Supporting Information

A Multifunctional Fullerene Derivative for Interface Engineering in Perovskite Solar Cells

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Materials.

5-hydroxyisophthalic acid (99%), 4-dimethylaminopyridine (DMAP) (99%) were purchased from Chem Greatwall. PCC (Pyridinium Chlorochromate) (98%), octyl 2-cyanoacetate (99%) was purchased from J&K scientific Co., Ltd. $LiAlH_4$ (97%) was purchased from Aladdin, p-toluenesulfonic acid (PTSA) (98%) and N,N-diisopropylcarbodiimide (DIPC) (98%) were purchased from Energy Chemical. SiO_2, $(NH_4)_2HPO_3$, H_2SO_4, HCl, anhydrous magnesium sulfate, methanol, ethyl acetate, petroleum ether, alcohol, toluene, dichloromethane, tetrahydrofuran, sodium hydrogen carbonate and o-dichlorobenzene were purchased from Sinopharm Chemical Reagent Co., Ltd. All of these except tetrahydrofuran were used without further purification. Tetrahydrofuran was dried over sodium, and distilled before use. [6,6]-phenyl-C_{61}-butyric acid (PCBA) was synthesized according to the literature method.[1,2]

Characterization.

Device characterization

The area of devices is 0.108 cm^2. *J–V* characteristics of photovoltaic cells were taken using a Keithley 2400 source measure unit under a simulated AM1.5G spectrum. With an Oriel 9600 solar simulator, the light intensity was calibrated by KG-5 Si diode. The *J-V* measurements were carried out in nitrogen glove box. The devices were taken out of nitrogen glove box for external quantum efficiencies measurement and EQE was measured by Enli tech (Taiwan) measurement system. For transient photovoltage and current measurements, a white light bias was generated from an array of diodes (Molex 180081-4320) to simulate 0.5 sun bias light working condition. A pulsed red dye laser (Rhodamine 6G, 590nm) pumped by a nitrogen laser (LSI VSL-337ND-S) was used as the perturbation source, with a pulse width of 4 ns and a repetition frequency of 10 Hz. The intensity of the perturbation laser pulse was controlled to maintain the amplitude of transient V_{oc} below 5 mV so that the perturbation assumption of excitation light holds. The voltages under open circuit and currents under short circuit conditions were measured over a 1 MΩ and a 50 Ω resistor, and were recorded on a digital oscilloscope (Tektronix DPO 4104B).

Structure and optical characterization.

^{1}H NMR spectra were measured using a Varian Mercury-400 NMR. Time-of-flight mass spectra were recorded with a Broker MALDI-TOF mass system. Thermal gravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris 6, with a heating rate of 10 ^{o}C/min under nitrogen flow. Differential scanning calorimetry (DSC) was performed under nitrogen flushing at a heating rate of 10 ^{o}C/min with a NETZSCH (DSC-204) instrument. Film thicknesses were measured using a KLA Tencor profilometer. Transmittance spectra were acquired on a Cary 6000i UV-vis-NIR spectrophotometer. X-ray diffraction pattern (*2θ* scans) of perovskite deposited on the glass/ITO/TiO_2 with and without PCBB-2CN-2C8 substrates were obtained by using an X-ray diffractometer (Panalytical X'Pert Pro) under Cu-Kα radiation (λ=1.54050Å). The data were collected from 10 to 70° (2θ) with a 0.02° step size. The SEM images were collected by using an emission SEM (The Nova 230 NanoSEM), where the electron beam accelerated in the range of 500V to 30 kV. SKPM was performed on TiO_2 and TiO_2/PCBB-2CN-C8 surfaces in air, and carried out on a Park XE-120 (Park Systems Corp. Suwon, Korea) atomic force microscopy using Cr/Au coated conducting tips (SC18, Mikromash Tallinn, Estonia) with a resonance frequency of approximately 75 kHz and a spring constant of approximately 2.8 N/m. An AC voltage (3 V in amplitude and 10 kHz in frequency) is applied to the actuated cantilever, and the DC voltage applied to the tip that nullifies the tip-sample interaction is collected as the SP signal. Through a feedback loop, this electrostatic force was nullified by a DC bias applied to the tip, while the DC bias served as a direct measurement of the surface potential. Steady-state photoluminescence (PL) was analyzed using Horiba Jobin Yvon system with an excitation at 640 nm. Time-resolved photoluminescence was obtained using the time correlated single-photon counting technique (Picoharp 300), and the excitation was provided by a picosecond diode laser at the wavelength of 768 nm with a repetition frequency of 1 MHz (PDL 800B).

Table S1. *Values for TRPL characteristics of perovskite film on TiO_2 and TiO_2/PCBB-2CN-2C8.*

ETL	τ1	Ratio	τ2	Ratio
TiO_2	9.7	96.82%	172	3.18%
TiO_2/PCBB-2CN-2C8	3.6	99.98%	63.2	0.02%

$$hysteresis\ index = \frac{J_{RS}(0.8\ V_{oc}) - J_{FS}(0.8\ V_{oc})}{J_{RS}(0.8\ V_{oc})} \qquad (1)$$

Equation (1): $J_{RS}(0.8\ V_{oc})$ and $J_{FS}\ (0.8\ V_{oc})$ represent photocurrent density at 80% of V_{oc} for the reverse scan (RS) and forward scan (FS), respectively.

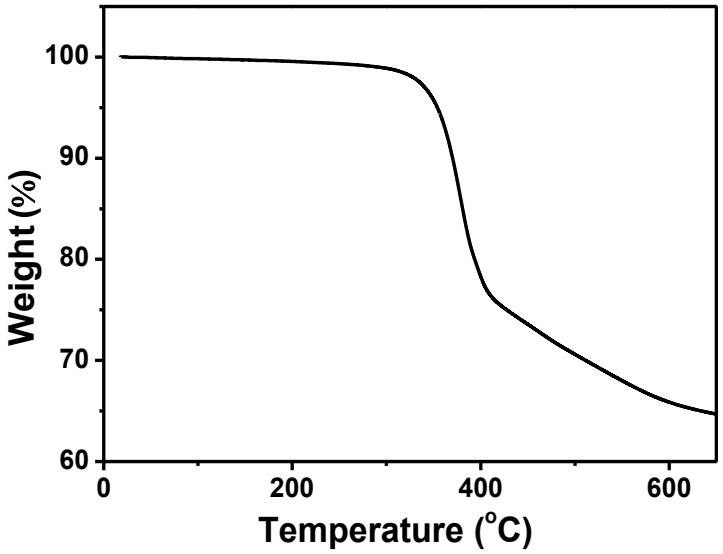

Figure S1. TGA thermogram of PCBB-2CN-2C8 at a heating rate of 10°C/min under N_2.

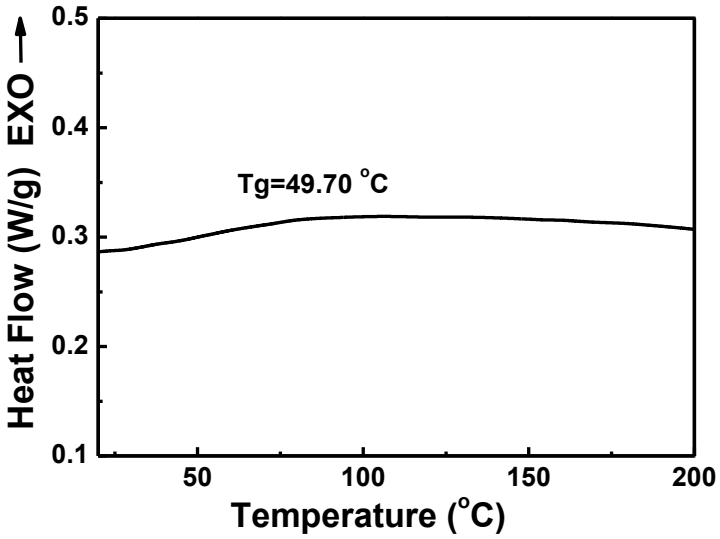

Figure S2. DSC analysis of PCBB-2CN-2C8 at a heating rate of 10 °C/min in N_2.

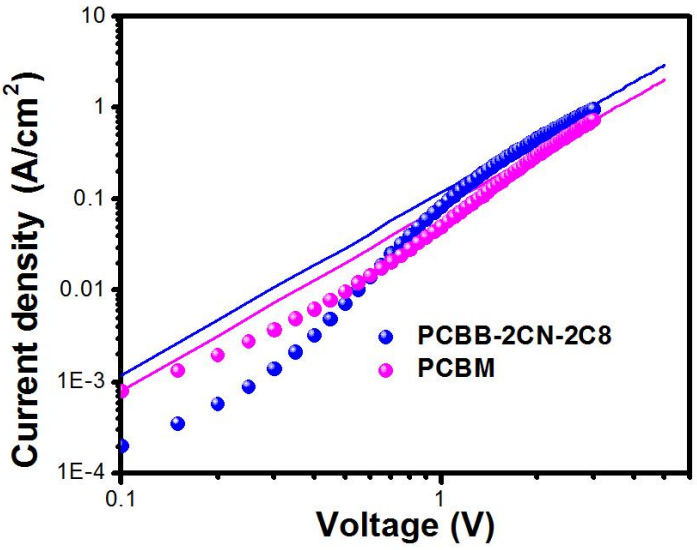

Figure S3. *J*−*V* characteristics of the electron-only devices based on PCBB-2CN-2C8 and PCBM for comparison with the structure of ITO/ZnO/fullerene derivative/ZnO/Al.

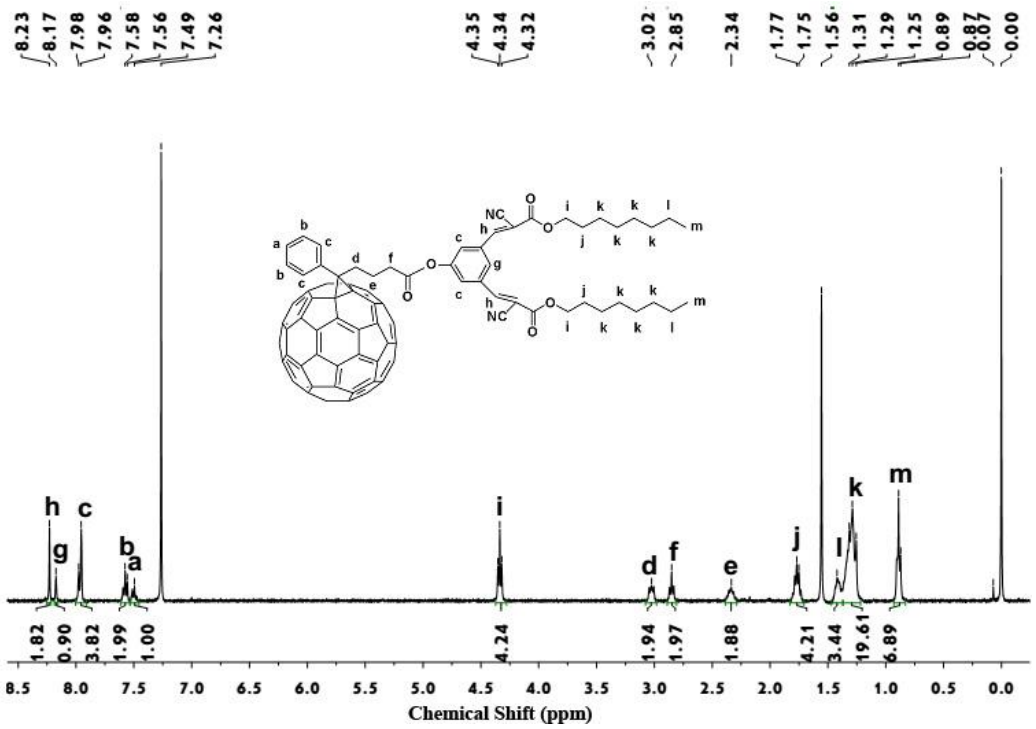

Figure S4. ^{1}H NMR spectrum of PCBB-2CN-2C8

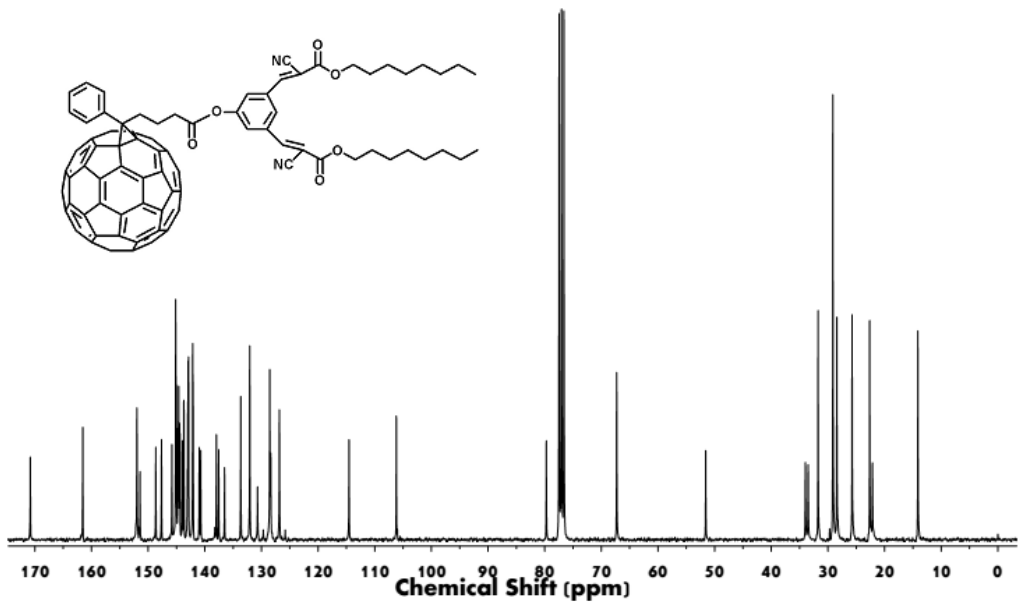

Figure S5. ^{13}C NMR spectrum of PCBB-2CN-2C8

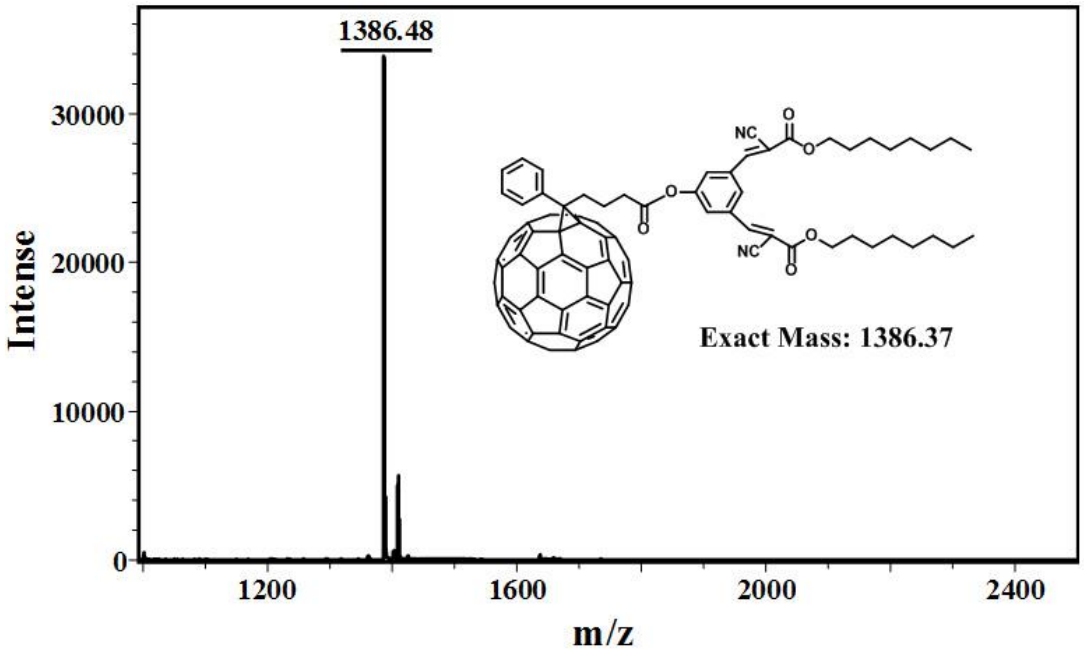

Figure S6. MALDI- TOF mass spectrum of PCBB-2CN-2C8.

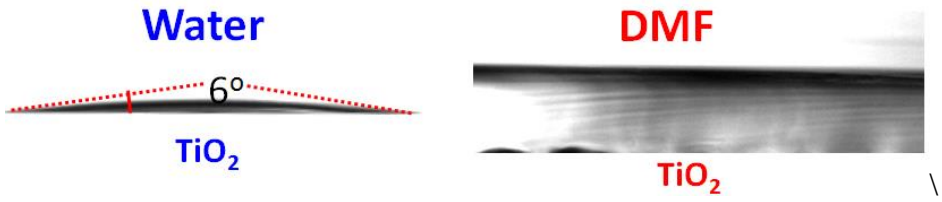

Figure S7. The images of water and DMF droplets contact angles on TiO_2 surfaces.

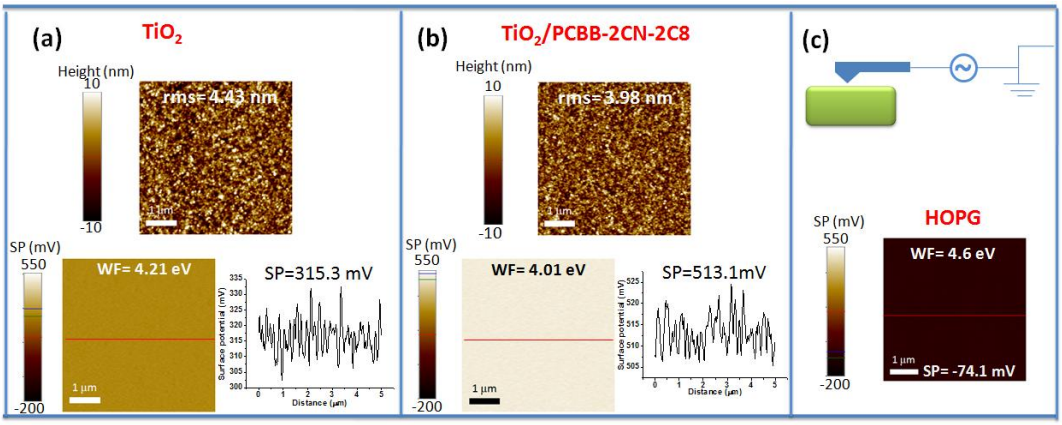

Figure S8. The AFM height and SKPM images of TiO_2 and TiO_2/PCBB-2CN-2C8 surfaces with their corresponding root-mean-square (rms), surface potential (SP) and work function (WF); (a) on TiO_2. (b) on TiO_2/PCBB-2CN-2C8. (c) on highly ordered pyrolytic graphite (HOPG) as standard sample.

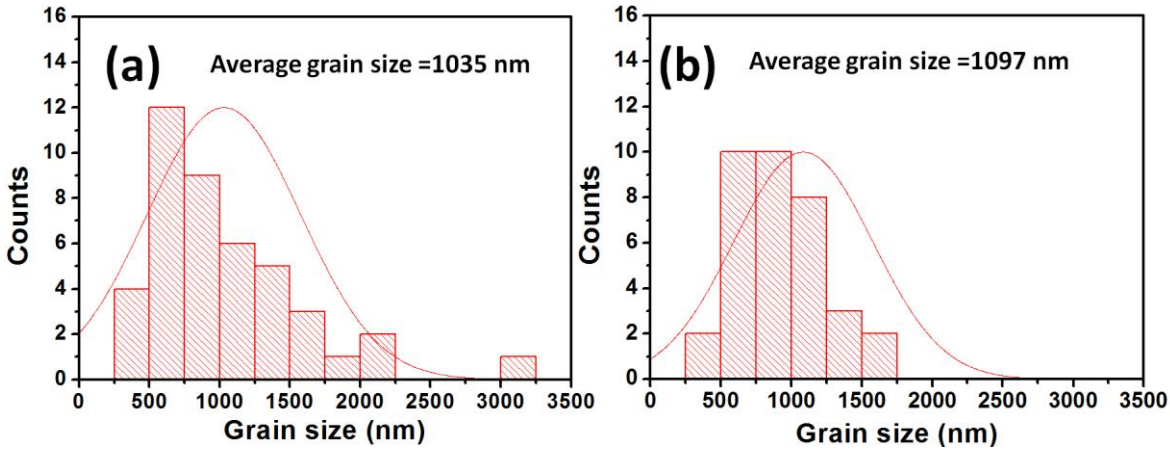

Figure S9. Grain size distribution of the perovskite film spin-coated on varied substrate: (a) on TiO_2; (b) on TiO_2/PCBB-2CN-2C8.

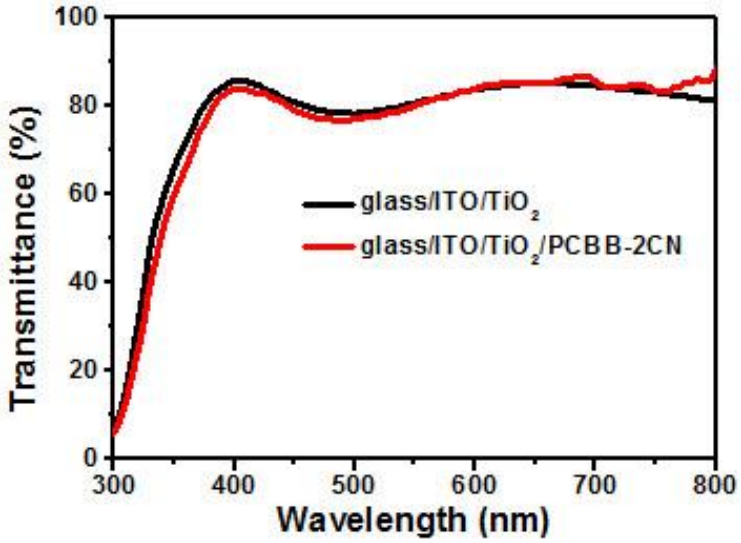

Figure S10. Transmittance spectra of glass/ITO substrates coated with TiO_2 or TiO_2/PCBB-2CN-2C8.

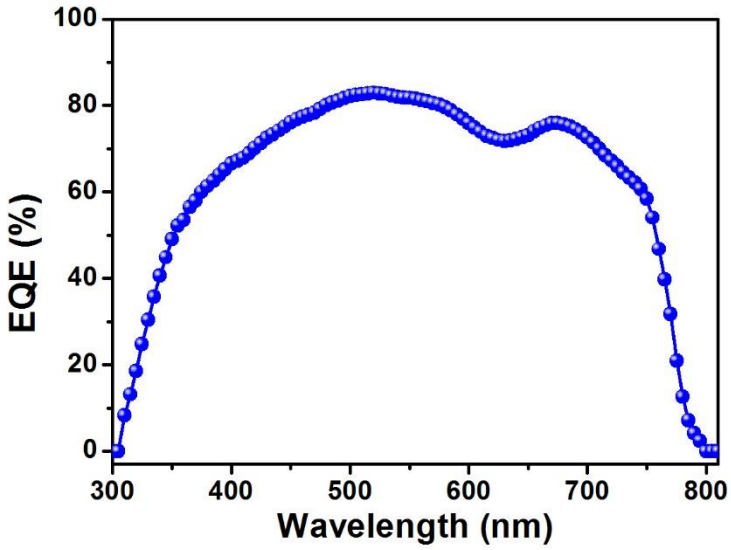

Figure S11. EQE spectrum of perovskite solar cell based on TiO_2/PCBB-2CN-2C8 ETL.

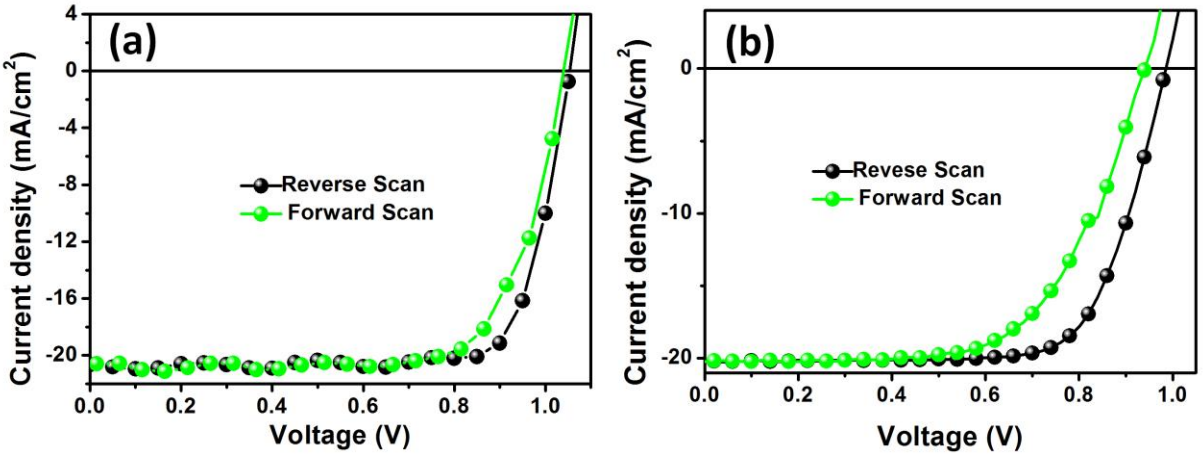

Figure S12. *J-V* curves in reverse and forward scan measured under 100 mW/cm^2 AM 1.5G illumination with the structure of glass/ITO/TiO_2/with or without PCBB-2CN-2C8/$CH_3NH_3PbI_3$/spiro-OMeTAD/Au: (a) TiO_2/PCBB-2CN-2C8 ETL based perovskite solar cell; (b) TiO_2 ETL based perovskite solar cell. Forward scan: 0 V→1.2 V, scan rate 200 mV/s, delay time 100 ms; Reverse scan: 1.2 V→0 V, scan rate 200 mV/s, delay time 100 ms.

REFERENCES

(1) Zhang, P.; Li, C.; Li, Y.; Yang, X.; Chen, L.; Xu, B.; Tian, W.; Tu, Y. *Chemical Communications* **2013**, *49*, 4917.
(2) Hummelen, J. C.; Knight, B. W.; LePeq, F.; Wudl, F.; Yao, J.; Wilkins, C. L. *The Journal of Organic Chemistry* **1995**, *60*, 532.