Supplementary Information (SI) for CrystEngComm.

Suppressed Surface Defect via Ligand Engineering with 2-Hexyldecanoic Acid for High Luminescence and Stable $CsPb_{1-x}Ni_xBr_3$ Perovskite Quantum Dots

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Materials

Cesium carbonate (Cs_2CO_3, 99.99%, TCI), lead bromide ($PbBr_2$, 99.99%, TCI), nickel bromide ($NiBr_2$, 99.99%, TCI), 1-octadecene (ODE, 90%, Sigma-Aldrich), oleylamine (OlAm, 70%, Sigma-Aldrich), oleic acid (OA, 90%, Sigma-Aldrich), 2-hexyldecanoic acid (DA, 99%, Sigma-Aldrich), *n*-hexane (95%, Sigma-Aldrich), and rhodamine B (analytical standard, Sigma-Aldrich) were used for the quantum yield (QY) measurement.

Synthesis of colloidal OA-$CsPbBr_3$ perovskite quantum dots (PQDs)

Cs_2CO_3 (0.1 g) and ODE (10 mL) were added to a three-necked flask, followed by the addition of OA (1 mL), under continuous stirring. The flask was gradually heated to 110 °C under vacuum. Subsequently, the solution was maintained under vacuum for 1 h for the complete dissolution of Cs_2CO_3. Subsequently, the solution was maintained under nitrogen atmosphere while the temperature was maintained at 110 °C. $PbBr_2$ (0.138 g) and ODE (10 mL) were added to another three-necked flask. The flask was heated to 120 °C under vacuum. Subsequently, the solution was maintained under vacuum for 1 h to remove impurities. Then, the flask was converted to a nitrogen atmosphere, and 1 mL of OlAm and 1 mL of OA were injected into the flask. The temperature then increased to 180 °C. Next, 1 mL of the cesium oleate precursor solution was injected into the lead precursor solution. After 5 s, the reaction was rapidly cooled with an ice bath until the temperature dropped below room temperature, preventing further growth. Then, the $CsPbBr_3$ solutions were purified via centrifugation for 5 min at 8000 rpm. Following the removal of the supernatant, the precipitate dried at ambient temperature. Then, *n*-hexane (2 mL) was added as a redispersion solvent, and the $CsPbBr_3$ PQDs were obtained after additional centrifugation at 8000 rpm for 5 min.

Synthesis of colloidal OA-$CsPb_{1-x}Ni_xBr_3$ PQDs

Cs_2CO_3 (0.1 g) and ODE (10 mL) were added to a three-necked flask, followed by the addition of OA (1 mL), under continuous stirring. The flask was gradually heated to 110 °C under vacuum. The solution was maintained under vacuum for 1 h for the complete dissolution of Cs_2CO_3. Then, the solution was maintained under nitrogen atmosphere while the temperature was maintained at 110 °C. $PbBr_2$ (0.138 g), $NiBr_2$, and ODE (10 mL) were added to another three-necked flask. This flask was gradually heated to 120 °C under vacuum, and the solution was maintained under vacuum for 1 h to remove impurities. Subsequently, the flask was converted to a nitrogen atmosphere. 1 mL of OlAm and 1 mL of OA were injected into the flask, and the temperature was increased to 180 °C. Subsequently, 1 mL of the cesium oleate precursor solution was injected into the lead precursor solution. After 5 s, the reaction was rapidly cooled with an ice bath until the temperature dropped below room temperature, preventing further growth. The $CsPbBr_3$ solutions were purified via centrifugation for 5 min at 8000 rpm. Following the removal of the supernatant, the precipitate dried at ambient temperature. Then, *n*-hexane (2 ml) was added as a redispersion solvent, and the $CsPbBr_3$ PQDs were obtained after an additional centrifugation at 8000 rpm for 5 min.

Synthesis of colloidal DA-$CsPb_{1-x}Ni_xBr_3$ PQDs

Cs_2CO_3 (0.1 g) and ODE (10 mL) were added to a three-necked flask, followed by the addition of DA (1 mL), under continuous stirring. The flask was gradually heated to 110 °C under vacuum. The solution was maintained under vacuum for 1 h for the complete dissolution of Cs_2CO_3 and under a nitrogen atmosphere at 110 °C. $PbBr_2$ (0.138 g), $NiBr_2$, and ODE (10 mL) were added to another three-necked flask. The flask was gradually heated to 120 °C under vacuum. Subsequently, the solution was maintained under vacuum for 1 h to remove impurities. The flask was then converted to a nitrogen atmosphere, and 1 mL of OlAm and 1 mL of DA were injected into the flask. Then, the temperature increased to 180 °C. Subsequently, 1 mL of the cesium oleate precursor solution was injected into the lead precursor solution. After 5 s, the reaction was rapidly cooled with an ice bath until the temperature dropped below room temperature, preventing further growth. Thereafter, the $CsPbBr_3$ solutions were purified via centrifugation at 8000 rpm for 5 min. Following the removal of the supernatant, the precipitate dried at an ambient temperature. Subsequently, *n*-hexane (2 ml) was added as a redispersion solvent, and the $CsPbBr_3$ PQDs were obtained after additional centrifugation at 8000 rpm for 5 min.

Fabrication of PQDs based diode

ITO substrates were washed with deionized water, acetone, and isopropanol in sequence by ultrasonic cleaning for 30 min before use, respectively. The PQDs solution of each precursor ratio was spin-coated at 1000 rpm for 30 s. Afterwards, MoO_3 and Ag were deposited in thicknesses of 5 nm and 100 nm, respectively, through thermal evaporation in a vacuum environment.

Characterizations

Ultraviolet-visible (UV-vis) absorption spectra of perovskite quantum dots (PQDs) in n-hexane were measured using a Perkin-Elmer Lambda 365 UV-vis spectrophotometer. The PL spectra were obtained using a Hitachi F-7000 fluorescence spectrophotometer while setting the absorbance of the reference (rhodamine B) and PQDs at ~0.1. An X-ray diffraction (XRD) analysis was performed using an X-ray spectrometer (Bruker AXS, D8-Advance) under CuKα radiation. The functional groups of the various PQD surface ligands and corresponding unbound ligands were analyzed using a Nicolet 6700 Fourier transform infrared (FT-IR) spectrometer. The relative quantum yields (QYs) of the various PQDs were calculated from both the UV-vis and PL results. The PQDs were subjected to transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) using a JEOL JEM-2100 instrument (JEOL JEM-ARM200F). Mapping images of the particles were obtained by applying TEM in combination with energy-dispersive spectrometry (EDS). The X-ray photoelectron spectroscopy (XPS) analysis of PQD thin films was performed using a K-alpha instrument (Thermo Fisher Scientific). The thermal stabilities of the various PQDs were evaluated through storage tests under 70 °C conditions. The PL and water stabilities of the various PQDs were evaluated through storage tests under ambient conditions.

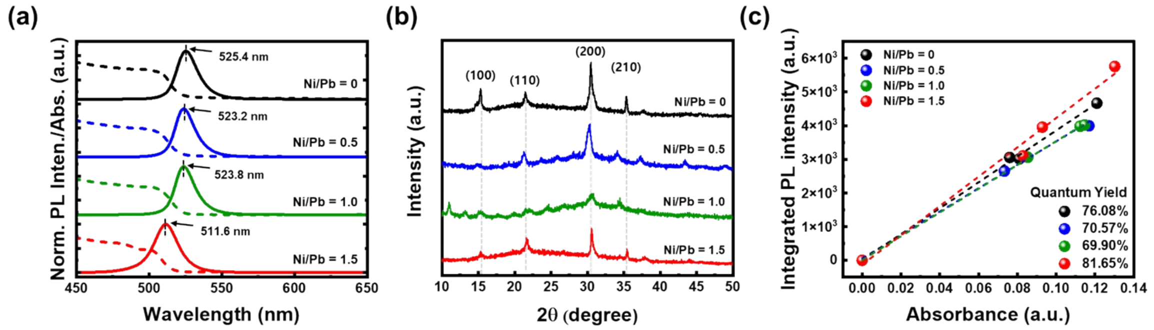

Fig. S1. (a) Normalized photoluminescence (PL) intensity/absorbance spectra, (b) X-ray diffraction (XRD) pattern, (c) relative quantum yield plots for the synthesized OA-CsPb$_{1-x}$Ni$_x$Br$_3$ perovskite quantum dots (PQDs) solution with various Ni/Pb ratios (0, 0.5, 1.0, and 1.5).

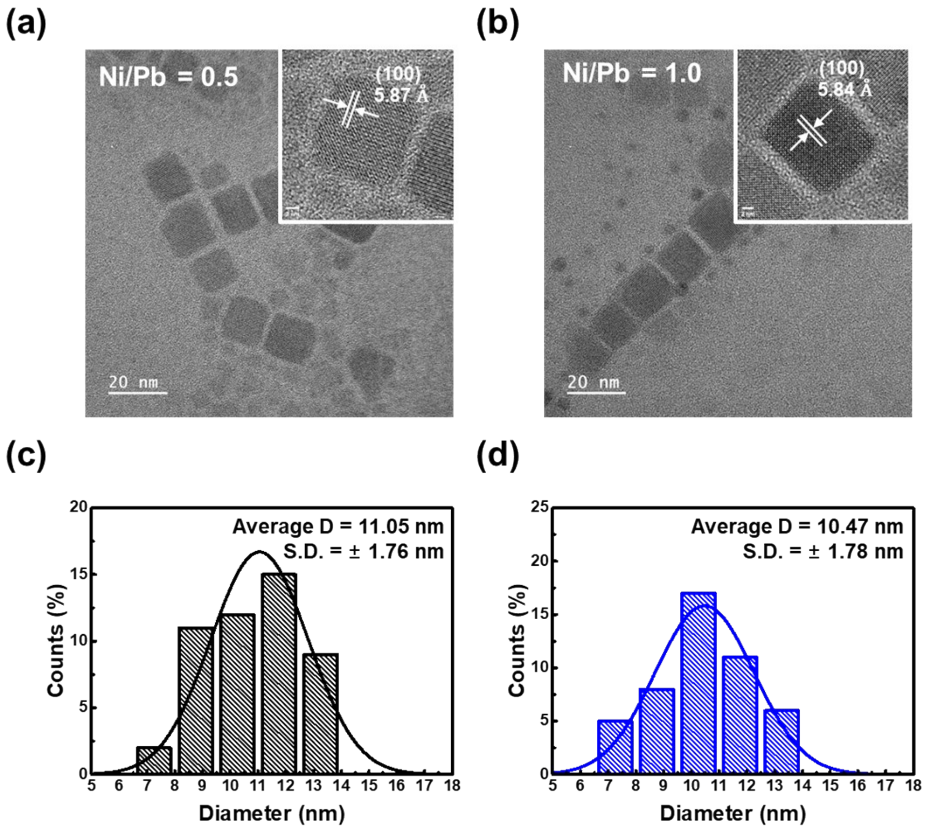

Fig. S2. Transmission electron microscopy (TEM) images and particle size distribution of (a), (c) Ni/Pb = 0.5, (b), (d) Ni/Pb = 1.0 ratio of the OA-$CsPb_{1-x}Ni_xBr_3$ PQDs solution.

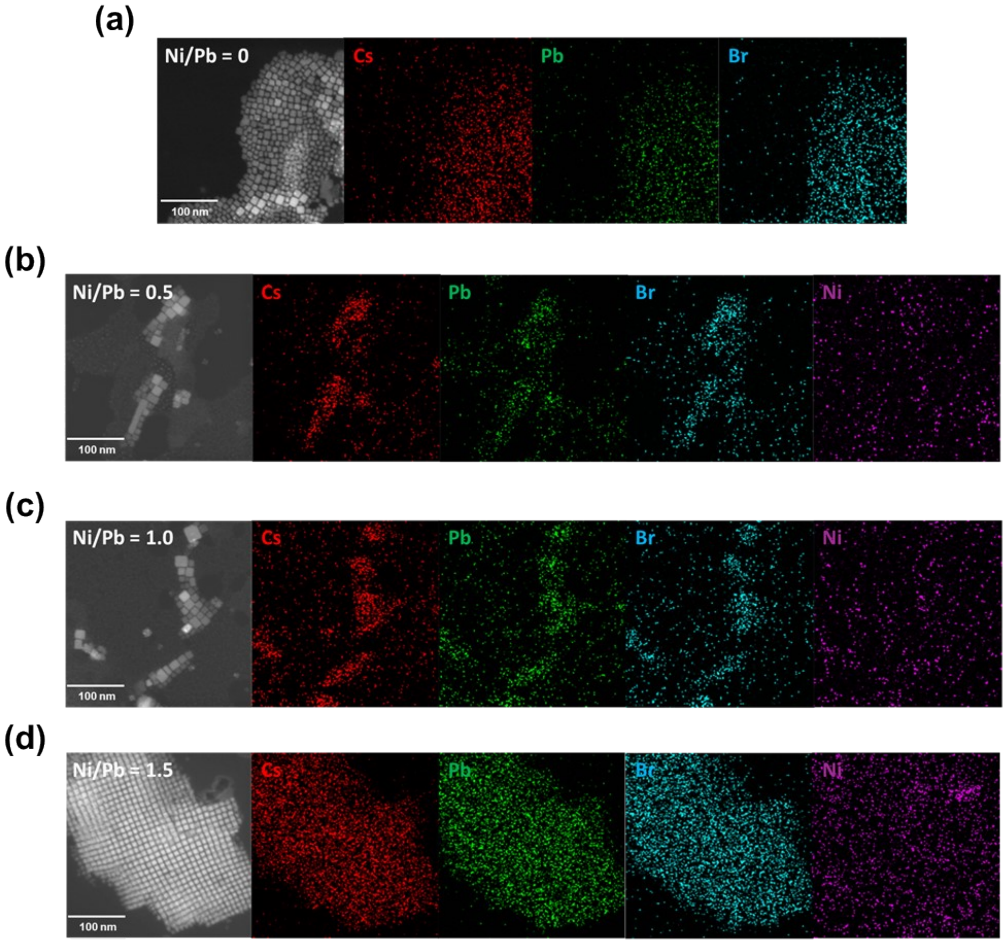

Fig. S3. High-angle annular dark-field scanning transmission electron microscopy (STEM-HAADF) images and mapping images of the OA-$CsPb_{1-x}Ni_xBr_3$ PQDs with (a) Ni/Pb = 0 (Cs, Pb, and Br), (b) Ni/Pb = 0.5 (Cs, Pb, Br, and Ni), (c) Ni/Pb = 1.0 (Cs, Pb, Br, and Ni), and (d) Ni/Pb = 1.5 (Cs, Pb, Br, and Ni) ratio.

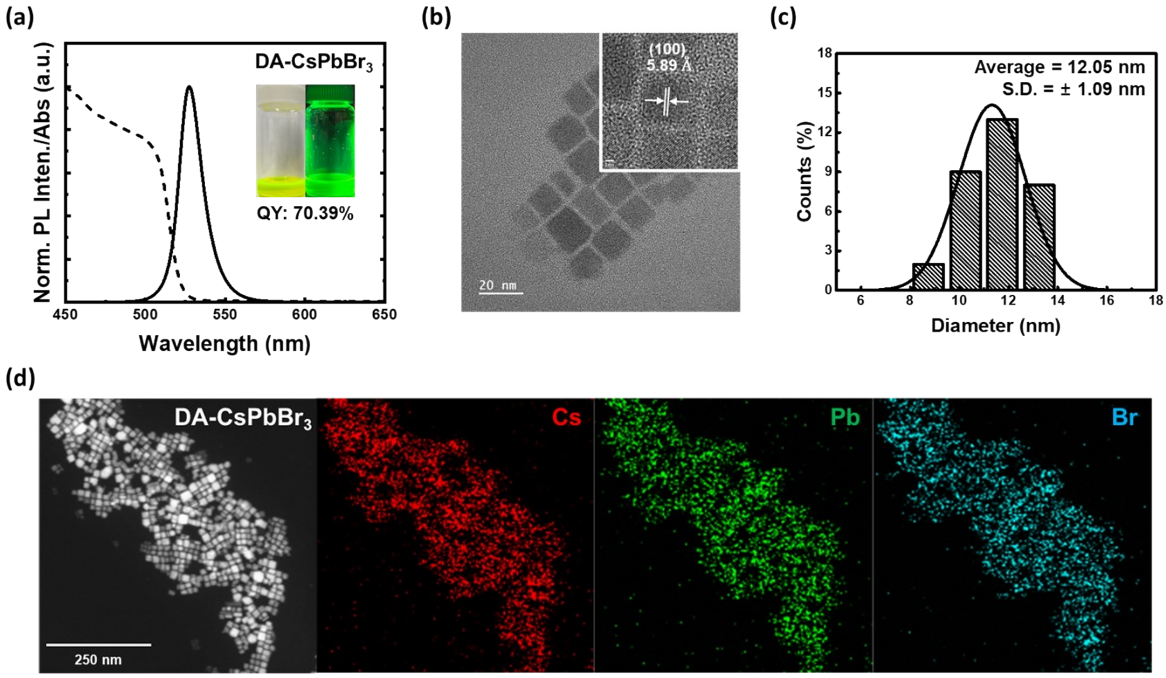

Fig. S4. (a) Normalized PL intensity/absorbance spectra, photograph (b) TEM image, (c) size distribution, and (d) STEM-HAADF mapping image (Cs, Pb, and Br) of DA-CsPbBr$_3$.

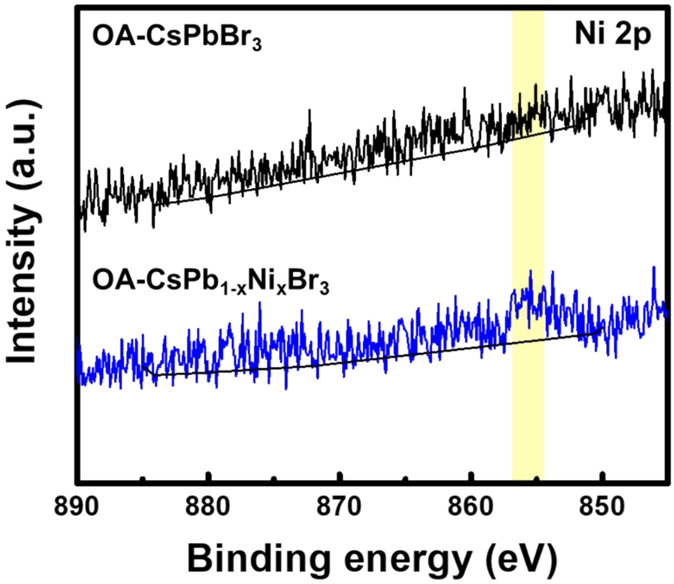

Fig. S5. XPS spectra of OA-CsPbBr$_3$ and OA-CsPb$_{1-x}$Ni$_x$Br$_3$ PQDs (Ni-2p).

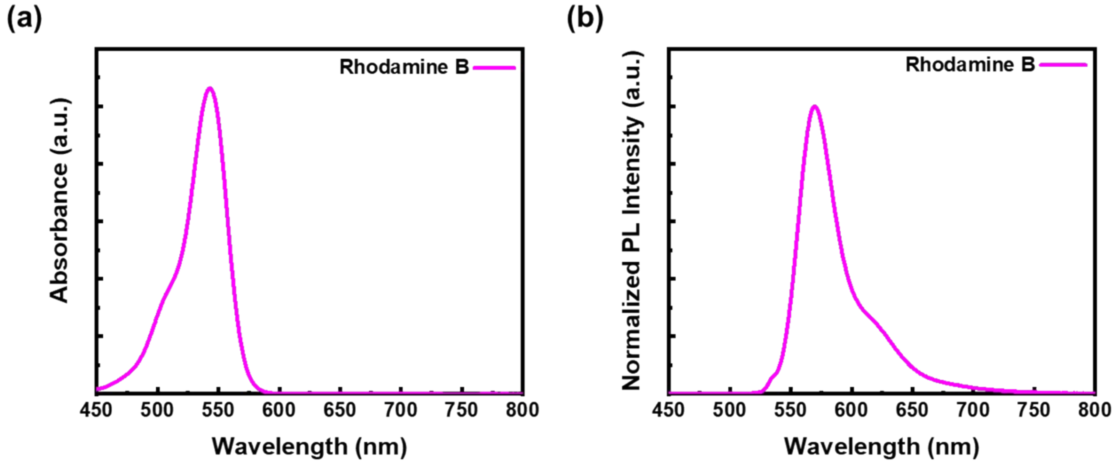

Fig. S6. (a) Absorption spectra and (b) normalized PL spectra of rhodamine B standard solution.

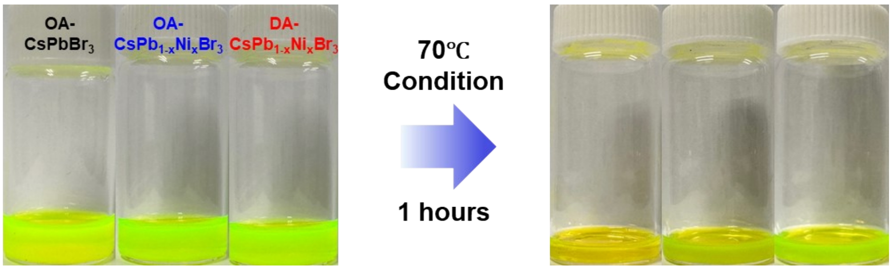

Fig. S7. Photograph of PQDs (OA-$CsPbBr_3$, OA-$CsPb_{1-x}Ni_xBr_3$, and DA-$CsPb_{1-x}Ni_xBr_3$) after thermal treatment under sunlight.

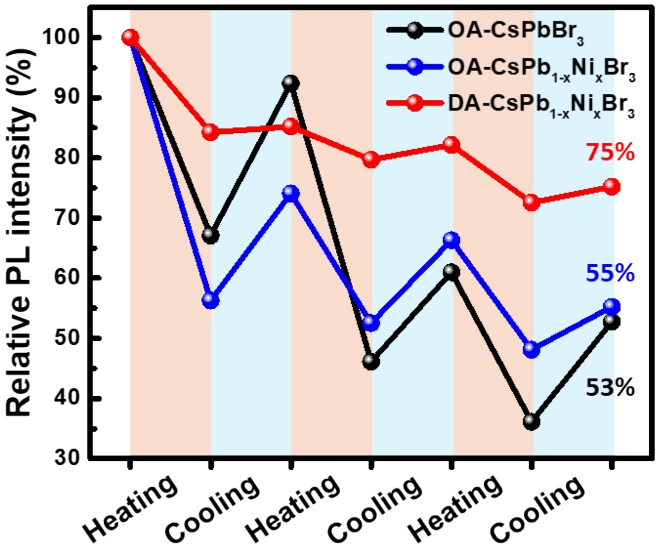

Fig. S8. PL intensity stability of temperature control cycle (heating, cooling) of OA-$CsPbBr_3$, OA-$CsPb_{1-x}NixBr_3$, and DA-$CsPb_{1-x}NixBr_3$ PQDs.

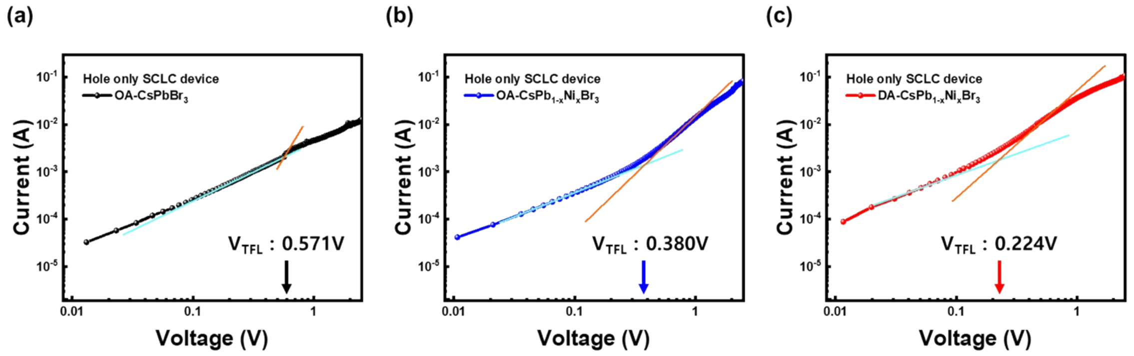

Fig. S9. J-V curves of a space-charge limited current (SCLC) device to measure the hole mobility of the ITO/QDs/MoO_3/Ag structures (a) OA-$CsPbBr_3$, (b) OA-$CsPb_{1-x}Ni_xBr_3$, and (c) DA-$CsPb_{1-x}Ni_xBr_3$ QDs.

Table S1. Factors value to calculate the relative QY of OA-$CsPb_{1-x}Ni_xBr_3$ PQDs with Ni/Pb ratio = 0, 0.5, 1.0, and 1.5.

Ni/Pb	**Solvent**	**Refractive index**	**Gradient (F/A)**	**Quantum Yield**
0	Hexane	1.375	3.86×10^4	0.761
0.5	Hexane	1.375	3.58×10^4	0.706
1.0	Hexane	1.375	3.55×10^4	0.699
1.5	Hexane	1.375	3.63×10^4	0.816

Table S2. Hole-only SCLC devices parameters of OA-$CsPbBr_3$, OA-$CsPb_{1-x}Ni_xBr_3$, and DA-$CsPb_{1-x}Ni_xBr_3$ QDs.

Sample	V_{TFL} (V)	Trap density (#/cm^3)	Hole mobility (cm^2/V·s)
OA-$CsPbBr_3$	0.571	2.12×10^{17}	5.17×10^{-6}
OA-$CsPb_{1-x}Ni_xBr_3$	0.380	1.41×10^{17}	1.74×10^{-5}
DA-$CsPb_{1-x}Ni_xBr_3$	0.224	8.30×10^{16}	3.95×10^{-5}