

Supporting Information

Suppression of Recombination Energy Losses by Decreasing the Energetic Offsets in Perylene Diimide-Based Nonfullerene Organic Solar Cells

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Materials. The perylene diimide-based nonfullerene acceptors, TPH-Se and T-2, and the donor PDBT-T1 were synthesized in our lab as reported previously.¹⁻³ The donors P3HT and PTB7-Th were purchased from Organic Nano Electronic. The donor PBDT-TS1 was purchased from Solarmer.

Measurements. UV-vis absorption spectra of the pure and blend films were acquired with a UV-vis spectrophotometer (Shimadzu UV-2600). All film samples were spin-cast onto the ITO/PEDOT:PSS substrate, as the photovoltaic device structure used in this work is ITO/PEDOT:PSS/Active layer/ZrAcac/Al. First, the ITO/PEDOT:PSS substrate was scanned as a blank to provide a spectral background, and then we measured the absorption spectra of samples. Cyclic voltammogram (CV) measurement was carried out on a Zahner IM6e electrochemical workstation with three electrodes, using a glassy carbon discs as the working electrode, Pt wire as the counter electrode, and Ag/AgCl electrode as the reference electrode at a scanning rate of 100 mVs⁻¹ under a nitrogen atmosphere. 0.1 mol l⁻¹ tetrabutylammoniumhexafluorophosphate (Bu₄NPF₆) dissolved in acetonitrile (HPLC grade) was employed as the supporting electrolyte. Polymers and small molecules were drop-cast the electrode from chloroform solutions (2mg ml⁻¹) to form thin films. Potentials were referenced to the ferrocene/ferroncenium (Fc/Fc⁺) redox couple by using ferrocene as the external standards in acetonitrile solutions.

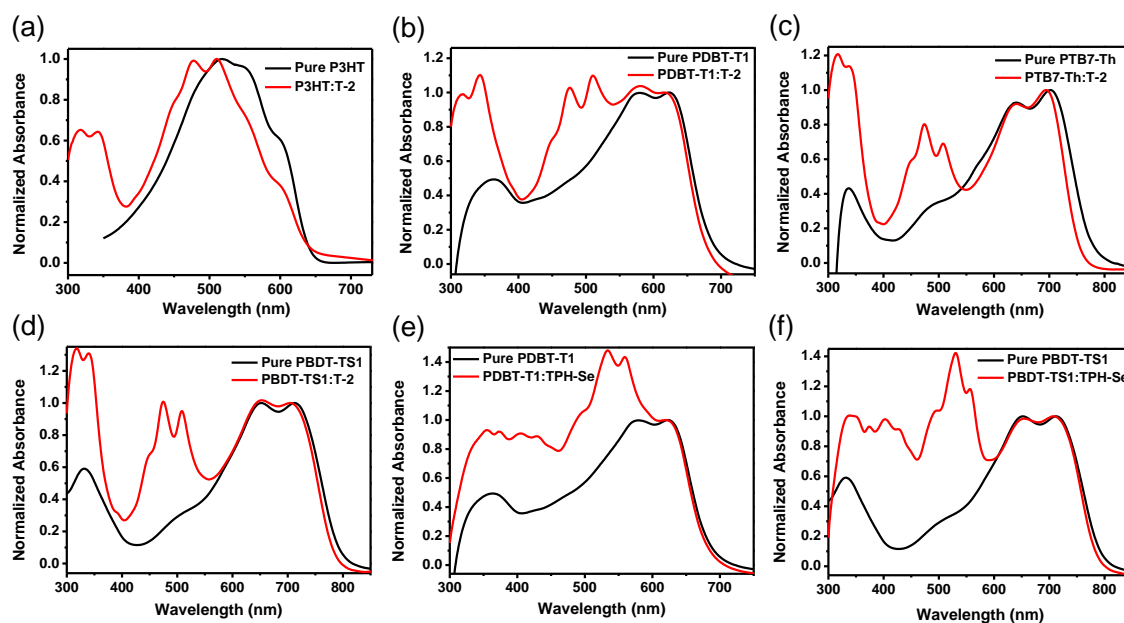


Figure S1. Normalized UV-vis absorptions of the (a) P3HT:T-2, (b) PDBT-T1:T-2, (c) PTB7-Th:T-2, (d) PBDT-TS1:T-2, (e) PDBT-T1:TPH-Se, and (f) PBDT-TS1:TPH-Se blend films and the corresponding donor films.

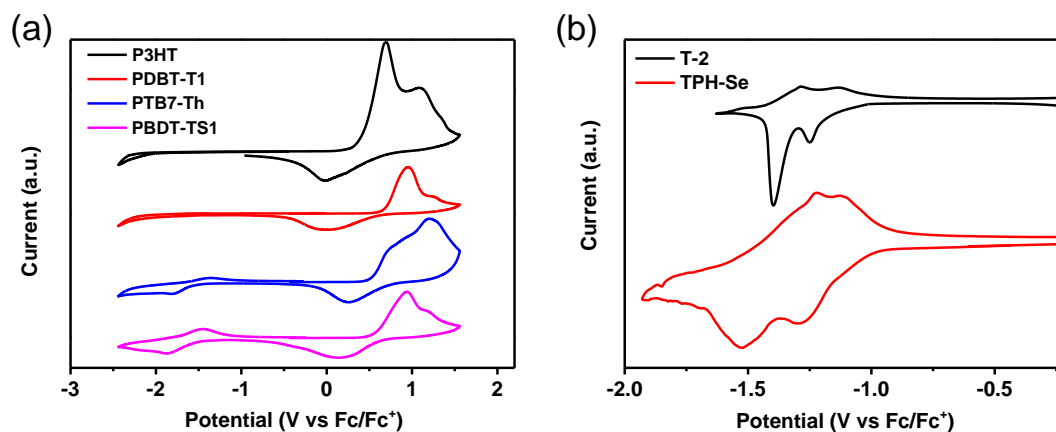


Figure S2. Cyclic voltammetry curves for (a) four polymer donors (P3HT, PDBT-T1, PTB7-Th, PBDT-TS1) and (b) two PDI-based small molecule acceptors (T-2, TPH-Se) in films, with a scan rate of 0.1 V s^{-1} (calibrated by Fc/Fc^+ redox couple).

Fabrication and Testing of OSC Devices: Prepatterned ITO-coated glass substrates were cleaned with detergent and ultrasonicated in deionized water, acetone and isopropanol for 20 min each and subsequently dried in an oven overnight. The substrates were treated by

ultraviolet-ozone for 30 min before using. PEDOT:PSS (Heraeus Clevious P VP. AI 4083, filtered at 0.45 μm) was spin-cast onto the ITO surface at 4000 r.p.m. for 30 s (the thickness is about 40 nm), and baked at 150 $^{\circ}\text{C}$ for 15 min in air. Then the active layers (D/A ratio 1:1) were spin-coated from CB solutions in a N_2 -filled glove box. The optimal active layer thickness was about 100 nm (measured on a Bruker Dektak XT profilometer). The ethanol solution of zirconium acetylacetonate (ZrAcac , 1.4 mg/mL) was spin-cast on the BHJ layer at 3500 r.p.m. for 30 s as the electron transport layer. Finally, a 100 nm Al electrode was deposited through a shadow mask under a vacuum about 1×10^{-4} Pa. The active area was 4.0 mm^2 . During the measurement, an aperture with the area of 3.14 mm^2 was used. Device current density-voltage (J - V) characteristics were recorded using a Keithley 2400 Source Measure Unit. The photocurrent was tested under AM 1.5G illumination at 100 mW cm^2 using a solar simulator (Class AAA solar simulator, Model 94063A, Oriel). The light intensity was calibrated using a standard Si solar cell and a readout meter (Model 91150V, Newport). The EQE spectra were acquired from a QEX10 Solar Cell EQE measurement system (PV measurement, Inc.).

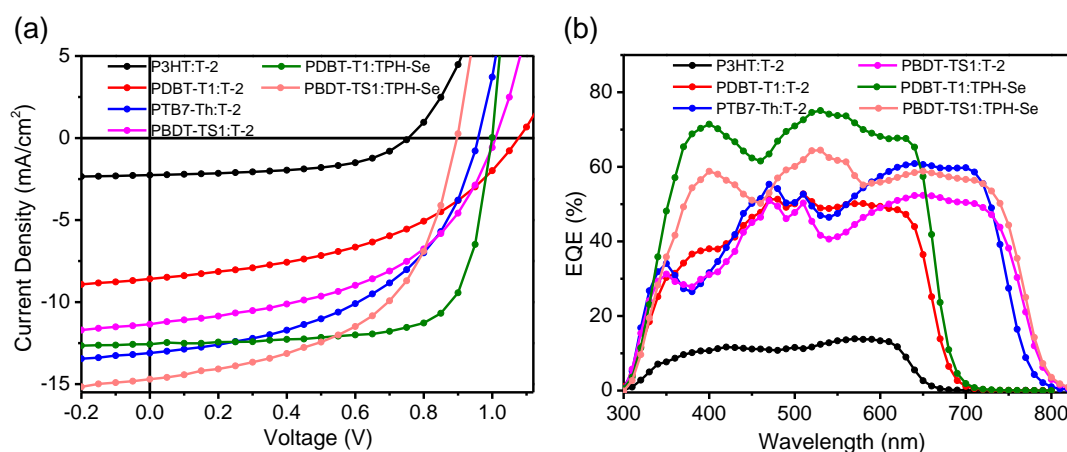


Figure S3. (a) Current density-voltage (J - V) characteristics of devices based those six blends and (b) the corresponding EQE spectra.

Table S1. Photovoltaic parameters of the nonfullerene OSCs studied in the work under the illumination of AM 1.5G, 100 mW cm⁻².

D:A	V_{oc} (V)	J_{sc} (mA cm ⁻²) ^a	FF (%)	PCE (%)	E_g (eV)	$q\Delta V_{oc}$ (eV) ^b
P3HT:T-2	0.76	2.26 (1.92)	54.2	0.92	1.92	1.16
PDBT-T1:T-2	1.08	8.59 (8.31)	45.1	4.18	1.86	0.78
PTB7-Th:T-2	0.97	13.11 (12.62)	49.2	6.18	1.64	0.67
PBDT-TS1:T-2	1.01	11.35 (11.58)	49.5	5.67	1.62	0.61
PDBT-T1:TPH-Se	1.01	12.57 (12.21)	72.2	9.17	1.86	0.85
PBDT-TS1:TPH-Se	0.91	14.70 (14.20)	53.4	7.04	1.62	0.71

^a J_{sc} values integrated from the EQE spectra; ^bCalculated according to the $q\Delta V_{oc} = E_g - qV_{oc}$.

AFM and TEM Characterizations: AFM measurement was performed on a Dimension Icon AFM (Bruker) in a tapping mode at ambient conditions. All film samples were spincoat on ITO/PEDOT:PSS substrates. TEM images of the active layers were obtained by using a JEOL JEM-1400 transmission electron microscope operated at 80 kV. The specimens for TEM investigation were prepared by spin casting the blend solutions on PEDOT:PSS substrates, then floating the films on a water surface, and transferring to TEM grids.

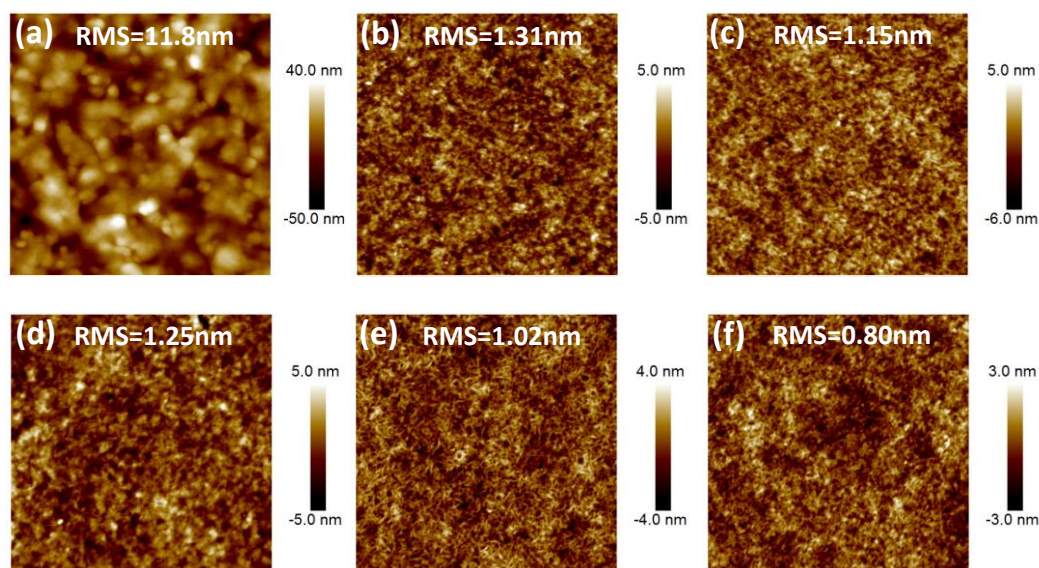


Figure S4. Tapping-mode AFM height images (2×2 μm) for blend films of (a) P3HT:T-2, (b) PDBT-T1:T-2, (c) PTB7-Th:T-2, (d) PBDT-TS1:T-2, (e) PDBT-T1:TPH-Se, and (f) PBDT-TS1:TPH-Se.

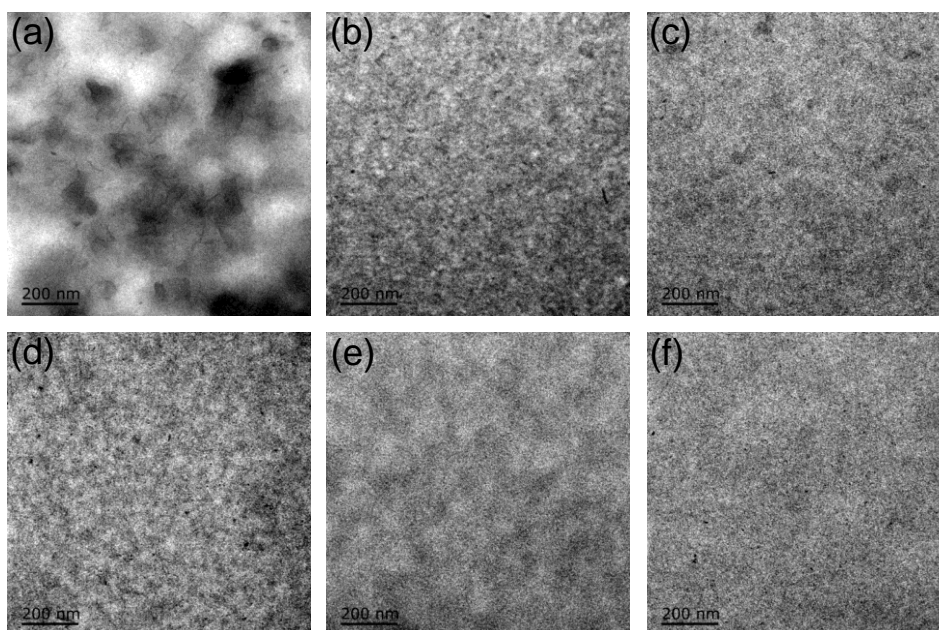


Figure S5. TEM images for blend films of (a) P3HT:T-2, (b) PDBT-T1:T-2, (c) PTB7-Th:T-2, (d) PBDT-TS1:T-2, (e) PDBT-T1:TPH-Se, and (f) PBDT-TS1:TPH-Se.

FTPS-EQE measurement. FTPS-EQE was recorded by using a Vertex 70 from Bruker Optics with an external detector option. A low-noise current amplifier (SR570) was used to amplify the photocurrent generated from the photovoltaic devices with illumination light modulated by the Fourier transform infrared (FTIR) instrument.

EL measurement. EL spectra were measured with an Andor spectrometer (Shamrock sr-303i-B, coupled to a Newton EMCCD Si arrow detector cooled to -60 °C). A Keithley 2400 external current/voltage source meter was connected to prepare solar cells comprising pristine or blend films to support an external electric field for EL measurements.

EQE_{EL} measurement. EQE_{EL} values were achieved from a home-built setup containing a Hamamatsu silicon photodiode 1010B, a Keithley 2400 SourceMeter for supplying voltages and recording the injected current, and a Keithley 485 for measuring the emitted light intensity.

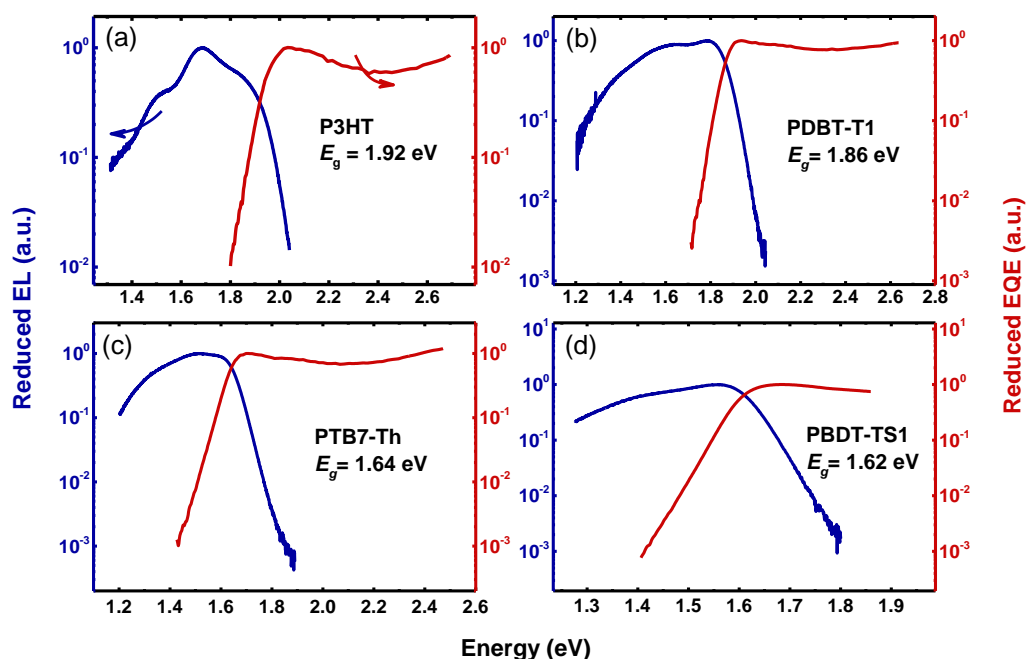


Figure S6. The optical gaps of (a) P3HT, (b) PDBT-T1, (c) PTB7-Th, and (d) PBDT-TS1 were determined from the crossing point between the normalized reduced FTPS-EQE and EL spectra.

References

- (1) Meng, D.; Fu, H.; Xiao, C.; Meng, X.; Winands, T.; Ma, W.; Wei, W.; Fan, B.; Huo, L.; Doltsinis, N. L.; et al. Three-Bladed Rylene Propellers with Three-Dimensional Network Assembly for Organic Electronics. *J. Am. Chem. Soc.* **2016**, *138*, 10184-10190.
- (2) Meng, D.; Fu, H.; Fan, B.; Zhang, J.; Li, Y.; Sun, Y.; Wang, Z. Rigid Nonfullerene Acceptors Based on Triptycene-Perylene Dye for Organic Solar Cells. *Chem. Asian. J.* **2017**, *12*, 1286-1290.
- (3) Huo, L.; Liu, T.; Sun, X.; Cai, Y.; Heeger, A. J.; Sun, Y. Single-junction Organic Solar Cells Based on a Novel Wide-bandgap Polymer with Efficiency of 9.7%. *Adv. Mater.* **2015**, *27*, 2938-2944.