

Supporting information

Enhanced Stability of Lead-free Double Perovskite $\text{Cs}_2\text{AgIn}_x\text{Bi}_{1-x}\text{Cl}_6$ Crystals under High Humidity Environment by Surface Capping Treatment

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Experimental Section

1.1. Materials

The cesium chloride (CsCl, 99.99%), silver chloride (AgCl, 99.5%), bismuth chloride (BiCl₃, 99.99%), indium chloride (InCl₃, 99.99%), dimethyl sulfoxide (DMSO, 99%), oleic acid (OA, 99%), isopropanol were purchased from Aladdin. The poly (vinylidene fluoride) (PVDF) purchased from Alfa Aesar. All the reagents were used without further purification.

1.2. Fabrication of ligand free Cs₂AgIn_xBi_{1-x}Cl₆ NCs with different In³⁺ content.

For the synthesis of ligand free Cs₂AgIn_xBi_{1-x}Cl₆ NCs, CsCl, AgCl, InCl₃ and BiCl₃ with molar ratio 2 : x : 1-x : 1 (x = 0, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 100%) was dissolved in DMSO to form precursor solution. Typically, 0.2 mmol CsCl, 0.1 mmol AgCl and 0.1 mmol BiCl₃ were dissolved in 5 mL DMSO to form the precursor solution. Then 100 μL precursor solution was injected into the 5 mL isopropanol under vigorous stirring. After that, the solution was centrifuged at 2000 rpm for 5 mins to discard the large crystals.

1.3. Fabrication of OA ligand capped Cs₂AgIn_{0.97}Bi_{0.03}Cl₆ NCs.

For the synthesis of OA ligand capped Cs₂AgIn_{0.97}Bi_{0.03}Cl₆ NCs, 0.2 mmol CsCl, 0.1 mmol AgCl, 0.01 mmol BiCl₃ and 0.09 mmol BiCl₃ were dissolved in 5 mL DMSO to form the precursor solution. Subsequently, 100 μL OA was added in 5 mL isopropanol to form the anti-solvent. Then 100 μL precursor solution was injected into the anti-solvent under vigorous stirring. After that, the solution was centrifuged at 2000 rpm for 5 mins to discard the large crystals.

1.4. Fabrication of PVDF capped Cs₂AgIn_{0.97}Bi_{0.03}Cl₆/PVDF CFs.

For the synthesis of PVDF capped Cs₂AgIn_{0.97}Bi_{0.03}Cl₆/PVDF CFs, 0.2 mmol CsCl, 0.1 mmol AgCl, 0.01 mmol BiCl₃ and 0.09 mmol BiCl₃ were dissolved in 5 mL DMSO to form the precursor

solution. Subsequently, 0.5 g PVDF powder was added to the precursor solution, which was stirred at room temperature for 1 h until the PVDF powder was completely dissolved. The above colloidal solution was then applied uniformly to the substrate using a blade applicator to form a film. The substrate was gradually heated (1 °C/min) to 130 °C to promote the formation of DP $\text{Cs}_2\text{AgIn}_{0.97}\text{Bi}_{0.03}\text{Cl}_6$. Afterwards, the film was held at 130 °C for 30 mins until the $\text{Cs}_2\text{AgIn}_{0.97}\text{Bi}_{0.03}\text{Cl}_6$ was completely crystallized. Finally, $\text{Cs}_2\text{AgIn}_{0.97}\text{Bi}_{0.03}\text{Cl}_6/\text{PVDF}$ CFs was obtained by natural cooling to room temperature.

1.5. LED device assembled by samples with different surface capping treatments.

To achieve highly efficient yellow light emitting LEDs, $\text{Cs}_2\text{AgIn}_{0.97}\text{Bi}_{0.03}\text{Cl}_6$ NCs-free, $\text{Cs}_2\text{AgIn}_{0.97}\text{Bi}_{0.03}\text{Cl}_6$ NCs-OA and $\text{Cs}_2\text{AgIn}_{0.97}\text{Bi}_{0.03}\text{Cl}_6/\text{PVDF}$ CFs were coated directly onto the surface of commercial UV LED chips without any encapsulation treatment, thus assembling them into yellow light emitting LED devices.

Characterization Methods

The morphology and microstructure of $\text{Cs}_2\text{AgIn}_x\text{Bi}_{1-x}\text{Cl}_6$ NCs-free, $\text{Cs}_2\text{AgIn}_{0.97}\text{Bi}_{0.03}\text{Cl}_6$ NCs-OA were analyzed using a high-resolution TEM (JEOL JEM-F200) and EDS detector (Oxford X-Max 65) attached to a transmission electron microscope was utilized to study the chemical compositions of the sample. The morphology and EDS spectra of $\text{Cs}_2\text{AgIn}_{0.97}\text{Bi}_{0.03}\text{Cl}_6/\text{PVDF}$ CFs were investigated by field emission scanning electron microscopy (SEM, FEI Quatan FEG 250) equipped with an energy dispersive spectrometer (EDS). All the elemental analysis was carried out via using a PerkinElmer Optima 7300 DV inductively coupled plasma-optical emission spectrometer (ICP-OES). The photoluminescence (PL) spectra, PL quantum yields (PLQYs) and time-resolved PL (TRPL) decay curves were recorded on an Edinburgh Instruments FLS 1000

spectrometer. The ultraviolet-visible (UV-Vis) absorption and transmittance spectra were recorded by PE Lambda 950. The X-ray diffraction (XRD) patterns were obtained using the DB-ADVANCE X-ray diffraction analyzer diffractometer. The FTIR spectra was measured by Bruker's Tensor 27 Fourier transform infrared spectrometers. The EL spectra of LED were collected by a Keithley 2400 sourcemeter and a Photo Research 670 spectrometer. High temperature and high humidity chambers (BDX-30F DONGGUAN BEIDOUXING TESTING EQUIPMENT CO. LTD) were adopted to provide constant humidity for the stability testing of LED devices in high humidity environments.

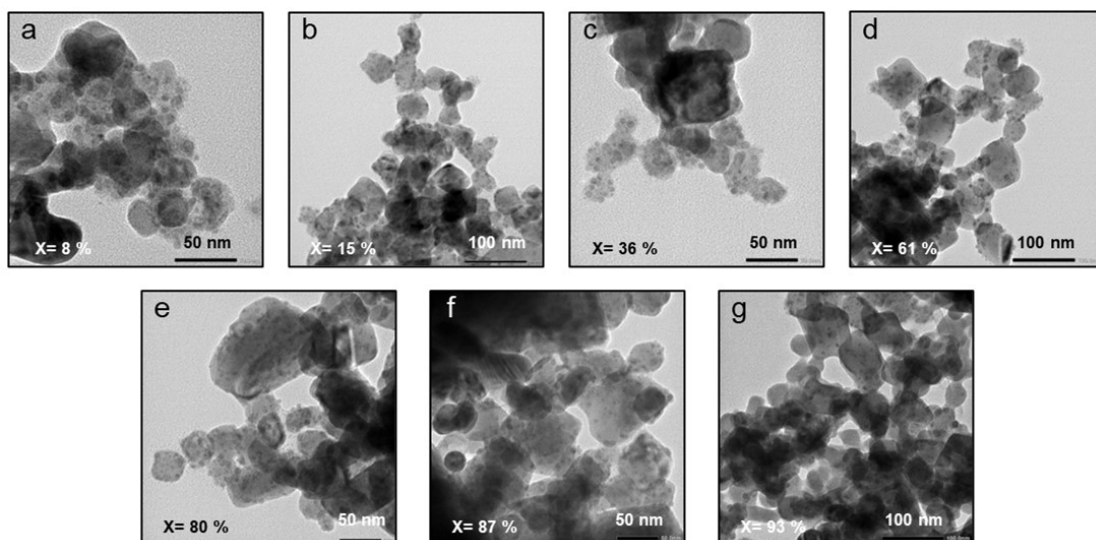


Fig. S1 (a-g) TEM images of $\text{Cs}_2\text{AgIn}_x\text{Bi}_{1-x}\text{Cl}_6$ NCs with different In^{3+} content ($x = 8\%$, 15% , 36% , 61% , 80% , 87% , 93%).

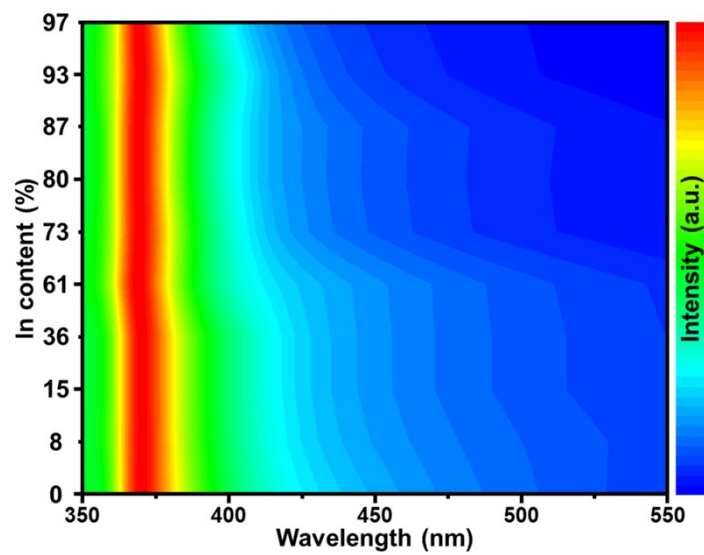


Fig. S2 Magnified views of Cs₂AgIn_xBi_{1-x}Cl₆ NCs absorption tails.

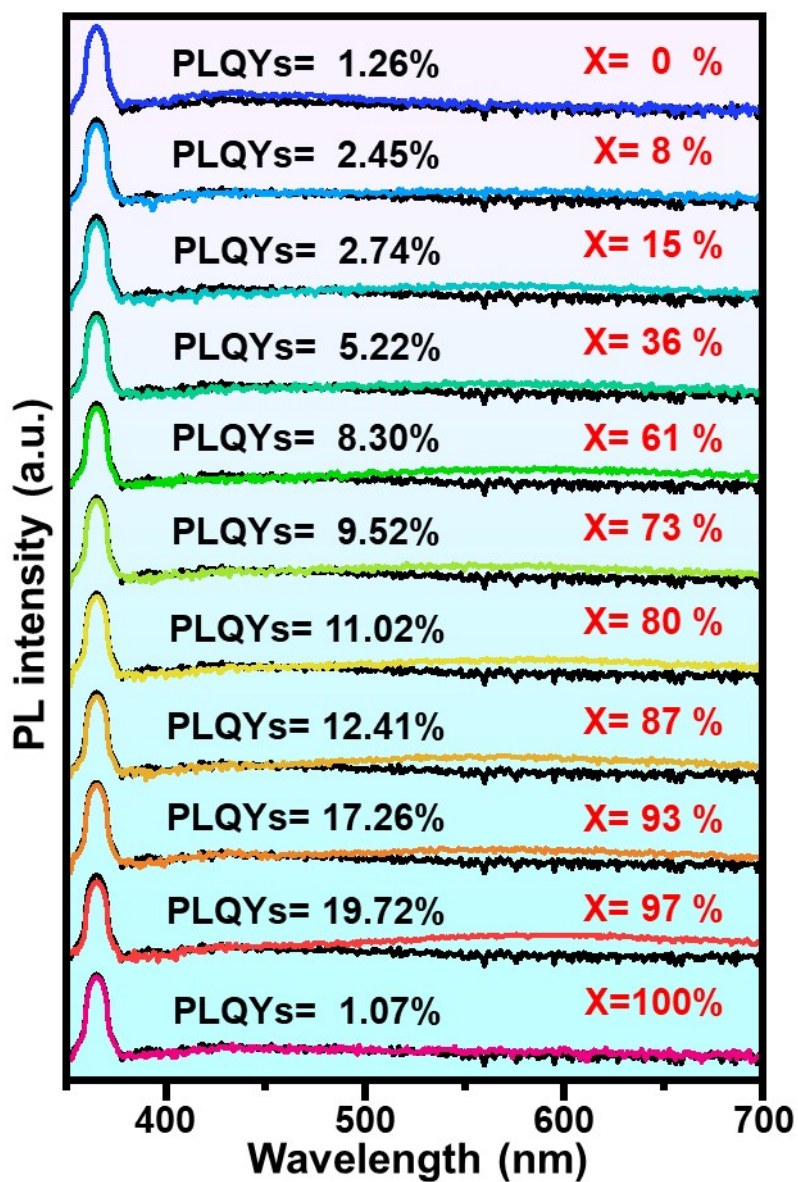


Fig. S3 The spectra for calculating the PLQYs values of $\text{Cs}_2\text{AgIn}_x\text{Bi}_{1-x}\text{Cl}_6$ NCs with different In^{3+} content. The black line is the spectrum of the background.

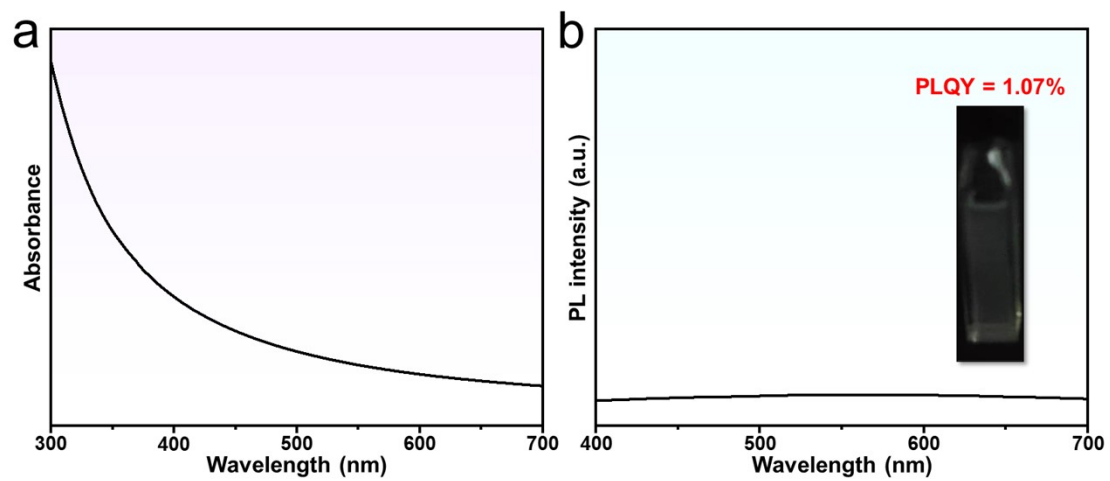


Fig. S4 (a) Absorbance and (b) PL spectra of $\text{Cs}_2\text{AgInCl}_6$ NCs. The inset in (b) displays the photograph and PLQY value corresponding to $\text{Cs}_2\text{AgInCl}_6$ NCs under a 365 nm UV light.

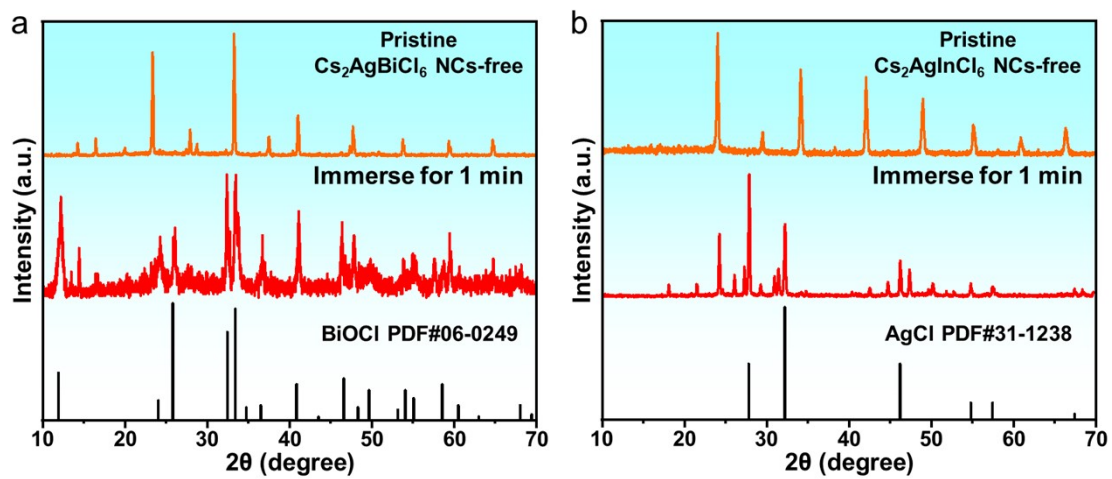


Fig. S5 XRD patterns of (a) $\text{Cs}_2\text{AgBiCl}_6$ NCs-free and (b) $\text{Cs}_2\text{AgInCl}_6$ NCs-free after immersion in the mixed solution (the volume ratio of isopropanol to water is 8:2) for 1 min respectively.

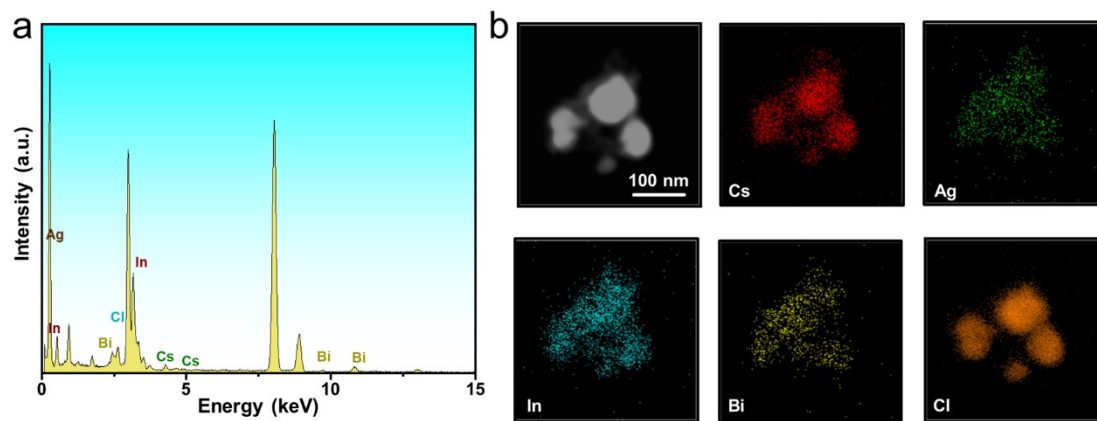


Fig. S6 (a) EDS spectrum and (b) elemental mapping of $\text{Cs}_2\text{AgIn}_{0.97}\text{Bi}_{0.03}\text{Cl}_6$ NCs-OA.

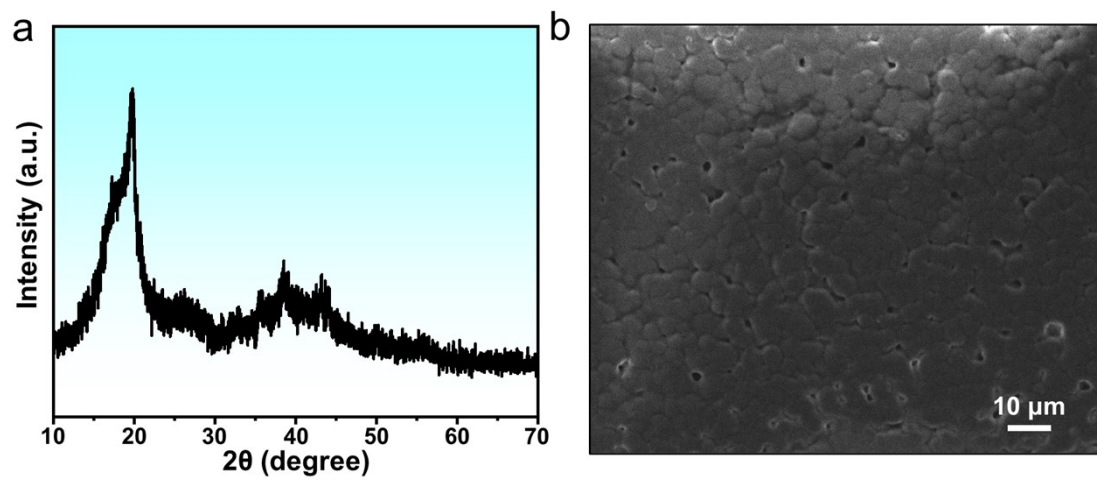


Fig. S7 (a) XRD pattern and b) SEM image of pure PVDF film.

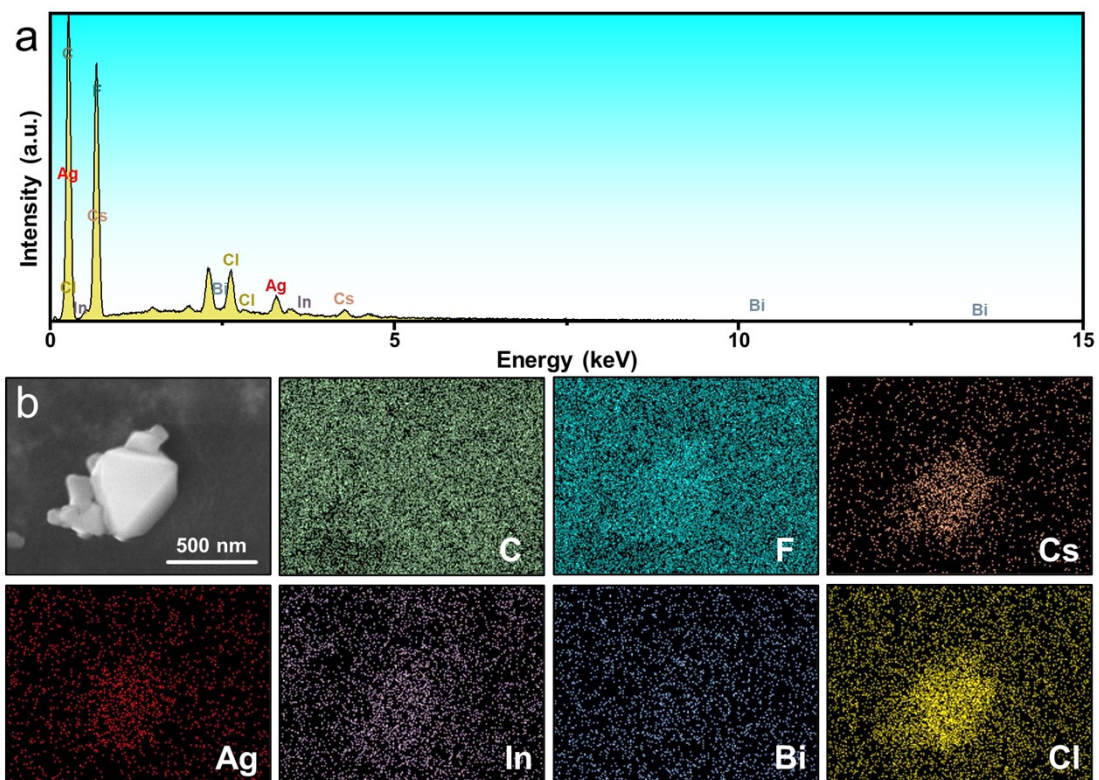


Fig. S8 (a) EDS spectrum and (b) elemental mapping of $\text{Cs}_2\text{AgIn}_{0.97}\text{Bi}_{0.03}\text{Cl}_6/\text{PVDF}$ CFs.

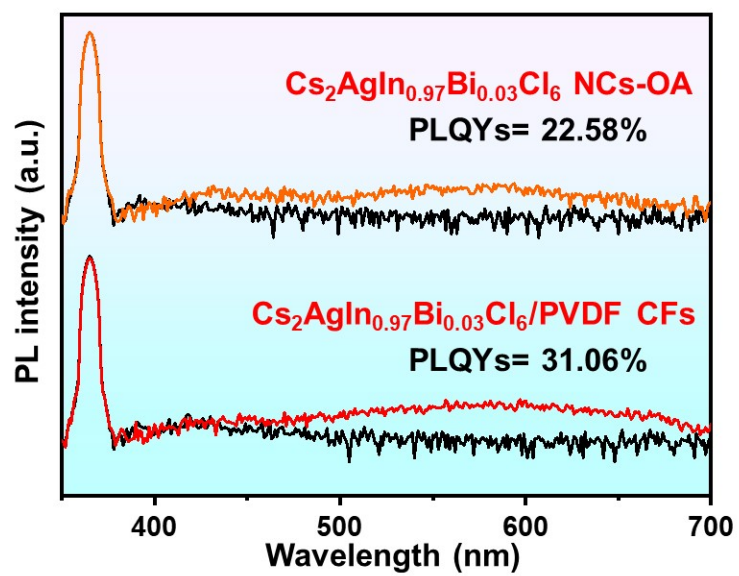


Fig. S9 The spectra for calculating the PLQYs values of $\text{Cs}_2\text{AgIn}_{0.97}\text{Bi}_{0.03}\text{Cl}_6$ NCs-OA and $\text{Cs}_2\text{AgIn}_{0.97}\text{Bi}_{0.03}\text{Cl}_6$ /PVDF CFs. The black line is the spectrum of the background.

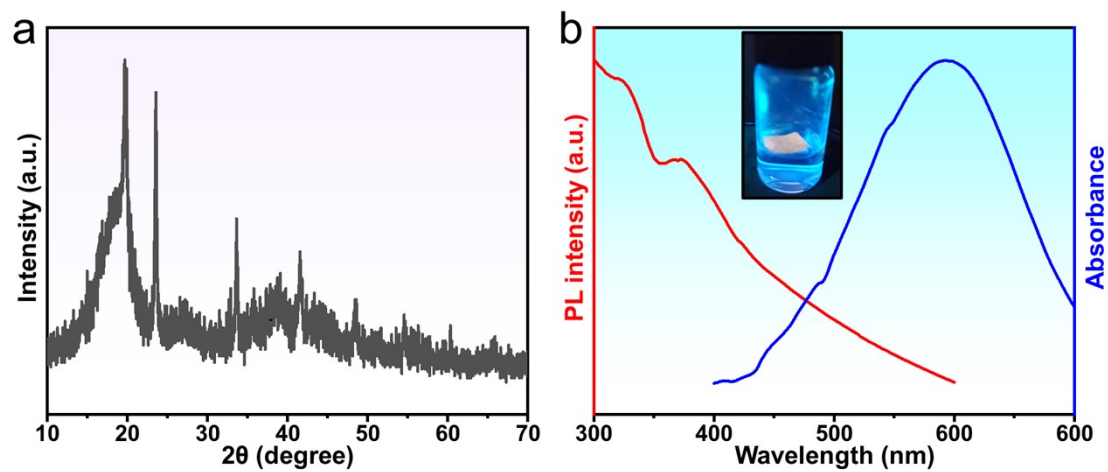


Fig. S10 (a) XRD patterns, (b) absorbance and PL spectra of $\text{Cs}_2\text{AgIn}_{0.97}\text{Bi}_{0.03}\text{Cl}_6/\text{PVDF}$ CFs after storage in water solution for ten days. The inset in (b) is a photograph under 365 nm UV light.

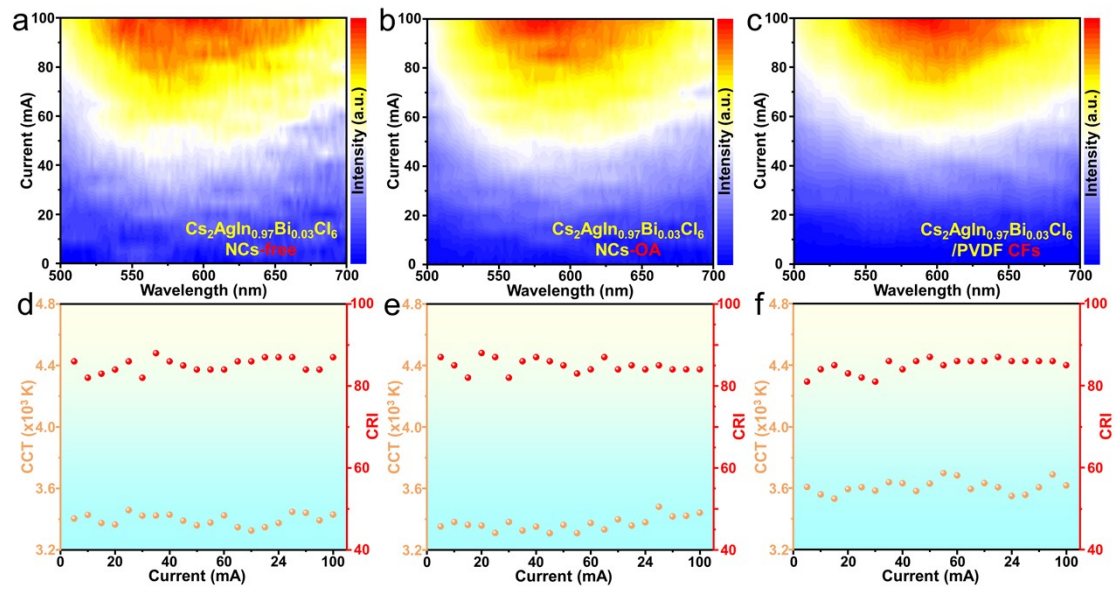


Fig. S11 Changes in the (a-c) EL spectra, (d-f) CRI (red dot) and CCT (yellow dot) of the LEDs at different drive currents.

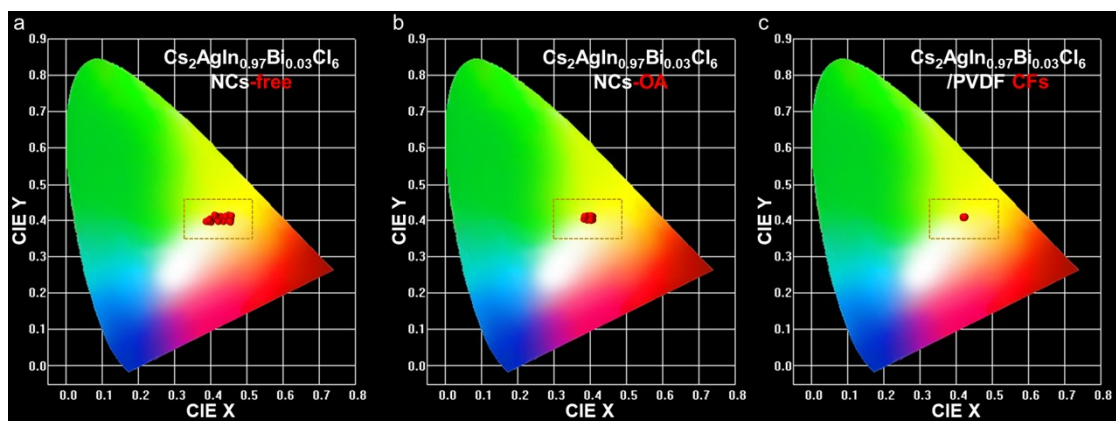


Fig. S12 (a-c) Changes in the CIE color coordinate of the LEDs at different operating times.

Table S1 ICP-OES results and calculations.

In/Bi feeding ratio (mol/mol)	In ³⁺ (g)	In ³⁺ (mol)	Bi ³⁺ (g)	Bi ³⁺ (mol)	In/Bi doping ratio (mol/mol)
0% / 100%	0	0	0.000056	2.67968E-07	0% / 100%
10% / 90%	0.000002	1.74189E-08	0.000044	2.10546E-07	8% / 92%
20% / 80%	0.000004	3.48377E-08	0.000041	1.96191E-07	15% / 85%
30% / 70%	0.000011	9.58038E-08	0.000035	1.6748E-07	36% / 64%
40% / 60%	0.000018	1.5677E-07	0.000021	1.00488E-07	61% / 39%
50% / 50%	0.000024	2.09026E-07	0.000016	7.65624E-08	73% / 27%
60% / 40%	0.000031	2.69993E-07	0.000014	6.69921E-08	80% / 20%
70% / 30%	0.000034	2.96121E-07	0.000009	4.30663E-08	87% / 13%
80% / 20%	0.000042	3.65796E-07	0.000006	2.87109E-08	93% / 7%
90% / 10%	0.000058	5.05147E-07	0.000003	1.43554E-08	97% / 3%
100% / 0%	0.000064	5.57404E-07	0	0	100% / 0%

Table S2 Bi-exponential fitting results of PL decays for Cs₂AgIn_{0.97}Bi_{0.03}Cl₆ NCs-free,Cs₂AgIn_{0.97}Bi_{0.03}Cl₆ NCs-OA and Cs₂AgIn_{0.97}Bi_{0.03}Cl₆/PVDF CFs.

	τ_1 (ns)	A ₁ (%)	τ_2 (ns)	A ₂ (%)	τ_{ave} (ns)
Cs ₂ AgIn _{0.97} Bi _{0.03} Cl ₆ NCs-free	10.0871	31.24	62.9341	68.76	59.3469
Cs ₂ AgIn _{0.97} Bi _{0.03} Cl ₆ NCs-OA	12.8348	25.91	74.3713	74.09	70.8688
Cs ₂ AgIn _{0.97} Bi _{0.03} Cl ₆ /PVDF CFs	17.1028	13.37	98.7725	86.63	96.6468

The PL decay curves of different samples were studied and the decay traces for the samples were well fitted with bi-exponential function $Y(t)$ based on nonlinear least-squares, using the following expression.

$$Y(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (S1)$$

where A_1 , A_2 are fractional contributions of time-resolved emission decay lifetimes τ_1 , τ_2 .

The average lifetime (τ_{ave}) of the different samples can be obtained by the following equation.

$$\tau_{ave} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \quad (S2)$$

Table S3. CIE coordinates, CCT, and CRI of WLEDs based on different lead-free DP.

Device structure	CIE coordinates	CCT (K)	CRI	Ref
UV LED/Cs ₂ AgIn _{0.7} Bi _{0.3} Cl ₆ /PMMA	(0.36, 0.35)	4443	≈91	1
UV LED/Cs ₂ (Na, Ag)InCl ₆ :7.09%Ho ³⁺	(0.40, 0.47)	-	75.4	2
UV LED/Cs ₂ Na _{0.4} Ag _{0.6} In _{0.995} Bi _{0.005} Cl ₆ :Mn ²⁺	(0.38, 0.42)	4323.4	82.6	3
UV LED/Cs ₂ Ag _{0.6} Na _{0.4} InCl ₆ :Bi ³⁺	(0.396, 0.448)	4054	-	4
UV LED/Cs ₂ AgIn _{0.833} Bi _{0.167} Cl ₆	(0.448, 0.444)	3119	85	5
UV LED/Cs ₂ Ag _{0.4} Na _{0.6} InCl ₆ :1%Bi ³⁺ -1% Ce ³⁺	(0.47, 0.45)	2769	84.1	6
UV LED/Cs ₂ NaInCl ₆ :2.5%Sb,45%Tb,3%Mn	(0.41, 0.39)	3371	89.2	7
UV LED/Cs ₂ NaInCl ₆ :Sb ³⁺ /Cs ₂ NaInCl ₆ :Rb ⁺ ,Sb ³⁺ / Cs ₂ NaInCl ₆ :Mn ²⁺ ,Sb ³⁺	(0.30, 0.35)	6772	91	8
UV LED/Cs ₂ AgIn _{0.9} Cr _{0.1} Cl ₆ /SrSi ₂ O ₂ N ₂ :Eu ²⁺ /CaAlSiN ₃ :Eu ²⁺	(0.3819, 0.4196)	4200	-	9
UV LED/Cs ₂ NaInCl ₆ :Sb ³⁺ /Sr ₂ Si ₅ N ₈ :Eu ²⁺ /β- SiAlON:Eu ²⁺	(0.3890, 0.4009)	3972.6	90.6	10
UV LED/Cs ₂ Na _{0.8} Ag _{0.2} BiCl ₆ /PMMA	(0.48, 0.44)	2600	85	11
UV LED/Cs ₂ AgIn _{0.97} Bi _{0.03} Cl ₆ -free	(0.39, 0.40)	3400	85	this work
UV LED/Cs ₂ AgIn _{0.97} Bi _{0.03} Cl ₆ -OA	(0.39, 0.40)	3400	85	this work
UV LED/Cs ₂ AgIn _{0.97} Bi _{0.03} Cl ₆ /PVDF	(0.41, 0.40)	3600	85	this work

Notes and references

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