

Surface polarization-induced emission and stability enhancement of CsPbX₃ nanocrystals

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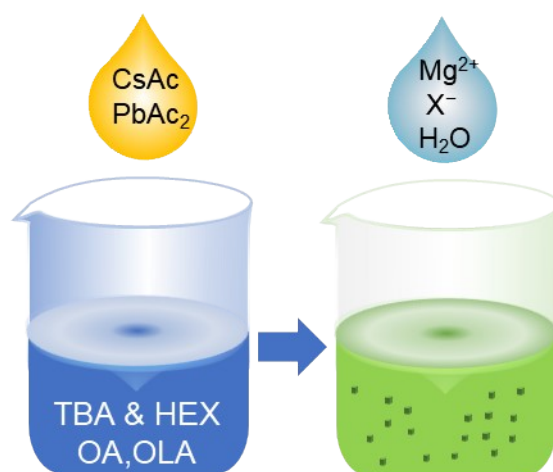


Figure S1. Schematic of the CSARP strategy.

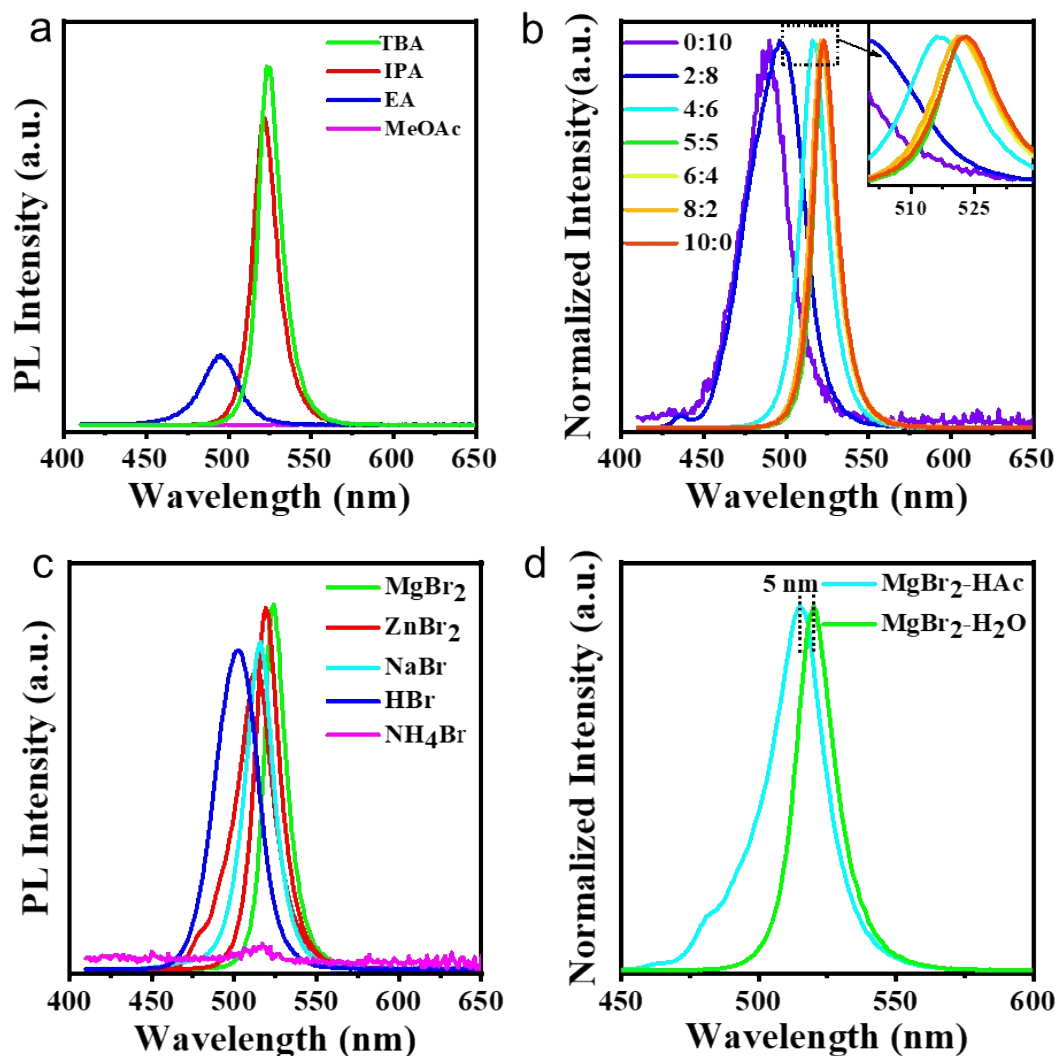


Figure S2. PL spectra of CSARP-CsPbBr₃ NCs synthesized using various: polar solvents (a), volume ratios of TBA to HEX (the PL intensity of 0:10 is 100 times enlarged) (b), metal bromines (c), and solvent for dissolving bromine precursors (d).

Supplementary note 1

We compared the effects of various polar solvents (including TBA: *tert*-butanol, IPA: isopropyl alcohol, EA: ethyl acetate, MeOAc: methyl acetate) on the PL properties of CSARP-CsPbBr₃ NCs, and the results suggested that TBA possessed the best performance. With the increasing of TBA ratio, red-shift of PL peaks have been

observed, which might be contributed to the varieties of the solubility of precursors. As the volume ratio of TBA to HEX increased to 5:5, the PL peaks were almost changeless. The PL intensity is extremely low when TBA is disappeared. We also employed various metal bromines as precursor (Figure S2c), which can provide sufficient Br^- ions and passivate the halide vacancy. We found that when MgBr_2 , ZnBr_2 , or NaBr was used as bromine precursor, the PLQY can be higher than 90%. As we mentioned in the main text, the small radius Mg^{2+} could lead to surface polarization effect and improved optical property and stability of CsPbX_3 NCs. Therefore, we believe that small radius metal cations play important roles for high PLQY. For HBr , an obvious blue-shift can be seen, this might be owned to its etching effect to CsPbBr_3 NCs. While, NH_4Br lead to fast PL decline, suggesting that the NH_4^+ ions might destroy the crystal structure of CsPbBr_3 NCs. Moreover, better optical property has been received when water was used as the solvent than that of HAc , which should be attributed to its surface passivation effect.¹

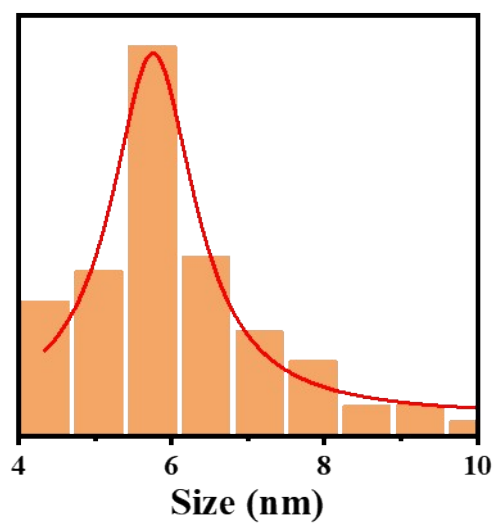


Figure S3. Size distribution histogram of NCs shown in Figure 1d. The NCs have an average size of 6.08 ± 0.36 .

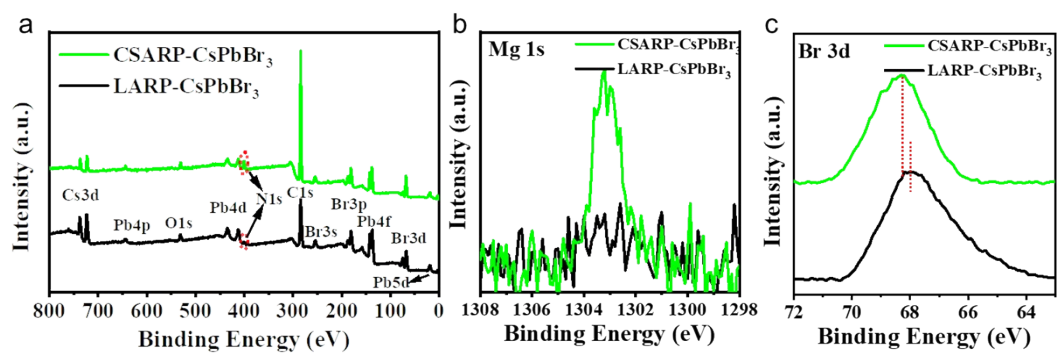


Figure S4. (a) XPS spectra of CSARP-CspbBr₃ and LARP-CspbBr₃. High-resolution XPS spectra of Mg 1s (b) and Br 3d (c) for CSARP-CspbBr₃ and LARP-CspbBr₃, respectively.

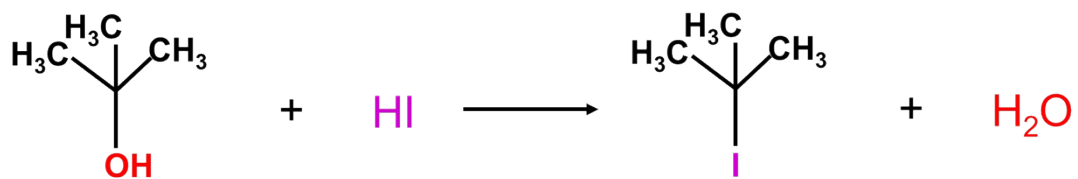


Figure S5. Nucleophilic substitution reaction (S_N1) between HI and TBA to generate TBI. The reaction can be completed rapidly at room temperature.

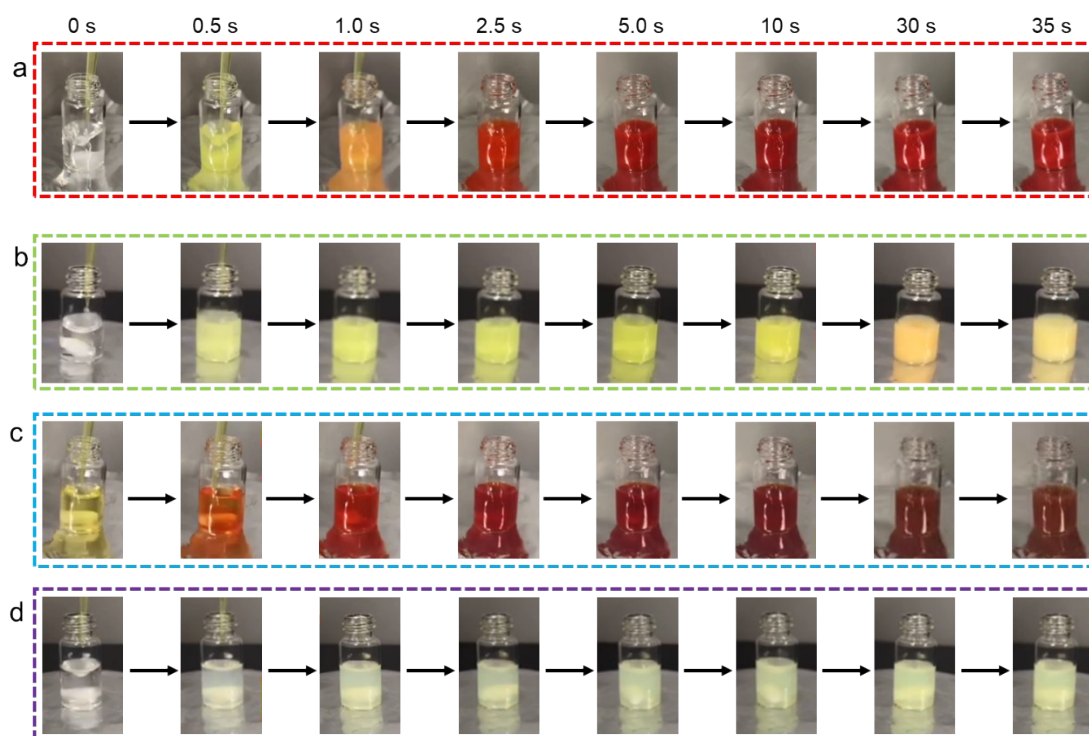


Figure S6. Photos of the formation process of CsPbI₃ NCs through CSARP strategy: (a) without any change; (b) without HI; (c) without HI but with additional TBI; (d) without TBA. At the very beginning in Figure S6c (0 s), the color of this solution is slightly yellow due to the emergence of TBI. These results clearly indicated that TBI is crucial for the successfully synthesis of CsPbI₃ NCs. More detailed information can be found in Video S1-4.

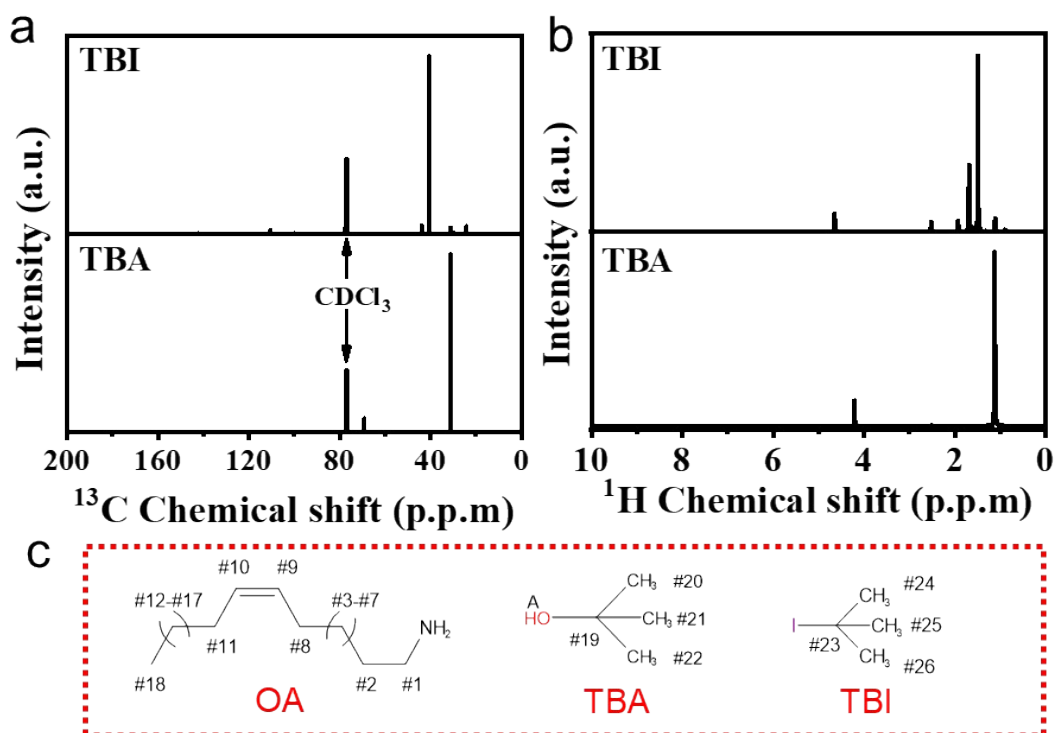


Figure S7. (a) ^{13}C NMR and (b) ^1H NMR spectra of TBI and TBA. (c) Molecular structure of OA, TBA, and TBI.

Supplementary note 2

In Figure 5d, the peaks located at 2.51 and 3.35 p.p.m can be indexed as deuterium DMSO- d_6 and water, respectively. In addition, the peaks of OLA (the peaks at 0.88, 1.24, 1.51, 1.99, 2.76, 5.33 p.p.m are assigned to the #18, #12-#17/#3-#7, #2, #8/11, #1, #9/10 on OLA, respectively), TBA, and TBI are also detected. The peaks located at 1.10 and 4.19 p.p.m are assigned to TBA, and the peaks located at 1.50 p.p.m is assigned to TBI. The inset of Figure 5d illustrate a magnified view near 1.5 p.p.m, which shows 6 splitting peaks. This should be owned to the coupling effect of adjacent nuclei, the number of splitting lines corresponding to the hydrogen on #2 of OLA should be 5 under first-order approximation, and the excess peaks can be corresponded to TBI.

Similarly, ^{13}C NMR spectrum shown in Figure 5e also reveals the emergence of TBI. The peak located at ~ 40.0 p.p.m is indexed to deuterium DMSO- d_6 . The peaks located at 14.4, 22.5, 40.0 and 130.1 p.p.m are assigned to the #18, #17, #1, #9/10 on OLA respectively. The peaks of 31.7 and 67.3 p.p.m should be TBA. The peaks at 40.0 and 45.6 p.p.m are assigned to TBI. In addition, we do not observe any peaks that can be assigned to $-\text{COOH}$, indicating the absence of OA or HAc on the surface of NCs. In general, the $-\text{COOH}$ should be coordinated with the Pb atom to form COO-Pb bond on the surface of NCs, the absence of $-\text{COOH}$ suggesting that there is no uncoordinated Pb atom, which further verifies the reduced surface defect and optimized surface passivation of the CSARP strategy.

Table S1. Detailed optical properties of samples with various halogen ratios.

Precursors molar ratios of MgCl ₂ :MgBr ₂ : MgI ₂	Emission peak (nm)	FWHM (nm)	Atom ratios of Cl:Br:I
1:0:0	409	9	100:0:0
2:1:0	447	13	66:34:0
1:1:0	465	17	55:45:0
1:2:0	494	18	30:70:0
0:1:0	512	16	0:100:0
0:2:1	545	44	0:96:4
0:1:1	586	52	0:84:16
0:1:2	630	43	0:52:48
0:0:1	658	42	0:0:100

Table S2. The volumes of HEX and TBA used for the synthesis of CSARP-CsPbX₃ NCs.

Precursors molar ratio of MgCl ₂ :MgBr ₂ : Mgl ₂	TBA (mL)	HEX (mL)
1:0:0	2	8
2:1:0	2.5	7.5
1:1:0	3	7
1:2:0	4	6
0:1:0	5	5
0:2:1	6	4
0:1:1	6.67	3.33
0:1:2	7	3
0:0:1	8	2

References

1. Zhang, X.; Bai, X.; Wu, H.; Zhang, X.; Sun, C.; Zhang, Y.; Zhang, W.; Zheng, W.; Yu, W. W.; Rogach, A. L., Water-assisted size and shape control of CsPbBr₃ perovskite nanocrystals. *Angew. Chem. Int. Ed.* 2018, 57 (13), 3337–3342.