Supporting Information

Optimization of Perovskite by 3D Twisted Diketopyrrolopyrrole for Efficient Perovskite Solar Cells

Bin Huang[a], Qingxia Fu[a], Qingyun Ai[a], Licheng Tan[a,b], Lie Chen*[a,b] and Yiwang Chen*[a,b]

[a] College of Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China.

[b] Jiangxi Provincial Key Laboratory of New Energy Chemistry/Institute of Polymers, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China.

Corresponding author. Tel.: +86 791 83968703; fax: +86 791 83969561. E-mail: ywchen@ncu.edu.cn (Y. Chen), chenlie@ncu.edu.cn (L. Chen).

Author contributions. B. Huang and Q. Fu contributed equally to this work.

Materials

Lithium diisopropylamide (LDA), 2-iso-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxoborolane, $(o\text{-tol})_3P$ and $Pd_2(DBA)_3$ were purchased from J&K Chemical Technology. 2,5-bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione and 1,1,2,2-tetrakis(4-bromophenyl)ethane were purchased from Suna Tech Inc. or CHEMSOON.

Experimental Section

1. Synthesis of 2,5-bis(2-ethylhexyl)-3-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (compound 2).

The LDA solution was added at -25 °C within 45 min to a 15 ml dry THF solution of 2,5-bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1.0 g, 1.9 mmol) and 2-iso-propoxy-4,4,5,5- tetramethyl-1,3,2-dioxoborolane (0.35 g, 1.9 mmol). This reaction mixture was stirred at 0 °C for 2 h and quenched with 10 mL of 1 M HCl solution. After extraction with dichloromethane (3 × 20 mL) the combined organic fractions were dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (eluent: hexane: ethyl acetate=1:1) to get the product as pink solid (0.86 g, 70%) (TPE-DPP_4).

2. Synthesis of 6,6',6'',6'''-((ethene-1,1,2,2-tetrayltetrakis(benzene-4,1-diyl))tetrakis(thiophene-5,2-diyl))tetrakis(2,5-bis(2-ethylhexyl)-3-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione).

1,1,2,2-tetrakis(4-bromophenyl)ethene (0.17 g, 0.26 mmol) and 2,5-bis(2-ethylhexyl)-3-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione. (0.84 g, 1.3 mmol) were taken in degassed dry THF (10 mL). The reaction container was loaded with the ligand (o-tol)$_3$P (20 mg), catalyst precursor $Pd_2(DBA)_3$ (15 mg) and purged with nitrogen for 10 min to remove dissolved oxygen. Degassed aqueous solution of K_3PO_4 (1 mL, 2 M) was added through syringe. The mixture was refluxed under nitrogen and the reaction was followed by TLC. Reaction was stopped after 48 hours. Then the reaction mixture was cooled to room temperature, washed with water. After extraction with dichloromethane (3 × 20 mL) the combined organic fractions were dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (eluent: hexane: ethyl acetate=5:1) to get the product as blue-black powder (0.5, 78%).

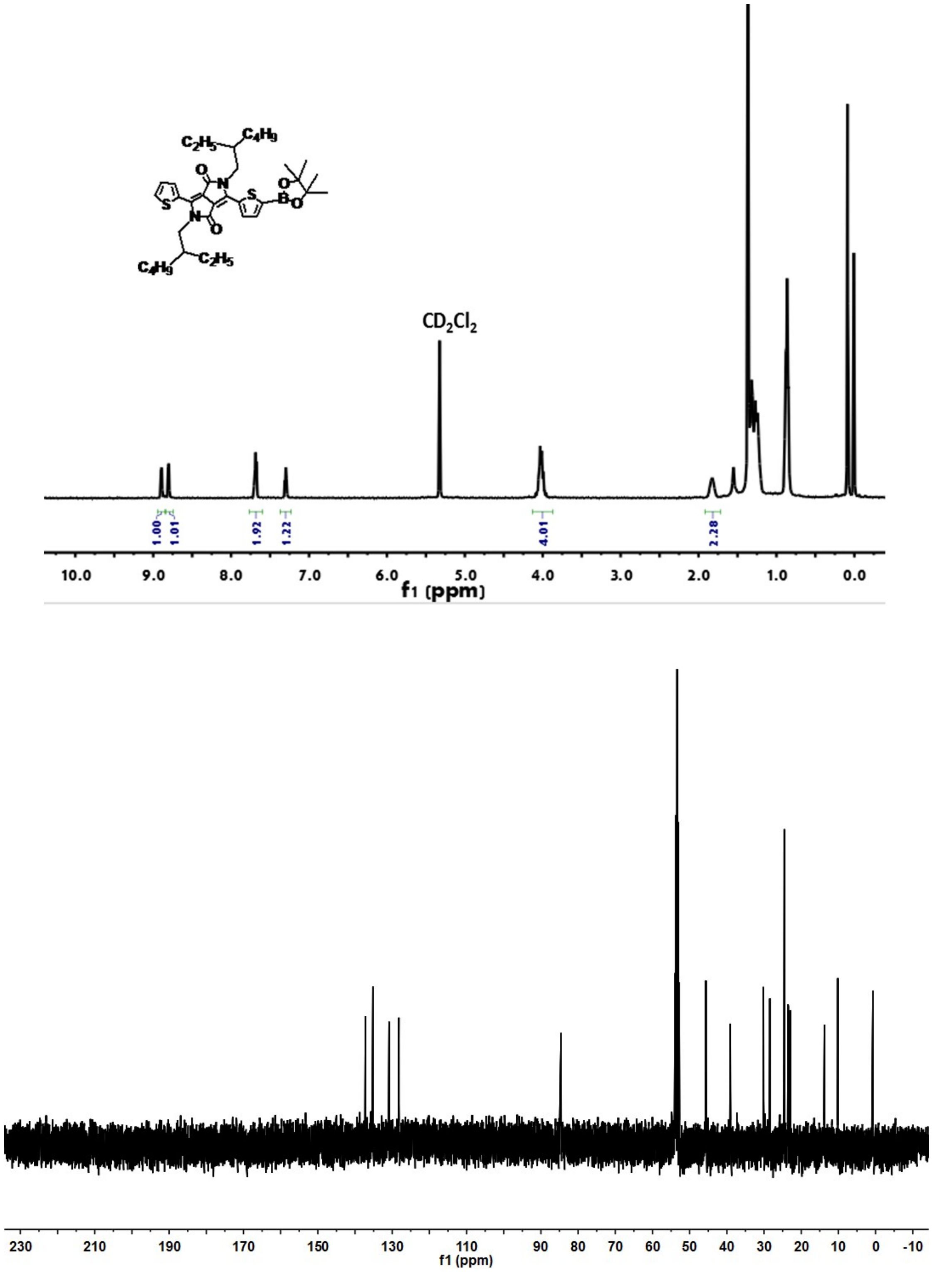

Figure S1. The ^{1}H NMR and ^{13}C of the intermediate compound 2.

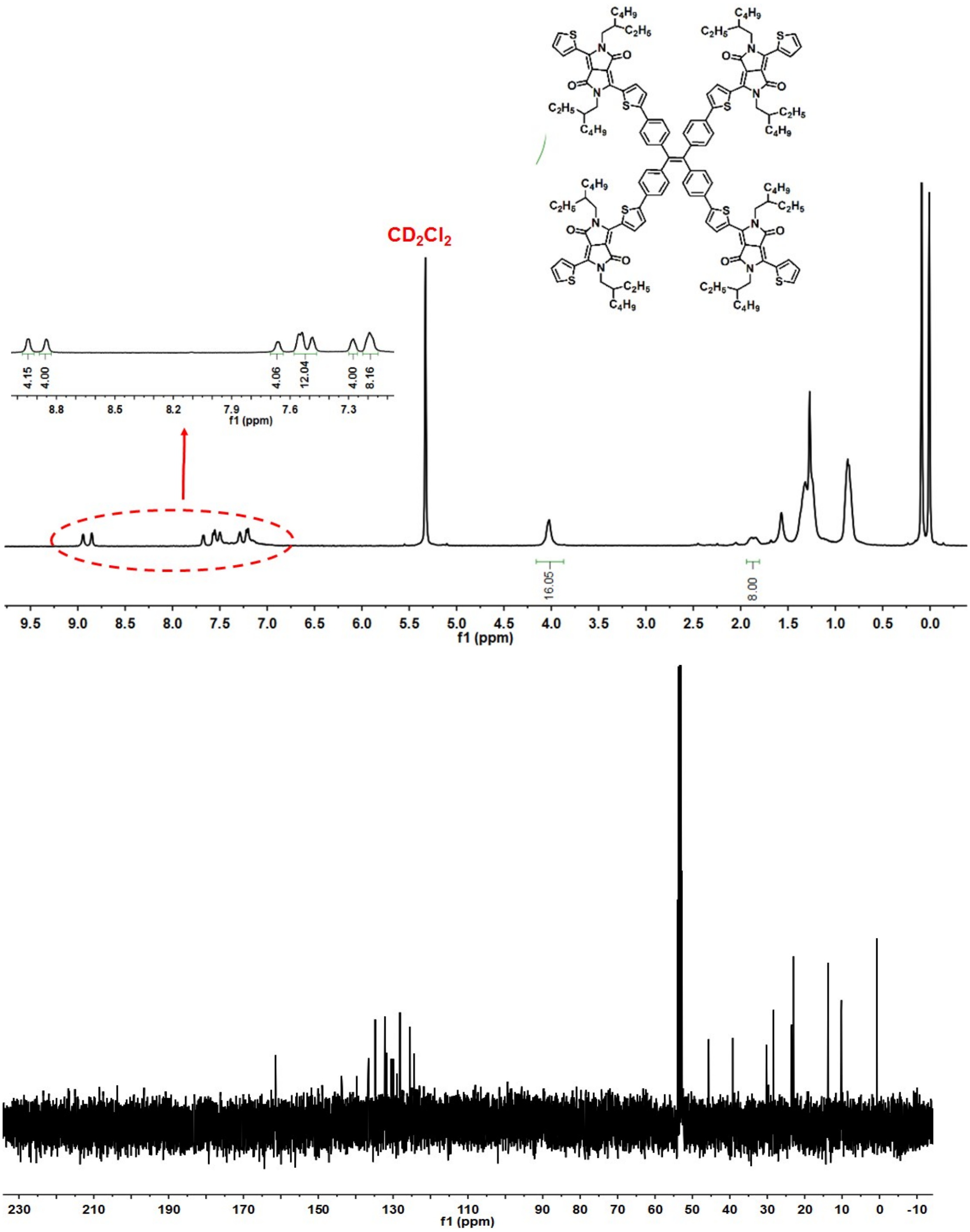

Figure S 2(a). The ^{1}H NMR and ^{13}C of the TPE-DPP$_4$.

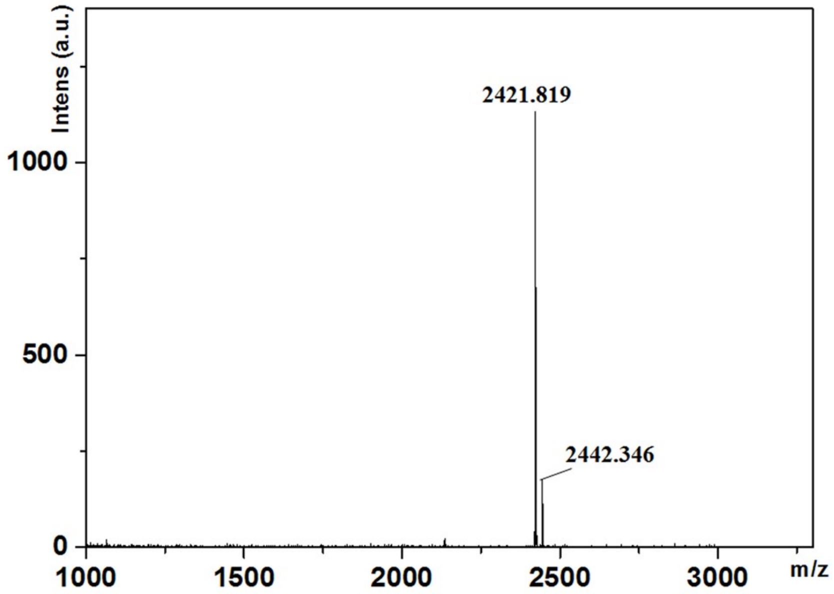

Figure S 2(b). MALDI-TOF of TPE-DPP$_4$

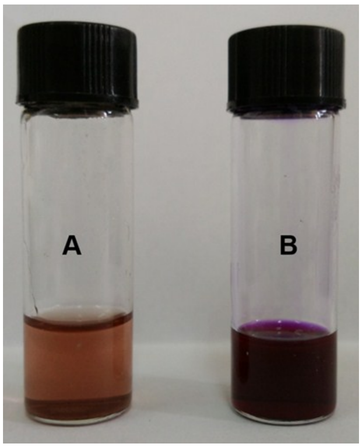

Figure S3. The photographs of (A) 0.5mg/ml PCBM/DMF solution. (B) 1 mg/ml TPE-DPP$_4$/DMF solution

Lead(II) iodide-TPE-DPP$_4$ solution Preparation: The Lead(II) iodide-TPE-DPP$_4$ solution was prepared by dissolved lead (II) iodide (PbI_2, Sigma-Aldrich, 99%, 462mg/mL) in anhydrous N,N-dimethylformamide (DMF, SigmaAldrich, 99.8%). The TPE-DPP$_4$ can be readily dispersed in DMF (2 mg ml^{-1}). Appropriate amount of TPE-DPP$_4$ were added into the PbI_2 solution. Mass percent of 0.01wt%, 0.02wt%, the solution was stirred at 60 °C overnight in argon glovebox. The solution was filtered with a 0.45 µm polyvinylidene fluoride filter before use.

Device Fabrication. The perovskite solar cells were fabricated on F-doped indium oxide (FTO) pattern glass substrates (Zhuhai Kaivo Optoelectronic Technology Co., Ltd. <15 Ω) with the following device configuration: FTO/c-TiO_2/mp-TiO_2/$CH_3NH_3PbI_3$/spiro-MeOTAD/ Ag. First, the FTO glass substrates were cleaned by sequential ultrasonic treatment in detergent, acetone, deionized water, and isopropyl alcohol for 15 min each and then dried with a nitrogen stream. Then the precleaned FTO glass substrates were treated by ultraviolet (UV)-ozone for 20 min in UV chamber. A 30 nm thick TiO_2 blocking layer was sequentially spin coated from a solution containing 0.3 M in n-butyl alcohol. The mesoporous TiO_2 layer was spin coated from a solution containing 1 g 18NRT Dyesol paste in 3.5 ml of EtOH at 5000rpm for 30 s. And the TiO_2 coated substrates were annealing at 500 ºC for 30 min. Then the meso-TiO_2 films were infiltrated with PbI_2 (Sigma-Aldrich, 99%) by spin-coating a PbI_2 with or with TPE-DPP$_4$ additive solution at 3500 rpm for 30 s, the films were dipped into CH_3NH_3I (10 mg/mL) (TCI, 99%) solution in isopropanol (Sigma-Aldrich) for 3 min, and then annealed at 105 °C for 10 min. The hole transport layer (HTM) solution was prepared by mixing 75 mg ml^{-1} spiroOMeTAD, 28 µl tert-butylpyridine and 17µl of bis(trifluoromethane) sulfonamide lithium salt (Li-TFSI) solution (520 mg in 1 ml acetonitrile) in 1 ml chlorobenzene. The HTM solution was spin-coated onto the perovskite film at 3000 rpm for 30 s. The substrates were kept in a desiccator overnight. Finally, a 100 nm thick Ag anode (thermal deposition rate of 1.0 Å/s) was deposited on the substrate through a shadow mask to give a device area of 0.06 cm^2 under a vacuum level of 10^{-4} Pa. All devices measurements were performed in an ambient environment (below 25% humidity) at room temperature.

Characterization: The nuclear magnetic resonance (NMR) spectra were collected on a Bruker ARX 600 NMR spectrometer with deuterated dichloromethane as the solvent and with tetramethylsilane (δ=0) as the internal standard. The ultraviolet–visible (UV) spectra and optical transmittance spectra of the samples were recorded on a Hitachi UV-3010 spectrophotometer. The cyclic voltammetry (CV) was performed on a CHI660C potentiostat equipped with electrochemical analysis system software and standard three-electrode configuration under an argon atmosphere at RT and a scan rate of 50 mV/s. Platinum rod, platinum wire, and saturated calomel electrode were used as working electrode, counter electrode, and reference electrode in a 0.1 mol/L Bu_4NPF_6-acetonitrile solution, respectively. The E_{HOMO} and E_{LUMO} are calculated as refer to the eqs (1) and (2).

$$E_{HOMO}=-(E_{ox}+4.4)\ \text{eV} \qquad (1),$$

$$E_{LUMO}=-(E_{red}+4.4)\ \text{eV} \qquad (2).$$

The illuminated current density-voltage (*J-V*) characteristics were characterized using Keithley 2400. The currents were measured under 100 mW cm^{-2} simulated AM 1.5 G irradiation (Abet Solar Simulator Sun2000). Atomic force microscopic (AFM) images were measured on a nanoscope III A (Digital Instruments) scanning probe microscope using the tapping mode. Scanning electron microscopy (SEM) imaging was conducted on SU8020 scanning electron microscope operated at an acceleration voltage of 8 kV. X-ray diffraction (XRD) measurements were performed with a Rigaku D/Max-B X-ray diffractometer with Bragg-Brentano parafocusing geometry, a diffracted beam monochromator, and a conventional cobalt target X-ray tube set to 40 KV and 30 mA. The ultraviolet-visible (UV-vis) spectra of the samples were recorded on a PerkinElmer Lambda 750 spectrophotometer. The photoluminescence spectra were measured by photoluminescence spectroscopy (Hitachi F-7000). Timeresolved photoluminescence were measured by an Edinburgh Instruments FLS920 spectrometer.

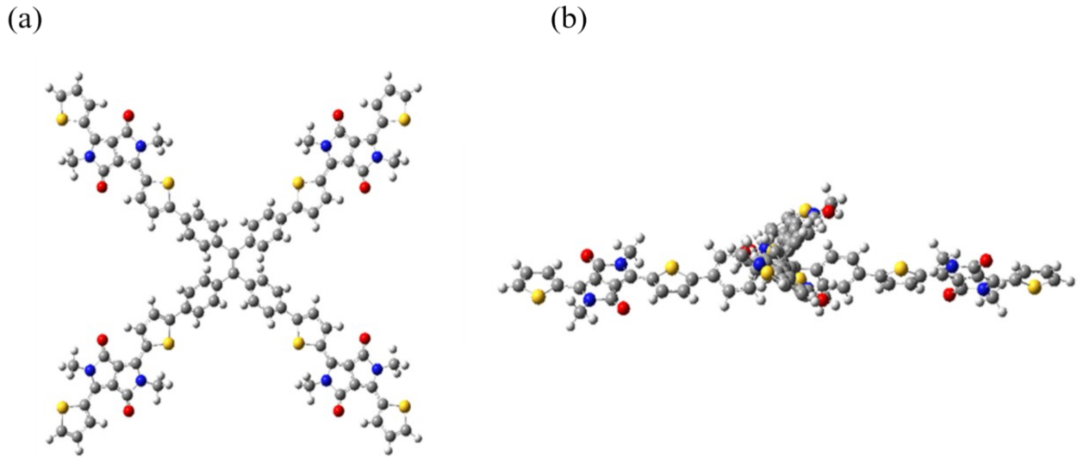

Figure S4. Density functional theory (DFT) simulations TPE-DPP4 spatial configuration of the molecule (a) top view, (b) side view.

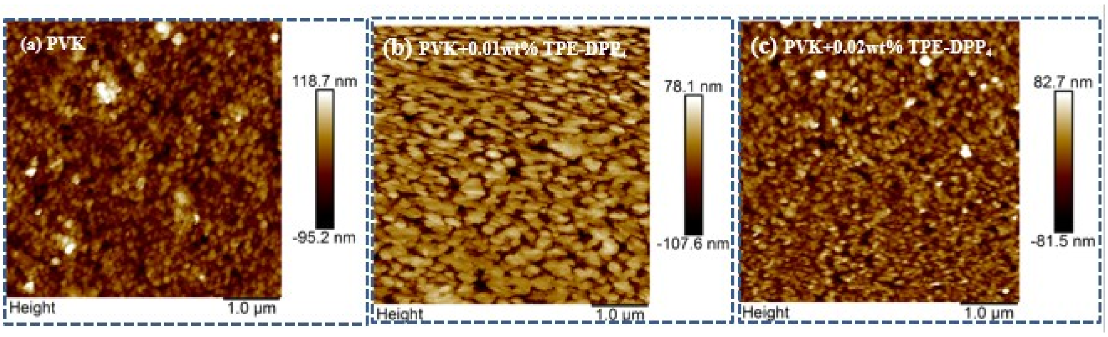

Figure S5. AFM morphology of (a) perovskite, (b) provskite+0.01wt% TPE-DPP$_4$ and (c) perovskite+0.02wt% TPE-DPP$_4$.

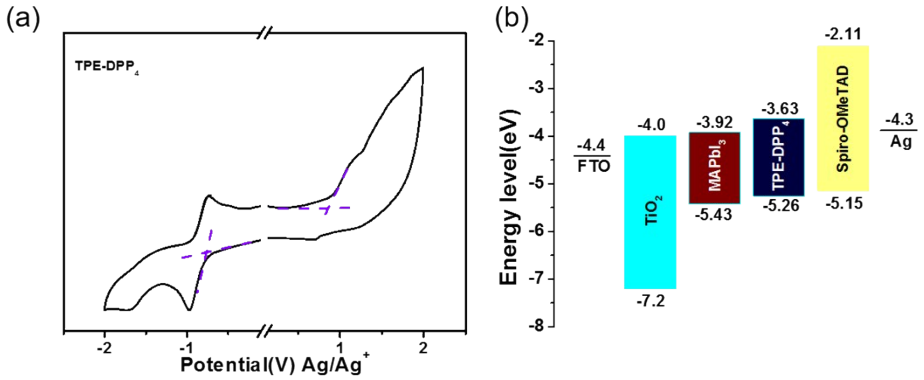

Figure S6: (a) Cyclic voltammetry (CV) of the copolymer TPE-DPP_4 thin film measured in a 0.1 M Bu_4NPF_6-CH_3CN solutions with a Pt electrode and an Ag/$AgNO_3$ reference electrode. (b) Energy-level diagram of the corresponding components in perovskite solar cell

Table S1. Energy levels of the TPE-DPP4

	E_{OX}(eV)	E_{RED} (eV)	E_{LUMO} (eV)	E_{HOMO} (eV)
TPE-DPP_4	0.86	-0.77	-3.63	-5,26

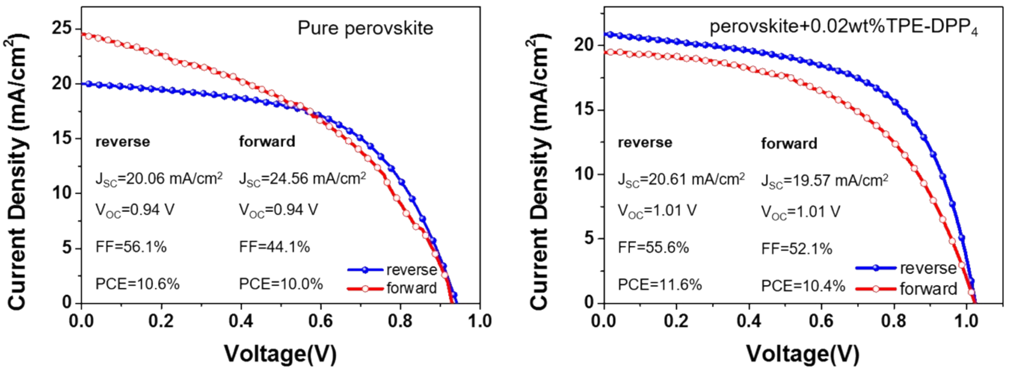

Figure S7. Forwar and reverse scan *J-V* curves for pure perovskite and perovskite+0.02wt%TPE-DPP$_4$ perovskite solar cells d

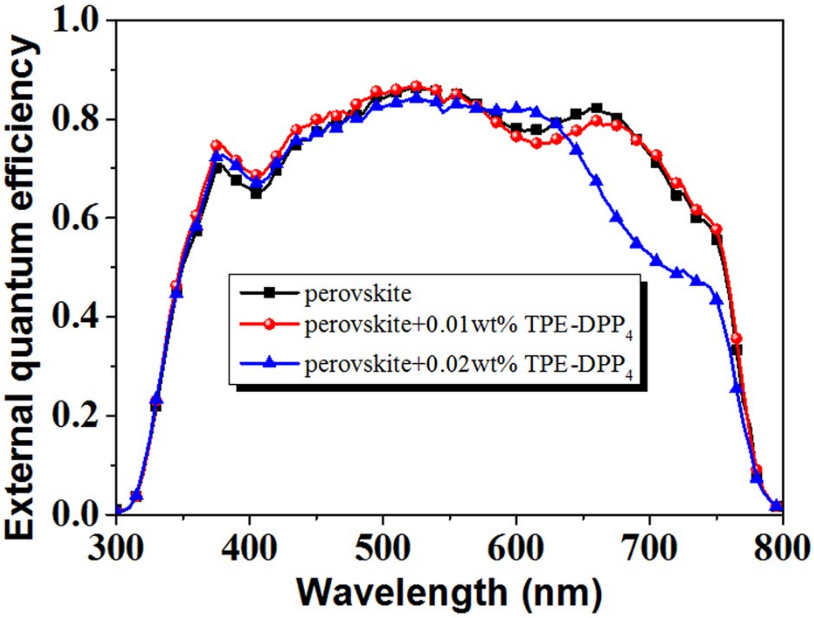

Figure S8. EQE curve of the perovskite cell based on perovskite and perovskite+TPE-DPP$_4$ hybrid films.