Supporting Information

Improved Stability of β-$CsPbI_3$ Inorganic Perovskite by π-Conjugated Bifunctional Surface Capped Organic Cations for High Performance Photovoltaics

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Materials

The cesium iodide (CsI, 99.999%), lead iodide (PbI_2, 99.9985%), 2,3-Naphthalenediamine (2,3-NDA, >97%) were purchased from Alfa Aesar. Dimethylammonium iodine (DMAI) was purchased from Borun Chemicals, and isopropanol (IPA) was purchased from J&K Scientific Ltd. Anhydrous dimethylformamide (DMF), bis(trifluoromethane) sulfonamide lithium salt (Li-TFSi) were purchased from Sigma-Aldrich. 4-tert-butylpyridine (tBP) was purchased from TCI Co., Ltd. Hydroiodic acid (HI, 57wt % in H_2O) was purchased from Acros organic. 2,3-$NDAI_x$ was synthesized by reacting 2,3-NDA powder (6 mmol) and hydroiodic acid (>57%, 15ml) in an ice bath for 7 h with continuous stirring. The precipitate was obtained by rotary evaporation at 60 ℃, washed with diethyl ether and then vacuum dried at 60 ℃ for 4 h. For 2,3-$NDAI_x$ salt, x is about 1.1~1.5 calculated from XPS measurement (Fig. 1d and Table S1).

Device fabrication

The FTO (TEC-7) substrate was coated with a compact TiO_2 (c-TiO_2) layer by spraying pyrolysis of 0.2 M Ti(IV)bis(ethyl acetoacetate)-diisopropoxide in 1-butanol

solution at 450 °C, followed by annealing at 450 °C for 1 h. The 0.6 M $CsPbI_3$ perovskite precursor was prepared by dissolving stoichiometric CsI, PbI_2, DMAI with 1:1:1.2 molar ratio in DMF. After that, the $CsPbI_3$ layer was spin-coated on 70 °C pre-heated c-TiO_2/FTO substrate (3000 rpm, 30 s), and dark brown layer was obtained after annealing at 210 °C for 5 min. The hole transport material (HTM) was spin-coated on the perovskite films, which consisted of 0.1 M spiro-MeOTAD, 0.035 M bis(trifluoromethane) sulfonamide lithium salt (LiTFSi), and 0.12 M 4-tert-butylpyridine (tBP) in chlorobenzene/acetonitrile (10:1, v/v) solution at 4000 rpm for 25 s. Finally, the Ag layer was deposited by thermal evaporation at a constant evaporation rate of 0.3 Å/s. All the process expecting for the metal evaporation were processed in a dry box with < 10% R.H.

Characterization

XRD patterns were measured by a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation. FTIR experiments were conducted on a Tensor 27 FTIR spectrometer (Nicolet 6700). The morphology was characterized using SEM (LEO1530VP). X-ray photoelectron spectroscopy (XPS, Thermo Fisher Escalab 250Xi, US) measurement was carried out by using an Al monochromatic X-ray at the power of 225 W. The *J-V* curves were measured by a Keithley 2401 source meter with voltage scan rate of 0.05 $V \cdot s^{-1}$. The solar cells were illuminated with a solar simulator (Enlitech's 3A light source) under simulated AM 1.5G illumination (100 $mW \cdot cm^{-2}$). The illuminated area was 0.12 cm^2. The light intensity was calibrated by a stand Si cell before test. The EQE was measured on a QE-3011 system (Enlitech).

Table S1. XPS analysis of 2,3-NDAI$_x$ powder.

	Name	Position	Area (%)	X(-NH_3^+:-NH_2)
2,3-NDAI$_x$	-NH_3^+	401.3	57.46	1.35
	-NH_2	398.97	42.54	

Table S2. Atomic ratios of Cs, Pb and I of perovskite films obtained from XPS results.

	Cs(%)	Pb(%)	I(%)	Cs/Pb	I/Pb
β-$CsPbI_3$	20.49	21.31	58.2	0.96	2.73
(2,3-NDAI$_x$)$CsPbI_3$	15.87	16.43	67.7	0.97	4.12

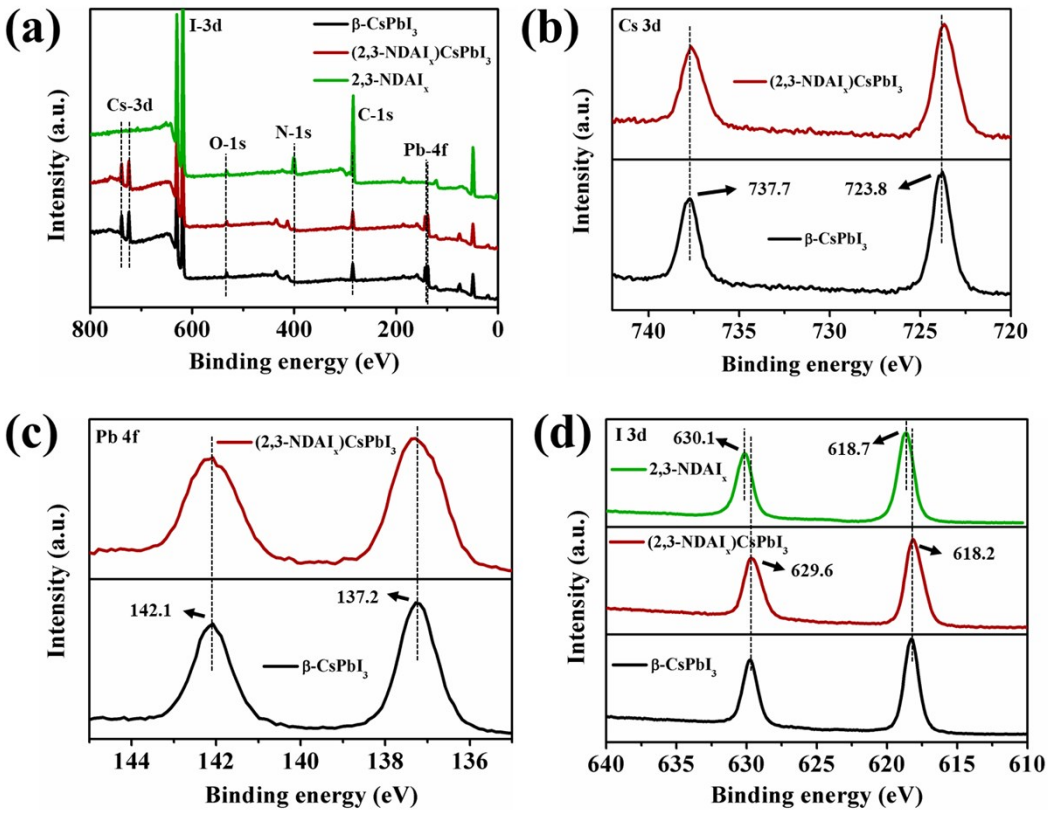

Fig. S1 (a) Survey XPS, (b) Cs 3d, (c) Pb 4f and (d) I 3d core-level XPS spectra for the β-$CsPbI_3$, (2,3-$NDAI_x$)$CsPbI_3$ and 2,3-$NDAI_x$.

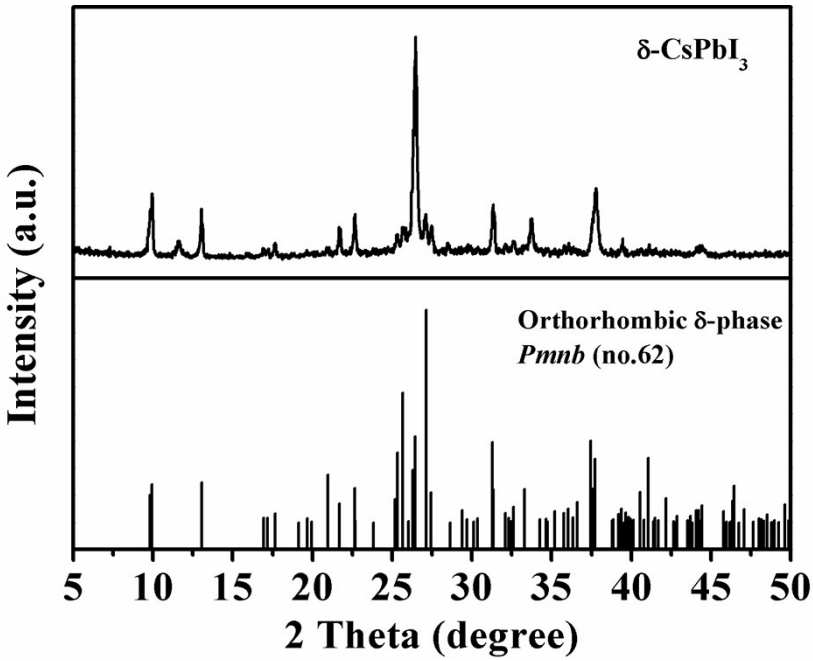

Fig. S2 XRD pattern of prepared yellow δ-$CsPbI_3$ and simulated orthorhomic δ-$CsPbI_3$ (space group *Pmnb*, no.62).

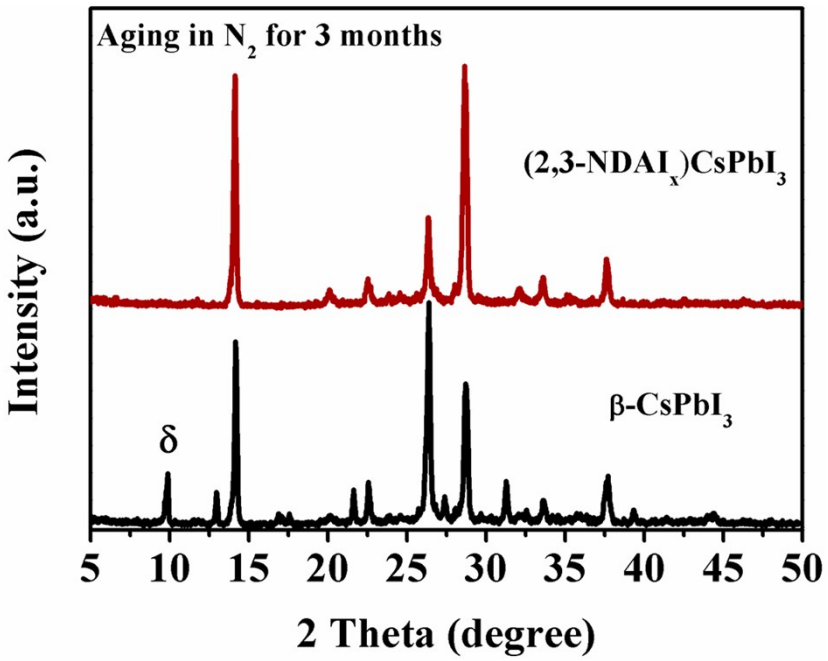

Fig. S3 XRD patterns of β-$CsPbI_3$ and (2,3-$NDAI_x$)$CsPbI_3$ after storage in nitrogen box for more than three months.

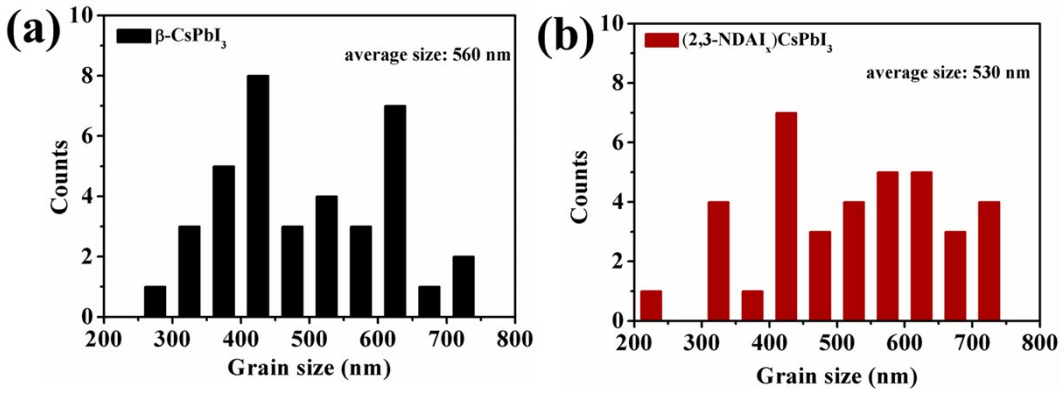

Fig. S4 Grain size distributions of the pristine β-$CsPbI_3$ and (2,3-$NDAI_x$)$CsPbI_3$ thin films.

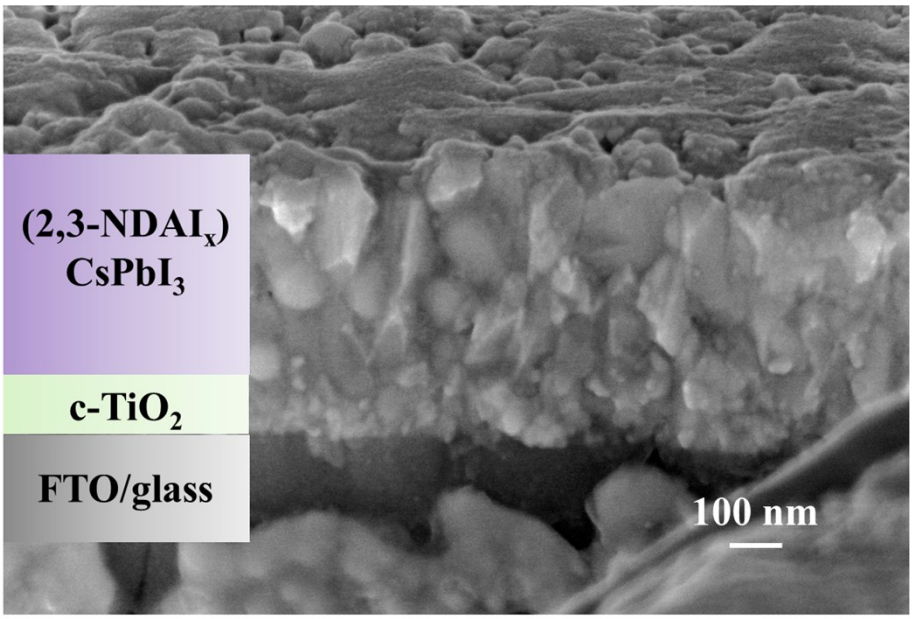

Fig. S5 The cross-sectional SEM image of (2,3-NDAI$_x$)CsPbI$_3$ deposited on c-TiO$_2$ layer.

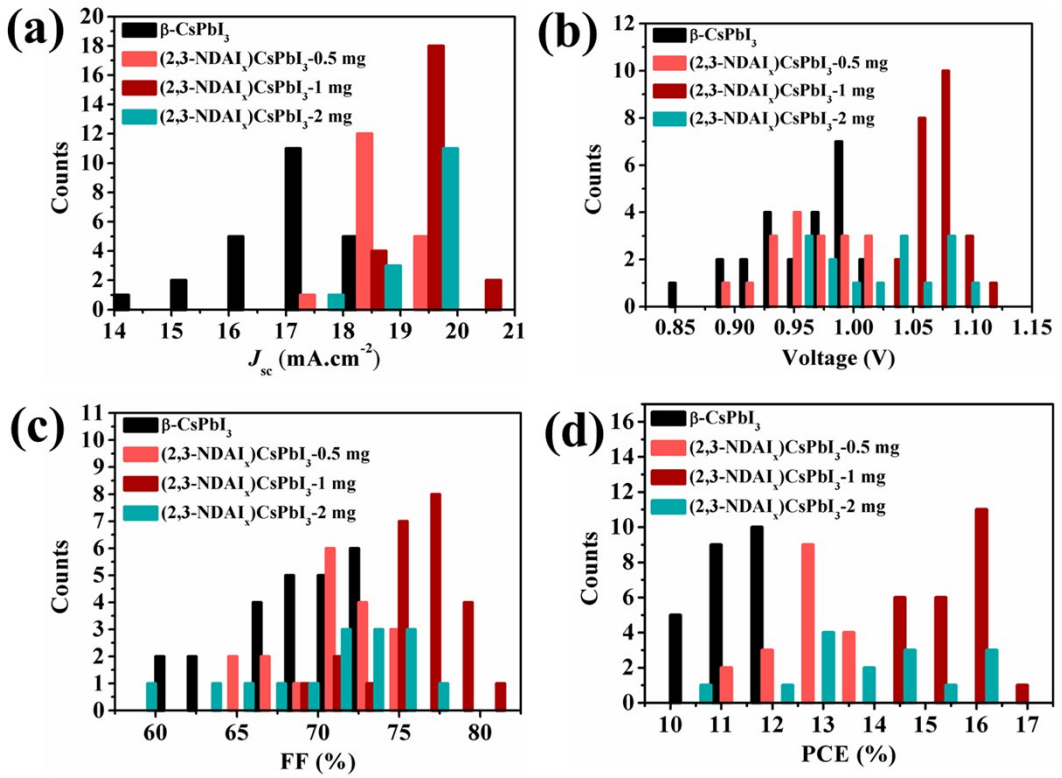

Fig. S6 Histograms of (a) J_{sc}, (b) V_{oc}, (c) FF and (d) PCE of β-$CsPbI_3$ and (2,3-$NDAI_x$)$CsPbI_3$ based PSCs with different concentration 2,3-$NDAI_x$ isopropyl alcohol solutions (0.5, 1.0, 2.0 mg/mL).

Table S3. The performances statistic of β-$CsPbI_3$ and (2,3-$NDAI_x$)$CsPbI_3$ based PSCs with different concentration 2,3-$NDAI_x$ isopropyl alcohol solutions (0.5, 1.0, 2.0 mg/mL).

	J_{sc} (mA.cm^{-2})	V_{oc} (V)	FF	PCE (%)
β-$CsPbI_3$	17.232±0.939	0.961±0.043	0.683±0.388	11.326±0.616
(2,3-$NDAI_x$)$CsPbI_3$-0.5 mg	18.707±0.364	0.965±0.034	0.704±0.032	12.692±0.564
(2,3-$NDAI_x$)$CsPbI_3$-1.0 mg	19.274±0.364	1.069±0.019	0.758±0.023	15.543±0.622
(2,3-$NDAI_x$)$CsPbI_3$-2.0 mg	19.127±0.451	1.021±0.047	0.698±0.048	13.824±1.577