

ADVANCED MATERIALS

Supporting Information

for *Adv. Mater.*, DOI: 10.1002/adma.201801117

Spontaneous Self-Assembly of Perovskite Nanocrystals into
Electronically Coupled Supercrystals: Toward Filling the
Green Gap

*Yu Tong, En-Ping Yao, Aurora Manzi, Eva Bladt, Kun Wang,
Markus Döblinger, Sara Bals, Peter Müller-Buschbaum,
Alexander S. Urban, Lakshminarayana Polavarapu,* and
Jochen Feldmann*

Copyright WILEY-VCH Verlag GmbH & Co. KGaA, 69469 Weinheim, Germany, 2018.

Supporting Information

Spontaneous Self-assembly of Perovskite Nanocrystals into Electronically Coupled Supercrystals: Toward filling the Green Gap

Yu Tong, En-Ping Yao, Aurora Manzi, Eva Bladt, Kun Wang, Markus Döblinger, Sara Bals, Peter Müller-Buschbaum, Alexander S. Urban, Lakshminarayana Polavarapu, and Jochen Feldmann*

Materials: Cs₂CO₃ (Cesium carbonate, 99%), PbCl₂ (lead (II) chloride, 98%), PbBr₂ (lead (II) bromide 98%), PbI₂ (lead (II) iodide 99%), 1-octadecene (technical grade 90%), oleic acid (technical grade 90%), oleylamine (technical grade 70%), acetone (HPLC, ≥99.8%), hexane (HPLC, grade ≥97.0%, GC), ethyl acetate (HPLC, ≥99.7%), nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O), ethylene glycol (reagent grade, ≥99.7%), ethylenediamine (≥99%), polyethylenimine (branched), zinc oxide nanoparticles dispersion (40 wt. % in butyl acetate) and LiF (Lithium fluoride, 99.99% were purchased from Sigma-Aldrich and used as received. The ZnO colloidal dispersion obtained from Sigma-Aldrich was diluted 10 times with ethyl acetate. PEDOT:PSS solution was purchased from Heraeus (Germany) and filtered before use. ITO glasses were purchased from SOLEMS (France), while the ITO coated PET flexible substrates were purchased from Solaronix (Switzerland). TPBi was purchased from Ossila (UK).

Synthesis of CsPbBr₃ supercrystals: The synthesis of CsPbBr₃ supercrystals (SCs) takes the merits of single-step ultrasonication assisted synthesis of perovskite nanocrystals (NCs), as reported in our previous work^[1, 2] In a typical synthesis, 10 ml of 1-octadecene, 1.5 ml of oleic acid and 1.5 ml of oleylamine were added to a mixture of 1 mmol of Cs₂CO₃ and 3 mmol of PbBr₂ precursor powders in a 20 ml glass bottle. The resultant mixture was subjected to tip sonication (SONOPULS HD 3100, BANDELIN) at a power of 30 W for 30 minutes, as

shown in Figure S1.^[2] During the sonication, the white color precursor powders dissolved in octadecene and the reaction mixture gradually transformed to yellow, indicating the formation of perovskite colloidal NCs. After 30 min of sonication, the reaction medium was cooled down to room temperature and then centrifuged at 6000 rpm for 15 min. The resultant sediment containing colloidal perovskite was dispersed in 3 ml of hexane for optical and morphological characterization. In order to obtain perovskite powders, the sediment was gently washed twice with hexane and ethyl acetate (to remove excess residual ligands) by centrifugation at 3000 rpm, and the obtained sediment was dried in air. It is worth mentioning that the purification of SCs by centrifugation was easier due to their heavy mass as compared to isolated NCs.

Composition tuning through halide ion exchange: At first, the halide ion (Cl & I) precursor solutions were prepared by dissolving 0.3 mmol of PbCl₂ or PbI₂ powers in a mixture of 10 ml of hexane, 0.3 ml of oleylamine and 0.3 ml of oleic acid at 100 °C under continuous stirring, as reported in our previous work.^[1] Then, the appropriate volume of halide (Cl & I) precursor solution was added to the as-synthesized CsPbBr₃ assemblies under vigorous stirring for 20 min. The halide ion exchange process can be clearly seen by the color change upon the addition of precursor solution. After the competition of ion exchange process, the SC colloids were purified by centrifugation at 6000 rpm for 15 min. The resultant sediment was dispersed in hexane for further characterization.

Preparation of bulk large size CsPbBr₃ colloidal crystals and thin films:

The bulk CsPbBr₃ colloidal crystals were also synthesized by modifying the tip-sonication approach developed by our group.^[1, 2] We have found that the size of the perovskite NCs increased by decreasing the concentration of ligand with respect to precursors. In typical synthesis, 10 ml of 1-octadecene, 0.5 ml of oleic acid and 0.5 ml of oleylamine were added to a mixture of 1 mmol of Cs₂CO₃ and 3 mmol of PbBr₂ precursor powders in a 20 ml glass bottle, followed by tip-sonication for 30 min. After completion of reaction, the product was

purified by centrifugation at 2000 rpm and the sediment was redispersed in hexane, yielding the CsPbBr₃ colloidal crystals. The purification process was repeated twice and the resultant sediment was dispersed in hexane for optical and morphological characterization. The bulk CsPbBr₃ film were prepared by annealing the NC film at 180 °C for 30 min, as reported previously.^[3]

Fabrication of light emitting diodes (LEDs):

First of all, selected area of indium tin oxide (ITO) coated substrates were etched using hydrochloride acid and zinc powders. Then, the substrates were ultrasonically cleaned with detergent, deionized water, acetone, and isopropyl alcohol. The substrates were further cleaned with oxygen plasma treatment. The cleaned substrates were used for the fabrication of LEDs both on rigid and flexible substrates by two different process as discussed below.

a) *Solution-processed method*: The device architecture can be seen in Figure 4a. At first, NiO_x precursor (1M nickel (II) nitrate hexahydrate in ethylene glycol with 50 µl/ml ethylenediamine) was spin-coated on ITO substrates at 4000 rpm followed by annealing at 300 °C for 1h, as described in the previous work.^[4] Then, a 10-time diluted CsPbBr₃ perovskite SC or isolated CsPbBr₃ NC colloidal dispersion was spin-coated on top of NiO_x at 6000 rpm. Afterwards, the PEI solution (20mg/ml in acetone) was spin-coated at 4000 rpm, followed by a subsequent spin-coating of ZnO NP colloid layer at 5000 rpm. The device fabrication ended with a thermal evaporation of Ag as cathode.

b) *Flexible LEDs*: The device architecture can be seen in Figure S14a. At first, PEDOT:PSS was spin-coated onto ITO coated PET substrate at 4000 rpm, and then annealed at 140 °C for 20 min. Then, the colloidal SC or NC dispersion was spin-coated at 6000 rpm, followed by a thermal evaporation of TPBi, LiF, and Ag to complete the fabrication of flexible LEDs.

Optical characterization: The extinction spectra of the samples were measured using Cary 5000 UV-Vis-NIR spectrophotometer. The PL and PL quantum yield measurements were performed using Varian Cary Eclipse fluorescence spectrophotometer (Agilent Technologies)

and Fluorolog-3 FL3-22 (Horiba Jobin Yvon GmbH) spectrometer equipped with an integrating sphere, respectively. Electroluminescence (EL) of the prepared LEDs were recorded using Fluorolog-3 FL3-22 spectrometer at different voltages (using Keithley 2400 Sourcemeter). Time-resolved PL measurements were performed using a time-correlated single photon counting (TCSPC) system (PicoQuant PicoHarp 300) by exciting the colloidal samples with a NKT photonics femtosecond pulsed laser.

Morphological characterization: The morphology of the prepared perovskite crystals were characterized by bright field transmission electron microscopy (BF-TEM) (JEOL JEM-1011 with an 80kV accelerating voltage), high angle annular dark field scanning TEM (HAADF-STEM) (cubed FEI Titan microscope operating at 300 kV) and scanning electron microscopy (SEM) using a Gemini Ultra Plus at an electron accelerating voltage of 3 kV. X-ray diffraction (XRD) measurements were performed with a BRUKER D8 ADVANCE diffractometer using 8 keV Cu-K α X-ray source. The reference cubic and orthorhombic phase CsPbBr₃ XRD patterns were taken from the crystallography open database (COD).

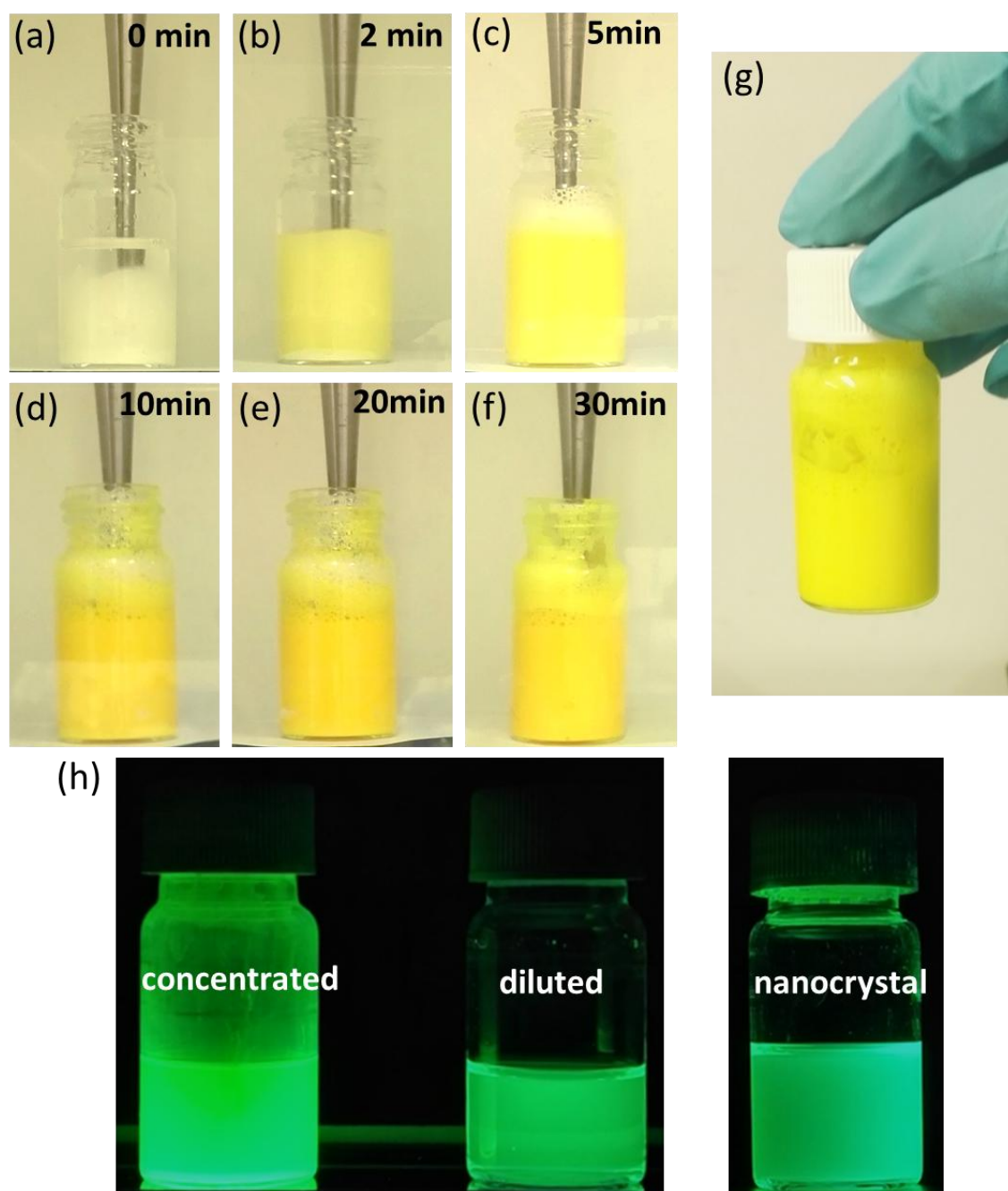


Figure S1. a-f) Photographs of the reaction medium recorded at different reaction times of CsPbBr₃ SC synthesis. g) Photograph of the as-prepared SC colloidal dispersion after completion of the reaction. h) Photographs of the as-prepared, diluted SC and NC colloidal dispersion under UV-light (367 nm) illumination. One can see that concentrated SC colloidal solution exhibit pure green emission, whereas the diluted SC colloidal solutions shows cyan-green emission similar to the isolated NC colloidal dispersion.

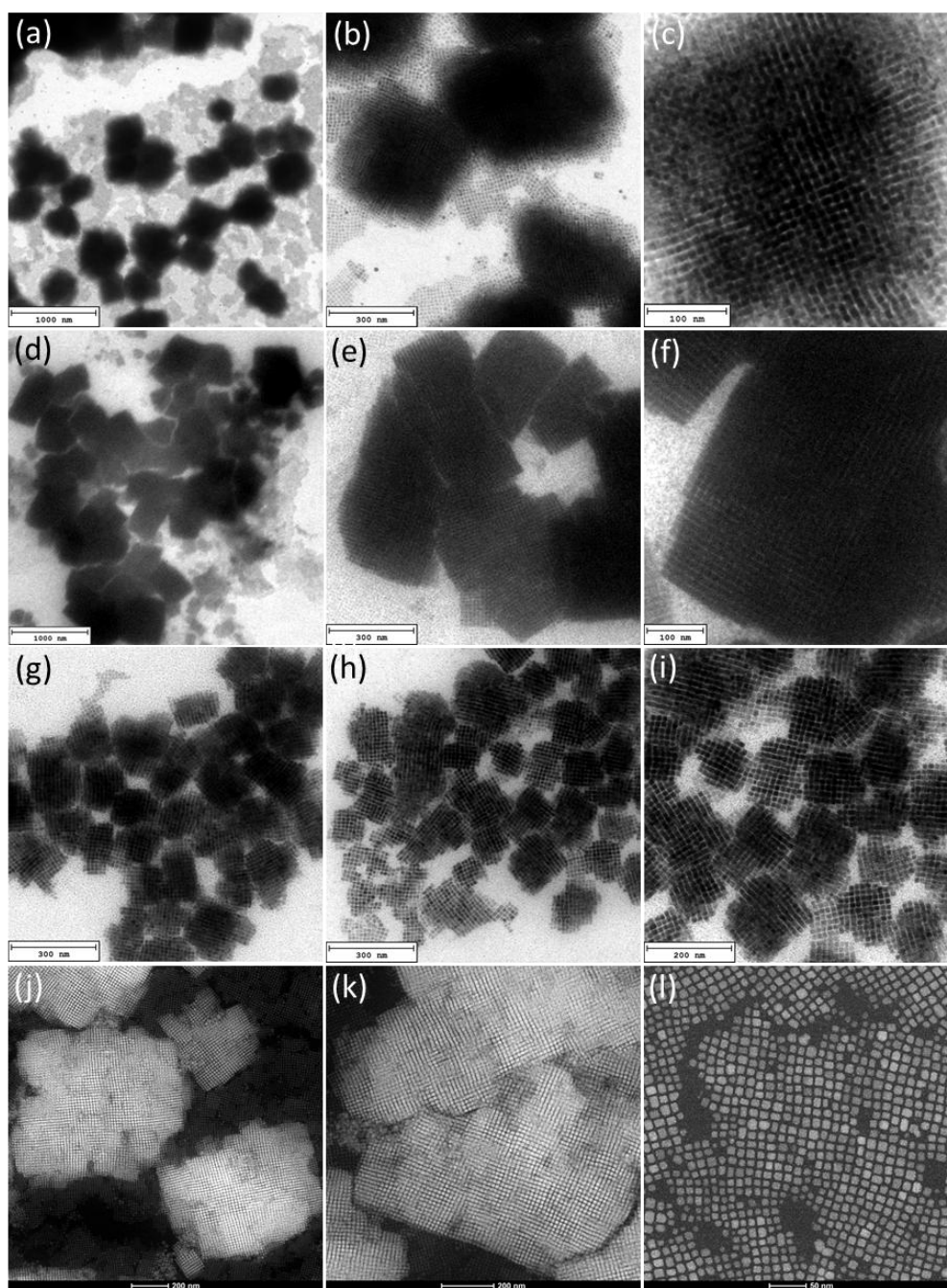


Figure S2. A broad overview of TEM (a-i) and HAADF-STEM (j & k) images of SCs in different magnifications. At low magnification, the SCs can be identified as large polyhedral crystals with dark color, however the structure of superlattices can't be clearly seen in both TEM and HAADF-STEM. Once zoomed in, one can see that the SCs are actually made of nanocube building blocks. (l) HAADF-STEM image of isolated CsPbBr₃ NCs obtained at low precursor concentration. The different between isolated NCs and SCs can be clearly seen in the images.

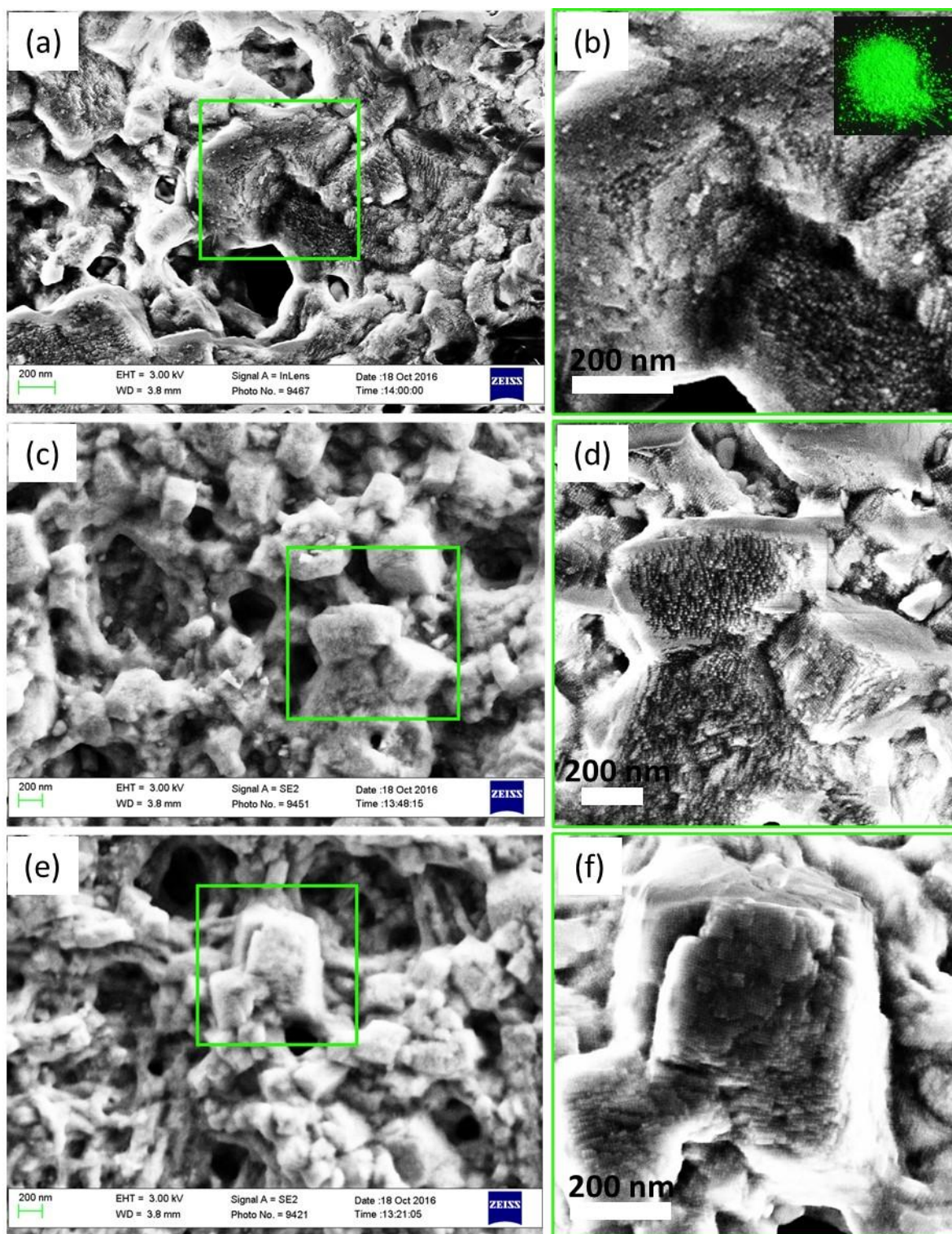


Figure S3. A broad overview of SEM images of SCs with different magnifications. The polyhedral shape of the supercrystals can be seen at low magnification (a, c and e), while the images recorded at higher magnification (b, d and f) shows that these polyhedral crystals are made of NC repeating units of size 10-15 nm.

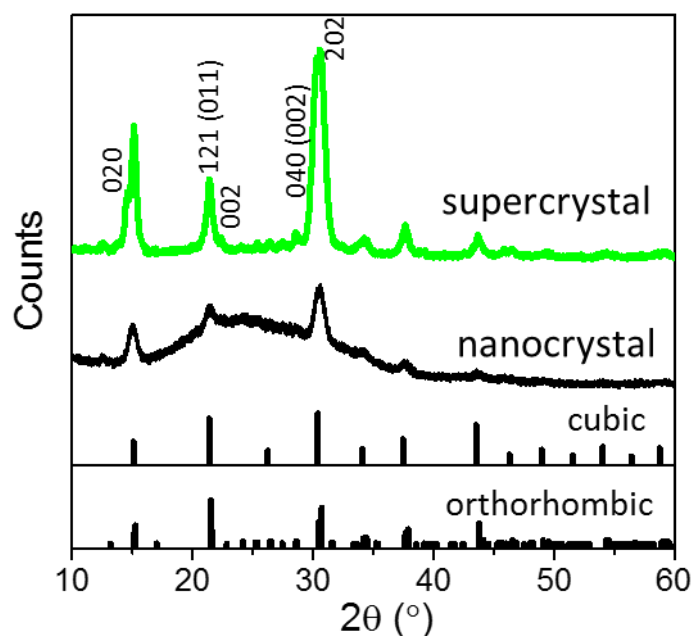


Figure S4. XRD data of SC film in comparison with nanocrystal. The patterns of cubic and orthorhombic phase CsPbBr₃ perovskite are also shown as references. Both SC and NC films show similar Bragg peak positions assigning to either orthorhombic or cubic phase. The SC films show background free XRD peaks due to high density of the NCs in the films. The diffraction peaks are indexed based on the reference pattern of orthorhombic phase while the Miller indices in brackets represent the cubic phase.

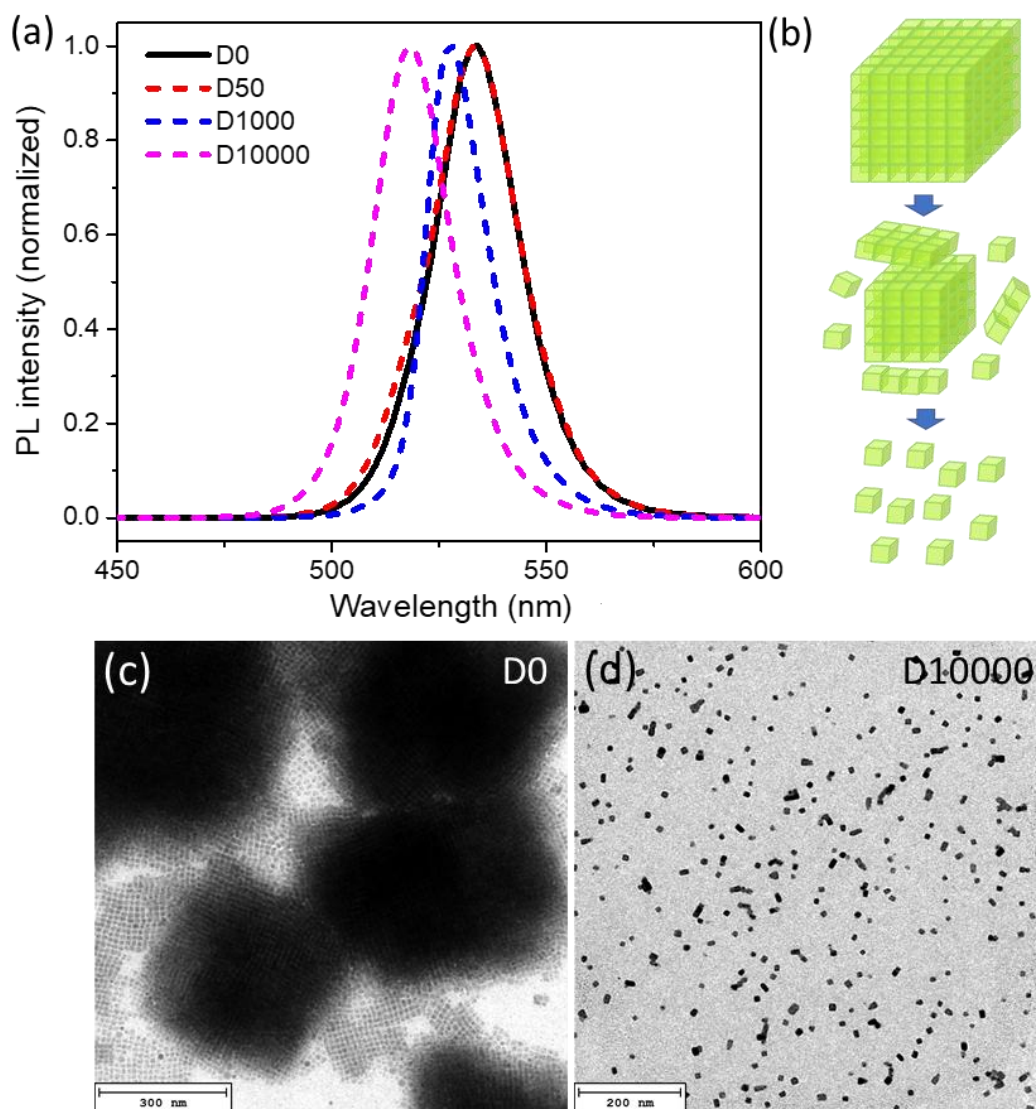


Figure S5. (a) PL spectra of SC colloidal dispersions of different dilutions (0 to 10000). (b) Schematic illustration showing the disassembly of SCs into NCs by dilution. (c and d) corresponding TEM images of the colloids before and after dilution (D10000 times), respectively.

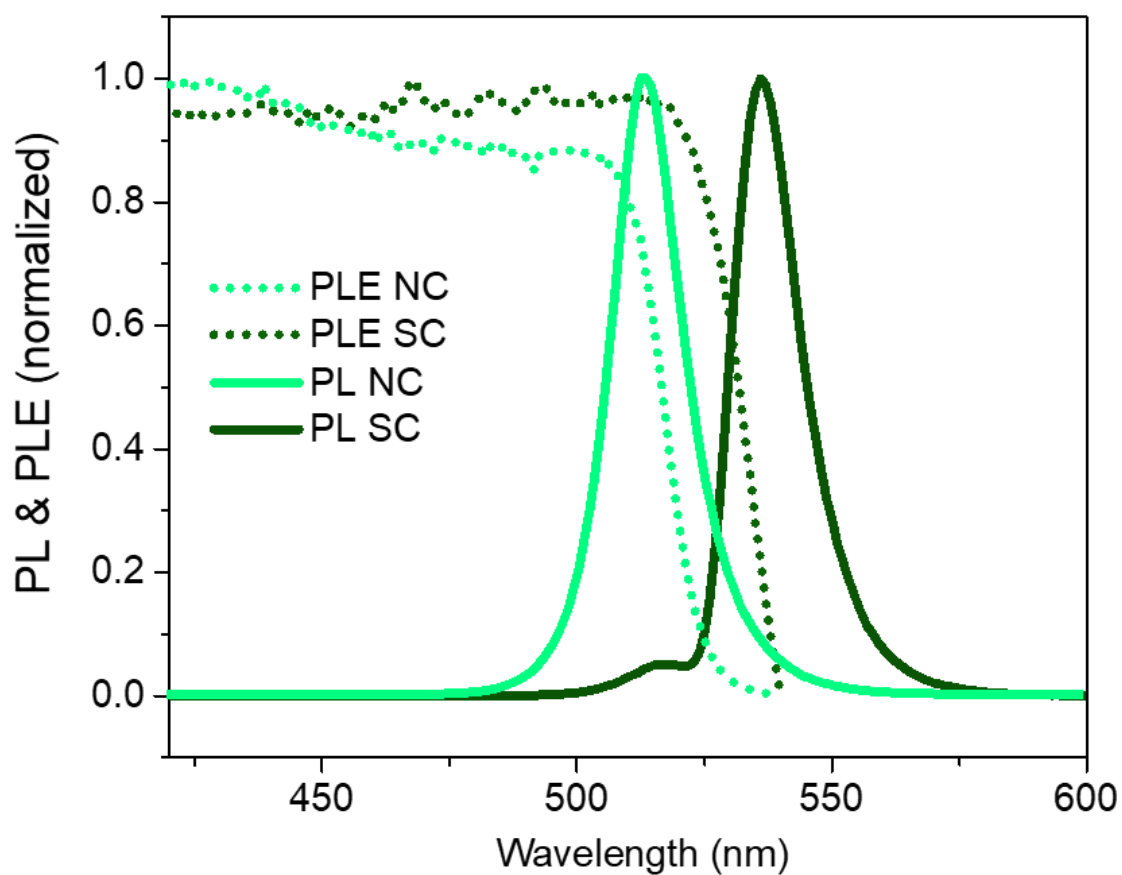


Figure S6. Photoluminescence excitation (PLE) (dotted lines) and PL spectra (solid lines) of NC (light green color) and SC (dark green color) films. It can be seen that the PLE of the SCs exhibit obvious redshift compared with that of the uncoupled NCs.

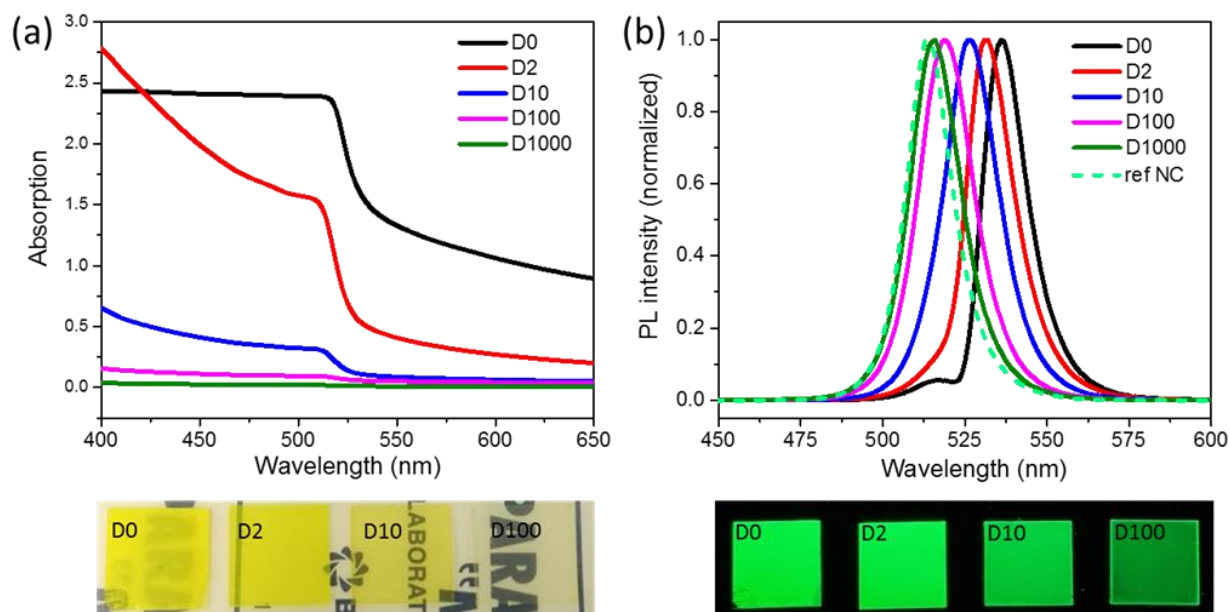


Figure S7. a) Absorption spectra of perovskite films prepared by spin-coating SC colloidal dispersion with varied dilutions (top) and the photograph of the films (bottom) recorded under room light. b) The corresponding PL spectra (top) and the photograph of the films (bottom) under UV light illumination. The PL spectra are normalized with respects of the perovskite film made of isolated NCs, which is also presented as a reference. Both the absorption onset and the PL peak position of the film show continuous blueshift with increasing dilution, and the PL spectra of the films made of diluted SCs (D1000) resembles that of isolated NC films, suggesting that the SCs disassemble into isolated NCs by dilution.

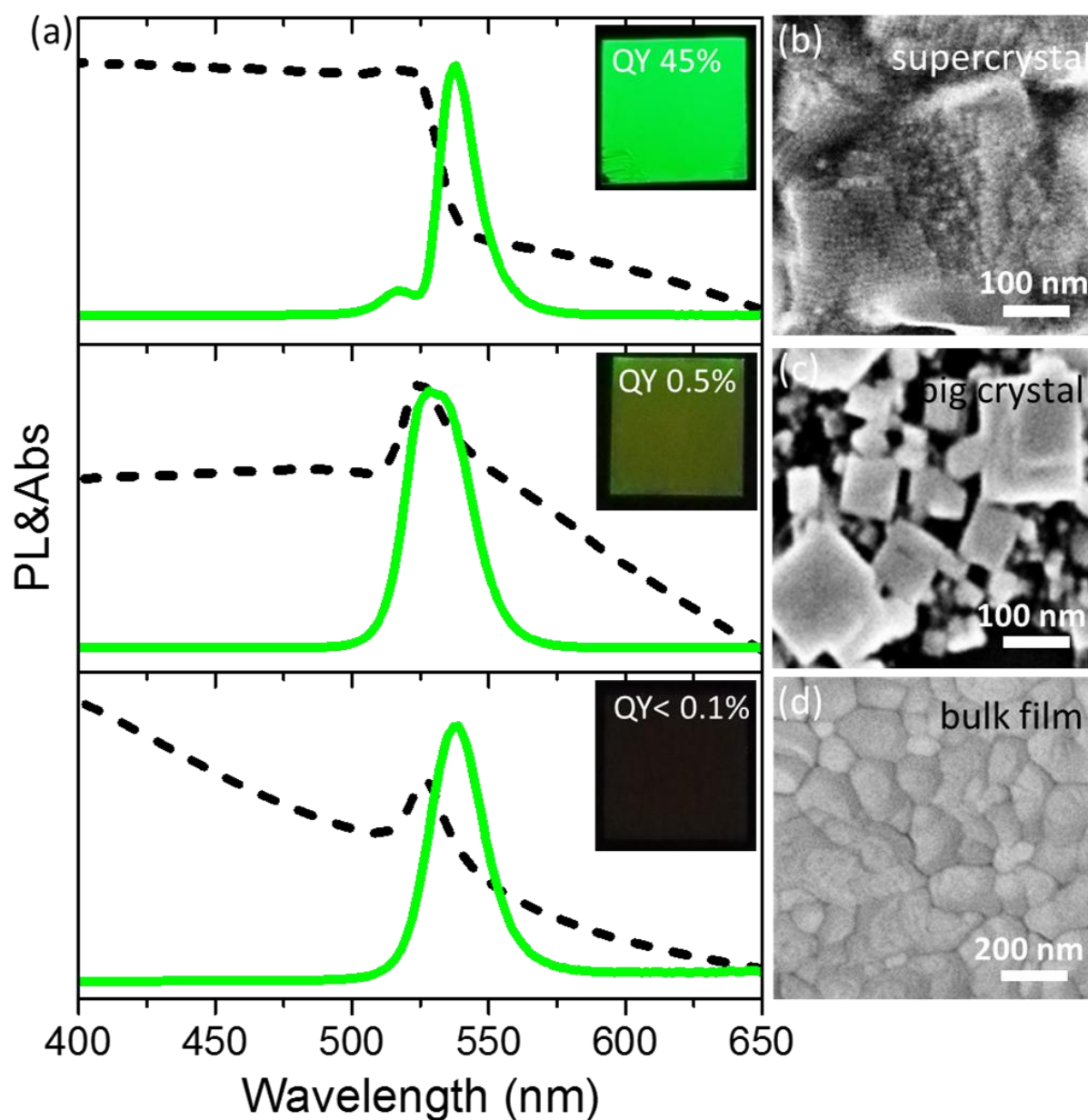


Figure S8. Comparison of morphology and optical properties between CsPbBr₃ perovskite made of SCs, bulk-like large crystals and bulk films of. a) Absorption and PL spectra of SCs (top), large colloidal crystals (middle) and bulk film (bottom). The insets show the photographs of the films under UV (367 nm) light illumination and PL quantum yield of the each sample. (b-d) SEM images of the corresponding films shown in (a).

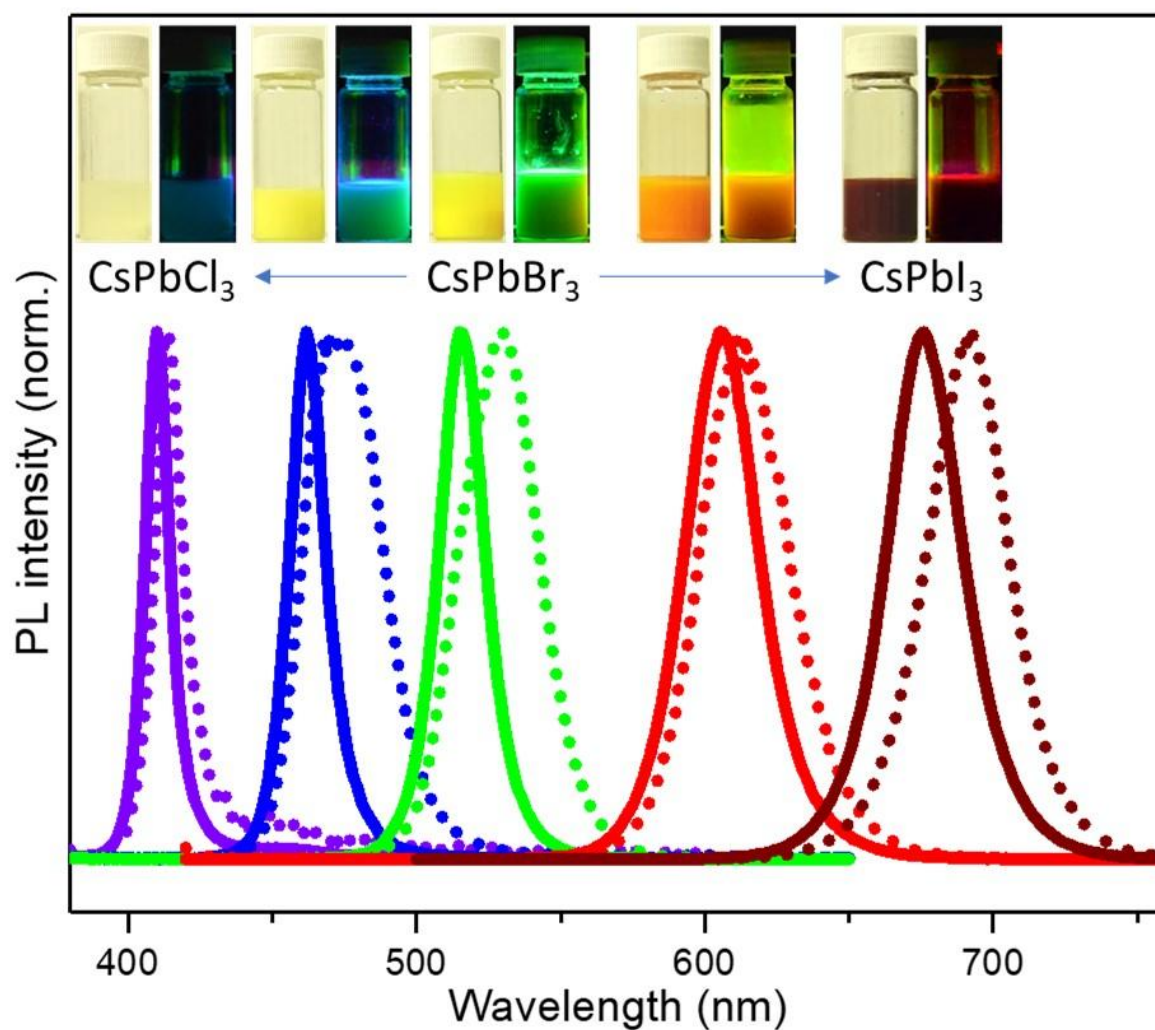


Figure S9. PL spectra of the concentrated (dotted lines) and diluted (solid lines) CsPbX₃ SC colloidal dispersions obtained by halide ion exchange on the CsPbBr₃ SC colloids. The photographs of the concentrated CsPbX₃ SC colloidal dispersions with different halide compositions under room light and UV illumination are shown in the inset.

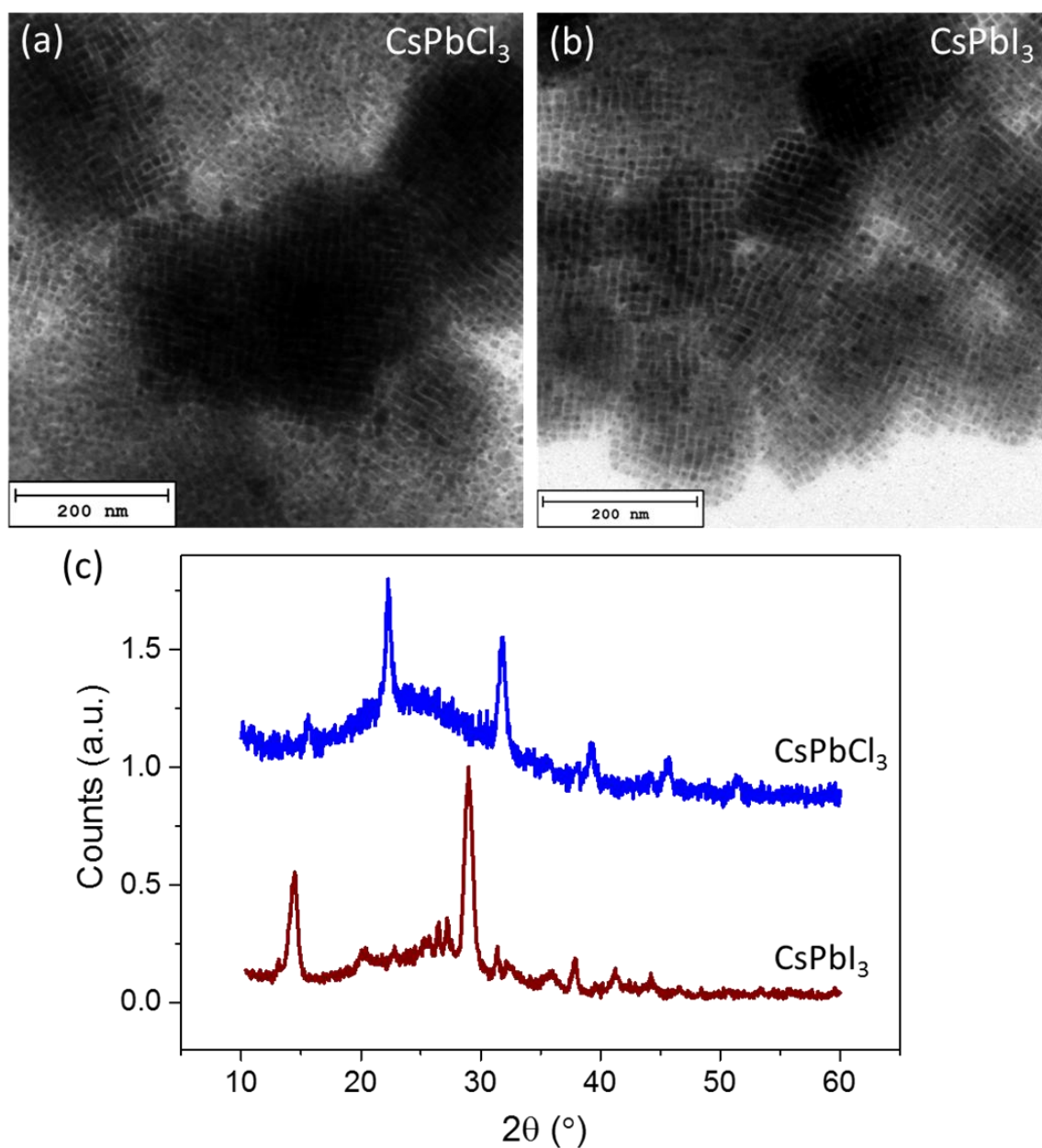


Figure S10. TEM images (a, b) and XRD patterns (c) of the CsPbCl₃ and CsPbI₃ SCs obtained by halide ion exchange on the as-synthesized colloidal CsPbBr₃ SCs. As shown by TEM images, assemblies can still be maintained after ion exchange. The XRD data demonstrate that the crystalline phase (orthorhombic or cubic) of the NCs in the assemblies remains unchanged after ion exchange.

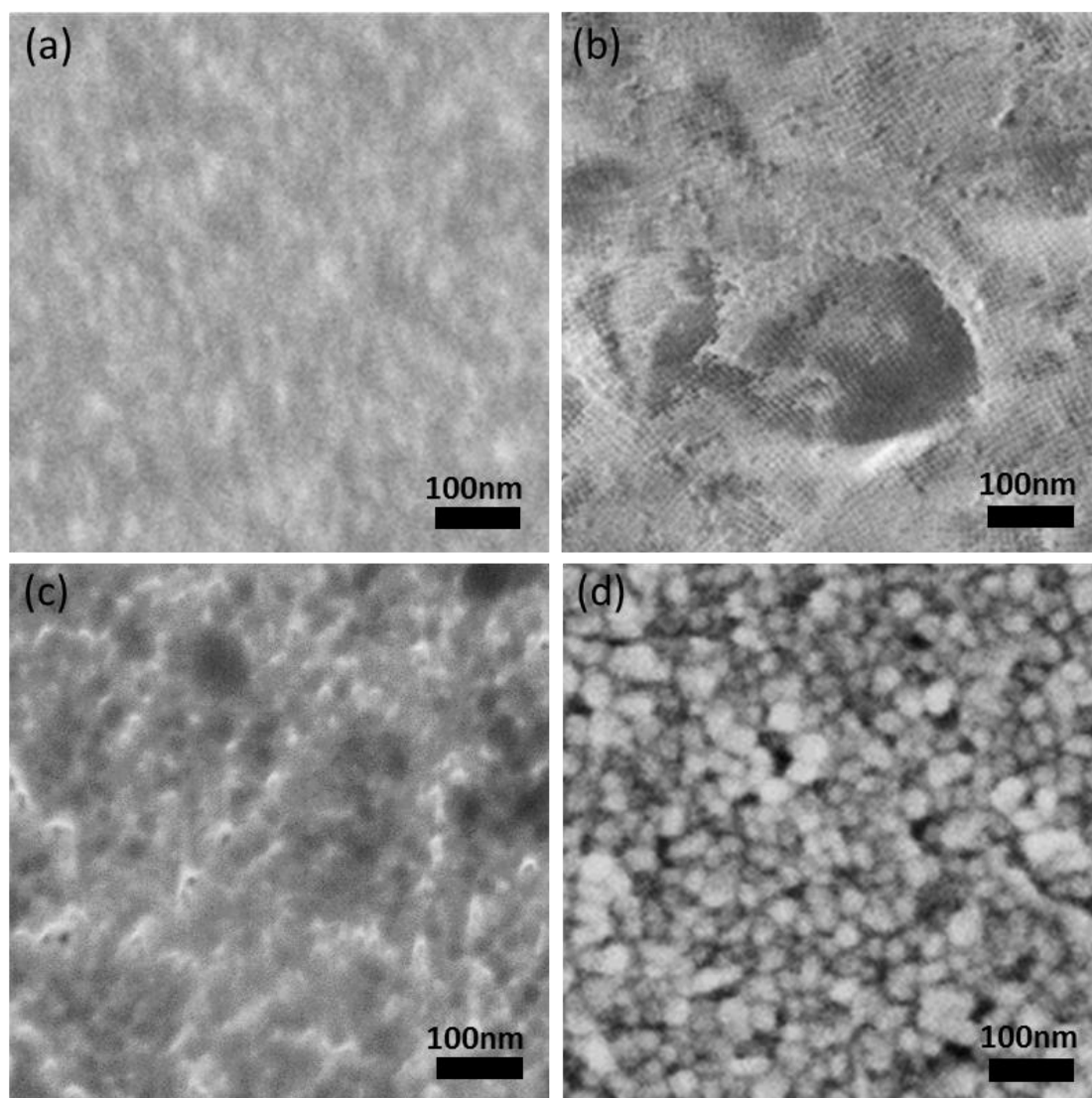


Figure S11. Top view SEM images of each functional layers in the solution-processed LED device. a) NiO_x b) perovskite c) PEI d) ZnO. It can be seen that each layer shows reasonable uniformity and pinhole free morphology. Especially, the perovskite film shows closely packed SCs exhibiting electronic coupling as aforementioned and manifests the pure green EL.

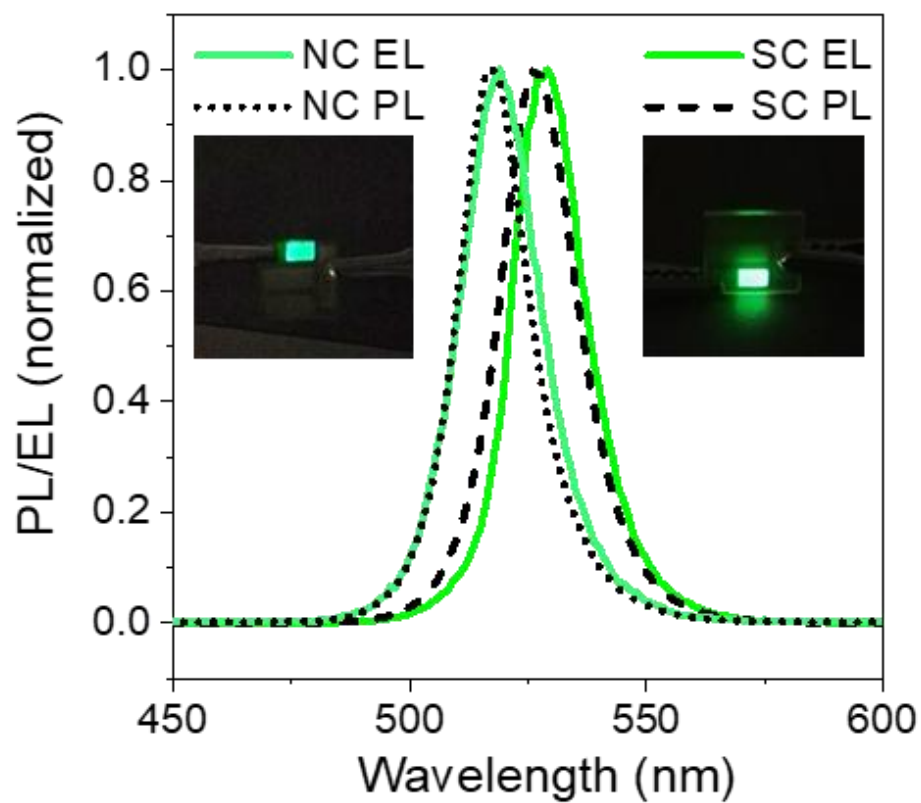


Figure S12. Comparison of the EL of LEDs fabricated using perovskite SCs and isolated NCs in the emitting layer. Both the NC and SC LEDs show strong, bright PL and EL. Insets show the photographs of the LEDs made of NCs and SCs.

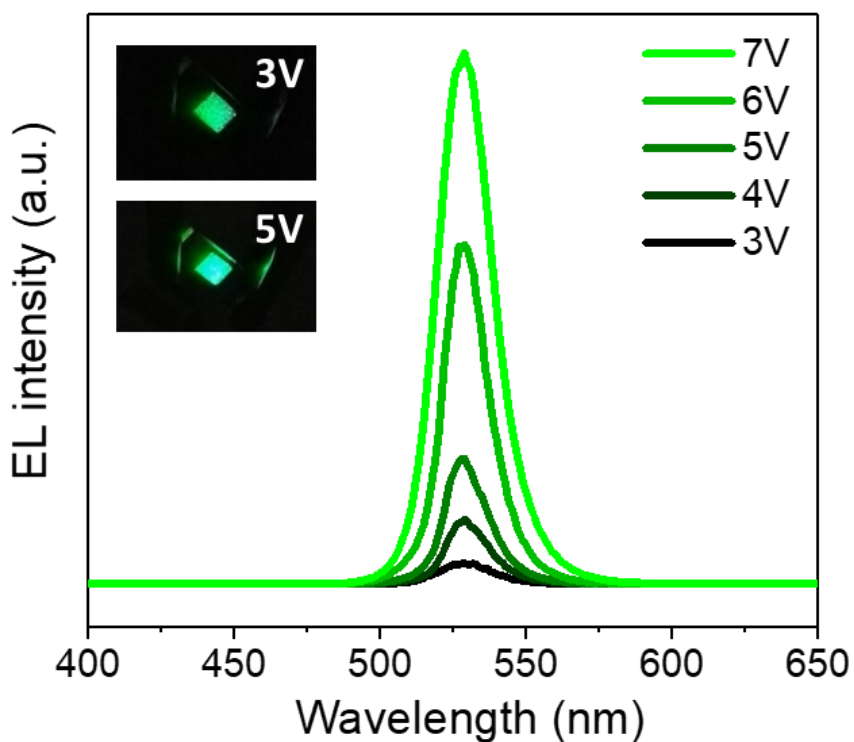


Figure S13. EL spectra of the solution-processed LED made of CsPbBr₃ SCs at different driving voltage. The EL intensity increased dramatically with the driving voltage while the peak position almost maintained the same at 530nm. Insets are the photos of the LED working at 3V (top) and 5V (bottom).

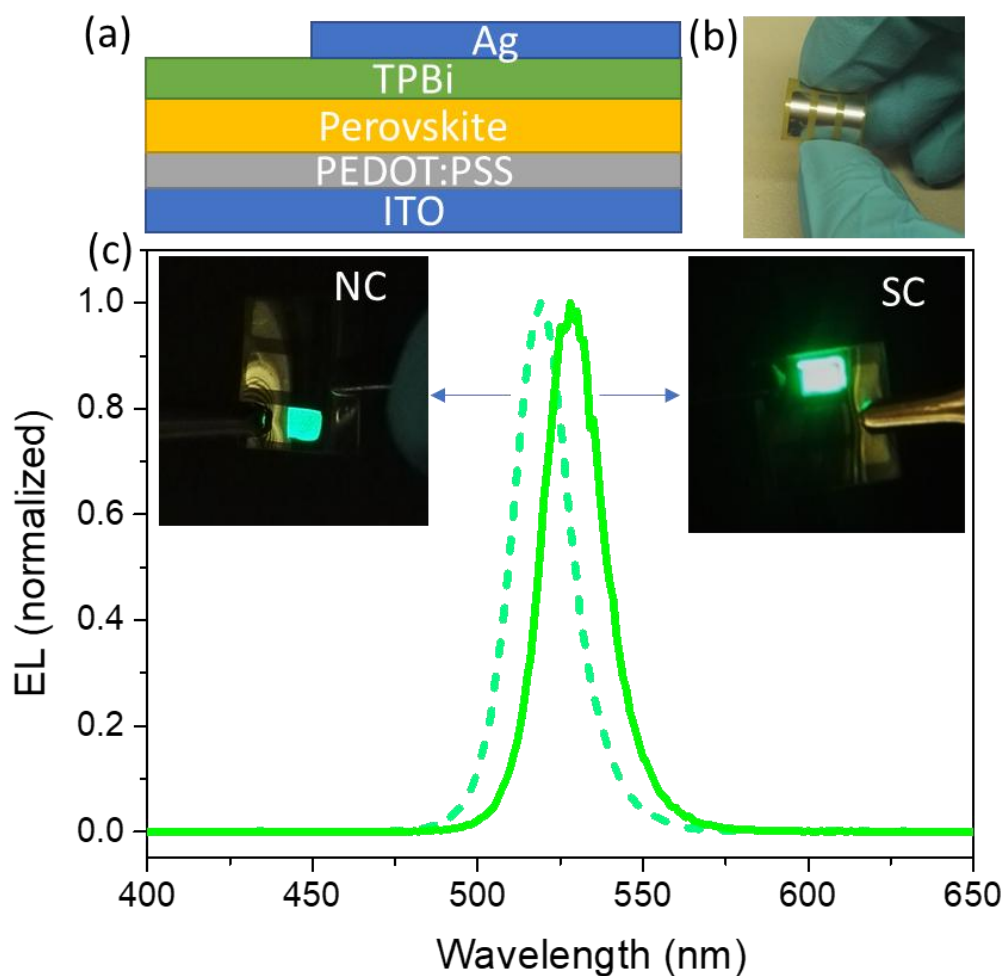


Figure S14. (a) Device architecture of flexible LED made out of CsPbBr₃ NCs or SCs. (b) Photograph of the fabricated flexible LED. (c) EL spectra of the flexible LEDs made out of CsPbBr₃ NCs (dashed line) or SCs (solid line). Photographs of the corresponding flexible LEDs working at a certain bending angle are shown in the insets.

References

- [1] Y. Tong, B. J. Bohn, E. Bladt, K. Wang, P. Müller-Buschbaum, S. Bals, A. S. Urban, L. Polavarapu, J. Feldmann, *Angew. Chem. Int. Ed.* **2017**, *56*, 13887.

- [2] Y. Tong, E. Bladt, M. F. Aygüler, A. Manzi, K. Z. Milowska, V. A. Hintermayr, P. Docampo, S. Bals, A. S. Urban, L. Polavarapu, J. Feldmann, *Angew. Chem. Int. Ed.* **2016**, 55, 13887.
- [3] J. B. Hoffman, G. Zaiats, I. Wappes, P. V. Kamat, *Chem. Mater.* **2017**, 29, 9767.
- [4] E.-P. Yao, Z. Yang, L. Meng, P. Sun, S. Dong, Y. Yang, Y. Yang, *Adv. Mater.* **2017**, 29, 1606859.