

# Printable CsPbI<sub>3</sub> Perovskite Solar Cells with PCE of 19% via an Additive Strategy

Xiaoming Chang, Junjie Fang, Yuanyuan Fan, Tao Luo, Hang Su, Yalan Zhang, Jing Lu, Leonidas Tsetseris, Thomas D. Anthopoulos,\* Shengzhong (Frank) Liu,\* and Kui Zhao\*

All-inorganic CsPbI<sub>3</sub> holds promise for efficient tandem solar cells, but reported fabrication techniques are not transferrable to scalable manufacturing methods. Herein, printable CsPbI<sub>3</sub> solar cells are reported, in which the charge transporting layers and photoactive layer are deposited by fast blade-coating at a low temperature ( $\leq 100$  °C) in ambient conditions. High-quality CsPbI<sub>3</sub> films are grown via introducing a low concentration of the multifunctional molecular additive Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, which reconciles the conflict between air-flow-assisted fast drying and low-quality film including energy misalignment and trap formation. Material analysis reveals a preferential accumulation of the additive close to the perovskite/SnO<sub>2</sub> interface and strong chemisorption on the perovskite surface, which leads to the formation of energy gradients and suppressed trap formation within the perovskite film, as well as a 150 meV improvement of the energetic alignment at the perovskite/SnO<sub>2</sub> interface. The combined benefits translate into significant enhancement of the power conversion efficiency to 19% for printable solar cells. The devices without encapsulation degrade only by  $\approx 2\%$  after 700 h in air conditions.

Perovskite semiconductors have emerged as exciting new materials for solar cells due to their unique combination of strong light absorption<sup>[1]</sup> and superb charge carrier mobility.<sup>[2]</sup> Power conversion efficiencies (PCEs) of perovskite solar cells (PSCs) have risen from 3.8% to a certified 25.2%,<sup>[3–6]</sup> which already rival those of other thin-film photovoltaic (PV) devices. One significant advantage of perovskite materials is their ability to be solution-processed at low temperature, which makes perovskite solar cells promising candidates for a high-performance, scalable and low-cost vacuum-free PV technology. Such fast and scalable fabrication paradigms are becoming important for fulfilling the anticipated rapid expansion of PV manufacturing from the annual PV installation of 99.1 gigawatt (GW) in 2017<sup>[7,8]</sup> to the targeted 1780 GW in 2050.<sup>[9]</sup>

Ambient scalable fabrication techniques, such as blade-coating, which facilitate easy entry into mature industrial processes, were first explored for methylammonium (MA) based organic-inorganic perovskite solar cells.<sup>[10,11]</sup> Based on detailed understanding of the phase transitions from disordered sol-gel to solvated intermediate and final perovskites,<sup>[12–15]</sup> the growth can be well-controlled for a smooth and highly crystalline film with suppressed charge trap concentration. As a result, the PCE of organic-inorganic perovskite solar cells based on ambient blade-coating recently increased to 21.9% for an 8 mm<sup>2</sup> single cell.<sup>[16]</sup> Unfortunately, MA-based perovskite solar cells suffer from poor thermal stability because of the volatile MA<sup>+</sup> cation. Replacing MA<sup>+</sup> with Cs<sup>+</sup> cations (e.g., CsPbI<sub>3</sub>) has allowed for significantly improved thermal stability and a slight increase of the bandgap ( $\approx 1.7$  eV), which together hold promise for efficient tandem solar cells.<sup>[17–22]</sup>


However, from a materials point of view, all-inorganic CsPbI<sub>3</sub> perovskite tends to form a thermodynamically stable  $\delta$ -phase instead of the optically active black phases ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) at operating temperature of solar cells.<sup>[23–26]</sup> Importantly, the phase degradation of active black phases is accelerated in ambient conditions due to its sensitivity to moisture. For these reasons, all high-performance CsPbI<sub>3</sub> solar cells reported to date—without exception—have been fabricated in an inert atmosphere via spin-coating.<sup>[21,23,27]</sup> Recent findings showed that a more stable  $\beta$ -CsPbI<sub>3</sub> than other black phases can be deposited at a low temperature in an inert atmosphere.<sup>[21,23]</sup> However, our previous

X. Chang, J. Fang, Y. Fan, T. Luo, H. Su, Y. Zhang, J. Lu, Prof. S. (F.) Liu, Prof. K. Zhao  
Key Laboratory of Applied Surface and Colloid Chemistry  
Ministry of Education  
Shaanxi Key Laboratory for Advanced Energy Devices  
Shaanxi Engineering Lab for Advanced Energy Technology  
School of Materials Science and Engineering  
Shaanxi Normal University  
Xi'an 710119, China  
E-mail: zhaok@snnu.edu.cn

H. Su, Prof. S. (F.) Liu  
Dalian National Laboratory for Clean Energy  
iChEM  
Dalian Institute of Chemical Physics  
Chinese Academy of Sciences  
Dalian 116023, China  
E-mail: szliu@dicp.ac.cn

Prof. L. Tsetseris  
Department of Physics  
National Technical University of Athens  
Athens GR-15780, Greece

Prof. T. D. Anthopoulos  
King Abdullah University of Science and Technology (KAUST)  
KAUST Solar Center (KSC) and Physical Science  
and Engineering Division (PSE)  
Thuwal 23955–6900, Saudi Arabia  
E-mail: thomas.anthopoulos@kaust.edu.sa

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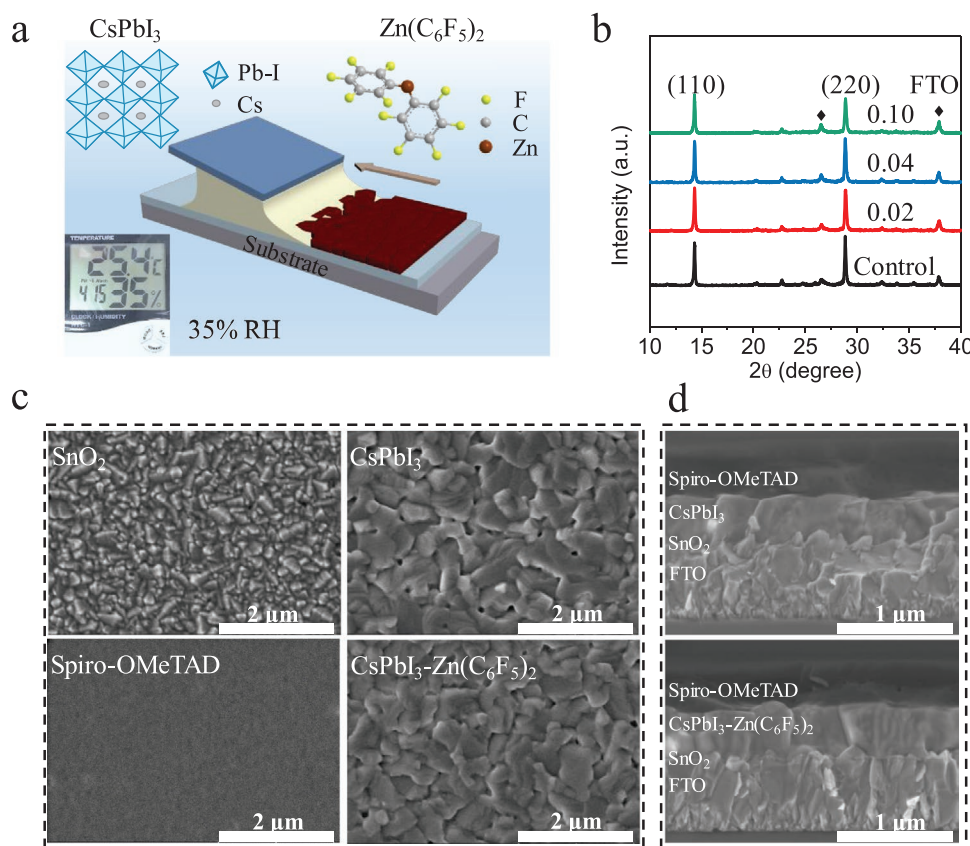
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observation indicated that, in the case of ambient scalable fabrication of all-inorganic perovskite (e.g.,  $\text{CsPbI}_2\text{Br}$ ) solar cells, a slow drying process during low-temperature deposition allows for moisture attack, which suppresses crystallization of the precursors.<sup>[13]</sup> Such unwanted moisture attack to perovskite films can in principle be suppressed during fast ambient crystallization processes such as those used for scalable manufacturing. However, from a thermodynamics point of view, the fast crystallization generally results in poor film formation and high trap concentrations, which in turn decrease both the efficiency and operating stability of solar cells. Therefore, to realize ambient scalable fabrication of high-performance  $\text{CsPbI}_3$  solar cells, it is critically important to reconcile the conflict between fast deposition and film quality including energy misalignment and trap formation.

Here, we report high-performance printable  $\text{CsPbI}_3$  solar cells realized via blade-coating  $\text{SnO}_2$ ,  $\text{CsPbI}_3$ , and spiro-OMeTAD layers at  $\leq 100^\circ\text{C}$  in ambient conditions. Airflow introduced straight after the blade helps to accelerate evaporation of the  $\text{CsPbI}_3$  ink and suppress moisture attack during crystal nucleation and growth. The molecular additive  $\text{Zn}(\text{C}_6\text{F}_5)_2$ <sup>[28]</sup> at a low concentration level of  $0.04 \text{ mmol L}^{-1}$  was introduced into perovskite solution to improve optoelectronic properties of the blade-coated  $\text{CsPbI}_3$  film. The location of  $\text{Zn}(\text{C}_6\text{F}_5)_2$  and

its interaction with perovskite, were investigated using time-of-flight secondary-ion mass spectroscopy (TOF-SIMS), optical absorption spectroscopy, X-ray diffraction (XRD) measurements, and theoretical calculations. The results show that the presence of  $\text{Zn}(\text{C}_6\text{F}_5)_2$  does not influence the crystal structure and crystallite size of  $\text{CsPbI}_3$ , but chemisorbs on perovskite surface, leading to the formation of energy gradients within the perovskite layer and an improved energy band alignment at the perovskite/ $\text{SnO}_2$  interface. Additionally,  $\text{Zn}(\text{C}_6\text{F}_5)_2$  suppresses trap formation within the perovskite film fabricated in ambient air. The combined effects result to printable  $\text{CsPbI}_3$  solar cells with PCE = 19%, which is significantly higher than control pristine cells (16.97%), primarily due to improvements in the open-circuit voltage ( $V_{oc}$ ) and fill factor (FF).

Printable  $\text{CsPbI}_3$  solar cells were realized via blade-coating in ambient air with the relative humidity (RH) at  $\approx 35\%$  (Figure 1a). Films of  $\text{SnO}_2$ ,  $\text{CsPbI}_3$ , and spiro-OMeTAD were blade-coated at  $\leq 100^\circ\text{C}$  substrates and used as the electron transporting layer, photoactive layer, and hole transporting layer, respectively. Landau–Levich flow is created when the blade spreads the precursor solution with a high speed of  $1.5 \text{ m min}^{-1}$ . Airflow was introduced right after the blade to accelerate evaporation of the ink. This enables scalable fabrication of smooth and uniform films of  $\text{SnO}_2$ ,  $\text{CsPbI}_3$ , and spiro-OMeTAD. To tune the



**Figure 1.** Scalable ambient fabrication. a) Schematic of blade-coating for the  $\text{SnO}_2$ ,  $\text{CsPbI}_3$  perovskite, and Spiro-OMeTAD layers. The ambient humidity is  $\approx 35\%$  RH. Room temperature is  $\approx 25^\circ\text{C}$ . The substrate temperature ranges from 25 to  $100^\circ\text{C}$ . The  $\text{Zn}(\text{C}_6\text{F}_5)_2$  is introduced into  $\text{CsPbI}_3$  as an additive. b) XRD patterns of the neat  $\text{CsPbI}_3$  (control) films and the  $\text{CsPbI}_3$  films treated with different concentration ( $\text{mmol L}^{-1}$ ) of  $\text{Zn}(\text{C}_6\text{F}_5)_2$  additive. c) Top-view SEM images of the blade-coated  $\text{SnO}_2$ , Spiro-OMeTAD, neat  $\text{CsPbI}_3$  and  $\text{CsPbI}_3\text{-Zn}(\text{C}_6\text{F}_5)_2$  films. d) Cross-section SEM image of the blade-coated neat  $\text{CsPbI}_3$  and  $\text{CsPbI}_3\text{-Zn}(\text{C}_6\text{F}_5)_2$  films.

**Table 1.** The PV performance statistics of the CsPbI<sub>3</sub> and CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> based PSCs (39 devices).

Sample		$V_{oc}$ [V]	$J_{sc}$ [mA cm <sup>-2</sup> ]	$FF$ [%]	PCE [%]
CsPbI <sub>3</sub>	average	1.05 ± 0.02	19.29 ± 0.54	77.39 ± 2.00	15.74 ± 0.66
	max	1.07	19.87	79.63	16.97
CsPbI <sub>3</sub> -Zn(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>	average	1.10 ± 0.02	20.21 ± 0.42	80.94 ± 0.65	18.00 ± 0.47
	max	1.12	20.67	81.98	19.00

optoelectronic properties of the CsPbI<sub>3</sub> film, a low concentration of fluoride-containing Lewis acid material Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> was introduced as an additive. It has recently been shown that addition of minute amount of Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> in organic semiconducting blends plays a dual role, first acting as a p-dopant, and second as a microstructure modifier due to its ability to control the crystallization dynamics of the small-molecule component present in the blend.<sup>[28]</sup>

We first evaluated the crystal structure of the CsPbI<sub>3</sub> films due to its critical effect on optoelectronic properties. For this purpose the blade-coated CsPbI<sub>3</sub> films were treated with thermal annealing in ambient conditions at 180°C for 20 min. The XRD analysis shows two main diffraction peaks at  $2\theta = 14.2^\circ$  and  $28.6^\circ$ , which can be indexed to the (110) and (220) reflections of the  $\beta$ -CsPbI<sub>3</sub> (P4/mbm) phase (Figure 1b). These are consistent with recent reports<sup>[23,29]</sup> and indicates a preferred orientation in the (110) direction (Figure S1, Supporting Information). We note that the often-observed diffraction peaks at  $9.9^\circ$ ,  $13.2^\circ$ , and  $22.8^\circ$  assigned to the orthorhombic (Pnma) yellow  $\delta$ -phase<sup>[30]</sup> are completely absent suggesting the phase pure  $\beta$ -CsPbI<sub>3</sub> films. On the other hand, the Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>-containing CsPbI<sub>3</sub> films, hereafter abbreviated as CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, exhibit almost identical diffraction pattern with the control (i.e., pristine CsPbI<sub>3</sub>) layer. Increasing Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> concentration from 0 to 0.02, 0.04, and 0.10 mmol L<sup>-1</sup> does not lead to noticeable variations in the peak position and crystal orientation. This indicates that the Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> treatment does not alter the CsPbI<sub>3</sub> crystal structure. The full width at half maxima values of the diffraction peak (220) for all CsPbI<sub>3</sub> films show a negligible variation in the range of  $\approx 0.15$ – $0.18^\circ$ , indicating almost identical crystal size irrespective of the additive treatment. In short, we demonstrated  $\beta$ -CsPbI<sub>3</sub> film growth via an ambient scalable deposition method. Addition of low concentrations of Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> does not affect the CsPbI<sub>3</sub> crystal structure and size.

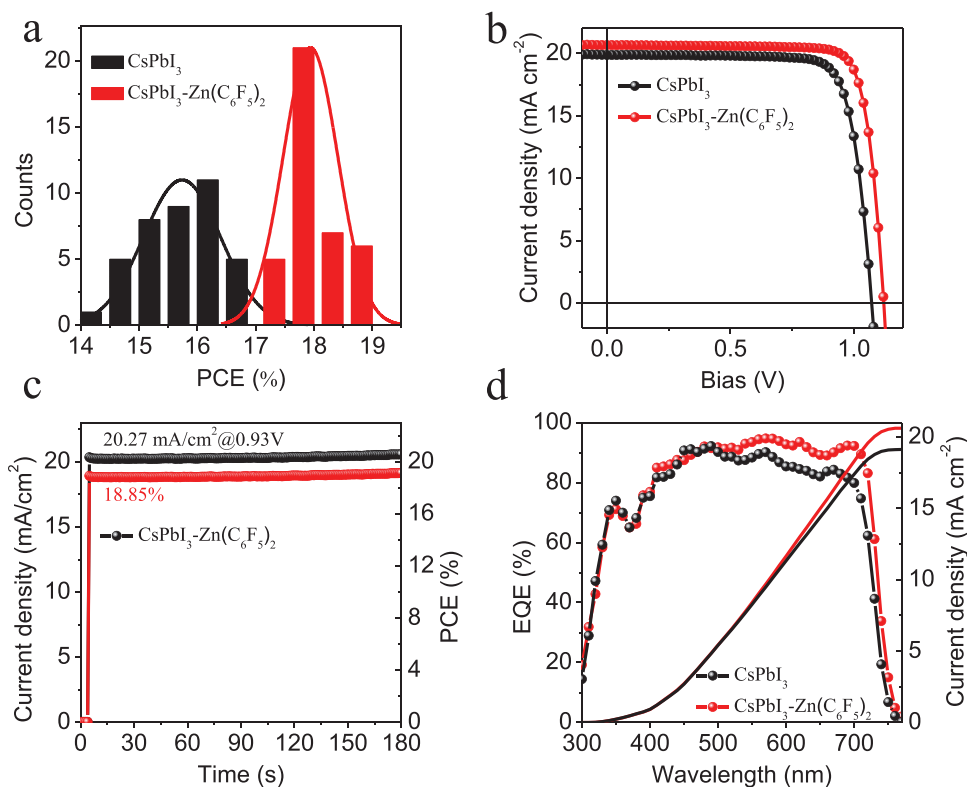
Next, we investigated the morphology of blade-coated layers of SnO<sub>2</sub>, CsPbI<sub>3</sub>, and Spiro-OMeTAD. Scanning electron microscopy (SEM) analysis reveals a compact surface for the SnO<sub>2</sub> layer with 20- to 300-nm-sized grains (Figure 1c). The Spiro-OMeTAD film is uniform without noticeable blemishes or pinholes. High uniformity with densely packed submicron-sized grains was observed for both the control CsPbI<sub>3</sub> and the CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> films. Addition of Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> did not change the grain size and uniformity of the CsPbI<sub>3</sub> film, in agreement with the XRD results. Figure 1d shows the cross-sectional SEM images of a complete device based on SnO<sub>2</sub>, CsPbI<sub>3</sub>, and spiro-OMeTAD layers. The layer thickness of SnO<sub>2</sub>, CsPbI<sub>3</sub>, and spiro-OMeTAD are  $\approx 30$ , 400–450, and  $\approx 700$  nm, respectively. The CsPbI<sub>3</sub> grains appear well connected in both pristine CsPbI<sub>3</sub> and CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> films, without noticeable difference on grain packing. Again, these observations indicate that

incorporation of Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> is unable to change the morphology of CsPbI<sub>3</sub> films via ambient blade-coating.

Printable solar cells were constructed with the planar device configuration of FTO/SnO<sub>2</sub>/Perovskite/Spiro-OMeTAD/Au. The active cell area is 0.09 cm<sup>2</sup> and the device was measured under ambient conditions (humidity of  $\approx 40\%$  RH, room temperature of 25°C). The average PCE (PCE<sub>ave</sub>) for the control CsPbI<sub>3</sub> cell is 15.74(±0.66)% (Table 1 and Figure 2a). The PCE<sub>ave</sub> values increase to a peak of 18.00(±0.47)% for devices treated with 0.04 mmol L<sup>-1</sup> Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>. Increasing the additive concentration further leads to a decline in cell efficiency (Figure S2, Supporting Information). The PCE histogram for optimized CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> cells exhibits a narrow PCE distribution suggesting improved reproducibility (Figure 2a), which is particularly important for scalable manufacturing. The significantly enhanced PCE<sub>ave</sub> for CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> solar cells in contrast to the control is ascribed to the sharp increases in  $V_{oc}$  and  $FF$ , along with a slight improvement in short-circuit current ( $J_{sc}$ ). For example, the  $V_{oc}$  increases prominently from 1.05(±0.02) to 1.10(±0.02) V, along with an increase in the  $FF$  from 77.39(±2.00)% to 80.94(±1.15)%. However, a slight increase from 19.29(±0.54) to 20.21(±0.42) mA cm<sup>-2</sup> is observed in  $J_{sc}$ . We achieved the highest PCE of 19.00% for the optimized CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> devices, with a  $V_{oc}$  of 1.12 V, a  $J_{sc}$  of 20.67 mA cm<sup>-2</sup>, and a  $FF$  of 81.98% (Table 1 and Figure 2b). This is on par with the best performance metrics reported to date for CsPbI<sub>3</sub>-based solar cells fabricated under inert atmosphere via spin-coating.<sup>[13]</sup> This excellent photovoltaic performance highlights the tremendous potential of Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> as a functional additive for printable solar cells.

We further conducted operational stability measurements under AM 1.5G one-sun illumination conditions in air (at 25°C, and  $\approx 40\%$  RH) (Figure 2c). A stabilized 18.85% output of a champion CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> cell was obtained within 3 min continuous illumination. Figure S3, Supporting Information shows PCE evolution of the devices without encapsulation in air condition (dark environment, 20% RH, 25°C), which degrade only by  $\approx 2\%$  after 700 h. The external quantum efficiency (EQE) shows higher intensity in the range of 500–730 nm for the CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> as compared to the control cell, hinting to the possibility of higher charge extraction efficiency. The integrated current from the EQE spectra is 20.61 mA cm<sup>-2</sup> for the CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> cell, which is within the 5% deviation from the measured  $J_{sc}$ . The integrated current is slightly higher to that calculated for the control cell (19.16 mA cm<sup>-2</sup>) (Figure 2d), in agreement with the higher  $J_{sc}$  measured from the  $J$ - $V$  characteristics under simulated illumination.

In order to understand why the addition of a small amount of Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> improves the  $V_{oc}$  and  $FF$ , we carried out a range of complementary characterization measurements. TOF-SIMS



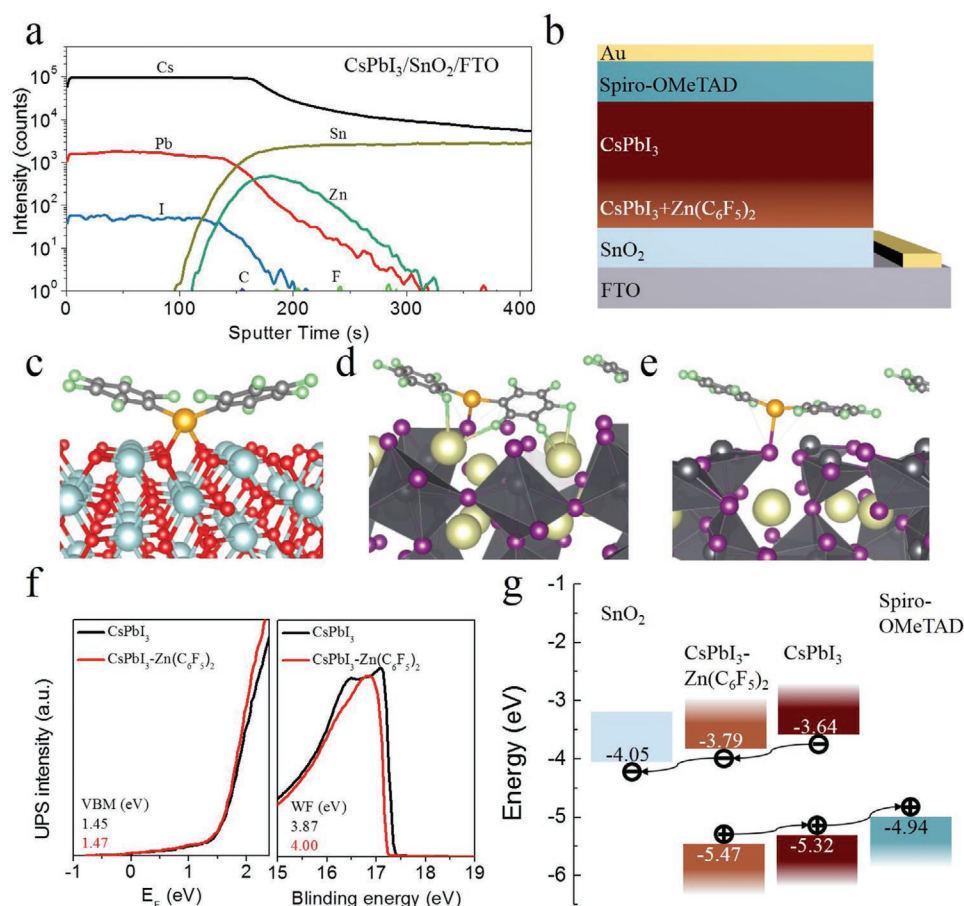
**Figure 2.** Photovoltaic performance. a) Efficiency histogram of the control CsPbI<sub>3</sub> and the CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> films based solar cells (effective cell area of 0.09 cm<sup>2</sup>, 39 devices). b) J–V curves of the champion cell for the control CsPbI<sub>3</sub> and the CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> based solar cells. c) Stabilized output curves of the champion CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>-based solar cells. d) The EQE for the control CsPbI<sub>3</sub> and the CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>-based solar cells.

was first performed to probe the depth profiles of the atomic species throughout the CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> film on the SnO<sub>2</sub>/FTO substrate (Figure 3a). Signals signifying the presence of Zn, C, and F associated with Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> are not observed in the bulk of the CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> layers, but do appear close to the perovskite/SnO<sub>2</sub> interface, where a rapid increase in their intensities is clearly observed along declining signals for Cs, Pb, and I. The 3D reconstructed images of the elemental distribution are displayed in Figure S4, Supporting Information, which highlights the preferential accumulation of Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> molecules at the bottom of the perovskite layer. X-ray photoelectron spectroscopy analysis on the surface of the pristine CsPbI<sub>3</sub> and the CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> films indicates a similar elemental distribution, suggesting an absence of Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> on the perovskite surface (Figure S5, Supporting Information). It can thus be deduced from these measurements that the Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> additive prefers to accumulate close to the perovskite/SnO<sub>2</sub> interface, as illustrated in Figure 3b.

We then probe the role of the Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> at the perovskite/SnO<sub>2</sub> interface. We first introduced a low concentration of Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> into PbI<sub>2</sub> solution and found a blue-shift of the absorption (Figure S6a, Supporting Information), which suggests an interaction between the Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> and the PbI<sub>2</sub>. Further evidences were found that the PbI<sub>2</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> film is optically more transparent than pristine PbI<sub>2</sub> layers of the same thickness. The PbI<sub>2</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> film exhibits significantly lower absorption intensity and crystallinity than the pristine PbI<sub>2</sub> film (Figure S6b–d, Supporting Information). Atomic-scale details

of the interactions between the Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> and the constituent parts of the perovskite/SnO<sub>2</sub> interface were further investigated using density functional theory (DFT) calculations. The findings indicate that a Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> molecule interacts, indeed, strongly, with both the (001) surface of SnO<sub>2</sub> and the (001) surface of  $\beta$ -CsPbI<sub>3</sub> (either I-terminated, or Pb-terminated) (Figure 3c–e). For example, the Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> molecule binds strongly to the surface of SnO<sub>2</sub> by forming two Zn–O bonds with a binding energy of 3.41 eV (Figure 3c). The electronic densities of states show a negligible influence of this chemisorption on electronic properties of the SnO<sub>2</sub> surface. A Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> molecule also chemisorbs strongly on  $\beta$ -CsPbI<sub>3</sub> through Zn–I bonds, with binding energies of 3.35 eV and 3.84 eV for the Pb-terminated and I-terminated CsPbI<sub>3</sub> surfaces (Figure 3d,e), respectively. Furthermore, strong F–Cs interaction was found between the Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> and CsPbI<sub>3</sub>, as confirmed by the relatively short Cs–F distances of 3.10–3.20 Å. These results indicate a strong chemisorption of the Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> on perovskite and SnO<sub>2</sub> surface.

To gain insight into the role of the strong chemisorption of the Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> on electronic properties of CsPbI<sub>3</sub>, we performed ultraviolet photoelectron spectroscopy (UPS) on blade-coated films to evaluate the energetic alignment (Figure 3f and Figure S7, Supporting Information). For this purpose we increased the Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> concentration to 0.40 mmol L<sup>-1</sup> and decreased the layer thickness to <50 nm in order to ensure that the concentration of Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> on the film's interface



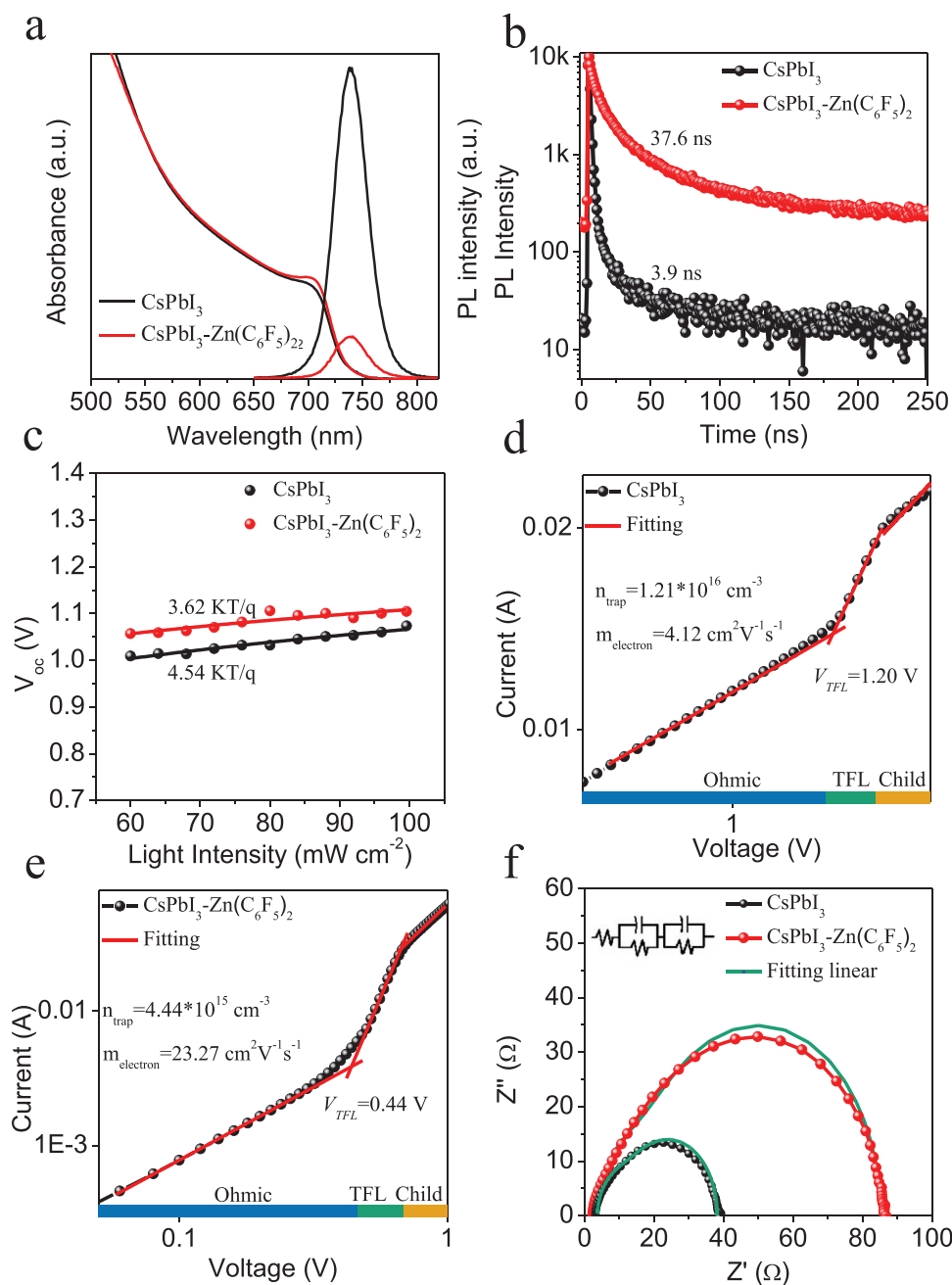
**Figure 3.** Location of  $\text{Zn}(\text{C}_6\text{F}_5)_2$  and energetic band alignment. a) The characterization of TOF-SIMS for  $\text{CsPbI}_3\text{-Zn}(\text{C}_6\text{F}_5)_2$  perovskite sample. b) A scheme showing a preferential accumulation of  $\text{Zn}(\text{C}_6\text{F}_5)_2$  at the  $\text{CsPbI}_3/\text{SnO}_2$  interface. c) A  $\text{Zn}(\text{C}_6\text{F}_5)_2$  molecule chemisorbed on the (001) surface of  $\text{SnO}_2$ . d) An I-terminated (001) surface of  $\text{CsPbI}_3$ . e) A Pb-terminated (001) surface of  $\text{CsPbI}_3$  (Sn: light blue, O: red, Cs: light yellow, Pb: dark gray, I: purple, C: gray, F: green, Zn: orange spheres). f) UPS spectra of the  $\text{CsPbI}_3$  and  $\text{CsPbI}_3\text{-Zn}(\text{C}_6\text{F}_5)_2$  films. g) The energy diagrams of a complete solar cell showing the formation of an energy gradient within  $\text{CsPbI}_3\text{-Zn}(\text{C}_6\text{F}_5)_2$  films and a better energetic alignment at the  $\text{CsPbI}_3/\text{SnO}_2$  interface.

is detectable. Indeed, we observed decreases from  $-3.64$  to  $-3.79$  eV for the conduction band minimum (CBM) and from  $-5.32$  to  $-5.47$  eV for the valence band maximum, respectively, for the  $\text{CsPbI}_3$  film with additive treatment. These results indicate that for  $\text{CsPbI}_3\text{-Zn}(\text{C}_6\text{F}_5)_2$  films in which the  $\text{Zn}(\text{C}_6\text{F}_5)_2$  molecules accumulate close to the perovskite/ $\text{SnO}_2$  interface, an energy gradient exists (Figure 3g). This leads to the formation of a built-in band alignment within the perovskite film, which is beneficial for internal charge separation and charge transfer between the top  $\text{CsPbI}_3$  layer and the bottom  $\text{CsPbI}_3\text{-Zn}(\text{C}_6\text{F}_5)_2$  layer. Furthermore, the presence of  $\text{Zn}(\text{C}_6\text{F}_5)_2$  improves the energetic alignment of the CBM by 150 meV at the perovskite/ $\text{SnO}_2$  interface. In summary, the existence of an energy gradient within the perovskite film and advantageous energetic alignment at the perovskite/ $\text{SnO}_2$  interface account for the increased  $V_{\text{oc}}$ .

Though perovskite vacancies are believed to be shallow electronic traps,<sup>[31]</sup> they can form deep traps particularly in layers grown in ambient conditions due to the absorption of water and oxygen at vacancy sites. To ascertain whether the chemisorption influences the formation of vacancies, we studied the trap passivation and charge extraction as both relate to

$V_{\text{oc}}$  and FF of the solar cell. We observe a negligible effect of  $\text{Zn}(\text{C}_6\text{F}_5)_2$  on the absorption intensity and the absorbance edge of the  $\text{CsPbI}_3$  films (Figure 4a), which remains at  $\approx 1.69$  eV ( $\approx 734$  nm) (Figure S8, Supporting Information). Surprisingly, addition of  $\text{Zn}(\text{C}_6\text{F}_5)_2$  leads to a sevenfold decrease in the photoluminescence (PL) intensity of the  $\text{CsPbI}_3\text{-Zn}(\text{C}_6\text{F}_5)_2$  layer deposited on  $\text{SnO}_2$ . This suggests a much improved charge transfer at the  $\text{CsPbI}_3\text{-Zn}(\text{C}_6\text{F}_5)_2/\text{SnO}_2$  interface, which agrees well with the improved energetic alignment at the interface (Figure 3d). Time-resolved PL (TRPL) reveals an important difference in the charge carrier lifetime of the perovskite films (Figure 4b). The lifetime extracted for a  $\text{CsPbI}_3\text{-Zn}(\text{C}_6\text{F}_5)_2$  film deposited on glass exhibits is much higher ( $\tau_{\text{ave}} = 37.6$  ns) than that measured for the control pristine layer ( $\tau_{\text{ave}} = 3.9$  ns). This significantly increased charge carrier lifetime indicates trap passivation induced by the presence of  $\text{Zn}(\text{C}_6\text{F}_5)_2$  in the  $\text{CsPbI}_3$  film.

Further evidence for  $\text{Zn}(\text{C}_6\text{F}_5)_2$ -mediated trap passivation were obtained by analyzing the dependence of  $V_{\text{oc}}$  on the light intensity (Figure 4c). The  $V_{\text{oc}}$  varies linearly with the light intensity for both the control and  $\text{CsPbI}_3\text{-Zn}(\text{C}_6\text{F}_5)_2$  cells. The trap-assisted recombination can be well reflected by the



**Figure 4.** Photophysical properties of CsPbI<sub>3</sub> films. a) Comparison of UV-vis and PL spectra for CsPbI<sub>3</sub> and CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> films. b) TRPL of perovskite films. c) Open-circuit voltage versus light intensity of CsPbI<sub>3</sub>- and CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>-based cells. d) Dark I-V measurement of the electron-only device for CsPbI<sub>3</sub> films. e) Dark I-V measurement of the electron-only device for CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> films. f) Electrical impedance spectroscopy (EIS) of cells based on the CsPbI<sub>3</sub> and CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> films.

deviation between the slope and the value of ( $kT/q$ ) ( $k$  is the Boltzmann constant,  $T$  is temperature, and  $q$  is the electric charge). We observed a decrease from 4.54, for the control CsPbI<sub>3</sub>, to 3.62  $kT/q$  for the CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> cell, suggesting a less pronounced trap-assisted recombination in good agreement with our TRPL data (Figure 4b). Since  $V_{oc}$  and FF are related to nonradiative recombination involving traps, the additive-mediated trap passivation should account for the improved  $V_{oc}$  and FF in a complete solar cell.

In light of the proposed energetic alignment mechanism, we further explored its effect on the charge carrier mobility. Dark I-V characteristics were measured for electron-only devices comprised of glass/FTO/SnO<sub>2</sub>/perovskite/PCBM/Ag (Figure 4d,e). The electron mobility can then be determined using the Mott-Gurney Law.<sup>[32]</sup>

$$\mu = \frac{8J_D L^3}{9\epsilon_0 \epsilon_r V^2} \quad (1)$$

where,  $\epsilon_0$  is the vacuum permittivity,  $\epsilon_r$  the relative dielectric constant,  $J_D$  the current density,  $L$  the distance between the electrodes (layer thickness), and  $V$  the applied voltage. The trap density, on the other hand, can be determined from the dark  $I$ - $V$  characteristics using space-charge-limited current model.<sup>[33]</sup>

$$n_{\text{trap}} = \frac{2\epsilon_0\epsilon_r V_{\text{TFL}}}{eL^2} \quad (2)$$

where,  $V_{\text{TFL}}$  is the onset voltage of the trap-filled limit region, and  $e$  is the elementary charge. The electron mobilities were estimated to be 16.26 ( $\pm 4.63$ ) and 3.71 ( $\pm 0.58$ )  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  for the  $\text{CsPbI}_3$ - $\text{Zn}(\text{C}_6\text{F}_5)_2$  and the control  $\text{CsPbI}_3$  films, respectively. The trap densities determined are  $4.72 (\pm 0.68) \times 10^{15}$  and  $1.25 (\pm 0.71) \times 10^{16} \text{cm}^{-3}$  for the  $\text{CsPbI}_3$ - $\text{Zn}(\text{C}_6\text{F}_5)_2$  and the control  $\text{CsPbI}_3$  films, respectively. The remarkably improved electron mobility and decreased trap density agree with UPS and TRPL findings, and indicate that addition of  $\text{Zn}(\text{C}_6\text{F}_5)_2$  improves the energetic alignment while suppressing the formation of unwanted vacancies.

Interestingly, we also observed an improvement of the recombination resistance at the perovskite/ $\text{SnO}_2$  interface upon  $\text{Zn}(\text{C}_6\text{F}_5)_2$  addition. Electrical impedance spectroscopy was performed to investigate the values of the recombination resistance ( $R_{\text{rec}}$ ) complete cells comprised of glass/FTO/ $\text{SnO}_2$ /perovskite/spiro-OMeTAD/Au (Figure 4f). Evidently, the  $R_{\text{rec}}$  values increase significantly from 9.44 to 66.38  $\Omega$  upon  $\text{Zn}(\text{C}_6\text{F}_5)_2$  addition, suggesting reduced charge recombination at the perovskite/ $\text{SnO}_2$  interface. The result is consistent with observations of more efficient electron extraction and the passivation effect (Figure 4a,b).

We reported the development of the first high-performance, printable  $\text{CsPbI}_3$  solar cells via ambient blade-coating technique. High quality  $\text{CsPbI}_3$  films were realized via a combination of air-flow-assisted drying and the addition of the organic Lewis acid  $\text{Zn}(\text{C}_6\text{F}_5)_2$ . Extensive material and device analysis reveal that the  $\text{Zn}(\text{C}_6\text{F}_5)_2$  accumulates close to the perovskite/ $\text{SnO}_2$  interface. The strong chemisorption of the  $\text{Zn}(\text{C}_6\text{F}_5)_2$  at the  $\text{CsPbI}_3$  surface leads to the formation of built-in potential, a 150-meV improvement of the energetic alignment at the perovskite/ $\text{SnO}_2$  interface, and suppressed trap formation within perovskite layer. The work highlights the use of functional additives as an effective strategy to reconcile the issues arising from the conflict between fast deposition and film quality, including energy misalignment and trap formation, all particular relevant for ambient scalable manufacturing of perovskite solar cells.

## Experimental Section

See experimental details in the Supporting Information.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Author Contributions

K.Z. designed the project and supervised the work. X.C. performed most of the experiments. J.F. and H.S. helped with the device fabrication. Y.F. helped with the SEM analysis. J.L. helped acquire the TRPL data. T.D.A. and L.T. assisted with the DFT calculation. T.L. and Y.Z. contributed to useful discussions. All authors contributed to the writing and improvement of the manuscript.

## Keywords

$\text{CsPbI}_3$  perovskite solar cells, energy alignment, passivation, printable devices

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## Supporting Information

### Printable CsPbI<sub>3</sub> Perovskite Solar Cells with PCE of 19% via an Additive Strategy

Xiaoming Chang,<sup>1</sup> Junjie Fang,<sup>1</sup> Yuanyuan Fan,<sup>1</sup> Tao Luo,<sup>1</sup> Hang Su,<sup>1,2</sup> Yalan Zhang,<sup>1</sup> Jing Lu,<sup>1</sup> Leonidas Tsetseris,<sup>3</sup> Thomas D. Anthopoulos,<sup>4,\*</sup> Shengzhong (Frank) Liu,<sup>1,2,\*</sup> Kui Zhao<sup>1,\*</sup>

X. Chang, J. Fang, Y. Fan, T. Luo, H. Su, Y. Zhang, J. Lu, Prof. K. Zhao

<sup>1</sup>Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education; Shaanxi Key Laboratory for Advanced Energy Devices; Shaanxi Engineering Lab for Advanced Energy Technology, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710119, China.

E-mail: [zhaok@snnu.edu.cn](mailto:zhaok@snnu.edu.cn)

H. Su, Prof. S. (F). Liu

<sup>2</sup>Dalian National Laboratory for Clean Energy; iChEM, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China.

Email: [szliu@dicp.ac.cn](mailto:szliu@dicp.ac.cn)

Prof. L. Tsetseris

<sup>3</sup>Department of Physics, National Technical University of Athens, Athens GR-15780, Greece.

Prof. T. D. Anthopoulos

<sup>4</sup>King Abdullah University of Science and Technology (KAUST), KAUST Solar Center (KSC) and Physical Science and Engineering Division (PSE), Thuwal 23955-6900, Saudi Arabia.

E-mail: [thomas.anthopoulos@kaust.edu.sa](mailto:thomas.anthopoulos@kaust.edu.sa)

## Experimental Section

*Material preparation:* The SnO<sub>2</sub> precursor (Tin (IV) oxide, 15% in H<sub>2</sub>O colloidal dispersion) was purchased from Alfa Aesar. *N,N*-dimethylformamide (DMF, 99.8%). Dimethyl sulfoxide (DMSO, 99.9%) was purchased from Sigma-Aldrich. Bis(pentafluorophenyl)zinc (Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, 99.7%) was purchased from J&K Scientific Ltd. Cesium iodide (CsI, 99.9%) and HPbI<sub>3</sub> was purchased from p-OLED.

*Solution preparation:* CsPbI<sub>3</sub> precursor solution: HPbI<sub>3</sub> (0.44 g) and CsI (0.18 g) were dissolved in 1 mL (DMF: DMSO = 4:1) and stirred at 25°C in N<sub>2</sub>-filled glove box for 12 h. Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> was dissolved in DMF and stirred at 25°C in N<sub>2</sub>-filled glove box for 20 min. The Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> solution was added into the CsPbI<sub>3</sub> precursor solution with concentration of 0.02, 0.04, 0.10 mmol L<sup>-1</sup> immediately. The Spiro-OMeTAD solution was consisted of 80 mg Spiro-OMeTAD, 22 µL lithium bis(trifluoromethanesulfonyl) imide solution (520 mg in 1 mL acetonitrile) and 30 µL 4-tert-butylpyridine and 1 mL chlorobenzene. The concentration of SnO<sub>2</sub> solution was decreased by 8-fold prior to usage.

*Device Fabrication:* The FTO glass (2.9 cm × 2.9 cm) was cleaned using acetone, isopropanol and ethanol and then dried in a N<sub>2</sub> flow before treated by O<sub>3</sub> plasma for 18 min. The key layers of SnO<sub>2</sub>, CsPbI<sub>3</sub>, and Spiro-OMeTAD were blade-coated at 100°C, 85 °C and 40 °C substrates at a speed of 1.5 m min<sup>-1</sup> in ambient conditions. To suppress moisture attack to the CsPbI<sub>3</sub> crystallization, air-flow was introduced after the blade to accelerate drying and crystallization of perovskite ink. The layers of SnO<sub>2</sub> and CsPbI<sub>3</sub> were then treated with thermal annealing at 150°C for 30 min and at 180°C for 20 min respectively.

The device fabrication for the CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> PSCs is the same with that for the CsPbI<sub>3</sub> PSCs. Finally, 70 nm of gold electrodes on the top of the cell were prepared by thermal evaporation.

### **Film characterizations**

*X-ray diffraction (XRD):* The crystal structures of perovskite films were characterized using XRD on a Rigaku Smart Lab (X-ray Source: Cu K $\alpha$ ,  $\lambda$  = 1.54 Å).

*Scanning electronic morphology (SEM):* The surface morphologies of SnO<sub>2</sub>, perovskite and Spiro-OMeTAD films were characterized by SEM (FE-SEM; SU-8020, Hitachi).

*UV-Vis absorption:* Absorption spectra were measured on a PerkinElmer UV-Lambda 950 instrument.

*Time-of-flight secondary-ion mass spectroscopy (TOF-SIMS):* TOF-SIMS with in situ ion sputtering was used to investigate CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> perovskite samples by Ion TOF Gmhb5.

*Photoluminescence (PL):* Steady-state photoluminescence (PL) (excitation at 510 nm, front-side excitation) and time-resolved photoluminescence (TRPL) (excitation at 510 nm, front-side excitation) were measured with a PicoQuant FT-300.

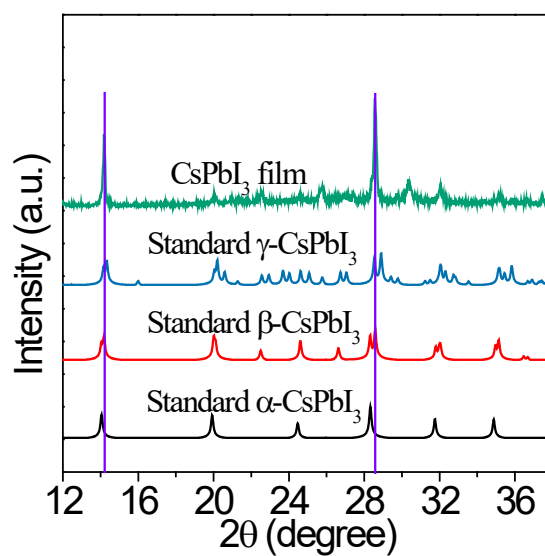
*Ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS):* UPS and XPS results were acquired on a photoelectron spectrometer (ESCALAB 250Xi, Thermo Fisher Scientific).

*Impedance spectroscopic measurements (EIS):* EIS were carried out on an electrochemical workstation (IM6ex, Zahner, Germany) with the frequency range from 10 Hz to 4 MHz at open-circuit voltage in the dark conditions.

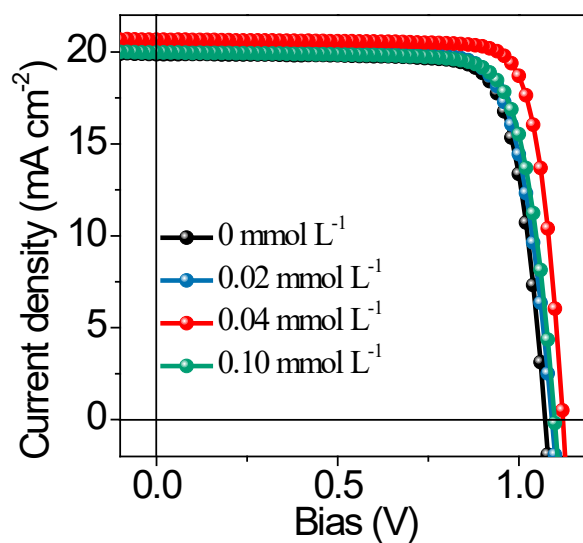
*Density Functional Theory (DFT):* DFT calculations were performed with the Perdew-Wang (PW) generalized-gradient approximation (GGA) exchange-correlation (xc) functional,<sup>[1]</sup> and projector-augmented waves,<sup>[2]</sup> as implemented in the code Quantum Espresso.<sup>[3]</sup> Van der Waals interactions were included with the so-called DFT-D2 scheme.<sup>[4]</sup> The energy cutoff for the plane wave basis was set at 100 Rydberg and large supercell slabs were used to simulate the surfaces of SnO<sub>2</sub> and  $\beta$ -CsPbI<sub>3</sub> with or without adsorbed molecules. Structures were rendered with the software VESTA.<sup>[5]</sup> Due to the large size of the employed supercells, it was not possible to apply post-DFT corrections (e.g. through so-called hybrid xc-functionals) to remedy the well-known underestimation of the energy band gap problem by standard xc-functionals such as the PW-GGA one.

*Device characterizations:* The J-V performance of the perovskite solar cells was analyzed using a Keithley 2400 SourceMeter under ambient conditions at room temperature, and the illumination intensity was 100 mW cm<sup>-2</sup> (AM 1.5G Oriel solar simulator). The scan range was 3.0 V – -0.1 V, and the bias step was 0.02 V. The power output of the lamp was calibrated using an NREL-traceable KG5-filtered silicon reference cell. The EQE was characterized on a QTest Station 2000ADI system (Crowntech Inc., USA), and the light source was a 300 W xenon lamp. The monochromatic light intensity for the EQE

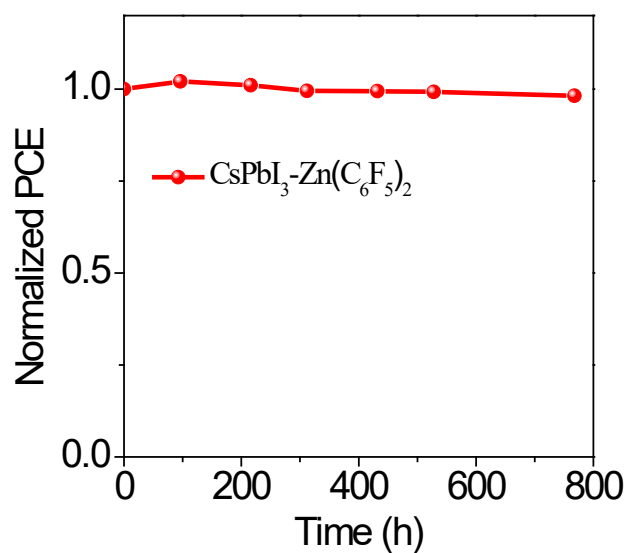
measurement was calibrated with a reference silicon photodiode. The dark J-V characteristics of the electron-only devices were measured by a Keithley 2400 SourceMeter.



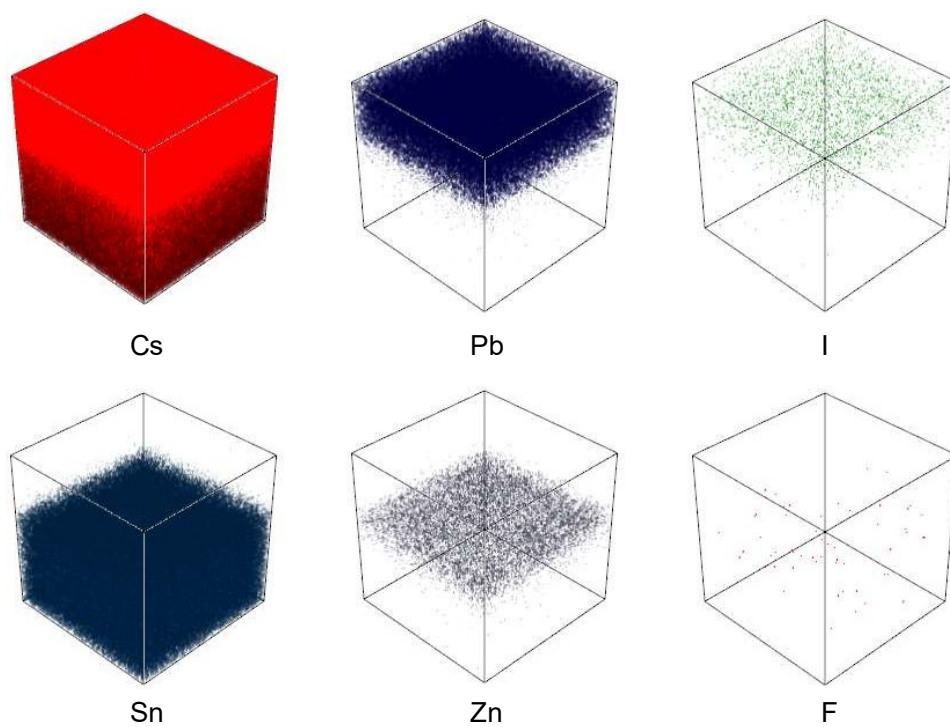
**Figure S1.** Comparison of XRD patterns of blade-coated CsPbI<sub>3</sub> films on ITO substrate with standard XRD patterns (Marronnier et al (2018)) of  $\alpha$ -CsPbI<sub>3</sub>,  $\beta$ -CsPbI<sub>3</sub> and  $\gamma$ -CsPbI<sub>3</sub>.



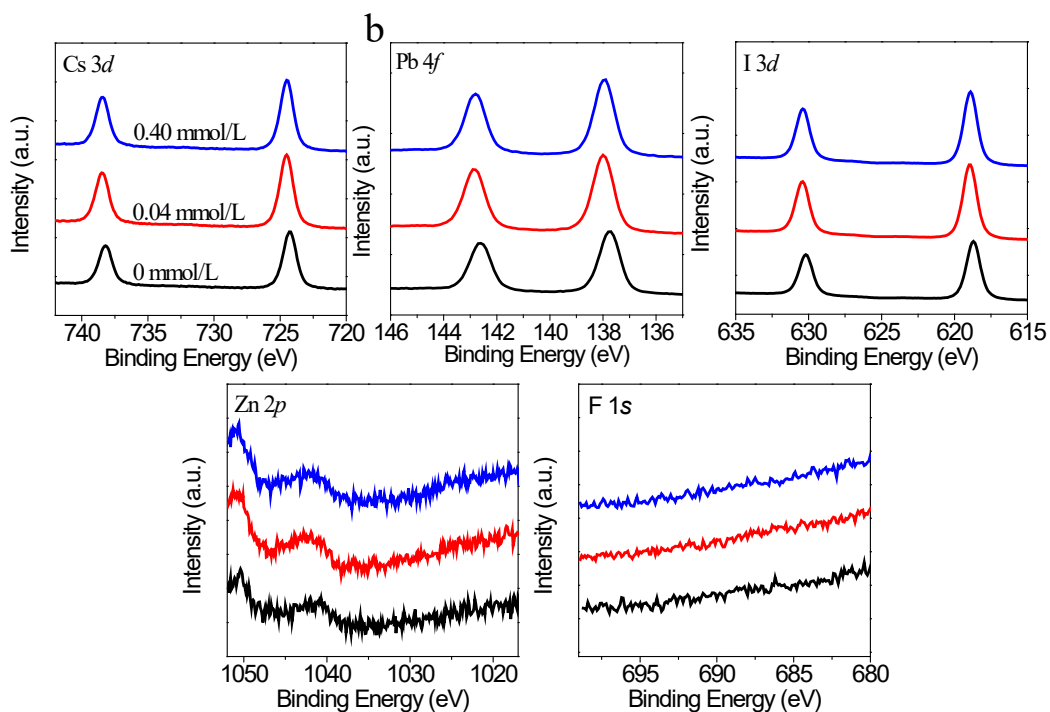
**Figure S2.**  $J$ - $V$  curves of the champion  $\text{CsPbI}_3$  perovskite solar cells with various  $\text{Zn}(\text{C}_6\text{F}_5)_2$  concentrations.



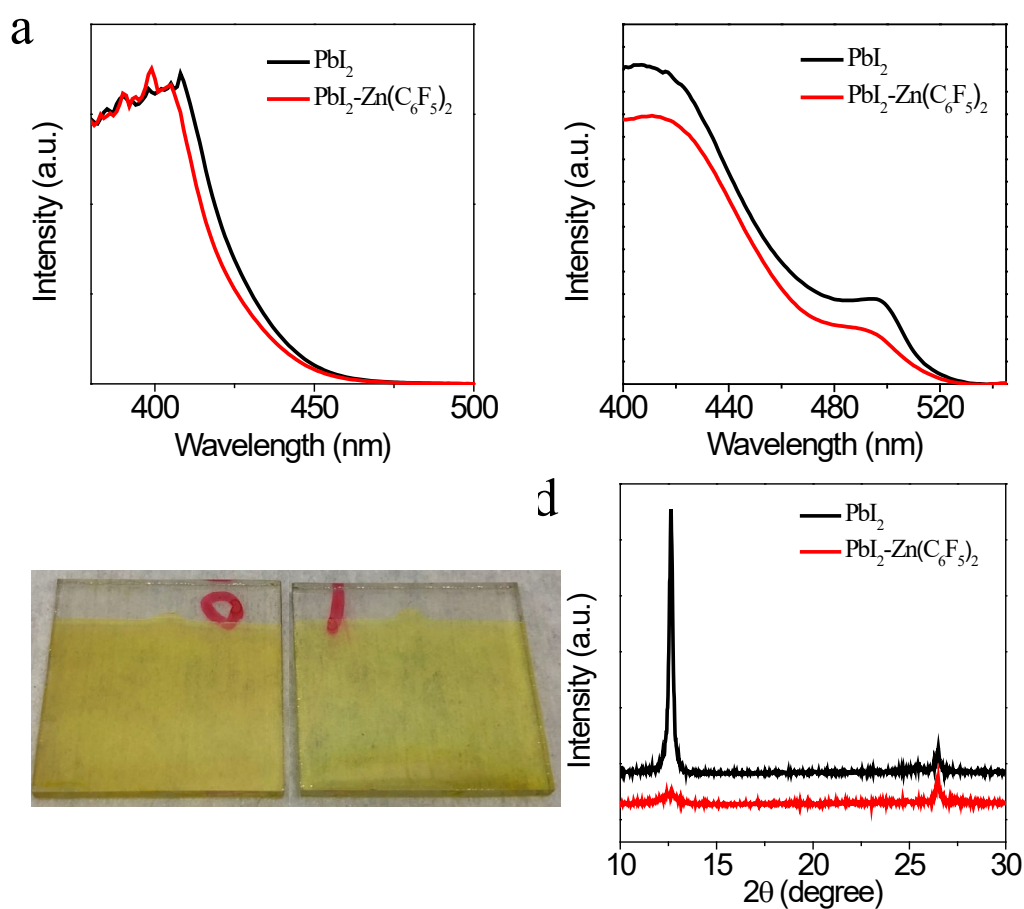
**Figure S3.** The stability of the non-encapsulated  $\text{CsPbI}_3$ - $\text{Zn}(\text{C}_6\text{F}_5)_2$  solar cells exposed to the ambient environment at 20% RH in the dark at room temperature.



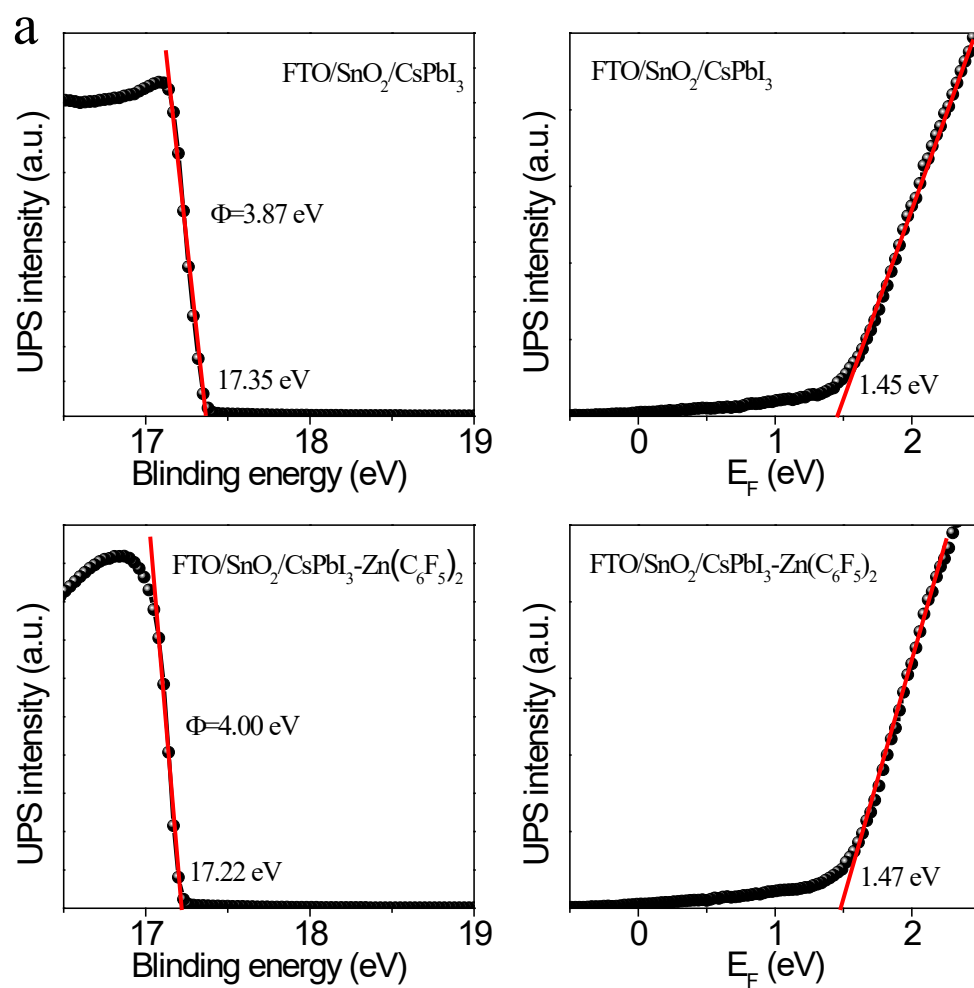
**Figure S4.** 3D reconstructed images of (a) Cs, (b) Pb, (c) I, (d) Sn, (e) Zn and (f) F in  $\text{CsPbI}_3\text{-Zn}(\text{C}_6\text{F}_5)_2$  perovskite film as obtained from the TOF-SIMS analysis.



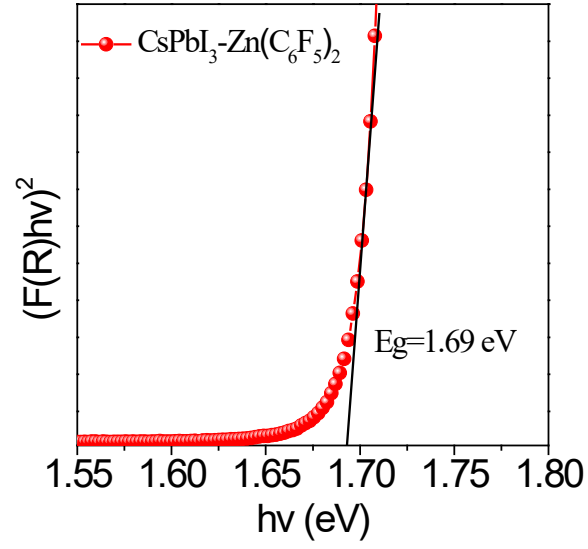
**Figure S5.** (a) Cs 3d, (b) Pb 4f, (c) I 3d, (d) Zn 2p and (e) F 1s core-level spectra for the CsPbI<sub>3</sub> perovskite films with Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> concentrations of 0, 0.04, and 0.40 mmol L<sup>-1</sup>.



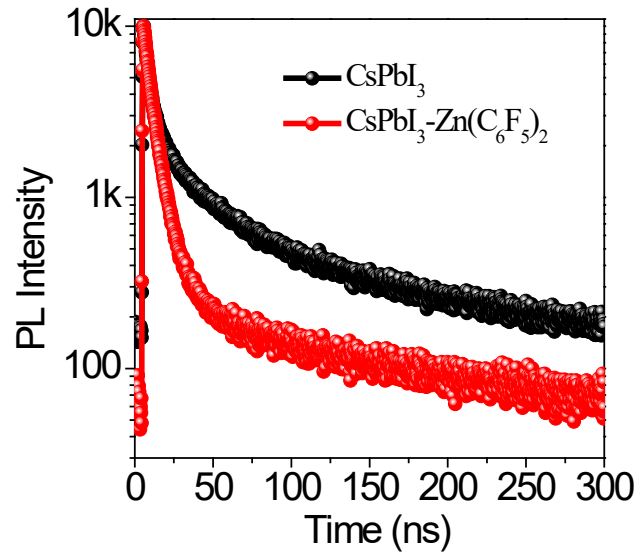
**Figure S6.** (a) Comparison of UV-Vis spectra for  $\text{PbI}_2$  and  $\text{PbI}_2\text{-Zn}(\text{C}_6\text{F}_5)_2$  solutions (DMF). (b) Comparison of UV-Vis spectra for  $\text{PbI}_2$  and  $\text{PbI}_2\text{-Zn}(\text{C}_6\text{F}_5)_2$  films. (c) Images of  $\text{PbI}_2$  and  $\text{PbI}_2\text{-Zn}(\text{C}_6\text{F}_5)_2$  films. (d) Comparison of XRD for  $\text{PbI}_2$  and  $\text{PbI}_2\text{-Zn}(\text{C}_6\text{F}_5)_2$  films.



**Figure S7.** UPS spectra (He-I with photon energy of 21.22 eV) of the CsPbI<sub>3</sub> and CsPbI<sub>3</sub>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> perovskite films deposited on FTO/SnO<sub>2</sub>.



**Figure S8.** Tauc plot of  $\text{CsPbI}_3\text{-Zn}(\text{C}_6\text{F}_5)_2$  assuming a direct band gap.



**Figure S9.** Time-resolved photoluminescence (TRPL) of perovskite layer deposited on  $\text{SnO}_2$ .

**Table S1.** The TRPL statistics of perovskite layer deposited on glass.

Sample	$\tau_1$ (ns)	$\tau_2$ (ns)	$\tau_{ave.1}$ (ns)	$\tau_{ave.2}$ (ns)
CsPbI <sub>3</sub>	14.3	1.1	3.9	1.4
CsPbI <sub>3</sub> -Zn(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>	58.41	8.1	37.6	16.3

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