## **Supporting information**

## Polymer-passivated Inorganic Cesium Lead Mixed-halide Perovskites for Stable and Efficient Solar Cells with High Open-Circuit Voltage over 1.3 V

Qingsen Zeng, Xiaoyu Zhang, Xiaolei Feng, Siyu Lu, Zhaolai Chen, Xue Yong, Simon

A. T. Redfern, Haotong Wei, Haiyu Wang, Huaizhong Shen, Wei Zhang, Weitao Zheng, Hao Zhang, John S. Tse and Bai Yang\*

Q. Zeng, Dr. X. Zhang, Dr. S. Lu, Dr. H. Shen, Prof. H. Zhang, Prof. B. Yang

State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun, 130012, P. R. China. E-mail: byangchem@jlu.edu.cn

Dr. X. Zhang, Prof. W. Zhang, Prof. W. Zheng

Department of Materials Science, Key Laboratory of Mobile Materials MOE, State Key Laboratory of Automotive Simulation and Control, Jilin University, Changchun, 130012, China.

Dr. Z. Chen, Dr. H. Wei

Department of Mechanical and Materials Engineering, University of Nebraska-Lincoln, Lincoln, Nebraska 68588, USA.

X. Feng

State Key Laboratory of Superhard Materials, Jilin University, Changchun, 130012, C hina.

Dr. X. Yong, Prof. J.S. Tse

Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, S7N5E2, Canada.

Prof. S. A. T. Redfern

Department of Earth Sciences, University of Cambridge, Downing Street, Cambirdge, CB2 3EQ, UK.

Prof. H. Wang

State Key Laboratory on Integrated Optoelectronics College of Electronic Science and Engineering, Jilin University, Changchun, 130012, P. R. China.

**Chemicals.** All chemicals were used without further purification. Cesium carbonate  $(Cs_2CO_3, 99.9\%)$ , oleic acid (OA, technical grade 90%), oleylamine (OLA, technical grade 70%), 1-octadecene (ODE, technical grade 90%), chlorobenzene (anhydrous, 99.8%), regioregular poly(3-hexylthiophene) (P3HT)(99.995% trace metals basis, average  $M_n$  15,000-45,000), 4-tert-butylpyridine (TBP), bis(trifluoromethylsulfonyl)amine lithium salt (Li-TFSI), and acetonitrile (anhydrous, 99.8%) were purchased from Sigma Aldrich. Lead (II) iodide (PbI<sub>2</sub> 99.9985%) was purchased from Alfa Aesar. Lead bromide (PbBr<sub>2</sub> 99.99%), lead (II) acetate trihydrate (Pb(OAc)<sub>2</sub> 3H<sub>2</sub>O, 99.999%) and methyl acetate (MeOAc, anhydrous 99.5%) were purchased from Aladdin. Hexane (HPLC  $\geq$ 97%), isopropanol (IPA HPLC  $\geq$ 97%) and toluene (anhydrous 99.8%) were purchased from Yu Wang Group. Tetrabutyl titanate and hydrochloric acid (HCl, AR) was purchased from Sinopharm Group Co. Ltd.

**Characterization.** UV-visible absorption spectra were obtained using a Shimadzu 3600 UV-visible-NIR spectrophotometer and photoluminescence (PL) spectra on a Cary Eclipse spectrofluorimeter. Time-resolved PL measurements were performed on a time-correlated single-photon counting (TCSPC) system under right-angle sample geometry using mini- $\tau$  miniaturefluorescence lifetime spectrometer (Edinburgh Instruments). A 405 nm picosecond diode laser (EPL-405, repetition rate 5 MHz, 64.8 ps) was used to excite the samples. The detail morphologies of the samples were observed on a Tecnai G2 S-Twin F20 at an accelerating voltage of 200 kV via a transmission electron microscopy (TEM) and a JEM-2100F high resolution transmission electron microscopy (HRTEM). Scanning electron microscopy (SEM) images were recorded on a SU8020 electron microscope and the Energy Disperse Spectroscopy (EDS) and mapping measurements for elemental analysis were

conducted on a Bruker Energy Dispersive Spectrometer based on the SEM instrument. XRD data were collected using a PANalytical B.V.-Empyream Diffractometer with Cu K $\alpha$  radiation. X-ray photoelectron spectroscopy (XPS) was investigated by using a VG ESCALAB MKII spectrometer. CsPbI<sub>2</sub>Br and doped-P3HT samples for UPS measurements were fabricated on glass/Cr(10nm)/Au(100nm) substrates. The energy band values were measured in an integrated ultrahigh vacuum system equipped with multitechnique surface analysis system (VG ESCALAB MK II spectrometer). A negative bias voltage was applied to the samples in order to shift the spectra from the spectrometer threshold.

**Femtosecond transient absorption**: The transient absorption (TA) setup consisted of 400 nm pump pulses generated from 800 nm laser pulses (100 fs duration, 250 Hz repetition rate) generated from a mode-locked Ti: sapphire laser/amplifier system (Solstice, Spectra-Physics) and broadband white-light probe pulses generated from 2-mm-thick water. The relative polarization of the pump and the probe beams was set to the magic angle. The transient absorption spectra data were collected via a fiber coupled spectrometer connected to a computer. CsPbI<sub>2</sub>Br (120 nm) films for TA measurements were spin-coated on quartz substrate and encapsulated with quartz to prevent sample degradation from humidity exposure.

**Computational details**: All the calculations were performed by using CP2K.<sup>[1]</sup> Electronic orbitals were expanded using the molecularly optimized MOLOPT double  $\zeta$ -valence polarized basis set, a mixed Gaussian and plane wave basis set. The Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional was employed.<sup>[2]</sup> The structural optimizations were performed using the Broyden-Fletcher-Goldfarb-Shanno algorithm until forces on all atoms were less than 10<sup>-4</sup> Ha/Bohr. 110 surface of CsPbI<sub>3</sub> were chosen since the 110 surface were found to be the stable surface.<sup>[3]</sup> I atoms at the

interface were substituted by Br to account for the effect of Br. Pb-Br antisite defects were considered in the case of 110 surface.



**Figure S1:** Plots of PCE against  $E_g$  for all inorganic perovskite solar cells reported so far.

Table	<b>S1</b> :	A	summary	of	the	detail	performance	parameters	of	reported	Cs-based
inorga	nic s	ola	r cells.								

Perovskites	Deposition method & atmosphere	Device structure	V <sub>oc</sub> (V)	Energy loss (eV)	PCE (%)	Steady-state PCE (%)	e Ref.
CsPbBr <sub>3</sub>	Solution & Open-air	FTO/c-TiO2/mp-TiO2/P/Spiro-MeOTAD/Au	1.32	0.98	5.95	-	29
CsPbBr <sub>3</sub>	Solution & Open-air	FTO/c-TiO <sub>2</sub> /mp-TiO <sub>2</sub> /P/PTAA/Au	1.25	1.05	6.2	-	32
CsPbBr <sub>3</sub>	Solution & Open-air	FTO/c-TiO <sub>2</sub> /mp-TiO <sub>2</sub> /P/Carbon	1.24	1.06	6.7	-	31
CsPbBr <sub>3</sub>	QD solution & Open-air	FTO/TiO <sub>2</sub> /P/Spiro-MeOTAD/Au	1.50	0.88	5.4	3.2	22
CsPbBr <sub>3</sub>	Solution & Open-air	FTO/c-TiO <sub>2</sub> /mp-TiO <sub>2</sub> /P/Carbon	1.24	1.06	3.9	-	30
CsPbBr <sub>2</sub> I	Evaporation & Air-free	FTO/TiO <sub>2</sub> /P /Au	0.96	1.09	4.7	-	33
CsPbBr <sub>2</sub> I	Solution & Air-free	FTO/c-TiO <sub>2</sub> /mp-TiO <sub>2</sub> /P/Spiro-MeOTAD/Au	1.23	0.82	8.02	6.7	25
CsPbBr <sub>2</sub> I	Solution & Open-air	FTO/c-TiO2/mp-TiO2/P/Spiro-MeOTAD/Au	1.12	0.93	6.3	6.3	37
CsPbBrI <sub>2</sub>	Solution & Air-free	ITO/PEDOT:PSS/P/PCBM/BCP/Al	1.12	0.78	6.8	6.5	17
CsPbBrI <sub>2</sub>	Solution & Air-free	FTO/TiO <sub>2</sub> /P/Spiro-MeOTAD/Ag	1.11	0.81	9.8	5.6	36
$Cs_{0.925}K_{0.075}P$ bBrI <sub>2</sub>	Solution & Open-air	FTO/TiO2/P/Spiro-MeOTAD/Au	1.18	0.74	10.0	9.2	20
CsPbBrI <sub>2</sub>	Solution & Open-air	FTO/TiO <sub>2</sub> /P/Spiro-MeOTAD/Ag	1.10	0.80	10.3	-	19
CsPbBrI <sub>2</sub>	Solution & Open-air	FTO/TiO <sub>2</sub> /P/Spiro-MeOTAD/Au	1.23	0.69	10.7	9.5	26
CsPbBrI <sub>2</sub>	Evaporation & Air-free	ITO/Ca/C <sub>60</sub> /P/TAPC/TAPC:MoO <sub>3</sub> /Ag	1.15	0.67	11.8	11.5	34
CsPbBrI <sub>2</sub>	Solution & Air-free	FTO/TiO <sub>2</sub> /P/Spiro-MeOTAD/Au	1.19	0.73	10.3	9.3	27
CsPb <sub>0.98</sub> Sr <sub>0.02</sub> I <sub>2</sub> Br	Solution & Air-free	FTO/c-TiO2/mp-TiO2/P/P3HT/Au	1.07	0.81	11.2	10.8	28
CsPbI <sub>3</sub>	Evaporation & Air-free	ITO/Ca/C <sub>60</sub> /P/TAPC/TAPC:MoO <sub>3</sub> /Ag	0.97	0.75	9.4	-	34
CsPbI <sub>3</sub>	Evaporation & Air-free	FTO/TiO <sub>2</sub> /P/P3HT/Al	1.06	0.66	10.5	8.2	35
CsPbI <sub>3</sub>	Solution & Air-free	ITO/PEDOT:PSS/P/PCBM/Al/Ca	0.85	0.88	2.9	1.7	16
CsPbI <sub>3</sub>	Solution & Air-free	FTO/c-TiO2/mp-TiO2/P/P3HT/MoO3/Au	0.74	0.98	4.68	-	24
CsPbI <sub>3</sub>	Solution & Open-air	FTO/TiO <sub>2</sub> /P/Spiro-MeOTAD/Ag	0.66	1.06	4.13	1.88	18
CsPbI <sub>3</sub>	QD solution & Open-air	FTO/TiO <sub>2</sub> /P/Spiro-MeOTAD/MoO <sub>x</sub> /Al	1.23	0.52	10.77	7.9	23
CsPbBrI <sub>2</sub>	QD solution & Open-air	ITO/TiO <sub>2</sub> /P/P3HT/Au	1.32	0.50	12.02	9.5 Th	is work



**Figure S2:** SEM energy-dispersive spectroscopy (SEM-EDS) analysis for as-prepared CsPbI<sub>2</sub>Br NCs shows Cs:Pb:I:Br =  $0.944 (\pm 0.03):1.00 (\pm 0.04):2.18 (\pm 0.05):1.15 (\pm 0.05).$ 



**Figure S3:** FTIR spectra showing the IR transmission of CsPbI<sub>2</sub>Br QD films with and without isopropyl alcohol (IPA) treatment. The vibrations at 2923 cm<sup>-1</sup> and 2852 cm<sup>-1</sup> are  $v_{asym}$  (C-H) and  $v_{sym}$  (C-H), respectively, which are associated with the original long chain ligands. As shown, organic ligands have almost been removed from the CsPbI<sub>2</sub>Br film after IPA washing.

Samples	$\tau_1$ (ns)	$\mathbf{f}_1$	$\tau_2(ns)$	$\mathbf{f}_2$	$\tau_3$ (ns)	f3	$\chi^2$	$ au_{ave}^{\ \ b}$
		(%)		(%)		(%)		(ns)
As-prepared	0.47	37.5	0.48	48.2	2.45	14.3	0.996	0.76
IPA-washed	0.55	56.1	2.64	32.4	14.29	11.5	0.996	2.81
Annealed (CsPbI <sub>2</sub> Br)	2.09	7.9	5.19	60.4	11.41	31.7	0.999	6.91
CsPbI <sub>2</sub> Br/P3HT	6.26	47.8	17.56	13.1	31.13	39.1	0.996	14.8
CsPbI <sub>2</sub> Br/P3HT, annealed	0.43	30.4	0.44	31.1	1.63	38.5	0.996	0.89
CsPbI <sub>2</sub> Br/ spiro-MeOTAD	1.83	30.5	1.84	69.1	4.73	0.4	0.999	1.85

Table S2: Summary of TRPL triple exponential fitting parameters.<sup>a</sup>

<sup>a</sup>Normalized time-resolved photoluminescence data are fit to the following exponential equation:<sup>[4]</sup>

Intensity = 
$$f_1 e^{-t/\tau_1} + f_2 e^{-t/\tau_2} + f_3 e^{-t/\tau_3} + b$$

 $^{b}Average$  lifetime,  $\tau_{ave},$  are calculated by

$$\tau_{\text{ave}} = f_1 \tau_1 + f_2 \tau_2 + f_3 \tau_3$$



**Figure S4:** The SEM-EDS and XPS measurements are conducted to detect the change of element content of CsPbI<sub>2</sub>Br films in the bulk and on the surface during the ligand treatment process, respectively. The SEM-EDS presents an increase of the Pb/Cs ratio from 1.00 ( $\pm$ 0.04): 0.944 ( $\pm$ 0.03) to 1.00 ( $\pm$ 0.03) : 0.862 ( $\pm$ 0.02) after IPA (saturated PbAc<sub>2</sub>) washing. In addition, the XPS spectra suggest that the surface Pb content increases most obviously compared with the Cs, I and Br, while the C content decrease sharply due to the remove of ligands, which is consistent with the results of IR spectra (**Figure S3**).



**Figure S5:** The XPS spectra of Cs 3d, Pb 4f and S 2p in the CsPbI2Br, CsPbI2Br/P3HT(~8 nm) bilayer, and P3HT films. When 8 nm P3HT is deposited on the CsPbI<sub>2</sub>Br surface, the binding energy of Cs 3d and Pb 4f shifts towards the lower binding energy and the binding energy of S 2p goes higher. As we know, the increase or decrease in binding energy of an element indicates the enhancement or weakening of effective positive charge around it. Therefore, the XPS results demonstrate that the interaction is indeed built between the S atoms and Pb (Cs) atoms, and the electrons on S atoms partly transfer to Pb<sup>2+</sup> and Cs<sup>+</sup>, thus leading to reduced binding energy and increased average electron density of Pb and Cs atoms. This is consistent with the calculated results.



**Figure S6:** SEM image of the annealed CsPbI<sub>2</sub>Br/ P3HT bilayer. The CsPbI<sub>2</sub>Br was annealed at 265 °C, and P3HT was annealed at 200 °C.



**Figure S7:** The reverse-scan J-V curves of CsPbI<sub>2</sub>Br solar cells with P3HT layer annealed at different temperature. RT is room temperature. The device performance degrades once annealing temperature of P3HT is over 200 °C.

**Table S3:** Photovoltaic parameters of the CsPbI<sub>2</sub>Br solar cells with the P3HT layer annealed at different temperature.

Annealing	$V_{OC}\left(\mathbf{V}\right)$	$J_{SC}$ (mA cm <sup>-2</sup> )	FF	PCE (%)	$R_s \left(\Omega \ \mathrm{cm}^2\right)^{\mathrm{a}}$
temperature (°C)					
RT	1.25	12.22	0.584	8.92	23.5
100 °C	1.27	12.90	0.631	10.34	17.5
200 °C	1.32	13.18	0.675	11.74	12.4

<sup>a</sup>The series resistance ( $R_s$ ) are calculated from the J-V curves.

The  $V_{OC}$  increases with the increased annealing temperature due to reduced energy disorder of P3HT. A high  $V_{OC}$  of 1.32 V with  $E_{loss}$  of 0.5 eV is achieved, demonstrating that the modification of interface with P3HT facilitated the charge extraction and transportation. In addition, the decreased series resistance ( $R_s$ ) agrees well with the results that hole transfer from CsPbI<sub>2</sub>Br to P3HT is enhanced after annealing.



**Figure S8:** UPS spectra of  $CsPbI_2Br$  and P3HT films. The left panel shows the secondary electron cut-off region and the right panel shows the magnified spectra near Femi edge.



**Figure S9:** (a) External quantum efficiency curve and integrated current density of a CsPbI<sub>2</sub>Br solar cells. (b) Bandgap determination from EQE measurements indicates a bandgap of 1.82 eV for the CsPbI<sub>2</sub>Br films.



**Figure S10:** The *J-V* curves of the CsPbI<sub>2</sub>Br solar cells based on P3HT and spiro-MeOTAD hole transport layers under dark condition. Diode ideality factor n (departure from unity) is an important factor to characterize trap-assisted and tail state recombination.<sup>[5,6]</sup> n can be extracted from the dark J–V curve based on **Equation S1**. The n values of the two perovskite solar cells are calculated from the linear slopes derived from the dark J–V curves. Compared to the spiro-MeOTAD-based device (n=2.06), the n value of the P3HT-based solar cell is 1.89. It indicates that there is less trap-assisted charge carrier recombination when P3HT is used as hole transport layer.

## **Equation S1**

$$J_{inj} = J_{0,n} e^{\frac{qV}{nTk_B}}$$

 $J_{0,n}$  is reverse saturation dark current density, n is diode ideality factor,  $k_B$  is Boltzmann constant, T is tempreture, q is elementary charge.  $J_{inj}$  is current density of perovskite solar cells in the dark.



Figure S11: J-V curves in reverse and forward sweep for CsPbI<sub>2</sub>Br solar cells.



**Figure S12:** Champion solar cell stabilized power output measurement held at a constant voltage of 0.99 V (PCE in blue; current density in red).



**Figure S13:** (a) The long-term stabilized power output of the CsPbI<sub>2</sub>Br device without encapsulation in open-air. (b) The PL spectra for the corresponding CsPbI<sub>2</sub>Br films measured as a function of exposure time (the light intensity is 100 mW cm<sup>-2</sup>). (c)-(f) Top view SEM image of CsPbI<sub>2</sub>Br film (c) and the corresponding EDS elemental mapping of <sup>79</sup>Br (d, blue), <sup>127</sup>I (e, red) and overlap of the <sup>79</sup>Br (red) and <sup>127</sup>I (blue) signals (f). Scale bar: 1  $\mu$ m.

The elemental distributions of <sup>79</sup>Br and <sup>127</sup>I across a freshly annealed CsPbI<sub>2</sub>Br film are given in **Figure S13**b and c, with their overlap signals shown in **Figure S13**d. The "blue" spots have high <sup>79</sup>Br intensities while the "red" spots have high <sup>127</sup>I intensities. Combining the elemental maps reveals an elemental distribution inhomogeneity, indicating the segregation of CsPbI<sub>2</sub>Br films. Similar phenomenon has already been observed in hybrid perovskite films yielding 20% efficient solar cells, which reveals that the mixed perovskite film intrinsically segregates into iodide-rich perovskite nanodomains on a length scale of up to a few hundred nanometers.<sup>[7]</sup>

The stabilized PCE of our device decreases to its half after illumination for an hour under constant, 1-sun illumination (**Figure S13**e). Photo-induced phase separation in mixed halide perovskite is a consequence of the unique electromechanical properties

of this class of materials.<sup>[8]</sup> As shown in **Figure S13**f, a 13 nm red-shift in the PL peak of CsPbI<sub>2</sub>Br film is observed at the same time during illumination, demonstrating that photoexcitation has caused halide segregation. This is accompanied by the formation of iodide-rich minority, which would act as recombination center traps,<sup>[9]</sup> and lead to device efficiency decrease. Zhao' Group in their recent work revealed that the activation energy for ion migration of the inorganic CsPbI<sub>2</sub>Br sample (0.45 eV) was much larger than that of MA-based hybrid one (0.07 eV).<sup>[10]</sup> Light-induced halide segregation could be eliminated completely in their work, indicating that inorganic CsPbI<sub>2</sub>Br mixed-halide perovskites are promising materials for achieving photostable perovskite solar cells. In addition, preparation in inert ambient and adding a UV filter may be helpful to enhance the light stability.<sup>[10]</sup>

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