

Electronic Supplementary Information

for

Dual functional phosphate-ester BODIPY regulation achieved stable CsPbBr₃ nanocrystals for optical anti-counterfeiting

Xiaoxia Feng*, Ruicong Li, Jinli Liu, Qian Ma, Yixin Yang, Wenyuan Zhang,
Jiacheng Liu

Key Laboratory of Eco-Functional Polymer Materials of the Ministry of Education
Key Laboratory of Bioelectrochemistry & Environmental Analysis of Gansu Province
College of Chemistry and Chemical Engineering Northwest Normal University
Lanzhou 730070, P. R. China

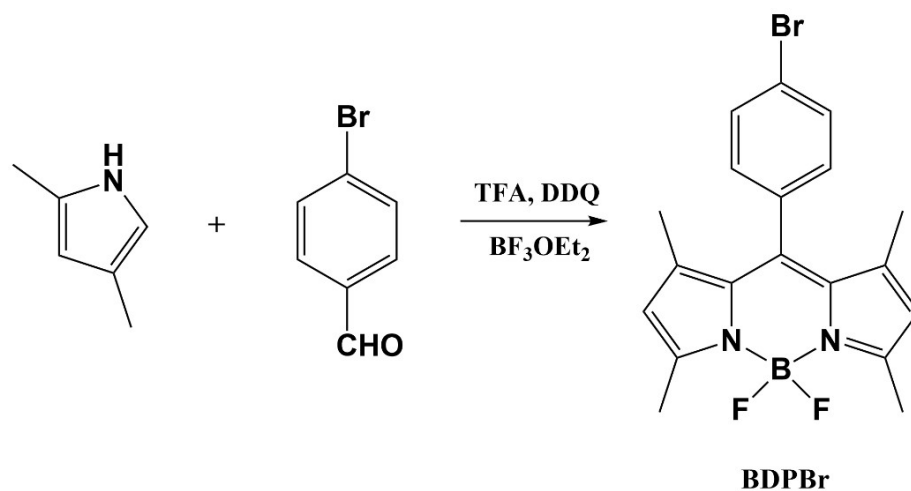
E-mail: fengxx@nwnu.edu.cn

- 1. Experimental Section**
- 2. Supplementary Figures**
- 3. Supplementary Tables**
- 4. Supplementary References**

1. Experimental Section

1.1 Experimental details

1.1.1. Synthesis of BDPBr



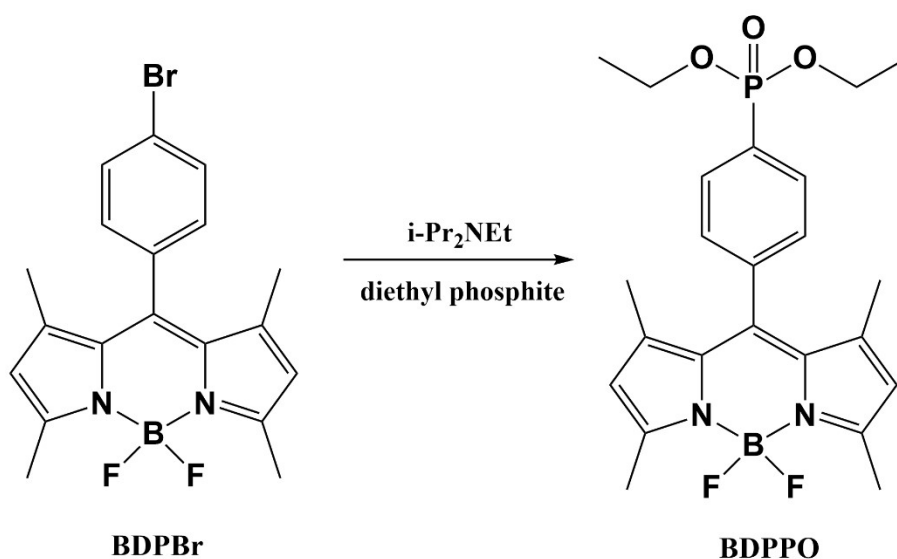
Schema S1. The synthesis route of BDPBr molecule.

Trifluoroacetic acid (TFA:0.3 mL, 2.70 mmol) was added dropwise to a stirred solution of 2,4-dimethyl pyrrole (2.57 mL, 27.02 mmol) and 4-bromobenzaldehyde (2.5 g, 13.51 mmol) in anhydrous CH_2Cl_2 (150 mL). The reaction mixture was stirred at room temperature under N_2 in a darkened flask overnight. Then, the DDQ (3.07 g, 13.51 mmol) was added in a single portion, and the mixture was stirred at room temperature for 3 h. Subsequently, the triethylamine (4.5 mL, 44.7 mmol) and $\text{Et}_2\text{O}\cdot\text{BF}_3$ (6.3 mL, 44.7 mmol) were added, and the mixture was stirred at room temperature overnight. The reaction mixture was washed and extracted by H_2O (2×150 mL) and brine (2×100 mL)¹. Then the solvent was removed to yield a dark-green solid. Purification using column chromatography on silica gel afforded the intended orange solid product (PE:DCM = 2:1), yield: 0.95 g (35.05 %).

^1H NMR (400 MHz, CDCl_3): δ 7.61-7.56 (m, 2H), 7.14-7.09 (m, 2H), 5.93 (s, 1H), 5.24 (s, 1H), 2.55 (s, 6H), 1.36 (s, 6H).

HRMS (ESI⁺): m/z $[\text{M}]^+$ calcd for $\text{C}_{19}\text{H}_{18}\text{BBrF}_2\text{N}_2$: 402.0701; found: 402.0701.

1.1.2. Synthesis of BDPPO



Schema S2. The synthesis route of BDPPPO molecules.

The $[\text{Pd}(\text{PPh}_3)_4]$ (3.0 g, 2.6 mmol) and BDPBr (10.41 g, 25.9 mmol) were dissolved in anhydrous DMSO (300 mL) under N_2 . $i\text{-Pr}_2\text{NEt}$ (10.11 mL, 78.2 mmol) and diethyl phosphite (10.81 mL, 31.2 mmol) were added subsequently and the solution was heated to 90 °C for 42 h. Then the H_2O (350 mL) was added to the reaction mixture and the suspension was extracted with CH_2Cl_2 (400 mL)². The organic layer was washed and extracted with H_2O (1×150 mL) and brine (1×150 mL), the solvent was removed to yield an orange solid. Purification using column chromatography on silica gel afforded the intended orange solid product (EtOAc: DCM = 1:10), yield: 3.31 g (27.77 %).

^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 7.90-7.82 (m, 2H), 7.61-7.54 (m, 2H), 6.17 (s, 2H), 4.09-3.99 (m, 4H), 2.46-2.41 (s, 3H), 2.03-1.89 (m, 3H), 1.50-1.39 (m, 3H), 1.31-1.29 (s, 9H).

HRMS (ESI⁺): m/z $[\text{M}]^+$ calcd for $\text{C}_{23}\text{H}_{28}\text{BF}_2\text{N}_2\text{O}_3\text{P}$: 460.1794; found: 483.1794. (M+Na)

1.2 Stability test

1.2.1 Long-time air stability

The CsPbBr_3 NCs or BDPPPO- CsPbBr_3 NCs toluene dispersions (0.8 mg/mL) was placed under air aged for 30 days (humidity 40%, room temperature), and the PL spectrum was tested in different time.

1.2.2 Water-stability

1 mL of deionized water was added to 2 mL CsPbBr₃ or BDPPPO-CsPbBr₃ NCs toluene dispersions (1.0 mg/mL), respectively. The PL spectrum was recorded with time at room temperature.

1.2.3 Photo-stability

The CsPbBr₃ NCs or BDPPPO-CsPbBr₃ NCs were dispersed in toluene solution (2.0 mg/mL), respectively. Then, the suspension was irradiated under the UV light for different times at room temperature, and the supernatants were diluted for detection.

1.2.4 Thermal-stability

The CsPbBr₃ NCs or BDPPPO-CsPbBr₃ NCs was dispersed in toluene solution (0.8 mg/mL), and then heated to different temperature (20-80 °C) or cooled to 20 °C for thermal stability testing.

The CsPbBr₃ NCs or BDPPPO-CsPbBr₃ NCs was deposited on the FTO glass, respectively, and the samples were heated to 100 °C and then cooled to room temperature to observe their fluorescence changes.

1.3 DFT calculations

We use density functional theory (DFT) to calculate the complexation energy of P=O:Cs and P=O:Pb. Firstly, the molecular geometry was optimized with M06-2X as functional and def2-SVP as the basis group for H, C, N, O, B, F, P, Pb and Cs atoms. Then, M06-2X as functional and def2-TZVP as the basis group was used to calculate the single electric energy and obtain the complexation energy by difference.

1.4 Time-resolved photoluminescence spectra

The time-resolved photoluminescence spectra of CsPbBr₃ and BDPPPO-CsPbBr₃ in toluene were measured, and they can be well fitted to triple exponential kinetic function³, $I = A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2} + A_3e^{-t/\tau_3}$.

The average fluorescent lifetime for each sample was calculated using:

$$\tau_{avg} = \frac{\sum_{i=1}^3 (A_i \tau_i^2)}{\sum_{i=1}^3 (A_i \tau_i)}$$

where A_i and τ_i are the respective fractional amplitude and lifetime, respectively.

1.5 Anti-counterfeiting test

The BDPPPO-CsPbBr₃ and CsPbBr₃ NCs were severally dispersed in toluene solution (2.0 mg/mL). They were used to draw patterns of cycle identification and fragmentary leaf on ordinary filter paper, respectively. The patterns were almost invisible in daylight and the green pattern appeared upon exposure on the 365 nm UV light.

(1) In **Fig. 5b**, the pure water was sprayed on the patterns, only the cycle identification was displayed on the paper because the water stability of BDPPPO-CsPbBr₃ NCs is higher than that of CsPbBr₃ NCs, which could achieve the purpose of one-time optical anti-counterfeiting.

(2) In **Fig. 5c**, the coated filter paper is placed on the heating plate. The fragmentary leaf might disappear due to the poor thermal stability of CsPbBr₃ under heating to 100 °C, while the cycle identification was preserved. After cooling to room temperature, all patterns were revealed again, achieving the reversible optical anti-counterfeiting.

2. Supplementary Figures

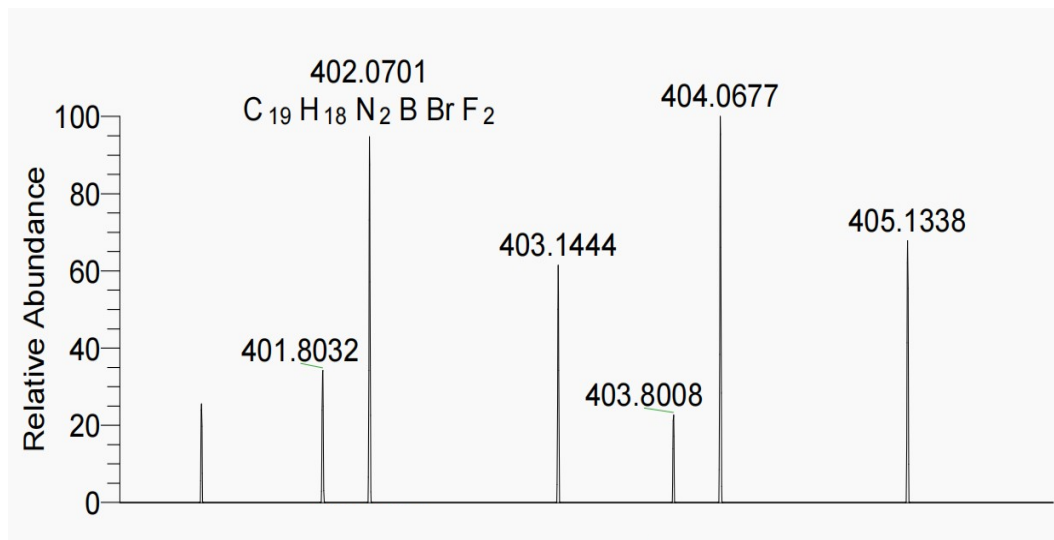


Fig. S1 The HRMS spectrum of BDPBr.

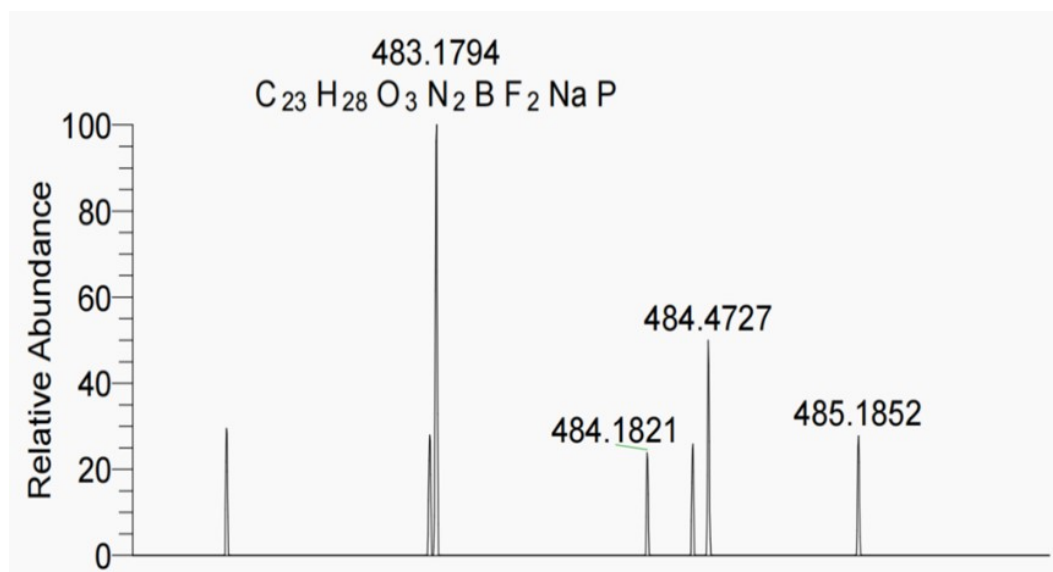


Fig. S2 The HRMS spectrum of BDPPPO.

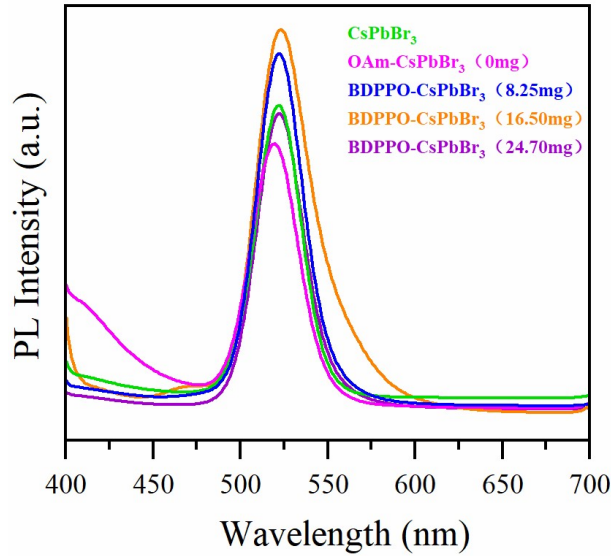


Fig. S3 The effect of various amounts BDPPPO on fluorescence intensity.

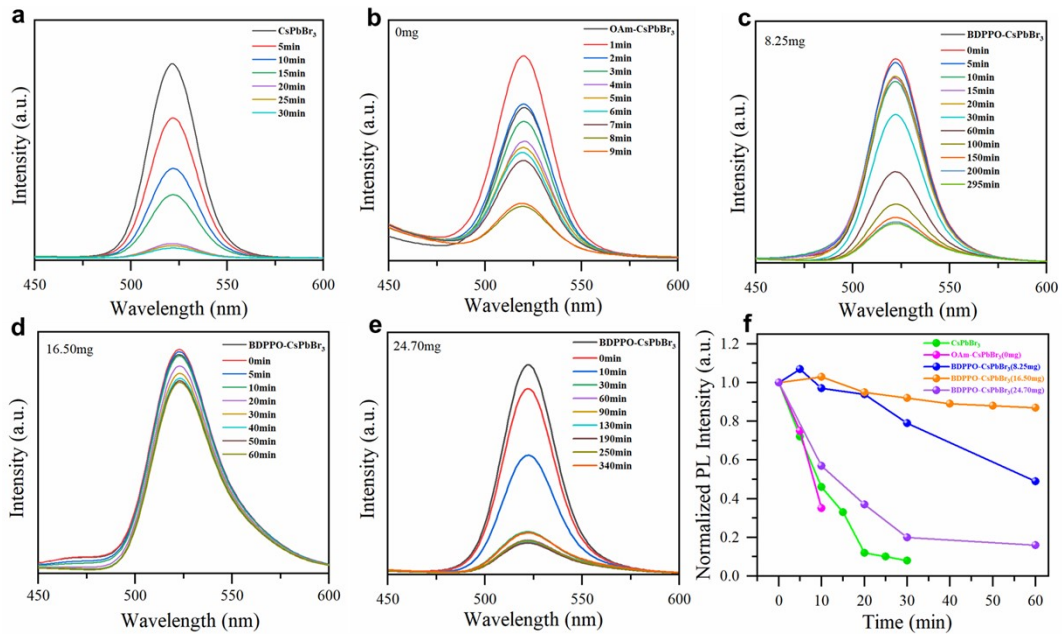


Fig. S4 The effect of various amounts BDPPPO on water stability of the BDPPPO-CsPbBr₃. (a) CsPbBr₃ (0.05 mL OAm, 0.10 mL OA), (b) OAm-CsPbBr₃ (only 0.05 mL OAm, without BDPPPO or OA), (c-e) BDPPPO-CsPbBr₃ (0.05 mL OAm, 8.25 mg BDPPPO (c)/16.50 mg BDPPPO (d)/24.70 mg BDPPPO (e)). (f) The normalized PL intensity about water stability. The stability of samples against water was tested by adding 1 mL of water into 2 mL of CsPbBr₃/BDPPPO-CsPbBr₃ toluene solution.

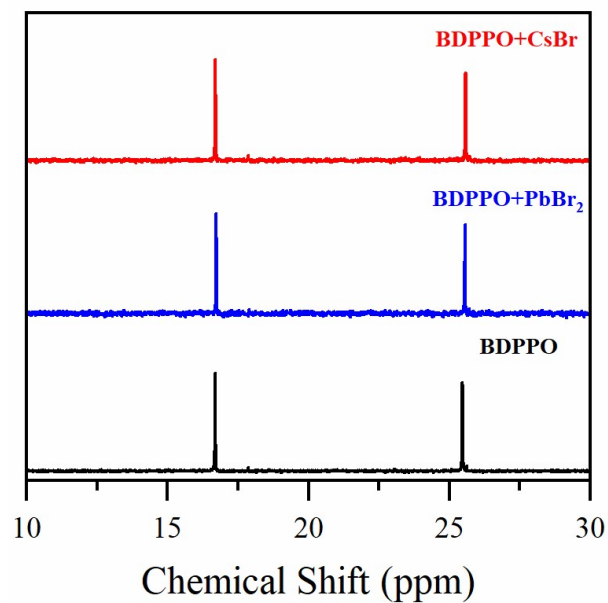


Fig. S5 ^{31}P NMR spectroscopy of pristine BDPPO and BDPPO mixed with CsBr and PbBr_2 recorded in DMSO-d_6 .

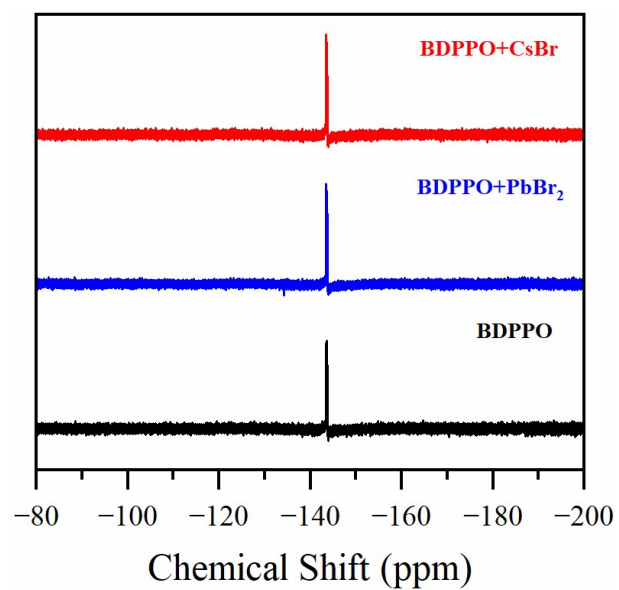


Fig. S6 ^{19}F NMR spectroscopy of pristine BDPPO and BDPPO mixed with CsBr and PbBr_2 recorded in DMSO-d_6 .

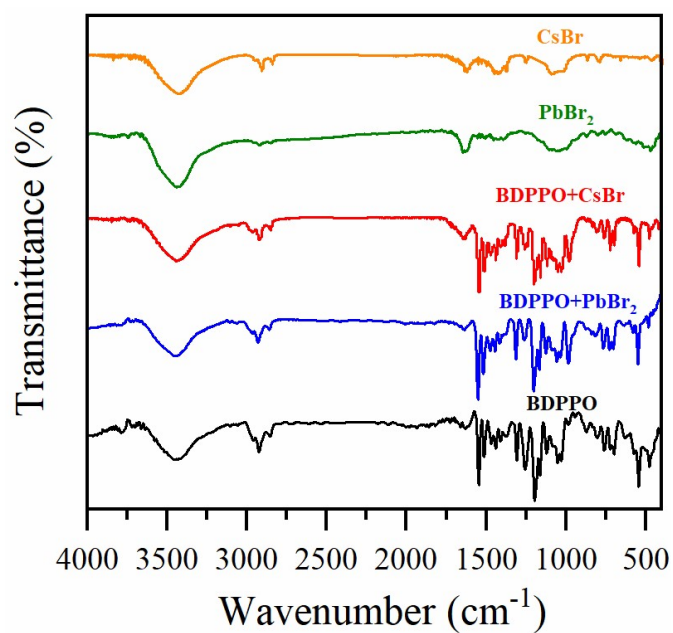


Fig. S7 The full FTIR spectrum at 4000-400 cm^{-1} for CsBr, PbBr_2 , BDPPO+CsBr, BDPPO+ PbBr_2 , BDPPO.

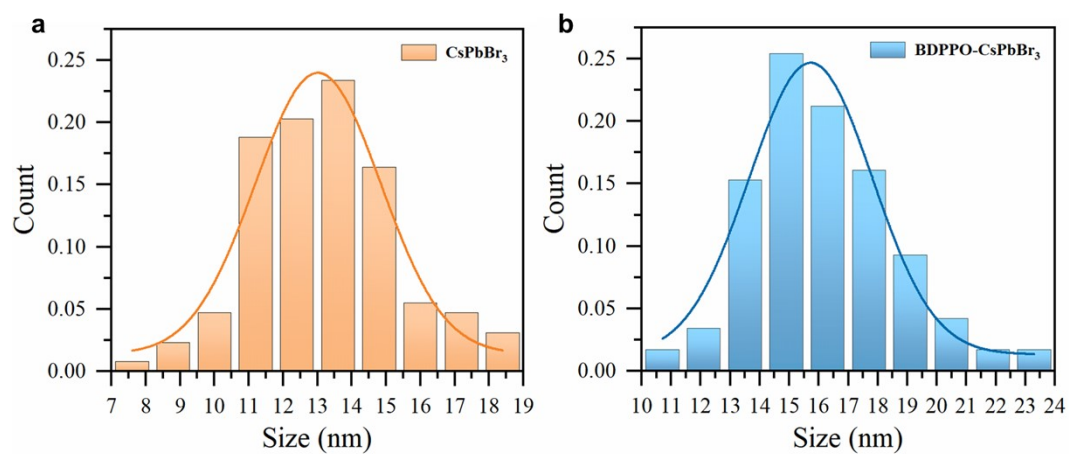


Fig. S8 Size distribution of (a) CsPbBr_3 and (b) BDPPO- CsPbBr_3 .

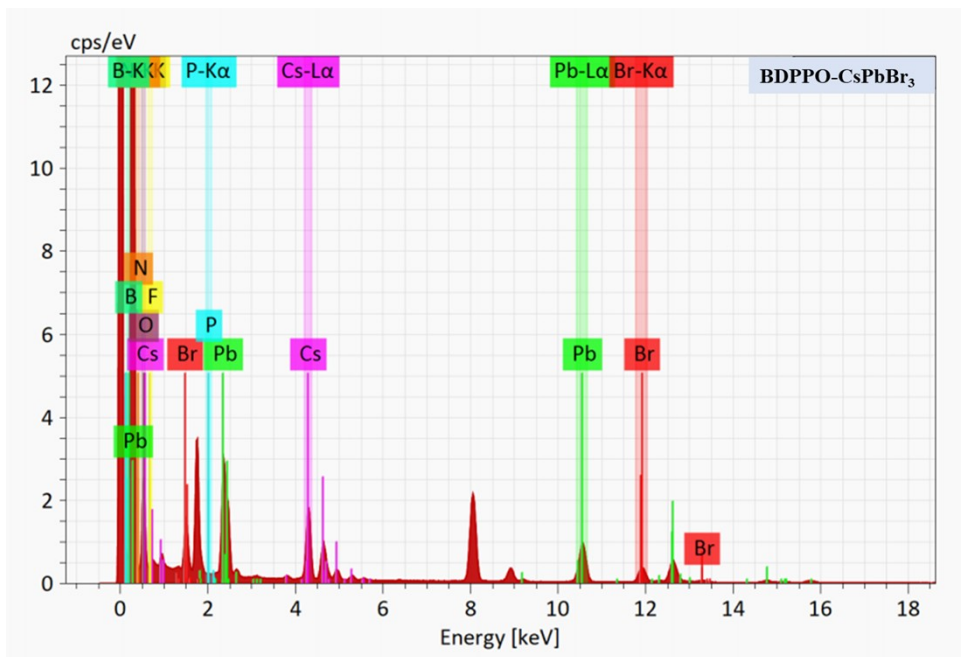


Fig. S9 EDX spectra of BDPPPO-CsPbBr₃.

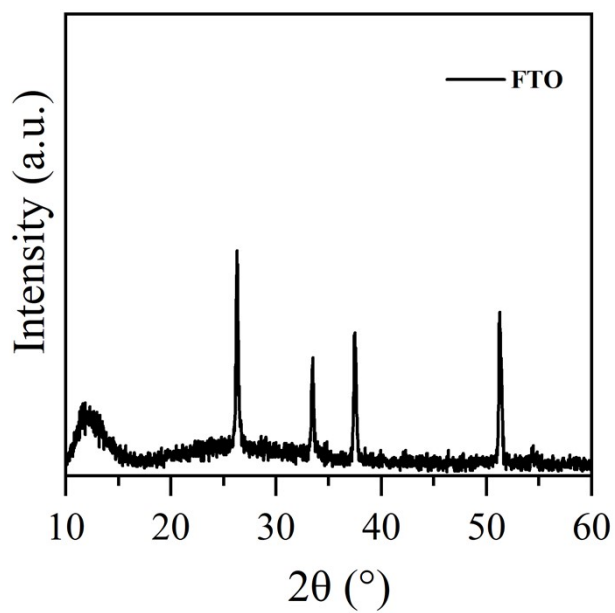


Fig. S10 XRD pattern of FTO glass.

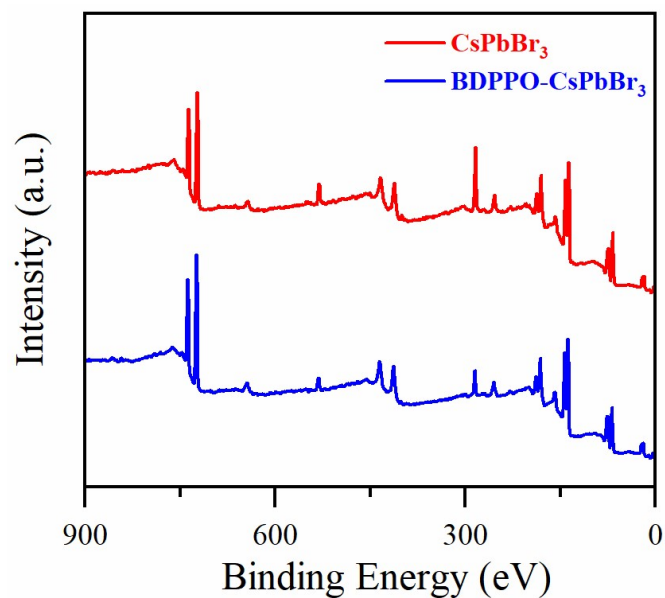


Fig. S11 The full survey XPS of CsPbBr₃ and BDPPPO-CsPbBr₃.

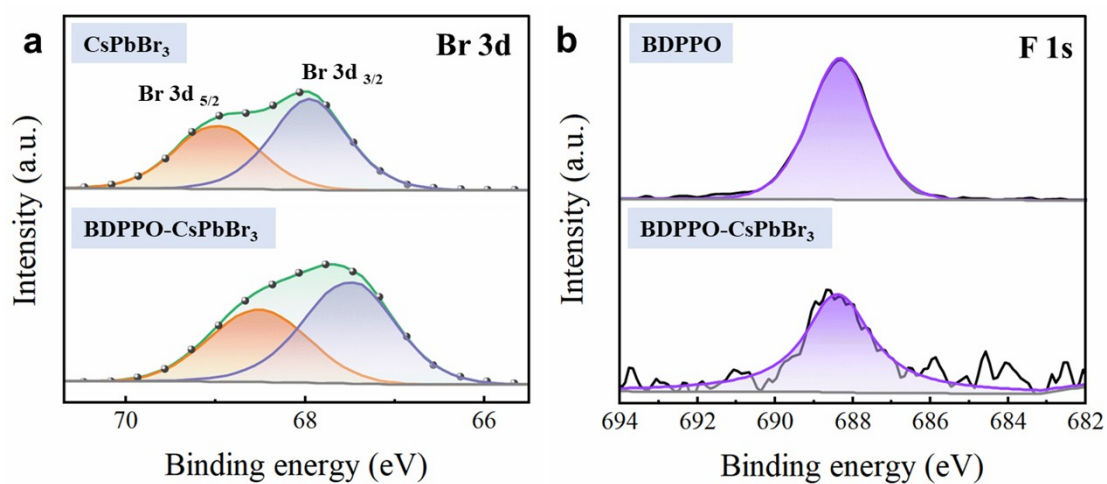


Fig. S12 XPS spectra of CsPbBr₃ and BDPPPO-CsPbBr₃, Br-3d (a), F-1s (b).

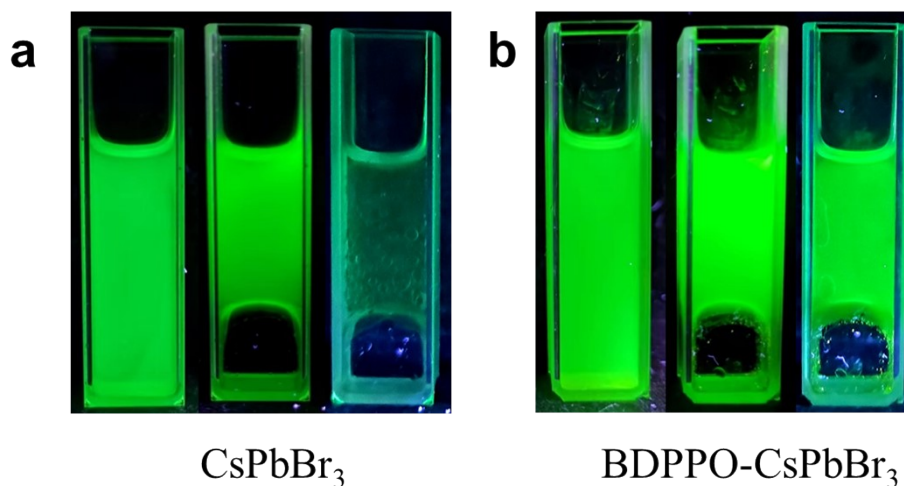


Fig. S13 The digital images obtained under UV light of CsPbBr₃ and BDPPO-CsPbBr₃ before and after adding water (excited at 365 nm). (a) CsPbBr₃: fresh (left), immediately adding water (middle), after adding water for 30 mins (right), (b) BDPPO-CsPbBr₃: fresh (left), immediately adding water (middle), after adding water for 120 mins (right).

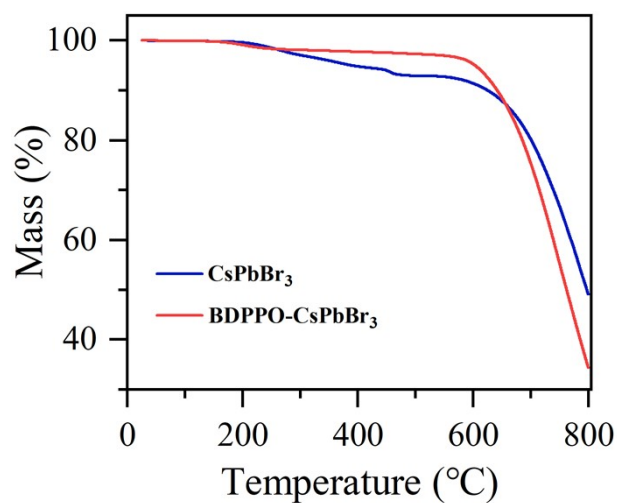


Fig. S14 Thermogravimetric curve of CsPbBr₃ and BDPPO-CsPbBr₃.

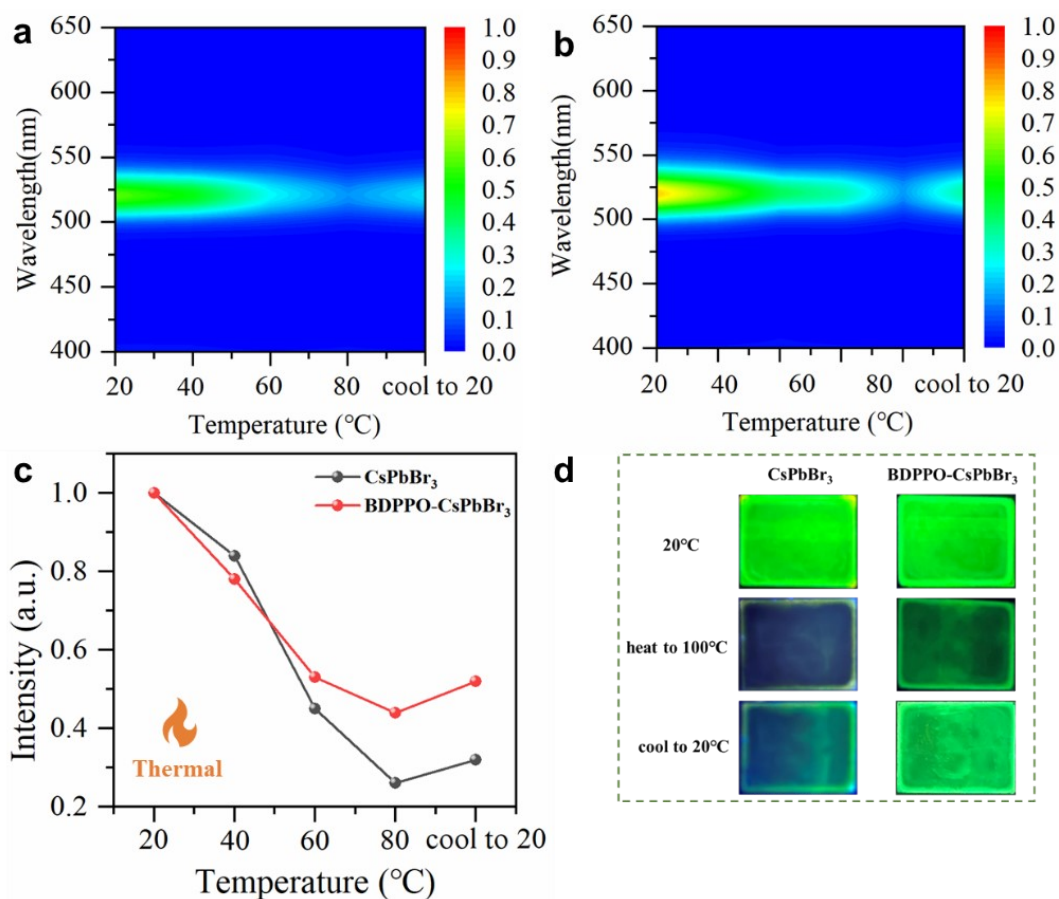


Fig. S15 (a-c) Thermal-stimuli response of the corresponding samples in toluene solution, (d) The corresponding samples deposited on the FTO glass.

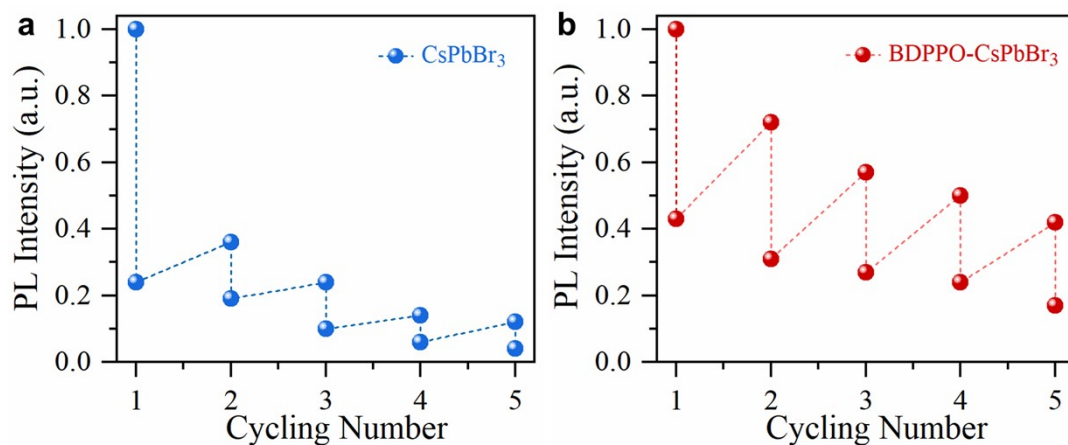


Fig. S16 Normalized PL intensity plot of CsPbBr₃ (a) and BDPPPO-CsPbBr₃ (b) dispersed in toluene solution at two typical temperature points (20 °C and 100 °C).

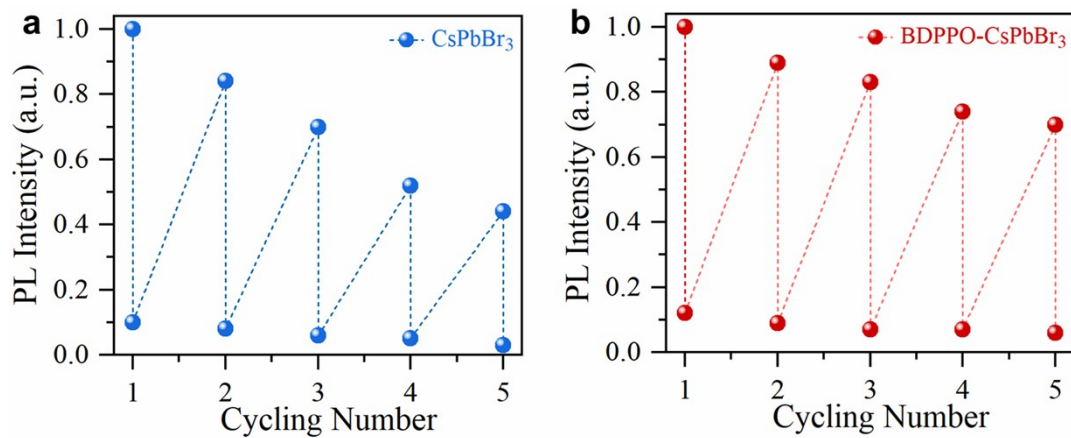


Fig. S17 Normalized PL intensity plot of CsPbBr₃ (a) and BDPPPO-CsPbBr₃ (b) deposited on the FTO at two typical temperature points (20 °C and 100 °C).

3. Supplementary Tables

Table S1. The summary of XPS data of CsPbBr₃ and BDPPPO-CsPbBr₃.

Element		Bind Energy (eV)		
		CsPbBr ₃	BDPPPO-CsPbBr ₃	Shifts
Pb	4f _{7/2}	142.657	142.461	-0.196
	4f _{5/2}	137.761	137.552	-0.209
Cs	3d _{3/2}	738.058	737.534	-0.524
	3d _{5/2}	724.129	723.605	-0.524
Br	3d _{5/2}	68.989	68.504	-0.485
	3d _{3/2}	67.932	67.468	-0.464
O	1s	530.551	530.922	0.371
		532.312	532.303	0.009
			533.41	
F	1s	688.326	688.462	0.136

Table S2. The fluorescence lifetimes of corresponding samples exhibit a triple exponential decay model.

Sample	A1	τ_1 (ns)	A2	τ_2 (ns)	A3	τ_3 (ns)	τ_{avg} (ns)
CsPbBr ₃	0.033	1.68	0.014	7.92	0.003	34.20	16.66
BDPPPO-CsPbBr ₃	0.032	1.46	0.014	7.61	0.004	38.97	22.49

4. Supplementary References

1. L. H. Davies, J. F. Wallis, M. R. Probert and L. J. Higham, *Synthesis*, 2014, **46**, 2622-2628.
2. F. Lv, H. Li, Q. Wu, X. Guo, H. Zhang, C. Yu, L. Jiao and E. Hao, *Chem. Commun.*, 2022, **58**, 3937-3940.
3. K. A. Brown, Q. Song, D. Mulder and P. King, *ACS nano*, 2014, **8**, 10790-10798.