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Supporting information

Energy Level Modification of Perovskite Nanocrystals by Dipole Ligand Treatment for Green Light-Emitting Diodes

Wenda Sun [a], Yue Li [a], Xiangxiang Chen [a], Huanxin Yang [a], Libing Zhang [b], Xiyan Li [a]*

[a] Institute of Photoelectronic Thin Film Devices and Technology, Nankai University; Tianjin Key Laboratory of Efficient Utilization of Solar Energy, Nankai University; Engineering Research Center of Thin Film Photoelectronic Technology of Ministry of Education, Nankai University; State Key Laboratory of Photovoltaic Materials and Cells, Nankai University; Academy for Advanced Interdisciplinary Studies (AAIS), Nankai University, Tianjin 300350, China.

[b] Tianjin Key Laboratory of Molecular Optoelectronic, Department of Chemistry, Tianjin University, Tianjin 300072, China.

* Corresponding author.

E-mail: xiyan.li@nankai.edu.cn

Materials

Cesium carbonate (Cs_2CO_3, 99.99%, Alfa Aesar), n-Octanoic acid (OTAC, 99%, Macklin), Formamidine acetate (FAAc, 99.5%, Macklin), Sodium carbonate (Na_2CO_3, 99.99%, Aladdin), Lead bromide ($PbBr_2$, 98%, Alfa Aesar), Tetraoctylammonium bromide (TOAB, 98%, Aladdin), Didodecyldimethylammonium Bromide (DDAB, 98%, Aladdin), Toluene (Tol, 99.7%, Tianjin Fengchuan), Ethyl acetate (EtAc, 99%, Macklin), n-octane (OCT, 99%, water ≤ 50ppm, J&K Scientific). Benzoic acid (BA, 99%, Sigma), 4-(Trifluoromethyl)benzoic acid (CF_3BA, 98%, Macklin), 4-Dimethylaminobenzoic acid (DMABA, 98%, Aladdin), Oleylamine (OLA, 80-90%, Macklin). Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS 4083,Heraeus), poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA) was purchased from Xi'an Polymer Light Technology Corp. 2,4,6-tris[3-(diphenylphosphinyl)phenyl]-1,3,5-triazine (PO-T2T) and lithium fluoride (LiF) were purchased from Luminescence Technology Corp. The ZnCdSe/ZnCdS/ZnS core/shell/shell quantum dots (ZnCdSe) was purchased from Boyijing New Materials Technology Co., Ltd. All chemicals were used directly without purification. The patterned ITO glasses were purchased from Yingkou You Xuan Trade Co., Ltd. And ultrasonically cleaned with soapy water, deionized water, ethyl alcohol (20 min each) for further use.

Purification of precursor

For A site precursor preparation, Cs_2CO_3 and Na_2CO_3 were respectively placed in two centrifuge tubes and fully dissolved with OTAC to obtain 0.1 M Cs-OTAC and Na-OTAC solution. FAAc was dissolved with OTAC to obtain 0.2 M FA-OTAC solution. The A site precursor used for the reaction is uniformly mixed from the above several solutions. Specifically, 2.2 ml Cs-OTAC, 0.8 ml Na_2CO_3, 0.48 ml FA-OTAC and 0.96 ml OTAC was mixed and diluted with 4.45 ml toluene.

For Pb precursor preparation, 458.8 mg $PbBr_2$, 1.3669 g TOAB and 25 ml Tol were mixed in a 50 ml centrifuge tube and stirred at room temperature until all the powder dissolved.

DDAB was dissolved in Tol to form 12 mg/ml DDAB solution.

Synthesis and purification

2.2 ml A site precursor was injected into 10 ml Pb precursor under vigorous stirring. After 2 min, 3.35 ml DDAB solution (12 mg/ml in Tol) was injected. After 2 min, the crude solution was centrifuged at 8000 rpm for 1 min, and the supernatant was collected for purification. EtAc was then added to the supernatant at a volume ratio of 2:1 and centrifuged at 8000 rpm for 2 min. The precipitate was collected after centrifugation and dispersed in 4 ml Tol. The above purification process was repeated one more time and the precipitate was finally dispersed in 1.5 ml OCT.

Ligand exchange

BA, CF_3BA or DMABA was mixed with equal amount of OLA to form ligand pair solution. After the first round of purification, the ligand pair solution was added into NCs solution, and then add EtAc for second round of purification.

LED fabrication

The clean and dried ITO glasses were treated with plasma for 15 min. The PEDOT:PSS solution was filtered by 0.45 μm PVDF filter and spin-coated onto the ITO glasses at 4000 rpm for 40 s and then baked at 160 °C for 15 min in air. After that, the substrates were transferred to a nitrogen glove box for fabricate other layers. The PTAA (5 mg/ml in CB) was spin coated at 2000 rpm for 40 s followed by annealing at 170 °C for 10 min. After the substrates were cooled down to room temperature, the QDs dispersed in OCT was spin-coated at 3000 rpm for 40s. No annealing was needed for QDs film, and PO-T2T (35 nm), LiF (1 nm), and Al (100 nm) were deposited by thermal evaporation under a high vacuum ($< 4 \times 10^{-4}$ Pa). The active area of LEDs was 0.086 cm^2.

Indicator devices fabrication

The indicator devices fabrication are the same as that of LED, except that the indicator solution was spin-coated at a speed of 3000 rpm and annealing at 100°C for 10 min.

LED characterization

The LED devices was not encapsulated and tested in a nitrogen glove box. The J-V-L and EL characteristics was measured using PR-735 spectroradiometer coupled with a Keithley 2400 source meter under a scanning rate of 0.2V s^{-1}. The EQE was calculated using the following equation:

$$EQE = \eta_A \frac{\pi q}{683hc} \frac{\int_{visible} I(\lambda)\lambda d\lambda}{\int_{visible} I(\lambda)V(\lambda)d\lambda}$$

Where η_A is the current efficiency; $I(\lambda)$ is the intensity of EL spectrum signal; $V(\lambda)$ is 1924 CIE standard visual efficiency function.

The above electroluminescence characteristics of LED were cross-checked by a system comprising a sphere-spectrometer system (QE65 Pro, FOIS-1-FL integration sphere). The T_{50} lifetime of LEDs was conducted using sphere-spectrometer system, but under a constant current density condition with initial luminance of 300 cd cm^{-2}.

Other characterizations

Absorption spectra were recorded from a UV–visible–near-infrared system (Yoke Instrument N6000). Steady-state and time-resolved photoluminescence spectra were both measured using a photoluminescence spectrophotometer (FS5, Edinburgh Instruments). The PLQY were calculated followed the methods suggested by IUPAC using Fluorescein as standard dye. The crystal structure of the samples was measured using a Rigaku Smart Lab X-ray diffractometer (XRD) with Cu radiation. Ultraviolet photoelectron spectroscopy (UPS) measurements were conducted on a Thermo ESCALAB Xi^+ with He radiation. An HP 4284A LCR instrument was used to conduct CV characterization of the PeLED devices. The J-V cure of hole-only and electron-only devices were measured using Keithley 2400 source meter. Electrochemical impedance spectroscopy (EIS) was obtained by CHI760E electrochemical workstation (Chenhua Instrument Shanghai Co., Ltd, China).

Calculations of energy level:

The energy level, Fermi level (E_F), valence band maximum (VBM), conduction band minimum (CBM) based on UPS measurements with the following formula:

$$E_F = E_{cutoff} - E_{He}$$

$$E_{VBM} = E_F - E_{onset}$$

$$E_{CBM} = E_{VBM} + E_g$$

Were E_{He} is the energy of the He emission line (21.22 eV) and E_g is the band gap, and the $E_{cutoff}$and E_{onset} are obtained from the cut-off region and valence zone in the UPS measurement results, respectively.

AIMD calculations

We set the plane-wave cutoff energy at 500 eV and employed the DZVP Gaussian basis set for all elements to ensure precise electronic structure characterization. Furthermore, we applied the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) for the treatment of exchange-correlation effects, while dispersion interactions were corrected using the RB3LYP method. This methodological framework enabled us to achieve results of high accuracy within reasonable computational limits.

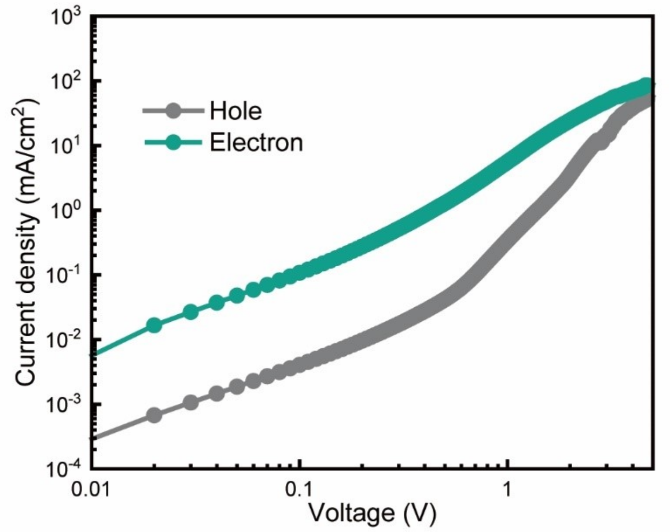

Figure S1. The J-V cures of hole-only device (ITO/PEDOT:PSS/PTAA/Pristine-NCs/MoO_3/Au) and electron-only (ITO/SnO/Pristine-NCs/PO-T2T/LiF/Al) device.

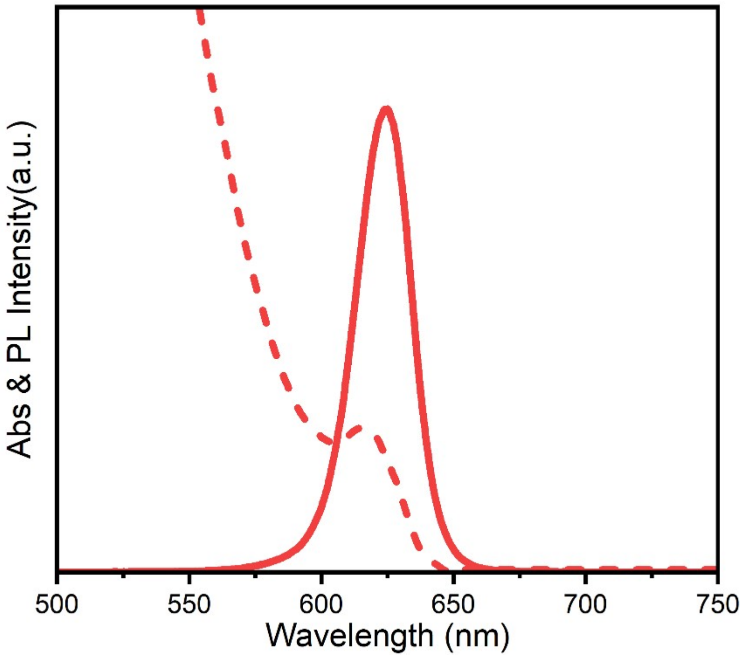

Figure S2. The Absorption and PL spectra of ZnCdSe solution.

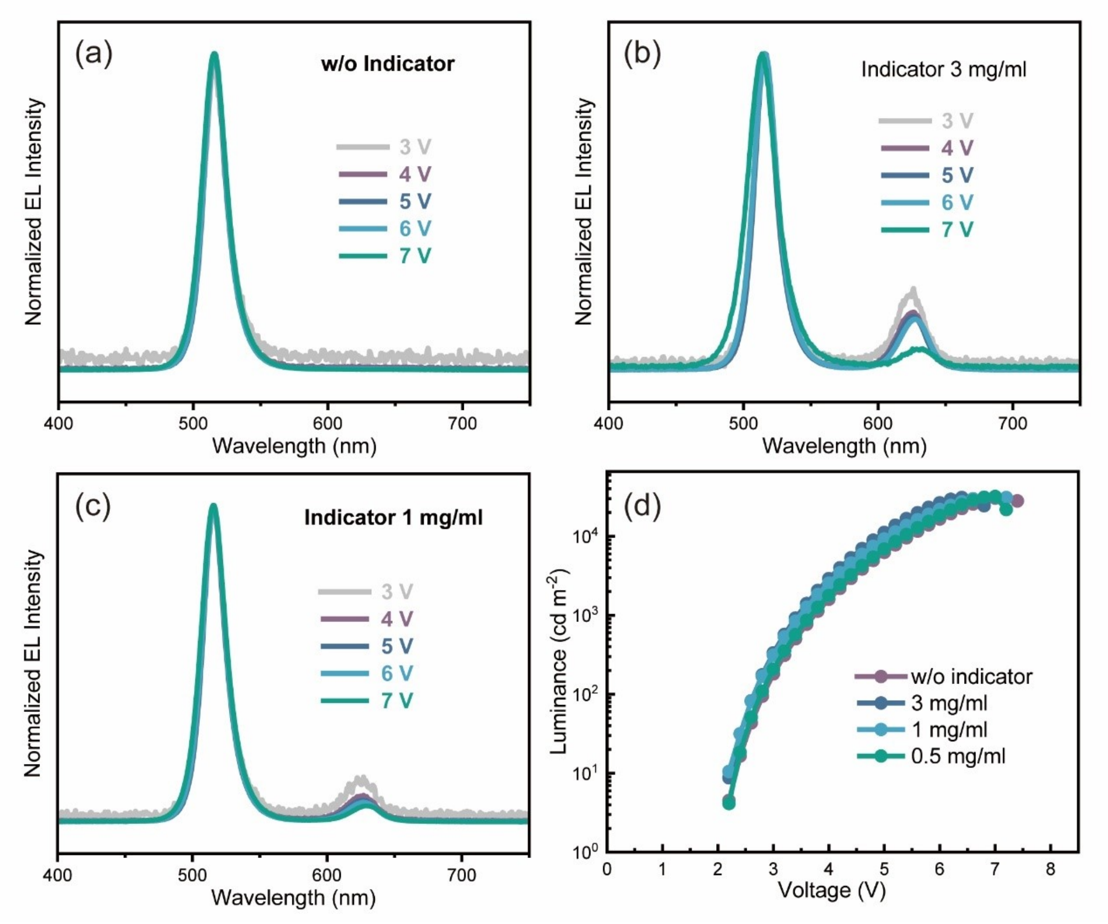

Figure S3. (a-c) EL spectrum of indicator devices with different indicator concentrations (d) The L-V cure of indicator devices.

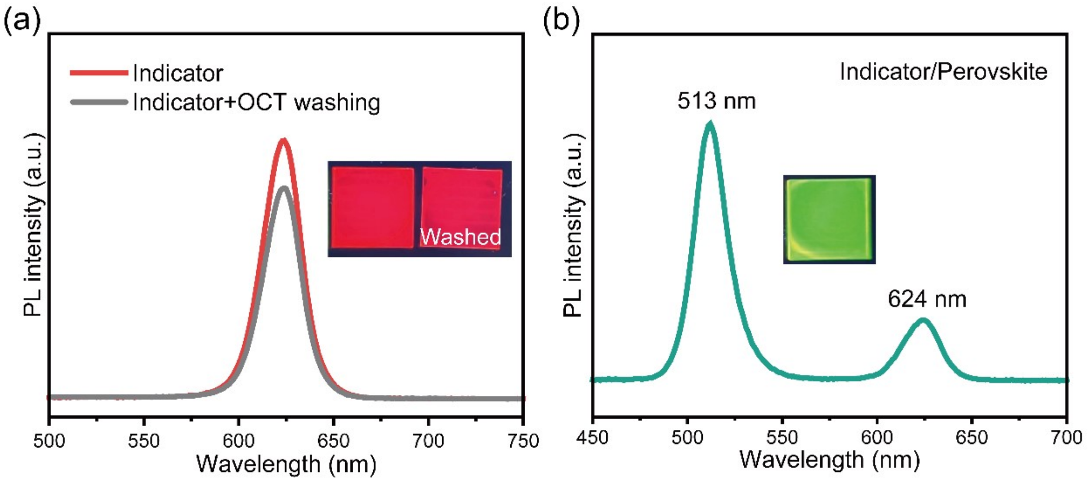

Figure S4. (a) The PL intensity of spin-coated Cd-based quantum dot film and Cd-based quantum dot film after OCT washing. (b) The PL intensity of Cd-based quantum dot film followed by spin-coating of perovskite film.

We conducted additional experiments to further verify the solvent-resistant property of the spin-coated Cd-based quantum dots. For one sample, the 1mg/ml Cd-based quantum dot solution was spin-coating on the glass substrate followed by annealing at 100 °C for 10 min. For another sample, the OCT solution was spin coat on the cooled Cd-based quantum dots substrate. The PL intensity of the two samples was shown in Figure S4a, the film retains a strong fluorescence after OCT washing, indicating that the Cd-based quantum dots were not completely washed away. The PL of Cd-based quantum dots/perovskite film was also shown in Figure S4b, the peak at 624 nm corresponds to the luminescence of Cd-based quantum dots.

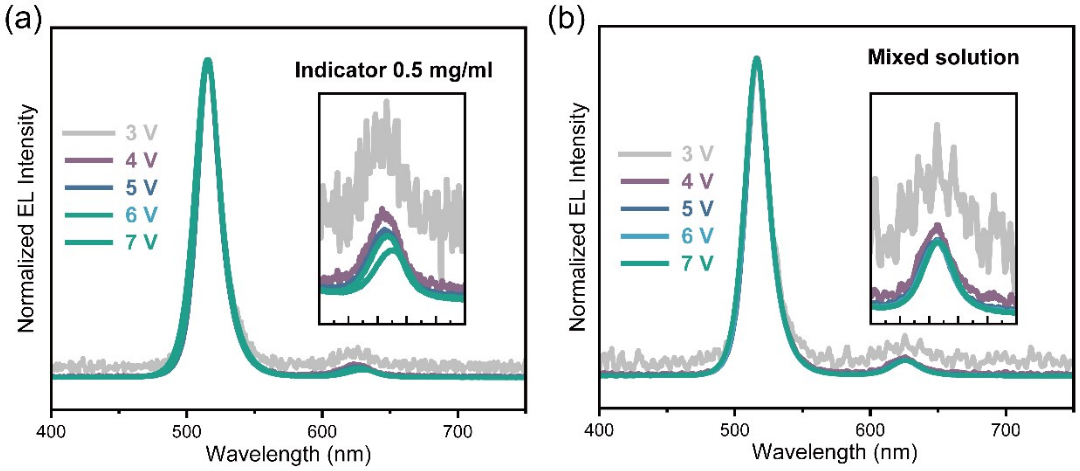

Figure S5. The EL spectrum under different voltages.

In order to verify whether the Cd-based quantum dots are still fixed at the interface after the spin-coating of perovskite solution, we fabricated LED device using mixed solution of Cd-based and perovskite quantum dot (Cd-based quantum dot 0.5 mg/ml, perovskite 25 mg/ml). In indicator device, if the Cd-based quantum dots was dissolved by the perovskite OCT solution, the trend of EL spectrum under different voltages should be similar with the device using mixed quantum dot solution as light emitting layer. The EL spectrum was shown below, under different voltages the two devices exhibit different EL behavior of Cd-based quantum dots, indicating that the distribution positions of Cd-based quantum dots in the two devices are different.

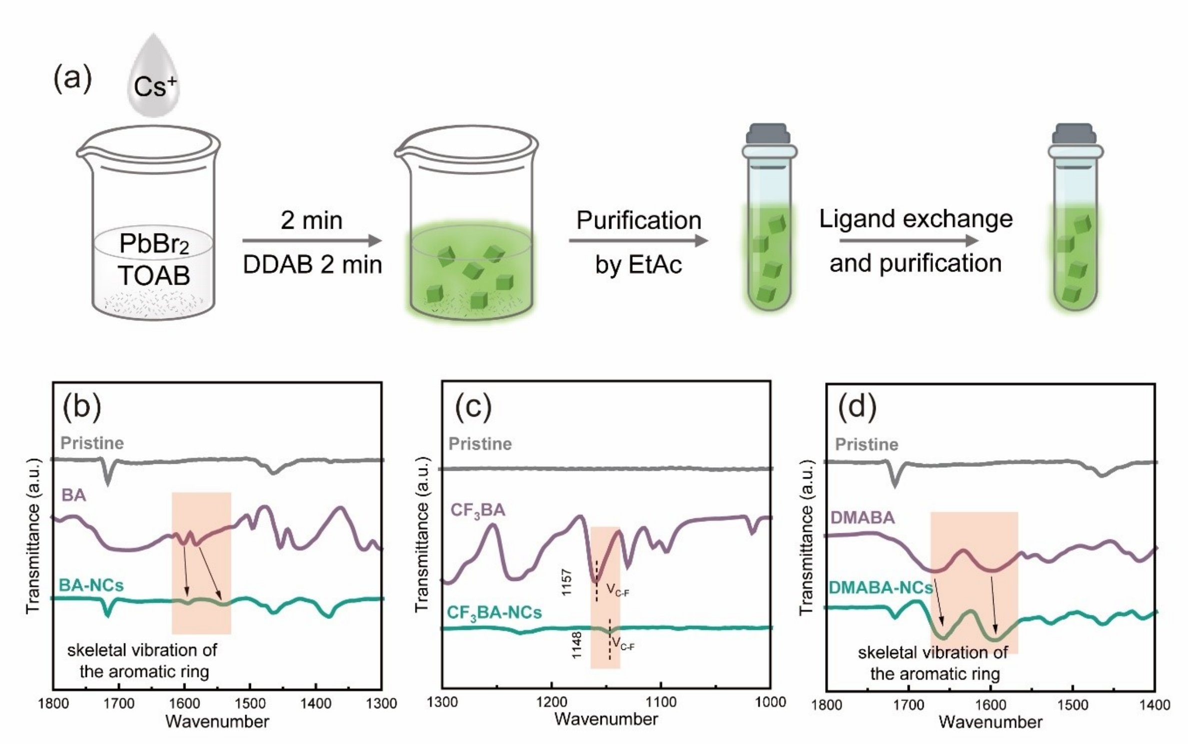

Figure S6. (a) The schematic illustration of synthesis and ligand exchange process. (b) FT-IR pectra of ligands and ligand treated NCs.

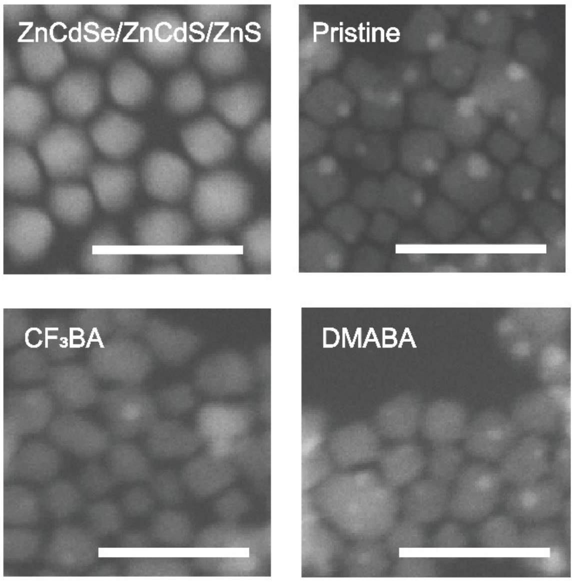

Figure S7. The TEM of Cd-based quantum dot (ZnCdSe/ZnCdS/ZnS core/shell/shell quantum dots) and ligand treated perovskite nanocrystal.

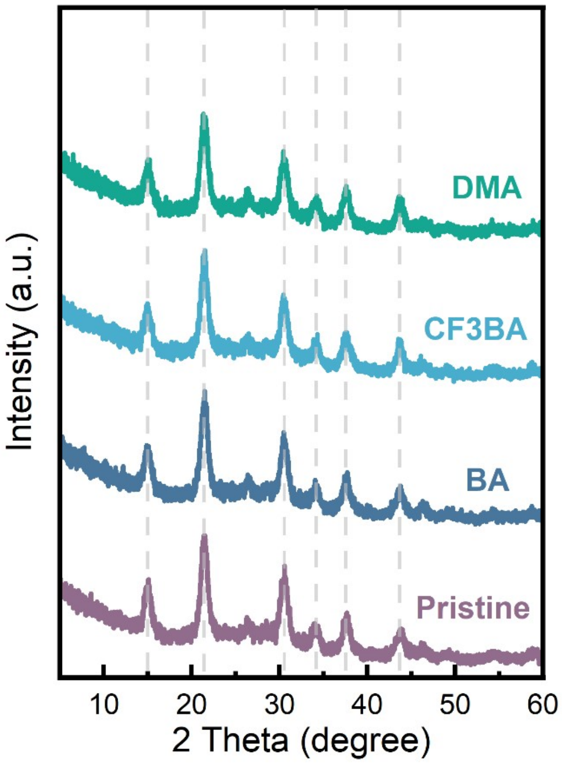

Figure S8. XRD spectra of different NCs.

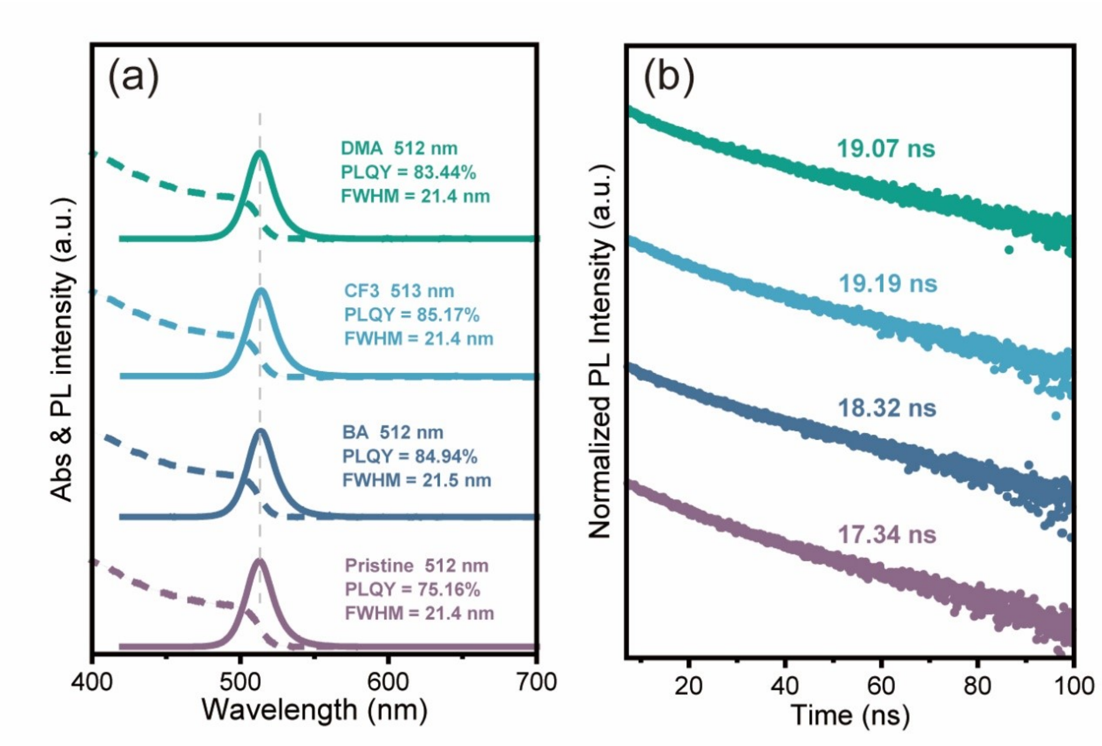

Figure S9. (a) Absorption and PL spectra of different NCs solution. (b) Time-resolved photoluminescence spectra of different NCs solution

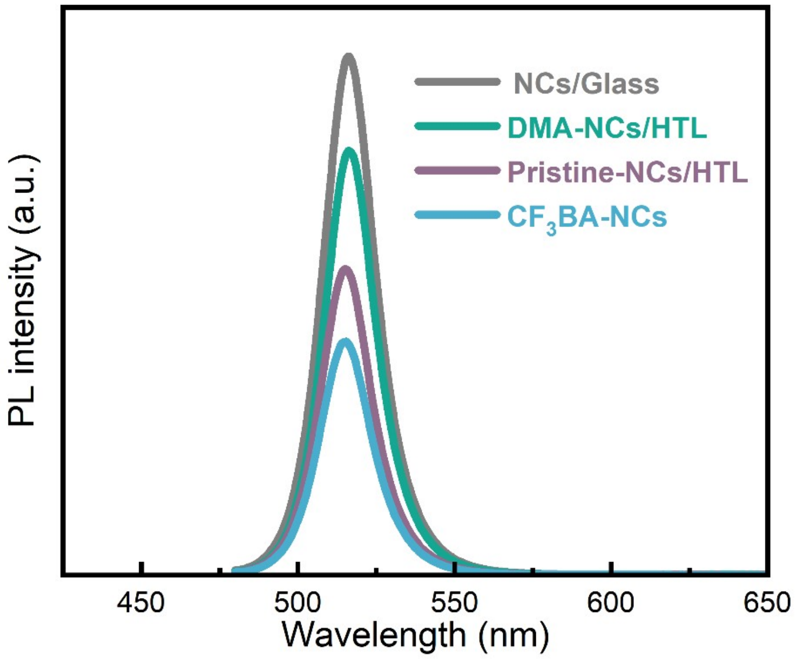

Figure S10. PL spectra of different NCs on PTAA.

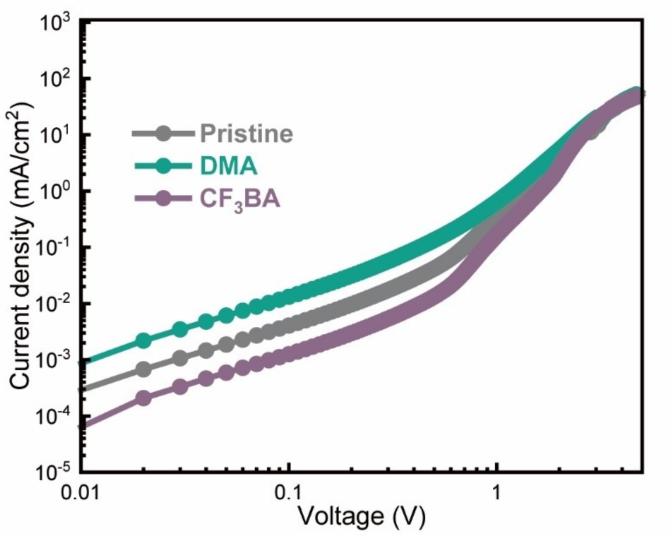

Figure S11. The J-V cures of hole-only device (ITO/PEDOT:PSS/PTAA/NCs/MoO$_3$/Au) with different perovskite NCs.

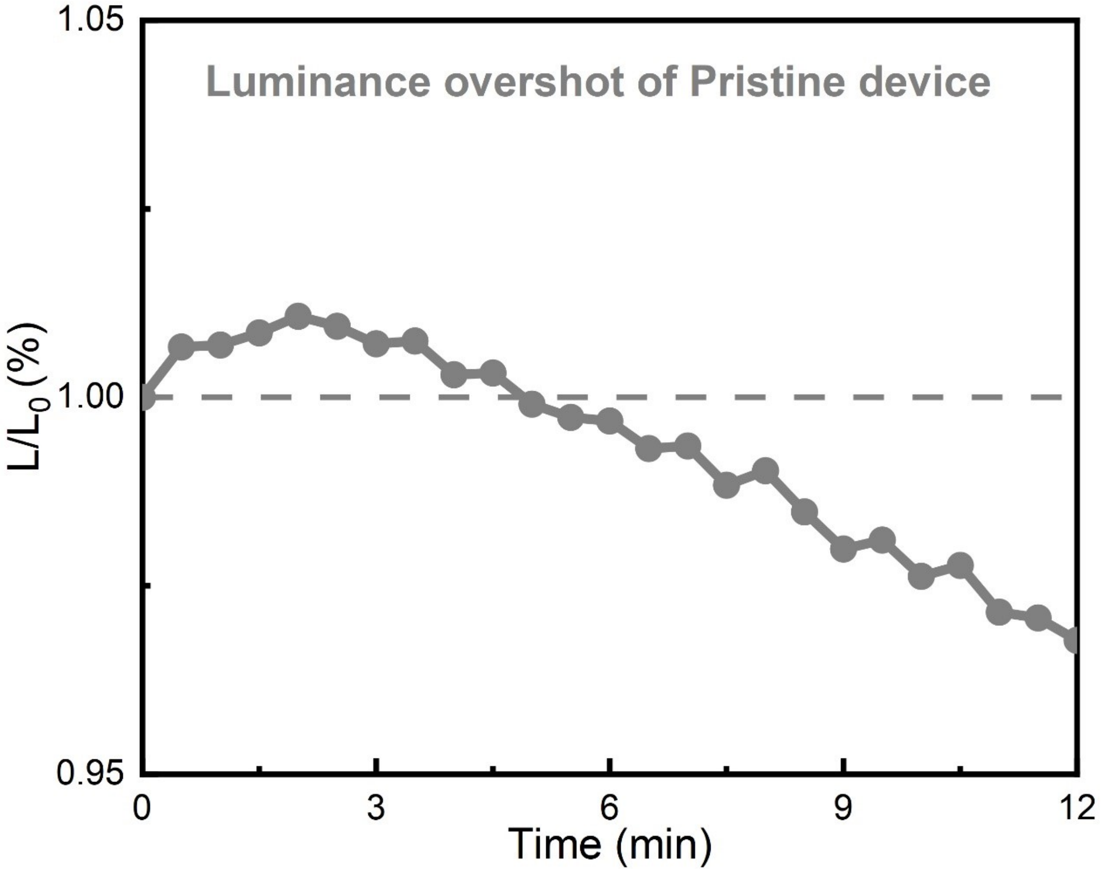

Figure S12. Luminance overshot of Pristine-device within the first 5 minutes.

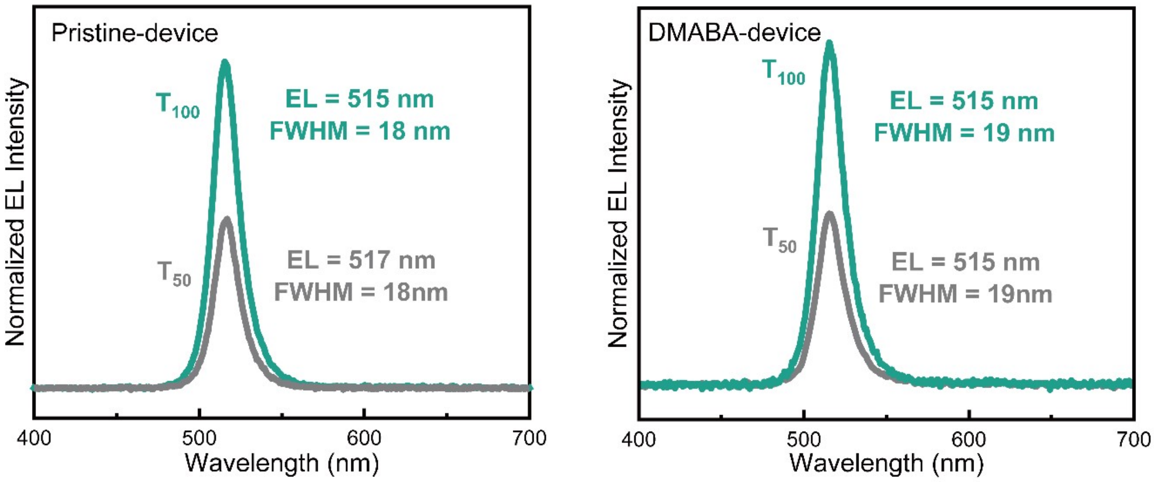

Figure S13. The EL spectra of Pristine and DMABA-device from T_{100} to T_{50}.

Table S1. The TRPL decay fitting parameters of NCs solution.

	F_1(%)	A_1	τ_1(ns)	F_2(%)	A_2	τ_2(ns)	τ_{avg}(ns)
Pristine	44.20	1.27	8.86	55.80	0.59	24.07	17.35
BA	28.70	1.12	6.68	71.30	0.81	23.00	18.32
CF_3BA	40.20	1.24	8.80	59.80	0.62	26.18	19.19
DMABA	30.00	1.12	7.37	70.00	0.80	24.09	19.08

The decay curves were fitted using the following exponential decay equation:

$$I(t) = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} + A_0$$

where A_1, A_2 and A_3 are the pre-exponential factors, A_0 is a constant, t is PL decay time, τ_1 $\tau_2$and τ_3 are characteristic lifetimes.

The average lifetime τ_{avg} was calculated from the following equation:

$$\tau_{avg} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

Table S2. The TRPL decay fitting parameters of NCs on PTAA HTL film.

	F_1 (%)	A_1	T_1	F_2 (%)	A_2	T_2	F_3 (%)	A_3	T_3	T (ns)
Pristine/Glass	/	/	/	40.11	0.53	6.71	59.89	0.25	21.24	14.90
Pristine/PTAA	17.80	0.81	1.16	33.40	0.34	5.15	48.80	0.11	24.63	13.95
DMA-NCs/ PTAA	10.80	0.70	1.10	30.30	0.39	5.44	58.90	0.16	26.69	17.49
CF_3BA-NCs/ PTAA	28.20	0.94	0.89	43.00	0.34	3.73	28.80	0.06	15.45	6.30

The decay curves were fitted using the following exponential decay equation:

$$I(t) = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} + A_3 e^{-\frac{t}{\tau_3}} + A_0$$

where A_1, A_2 and A_3 are the pre-exponential factors, A_0 is a constant, t is PL decay time, τ_1 $\tau_2$and τ_3 are characteristic lifetimes.

The average lifetime τ_{avg} was calculated from the following equation:

$$\tau_{avg} = \frac{A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3}$$

Table S3. The TREL decay fitting parameters of Pristine and DMA-device.

	F_1(%)	A_1	τ_1(μs)	F_2(%)	A_2	τ_2(μs)
Pristine	19.85	0.69	0.17	80.15	0.32	1.48
DMA	74.79	0.89	0.18	25.21	0.09	0.60

The decay curves were fitted using the following exponential decay equation:

$$I(t) = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} + A_0$$

where A_1, A_2 and A_3 are the pre-exponential factors, A_0 is a constant, t is PL decay time, τ_1 $\tau_2$and τ_3 are characteristic lifetimes.

The average lifetime τ_{avg} was calculated from the following equation:

$$\tau_{avg} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

Table S4. The fitting parameters extracted from equivalent-circuit model.

	Rs	Rt (Ω)	Ct(nF)	Rr (Ω)	Cr (nF)
Pristine	295	1404	21.3	51978	3.8
DMA	193	924	16.7	36077	3.6