

Supporting Information

Efficient and UV-Stable Perovskite Solar Cells Enabled by Side Chain-Engineered Polymeric Hole-Transporting Layers

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Experimental Section

Materials: P8TTT, PII2T8T, and PII2T8T polymers were prepared as described in our previous works.^{39, 40} Formamidinium iodide (FAI) and methylammonium bromide (MABr) were purchased from Xi'an p-OLED. Lead iodide (99.9985%) and lead bromide(99.999%) were purchased from Alfa Aesar. PEDOT:PSS (Clevios P VP AI 4083) were purchased from

H. C. Stark Company. Other used materials or precursors were purchased from Sigma-Aldrich without further purification except notifications.

Photovoltaic Device Fabrication and Characterization: ITO glass ($15 \Omega \text{ sq}^{-1}$) was cleaned through sequential sonication with deionized water, acetone, and isopropyl alcohol for 20 min, respectively. The cleaned ITO substrates were then treated by UV ozone for 15 min before use. The PEDOT:PSS and studied polymeric HTLs were spin-coated at 4000 rpm for 30 s, followed by annealing at 150 °C for 20 mins. The precursor solution of the polymeric HTLs was prepared with a concentration of 5-7 mg mL⁻¹ in chlorobenzene. The perovskite layers were prepared by the solvent-washing technique in a glove box, for which the perovskite precursor solution ((FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}) was spin-coated onto the above prepared films at 5000 rpm for 30 s, and during the last 15 s of the second spin-coating step, the substrate was treated with the drop-casting of chlorobenzene (0.1 mL).⁴¹ The as-spun films were then annealed at 100 °C for ~ 45 min. For the samples based on the studied polymeric HTLs, owing to their non-wetting surface, the perovskite precursor solution was spin-coated twice before annealing. Afterward, the PCBM ETL (15 mg mL⁻¹ in chloroform) was spin-coated on top of the perovskite layer at 2000 rpm for 30 s and BCP (2 mg mL⁻¹ in isopropyl alcohol) was spin-coated on top of the PCBM at 3000 rpm for 30 s. Finally, a 100-nm thick top Ag electrode was evaporated under high vacuum.

The *J-V* characteristics were measured under AM 1.5 G solar irradiance (100 mW cm⁻²) using a Newport Class A solar simulator (94021A, a Xenon lamp with an AM 1.5G filter) in

air at room temperature and recorded using a Keithley 2400 source meter unit. The active area of each device aperture was 0.10 cm^2 and a mask of 0.06 cm^2 was used during the measurement and the steady-state power output test. The EQE spectra were recorded by a setup consisting of a xenon light source, a monochromator, and a potentiostat. The morphology of the perovskite films was characterized by a high-resolution scanning electron microscopy (JEOL -7100F). X-ray diffraction (XRD) patterns were obtained with smart lab instruments Cu $K\alpha$ beam ($\lambda = 1.54 \text{ \AA}$). The absorption spectra were measured by a Hitachi model U-3010 UV-vis spectrophotometer. Steady-state PL spectra were recorded using a 514.5 nm ultrafast laser as the excitation light source (Laser sources: Ar ion laser, 50 mW). The transient PL spectra were recorded on a fluorescence spectrometer with a 400 nm pulsed laser generated from the second-harmonic generator to excite the samples. The ambient stability was traced by storing the samples at room temperature ($25 \text{ }^\circ\text{C}$) with a relative humidity of $50 \pm 10 \%$ without under illumination. For UV-stability test, the device was continuously illuminated under a 365-nm UV lamp (5 mW cm^{-2}) (Spectronics brand Corded Hand-Held UV lamp) at ambient environment. For the thermal property analysis, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were carried out in a nitrogen atmosphere at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ using the TA Instruments (Q-50 and Q-100), respectively.

Table S1. The optoelectronic properties of the studied polymers summarized from our previous works.[39, 40]

Polymers	UV-Vis absorption		CV	Mobility
	λ_{max}^{film} (nm)	E_g^{opt} (eV)	HOMO/LUMO (eV)	($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) (Max. Value)
P8TTT	300, 359, 481	2.03	-5.33, -2.72	$(5.0 \pm 0.3) \times 10^{-5}$
PII2T8T	299, 437, 623, 674	1.63	-5.38, -3.75	$(1.3 \pm 0.3) \times 10^{-3}$
PII2T8TSi	300, 440, 626, 675	1.63	-5.32, -3.69	$(3.0 \pm 0.2) \times 10^{-2}$

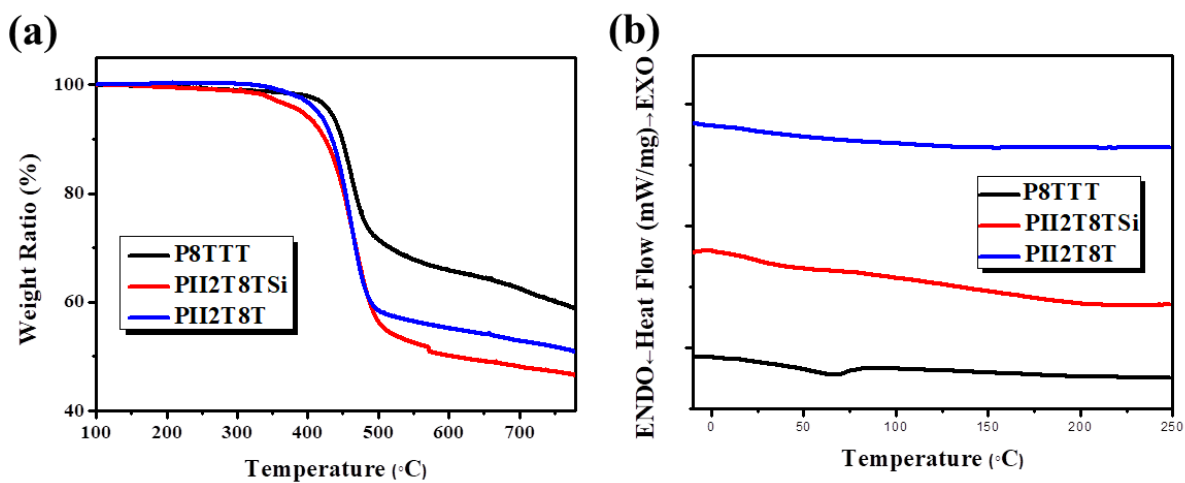


Figure S1. The (a) TGA and (b) DSC curves of the studied polymers.

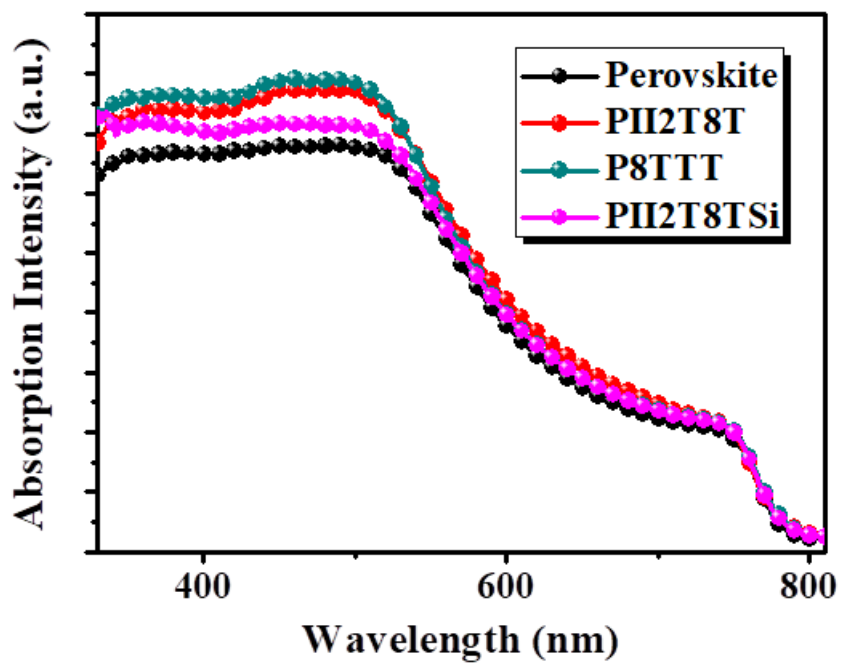


Figure S2. UV-vis absorption spectra of the bilayered perovskite/HTL samples.

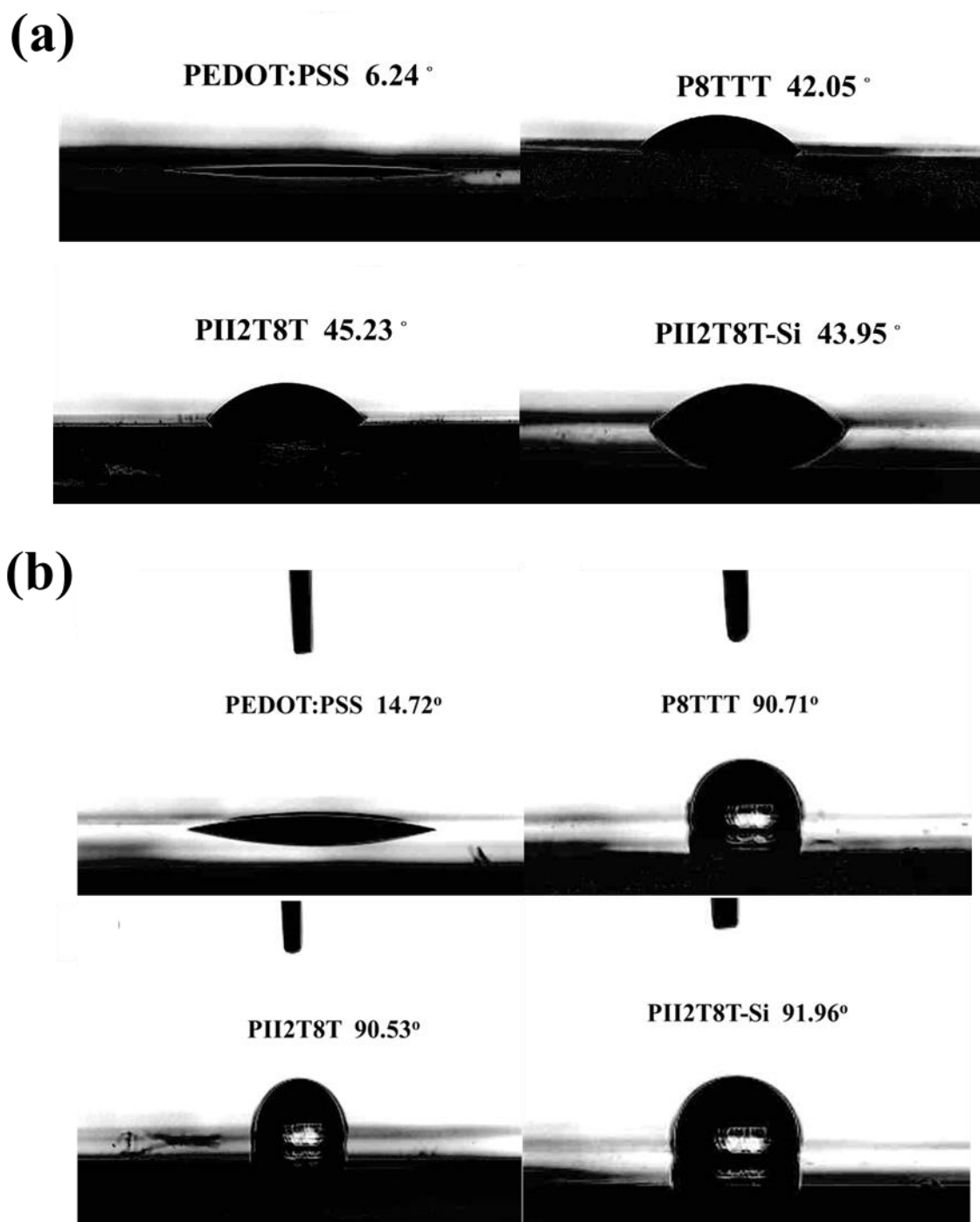


Figure S3. (a) DMF and (b) water contact angle analyses of the studied polymeric HTLs.

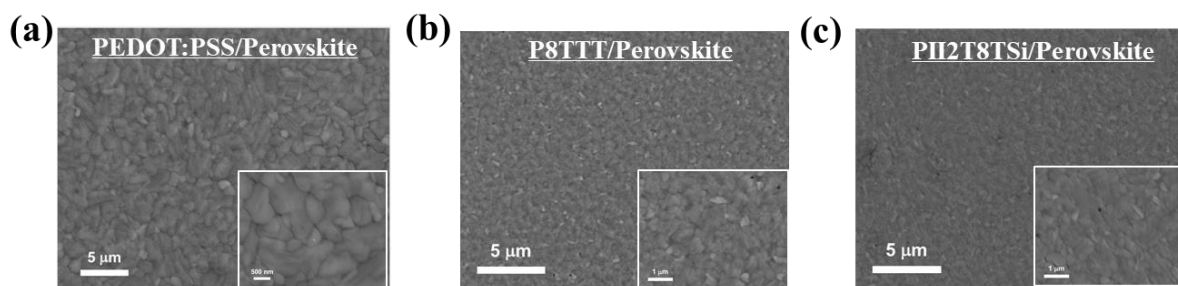


Figure S4. SEM images of the perovskite film deposited on PEDOT:PSS, P8TTT, PII2T8TSi HTLs, respectively.

Table S2. Summary of the parameters fitted from the time-resolved PL spectra. Note: The fitting functions of the double-exponential equation was $y = y_0 +$

$$A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right).$$

Sample	A_1	τ_1 (ps)	A_2	τ_2 (ps)
Perovskite	0.228	1.58	0.768	114.51
PEDOT:PSS	0.243	1.52	0.748	18.24
P8TTT	0.168	2.59	0.810	44.27
PII2T8T	0.190	1.97	0.797	16.93
PII2T8TSi	0.246	0.51	0.765	26.17

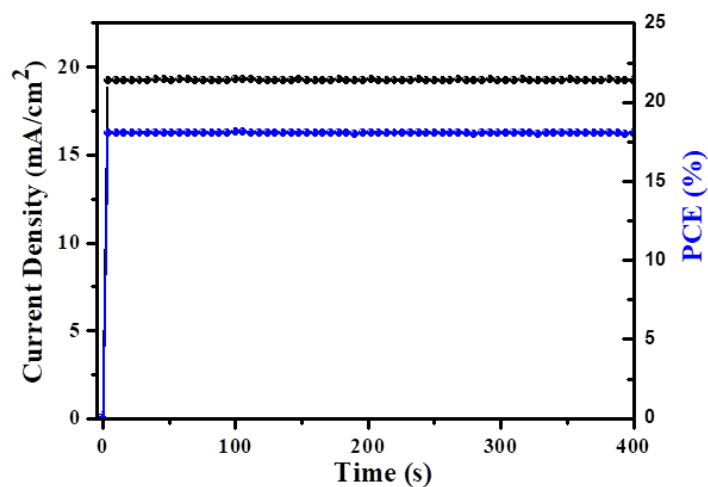


Figure S5. The stabilized photocurrent density (black) and PCE (blue) of the PII2T8T-based PVSC obtained at the maximum power point voltage 0.88 V.

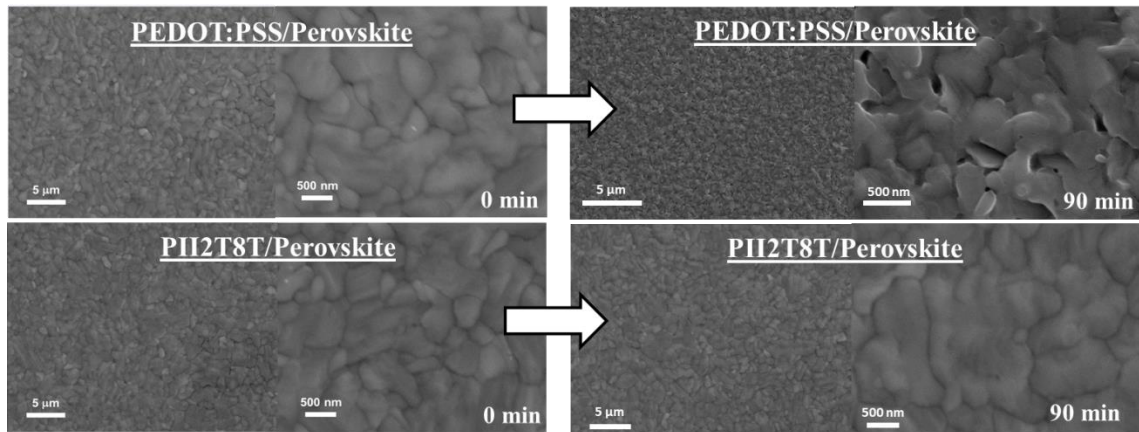


Figure S6. The SEM images of the bilayered (a) PEDOT:PSS/perovskite and (b) PII2T8T/perovskite samples before (0 mins) and after (90 min) aging under UV irradiation.

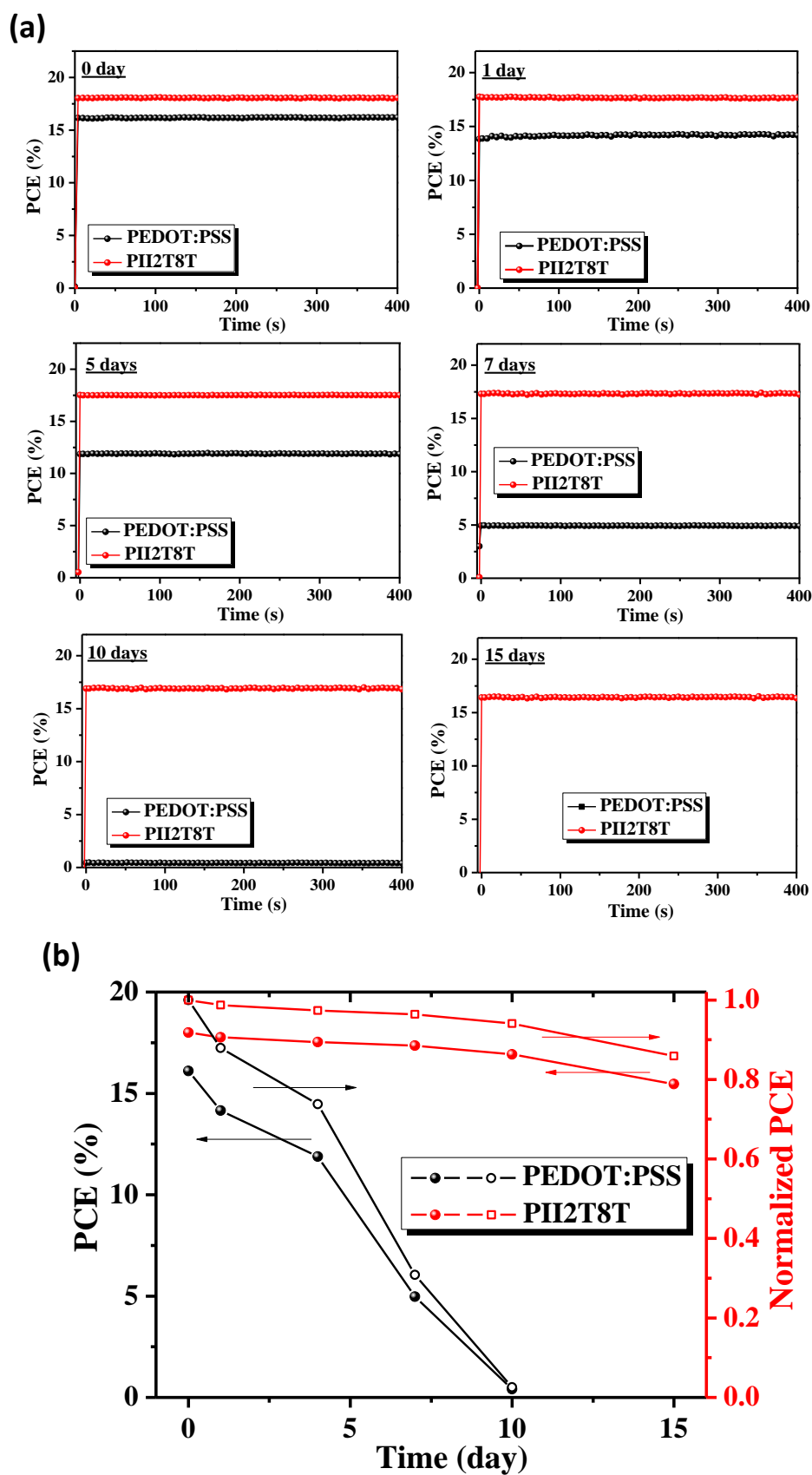


Figure S7. (a) The device's maximum power point under working condition tracked after different storage time at room temperature with a relative humidity of $50 \pm 10 \%$. (b) Their corresponding ambient stability test as a function of storage time.