTTE:Ph(PDI) ₃	-	$3.98 \pm (0.03)$	-	$1.30 \pm (0.03)$
Neat Ph(PDI) ₃	22.3	$4.66 \pm (0.07)$	24.3	0.98 ± (0.01)

Table S9. (100) in-plane (IP) and (010) out-of-plane (OoP) *d*-spacings and correlation lengths of pristine and blend polymer films.

All the values are reported as averages from 3 separate datasets.

12. X-ray. Film 20 X-ray Diffraction (GIXRD)

Sample films were prepared using the same conditions as the GIWAXS measurements on 2 cm × 2 cm ZnO/Si substrates (see more details in the GIWAXS section above). Out-of-plane (OoP) grazing incidence 20 X-ray diffraction (GIXRD) measurements were conducted on a Rigaku Smartlab (Jerome B. Cohen X-ray Diffraction Facility, NU) with monochromated CuK α radiation ($\lambda = 1.541$ Å). X-ray beam was aligned sequentially by performing $\theta/2\theta$, Z, Ry, Z scans, and the final Z scan value was set at 50% of maximal intensity. The slit was then changed from PSA open to PSA 0.5 deg. Omega was set as 0.2, and 2 θ was scanned from 3° to 30°. Step was set as 0.03°, and speed was set as 10°/min.

Data analysis was performed in Origin 9 software. The diffraction peak 2θ values were fitted using the Gaussian function in the software package. The Bragg's equation:



 $n\lambda = 2d\sin\theta$

was used to obtain the stacking distances d (n = 1). The GIXRD results agree with the GIWAXS measurements (*vide supra*), confirming the amorphous nature of neat and blend films.

Figure S23. (a) Schematic diagram of GIXRD experiment, (b) GIXRD curves of neat and BHJ blend films.

13. Transient Absorption (TA) Spectroscopy

All the films were spin-coated onto clean glass substrates (VWR, 25 mm × 25 mm) in the Ar-filled glovebox. **PBDTT-FTTE:Ph(PDI)**₃ and **PBDTTF-FTTE:Ph(PDI)**₃ blend films were spin-coated, applying the same conditions as the optimized OPV devices (see the details in solar cell fabrication section). For the control experiments, neat **PBDTT-FTTE** and **PBDTTF-FTTE** films were spin-coated from 11 mg/mL 1,2-dichlorobenzene solution (1000 rpm, 120 s), and neat **Ph(PDI)**₃ films were spin-coated from 22 mg/mL 1,2-dichlorobenzene solution (1000 rpm, 120 s). Samples were enclosed in a cryostat to prevent degradation and O₂ quenching.

Transient absorption (TA) experiments for thin films were performed as described previously.¹⁸ Briefly, ~ 40% of the output of a 1 kHz amplified Ti:sapphire system at 827 nm (1 W, 100 fs, Spitfire, Spectra Physics) is used to pump a laboratory-constructed optical parametric amplifier that is then tuned to the specific excitation wavelength. The pump is depolarized to minimize polarization-specific dynamics. The pump spot size was set to 1 mm diameter (1/*e*) and the pulse energy is attenuated to be <100 nJ/pulse to minimize singlet-singlet annihilation. The probe in the fsTA experiment is generated using 10% of the remaining output by driving continuum generation in a sapphire plate (430-850 nm) or a proprietary crystal from Ultrafast Systems (850-1600 nm). In the nsTA experiment, the probe is generated in a separately delayed broadband laser system (EOS, Ultrafast Systems, LLC). Pump and probe are spatially and temporally overlapped at the sample. The transmitted probe is detected on a commercial spectrometer (customized Helios-EOS, Ultrafast Systems, LLC).

Prior to kinetic analysis, the fsTA data are background/scatter-subtracted and chirp-corrected, and the visible and NIR data sets are spectrally merged (Surface Xplorer 4, Ultrafast Systems, LLC). The kinetic analysis was performed using home written programs in MATLAB and was based on a global fit to selected single-wavelength kinetics. The time-resolution is given as w = 300 fs (full width at half maximum, FWHM); the assumption of a uniform instrument response across the frequency domain and a fixed time-zero (t_0) is implicit in global analysis.

The kinetic data from multiple different wavelengths are fit using the global analysis described below. Each wavelength is given an initial amplitude that is representative of the spectral intensity at time t_0 and varied independently to fit the data. The time/rate constants and t_0 are shared between the various kinetic data and are varied globally across the kinetic data in order to fit the model(s) described below.

To fit the data for the control samples (neat $Ph(PDI)_3$, PBDTT-FTTE, PBDTTF-FTTE films) we use a first-order kinetic model with rate matrix K:

$$K = \begin{bmatrix} -k_1 & 0 & 0 & 0 \\ k_1 & -k_2 & 0 & 0 \\ 0 & k_2 & -k_3 & 0 \\ 0 & 0 & k_4 & 0 \end{bmatrix}$$
(Eqn. S1)

The MATLAB program numerically the solves the first-order differential equations through matrix methods,¹⁹ then convolutes the solutions with a Gaussian instrument response function with width w, before employing a least-squares fitting using a Levenberg-Marquardt or Simplex method to find the parameters which result in matches to the kinetic data.

For the **PBDTT-FTTE:Ph(PDI)**₃ and **PBDTTF-FTTE:Ph(PDI)**₃ blend films, we use a nonlinear kinetic model to properly account for bimolecular recombination of the free charge carriers (k_{FC}) :

$$\frac{dA}{dt} = -k_1[A]$$

$$\frac{dB}{dt} = +k_1[A] - k_2[B] \qquad (Eqn. S2)$$

$$\frac{dC}{dt} = +k_2[B] - k_3[C]$$

$$\frac{dD}{dt} = +k_3[C] - k_{FC}[D]^2$$

The low pulse energy used in the experiment (<100 nJ/pulse) minimizes the influence of singletsinglet annihilation otherwise present in low-fluence experiments that we have reported previously.¹⁸

The MATLAB program solves the higher-order system of differential equations numerically using the Runge-Kutta algorithm, then convolutes the solutions with a Gaussian instrument response function with width *w*, before employing a least-squares fitting to find the parameters which result in matches to the kinetic data.

Once the fit parameters are established, they are fed directly into the differential equations, which were solved for the populations of the states in model—i.e., A(t), B(t), C(t), and D(t). Finally, the raw data matrix (with all the raw data) is deconvoluted with the populations as functions of time to produce the spectra associated with each state (evolution-associated spectra, or EAS).



Figure S24. Time-resolved fsTA spectra at selected time points of film $Ph(PDI)_3$ with $\lambda_{ex} = 520$ nm.



Figure S25. Analysis of the raw **PBDTT-FTTE** pristine film data with $\lambda_{ex} = 700$ nm as described in the text. (a) Time-resolved spectra at selected time points of film **PBDTT-FTTE** with $\lambda_{ex} = 700$ nm. (b) Evolution-associated spectra, τ_1 is the decay of species A to species B, etc. with time constants $\tau = 1/k$ shown in (c). (c) Kinetic fits to the raw data at the indicated wavelengths with the kinetic model described by **Eqn. S1**. (d) Model population kinetics, distribution of species in time.



Figure S26. Analysis of the raw **PBDTTF-FTTE** pristine film data with $\lambda_{ex} = 700$ nm as described in the text. (a) Time-resolved spectra at selected time points of film **PBDTTF-FTTE** with $\lambda_{ex} = 700$ nm. (b) Evolution-associated spectra, τ_1 is the decay of species A to species B, etc. with time constants $\tau = 1/k$ shown in (c). (c) Kinetic fits to the raw data at the indicated wavelengths with the kinetic model described by **Eqn. S1**. (d) Model population kinetics, distribution of species in time.



Figure S27. Analysis of the raw PBDTT-FTTE:Ph(PDI)₃ blend film data with $\lambda_{ex} = 520$ nm as described in the text. (a) Time-resolved spectra at selected time points of PBDTT-FTTE:Ph(PDI)₃ blend film with $\lambda_{ex} = 520$ nm. (b) Evolution-associated spectra, τ_1 is the decay of species A to species B, etc. with time constants $\tau = 1/k$ shown in (c). (c) Kinetic fits to the raw data at the indicated wavelengths with the kinetic model described by Eqn. S2. (d) Model population kinetics, distribution of species in time.



Figure S28. Analysis of the raw **PBDTT-FTTE:Ph(PDI)**₃ blend film data with $\lambda_{ex} = 700$ nm as described in the text. (a) Time-resolved spectra at selected time points of **PBDTT-FTTE:Ph(PDI)**₃ blend film with $\lambda_{ex} = 700$ nm. (b) Evolution-associated spectra, τ_1 is the decay of species A to species B, etc. with time constants $\tau = 1/k$ shown in (c). (c) Kinetic fits to the raw data at the indicated wavelengths with the kinetic model described by **Eqn. S2**. (d) Model population kinetics, distribution of species in time.



Figure S29. Analysis of the raw **PBDTTF-FTTE:Ph(PDI)**₃ blend film data with $\lambda_{ex} = 520$ nm as described in the text. (a) Time-resolved spectra at selected time points of **PBDTTF-FTTE:Ph(PDI)**₃ blend film with $\lambda_{ex} = 520$ nm. (b) Evolution-associated spectra, τ_1 is the decay of species A to species B, etc. with time constants $\tau = 1/k$ shown in (c). (c) Kinetic fits to the raw data at the indicated wavelengths with the kinetic model described by Eqn. S2. (d) Model population kinetics, distribution of species in time.



Figure S30. Analysis of the raw **PBDTTF-FTTE:Ph(PDI)**₃ blend film data with $\lambda_{ex} = 700$ nm as described in the text. (a) Time-resolved spectra at selected time points of **PBDTTF-FTTE:Ph(PDI)**₃ blend film with $\lambda_{ex} = 700$ nm. (b) Evolution-associated spectra, τ_1 is the decay of species A to species B, etc. with time constants $\tau = 1/k$ shown in (c). (c) Kinetic fits to the raw data at the indicated wavelengths with the kinetic model described by **Eqn. S2**. (d) Model population kinetics, distribution of species in time.



Figure S31. nsTA spectra at selected time points of PBDTT-FTTE:Ph(PDI)₃ blend film with $\lambda_{ex} = 520$ nm.



Figure S32. nsTA spectra at selected time points of **PBDTTF-FTTE:Ph(PDI)**₃ blend film with $\lambda_{ex} = 520$ nm.



Figure S33. Raw kinetic traces for the polymer cation decay of **PBDTT-FTTE:Ph(PDI)**₃ and **PBDTTF-FTTE:Ph(PDI)**₃ blends monitored at 1150 nm in the nanosecond regime with their kinetic fits. $\lambda_{ex} = 520$ nm. The kinetics were fit to a sum of three exponential decays convoluted with a Gaussian instrument response.

A Excitation 700 nm



Figure S34. The proposed photophysical process in current polymer: **Ph(PDI)**₃ OPV systems under (a) $\lambda_{ex} = 700$ nm or (b) $\lambda_{ex} = 520$ nm laser excitation, respectively. S₁ and T₁ are the lowest-energy spin-singlet and spin-triplet excited states, respectively. The formation of interfacial ¹CT state that separates into free charges (FCs) efficiently, while in turn the bimolecular recombination of free electrons and holes leads to the formation of ¹CT state. ¹CT is the spin-singlet charge-transfer state. GS is the ground state. FRET is Förster resonance energy transfer.

14. Computation

14.1. Dipole calculations

The ground state dipole moment (p_g) was calculated using the optimized geometry for each oligomer (monomer, N = 1; dimer, N = 2; trimer, N = 3; tetramer, N = 4) using a B3LYP functional and 6-31G(d) basis set. The excited state dipole moment (p_e) was calculated using the same optimized geometry linear-response TDDFT with a ω B97X-D3 functional to get the CT nature of the exciton modeled with a range-tuned functional. The cc-pVDZ basis set was used. A cc-pVTZ basis was used on the smaller oligomers (N = 1,2), but the dipole moments did not change by more than 10 %. The Q-Chem electronic structure package was used for the DFT and TDDFT calculations.^{20, 21} The dipole difference Δp_{eg} is calculated using the Euclidean distance between p_g and p_e or

$$\Delta p_{eg} = \sqrt{\left(p_e^x - p_g^x\right)^2 + \left(p_e^y - p_g^y\right)^2 + \left(p_e^z - p_g^z\right)^2}$$
(Eqn S3)

The angle between the two dipole moments (θ_{eg}) is just the vector projection definition or

$$\theta_{eg} = \cos^{-1} \frac{\boldsymbol{p}_g \cdot \boldsymbol{p}_e}{|\boldsymbol{p}_g| |\boldsymbol{p}_e|}$$
(Eqn S4)

The dipole moment calculations for the N = 1-4 oligomers for **PBDTTF-FTTE** and **PBDTT-FTTE** polymers is summarized in **Tables S10-S13**. The oligomer geometries for each dipole calculation is shown after corresponding table in **Figures S35-S38**.

lsomer	PBDTT-FTTE	PBDTTF-FTTE
	x y z	x y z
p _g (Debye)	-2.4000, -0.7197, 0.1621	-2.4987, -1.7446, 0.1498
p _e (Debye)	-4.7969, -2.1702, 0.3278	-3.6705, -2.6854, 0.2432
p _{tr} (Debye)	2.3158, 2.2564, 0.0296	1.9927, 2.5634, -0.0140
	Total	Total
p _g (Debye)	2.51083	3.05116
p _e (Debye)	5.27517	4.55446
p _{tr} (Debye)	3.23344	3.24686
Δp_{eg} (Debye)	2.80652	1.50564
$ heta_{eg}$ (°)	7.63601	1.28915
Gap (eV)	3.4237	3.4454

Table S10. Monomer (N = 1) dipole moments.



Figure S35. Monomer optimized geometries for (A) PBDTT-FTTE and (B) PBDTTF-FTTE.

Isomer	PBDTT-FTTE	PBDTTF-FTTE		
	x y z	x y z		
p _g (Debye)	-4.2335, 1.4371, 0.5754	-3.6246, 2.3597, 0.6438		
p _e (Debye)	-3.1618, 1.0306, 0.4329	-2.4051, 2.0454, 0.5757		
p _{tr} (Debye)	5.6308, 0.6682, -0.1726	5.4662, 0.3642, -0.2763		
	Total	Total		
p _g (Debye)	4.50765	4.37269		
p _e (Debye)	3.35358	3.2093		
p _{tr} (Debye)	5.67293	5.48528		
Δp_{eg} (Debye)	1.15503	1.26119		
θ _{eg} (°)	0.695883	7.45322		
Gap (eV)	2.8904	2.8881		

Table S11. Dimer (N = 2) dipole moments.



Figure S36. Dimer optimized geometries for (A) PBDTT-FTTE and (B) PBDTTF-FTTE.

Isomer	PBDTT-FTTE	PBDTTF-FTTE			
	x y z	x y z			
p _g (Debye)	-3.1365 , 3.7425, 0.0280	-6.1296, 2.9579, -0.0332			
p _e (Debye)	2.2060, 3.2532, 0.2942	5.1465, 2.1926, 0.2987			
p _{tr} (Debye)	6.9961, -0.6773, -0.1272	7.0377, -0.6863, -0.1099			
	Total	Total			
p _g (Debye)	4.88311	6.80605			
p _e (Debye)	3.94161	5.60207			
p _{tr} (Debye)	7.02996	7.07194			
Δp_{eg} (Debye)	5.37146	11.3069			
$ heta_{eg}$ (°)	74.1271	131.112			
Gap (eV)	2.6816	2.6734			

Table S12. Trimer (N = 3) dipole moments.



Figure S37. Trimer optimized geometries for (A) PBDTT-FTTE and (B) PBDTTF-FTTE.

lsomer	PBDTT-FTTE	PBDTTF-FTTE			
	x y z	x y z			
p _g (Debye)	-4.4177, 4.4856, 0.1778	-7.7753, 3.7247, 0.6688			
p _e (Debye)	3.5432, 3.7314, 0.5427	7.0670, 2.7658, 0.1068			
p _{tr} (Debye)	7.9932, -0.6706, -0.2283	8.0372, -0.5663, -0.3739			
	Total	Total			
p _g (Debye)	6.29828	8.64731			
p _e (Debye)	5.17418	7.5897			
p _{tr} (Debye)	8.02453	8.0658			
Δp_{eg} (Debye)	8.00487	14.8839			
$ heta_{eg}$ (°)	87.9227	132.78			
Gap (eV)	2.5939	2.6125			

Table S13. Tetramer (N = 4) dipole moments.



Figure S38. Tetramer optimized geometries for (A) PBDTT-FTTE and (B) PBDTTF-FTTE.

14.2. Frontier Molecular Orbitals



Figure S39. HOMO of **PBDTT-FTTE** trimer. Isosurface contour value is +/- 0.01.



Figure S40. LUMO of PBDTT-FTTE trimer. Isosurface contour value is +/- 0.01.



Figure S41. HOMO of PBDTTF-FTTE trimer. Isosurface contour value is +/- 0.01.



Figure S42. LUMO of PBDTTF-FTTE trimer. Isosurface contour value is +/- 0.01.

14.3. Exciton delocalization

The electron-hole separation calculated from the spatial distance between the center of the hole and electron positions from the decomposed TDDFT wavefunction.²² We summarize the electron-hole separation R_{eh} in **Table S14** for the set of oligomers for **PBDTT-FTTE** and **PBDTTF-FTTE**.

	PBDTT-FTTE			PBDTTF-FTTE				
N	1	2	3	4	1	2	3	4
R _{eh} (A)	0.648	0.121	0.171	0.109	0.362	0.280	0.207	0.122

 Table S14. Exciton electron-hole separation.

14.4. Potential energy surface calculations

The potential energy surface calculations were run using an optimized geometry search at each torsion angle. The angles were chosen in 10° steps over the full range -180° to 180° due to the asymmetry of the fluorination. The functional used was B3LYP and a 6-31G(d) basis set. The energy scale was set from the minimum energy found such that in **Figures S43-46**, $E = E_{opt} - E_{min}$. Four torsion angles were considered for the potential energy surface calculations; two along the backbone (one on each side of the **FTTE** unit; ϕ_1 and ϕ_2) and two on the thiophene side-chains ϕ_{S1} and ϕ_{S2} (see inset of **Figures S43-46** for angle assignment).



Figure S43. The 1D potential energy surface of the during the rotation of the ϕ_1 torsion angle for the **PBDTTF-FTTE** polymer (black circle) and the **PBDTT-FTTE** polymer (red square). The minimum energy angle is circled at 30°.



Figure S44. The 1D potential energy surface of the during the rotation of the ϕ_2 torsion angle for the **PBDTTF-FTTE** polymer (black circle) and the **PBDTT-FTTE** polymer (red square). The minimum energy angle is circled at 160°.



Figure S45. The 1D potential energy surface of the during the rotation of the ϕ_{S1} torsion angle for the **PBDTTF-FTTE** polymer (black circle) and the **PBDTT-FTTE** polymer (red square). The minimum energy angle is circled at 130°.



Figure S46. The 1D potential energy surface of the during the rotation of the ϕ_{S2} torsion angle for the **PBDTTF-FTTE** polymer (black circle) and the **PBDTT-FTTE** polymer (red square). The minimum energy angle is circled at 120°.

15. References

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