
Efficient and stable warm-white emissive lead-free halide double perovskites

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Lighting accounts for one fifth of global electricity consumption¹. Materials with efficient and stable white emission are ideal for lighting but are fundamentally difficult to achieve. Metal halide perovskites demonstrate outstanding emission properties^{2,3}; however, the best previous materials contain lead, and show unsatisfactory stability. Here we report a lead-free double perovskite that exhibits efficient and stable white emission via self-trapped excitons (STEs) originating from the Jahn-Teller distortion of [AgCl₆] octahedron in the excited state (ES). By alloying Na cations into Cs₂AgInCl₆, we break the dark transition by manipulating the parity of the STE wave function and reduce the semiconductor's electronic dimensionality⁴, leading to an increase of photoluminescence (PL) efficiency by three orders of magnitude. The optimally alloyed Cs₂(Ag_{0.60}Na_{0.40})InCl₆ with 0.04% Bi doping emits warm white light with a remarkable $(86 \pm 5)\%$ quantum efficiency, and works for over 1000 hours without encapsulation. We anticipate that these results will stimulate research on single-emitter-based white emissive phosphors and diodes for next-generation lighting and display technologies.

Metal halide perovskites have rapidly advanced the field of optoelectronic devices because of their exceptional defect tolerance, low-cost solution processing and tunable

emission across the visible spectrum⁵⁻⁸. For example, the photoluminescence quantum yield (PLQY) of perovskite nanocrystals has now reached close to unity^{9,10}, and green and red electroluminescent devices have been reported to having external quantum efficiencies (EQE) reaching 20.1%¹¹⁻¹⁴. For lighting applications, white emission from a single emitter layer is of particular interest, for this simplifies device structure, and avoids self-absorption and color instability seen in mixed and multiple emitters¹⁵.

Broadband and white emission typically originate from STEs that exist in semiconductors having localized carriers and a soft lattice¹⁶⁻¹⁸. Hybrid metal halide perovskites, particularly those with low dimensional crystal structures^{15,19-21}, have received considerable attention as broadband emissive materials; but high PLQY has been relatively rarely achieved²¹. Remaining challenges include reliance on water soluble lead-based materials; unsatisfactory stability; and the need to increase the mechanistic understanding of the origins of white emission.

We focused herein on the double perovskite $\text{Cs}_2\text{AgInCl}_6$ as a promising warm-white emissive material in view of its broad spectrum covering 400 nm - 800 nm and its all-inorganic and lead-free nature²²⁻²⁴. We first performed first-principles density functional theory, many-body perturbation theory within GW approximation, and Bethe-Salpeter Equation (BSE) calculations to understand the origins of the broadband emission in $\text{Cs}_2\text{AgInCl}_6$. GW -BSE calculations indicate that the lowest exciton, which has a binding energy E_b of 0.25 eV, is dark due to fact that the associated transition is

1 parity-forbidden²⁴ (Fig. 1a). This exciton was calculated with the crystal structure fixed
 2 in its ground state (GS) equilibrium, which represents the situation of the free exciton
 3 (FE). We then investigated exciton-phonon coupling by relaxing the lattice, which
 4 represents the situation of the STE (Fig. 1b). We found that the STE in Cs₂AgInCl₆
 5 arises from a strong Jahn-Teller distortion of the [AgCl₆] octahedron (Inset of Fig. 1b),
 6 i.e., the Ag-Cl bonds are elongated by 0.08 Å in the axial direction but compressed by
 7 0.2 Å in the equatorial plane. Hole trapping at Ag atoms that changes the electronic
 8 configuration of Ag to 4d⁹ favors a Jahn-Teller distortion. The STE has the same orbital
 9 character as that of the FE, indicating a parity-forbidden transition. The self-trapping
 10 energy E_{ST} and lattice deformation energy E_D , which are the excited and ground state
 11 energy differences between the STE and FE configurations, as shown in the
 12 configuration coordinate (cc) diagram of Fig. 1c, were calculated to be 0.53 eV and
 13 0.67 eV, respectively. The emission energy is thus calculated to be $E_{PL} = E_g - E_{ST} -$
 14 $E_D - E_b = 1.82$ eV, where E_g is 3.27 eV based on *GW* calculation and experimental
 15 results. This value agrees with the experimental PL peak value of 2 eV²². The phonon
 16 frequency $\hbar\Omega_g$ of the ground state obtained by fitting the cc diagram is 18.3 meV, and
 17 this agrees well with one particular phonon eigenmode of 17 meV. The corresponding
 18 eigenvector shows displacement in agreement with the Jahn-Teller distortion (Extended
 19 Data Fig. 1), consistent with the view that Jahn-Teller distortion is responsible for STE
 20 formation in Cs₂AgInCl₆. Strong electron-phonon coupling, which is necessary for STE
 21 formation, is confirmed by the large Huang-Rhys²⁵ factor ($S = E_D/\Omega_g$) of 37,
 22 consistent with experiment results (Extended Data Fig. 2). With the phonon frequency

1 $\hbar\Omega_e = 17.4$ meV of the excited state, we can estimate the exciton self-trapping time as
 2 $\tau = 2\pi/\Omega_e = 238$ fs, which indicates an ultrafast transition from FE to STE following
 3 photoexcitation. The calculated PL spectrum and the comparison with experimental
 4 data are shown in Fig. 1d. Overall the agreement is good, except for the small deviations
 5 at 400-450 nm, which could be the FE emission not accounted for in our calculations.

6

7 The above theoretical analysis indicates extremely low PLQY for pure $\text{Cs}_2\text{AgInCl}_6$.

8 PLQY is defined as the ratio of the radiative recombination rate (k_{rad}) to the sum of

9 radiative and non-radiative (k_{non}) recombination rates. From Fermi's golden rule,

10 k_{rad} is proportional to the transition dipole moment (TDM, μ): $\mu = \langle \varphi_h | \hat{\mu} | \varphi_e \rangle$

11 where φ_e and φ_h are the electron and hole wave functions, $\hat{\mu}$ is the electric dipole

12 operator. The dark transition of FE and STE in $\text{Cs}_2\text{AgInCl}_6$ results in extremely low

13 radiative recombination rates, leading to low PLQY (<0.1%, Extended Data Fig. 2d).

14 Increasing k_{rad} and reducing k_{non} provide two strategies to enhance the PLQY. The

15 first and most critical step toward improving the PLQY is to break the parity-forbidden

16 transition by manipulating the symmetry of the STE wave function. A practical

17 approach is to partially substitute Ag with an element that can sustain the double

18 perovskite structure, but with a distinctively different electronic configuration than Ag,

19 as such a group-IA element (alkali metal). We therefore explored alloying Na into

20 $\text{Cs}_2\text{AgInCl}_6$. Broadband emission was also observed in pure $\text{Cs}_2\text{NaInCl}_6$ (Extended

21 Data Fig. 3) but with very low efficiency due to strong phonon emission, as indicated

22 by a simulated high Huang-Rhys factor of 80 at excited state. The Huang-Rhys factor

can potentially serve as the figure-of-merit for the design of efficient white emission from STEs (discussed in Extended Data Table 1). Since the lattice mismatch between $\text{Cs}_2\text{NaInCl}_6$ and $\text{Cs}_2\text{AgInCl}_6$ is as low as 0.30% (Supplementary Table S1), we anticipated that Na^+ could be incorporated uniformly into $\text{Cs}_2\text{AgInCl}_6$ without causing detrimental defects and phase separation. For the synthesis, CsCl , NaCl , AgCl and InCl_3 precursors were mixed into HCl solution in a hydrothermal autoclave which was heated for a given time and then slowly cooled down, resulting in white precipitates as final products. This straightforward synthesis has over 90% product yield.

X-ray diffraction patterns of a series of compositions (Fig. 2a) confirmed the pure double perovskite phase. The intensity of the (111) diffraction peak marked * is related to the Na/Ag composition by a dispersion factor of Na, Ag and In atoms²⁶. These agree well with compositions determined using inductively coupled plasma optical emission spectrometry (Supplementary Table S3). This observation also suggests a high degree of B(I) and B'(III) site ordering and negligible antisite defects (Supplementary Fig. S2). The refined lattice parameters follow a linear increase upon Na substitution, indicating solid-solution behavior with Na^+/Ag^+ randomly distributed²⁷ at B(I) site in $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{InCl}_6$ (Extended Data Fig. 4, Supplementary Fig. S3). Upon Na alloying, an evident excitonic absorption peak emerged near 365 nm, and a three-orders-of-magnitude enhancement in the intensity of white emission was obtained compared to the pure $\text{Cs}_2\text{AgInCl}_6$ and $\text{Cs}_2\text{NaInCl}_6$ (Fig. 2b). A similar phenomenon was also found in Li doped $\text{Cs}_2\text{AgInCl}_6$ and Na doped $\text{Cs}_2\text{AgSbCl}_6$ (Extended Data Fig. 5), suggesting the general nature of alkali metal-induced PL enhancement in double perovskites. We then

recorded the PL spectra of a series of $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{InCl}_6$ powders by varying the measurement temperatures, and found that the extracted activation energy (Supplementary Fig. S6-7) increases monotonically with increased Na content, suggesting suppressed non-radiative process and thermal quenching upon Na alloying. With optimized Na content, Bi doping and slow cooling, we obtained the highest PLQY of $(86 \pm 5)\%$ at a Na content of $\sim 40\%$ (Fig. 2c, Supplementary Fig. S8). To our best knowledge, this PLQY represents the highest efficiency reported for white-emitting materials (Supplementary Table S4). The best-performing white emissive lead halide perovskites $\text{C}_4\text{N}_2\text{H}_{14}\text{PbBr}_4^{28}$ and $\text{CuGaS}_2/\text{ZnS}$ quantum dots²⁹ exhibit PLQYs of 20% and 73%, respectively. The Bi^{3+} incorporation is believed to improve crystal perfections and promote exciton localization³⁰, further enhancing the PLQY (Extended Data Fig. 6).

The STE origin of the white emission is further experimentally confirmed via emission-wavelength-dependent photoluminescence excitation (PLE) spectra (Fig. 2d). For emission from 460 to 700 nm, the PLE spectra exhibit identical shape and features, indicating that the white emission is from the relaxation version of the same excited state. Experimental observations that the PLE spectra decrease to nearly zero at wavelength above 400 nm, the emission intensity from $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ exhibits a linear dependence on the excitation power (Fig. 2e), and the independence of PLQY results on the photoexcitation power (Supplementary Fig. S9) all suggest that the emission does not arise from permanent defects. Surface defect emission is also ruled

out by the comparable PL intensity of single crystals and ball-milled powders (Supplementary Fig. S10). The transient absorption data further provide direct evidence for STEs¹⁷. With 325 nm-wavelength laser photoexcitation, $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ exhibited a broad photoinduced absorption at energies that extends across the visible spectrum (Fig. 2f, Supplementary Fig. S11), with an onset time of ca. 500 fs, consistent with our calculated exciton self-trapping time.

We performed further theoretical analysis to understand the trend of PLQY change as a function of Na content. In Fig. 3a, we show the calculated TDM of $\text{Cs}_2\text{Ag}_{1-x}\text{Na}_x\text{InCl}_6$ as a function of Na concentrations. It is clear that with the increase of Na content, the TDM first increases and then decreases, echoing the observed composition-dependent PLQY. Fig. 3b compares the electron wave function of the STE before and after the Na replacement. Na incorporation breaks the inversion symmetry of the $\text{Cs}_2\text{AgInCl}_6$ lattice, and this changes the electron wave function at the Ag site from symmetric to asymmetric, resulting in a parity change in the STE wave function and consequently allowing for radiative recombination. Since Na^+ contributes to neither the conduction band minimum nor the valence band maximum of the alloy, the second effect of Na incorporation is to reduce the electronic dimensionality⁴ of the $\text{Cs}_2\text{AgInCl}_6$ lattice by partially isolating the $[\text{AgCl}_6]$ octahedra (Supplementary Fig. S12). The newly-formed $[\text{NaCl}_6]$ octahedra serve as barriers to confine the spatial distribution of the STE (Fig. 3c), thus enhancing the electron and hole orbital overlap and increasing TDM. For example, the radius of the STE is reduced from more than 20 Å for the pure $\text{Cs}_2\text{AgInCl}_6$ to only 9 Å with 50% Na incorporation, which increases the TDM from zero to 0.07

a.u.

Two reasons account for the decreased PLQY upon further increasing the Na content. For Na-rich compounds, the electron remains strongly confined within a single In octahedron (In 5s and Cl 3p), and the hole is always located on the Ag 4d orbital and the neighboring Cl 3p orbitals (Fig. 3d), thereby the orbital spatial overlapping between electrons and holes for the STE, and hence the TDM, is dramatically reduced. Another factor is the increased non-radiative loss in the Na-rich alloy. We found that the ES curve and GS curve cross in the cc diagram of pure Cs₂NaInCl₆ (Fig. 3e), which means that photoexcited electrons can directly recombine with holes through the intersection with phonon emission. Diminished TDM and enhanced non-radiative recombination rates explain the decreased PLQY for Na-rich alloys.

The PL spectrum of the best-performing Cs₂Ag_{0.60}Na_{0.40}InCl₆ powder exhibits a high overlap with the sensitivity of the human eye to optical wavelengths (i.e. the luminosity function) (Fig. 3a), which enables a theoretical luminous efficacy that reaches ~373 lm/W. Emission stability is another key, yet very challenging, parameter for lighting applications. The Cs₂Ag_{0.60}Na_{0.40}InCl₆ materials demonstrated little emission degradation when tested from 233 K to 343 K. A version of the material slightly richer in Na (Na/(Ag+Na)=0.46) showed stable emission up to 393 K (Supplementary Fig. S13). We further annealed our Cs₂Ag_{0.60}Na_{0.40}InCl₆ powders at 150°C on a hotplate for 1000 hours and observed little PL decay of the white emission (Fig. 4b). We propose that its strongly bound excitons and nearly defect-free lattice prevent PL quenching,

and that the all-inorganic composition also helps resist thermal stress (decomposition temperature up to ~863 K, Supplementary Fig. S14).

We fabricated a white emissive LED by directly pressing the $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ powders onto a commercial UV LED chip without epoxy nor silica encapsulation. With the contribution from the blue light of UV LED chip (380~410 nm), the device has CIE coordinates (0.394, 0.444) located at warm-white point with a CCT of 4075 K, which fulfills the requirements for indoor lighting. The white LED showed negligible emission intensity change when operated at ~5000 cd/m^2 over 1000 hour in air without encapsulation (Fig. 4c). The outstanding photometric performance, combined with ready manufacture, together indicate promise in white phosphor applications.

The broadband emission associated with STE provides a new strategy to produce single material-based, white-emissive electroluminescence (EL). We thus fabricated prototype double-perovskite based EL devices. XRD confirmed the pure phase of the thermally-evaporated $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ film, which showed bright and uniform warm-white PL under ultraviolet lamp excitation (Fig. 4d). Our EL device demonstrated an applied bias-insensitive broadband emission, and a peak current efficiency of 0.11 Cd/A^{-1} mainly limited by and the relatively low quality of $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ films compared to their bulk counterparts (Supplementary Fig. S15-17). Further research should focus on optimizing emitting layer quality and device configuration to increase the performance of EL devices.

In summary, Na alloying into $\text{Cs}_2\text{AgInCl}_6$ breaks the parity-forbidden transition and reduces its electronic dimensionality, leading to efficient white emission via radiative recombination of self-trapped excitons. This white emissive material also demonstrates outstanding stability and low-cost manufacture, indicating promise for solid state lighting. We believe that halide double perovskites hold great potential for display and lighting applications and merit further study along the path to realizing their full potential.

References

1. Sun, Y. *et al.* Management of singlet and triplet excitons for efficient white organic light-emitting devices. *Nature* **440**, 908–912 (2006).
2. Tan, Z. K. *et al.* Bright light-emitting diodes based on organometal halide perovskite. *Nature Nanotechnol.* **9**, 687–692 (2014).
3. Cho, H. *et al.* Overcoming the electroluminescence efficiency limitations of perovskite light-emitting diodes. *Science* **350**, 1222–1225 (2015).
4. Xiao, Z. *et al.* Searching for promising new perovskite-based photovoltaic absorbers: the importance of electronic dimensionality. *Mater. Horiz.* **4**, 206–216 (2017).
5. Kojima, A., Teshima, K., Shirai, Y. & Miyasaka, T. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *J. Am. Chem. Soc.* **131**, 6050–6051 (2009).
6. Burschka, J. *et al.* Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature* **499**, 316–319 (2013).
7. Lee, M. M., Teuscher, J., Miyasaka, T., Murakami, T. N. & Snaith, H. J. Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites. *Science* **338**, 643–647 (2012).
8. Yin, W.-J., Shi, T. & Yan, Y. Unique properties of halide perovskites as possible origins of the superior solar cell performance. *Adv. Mater.* **26**, 4653–4658 (2014).
9. Protesescu, L. *et al.* Nanocrystals of cesium lead halide perovskites (CsPbX_3 , X=Cl, Br, and I): novel optoelectronic materials showing bright emission with wide color gamut. *Nano Lett.* **15**, 3692–3696 (2015).
10. Zhou, Q. *et al.* *In situ* fabrication of halide perovskite nanocrystal embedded polymer composite films with enhanced photoluminescence for display backlights. *Adv. Mater.* **28**, 9163–9168 (2016).
11. Wang, N. *et al.* Perovskite light-emitting diodes based on solution-processed self-organized multiple quantum wells. *Nature Photon.* **10**, 699–704 (2016).
12. Yuan, M. *et al.* Perovskite energy funnels for efficient light-emitting diodes. *Nature*

- 1 *Nanotechnol.* **11**, 872-877 (2016).
- 2 13. Yang, X. *et al.* Efficient green light-emitting diodes based on quasi-two-dimensional
- 3 composition and phase engineered perovskite with surface passivation. *Nature Commun.* **9**, 570
- 4 (2018).
- 5 14. Zhao, B. *et al.* High-efficiency perovskite-polymer bulk heterostructure light-emitting diodes.
- 6 *arXiv preprint arXiv:1804.09785* (2018).
- 7 15. Dnhner, R. E., HoKe, T. K. & Karunadasa. I. H. Self-assembly of broadband white-light
- 8 emitters. *J. Am. Chem. Soc.* **136**, 1718-1721 (2014).
- 9 16. Song, K. S. & Williams, R. T. *Self-Trapped Excitons; Optical Sciences*; Springer New York:
- 10 New York (2008).
- 11 17. Smith, M. D. & Karunadasa, H. I. White-Light Emission from Layered Halide Perovskites. *Acc.*
- 12 *Chem. Res.* **51**, 619– 627 (2018).
- 13 18. Ueta, M. *et al.* *Excitonic Processes in Solids*; Springer: Berlin, Heidelberg (1986).
- 14 19. Dnhner, R. E., Jaffe, A., Bradshaw, R. L. & Karunadasa. I. H. Intrinsic White-Light Emission
- 15 from Layered Hybrid Perovskites. *J. Am. Chem. Soc.* **136**, 13154-13157 (2014).
- 16 20. Mao, L., Wu, Y., Stoumpos, C. C., Wasielewski, M. R. & Kanatzidis, M. G. White-light
- 17 emission and structural distortion in new corrugated two-dimensional lead bromide
- 18 perovskites. *J. Am. Chem. Soc.* **139**, 5210-5215 (2017).
- 19 21. Zhou, C. *et al.* Luminescent zero-dimensional organic metal halide hybrids with near-unity
- 20 quantum efficiency. *Chem. Sci.* **9**, 586-583 (2018).
- 21 22. Volonakis. G. *et al.* Cs₂InAgCl₆: A new lead-free halide double perovskite with direct band Gap.
- 22 *J. Phys. Chem. Lett.* **8**, 772-778 (2017).
- 23 23. Zhao, X. G. *et al.* Cu–In Halide Perovskite Solar Absorbers. *J. Am. Chem. Soc.* **139**, 6718-6725
- 24 (2017).
- 25 24. Meng, W. *et al.* Parity-forbidden transitions and their impact on the optical absorption
- 26 properties of lead-free metal halide perovskites and double perovskites *J. Phys. Chem.*
- 27 *Lett.* **8**, 2999– 3007 (2017).
- 28 25. Huang, K. & Rhys, A. Theory of light absorption and non-radiative transitions in F-centres.
- 29 *Proc. R. Soc. London. Ser. A. Math. Phys. Sci.* **204**, 406 LP-423 (1950).
- 30 26. Lim, T.-W. *et al.* Insights into cationic ordering in Re-based double perovskite oxides. *Sci. Rep.*
- 31 **6**, 19746 (2016).
- 32 27. Maughan, A. E. *et al.* Defect tolerance to intolerance in the vacancy-ordered double perovskite
- 33 semiconductors Cs₂SnI₆ and Cs₂TeI₆. *J. Am. Chem. Soc.* **138**, 8453– 8464 (2016).
- 34 28. Yuan, Z. *et al.* One-dimensional organic lead halide perovskites with efficient bluish white-light
- 35 emission. *Nature Commun.* **8**, 14051 (2017).
- 36 29. Kim, J.-H. *et al.* White electroluminescent lighting device based on a single quantum dot emitter.
- 37 *Adv. Mater.* **28**, 5093-5098 (2016).
- 38 30. Moser, F., & Lyu, S. Luminescence in pure and I-doped AgBr crystals. *J. Lumin.* **3**, 447-458
- 39 (1971).

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41 **Figure 1 | Computational studies of the STE in Cs₂AgInCl₆.** (a) *GW* band structure of Cs₂AgInCl₆.

42 The orbital characters and FE wave function are visualized by plotting as a fatband structure. The

43 green, blue, cyan and red colors denote Cl 3*p*, Ag 4*d*, In 5*s* and Ag 5*s* orbitals, respectively. The

magenta circles display the lowest FE amplitude $|A_{vck}^{S1}|$ with the exciton wave function $|S1\rangle = \sum_{vck} A_{vck}^{S1} |\nu c\rangle$, where ν and c are valence and conduction states, k is the wave vector. $|S1\rangle$ is derived from the electron and hole states with the same parity (labels at Γ and X) along ΓX , implying a dark transition. **(b)** STE of $\text{Cs}_2\text{AgInCl}_6$. Cs atoms are omitted for clarity. The cyan and magenta isosurfaces represent the electron and hole charge densities ($\rho = \langle\psi|\psi\rangle$), respectively. The electron state is rather spread (marked by the red dash circle) and the hole state is compact (marked by the black dashed circle), consistent with the small (large) effective mass of the conduction (valence) band in panel a. Inset shows the Jahn-Teller distortion of the $[\text{AgCl}_6]$ octahedron. Here the isosurface of hole is obvious, whereas the isosurface of electron is invisible due to its small density. **(c)** Configuration coordinate diagram for the STE formation. GS: ground state; ES: excited state. E_{ST} , E_D , and E_{PL} are energies of self-trapping, lattice deformation, and emission, respectively. **(d)** Calculated PL spectrum compared with experimental result. The calculated line shapes were shifted to align the maximum with that of the experimentally measured curves for better comparison.

Figure 2 | Characterization of $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{InCl}_6$ with different Na content. All samples were doped using a small amount (0.04%, atomic ratio to In) of Bi, and the compositions were determined from inductively coupled plasma optical emission spectrometry results (Supplementary Table S3). **(a)** X-ray diffraction (XRD) patterns of $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{InCl}_6$ powders with different Na content, the * marked (111) diffraction peak. **(b)** The optical absorption (solid lines) and PL spectra (dash lines) of pure $\text{Cs}_2\text{AgInCl}_6$ and $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$. **(c)** The activation energy and PLQY of $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{InCl}_6$ powder versus Na content. **(d)** Excitation spectra of PL monitored at different wavelength. **(e)** Emission intensity versus excitation power for $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$. **(f)** Transient absorption spectra for $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ (laser pulse: 325 nm, $4\mu\text{J}/\text{cm}^2$), $\Delta A/A$ is the optical density. The irregular peaks located at ~ 650 nm are from frequency doubling of the pumping light. Note that measurements are based on the $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{InCl}_6$ powder.

Figure 3 | Mechanistic investigations of PLQY in $\text{Cs}_2\text{Ag}_{1-x}\text{Na}_x\text{InCl}_6$. **(a)** Transition dipole moment μ as a function of Na content in $\text{Cs}_2\text{Ag}_{1-x}\text{Na}_x\text{InCl}_6$. Given the assumption of constant non-radiative recombination, the PLQY is proportional to μ . **(b)** Parity change of the electron wave function (isosurface at Ag site) of the STE before and after Na incorporation. **(c)** Manual configuration showing the strengthened STE confinement by the surrounding $[\text{NaCl}_6]$ octahedra. The STEs are confined within two lattice parameters (c.f. Fig. 1b) surrounded by the $[\text{NaCl}_6]$ octahedra. **(d)** STE of Na-rich $\text{Cs}_2\text{Ag}_{1-x}\text{Na}_x\text{InCl}_6$. The STE is located in two neighboring octahedra ($[\text{AgCl}_6]$ - $[\text{InCl}_6]$) with the hole derived from the Ag $4d/\text{Cl } 3p$ orbitals while the electron composed of In $5s/\text{Cl } 3p$ orbitals. **(e)** Cc diagram of the STE (Inset) formation in $\text{Cs}_2\text{NaInCl}_6$. The STE is located within a single distorted $[\text{InCl}_6]$ octahedron. The hole is the well-known V_k center, i.e., Cl_2^- dimer ion, while the electron is derived of In $5s/\text{Cl } 3p$ orbitals. The separation of the electron and hole makes the optical transition very weak. In panels b-e, the cyan and magenta isosurfaces denote electron and hole, respectively.

Figure 4 | $\text{Cs}_2\text{Ag}_{1-x}\text{Na}_x\text{InCl}_6$ based white emission. **(a)** Comparison of the luminosity function

(plotted in dash line) and PL spectra of $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ measured at different temperature from 233 K to 343 K. **(b)** PL stability of $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ against continuous heating at 150°C on a hotplate, measured after recovering to room temperature. **(c)** Operational stability of $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ down conversion devices, measured in air without any encapsulation. **(d)** XRD patterns of $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ film (Inset: quartz substrate, 300 nm thick and 500 nm thick $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ films under 254 nm UV lamp illumination).

Supplementary Information is available in the online version of the paper.

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Author Contributions J. T. supervised the whole project. J-J. L., S-R. L. and J. L. designed and performed most of the experiments and analyzed the data; X. W. performed most of the theoretical calculations and analysis (*GW*-BSE, STE, PL) under the guidance of Y-F. Y.; S-R. L. discovered the phosphor; L. Y. contributed in EL device optimization; L. G. carried out TA experiments; M-Y. L assisted in data analysis

and PL measurement; Y. G. and J. E. carried out the electron microscopy measurements and analyzed the results; Y-H. F. and L-J. Z. simulated the band alignment and the contour plots of the VBM and CBM charge densities; C-Y. Z. and S-Y. J. provided some optical measurements; Q-S. D, F-S. M., L-D. W., W-X. L. and J-B. H. helped in PLQY measurement and EL device fabrication; G-D. N. involved in data analysis and experiments design; Y- F. Y. helped manuscript writing; J-J. L., X. W., E. H. S. and J. T. wrote the paper; all authors commented on the manuscript.

Author Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to J. T. (jtang@mail.hust.edu.cn) and Y-F. Y. (yanfa.yan@utoledo.edu).

METHODS

Materials. Cesium chloride (CsCl, 99.99%), silver chloride (AgCl, 99.99%), sodium chloride (NaCl, 99.99%), lithium chloride (LiCl, 99.9%), anhydrous indium chloride (InCl_3 , 99.999%), anhydrous bismuth chloride (BiCl_3 , 99.999%), anhydrous antimony chloride (SbCl_3 , 99.99%), zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} > 98\%$), tetramethylammonium hydroxide (TMAH, 98%) and polyethylenimine (PEIE) were purchased from Sigma Aldrich. Molybdenum oxide (MoO_3 , 99%) and 4,4'-Cyclohexylidenebis[N,N-bis(4-methylphenyl) benzenamine] (TAPC, 99%) were purchased from Guangdong Aglaia Optoelectronic Materials Company. Hydrochloric acid, ethanol, acetone, isopropanol, ethyl acetate, 1-butanol and dimethyl sulphoxide (DMSO, 99%) were purchased from Sinopharm Chemical Reagent Company. Patterned ITO-glass substrates (sheet resistance, $15 \Omega \text{ sq}^{-1}$) were purchased from Guangdong Xiangcheng Technology Company. All materials were used as received.

Synthesis of alloyed double perovskite materials. As double perovskites are generally impurity sensitive, Teflon autoclave should soaked with aqua regia for a whole night and raw materials with high-purity should be used. Then, 1 mmol anhydrous InCl_3 , ~ 0.005 mmol anhydrous BiCl_3 and 2 mmol CsCl were first dissolved in 5 mL 10 M HCl in a 25 mL Teflon autoclave. Then x mmol of AgCl and $1-x$ mmol of NaCl were added and the solution was heated at 180°C for 12 hours in a stainless steel Parr autoclave. The solution was then steadily cooled to 50°C with a speed of 3°C per hour (the cooling process was key in determining the PLQY of products). The as-prepared crystals were then filtered out and washed with isopropanol and dried in a furnace at 60°C . Na doped $\text{Cs}_2\text{AgSbCl}_6$ was synthesized by similarly substituting the above-mentioned InCl_3 with SbCl_3 , and Li doped $\text{Cs}_2\text{AgInCl}_6$ was achieved by mixing 20 mmol LiCl with 1 mmol $\text{Cs}_2\text{AgInCl}_6$ into a 25 mL Teflon autoclave contained 4 mL

10 M HCl, and then follow exactly the procedure for $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{InCl}_6$ synthesis.

Characterization and calibration of the PLQY of $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{InCl}_6$. The PLQY was measured using an absolute PL measurement system (Hamamatsu Quantaurus-QY) at Tsinghua University. The excitation wavelength was set as 365 nm, and step increments and integration time were set as 1 nm and 0.5 s per data point. Commercial YAG:Ce³⁺ powder purchased from Hunan LED Company with standard PLQY (80%~85%, 460 nm excitation) was applied to calibrate our system.

Electroluminescence devices fabrication. Colloidal ZnO nanocrystals were synthesized following a published recipe³¹. Patterned indium-doped tin oxide (ITO) substrates were cleaned by sequential sonication in acetone, ethanol and deionized water for 30 min in each bath. After drying, solutions of PEIE in isopropanol (0.4 wt%) were spin-coated onto the ITO substrates at 5,000 rpm for 60 s, followed by a layer of ZnO nanocrystals spun at a speed of 3,000 rpm for 60 s, and a further PEIE layer (0.4 wt% in 2-methoxyethanol) spin-coated at 5,000 rpm for 60 s. The $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ film was deposited by thermal evaporation of CsCl, AgCl, NaCl, InCl₃ and BiCl₃ in separate crucibles at a stoichiometric molar ratio of 2:0.6:0.4:1:~0.005. The evaporation rate was monitored by the quartz microbalance. After the pressure of the evaporator chamber (Fangsheng Technology, OMV-FS300) was pumped down to 6×10^{-6} mTorr, one precursor was heated slowly to achieve a desirable deposition rate (CsCl: 0.10-0.20 Å/s, NaCl: 0.01-0.03 Å/s, AgCl: 0.05-0.10 Å/s, InCl₃: 0.10-0.20 Å/s, BiCl₃: 0.01 Å/s). The shutter was then manually opened until certain thickness was deposited. The evaporation sequence was CsCl, InCl₃, BiCl₃, NaCl and AgCl in order. Then, the $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ film was exposed to air for 5 min, and further annealed at 150 °C in N₂ for 5 min to promote its crystallization. Afterwards, 40 nm thick TAPC layers were deposited at a 0.10-0.20 Å/s speed, followed by the MoO₃/Al electrode deposition to complete the device (device area 4 mm²).

Materials characterization. Powder XRD measurements were performed by grinding $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{InCl}_6$ crystals into fine powders in a mortar using Philips X pert pro MRD diffractometer with the Cu K α radiation. High-resolution XRD measurements were conducted on the powder diffractometer (D8 ADVANCE, Bruker) using a Cu K α rotating anode. The absorption and reflectance spectra was measured on a UV-vis spectrophotometer (PerkinElmer Instruments, Lambda 950) with an integrating sphere, which were calibrated by measuring a reference material (MgO powder) at the same time. The PL and PLE measurements were carried out using an Edinburgh Instruments Ltd UC920. The temperature-dependent PL spectra were measured using Horiba JobinYvon, LabRAM HR800 excited by a 325 nm wavelength Nd-YAG laser and temperature ranging from 80 to 500 K using a liquid nitrogen cooler. The intensity-dependent PL measurement was also carried out by using picosecond pulse diode laser (Light Conversion, Pharos) with 365 nm output wavelength and 50-ps pulse width, and

the pulse intensity was monitored by a power meter (Ophir PE10BF-C). The powder density was controlled by neutral density filters (Light Conversion, Pharos). The PL lifetime measurement was based on the time-correlated single photon counter technology. The excitation beam was picosecond pulse diode laser (Light Conversion, Pharos) with 365 nm output wavelength and 50-ps pulse width. For transient absorption measurement, an amplified Yb:KGW laser (Light Conversion, Pharos) with a 5 kHz repetition rate was used to generate femtosecond laser pulses. Pump wavelength: 325 nm; intensity: $4 \mu\text{J cm}^{-2}$. A crystal with about $0.2 \times 1.0 \times 1.0 \text{ mm}^3$ size was placed on the glass substrate during the measurement. Inductively coupled plasma optical emission spectrometer (ICP-OES) measurements were carried out on Perkin Elmer Optima 7300DV with $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{InCl}_6$ powders dissolved in HCl. Thermal gravimetric analysis (TGA) were obtained using a PerkinElmer Diamond TG/DTA6300, conducted at a heating rate of $10 \text{ }^\circ\text{C/min}$ from room temperature to $800 \text{ }^\circ\text{C}$ in N_2 flow with an alumina crucible. $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ thin film fabricated by thermal evaporation was characterized by SEM (FEI Nova NanoSEM450, without Pt coating), UPS (Specs UVLS, He I excitation, 21.2 eV, referenced to the Fermi edge of argon etched gold). Stability against heat was measured by simply putting the powders onto a $150 \text{ }^\circ\text{C}$ hotplate, and PL intensity was measured after a certain time interval. Note that all these measurements are based on the powder except for the EL parts.

Transmission electron microscopy analysis. TEM specimens were prepared by crushing the as-grown single crystals and then drop cast onto a TEM copper grid which was covered by an ultrathin carbon film. TEM characterization was carried out on a JEOL 2100F TEM with a field emission gun at 200 kV in the Monash Centre for Electron Microscopy (MCEM). Low dose selected area electron diffraction (SAED) and scanning electron nanobeam diffraction (SEND) were performed to avoid beam damage. Using a nominal current density of 2 pA/cm^2 no change in lattice parameters was observed after several minutes' exposure. For SEND measurement, a step size of 5 nm was used and a dataset of 10×10 diffraction patterns of 2048×2048 pixels were collected from a squared region of $50 \times 50 \text{ nm}^2$. We deployed a Digital Micrograph script developed in J.M. Zuo's group at University of Illinois at Urbana-Champaign for automatic control of the scanning coils and pattern acquisition.

First-principles density functional theory (DFT), many-body perturbation theory (*GW*), and Bethe-Salpeter Equation (BSE) calculations DFT, *GW*, and BSE calculations were performed using VASP code^{32,33} with projector augmented-wave (PAW)³⁴ potentials. A kinetic energy cutoff of 520 eV and Γ centered k mesh of $4 \times 4 \times 4$ were employed. The band gaps of both $\text{Cs}_2\text{AgInCl}_6$ and $\text{Cs}_2\text{NaInCl}_6$ were found quite sensitive to the bond length, thus we used more accurate PBE0³⁵ functional to relax the atomic coordinates with the force tolerance of 0.01 eV/\AA while keeping the lattice parameters fixed at their experimental values. With the relaxed coordinates, *GW*

calculations were performed on top of the PBE³⁶ wave function. Partial self-consistency on the Green's function (G) only, the GW_0 scheme, was adopted. An energy cutoff of 200 eV for the response function, 200 real frequency grids for the dielectric function and 1000 bands were used for the GW calculations. The results were further extrapolated to infinite basis sets and number of bands³⁷. GW band structures were obtained using wannier interpolation via the wannier90 code³⁸. BSE calculations were performed on top of the GW quasiparticle energies. The number of occupied/virtual states of 2/2 and 24/4 were used for $\text{Cs}_2\text{AgInCl}_6$ and $\text{Cs}_2\text{NaInCl}_6$, respectively, to converge the several low-lying exciton states. The exciton binding energies were extrapolated to infinitely dense k meshes. For finer k mesh, the GW calculations are computationally prohibitive. We used wannier interpolation to interpolate the GW quasiparticle energies and model dielectric function³⁹ ϵ_q which is fitted from the one obtained on a coarser grid to interpolate the dielectric function. ($\epsilon_q = 1 + [(\epsilon_\infty - 1)^{-1} + \alpha q^2 + \beta q^4]^{-1}$, ϵ_∞ is the static dielectric constant, q is wave vector, α and β are fitting parameters.)

STE calculation To study the STE properties, we used the restricted open-shell Kohn-Sham (ROKS) theory⁴⁰⁻⁴² as implemented in the cp2k code⁴³. A supercell with a single Γ point was used in the calculation. The DZVP molecularly optimized basis sets⁴⁴, PBE exchange-correlation functional and GTH pseudopotentials⁴⁵ were used. The energy cutoffs of 300 Ry and 1200 Ry were used for $\text{Cs}_2\text{AgInCl}_6$ and $\text{Cs}_2\text{NaInCl}_6$, respectively. The delocalization error of the PBE functional was removed using the scaled Perdew-Zunger self-interaction correction (PZ-SIC)^{46,47} only on the unpaired electrons⁴⁸. The scaling parameter α of the Hartree energy was fitted to reproduce the exciton binding energies calculated by the GW -BSE approach. The exciton binding energy within the ROKS framework is calculated as $E_b = E_g - (S_1 - E_0)$, where S_1 and E_0 are the first excited singlet state and ground state energies, respectively. We obtained α of 0.30 and 0.34 for $\text{Cs}_2\text{AgInCl}_6$ and $\text{Cs}_2\text{NaInCl}_6$, respectively. Since the present SIC scheme is not meant to correct the band gap, the ES curves in the cc diagrams were shift by aligning the FE energy with that from GW -BSE calculations. A supercell with size of $21.0 \times 21.0 \times 21.0 \text{ \AA}^3$ was found enough to converge both the FE and STE of $\text{Cs}_2\text{NaInCl}_6$. However, for $\text{Cs}_2\text{AgInCl}_6$, due to the small effective mass of the electron, a supercell with size as large as $41.9 \times 41.9 \times 41.9 \text{ \AA}^3$ is needed. For completely delocalized state, the SIC is zero. Thus we neglected the SIC on the electron wave function of the STE in $\text{Cs}_2\text{AgInCl}_6$. This can safely reduce the supercell size to only $20.9 \times 20.9 \times 20.9 \text{ \AA}^3$. For the alloyed double perovskites, we used supercell of $21.0 \times 21.0 \times 21.0 \text{ \AA}^3$ and α of 0.34.

Configuration coordinate diagram and PL spectra calculation

Cc diagram was constructed by linear interpolating the coordinates between the FE and STE configurations and then calculating both the GS and ES energies at each coordinate.

1 The coordinate difference between the FE and STE configurations is $\Delta Q =$
 2 $\sqrt{\sum_{\kappa,i} m_{\kappa} (R_{\kappa,i}^e - R_{\kappa,i}^g)^2}$, here κ labels the atoms, $i = (x, y, z)$, m is the atomic mass,
 3 R the atomic coordinates with e and g for the excited and ground state, respectively.
 4 The calculated ΔQ is 4.35 and 9.16 $\text{\AA}\sqrt{amu}$, respectively, for $\text{Cs}_2\text{AgInCl}_6$ and
 5 $\text{Cs}_2\text{NaInCl}_6$. The phonon frequency Ω was obtained by a third-order polynomial
 6 $(\frac{1}{2}\Omega Q^2 + \lambda Q^3)$ fit of the ES or GS curve. The normalized PL intensity in the leading
 7 order can be written as⁴⁹ $I(h\nu) = C\nu^3 A(h\nu)$ where $h\nu$ is the photon energy and C is
 8 the normalization factor, which includes the transition dipole moments for dipole-
 9 allowed transitions and magnetic dipole moments and electric quadruple moments for
 10 dipole-forbidden transitions. A is the normalized spectral function, under Franck-
 11 Condon approximation:

$$12 \quad A(h\nu) = \sum_{m,n} w_m(T) |\langle \chi_{gn} | \chi_{em} \rangle|^2 \delta(E_{ZPL} + \hbar\omega_m - \hbar\omega_n - h\nu) \quad (1)$$

13 $w_m(T) = e^{-\hbar\omega_m/k_B T}$ is the thermal occupation factor of the excited state phonons
 14 with energy of $\hbar\omega_m = (\frac{1}{2} + m)\hbar\Omega_m$, where Ω_m is the phonon frequency and m the
 15 corresponding quantum number. n denotes the ground state related quantity. E_{ZPL} is
 16 the zero phonon line energy which is the energy difference between the minima of the
 17 ES and GS curves plus the zero point energy difference $\frac{1}{2}\hbar(\Omega_e - \Omega_g)$. χ_{em} and χ_{gn}
 18 are the harmonic phonon wave functions of the excited and ground states, respectively.

19 The Franck-Condon factors $|\langle \chi_{gn} | \chi_{em} \rangle|^2$ were calculated by the recurrence method⁵⁰.
 20 The δ function in Eq. 1 was replaced by the Lorentzian with a broadening parameter
 21 of 0.03 eV which is around the phonon cutoff frequency of $\text{Cs}_2\text{AgInCl}_6$ (Extended Data
 22 Fig. 2).

23 **LED devices on the UV chips.** GaN based UV chips (14 W output, 365-370 nm peak
 24 emission) were purchased from Taiwan Epileds Company. The $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$
 25 crystals was ball-milled into fine powder, and the powder was painted onto the
 26 commercial chips without encapsulation. The LEDs were driven by a Keithley 2400
 27 source meter, and the emission spectra and intensity were recorded by a PHOTO
 28 RESEARCH SpectraScan PR655 photometer. For the device stability test, the LED was
 29 continuously powered by a Keithley 2400 at a fixed current, and the initial brightness
 30 was set as $\sim 5000 \text{ cd m}^{-2}$. Devices performance was monitored after a certain time
 31 interval.

32 **EL device performance measurement.** The density-voltage, luminance-voltage
 33 characteristics and EL spectra of the devices were collected by a Photo Research
 34 SpectraScan PR655 photometer and a Keithley 2400 Source Meter constant current
 35 source. All the experiments were carried out at room temperature under ambient
 36 conditions in dark.

Calculation and comparison of Huang-Rhys factor. In principle, Huang-Phys factor (S) reflects how strongly electrons couple to phonons, which can be obtained by fitting the temperature dependent full width at half maxima (FWHM) of PL peaks using the following equation⁵¹

$$FWHM = 2.36\sqrt{S}\hbar\omega_{phonon}\sqrt{\cot\frac{\hbar\omega_{phonon}}{2k_bT}} \quad (2)$$

where $\hbar\omega_{phonon}$ is phonon frequency, T is a temperature, and k_b is Boltzmann constant, respectively. For $\text{Cs}_2\text{AgInCl}_6$, S and $\hbar\omega_{phonon}$ are calculated as 38.7 and 20.1 meV, in good agreement with our simulation results (37 and 17.4 meV). Extended Data Table 1 lists S values of a few representative compounds. The Huang-Rhys factor of $\text{Cs}_2\text{AgInCl}_6$ is 38.7, which is larger than that of many common emitters such as CdSe, ZnSe, indicating the easy formation of STE in $\text{Cs}_2\text{AgInCl}_6$. For comparison, the formation of STEs is also found in materials with high Huang-Rhys factor⁵⁵, such as $\text{Cs}_3\text{Sb}_2\text{I}_9$, $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{Rb}_3\text{Sb}_2\text{I}_9$. However, for efficient STE emission, S should not be overly large because otherwise excited state energy will be dissipated by phonons, as the case in $\text{Cs}_2\text{NaInCl}_6$. This is because S also influences PL emission by radiative rate, as described by Equation 1. If we assume the ground and excited states have similar phonon frequency, the Franck-Condon factor (F , at zero temperature) can be simplified as

$$F = |\langle\chi_n|\chi_0\rangle|^2 = \frac{e^{-S}S^n}{n!} \quad (3)$$

The PL peak appears at $n \approx S$, so

$$F_{max} = \frac{e^{-S}S^S}{S!} \quad (4)$$

which is a monotonic decreasing function of S . As the PL intensity $I \propto F$, the larger the S , the smaller the radiative rate, and the lower the emission efficiency. Thereby, S value could potentially serve as the figure-of-merit for the design of efficient emission from self-trapped excitons. The ideal value of the Huang-Rhys parameter can neither be too big nor too small for efficient STE emitters.

Mechanistic study of Bi^{3+} doping. Extended Data Figure 6 provides relevant information to understand the effect of Bi^{3+} incorporation for PLQY improvement. For Bi doped $\text{Cs}_2\text{AgInCl}_6$ sample, XRD measurement revealed smaller full-width at half-maxima (FWHM, from 0.058° to 0.034°) of the diffraction patterns, and optical measurement demonstrated diminished sub-bandgap absorption after 400 nm and increased photoluminescence lifetime (from 2971 ns (70%) to 5989 ns (97%)). As In^{3+} is one deep defect in $\text{Cs}_2\text{AgInCl}_6$, and isovalent doping helps to reduce vacancy defects in perovskite, we thus believe Bi doping passivates defects and suppress non-radiative recombination loss. Additionally, theoretical simulation indicated that Bi doping introduces a shallow state right above the VBM, forms nanoelectronic domains in the

matrix that concentrate holes. The holes finally relax to Ag sites through Bi 6s/Ag 4d orbital hybridization and lattice interaction, promoting exciton localization, just like I doped AgBr for STE emission. Therefore, Bi doping improves crystal quality and promotes radiative recombination, enhancing PLQY.

Data Availability. The data sets analysed during the study are available from the corresponding authors upon request.

References

31. Dai, X. *et al.* Solution-processed, high-performance light-emitting diodes based on quantum dots. *Nature* **515**, 96-99 (2014).
32. Kresse, G. & Furthmüller, J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).
33. Kresse, G. & Furthmüller, J. Efficiency of *ab initio* total energy calculations for metals and semiconductors using a plane wave basis set. *Comput. Mat. Sci.* **6**, 15 (1996).
34. Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953–17979 (1994).
35. Perdew, J. P., Ernzerhof, M. & Burke, K. Rationale for mixing exact exchange with density functional approximations. *J. Chem. Phys.* **105**, 9982–9985 (1996).
36. Perdew, J., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
37. Klimeš, J., Kaltak, M., & Kresse, G. Predictive *GW* calculations using plane waves and pseudopotentials. *Phys. Rev. B* **90**, 075125 (2014).
38. Mostofi, A. A. *et al.* wannier90: A tool for obtaining maximally-localised Wannier functions. *Comput. Phys. Commun.* **178**, 685–699 (2008).
39. Cappellini, G. *et al.* Model dielectric function for semiconductors. *Phys. Rev. B* **47**, 9892 (1993).
40. Kowalczyk, T., Tsuchimochi, T., Chen, P. T., Top, L. & Van Voorhis, T. Excitation energies and Stokes shifts from a restricted open-shell Kohn-Sham approach. *J. Chem. Phys.* **138**, (2013).
41. Filatov, M. & Shaik, S. A spin-restricted ensemble-referenced Kohn-Sham method and its application to diradicaloid situations. *Chem. Phys. Lett.* **304**, 429–437 (1999).
42. Frank, I., Hutter, J., Marx, D. & Parrinello, M. Molecular dynamics in low-spin excited states. *J. Chem. Phys.* **108**, 4060–4069 (1998).
43. Hutter, J., Iannuzzi, M., Schiffmann, F. & VandeVondele, J. Cp2k: Atomistic simulations of condensed matter systems. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **4**, 15–25 (2014).
44. VandeVondele, J. & Hutter, J. Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases. *J. Chem. Phys.* **127**, 114105 (2007).
45. Goedecker, S., Teter, M. & Hutter, J. Separable dual-space Gaussian pseudopotentials. *Phys. Rev. B* **54**, 1703–1710 (1996).
46. Perdew, J. P. & Zunger, A. Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B* **23**, 5048–5079 (1981).
47. VandeVondele, J. & Sprik, M. A molecular dynamics study of the hydroxyl radical in solution applying self-interaction-corrected density functional methods. *Phys. Chem. Chem. Phys.* **7**, 1363 (2005).
48. d’Avezac, M., Calandra, M. & Mauri, F. Density functional theory description of hole-trapping in SiO₂: A self-interaction-corrected approach. *Phys. Rev. B* **71**, 205210 (2005).

-
- 1 49. Alkauskas, A., Lyons, J. L., Steiauf, D. & Van De Walle, C. G. First-principles calculations of
2 luminescence spectrum line shapes for defects in semiconductors: The example of GaN and
3 ZnO. *Phys. Rev. Lett.* **109**, 267401 (2012).
- 4 50. Ruhoff, P. T. Recursion relations for multi-dimensional Franck-Condon overlap integrals. *Chem.*
5 *Phys.* **186**, 355–374 (1994).
- 6 51. Stadler, W. *et al.* Optical investigations of defects in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$. *Phys. Rev. B* **51**, 10619 (1995).
- 7 52. Türeci, V. *et al.* Effect of random field fluctuations on excitonic transitions of individual CdSe
8 quantum dots. *Phys. Rev. B* **61**, 9944 (2000).
- 9 53. Zhao, H., & Kalt, H. *et al.* Energy-dependent Huang-Rhys factor of free excitons. *Phys. Rev. B*,
10 **68**, 125309 (2003).
- 11 54. Leung, C. H. & Song, K. S. On the luminescence quenching of F centers in alkali halides. *Solid*
12 *State Commun.* **33**, 907 (1980).
- 13 55. Mulazzi, E., & Terzi, N. Evaluation of the Huang-Rhys factor and the half-width of F-band in
14 KCl and NaCl crystals. *J. Phys. Colloq.* **28**, 49-54 (1967).
- 15 56. Schulz M *et al.* Intensity dependent effects in silver chloride: bromine - bound exciton and
16 biexciton states. *Phys. status solidi B* **177**, 201-212 (1993).
- 17 57. McCall, K. M. *et al.* Strong electron-phonon coupling and self-trapped excitons in the defect
18 halide perovskites $\text{A}_3\text{M}_2\text{I}_9$ (A = Cs, Rb; M = Bi, Sb). *Chem. Mater.* **29**, 4129–4145 (2017).
- 19 58. Andrews, L. J. *et al.* Thermal quenching of chromium photoluminescence in ordered
20 perovskites. I. Temperature dependence of spectra and lifetimes. *Phys. Rev. B* **34**, 2735 (1986).
- 21

Extended Data Figure 1| Phonon band structure of Cs₂AgInCl₆ and the zone-center Jahn-Teller phonon mode (inset). The phonon band structure was calculated by the finite difference method with the supercell approach. The consistent displacement pattern of the phonon eigenvector compared with that of the lattice distortion during the STE formation, and the consistent phonon eigen frequency compared with the phonon frequency fitted from the cc diagram confirms that the Jahn-Teller phonon mode coupled with the photoexcited excitons is responsible for the STE formation in Cs₂AgInCl₆.

Extended Data Figure 2| The emission characterizations of pure Cs₂AgInCl₆. **a**, The broad PL spectrum of Cs₂AgInCl₆ measured at room temperature. **b**, The temperature-dependent PL spectra of the pure Cs₂AgInCl₆. **c**, The fitting results of full width at half maximum (FWHM) as a function of temperature. **d**, The PLQY of Cs₂AgInCl₆. The reference is bare integrating sphere without sample.

Extended Data Figure 3| The electronic and optical properties of Cs₂NaInCl₆. **a**, *GW* calculated band structure. The *GW* band gap is 6.42 eV. The lowest exciton with binding energy of 0.8 eV is dark. The first bright exciton has a binding energy of 0.44 eV. **b**, Calculated optical absorption and PL spectra are compared with experimental results.

1 **Extended Data Table 1. Comparison of the Huang-Rhys factors.**

Compounds	Huang-Rhys factor
CdSe^{52}	1
ZnSe^{53}	0.31
$\text{NaCl}^{54,55}$	42
AgCl:Br^{56}	22
$\text{Cs}_3\text{Bi}_2\text{I}_9^{57}$	79.5
$\text{Cs}_3\text{Sb}_2\text{I}_9^{57}$	42.7
$\text{Rb}_3\text{Sb}_2\text{I}_9^{57}$	50.4
$\text{Cs}_2\text{NaYCl}_6^{58}$	6.99
$\text{Cs}_2\text{NaInCl}_6$	80(ES)/188(GS)*
$\text{Cs}_2\text{AgInCl}_6$	38.7
$\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$	40.9
$\text{Cs}_2\text{Ag}_{0.16}\text{Na}_{0.84}\text{InCl}_6$	51.0

2 Note Huang-Phys factors for CdSe, ZnSe, NaCl and AgCl:Br are adopted from
 3 literatures, $\text{Cs}_2\text{NaInCl}_6$ is simulation result, and all other values are obtained from the
 4 fitting results of temperature dependent FWHM of PL data at relatively low
 5 temperature region (Extended Data Fig. 2c and Supplementary Fig. S1).

6
 7 * Normally the Huang-Phys factors of GS and ES are quite close⁴⁹, as it is generally
 8 assumed that the ground state and excited state have the same phonon frequency.
 9 However, for $\text{Cs}_2\text{NaInCl}_6$ the difference is quite large.

10

Extended Data Figure 4| The alloy behavior of $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{InCl}_6$. **a**, XRD patterns of $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{InCl}_6$ shifted to lower degrees with increasing sodium substitution, **b**, the refined lattice parameters plotted as a function of nominal x in $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{InCl}_6$, which follows a linear increase upon sodium substitution. See Supplementary Fig. S2 for the characterization detail. Note that selected-area electron diffraction and scanning electron nanobeam diffraction analysis (Supplementary Fig. S4-5) also suggest the existence of microscopic super-lattice (Na/Ag ordering).

Extended Data Figure 5| The PL enhancement of doped double perovskite powders. **a**, The PL spectra of pure $\text{Cs}_2\text{AgInCl}_6$ and Li doped $\text{Cs}_2\text{AgInCl}_6$. **b**, The PL spectra of pure $\text{Cs}_2\text{AgSbCl}_6$ and Na doped $\text{Cs}_2\text{AgSbCl}_6$.

Extended Data Figure 6| Characterization the effect of Bi doping in $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{InCl}_6$. **a**, high-resolution single crystal X-ray diffraction towards (111) peaks of $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ with and without Bi doping **b**, absorption spectra of various materials from 500 nm to 950 nm wavelength, **c**, comparison of PLQY results, **d**, the comparison of PL lifetime, **e**, the comparison of the total DOS between pure $\text{Cs}_2\text{AgInCl}_6$ and that with Bi doping. Inset: The band alignment of $\text{Cs}_2\text{AgInCl}_6$ and Bi doped $\text{Cs}_2\text{AgInCl}_6$. The small shallow peak marked by arrow is derived from the Bi 6s states which hybridize with the Ag 4d states. **f**, the PDOS of Bi doped $\text{Cs}_2\text{AgInCl}_6$.