**Supporting Information**.

## Formation Mechanisms of CsPbBr<sub>3</sub>/Cs<sub>4</sub>PbBr<sub>6</sub> Micr oscale Composites Assisted by Imidazolium Cation s and Their Device Application

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Figure. S1. Schematic diagram of synthesizing the MCs, with inset photos showing the products under natural light and UV light, respectively.



Figure S2. (a) PXRD analysis of intermediate samples from acetone. Impurities fitted well with the patterns of cubic CsBr #73-0391. (b) SEM images of the intermediates and their final products.



Figure S3. EDS element analysis of intermediate using acetone as anti-solvent.



Figure S4. HRTEM images of MCs obtained from acetone.



Figure S5. TEM images and the size distribution of HI-NCs (left blue block) and MCs prepared in<br/>toluenetoluene(rightgreenblock).



Figure S6. (a) 3D and (b) 2D differential charge density of CsPbBr<sub>3</sub> (100) dimethyimidazolium attached surface.



Figure S7. (a) Photos taken during the reprecipitation process. emission and excitation spectrum of (b) the DMSO precursor and (c) the THF supernatant in the intermediate.

The PL lifetime fitted with the decay curves exponentially by the following equation:

$$y = y_0 + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$$

where  $\tau_1$  is the lifetime of exciton recombination pathway of the emission and  $\tau_2$  the lifetime of defect-related PL process, while their weights are represented by  $A_1$  and  $A_2$ , respectively.

	$\tau_1(ns)$	$\tau_2(ns)$	A <sub>1</sub> /(A <sub>1</sub> +A <sub>2</sub> )
HI-NCs	5.6	15	80%
MCs (toluene)	5.8	41	74%
MCs (THF)	6.1	44	78%
MCs (pyridine)	3.1	18	72%
MCs (acetone)	5.3	29	76%

Table S1 The multi-exponential fitting results of the HI-NCs and MCs.



**Figure S8**. (a) impacts of ligands in the MCs product. From right, no ligands, 1/3 of the default [C14mim]Br, default [C14mim]Br, 3 times the default [C14mim]Br, [C8mim]Br, [C10mim]Br, [C10mim]Br, [C10mim]Br and [C16Py]Br were used as ligands, and the MCs were stored in cyclohexane. The upper photo was taken under UV light and the lower one under daylight. (b) PL spectrum of the MCs featuring samples using different amount of ligands ([C14mim]Br). (c) PL spectrum of samples using different ligands.



Figure S9. SEM images of the MCs coming from THF using (a) C16PyBr, (b) no ligands and (c) OA/OAm as ligands. The cyan-blue bar represents 20  $\mu$ m and the yellow bar is 5  $\mu$ m.



**Figure S10**. (a) PL spectrum of the MCs all capped with [C14mim]Br prepared in the corresponding solvents and HI-NCs capped with OA/OAm, the inset table shows the peak location and the fitted FWHM.