Supporting Information

Chlorine Vacancy Passivation in Mixed-Halide Perovskite Quantum Dots by Organic Pseudohalides Enables Efficient Rec. 2020 Blue Light-Emitting Diodes

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Chemicals. All chemicals were used as received without further purification: cesium carbonate (Cs_2CO_3, 99.995%, Sigma-Aldrich), PbO (98%, Sigma-Aldrich), oleic acid (OA, technical grade 90%, Alfa Aesar), n-oleylamine (OAm, 70%, Sigma-Aldrich), 1-octadecene (ODE, technical grade 90%, Sigma-Aldrich), toluene (Honeywell Burdick & Jackson), OAmCl (≥99.5%, Xi'an Polymer Light Technology Corp.), and OAmBr (≥99.5%, Xi'an Polymer Light Technology Corp.).

$CsPb(Br_xCl_{1-x})_3$ QD synthesis and purification. $CsPb(Br_xCl_{1-x})_3$ QDs were synthesized according to a well-established synthesis protocol.[1-6] For a typical procedure, Cs_2CO_3 (0.2 mmol), PbO (0.4 mmol), ODE 20 ml, OA 4ml, and OAm 2ml were added into a 250mLflask. The solution was heated to 120 ˚C and kept for 1 hour in order to dissolve the chemicals and get rid of oxygen and moisture. It was then purged 3 times with inert gas and heated to 200 ˚C. The $CsPb(Br_xCl_{1-x})_3$ QDs were formed after the injection of a mixture of OAmBr (1.19 mmol) and OAmCl (0.835 mmol) in 2ml OAm. The crude solution was centrifuged at 8000 rmp for 5 minutes. Then, the supernatant was removed, and the precipitate was collected and re-dispersed in 10 mL toluene. One more centrifugation was required to purify the final QDs, with 8000 rmp for 1 minute in order to remove larger QDs.

LED fabrication. The patterned ITO/glass substrates were sequentially cleaned with soap, deionized water, acetone, and isopropanol under ultrasonication. The ITO/glass substrates were then dried with N_2 blow and treated with ultraviolet (UV) ozone for 15 min. Poly(9,9-dioctylfluorene-alt-N-(4-sec-butylphenyl)-diphenylamine) (TFB) dissolved in chlorobenzene at 5 mg/ml was firstly spin-coated on treated ITO substrates at 6000 rpm, and followed by annealing

at 120 °C for 15 min. Then a thin film of nafion perfluorinated resin (PFI) (0.05 wt% in isopropanol) was deposited at 6000 rpm and dried at 120 °C for 15 min. QDs were dispersed in n-hexane with concentration about 12 mg/ml and spin-coated on the top of substrates. For DAT treated device, DAT with concentration of ~0.1 mg/ml was added into QDs dispersion. Finally, films were transferred to evaporation chamber, where 40 nm tris(2,4,6-triMethyl-3-(pyridin-3-yl)phenyl)borane (3TPYMB), 1.6 nm Liq, and 100 nm Al were deposited. Before measurement, all devices were encapsulated.

LED characterization. The current-voltage characteristics were measured with a computer controlled Keithley 2400 source meter. Electroluminescence spectra were collected by using a photonic multichannel analyzer PMA-12 (Hamamatsu C10027-01). The external quantum efficiency of the devices (calculated in the range of 300-980 nm) was obtained by measuring the light intensity in the forward direction by using an integrating sphere (Hamamatsu A10094). All the measurements were carried out in ambient air.

Density functional theory (DFT) calculations. We carried out the DFT calculations using projector augmented wave (PAW) method as implemented in the Vienna ab initio Simulation Package (VASP). The PerdewBurke-Ernzerhof (PBE) formulation of the generalized gradient functional (GGA) for exchange-correlation energy was used. The energy cutoff for the wave function expanded in the plane-wave basis was 500 eV. Monkhorst−Pack-type k-meshes of 6×6×6 and 6×6×1 were used for the cubic-phase bulk $CsPbCl_3$, and the 2×2 slabs are exposing the (001) surface, respectively. We considered three slab models of (*i*) the ideal $CsPbCl_3$ slab, (*ii*) with the removed Cl on the surface, and (*iii*) with the surface filled SCN^-. All the slabs were separated by

both top and bottom vacuum layers (~10 Å) to prevent spurious inter-slab interactions. Each structure was optimized until the forces on every single atom were smaller than 0.01 eV/Å. The molecular graphics viewer VESTA was used to plot crystal structures and charge densities.

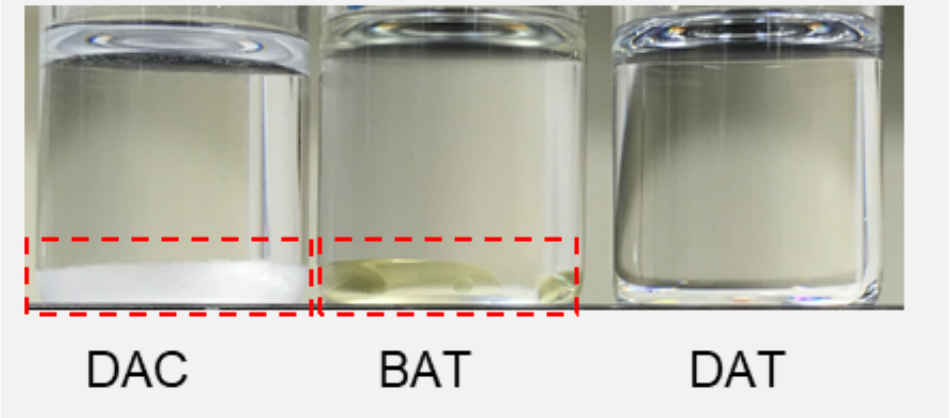

Figure S1. Photographs of dispersing 50 mg of n-dodecylammonium chloride (DAC; $C_{12}H_{25}NH_3Cl$), n-butylammonium thiocyanate (BAT; $C_4H_9NH_3SCN$), and n-dodecylammonium thiocyanate (DAT; $C_{12}H_{25}NH_3SCN$) into 2 ml toluene.

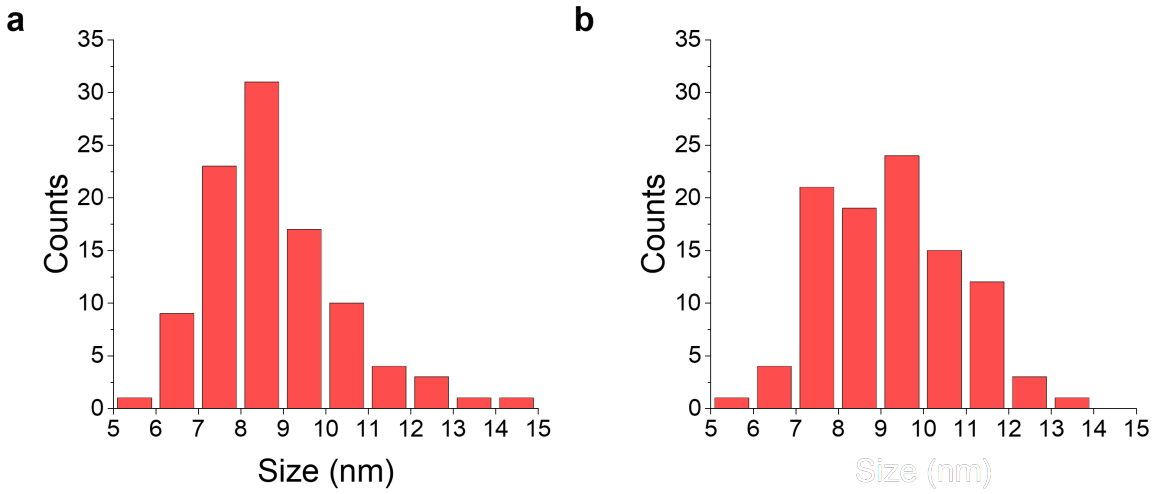

Figure S2. Size distribution of (**a**) the pristine MHP QDs and (**b**) DAT-treated MHP QDs.

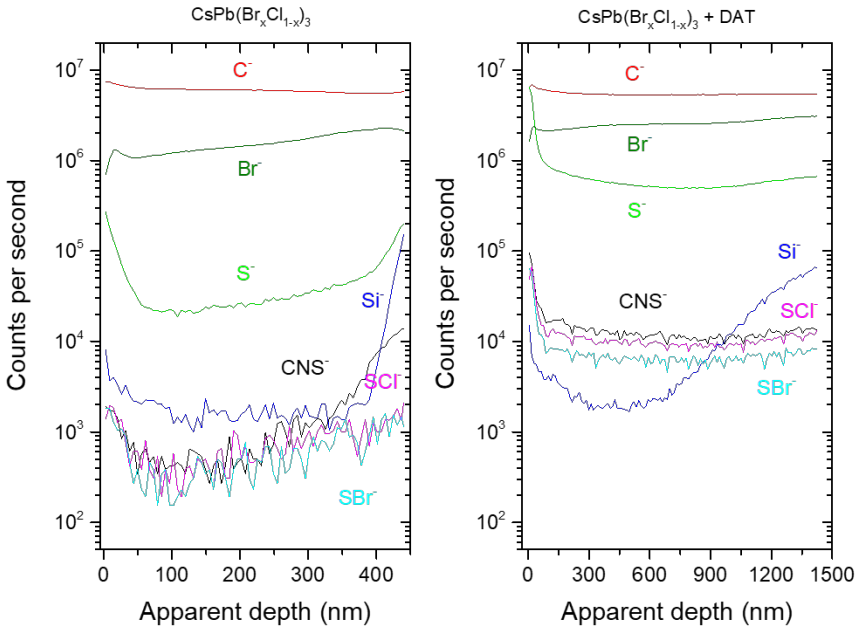

Figure S3. SIMS depth profiles of the drop-casted pristine MHP QD films and DAT-treated MHP QD films.

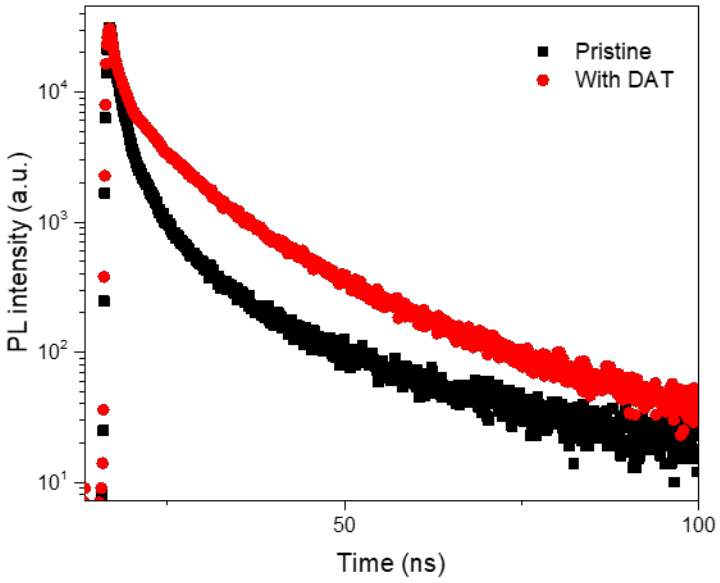

Figure S4. Time-resolved photoluminescence (PL) decay of pristine MHP QD films and DAT-treated MHP QD films.

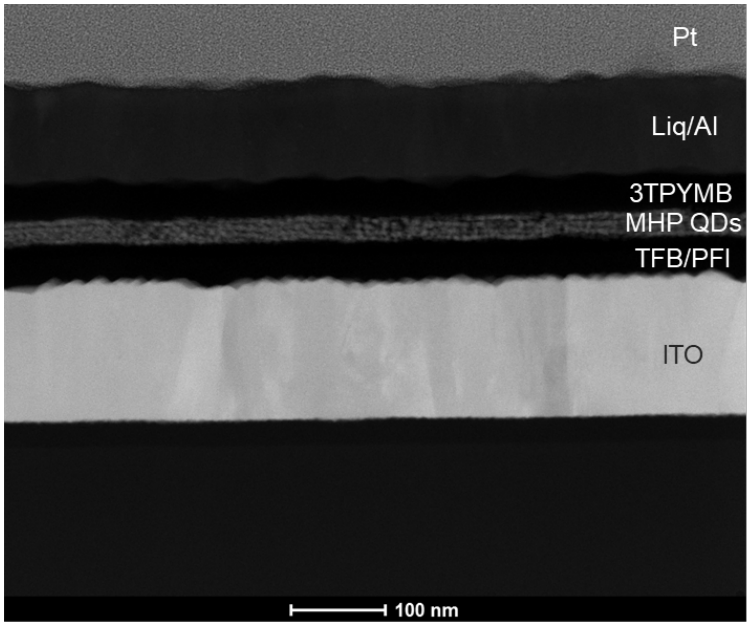

Figure S5. Cross-sectional high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the MHP QD LEDs.

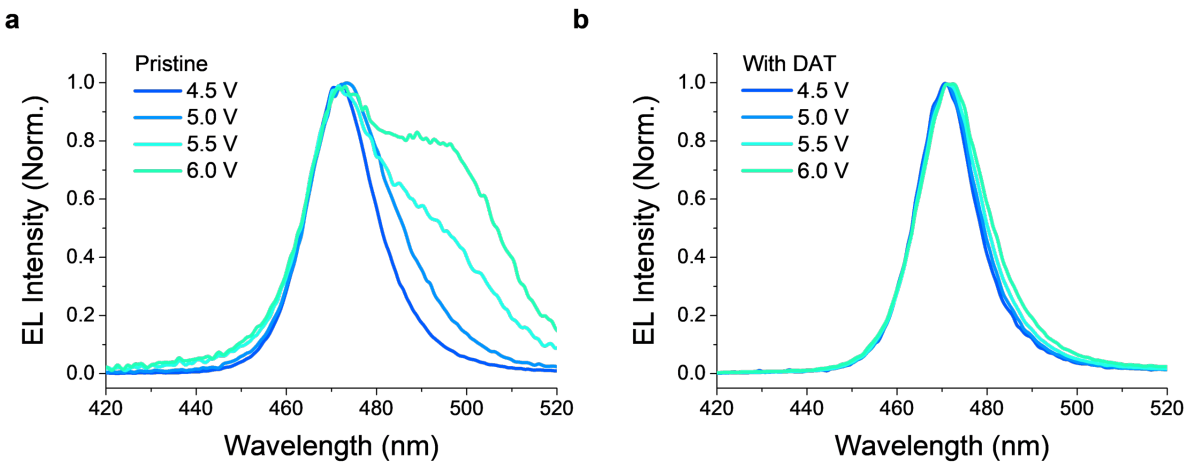

Figure S6. (**a**, **b**) normalized EL spectra for (**a**) pristine device and (**b**) the DAT-treated device.

References

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