Supporting information

Advanced Lead-free Double Perovskite/Silica Hybrid Nanocrystals for Highly Stable Light-Emitting Diodes

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Experimental Section

1.1. Materials

The cesium chloride (CsCl, 99.99%), silver chloride (AgCl, 99.5%), bismuth chloride ($BiCl_3$, 99.99%), indium chloride ($InCl_3$, 99.99%), dimethyl sulfoxide (DMSO, 99%), and isopropanol (IPA) were purchased from Aladdin. The KIT-6 mesoporous molecular sieve was purchased from Nanjing XFNANO Co. Ltd. All the reagents were used without further purification.

1.2. Fabrication of $Cs_2AgIn_xBi_{1-x}Cl_6$@KIT-6 NCs with different In^{3+} content.

Synthesis of $Cs_2AgIn_xBi_{1-x}Cl_6$@KIT-6 NCs by in situ assembling method. Firstly, CsCl, AgCl, $InCl_3$ and $BiCl_3$ with molar ratio 2 : x : 1-x : 1 (x = 100%、90%、80%、70%、60%) was dissolved in DMSO to form precursor solution. Subsequently, some amount of KIT-6 mesoporous molecular sieve was added into the precursor solution, and stirring continuously for three hours until complete mixing. Finally, 500 mL of IPA was rapidly added into the mixed solution under vigorous stirring. Further, the crude product was collected by centrifugation, and it was dried at 80 °C for 10 h to obtained $Cs_2AgIn_xBi_{1-x}Cl_6$@KIT-6 NCs powder. Typically, 0.2 mmol CsCl, 0.1 mmol AgCl and 0.1 mmol $InCl_3$ were dissolved in 5 mL DMSO to form the precursor solution. Subsequently, 0.2 g of KIT-6 mesoporous molecular sieve was added into the precursor solution, and stirring continuously for three hours until complete mixing. Finally, 500 mL of IPA was rapidly added into the mixed solution under vigorous stirring. After that, the solution was centrifuged at 8000 rpm for 5 min to collected the crude product, and it was dried at 80 °C for 10 h to obtained $Cs_2AgBiCl_6$@KIT-6 NCs.

1.3. Fabrication of $Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$ NCs.

For the synthesis of $Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$ NCs, 0.2 mmol CsCl, 0.1 mmol AgCl, 0.01 mmol

$BiCl_3$ and 0.09 mmol $InCl_3$ were dissolved in 5 mL DMSO to form the precursor solution. Subsequently, 500 mL of IPA was rapidly added into the precursor solution under vigorous stirring. After that, the solution was centrifuged at 8000 rpm for 5 min to collected the crude product, and it was dried at 80 °C for 10 h to obtained $Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$ NCs.

1.4. LED devices assembled from different samples.

To achieve highly efficient yellow light emitting LEDs, $Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$ NCs and $Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$@KIT-6 NCs after PMMA encapsulation were coated on the surface of a commercial UV LED chip (Shenzhen Xin Kai photoelectric Co Ltd.), dried overnight at room temperature, thus assembling them into yellow light emitting LED devices.

Characterization Methods

The morphology and microstructure of $Cs_2AgIn_xBi_{1-x}Cl_6$@KIT-6 NCs and $Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$ NCs were analyzed using a high-resolution TEM (JEOL JEM-F200). 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. X-ray photoelectron spectroscopy (XPS) spectra were measured by a Thermo Fisher ESCALA670B Xi^+. The PL spectra of the samples at different temperatures were collected by Photo Research 670 spectrometer after heating the samples using a heater (MS7-H550-S, DLAB, China) and under 365 nm UV light irradiation. The EL spectra of LED were collected by a Keithley 2400 sourcemeter and a Photo

Research 670 spectrometer. The thermal infrared imager was used to detect temperature and record thermal images (FOTRIC, USA). Specific surface areas were calculated using the BET (Brunauer−Emmett−Teller) method with N_2 adsorption−desorption isotherms recorded on a Micromeritics TriStar II 3020 specific surface and porosity analyzer.

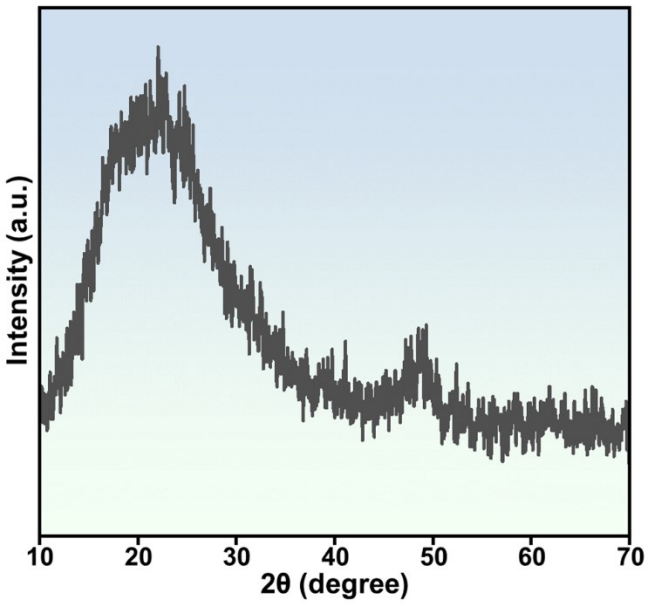

Fig. S1 XRD patterns of amorphous KIT-6 mesoporous molecular sieve.

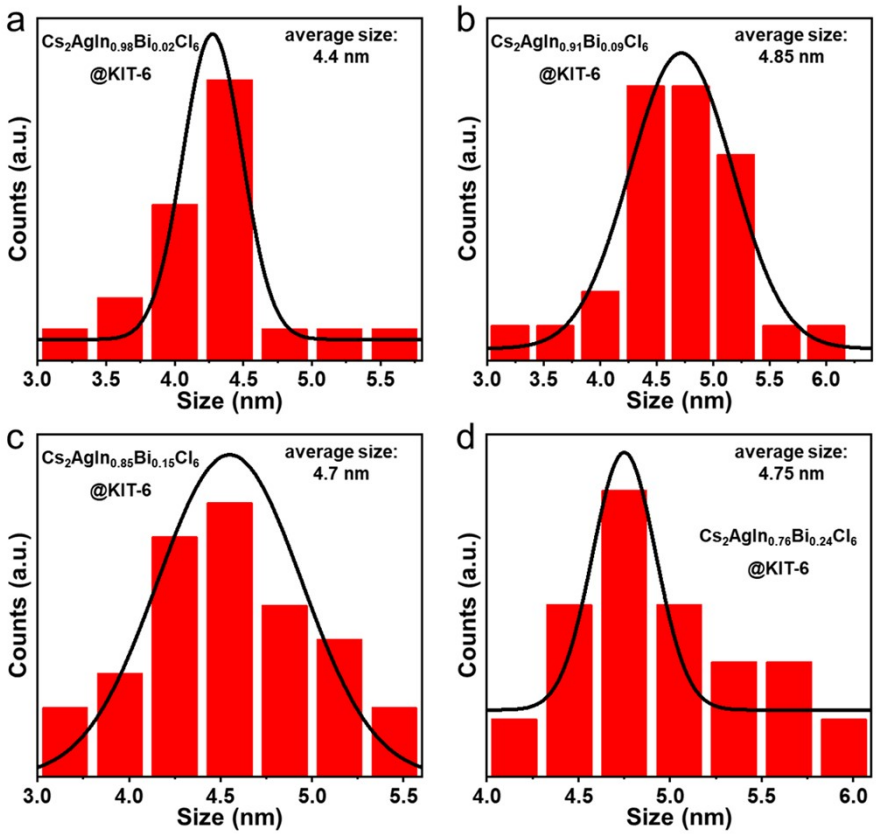

Fig. S2 The size of $Cs_2AgIn_xBi_{1-x}Cl_6$ NCs in $Cs_2AgIn_xBi_{1-x}Cl_6$@KIT-6 NCs. (a) X=98%, (b) X=91%, (c) X=85% and (d) X=76%,

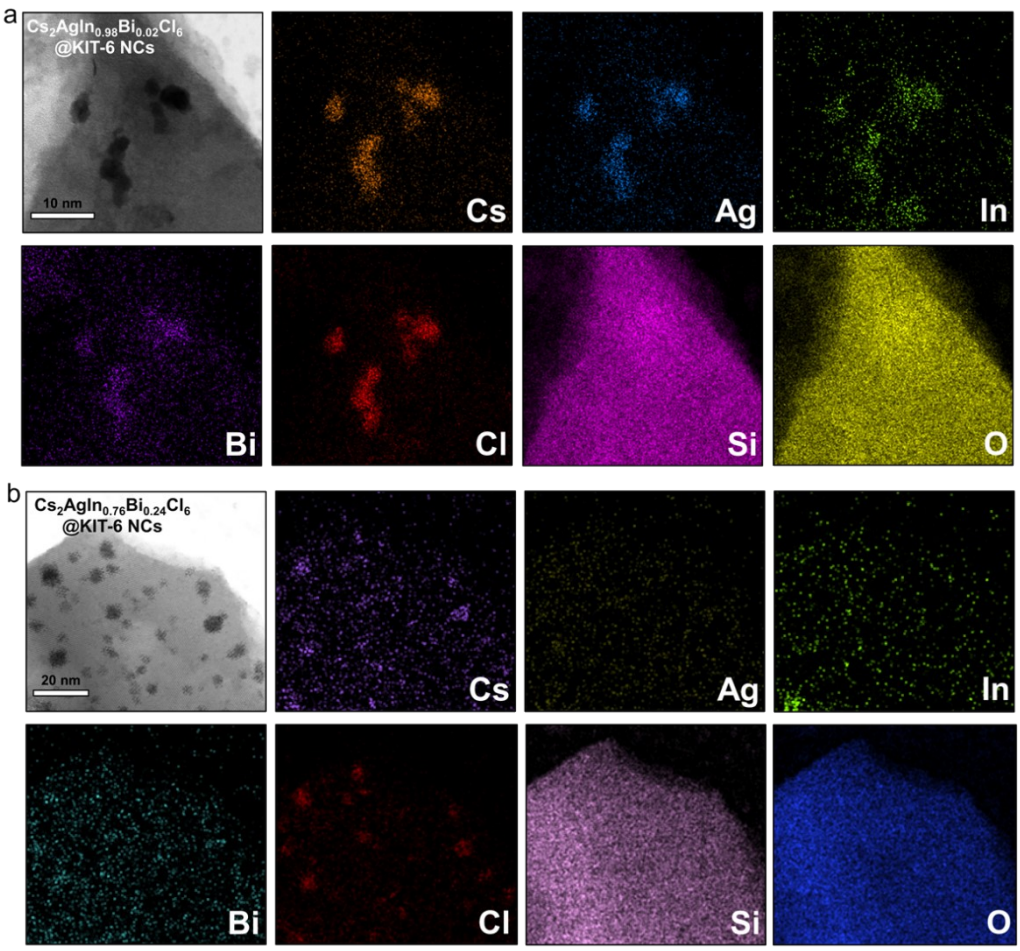

Fig. S3 The elemental mapping spectra of (a) $Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$@KIT-6 NCs and (b) $Cs_2AgIn_{0.76}Bi_{0.24}Cl_6$@KIT-6 NCs.

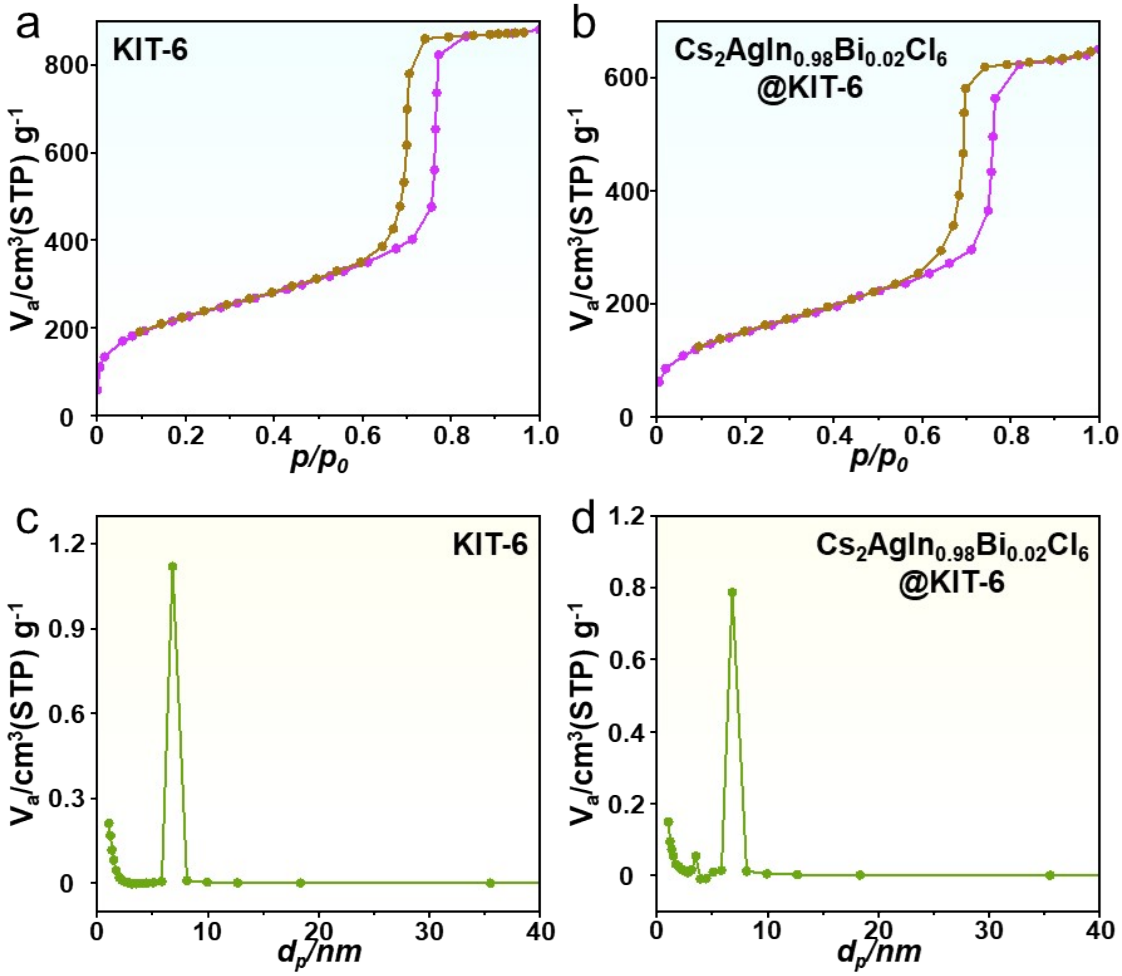

Fig. S4 Nitrogen adsorption-desorption isotherm diagram of (a) KIT-6 and (b) $Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$@KIT-6 NCs, respectively. Pore diameter distribution curves of (c) KIT-6 and (d) $Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$@KIT-6 NCs, respectively

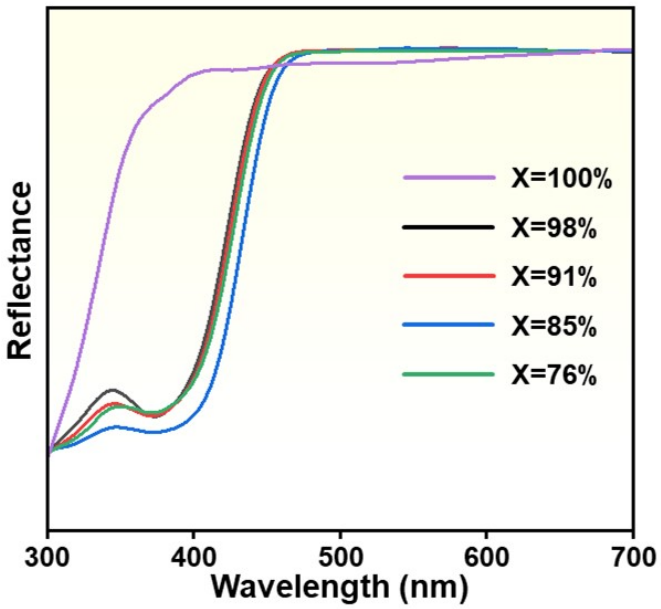

Fig. S5 UV-vis reflectance spectra of $Cs_2AgIn_xBi_{1-x}Cl_6$@KIT-6 NCs with different In^{3+} content.

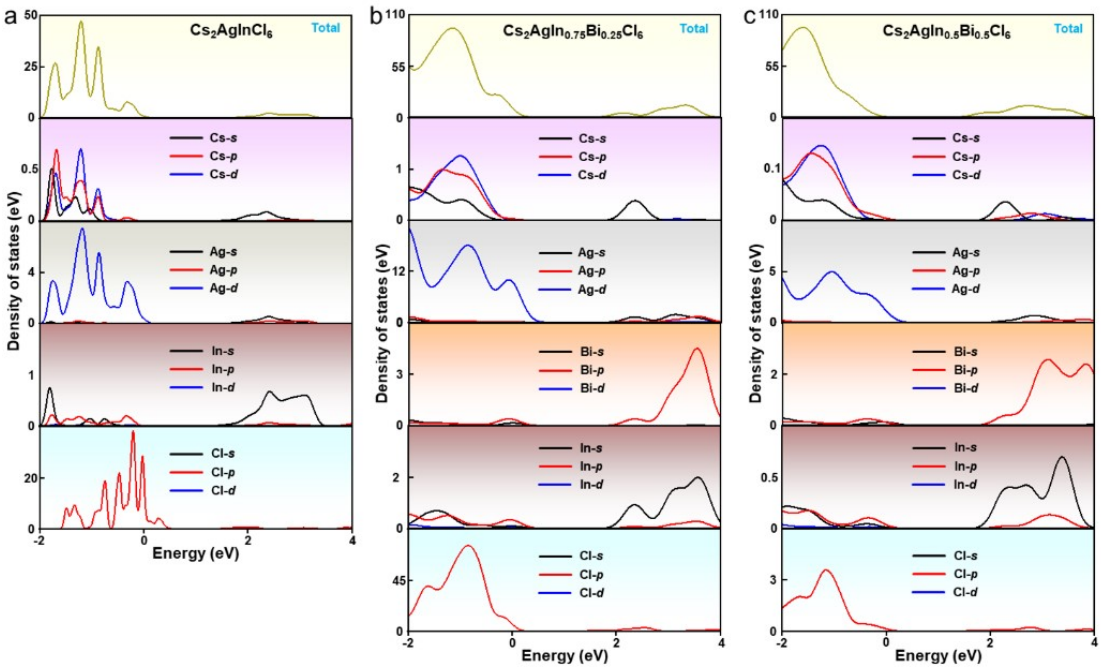

Fig. S6 The total and partial density of states of (a) $Cs_2AgInCl_6$, (b) $Cs_2AgIn_{0.75}Bi_{0.25}Cl_6$ and (c) $Cs_2AgIn_{0.5}Bi_{0.5}Cl_6$ from the PBE+SOC calculations.

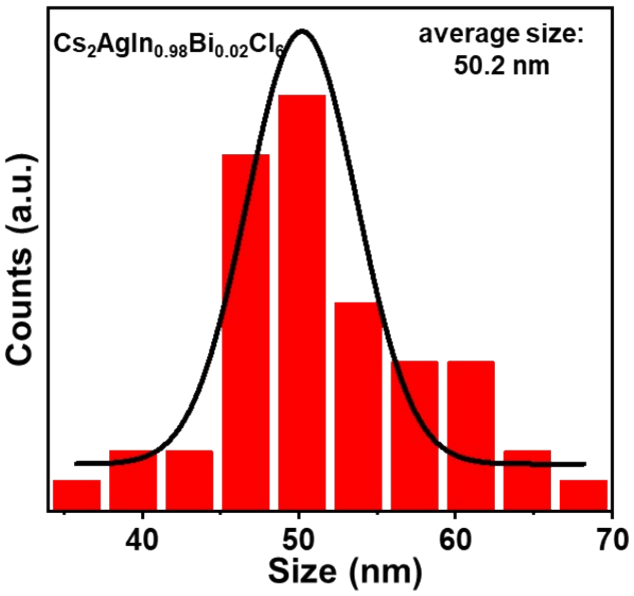

Fig. S7 The size of $Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$ NCs.

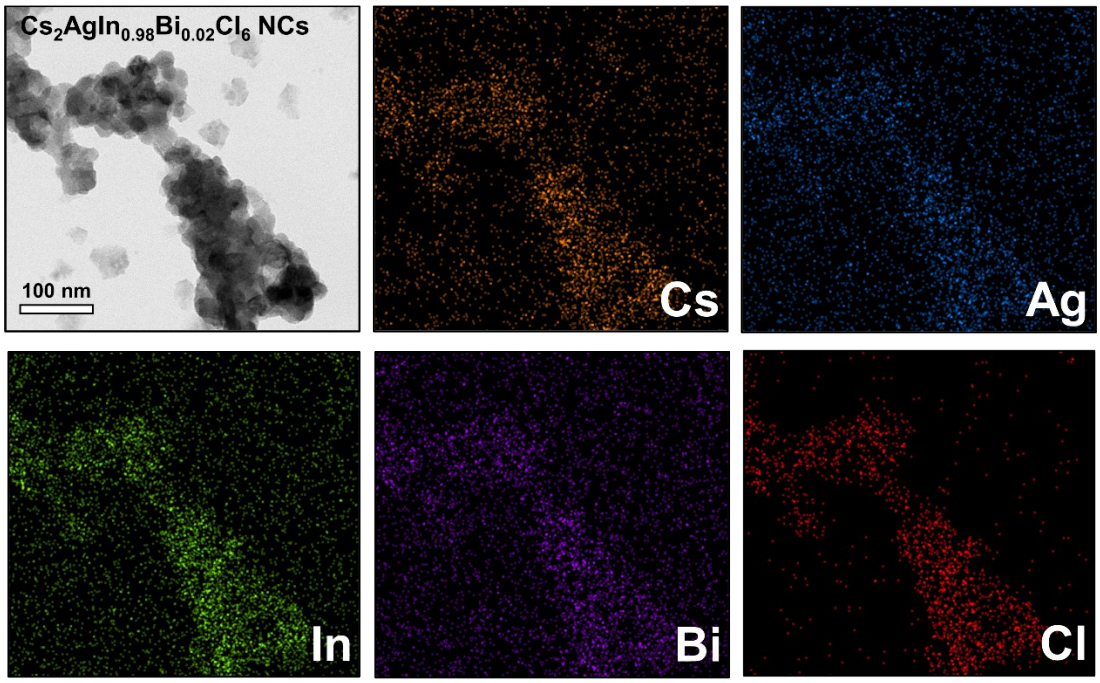

Fig. S8 The elemental mapping spectra of $Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$ NCs.

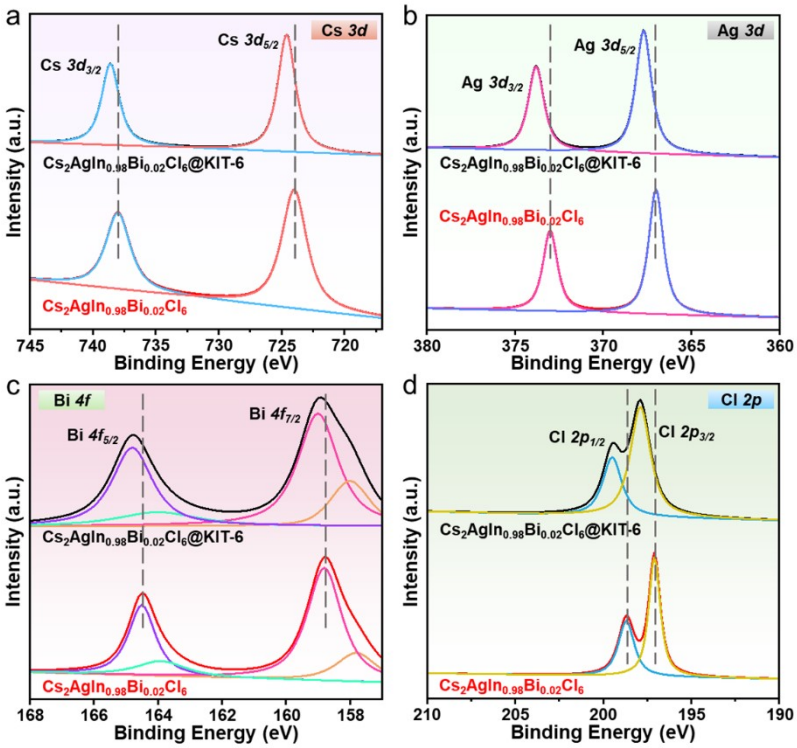

Fig. S9 The high-resolution XPS spectra of (a) Cs 3d, (b) Ag 3d, (c) Bi 4f and (d) Cl 2p.

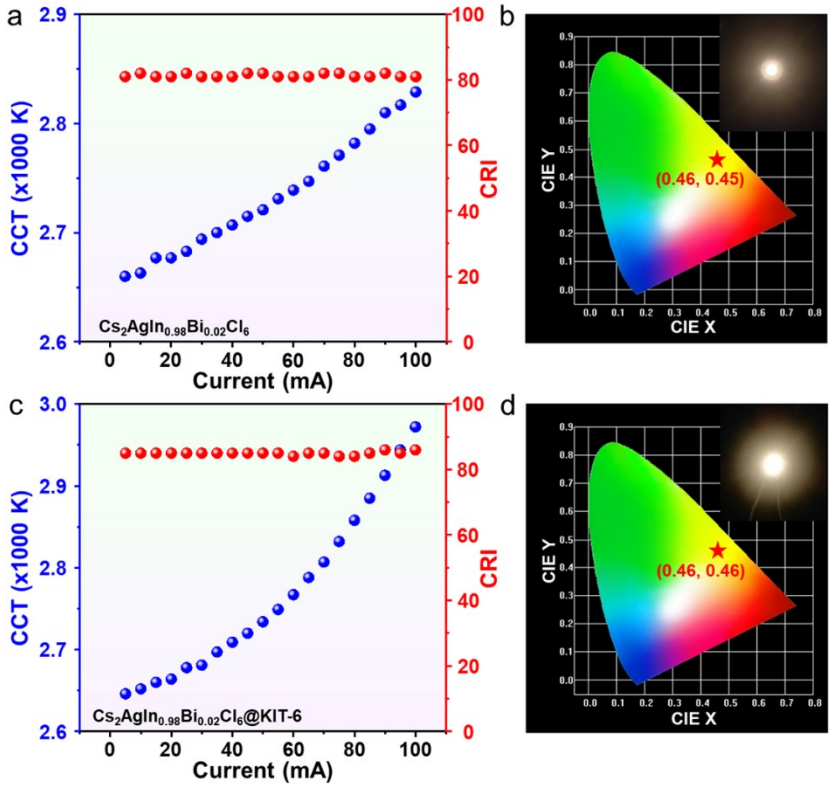

Fig. S10 The CCT values (blue) and CRI values (red) of LED devices assembled with (a) $Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$ NCs and (c) $Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$@KIT-6 NCs at different drive currents. (b, d) The CIE color coordinates of LED devices driven at 100 mA. The insets in (b, d) are photographs of the corresponding LED in operation.

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)
100% / 0%	0.000061	5.31276E-07	0	0	100% / 0%
90% / 10%	0.000053	4.616E-07	0.0000021	1.00488E-08	98% / 2%
80% / 20%	0.000047	4.09343E-07	0.0000083	3.97167E-08	91% / 9%
70% / 30%	0.000042	3.65796E-07	0.0000135	6.45995E-08	85% / 15%
60% / 40%	0.000035	3.0483E-07	0.0000201	9.61815E-08	76% / 24%

Table S2 Comparison of detailed parameters on the BET surface area and pore volume of KIT-6 and $Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$@KIT-6.

Sample	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)
KIT-6	0.000061	5.31276E-07
$Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$@KIT-6	0.000035	3.0483E-07

Table S3 Bi-exponential fitting results of PL decays for $Cs_2AgIn_xBi_{1-x}Cl_6$@KIT-6 NCs with different In^{3+} content.

	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_{ave} (ns)
$Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$@KIT-6 NCs	4.1521	79.8	29.9278	22.2	20.7981
$Cs_2AgIn_{0.91}Bi_{0.09}Cl_6$@KIT-6 NCs	4.8363	81.3	27.1463	18.7	17.421
$Cs_2AgIn_{0.85}Bi_{0.15}Cl_6$@KIT-6 NCs	3.0131	84.3	24.0626	15.7	15.5935
$Cs_2AgIn_{0.76}Bi_{0.24}Cl_6$@KIT-6 NCs	2.9415	87.6	21.7309	12.4	12.5458

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 S4 Bi-exponential fitting results of PL decays for pure $Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$ NCs and $Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$@KIT-6 NCs

	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_{ave} (ns)
pure $Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$ NCs	3.2013	81.4	26.1434	18.6	18.1519
$Cs_2AgIn_{0.98}Bi_{0.02}Cl_6$@KIT-6 NCs	4.1521	79.8	29.9278	22.2	20.7981