Electronic Supplementary Information

Simultaneous hole transport and defect passivation enabled by a dopant-free single polymer for efficient and stable perovskite solar cells

Xiaoqing Jiang,^{a, #} Xuan Liu,^{a, b, #} Jiafeng Zhang,^{a, b} Sajjad Ahmad,^{a, b} Dandan Tu,^{a, b} Wei Qin,^a Tonggang Jiu,^c Shuping Pang,^c Xin Guo,^{a, *} and Can Li ^{a, *}

^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, 457 Zhongshan

Road, Dalian 116023, China

E-mail: guoxin@dicp.ac.cn; canli@dicp.ac.cn

^b University of Chinese Academy of Sciences, Beijing 100049, China.

^{*c*} Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, P.R. China.

[#] X. Jiang and X. Liu contributed equally to this work.

Materials and methods

The PbBr₂ and PbI₂ were purchased from TCI chemical Ltd. The MAI, FAI and MABr were purchased from Xi'an Polymer Light Technology Corp, China. All solvents were purchased from Sigma without any further purification.

¹H NMR spectra were recorded on a Bruker 400 MHz AVANCE III with tetramethylsilane as an internal reference. The UV-vis absorption spectra were performed by Cary 5000 UV-Vis-NIR spectrophotometer, Varian Inc, USA. Cyclic voltammetry (CV) was carried out on a CHI600D electrochemical workstation at a scan rate of 50 mV s⁻¹ with an Ag/AgCl as the reference electrode. Redox potentials of PBDT-Nx were measured in acetonitrile solution with 0.1 M TBAPF₆ as the supporting electrolyte. A glassy carbon electrode with a surface area of 0.785 cm² was used as the working electrode. The counter electrode was a platinum wire and Ag/AgCl as the reference electrode. The redox potential was calibrated against Fc/Fc⁺ as an external standard. Scanning electron microscopy (SEM) was performed on a Quanta 200F microscope (FEI Company) with an accelerating voltage of 20 kV. Two dimensional Grazing-incidence X-ray diffraction (2D GIXD) measurements were conducted using the Beamline BL14B1 at the Shanghai Synchrotron Radiation Facility (SSRF) with the incident photon energy of 10 keV (wavelength of 1.2398 angstrom) at an incident angle of 0.13° and an exposure time of 30 s. The charge carrier mobilities were measured from the space-charge-limited current (SCLC) method. The conductivities of the polymers were determined by using a two-contact electrical conductivity set-up, which were performed by following a published procedure.^[1] The time-resolved photoluminescence spectra were recorded on a FLS920 fluorescence spectrometer (Edinburgh Instruments) in air at room temperature. A picosecond pulsed diode laser (406.8 nm) was used as the excitation source. X-ray photoelectron spectroscopy (XPS) was carried out on a ESCALAB 250 Xi photoelectron spectroscopy (Thermo Fisher Scientific) with Al Ka radiation source and all the binding energies were calibrated by C 1s (284.8 eV) as a reference. Electrochemical impedance spectroscopy (EIS) measurements were performed with a bias of 0.6 V in the frequency range of 1 MHz to 0.1 Hz under 1 sun illumination at room temperature using an electrochemical workstation (CHI600D). Differential scanning calorimetry (DSC) was carried out with a thermal analyzer (NETZSCH DSC 206, Germany), measured from 40 °C to 250 °C at a heating rate of 10 °C /min. Thermogravimetric analysis (TGA) was performed using thermal gravimetric analyzer (NETZSCH TG209, Germany) with a ramp of 10 °C/min under N₂ from 50 °C to 580 °C.



Figure S1. Thermogravimetric analysis (TGA) curves of PBDT-Nx.



Figure S2. Differential scanning calorimetry (DSC) curves of PBDT-Nx at a heating rate of 10 °C min⁻¹.



Figure S3. Cyclic voltammetry (CV) curves of a) PBDT-N0, PBDT-N5, PBDT-N20 and b) Ferrocene (Fc). The HOMO and LUMO energy levels were calculated by E_{HOMO} =-($E_{onset, ox}$ - E_{Fc} +5.1) eV and E_{LOMO} =-($E_{onset, red}$ - E_{Fc} +5.1) eV (E_{Fc} = 0.05 eV).



Figure S4. Normalized UV-Vis absorption spectra of a) PBDT-N0, b) PBDT-N5, c) PBDT-N20 in chlorobenzene solutions (10⁻⁵ M) and in films



Figure S5. Integrated and normalized (010) peak intensities of PBDT-Nx films plotted as a function of the azimuthal angle.



Figure S6. Schematic of hole-only device for measuring the hole mobility.



Figure S7. a) Current-voltage characteristics of PBDT-Nx based films; and b) schematic of the device for the conductivity test. The conductivity was calculated by the equation $\sigma = L/(R \cdot \mu \cdot d)$, where L is the channel length; R is the film resistance, μ is the channel width, and d is the film thickness, respectively. The conductivity of polymers are estimated to be 1.0×10^{-4} S cm⁻¹ (PBDT-N0), 1.3×10^{-4} S cm⁻¹ (PBDT-N5) and 4.2×10^{-4} S cm⁻¹ (PBDT-N20), respectively.^[1]



Figure S8. Steady-state PL spectra of perovskite films without treatment and treated with DMBA or PBDT-Nx polymers



Figure S9. *J-V* characteristics of PSCs based on dopant-free PBDT-Nx, Spiro-OMeTAD and doped Spiro-OMeTAD as the HTM. The hysteresis indexes are calculated to be 0.23 (PBDT-N0), 0.16 (PBDT-N5) and 0.12 (PBDT-N20), respectively, according to $HI=(J_{RS}(0.8V_{oc})-J_{FS}(0.8V_{oc}))/J_{RS}(0.8V_{oc}).^{[2]}$



Figure S10. Stabilized PCE and J_{sc} as a function of time for doped Spiro-OMeTADbased PSC measured at maximum power point voltage of 0.90 V.

Polymer	Out-of-plane (010) peak (Å ⁻¹)	π - π stacking distance (Å)
PBDT-N20	1.64	3.82
PBDT-N5	1.62	3.87
PBDT-N0	1.58	3.97

Table S1. 2D GIXD packing parameters for PBDT-Nx films.

References

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