

## Supporting Information

### **Critical role of metal ions on surface engineering toward brightly luminescent and stable cesium lead bromide perovskite quantum dots**

Congyang Zhang<sup>a</sup>, Bo Wang<sup>a</sup>, Qun Wan<sup>a</sup>, Long Kong<sup>a</sup>, Weilin Zheng<sup>a</sup>, Zhichun Li<sup>a</sup>, Liang Li<sup>a,c,\*</sup>

*<sup>a</sup>School of Environmental Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China.*

*<sup>b</sup>Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, P.R. China*

## **Experimental section**

### **Materials**

Cesium carbonate ( $\text{Cs}_2\text{CO}_3$ , 98%), lead bromide ( $\text{PbBr}_2$ , 98%), 1-octadecene (ODE, 90%), oleic acid (OA, 90%), oleylamine (OAm, 90%), dimethylammonium bromide (DDAB, 98%), methyl acetate (98%),  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (99.99%), zinc acetate dihydrate ( $\text{Zn}(\text{Ac})_2\cdot 2\text{H}_2\text{O}$ , 99.995% metals basis), tetramethylammonium hydroxide (TMAH, 97%) are purchased from Aladdin. Indium acetate ( $\text{In}(\text{Ac})_3$ , 99.99%) are purchased from Alfa Aesar. Perfluoro-3,6,9-trioxatridecanoic acid (98%) is purchased from Fluorochem. All the chemicals were used without further purification.

### **Synthesis of $\text{CsPbBr}_3$ QDs**

Firstly, the cesium oleate (CsOA) precursor (0.5 M) was prepared based on previous report. Then, 20 mL ODE, 5 mL of OAm, 5 mL of OA, and 2 mmol  $\text{PbBr}_2$  were loaded into a 100 mL three-neck flask, degassed at 120 °C for 30 min. Then, the temperature was raised to 180 °C under argon atmosphere until  $\text{PbBr}_2$  salt had completely dissolved. 1 mL of CsOA precursor was injected. After 5 s, the reaction was immediately quenched by an ice-water bath. The crude solution was purified through precipitation by methyl acetate, centrifugation, and then dispersion in 20 mL toluene.

### **Metal ions-assistant ligand surface engineering for $\text{CsPbBr}_3$ QDs**

10 mL of as-synthesized  $\text{CsPbBr}_3$  QDs/toluene solution was loaded into a bottle. 1 mL of  $\text{S}^{2-}$ -DDA<sup>+</sup> ligand solution (preparation method can be found in the previous report) was added into the PQD solution for ligand exchange 60 min with magnetic stirring. Then 60 mg of  $\text{In}(\text{Ac})_3$  powder was added and stirred for 1 h at 60 °C. After the reaction, the final mixture solution was centrifugation at 10000 rpm for 3 minutes to remove the residue metal salt. Then methyl acetate was added to precipitate and separate products from the above solution via centrifugation. The precipitates were collected and dispersed in 10 mL toluene as the  $\text{CsPbBr}_3$ -Ex-In QDs sample for further characterization. For the  $\text{CsPbBr}_3$ -Ex QDs sample, the  $\text{CsPbBr}_3$  QDs with ligand exchange were purified similar to the above process and also dispersed in 10 mL toluene. For the device application, the obtained PQDs precipitates were dispersed in 2 mL hexane.

### **Device Fabrication**

PEDOT: PSS (Baytron P VP Al 4083) was spin-coated onto the cleaned ITO-coated glass at 4000

rpm for 30 s and baked at 140 °C for 20 min, and then transferred into glovebox. Poly-TPD (Xi'An p-OLED Co.)/chlorobenzene solution (10 mg/mL) was spin-coated at 4000 rpm for 30 s and then annealing at 110 °C for 30 min. As the emitting layer, the CsPbBr<sub>3</sub> QD in hexane solution was spin-coated at 1500 rpm for 30 s. Finally, TPBi, LiF, and Al were deposited by thermal evaporation.

The electron-only and hole-only devices adopt the configuration of ITO/ZnO/PQD/ZnO (HFE 7100)/Al and ITO/PEDOT/Poly-TPD/PQD/MoO<sub>3</sub>/Al respectively. The ZnO or ZnO (HFE 7100) layer in electron-only devices was prepared by spin-coating the ZnO or ZnO (HFE 7100) NC solution at 2000 rpm for 30 s and then baked at 100 °C for 10 min. The ZnO or ZnO (HFE 7100) NC solution were prepared from our previous work.<sup>4</sup> The MoO<sub>3</sub> layer (10 nm) in hole-only devices was deposited through thermal evaporation under high vacuum.

### **Characterization and device measurements**

The transmission electron microscopy (TEM) images were obtained from the FEI Talos F200X TEM instruments. The XRD characterization was conducted by a Shimadzu XRD-6100 diffractometer with Cu K<sub>α</sub> radiation. UV-vis spectra were recorded by a T-6 UV-visible spectrophotometer. PL spectra were taken by an F-380 fluorescence spectrometer (Tianjin Gangdong Sci. & Tech. Development Co., Ltd., China). The PL lifetimes were measured by a PTI QM/TM/IM time-resolved fluorescence spectrofluorometer. The absolute PLQY values were obtained by a fluorescence spectrometer with an integrated sphere executed at the 450 nm LED light source. For the photostability measurement of PQD solution, all the samples were adjusted to the same optical density (Abs = 1.5, 450 nm) in the quartz cuvettes (sealed) and illuminated with the 450 nm LED light (175 mW/cm<sup>2</sup>) under ambient atmosphere. The PL emission spectra were recorded at every periodic interval. The chemical compositions of PQDs surface were determined by the XPS (Kratos Axis Ultra<sup>DLD</sup>, all the binding energies were calibrated with the C 1 s peak at 284.8 eV). The electroluminescence spectra were measured using an Ocean Optics USB 2000 spectrometer. The luminance-current-voltage (L-I-V) characteristics were measured simultaneously with a Keithley 2400 source and Konica Minolta LS-160 luminance meter in air and at room temperature.

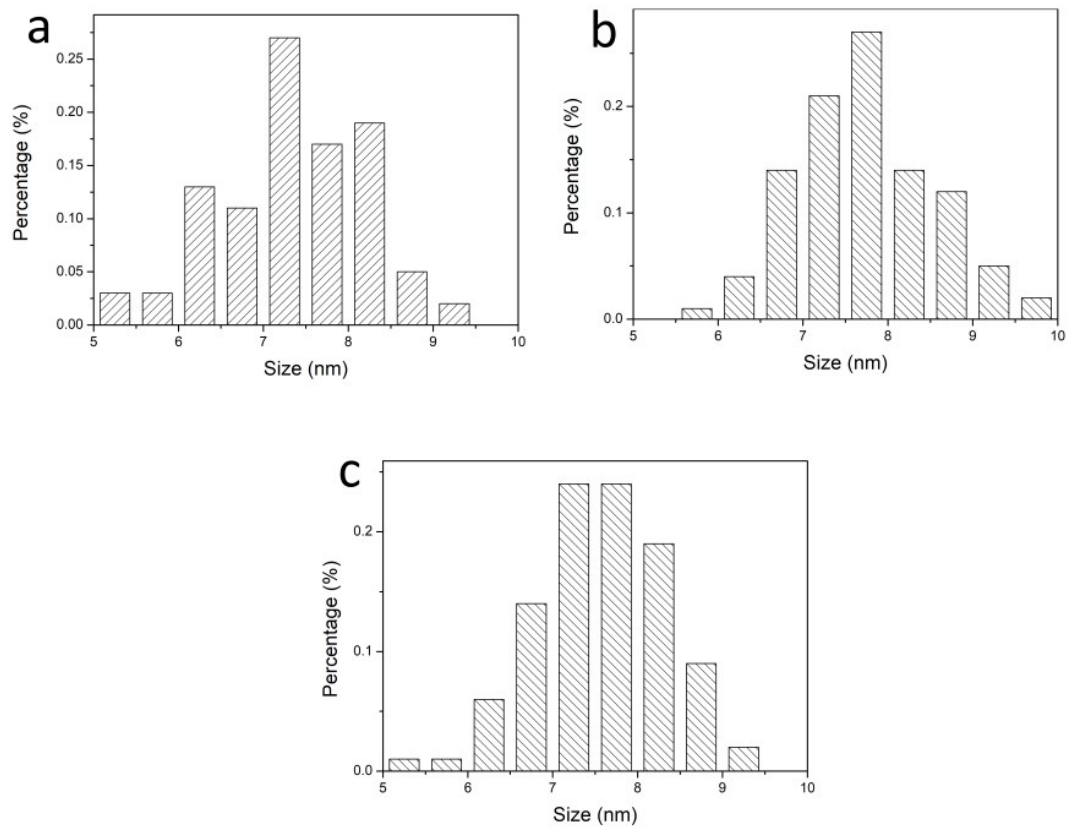


Figure S1 Size distribution histograms of the CsPbBr<sub>3</sub>, CsPbBr<sub>3</sub>-Ex, and CsPbBr<sub>3</sub>-Ex-In QDs.

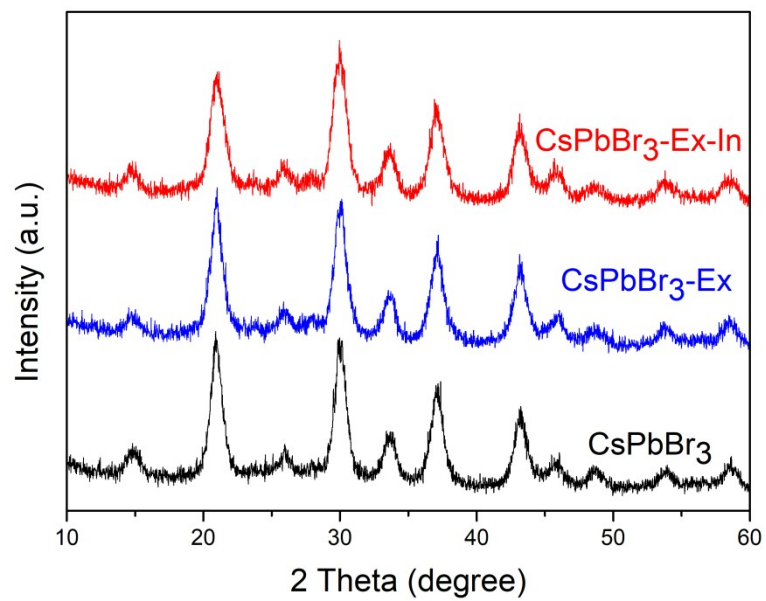


Figure S2 XRD pattern of the CsPbBr<sub>3</sub>, CsPbBr<sub>3</sub>-Ex, and CsPbBr<sub>3</sub>-Ex-In QDs samples.

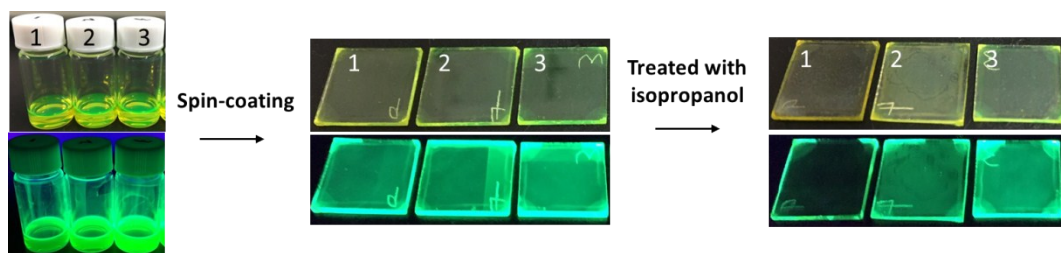


Figure S3 Stability test of PQD films (1: CsPbBr<sub>3</sub>, 2: CsPbBr<sub>3</sub>-Ex, 3: CsPbBr<sub>3</sub>-Ex-In) against a polar solvent of isopropanol.

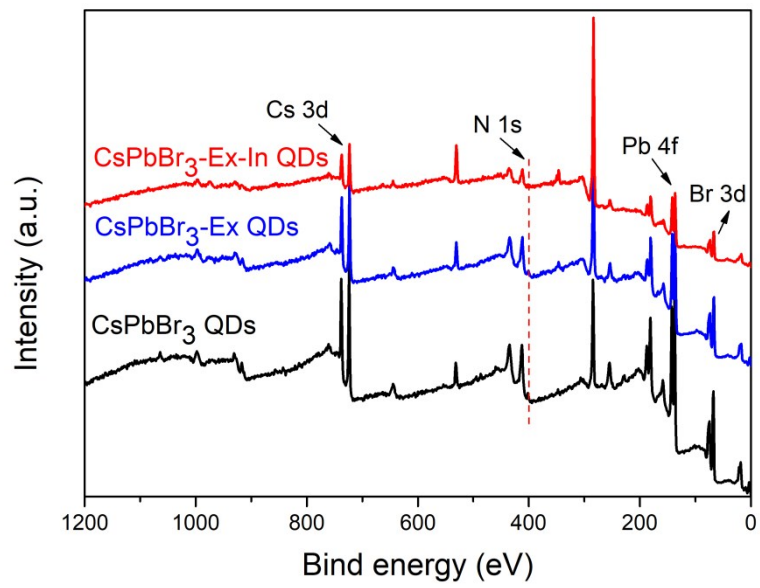


Figure S4 XPS spectrum of the CsPbBr<sub>3</sub>, CsPbBr<sub>3</sub>-Ex, and CsPbBr<sub>3</sub>-Ex-In QDs

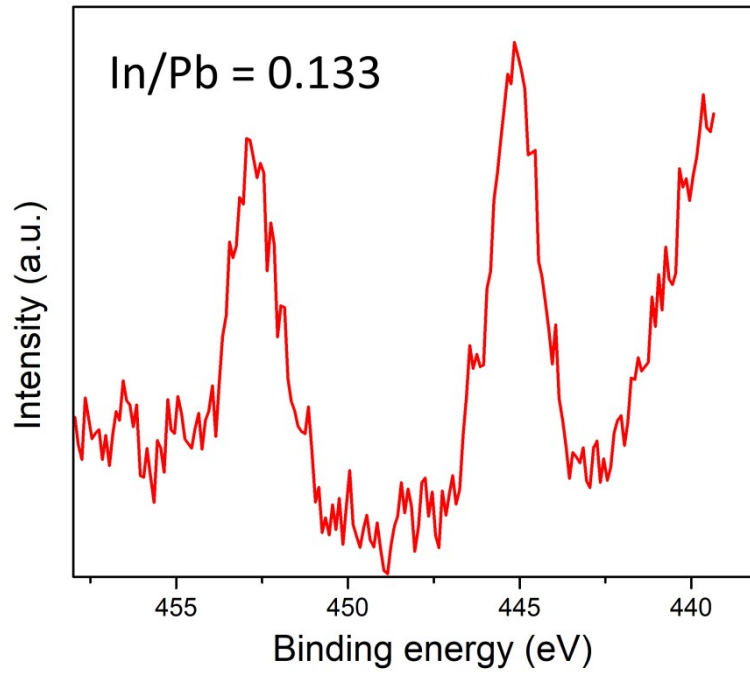


Figure S5 High resolution In 3d XPS spectrum of the CsPbBr<sub>3</sub>-Ex-In QDs



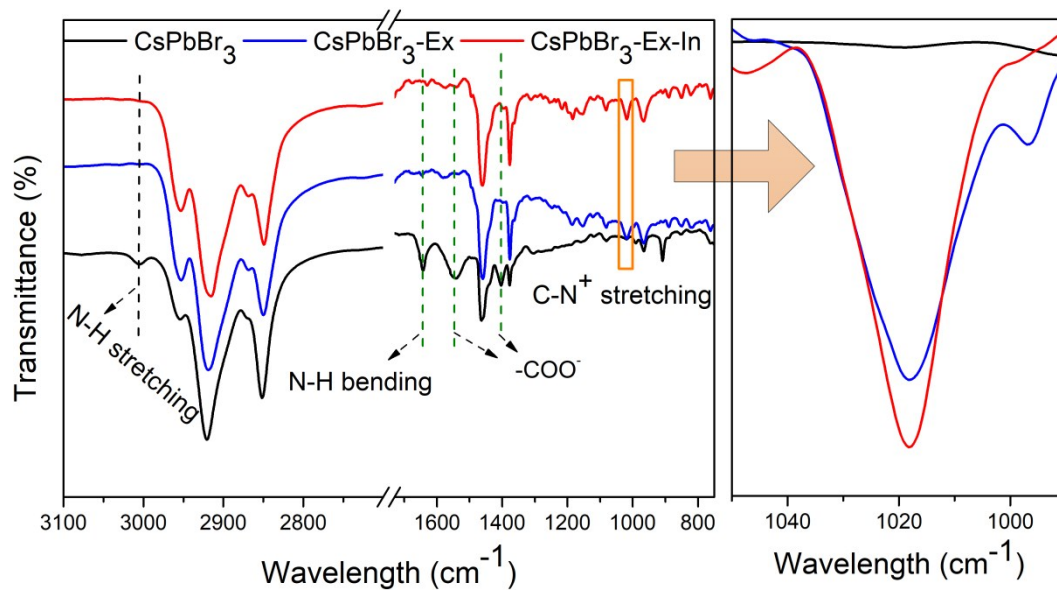


Figure S6 FTIR spectrum of the CsPbBr<sub>3</sub>, CsPbBr<sub>3</sub>-Ex, and CsPbBr<sub>3</sub>-Ex-In QDs.

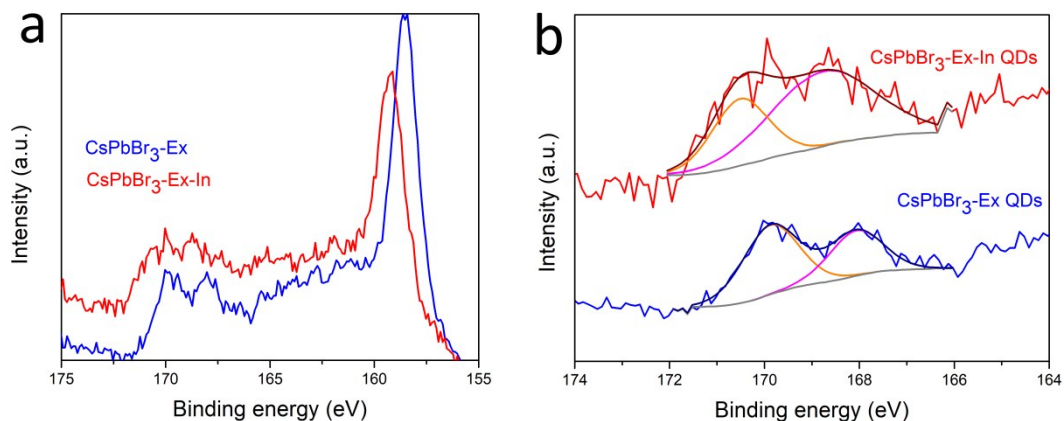


Figure S7 High resolution S2p XPS spectrum of the CsPbBr<sub>3</sub>-Ex and CsPbBr<sub>3</sub>-Ex-In QDs.

**Note:** From this result, the S 2p XPS spectra mainly contain two parts. The spectra peaks at about 158 eV may originate from the sulfur of the DDA<sup>+</sup>-S<sup>2-</sup> ligand. The weak peaks at higher energy (166-170 eV) should be ascribed to the higher valence state sulfur, such as oxidation of sulfur SO<sub>3</sub><sup>2-</sup> or SO<sub>4</sub><sup>2-</sup>, which could be slow oxidized in ambient atmosphere.<sup>1</sup> Obviously, after In(Ac)<sub>3</sub> treatment, the main spectrum peak of the CsPbBr<sub>3</sub>-Ex-In QDs shift to larger binding energy. Despite, due to the possible spectra overlap of S 2p and Cs 4p<sub>3/2</sub>,<sup>2,3</sup> it seems difficult to distinguish the sulfur signal from the main spectra peaks. Therefore, we further compare the weak peaks at higher energy, which also show slight shift toward higher binding energy. All the above results have demonstrated the interaction of metal ions with sulfur on PQD surface.

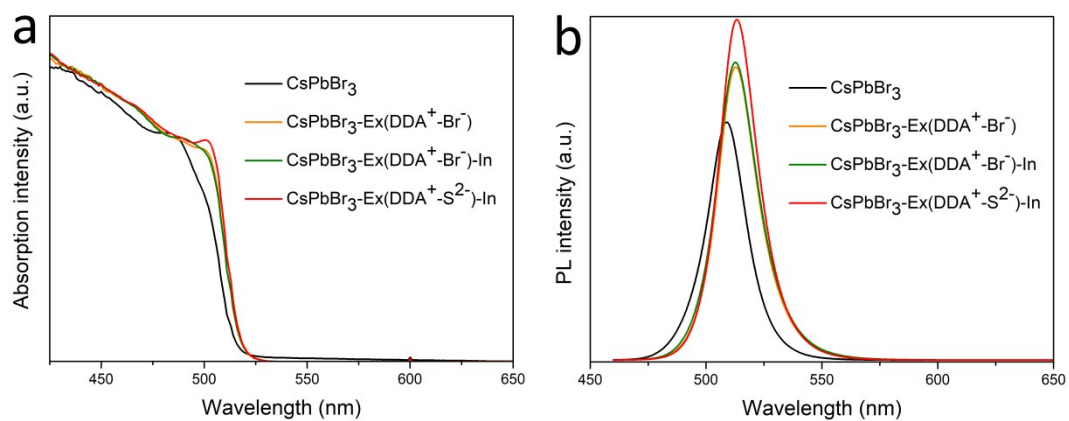


Figure S8 UV-vis absorption and PL spectra spectrum of the CsPbBr<sub>3</sub>, CsPbBr<sub>3</sub>-Ex (DDA<sup>+</sup>-Br<sup>-</sup>), and CsPbBr<sub>3</sub>-Ex(DDA<sup>+</sup>-Br<sup>-</sup>)-In, and CsPbBr<sub>3</sub>-Ex(DDA<sup>+</sup>-S<sup>2-</sup>)-In QDs samples.

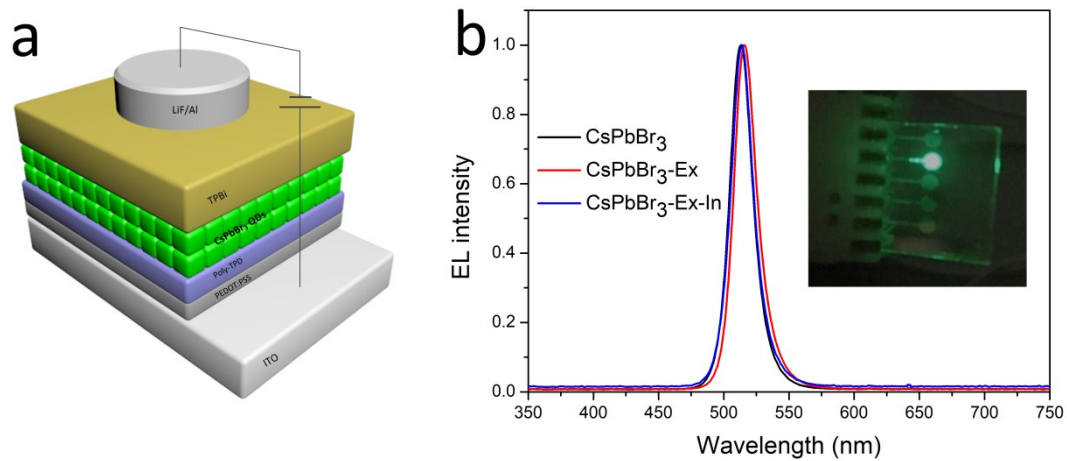


Figure S9 (a) Schematic of the device structure and (b) EL spectra of the Pe-QLED based on CsPbBr<sub>3</sub>, CsPbBr<sub>3</sub>-Ex, and CsPbBr<sub>3</sub>-Ex-In QDs. The inset is the photograph of an operating Pe-QLED with CsPbBr<sub>3</sub>-Ex-In QDs.

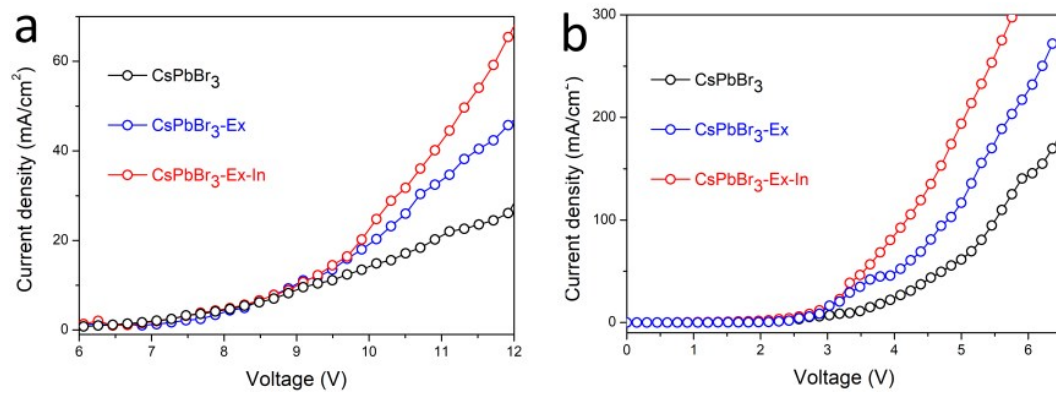


Figure S10 Current density-voltage characteristics of electro-only and hole-only devices with configuration of ITO/ZnO/PQD/ZnO (HFE 7100)/Al and ITO/PEDOT/Poly-TPD/PQD/MoO<sub>3</sub>/Al respectively.

## References

- 1 Z. Li, W. Yao, L. Kong, Y. Zhao and L. Li, *J. Am. Chem. Soc.*, 2015, **137**, 12430-12433.
- 2 H. Sun, Z. Li, L. Kong, B. Wang, C. Zhang, Q. Yuan, S. Huang, Y. Liu and L. Li, *Chem. Commun.*, 2018, **54**, 9345-9348.
- 3 M. V. Elizarov, O. V. Lozkina, D. I. Yeletz, A. V. Emeline , V. K. Ryabchuk and A. A. Murashkina, *Journal of Physics: Conference Series*, 2018, **993**, 1-5
- 4 C. Zhang, B. Wang, W. Zheng, S. Huang, L. Kong, Z. Li, G. He, L. Li, *Nano Energy* 2018, **51**, 358-365.