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ADVANCED MATERIALS INTERFACES

Supporting Information

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Modulate Molecular Interaction between Hole Extraction
Polymers and Lead Ions toward Hysteresis-Free and Efficient
Perovskite Solar Cells

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1. General Information.

Instrument. ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker Advance III 400 (400 MHz) nuclear magnetic resonance (NMR) spectroscope. MALDI-TOF MS spectra were measured on a Walters Maldi Q-TOF Premier mass spectrometry. Molecular weight and molecular weight distribution indices of the synthesized polymers were measured with a Waters GPC using THF as eluent and polystyrene as standard. Thermogravimetric analysis (TGA) was carried out on a WCT-2 thermal balance under protection of nitrogen at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. UV-vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. The size distributions of PbI_2 (0.5 M in DMF) was measured by dynamic light scattering with zeta potential analyzer. Cyclic voltammetry (CV) was done on a CHI600A electrochemical workstation with Pt disk, Pt plate, and standard calomel electrode (SCE) as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 M Bu_4NPF_6 CH_2Cl_2 solution. The CV curves were recorded versus the potential of SCE, which was calibrated by the ferrocene-ferrocenium (Fc/Fc^+) redox couple (5.1 eV below the vacuum level). The SEM data were scanned by S-4800 (Hitachi) field-emission scanning electron microscope (FESEM). X-Ray diffraction (XRD) pattern was obtained by Bede D1 system high-resolution X-Ray diffractometer. The PL spectra (steady state and transient spectra) were measured using an FluoroMax-4 HORIBA Jobin Yvon spectrofluorometer. Calculations were performed in the Density Functional Theory (DFT) framework as implemented in the GAUSSIAN software suite using the B3LYP exchange correlation functional and 6-31G**//LanL2DZ (or Def2-TZVP) basis set. The in-situ interfacial characterizations (SRPES and NEXAFS) were performed at the Catalysis and Surface Science Endstation at the BL11U beamline in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. The detailed description of the ultrahigh vacuum system of this endstation can be found elsewhere.^[1] The PbI_2 deposition was carried out in a molecular beam epitaxy (MBE) chamber and then transported to an analysis chamber without any air exposure. The S 2p and O 1s XPS spectra were measured with photon energies of 600 eV and 240 eV, respectively. The valence-band spectra were determined with a photon energy of 40 eV and sample bias of -5.0 V was applied to observe the secondary electron cutoff. For the surficial sensitive detection, the S L-edge and O K-edge NEXAFS measurements were carried out in the partial electron yield (PEY) mode.

Materials. All reagents and solvents, unless otherwise specified, were purchased from Aladdin, Aldrich and J&K Scientific Ltd. and used without further purification. PC_{61}BM was purchased from American Dyes Source, Inc. $\text{CH}_3\text{NH}_3\text{I}$ (MAI) was purchased from Shanghai Materwin New Materials Co. Ltd.

2. Perovskite solar cells fabrication.

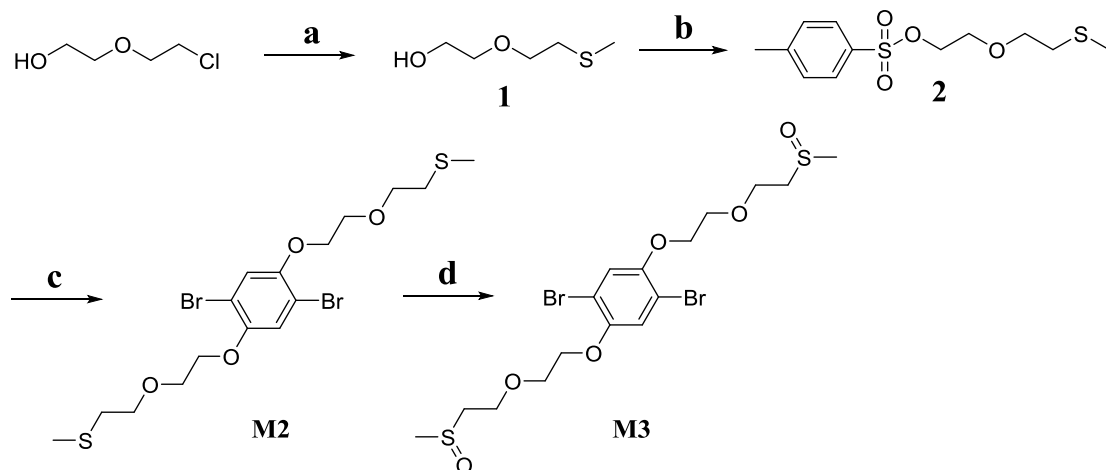
Prior to fabrication, the substrates were cleaned by sonication using detergent, deionized water, acetone, and isopropanol sequentially for every 15 min followed by 15 min of ultraviolet ozone (UV-ozone) treatment. The substrates were transferred to a glovebox. PB2T -, PB2T-S and PB2T-SO films were fabricated by spin-coating chloroform solutions with a concentration of 2 mg mL^{-1} on the ITO substrates in glove-box. The films are free of annealing.

PbI_2 (1 M) and DMSO (1 M) were dissolved in DMF under stirring at $70\text{ }^\circ\text{C}$. The solution was kept at $70\text{ }^\circ\text{C}$ during the whole procedure. The solution was then spin coated on the HEM

film at 6000 rpm for 60 s. Then a solution of MAI in 2-propanol (IPA) (50 mg mL^{-1}) was dropped and spin-coated at 6000 rpm for 60 s. Afterwards, the as prepared films were heated at 90°C for 15 min. After cooling down, a layer of [6,6]-phenyl-C61-butyric acid methyl ester (PC_{61}BM , 20 mg mL^{-1} in chlorobenzene) was spin-coated at 2000 rpm for 45 s. A hole-blocking layer was deposited via spin-coating ZnO nanoparticles in ethanol at 4000 rpm for 30 s on the top of PC_{61}BM layer. Subsequently, samples were loaded into a vacuum deposition chamber (background pressure $\approx 5 \times 10^{-4} \text{ Pa}$) to deposit a 100 nm thick Al cathode with a shadow mask. For the BCP based devices, a layer of BCP (0.5 mg mL^{-1} in ethanol) was spin-coated at 3000 rpm after PC_{61}BM . Subsequently, samples were loaded into a vacuum deposition chamber to deposit a 100 nm Ag cathode. To specify the illuminated area, we used an aperture (shadow mask) with an area of 0.06 cm^2 , whereas the total device area defined by the overlap of the electrodes was approximately 0.12 cm^2 . The thickness of perovskite layer is around 300 nm.

The J-V characteristics were measured with Keithley 2400 measurement source units with the devices maintained at room temperature in glove-box. The photovoltaic response was measured under a calibrated solar simulator (Enli Technology) at 100 mW cm^{-2} , and the light intensity was calibrated with a standard photovoltaic reference cell. The devices were stored in glove-box in dark overnight before measurement. The forward J-V scans were measured from -0.1 V to 1.2 V with a scan rate of 0.05 V s^{-1} and a voltage step of 0.01 V while the reverse J-V scans were measured from 1.2 V to -0.1 V with a scan rate of 0.05 V s^{-1} and a voltage step of 0.01 V . For MPP measurement, the interval is 1 s with a constant applied bias. The EQE spectrum was measured using a QE-R Model of Enli Technology.

3. Synthesis of PB2T-O, PB2T-S and PB2T-SO.



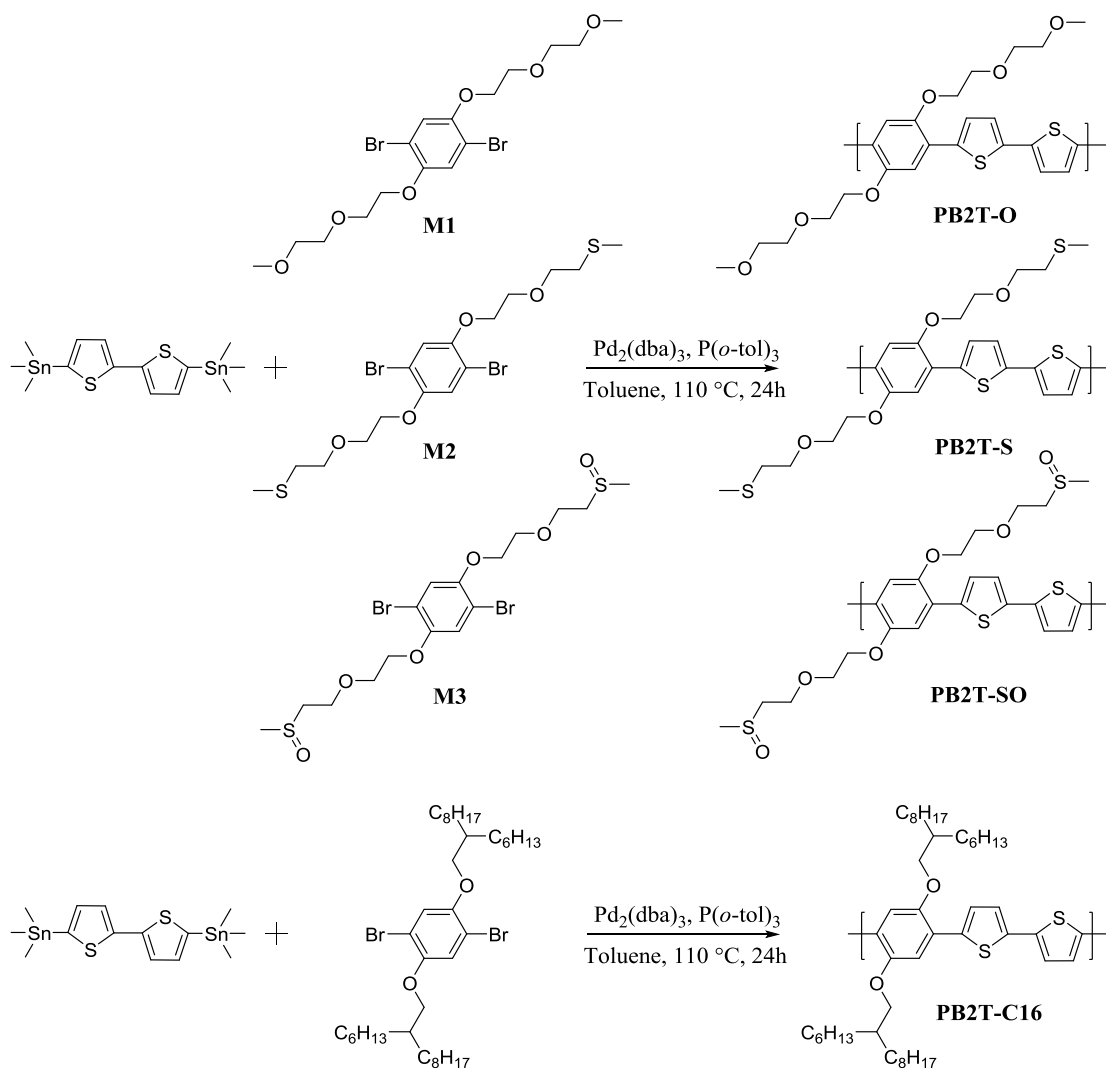


Figure S1. Synthetic route of PB2T-O, PB2T-S, PB2T-SO and PB2T-C16.

(a) Sodium methanethiolate, dioxane, reflux; (b) NaOH, *p*-toluenesulfonyl chloride, THF, 0 °C; (c) 2,5-dibromo-1,4-benzenediol, K₂CO₃, DMF, 70 °C; (d) *m*-chloroperbenzoic acid, CH₂Cl₂, 0 °C.

1,4-Dibromo-2,5-bis(2-(2-methoxyethoxy)ethoxy)benzene (M1) was synthesized following the reported procedure.^[2]

2-(2-(Methylthio)ethoxy)ethan-1-ol (1) was synthesized following the reported procedure.^[3]

2-(2-(Methylthio)ethoxy)ethyl 4-methylbenzenesulfonate (2). NaOH (0.7 g, 17.5 mmol) and 2-(2-(methylthio)ethoxy)ethan-1-ol (1.6 g, 11.8 mmol) were dissolved into 3.5 mL water and 28 mL THF in a clean flask during ice bath. *p*-Toluenesulfonyl chloride (2.47g, 12.9 mmol) in 3.5 mL THF was dropped into the mixture while maintaining the temperature below 5 °C. The mixture was stirred for 5 h and water was added. The mixture was extracted with chloroform. The combined organic part was washed with water and dried with MgSO₄. The solution was evaporated in vacuum to give the pure compound as a light yellow liquid (2.15 g, 63%). ¹H NMR (400 MHz, CDCl₃), δ 7.81 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 4.19

– 4.14 (m, 2H), 3.67 (dd, J = 5.4, 4.1 Hz, 2H), 3.59 (t, J = 6.7 Hz, 2H), 2.61 (t, J = 6.7 Hz, 2H), 2.45 (s, 3H), 2.11 (s, 3H).

1,4-Dibromo-2,5-bis(2-(2-methylthioethoxy)ethoxy)benzene (M2). Under N₂ atmosphere, to a solution of 2,5-dibromo-1,4-benzenediol (0.9 g, 3.3 mmol) and K₂CO₃ (2.3 g, 16.7 mmol) in 30 mL dry DMF, 2-(2-(methylthio)ethoxy)ethyl 4-methylbenzenesulfonate (2.15 g, 7.4 mmol) in 4 mL dry DMF was added dropwise during ice bath. After reacting for 30 min, the mixture was heated to 70 °C for another 8 h. Then water was added and the mixture was extracted with chloroform. The combined organic part was washed by water and dried with MgSO₄. The solution was evaporated in vacuum to give a crude product, which was purified by column using hexane as eluent. A sticky liquid (0.91 g, 54%) was obtained as the final product. ¹H NMR (400 MHz, CDCl₃), δ 7.16 (s, 1H), 4.15 - 4.10 (m, 2H), 3.88 – 3.84 (m, 2H), 3.78 (t, J = 6.8 Hz, 2H), 2.72 (t, J = 6.8 Hz, 2H), 2.16 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.31 (s), 119.16 (s), 111.40 (s), 71.05 (s), 70.22 (s), 69.28 (s), 33.58 (s), 16.14 (s).

1,4-Dibromo-2,5-bis(2-(2-methylsulfoethoxy)ethoxy)benzene (M3). To a solution of M2 (400 mg, 0.79 mmol) in 10 mL CH₂Cl₂ at 0 °C, 10 mL CH₂Cl₂ solution of *m*-chloroperbenzoic acid (85% purity, 322 mg, 1.58 mmol) was dropped slowly. After 16 h, the mixture was washed with saturated NaHCO₃ solution and the organic phase was dried with anhydrous MgSO₄. Removal of the solvent by evaporation gave a white solid (320 mg, 75%). ¹H NMR (400 MHz, CDCl₃), δ 7.15 (s, 1H), 4.15 - 4.10 (m, 2H), 4.08 – 3.97 (m, 2H), 3.91 – 3.86 (m, 2H), 3.08 – 2.88 (m, 2H), 2.65 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.22 (s), 119.05 (s), 111.32 (s), 69.90 (s), 69.67 (s), 63.96 (s), 54.74 (s), 39.26 (s). Exact Mass = 536.29, MS (MALDI-TOF) = 536.106.

PB2T-O. Under N₂ atmosphere, to a three-necked flask, M1 (100 mg, 0.21 mmol), 5,5'-bis(triMethylstannyl)-2,2'-bithiophene (104 mg, 0.21 mmol) and 2 mL anhydrous toluene were added. After deoxygenating for 30 min, Pd₂(dba)₃ (4 mg) and P(*o*-tol)₃ (5.2 mg) were added and the mixture was heated to 110 °C for 24 h. The mixture was cooled to room temperature and precipitated in hexane. The precipitate was purified by Soxhlet extraction (hexane, acetone, chloroform). The chloroform part was evaporated in vacuum to give the final product as a red solid (50 mg, 50%). ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, J = 3.7 Hz, 2H), 7.31 (s, 2H), 7.22 (d, J = 3.7 Hz, 2H), 4.28 (dt, J = 41.2, 4.6 Hz, 4H), 4.05 – 3.91 (m, 4H), 3.78 (dt, J = 11.9, 4.4 Hz, 4H), 3.62 (dt, J = 11.4, 5.7 Hz, 4H), 3.41 (s, 6H).

PB2T-S (PB2T-SO) was polymerized by the same procedure as PB2T-O using M2 (or M3) and 5,5'-bis(triMethylstannyl)-2,2'-bithiophene and obtained as a red solid. PB2T-S: ¹H NMR (400 MHz, CDCl₃) δ 7.54 (s, 2H), 7.31 (s, 2H), 7.23 (s, 2H), 4.32 (s, 4H), 3.99 (s, 4H), 3.86 – 3.73 (m, 4H), 2.78 (t, J = 6.6 Hz, 4H), 2.15 (s, 6H). PB2T-SO: ¹H NMR (400 MHz, CDCl₃) δ 7.53 (s, 2H), 7.28 (s, 2H), 7.23 (s, 2H), 4.32 (s, 4H), 4.12 – 3.96 (m, 8H), 3.12 – 2.86 (m, 4H), 2.58 (s, 6H).

PB2T-C16 was polymerized by the same procedure as PB2T-O using 1,4-dibromo-2,5-bis((2-hexyldecyl)oxy)benzene and 5,5'- bis(triMethylstannyl)-2,2'-bithiophene and obtained as a red solid. ¹H NMR (400 MHz, CDCl₃) δ 7.47 (s, 2H), 7.28 (s, 2H), 7.18 (s, 2H), 4.04 (s, 4H), 1.95 (d, J = 6.0 Hz, 2H), 1.69 – 1.19 (m, 48H), 0.86 (t, J = 6.4 Hz, 12H).

The molecular weights and molecular weight distribution indices of the synthesized polymers were measured by GPC using THF as eluent. However, due to the low solubility of PB2T-O, PB2T-S and PB2T-SO with polar side chains, only the low-Mn fraction could be dissolved in THF and the high-Mn fraction was filtered before running GPC. So the measured Mn of

PB2T-O, PB2T-S and PB2T-SO were 4.0, 4.2 and 4.1 kDa, with a polymer dispersity index (PDI) of 1.35, 1.24 and 1.41, respectively. The reference polymer PB2T-C16 which was polymerized using the same procedure as the above three polymers, has good solubility in THF and the measured M_n of PB2T-C16 was 42.3 kDa, with a PDI of 1.85.

4. Characterization of PB2T-O, PB2T-S and PB2T-SO and corresponding perovskite solar cells.

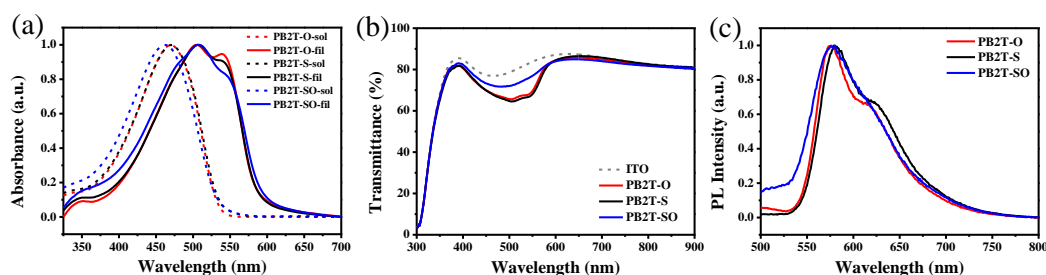


Figure S2. (a) UV-vis absorption spectra of HEMs in dilute solutions and thin films. (b) UV-vis transmittance of ITO with/without three HEMs. (c) PL emission spectra of HEMs in thin films.

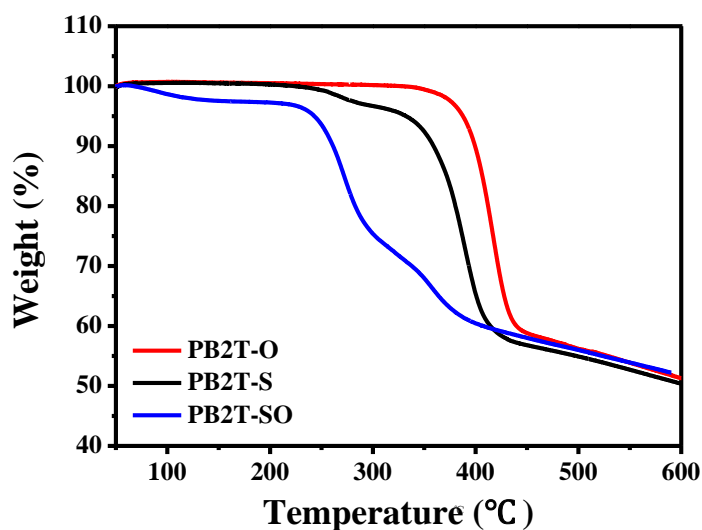


Figure S3. Thermogravimetric analysis (TGA) of PB2Ts with scan rate of 10°C /min under N_2 atmosphere.

Table S1 Calculated bonding energy of different end groups with Pb^{2+} .

	Basis set	Me_2O	Me_2S	Me_2SO
Bonding energy	6-31G**//LanL2DZ	-89.4	-91.9	-137.3

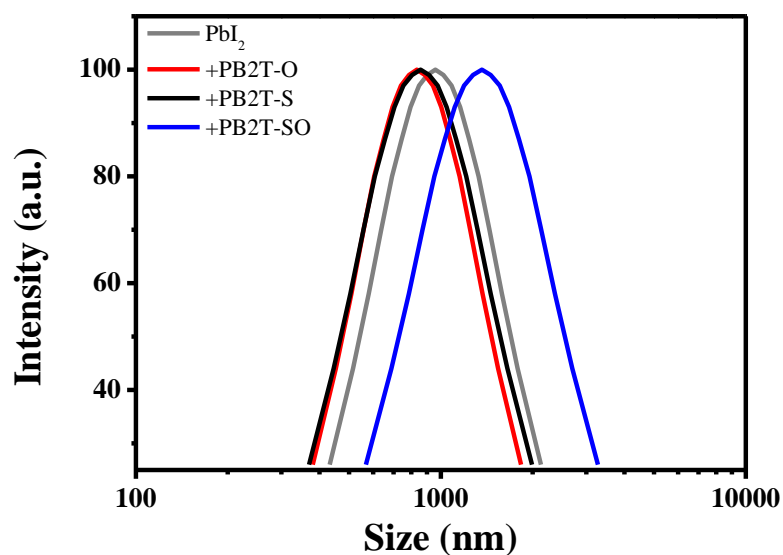


Figure S4. Size distributions of $\text{PbI}_2(\text{HEM})_x$ complexes in CPS detected by dynamic light scattering. The polydispersity index for PbI_2 , PB2T-O, PB2T-S and PB2T-SO are 0.265, 0.257, 0.300 and 0.328.

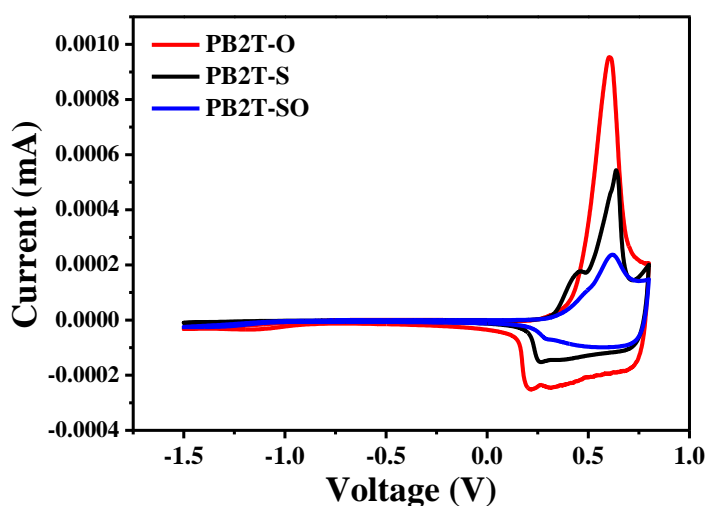


Figure S5. Cyclic voltammograms (CV) of HEMs.

Hole mobility test. The charge carrier mobility of the Trux-OMeTAD films were measured using the space-charge-limited current (SCLC) method. Hole-only devices were fabricated in

a structure of ITO/PEDOT:PSS/HEM/MoO₃/Al. The device characteristics were extracted by modeling the dark current under forward bias using the SCLC expression described by the Mott-Gurney law:

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3} \quad (1)$$

Here, $\varepsilon_r \approx 3$ is the average dielectric constant of the film, ε_0 is the permittivity of the free space, μ is the carrier mobility, $L \approx 50$ nm is the thickness of the film, and V is the applied voltage.

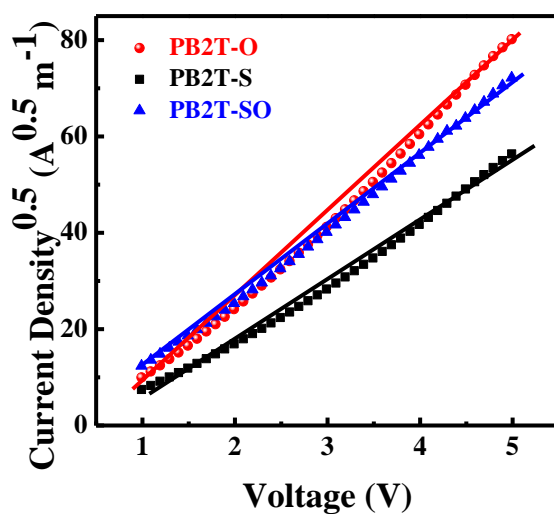


Figure S6. $J^{0.5}$ - V curves of hole-only devices with a architecture of ITO/PEDOT:PSS/HEM/MoO₃/Al.

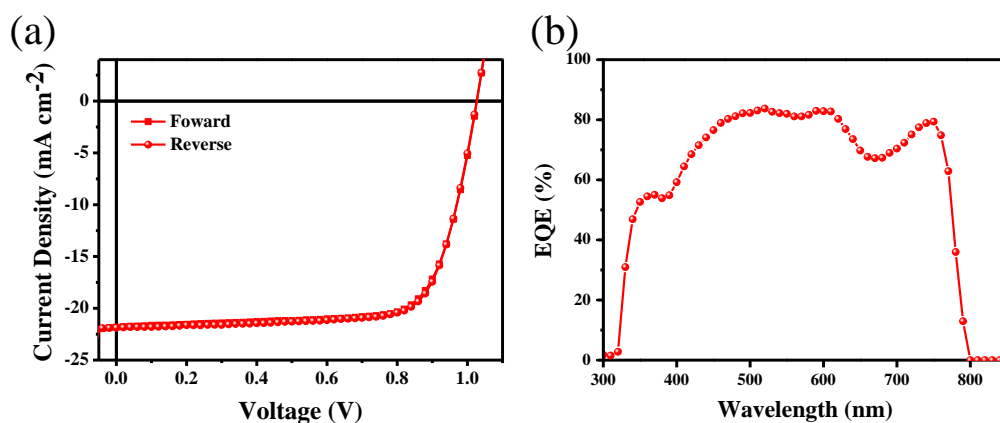


Figure S7. (a) J-V curve and (b) EQE spectrum of the devices with a structure of ITO/PB2T-O/perovskite/PC₆₁BM/BCP/Ag.

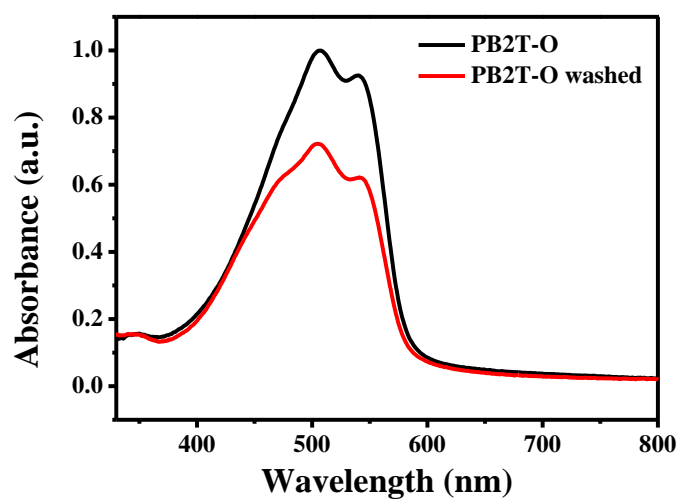


Figure S8. Normalized UV-vis absorption spectra of PB2T-O thin film before/after being washed by DMF.

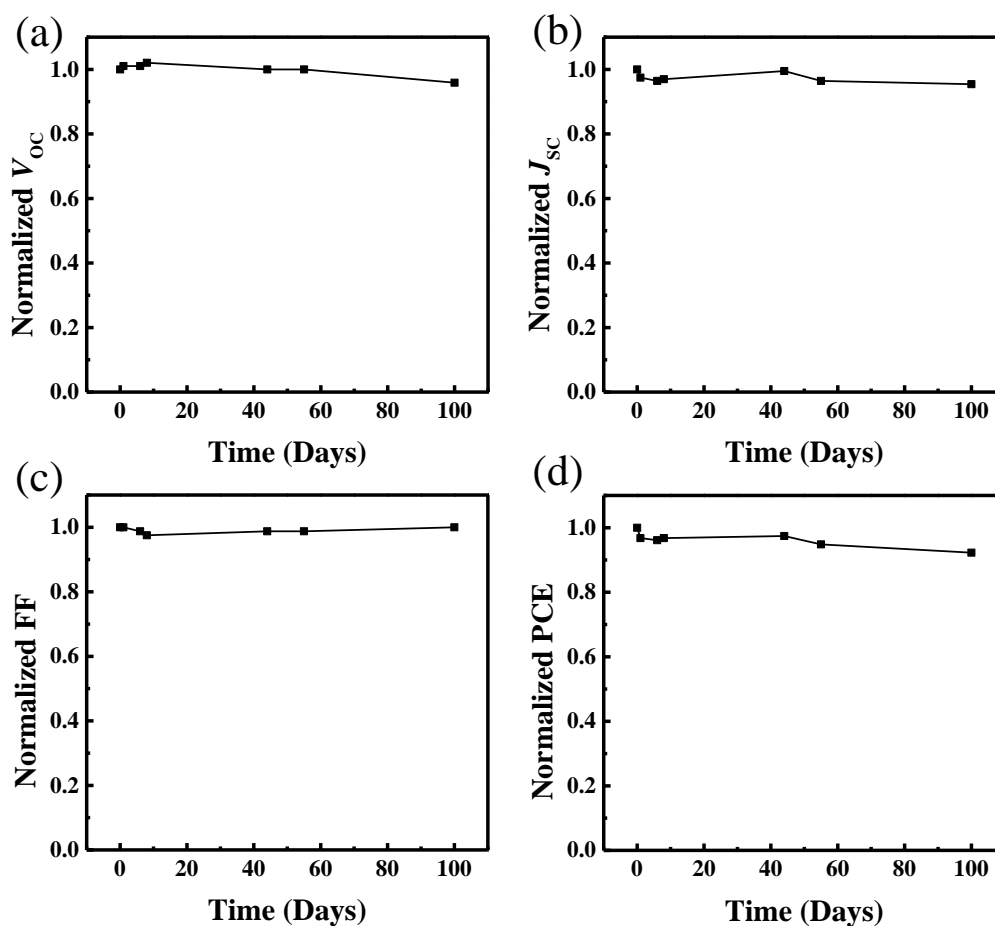


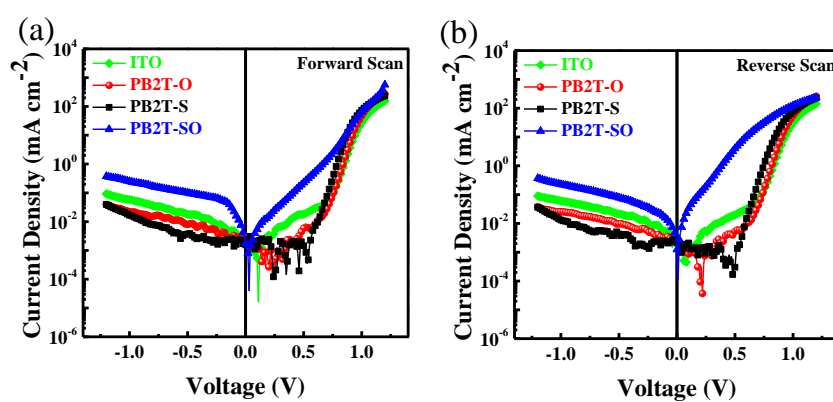
Figure S9. PB2T-O based PVSC device parameters (a) V_{OC} , (b) J_{SC} , (c) FF and (d) PCE stored in a glove box over 100 days.

Table S2 PB2T-O based PVSC device parameters stored in a glove box over 100 days.

Storage Time [Days]	V_{OC} [V]	J_{SC} [mA cm ⁻²]	FF	PCE [%]
0	0.97	19.7	0.81	15.5
1	0.98	19.2	0.81	15.0
6	0.98	19.0	0.80	14.9
8	0.99	19.1	0.79	15.0
44	0.97	19.6	0.80	15.1
55	0.97	19.0	0.80	14.7
100	0.93	18.8	0.81	14.3

Table S3 Time-Resolved PL Measurements.

sample	τ_1 (ns)	frac.1	τ_2 (ns)	frac.2	ave. (ns)
none	2.0	3.8%	38.7	96.2%	37.3
PB2T-O	0.8	34.8%	27.7	65.2%	18.3
PB2T-S	1.7	15.3%	25.7	84.7%	22.0
PB2T-SO	0.9	54.4%	7.8	45.6%	4.0

**Figure S10.** Current–voltage curves of the devices under dark condition.

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