

New Donor Polymer with Tetrafluorinated Blocks for Enhanced Performance in Perylenediimide-Based Solar Cells

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Materials and Methods

Common solvents, tetrakis(triphenylphosphine)palladium ($\text{Pd}(\text{PPh}_3)_4$) and *N,N*-dimethylformamide (DMF) (anhydrous, 99.8%) were purchased from Sigma Aldrich and used without further purification. Toluene was purified via a Grubbs type column.

Density Functional Theory (DFT) calculations were performed by using QChem¹ and the results were visualized on jMol.² Elemental analyses (EA) of the polymer samples were performed by Midwest Microlab LLC, Indianapolis, IN. Gel Permeation Chromatography (GPC) of the polymers was performed on Polymer Laboratories PL-GPC 220 instrument equipped with a set of three PLgel 10 μm mixed-B columns and dual detector system. Polymer solutions of ~ 0.5 mg/mL were prepared on 1,2,4-trichlorobenzene by heating and stirring for 3 h at 150 $^\circ\text{C}$, and experiments were run in the same solvent at same temperature, and data analyzed vs polystyrene standards. Differential scanning calorimetry (DSC) was performed on an indium-calibrated Mettler-Toledo DSC822e with a heating ramp of 10 $^\circ\text{C}/\text{min}$. Thermograms from the second heating-cooling cycle are reported. Thermogravimetric analysis (TGA) was performed on Mettler-Toledo TGA/SDTA851e with the decomposition temperature (T_d) reported for loss of 5 % of the initial weight of the sample. Cyclic Voltammetry (CV) was performed on a C3 Cell Stand electrochemical station equipped with BAS Epsilon software (Bioanalytical Systems, Inc., Lafayette, IN). The analyte and ferrocene were dissolved in dry methylene chloride (concentration $\sim 1\text{mM}$ for both), along with the electrolyte tetrabutylammonium hexafluorophosphate (concentration 0.1 M). All scans were performed at 100 mV/s under inert atmosphere. A platinum working electrode (3 mm diameter), a Pt-wire counter electrode and a Ag-wire pseudo-reference electrode were employed. Polymers films were drop-cast onto working electrode. Steady state UV-Vis absorption spectra were recorded on Varian Cary 50 Scan UV-Vis spectrophotometer. Film fluorescence spectra were measured with Horiba NanoLog TCSPC spectrophotometer with the films angled at 30 $^\circ$ to the excitation beam. Tapping mode AFM were obtained with a JOEL JSPM-5200 atomic force microscope. Grazing incidence wide angle x-ray scattering (GIWAXS) measurements were performed at Beamline 8-ID-E³ of the Advanced Photon Source at Argonne National Laboratory as per previously described methods.⁴ X-ray beam of $\lambda = 1.6868$ \AA was used, and data were collected on a Pilatus 1M pixel array detector. All spectra were normalized with respect to exposure time and attenuation, and corrected for detector non-uniformity and efficiency, and converted to q -space using the GIXSGUI package for Matlab.⁵

OFET devices were fabricated as follows. The surfaces of heavily doped silicon substrates with a 300 nm thick thermally grown SiO_2 layer (WRS Materials) were cleaned with ultrasonication in warm acetone and isopropyl alcohol, and were then treated with O_2 plasma for 1 min. Around 80 nm thick film of organic semiconductors were spun coated with from a $\sim 7\text{mg}/\text{mL}$ solution of the polymer in chlorobenzene. Transistor fabrication was complete when 30 nm thick top Au electrodes were deposited through shadow masks. The resulting devices had channel lengths and widths of 50 and 1000 μm , respectively. Devices were tested in ambient conditions in the dark with an Agilent B1500A semiconductor parameter analyzer. Mobilities were extracted from saturated regimes by averaging results for at least 4 devices.

Organic photovoltaic (OPV) devices were fabricated and tested according to previously reported procedures⁴ except for the solvent used and device thicknesses, which are detailed in the main text. Light intensity based measurements were made by using neutral density filters and a

calibrated light source that radiates at one-sun intensity Femtosecond Transient Absorption (fsTA) Spectroscopy. Transient spectra were collected using 10 nJ, 100 fs pump pulses focused to a spot size of 1 mm and operating at a 100 kHz repetition rate in order to minimize excitation density and avoid exciton annihilation. All samples were excited at 525 nm. Details of the transient absorption instrumentation and experimental methodology have been reported previously.⁴ The measurements for intensity based experiments were performed as follows: on a **PBTZF4:bPDI2P** film by exciting a circular spot of 1 mm diameter of with a 10, 20 and 50 nJ laser energy and the fsTA data was integrated over 730-750 nm to obtain the kinetic profile of CS states generated under differing excitation intensities.

Polymers Synthesis

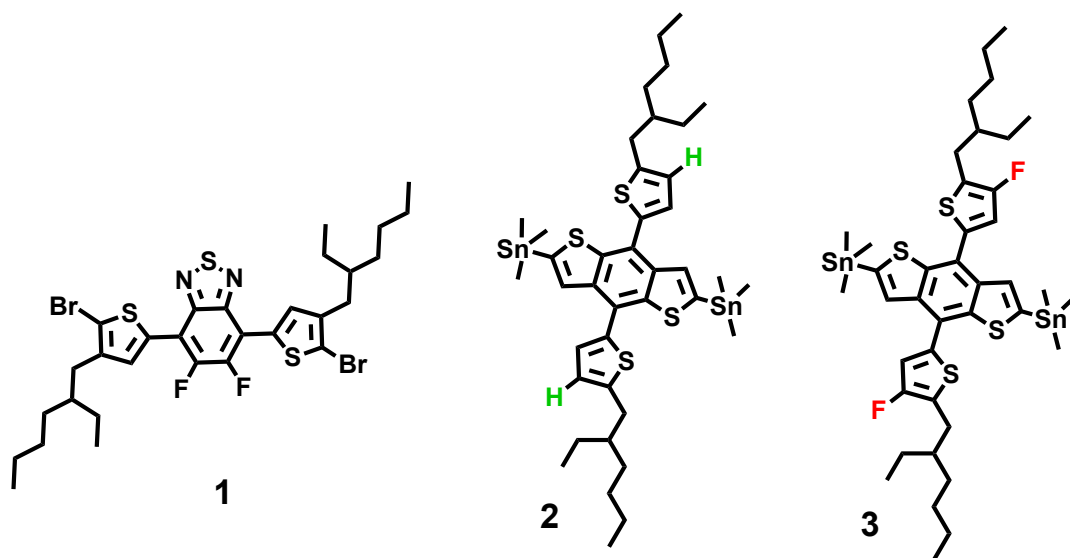


Figure S1. Chemical structure of functionalized building blocks used for the polymers (**PBTZF2/F4**) synthesis.

Building blocks 5,6-difluoro-4,7-dithien-2-yl-2,1,3-benzothiadiazole (**1**),⁶ 4,8-bis(thiophene-2-yl)-benzo[1,2-b:4,5-b']dithiophene (**2**),⁷ 4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene, (**3**),⁸ were synthesized as reported in the literature. **PBTZF4** was synthesized under inert atmosphere (N_2) via modified Stille-coupling reaction. Building blocks **1** (75.8 mg, 1.05×10^{-4} mol) and **2** (99.0 mg, 1.05×10^{-4} mol) were charged into a sealable flame-dried vial, followed by the addition of 5 ml dry solvent (3:1 toluene:DMF mixture by volume). The solution was then purged with N_2 for 10 min and the catalyst $Pd(PPh_3)_4$ (3.6 mg, 3 mol%) added. The vessel was then sealed with a Teflon cap and heated at 110 °C under stirring. The reaction mixture was allowed to cool and, while maintaining inert conditions, $Pd(PPh_3)_4$ (1 mg) and 2-(tributylstannyl)thiophene (20 mg, 0.5 eq) were added and the flask resealed. The reaction mixture was then stirred for 12 h at 110 °C, and allowed to cool down. This was followed by addition of 3-bromothiophene (51.6 mg, 3 eq.) into the reaction mixture under inert conditions and resealing of the vessel, stirred for another 12 h at 110 °C. The reaction mixture was cooled down to room temperature and transferred into a vessel containing 200 mL MeOH. The precipitate was filtered off and transferred into a cellulose thimble. After

sequential Soxhlet purification with MeOH, acetone, hexanes and chloroform, the final compound was extracted with chlorobenzene. The chlorobenzene fraction was re-precipitated in MeOH, filtered off, and dried in vacuum overnight to obtain 71 mg solid (57% yield). Elemental composition calculated for $C_{64}H_{74}F_4N_2S_7$: C, 65.60; H, 6.36; N, 2.39; found C, 65.11; H, 6.09; N, 2.30; $M_n = 17.0$ kDa; PDI = 1.72. Polymer **PTBZF2** was synthesized and isolated similar manner (39% yield). Elemental composition calculated for $C_{64}H_{76}F_2N_2S_7$: C, 67.68; H, 6.74; N, 2.47; found C, 65.67; H, 6.54; N, 2.20. $M_n = 17.2$ kDa; PDI = 1.59.

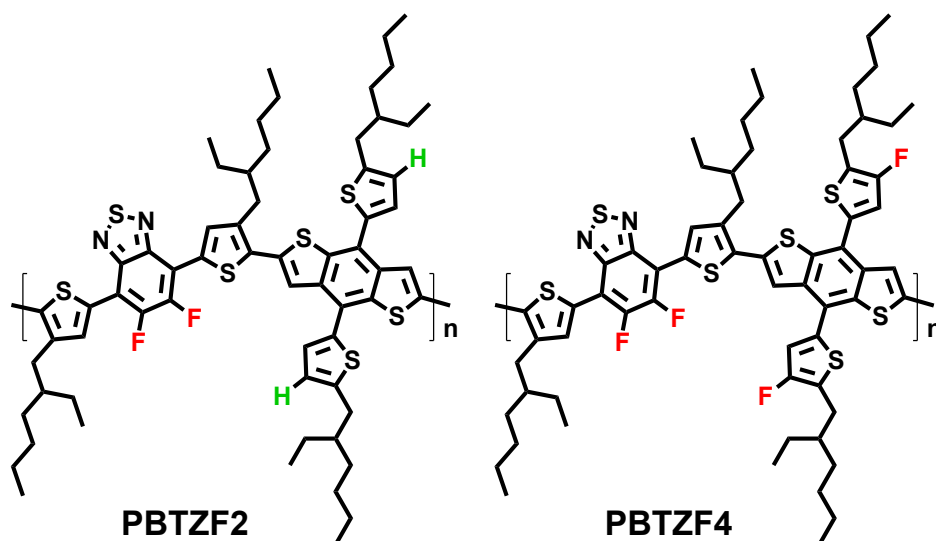


Figure S2. Chemical structure of polymers **PBTZF2/F4**.

DSC/TGA Thermograms

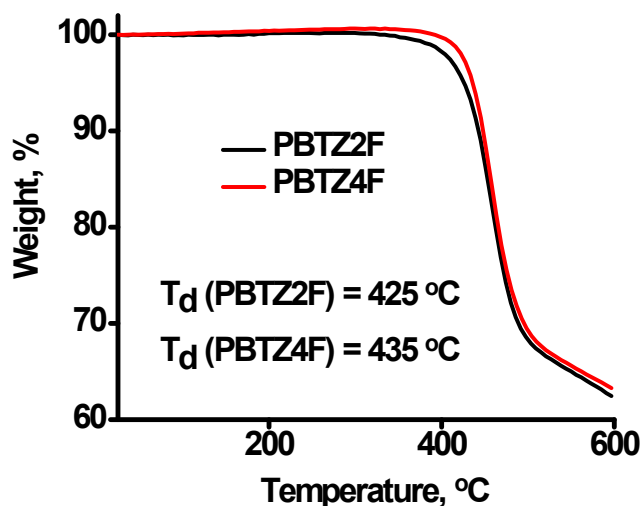


Figure S3. TGA thermograms of **PBTZF2/F4**.

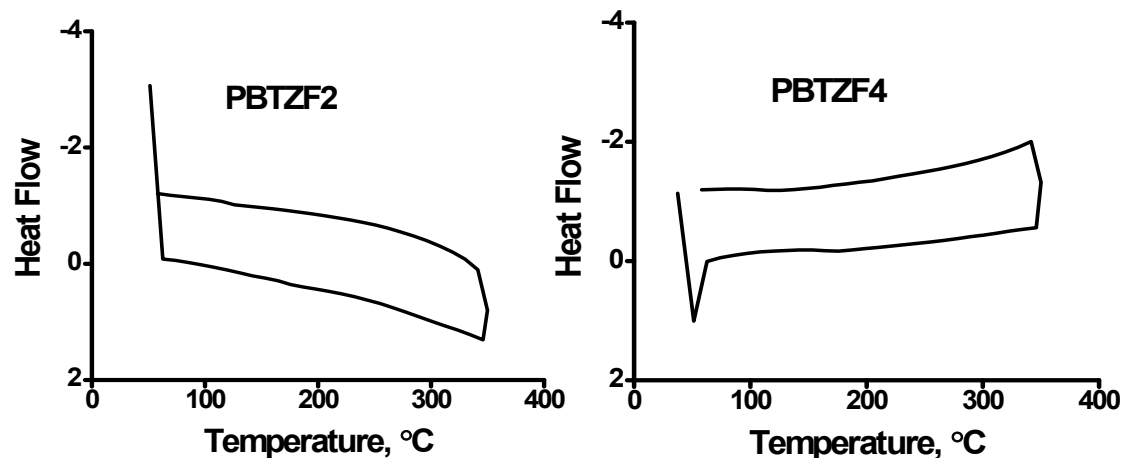


Figure S4. DSC heating (heat flow, endo up) and cooling traces for **PBTZF2/F4**.

DFT Calculations

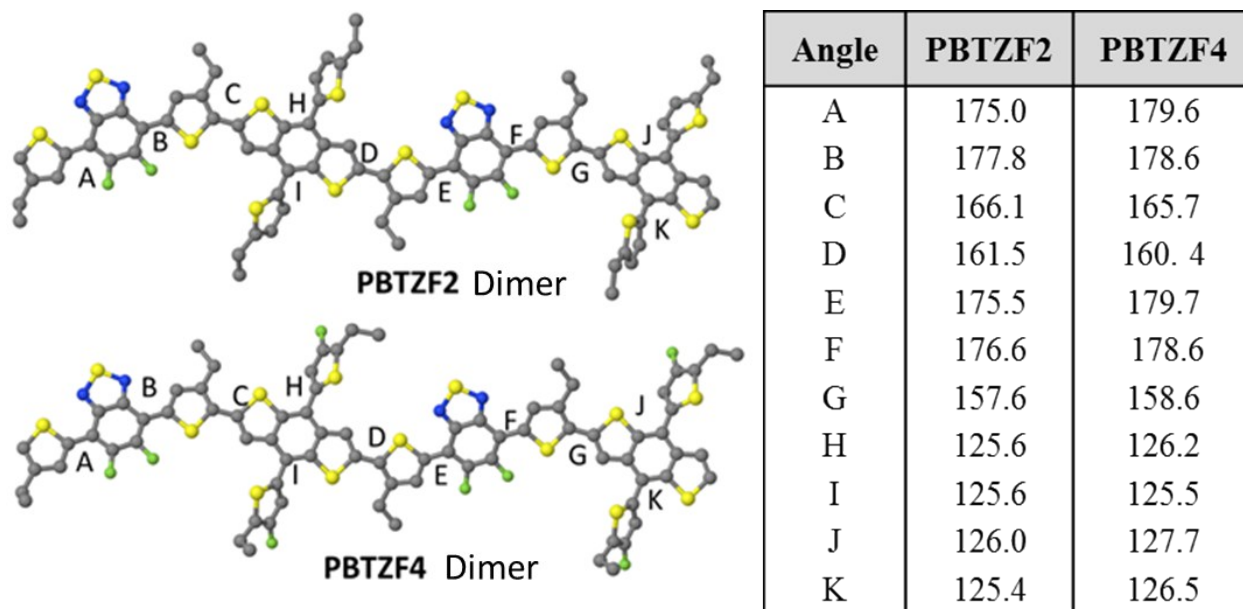


Figure S5a. Geometry optimized structures of the **PBTZF2/F4** model compounds (two repeating units). CCC dihedral angles were measured in each case. All angles refer to the angle of rotation of adjacent aromatic rings around the single bonds indicated.

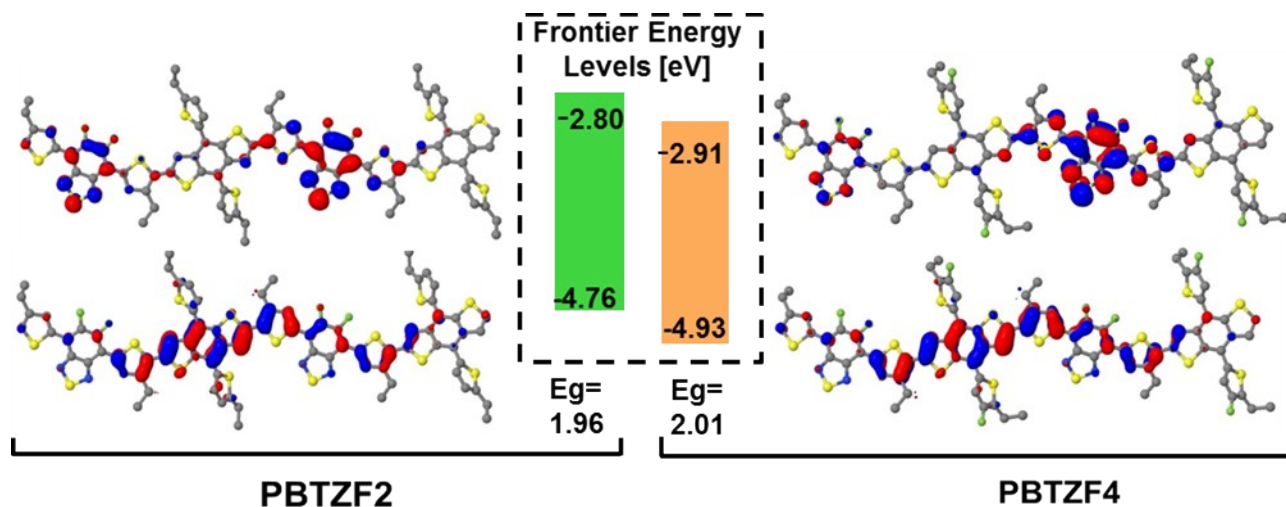


Figure S5b. Frontier orbitals and energy levels of PBTZF2/F4 model compounds.

Cyclic Voltammetry (CV)

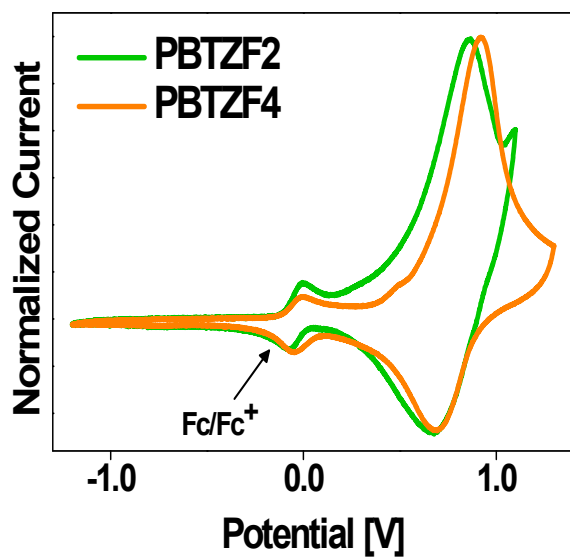


Figure S6. CV of the polymers with midpoint of the Fc/Fc⁺ internal standard redox peak calibrated to 0.0 V.

UV-vis Spectra

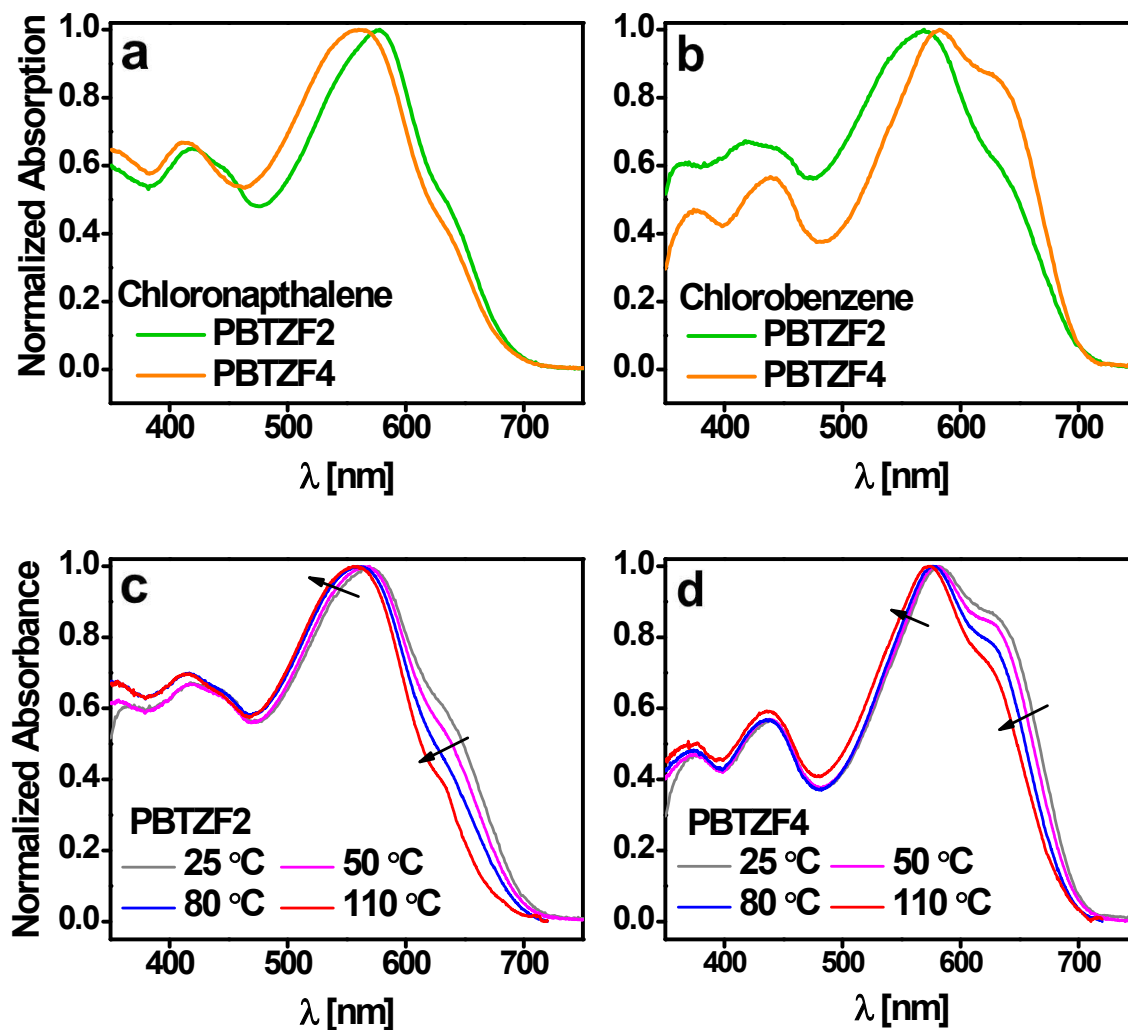


Figure S7. UV-vis spectra of the polymers in 1-chloronaphthalene (a) and in chlorobenzene (b) ($\sim 1 \times 10^{-5}$ M). c,d. variable temperature spectra in chlorobenzene.

Photoluminescence Spectra

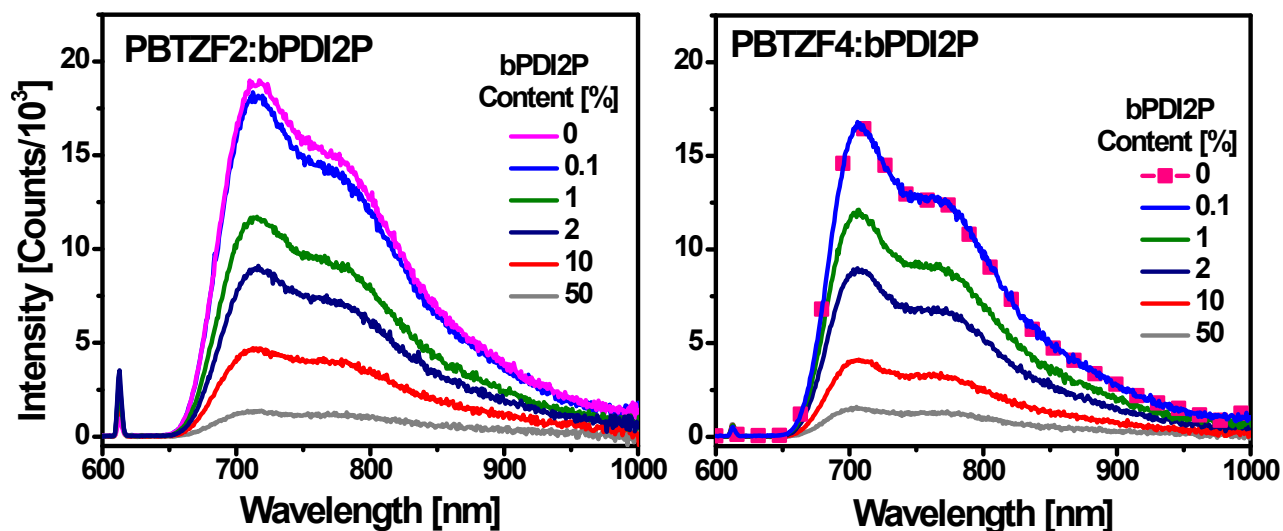


Figure S8. Photoluminescence spectra of films with different polymer:bPDI2P content. Excitation energy (615 nm) is lower than the band gap of the bPDI2P (~600 nm).

Table S1. Photoluminescence Quenching (Δ PL) of PBTZF2/F4.^a

bPDI2P content [%]	Δ PL [%]	
	PBTZF2	PBTZF4
0	-	-
0.1	5	<1
1	38	27
2	52	46
10	73	74
50	94	92

^a Films spuncast on ZnOx coated glass slides from chlorobenzene solution of the blends (5 mg/mL by polymer). Photoluminescence values are absorbance corrected.

OPV Performance Optimization

Table S2. Summary of OPV Performance Optimization*

Donor	Anneal. [°C]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
PBTZF4	-	1.118	10.02	49.5	5.55^b
PBTZF4	100	1.117	9.76	48.4	5.27
PBTZF4	200	1.117	8.68	48.3	4.68
PBTZF2	-	0.993	9.21	40.0	3.68^b
PBTZF2	100	0.997	7.07	43.0	3.03

*Performance of best device of ITO/ZnO_x/polymer:bPDI2P/MoO₃/Ag device structure with ~85 nm thick polymer:bPDI2P films spuncast from chlorobenzene solution. ^a wt:wt ratio. ^b Performance parameters of the highest performing devices for each polymer are highlighted in bold and are discussed in the main text.

fsTA Spectroscopy

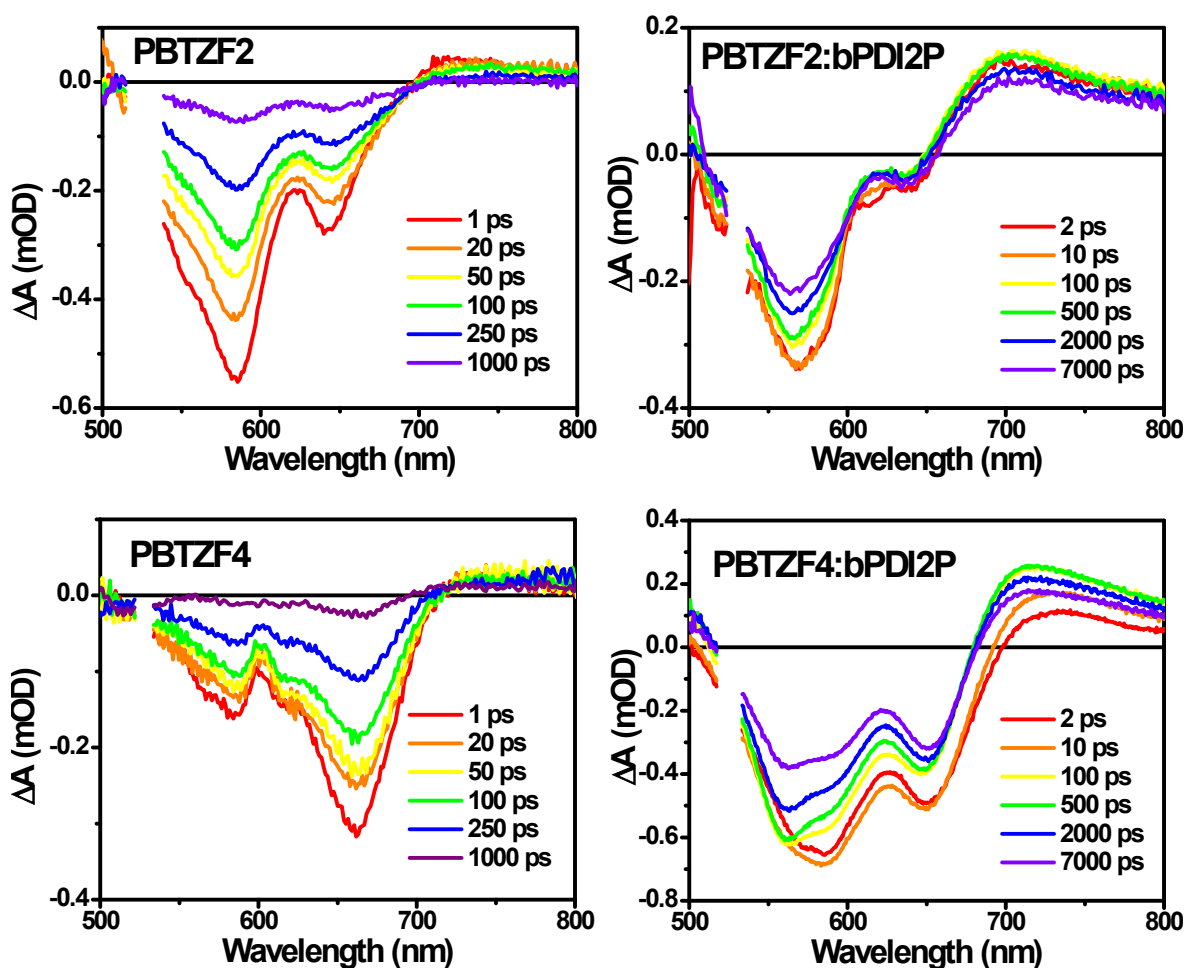


Figure S9. fsTA spectra of pristine polymer films and polymer:bPDI2P blend films.

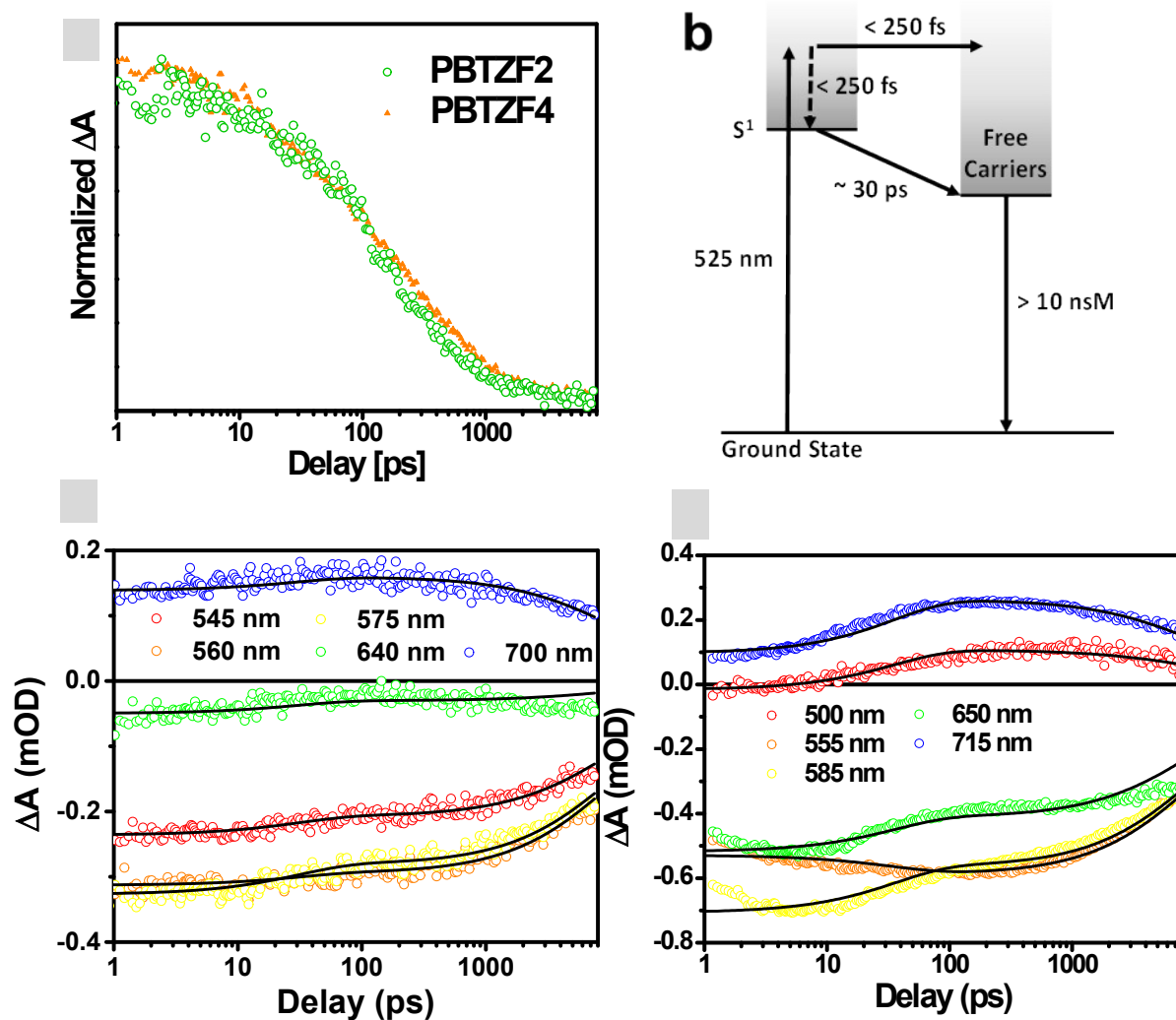


Figure S10. a. Decay kinetics of the excited states of the indicated neat polymer films with biexponential decay constants of 100 ps and 530 ps for **PBTZF2** and 29 ps and 410 ps for **PBTZF4**. b. Model proposed for charge separation and recombination processes in the blends. c,d. Agreement between fsTA data obtained (points) and the fits according to the proposed model (lines) the **PBTZF2:bPDI2P** and **PBTZF4:bPDI2P** blends, respectively.

Light Intensity and Photocurrent

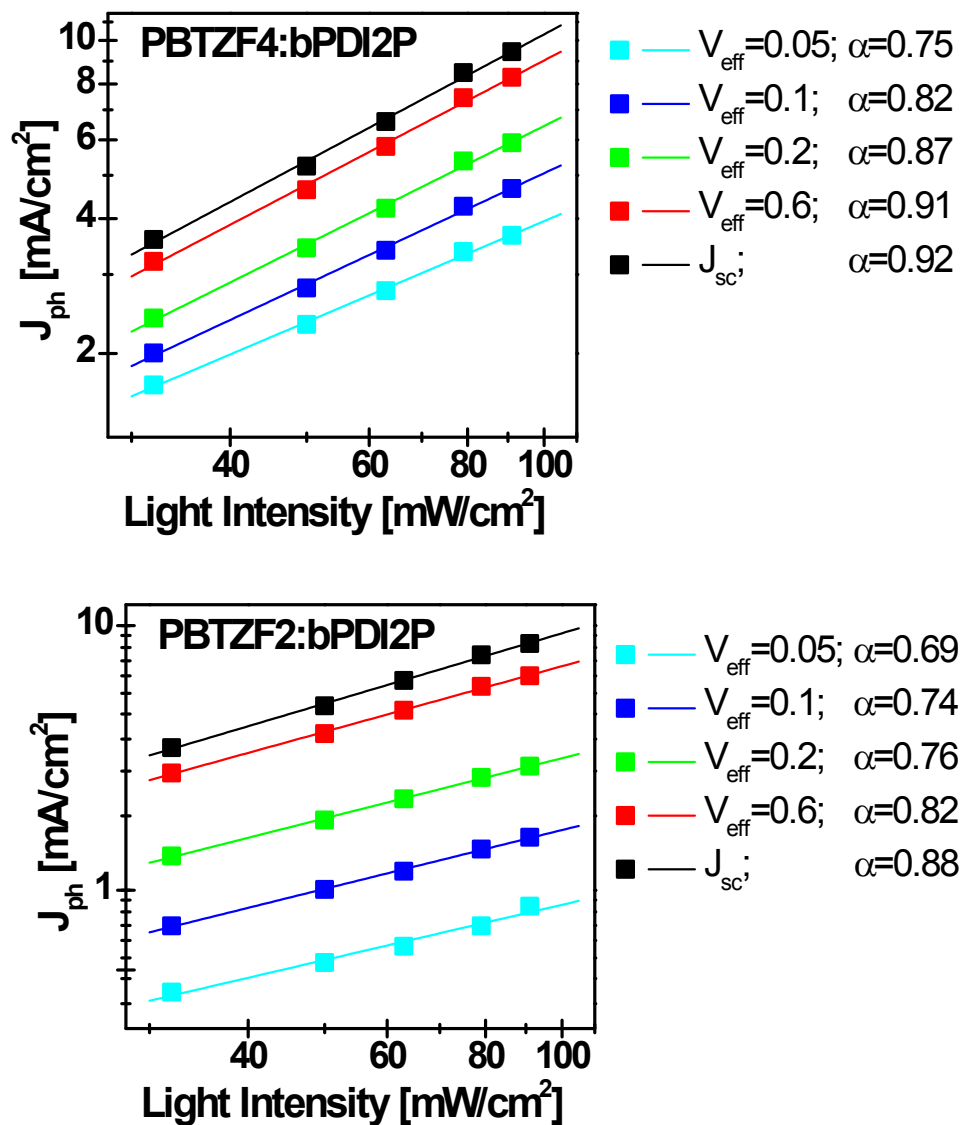


Figure S11. J_{ph} – Light-Intensity plots at different V_{eff} . Slopes of the lines (α) are shown.

GIWAXS

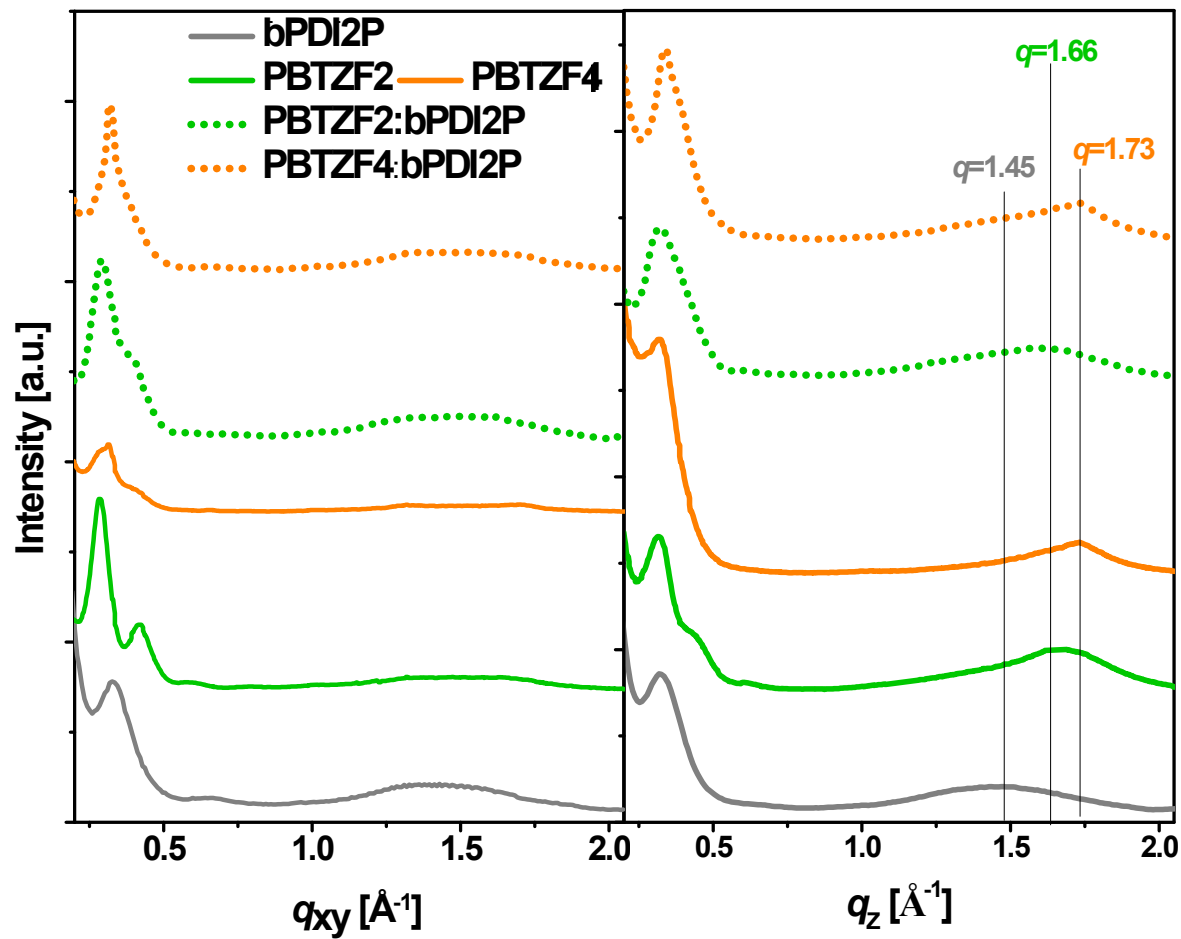
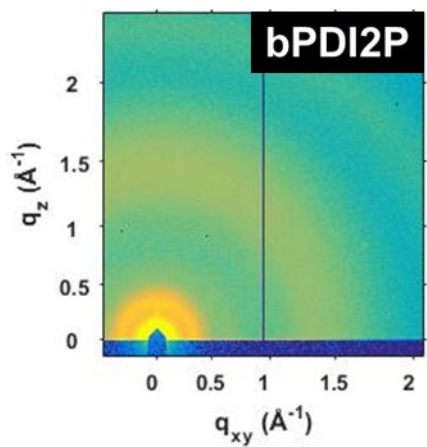


Figure S12. 2D GIWAXS spectra of **bPDI2P** (top); in-plane (bottom left) and out-of-plane (bottom right) line cuts of the 2D GIWAXS spectra.

AFM

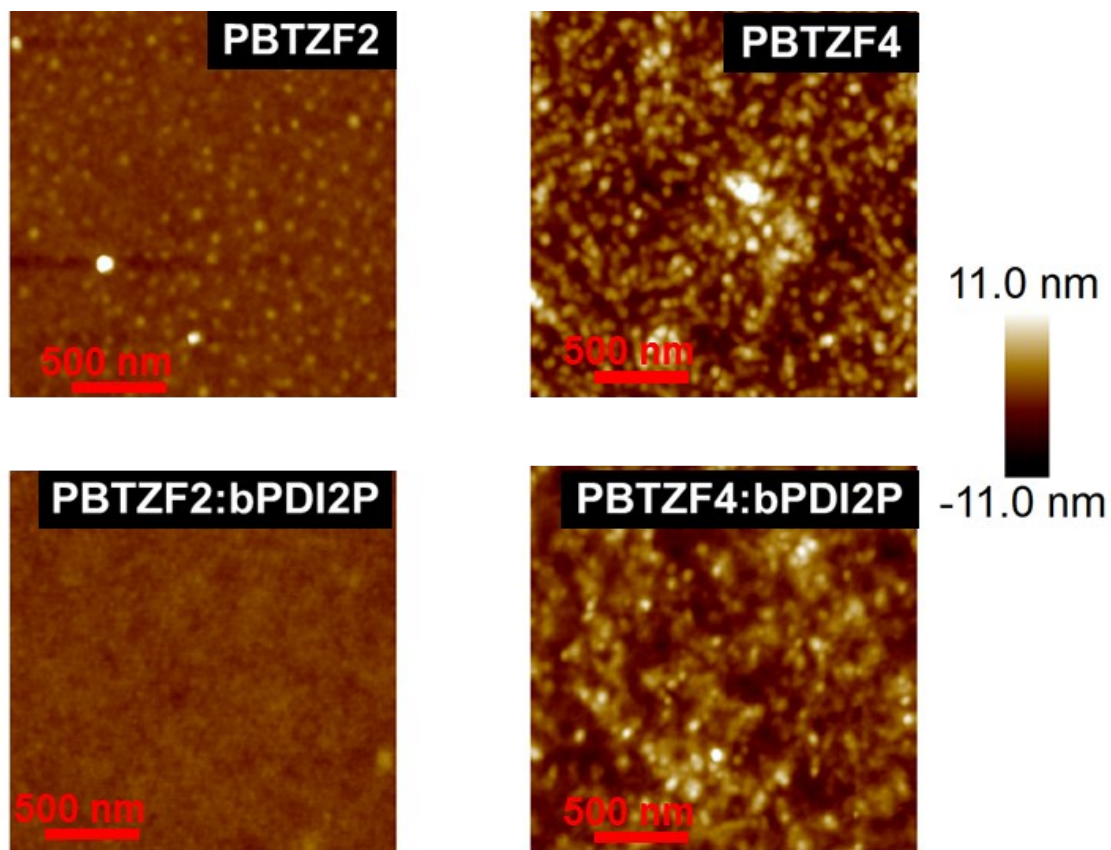


Figure S13. AFM (height) images for neat and blend polymer films. Rq roughness: **PBTZF2** (0.51 nm), **PBTZF4** (2.1 nm), **PBTZF2:bPDI2P** (0.39 nm), **PBTZF4:bPDI2P** (1.82 nm).

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