

Mechanical Milling Processed Highly Luminescent Cs-Pb-Br Perovskite Emitters

**Teng Zhang,^{a*} Youru Bai,^a Shaohuan Feng,^a Qifan Xue,^{b,c*}
Xiaotian Hu,^{d*} Xueqing Xu,^{c*} Heyuan Liu,^a Yuriy N. Luponosov,^e
Muhammad Bilal Khan Niazi^f and Xiyu Li^{a*}**

^a School of Materials Science and Engineering, China University of Petroleum (East China), Qingdao, 266580, P. R. China.

^b State Key Laboratory of Luminescent Materials and Devices, Institute of Polymer Optoelectronic Materials and Devices, School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, P. R. China.

^c Key Laboratory of New and Renewable Energy Research and Development, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, P. R. China

^d College of Chemistry and Chemical Engineering/Institute of Polymers and Energy Chemistry (IPEC)/Jiangxi Provincial Key Laboratory of New Energy Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

^e Enikolopov Institute of Synthetic Polymeric Materials of the Russian Academy of Sciences, Moscow 117393, Russia.

^f School of Chemical & Materials engineering, National University of Sciences & Technology, Islamabad, Pakistan

1. Experimental Section

1.1 Materials

Lead bromide (PbBr_2 , AR, 99.0%, Aladdin), Cesium bromide (CsBr , 99.5% metals basis, Aladdin), Oleylamine (OAM, 80-90%, Macklin), oleic acid (OA, 90%, Energy Chemical), n-Octylamine (90%, Macklin), n-Butylamine ($\geq 99.5\%$ (GC), Macklin), Toluene (AR, Tianjin Fuyu Fine Chemical Co., Ltd.), Dichloromethane (AR, Tianjin Fuyu Fine Chemical Co., Ltd.), Poly methyl methacrylate (PMMA, Average $M_w \sim 15000$ (GPC), J&K). All chemicals were used as received without further purification.

1.2 Synthesis of the Cs-Pb-Br NCs

Cs-Pb-Br NCs were synthesized by the ambient conditioned ball milling (DECO-PBM-AD-0.4L, Changsha Deke Co., Ltd.). To start with, 1.835g PbBr_2 (0.5mmol) and 1.064g CsBr (0.5 mmol) were added into the 100ml ball milling cans. The ball milling process has been set to 30 minutes with a rotation speed of 700 rpm/minutes. The milling balls added into the cans have been set to the following three conditions: A two large zirconia ceramic grinding balls (4.6g in total); B two large balls, six middle balls (7g in total) and C: three large balls, ten middle balls (10.9g). The mass ratio between the precursor and the milling balls corresponding to 1:1.16 (condition A), 1:2.41 (condition B) and 1:3.76 (condition C). The condition B was used for further optimization due to high PLQY.

Since dry-milled perovskite powders were not emissive, oleic acid (OA), oleylamine (OAM), octylamine (OLA) and butyl amine (BLA) were added into the milling cans

and an extra grinding time of 0.5 h was needed to prepare highly emitting NCs. After the wet-ball milling process, 8 ml toluene was added into the ball milling cans. The prepared products were centrifuged at 10000 rpm and redispersed in toluene several times to collect highly emitting Cs-Pb-Br perovskite NCs. The Cs-Pb-Br perovskite ink (0.5 ml, 0.75 ml, 1 ml and 1.25ml) has been mixed with 0.2g PMMA dissolved in 2 ml dichloromethane. These mixtures have been dropped on the glass substrate for XRD and stability characterization. As for the precursor engineering case, the precursor ratio has been set to Cs/Pb=1, 1.25 and 1.5.

2. Characterization Section

The X-ray diffraction (XRD) were conducted by X-ray diffraction (Ultima IV, Rigaku, Japan) equipped with Cu Ka ($\lambda=1.5418\text{\AA}$) radiation. The XRD results were analyzed with the Jade 6.0 software. The ultraviolet and visible (UV-vis) absorption characteristics have been collected by the U-3900 (hitachi). Fourier Transform Infrared Spectroscopy (FTIR) analysis has been measured with a Nicolet IS50 (Thermo fisher) spectrometer. The high resolution X-ray photoelectron spectroscopy (XPS) analysis has been performed with the K-Alpha (Thermo fisher) equipped with Al Ka ($h\nu=1486.68\text{eV}$) source. The XPS signal have been calibrated with the C 1s peak at 284.5 eV. As for the fluorescent characteristics, the steady-state photoluminescence (PL) spectrum have been conducted on FLS980 (Edinburgh) with a 400 nm excitation. The TRPL analysis was also collected by FLS980 (Edinburgh). The absolute PL quantum yield (PLQY) was collected with an integrating sphere embedded in the Edinburgh FLS980 instrument. The transmission electron microscope (TEM) images

and high resolution TEM (HR-TEM) images were pictured by Talos F200X (Thermo fisher).

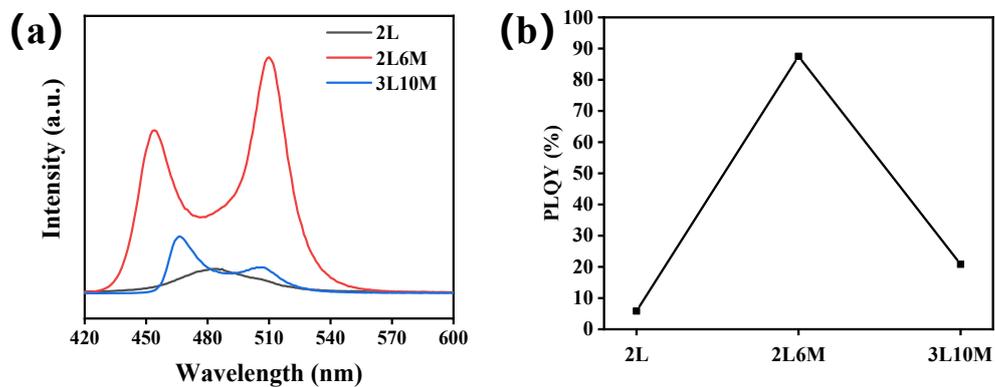


Figure S1. Milling ball dependent steady-state PL spectrum (a) and the corresponding PLQY variation (b). Here, L and M stand for large (small) ball with a mass of 2.3g and 0.4g. A 400 nm laser has been used for the steady-state PL characterization.

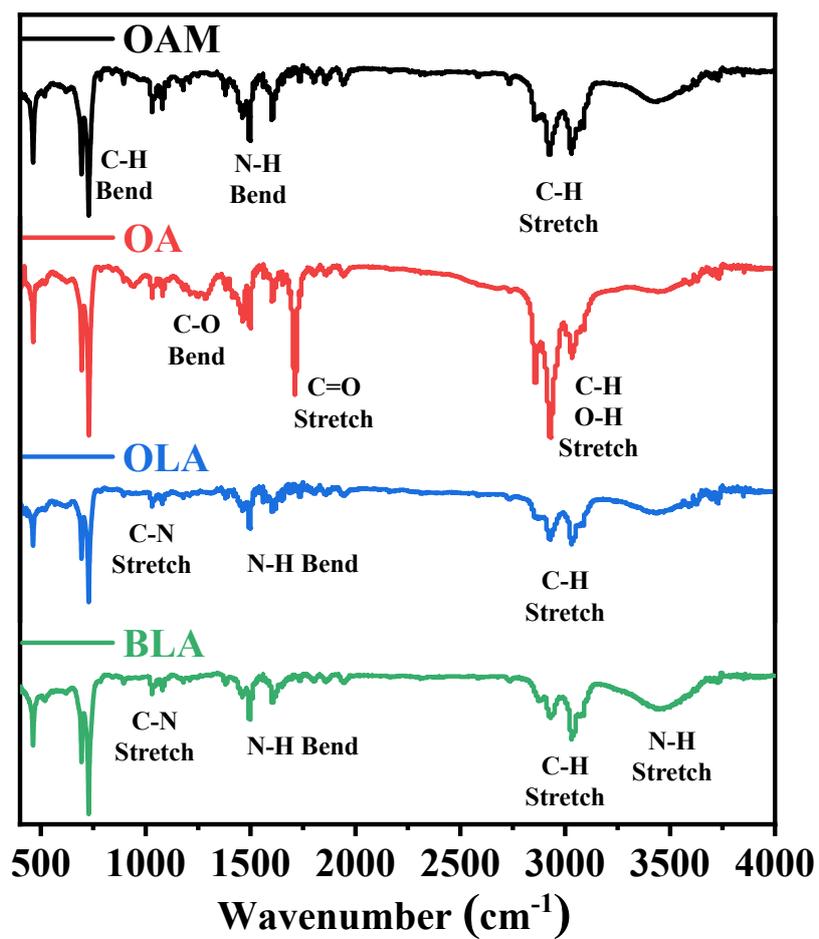


Figure S2. FTIR spectrum of the surfactant functionalized Cs-Pb-Br NCs dispersed in toluene.

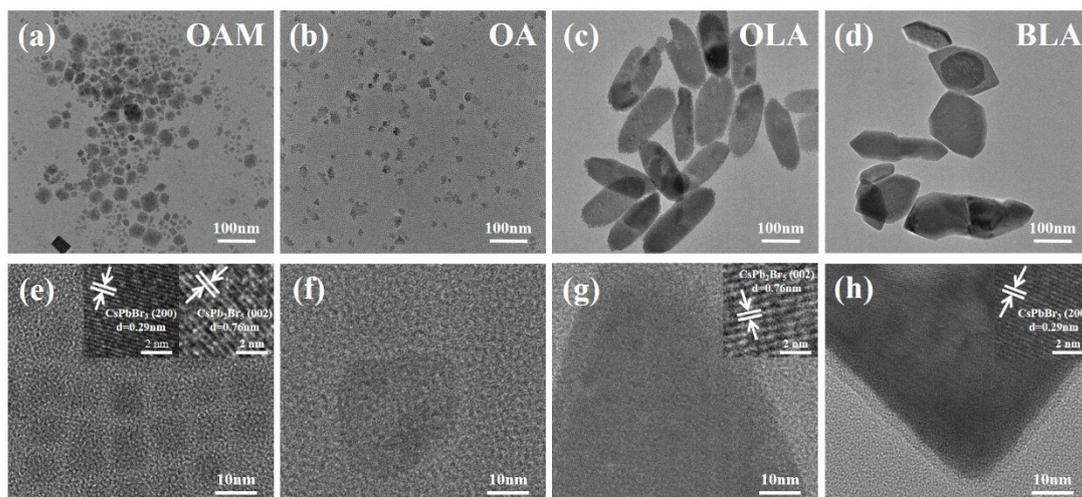


Figure S3. TEM images and the HRTEM images of the synthesized OAM functionalized NCs (a, e), OA functionalized NCs (b, f), OLA functionalized NCs (c, g) and BLA functionalized NCs (d, h).



Figure S4 Photographs of the Cs-Pb-Br NCs coated glass substrates under UV light illumination during a two-month storage.

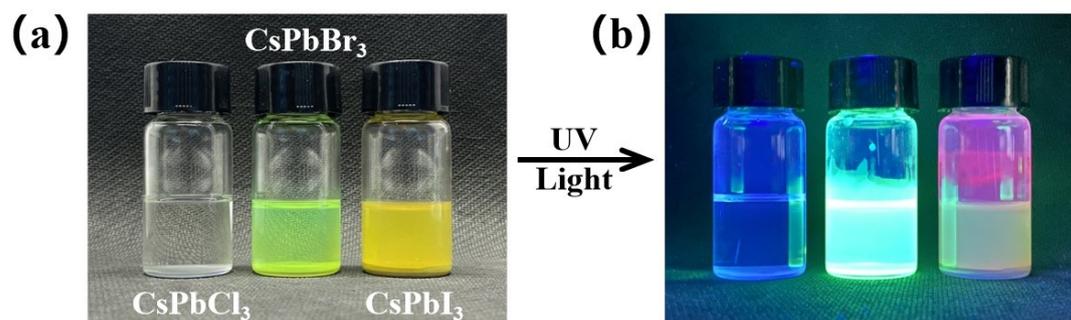


Figure S5. The emission characteristics of the CsPbX₃ (X=Cl, Br, I) emitters dispersed in toluene.

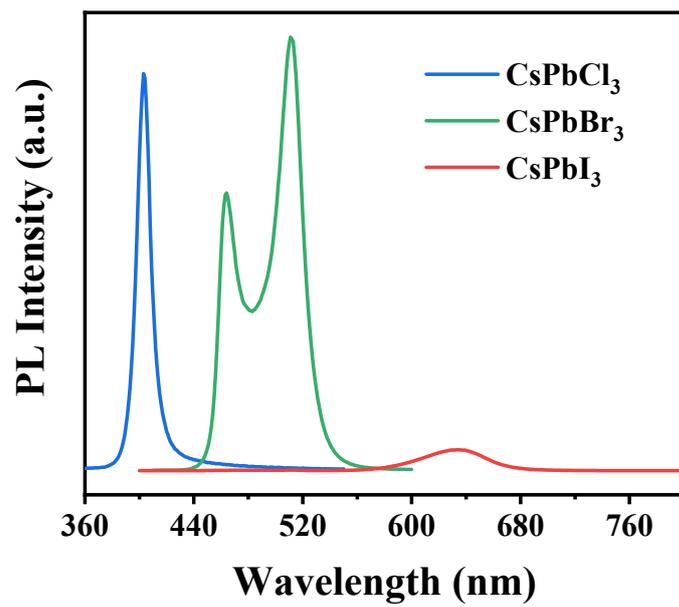


Figure S6. The PL spectrum of the CsPbX₃ (X=Cl, Br, I) emitters dispersed in toluene.

Table S1. The corresponding time constant extracted from the TRPL characterization recorded in Figure 2b.

	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_{ave} (ns)
OAM-functionalized	2.64	14.14	14.93	85.86	14.58
OA-functionalized	1.22	72.47	7.91	27.53	5.98
OLA-functionalized	1.66	33.31	5.21	66.69	4.73
BLA-functionalized	0.12	35.66	4.07	64.34	4.01