

Supporting Information

Spray-driven Halide Exchange in Solid-State CsPbX₃ Nanocrystal Films

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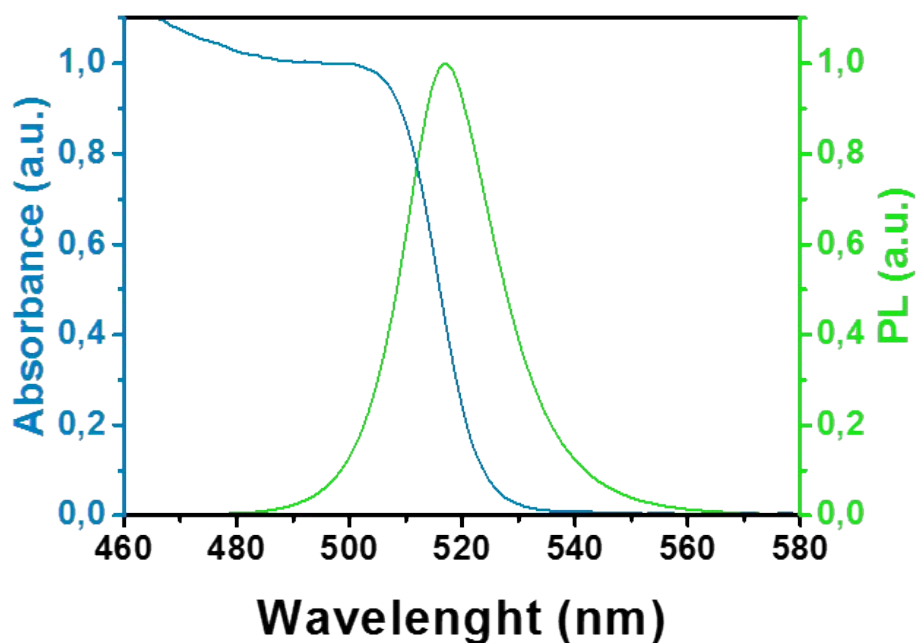


Figure S1. Absorbance and PL spectra of as-synthesized CsPbBr₃ NCs.

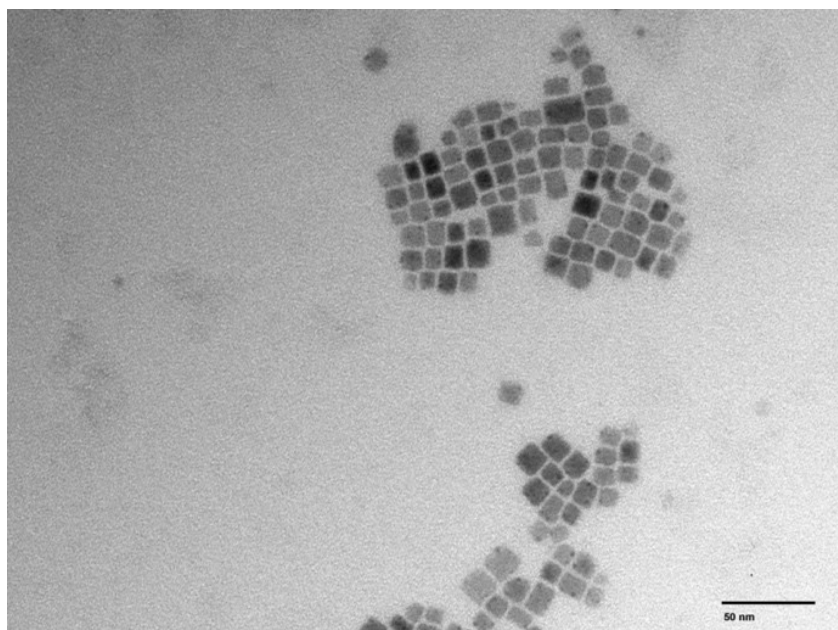


Figure S2. TEM image of as-synthesized CsPbBr₃ NCs (scale bar: 50 nm).

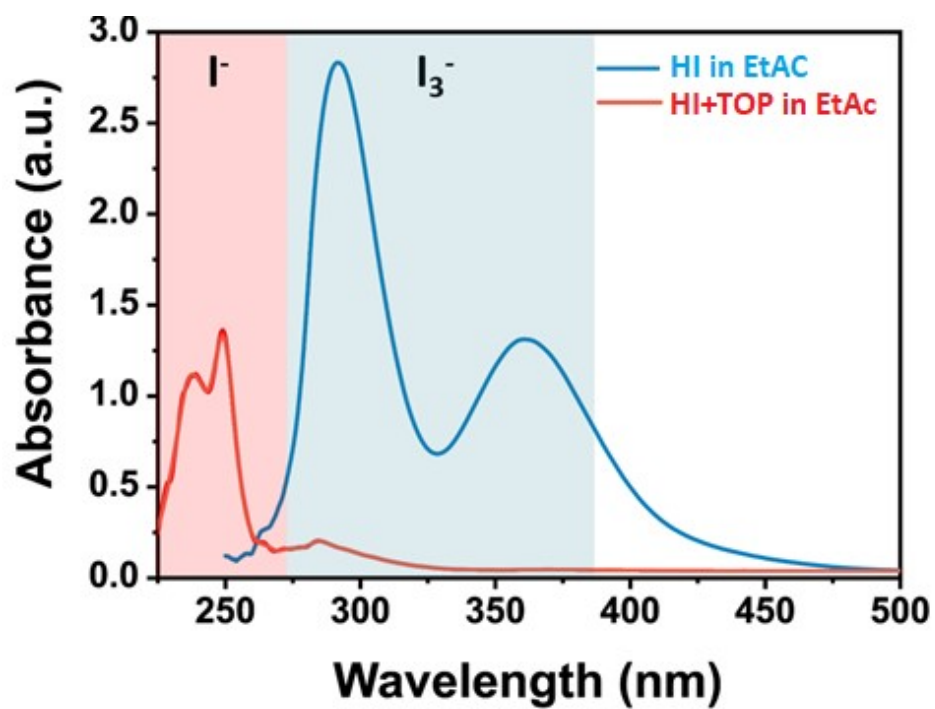


Figure S3. UV-Vis spectra of HI and HI-TOP in EtOAc.

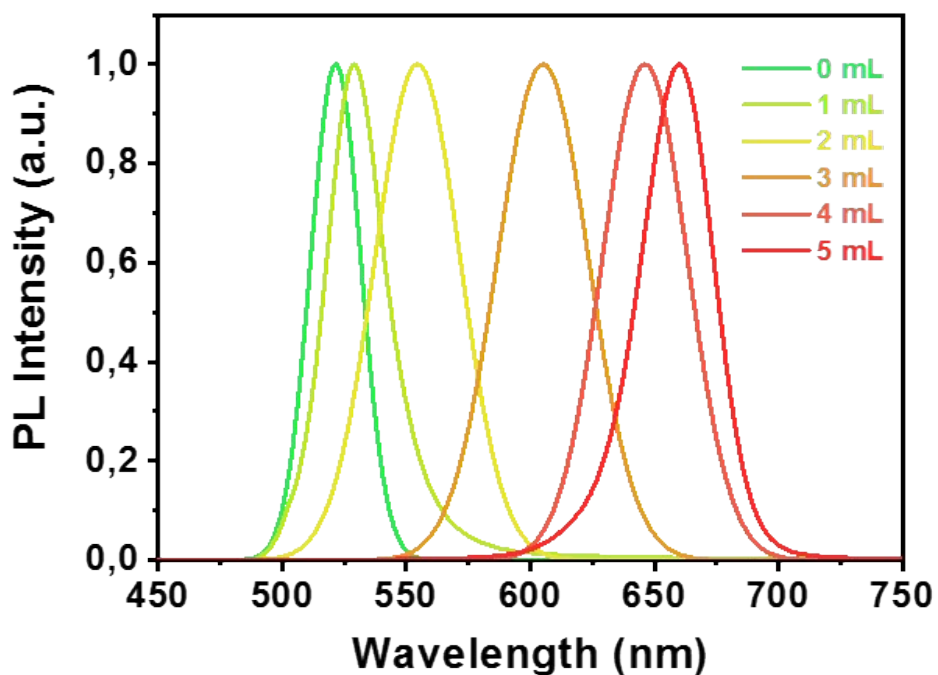


Figure S4. PL spectra after anion exchange implemented by spraying different volumes of 66 mM HI in EtOAc

Sprayed Volume (mL)	PL (nm)	PLQY _{Drybox} (%)
0	505	56
1	530	4
2	560	8
3	609	20
4	645	63
5	664	42

Table SI Summarized optical properties of CsPbBr_{3-x}I_x thin films synthesized inside a drybox (RH ≤ 20%) as a function of the sprayed volume of the iodine precursor solution. Anion exchanged thin film samples were obtained, spraying a 33 mM HI- and 11 mM TOP solution in EtAc.

Sprayed Volume (mL)	PL (nm)	PLQY _{Drybox} (%)
0	505	56.2
2	545	<1
4	560	6.3
6	590	19.3
8	610	83.1
10	640	60,1

Table SII Summarized optical properties of CsPbBr_{3-x}I_x thin films synthesized inside a drybox (RH ≤ 10 %) as a function of the sprayed volume of the iodine precursor solution. Anion exchanged thin film samples were obtained, spraying a 15 mM HI- and 5.5 mM TOP solution in EtAc.

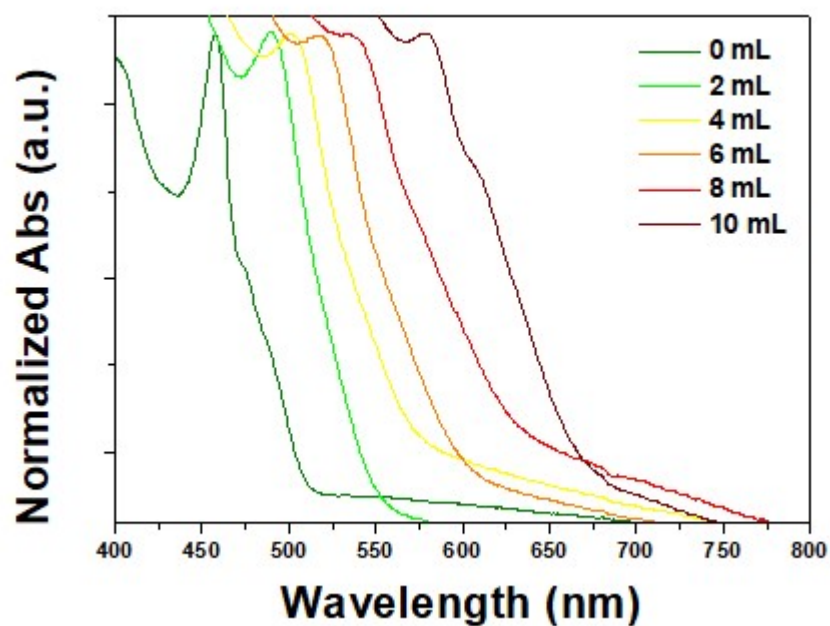


Figure S5 Normalized absorbance spectra of anion exchanged CsPbBr_{3-x}I_x films as a function of sprayed Volume of iodine solution precursor. Samples were obtained under low humidity conditions (RH ≤ 10%).

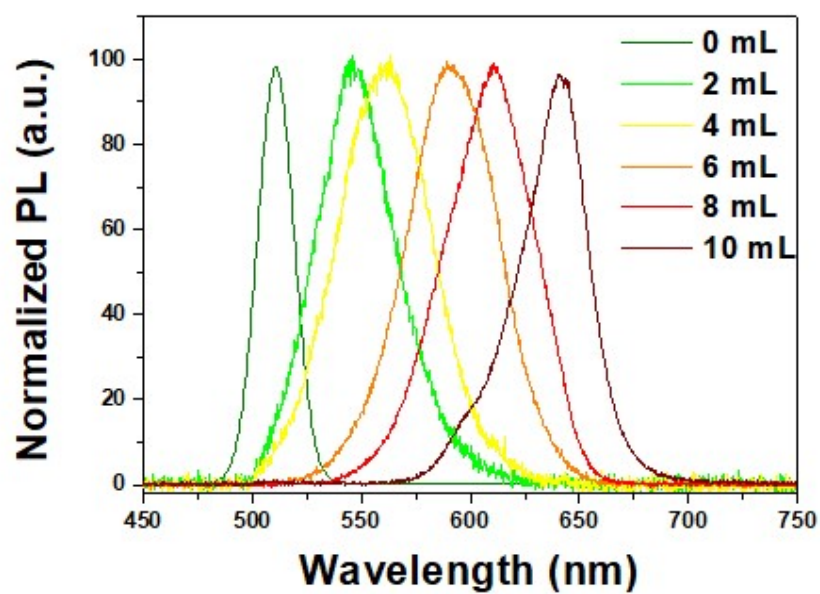


Figure S6 Normalized photoluminescence spectra of CsPbBr_{3-x}I_x thin films as a function of the sprayed volume of iodine precursor solutions. Samples were obtained under low humidity conditions (RH ≤ 10- 20%).

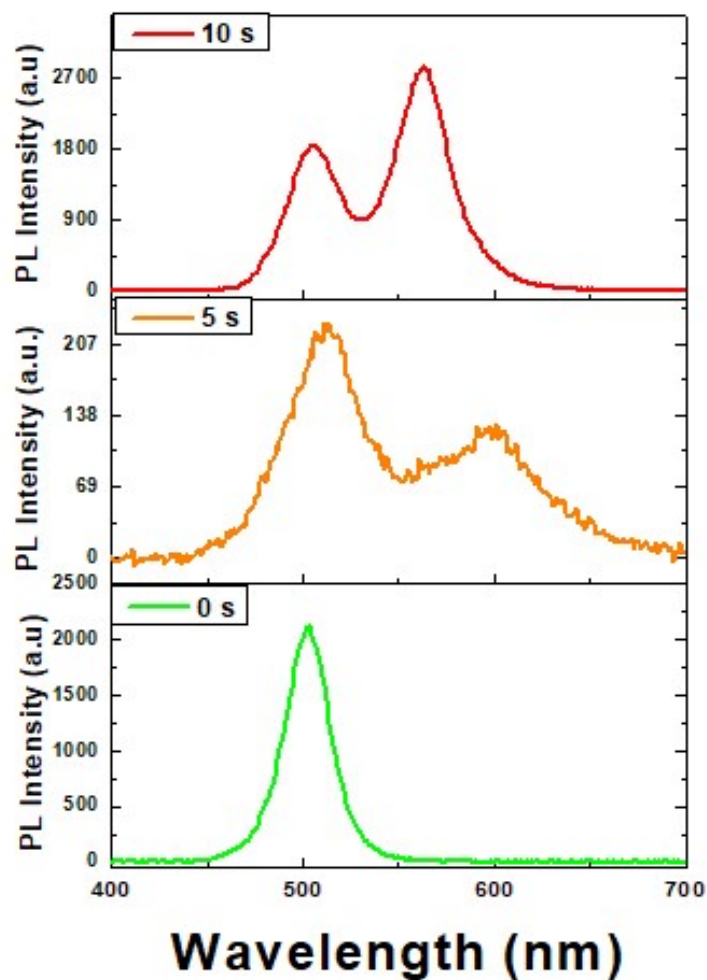


Figure S7 Photoluminescence spectra of CsPbBr_{3-x}I_x films after dipping in a solution containing 33 mM HI and 11 mM TOP in ethyl acetate.

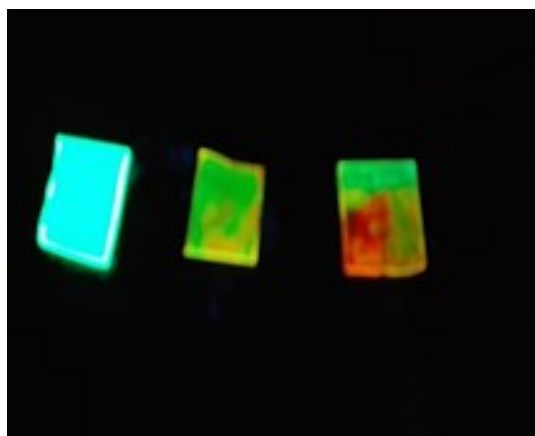


Figure S8 CsPbBr_{3-x}I_x films obtained by dipping-driven anion exchange in a 33 mM HI- 11 mM TOP solution in ethyl acetate.

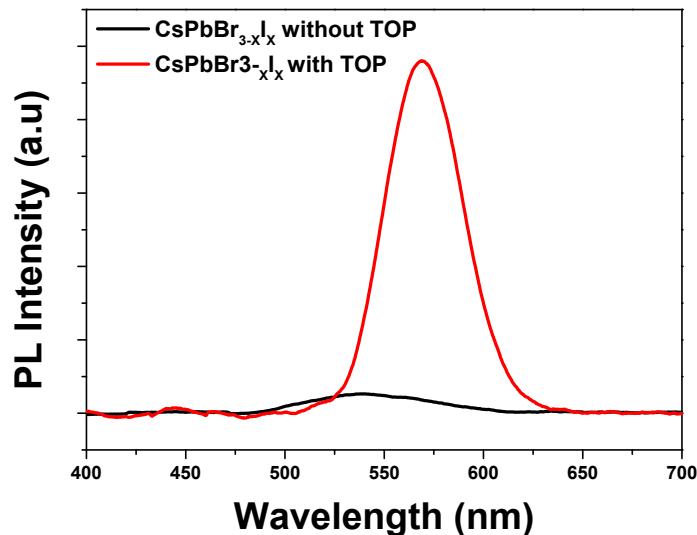


Figure S9. Trioctylphosphine effect in the optical properties of anion exchanged $\text{CsPbBr}_{3-x}\text{I}_x$ nanocrystalline thin films.

To clarify the role of TOP, we carried out the spray-driven anion exchange reactions on CsPbBr_3 thin films with and without TOP in the HI solution. Without TOP, we observe a typical redshift on the PL of $\text{CsPbBr}_{3-x}\text{I}_x$ films (see Figure S9, Support information) together with a drastic decrease of PLQY (PLQY < 1%).

However, ^{31}P NMR reveals that TOP is oxidized to TOPO when I_3^- is reduced to I^- (Figure S10 in SI). TOPO is also a well-known capping agent able to stabilize CsPbX_3 NCs. To clarify the role of TOP, we carried out the spray-driven anion exchange reactions on CsPbBr_3 thin films with and without TOP in the HI solution. Without TOP, we observe a typical redshift on the PL of $\text{CsPbBr}_{3-x}\text{I}_x$ films (see Figure S9, Support information) together with a drastic decrease of PLQY (PLQY < 1%) owing to oleylammonium ligand may be removed from nanocubes surface during processing as proved by FTIR (Fig S 11). The presence of TOPO after the halide exchange is confirmed by ^1H and ^{31}P NMR (Figure S10 in SI) and FTIR (Figure S11 in SI).

In the case that spray-driven anion exchange was carried out with HI solution in ethyl acetate, there is a red shift in the absorbance and PL peak of perovskite thin films, but PLQY decreased drastically owing to oleylammonium ligand may be removed from nanocubes surface during processing as proved by FTIR (Fig S 11)

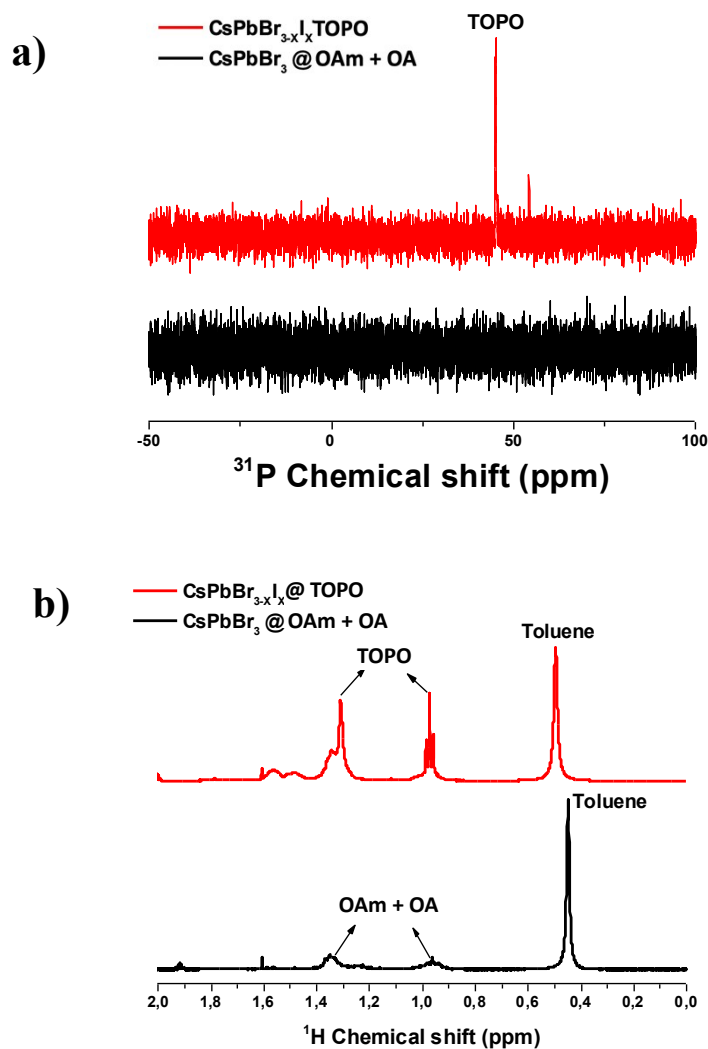


Figure S10. a) ³¹P NMR and b) ¹H NMR spectra from CsPbBr₃ and CsPbBr_{1.3}I_{1.7} NCs obtained after spray-driven halide exchange. All samples were measured in toluene- d₈.

³¹P NMR reveals a singlet signal centred at 45 ppm that was assigned to the formation of trioctylphosphine oxide[48]. TOP is oxidized to TOPO when I₃⁻ is reduced to I⁻ (Figure S10 in SI). TOPO is also a well-known capping agent able to stabilize CsPbX₃ NCs. The presence of TOPO after the halide exchange is also confirmed by ¹H (Figure S10b in SI) and FTIR (Figure S11 in SI). Moreover, in 1H NMR spectra, we observe a multiplet centred at 1.3 ppm and a triplet centred at 0.9 ppm characteristics of H nucleus in a single bond C-H in oleylamine and oleic acid [47]. These signals increase in intensity, as observed in figure S10, due to the attachment of TOPO on the surface of CsPbBr₃-XIX NCs.

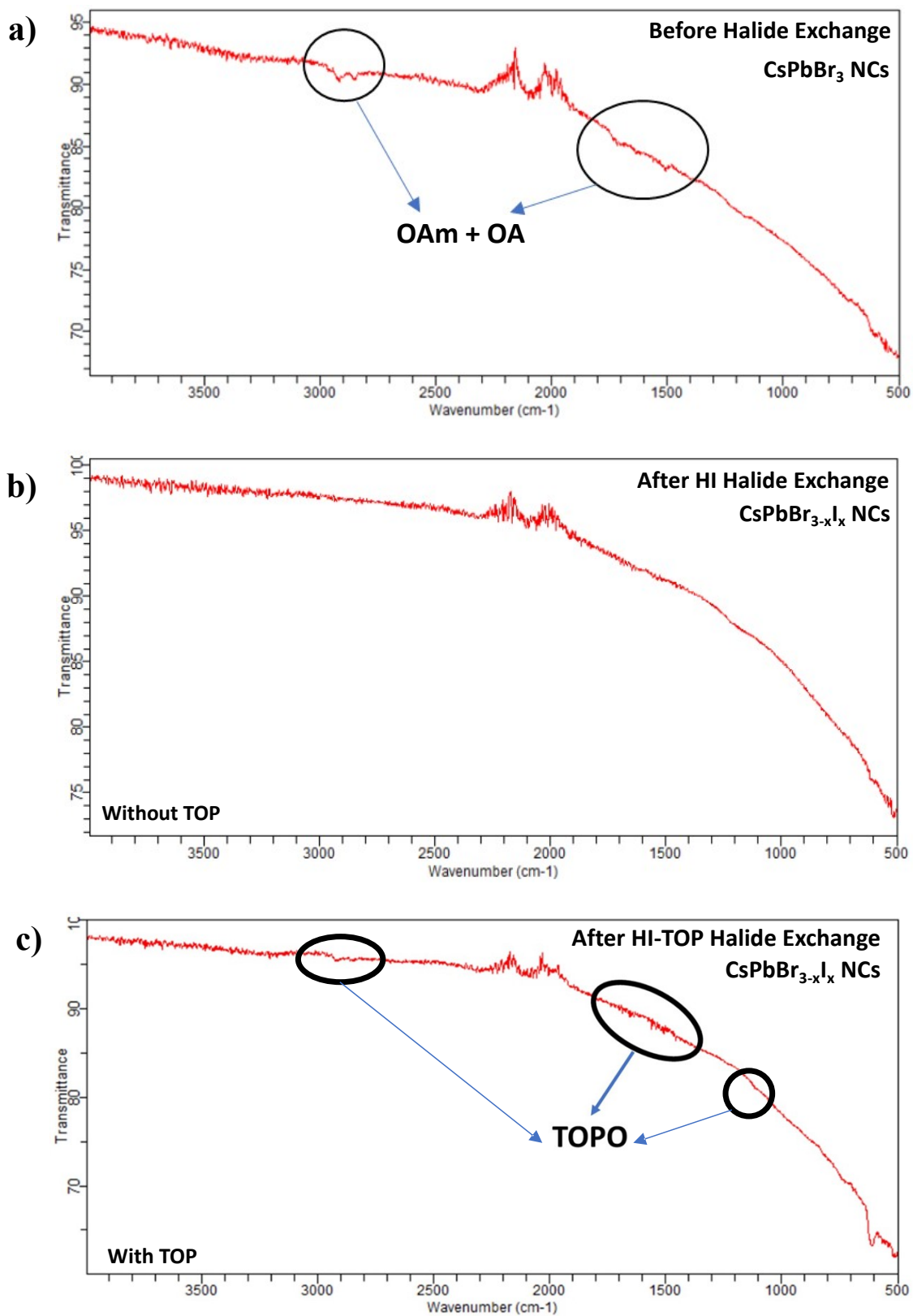


Figure S11 FTIR Spectra recorded from a) CsPbBr₃, b) CsPbBr_{1.3}I_{1.7} obtained by spray processing with HI solution in ethyl acetate, c) CsPbI_xBr_{3-x} synthesized by spray processing with 33 mM HI and 11 mM TOP solution in ethyl acetate

Figure S11a shows the FTIR spectrum of CsPbBr₃ NC thin films before halide exchange. We observe peaks between 2800- 3000 cm⁻¹ and 1800- 1600 cm⁻¹, characteristics of C-H stretching and bending modes from OAm and OA ligands. When halide exchange is carried out with HI solution (without TOP), no peaks between 2800- 3000 cm⁻¹ and 1700- 1300 cm⁻¹ are observed. Most probably, OAm and OA are removed by EtOAc. On the other hand, when halide exchange is carried out with HI-TOP solutions, new peaks appear at 2900 and 1800 cm⁻¹, corresponding to the C-H stretching and bending modes of TOPO. Stretching of P=O is observed around 1400 cm⁻¹.

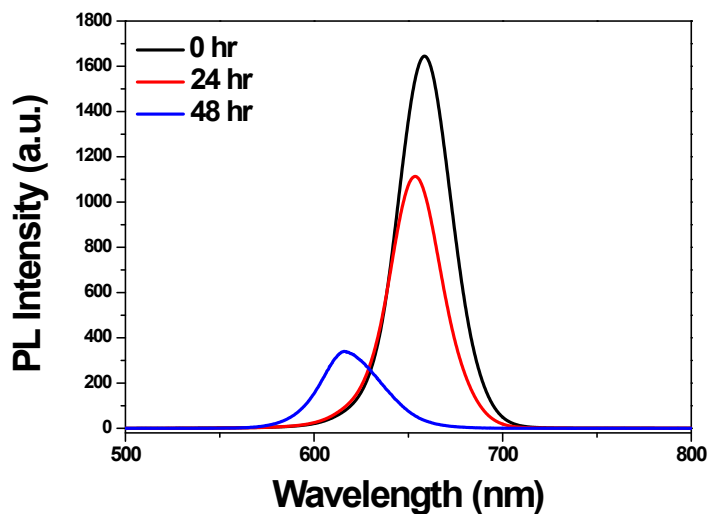


Figure S12. Stability test of CsPbBr_{3-x}I_x nanocrystal thin films under ambient conditions (Moisture and room temperature).

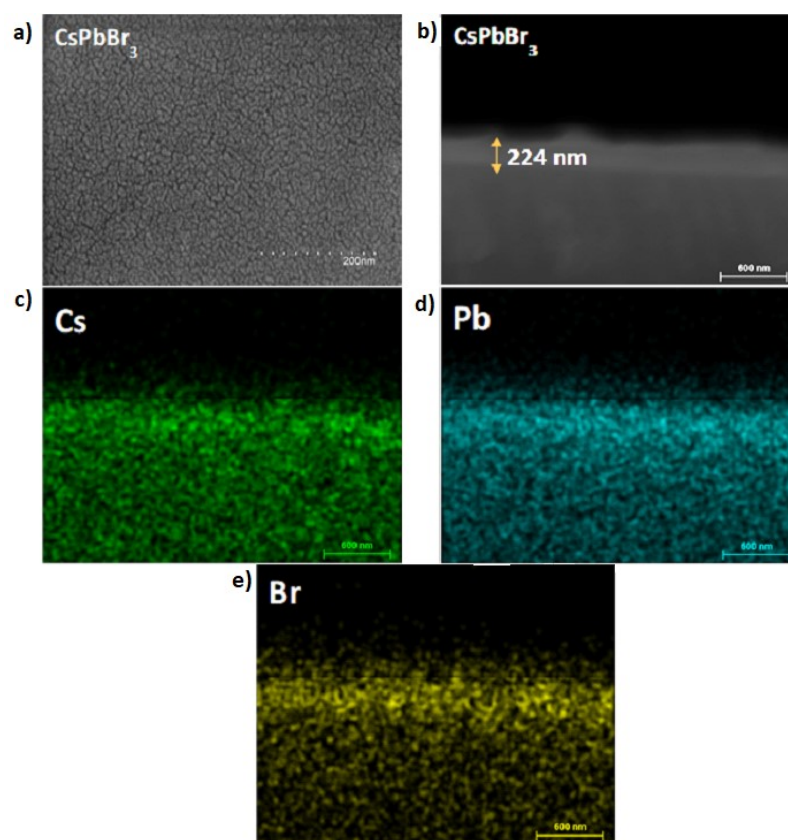


Figure S13 SEM Images (a) Superficial, b) Cross- section) and c-e) elemental mapping obtained from cross-section of CsPbBr₃ NCs film.

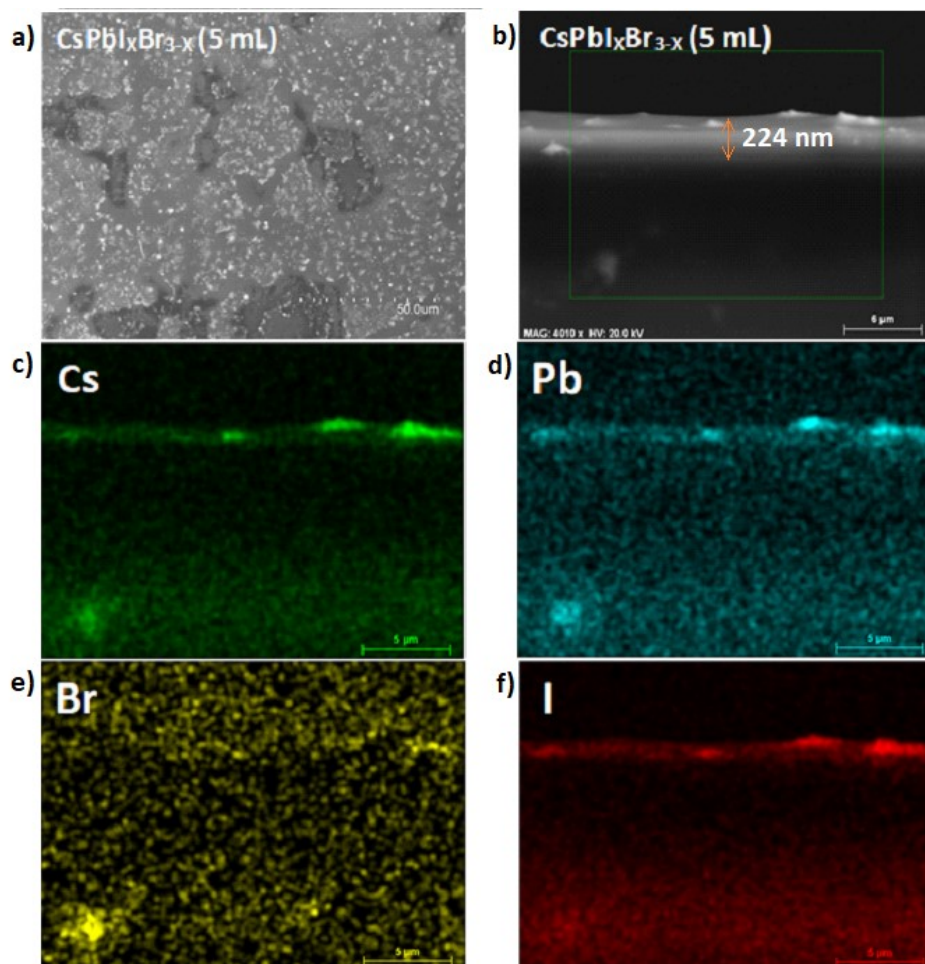


Figure S14 SEM Images (a) Superficial and (b) Cross-section) images from $\text{CsPbBr}_{3-x}\text{I}_x$ films and (c-f) elemental mapping obtained from a cross-section of $\text{CsPbBr}_{3-x}\text{I}_x$. The sample was obtained after spraying 5 mL of 33 mM HI- 11 mM TOP solution in ethyl acetate.