

Supporting information

Electron Extraction Layer based on Diketopyrrolopyrrole/ Isoindigo to Improve the Efficiency of Inverted Perovskite Solar Cells

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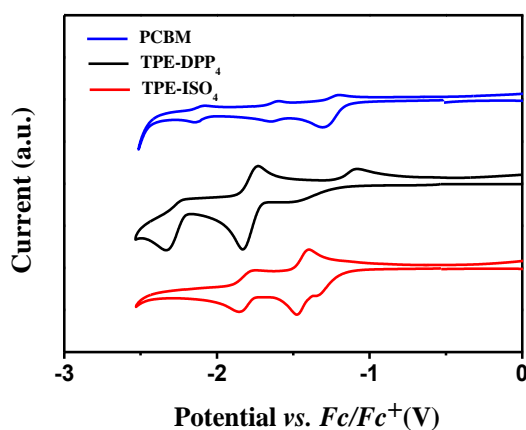


Fig. S1 Cyclic voltammograms of PCBM, TPE-DPP₄ and TPE-ISO₄.

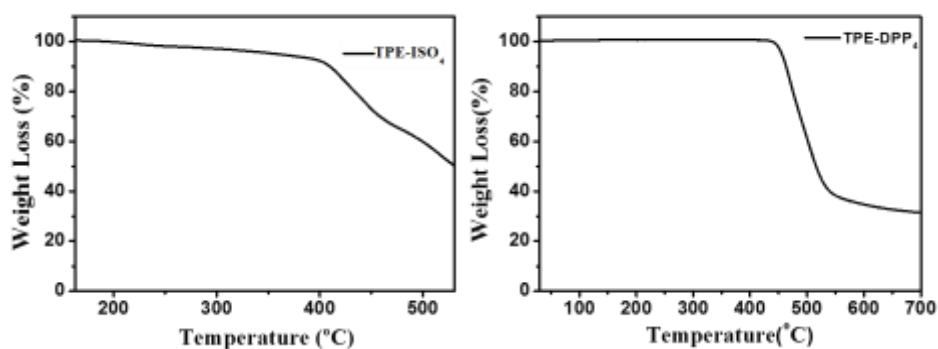


Fig. S2 TGA of TPE-DPP₄ and TPE-ISO₄ at N₂ atmosphere, heating rate of 10 °C min⁻¹.

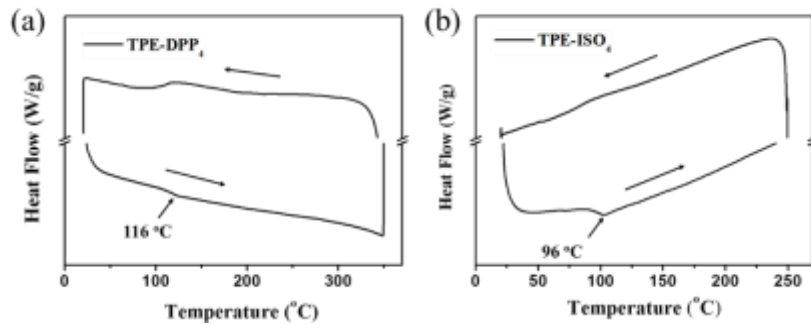


Fig. S3 DSC curves of (a) TPE-DPP₄ and (b) TPE-ISO₄ at the second heating-cooling cycle.



Fig. S4 The cross-sectional scanning electron microscopy (SEM) image of the device.

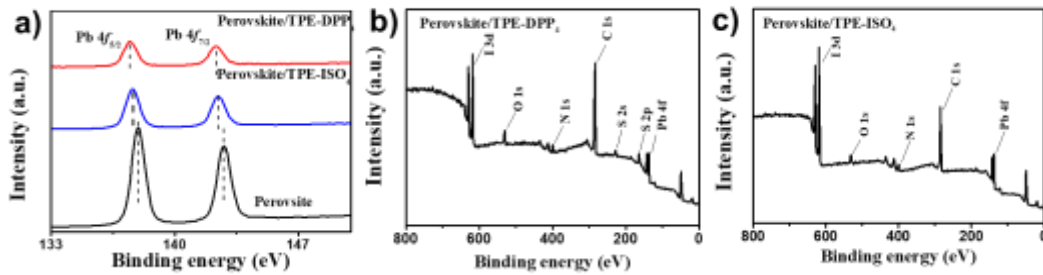


Fig. S5 a) XPS peak of Pb 4f obtained from perovskite film with or without the interlayers. XPS spectra of perovskite film spin-coated with (a) TPE-DPP₄ and (b) TPE-ISO₄, respectively.

Table S1. Photovoltaic parameters of the inverted planar devices with and without the interlayers under forward and reverse scans. The optimal concentration is 2 mg ml⁻¹.

Device structure	Scan direction	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
TPE-DPP ₄ /C ₆₀	Forward	1.050	22.03	0.80	18.44
	Reverse	1.049	21.99	0.79	18.16
TPE-ISO ₄ /C ₆₀	Forward	1.036	21.86	0.80	18.19
	Reverse	1.035	21.87	0.78	17.76
C ₆₀	Forward	1.015	21.39	0.78	16.87
	Reverse	1.010	21.40	0.76	16.38

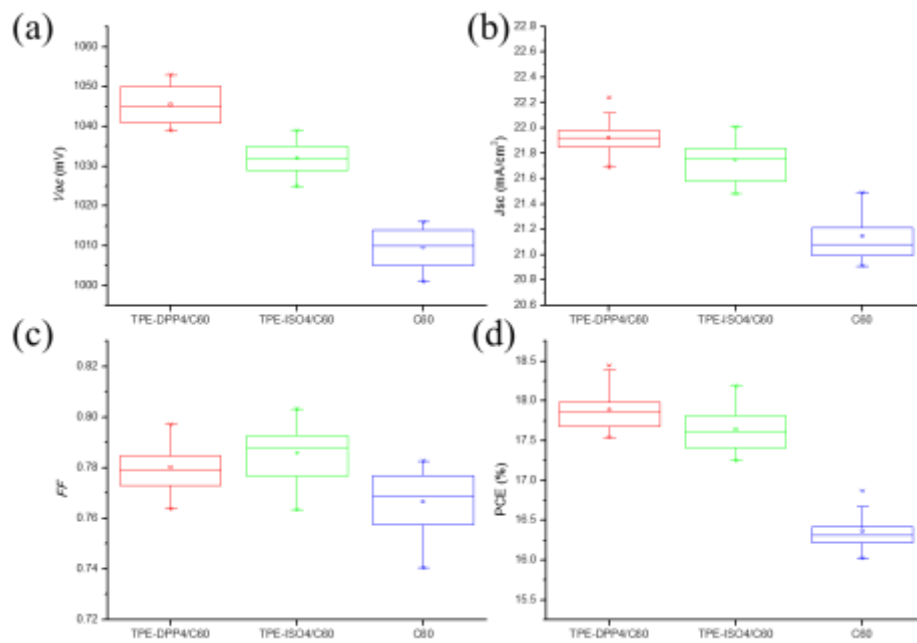


Fig. S6 Statistics of photovoltaic parameters (a) V_{oc} , (b) J_{sc} , (c) FF, and (d) PCE of 20 PSCs containing different interlayers measured under AM 1.5 G illumination (100 mW cm⁻²).

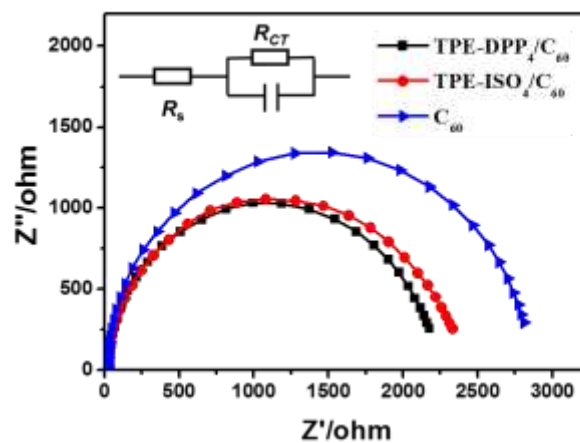


Fig. S7 EIS of PSCs with different interlayers under dark condition at 0.9 V forward bias. The inset is equivalent

circuit model, R_S : series resistance, R_{CT} : charge transfer resistance.

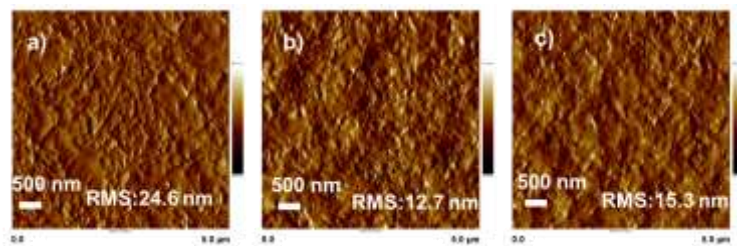


Figure S8. AFM images of a) perovskite film, and perovskite film covered by b) TPE-DPP₄ and c) TPE-ISO₄.

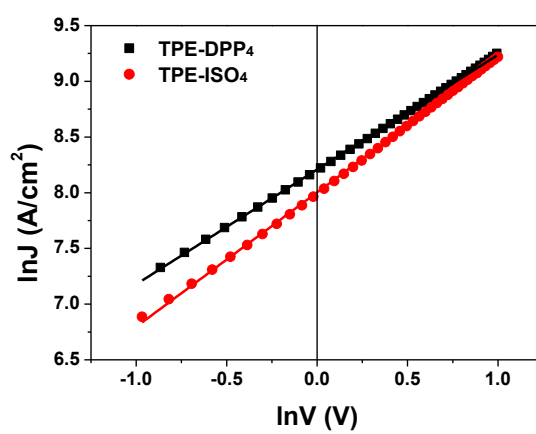
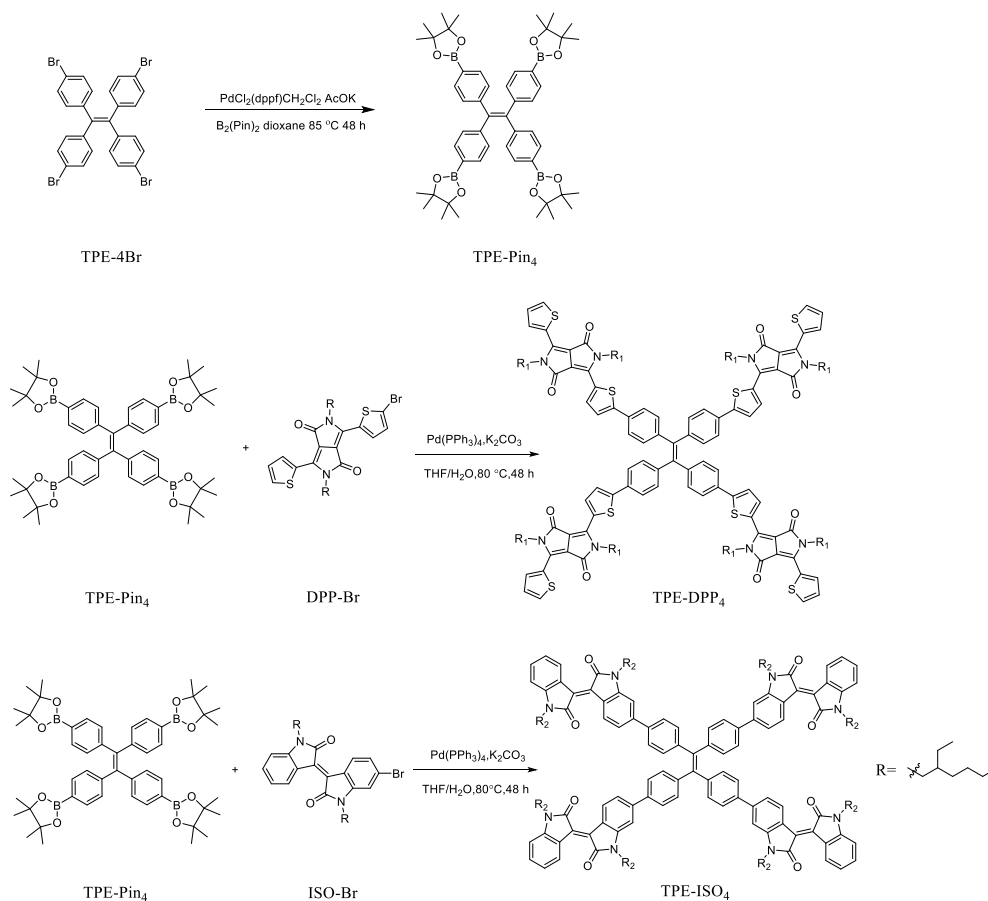


Figure S9. Electron mobility of TPE-DPP₄ and TPE-ISO₄ measured by the SCLC method.



Scheme S1. The synthetic routes for TPE-DPP₄ and TPE-ISO₄.

Experimental section

Materials and instruments

Unless otherwise stated, all starting materials were purchased from commercial suppliers (Sigma–Aldrich and Energy Chemical) and used without further purification, including P3CT (Rieke Metals), PbI₂ (p-OLED, >99.99 %), MAI (p-OLED, ≥99.5 %), PCBM (p-OLED, ≥99 %), C₆₀ (p-OLED), BCP (p-OLED), DMF (Sigma-Aldrich, 99.8 %), DMSO (Sigma-Aldrich, 99.8 %) and CB (Sigma-Aldrich, 99.8 %). Tetrahydrofuran (THF) and toluene were freshly distilled over Na-K alloy under Ar atmosphere before uage. Nuclear magnetic resonance (NMR) spectra were obtained

from a BRUKER AVANCE III 600 MHz NMR Instrument. HRMS was measured on Thermo Scientific Q Exactive instrument. UV/Vis absorption spectra were recorded on a Shimadzu UV-2450 absorption spectrophotometer. Fluorescence spectra were measured on a Hitachi F-4600 FL Spectrophotometer. The PL lifetimes were measured by a single photon counting spectrometer from Edinburgh Instruments (FLS920) with a Picosecond Pulsed UV-LASTER (LASTER377) as the excitation source. Field-emission SEM (FE-SEM) images were taken on JSM-7800F. AFM images were collected in air on a Bruker AFM using a tapping mode. Thermal gravimetric analysis (TGA) was performed on a TGA Q50 at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. Differential scanning calorimetry (DSC) measurement was performed on a DSC Q20 instrument at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. X-ray photoelectron spectroscopy (XPS) was recorded on ESCALAB 250 Xi device.

TPE-4Br, TPE-Pin₄, DPP-Br, ISO-Br and TPE-DPP₄ were prepared according to reported literatures.^[1-3]

Synthesis of TPE-ISO₄

A mixture of compound 1 (70 mg, 0.084 mmol), compound 3 (227 mg, 0.38 mmol), Pd(PPh₃)₄ (28 mg, 0.024 mmol), K₂CO₃ (116 mg, 0.84 mmol), THF (8 mL) and H₂O (4 mL) were placed in a Schlenk tube under an argon atmosphere and were stirred at 60 °C for 48 h. After cooling to room temperature, the reaction was quenched by adding water, and then was extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous Na₂SO₄. After evaporation of solvents, the residue

was purified by column chromatography over silica gel using petroleum ether/dichloromethane (3:1) as the eluent to give a brown solid (85 mg, 45%). ^1H NMR (600 MHz, CDCl_3): δ 9.21 (d, 4H, $J = 8.4$ Hz), δ 9.16 (d, 4H, $J = 7.8$ Hz), δ 7.50 (d, 8H, $J = 7.8$ Hz), δ 7.33 (t, 4H, $J = 7.8$ Hz), δ 7.28 (d, 12H, $J = 13.8$ Hz), δ 7.04 (d, 4H, $J = 7.8$ Hz), δ 6.98 (s, 4H), δ 6.77 (d, 4H, $J = 7.8$ Hz), δ 3.69 (m, 16H), δ 1.87 (m, 8H), δ 0.82 (m, 64H) δ 0.89 (m, 48H). ^{13}C NMR (150 MHz, CDCl_3): δ 168.61, 168.38, 145.89, 145.15, 144.21, 143.63, 140.79, 138.66, 133.00, 132.12, 130.86, 130.23, 129.72, 128.84, 126.39, 122.11, 121.86, 121.04, 120.57, 108.10, 106.14, 65.53, 44.27, 37.74, 37.63, 30.80, 30.61, 28.77, 24.22, 24.15, 23.05, 19.18, 14.02, 13.68, 10.78, 10.72. MALDI-TOF-MS: calcd for $\text{C}_{154}\text{H}_{180}\text{N}_8\text{NaO}_8$ $[\text{M}+\text{Na}]^+$: 2292.3816, found 2292.3804.

Device fabrication

The indium tin oxide (ITO) glass substrates were sequentially washed by sonication using detergent, deionized water, ethanol and acetone. The hole transporting layer P3CT-Na was formed on ITO substrates by spin coating at 4000 rpm for 60 s followed by annealing at 140 °C for 30 min. Then the samples were transferred into a N_2 -filled glovebox. A $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor solution (1.4 M in DMF: DMSO mixed solution with a v/v of 4:1) was spin-coated in a two-step program at 400 and 5000 rpm for 3 and 30 s, respectively. During the second step, 200 μL of chlorobenzene was poured on the spinning substrate at 10 s after the start-up. Next, the as-spun perovskite layer was annealed on a hot plate at 60 °C for 1 min and at 80 °C for 2 min to drive off solvent and form the perovskite phase. Then TPE-DPP₄ or TPE-ISO₄ solutions in chlorobenzene were spin-coated (5000 rpm) onto the perovskite layer. To fabricate

ITO/P3CT-Na/Perovskite/TPE-DPP₄ or TPE-ISO₄/C₆₀/BCP/Ag device, C₆₀ (40 nm) and BCP (6 nm) were evaporated under high vacuum on top of the interlayer. Finally, a 100 nm thick Ag electrode was deposited through a shadow mask. The active area of our device is 0.09 cm². Electron-only devices are fabricated with the structure of FTO/TiO₂/TPE-DPP₄ or TPE-ISO₄/BCP (4 nm)/Al (100 nm). Mobility is extracted by fitting the current density-voltage curves using the space-charge limited current (SCLC) method.

References

- [1] Liu Y, Mu C, Jiang K, et al. A Tetraphenylethylene Core-Based 3D Structure Small Molecular Acceptor Enabling Efficient Non-Fullerene Organic Solar Cells [J]. *Advanced Materials*, **2015**, 27(6):1015.
- [2] Mei J, Graham K R, Stalder R, et al. Synthesis of isoindigo-based oligothiophenes for molecular bulk heterojunction solar cells [J]. *Organic Letters*, **2010**, 12(4):660.
- [3] Rananaware A, Gupta A, Li J, et al. A four-directional non-fullerene acceptor based on tetraphenylethylene and diketopyrrolopyrrole functionalities for efficient photovoltaic devices with a high open-circuit voltage of 1.18 V [J]. *Chemical communications*, **2016**, 52(55): 8522-8525.