## Supporting Information

# Multivariant ligands stabilize anionic solvent-oriented α-$CsPbX_3$ nanocrystals at room temperature

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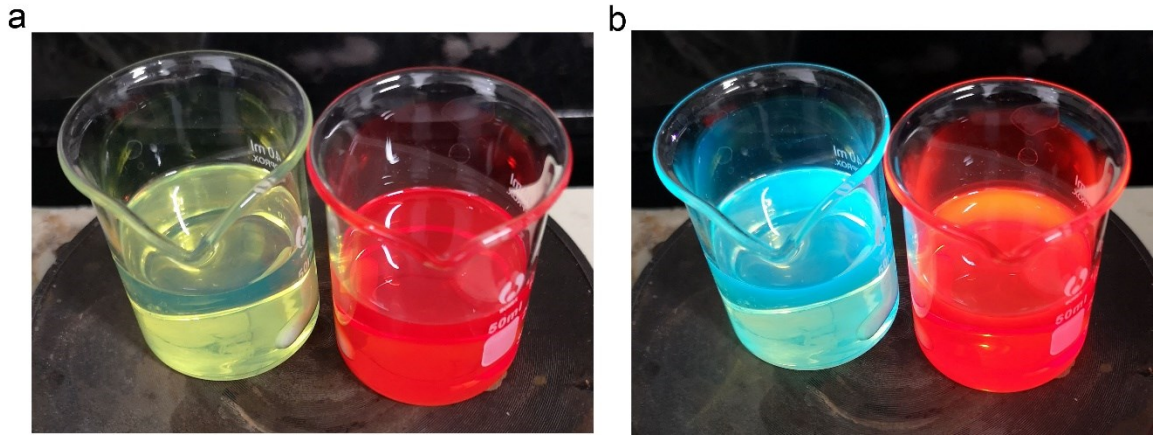


**Fig S1.** Temperature fluctuation effect. The $CsPbX_3$ (X= Br, I) were obtained in OA / OLA / toluene at R.T. (a) Photograph under daylight. (b) Photograph under 365 nm excitation after centrifuging for one minute at 4000 RPM (The heat produced by centrifugal process). The color of $CsPbBr_3$ changes from sky-blue to cyan.

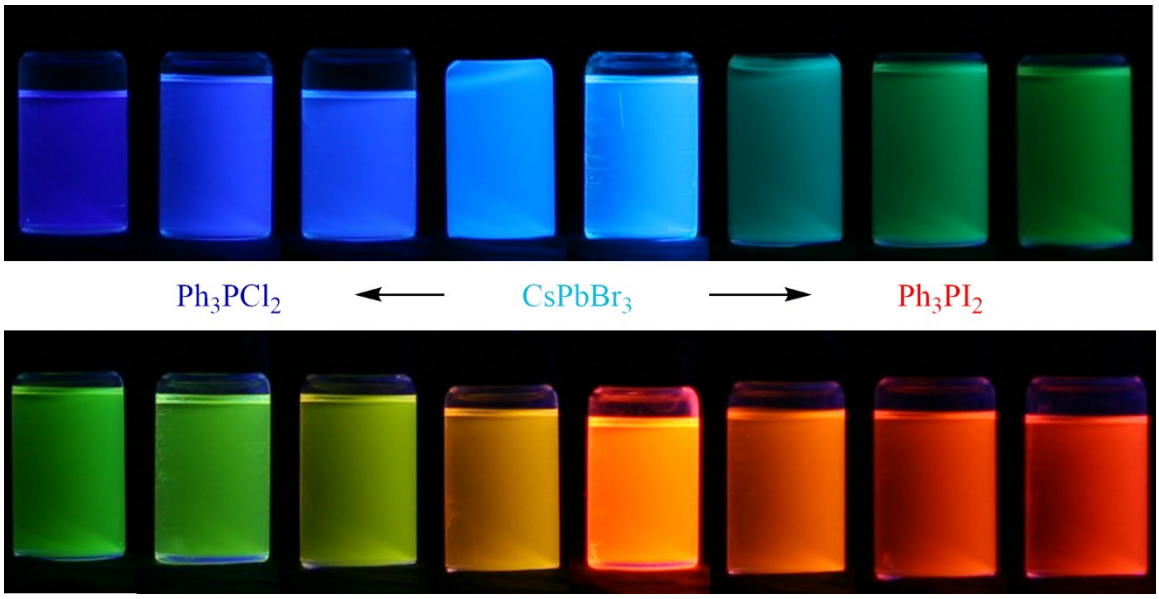


**Fig S2.** Ion exchange property. Rapid PL change at R.T. was induced by adding stoichiometric $Ph_3PCl_2$ or $Ph_3PI_3$ to $CsPbBr_3$ solution. This exchange reaction was completed immediately by shaking mixture solution.

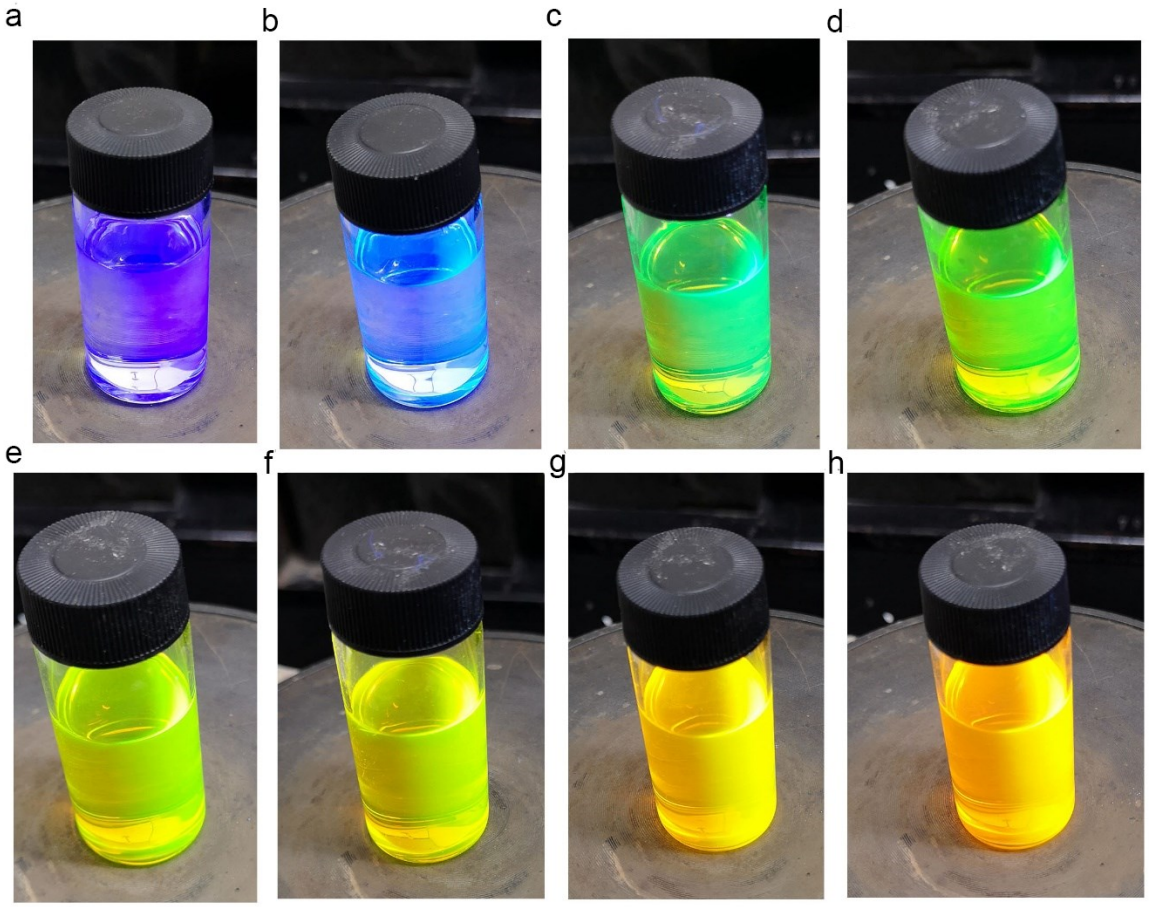


**Fig S3.** Ion exchange stability. The all $CsPbX_3$ NCs were obtained in OA / OLA / $CH_3Cl_3$ at R.T. Adding $Ph_3PCl_2$ or $Ph_3PI_2$ to optimized $CsPbBr_3$ solution. (a) $CsPbCl_3$ NCs. (b) $CsPbBr_3$ NCs. (c-h) $CsPbBr_{3-x}I_x$ NCs. All alloyed NCs show no fluorescence intensity reduction.

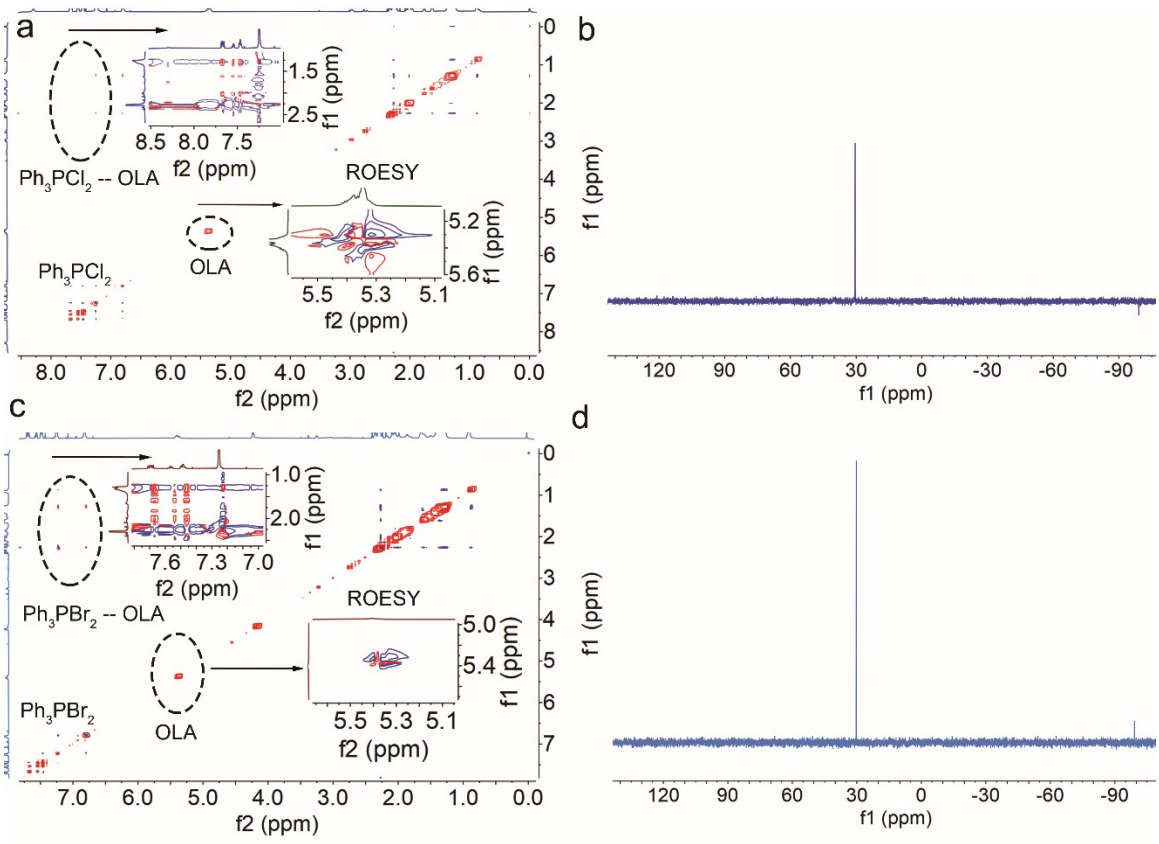


**Fig S4.** The ROESY characterized NCs were obtained in OA / OLA / $Ph_3P$ / $C_6Cl_6$ / $CD_3Cl$ for $CsPbCl_3$ NCs at R.T. and in OA / OLA / $CD_3Cl$ for $CsPbBr_3$ NCs at R.T. Two-dimensional ROESY of the (a) $CsPbCl_3$ and (c) $CsPbBr_3$ NCs. $^{31}$P-NMR of (b) $CsPbCl_3$ and (d) $CsPbBr_3$ NCs.

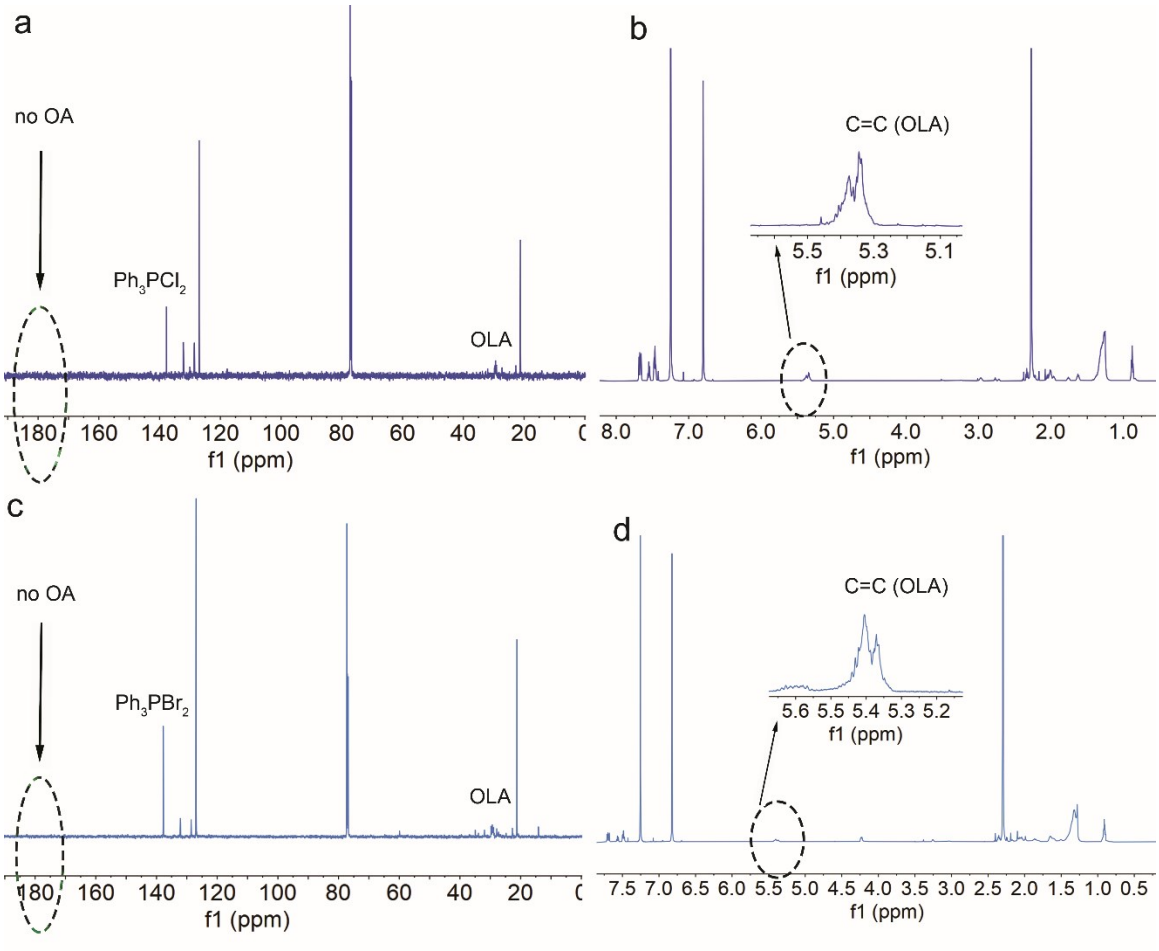


**Fig S5.** NMR characterized NCs were obtained in OA / OLA / $Ph_3P$ / $C_6Cl_6$ / $CD_3Cl$ for $CsPbCl_3$ NCs at R.T. and in OA / OLA / $CD_3Cl$ for $CsPbBr_3$ NCs at R.T. $^{13}$C-NMR spectrum of (a) $CsPbBr_3$ NCs. (c) $CsPbCl_3$ NCs. $^{1}$H-NMR spectrum of (b) $CsPbBr_3$ NCs. (d). $CsPbCl_3$ NCs. The top-right insert is $^{1}$H-NMR spectrum of OLA.

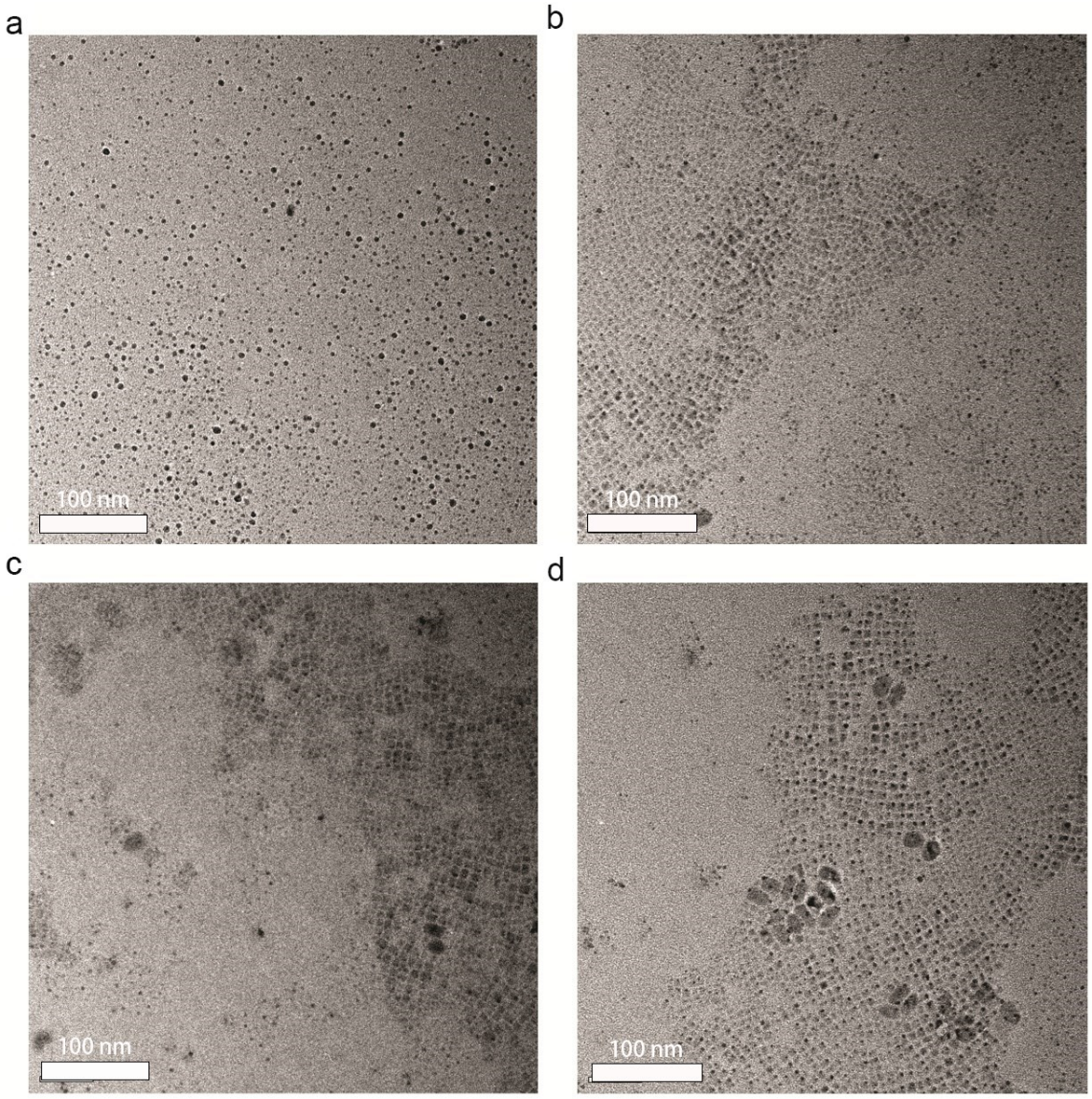


**Fig S6.** TEM of $CsPbCl_3$ NCs obtained in OA / OLA / $Ph_3P$ / $C_6Cl_6$ / $CD_3Cl$ at different reaction time of (a) 5 min (b) 10 min. (c) 20 min. (d) 40 min. Morphology evolution from initial dotted shape to small square size indicates nucleation growth of $CsPbCl_3$ NCs. The scale bars are 100 nm.

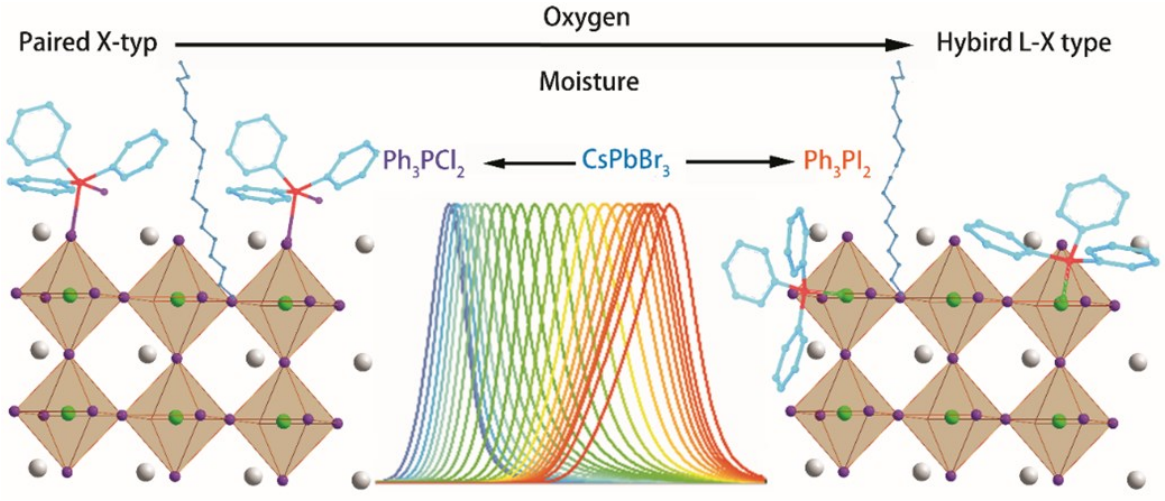


Fig S7. Ligands evolution model of $CsPbX_3$ NCs. The initial ligands are paired-X-type ligands with R-$NH_3^+$ and $Ph_3PX_2$. After destroyed by moisture, the surface ligands were hybrid L-X type with R-$NH_3^+$ and $Ph_3PO$.

**Movie S1.** rapid synthesis of blue $CsPbBr_3$ NCs.

In a typical synthesis, metal precursor solution was dropped into $CH_3Cl$ (bromine was diluted in $CH_3Cl$) at room temperature. The stirred solution immediately shows blue fluorescence.

**Movie S2.** rapid synthesis of orange $CsPbI_3$ NCs

In a typical synthesis, metal precursor solution was dropped into toluene (iodine was ultrasonically dissolved in toluene) at room temperature. The stirred solution immediately shows orange fluorescence.