

Supporting Information

Enhanced Photothermal Stability of In-situ Grown FAPbBr₃ Nanocrystals in Polyvinylidene Fluoride by Incorporation of Cd²⁺ Ions

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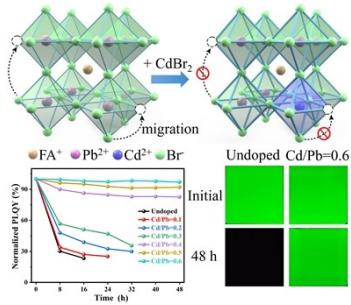
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We reported the enhanced photothermal stability of in-situ grown FAPbBr₃ perovskite nanocrystals in polyvinylidene fluoride by incorporation of Cd²⁺ ions, which with potential applications in backlight devices.

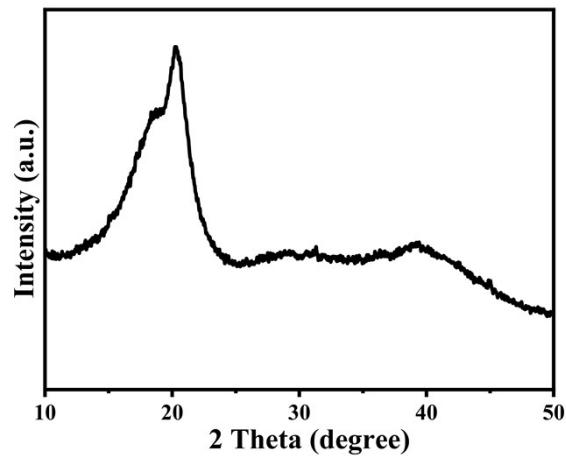


Fig. S1 XRD patterns of pure PVDF film.

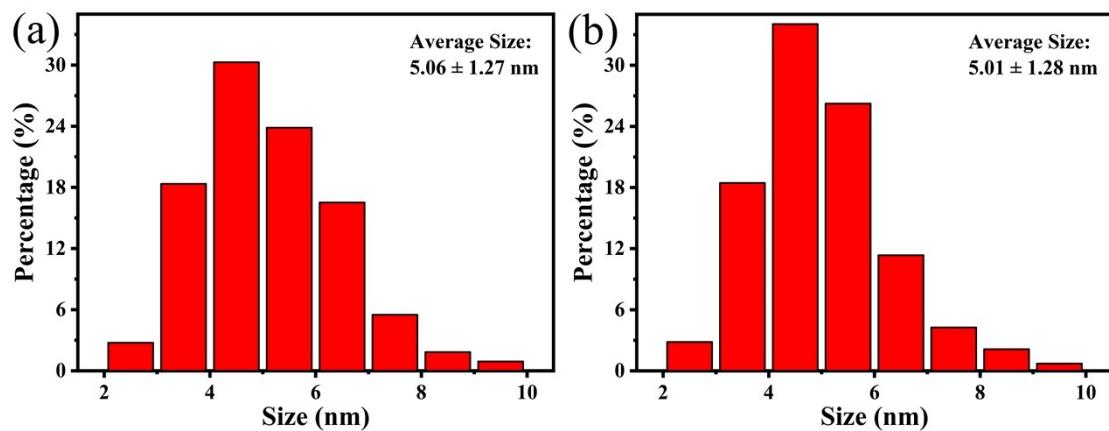


Fig. S2 Grain size distribution histograms of undoped FAPbBr₃ PNCs (a) and Cd²⁺-doped FAPbBr₃ (Cd/Pb = 0.6) PNCs (b).

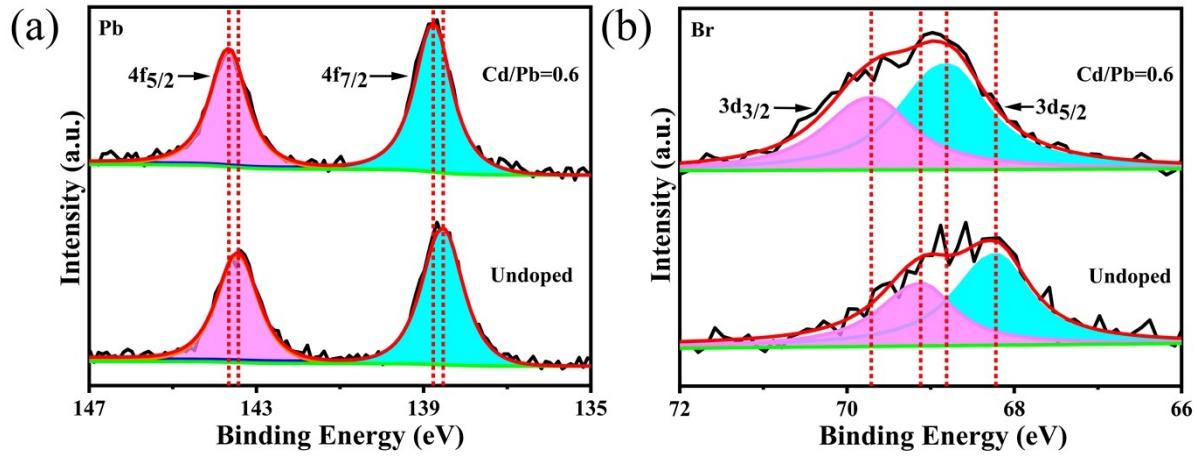


Fig. S3 XPS spectra of Pb 4f (a) and Br 3d (b) in purified undoped $FAPbBr_3$ and Cd^{2+} -doped $FAPbBr_3$ ($Cd/Pb = 0.6$) PNCs.

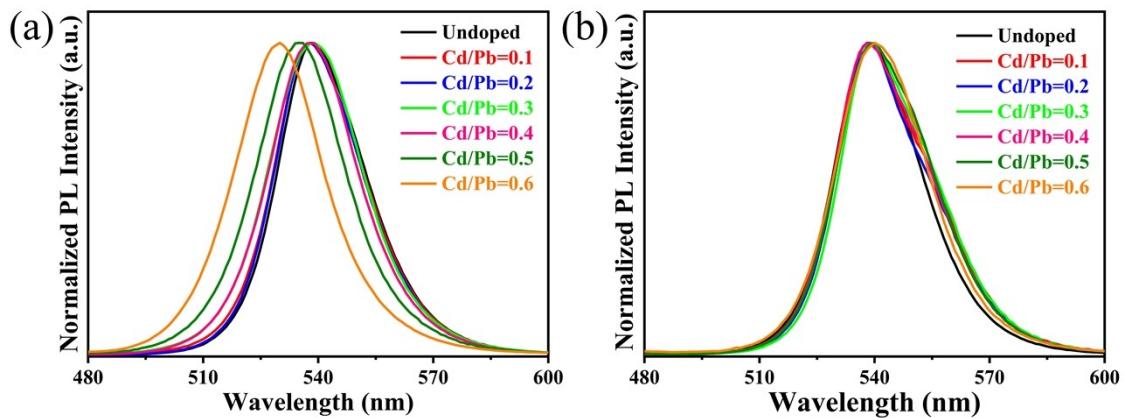


Fig. S4 Normalized PL spectra of Cd^{2+} -doped (Cd/Pb varied from 0.1 to 0.6) and undoped $FAPbBr_3@PVDF$ films before (a) and after (b) annealing at 393 K for half an hour.

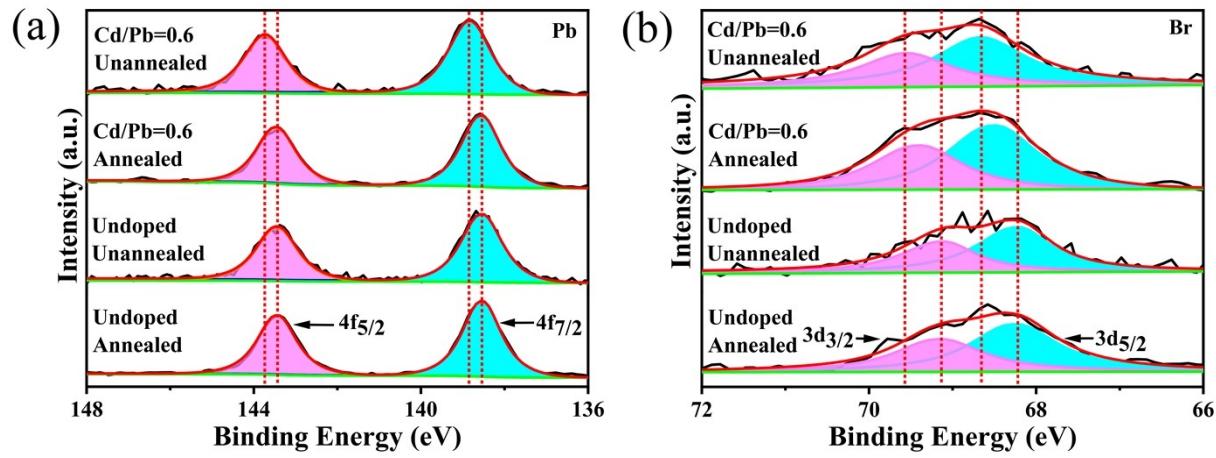


Fig. S5 XPS spectra of Pb 4f (a) and Br 3d (b) of purified undoped FAPbBr_3 PNCs and Cd^{2+} -doped FAPbBr_3 ($\text{Cd}/\text{Pb} = 0.6$) PNCs before and after annealing at 393 K for half an hour.

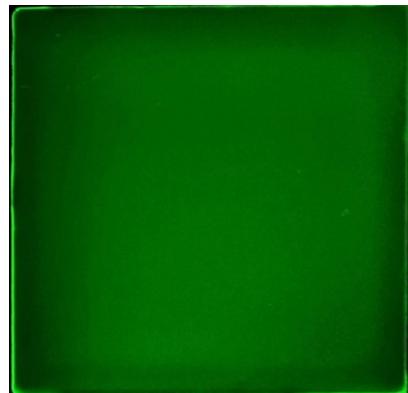


Fig. S6 The digital photograph of Cd^{2+} -doped $\text{FAPbBr}_3@\text{PVDF}$ ($\text{Cd}/\text{Pb} = 0.7$) film, under UV irradiation at 365 nm.

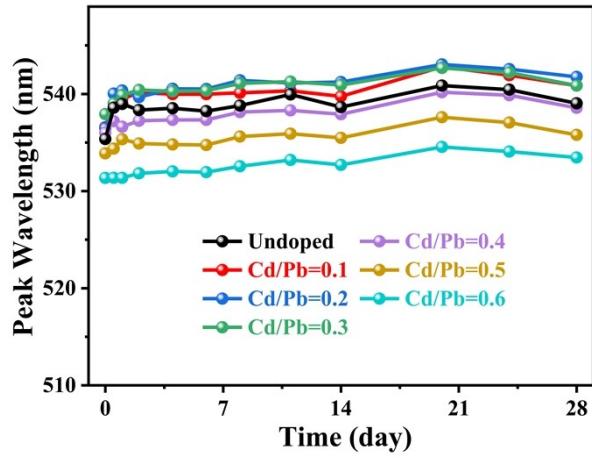


Fig. S7 PL peak wavelength evolution after different periods in an oven at 333 K of Cd²⁺-doped (Cd/Pb varied from 0.1 to 0.6) and undoped FAPbBr₃@PVDF films.

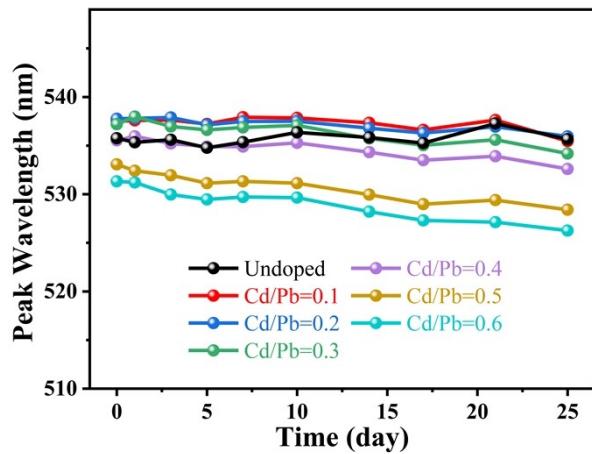


Fig. S8 PL peak wavelength evolution after different periods under continuous blue-light irradiation (460 nm, 13 mW/cm² at film surface) of Cd²⁺-doped (Cd/Pb varied from 0.1 to 0.6) and undoped FAPbBr₃@PVDF films.

Processing

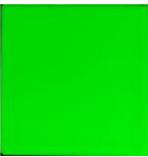
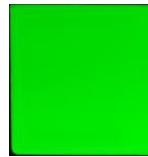
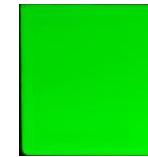
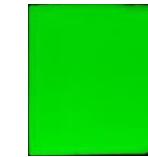
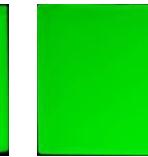
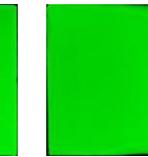
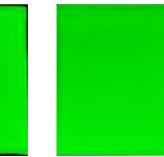
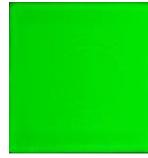
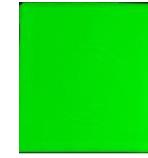
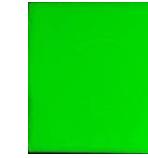
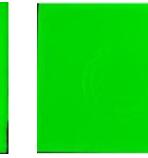
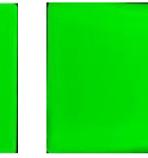
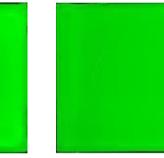
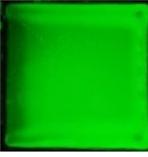
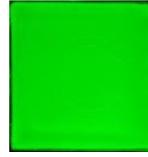
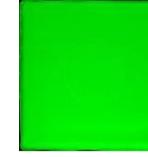
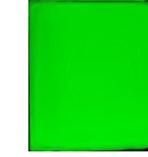
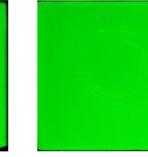
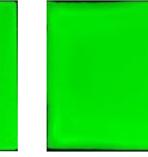
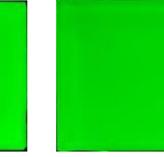
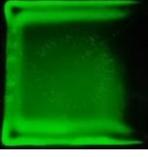
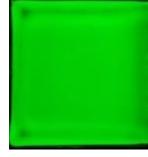
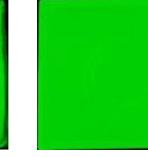
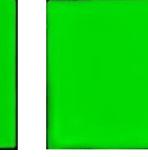
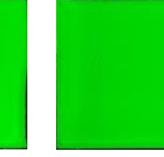
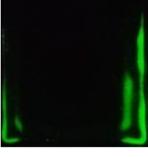
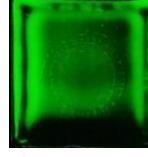
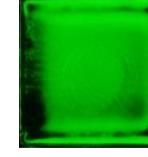
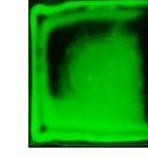
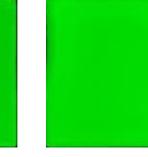
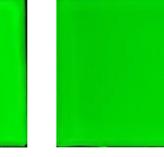
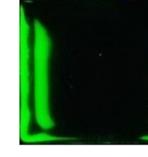
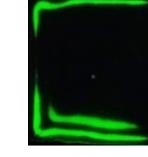
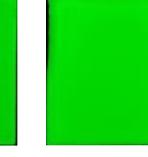
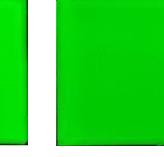
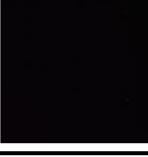
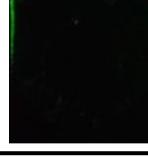
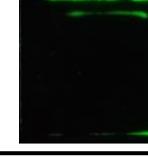
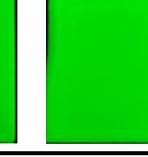
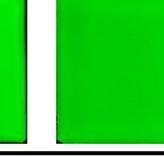
time	Undoped	Cd/Pb = 0.1	Cd/Pb = 0.2	Cd/Pb = 0.3	Cd/Pb = 0.4	Cd/Pb = 0.5	Cd/Pb = 0.6
0 h							
8 h							
16 h							
24 h							
32 h							
40 h							
48 h							

Fig. S9 The digital photographs under UV irradiation at 365 nm of Cd²⁺-doped (Cd/Pb varied from 0.1 to 0.6) and undoped FAPbBr₃@PVDF films treated in the environment of 333 K and blue-light (460 nm, 13 mW/cm²) irradiation for different time.

Table S1. The binding energy of Pb 4f and Br 3d in Cd²⁺-doped (Cd/Pb varied from 0.1 to 0.6) and undoped FAPbBr₃@PVDF films.

sample	Binding Energy (eV)		Binding Energy (eV)	
	Br ⁻ 3d _{5/2}	Br ⁻ 3d _{3/2}	Pb ²⁺ 4f _{7/2}	Pb ²⁺ 4f _{5/2}
Cd/Pb = 0.6	68.69	69.66	138.79	143.69
Cd/Pb = 0.5	68.64	69.65	138.73	143.63
Cd/Pb = 0.4	68.58	69.60	138.62	143.49
Cd/Pb = 0.3	68.48	69.46	138.61	143.47
Cd/Pb = 0.2	68.35	69.35	138.54	143.41
Cd/Pb = 0.1	68.28	69.26	138.53	143.40
Undoped	68.15	69.13	138.48	143.35

Table S2. Comparison of stability parameters of halide perovskites

Perovskite	Treatment	Emission peak (nm)	PLQY (%)	Photostability	Thermostability	Ref.
CsPbBr ₃	Integrated with mesoporous silica nanoparticles.	519		80% (96 h, 365 nm, 6 W)		1
CsPbBr ₃	Silica-coated	519	87	80% (168 h, 365 nm, 16 W)	85% (293 K heat up to 393 K)	2
CsPbBr ₃	Encapsulated in Dimethicone	522		55% (2 h, UV)	56% (273 K heat up to 353 K),	3
CsPbBr ₃	Encapsulate with a poly-diphenylvinylphosphine-styrene copolymer	518	90	64% (142 h, 365 nm)		4
CsPbBr ₃	Surface treatment using ammonium hexafluorosilicate		84	93% (53 h, 450 nm, 175 mW/cm ²)	90% (293 K heat up to 353 K)	5
CsPbBr ₃	Anchoring on BN nanosheets	523	71	95% (96 h, 365 nm)	50% (303 K heat up to 373 K),	6
CsPbBr ₃	Assembled on natural mineral halloysite nanotubes	526	56	82% (144 h, 365 nm)	60% (298 K heat up to 393 K)	7
CsPbBr ₃	N-alkylmonoamine ligands	515	96	80% (1 h, 450 nm, 9.3 mW/mm ²)		8
CsPbBr ₃ /CsPb ₂ Br ₅	Coordinated with partially hydrolyzed poly (methyl methacrylate) and polyethylenimine	520	75	60% (120 h, 365 nm, 2W)		9
CsPbCl ₃	Mn ²⁺ -doped	396, 587	54	40% (1 h, 2000 W)		10
CsPbCl ₃	Zn ²⁺ -doped	409	88	46% (70 h, 365 nm, 6W)	47% (273 K heat up to 413 K)	11
CsPbCl ₃	Cd ²⁺ -doped	406	98	60% (260 h, 365 nm, 8W)		12
CsPbCl ₃	Cd ²⁺ -doped and CdCl ₂ surface passivation	381	60	83% (168 h, 330 nm, 8 W)	54% (3 h, 358 K)	13
CsPb(Br/Cl) ₃	Cu ²⁺ -doped	455	80		75% (annealing at 523K)	14
CsPbBr ₃	Cu ²⁺ -doped	506	95		50% (annealing at 523K)	
CsPbBr ₃	Sn ²⁺ -doped	512	82		93% (105 min, 353K)	15
FAPbBr ₃	Cd ²⁺ -doped	530	75	96% (360 h, 460 nm, 13 mW/cm ²)	97% (48 h, 333 K and blue-light irradiation)	This work

References

1. 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. Engl.*, 2016, **55**, 7924-7929.
2. F. Gao, W. Q. Yang, X. L. Liu, Y. Z. Li, W. Z. Liu, H. Y. Xu and Y. C. Liu, *Chem. Eng. J.*, 2021, **407**, 128001.
3. Y. G. Yang, Q. Q. Li, Y. F. Liu, R. Cong, Y. Sun, J. S. Hou, M. Y. Ge, J. C. Shi, F. Zhang, G. Y. Zhao, N. Zhang, Y. Z. Fang and N. Dai, *ACS Appl. Nano Mater.*, 2020, **3**, 4886-4892.
4. W. Q. Yang, L. L. Fei, F. Gao, W. Z. Liu, H. Y. Xu, L. L. Yang and Y. C. Liu, *Chem. Eng. J.*, 2020, **387**, 124180.
5. Q. Zhang, Z. Li, M. Liu, L. Kong, W. Zheng, B. Wang and L. Li, *J. Phys. Chem. Lett.*, 2020, **11**, 993-999.
6. M. M. Yu, X. He, D. Y. Li, J. Lin, C. Yu, Y. Fang, Z. Y. Liu, Z. L. Guo, Y. Huang and C. C. Tang, *J. Mater. Chem. C*, 2021, **9**, 842-850.
7. J. Hao, X. Qu, L. Qiu, G. Li, Y. Wei, G. Xing, H. Wang, C. Yan, H. S. Jang, Z. Cheng and J. Lin, *Adv. Opt. Mater.*, 2018, **7**, 1801323.
8. W. K. Lin, G. X. Chen, E. L. Li, H. X. Xie, G. Peng, W. J. Yu, H. P. Chen and T. L. Guo, *Org. Electron.*, 2020, **86**, 105869.
9. G. Jiang, C. Guhrenz, A. Kirch, L. Sonntag, C. Bauer, X. Fan, J. Wang, S. Reineke, N. Gaponik and A. Eychmuller, *ACS Nano*, 2019, **13**, 10386-10396.
10. H. Liu, Z. Wu, J. Shao, D. Yao, H. Gao, Y. Liu, W. Yu, H. Zhang and B. Yang, *ACS Nano*, 2017, **11**, 2239-2247.
11. V. Naresh and N. Lee, *ACS Appl. Nano Mater.*, 2020, **3**, 7621-7632.
12. N. Mondal, A. De and A. Samanta, *ACS Energy Lett.*, 2019, **4**, 32-39.

13. Y. Zhang, X. Cheng, D. Tu, Z. Gong, R. Li, Y. Yang, W. Zheng, J. Xu, S. Deng and X. Chen, *Angew. Chem. Int. Ed. Engl.*, 2021, **60**, 9693-9698.
14. C. Bi, S. Wang, Q. Li, S. V. Kershaw, J. Tian and A. L. Rogach, *J. Phys. Chem. Lett.*, 2019, **10**, 943-952.
15. D. Yan, Q. Mo, S. Zhao, W. Cai and Z. Zang, *Nanoscale*, 2021, **13**, 9740-9746.