Boosting the Self-Trapped Exciton Emission in Alloyed Cs$_2$(Ag/Na)InCl$_6$ Double Perovskite via Cu$^+$ Doping

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1. Introduction

All-inorganic 3D lead-free double perovskites (DPs) with the general formula A$_x$B$^+$$^+$B$^{III}$X$_6$ ($A = \text{Rb}^+$, Cs$^+$; $B^+ = \text{K}^+$, Ag$^+$, Na$^+$; $B^{III} = \text{In}^{3+}$, Bi$^{3+}$, Sb$^{3+}$; $X = \text{Cl}^-$, Br$^-$, I$^-$) have recently evoked considerable interest in a wide range of research fields owing to their intriguing optoelectronic properties. [1] These DPs, while preserving the merits of 3D lead halide perovskites (typically CsPbX$_3$) including long carrier diffusion distance, large absorption coefficient, and tunable bandgap, are superior to CsPbX$_3$ in terms of the toxicity and stability issues, and the freedom of tunability via B site engineering. [2] Therefore, they are ideal candidates as alternatives to lead halide perovskites and as a new generation of optoelectronic materials for various applications such as solar cells, photodetectors, and light-emitting diodes (LEDs). [3] In contrast to CsPbX$_3$ with corner-sharing [PbX$_6$]$^{2-}$ octahedra, the structural units of DPs are characterized by alternating [B$^+$$^+$X$_6$]$^{2-}$ and [B$^{III}$X$_6$]$^{3-}$ octahedra. [4] As a result, the electronic dimensionality of DPs is reduced in comparison with that of CsPbX$_3$, leading to many fascinating characteristics such as strong electron–phonon coupling, large exciton binding energy, and broadband self-trapped exciton (STE) emission with a large Stokes shift. [5] Nonetheless, because of the nature of indirect bandgap or direct bandgap with parity-forbidden transitions, these DPs normally suffer from a low photoluminescence (PL) efficiency, [6] which limits their application as light-emitting materials in many technological fields.

To circumvent the limitation of DPs, it is essential to modify their bandgap and transition attributes by engineering the B site of the materials through metal ion doping or alloying. [7] In this regard, d-, f-, and s-electron ions such as Mn$^{2+}$, Cr$^{3+}$, Tb$^{3+}$, Yb$^{3+}$, Er$^{3+}$, Bi$^{3+}$, In$^{3+}$, and Sb$^{3+}$ have been established as effective dopants in DPs to modulate their electronic structures and boost their PL efficiencies. [8] Specifically, broadband white-light emission with a quantum yield (QY) of 86% was realized in the alloyed Cs$_2$(Ag$_{0.60}$/Na$_{0.40}$)InCl$_6$: Bi$^{3+}$ crystals by breaking the parity-forbidden transition through lowering the symmetry of the STE wavefunction. [9] However, the maximum excitation band of the crystals at the high energy region (325 nm) is not optimal for a commercial near-UV (NUV, >350 nm) LED chip. Although many efforts have been devoted to tailoring both the excitation and emission of STEs in Cs$_2$(Ag/Na)InCl$_6$ DPs, [10] the fundamental photophysics involved in the doping effect especially the dynamics of STEs remains elusive and not fully understood.
Herein, we report a unique strategy based on Cu$^{+}$ doping to boost the STE emission in the alloyed Cs$_2$(Ag/Na)InCl$_6$ DPs. The effect of Cu$^{+}$ doping on the electronic structure and optical properties of Cs$_2$(Ag/Na)InCl$_6$ and the STE dynamics are comprehensively surveyed by means of temperature-dependent PL and ultrafast femtosecond transient absorption (fs-TA) spectroscopies. The as-synthesized Cs$_2$(Ag/Na)InCl$_6$:Cu$^{+}$ single crystals with different Na–Ag alloying ratios and Cu$^{+}$ doping concentrations were synthesized via a modified solvothermal method. The results show that the actual Na–Ag alloying ratios of the crystals were generally consistent with its feeding ratios (Table S1, Supporting Information), and an optimal Na–Ag alloying ratio of 2:3 was identified by powder X-ray diffraction (XRD) and PL measurements (Figures S2 and S3, Supporting Information). To this regard, we fixed the Na–Ag alloying ratio of 2:3 and investigated the effect of Cu$^{+}$ doping on the optical properties of the alloyed Cs$_2$(Ag/Na)InCl$_6$ (the formula was used throughout for convenience). In contrast to that of Na–Ag alloying, only a small amount of Cu$^{+}$ (1.4 mol%) was found in the crystals even at a high feeding ratio (40 mol%) of Cu to (Na + Ag) (Table S2, Supporting Information). Powder XRD measurements show that all diffraction peaks of the Cu$^{+}$-doped samples can be well indexed.

2. Results and Discussion

The alloyed Cs$_2$(Ag/Na)InCl$_6$ crystal is characterized by a 3D DP structure (space group Fm$\overline{3}$m) consisting of alternating [MCl$_6$]$^{3-}$ (M = Ag or Na) and [InCl$_6$]$^{3-}$ corner-sharing octahedra with Cs$^+$ ions occupying the voids in between (Figure 1a). Cu$^{+}$ dopants are supposed to substitute the octahedral Ag$^+$ site. Cs$_2$(Ag/Na)InCl$_6$:x%Cu$^+$ single crystals with different Na–Ag alloying ratios and Cu$^{+}$ doping concentrations were synthesized via a modified solvothermal method. The as-synthesized crystals have a mean size around 100–400 μm (Figure S1, Supporting Information). The Na–Ag alloying ratios and Cu$^{+}$ doping concentrations were controlled by varying the feeding ratios of the metal precursors between Na, Ag, and Cu, and checked by inductively coupled plasma–atomic emission spectroscopy (ICP–AES). The results show that the actual Na–Ag alloying ratios of the crystals were generally consistent with its feeding ratios (Table S1, Supporting Information), and an optimal Na–Ag alloying ratio of 2:3 was identified by powder X-ray diffraction (XRD) and PL measurements (Figures S2 and S3, Supporting Information). To this regard, we fixed the Na–Ag alloying ratio of 2:3 and investigated the effect of Cu$^{+}$ doping on the optical properties of the alloyed Cs$_2$(Ag/Na)InCl$_6$ (the formula was used throughout for convenience). In contrast to that of Na–Ag alloying, only a small amount of Cu$^{+}$ (1.4 mol%) was found in the crystals even at a high feeding ratio (40 mol%) of Cu to (Na + Ag) (Table S2, Supporting Information). Powder XRD measurements show that all diffraction peaks of the Cu$^{+}$-doped samples can be well indexed.
into cubic Cs$_2$AgInCl$_6$ (ICSD No. 19 130) without any observable impurities, indicating pure phase and high crystallinity of the resulting crystals (Figure 1b). The diffraction peaks of the crystals (e.g., at 23.6°) shift to higher angles with increasing the Cu$^+$ concentration, suggesting a lattice contraction induced by the substitution of Ag$^+$ (0.126 nm) with smaller Cu$^+$ (0.096 nm). X-ray photoelectron spectroscopy (XPS) exhibits the signals of binding energies typical for Cs$^+$ (3d), Ag$^+$ (3d), Na$^+$ (1s), In$^{3+}$ (3d), Cl$^-$ (2p), and Cu$^+$ (2p) in Cs$_2$Ag/NaInCl$_6$: 1.0 mol%Cu$^+$ (Figure S4, Supporting Information), confirming the monovalent state of Cu in Cs$_2$(Ag/Na)InCl$_6$ and its successful doping into the crystal lattice.

Figure 1c and Figure S5 (Supporting Information) show the optical absorption spectra of the undoped and Cu$^+$-doped Cs$_2$(Ag/Na)InCl$_6$ crystals. The crystals display a broad absorption band ranging from 350 to 650 nm, with its maximum shifting from 380 to 410 nm upon Cu$^+$ doping. This indicates that Cu$^+$ doping may lower the bandgap energy of Cs$_2$(Ag/Na)InCl$_6$ crystals, as confirmed by Tauc plots of the absorption spectra (inset of Figure 1c), whereby the optical bandgap of the crystals was estimated to decrease from 2.85 eV in Cs$_2$(Ag/Na)InCl$_6$ to 2.30 eV in Cs$_2$(Ag/Na)InCl$_6$: 1.0%Cu$^+$. Such a bandgap decrease is related to the overlap of Cu-3d orbital with Cl-3p orbital in the valence band of the crystals,[11] as confirmed by density-functional theory (DFT) calculations. We chose a 5 × 1 × 1 supercell of 200 atoms to build the alloyed Cs$_2$(Ag/Na)InCl$_6$ system with 12 Ag atoms and 8 Na atoms, then one Cu atom was introduced to substitute one Ag atom, achieving the Cu$^+$ doping concentration of 5.0 mol%. According to the calculated density of states (DOS) and band structures (Figure S6, Supporting Information), the conduction band minimum (CBM) of Cs$_2$(Ag/Na)InCl$_6$ is contributed mainly from In-5s orbitals and the valence band maximum (VBM) is composed of Cl-3p and Ag-5d orbitals. In-doped Cs$_2$(Ag/Na)InCl$_6$ system was used for calculation, it can be concluded from the DFT calculation that Cu$^+$ doping brings about a new VBM above the original VBM, which results in a evident bandgap reduction of Cs$_2$(Ag/Na)InCl$_6$ upon Cu$^+$ doping.

Under UV excitation at 365 nm, the crystals exhibited bright yellow PL with a broad emission band (full-width at half maximum (FWHM) of ≈590 meV) covering from 400 to 800 nm (Figure 1d), which can be ascribed to the intrinsic STE emission arising from the strong Jahn–Teller distortion of the [AgCl$_6$]$^{3-}$ octahedra.[60] The PL intensity of the crystals is increased gradually with increasing the Cu$^+$ doping concentration from 0 to 1.0 mol% and then decreased at higher Cu$^+$ concentrations, in parallel with the increased PLQY of the crystals from 19.0% ± 0.4% in Cs$_2$(Ag/Na)InCl$_6$ to 62.6% ± 0.6% in Cs$_2$(Ag/Na)InCl$_6$: 1.0%Cu$^+$. PL excitation spectra of the crystals showed an evident redshift in the optimal excitation band from 310 to 365 nm upon Cu$^+$ doping (Figure 1d), which is highly desirable for their application as emitters in NUV-converted WLEDs. Further wavelength-dependent PL excitation and emission spectra showed identical excitation and emission bands (Figure S7, Supporting Information), confirming the single luminescent center of STEs in Cs$_2$(Ag/Na)InCl$_6$: 1.0%Cu$^+$ crystals. Intriguingly, we observed that the enhancement in PL intensity and PLQY of the crystals was accompanied by a decrease in PL lifetime (Figure 1e; Figure S8, Supporting Information). The effective PL lifetime of the crystals decreased from 6.4 to 3.9 μs with increasing the Cu$^+$ concentration from 0 to 1.0 mol% and then increased to 5.2 μs at 1.4 mol% of Cu$^+$ doping (Table S3, Supporting Information).

This indicates that the enhancement in PL intensity and PLQY of the crystals is contributed mainly from the increased radiative decay rate of STEs. The radiative decay rate of STEs was derived, with the value increasing from 3.0 × 10$^4$ s$^{-1}$ in Cs$_2$(Ag/Na)InCl$_6$ to 1.6 × 10$^5$ s$^{-1}$ in Cs$_2$(Ag/Na)InCl$_6$: 1.0%Cu$^+$ (Table S3, Supporting Information). The remarkable increase in radiative recombination rate of STEs can be attributed to the symmetry breakdown of the [AgCl$_6$]$^{3-}$ octahedron as well as the electron wavefunction at the Ag$^+$ site due to Cu$^+$ substitution-induced lattice contraction, which may lead to a parity change in the STE wavefunction and thereby promote the radiative recombination rate of STEs, as previously reported by Tang et al. in Cs$_2$(Ag/Na)InCl$_6$: Bi$^{3+}$ crystals.[3a]

To gain deep insights into the effect of Cu$^+$ doping on the STE emission of Cs$_2$(Ag/Na)InCl$_6$, we carried out temperature-dependent PL spectroscopic measurements. Figure 2a,b and Figure S9 (Supporting Information) show the temperature-dependent PL emission spectra (77–320 K) of the undoped and 1.0 mol% Cu$^+$-doped Cs$_2$(Ag/Na)InCl$_6$ crystals under excitation at 365 nm. The PL intensities of the crystals decreased gradually with increasing the temperature from 77 to 320 K, along with the emission bands broadening from 572 and 495 meV in Cs$_2$(Ag/Na)InCl$_6$ and Cs$_2$(Ag/Na)InCl$_6$: 1.0%Cu$^+$, respectively, as a result of accelerated nonradiative relaxation and enhanced electron-phonon coupling of STEs at higher temperatures.[15] Based on the Arrhenius plot of the integrated PL intensity versus the inverse temperature (Figure 2c,d)[16]

$$I(T) = \frac{I_0}{1 + A \exp \left( -\frac{E_a}{k_B T} \right)}$$

where $I_0$ and $I$ represent the observed and radiative decay times, respectively. Therefore, we deduced that the improved PLQY along with the decreased PL lifetime observed in Cu$^+$-doped Cs$_2$(Ag/Na)InCl$_6$ originated mainly from the increased radiative decay (or recombination) rate of STEs caused by Cu$^+$ doping. By taking the measured PL lifetimes into Equation (1), the radiative decay rate of STEs was derived, with the value increasing from 3.0 × 10$^4$ s$^{-1}$ in Cs$_2$(Ag/Na)InCl$_6$ to 1.6 × 10$^5$ s$^{-1}$ in Cs$_2$(Ag/Na)InCl$_6$: 1.0%Cu$^+$ (Table S3, Supporting Information).
where \( I(T) \) and \( I_0 \) are integrated PL intensities at \( T \) and 0 K, respectively, \( A \) is a constant, \( k_B \) is the Boltzmann constant, and \( E_a \) is the activation energy. The activation energies of STEs were determined to be 58.2 and 208.2 meV in Cs₂(Ag/Na)InCl₆ and Cs₂(Ag/Na)InCl₆: 1.0%Cu\(^+\) respectively. According to the Boltzmann distribution law and Fermi’s Golden Rule, the radiative decay rate \( (k_r) \) of excitons can be expressed as follows: \(^{17}\)

\[
k_r(T) = \frac{ne^2\omega^2}{3\epsilon_0e^2m_0} f_0 \left( \frac{\mu E_x}{m_0} \right)^{3/2} \frac{1 - e^{-\Delta E/k_B T}}{\Delta E} \tag{3}
\]

where \( C \) is a constant dictated by the refractive index (\( n \)), the transition frequency (\( \omega \)), the vacuum permittivity (\( \epsilon_0 \)), the electron mass (\( m_e \)), the equivalent exciton mass (\( \mu \)), and the exciton mass (\( M \)) of the materials, and \( \Delta E \) is the energy line width. It is clear that \( k_r \) is proportional to the \( 3/2 \) power of \( E_x \). Therefore, the radiative recombination rate \( (k_r) \) of STEs in the crystals was significantly improved after Cu\(^+\) doping, in view of the larger activation energy \( (E_x) \) of STEs in Cs₂(Ag/Na)InCl₆: 1.0%Cu\(^+\) (208.2 meV) than in Cs₂(Ag/Na)InCl₆ (58.2 meV). This agrees well with the observation that Cu\(^+\) doping resulted in decreased PL lifetime of the crystals. To unveil the influence of electron–phonon coupling, we analyzed the temperature dependence of the emission band broadening using the equation\(^{18}\)

\[
\text{FWHM} = 2.36 \sqrt{S} \frac{\hbar \omega_{\text{phonon}}}{k_B T} \sqrt{\coth \left( \frac{\hbar \omega_{\text{phonon}}}{2 k_B T} \right)} \tag{4}
\]

where \( S \) and \( \hbar \omega_{\text{phonon}} \) are Huang-Rhys factor and phonon energy, respectively. The phonon energy \( (\hbar \omega_{\text{phonon}}) \) and Huang-Rhys factor \( (S) \) were calculated to be 29.6 meV and 41.1 for Cs₂(Ag/Na)InCl₆ and 28.8 meV and 43.4 for Cs₂(Ag/Na)InCl₆: 1.0%Cu\(^+\), respectively (Figure 2e,f), which are generally consistent with those reported in Cs₂AgInCl₆ and Cs₂(Ag/Na)InCl₆.\(^{3a,7a}\) The fitted phonon energies were also close to that (36.5 meV) of the A$_{1g}$ longitudinal optical phonon mode of [InCl₆]$^{3-}$ octahedron determined by Raman spectra (Figure S10, Supporting Information), suggesting a dominant phonon mode of A$_{1g}$ involved in the electron–phonon coupling.\(^{19}\) Such large \( S \) values indicate strong electron–phonon coupling, which favors the formation of STEs in the soft lattice of Cs₂(Ag/Na)InCl₆: 1.0%Cu\(^+\) and accounts for the broadband (≈590 meV) and large Stokes shift (240 nm) of the STE emission (Figure S11, Supporting Information).

To probe the ultrafast photophysical processes involved in the photoexcitation of the crystals, we performed fs-TA...
Figure 3. Contour plots of the fs-TA spectra of a) Cs₂(Ag/Na)InCl₆ and b) Cs₂(Ag/Na)InCl₆: 1.0%Cu⁺ upon excitation with a 365 nm fs-pulsed laser. The rise portion of the normalized PIA kinetic curves of c) Cs₂(Ag/Na)InCl₆ and d) Cs₂(Ag/Na)InCl₆: 1.0%Cu⁺ in the probe region from 500 to 620 nm. e) Normalized PIA decay curves of Cs₂(Ag/Na)InCl₆ at 575 nm and Cs₂(Ag/Na)InCl₆: 1.0%Cu⁺ at 530 nm. f) Configuration coordinate diagram of Cs₂(Ag/Na)InCl₆, showing the electronic transitions involved in the STE emission. GS and FE denote the ground state and free exciton, respectively.

Figure 3a,b shows the contour plots of the fs-TA spectra of the undoped and 1.0 mol% Cu⁺-doped Cs₂(Ag/Na)InCl₆ upon excitation with a 365 nm fs-pulsed laser under identical conditions. Both samples exhibited a positive photoinduced absorption (PIA) in the probe region from 470 to 640 nm, which can be an evidence for the formation of STEs in the crystal lattice.[20] Moreover, it was observed that the PIA signal of Cu⁺-doped sample was significantly enhanced and blue-shifted to 530 nm in comparison with that (575 nm) of the undoped one. The blueshift in PIA of STEs is due to the effect of Cu⁺ alloying on the bandgap of Cs₂(Ag/Na)InCl₆, as proved by the steady-state optical absorption spectra. The enhanced PIA of STEs implies that Cu⁺ doping may increase the density of the photo-generated STEs in Cs₂(Ag/Na)InCl₆ lattice and thereby boost the STE emission. Further kinetic traces of PIA in the probe region from 500 to 620 nm displayed an identical rise time of ≈500 and ≈300 fs for the undoped and Cu⁺-doped samples, respectively (Figure 3c,d), indicating that the broadband PIA of both samples originated from a single excited STE state. Such an ultrafast rise time in PIA is closely related to the Jahn–Teller distortion of [AgCl₆]⁵⁻ octahedra, which agrees well with the STE formation time as previously reported by Han et al.[20] Therefore, the formation time of STEs in the crystals decreased after Cu⁺ doping, which is beneficial for STE generation and accounts for the increased STE density in Cu⁺-doped sample. Figure 3e compares the PIA decay curves of Cs₂(Ag/Na)InCl₆ at 575 nm and Cs₂(Ag/Na)InCl₆: 1.0%Cu⁺ at 530 nm. By biexponential fitting to the PIA decay curves, two distinct decay components were derived: a fast decay associated with the nonradiative relaxation of STEs to the quenching centers such as lattice or surface defects, and a slow decay related to the radiative recombination of STEs through photon emission.[9b] It was found that the contribution of nonradiative relaxation in Cs₂(Ag/Na)InCl₆: 1.0%Cu⁺ (23.7%) was much less than that in pristine Cs₂(Ag/Na)InCl₆ (48.2%; Table S4, Supporting Information). These results demonstrate unambiguously that Cu⁺ doping promotes the radiative recombination process of STEs to the quenching centers such as lattice or surface defects, and a slow decay related to the radiative recombination of STEs through photon emission.[9b] It was found that the contribution of nonradiative relaxation in Cs₂(Ag/Na)InCl₆: 1.0%Cu⁺ (23.7%) was much less than that in pristine Cs₂(Ag/Na)InCl₆ (48.2%; Table S4, Supporting Information). These results demonstrate unambiguously that Cu⁺ doping promotes the radiative recombination process of STEs to the quenching centers such as lattice or surface defects, and a slow decay related to the radiative recombination of STEs through photon emission.[9b] It was found that the contribution of nonradiative relaxation in Cs₂(Ag/Na)InCl₆: 1.0%Cu⁺ (23.7%) was much less than that in pristine Cs₂(Ag/Na)InCl₆ (48.2%; Table S4, Supporting Information). These results demonstrate unambiguously that Cu⁺ doping promotes the radiative recombination process of STEs to the quenching centers such as lattice or surface defects, and a slow decay related to the radiative recombination of STEs through photon emission.[9b] It was found that the contribution of nonradiative relaxation in Cs₂(Ag/Na)InCl₆: 1.0%Cu⁺ (23.7%) was much less than that in pristine Cs₂(Ag/Na)InCl₆ (48.2%; Table S4, Supporting Information). These results demonstrate unambiguously that Cu⁺ doping promotes the radiative recombination process of STEs to the quenching centers such as lattice or surface defects, and a slow decay related to the radiative recombination of STEs through photon emission. Furthermore, we evaluated the stability of Cs₂(Ag/Na)InCl₆: Cu⁺ crystals. The XRD pattern, PL spectrum, and PL intensity of Cs₂(Ag/Na)InCl₆: 1.0%Cu⁺ remained essentially unchanged.
after their storage in the air over 22 months, manifesting the excellent air stability of the crystals (Figure 4a,b). Temperature-dependent XRD measurements showed that the diffraction peaks of the crystals were nearly the same and matched well with cubic Cs₂AgInCl₆ (ICSD No. 19130) in the temperature range of 20–400 °C (Figure 4c), revealing the prominent structure stability of the crystals. Further temperature-dependent PL emission spectra showed that Cu⁺ doping can also improve the thermal stability of Cs₂AgInCl₆ crystal (Figure S12, Supporting Information). The integrated PL intensities of the undoped and Cu⁺-doped samples remained 76.2% and 88.4%, respectively, at 150 °C compared with their initial intensities at room temperature (RT; Figure 4d). Such outstanding air, structure, and thermal stability of Cs₂(Ag/Na)InCl₆:Cu⁺ crystals, along with the high PLQY (62.6%) and broad emission band at ≈605 nm, makes them an ideal candidate as an efficient yellow-emitting phosphor in WLEDs. For this purpose, we fabricated a WLED by encapsulating Cs₂(Ag/Na)InCl₆:1.0%Cu⁺ with the blue phosphor BaMgAl₁₀O₁₇:Eu²⁺ onto a commercial 365-nm NUV chip. The as-fabricated WLED device exhibited bright electroluminescence (EL) at a drive current of 25 mA, with a color coordinate of (0.374,0.380) in CIE 1931, a color-rendering index (Ra) of 86, and a white light correlated color temperature (CCT) of 4060 K (Figure 4e,f), thus validating the promise of Cs₂(Ag/Na)InCl₆:Cu⁺ DPs in solid-state lighting.

3. Conclusions

In summary, we have systematically investigated the optical properties and excited-state dynamics of Cu⁺-doped Cs₂(Ag/Na)InCl₆ crystals. The substitution of Ag⁺ by a small amount (1.0 mol%) of Cu⁺ resulted in the boosted STE emission of Cs₂(Ag/Na)InCl₆ at 605 nm, with PLQY increasing from 19.0% to 62.6% and excitation band shifting from 310 to 365 nm. Mechanistic investigation through temperature-dependent PL and femtosecond transient absorption spectroscopies unraveled that the remarkable PL enhancement was ascribed to the increased density and radiative recombination rate of STEs, as a result of symmetry breakdown of the STE wavefunction at the octahedral Ag⁺ site induced by Cu⁺ doping. Besides, Cu⁺ doping also improved the thermal stability of the crystals, retaining 88.4% of the RT PL intensity at 150 °C. These results reveal the great potential of Cu⁺-doped Cs₂(Ag/Na)InCl₆ as an efficient NUV-converted yellow-emitting phosphor in WLEDs, which may open up a new avenue for the exploration of novel luminescent lead-free DPs via metal ion doping toward versatile applications such as solid-state lighting.

4. Experimental Section

Chemicals and Materials: CsCl (99.9%), AgCl (99.9%), CuCl (99.9%), NaCl (99.9%), and isopropanol (99.5%) were purchased from Aladdin...
(Shanghai, China). In(CH\textsubscript{3}CO\textsubscript{2})\textsubscript{3} (99.99%) was purchased from Sigma-Aldrich (Shanghai, China). HCl was of analytical grade and purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). All the chemical reagents were used as received without further purification.

Synthesis of Cs\textsubscript{2}(Ag/Na)InCl\textsubscript{6} Single Crystals: Cs\textsubscript{2}(Ag/Na)InCl\textsubscript{6} single crystals were synthesized via a modified solvothermal method. In a typical synthesis of Cs\textsubscript{2}(Ag\textsubscript{0.6}Na\textsubscript{0.4})InCl\textsubscript{6}, 2 mmol of CsCl, 0.6 mmol of AgCl, 0.4 mmol of NaCl, and 1 mmol of In(CH\textsubscript{3}CO\textsubscript{2})\textsubscript{3} were mixed with 10 ml of HCl in a 25 ml Teflon-lined autoclave. The mixture was heated to 180 °C for 12 h and then cooled down to RT naturally. The products were collected by centrifugation, washed twice with isopropanol, and finally dried at 60 °C in a vacuum for 24 h. For synthesizing Cs\textsubscript{2}(Ag/Na)InCl\textsubscript{6} of different Na–Ag alloying ratios, different molar ratios of Na to Ag with 1 mol total amount of (Na + Ag) precursors were used under otherwise identical conditions. The actual Na–Ag alloying ratios of the crystals were identified by ICP–AES.

Synthesis of Cu\textsuperscript{+}-Doped Cs\textsubscript{2}(Ag/Na)InCl\textsubscript{6} Single Crystals: In a typical synthesis of 20 mol% (nominal concentration) Cu\textsuperscript{+}-doped Cs\textsubscript{2}(Ag/Na)InCl\textsubscript{6}, 2 mmol of CsCl, 0.6 mmol of AgCl, 0.4 mmol of NaCl, 0.2 mmol of CuCl, and 1 mmol of In(CH\textsubscript{3}CO\textsubscript{2})\textsubscript{3} were mixed with 10 ml of HCl in a 25 ml Teflon-lined autoclave. The mixture was heated to 180 °C for 12 h and then cooled to RT naturally. The products were collected by centrifugation, washed twice with isopropanol, and finally dried at 60 °C in a vacuum for 24 h. For synthesizing Cs\textsubscript{2}(Ag/Na)InCl\textsubscript{6}:x\textsuperscript{+}Cu\textsuperscript{+} of different Cu\textsuperscript{+} doping concentrations, different molar ratios of Cu to (Na + Ag) with fixed feeding amounts of Na (0.4 mmol of NaCl) and Ag (0.6 mmol of AgCl) were used under otherwise identical conditions. The nominal Cu\textsuperscript{+} doping concentration was defined by the molar ratio of Cu to (Na + Ag) in the precursors, and the actual Cu\textsuperscript{+} doping concentrations were identified by ICP–AES.

Theoretical Calculations: DFT calculations were carried out using the Vienna ab initio simulation package (VASP). A 5 × 1 × 1 supercell of 200 atoms was chosen to build the alloyed Cs\textsubscript{2}(Ag/Na)InCl\textsubscript{6} system, in which 8 of 20 Ag atoms were replaced by Na atoms, making Na–Ag ratio of 2:3. Furthermore, the Cu\textsuperscript{+} doped Cs\textsubscript{2}(Ag/Na)InCl\textsubscript{6} system was modeled with additional one Ag atom substituted by one Cu atom, creating Cu\textsuperscript{+} doping concentration of 5.0 mol%. The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) function was employed to describe exchange-correlation interactions. The projector augmented wave (PAW) pseudopotentials were used to describe the electron–ion interactions. For expanding electronic wave functions, the cutoff energy of plane-wave basis was set as 500 eV, and a Monkhorst–Pack k mesh of 1 × 5 × 5 was used to sample the Brillouin zone. The convergence threshold of 10\textsuperscript{−5} eV\textsuperscript{Å\textsuperscript{2}} was adopted for total energy calculation, and the force convergence criteria were set at 0.02 eV\textsuperscript{Å\textsuperscript{−1}} per atom in geometry relaxation. Structural and Optical Characterization: Powder XRD patterns were collected with an X-ray diffractometer (MiniFlex2, Rigaku) using Cu K\alpha radiation (λ = 0.154187 nm). ICP analysis was conducted on an ICP–AES spectrometer (Ultima2, Jobin Yvon). The scanning electron microscopy (SEM) measurements were performed by using a JSM-6700F SEM. XPS measurements were performed on a Thermo Fisher ESCALAB 250Xi using Al K\alpha (1486.6 eV) and He I\alpha (220 eV) as the radiation sources. Raman spectra were recorded using a micro-Raman spectrometer (Invia Reflex) with an excitation laser source of 532 nm. Optical absorption spectra were translated from the corresponding diffuse reflectance spectra that were recorded with a Perkin–Elmer Lambda 950 UV–vis–NIR spectrometer by using BaSO\textsubscript{4} as a reference. PL excitation spectra, PL emission spectra, and PL decay curves were measured on the FLS980 spectrometer (Edinburgh) equipped with both continuous xenon (450 W) and pulsed flash lamps. PL photographs were taken by using a Huawei P30Pro cell phone without using any filter. The absolute PLQYs of the samples were measured via a pulsed flash lamp and decay curve instrument (EDX1800, Edinburgh) equipped with an excimer laser (308 nm) as the light source. A standard tungsten filament was used to correct the optical response of the instrument. For temperature-dependent PL measurements, the samples were placed on the thermal stage (77–873 K, THMS 600, Linkam Scientific Instruments) and excited with the continuous xenon lamp. The ultrafast fs-TA measurements were conducted under a pump wavelength of 365 nm on Helios (Ultrafast systems) spectrometers using a regeneratively amplified femtosecond Ti:sapphire laser system (Spitfire Pro-F1KXP, Spectra-Physics).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Cu\textsuperscript{+} doping, double perovskite, excited-state dynamics, photoluminescence, self-trapped exciton

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