

Supporting Information

Phototriggered Color Modulation of Perovskite Nanoparticles for High Density Optical Data Storage

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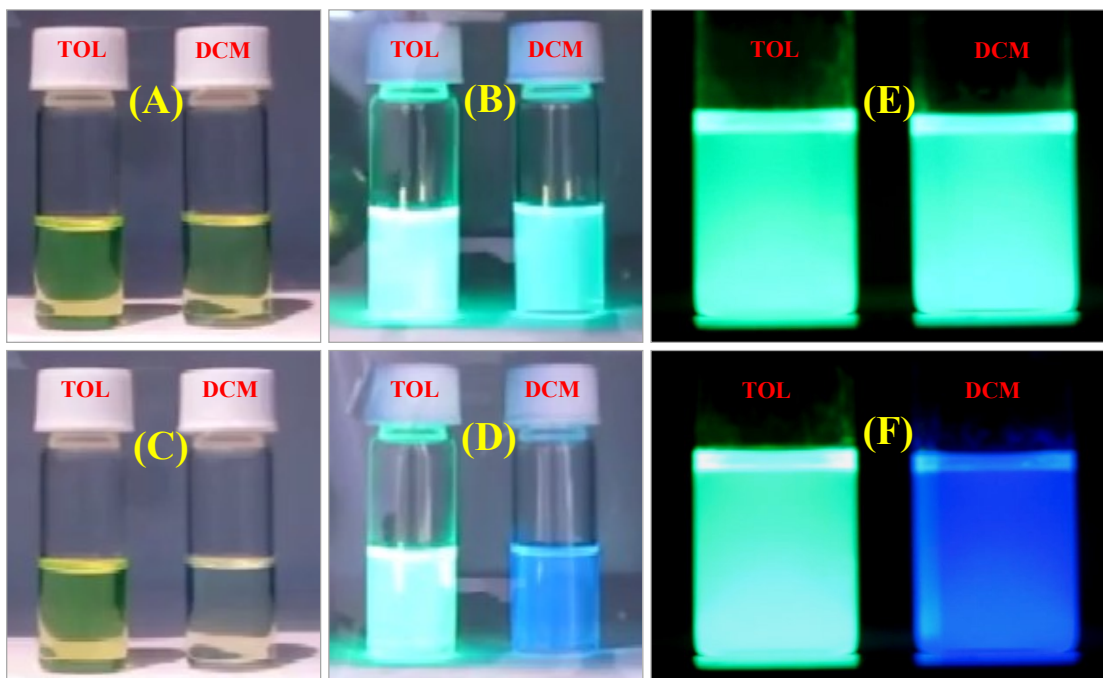


Figure S1. Photos of OAm-CsPbBr₃-TOL and OAm-CsPbBr₃ PNCs-DCM solutions.

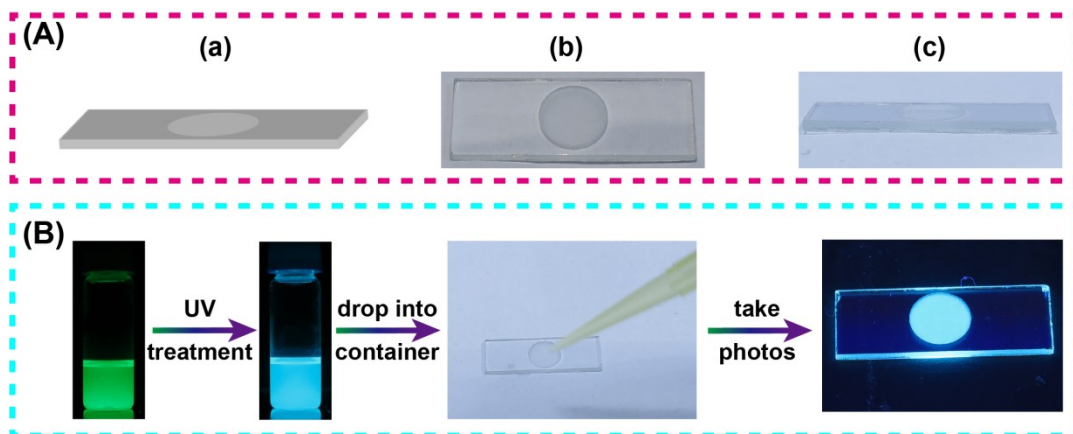


Figure S2. (A) Schematic diagram of a homemade circular glass cell fabricated on a glass slide by laser etching (a), the top view (b) and side view (c) of the fabricated circular glass cell. (B) The general procedures to acquire photos shown in Figure 1A including: treating the OAm-PNCs-DCM dispersion with UV light, dropping some of the UV-irradiated OAm-PNCs-DCM dispersion into the circular glass cell, and taking the fluorescence photo.

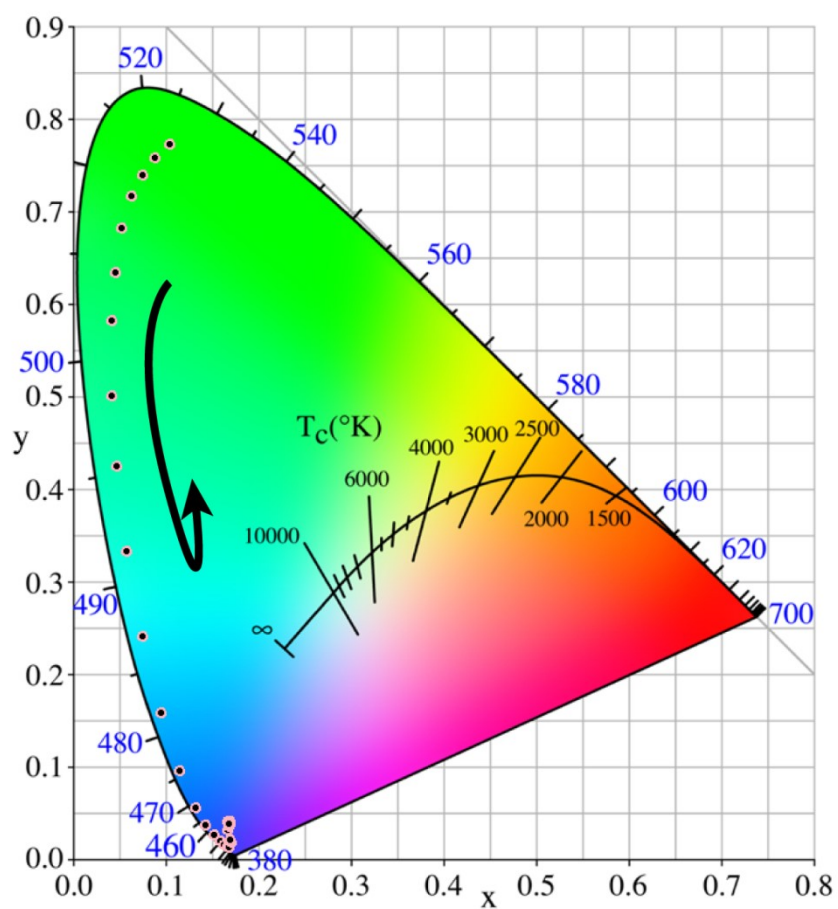


Figure S3. CIE chart converted from the PL spectra of OAm-CsPbBr₃ PNCs-DCM with different illumination time.

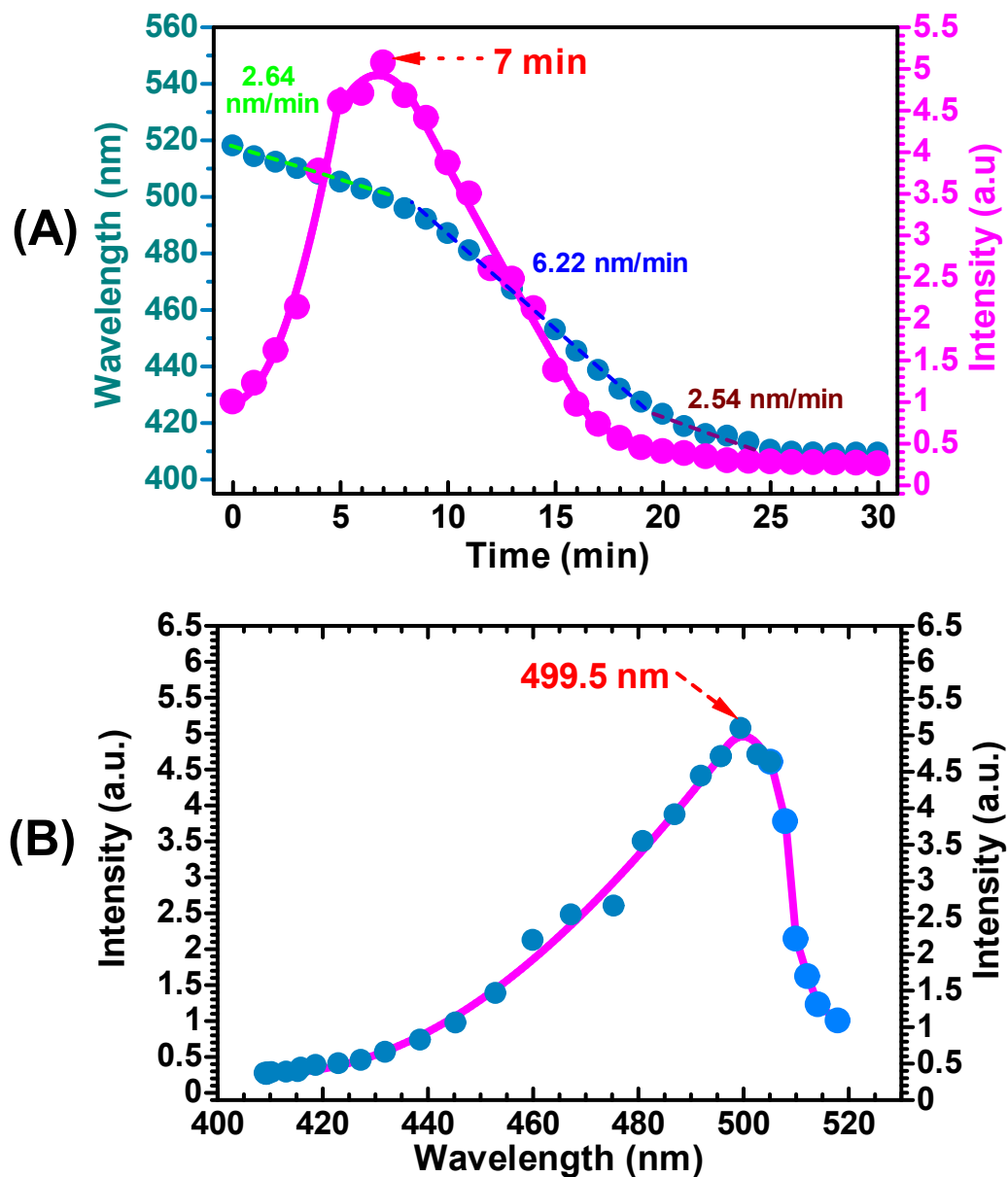


Figure S4. (A) Variation of maximum emission wavelength (cyan dots) and intensity (pink dots) of OAm-CsPbBr₃ PNCs-DCM with UV exposure time; (B) Plot of maximum emission intensity versus wavelength.

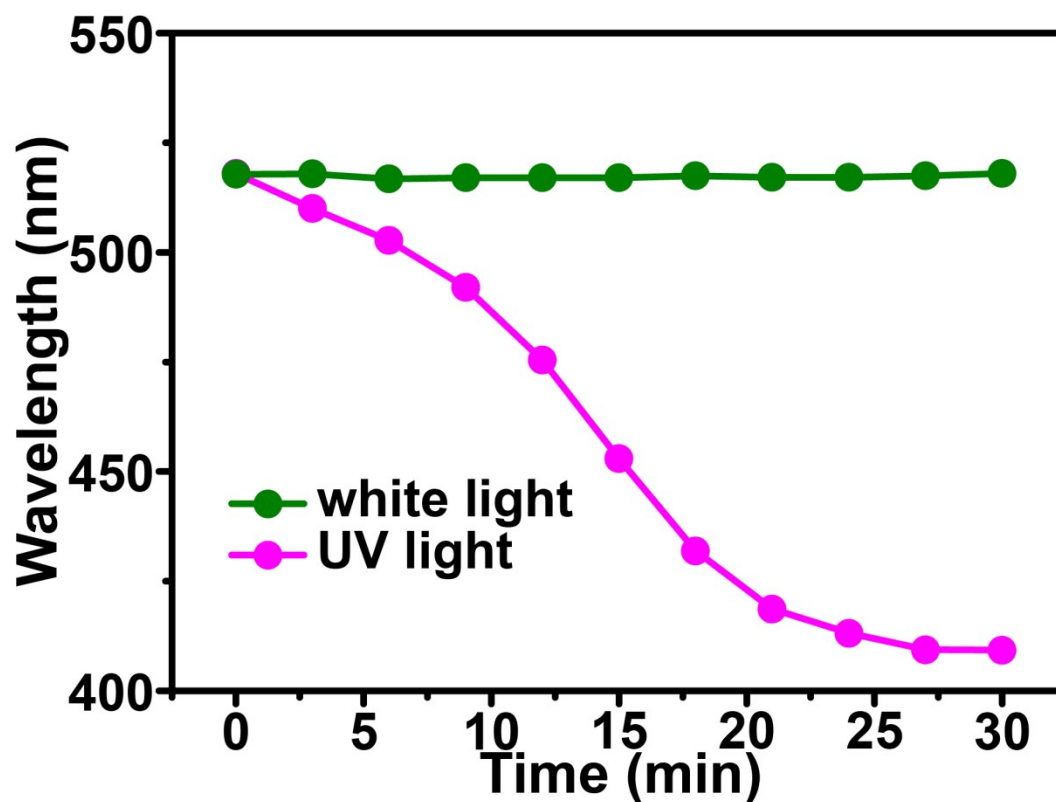


Figure S5. Comparison in variation of the maximum emission wavelength of OAm-PNCs-DCM with time under white light exposure (green curve) to that under UV light exposure (pink curve).

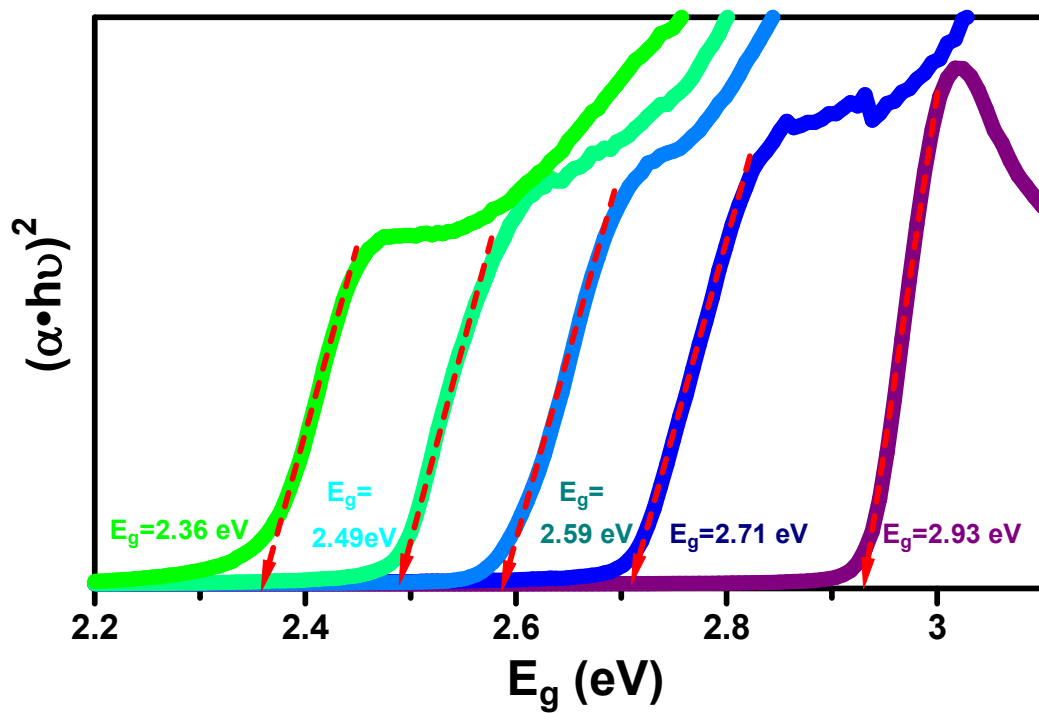


Figure S6. Tauc plots obtained from UV-vis absorption spectra (Figure 2B) for OAm-PNCs after exposing OAm-CsPbBr₃ PNCs to UV light for different time.

Table S1. Variation of optical properties of OAm-PNCs after exposing OAm-CsPbBr₃ PNCs to UV light for different time

UV exposure time (min)	0	9	12	16	21
Maximum emission wavelength (nm)	518	492	475	445	417
UV-vis absorption peak (nm)	505	482	462	437	411
Bandgap energy (eV)	2.36	2.49	2.59	2.71	2.93
XRD (200) peak (degree)	30.40	30.70	30.92	31.26	31.76

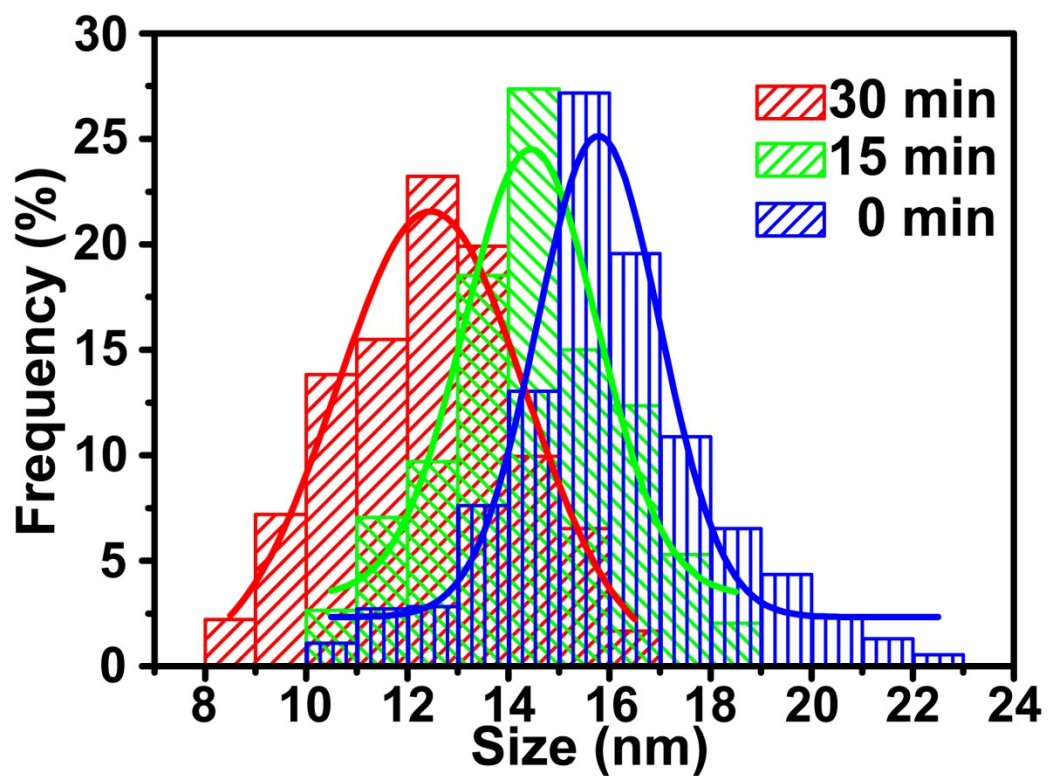


Figure S7. Size distribution of PNCs after irradiating OAm-CsPbBr₃-DCM for 0 min, 15 min, 30 min, collected by TEM.

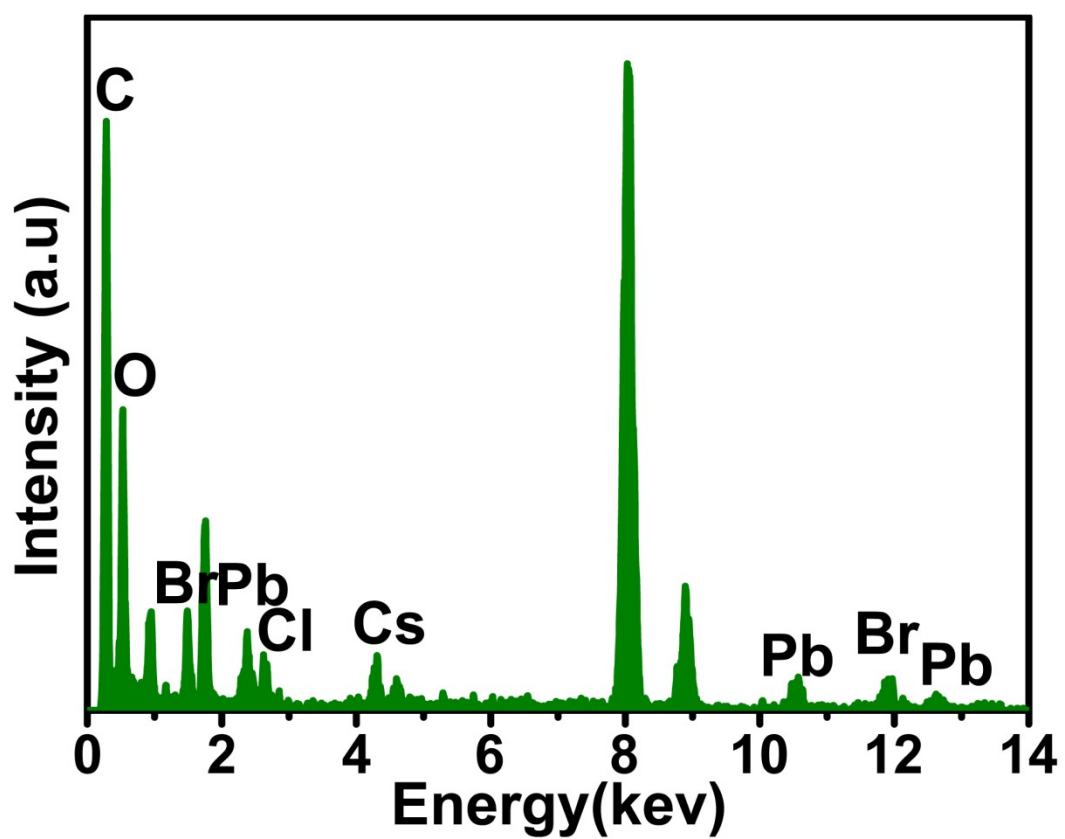


Figure S8. EDS pattern obtained for OAm-CsPbBr₃ PNCs-DCM with 15 min photo-treatment.

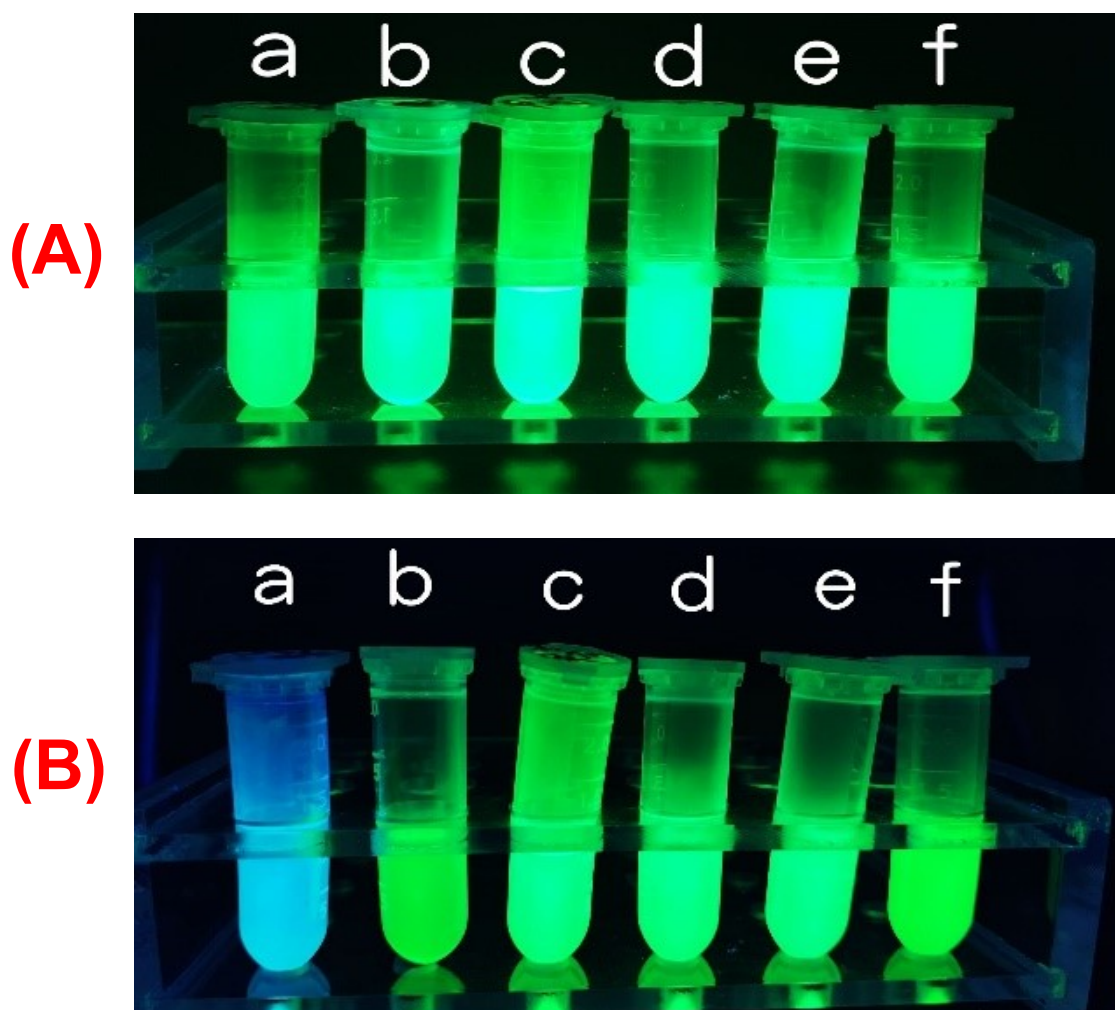


Figure S9. Effect of dispersion solvent type on the fluorescence color change of OAm-CsPbBr₃ PNCs before (A) and after (B) 10 min UV-exposure. The solvents investigated were: (a) DCM; (b) Benzene; (c) Toluene; (d) n-Hexane; (e) Cyclohexane; and (f) Ethyl ether.

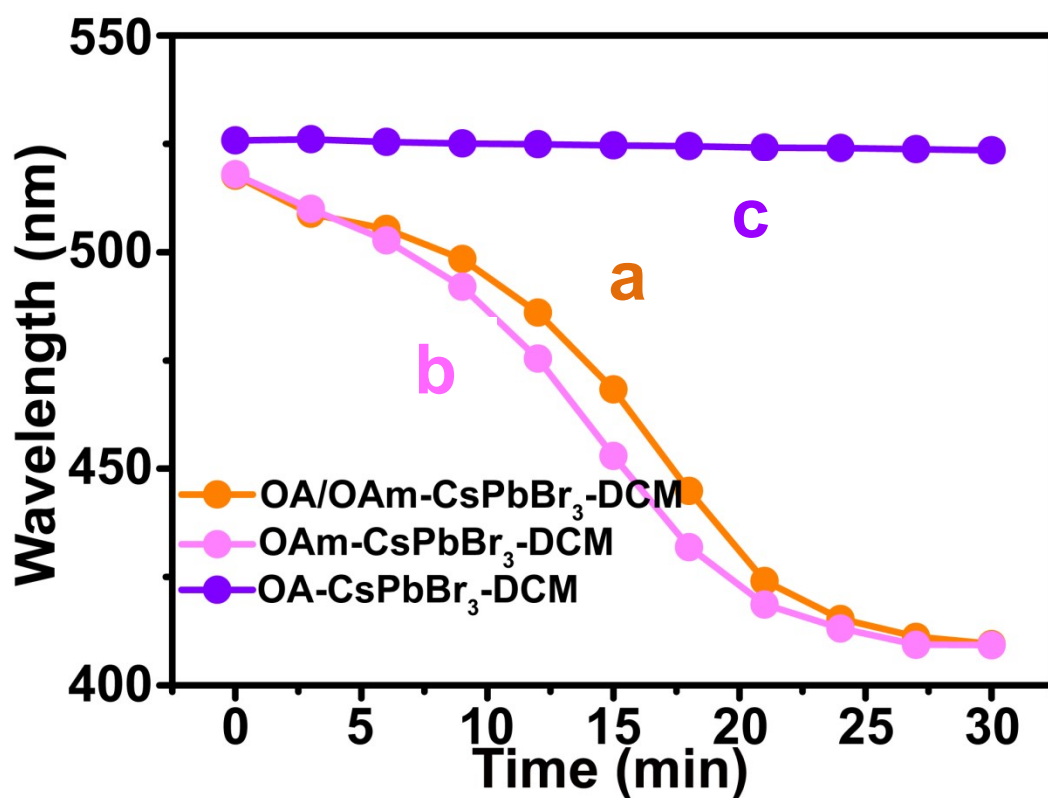


Figure S10. Maximum emission wavelengths obtained for OA/OAm-CsPbBr₃ PNCs-DCM (a), OAm-CsPbBr₃ PNCs-DCM (b) and OA-CsPbBr₃ PNCs-DCM (c) at different UV-exposure time.

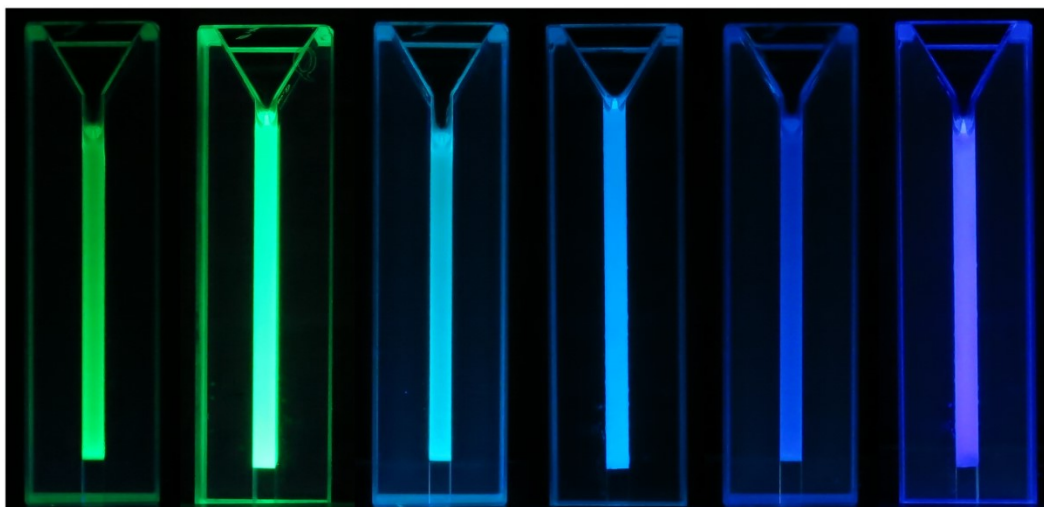


Figure S11. The images of ODA-CsPbBr₃ PNCs-DCM with different illumination time recorded under 365 nm ultraviolet light excitation.

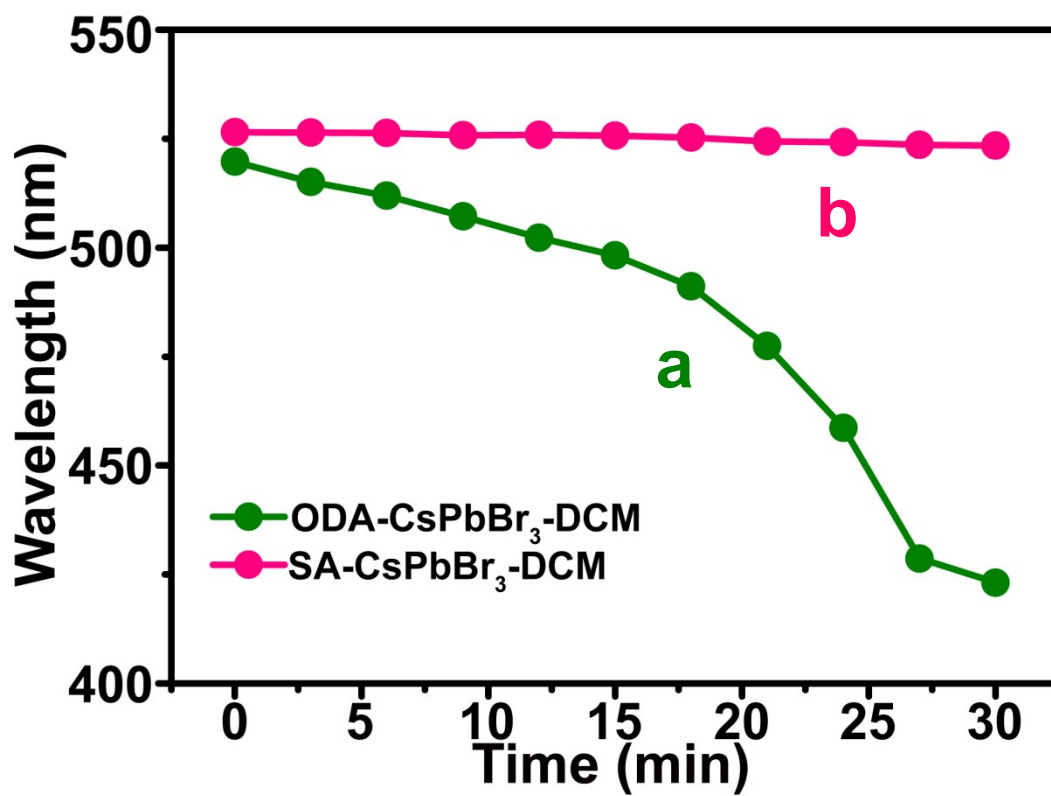


Figure S12. PL maximum emission wavelength of ODA-CsPbBr₃ PNCs-DCM and SA-CsPbBr₃ PNCs-DCM at different UV irradiated time.

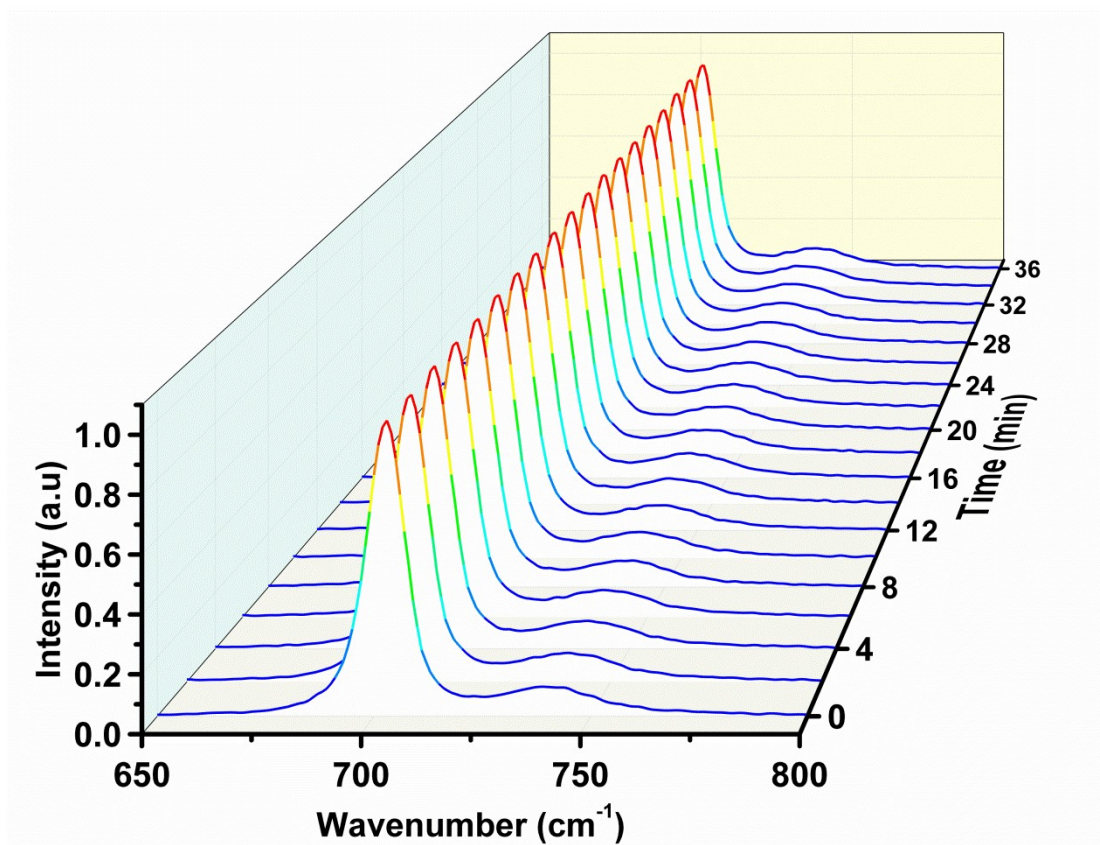


Figure S13. Variation of Raman spectrum of DCM with UV irradiation time in the presence of only OAm (i.e. without PNCs).

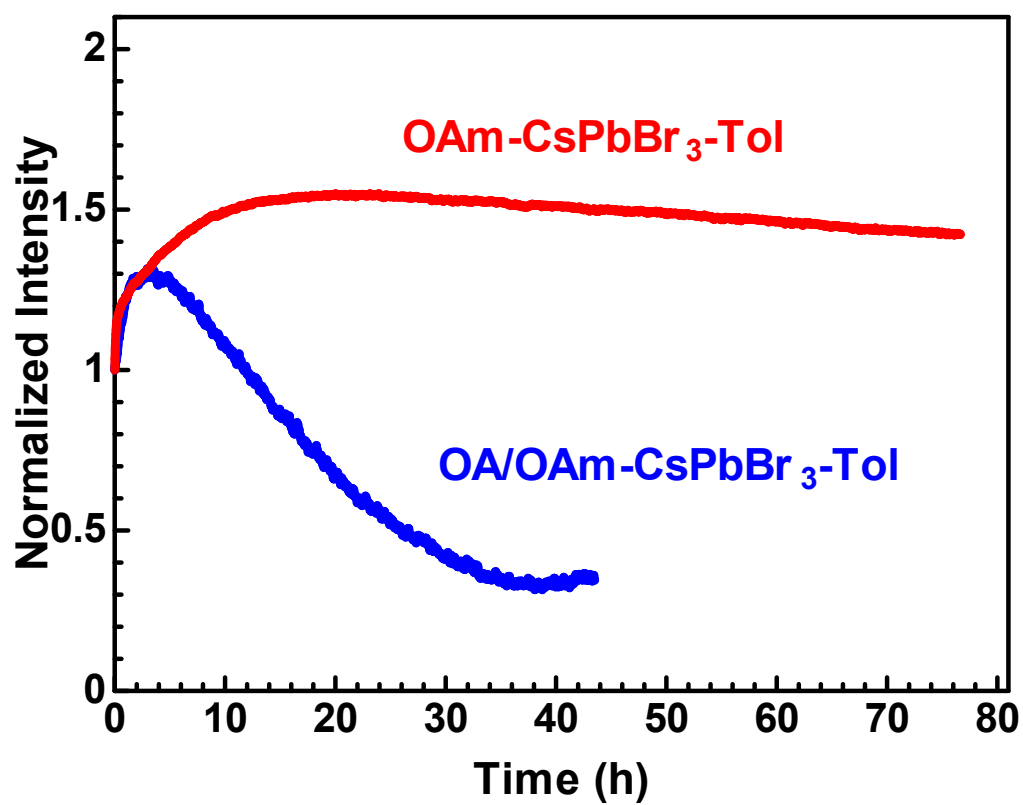


Figure S14. Comparison in UV-stability between OAm-CsPbBr₃ PNCs and OA/OAm-CsPbBr₃ PNCs in toluene.

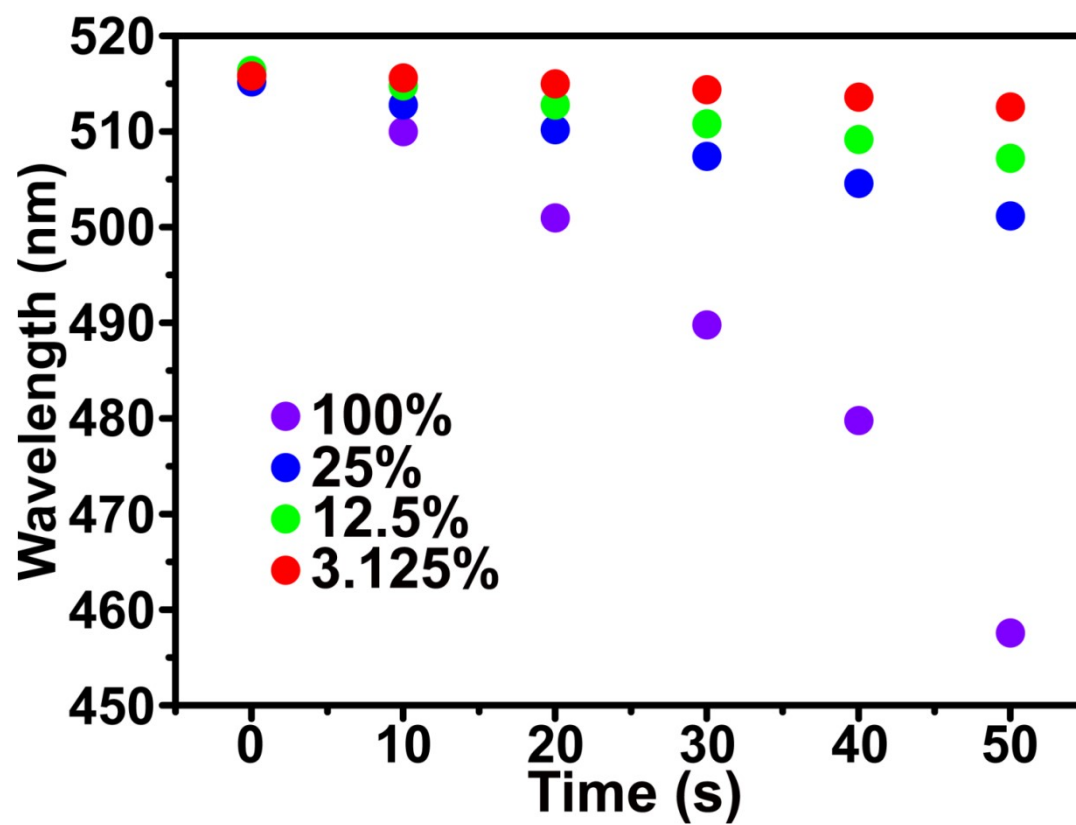


Figure S15. Effect of UV light power on the kinetics of PL color change.

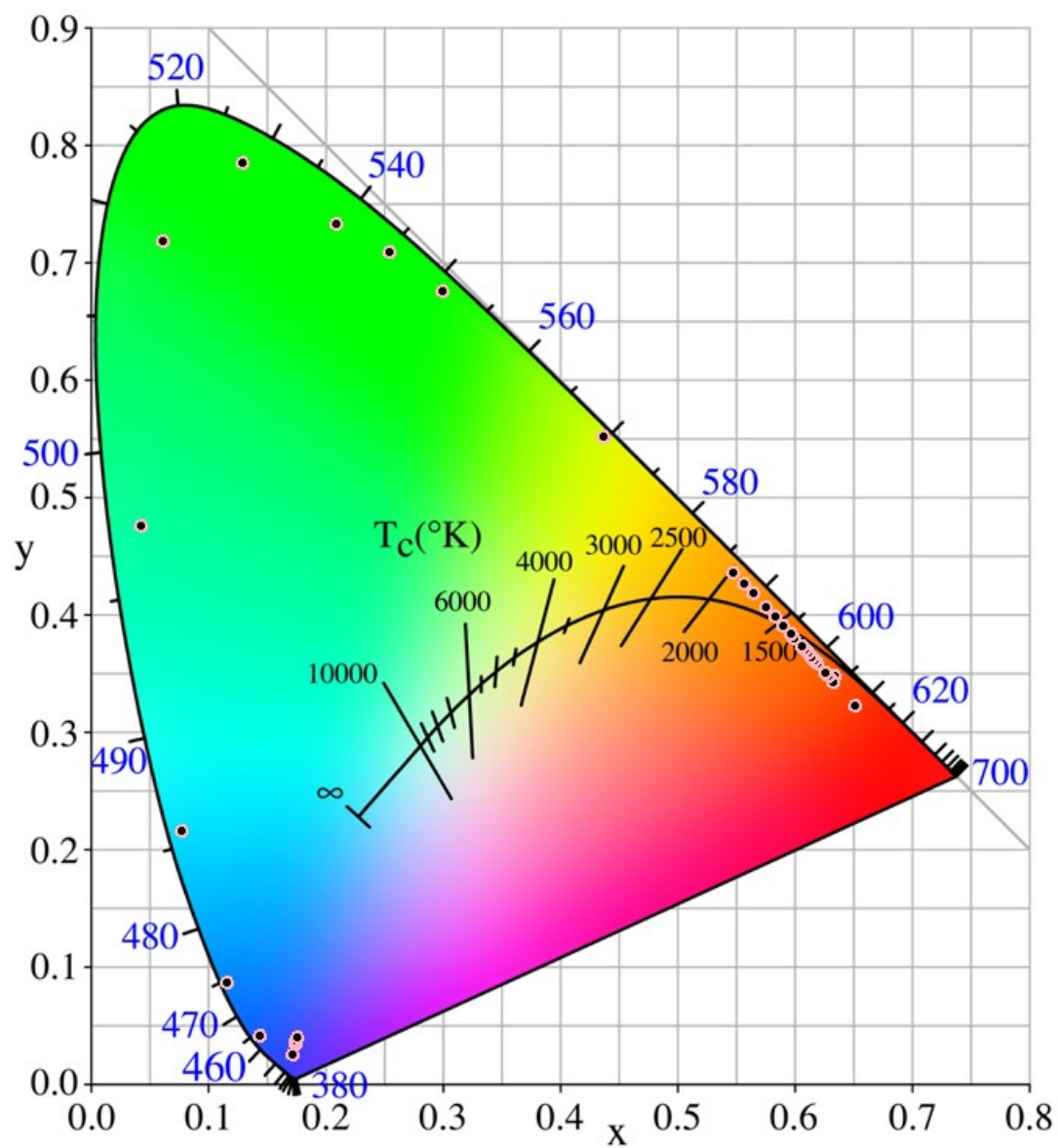


Figure S16. CIE chart converted from the PL spectra of OAm-CsPb(Br_{0.4}I_{0.6})₃-DCM system with different illumination time.

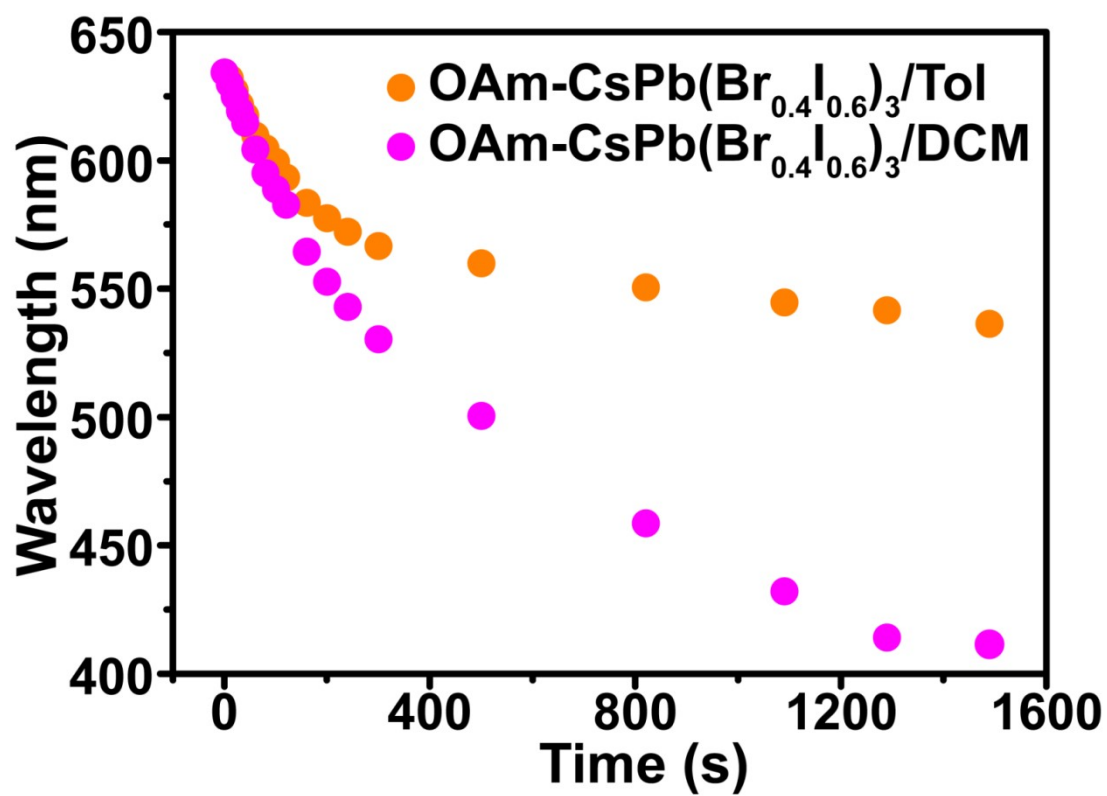
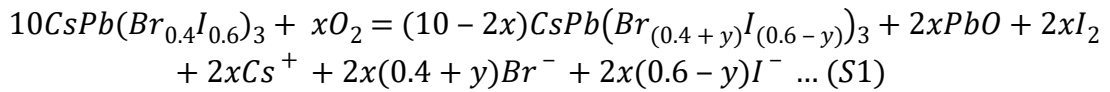


Figure S17. Scatter plot of PL emission of OAm-CsPb(Br_{0.4}I_{0.6})₃ PNCs-Tol and OAm-CsPb(Br_{0.4}I_{0.6})₃ PNCs-DCM at different UV irradiation time.

Reaction equations proposed for UV light-induced oxidation of OAm-CsPb(Br_{0.4}I_{0.6})₃ PNCs in toluene (i.e. without Cl⁻ ion exchange).



Then

The amounts (mol) of elements before the reaction (see left items of the reaction equation):

$$N_{Cs}=10;$$

$$N_{Pb}=10;$$

$$N_{Br}=10 \times 0.4 \times 3=12;$$

$$N_I=10 \times 0.6 \times 3=18;$$

$$N_O=2x$$

The amounts (mol) of elements after the reaction (see right items of the reaction equation):

$$N_{Cs}=10-2x+2x=10;$$

$$N_{Pb}=10-2x+2x=10;$$

$$N_{Br}=(10-2x) \times (0.4+y) \times 3+2x \times (0.4+y)=(30-4x) \times (0.4+y);$$

$$N_I=(10-2x) \times (0.6-y) \times 3+2x \times (0.6-y)+4x=(30-4x) \times (0.6-y)+4x;$$

$$N_{O_2}=2x$$

The amounts of elements after the reaction should be the same as those before the reaction, then:

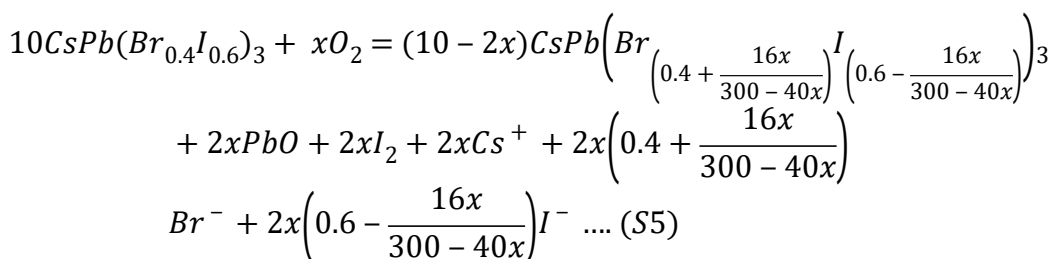
$$N_{Br}=(30-4x) \times (0.4+y)=12 \dots \dots \dots (S2);$$

$$N_I=(30-4x) \times (0.6-y)+4x=18 \dots \dots \dots (S3);$$

Then it can be obtained from S2 or S3

$$y=16x/(300-40x) \dots \dots \dots (S4)$$

Finally, we can obtain S5 by combining S1 with S4:



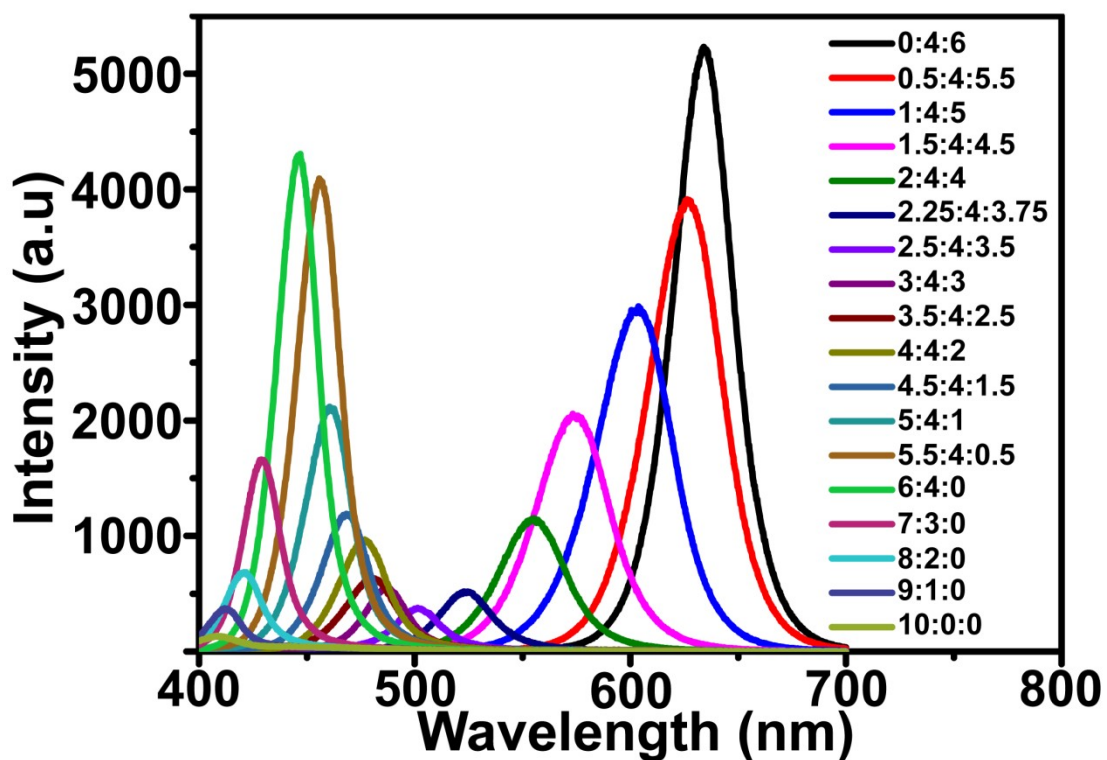


Figure S18. Fluorescence spectra obtained for a serial of CsPb(Cl_xBr_{0.4}I_{0.6-x})₃ PNCs. The serial PNCs were prepared by keeping the amount of Br⁻ unchanged while decreasing the amount of I⁻ and increasing the amount of Cl⁻ to simulate the photo-induced oxidation and ion exchange processes shown in Equation 8.

Table S2. The maximum fluorescence emission wavelength and intensity obtained for CsPb(Cl_xBr_{0.4}I_{0.6-x})₃ PNCs

	Cl:Br:I	CsPb(Cl _x Br _{0.4} I _{0.6-x}) ₃	λ _{max} (nm)	Intensity	Normalized intensity	
1	0:4:6	CsPb(Br _{0.4} I _{0.6}) ₃	635	5234	100	strong
2	0.5:4:5.5	CsPb(Cl _{0.05} Br _{0.4} I _{0.55}) ₃	626	3912	75	
3	1:4:5	CsPb(Cl _{0.1} Br _{0.4} I _{0.5}) ₃	604	2986	57	
4	1.5:4:4.5	CsPb(Cl _{0.15} Br _{0.4} I _{0.45}) ₃	573	2055	39	
5	2:4:4	CsPb(Cl _{0.2} Br _{0.4} I _{0.4}) ₃	555	1151	22	
6	2.25:4:3.75	CsPb(Cl _{0.225} Br _{0.4} I _{0.375}) ₃	523	517.9	10	weak
7	2.5:4:3.5	CsPb(Cl _{0.25} Br _{0.4} I _{0.35}) ₃	501	375.3	7	
8	3:4:3	CsPb(Cl _{0.3} Br _{0.4} I _{0.3}) ₃	487	553.3	11	
9	3.5:4:2.5	CsPb(Cl _{0.35} Br _{0.4} I _{0.25}) ₃	479	637.2	12	
10	4:4:2	CsPb(Cl _{0.4} Br _{0.4} I _{0.2}) ₃	477	968.6	18	strong
11	4.5:4:1.5	CsPb(Cl _{0.45} Br _{0.4} I _{0.15}) ₃	468	1190	23	
12	5:4:1	CsPb(Cl _{0.5} Br _{0.4} I _{0.1}) ₃	462	2118	40	
13	5.5:4:0.5	CsPb(Cl _{0.55} Br _{0.4} I _{0.05}) ₃	456	4093	78	
14	6:4:0	CsPb(Cl _{0.6} Br _{0.4}) ₃	447	4307	82	
15	7:3:0	CsPb(Cl _{0.7} Br _{0.3}) ₃	429	1662	32	
16	8:2:0	CsPb(Cl _{0.8} Br _{0.2}) ₃	421	685.4	13	
17	9:1:0	CsPb(Cl _{0.9} Br _{0.1}) ₃	412	373.1	7	weak
18	10:0:0	CsPbCl ₃	409	135.4	3	

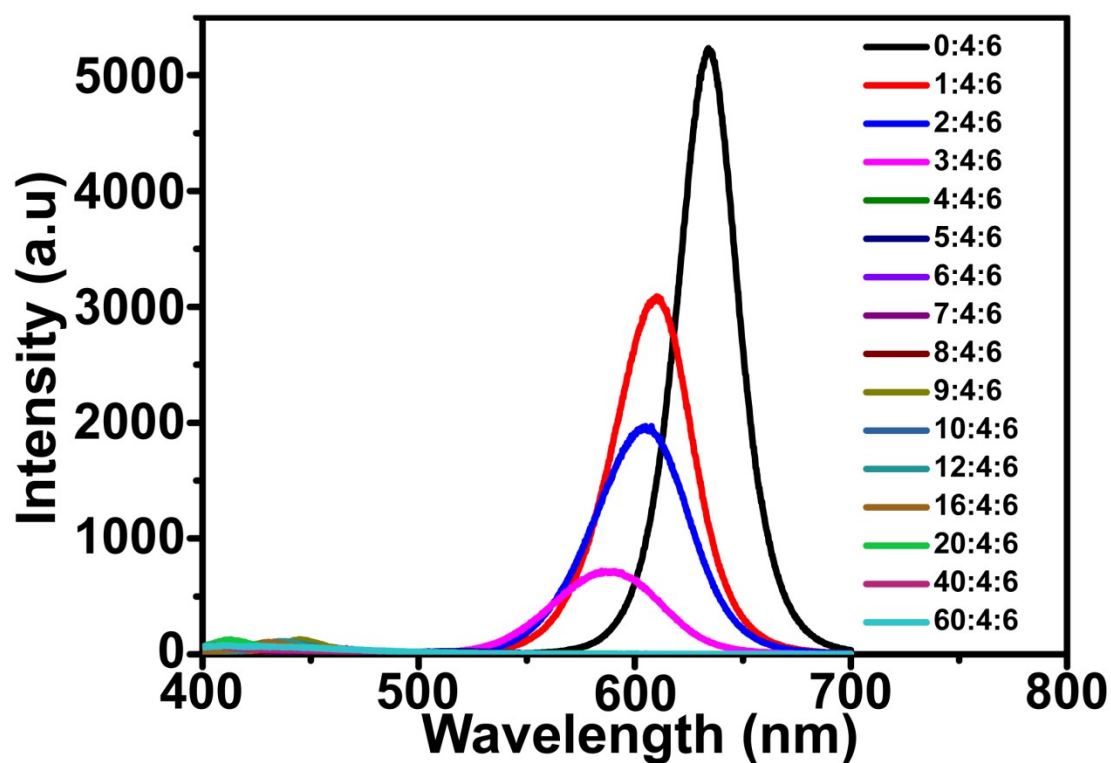


Figure S19. Fluorescence spectra obtained for a serial $\text{CsPb}(\text{Cl}_x\text{Br}_{0.4}\text{I}_{0.6})_3$ PNCs. The serial PNCs were prepared by keeping the amount of Br^- and I^- unchanged while increasing the amount of Cl^- to simulate sole photo-induced ion exchange processes (Equation S6).

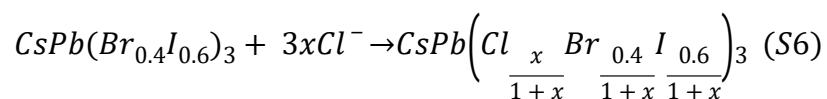


Table S3. The maximum fluorescence emission wavelength and intensity obtained for $\text{CsPb}(\text{Cl}_{x/(1+x)}\text{Br}_{0.4/(1+x)}\text{I}_{0.6/(1+x)})_3$ PNCs

	Cl:Br:I	$\text{CsPb}(\text{Cl}_{x/(1+x)}\text{Br}_{0.4/(1+x)}\text{I}_{0.6/(1+x)})_3$	λ_{max} (nm)	Intensity	Relative intensity	
1	0:4:6	$\text{CsPb}(\text{Br}_{0.4}\text{I}_{0.6})_3$	635	5234	100	strong
2	1:4:6	$\text{CsPb}(\text{Cl}_{0.091}\text{Br}_{0.364}\text{I}_{0.545})_3$	610	3089	59	
3	2:4:6	$\text{CsPb}(\text{Cl}_{0.167}\text{Br}_{0.333}\text{I}_{0.500})_3$	608	1971	38	
4	3:4:6	$\text{CsPb}(\text{Cl}_{0.231}\text{Br}_{0.308}\text{I}_{0.461})_3$	585	719.6	14	
5	4:4:6	$\text{CsPb}(\text{Cl}_{0.286}\text{Br}_{0.286}\text{I}_{0.428})_3$	(451)	(27.74)	(0.5)	weak
6	5:4:6	$\text{CsPb}(\text{Cl}_{0.333}\text{Br}_{0.267}\text{I}_{0.400})_3$	517 (455)	26 (31.27)	0.5 (0.6)	
7	6:4:6	$\text{CsPb}(\text{Cl}_{0.375}\text{Br}_{0.250}\text{I}_{0.375})_3$	(456)	(56.01)	(1)	
8	7:4:6	$\text{CsPb}(\text{Cl}_{0.412}\text{Br}_{0.235}\text{I}_{0.353})_3$	485 (450)	21 (33.76)	0.4 (0.6)	
9	8:4:6	$\text{CsPb}(\text{Cl}_{0.445}\text{Br}_{0.222}\text{I}_{0.333})_3$	(452)	(71.8)	(1)	
10	9:4:6	$\text{CsPb}(\text{Cl}_{0.474}\text{Br}_{0.210}\text{I}_{0.316})_3$	(445)	(129.4)	(2)	
11	10:4:6	$\text{CsPb}(\text{Cl}_{0.500}\text{Br}_{0.200}\text{I}_{0.300})_3$	(440)	(103.8)	(2)	
12	12:4:6	$\text{CsPb}(\text{Cl}_{0.545}\text{Br}_{0.182}\text{I}_{0.273})_3$	(436)	(114.1)	(2)	
13	16:4:6	$\text{CsPb}(\text{Cl}_{0.615}\text{Br}_{0.154}\text{I}_{0.231})_3$	(432)	(105.9)	(2)	
14	20:4:6	$\text{CsPb}(\text{Cl}_{0.667}\text{Br}_{0.133}\text{I}_{0.200})_3$	(412)	(127.7)	2	
15	40:4:6	$\text{CsPb}(\text{Cl}_{0.800}\text{Br}_{0.080}\text{I}_{0.120})_3$	(407)	(75.76)	(1)	
16	60:4:6	$\text{CsPb}(\text{Cl}_{0.857}\text{Br}_{0.057}\text{I}_{0.086})_3$	(407)	(76.47)	(1)	

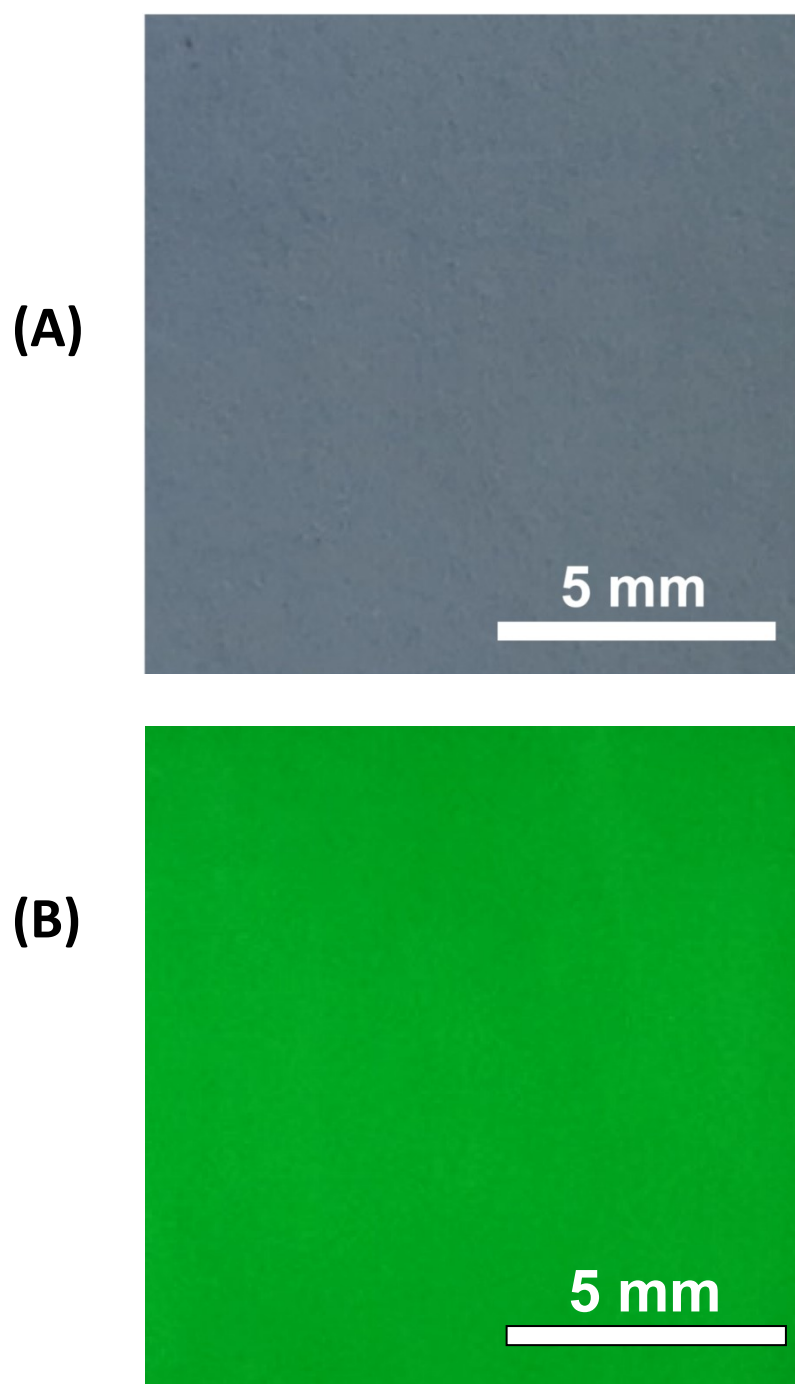


Figure S20. Photographs of PNCs-UCR-DCM film under white light (A) and UV light (B).

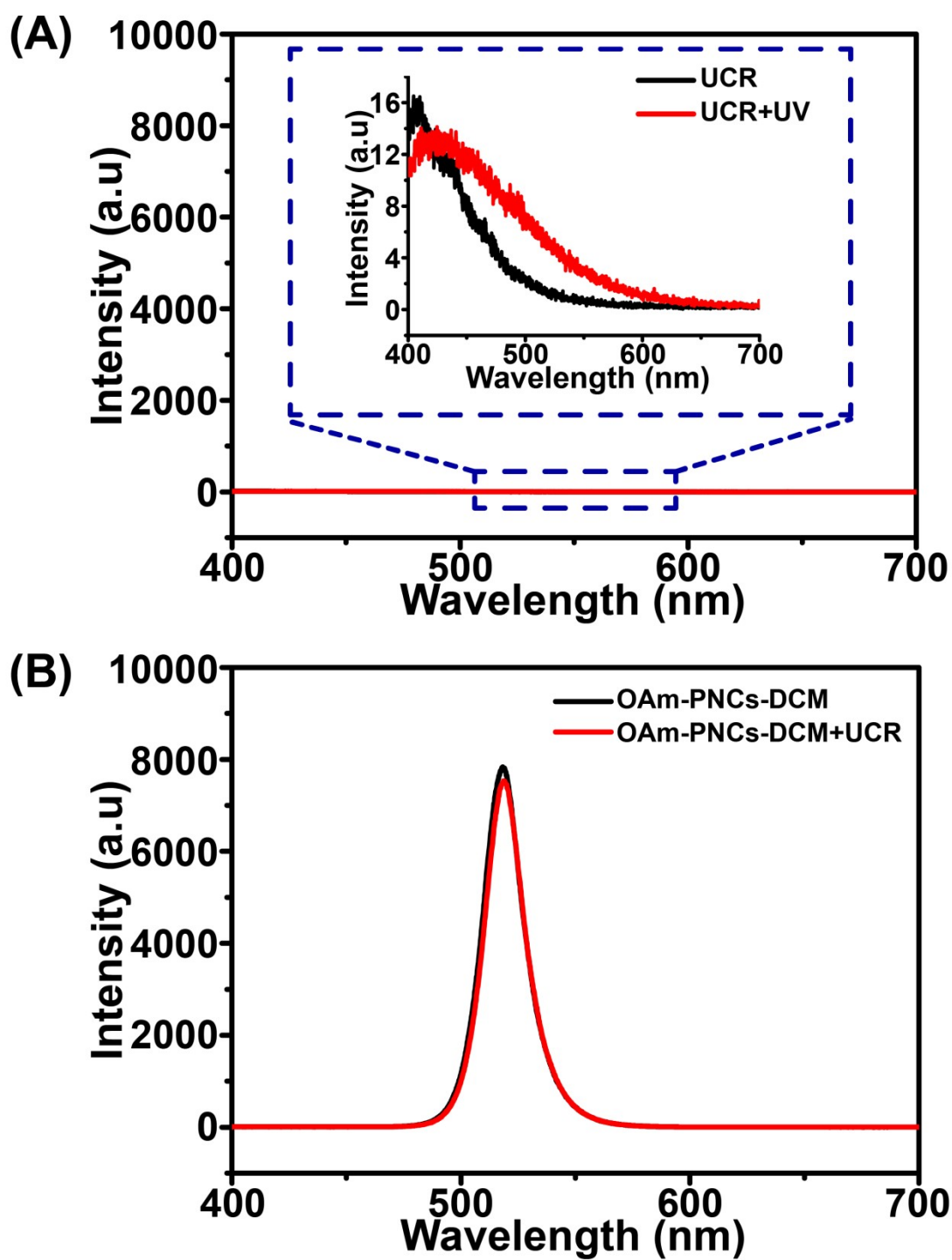


Figure S21. (A) The fluorescence spectra of UCR with (red line) and without (black line) UV irradiation. (B) The fluorescence spectra of OAm-PNCs-DCM solution with (red line) and without (black line) the addition of UCR.

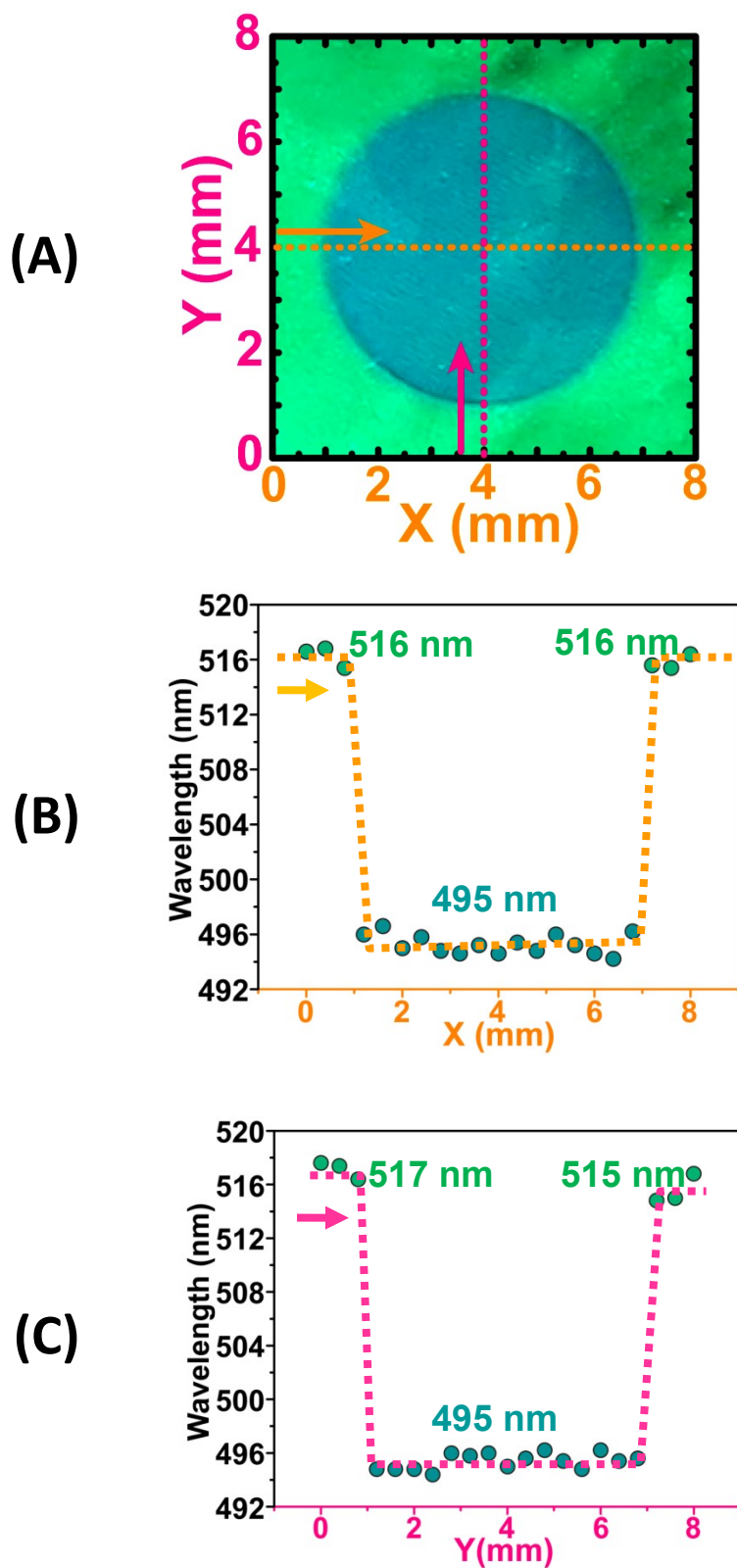


Figure S22. Cyan emissive disk-shaped pattern (A) painted on a green emissive PNCs thin film by a 355-nm laser beam (20 scans), and maximum emission wavelengths probed along X-axis (B) and Y-axis (C) by a USB fiber optical spectrophotometer.

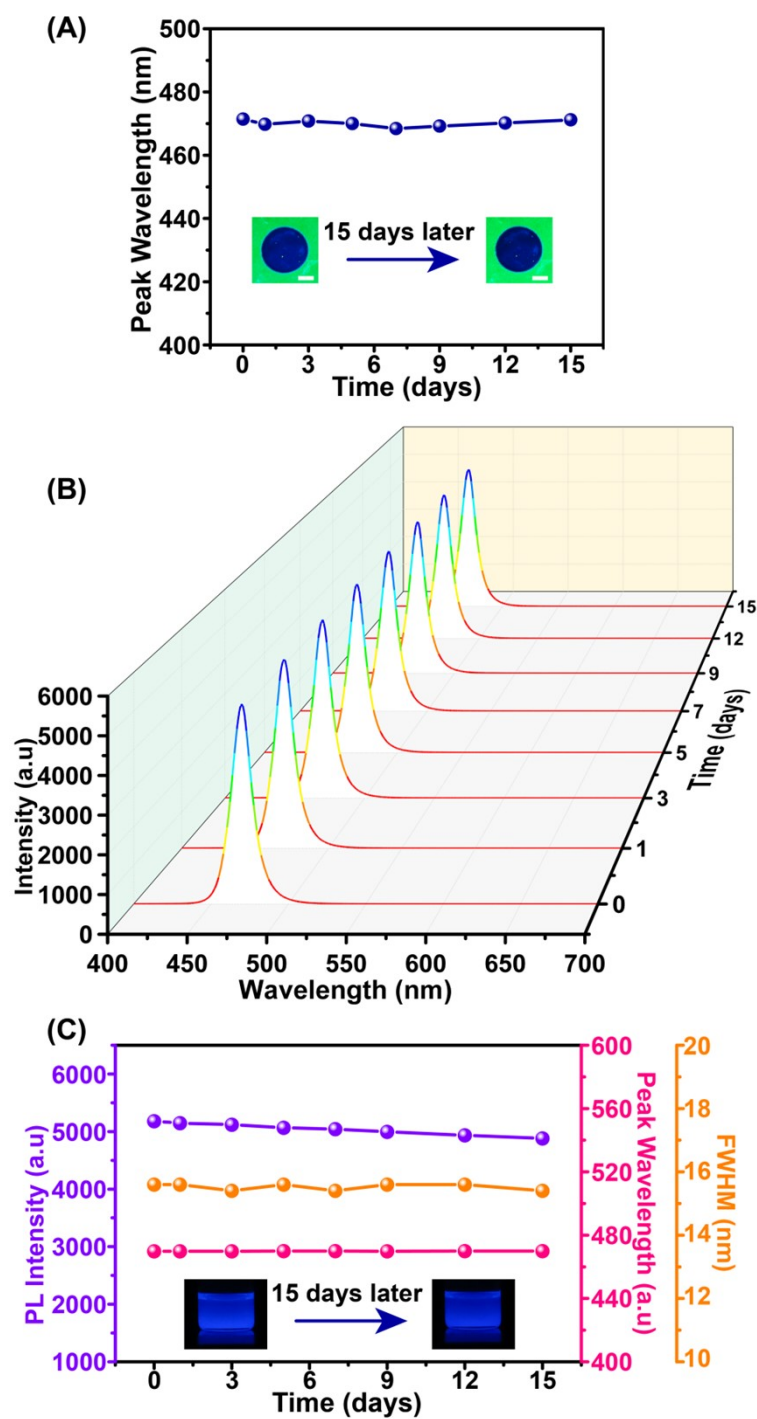


Figure S23. (A) The peak wavelength of the laser-printed pattern with storage time. Inset: the fluorescence photo of the pattern before and after storing for 15 days, scale bar: 2 mm. (B) The spectral stability of OAm-PNCs-DCM solution after stopping UV irradiation. (C) The variations of PL intensity, peak wavelength and FWHM of the OAm-PNCs-DCM solution with time after stopping UV irradiation. Inset: fluorescence photos of the UV light-produced blue emissive OAm-PNCs-DCM solution before and after being stored for 15 days.

The fluorescence quantum yields (FQY) of PNCs are estimated by following Equation^{S1}:

$$Q = Q_R \cdot \frac{I}{I_R} \cdot \frac{OD_R}{OD} \cdot \frac{n^2}{n_R^2}$$

The Q is FQY of samples, I is the measured integrated emission intensity, OD is the optical density of sample which is tested at 365-nm absorbance by UV-Vis spectrophotometer, n is the refractive index of sample, the subscript R is the reference fluorophore of known quantum yield. In this work, quinine sulfate was selected to the reference fluorophore. $Q_R=0.54$, $n_R=1.33$, $n=1.42$, then the Equation is simplified as followed:

$$\begin{aligned} Q &= 0.54 \cdot \frac{I}{I_R} \cdot \frac{OD_R}{OD} \cdot \frac{1.42^2}{1.33^2} \\ &= 0.62 \cdot \frac{I}{I_R} \cdot \frac{OD_R}{OD} \end{aligned}$$

The OD_R and I_R are fixed value as the same reference fluorophore, so the FQY of PNCs can be estimated by simply determine the integrated emission intensity and the absorbance of measured samples, after normalizing the absorbance, the comparison of FQY of PNCs was easily made by measurement of integrated emission intensity.

The concentration of PNCs in DCM was calculated to be 1.9×10^{-3} mol/L or 1.1 mg/mL with the intrinsic absorption coefficient reported before as follow:^{S2}

$$\mu_i = \frac{A}{f \cdot L} \ln 10 \quad (1)$$

$$f = \frac{V(CsPbBr_3)}{V(solution)} \quad (2)$$

$$V(CsPbBr_3) = \frac{n \cdot M}{\rho} \quad (3)$$

$$C(CsPbBr_3) = \frac{n}{V(solution)} \quad (4)$$

where μ_i is the intrinsic absorption coefficient of CsPbBr₃ in solution with a value of 8.7×10^4 cm⁻¹ at 400 nm, A is absorbance at 400 nm, f is volume fraction of CsPbBr₃ in DCM solution, L is optical path length of the sample, $V(CsPbBr_3)$ is the volume of CsPbBr₃ crystals, $V(solution)$ is volume of DCM solution, n , M , ρ is the amount of substance, molar mass and density.

Then the $C(CsPbBr_3)$ can be obtained as follow:

$$\begin{aligned} C(CsPbBr_3) &= \frac{A \cdot \ln 10 \cdot \rho(CsPbBr_3)}{\mu_i \cdot L \cdot M(CsPbBr_3)} \quad (5) = \frac{0.094 \times 100 \times 2.303}{8.7 \times 10^4 \text{ cm}^{-1} \times 1 \text{ cm}} \\ &= 1.9 \times 10^{-6} \text{ mol.cm}^{-3} = 1.9 \times 10^{-3} \text{ mol.L}^{-1} = 1.1 \text{ mg.m} \end{aligned}$$

The loading (w%) of PNCs in the wet film (PNCs-DCM-UCR) and in the dried film (PNCs-UCR) were calculated as follows.

(1) In the wet film (PNCs-DCM-UCR):

$$\begin{aligned} w\%(CsPbBr_3) &= \frac{w(CsPbBr_3)}{w(CsPbBr_3) + w(DCM) + w(UCR)} \quad (6) = \frac{1.1 \text{ mg}}{1.1 \text{ mg} + 1 \text{ mL}} \\ &= 0.047\% \end{aligned}$$

(2) In the dried film (PNCs -UCR):

$$\begin{aligned} w\%(CsPbBr_3) &= \frac{w(CsPbBr_3)}{w(CsPbBr_3) + w(UCR)} \quad (7) = \frac{1.1 \text{ mg}}{1.1 \text{ mg} + 1 \text{ mL} \times 1.024 \text{ g.cm}^{-3}} \\ &= 0.11\% \end{aligned}$$

References

- (S1) H. Wu, Y. Chen, W. Zhang, M. S. Khan, Y. Chi, *ACS Appl. Nano Mater.* 2021, **4**, 11791.
- (S2) J. Maes, L. Balcaen, E. Drijvers, Q. Zhao, J. De Roo, A. Vantomme, F. Vanhaecke, P. Geiregat and Z. Hens, *J. Phys. Chem. Lett.* 2018, **9**, 3093.