Electronic Supplementary Information (ESI)

Promotion of performances of quantum dot solar cell and its tandem solar cell with low bandgap polymer (PTB7-Th):$PC_{71}BM$ by water vapor treatment on quantum dot layer on its surface

Yi-Lun Li, Po-Nan Yeh, Sunil Sharma and Show-An Chen*

Synthesis of PbS QDs

PbS QDs were synthesized in accordance with the procedure in reference [S1]. 0.45 g (2 mmol) PbO, 1.5 mL OA and 18 mL ODE were mixed in three-necked flask under vacuum at 90˚C overnight to remove residual water. Once the solution turned to clear, indicating a formation of lead oleate, the flask then heated to 110˚C under nitrogen. 210 μL TMS in 10 mL ODE was rapidly injected into the lead oleate solution using syringe under nitrogen at 110˚C. The solution changed to brown color immediately, indicating a formation of OA-capped PbS QDs. The QDs solution was removed from the heating mantle and then rapid cooled to room temperature by water bath. The QDs were precipitated by adding 100-200 mL acetone and centrifuged at 8000 rpm for 10 minutes under ambient condition. The supernatant was discarded and the QDs were redispersed in hexane. Sediment was precipitated by acetone, centrifuged and redispersed in hexane. These processes were repeated for three times and the resulting QDs were redispersed in octane (25 mg/mL). The oleic acid capped PbS QDs solution

in octane were filtered through a 0.22 μm PTFE syringe filter and stored in nitrogen-filled glove box. The first absorption peak of oleic acid capped PbS QD is located in the range of 915 nm as shown in **Fig.S1**.

Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized in accordance with the procedure in reference [S2]. 2.95 g (13.4 mmol) of zinc acetate dehydrate was dissolved in methanol (125 mL) under vigorous stirring at about 70℃. Then, a solution of potassium hydroxide (1.48g) in dry methanol (65 mL) was added dropwisely under nitrogen atmosphere. The reaction mixture was stirred for 2.5 h at 70℃ until the solution turned to turbid. The resulting solution was centrifuged at 5000 rpm for 10 minutes under ambient conditions. The supernatant was discarded and dry methanol was added to ZnO nanoparticles precipitate. These procedures were repeated twice and the resulting ZnO nanoparticles were redispersed in n-butanol under nitrogen atmosphere. The ZnO nanoparticle solution were filtered through a 0.22 μm PTFE syringe filter and stored in nitrogen-filled glove box.

Preparation of indium doped ZnO precursor solution

The InZnO precursor solution was prepared by dissolving zinc acetate dihydrate (991.5 mg), indium (III) chloride (9.85 mg, 1% mole ratio) and monoethanolamine (0.252 g) in 2-methoxyethanol (10 ml) under stirring for 8 h for hydrolysis reaction and aging.

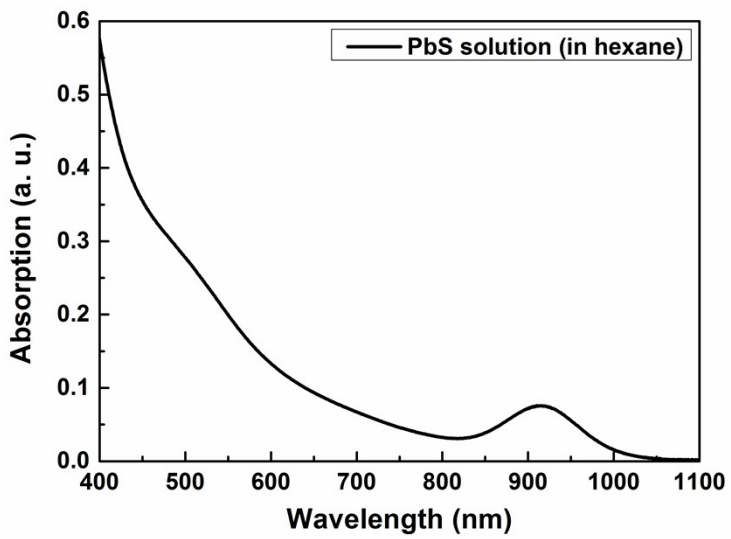

Fig. S1 Absorption of oleic acid capped PbS QD solution (in hexane). The first absorption peak is located at 915 nm.

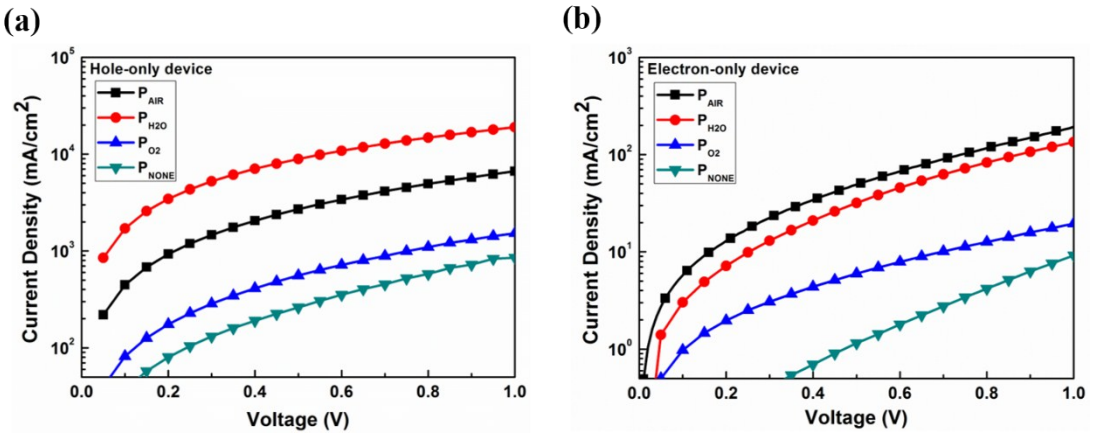

Fig. S2 Current density versus voltage of (a) the hole-only device and (b) the electron-only devices under various treaments. The structure of hole-only device is ITO/PEDOT (30 nm)/PbS-I (60 nm)/PbS-EDT (20 nm)/Au (100 nm) and electron-only device is: ITO/InZnO (30 nm)/PbS-I (60 nm)/PbS-EDT (20 nm)/LiF (0.6 nm)/Al (100 nm).

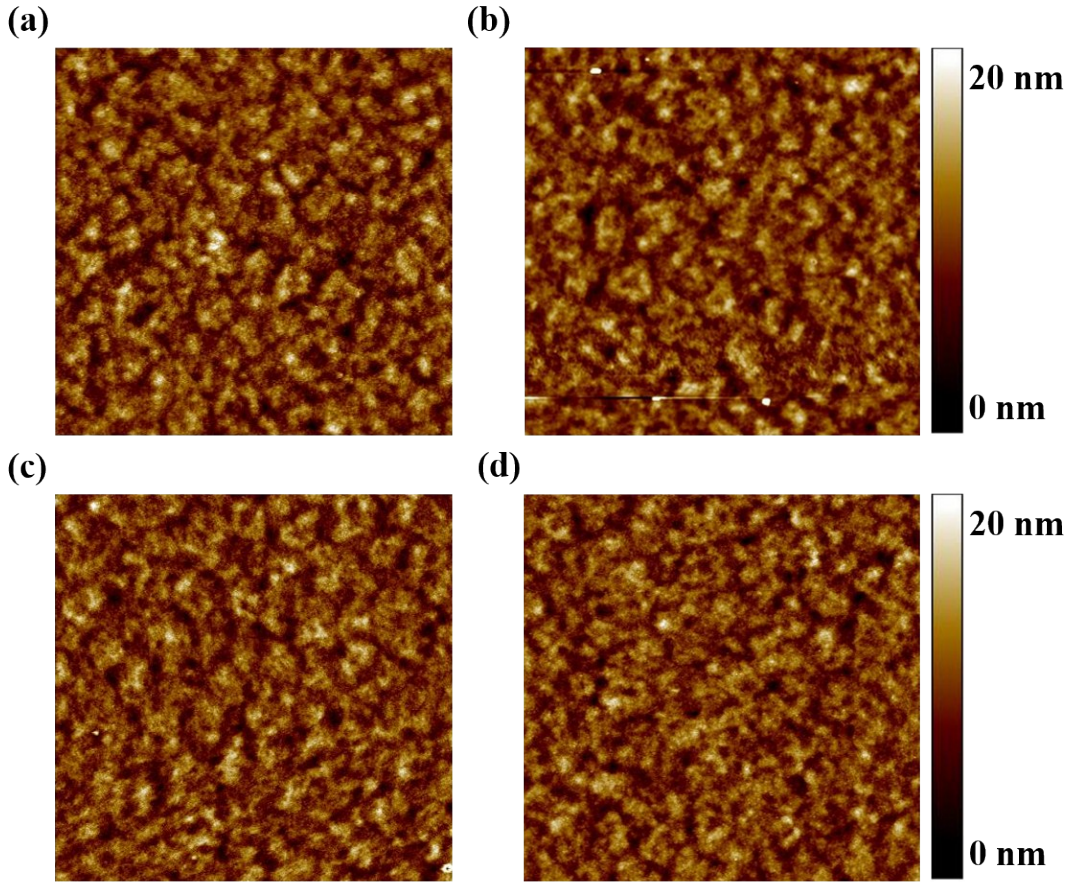

Fig. S3 AFM (5x5 μm) topographical images using tapping mode: PbS-EDT film was treated in (a)air, (b)water vapor, (c)oxygen environments; and (d)pristine PbS-EDT film. The roughness are (a)1.91 nm, (b)1.87 nm, (c)1.93 nm, (d)1.89 nm, respectively.

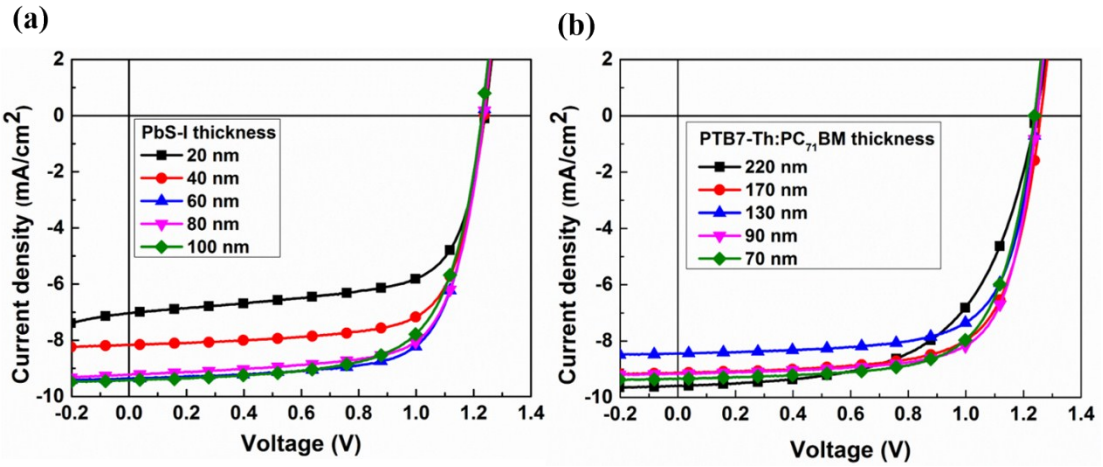

Fig. S4 Current density-voltage curves of the hybrid tandem solar cell with various thicknesses of (a) PbS-I film in the bottom cell and (b) PTB7-Th:$PC_{71}BM$ film in the top cell. The hybrid tandem device structure is: ITO/InZnO (30 nm)/PbS-I (various thicknesses)/PbS-EDT (20 nm)/MoO_3 (10 nm)/Au (0.5 nm)/ZnO NP (30 nm)/PTB7-Th:$PC_{71}BM$ (various thicknesses)/MoO_3 (10 nm)/Ag (100 nm).

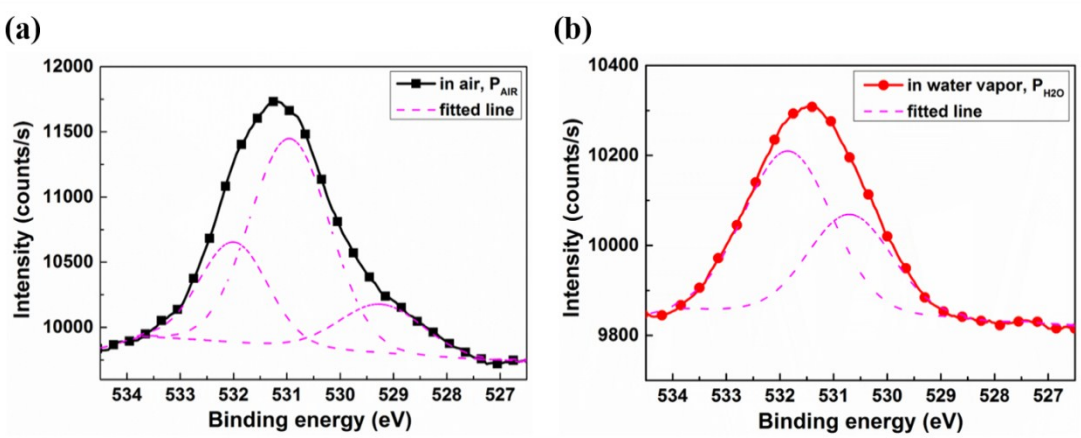

Fig. S5 XPS spectra of O 1s signals of PbS-EDT film under **(a)** air treatment, $\mathbf{P_{AIR}}$, and **(b)** water vapor treatment, $\mathbf{P_{H2O}}$, and those deconvoluted results The intensity profile of $\mathbf{P_{AIR}}$ is deconvoluted into three peaks assuming the presence of the three species with their O1s binding energy peaks at PbO (529.2 eV), $PbSO_3$ (530.9 eV) and $PbSO_4$ (531.9 eV). And, the intensity profile of $\mathbf{P_{H2O}}$ is deconvoluted into two peaks, $PbSO_3$ (530.7 eV) and $PbSO_4$ (531.8 eV). The mole fractions of PbO, $PbSO_3$ and $PbSO_4$ are 24.4%, 40.8% and 35.8% in $\mathbf{P_{AIR}}$ and those of $PbSO_3$ and $PbSO_4$ are 36.9% and 63.1% in $\mathbf{P_{H2O}}$. The sample is ITO/PbS-EDT (20 nm) with different treatment.

Table S1. Hole and electron mobility of PbS-I/PbS-EDT film under various treatment determined using the hole-only device and the electron-only devices along with the use of space charge limited current equation in the calculation. The structure of hole-only device is: ITO/PEDOT (30 nm)/PbS-I (60 nm)/PbS-EDT (20 nm)/Au (100 nm) and electron-only device is: ITO/InZnO (30 nm)/PbS-I (60 nm)/PbS-EDT (20 nm)/LiF (0.6 nm)/Al (100 nm). And Conductivity measurement using four probe method for the sample, PbS-EDT film under various treatments.

Process	Hole mobility ($cm^2\ V^{-1}\ s^{-1}$)	Electron mobility ($cm^2\ V^{-1}\ s^{-1}$)	Surface Conductivity ($S\ cm^{-1}$)
$\mathbf{P_{AIR}}$	1.83×10^{-4}	5.19×10^{-6}	2.94×10^{-4}
$\mathbf{P_{H2O}}$	5.35×10^{-4}	3.80×10^{-6}	5.52×10^{-4}
$\mathbf{P_{O2}}$	4.14×10^{-5}	5.64×10^{-7}	2.27×10^{-4}
$\mathbf{P_{NONE}}$	2.21×10^{-5}	1.24×10^{-7}	8.96×10^{-5}

Table S2. The tandem solar cell performance of various PbS-I film thicknesses. The device structure is: ITO/InZnO (30 nm)/PbS-I/PbS-EDT (20 nm)/MoO_3 (10 nm)/Au (0.5 nm)/ZnO NP (30 nm)/PTB7-Th:$PC_{71}BM$ (90 nm)/MoO_3 (10 nm)/Ag (100 nm)

PbS-I film thickness	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]	R_{SH} [Ω cm^2]	R_S [Ω cm^2]
20 nm	1.24	7.03	67.1	5.85	878	13.8
40 nm	1.24	8.16	71.5	7.22	2908	12.1
60 nm	1.24	9.36	71.1	8.22	3291	11.4
80 nm	1.23	9.22	70.6	8.05	2260	11.4
100 nm	1.23	9.41	67.5	7.80	2863	11.4

Table S3. The tandem solar cell performance of various PTB7-Th:$PC_{71}BM$ thicknesses. The device structure is: ITO/InZnO (30 nm)/PbS-I (60 nm)/PbS-EDT (20 nm)/MoO_3 (10 nm)/Au (0.5 nm)/ZnO NP (30 nm)/PTB7-Th:$PC_{71}BM$/MoO_3 (10 nm)/Ag (100 nm)

PTB7-Th:$PC_{71}BM$ thickness	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]	R_{SH} [Ω cm^2]	R_S [Ω cm^2]
220 nm	1.24	9.59	59.0	7.04	1977	19.0
170 nm	1.26	9.13	69.5	7.99	3535	13.7
130 nm	1.25	8.45	69.8	7.36	3507	12.0
90 nm	1.25	9.16	71.7	8.20	4015	10.9
70 nm	1.24	9.30	68.8	7.92	3310	11.3

References:

[S1] M. A. Hines and G. D. Scholes, *Adv. Mater.*, 2003, **15**, 1844.

[S2] P.-N. Yeh, T.-H. Jen, Y.-S. Cheng and S.-A. Chen, *Solar Energy Materials & Solar Cells,* 2014, **120**, 728.