

Supporting Information

Linear Conjugated Tetramer as a Surface-modified Layer to Increase Perovskite Solar Cell Performance and Stability

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1. Materials and Characterization

IDTT was purchased from Derthon Optoelectronic Materials Co., CH₃NH₃I (MAI) and Br-PDI were synthesized by using previously reported methods in the literature.²³ PbI₂ (99.999%) was purchased from Alfa Aesar. PMMA and F4-TCNQ were purchased from Xi'an Polymer Light Technology Corp. (China). PTAA was purchased from 1-Material (Canada). [6,6]-Phenyl-C₆₁-butyric acid methyl ester (PCBM) and 4,7-diphenyl-1,10-phenanthroline (Bphen) were purchased from Nichem Fine Technology Co. Ltd. (Taiwan). N,N-dimethylformamide (DMF, 99.5%), dimethylsulfoxide (DMSO, 99.5%), 2-butanol (99.5%), chlorobenzene (99.5%), ethyl acetate (99.5%) and ethanol (99.5%) were purchased from Sigma Aldrich. 3,4,9,10-Perylenetetracarboxylic dianhydride, tris(dibenzylideneacetone)dipalladium and tris(2-methylphenyl)phosphine were purchased from Aladdin (China). The indium-tin-oxide (ITO) on glass was purchased from Xiangcheng Science and Technology Co. Ltd. Other commercially available reagents were purchased from TCI Chemical Co. and used without further purification unless otherwise stated. Solvents for chemical reactions were purified according to the standard procedures. All chemical reactions were carried out under an inert atmosphere.

¹H and ¹³C NMR spectra were recorded using a 400 MHz Bruker NMR spectrometer in CDCl₃ at 293 K using TMS as a reference. The accurate mass correction was measured with matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectrometer (MALDI micro MX). UV-Vis spectra were measured with the UV-Vis spectrophotometer (Model HP8453) in a 1 cm quartz cell. Cyclic voltammetry (CV) were recorded on a BSA100B/W electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode and Hg/Hg₂Cl₂ electrode as the reference electrode. 0.05 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) dissolved in dichloromethane was employed as the supporting electrolyte, which was calibrated by the ferrocene/ferroncenium (Fc/Fc⁺) as the redox couple. The energy level of Fc/Fc⁺ is 5.08 eV relative to vacuum. Thermogravimetric analysis (TGA) was carried out using

a Mettler Toledo TGA/SDTA 851e at a heating rate of 10 °C min⁻¹ under the nitrogen flow of 20 mL min⁻¹.

2. Device fabrication and measurement

Device Fabrication: The 5 wt% F4-TCNQ doped PTAA precursor solution (5 mg mL⁻¹) was prepared by dissolving PTAA and F4-TCNQ in chlorobenzene. The PMMA precursor solution (0.5 mg mL⁻¹) was prepared by dissolving PMMA in ethyl acetate. The MAPbI₃ precursor solution was prepared by dissolving 1.037 g PbI₂ and 0.376 g MAI (PbI₂:MAI molar ratio = 1:1.05) into 1.35 mL DMF and 0.15 mL DMSO mixed solvent. The IDTT2FPDI precursor solutions of different concentrations (5-20 mg mL⁻¹) were prepared by dissolving in chlorobenzene. The 10 mg mL⁻¹ PCBM precursor solution was prepared by dissolving PCBM in chlorobenzene. The 0.7 mg mL⁻¹ Bphen precursor solution was prepared by dissolving Bphen in ethanol.

The perovskite solar cells were fabricated as follows. First, the indium tin oxide (ITO) substrates (2×2 cm²) were ultrasonically and subsequently cleaned with deionized water, acetone, and isopropanol for 15 min, respectively. Then, the substrates were dried by blowing nitrogen and then treated with O₃ plasma for 15 min before use. After that, a PTAA:F4-TCNQ precursor solution was spin-coated on the cleaned ITO at 6000 revolutions per minute (rpm) for 20 s. Then, the films were annealed at 100 °C on a hot plate for 2 min. For the deposition of the thin passivation layer, the PMMA precursor solution was spin-coated on the top of the ITO/PTAA:F4-TCNQ substrates at 6000 rpm for 20 s, and then annealed at 100 °C for 2 min. After the substrates were cooled down, the MAPbI₃ precursor solution was spin-coated on the ITO/PTAA:F4-TCNQ/PMMA substrates at 6000 rpm for 20 s. 300 μL 2-butanol was used as the anti-solvent and was dropped on the wet MAPbI₃ precursor film for 8 s during the spin-coating process, and then the films were annealed at 100 °C for 10 s. The above spin-coating processes were conducted in a glove box under a nitrogen atmosphere and with a real-time humidity of <1 ppm. Finally, the perovskite films were transferred on a hot plate, first annealed in ambient air (at 100 °C, for 15 min,

with a real-time humidity of 55–65%), and then annealed under the DMSO atmosphere with the same temperature and time. For the DMSO atmosphere, 100 μL DMSO was dropped into a small ceramic crucible, and then a glass Petri dish was used to cover the samples and crucible. After the films were cooled down, the IDTT2FPDI precursor chlorobenzene solution (5–20 mg mL^{-1}) was spin-coated on the perovskite layer at 1500–2500 rpm for 30–60 s, which could obtain the IDTT4PDI film with different thicknesses (7–28 nm). The thickness of the IDTT4PDI film on the perovskite layer was measured by the stylus profiler (KLA D600). Then, the PCBM precursor solution was spin-coated on the IDTT2FPDI layer at 2500 rpm for 30 s. Then, the Bphen precursor solution was spin-coated without additional annealing. The devices were completed by evaporating a 100 nm thick aluminum film as the electrode. The active device area was set as 0.12 cm^2 ($0.3 \times 0.4 \text{ cm}^2$) by the overlapping area between the top Al cathode and the bottom ITO anode.

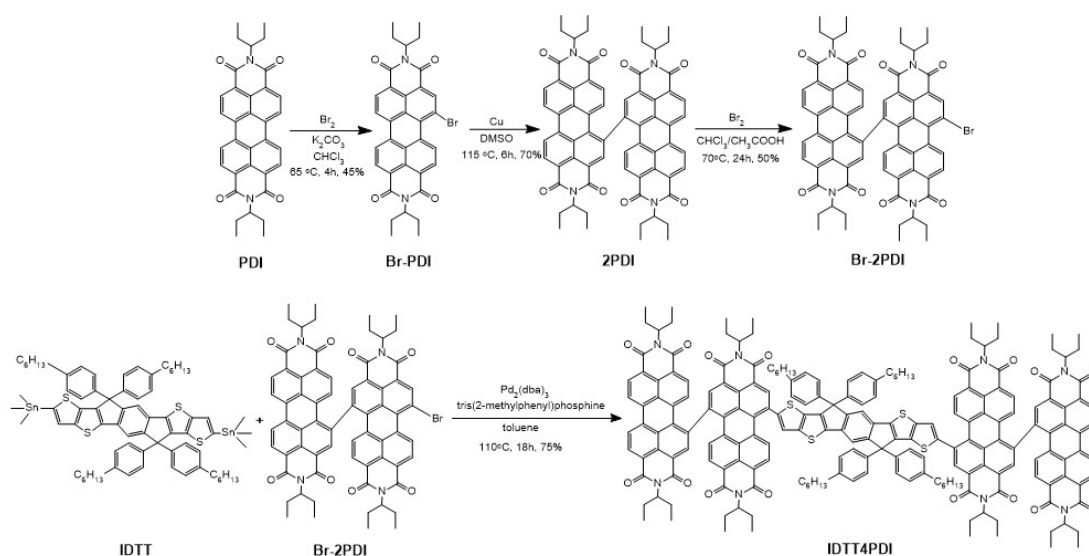
The electron-only devices for PCBM or IDTT2FPDI films were fabricated as follows. The 1.5 M ZnO precursor solution was spin-coated on the cleaned ITO at 4000 rpm for 30 s and then annealed at 200 $^{\circ}\text{C}$ for 30 min. After the films were cooled down, the PCBM or IDTT2FPDI chlorobenzene solution (20 mg mL^{-1}) was spin-coated at 1000 rpm for 30 s without additional annealing. Finally, Ca (10 nm) and Al (100 nm) films were evaporated on top of the active layer as the electrode.

The electron-only devices for perovskite films were fabricated as follows. The 0.5 M SnO_2 precursor solution was spin-coated on the cleaned ITO at 2000 rpm for 30 s and then annealed at 150 $^{\circ}\text{C}$ for 30 min. The rest of the fabrication steps is similar to the fabrication of PSCs.

Device Characterization: SEM images were obtained with a Zeiss Supra 55 microscope. AFM images were obtained from Bruker Dimension Icon AFM. A sun simulator (Zolix Sirius-SS) was used to provide the simulated solar irradiation (AM 1.5G, 100 mW cm^{-2}). J - V characteristics were measured using a Keithley 2400 source meter. The output of the light source was adjusted using a calibrated silicon photodiode (ABET technology). The J - V curves were measured by forward scan from -0.5 to 1.5 V and reverse scan from 1.5 to -0.5 V. The EQE was measured using a

power source (Zolix Sirius-SS) with a monochromator (Zolix Omni- λ) and a source meter (Keithley 2400). The stability of the PSCs was kept in the dark condition at room temperature and under controlled humidity of about 25% room humidity (RH). The samples were taken out to be tested in the forward scan rate of 0.1 V/s after every 12 hours. The FLIM measurements and TRPL decay traces were measured by a Leica TCS SP8 system using the TCSPC technique with laser excitation at 600 nm and detection at 770 nm. The steady-state PL spectra were measured by the fluorescence spectrophotometer (OmniPL-microS, Zolix, China), a 600 nm continuous wave laser came into the films from the air side. Water contact angles were measured by the contact angle instrument (SZ-CAMD33, China).

3. Synthesis



Scheme S1. Synthetic route of IDTT4PDI.

2PDI: A mixture of Br-PDI (0.5 g, 0.82 mmol) and copper powder (0.53 g, 8.28 mmol) in dry DMSO (30 mL) was stirred at 115°C under an argon atmosphere. After 6 hours, water was added and the mixture was extracted with dichloromethane. The organic layers were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by silica gel

column chromatography with dichloromethane:ethyl acetate (100:1, v/v) as eluent to afford 2PDI (70 %, 0.61 g, 0.57 mmol). ^1H NMR (400 MHz, CDCl_3 , 25 °C) : δ (ppm) = 8.84-8.79 (d, 8H), 8.51-8.49 (d, 2H), 8.20-8.17 (d, 4H), 5.01-4.94 (m, 4H), 2.22-1.88 (m, 8H), 1.87-1.83 (m, 8H), 0.92-0.87 (t, 24H).

Br-2PDI: 2PDI (0.5 g, 0.47 mmol) was added to the mixed solvents of chloroform (10 mL) and acetic acid (10 mL), and stirred at room temperature under an argon atmosphere. Then a solution of bromine (2.85 mL, 56.64 mmol) in chloroform (10 mL) was added to the solution, and then the mixture was stirred at 70 °C for 24 hours. After the reaction, the excess bromine was removed by adding saturated aqueous sodium sulfite solution. Then water was added and the mixture was extracted with dichloromethane. The organic layers were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography with dichloromethane:ethyl acetate (100:1, v/v) as eluent to obtain Br-2PDI (50 %, 0.27 g, 0.24 mmol). ^1H NMR (400 MHz, CDCl_3 , 25 °C) : δ (ppm) = 9.81-9.79 (d, 1H), 8.92-8.62 (m, 12H), 5.03-4.97 (m, 4H), 2.23-2.21 (m, 8H), 1.86-1.83 (m, 8H), 0.85-0.82 (t, 24H).

IDTT4PDI: Br-2PDI (0.3 g, 0.26 mmol), IDTT (0.15 g, 0.11 mmol), $\text{Pd}_2(\text{dba})_3$ (24 mg, 0.026 mmol) and tris(2-methylphenyl)-phosphine (32 mg, 0.10 mmol) were added to 10 mL dry toluene and stirred at 110 °C under an argon atmosphere. After 18 hours, the solvent was stripped off by a rotary evaporator, and the crude product was purified by silica gel column chromatography with dichloromethane:ethyl acetate (50:1, v/v) as eluent to obtain IDTT4PDI (75%, 0.26 g, 0.084 mmol). ^1H NMR (400 MHz, CDCl_3 , 25 °C) : δ (ppm) = 8.83-8.79 (m, 8H), 8.53-8.09 (m, 16H), 7.69-7.63 (m, 4H), 7.22-7.18 (m, 18H), 5.01-4.98 (m, 8H), 2.64-2.54 (m, 8H), 2.20-2.17 (m, 16H), 1.90-1.86 (m, 16H), 1.34-1.25 (m, 32H), 0.91-0.85 (t, 60H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) : δ (ppm) = 168.95, 156.60, 148.42, 148.35, 142.34, 142.05, 138.73, 138.14, 136.30, 135.52, 134.10, 133.47, 133.32, 131.63, 128.70, 128.64, 127.49, 125.93, 122.36, 57.38, 35.60, 31.79, 31.68, 31.29, 29.34, 29.18, 24.96, 24.94, 22.68, 22.60, 14.13, 14.08, 11.44, 11.29; MALDI-TOF-MS: calculated for $\text{C}_{204}\text{H}_{186}\text{N}_8\text{O}_{16}\text{S}_4$, 3131.287 [M] $^-$, found 3131.406.

4. Supporting table and figures

Table S1. Device performance of perovskite solar cells with different IDTT4PDI film thickness.

Thickness	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF [%]	PCE [%]
0	22.68	1.076	71.3	17.41
7	23.83	1.108	70.8	18.70
14	23.91	1.123	74.9	20.12
19	23.63	1.117	72.3	19.10
21	23.77	1.082	73.1	18.80
24	23.76	1.074	73.5	18.76
28	23.57	1.076	73.9	18.76

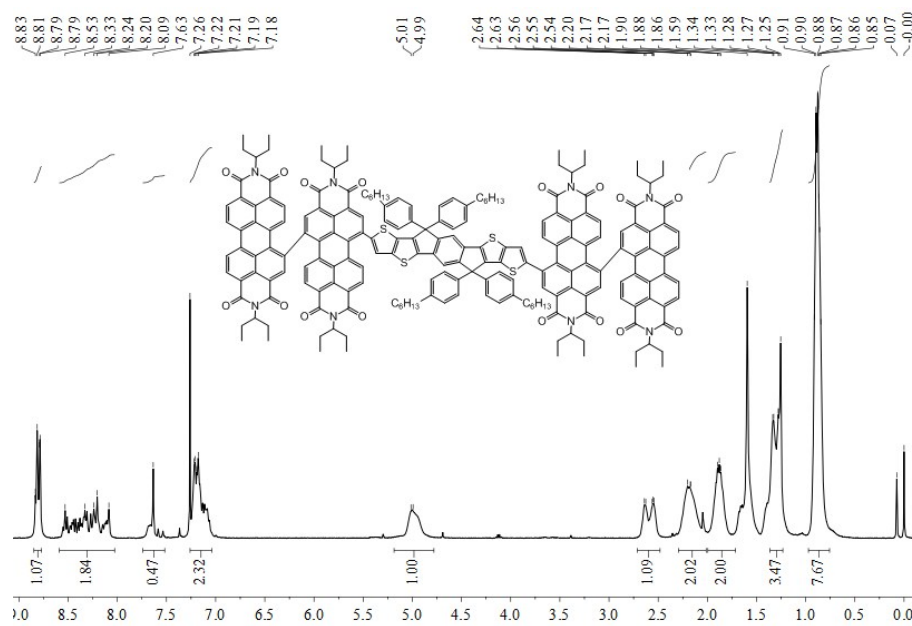


Figure S1. ¹H NMR spectrum of IDTT4PDI in CDCl₃.

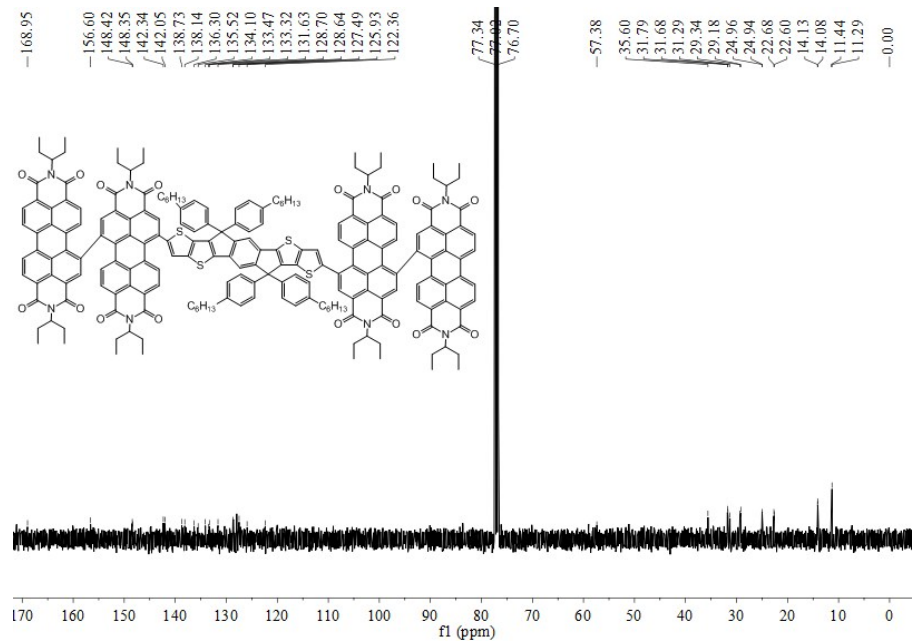


Figure S2. ¹³C NMR spectrum of IDTT4PDI in CDCl₃.

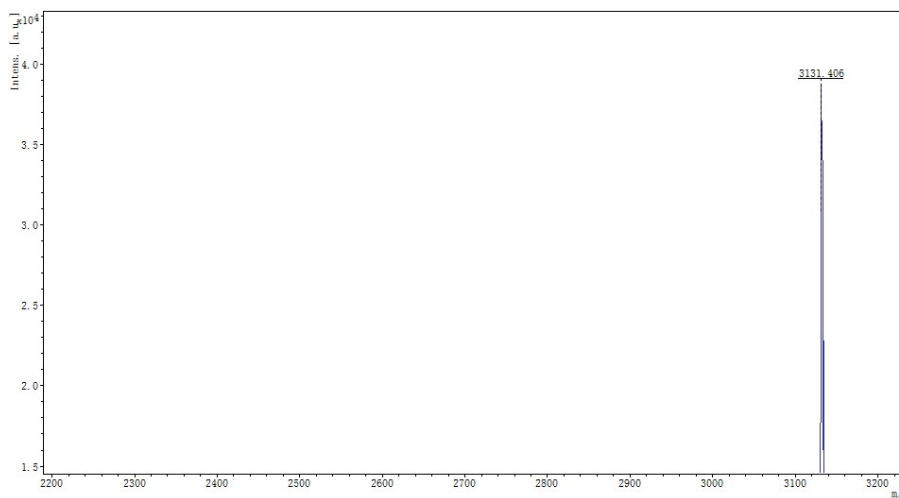


Figure S3. MALDI-TOF mass spectrum of compound IDTT4PDI.

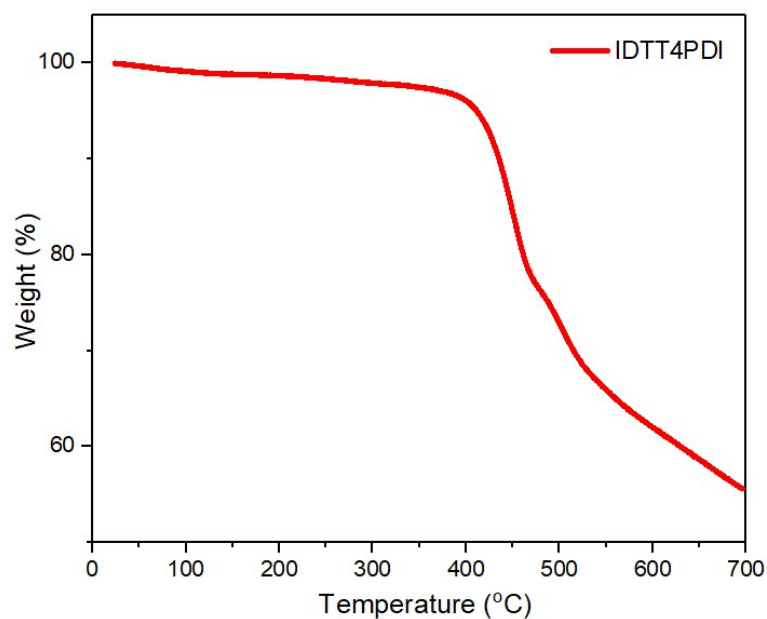


Figure S4. Thermal gravimetric analysis plot of IDTT4PDI.

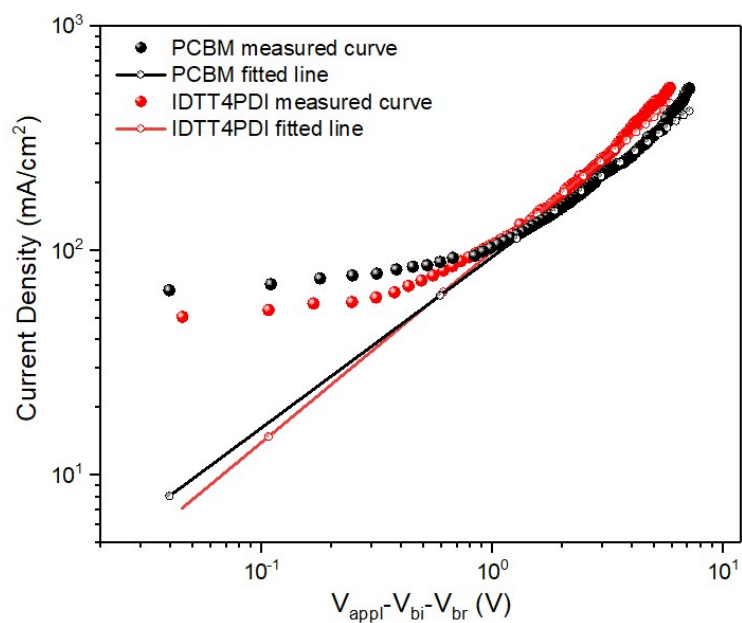


Figure S5. Current density-voltage traces of electron-only devices based on PCBM or IDTT4PDI films by space charge limited current method.

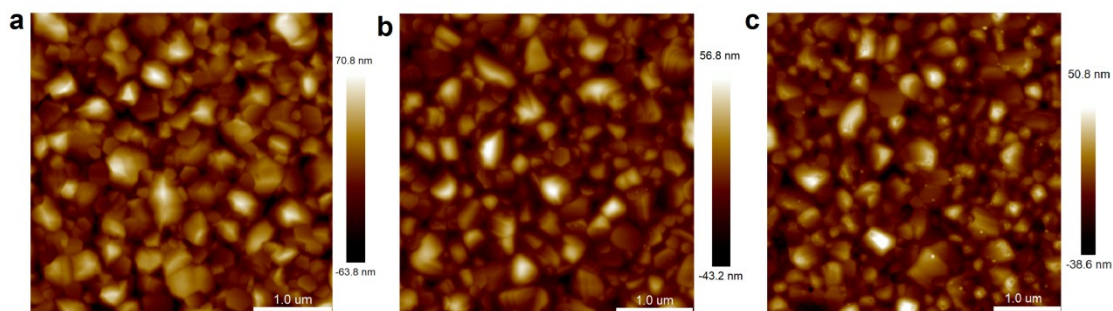


Figure S6. AFM images of the bare perovskite film (RMS = 18.4 nm) (a), PCBM-coated perovskite film (RMS = 14.2 nm) (b), and IDTT4PDI-coated perovskite film (RMS = 11.9 nm) (c) on ITO substrates.

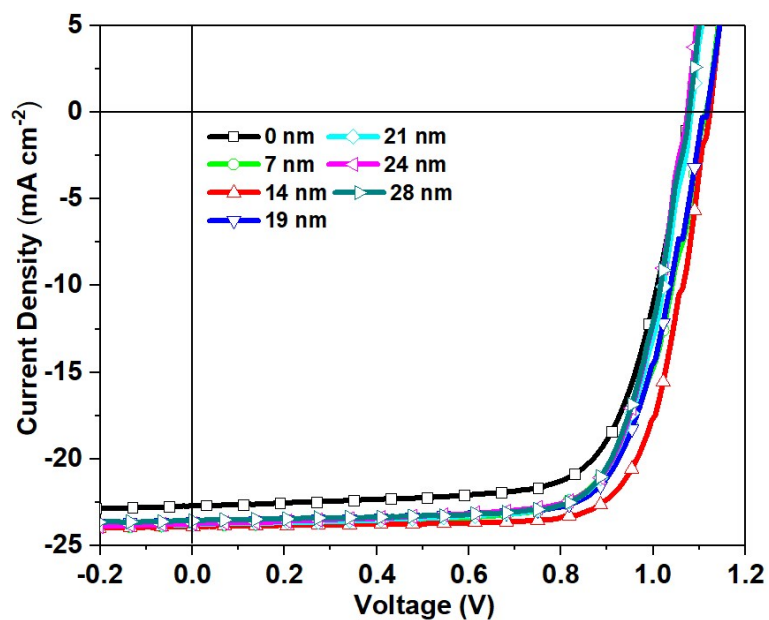


Figure S7. J - V curves of perovskite solar cells with different thickness of the IDTT4PDI as the surface-modified layer.

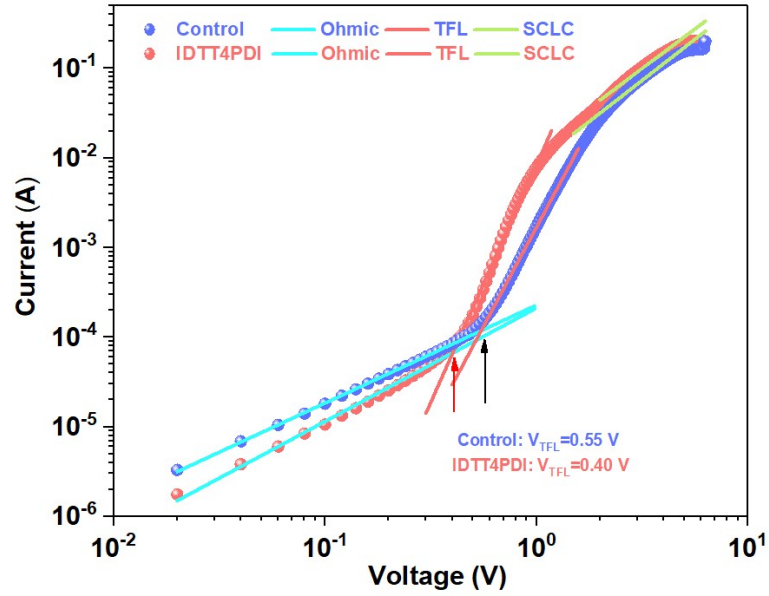


Figure S8. Current density-voltage traces of the control and IDTT4PDI-based devices by space charge limited current method.

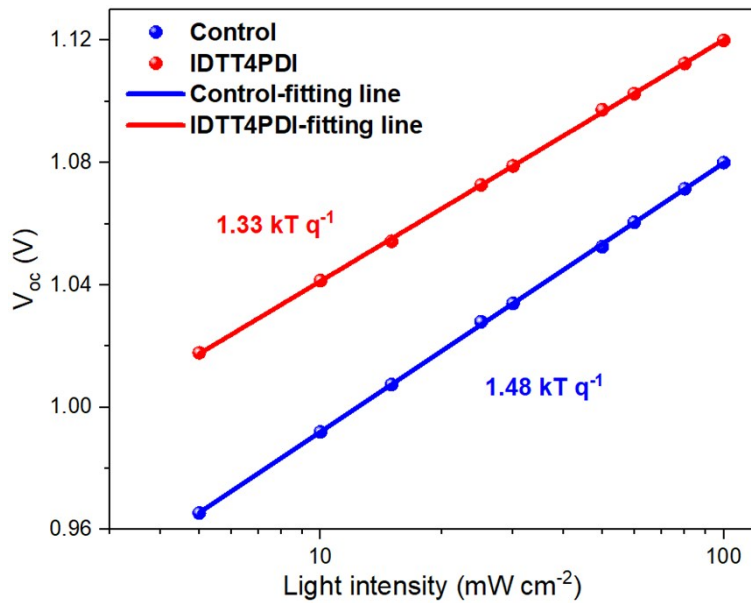


Figure S9. The measured V_{oc} versus light intensity for control and IDTT4PDI-based devices (symbols), together with linear fits to the data (solid lines).

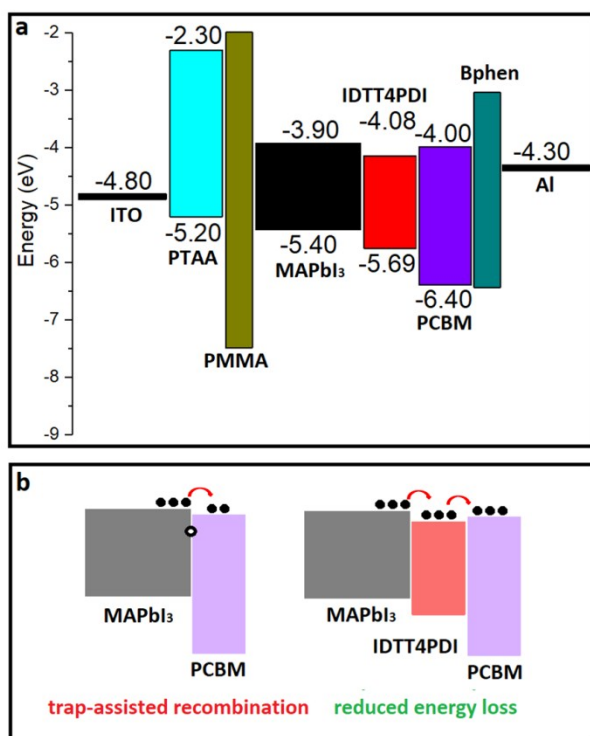


Figure S10. (a) The energy level alignments of inverted perovskite solar cells; (b) working mechanism of IDTT4PDI as an interface engineering layer.

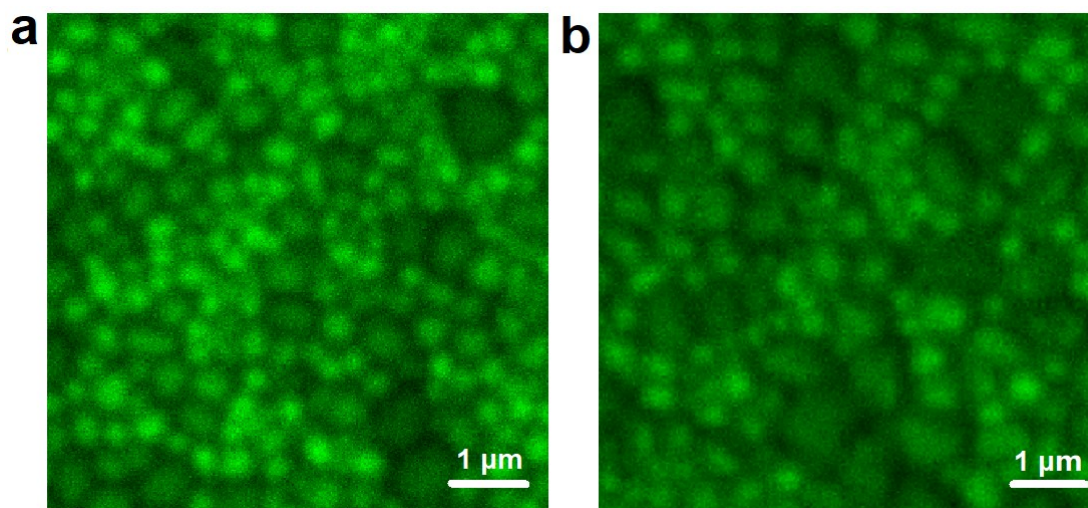


Figure S11. Fluorescence lifetime imaging microscopy images of the control (a) and IDTT4PDI-based (b) perovskite films.

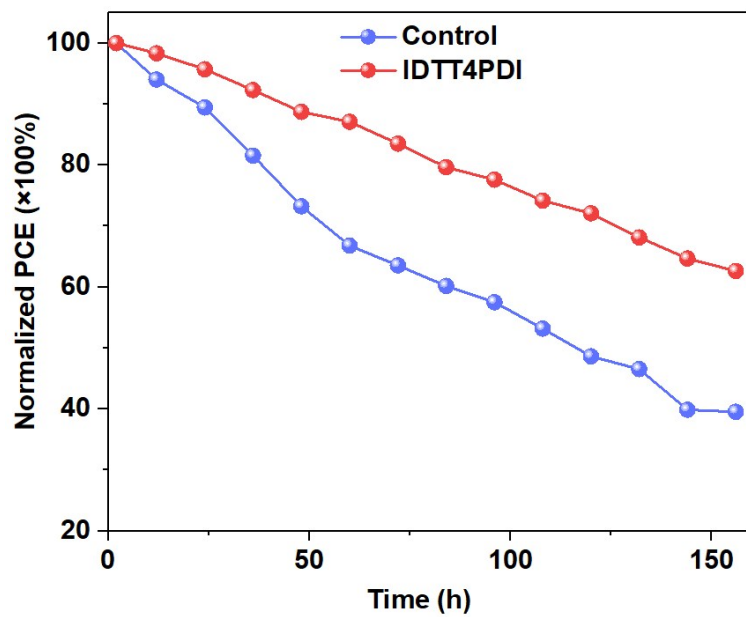


Figure S12. Stability measurement of the control and IDTT4PDI-based devices under 25% humidity conditions.