Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information: Designing Efficient Ligands Exchange for Stable Perovskite Quantum Dots Synthesis

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Perovskite Nanocrystals· Light-emitting Diodes· In-situ Ligand Exchange· High Stability· Strong Ligands

Method

Materials. Cesium carbonate (Cs_2CO_3, Sigma-Aldrich 99.995%), oleylamine (OAm, Aladdin 90%), lead (II) bromide ($PbBr_2$ Aladdin 99.999%), 1-octadecene (ODE, Sigma-Aldrich 90%), Bis(2-ethylhexyl) phosphate (DEHPA, TCI 97%), didodecylamine (DDDAM, TCI 97%), hydrogen bromide (HBr, alfa), hexane (Aladdin 99%), methyl acetate (MeOAc, Aladdin anhydrous 99.5%), oleic acid (OA, Sigma-Aldrich 90%), ethyl acetate (Aladdin anhydrous 99.5%), 3-(N,N-dimethyloctadecylammonio)propanesulfonate (ASC18, Aladdin, 99.8%, abbreviation C_3-S), octane (Aladdin 99%), mesitylene (Aladdin 99%), chlorobenzene (CB, Mackin, 99.8%), polymethylmethacrylate (PMMA, Sigma-Aldrich), (1,3,5-Benzinetriyl)-tris(1-phenyl-1H-benzimidazole) (TPBi), 2,4,6-tris(3-(diphenylphosphoryl)phenyl)-1,3,5-triazine (PO-T2T, 99.5%), Lithium fluoride (LiF) are from Xi’an Polymer Light Technology. The perovskite nanocrystals synthesis method is modified from the method previous reported by our group[1]. Details are described as following:

Preparations of Cs-oleate precursor. 0.75 mmol of Cs_2CO_3, and 9 mL ODE with 1 mL OA were placed together in a 50 mL three-necked round bottom flask. The mixture solution was heated to 40 °C and vacuum dried for 30 minutes. Then, the temperature was increased to 100 °C, and continued vacuum drying for 1 hour. Then argon was pumped into the flask and continued degassing for 30 minutes. After completely removing H_2O and O_2. The clear Cs-Oleate solution was obtained.

Synthesis of C_3-S-HBr. In a 50 mL three-necked flask, 172 mg C_3-S with 4 mL mesitylene was degassed using argon flow for 30 min at room temperature. 100 μL of HBr was injected and the temperature was elevated to 130 °C in the argon atmosphere. The reaction between C_3-S and HBr was continued for 1 hour and formed a transparent rufous solution. The temperature of the C_3-S-HBr solution was kept at 130 °C before use.

Synthesis of OA/OAm or DEHPA $CsPbBr_3$ nanocrystals. In a 50 mL three-necked flask, 138 mg $PbBr_2$ with 10 mL ODE was vacuum dried at 40 °C for 30 minutes. Then, the temperature was increased to 100 °C, and continued vacuum drying for 1 hour. The argon flow was pumped into the flask and kept the lead halide precursor in the argon atmosphere. 1 mL OA and 1 mL OAm (or 0.9 ml DEHPA with 1 mL OAm) were injected into the mixtures to dissolve the $PbBr_2$. After the $PbBr_2$ was completely dissolved and formed a clear solution, the temperature was increased to 160 °C. 0.8 mL Cs-oleate precursor solution was quickly injected into the flask at 160 °C. After 5 seconds, the flask was swiftly cooled by an ice water bath. The nanocrystals were first purified using methyl acetate. Ethyl acetate was used for the second purification.

Synthesis of C_3-S-HBr $CsPbBr_3$ nanocrystals. All the synthesis procedures until Cs-oleate injection are the same. After injection of Cs-oleate, 2 mL C_3-S-HBr was injected for ligand exchange immediately. Then, 0.3 mmol DDAm dissolved in toluene was injected for further ligand exchange. The flask was swiftly cooled by an ice water bath. The nanocrystals were first purified using methyl acetate. Ethyl acetate was used for the second purification.

Device Fabrications: The device fabrication process is modified from our previous report[2]. The ITO pattern glass substrate was cleaned with acetone, isopropanol, and ethanol in turn. Each time, it was ultrasonic for 15 minutes. After cleaning, it was treated with ultraviolet ozone for 15 minutes to adjust the ITO work function. An aqueous solution of PEDOT: PSS was spin-coated on ITO glass substrate at 2000 rpm for 40 s, and then annealed at 150 °C for 30 minutes; Then, it was transferred to the glove box with nitrogen, 8 mg/mL PTAA chlorobenzene solution was spin-coated onto the PEDOT: PSS layer and bake for 15 min at 120 °C. 15 mg/mL perovskite nanocrystal octane solution was spin-coated at 2000 rpm for 30 s, and then annealed at 80 °C for 10 min. 5 nm TPBi, 35 nm PO-T2T, 1 nm LiF and 100 nm Al electrodes were evaporated under $2*10^{-4}$ Pa pressure.

UV-Vis UV-vis absorption spectra were obtained by Perkin-Elmer Lambda 950.TEM and HRTEM of nanocrystals were obtained by a Talos F200X with 200 kV acceleration voltage. Photoluminescence spectra profiles were obtained by Horiba FL3-111 with an excitation source at 400 nm. Photoluminescence quantum yield was obtained by Otsuka QE2100. Time-resolved PL decay spectra of nanocrystals were obtained by Horiba FL3-111. The XRD spectra of nanocrystal film were obtained by a Bruker D8 Advanced Davinci using Cu Kα radiation ($\lambda = 1.5418$ Å). FTIR spectra were collected using a Cary660+620 attenuated total reflectance FTIR system. All nanocrystal solid film samples were cast on glass substrates. XPS measurements were performed using an ESCALAB 250Xi with a base pressure of $\sim10^{-9}$ torr. The X-ray radiation is Al Kα emission (1486.7 eV, take-off angle, 75°).

Device characterization. The electroluminescence performance of devices was measured with the same setup reported before. Electroluminescence spectra were obtained using an Ocean Optics USB 2000+ spectrometer with the devices driven at a constant current with a Keithley 2400 source meter. The J-L-V characteristics of the devices were taken under ambient conditions with a Keithley 2400 source meter measuring the sweeping voltages and currents and a Keithley 6485 Picoammeter together with a calibrated silicon detector (Edmund) measuring light intensities. Luminance was calibrated using a photometer (Spectra Scan PR655) with the assumption of the Lambertian emission pattern of all devices. The operational lifetime test was conducted under ambient conditions at room temperature (22±2℃) using a commercialized lifetime test system (Guangzhou Jinghe Equipment Co., Ltd). The devices were encapsulated with Nagase UV epoxy resin XNR5516Z(C)-SA1 and capping glasses. The Lifetime of PeLEDs was measured through a commercialized lifetime test system (Guangzhou Jinghe Equipment Co., Ltd) under ambient conditions.

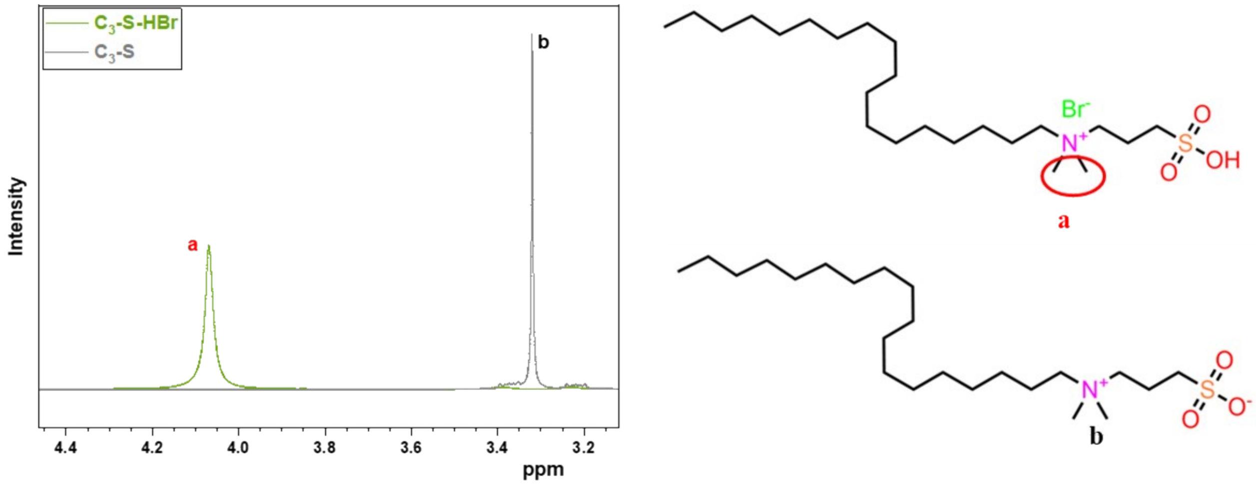

Figure S1 ^{1}H-NMR of synthesized C_3-S-HBr and C_3-S

The raw material 3-(N,N-dimethyloctadecylammonio)propanesulfonate (C_3-S) is highly possible a kind of dimer. The peak of 3.32 ppm is attributed to methyl near the ammonium group. After reacting with hydrobromic acid, the dimer structure is broken, the possible product molecular structure is shown in Figure S1. The peak of methyl group at 3.32 ppm shifts to 4.06 ppm due to chemical environment change.

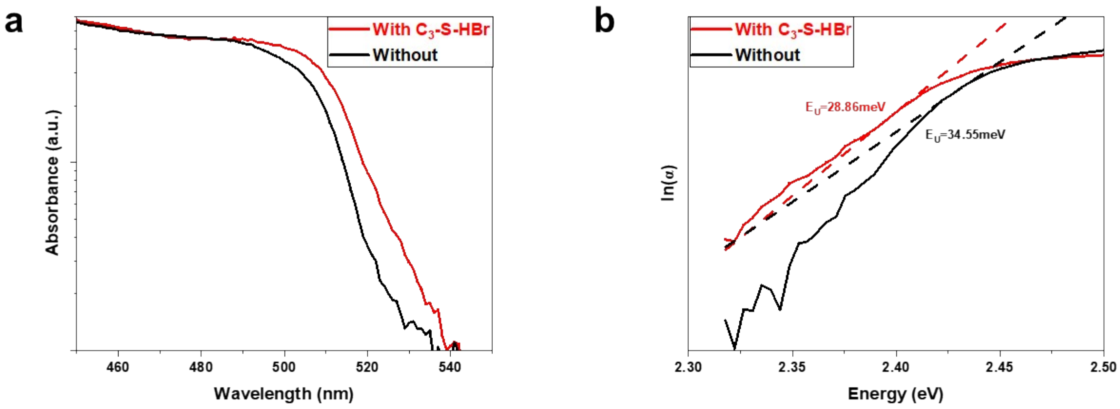

Figure S2 (a) Urbach tail (b) Urbach energy diagram for perovskite nanocrystals with or without C_3-S-HBr resurfacing agent.

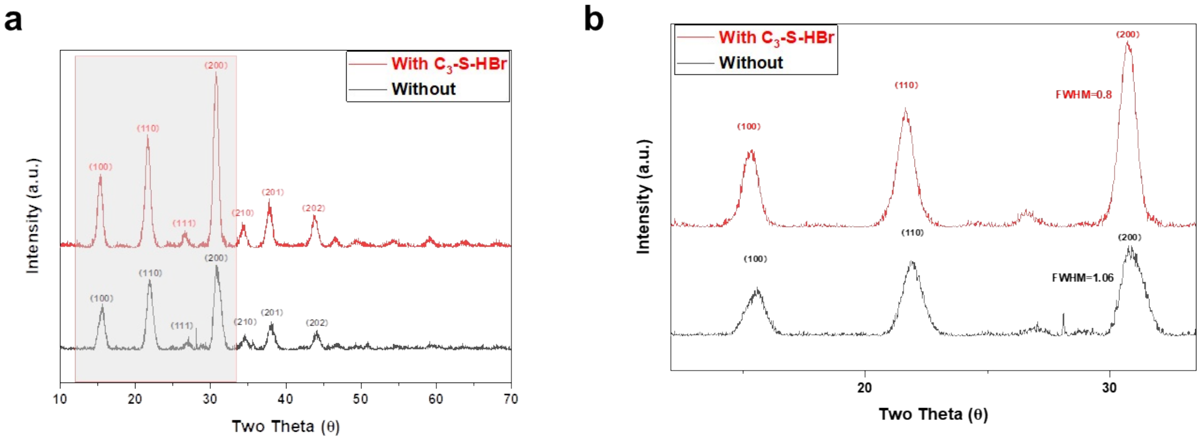

Figure S3 X-ray refraction patterns of synthesized perovskite nanocrystal films.

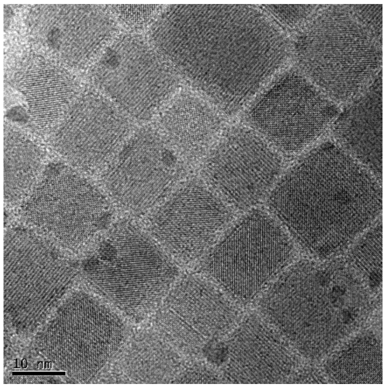

Figure S4 TEM image of C_3-S-HBr perovskite nanocrystals.

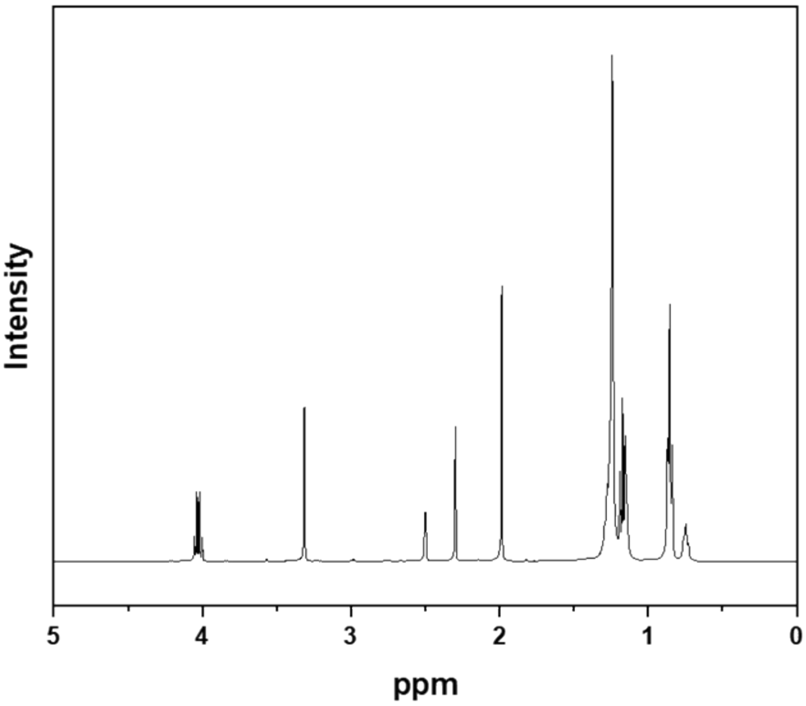

Figure S5 ^{1}H-NMR of synthesized C_3-S-HBr perovskite nanocrystals.

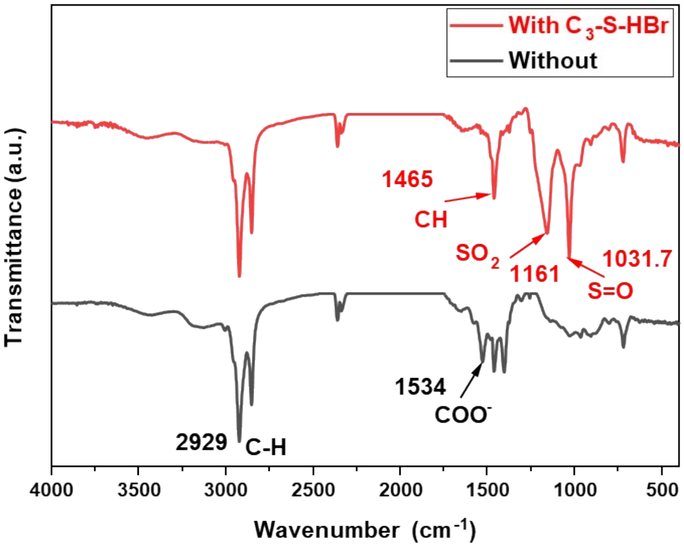

Figure S6 Comparison of FTIR characterization of perovskite nanocrystal films with/without C_3-S-HBr passivation.

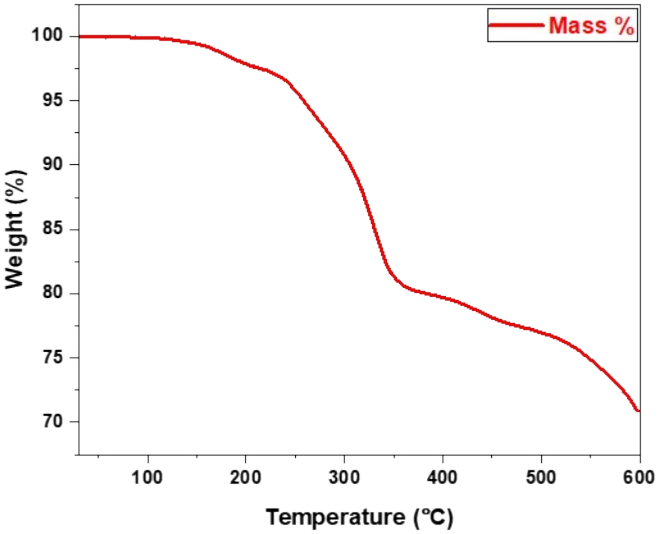

Figure S7 TGA of synthesized C_3-S-HBr perovskite nanocrystals.

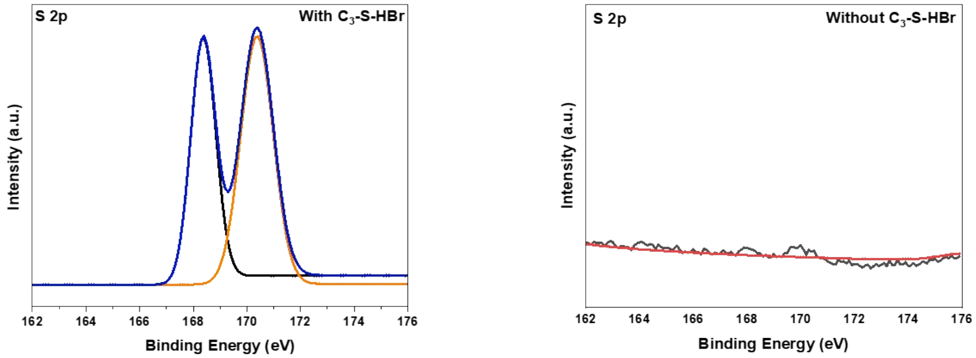

Figure S8 XPS S 2p spectra of synthesized nanocrystal films with or without C_3-S-HBr.

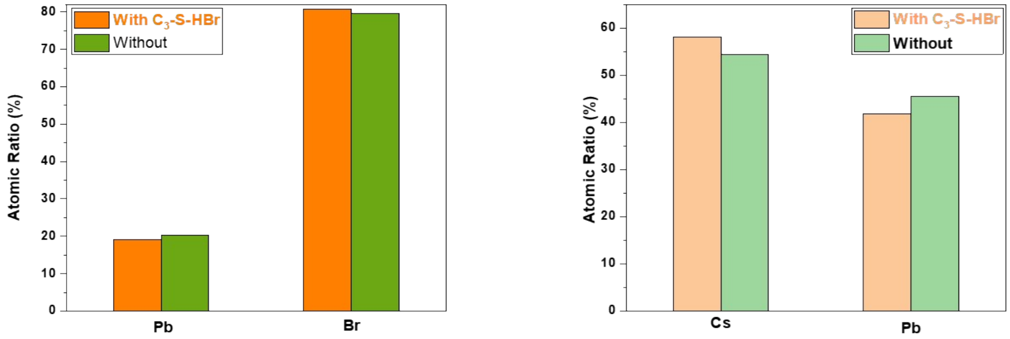

Figure S9 Calculated elemental ratio of synthesized nanocrystal films with or without C_3-S-HBr.

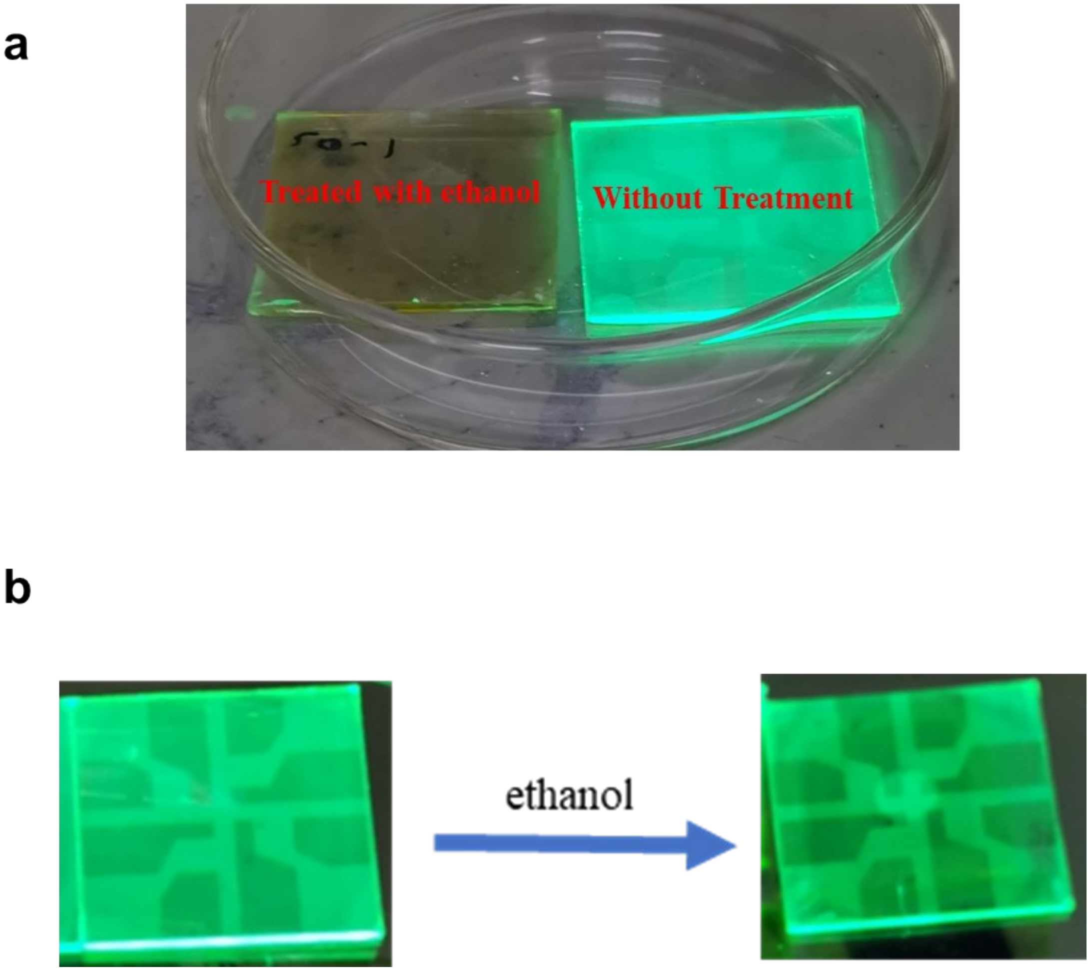

Figure S10 (a) OA/OAm, (b) C_3-S-HBr perovskite nanocrystal film treated with ethanol by spin coating.

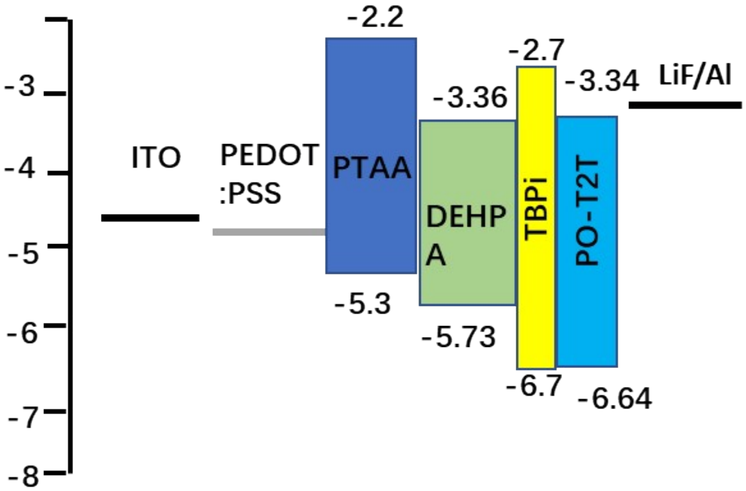

Figure S11 Energy diagram of fabricated perovskite QLEDs

Table S1 Parameters used for fitting the PL decay of perovskite nanocrystal film.

	τ1(ns)	τ2(ns)	τ3(ns)	B_1	B_2	B_3	τeff.(ns)
C_3-S LHP film	9.87	2.60	28.86	2212.309	2268.873	351.5839	13.82
DEHPA LHP film	8.52	34.41	2.71	1578.861	146.9923	3109.993	11.56
OA/OAm LHP film	35.72	4.12		66.69305	5233.949		7.26

The OA/OAm nanocrystals passivated with C_3-S showed an effective exciton lifetime of 12.20 ns[1]. The QLED based on the nanocrystals has a peak EQE of 12.52%.

Table S2 Comparison of PL stability of perovskite nanocrystal film.

Material	**PL Stability**	**Reference**
CsPbBr3 QDs film	50% of initial QY after 400 mins (UV365+RH.70%)	Angew. Chem. Int. Ed. 2023, e202303462
CsPbBr3 QDs film	30% of initial QY after 960 mins (UV254+RH.30%)	Nat. Photonics 15, 843-849 (2021)
CsPbBr3 film	~35% of initial QY after 600 mins (RH.50%)	Adv. Mater 33, 2103268 (2021)
CsPbBr3 QDs film	90% of initial QY after 960 mins (UV254+RH.80%)	This work

Reference

1 X. Zhang, Q. Wang, Z. Yao, M. Deng, J. Wang, L. Qian, Y. Ren, Y. Yan and C. Xiang, *Adv. Sci.*, , DOI:10.1002/advs.202304696.

2 C. Xiang, L. Wu, Z. Lu, M. Li, Y. Wen, Y. Yang, W. Liu, T. Zhang, W. Cao, S. W. Tsang, B. Shan, X. Yan and L. Qian, *Nat. Commun.*, 2020, **11**, 1–9.