

## Supporting Information for

# **Stability and efficiency improved perovskite solar cells through tuning the hydrophobicity of hole transport layer with organic semiconductor<sup>†</sup>**

Chongyang Xu,<sup>a</sup> Zhihai Liu,<sup>b</sup> and Eun-Cheol Lee,<sup>\*a</sup>

<sup>a</sup>*Department of Physics, Gachon University, Seongnam, 13120, Republic of Korea*

<sup>b</sup>*School of Opto-Electronic Information Science and Technology, Yantai University, Shandong 264005, China*

*\*Corresponding authors. E-mail address: elee@gachon.ac.kr*

## Experimental Section

### Chemicals and reagents

Lead iodide ( $\text{PbI}_2$ ), CB, dimethyl sulfoxide (DMSO, anhydrous, 99.8%) and N,N-dimethylformamide (DMF) were purchased from Sigma-Aldrich (USA). PTB7 was obtained from 1-Material Inc (Canada), while PEDOT:PSS (Clevios PVP AI 4083) was acquired from H.C. Starck company (Germany) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) was purchased from Nano-C Inc. (USA). Methylammonium iodide (MAI) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) were purchased from Xi'an Polymer Light Technology Corp (China), while patterned indium tin oxide (ITO) glasses were purchased from Ying Kou You Xuan Trade Co., Ltd. (China).

### Device fabrication

The experimental samples were fabricated on the ITO glasses with a configuration of ITO/PEDOT:PSS/PTB7/perovskite/PCBM/BCP/Ag as shown in Fig. 1a. The glass substrates with an ITO anode were cleaned sequentially with detergent, deionized water, and isopropanol (IPA). Following this, a 20-min treatment using ultraviolet–ozone ( $\text{UV-O}_3$ ) was performed. PEDOT:PSS was spin-coated on the ITO glasses at 4,000 rpm for 30 s followed by thermal annealing at  $140^\circ\text{C}$  for 15 min. The PTB7 solutions were prepared by adding 1, 3 and 6 mg of PTB7 in 1 mL of CB solvent to make different concentrations based on the corresponding experiments. Then, the prepared PTB7 solution was spin-coated at 5,000 rpm for 40 s and thermally annealed at  $120^\circ\text{C}$  for 30 min. The perovskite precursor solution was prepared by dissolving  $\text{PbI}_2$  and MAI (molar ratio 1:1) in an anhydrous mixture of DMF and DMSO (4:1, v:v) to obtain a precursor with a concentration of 1.2 M, which was then stirred for 15 h at  $60^\circ\text{C}$ . The perovskite film was deposited by spin-coating the as-prepared precursor at 4,000 rpm for 30 s in a nitrogen-filled glove box. During the spin-coating process, CB (200  $\mu\text{L}$ ) was quickly dropped onto the samples at a delay time of 8 s after commencing the spin-coating. The samples were subsequently annealed on a hot plate at  $100^\circ\text{C}$  for 10 min. Next, a 50  $\mu\text{L}$   $\text{PC}_{61}\text{BM}$  solution (30  $\text{mg mL}^{-1}$  in CB) was spin-coated at 1,500 rpm for 30 s to form the ETL before a 70  $\mu\text{L}$  BCP solution (0.5 mg

mL<sup>-1</sup> in IPA) was spin-coated onto the surface of the ETL at 4,000 rpm. Finally, a 100-nm thick Ag electrode was coated on top of the samples (working area of 0.1 cm<sup>2</sup>) using a thermal evaporator under high vacuum (<6.0 × 10<sup>-6</sup> Torr).

### **Characterization**

Top-view and cross-sectional scanning electron microscope (SEM) images were obtained using a JSM-7500F Field Emission SEM (JOEL, Japan) at an acceleration voltage of 20 kV. The steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra were measured using a spectrometer (FLS920, Edinburgh Instruments, UK). The current density-voltage (*J-V*) characteristics of the PSCs were measured under an irradiation intensity of 100 mW cm<sup>-2</sup> (AM 1.5), while the external quantum efficiency (EQE) of the PSCs was measured using a Solar Cell incident photon-to-current efficiency measurement system (Solar Cell Scan 100, Zolix, China). The space charge limited current (SCLC) of the hole-only device with a configuration of ITO/PEDOT:PSS/HTL/MAPbI<sub>3</sub>/MoO<sub>3</sub>/Ag was obtained via a 2400 SourceMeter in a dark environment with a bias voltage of 1 V. Meanwhile, the electrochemical impedance spectroscopy (EIS) of the devices was performed in a dark environment using an electrochemical workstation (CH Instruments, USA), while the ultraviolet-visible (UV-vis) absorption spectra were recorded on a UV-vis-NIR 3600 spectrometer (Shimadzu, Japan). X-ray diffraction (XRD) measurements were carried out using a Rigaku Smart Lab X-ray diffractometer (Japan) with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at room temperature, while the ultraviolet photoelectron spectroscopy (UPS) was performed using a Kratos Axis Ultra X-ray and ultraviolet photoelectron spectroscope (Kratos Analytical, UK). Finally, X-ray photoelectron spectroscopy was performed using a PHI 5300 ESCA Perkin-Elmer spectrometer.

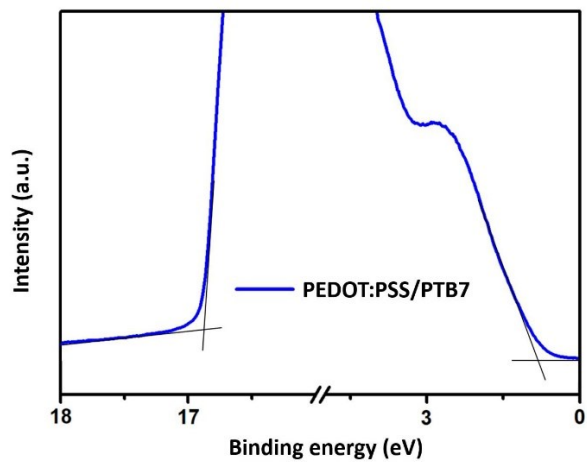


Fig. S1. UPS spectra of PEDOT:PSS/PTB7.

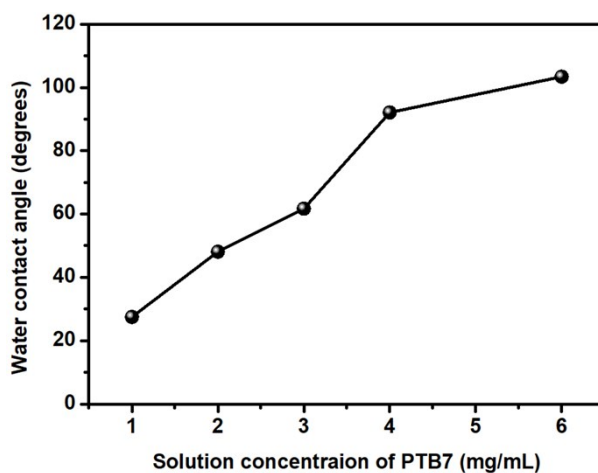


Fig. S2. Water contact angles in terms of various concentrations of PTB7 solution.

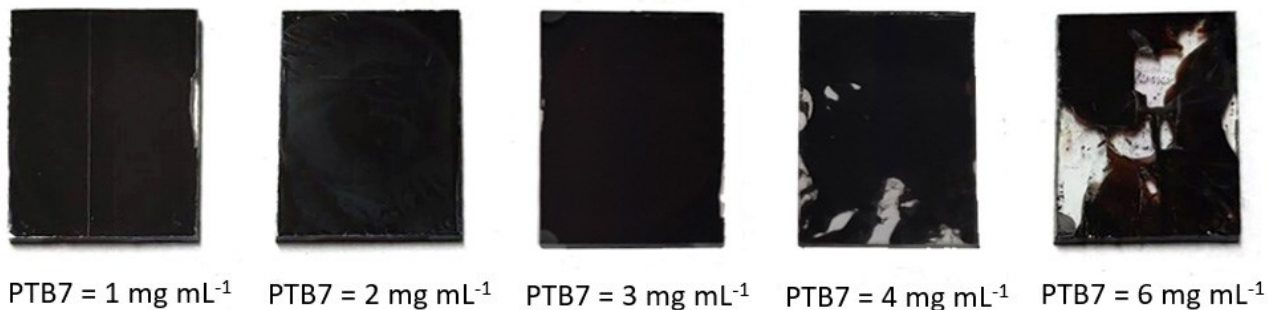


Fig. S3. Photos of perovskite films deposited on PTB7 layers formed under various solution concentrations.

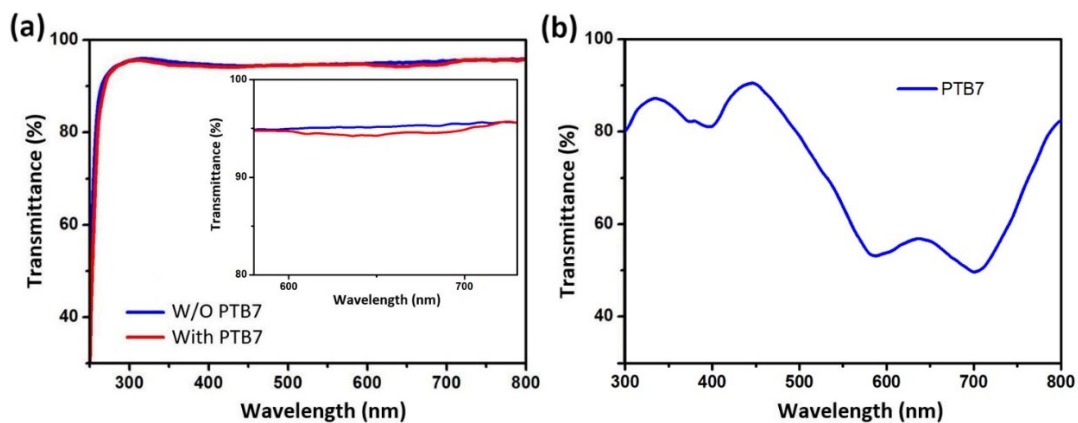


Fig. S4. Transmittance spectra for (a) PEDOT:PSS and PDEOD:PSS/PTB7 and (b) single PTB7 film.

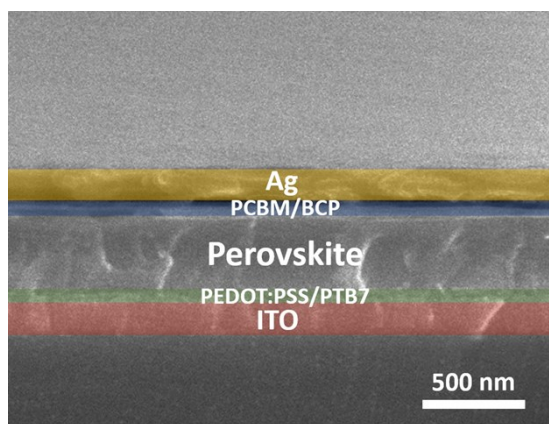


Fig. S5. Cross-sectional SEM image of a PSC.

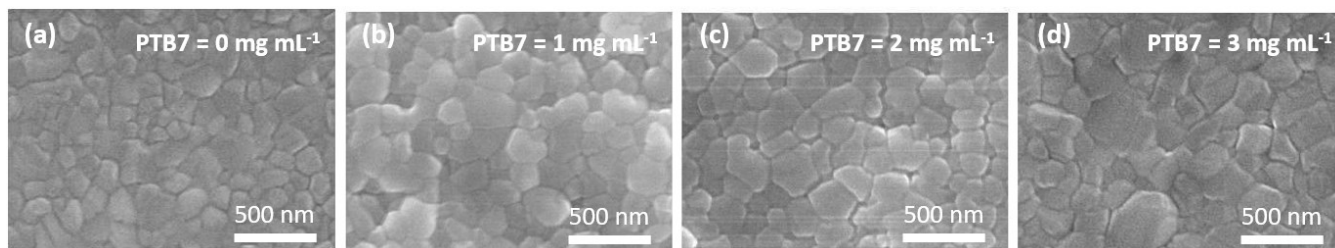


Fig. S6. Top-view SEM images of perovskite films on the PEDOT:PSS layers modified with PTB7 with different concentrations.

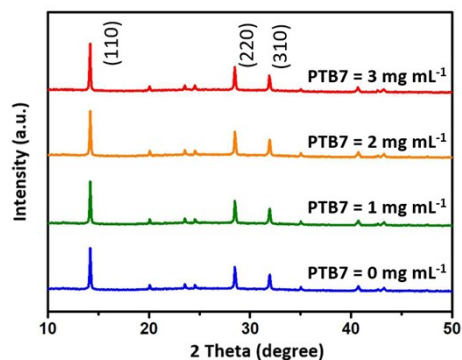


Fig. S7. XRD spectra for perovskite films on the PEDOT:PSS layers modified with PTB7 with different concentrations.

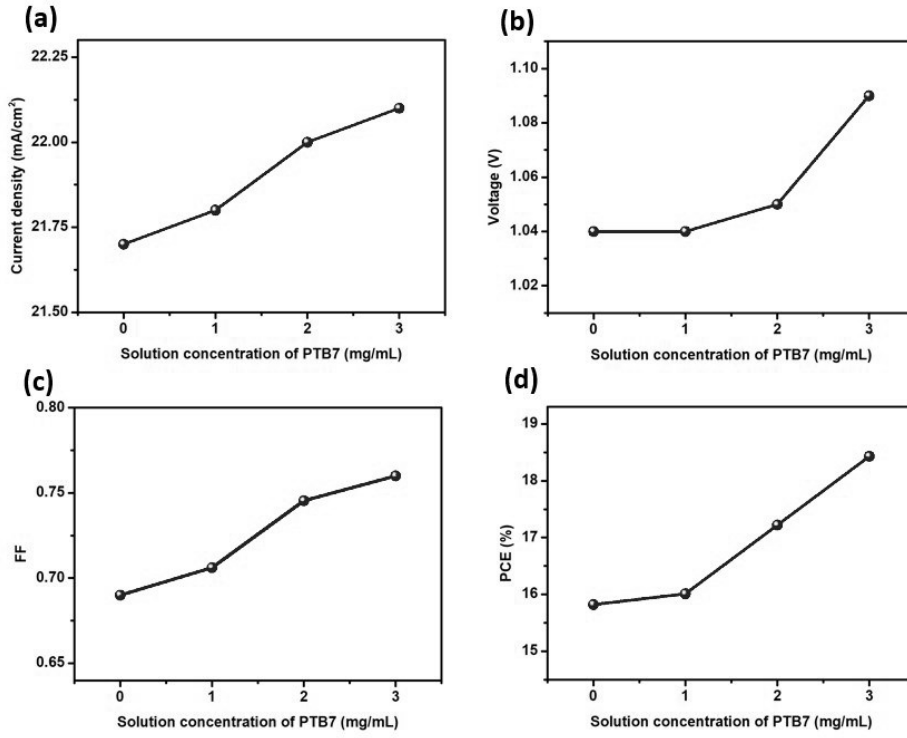


Fig. S8. The variation for  $J_{sc}$ ,  $V_{oc}$ , FF, and PCE of the PSCs with PTB7 layers deposited under different solution concentrations.

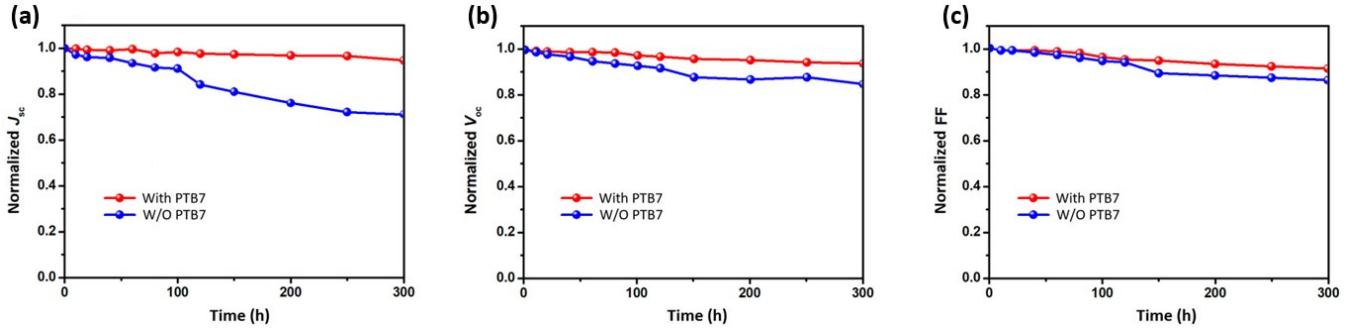


Fig. S9. The normalized  $J_{sc}$ ,  $V_{oc}$ , and FF of PSCs stored for 300 h without encapsulation.

Table S1. The fundamental constants and parameter for calculating trap densities of the PSCs based on different kinds of PTB7 film.

$L$ (nm)	$e$ (C)	$\epsilon_0$ ( $\text{F m}^{-1}$ )	$\epsilon$
400	$1.602 \times 10^{-19}$	$8.854 \times 10^{-12}$	32 [1]

## Reference

1. W.-G. Li, H.-S. Rao, B.-X. Chen, X.-D. Wang and D.-B. Kuang, *J. Mater. Chem. A*, 2017, **5**, 19431-19438.