

Tailoring Charge Donor-Acceptor Interaction in CsPbBr₃ Perovskite Nanocrystals through Ligand Exchange

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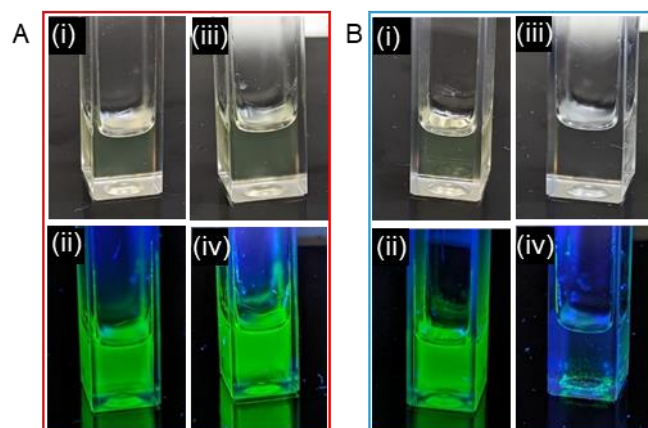


Figure S1. Stability of CsPbBr₃ PNCs after ligand-exchange with different amounts of butylamine. (A) Cuvette images of CsPbBr₃ PNC solution (i/ii) immediately and (iii/iv) two hours after the treatment with 2 μL of butylamine. (B) Cuvette images of CsPbBr₃ PNC solution (i/ii) immediately and (iii/iv) two hours after the treatment with 10 μL of butylamine. (i/iii) and (ii/iv) in A and B are the images under room light and UV light, respectively.

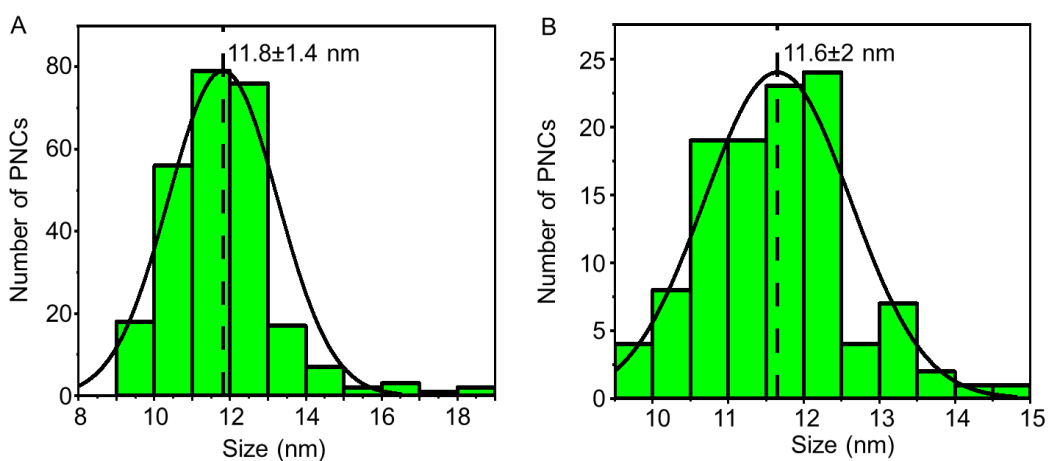


Figure S2. Size distribution histograms for (A) oleylamine (OlAm)-capped and (B) butylamine (ButAm)-capped CsPbBr₃ perovskite nanocrystals (PNCs).

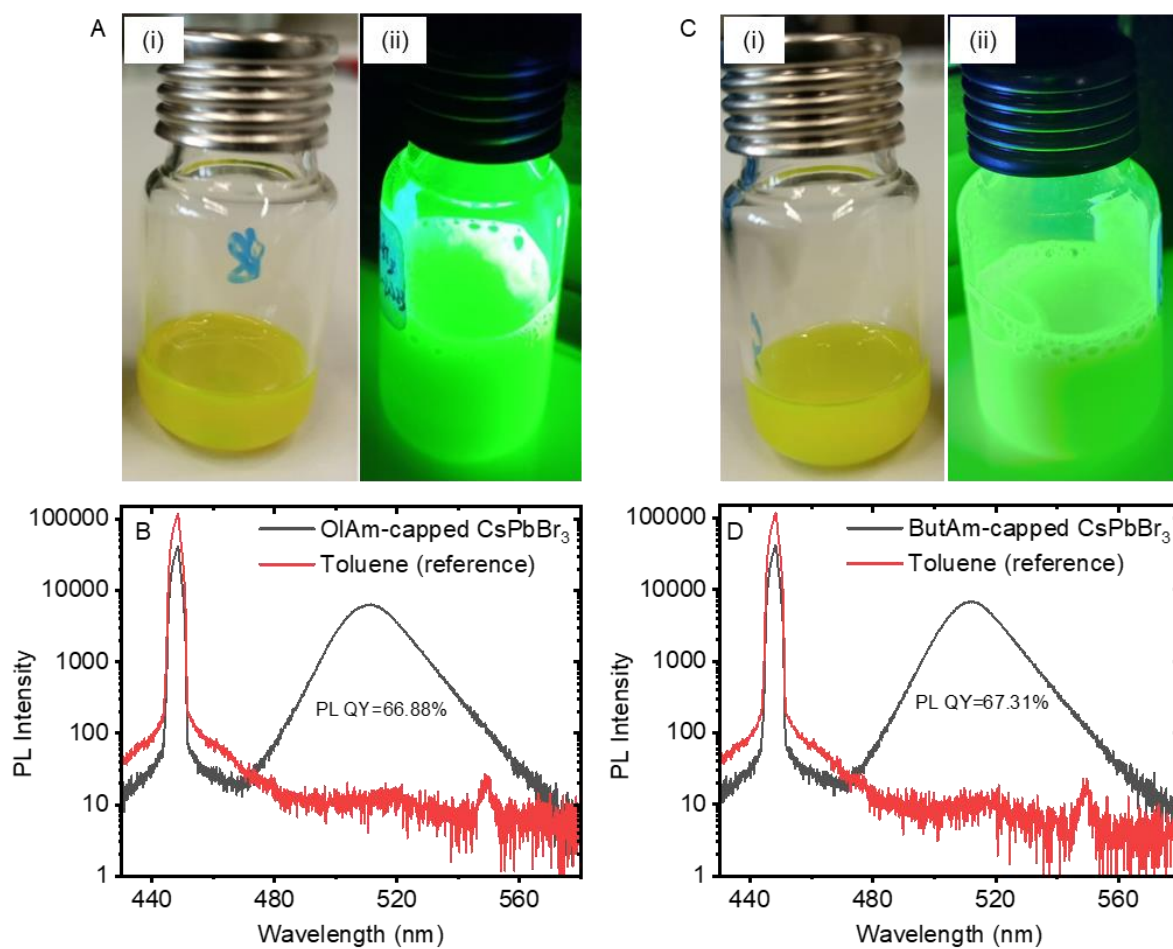


Figure S3. (A, B) Colloidal solutions of (A) OlAm-capped and (B) ButAm-capped CsPbBr₃ PNCs (i) at room light and (ii) under 365 nm UV lamp excitation. (B, C) Photoluminescence (PL) spectra recorded with an integrating sphere in a PL spectrometer for the absolute PL quantum yield (QY) measurements of (B) OlAm-capped and (D) ButAm-capped CsPbBr₃ PNC colloidal solutions. Toluene was used as the reference.

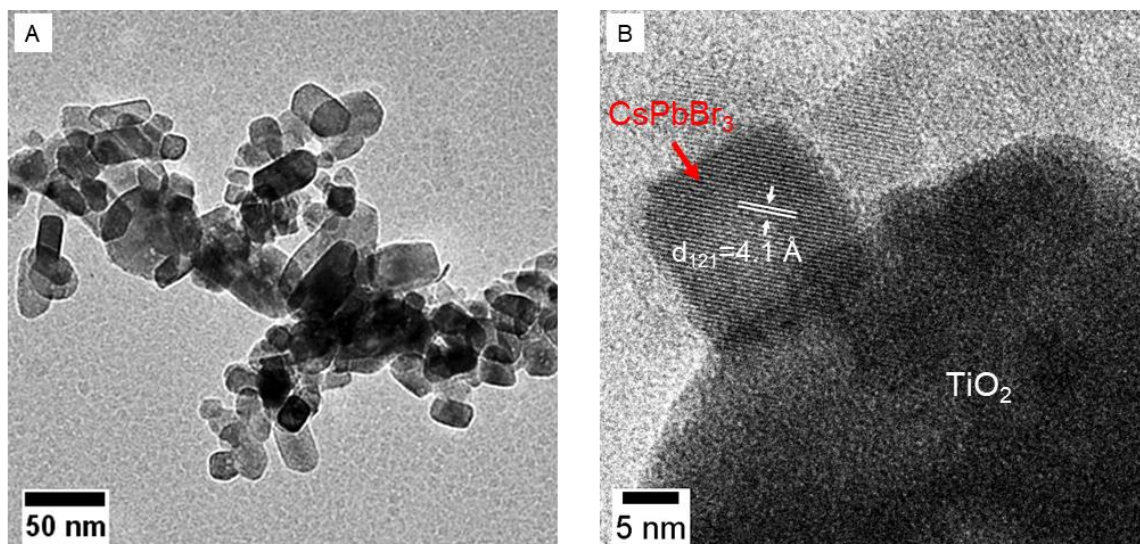


Figure S4. Transmission electron microscopy (TEM) images of (A) TiO₂ nanoparticles and (B) a CsPbBr₃ PNC on the TiO₂ nanoparticle showing a donor-acceptor interface. A lattice fringe of 4.1 Å in CsPbBr₃ PNC corresponds to the (121) plane of an orthorhombic crystal structure of the bulk CsPbBr₃, as reported in ref. 1.

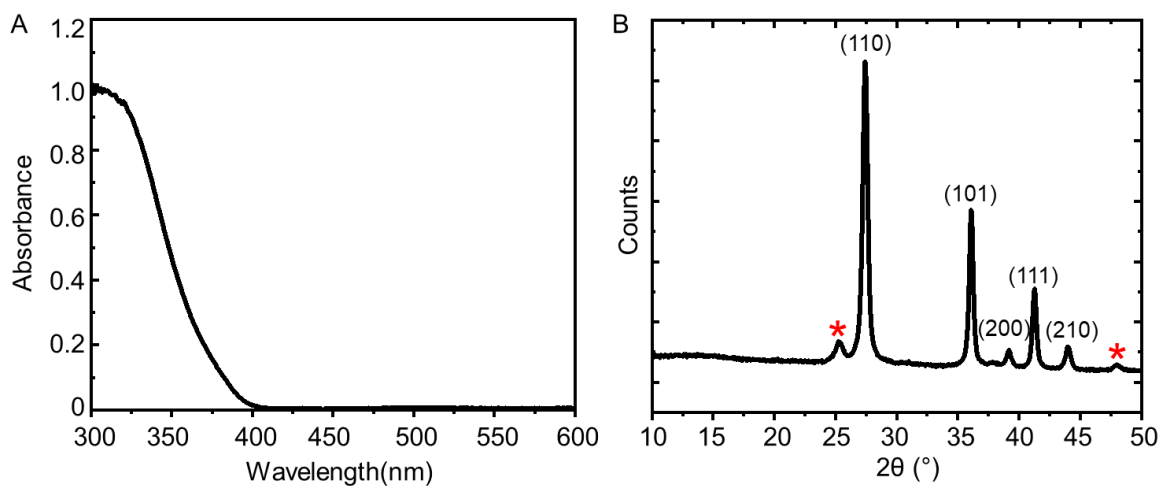


Figure S5. (A) UV-Visible absorption spectrum of TiO₂ nanoparticle suspension. (B) Powder X-ray diffraction (XRD) pattern of TiO₂ nanoparticles. The indexed XRD peaks are for Rutile phase, while the XRD peaks labelled with (*) are for the Anatase phase of TiO₂. The XRD peaks are analysed by comparing them with those from ref. 2.

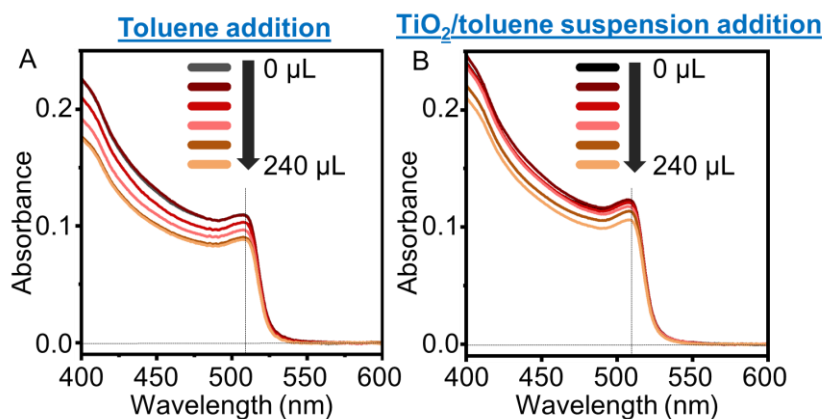


Figure S6. Absorption spectra of butylamine-capped CsPbBr₃ PNCs with the (A) addition of toluene and (B) TiO₂-suspended toluene at different volumes (indicated in the inset), indicating colloidal as well as material stability under dilution.

In Figure S6, we see only a gradual decrease in the absorption peak which is due to the dilution, but without the appearance of any addition bands in the absorption spectra in both the cases. This suggests that the PNCs are stable during the addition of TiO₂ or dilution. Further, we do not observe significant scattering at higher wavelength region, tailing at the absorption onset, or broadening of the absorption peak in the absorption spectra, suggesting that the colloidal stability is intact.

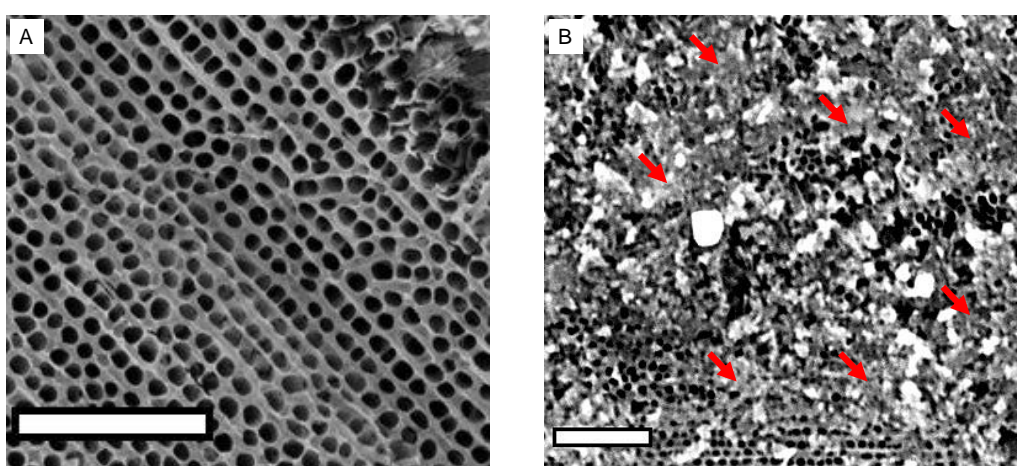


Figure S7. Scanning electron microscopy images of (A) anodically-grown bare TiO₂ nanotubes and (B) TiO₂ nanotubes with CsPbBr₃ PNCs deposited on the top. Some patches of deposited PNCs are indicated by red arrows. Scale bars in both images are 1 μm.

Dilution correction for the PL spectra of CsPbBr₃ PNCs in presence of quencher (TiO₂)

The addition of toluene causes a decrease in PL intensity of PNC solution due to the dilution effect. Therefore, to separate out the effect of dilution from the effect of charge transfer interaction on the PL intensity of PNC solution, two separate set of experiments were carried out. In the first experiment, TiO₂ suspended in toluene was added to PNC solution following a step wise manner as presented in the main text and the corresponding PL spectra were recorded. In the second set of experiments, similar volume of only toluene (but without TiO₂) was added in a step wise manner to the PNC solution to obtain a set of corresponding PL spectra. The data from both experiments were compared to subtract out the effect of toluene dilution.

We divide the PNC solution into 2 cuvettes (cuvette1 and cuvette2), each having equal volume. We take cuvette1, record the initial PL intensity (P_1) and add 20 μ L (TiO₂/toluene suspension) to it, which causes a decrease in the PL intensity to P_1' . This decrease is ascribed to the combined effect of charge transfer and dilution.

Again, we take cuvette2, record the initial PL intensity (P_2) and add 20 μ L of pure toluene to it, causing decrease in PL intensity to P_2' . This decrease in PL intensity is now ascribed to only the dilution effect.

For the dilution correction on PL spectra, we carry out a two-step calculation:

$$(P_2 - P_2' / P_2) = Z \quad (\text{dilution factor})$$

$$P_1' + (P_1 \times Z) = \text{Corrected PL intensity (without the dilution effect of solvent, toluene)}$$

The same process was repeated for all the subsequent step wise addition of TiO₂ suspension to the PNC solution.

References

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