# Self-Assembled Halide Perovskite Quantum Dots in Polymer Thin Films Showing Temperature-Controlled Exciton Recombination

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## Materials and Methods

### Chemicals

We used the following chemicals without any further purification, such as Formamidine hydrobromide (FABr, TCI, >98.0%), lead (II) bromide ($PbBr_2$, Sigma-Aldrich, ≥98%), *n*-octylamine hydrobromide (TCI, >98.0%), oleic acid (TCI, >85.0%), polybutadiene (PBD, Sigma-Aldrich, average $M_w$ ~200,000), dehydrated *N, N*-dimethylformamide (DMF, Fujifilm Wako), 1-octadecene (TCI, >90.0%), acetone (Fujifilm Wako, ≥99.5%), hexane (Fujifilm Wako, >96.0%), and toluene (Fujifilm Wako, ≥99.5%).

### Synthesis procedure of $FAPbBr_3$ PQDs

Colloidal $FAPbBr_3$ perovskite quantum dots (PQDs) were synthesized by a modified hot injection method.[5] The precursor solution was prepared by dissolving FABr (0.2 mmol, 25 mg) and $PbBr_2$ (0.2 mmol, 73.4 mg) in 400 µL of dry DMF. *n*-octylammonium bromide (0.12 mmol, 25.2 mg), oleic acid (0.63 mmol, 200 µL), and 4 mL of 1-octadecene were mixed in a three-neck flask. This ligand solution was kept under a vacuum for 15 min and then continuously stirred at 80 °C under argon flow for 10 min. The precursor solution was added to the ligand solution. Then, a mixture (1:1 v/v) of acetone and hexane was added and immediately transferred into an ice water bath to quench the reaction. 100 µL of the as-prepared PQD solution was added to the 3 mL of toluene under vigorous stirring. The solution was centrifuged

at 14500 rpm for 5 min, and the supernatant that includes DMF was discarded. The precipitate was redispersed in toluene for further studies.

**Preparation of a PQD-PBD film**

The purified PQD solution (10 mg/mL) was mixed with 25 mg/mL PBD in toluene. The mixture was sonicated for 5 minutes. 5 μL of the mixture was dropped on a glass coverslip (25 × 50 $mm^2$).

**Characterization of PQDs**

The absorption and steady-state PL spectra of a PQD solution were recorded using a UV-vis spectrometer (Evolution 220, Thermo Fischer Scientific) and a fluorescence spectrometer (F-4500, Hitachi). The morphologies of PQDs were observed using a scanning transmission electron microscope (STEM, HD-2000 microscope, HITACHI) operated at 200 kV. We prepared STEM samples by dropping the PQD colloidal solution on the copper grid with carbon film (Okenshoji). X-ray diffraction (XRD) and small-angle x-ray scattering (SAXS) profiles of PQD film and PQD-polymer film were recorded on an X-ray diffractometer (SmartLab, RIGAKU) with a *Cu Kα* (λ = 0.15406 nm) X-ray source. Samples were deposited on glass slides and Kapton films for XRD and SAXS measurements, respectively.

**PL decay recording**

Time-resolved PL measurements were carried out on an inverted microscope (IX71, OLYMPUS). PL decays were measured by exciting the samples with femtosecond laser pulses (405 nm, 150 fs, 200 kHz) emitted from an optical parametric amplifier (Coherent OPA-9400). The PL from the sample was collected by 10x objective lens and passed through a 440 nm long-pass filter. Streak camera images of photons emitted from the excited samples were recorded for 2 min using an assembly of a polychromator (model 250IS, Chromex) and a Streak-camera (model C4334, Hamamatsu).

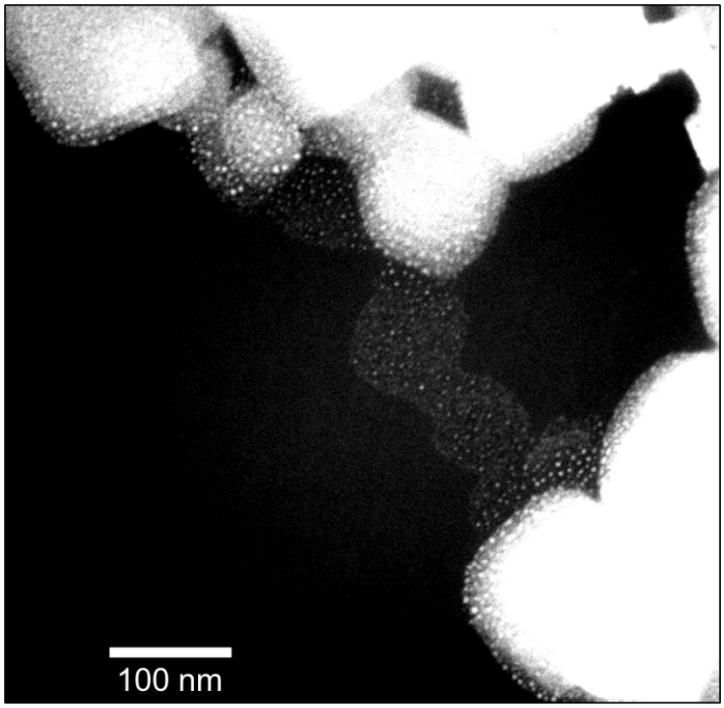


Fig. S1. A STEM image of a PQD-PBD thin film

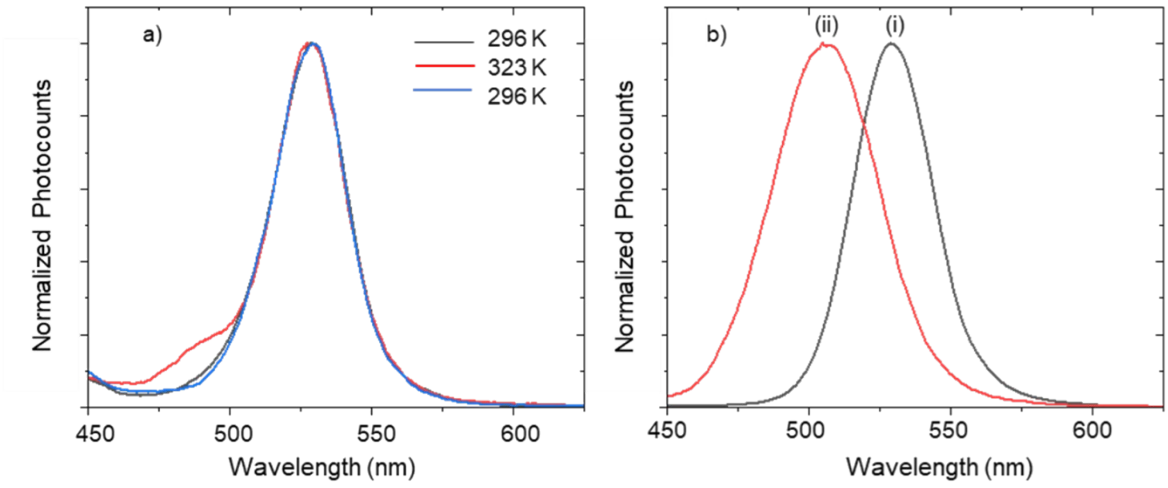


Fig. S2. PL spectra of a PQD-only film (a) at different temperatures and [b (i)] before and [b (ii)] after applying a lateral mechanical force > 4N.

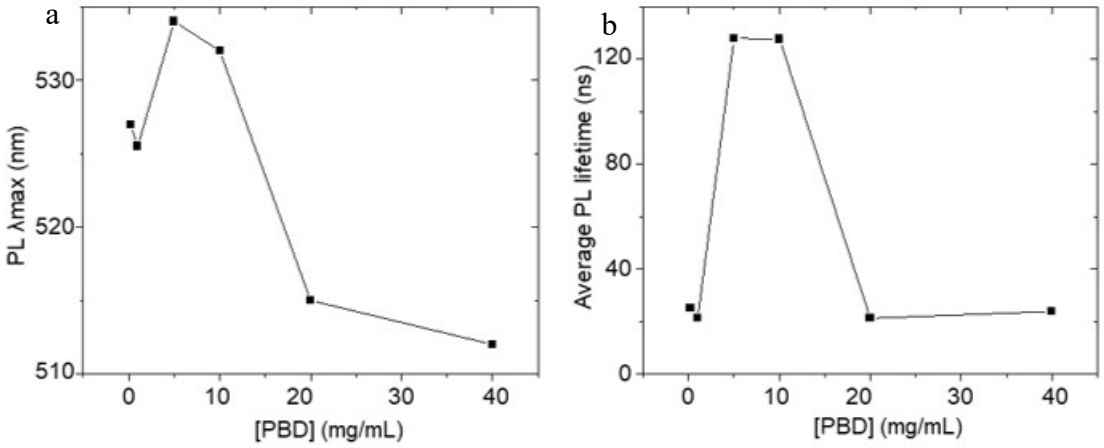


Fig. S3. (a) PL spectral maxima (λmax) and (b) average PL lifetimes of PQD assemblies in PQD-PBD films, as a function of PBD concentration in the precursor solutions of the films.

**Author contributions**

VB conceived the project. MFK prepared the PQD and PQD– PBD samples. TO conducted the STEM and XRD experiments. MFK collected the PL images and steady-state absorption, and PL spectra. MFK, TO, and VB conducted the TRPL experiments. MFK and TO analyzed the data. MFK wrote the manuscript draft, and TO and VB finalized it.