Electronic Supplementary Material (ESI) for Nanoscale.

*Supporting Information*

# Photoinduced Photoluminescence Enhancement in Self-assembled Clusters of Formamidinium Lead Bromide Perovskite Nanocrystals

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## Experimental Section

**Synthesis of $FAPbBr_3$ PNC:** $FAPbBr_3$ PNC was prepared as follows. Octylammonium bromide (25.2 mg, 0.12 mmol) was dissolved in a mixture of oleic acid (170 mg, 0.6 mmol) and octadecene (4 mL) by stirring at 80 °C. Subsequently formamidinium bromide (25 mg, 0.20 mmol dissolved in 200 µL of DMF) and lead (II) bromide (73.4 mg, 0.2 mmol dissolved in 250 µL of DMF) were added to the solution of octylammonium bromide. The PNCs were precipitated by the addition of a mixture of hexane and acetone (8:1, v/v). The mixture was centrifuged at 7000 rpm for 10 min, and the supernatant was decanted. The residual PNCs from the precipitate were washed repeatedly with acetone and dried in air.

**Thin Film Preparation:** ca 1 mg of the dried PNC sample was dispersed in toluene (1 mL), which was followed by sonication for 10 minutes. This stock solution was diluted into 0.1 mg/mL with toluene. Thin films of PNC were prepared by drop-casting of 100 µL PNC solution on $24\times50$ mm$^2$ glass coverslips. The samples were dried under a laminar flow of air. Initially, the ligand-capped PNCs were well dispersed in toluene. During the gradual evaporation of the drop-cast, the long-chain alkyl ligands, octylammonium bromide and oleic acid, assist in the assemblage of PNCs into close-packed clusters, thus providing us with uniform thin films.

**$C_{60}$-Doped Thin Film Preparation:** Thin films of $C_{60}$-doped PNCs were prepared by following the method like the preparation of undoped thin film described above. Typically, to the PNC stock solution (1 mg/mL in toluene), 1.4 weight% of $C_{60}$ (14 µg) was added, and the mixture was sonicated for 30 min. The stock solution containing $C_{60}$ was further diluted 10 times with toluene. Thin films of $C_{60}$-doped PNCs were prepared by drop-casting of 100 µL of the dilute solution on 24×50 $mm^2$ glass coverslips and drying.

**Characterization of PNC:** PNCs were characterized by using FEI-TECNAI T30 high resolution transmission electron microscope (HR-TEM), at the accelerating voltage of 300 kV. The TEM samples were prepared by drop-casting of a PNC solution onto a carbon coated copper grid at ambient conditions and the solvent was removed under vacuum. X-ray diffraction study was carried out for film samples with PANalytical 'X'Pert PRO (Model No. PW 3040/60) using Cu-K $\alpha$ radiation ($\lambda$ = 1.5406 Å). Electronic absorption spectra were recorded on a Shimadzu UV-2600 UV-vis spectrophotometer and the emission spectra were recorded on a SPEX-Fluourolog spectrofluorimeter. The surface chemical composition and the oxidation states of the constituent elements in PNCs were analyzed using X-ray photoelectron spectroscopy (XPS) using PHI 5000 Versa Probe II having Al kα monochromatic source.

The excitation light source used for time-resolved PL was 400 nm (140 fs) pulses generated from the SHG crystal of an optical parametric amplifier (Coherent OPA 9400), which was pumped at 200 kHz by a regenerative amplifier (Coherent RegA 9000). RegA was seeded by a mode-locked Ti:Sapphire laser (Coherent Mira 900F). PL decays were recorded using an assembly of a polychromator (model 250IS, Chromex) and a photon-counting Streak-camera (model C4334, Hamamatsu). The fluorescence signals were filtered through a 440 nm long-pass filter, focused at the entrance slit of the polychromator, and detected using the Streak-camera. Laser power was varied by using neutral density filters.

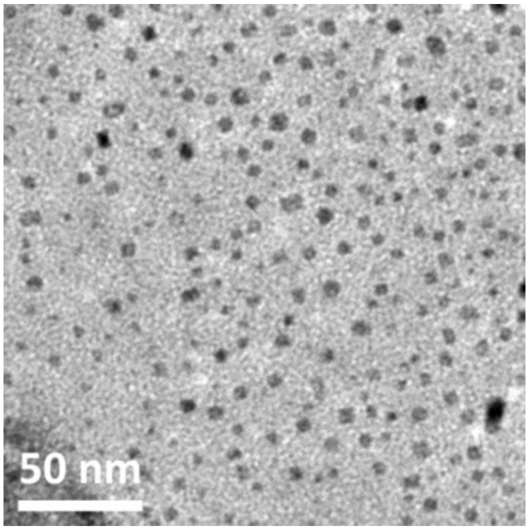

**Figure S1.** TEM image of $FAPbBr_3$ PNCs.

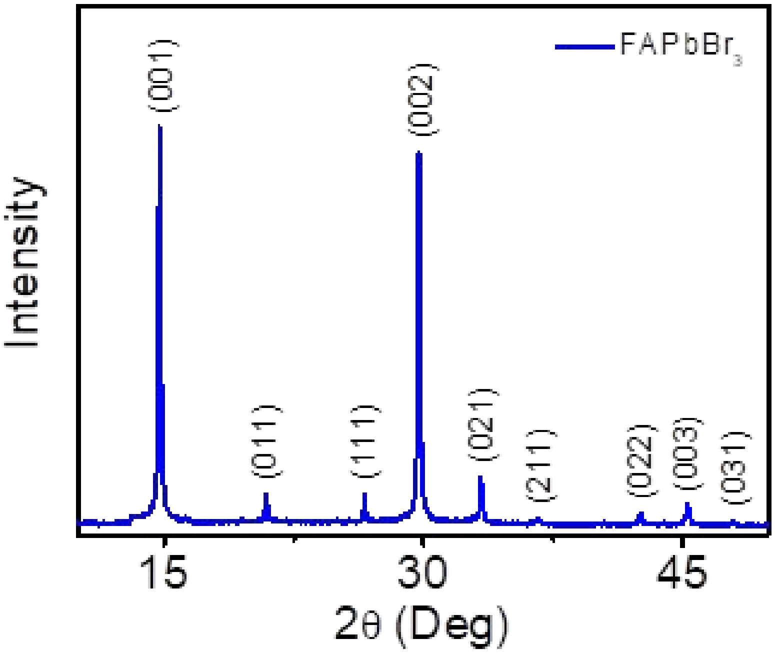

**Figure S2.** XRD of $FAPbBr_3$ PNC.

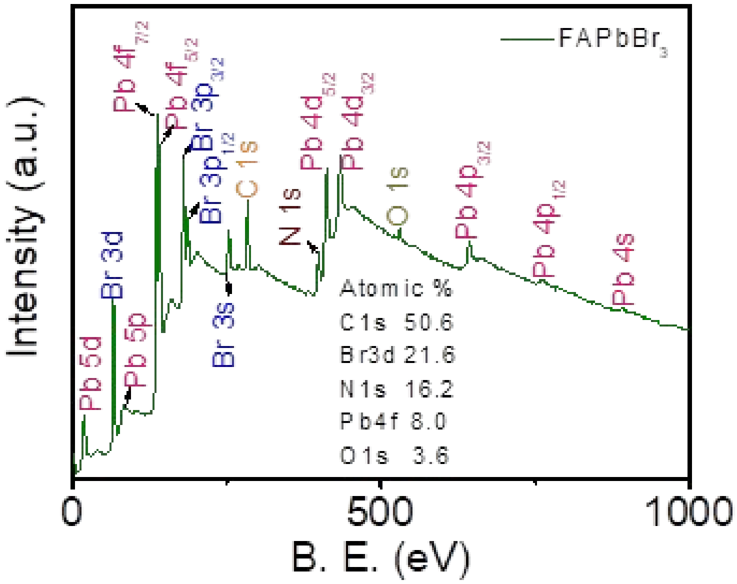

**Figure S3.** XPS of $FAPbBr_3$ PNC.

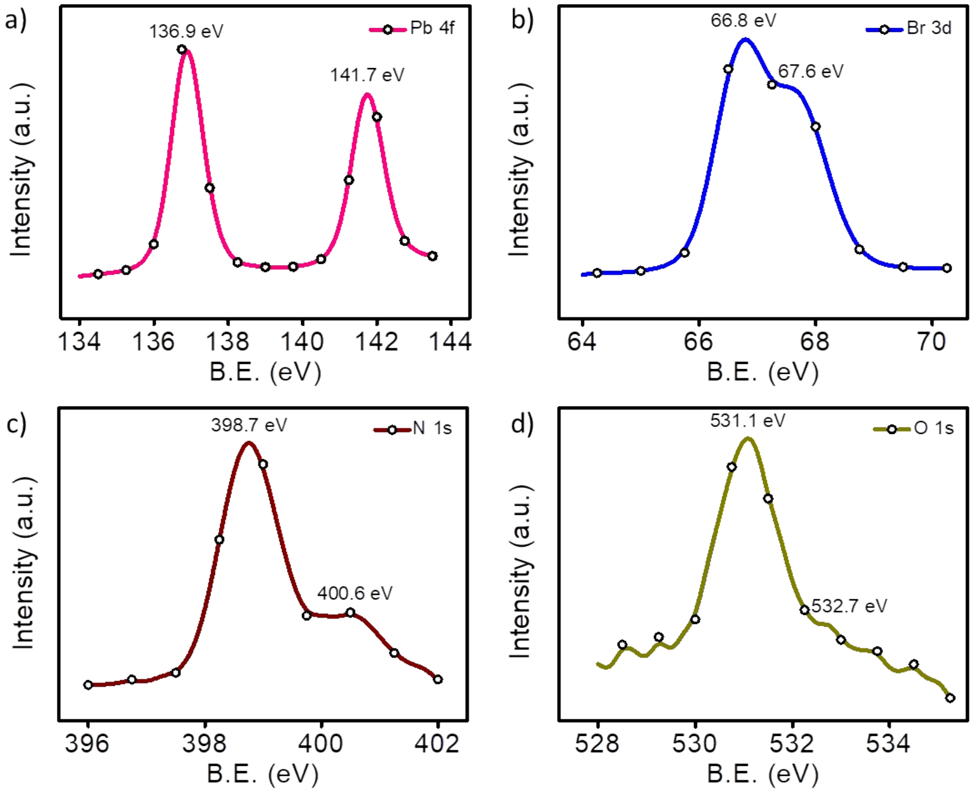

**Figure S4.** XPS of PNCs corresponding to a) Pb 4f, b) Br 3d, c) N 1s, and d) O 1s.

XPS data of PNCs are shown in **Figure S3** and **S4**. Two symmetric peaks of Pb 4f (**Figure S4a**) at 136.9 eV and 141.7 eV correspond to Pb $4f_{7/2}$ and Pb $4f_{5/2}$ levels. Absence of any peak at the lower-binding energy side indicates the absence of metallic lead. The Br 3d peaks (**Figure S4b**) were fitted into two peaks centered at 66.8 and 67.6 eV, which correspond to the inner and surface $Br^-$ ions of PNCs, respectively. The N 1s spectrum (**Figure S4c**) has two peaks, indicating the presence of two existing chemical states of N. The peak at 398.7 eV can be attributed to octylammonium ligand, while the peak at 400.6 eV originates from formamidinium salt. XPS of the O 1s (**Figure S4d**) contains two peaks. The lower energy peak at 531.1 eV corresponds to two non-equivalent O atoms of carboxylic acid, while the higher energy state peak at 532.7 eV can be assigned to two chemically equivalent O atoms from carboxylate species of deprotonated oleic acid. The elemental composition obtained from XPS was C:N:Pb:Br:O = 6.33:2.03:1.00:2.70:0.45. The ratio of Pb:Br was found to be 1.00:2.70 which is very close to the ideal value (1.00:3.00). The excessive carbon, nitrogen and oxygen (C:N:O = 3.33:0.03:0.45) are from the capping ligands such as octyl ammonium and oleate ions. The capping ligand, oleic acid, can replace certain bromide ions from $PbBr_2$ to form Pb-oleate on the surface of PNCs, which leads to a slight decrease of bromide concentration.[1]

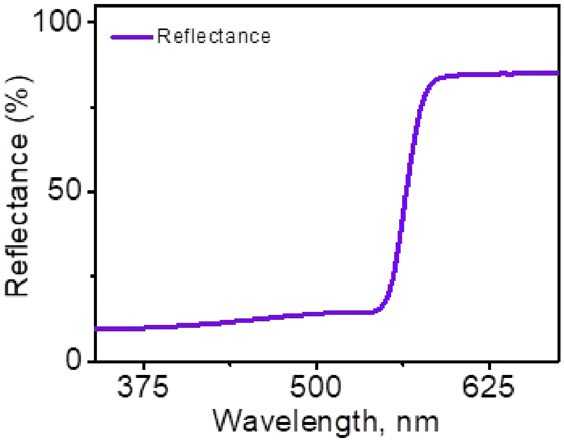

**Figure S5.** Reflectance spectrum of a $FAPbBr_3$ PNC film.

## Reference

1. H. Huang, J. Raith, S. V. Kershaw, S. Kalytchuk, O. Tomanec, L. Jing, A. S. Susha, R. Zboril and A. L. Rogach, *Nat. Commun.,* 2017, **8**, 996.