

Supporting Information

Surface modification strategy based on molecular engineering of organic cation toward spectrally stable deep-blue emission perovskites

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Experimental Methods

Materials.

Cesium carbonate (Cs_2CO_3 , 99.0%), oleic acid (OA, 90.0%), oleylamine (OLA, 90.0%), 4,4'-diaminobiphenyl (99.0%), 3,3',4,4'-biphenyltetramine (99.0%), hydrochloric acid (H_2O , 36%), lead bromide (PbBr_2 , 99.0%), lead chloride (PbCl_2 , 99.0%), 1-octadecene (ODE, 90.0%), ethyl acetate (EA, 99.5%), ethanol (EtOH, 99.5%), petroleum ether (PET, 99.5%). All chemicals were directly used without further purification.

Synthesis of Cs-oleate solution.

Cs_2CO_3 (0.8 g), OA (2.5 mL) and ODE (30.0 mL) were loaded into a 100 mL round bottom flask and heated under N_2 at 130 °C for 1 h. The mixture was then heated to 150 °C for 30 min until Cs_2CO_3 powder totally dissolved. The solution was cooled down to room temperature and stored in the desiccator.

Synthesis of 4,4'-diaminobiphenyl hydrochloride (named as 2N).

4,4'-diaminobiphenyl (3 mmol) and EtOH (50 mL) were loaded into a 100 mL single-neck round bottom flask and stirred in the ice water bath for 20 min. 1 mL of hydrochloric acid was added to the flask every 20 min, repeat 3 times and continue stirring for 8 h. The obtained product was subjected to rotary evaporation to remove the solvent and then ultrasonically cleaned with an EtOH/PET mixed solvent for 3 times, and the obtained product was placed in a vacuum oven and heated to 50 °C to dry overnight.

Synthesis of 3,3',4,4'-biphenyltetramine hydrochloride (named as 4N).

3,3',4,4'-biphenyltetramine (3 mmol) and EtOH (50 mL) were loaded into a 100 mL single-neck round bottom flask and stirred in the ice water bath for 20 min. 2 mL of hydrochloric acid was added to the flask every 20 min, repeat 3 times and continue stirring for 8 h. The obtained product was subjected to rotary evaporation to remove the solvent and then ultrasonically cleaned with an EtOH/PET mixed solvent for 3 times, and the obtained product was placed in a vacuum oven and heated to 50 °C to dry overnight.

Synthesis of $\text{CsPbBr}_{3-x}\text{Cl}_x$.

PbX_2 (0.72 mmol), OLA (2 mL), OA (2 mL), 2N (or 4N) and ODE (20.0 mL) were loaded into a

50 mL 2-neck round bottom flask and heated under N₂ at 100 °C for 40 min until PbBr₂ powder totally dissolved (Table S1-S3). Then Cs-oleate solution preheated to 80 °C (2 mL) was injected quickly into the solution. The mixture was kept at 100 °C for 20 min. Then the mixture was cooled down to room temperature quickly by ice-water bath. EA was added to the mixture to 200 mL and stirred for 20 min. The product was obtained by centrifuging and purified by moderate EA and then dried at 50 °C in a vacuum oven.

Table S1 The dosage of PbX₂.

	PbBr ₂	PbCl ₂
CsPbBrCl ₂	0.0881 g (0.24 mmol)	0.1335 g (0.48 mmol)
CsPbBr ₂ Cl	0.1762 g (0.48 mmol)	0.0667 g (0.24 mmol)

Table S2 The dosage of ligands (CsPbBr_{3-x}Cl_x-2N).

	2N	OA	OLA
CsPbBr _{3-x} Cl _x -0	0	2.0 mL	2.0 mL
CsPbBr _{3-x} Cl _x -2N 0.06 mmol	0.0154 g	2.0 mL	2.0 mL
CsPbBr _{3-x} Cl _x -2N 0.12 mmol	0.0309 g	2.0 mL	2.0 mL
CsPbBr _{3-x} Cl _x -2N 0.18 mmol	0.0463 g	2.0 mL	2.0 mL

Table S3 The dosage of ligands (CsPbBr_{3-x}Cl_x-4N).

	4N	OA	OLA
CsPbBr _{3-x} Cl _x -0	0	2.0 mL	2.0 mL
CsPbBr _{3-x} Cl _x -4N 0.06 mmol	0.0216 g	2.0 mL	2.0 mL
CsPbBr _{3-x} Cl _x -4N 0.12 mmol	0.0432 g	2.0 mL	2.0 mL
CsPbBr _{3-x} Cl _x -4N 0.18 mmol	0.0648 g	2.0 mL	2.0 mL

Characterization.

Solid XRD patterns were recorded using an X-ray diffractometer with SmartLab system. TEM images were obtained from the JEOL-2100F electron microscope. FT-IR tests were performed on a Nicolet 6700 FTIR spectrometer with KBr disks. The contents of halogens were obtained from EDS of HITACHI SU8010 scanning electron microscope. Absorption spectra were obtained by Cary7000 UV-Vis-NIR Spectrophotometer with a calibrated integrating sphere. Solid PL spectra, three-dimensional PL spectra, PLQYs and lifetimes were collected by a FLS1000 spectrophotometer ($\lambda_{\text{ex}} = 360$ nm). The density functional theory calculations were performed on 2N and 4N to obtain the overall charge number in the -NH₃⁺.

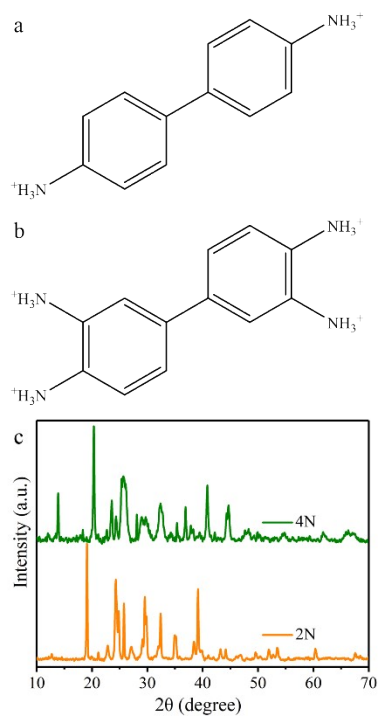


Figure S1 The structure of organic cations: 2N (a) and 4N (b). (c) XRD patterns of 2N and 4N.

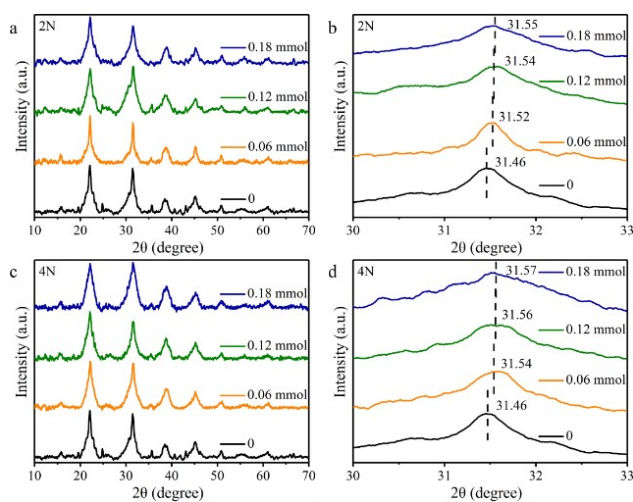


Figure S2 Full and enlarged (from 30 to 33 degree) XRD patterns of CsPbBrCl_2 before and after the modification with 2N (a, b) and 4N (c, d).

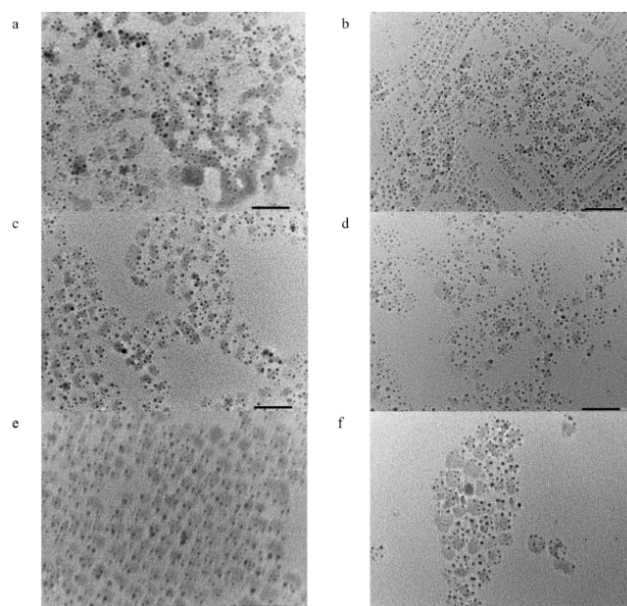


Figure S3 TEM images of CsPbBrCl₂ (a 0, c 0.06 mmol 2N, e 0.06 mmol 4N) and CsPbBr₂Cl (b 0, d 0.06 mmol 2N, f 0.06 mmol 4N) before and after the modification with 2N and 4N (scale bar is 50 nm).

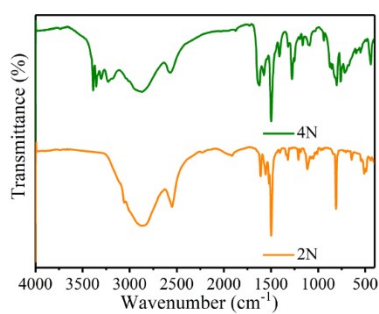


Figure S4 FT-IR spectra of 2N and 4N.

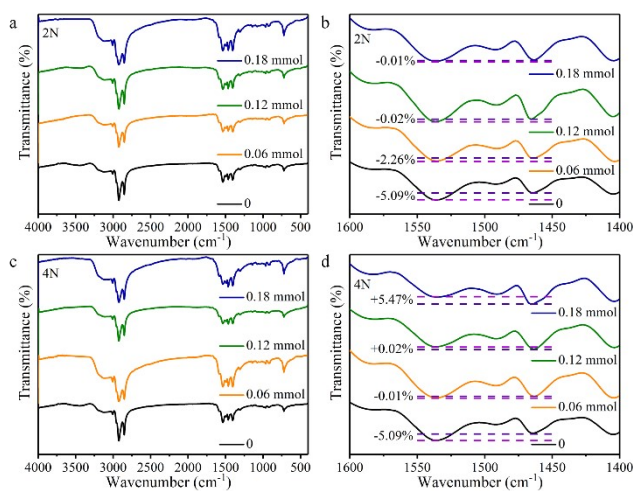


Figure S5 Full and enlarged (from 1400 to 1600 cm⁻¹) FT-IR spectra of CsPbBrCl₂ before and after

the modification with 2N (a, b) and 4N (c, d).

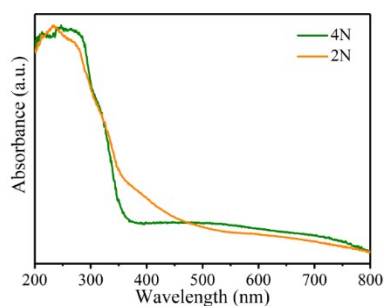


Figure S6 Absorption spectra of 2N and 4N.

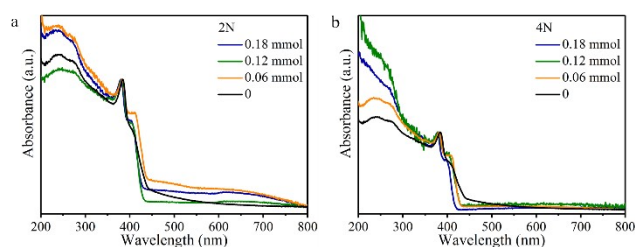


Figure S7 Absorption spectra of CsPbBrCl₂ before and after the modification with 2N (a) and 4N (b).

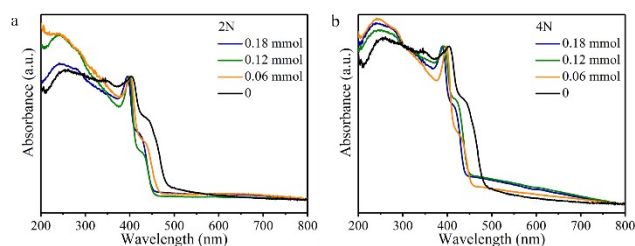


Figure S8 Absorption spectra of CsPbBr₂Cl before and after the modification with 2N (a) and 4N (b).

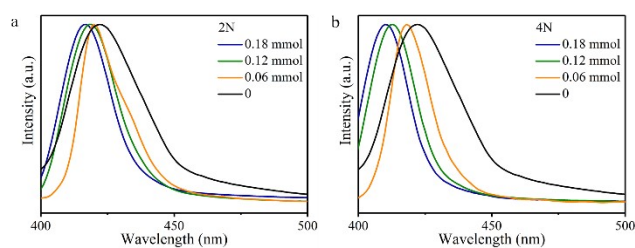


Figure S9 PL spectra ($\lambda_{\text{ex}} = 360 \text{ nm}$) of CsPbBrCl₂ before and after the modification with 2N (a) and 4N (b).

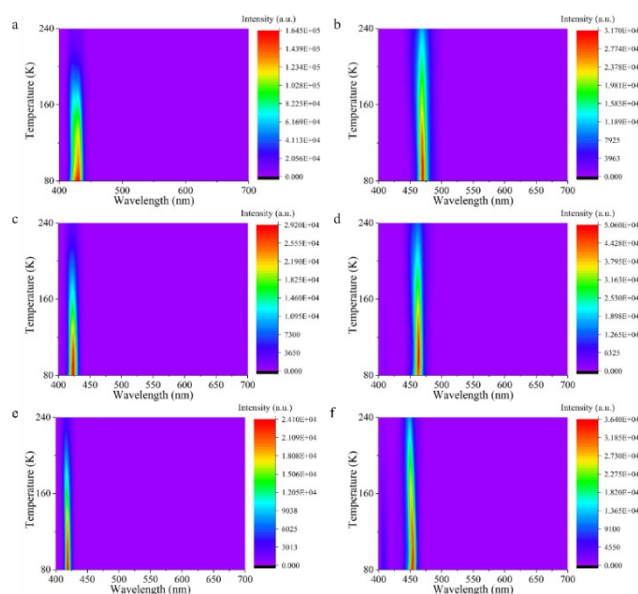


Figure S10 Three-dimensional PL spectra ($\lambda_{\text{ex}} = 360$ nm) of the emission wavelength-temperature-emission intensity of CsPbBrCl₂ (a 0, c 0.06 mmol 2N, e 0.06 mmol 4N) and CsPbBr₂Cl (b 0, d 0.06 mmol 2N, f 0.06 mmol 4N) before and after the modification with 2N (c, d) and 4N (e, f).

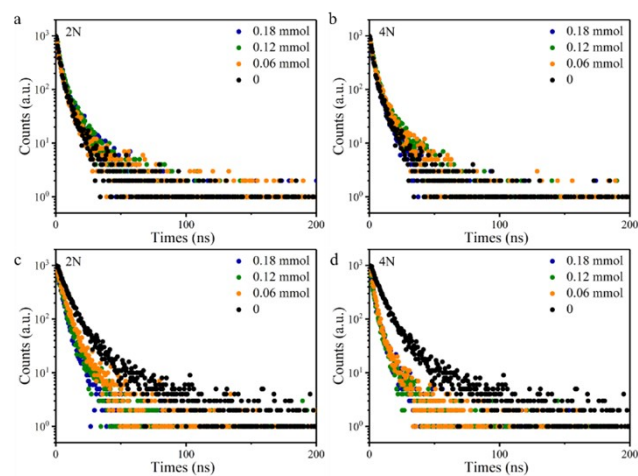


Figure S11 (a, b) PL decay curves ($\lambda_{\text{ex}} = 360$ nm) of CsPbBrCl₂ before and after the modification with 2N (a) and 4N (b). (c, d) Fluorescence decay curves ($\lambda_{\text{ex}} = 360$ nm) of CsPbBrCl₂ before and after the modification with 2N (c) and 4N (d).

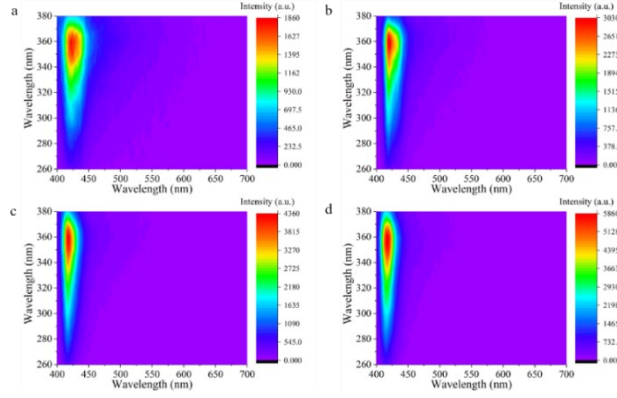


Figure S12 Three-dimensional PL spectra ($\lambda_{\text{ex}} = 360 \text{ nm}$) of emission wavelength-excitation wavelength-emission intensity of CsPbBrCl₂ before (a) and after the modification with 2N: 0.06 mmol (b), 0.12 mmol (c) and 0.18mmol (d).

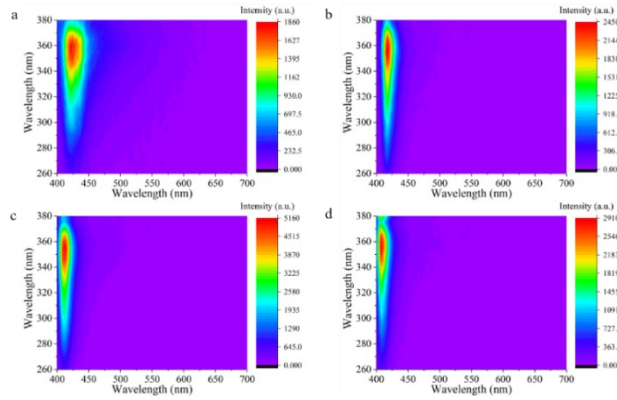


Figure S13 Three-dimensional PL spectra ($\lambda_{\text{ex}} = 360 \text{ nm}$) of emission wavelength-excitation wavelength-emission intensity of CsPbBrCl₂ before (a) and after the modification with 4N: 0.06 mmol (b), 0.12 mmol (c) and 0.18mmol (d).

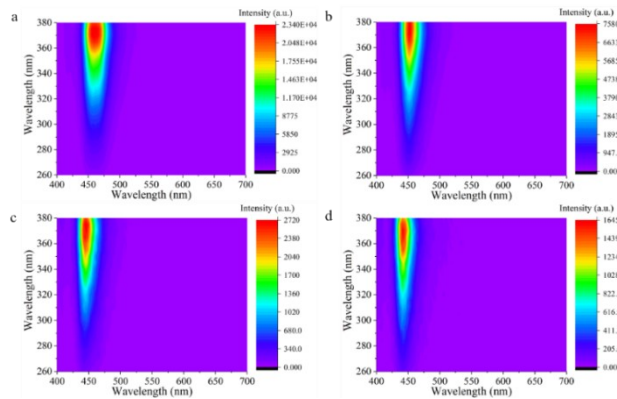


Figure S14 Three-dimensional PL spectra ($\lambda_{\text{ex}} = 360 \text{ nm}$) of emission wavelength-excitation wavelength-emission intensity of CsPbBr₂Cl before (a) and after the modification with 2N: 0.06 mmol (b), 0.12 mmol (c) and 0.18mmol (d).

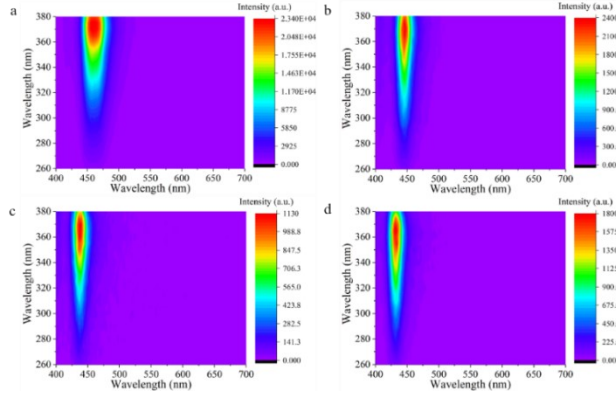


Figure S15 Three-dimensional PL spectra ($\lambda_{\text{ex}} = 360 \text{ nm}$) of emission wavelength-excitation wavelength-emission intensity of CsPbBr₂Cl before (a) and after the modification with 4N: 0.06 mmol (b), 0.12 mmol (c) and 0.18mmol (d).

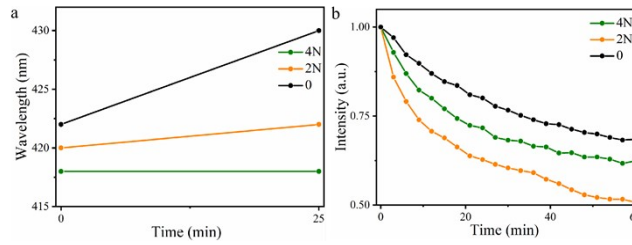


Figure S16 (a) The change on the emission wavelength under stronger illumination of CsPbBrCl₂ before and after modification with 2N and 4N ($\lambda_{\text{ex}} = 360 \text{ nm}$). (b) The change on the emission intensity under weaker illumination of CsPbBrCl₂ before and after modification with 2N and 4N ($\lambda_{\text{ex}} = 360 \text{ nm}$).

Table S4 Elemental composition of CsPbBrCl₂ before and after the modification with 2N.

	Cs	Pb	Br	Cl	(Br+Cl)/Pb	Cl/(Cl+Br)
0	1	0.81	1.05	2.36	4.20	0.69
0.06 mmol	1	0.84	1.01	2.52	4.20	0.71
0.12 mmol	1	0.85	1.00	2.64	4.27	0.72
0.24 mmol	1	0.85	0.91	2.69	4.23	0.75

Table S5 Elemental composition of CsPbBrCl₂ before and after the modification with 4N.

	Cs	Pb	Br	Cl	(Br+Cl)/Pb	Cl/(Cl+Br)
0	1	0.81	1.05	2.36	4.20	0.69
0.06 mmol	1	0.87	0.89	2.77	4.21	0.76
0.12 mmol	1	0.89	0.84	2.91	4.21	0.78
0.24 mmol	1	0.95	0.78	3.31	4.31	0.81

Table S6 Elemental composition of CsPbBr₂Cl before and after the modification with 2N.

	Cs	Pb	Br	Cl	(Br+Cl)/Pb	Cl/(Cl+Br)
0	1	0.88	1.97	1.22	3.65	0.38
0.06 mmol	1	0.83	1.79	1.48	3.95	0.45
0.12 mmol	1	0.86	1.75	1.69	4.00	0.49
0.24 mmol	1	0.85	1.61	1.86	4.05	0.54

Table S7 Elemental composition of CsPbBr₂Cl before and after the modification with 4N.

	Cs	Pb	Br	Cl	(Br+Cl)/Pb	Cl/(Cl+Br)
0	1	0.88	1.97	1.22	3.65	0.38
0.06 mmol	1	0.84	1.74	1.70	4.08	0.49
0.12 mmol	1	0.84	1.67	1.93	4.29	0.54
0.24 mmol	1	0.93	1.66	2.38	4.36	0.59

Table S8 Maximum absorption wavelength of CsPbBr_{3-x}Cl_x.

	0	0.06 mmol	0.12 mmol	0.24 mmol
CsPbBrCl ₂ -2N	384 nm	383 nm	382 nm	380 nm
CsPbBrCl ₂ -4N	384 nm	381 nm	379 nm	378 nm
CsPbBr ₂ Cl-2N	404 nm	402 nm	399 nm	395 nm
CsPbBr ₂ Cl-4N	404 nm	398 nm	392 nm	389 nm

Table S9 Maximum PL emission wavelength of CsPbBr_{3-x}Cl_x.

	0	0.06 mmol	0.12 mmol	0.24 mmol
CsPbBrCl ₂ -2N	422 nm	420 nm	419 nm	417 nm
CsPbBrCl ₂ -4N	422 nm	418 nm	413 nm	410 nm
CsPbBr ₂ Cl-2N	460 nm	454 nm	448 nm	444 nm
CsPbBr ₂ Cl-4N	460 nm	448 nm	438 nm	434 nm

Table S10 Photophysical properties of CsPbBrCl₂ before and after the modification with 2N.

	0	0.06 mmol	0.12 mmol	0.24 mmol
τ_1 (ns)	2.21	2.11	2.26	2.54
a_1 (%)	64.87	59.58	50.91	57.16
τ_2 (ns)	10.19	8.83	8.89	10.19
a_2 (%)	35.13	40.42	49.09	42.84

τ_{avg} (ns)	5.01	4.82	5.52	5.82
PLQY (%)	0.60	1.89	1.71	1.64
k_{r} (10^6 s^{-1})	1.20	3.92	3.10	2.82
k_{nr} (10^6 s^{-1})	198.24	203.34	178.16	169.03

Table S11 Photophysical properties of CsPbBrCl₂ before and after the modification with 4N.

	0	0.06 mmol	0.12 mmol	0.24 mmol
τ_1 (ns)	2.21	2.41	2.72	2.35
a_1 (%)	64.87	53.88	59.47	58.65
τ_2 (ns)	10.19	10.29	10.85	7.71
a_2 (%)	35.13	46.12	40.53	41.35
τ_{avg} (ns)	5.01	6.05	6.01	4.57
PLQY (%)	0.60	4.12	1.11	0.64
k_{r} (10^6 s^{-1})	1.20	6.81	1.85	1.40
k_{nr} (10^6 s^{-1})	198.24	158.59	164.51	217.53

Table S12 Photophysical properties of CsPbBr₂Cl before and after the modification with 2N.

	0	0.06 mmol	0.12 mmol	0.24 mmol
τ_1 (ns)	6.17	3.95	3.37	2.76
a_1 (%)	70.65	59.99	68.08	57.63
τ_2 (ns)	20.21	10.18	9.08	6.70
a_2 (%)	29.35	40.01	31.92	51.37
τ_{avg} (ns)	10.29	6.44	5.19	5.03
PLQY (%)	31.57	31.48	11.56	11.01
k_{r} (10^6 s^{-1})	30.67	48.88	22.26	21.89
k_{nr} (10^6 s^{-1})	66.49	106.38	170.33	176.92

Table S13 Photophysical properties of CsPbBr₂Cl before and after the modification with 4N.

	0	0.06 mmol	0.12 mmol	0.24 mmol
τ_1 (ns)	6.17	2.49	1.85	1.98
a_1 (%)	70.65	71.38	50.40	58.52
τ_2 (ns)	20.21	8.30	5.56	6.84
a_2 (%)	29.35	28.62	49.60	41.48
τ_{avg} (ns)	10.29	4.15	3.69	3.99
PLQY (%)	31.57	7.39	5.07	3.53

k_r (10^6 s^{-1})	30.67	17.79	13.74	8.84
k_{nr} (10^6 s^{-1})	66.49	222.91	257.33	241.58

Table S14 Stability on emission wavelength of CsPbBrCl₂ under ultraviolet light exposure.

	CsPbBrCl ₂ -2N		CsPbBrCl ₂ -4N	
	0	25 min	0	25 min
0	422 nm	430 nm	422 nm	430 nm
0.06 mmol	420 nm	422 nm	418 nm	418 nm
0.12 mmol	419 nm	419 nm	413 nm	413 nm
0.24 mmol	417 nm	417 nm	410 nm	410 nm

Table S15 Stability on emission wavelength of CsPbBr₂Cl under ultraviolet light exposure.

	CsPbBr ₂ Cl-2N		CsPbBr ₂ Cl-4N	
	0	25 min	0	25 min
0	460 nm	464 nm	460 nm	464 nm
0.06 mmol	454 nm	455 nm	448 nm	448 nm
0.12 mmol	448 nm	448 nm	438 nm	438 nm
0.24 mmol	444 nm	444 nm	434 nm	434 nm