Probing molecule-like isolated octahedra via phase stabilization of zero-dimensional cesium lead halide nanocrystals

Paulraj Arunkumar1, Han Bin Cho1, Kyeong Hun Gil1, Sanjith Unithrattil1, Yoon Hwa Kim1 & Won Bin Im1

Zero-dimensional (0D) inorganic perovskites have recently emerged as an interesting class of material owing to their intrinsic Pb2+ emission, polaron formation, and large exciton binding energy. They have a unique quantum-confined structure, originating from the complete isolation of octahedra exhibiting single-molecule behavior. Herein, we probe the optical behavior of single-molecule-like isolated octahedra in 0D Cesium lead halide (Cs4PbX6, X = Cl, Br/Cl, Br) nanocrystals through isovalent manganese doping at lead sites. The incorporation of manganese induced phase stabilization of 0D Cs4PbX6 over CsPbX3 by lowering the symmetry of PbX6 via enhanced octahedral distortion. This approach enables the synthesis of CsPbX3 free Cs4PbX6 nanocrystals. A high photoluminescence quantum yield for manganese emission was obtained in colloidal (29%) and solid (21%, powder) forms. These performances can be attributed to structure-induced confinement effects, which enhance the energy transfer from localized host exciton states to Mn2+ dopant within the isolated octahedra.
Over the past few years, inorganic lead halide perovskites have attracted great attention as a promising optoelectronic material for light-emitting devices, photodetectors, and low-threshold lasers, owing to their high photoluminescence quantum yield (PL QY), narrow emission, and tunable band gap. The basic building block in these materials is PbX\(_6\) octahedra (where X is a halogen), whose diverse connectivity can produce structures with various dimensionalities, ranging from three-dimensional (3D) to zero-dimensional (0D). The 3D inorganic perovskites, with general formula A\(_{n}\)PB\(_{n}\)X\(_{3n}\) (A = Cs, Rb, and X = Cl, Br, or I), consist of an extended network of corner-sharing PbX\(_6\) octahedra with cavities occupied by A ions. Despite being the most explored material, the poor chemical stability of 3D perovskites against moisture, inherent phase transformation, and ion migration make their low-dimensional counterparts more favorable for optoelectronic applications.

In particular, 0D inorganic perovskite-like Cs\(_4\)Pb\(_{x}\)Br\(_{6-x}\) system have crystal structure in which the PbX\(_6\) octahedra are decoupled from each other by the surrounding Cs\(^+\) ions. The complete isolation of octahedra leads to strong quantum confinement and exciton–phonon interactions, which in turn can result in exciton localization, self-trapping, and polaron formation. The optical features of 0D Cs\(_4\)Pb\(_{x}\)Br\(_{6-x}\) are governed by transitions between the electronic states of Pb\(^{2+}\) ions, and its broad ultraviolet (UV) emission has been assigned to the radiative decay of Frenkel excitons at Pb\(^{2+}\) sites. However, the origin of their PL in the visible range is still under debate because of mixed views on the efficient green luminescence (QY of 45%) of Cs\(_4\)PbBr\(_6\), which some studies have been attributed to the minor 3D CsPbBr\(_3\) nanoscale impurity, and others to Cs\(_4\)PbCl\(_6\) single crystals, assigning to Pb\(^{2+}\) ion emission, originating from the optical transitions of \(^{3}\)P\(_{0,1}\) \(\rightarrow\) \(^{1}\)S\(_0\) in the isolated PbCl\(_6\) octahedra, similar to Pb\(^{2+}\) doping in the alkali halide host. In addition, the coexistence of 3D CsPbCl\(_6\)-like impurity was noted by 414 nm emission in Cs\(_4\)PbCl\(_6\). While, Mohammed’s group reported Cs\(_4\)PbBr\(_6\) characteristic with two broad UV emissions at 340 nm (high-energy) and 400 nm (low-energy) attributing to Pb\(^{2+}\) ion and charge-transfer band denoted as “D-state”, respectively. D-state emission originates via the transfer of excited electrons from (PbBr\(_6\))^\(-\) octahedra to the Pb\(^{2+}\) occupying Cs sites (D-states), through their strong coupling in Cs\(_4\)Pb\(_{x}\)Br\(_{6-x}\) host. Therefore, 0D Cs\(_4\)Pb\(_{x}\)Br\(_{6-x}\) behave as an ideal host–guest system, with periodically doped individual PbX\(_6\) species in a wide band gap matrix. Moreover, although many reports attribute the green emission (512 nm) to the intrinsic property of Cs\(_4\)PbBr\(_6\), we believe it arise from the coexistence of CsPbBr\(_3\) impurity, similar to 414 nm emission of Cs\(_4\)PbCl\(_6\). Nevertheless, 0D cesium lead halide perovskites still represent largely unexplored and intriguing perovskite-like material, expected to exhibit interesting optoelectronic properties, due to their strongly localized excitons and high exciton binding energies (150 to 380 meV).

The coexistence of 3D CsPb\(_{x}\)Br\(_{6-x}\) impurity has precluded a detailed understanding on the optical properties of CsPb\(_{x}\)Br\(_{6-x}\), leading to a growing demand for their synthesis in pure form and their phase stabilization. Solvent washing has been recently reported for the synthesis of Cs\(_4\)PbBr\(_6\) free from CsPb\(_x\) impurity, which, however, is inadequate to treat the chloride compositions due to their poor solubility. As the inevitable coexistence of CsPb\(_x\) phase represents a major drawback, new synthetic strategies are of utmost interest for obtaining pure CsPb\(_{x}\)Br\(_{6-x}\) nanocrystals with reduced CsPb\(_x\) impurity.

Recently, the molecule-like behavior of Cs\(_4\)PbBr\(_6\) has been discussed in terms of charge carrier mobility and polaron formation, arising from weak interactions between isolated octahedra. Thus, understanding the fundamental optoelectronic behavior of 0D Cs\(_4\)Pb\(_{x}\)Br\(_{6-x}\) would promote the development of bulk perovskite-based devices. Incorporation of transition metal ions such as manganese (Mn\(^{2+}\)) in the semiconductor nanocrystal leads to interesting optoelectronic properties by modulating the electronic properties of the host, providing new routes for designing solid-state lighting and light-harvesting devices.

Hence, Mn\(^{2+}\) ions can serve as the sensitive probe for investigating the local structure of the host and altering its optical and electronic behavior. Thus far, the potential effect of isovalent cation doping on the isolated octahedral units of Cs\(_4\)PbX\(_6\) remains unexplored, particularly in terms of phase stabilization and optical properties.

In this work, we probe the optical behavior of isolated octahedra in the Cs\(_4\)Pb\(_{x}\)Br\(_{6-x}\) (X = Br, Cl) by introducing Mn\(^{2+}\) at the octahedral sites and explore its phase stabilization over commonly coexisting CsPb\(_x\)Br\(_{6-x}\) impurity. The luminescence measurements show that Mn\(^{2+}\) dopant significantly alter the optical properties of different host emissive states in the Cs\(_4\)Pb\(_{x}\)Br\(_{6-x}\). The dopant emission is controlled by adjusting the band gap of Cs\(_4\)Pb\(_{x}\)Br\(_{6-x}\) through halide identity, facilitating energy transfer for enhancing the dopant emission efficiency in both colloidal and solid forms. The quantum-confined structure of 0D Cs\(_4\)Pb\(_{x}\)Br\(_{6-x}\) further improves the stability of the host and efficiency of the dopant emission, particularly in their solid form.

**Results**

Mn\(^{2+}\)-doped Cs\(_4\)Pb\(_{x}\)Br\(_{6-x}\) nanocrystals. A series of 0D Cs\(_4\)Pb\(_{x}\)Br\(_{6-x}\) (X = Br, Cl) nanocrystals, doped with manganese, were synthesized via modified reverse microemulsion method (Supplementary Figure 1 and Supplementary Note 1). A short-chain alkylamine (octylamine) surfactant was employed instead of the previously reported long-chain oleylamine to control size and morphology. The exact composition of the synthesized undoped and Mn\(^{2+}\)-doped Cs\(_4\)Pb\(_{x}\)Br\(_{6-x}\) (denoted as mixed halide) analogs are Cs\(_4\)Pb\(_{x}\)Cl\(_{4-x}\) and Cs\(_4\)Pb\(_{x}\)Br\(_{4-x}\), respectively, with x varying from 0.05 (5% Mn) to 0.80 (80% Mn). The Pb/Mn ratios were estimated from inductively coupled plasma–optical emission spectroscopy (Supplementary Table 1). For simplicity, the synthesized samples were represented as Cs\(_4\)Pb\(_{x}\)Br\(_{6-x}\)X\(_{x}\) Mn\(_{y}\), where X = (Br/Cl), Cl, and Br, and y = percentage of Mn concentration with respect to displaced lead ions.

**Local and bulk structure.** The crystal structure of Cs\(_4\)Pb\(_{x}\)Br\(_{6-x}\) consists of caged PbX\(_6\) octahedra, isolated by interspersed Cs\(_2\)X\(_4\) bridges. Two types of Cs sites are present: the Cs(1) site form an alternating octahedra with PbX\(_6\), whereas the Cs(2) trigonal prisms share one triangular face to form infinite [CsPbX\(_3\)]\(^{3-}\) chains along the [001] direction. The synthesized samples were highly crystalline matching with the rhombohedral Cs\(_4\)Pb\(_{x}\)Br\(_{6-x}\) phase (X = Br, Cl) and space group: R\(_{3c}\) as presented in Fig. 1a. However, in the undoped Cs\(_4\)Pb\(_{x}\)Br\(_{6-x}\), the presence of 3D CsPb\(_x\)Br\(_{6-x}\) impurity were clearly apparent in all the halide analogs (Fig. 1a, Supplementary Figure 2, and Supplementary Note 2). Despite using high Cesium content (CsPb = 5:1), formation of undesired CsPb\(_x\)Br\(_{6-x}\) phase were observed in the undoped Cs\(_4\)Pb\(_{x}\)Br\(_{6-x}\) probably due to localized occurrence of Cs-deficient regions.

Upon Mn incorporation, the Bragg’s peak at 23° monotonically shifts to higher 2θ, suggesting the substitution of Pb\(^{2+}\) with smaller Mn\(^{2+}\) ion in Cs\(_4\)Pb\(_{x}\)Br\(_{6-x}\) (X = Br, Cl), which is also evident from the decrease in lattice parameters (Table 1, Supplementary Tables 2 to 4). Lattice contraction of 0.3% and volume change of 2%, after Mn (20% Mn) doping, resulted in the shortening of lead halide (Pb–Br/Cl) bond lengths and similar...
The strong bonding nature upon Mn doping is evidenced from high bond-dissociation energy of Mn–Cl (361 kJ mol$^{-1}$) than Pb–Br bonds (247 kJ mol$^{-1}$)$^{26}$. The valence states and substitution of Mn$^{2+}$ ions at the isolated octahedral PbX$_6$ sites was reaffirmed from X-ray photoelectron spectroscopy and electron spin resonance results, respectively (Supplementary Figures 3a to 3f and Supplementary Note 3)$^{22,27,28}$. Quantification of multiple crystalline phases (Cs$_4$PbX$_6$ and CsPbX$_3$) in the synthesized samples were estimated using Rietveld refinement of X-ray diffraction (XRD) results. Interestingly, Mn doping resulted in a decrease in the phase fraction (mass%) of 3D CsPbX$_3$ impurity, which further reduced with Mn content in both Br/Cl and Cl analogs, as shown in Fig. 1b. In other words, the phase fraction of 0D Cs$_4$Pb(Br/Cl)$_6$ with respect to the total (0D+3D) phase gradually increased from 86 to 100% upon increasing Mn concentration from 0 to 20%. This increase in the phase fraction of Cs$_4$PbX$_6$ was also apparent in the pure chloride analog (Supplementary Table 5, 6). The strong bonding nature upon Mn doping is evidenced from high bond-dissociation energy of Mn–Cl (361 kJ mol$^{-1}$) than Pb–Br bonds (247 kJ mol$^{-1}$)$^{26}$. The valence states and substitution of Mn$^{2+}$ ions at the isolated octahedral PbX$_6$ sites was reaffirmed from X-ray photoelectron spectroscopy and electron spin resonance results, respectively (Supplementary Figures 3a to 3f and Supplementary Note 3)$^{22,27,28}$.

**Fig. 1** Local and bulk structures of Mn$^{2+}$-doped Cs$_4$PbX$_6$. a X-ray diffraction patterns of Mn$^{2+}$-doped Cs$_4$PbX$_6$ series with different doping concentrations showing the rhombohedral structure is preserved after Mn-doping. Selected 2θ range of (22 to 24° and 29 to 31°) XRD patterns were presented. A monotonic shift of the XRD peak at Bragg’s angle at 23.4° towards higher 2θ is the result of progressive lattice contraction as the Mn$^{2+}$ concentration increases, due to the substitutional replacement of Pb$^{2+}$ with isovalent but smaller Mn$^{2+}$ ions. The additional impurity cubic phases of 3D CsPb(Br/Cl)$_3$, 3D CsPbCl$_3$, CsBr, Cs(Br/Cl), and CsCl were denoted as hash, asterisk, triangle, open circle, and closed circle, respectively. It is to be noted that the Cs:Pb precursor ratio was fixed at 5:1 for all the samples of Cs$_4$PbX$_6$ (Br, Cl, and Br/Cl). b Phase fraction of the desired 0D Cs$_4$PbX$_6$ perovskite with respect to 3D CsPbX$_3$ perovskite phase and segregation of CsX, with varying Mn concentration in the Cs$_4$PbX$_6$ synthesis. c Octahedral tilting/distortion without and with Mn doping (10% Mn) causing the phase stabilization of Cs$_4$Pb(Br/Cl)$_6$ structure. Electron density distribution profile derived from Maximum Entropy method for the d undoped Cs$_4$PbCl$_6$, e Cs$_4$PbCl$_6$:10% Mn, and f Cs$_4$PbCl$_6$:20% Mn, along the (010) plane. g Schematic representation of phase stabilization of Cs$_4$PbX$_6$ perovskite structure upon Mn$^{2+}$ incorporation.
the interconnected neighboring PbX$_6$ octahedra through the amine- and thiol-mediated extraction of PbBr$_2$, while the symmetry Cs$_4$Pb(Br/Cl)$_6$ upon Mn$_2$tilting (enhanced) results in the phase stabilization of low-symmetry rhombohedral Cs$_4$PbX$_6$ and high-symmetry cubic CsPbX$_3$. Therefore, enhanced octahedral tilting upon Mn substitution, result in the formation of only possible low-symmetry Cs$_4$PbX$_6$ phase; at the same time, destabilizing the cubic CsPbX$_3$ phase under Cs-rich condition. This phase stabilization of Cs$_4$PbX$_6$ via Mn substitution, might favor deeper investigation to their unexplored and intriguing properties.

**Electronic structure.** The changes in the electronic structure namely bonding nature and electron density distribution in the Cs$_4$PbCl$_6$ were analyzed with Mn incorporation via maximum entropy method (MEM) using XRD results. In the Cs$_4$PbCl$_6$, the electron density around Pb and Cl is anisotropic and highly resolved with no feature of electron sharing between Pb and Cl, resembling electrostatic attractive/repulsive forces (Fig. 1d). Upon Mn substitution a significant change in the local charge density around Pb atom was apparent, suggesting that Mn modulates the electronic structure of the 0D Cs$_4$PbBr$_6$ (Fig. 1e, f). With increasing Mn content, high electron density distribution between Pb and Cl atoms, suggests covalent bonding nature of (Pb/Mn)–Cl bonds (Supplementary Figure 6). This also supports the stronger (Pb/Mn)–Cl bonds or shorter bond lengths of Pb–Cl upon Mn doping, as observed from XRD. The change in local electron density after Mn-doping results in the lattice distortion (also evidenced from octahedral tilting, Fig. 1c) and could lead to electron-phonon (lattice) coupling and formation of polaron. Recently, the formation of polaron in the Cs$_4$PbBr$_6$ has been reported from density functional theory calculation and transient absorption measurements$^{10}$. In the present case, at variance with the undoped Cs$_4$PbX$_6$, a strong lattice distortion upon Mn incorporation could eventually enhance the electron-phonon coupling, leading to polaron formation. Therefore, it could be

| Formula | Cs$_4$Pb(Br/Cl)$_6$ | 5% Mn | 10% Mn | 20% Mn |
|---------|-------------------|-------|--------|--------|
| Space group | $I5_1c$ | $I5_1c$ | $I5_1c$ | $I5_1c$ |
| Composition | Cs$_4$PbBr$_2$Cl$_4$ | Cs$_4$Pb$_{0.95}$Mn$_{0.5}$Br$_{1.5}$Cl$_{1.5}$ | Cs$_4$Pb$_{0.9}$Mn$_{0.5}$Br$_{1.5}$Cl$_{1.5}$ | Cs$_4$Pb$_{0.8}$Mn$_{0.5}$Br$_{1.5}$Cl$_{1.5}$ |
| Wt. fraction | 87% | 94% | 100% | 92% |
| $a$/Å | 13.355(2) | 13.3465(1) | 13.3010(1) | 13.2653(2) |
| $c$/Å | 16.8135(4) | 16.8248(3) | 16.7800(3) | 16.7471(3) |
| $V$/Å$^3$ | 2597.22(6) | 2595.47(5) | 2570.94(5) | 2552.13(5) |
| $Z$ | 6 | 6 | 6 | 6 |

The number in the parentheses are the estimated standard deviation of the last significant figure.

Table 1 Structural parameters of Cs$_4$Pb(Br/Cl)$_6$ with varying concentration of Mn, calculated using the Rietveld refinement for Cs$_4$PbX$_6$. The versatility of the Cs–Pb–X ternary compounds (particularly Cs$_4$PbX$_6$ and Cs$_4$PbX$_3$) lies in their ability to interconversion via post-synthetic physical and chemical treatments. The post-synthetic conversion of cubic CsPbX$_3$ to rhombohedral Cs$_4$PbX$_6$ has been demonstrated via amine- and thiol-mediated extraction of PbBr$_2$, while the reverse conversion from Cs$_4$PbX$_6$ to Cs$_4$PbX$_3$ has been reported by the insertion of PbX$_2$, stripping of CsX, excess oleic acid, and by heat treatment (90 to 180°C). These post-synthetic conversion mechanisms are inadequate to explain the simultaneous formation of Cs$_4$PbX$_6$ and Cs$_4$PbX$_3$ phases, during synthesis. It has been demonstrated that the phase stabilization of perovskite semiconductors could be achieved by controlling the octahedral tilting via partially substituting Pb$^{2+}$ with other metal ions. For instance, substitution of smaller Mn$^{2+}$ into the cubic α-CsPbI$_3$ phase by reducing the octahedral rotation or tilting via a decrease in the bond angle of Pb–I–Pb below 180°, which is along the interconnected neighboring PbX$_6$ octahedra through the bridging halide ion. In the present case, a similar octahedral tilting (enhanced) results in the phase stabilization of low-symmetry Cs$_4$Pb(Br/Cl)$_6$ upon Mn$^{2+}$ incorporation. A decrease in the Pb–X bond length after Mn doping (10% Mn) to 2.950 Å, than undoped Cs$_4$Pb(Br/Cl)$_6$ (2.991 Å), resulted in an enhanced octahedral tilting, preventing the undesired high-symmetry cubic CsPbX$_3$ phase (Fig. 1c). Here, the octahedral tilting in the Cs$_4$PbX$_6$ (X = Br/Cl) is described based on the X–Pb–Cs$_1$ bond angle along c axis of the unit cell, which changes from 54.94° (undoped) to 54.76° upon Mn incorporation. This octahedral tilting would distort the PbX$_6$ octahedra, which subsequently lowers the symmetry of crystal structure. It is worth mentioning that only two stable compositions exist in the phase diagram of mixed CsX–PbX$_2$, under Cs-rich or Pb-deficient conditions viz., low-symmetry rhombohedral Cs$_4$PbX$_6$ and high-symmetry cubic CsPbX$_3$. Therefore, enhanced octahedral tilting upon Mn substitution, result in the formation of only possible low-symmetry Cs$_4$PbX$_6$ phase; at the same time, destabilizing the cubic Cs$_4$PbX$_3$ phase under Cs-rich condition. This phase stabilization of 0D Cs$_4$PbX$_6$ via Mn substitution, might favor deeper investigation to their unexplored and intriguing properties.
concluded that Mn$^{2+}$ incorporation modulates the electronic structure and favors the phase stabilization of Cs$_4$PbX$_6$, preventing the formation of undesirable CsPbX$_3$ impurity (Fig. 1g). Though the phase stabilization of Cs$_4$PbX$_6$ were concluded based on XRD results, this technique has its own limitation of insensitivity to detect any minor crystalline phase below 5%34. Henceforth, to further support the phase stabilization, optical characterization was exploited owing to its high sensitivity to detect even trace of fluorescent CsPbX$_3$ impurity.

The excitation and photoluminescence (PL) properties of Cs$_4$PbX$_6$ were measured in presence of Mn$^2+$ under 365 nm excitation, where X = Br/Cl and Cl, with Mn contents denoted as 0% Mn, 5% Mn, 10% Mn, and 20% Mn and the insets shows the respective samples under 365 nm UV lamp. The PL spectra presented are the PL intensities corrected using optical density. The asterisk mark denote the 3D CsPb(Br/Cl)$_3$ phases. FE-SEM images of the insets shows the respective samples under 254 nm UV lamp. The PL spectra presented are the PL intensities corrected using optical density. The lamp.

FIG. 2 Luminescent properties of Mn$^{2+}$-doped Cs$_4$PbX$_6$. a PL spectra of Mn$^{2+}$-doped Cs$_4$PbX$_6$ colloids were measured under 365 nm excitation, where X = Br/Cl and Cl, with Mn contents denoted as 0% Mn, 5% Mn, 10% Mn, and 20% Mn and the insets shows the respective samples under 365 nm UV lamp. b UV-Vis spectra of Mn$^{2+}$-doped Cs$_4$PbX$_6$ colloids. c PL spectra of Mn$^{2+}$-doped Cs$_4$PbX$_6$ colloids were measured under 290 nm excitation and the insets shows the respective samples under 254 nm UV lamp. The PL spectra presented are the PL intensities corrected using optical density. The asterisk mark denote the 3D CsPb(Br/Cl)$_3$ phases. FE-SEM images of d undoped Cs$_4$Pb(Br/Cl)$_6$ and e Cs$_4$Pb(Br/Cl)$_6$10% Mn, and f, g HR-TEM images of Cs$_4$Pb(Br/Cl)$_6$10% Mn. A lattice spacing of 0.31 nm corresponding to (131) plane of rhombohedral structure of Cs$_4$Pb(Br/Cl)$_6$.
emission corresponds to the band-edge emission of CsPbCl\(_3\) impurity\(^{12}\) and the hump ranging 450 to 480 nm is assigned to the quantum size effect of CsPbCl\(_3\). Upon Mn incorporation, a new emission at 400 nm arises from the D-state of Cs\(_4\)PbCl\(_6\), with less contribution from CsPbCl\(_3\), compared to undoped one, which completely disappeared with higher Mn (20% Mn) content (Supplementary Figure 4), reaffirming the phase stabilization of Cs\(_4\)PbX\(_6\) upon Mn incorporation.

The undoped and Mn\(^{2+}\)-doped Cs\(_4\)PbCl\(_6\) displayed blue and pinkish (combination of D-state 'blue' and Mn\(^{2+}\) 'orange') emission under 365 nm, respectively (Fig. 2a, inset). The dual UV absorption bands at 218 and 308 nm, are the characteristic features of Cs\(_4\)Pb(Br/Cl)\(_6\). The band gaps estimated from the absorption maxima are 3.83, 4.02, and 4.25 eV, for Cs\(_4\)PbBr\(_6\), Cs\(_4\)Pb(Br/Cl)\(_6\), and Cs\(_4\)PbCl\(_6\), respectively (Supplementary Figure 8a), which agrees with the earlier reports\(^{18}\). It is interesting to note the increase in Cs\(_4\)PbX\(_6\) host emission after Mn doping (Fig. 2a–c) in both mixed halide and chloride analog, similar to the perovskite nanocrystals\(^{38}\). The host emission increment is more prominent in the mixed halide (Br/Cl) analog than pure chloride, which is presumed to the passivation effect of chloride ion on the pre-existing defects of the host\(^{38}\). Therefore, Mn\(^{2+}\) doping significantly alters the competitive kinetics between the radiative and non-radiative relaxation process of the Cs\(_4\)PbX\(_6\) host.

The PL properties were investigated, by exciting at energies higher than band gap of host (290 nm), due to their strong absorption. Mn\(^{2+}\)-doped (Br/Cl) samples exhibited dual UV emissions at 372 nm and a hump at 324 nm, arising from optical 3P\(_{1,1,2} \to \) 1S\(_0\) transitions of Pb\(^{2+}\) ion\(^{35,39}\). The absorption maxima are 3.83, 4.02, and 4.25 eV, for Cs\(_4\)PbBr\(_6\), Cs\(_4\)Pb(Br/Cl)\(_6\), and Cs\(_4\)PbCl\(_6\), respectively. The dual UV absorption bands at 218 and 308 nm, are the characteristic features of Cs\(_4\)Pb(Br/Cl)\(_6\). The band gaps estimated from the absorption maxima are 3.83, 4.02, and 4.25 eV, respectively (Supplementary Figure 8a), which agrees with the earlier reports\(^{18}\). It is interesting to note the increase in Cs\(_4\)PbX\(_6\) host emission after Mn doping (Fig. 2a–c) in both mixed halide and chloride analog, similar to the perovskite nanocrystals\(^{38}\). The host emission increment is more prominent in the mixed halide (Br/Cl) analog than pure chloride, which is presumed to the passivation effect of chloride ion on the pre-existing defects of the host\(^{38}\). Therefore, Mn\(^{2+}\) doping significantly alters the competitive kinetics between the radiative and non-radiative relaxation process of the Cs\(_4\)PbX\(_6\) host.

The PL properties were investigated, by exciting at energies higher than band gap of host (290 nm), due to their strong absorption. Mn\(^{2+}\)-doped (Br/Cl) samples exhibited dual UV emissions at 372 nm and a hump at 324 nm, arising from optical 3P\(_{1,1,2} \to \) 1S\(_0\) transitions of Pb\(^{2+}\) ion\(^{35,39}\). The absorption maxima are 3.83, 4.02, and 4.25 eV, for Cs\(_4\)PbBr\(_6\), Cs\(_4\)Pb(Br/Cl)\(_6\), and Cs\(_4\)PbCl\(_6\), respectively. The dual UV absorption bands at 218 and 308 nm, are the characteristic features of Cs\(_4\)Pb(Br/Cl)\(_6\). The band gaps estimated from the absorption maxima are 3.83, 4.02, and 4.25 eV, respectively (Supplementary Figure 8a), which agrees with the earlier reports\(^{18}\). It is interesting to note the increase in Cs\(_4\)PbX\(_6\) host emission after Mn doping (Fig. 2a–c) in both mixed halide and chloride analog, similar to the perovskite nanocrystals\(^{38}\). The host emission increment is more prominent in the mixed halide (Br/Cl) analog than pure chloride, which is presumed to the passivation effect of chloride ion on the pre-existing defects of the host\(^{38}\). Therefore, Mn\(^{2+}\) doping significantly alters the competitive kinetics between the radiative and non-radiative relaxation process of the Cs\(_4\)PbX\(_6\) host. In addition, despite the unaltered Pb\(^{2+}\) emission, an enhanced Mn\(^{2+}\) emission in the mixed halides, was observed with increasing Mn concentration, due to efficient energy transfer from Pb\(^{2+}\) to Mn\(^{2+}\). The unusual red-shifted emission from 599 to 635 nm for Cs\(_4\)PbBr\(_6\):20% Mn sample, is attributed to the formation of Mn-to-Mn pairs at higher Mn concentration, which reduces the 4T\(_1\)–6A\(_{1}\) energy gap, resulting in the red shift of Mn\(^{2+}\) emission\(^{40}\). Hence, the phase stabilization of Cs\(_4\)PbX\(_6\) (X = Cl, Br/Cl) with Mn incorporation were demonstrated in the chloride-dominant system (above 60%), through XRD and optical results.

The Mn incorporation was also investigated in bromide analog (Cs\(_4\)PbBr\(_6\)) for monitoring phase stabilization via XRD and PL results (Supplementary Figures 2 and 8). With increasing Mn, the green emission (512 nm) of CsPbBr\(_3\) impurity decreased gradually, which completely disappeared above 70% Mn, suggesting the prevention of CsPbBr\(_3\) impurity in presence of Mn, agreeing with the XRD results. In the excitation wavelength range of 280 to 310 nm, the D-state emission gradually decreased, where Pb\(^{2+}\) emission remains dominant. While above 310 nm excitation, Pb\(^{2+}\) emission disappeared due to insufficient energy to excite its 3P\(_1\) levels, and only D-state is retained. Upon Mn doping, the D-state emission completely disappeared in the excitation wavelengths ranging, 280 to 310 nm, exhibiting only Pb\(^{2+}\) emission (Fig. 3b, c). The absence of D-state emission after Mn\(^{2+}\) doping is probably due to suppression of charge-transfer process from PbX\(_6\) octahedra to Pb\(^{2+}\) occupying Cs\(^{2+}\) site, primarily at high excitation energies (above 4.0 eV), where both Pb\(^{2+}\) and D-states are excited. Therefore, the presence of Mn\(^{2+}\) plays a key role in regulating the optical behavior of molecule-like isolated PbX\(_6\) octahedra in Cs\(_4\)PbX\(_6\) nanocrystals.

The energy transfer and direct excitation of 3P\(_1\) levels of Pb\(^{2+}\) (375 nm) and D-states (420 nm), were explored from excitation spectrum of 5% Mn\(^{2+}\)-doped Cs\(_4\)PbBr\(_6\):20% Mn sample, is attributed to the formation of Mn-to-Mn pairs at higher Mn concentration, which reduces the 4T\(_1\)–6A\(_{1}\) energy gap, resulting in the red shift of Mn\(^{2+}\) emission\(^{40}\). Hence, the phase stabilization of Cs\(_4\)PbX\(_6\) (X = Cl, Br/Cl) with Mn incorporation were demonstrated in the chloride-dominant system (above 60%), through XRD and optical results.

Moreover, Mn\(^{2+}\) emission is well-known to be sensitized by the host via energy transfer, where Pb\(^{2+}\) and D-state sensitizes at high and low excitation energies, respectively. Therefore, Mn\(^{2+}\) emission at varying excitation energies is determined from the absorption of the corresponding host state and efficiency of energy transfer from host states. The Mn\(^{2+}\) emission relative to the host emission (i.e., Pb\(^{2+}\) + D-state) was the highest at 280 nm, attributing to the efficient energy transfer from the Pb\(^{2+}\) state, which then gradually decreased at lower excitation energies, apart from 320 nm (Fig. 3e). Although the direct excitation of both Pb\(^{2+}\) and D-states is possible at 280 nm, Mn\(^{2+}\) is sensitized only through Pb\(^{2+}\) state, owing to the suppression of D-state in presence of Mn. The dominant Mn\(^{2+}\) emission at 320 nm...
Probing the host states at the isolated octahedron with Mn$^{2+}$ ion. Colloidal PL spectra measured at different excitation wavelengths ranging 280 to 365 nm for the a undoped Cs$_4$Pb(Br/Cl)$_6$ and b Cs$_4$Pb(Br/Cl)$_6$:5% Mn. c Emission intensities of Pb$^{2+}$ and D-state emission with varying excitation energies for the undoped and Mn-doped Cs$_4$Pb(Br/Cl)$_6$:5% Mn. d Excitation spectra of Cs$_4$Pb(Br/Cl)$_6$:5% Mn colloids by monitoring at 375 nm (Pb$^{2+}$ ion), and 420 nm (D-state). e PL intensity ratio of Mn$^{2+}$ to the host emission with respect to varying excitation energies. f PL intensity ratio of Mn$^{2+}$ to the host states with varying Mn concentration for Cs$_4$PbX$_6$ colloids, where X = (Br/Cl) and Cl. g Origin of host emissions namely Pb$^{2+}$ and D-state under high excitation energies, without and with Mn doping at high excitation energies. The solid, dashed, and curved arrows are denoted for optical excitation, emission, and energy transfer processes, respectively. h Strength of energy transfer from the host states namely Pb$^{2+}$ and D-state to the Mn$^{2+}$ emission are depicted. The upward, downward, and curved arrows are denoted for the optical excitation, emission, and energy transfer processes, respectively.

excitation, ascribed to the Mn$^{2+}$ sensitization from both D-state and partially from Pb$^{2+}$ ion. In addition, energy transfer from Pb$^{2+}$ to Mn$^{2+}$ was more efficient than from D-state (Fig. 3f, Supplementary Figure 10, and Supplementary Note 7). Moreover, the presence of Mn$^{2+}$ considerably suppresses the D-state emission by blocking the charge-transfer process from isolated octahedra to the D-state, especially at high excitation energies (about 4.3 eV, 280 nm excitation), where both the D-state and Pb$^{2+}$ could be directly excited (Fig. 3g). This may be caused by the weak coupling between electronically decoupled (Pb/Mn)$_6$ octahedra and D-state (Pb$^{2+}$ at Cs site) which deteriorates the charge transfer between them, due to strong Mn–Cl bond formation. The sensitization of Mn$^{2+}$ is predominantly occurs from Pb$^{2+}$ than the D-state, due to larger energy difference between Mn$^{2+}$ and Pb$^{2+}$ states (Fig. 3h). Moreover, the efficient energy transfer from Mn$^{2+}$ dopant in the wide band gap host, due to large energy difference between host and Mn$^{2+}$ levels, is well documented. The above results demonstrate that the Mn$^{2+}$ incorporation significantly affects the optical properties of host state in Cs$_4$PbX$_6$ nanocrystals.
Luminescence efficiency. The potential application of perovskite-like Cs$_4$PbX$_6$ as emitting layer in color-converting devices has been explored in colloidal and solid forms (thin films and powders) and is expected to have high conversion efficiency similar to other color converter viz. phosphor. High PL QY has been reported in perovskite colloids by employing ligands to stabilize the nanocrystals, and thin films (solids) of micron-sized grains. Here, although PL QY of undoped Cs$_4$Pb(Br/Cl)$_6$ nanocrystal is low (5%), the overall QY substantially increased to 32% upon Mn$^{2+}$ doping, under 365 nm excitation (Table 2, Supplementary Figure 11a, and Supplementary Note 8). Highest PL QY of 29% was obtained for Cs$_4$Pb(Br/Cl)$_6$10% Mn and Cs$_4$PbCl$_6$:10% Mn (Table 2), which is among the best values reported for Mn$^{2+}$ emission (Supplementary Table 8). Mn$^{2+}$ luminescence was the highest at lower (365 nm) and higher excitation energy (290 nm), for Cs$_4$Pb(Br/Cl)$_6$ and Cs$_4$PbCl$_6$, respectively, due to their suitable band gaps (determined by halide species), enabling efficient energy transfer to Mn$^{2+}$. The overall superior PL QY of Mn$^{2+}$-doped Cs$_4$PbX$_6$ colloids (X = Br/Cl, Cl) is attributed to the spatially confined zero-dimensional structure, and presence of dopant at the isolated octahedra favoring enhanced dopant emission through the localized excitons and high exciton binding energy (Supplementary Figure 11b to 11e). The reported exciton binding energies of Cs$_4$PbBr$_6$ and Cs$_4$PbCl$_6$ are 353 and 153 eV, respectively, compared to CsPbBr$_3$ (19 to 62 meV) and CsPbCl$_3$ (72 meV). These results suggest that the high luminescent Cs$_4$PbX$_6$ nanocrystals doped with Mn$^{2+}$ could represent promising emitting materials for efficient solid-state lighting applications.

In the Cs$_4$PbX$_6$ solids, a similar low PL QY was observed for undoped sample, but the overall PL QY increased markedly upon Mn doping in both mixed halide and chloride samples (Supplementary Figure 11e). PL QY of 21% was obtained for Mn$^{2+}$ emission in Cs$_4$PbCl$_6$ solids, under 290 nm excitation (Supplementary Table 9). The bright orange emission of Mn$^{2+}$-doped Cs$_4$PbX$_6$ in their solid form, is a unique feature among Mn$^{2+}$-doped perovskite solids (Fig. 4c). This remarkable PL QY and retention of dopant emission in solid form is the attributes of spatial confinement of the nanocrystals.

Table 2 PL quantum yield of the Cs$_4$PbX$_6$ colloids in n-octane medium

| Sample                   | $\lambda_{ex}$ (nm) | total QY (%) | QY (%) | Host emission (%) | Mn$^{2+}$ emission (%) |
|--------------------------|---------------------|--------------|--------|-------------------|------------------------|
| Cs$_4$PbBr$_6$           | 365                 | 60%          |        | 60                | 0                      |
| Cs$_4$Pb(Br/Cl)$_6$      | 365                 | 5%           |        | 5                 | 0                      |
| Cs$_4$Pb(Br/Cl)$_6$:5% Mn| 365                 | 32%          |        | 3                 | 27                     |
| Cs$_4$Pb(Br/Cl)$_6$:10% Mn| 365               | 23%          |        | 2                 | 21                     |
| Cs$_4$PbCl$_6$           | 290                 | 6%           |        | 6                 | 0                      |
| Cs$_4$PbCl$_6$:10% Mn    | 290                 | 32%          |        | 5                 | 27                     |
| Cs$_4$PbCl$_6$           | 365                 | 2%           |        | 2                 | 0                      |
| Cs$_4$PbCl$_6$:10% Mn    | 365                 | 15%          |        | 6                 | 9                      |

Fig. 4 Lifetime of Mn$^{2+}$-doped Cs$_4$PbX$_6$. Time-resolved PL spectra of Cs$_4$Pb(Br/Cl)$_6$ colloids excited at 375 nm and monitoring the D-state and Mn$^{2+}$ emission at 420 and 600 nm, respectively. c Images of Cs$_4$PbX$_6$ perovskite solids under 254 and 365 nm UV lamp, which are denoted by their respective halides and Mn concentrations.
confinement of low-dimensional Cs₄PbX₆ induced by isolated octahedra, eventually favoring a stable dopant emission in solids.

To further elucidate the emission properties of Cs₄PbX₆ host and Mn²⁺, time-resolved PL results were performed by monitoring the D-state (420 nm) and Mn²⁺ emission (600 nm), exciting at 375 nm (Fig. 4a, b, Supplementary Figures 12 to 14, and Supplementary Note 9). A nominal decrease in the average lifetime of D-state emission in Cs₄PbX₆ (X = Br/Cl and Cl) was observed with increasing Mn content (Supplementary Figure 13). For instance, the average lifetime of D-state decreased from 1.08 ns (undoped) to 0.82 ns (20% Mn), corroborating the Mn²⁺ sensitization by the Cs₄Pb(Br/Cl)₆ host (Table 3). A long lifetime was obtained for the Mn²⁺ emission in Cs₄Pb(Br/Cl)₆ and Cs₄PbCl₆ of 1.20 ms and 1.39 ms, respectively (Fig. 4b and Supplementary Figure 13b). The lifetime of D-states of Cs₄Pb(Br/Cl)₆ converged with three components namely 3.7 (slow), 2.6, and 0.40 ns (last two combined is fast), similar to the previous report. The first slow (radiative) component is assigned to D-state emission and the fast (non-radiative) component to the energy transfer process to Mn²⁺. A rise in the contribution of slow component with increasing Mn²⁺ content, agrees with the increase in D-state emission (Supplementary Figure 12). This suggests that the inclusion of chlorine species with Mn-doping (MnCl₂ precursor), passivates the pre-existing defects in the Cs₄Pb(Br/Cl)₆ host, resulting to an enhanced host PL efficiency. Hence, the passivation effect of chlorine in the Cs₄Pb(Br/Cl)₆ would contribute greatly to the PL efficiency of D-state rather than energy transfer to Mn²⁺ at 375 nm excitation. On the contrary, superior contribution of fast component in Cs₄PbCl₆,

illustrates the dominant energy transfer from D-state to Mn²⁺ (Supplementary Figures 13 and 14) at 375 nm excitation. The chloride passivation effect in the Cs₄PbCl₆ may be negligible as chloride content remain unchanged with increasing dopant concentration. Therefore, the D-state emission in mixed halide Cs₄Pb(Br/Cl)₆ is predominated by the passivation effect of chlorine over energy transfer to Mn²⁺, while in the Cs₄PbCl₆, energy transfer to Mn²⁺ dominated over passivation effect.

The mechanism of energy transfer from host states (Pb²⁺ and D-state) to Mn²⁺ in the mixed halide perovskite is further illustrated in the Fig. 5. The high PL QY of Mn²⁺-doped Cs₄PbX₆ is the attributes of structure-induced quantum confinement with high exciton binding energy favoring enhanced emission, compared to 3D CsPbX₃ perovskite (Fig. 5a). The superior PL QY of Mn²⁺-doped Cs₄Pb(Br/Cl)₆ and Cs₄PbCl₆ were observed at low (365 nm) and high excitation energy (290 nm), due to high absorption in their respective band gaps arising from halide identity. The Pb²⁺ ions are excited at high excitation energies (above 4.0 eV), leading to 375 nm emission, while D-states are excited at low excitation energies (below 4.0 eV), and both these states eventually generate Mn²⁺ emission through energy transfer (Fig. 5b). The presence of Mn²⁺ suppresses the charge transfer from isolated octahedra to the D-state, due to the weak coupling with the regular crystal lattice sites particularly at higher excitation energy. The enhanced overall PL QY of Mn²⁺-doped Cs₄PbX₆ in both colloidal and solid form is attributed to the synergistic effect of structural quantum confinement effect from the isolated octahedra and high exciton binding energies, facilitating dopant emission through enhanced energy transfer process.

### Table 3

| Mn content (%) | Average lifetime of D-state emission (ns) |
|----------------|------------------------------------------|
|                | Cs₄Pb(Br/Cl)₆ | Cs₄PbCl₆ |
| 0              | 1.08          | 1.47     |
| 5              | 1.00          | 0.44     |
| 10             | 0.85          | 2.50     |
| 20             | 0.82          | 0.32     |

**Discussion**

In conclusion, we rationalized the exceptional optical behavior of isolated octahedra in the zero-dimensional cesium lead halide structure by introducing Mn²⁺ dopants. Structural, PL, and lifetime results confirmed the incorporation of Mn²⁺ in the OD Cs₄PbX₆ lattice. The Mn²⁺ incorporation stabilized the Cs₄PbX₆ structure via enhanced octahedral tilting and limited compositional variation of Cs–Pb salts, suppressing the formation of CsPbX₃ impurity phase. The PL QY at a given excitation energy was determined by the energy transfer from the host states to Mn²⁺ and band gap of the host. A high PL QY for Mn²⁺...
emission was achieved in the colloidal (29%) and solid (21%, powder) forms; making the solid form of Cs$_4$PbX$_6$ as a promising emissive layer for light-emitting devices. The enhanced PL QY of the Mn$^{2+}$ emission was attributed to the synergistic effect of structure-induced spatial confinement of 0D Cs$_4$PbX$_6$ and electronically decoupled PbX$_6$ octahedra favoring dopant emission via localized exciton. The present work provides deep insight into the structural and molecular behavior of 0D perovskite-like Cs$_4$PbX$_6$ material and opens an avenue to design low-dimensional perovskites with photo and chemical stability for high-performance optoelectronic applications.

**Methods**

**Materials**

All the reagents were used without any purification. Cesium carbonate (Cs$_2$CO$_3$, 99.999% Kojundo), lead (II) bromide (PbBr$_2$, 99%, Sigma-Aldrich), lead (II) chloride (PbCl$_2$, 98%, Sigma-Aldrich), manganese (II) bromide (MnBr$_2$, 98%, Sigma-Aldrich) manganese (II) chloride tetrahydrate (MnCl$_2$, 4H$_2$O, 99%, Sigma-Aldrich), oleic acid (OA, 90%, Fluka), octylamine (OA, 97%, Sigma-Aldrich), N,N-dimethylformamide (DMF, 99.8%, Sigma-Aldrich), n-hexane (99.8%, Junsei, Japan), n-octane (98%, Sigma-Aldrich), 1-octadecene (95%, Sigma-Aldrich), hydrochloric acid (37%, Sigma-Aldrich), and hydrobromic acid (48%, Sigma-Aldrich) were employed for the synthesis.

**Synthesis of undoped and Mn$^{2+}$-doped Cs$_4$Pb(BO$_3$)$_6$ colloids.** The exact compositions of the synthesized undoped and Mn$^{2+}$-doped Cs$_4$Pb(BO$_3$)$_6$ series are Cs$_4$PbBr$_2$Cl$_4$ and Cs$_4$Pb$_{1-x}$Mn$_x$Br$_{2-2x}$Cl$_{1+2x}$, with $x = 0.05$ (5% Mn), 0.10 (10% Mn), and 0.20 (20% Mn), respectively. Mn$^{2+}$-doped Cs$_4$Pb(BO$_3$)$_6$ nanocrystals were synthesized by a reverse microemulsion method at room temperature, as reported earlier. PbBr$_2$ precursor was used as the lead precursor. A simultaneous anion (Cl$^-$) and cation (Mn$^{2+}$) inclusion were effected by employing MnCl$_2$, 4H$_2$O precursor for the synthesis of Mn$^{2+}$-doped Cs$_4$Pb(BO$_3$)$_6$. An optimal concentration of octylamine (OA) and oleic acid (OA) surfactants were used in facilitating the solubilization of Cs, Pb, and Mn precursors. The mixed MnCl$_2$, 4H$_2$O and PbBr$_2$ precursors, and the Cs-oleate precursor were synthesized separately. First, a mixture of 2.25 g of Cs$_2$CO$_3$ and 21.5 mL of OA was stirred and degassed at 130 °C, which is further maintained under vacuum for 1 h to generate a yellowish stock of Cs-oleate precursor. Second, 0.2 mL Cs-oleate precursor, 10 mL of n-hexane, 5 mL of OA were loaded into a 50-mL three-neck flask, followed by mild degassing (vacuum) for 5 min and Argon purging for 5 min. Third, a mixture of PbBr$_2$ and MnCl$_2$, 4H$_2$O (DMF, 1 mL), HCl (38 wt%, 19 mL), 0.10 mL OA, and 0.05 mL OA was swiftly injected into the flask, under vigorous stirring. Upon stirring for 10 min, white color crystals were formed, suggesting the formation of Mn$^{2+}$-doped Cs$_4$Pb(BO$_3$)$_6$. The as-synthesized nanocrystals were collected via centrifugation at 7000 rpm for 5 min followed by dispersion in 2 mL of n-octane for further characterization. The contents of Cs$_4$Pb(BO$_3$)$_6$ solids were pure white for the Cs$_4$PbCl$_6$, Cs$_4$PbCl$_6$Mn, and Cs$_4$Pb(Br$_2$Cl$_3$)$_{Mn}$, except Cs$_4$Pb(Br$_2$Cl$_3$) (pale greenish white), and Cs$_4$PbBr$_6$ (bright yellow).

**Synthesis of zero-dimensional Cs$_4$PbX$_6$ solids.** The as obtained colloidal samples dispersed in n-octane were centrifuged and re-dispersed in tert-butanol and hexane for further characterization. The samples were then dried overnight to get respective Cs$_4$PbX$_6$ solids. The body color of the zero-dimensional solids were pure white for the Cs$_4$PbCl$_6$, Cs$_4$PbCl$_6$Mn, and Cs$_4$Pb(Br$_2$Cl$_3$)$_{Mn}$ except Cs$_4$Pb(Br$_2$Cl$_3$) (pale greenish white), and Cs$_4$PbBr$_6$ (bright yellow).

**Characterization.** The synthesized zero-dimensional Cs$_4$PbX$_6$ nanocrystals were characterized by powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), electron spin resonance spectra (ESR), inductive coupled plasma-mass emission spectroscopy (ICP-OES), field-emission scanning electron microscope (FE-SEM), and high-resolution tunneling electron microscope (HR-TEM). The XRD was performed using a Philips X’Pert diffractometer with Cu Ka radiation, in the range of 10° to 120° with a step size of 0.026° with the synthesized powders. The structural information was derived from Rietveld refinement using the General Structure Analysis System (GSAS) software suite. The VESTA program was used to draw the crystal structure. The phase fractions of multiple phases were estimated using Rietveld refinement of XRD results considering full refinement of crystallographic and instrumental parameters as implemented in the GSAS program suite. The FE-SEM and HR-TEM images were recorded using a Hitachi S-4700 and FEI Tecnai F20 (200 kV), respectively, at Korea Basic Science Institute (KBSI), Gwangju, South Korea. The sample for TEM measurements were prepared by dispersing the nanocrystals in the ethanol medium. It is to be noted that the undoped and Mn$^{2+}$-doped Cs$_4$PbX$_6$ perovskite were unstable upon exposure to high-energy electron beam and tend to damage within short period of time. XPS was performed on the powder samples using VG Multilab 2000 instruments to identify the chemical state of the elements on the sample surface (below 10 nm), employing Al Kα as the X-ray source. The energy of the X-ray source (Al Kα) is 1480 eV with a line width of 0.5 eV. The chemical compositions of the synthesized samples were analyzed using ICP-OES (Perkin-Elmer, OPTIMA 8300), at KBSI, Gwangju, South Korea. ESR measurement was carried out using JEOL JES-FA200 with an X-band microwave frequency of 9.7 GHz, and field sweep from 0 to 100 mT. The liquid samples were taken in an ESR tube and frozen in liquid nitrogen at 173 K. All the spectra were recorded using the following ESR parameters: microwave power, 1 mW; modulation amplitude, 0.2 mT; modulation frequency, 100 kHz; and sweep time, 120 s.

Phololuminescence was measured using a Hitachi F-4500 fluorescence spectrophotometer over the wavelength range of 200 to 750 nm, using n-octane dispersions in a 1×1 cm quartz cuvette. UV-vis spectra were obtained using Optizen POP UV/Vs spectrophotometer. The lifetime was measured using a time-correlated single photon counting (TCSPC) system on FL920 Edinburgh instruments at Korean Advanced Institute of Science and Technology (KAIST), South Korea. Pulsed laser irradiation with 300 nm was used as the excitation source. Internal quantum efficiency was measured with 365 and 290 nm excitation using a xenon laser (Hamamatsu C9290-02) at the Korea Photonics Technology Institute (KOPTI), South Korea. Time-resolved photoluminescence measurement for Mn$^{2+}$ (600 nm) and Cs$_4$PbX$_6$ (420 nm) were recorded with a single 10 ns pulse at 1777 GHz, and Cs$_4$PbX$_6$ was excited using a single-mode pulsed diode laser as the excitation source (λmax = 375 nm) at Korea Basic Science Institute (KBSI), Daeje, South Korea.

Data availability

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

Received: 4 April 2018 Accepted: 16 October 2018

Published online: 08 November 2018

**References**

1. Profesescu, 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).

2. Huang, H., Bodnarchuk, M. I., Kershaw, S. V., Kovalenko, M. V. & Rogach, A. L. Lead halide perovskite nanocrystals in the research spotlight: stability and defect tolerance. ACS Energy Lett. 2, 2071–2083 (2017).

3. Saidaminov, M. I. et al. Pure Cs$_4$PbBr$_6$: highly luminescent zero-dimensional perovskite solids. ACS Energy Lett. 3, 2071–2083 (2017).

4. Yang, X. et al. Efficient green light-emitting diodes based on quasi-two-dimensional composition and phase engineered perovskite with surface passivation. Nat. Commun. 9, 570 (2018).

5. Saidaminov, M. I., Mohammed, O. F. & Bakr, O. M. Low-dimensional metal halide perovskites: the next big thing. ACS Energy Lett. 2, 889–896 (2017).

6. Bakr, O. M. & Mohammed, O. F. Powering up perovskite photovoltaics. Science 355, 1260–1261 (2017).
Ahmed, G. H. et al. Pyridine-induced dimensionality change in hybrid perovskite nanocrystals. Chem. Mater. 29, 4393–4400 (2017).

Akkerman, Q. A., Møgelfjord, D., De Angelis, F. & Manna, L. Fluorescent alloy CaPbMn$_3$I$_5$ perovskite nanocrystals with high structural and optical stability. ACS Energy Lett. 2, 2183–2186 (2017).

Meinardi, F. et al. Doped halide perovskite nanocrystals for reabsorption-free luminescent solar concentrators. ACS Energy Lett. 2, 3496–3503 (2016).

Yin, J. et al. Molecular behavior of zero-dimensional perovskites. Sci. Adv. 3, e1701793 (2017).

Andrews, R. H., Clark, S. J., Donaldson, J. D., Dewan, J. C., & Silver, J. Solid-state properties of materials of the type CaPb$_x$M$_{3-x}$X$_5$ (where M = Sn or Pb and X = Cl or Br). J. Chem. Soc. Dalton Trans. 767–770 (1983).

Nikl, M., Hmieloš, M. & Nitsch, K. Photoluminescence & decay kinetics of CaPb$_x$Pb$_{3-x}$ single crystals. Solid State Commun. 84, 1089–1092 (1992).

Nikl, M. et al. Photoluminescence of CsPbBr$_x$ crystals and thin films. Chem. Phys. Lett. 306, 280–284 (1999).

Kondo, S. et al. Fundamental optical absorption of CaPb$_x$Pb$_{3-x}$, Solid State Commun. 120, 141–144 (2001).

Yin, J. et al. Localized optical absorption in CaPb$_x$Br$_{3-x}$. J. Phys. Condens. Matter 14, 2093–2099 (2002).

Chen, D., Wan, Z., Chen, X., Yuan, Y. & Zhong, J. Large-scale room-temperature synthesis and optical properties of perovskite-related CaPb$_x$Br$_{3-x}$ fluorophores. J. Mater. Chem. C. 4, 10646–10653 (2016).

Li, X. et al. All inorganic halide perovskite nanosystem: synthesis, structural features, optical properties and optoelectronic applications. Small 13, 1603996 (2017).

Kakerna, Q. A. et al. Nearly monodisperse ionizer CaPb$_x$X$_3$(X = Cl, Br, I) nanocrystals, their mixed halide compositions, and their transformation into CsPb$_x$X$_3$ nanocrystals. Nano Lett. 17, 1924–1930 (2017).

Yin, J. et al. Intrinsic lead ion emissions in zero-dimensional CsPb$_x$Br$_{3-x}$ nanocrystals. ACS Energy Lett. 2, 2805–2811 (2017).

Zhang, Y. et al. Zero-dimensional CsPb$_x$Br$_{3-x}$ perovskite nanocrystals. J. Phys. Chem. Lett. 8, 961–965 (2017).

De Bastiani, M. et al. Inside perovskites: quantum luminescence from bulk CaPb$_x$Br$_{3-x}$ single crystals. Chem. Mater. 29, 7108–7113 (2017).

Miri, W. J., Jagadeeswararao, M., Das, S. & Nag, A. Colloidal Mn-doped cesium lead halide perovskite nanoplatelets. ACS Energy Lett. 2, 537–543 (2017).

Arunkumar, P. et al. Colloidal organolead halide perovskite with a high Mn solubility limit: a step toward Pb-free luminescent quantum dots. J. Phys. Chem. Lett. 8, 4161–4166 (2017).

Velasquez, M. et al. Growth and characterization of pure and Pr$_{3+}$-doped CaPb$_x$Br$_{3-x}$ crystals. J. Cryst. Growth 310, 5458–5463 (2008).

Moller, C. K. Crystal structure and photoconductivity of cesium plumbohalides. Nature 182, 1436–1436 (1958).

Luo, Y., & Kerr, J. Bond dissociation energies. CRC Handb. Chem. Phys. 89, 99 (2012).

Zhang, X. et al. Hybrid perovskite light-emitting diodes based on perovskite nanocrystals with organic–inorganic mixed cations. Adv. Mater. 29, 1606405 (2017).

Lindblad, R. et al. Electronic structure of CH$_3$NH$_3$PbX$_3$ perovskites: dependence on the halide moiety. J. Phys. Chem. C. 119, 1818–1825 (2015).

Palazon, F. et al. Changing the dimensionality of cesium lead bromide nanocrystals by reversible post-synthesis transformations with amines. Chem. Mater. 29, 4167–4171 (2017).

Liu, Z. et al. Ligand mediated transformation of cesium lead bromide perovskite nanocrystals to lead depleted CsPb$_x$Br$_{3-x}$ nanocrystals. J. Am. Chem. Soc. 139, 5309–5312 (2017).

Swarnkar, A., Mir, W. J. & Nag, A. Can B-site doping or alloying improve thermal- and phase-stability of all-inorganic CaPb$_x$X$_3$(X = Cl, Br, I) perovskites? ACS Energy Lett. 3, 286–289 (2018).

Nitsch, K. et al. Growth and characterization of crystals of incongruently melting ternary alkali lead chlorides. Phys. Status Solidi A 135, 565–571 (1993).

Schlenker, C., Dumas, J., Greenblatt, M., & van Smaalen, S. Physics and Chemistry of Low-Dimensional Inorganic Conductors (Plenum press, New York, 1996).

Newman, J. & et al. Parts per million powder X-ray diffraction. Anal. Chem. 87, 10950–10955 (2015).

Folkerts, H. F., Ghiani, F. & Blasse, G. Search for D-level emission of Pb$^{2+}$ in alkaline-earth amalgamates and gallates. J. Phys. Chem. Solids 57, 1639–1645 (1996).

Das Adhikari, S., Dutta, S. K., Dutta, A., Guria, A. K. & Pradhan, N. Chemically tailoring the dopant emission in manganese-doped CsPb$_x$Br$_{3-x}$ perovskite nanocrystals. Angew. Chem. Int. Ed. 56, 8746–8750 (2017).

Chen, W. et al. Crystal field, phonon coupling and emission shift of Mn$^{3+}$ in Zn$_x$Cd$_{1-x}$S nanocrystals. J. Phys. Chem. 99, 1120–1129 (2001).

Parobek, D. et al. Exciton-to-dopant energy transfer in Mn-doped cesium lead halide perovskite nanocrystals. Nano Lett. 16, 7376–7380 (2016).