

# Supporting Information

## *A Dual Functional Molecule for Perovskite/P3HT Interface to Achieve Stable Perovskite Solar Cells*

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### **Corresponding Author Footnote**

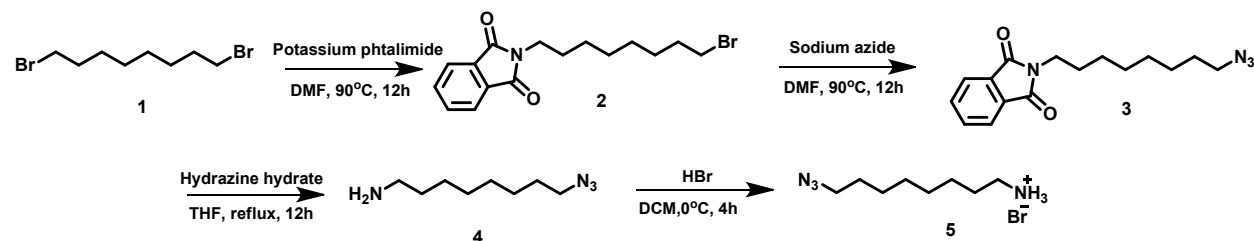
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## EXPERIMENTAL SECTION

### Synthesis details

#### Material synthesis and characterization



**Scheme S1.** Synthesis route for OAN<sub>3</sub>

#### N-(6-Bromohexyl)phthalimide

1,6-Dibromohexane (8.72 g, 35.8 mmol), potassium phthalimide (2.64 g, 14.2 mmol), and 50 mL of anhydrous DMF were added to a dry round bottom flask. The resulting solution was stirred at 90 °C for 16 hours under argon atmosphere. The cooled mixture was diluted with distilled water and extracted with dichloromethane. The combined organic layer was washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. The obtained crude product was purified by column chromatography using hexane-ethyl acetate (8:1, v/v) as the eluent which afforded a white solid (4.27 g, 89% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.86-7.81 (m, 2H), 7.73-7.68 (m, 2H), 3.67 (t, *J* = 7.3 Hz, 2H), 3.39 (t, *J* = 7.3 Hz, 2H), 1.83 (q, *J* = 7.3 Hz, 2H), 1.67 (q, *J* = 7.3 Hz, 2H), 1.41 (q, *J* = 7.3 Hz, 2H), 1.38-1.26 (m, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 168.48, 133.87, 132.17, 123.17, 37.99, 33.96, 32.74, 28.95, 28.59, 28.53, 28.06, 26.72

#### N-(6-Azidohexyl)phthalimide

To the solution of 0.86 g (13.3 mmol) of sodium azide in 50 mL of DMSO was added 4.09 g (12.1 mmol) of N-(6-Bromohexyl)phthalimide. The solution was stirred at room temperature for 4 h.

The resulting solution was then poured into 100 mL of water and extracted twice with 30 mL of diethyl ether. The combined organic layer was dried over MgSO<sub>4</sub> and concentrated at reduced pressure to get white solid (3.45g, Yield: 95%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ 7.86-7.81 (m, 2H), 7.73-7.68 (m, 2H), 3.67 (t, *J* = 7.3 Hz, 2H), 3.24 (t, *J* = 7.3 Hz, 2H), 1.83 (q, *J* = 7.3 Hz, 2H), 1.67 (q, *J* = 7.1 Hz, 2H), 1.58 (q, *J* = 7.1 Hz, 2H), 1.39-1.27 (m, 8H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 168.48, 133.87, 132.17, 123.17, 51.44, 37.98, 28.98, 28.97, 28.78, 28.52, 26.71, 26.61

### **N-(6-azidohexyl)ammonium bromide**

A round flask equipped with a magnetic stirrer was charged with N-(6-Azidohexyl)phthalimide (3.00 g, 9.99 mmol), hydrazine monohydrate (1.00g, 19.98 mmol, 2 equiv.) and 50 mL of ethanol. The reaction mixture was refluxed for 2 h, then the reaction mixture was cooled to room temperature. The solution was diluted with ethanol and filtered, the solution was then concentrated and dissolved in 10 mL DCM and washed with sodium hydroxide (10%) and dried over MgSO<sub>4</sub>. Then, the solution was concentrated to obtain an oil. The product was dissolved in 5 mL DCM and HBr (0.51 mL, 10.02 mmol) was added dropwise in an ice bath, the reaction mixture was stirred for 15 min, then the mixture was filtered and washed with diethyl ether to obtain a brown solid (2.06g, Yield: 82%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), 7.81-7.58 (br s, 3H), 3.30 (t, *J* = 7.3 Hz, 2H), 2.79-2.70 (br s, 2H), 1.51 (q, *J* = 7.3 Hz, 4H), 1.35-1.22 (br s, 8H). <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>) δ 51.08, 39.24, 28.83, 28.78, 28.65, 27.36, 26.49, 26.15

**Material.** Tin(II) chloride dihydrate, ethanol, acetone, acetonitrile, isopropanol, chlorobenzene, dimethyl sulfoxide (DMSO), and dimethylformamide (DMF) 4-tert-butylpyridine (tBP), bis(trifluoromethane)sulfonimide lithium salt (LiTFSI), were purchased from Sigma-Aldrich. Tin(IV) oxide colloidal dispersion was purchased from Alfa Aesar. Formamidinium iodide (FAI),

methylammonium bromide (MABr), and cobalt(III) tris(bis(trifluoromethylsulfonyl)imide) (FK209) were purchased from Dyesol. Lead(II) Iodide (PbI<sub>2</sub>) and lead(II) bromide (PbBr<sub>2</sub>) were purchased from TCI. 2,2',7,7'-tetrakis(N,N'-di-p-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) was purchased from NCT.

**Solar cell fabrication** ITO glass substrates were ultrasonic cleaned with deionized water and isopropanol in sequence with 5 min sonication each. Then, the ITO substrates were dried and treated by UV-ozone for 15 min. The SnO<sub>2</sub> solution (diluted by water with a v/v of 1:5) was spin-coated on the ITO glass substrate with 3000 rpm for 30 s, followed by thermal annealing at 100 °C for 30 min. After cooled down to room temperature, the substrates were treated by the UV-ozone for another 15 min. A perovskite precursor solution was made with 1.56 M  $\delta$ -FAPbI<sub>3</sub> and 20 mol% MACl in DMF:DMSO mixed solvent with a v/v of 8:1. The precursor solution was spin-coated onto the SnO<sub>2</sub> films via two respective steps: at 1000 rpm for 5 s and at 5000 rpm for 20 s, and 2 mL of diethyl ether was quickly dripped onto the rotating substrate within 5 s prior to the end. Then, the as-prepared film was heated on a hot plate at 100 °C for 60 min. For the OAN<sub>3</sub> treated samples, OAN<sub>3</sub> was dissolved in IPA, coated on the surface of perovskite film at 5000 rpm for 30 s, following by annealing at 105 °C for 5 min. The P3HT solution was prepared with the concentration of 10 mg/mL in the mixed solvent (chlorobenzene: diphenyl ether = 97:3 v/v). The P3HT solution was spin-coated on the perovskite layer at 3000 rpm for 30 s. Finally, 80 nm of counter electrode (Ag or Au) was deposited via thermal evaporation on top of the HTM layer.

**Device characterization.** Using a Keithley 2400 SMU and an Oriel xenon lamp (450 W) with an AM1.5 filter, the solar cells were characterized in air under AM 1.5G illumination of 100 mW/cm<sup>2</sup> (Oriel 1 kW solar simulator), which was calibrated with a KG5 filter certified by National Renewable Energy Laboratory (NREL). The current density-voltage (J-V) curves of all devices

(active area: 0.09 cm<sup>2</sup>) were measured by 0.1 V/s of scan rate. The stabilized power output was measured under the maximum power point voltage.

**IPCE measurement.** Constant 100 W Xenon lamp source with an automated monochromator filters and 0.76 mm x 1.0 mm rectangular spot size was used for incident-photon-to-current-efficiency (IPCE) spectra. The measurements were conducted in the wavelength range from 300 to 850 nm, chopped at 4 Hz (IQE-200B model).

**Photoluminescence Measurement.** The high resolution monochromator and hybrid photomultiplier detector (PMA Hybrid 40, PicoQuant GmbH) was employed to measure the PL. Time-resolved and steady-state photoluminescence measurements were conducted using prepared samples: glass/perovskite. Time-resolved photoluminescence measurements were performed using time correlated single photon counting (TCSPC) system (HAMAMATSU/C11367-31). For TCSPC measurements, a pulsed laser source was laser diode with a wavelength of 474 nm, a repetition rate of 100 kHz, fluence of ~ 4 nJ/cm<sup>2</sup> and a pulse width of 70 ps. The samples were excited from the glass side under ambient conditions.

**SCLC measurement.** The space charge limited current (SCLC) was measured by Keithley 2400 SMU. The device structures were ITO/poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)/perovskite/Spiro-OMeTAD/Au. The trap densities were calculated using the following equation

$$V_{\text{TFL}} = \frac{en_t d^2}{2\epsilon\epsilon_0}$$

where  $V_{\text{TFL}}$  is the trap-filled limit voltage,  $e$  is the elementary charge,  $n_t$  is the trap density,  $d$  is the film thickness,  $\epsilon$  is the dielectric constant, and  $\epsilon_0$  is the vacuum permittivity.

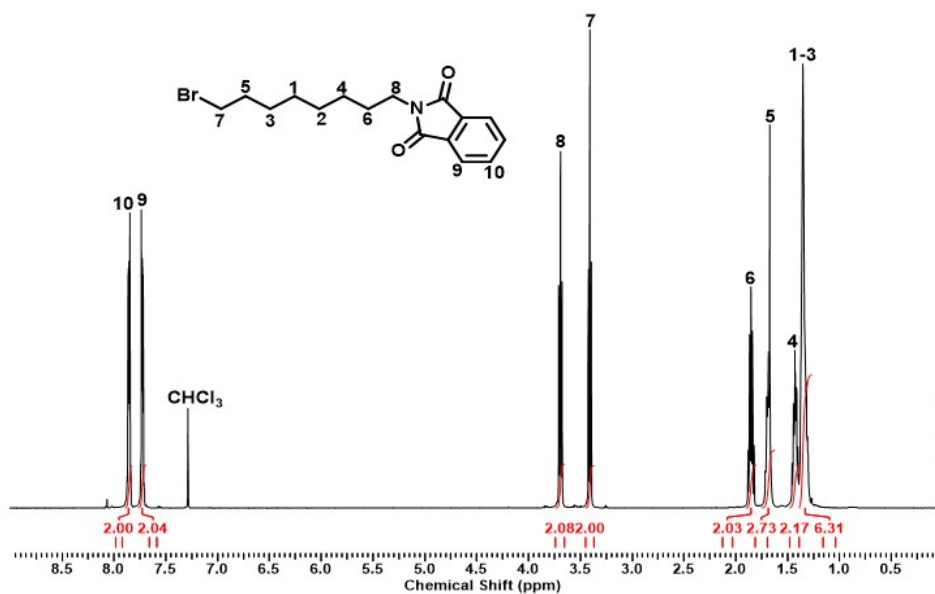
**UV-vis measurement.** The Ultraviolet-visible (UV-vis) absorption spectra were obtained using an Optizen Pop UV-vis spectrophotometer for glass/perovskite before and after treatment of OAN<sub>3</sub> additive.

**SEM measurement.** Field emission scanning electron microscope (FE-SEM, Hitachi S 4800) was employed for the surface of the perovskite layer and cross-section of perovskite solar cells.

**XRD measurement.** X-Ray diffraction analysis (XRD, Rigaku D/Max-2200/PC) was employed for perovskite crystal phase identification.

## Supplementary Figures and Tables

### [<sup>1</sup>H-NMR]



### [<sup>13</sup>C-NMR]

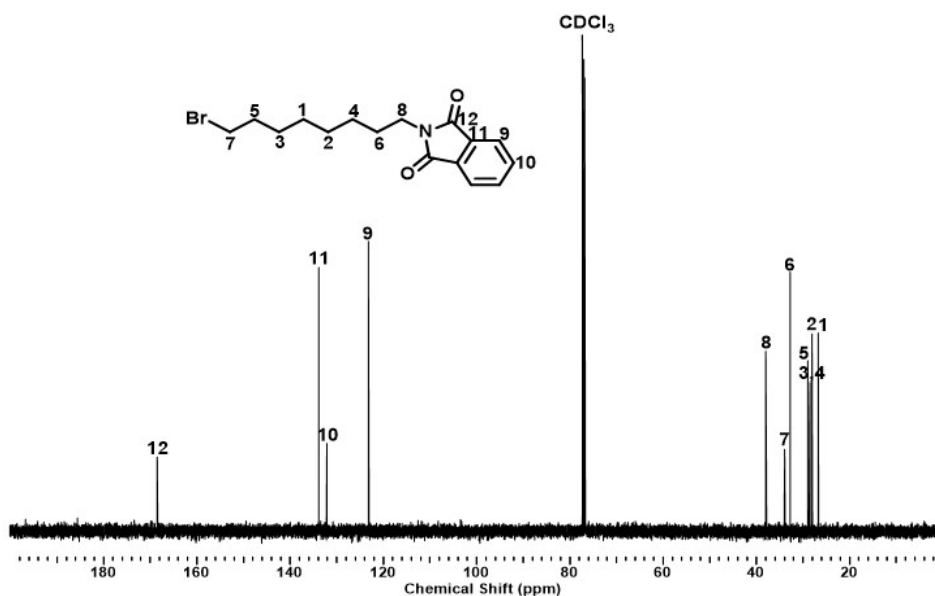
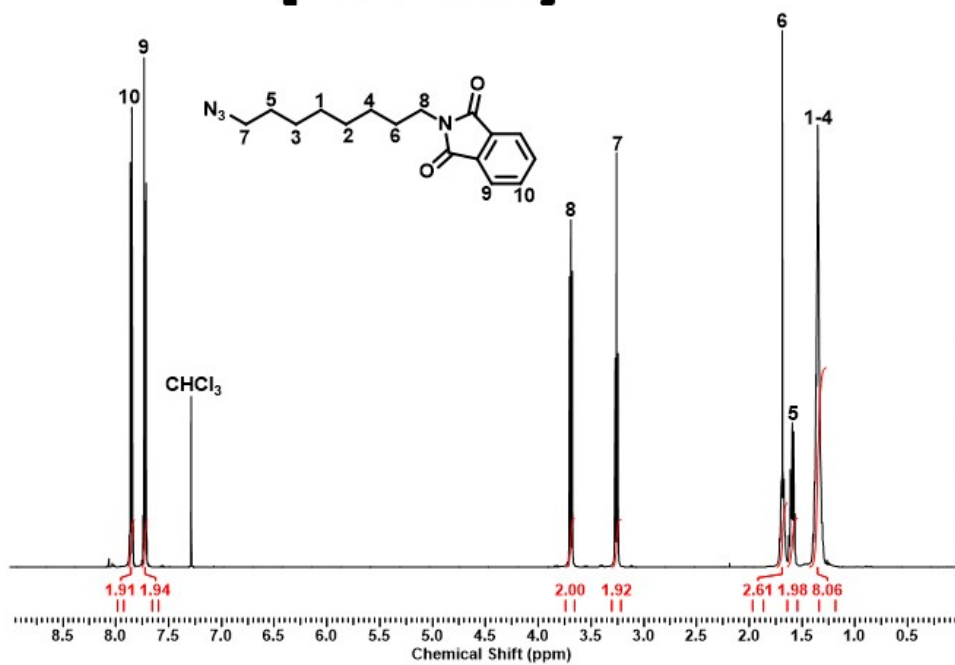


Figure S1. <sup>1</sup>H / <sup>13</sup>C NMR spectrum of 2

# [<sup>1</sup>H-NMR]



# [<sup>13</sup>C-NMR]

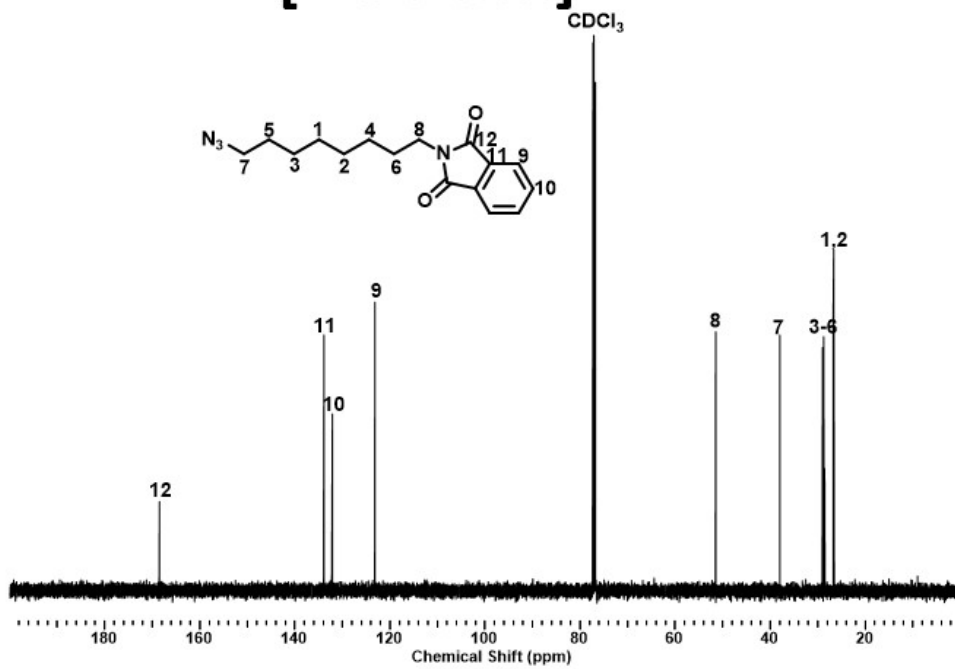
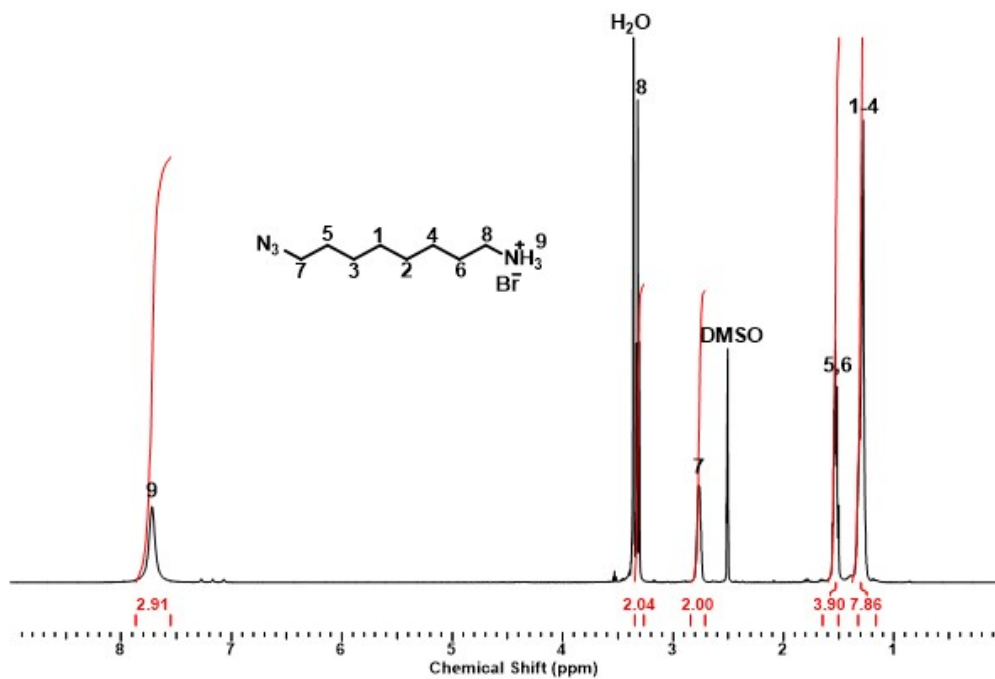


Figure S2. <sup>1</sup>H/<sup>13</sup>C NMR spectrum of 3



# [<sup>1</sup>H-NMR]



# [<sup>13</sup>C-NMR]

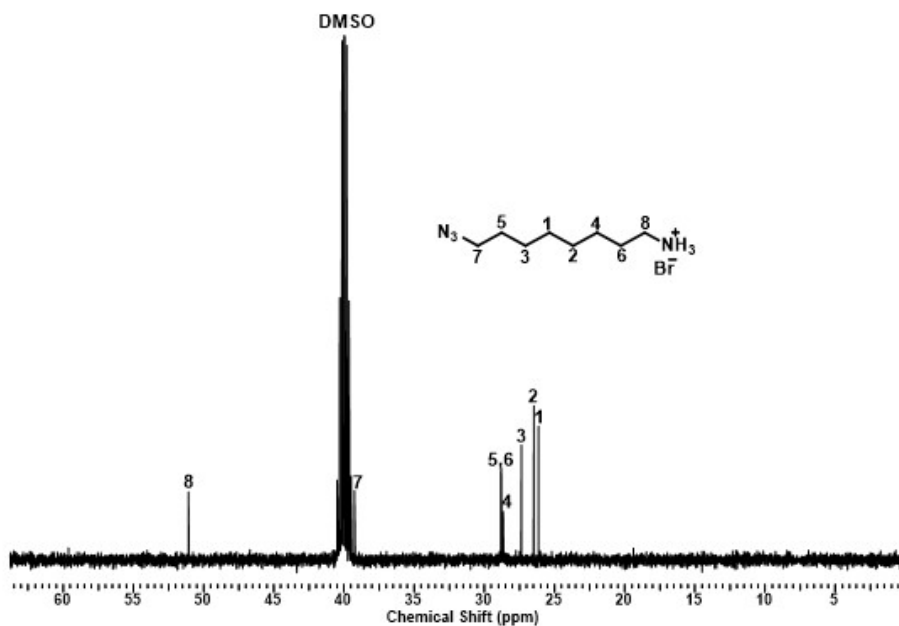
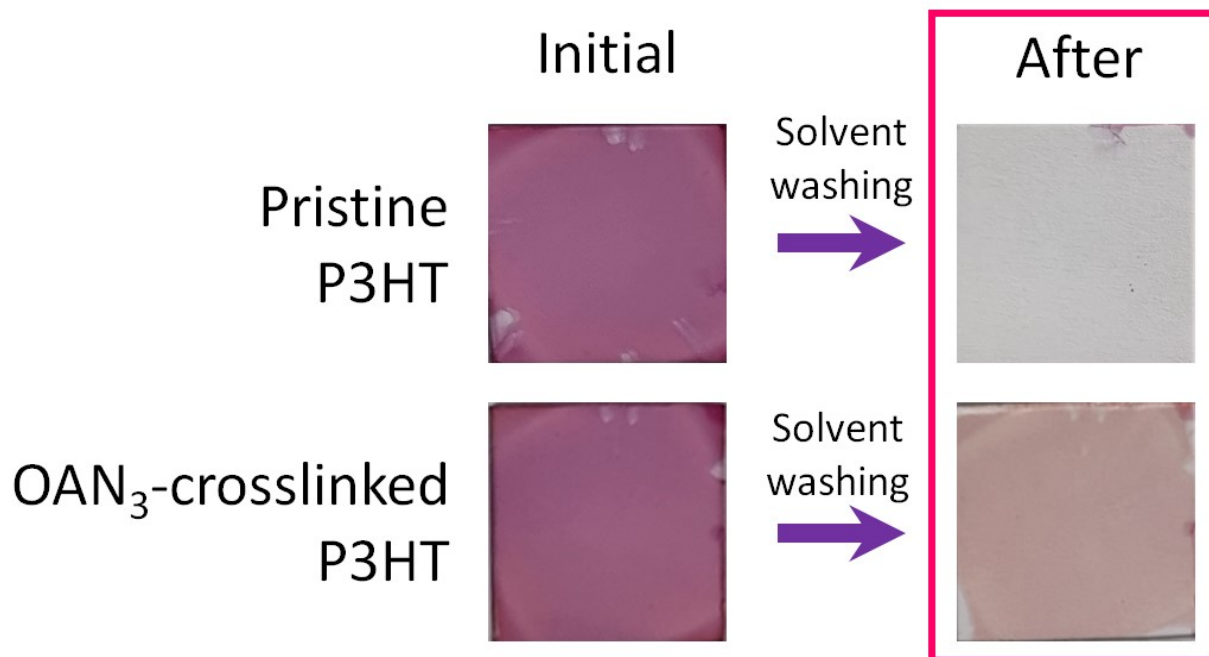
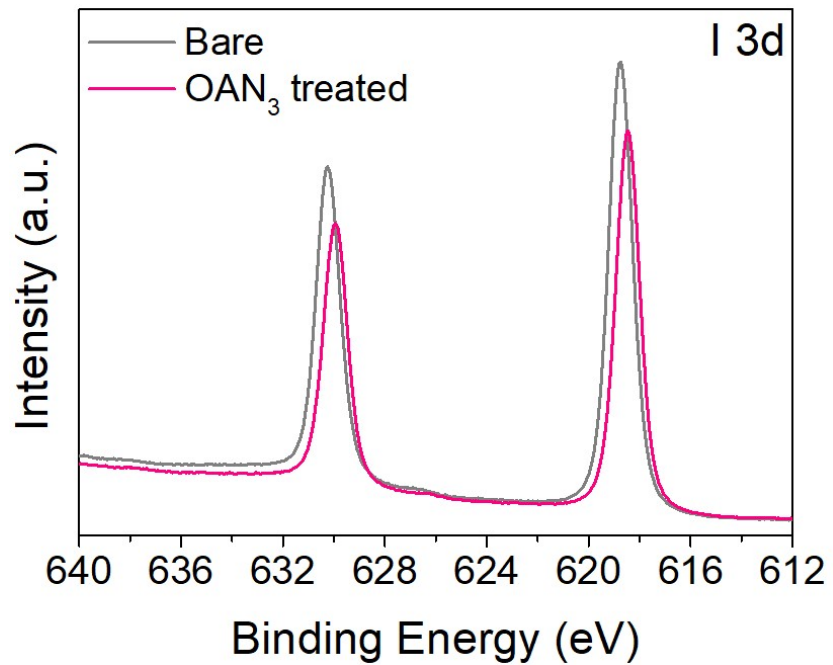


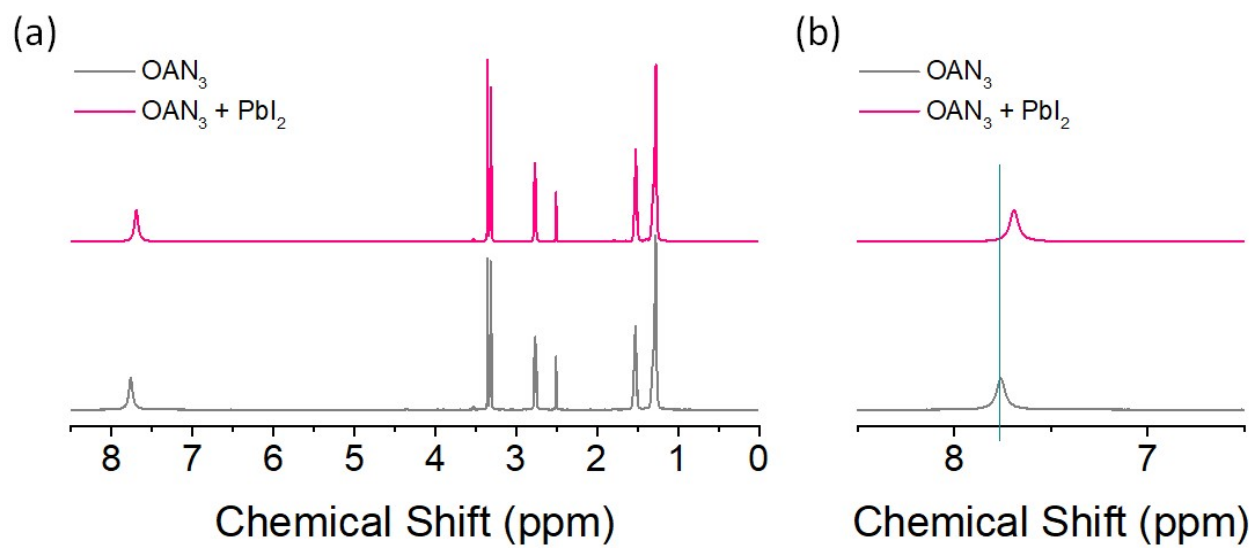
Figure S3. <sup>1</sup>H / <sup>13</sup>C NMR spectrum of 5



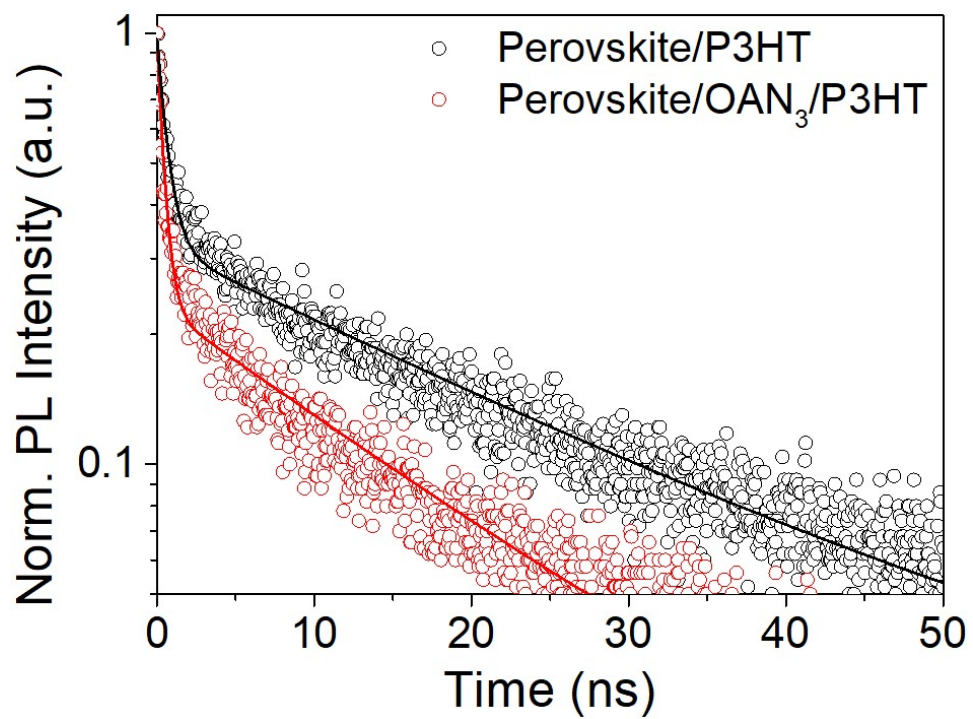
**Figure S4.** Film image of P3HT film before and after washing with chlorobenzene.



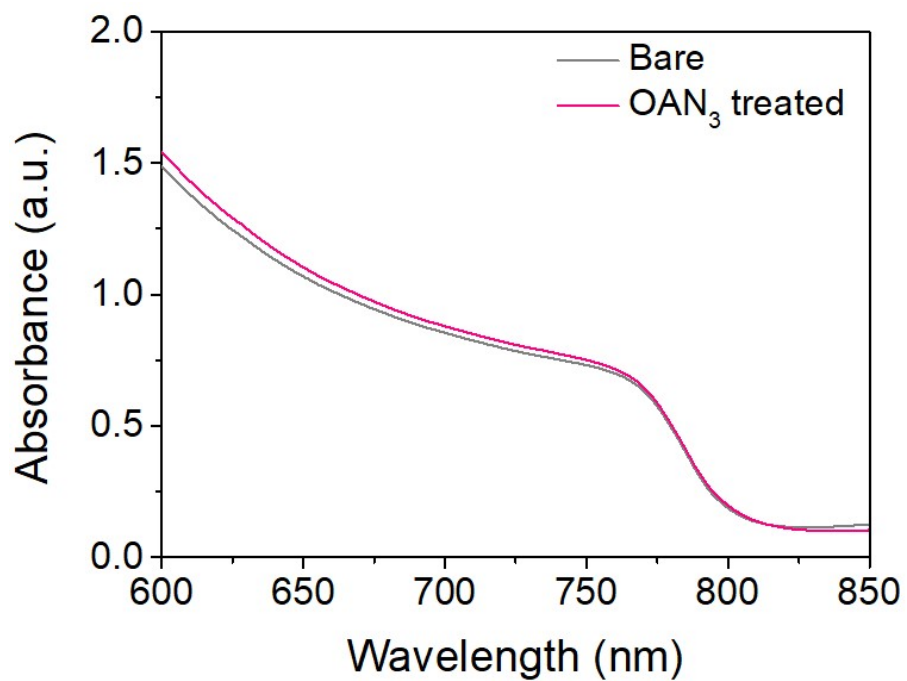
**Figure S5.** XPS spectrum of I 3d before and after OAN<sub>3</sub> introduction.



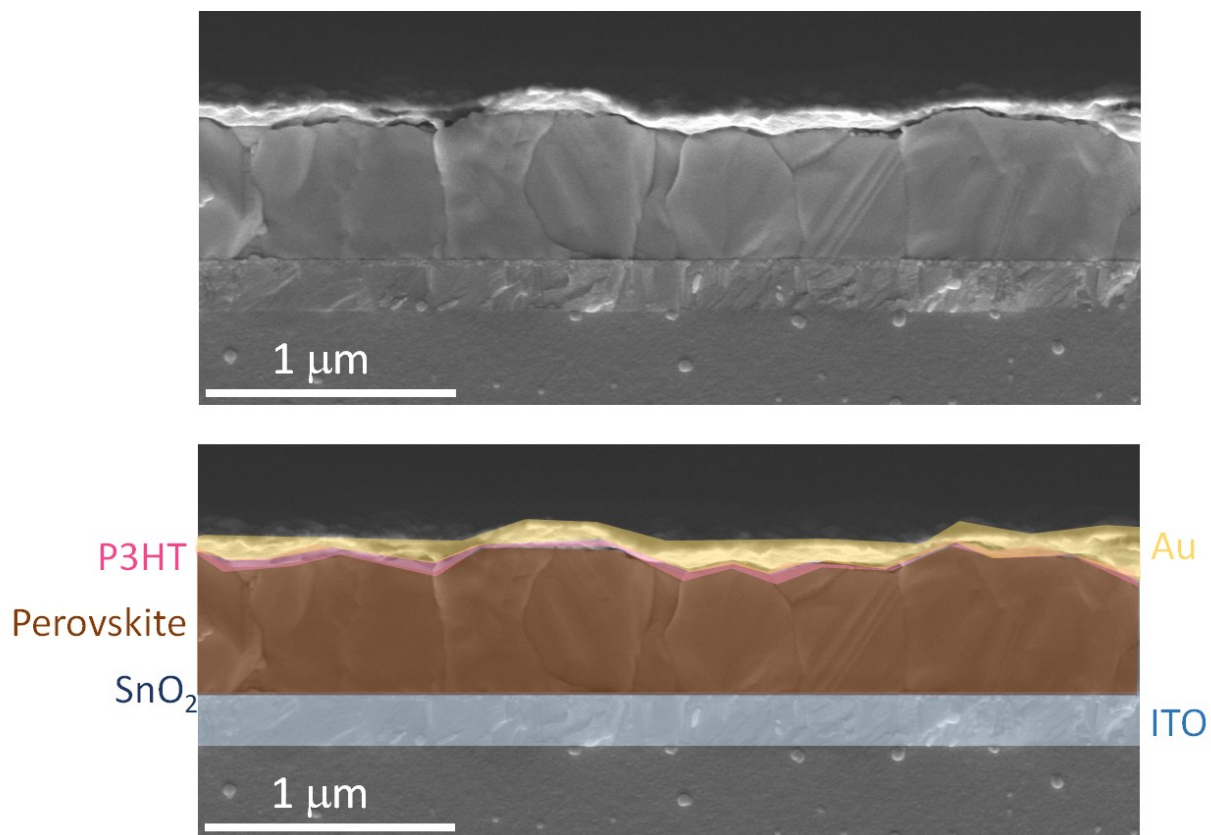
**Figure S6.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of OAN<sub>3</sub> and OAN<sub>3</sub>/PbI<sub>2</sub> mixture in the DMSO-*d*<sub>6</sub> solution.



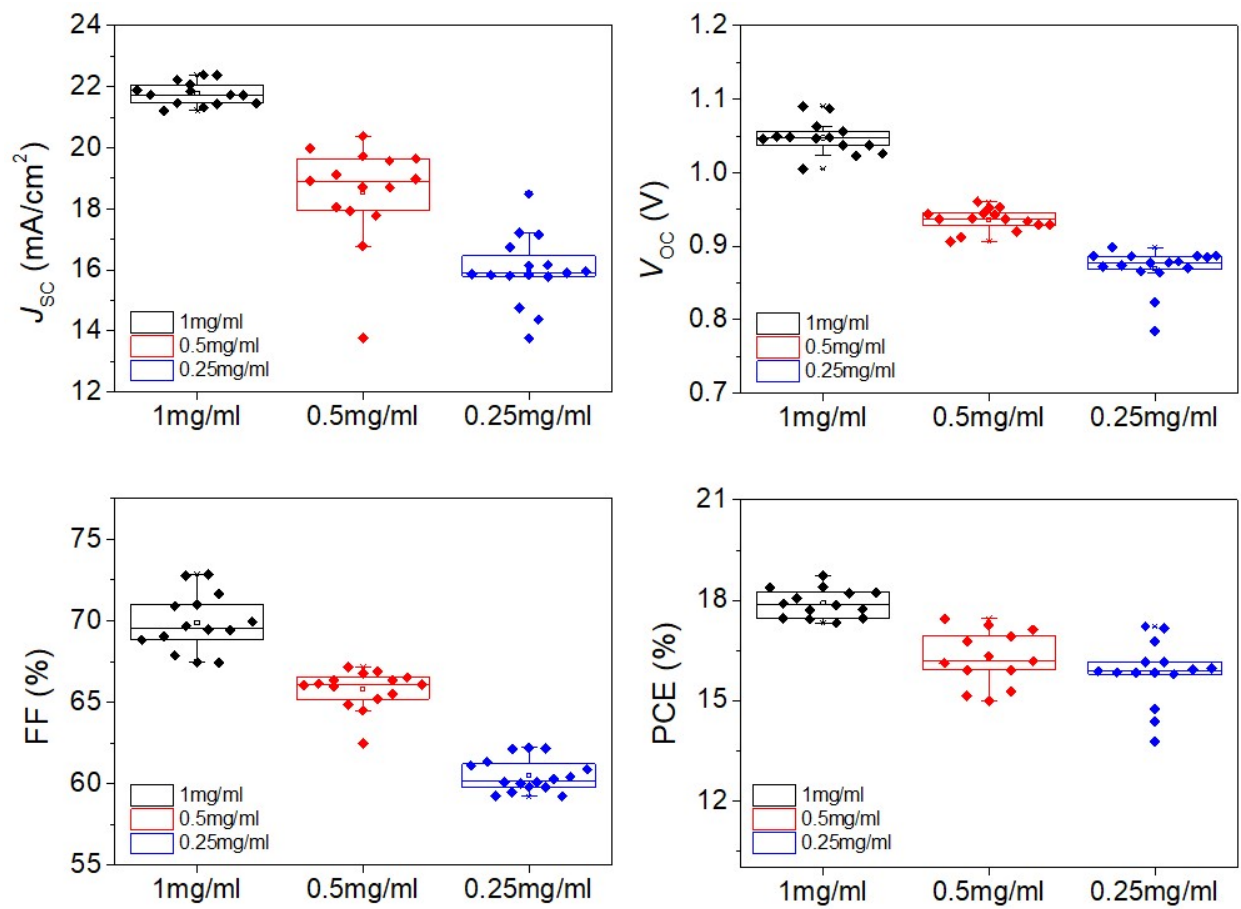
**Figure S7.** TRPL spectra of perovskite/P3HT and perovskite/OAN<sub>3</sub>/P3HT.



**Figure S8.** UV-Vis spectrum of perovskite before and after OAN<sub>3</sub> introduction.

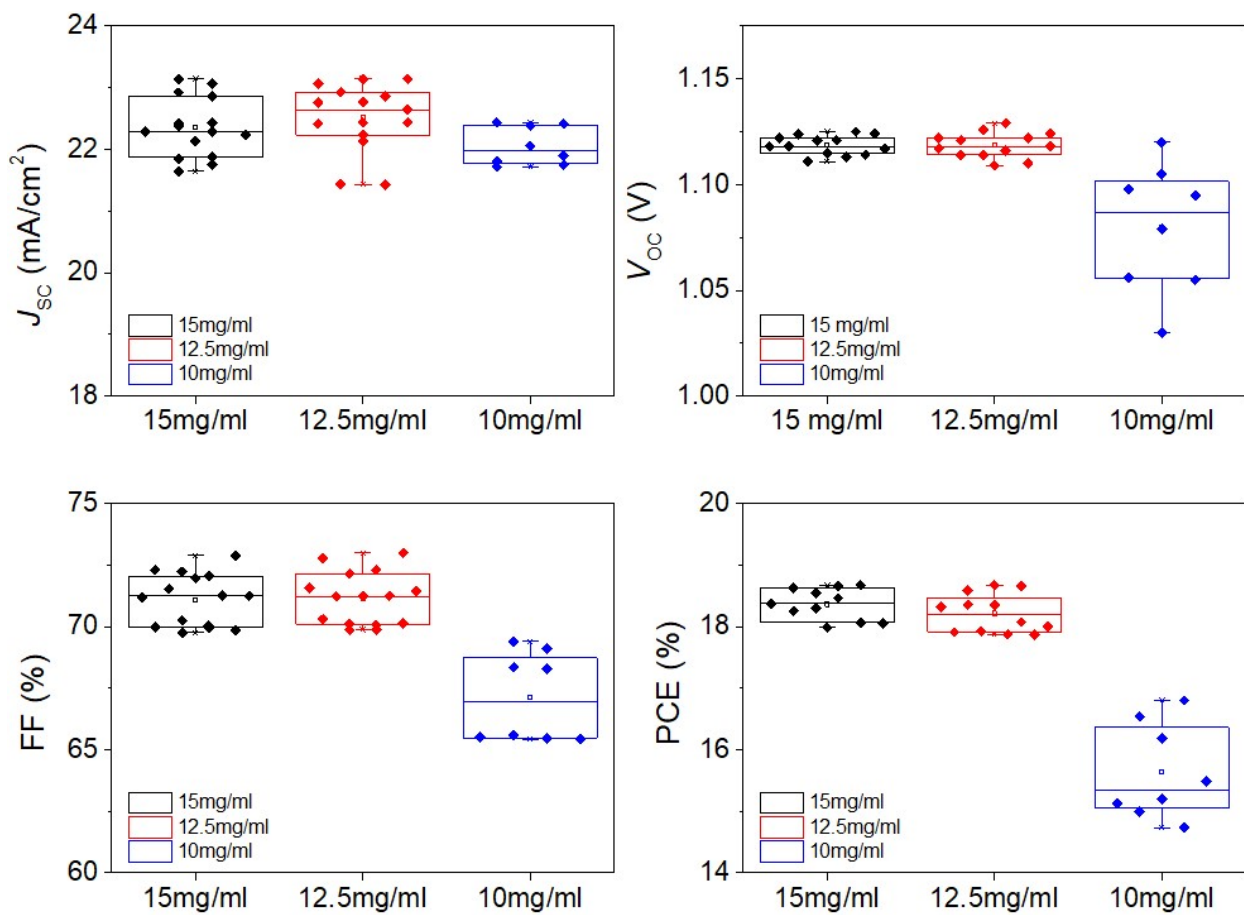


**Figure S9.** Cross-sectional SEM images of PSCs.

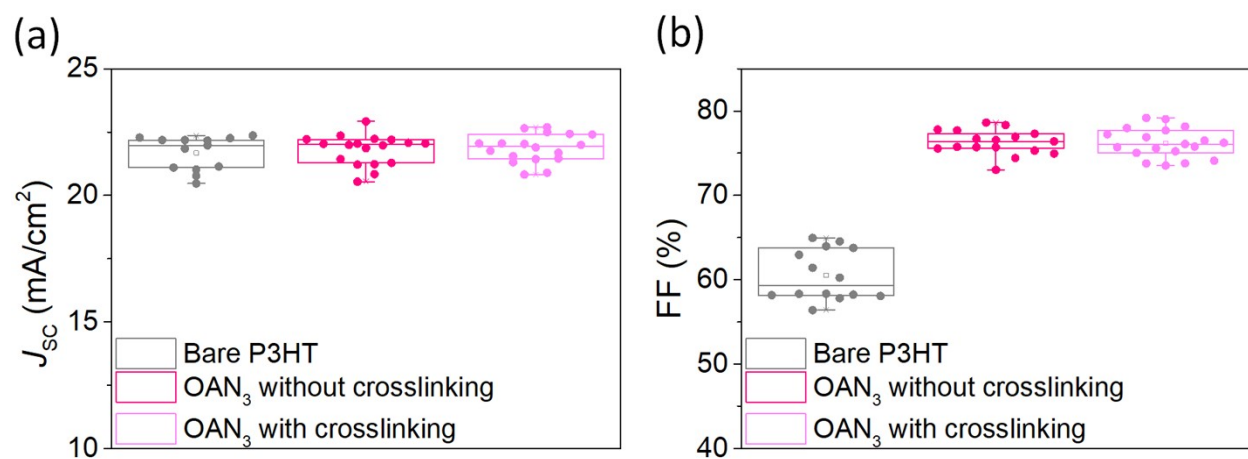


**Figure S10.** Photovoltaic parameters of PSCs with different OAN<sub>3</sub> concentration.

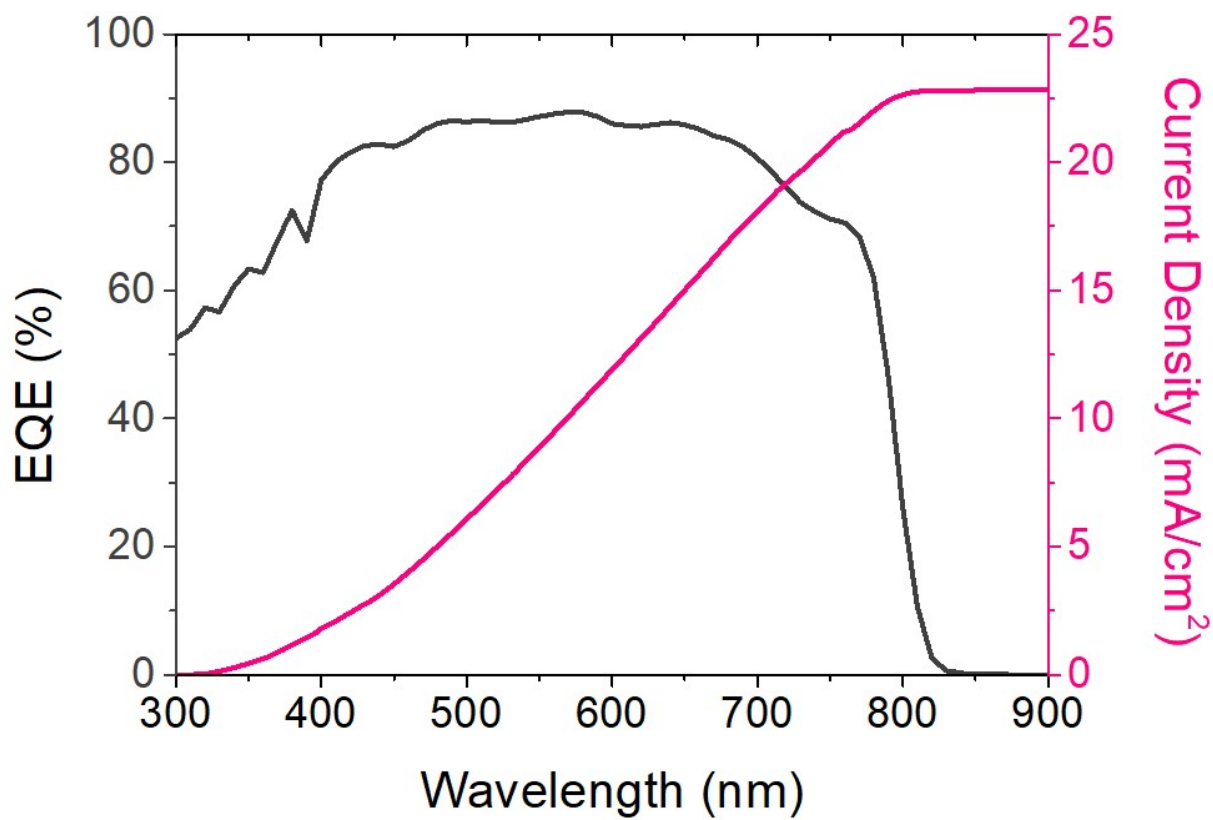




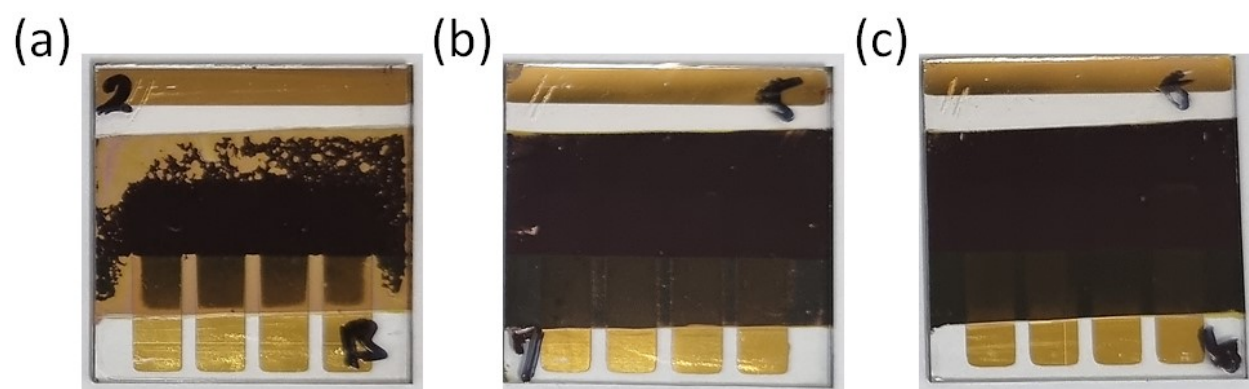
**Figure S11.** Photovoltaic parameters of PSCs with different P3HT concentration.



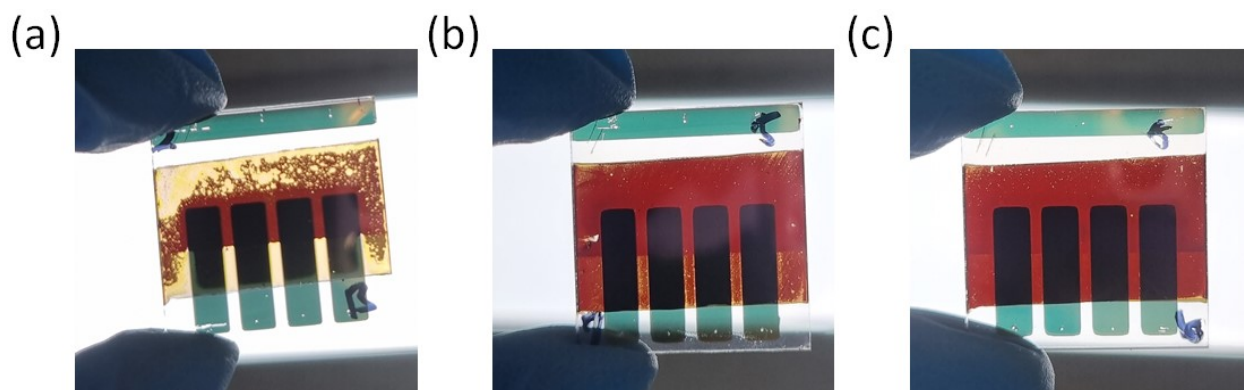
**Figure S12.**  $J_{sc}$  and FF of PSCs based on bare, OAN<sub>3</sub> treated before crosslinking, and after crosslinking.



**Figure S13.** External quantum efficiency spectrum for OAN<sub>3</sub> treated PSC.



**Figure S14.** PSC images of (a) bare PSCs and OAN<sub>3</sub> treated PSCs (b) before and (c) after crosslinking, after storage under RH:50~60%.



**Figure S15.** PSC images of (a) bare PSCs and OAN<sub>3</sub> treated PSCs (b) before and (c) after crosslinking, after storage under RH:50~60% (under LED illumination).