

Supporting Information

Stabilization of Organometallic Halide Perovskite Nanocrystals in Aqueous Solutions and Their Applications for Copper Ion Detection

Chunqing Ma,^{ab} Ming-Fai Lo ^{*ab} and Chun-Sing Lee^{*ab}

^aCenter of Super-Diamond and Advanced Films (COSDAF) and Department of Chemistry, City University of Hong Kong, Hong Kong SAR, P. R. China

^bCity University of Hong Kong Shenzhen Research Institute, Shenzhen 518057, Guangdong, P. R. China

*Email: mingflo@cityu.edu.hk and apcslee@cityu.edu.hk

Experimental Section

Fabrication of PNCs solutions and thin films

The PNCs solutions were prepared by antisolvent precipitation method without addition of capping ligands. A mixture of 0.1 mmol PEAI and 0.05 mmol PbI_2 was dissolved in 1 mL of DMF and was stirred for 1 h to form a precursor solution. 1 mL of precursor solution was dropped into 5 mL of toluene with vigorous stirring. Along with the mixing, strong green PL emission was observed. The solution was centrifuged at 1000 rpm for 10 mins to discard the precipitates, and a bright yellow colloidal solution was obtained. The PNCs thin films were fabricated via a blade-coated technique. The glass substrates were cleaned with deionized water and acetone. The PNCs solutions were centrifuged and blade-coated on the glass substrate to form PNCs film. The PNCs coated glass was dried at 80°C for 10 mins in air to remove residual solvent. It was then naturally cooled to room temperature.

Stabilities tests of PNCs in aqueous solution

Aqueous solutions with different PEAI concentrations (i.e. 0, 0.05, 0.15, 0.25, 0.5 M) were prepared by dissolve corresponding amounts of PEAI into water and stirred for 30 mins. Stabilities tests were conducted by immersing the PNCs films into the aqueous solutions. PL images were taken under UV illumination ($\lambda = 365 \text{ nm}$) after PNCs films immersing in different aqueous solutions for 1 min. XRD patterns were obtained after PNCs films immersing in different aqueous solutions for 1, 15, and 45 mins. Before the XRD measurement, the PNCs films were dried under vacuum for 10 min to remove residual solvent. The recyclable studies were conducted by immersing the PNCs films alternatively in water solution and 0.5 M PEAI aqueous solution for 4 cycles.

Metal ion detection

0.15 M PEAI aqueous solutions with different Cu^{2+} concentrations were prepared by dissolving corresponding amounts of CuCl_2 into the aqueous solutions and stirred for 30 mins. 0.15 M PEAI aqueous solutions with 5×10^{-2} M metal ions (i.e. Ca^{2+} , Na^+ , Mg^{2+} , K^+ , Ni^{2+} , Co^{2+} , Fe^{3+} , Zn^{2+}) were also prepared. The detection tests were conducted by immersing PNCs films into the aqueous solutions for 5 mins. Then their emission intensities and PL quenching effect were measured by PL.

Characterization

XRD results were obtained with a Philips X' Pert diffractometer with $\text{Cu K}\alpha$ radiation. PL spectra were recorded with a spectrofluorometer (Fluormax-4). Morphology and lattice structure were characterized with a transmission electron microscope (FEI/Philips Tecnai 12 BioTwin).

Table S1. Stability strategies for PNCs

Reference	Perovskite nanocrystals	Protective layer and process	Stable in water and method	Applications
1	CsPbX ₃	Didodecyl dimethylammonium sulphide; precipitation	No; insulation	Amplified spontaneous emission
2	CsPbX ₃	Adjacent ligands; X-ray treatment	1 day; insulation	No
3	CsPbX ₃	Trimethylaluminum cross-linking; vapor crosslinking	No; insulation	Light-emitting diodes
4	CsPbBr ₃	Silica particles; mixing method	No; insulation	Light-emitting diodes
5	CsPbBr ₃	AlO _x ; atomic layer deposition	1 hour; insulation	No
6	CsPbBr ₃	Polymethyl methacrylate; electrospun	Yes; insulation	sensors
7	CsPbBr ₃	Crosslinked polystyrene; swelling-shrinking strategy	100 hours; insulation	Light-emitting diodes
8	CsPbX ₃	Porous zeolite matrix; ion exchange	No; insulation	Light-emitting diodes
9	CsPbX ₃	Silica; mixing method	No; insulation	Light-emitting diodes
Our work	PEA₂PbI₄	No	2 months; inhibited diffusion	Copper ion detection

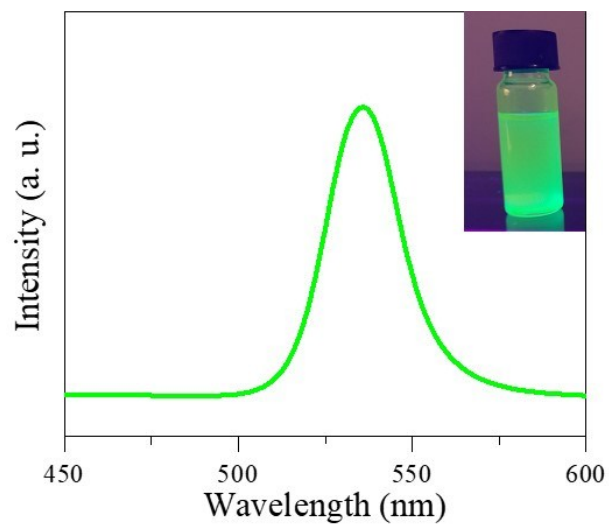


Fig. S1. PL spectrum of the pristine PEA₂PbI₄ PNCs. Inset is a picture of the PNCs solution taken under UV-illumination ($\lambda = 365$ nm).

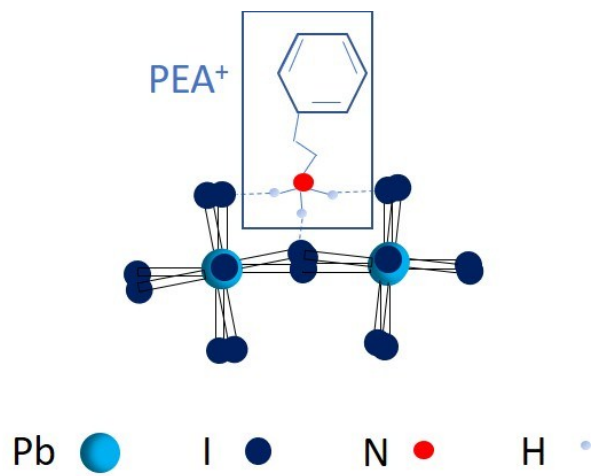


Fig. S2 Hydrogen-bonding scheme in PEA₂PbI₄ PNCs.

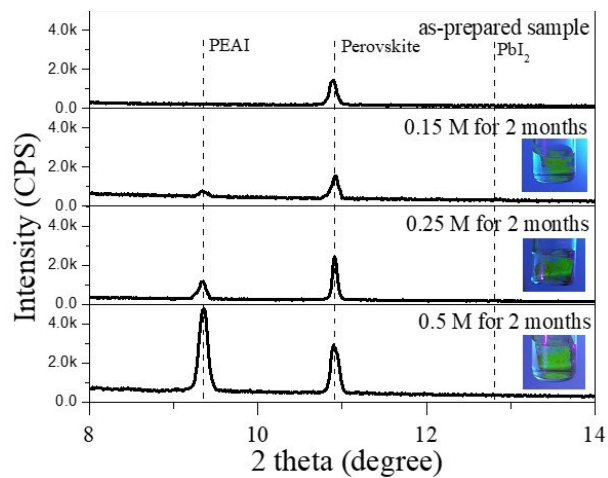


Fig. S3 XRD patterns of the as prepared sample (the top line) and samples after immersing in aqueous solutions with different PEA⁺ concentrations (0.15, 0.25, 0.5 M) for 2 months. Insets are the pictures taken under UV-illumination ($\lambda = 365$ nm).

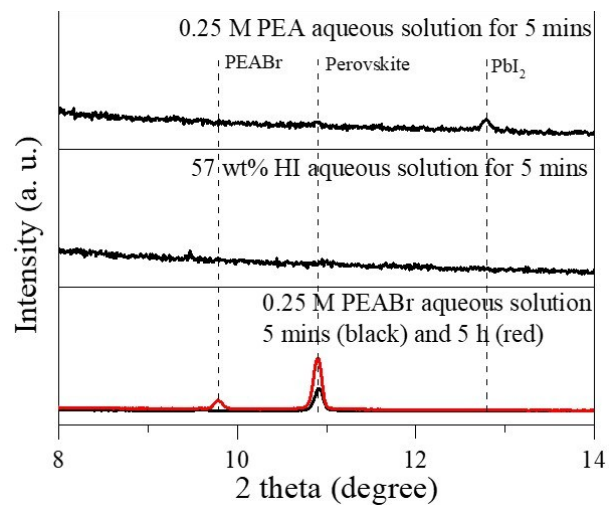


Fig. S4 XRD patterns of the PNCs after immersing in different aqueous solutions (0.25 M PEA, 57 wt% HI and 0.25 M PEABr aqueous solutions) for different times.

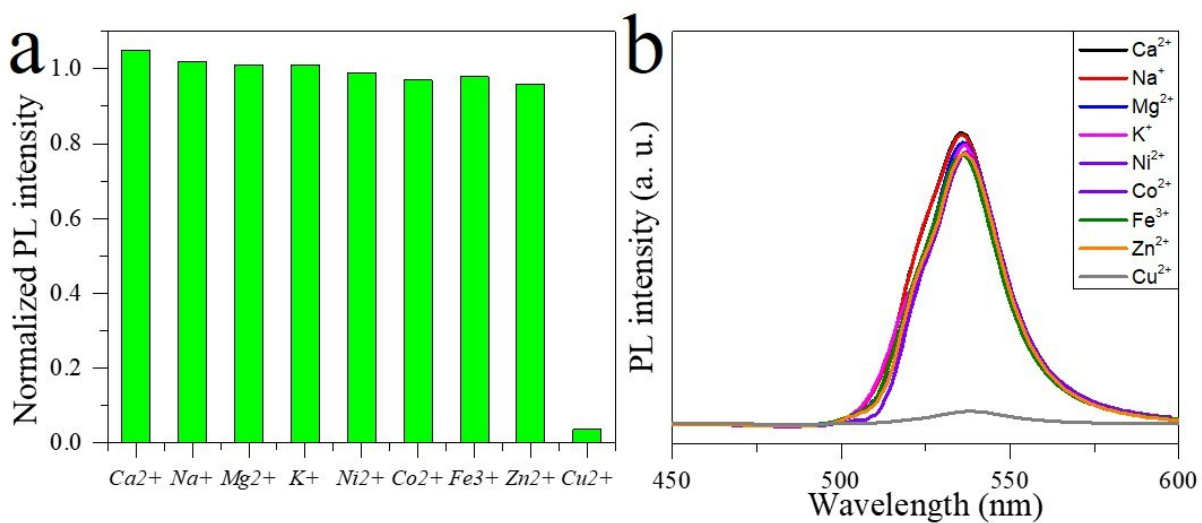


Fig. S5 (a) Effects of different metal ions on the PL intensity of the PNCs. (b) PL spectra of PNCs samples after immersing in different metal ion aqueous solutions. The concentration of metal ions is 5×10^{-2} M.

Reference

1. J. Pan, S. P. Sarmah, B. Murali, I. Dursun, W. Peng, M. R. Parida, J. Liu, L. Sinatra, N. Alyami and C. Zhao, *J. Phys. Chem. Lett.*, 2015, **6**, 5027-5033.
2. F. Palazon, Q. A. Akkerman, M. Prato and L. Manna, *ACS nano*, 2015, **10**, 1224-1230.
3. G. Li, F. W. R. Rivarola, N. J. Davis, S. Bai, T. C. Jellicoe, F. de la Peña, S. Hou, C. Ducati, F. Gao and R. H. Friend, *Adv. Mater.*, 2016, **28**, 3528-3534.
4. H. C. Wang, S. Y. Lin, A. C. Tang, B. P. Singh, H. C. Tong, C. Y. Chen, Y. C. Lee, T. L. Tsai and R. S. Liu, *Angew. Chem. Int. Ed.*, 2016, **55**, 7924-7929.
5. A. Loiudice, S. Saris, E. Oveisi, D. T. Alexander and R. Buonsanti, *Angew. Chem. Int. Ed.*, 2017, **56**, 10696-10701.
6. Y. Wang, Y. Zhu, J. Huang, J. Cai, J. Zhu, X. Yang, J. Shen and C. Li, *Nanoscale Horiz.*, 2017, **2**, 225-232.
7. Y. Wei, X. Deng, Z. Xie, X. Cai, S. Liang, P. a. Ma, Z. Hou, Z. Cheng and J. Lin, *Adv. Funct. Mater.*, 2017, **27**, 1703535.
8. J. Y. Sun, F. T. Rabouw, X. F. Yang, X. Y. Huang, X. P. Jing, S. Ye and Q. Y. Zhang, *Adv. Funct. Mater.*, 2017, **27**, 1704371.
9. C. Sun, Y. Zhang, C. Ruan, C. Yin, X. Wang, Y. Wang and W. W. Yu, *Adv. Mater.*, 2016, **28**, 10088-10094.