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Lead-free perovskites and their analogues have been extensively studied as a class of next-generation luminescent and optoelectronic materials. Herein, we report a new synthesis of colloidal $Cs_4M(II)Bi_2Cl_{12}$ (M(II) = Cd, Mn) nanocrystals (NCs) with unique luminescent properties. The obtained $Cs_4M(II)Bi_2Cl_{12}$ NCs show a layered double perovskite (LDP) crystal structure with good particle stability. Density functional theory calculations show that both samples exhibit a wide, direct band gap feature. Remarkably, the strong Mn-Mn coupling effect of the $Cs_4M(II)Bi_2Cl_{12}$ NCs results in an ultra-short Mn photoluminescence (PL) decay lifetime of around 10 µs, around two orders of magnitude faster than commonly observed Mn^{2+} dopant emission in NCs. Diluting the Mn^{2+} ion concentration through forming $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ ($0 < x < 1$) alloyed LDP NCs leads to prolonged PL lifetimes and enhanced PL quantum yields. Our study provides the first synthetic example of Bi-based LDP colloidal NCs with potentials for serving as a new category of stable lead-free perovskite-type materials for various applications.

Introduction

Owing to the advantageous optical and optoelectronic properties, lead-halide perovskites (ABX_3, A = methylammonium or MA, Cs, Rb, etc., B = Pb, X = Cl, Br, I) have been intensively investigated and triggered a range of their applications in the past decade.[1-13] However, the inclusion of the toxic lead element and the intrinsic instability of lead-halide perovskites have set obstacles for the implementation of such materials into a wide practice of applications.[14-16] To overcome these drawbacks, searching for possible lead-free perovskites has emerged as an important research subject and have drawn increased amount of attention in recent years.[17-21] To date, various lead-free perovskites and perovskite-analogues have been demonstrated including three dimensional (3D) double perovskites,[22-25] 2D Ruddlesden-Popper phase,[26, 27] Dion-Jacobson phase,[28] and other types of 2D perovskites,[29, 30] 0D perovskites,[31-33] vacancy-ordered perovskites,[34, 35] and other structures.[36, 37] In particular, lead-free perovskite analogues (LFPAs) refer to lead-free materials that possess characteristic structural motifs of perovskites, *i.e.,* perfect or distorted metal-halide octahedral units, yet do not strictly corner share these units in a cubic framework.[38] Consequently, the LFPAs often exhibit crystal structures with reduced symmetries and low dimensionalities which are determined by the manner of geometric connectivity of their metal-halide octahedral constituents.[39-41] In addition, given the enlarged compositional space, as well as the structural diversity and versatility of LFPAs, tuning the composition and/or crystal phase of the LFPAs through either direct synthesis or transformation post-synthesis has been demonstrated successfully in multiple systems.[32, 42, 43] Such controllable tuning in materials' composition and thus crystal structure has been validated as a unique and efficient means to manipulate the properties, especially the optoelectronic properties of the LFPA materials, rendering them an ideal platform for acquiring in-depth understandings of the composition-structure-property relationship of perovskite-type materials.

Very recently, a new class of LFPAs, *i.e.*, vacancy-ordered layered double perovskites (LDPs), has been theoretically predicted and experimentally obtained.[35, 44-54] LDPs with a chemical formula of $A_4M(II)M(III)_2X_{12}$ possess a unique crystal structure with a layer of divalent metal (*e.g.,* M(II) = Cu, Mn, Cd) halide octahedra (*i.e.,* $[M(II)X_6]^{4-}$), sandwiched between two layers of trivalent metal (*e.g.,* M(III) = Sb, Bi) halide octahedra (*i.e.,* $[M(III)X_6]^{3-}$) (**Figure 1a**).[52] The overall tri-layer motifs are separated by top and bottom vacancy layers along the [001] crystal direction of the LDP (**Figure 1a**).[44] The LDPs possess many unique properties compared to other LFPAs, such as direct band gap, improved material stability, rapid and steady photoelectrochemical response, inter- or intra-layer magnetic ordering, p-type conductivity, *etc.*.[44, 45, 48, 52] To date, several LDPs have been synthesized in powder or single crystal forms, including $Cs_4M(II)Sb_2Cl_{12}$ (M(II) = Cu, Mn, Cd), $Rb_4M(II)Sb_2Cl_{12}$ (M(II) = Cu, Mn), and $Cs_4M(II)Bi_2Cl_{12}$, (M(II) = Mn, Cd).[32, 35, 44, 47-49, 55-57] Examples of bringing such materials down to the nanoscale have been extremely rare. So far, only two examples have been demonstrated, both of which are in the Cu/Sb-based systems.[47, 48] Kuang *et al.* demonstrated a fabrication of

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$Cs_4CuSb_2Cl_{12}$ nanocrystals (NCs) using a top-down ultrasonic exfoliation technique, resulting in LDP NCs with reduced effective masses of the photogenerated carriers.[47] Very recently, we reported the first demonstration of colloidal synthesis of $Cs_4CuSb_2Cl_{12}$ NCs with a direct band gap of 1.79 eV. Furthermore, an intriguing crystal phase transformation may induce intriguing indirect-to-direct bandgap transition of these LDPs, which has been explored through adjusting the stoichiometry ratio of Cu and Ag components in the $Cs_4Cu_xAg_{(2-2x)}Sb_2Cl_{12}$ NCs.[48]

Herein, we report the first colloidal synthesis of Bi-based LDP NCs using a hot-injection method. Two types of LDP NCs, *i.e.*, $Cs_4MnBi_2Cl_{12}$ and $Cs_4CdBi_2Cl_{12}$ NCs, have been successfully synthesized. Density functional theory (DFT) calculations revealed that both samples possess a direct band gap with a large band gap energy, consistent with the experimental results. Moreover, we found that the close vicinity of Mn^{2+} ion centers in $Cs_4MnBi_2Cl_{12}$ NCs induced a strong Mn-Mn coupling, which led to an ultra-short photoluminescence (PL) lifetime and a low PL quantum yield (QY). To control the extent of this strong inter-Mn coupling, we have synthesized a series of $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ cationic alloyed LDP NCs, aiming to dilute the Mn^{2+} ion concentration. The resulting alloyed LDP NCs showed a reduction of Mn-Mn coupling interaction evidenced by prolonged PL lifetimes and drastically enhanced PL QYs. Our results provide insights into the structure-property relationship of the Cd- and Mn-containing Bi-based LDP NCs, which hold potentials for future implementation as a new category of optical and optoelectronic materials in a range of applications.

Results and Discussion

Synthesis of $Cs_4M(II)Bi_2Cl_{12}$ (M(II) = Cd, Mn) LDP NCs

Lead-free $Cs_4M(II)Bi_2Cl_{12}$ (M(II) = Cd, Mn) LDP NCs were synthesized using a hot-injection method (see details in SI).[58] Briefly, cesium carbonate, bismuth acetate, and cadmium acetate (or manganese acetate) were mixed in 1-octadecene. Oleic acid and oleylamine with a volume ratio of 3:1 were added to the mixture as the capping ligands. The mixture was then degassed under vacuum to remove water and oxygen. At 170 °C, benzoyl chloride was injected into the mixture to trigger the nucleation and growth of the NCs. The resultant LDP NCs can be isolated from 1-octadecene by adding isopropanol and further dispersed in non-polar solvents such as toluene.

The trigonal LDP crystal structure with a general formula of $A_4M(II)Bi_2X_{12}$ is derived from the conventional cubic ABX_3 perovskite structure. In short, by replacing the B cations in each (111) crystal plane of the cubic perovskite with a metal ion (either M^{2+} or Bi^{3+}) or a vacancy (V), while keeping the A and X sublattices intact, an alternating Bi-M-Bi-V pattern along the [001] direction (the original [111] direction of the cubic lattice) of the LDP crystal structure (a trigonal phase) can be formed (**Figure 1a**). X-ray diffraction (XRD) patterns of the two samples (*i.e.,* $Cs_4CdBi_2Cl_{12}$ and $Cs_4MnBi_2Cl_{12}$ NCs) unambiguously show a trigonal LDP crystal structure (space group: $R\overline{3}m$) with all the Bragg diffraction peaks matching well with the simulated standard peaks (**Figure 1b, c**). A set of characteristic triple peaks in the 2θ region of 27° – 30° can be assigned to the (116), (204) and (205) crystal planes of the LDP structure (**Figure 1b, c**). The lattice parameters of $a = b = 7.574$ Å , $c = 37.36$ Å, and $a = b = 7.542$ Å, $c = 37.16$ Å, were obtained through fitting the XRD patterns for the $Cs_4CdBi_2Cl_{12}$ and $Cs_4MnBi_2Cl_{12}$ LDP NCs, respectively (Figure S1, S2 and Table S1, S2). The slightly larger lattice constant of $Cs_4CdBi_2Cl_{12}$ compared with $Cs_4MnBi_2Cl_{12}$ is ascribed to the larger ionic radius of Cd^{2+} (95 pm) than Mn^{2+} (83 pm).[59] Broadening effect of all the Bragg diffraction peaks indicated finite crystal domain sizes on the nanometer scale (Table S1, S2). Consistently, transmission electron microscopy (TEM) images of the $Cs_4M(II)Bi_2Cl_{12}$ NCs show a sphere-like shape with average diameters of 11.8 ± 2.5 nm (for the Cd-containing case) and 11.6 ± 2.1 nm (for the Mn-containing case)

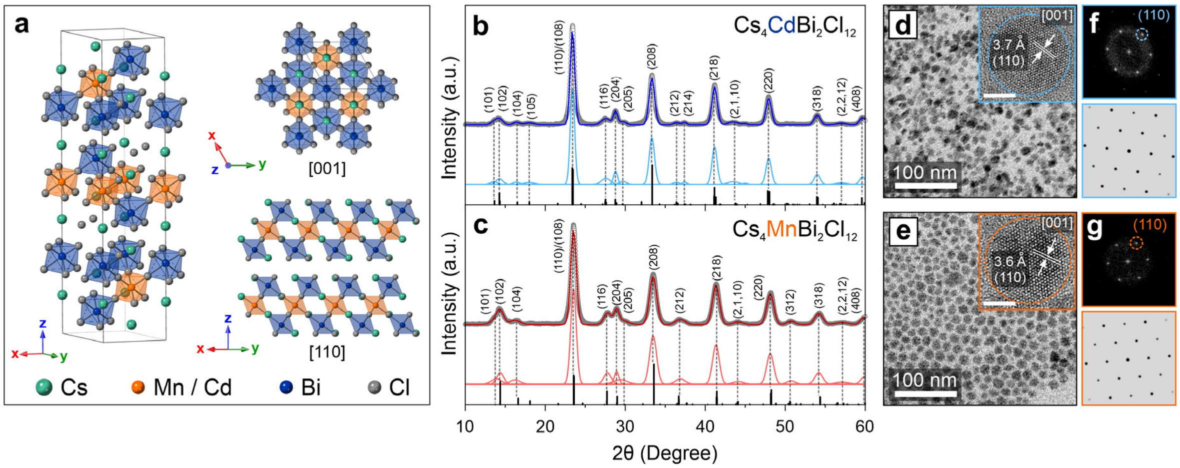

Figure 1. **(a)** Schematic illustration of the crystal structure of $Cs_4M(II)Bi_2Cl_{12}$, M(II) = Cd or Mn. Left: a unit cell of trigonal LDP; right: the crystal lattices viewed from [001] (top) and [110] (bottom) zone axes. **(b, c)** XRD patterns (grey circles) of the $Cs_4CdBi_2Cl_{12}$ (b) and $Cs_4MnBi_2Cl_{12}$ (c) NCs, fitted curves (blue and red lines) and constituent peaks (cyan and orange lines). Black bars represent the calculated diffraction peak positions. **(d, e)** TEM images of $Cs_4CdBi_2Cl_{12}$ (d) and $Cs_4MnBi_2Cl_{12}$ (e) NCs. Inset: high resolution (HR) TEM images, scale bar = 5 nm. **(f, g)** Fast Fourier transform (FFT) patterns of the corresponding HR TEM images (top) and the simulated electron diffraction patterns viewed from [001] zone axis (bottom).

(**Figure 1d, e**). The displayed *d*-spacings of 3.7 Å and 3.6 Å in the hexagonal lattice fringes for $Cs_4CdBi_2Cl_{12}$ and $Cs_4MnBi_2Cl_{12}$ NCs, respectively, were assigned to the (110) plane lattice viewed from the [001] zone axis of the trigonal LDP structure (**Figure 1a, d-g**). X-ray photoelectron spectroscopy (XPS) measurements confirmed the existence of Cs, Cd/Mn, Bi and Cl in the $Cs_4M(II)Bi_2Cl_{12}$ NCs (Figure S3). In addition, the inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements validated the stoichiometric Bi to M(II) ratio of ~ 2 (Table S3). Taken together, these results unequivocally proved the successful synthesis of $Cs_4CdBi_2Cl_{12}$ and $Cs_4MnBi_2Cl_{12}$ LDP NCs. Attempts to incorporate divalent metal ions other than Cd and Mn failed and often resulted in the formation of 2D $Cs_3Bi_2Cl_9$ perovskite-analogue NCs, in line with the theoretical prediction and experimental results of thermodynamically stable bulk Bi-based LDPs.[49, 52]

Next, optical property characterizations were carried out for both samples. The UV-vis absorption spectra show similar absorption profiles for both samples (**Figure 2a, b**). A clear absorption band with the peak at 331 nm (3.75 eV) was observed for the $Cs_4CdBi_2Cl_{12}$ NC sample, while a slightly blue-shifted peak position of 325 nm (3.82 eV) was obtained for the $Cs_4MnBi_2Cl_{12}$ NCs (**Figure 2a, b**). The corresponding band gaps were determined by Tauc plot analysis to be 3.49 eV for $Cs_4CdBi_2Cl_{12}$ NCs and 3.56 eV for $Cs_4MnBi_2Cl_{12}$ NCs, respectively (**Figure 2c, d**). The slightly wider band gap for the $Cs_4MnBi_2Cl_{12}$ NCs can be ascribed to a slightly compressed crystal lattices evidenced by the XRD and HR-TEM results (**Figure 1b-e**). These absorption profiles showed a high similarity to that of the previously reported 0D Cs_3BiCl_6 NCs with isolated $[BiCl_6]^{3-}$ octahedral units inside the lattice, indicating that the spin forbidden $^1S_0$ - $^3P_1$ electronic transition of Bi^{3+} ion is mainly responsible for the observed absorption band.[40, 60]

We further characterized the emission property of both $Cs_4M(II)Bi_2Cl_{12}$ LDP NCs. A very weak PL emission (centered at ~ 602 nm, PL QY < 0.1%) was detected for the $Cs_4CdBi_2Cl_{12}$ NCs (**Figure 2a**), which can be attributed to the $^3E_g \rightarrow {}^1A_{1g}$ electronic transition of the Cd^{2+} ion in a six-coordinated $[CdCl_6]^{4-}$ octahedral unit, in line with our previous report of Cd-doped $CsPbCl_3$ perovskite NCs.[55] In contrast, a relatively stronger PL emission centered at 628 nm with a PL QY of 0.4% was detected for the $Cs_4MnBi_2Cl_{12}$ LDP NCs (**Figure 2b**). This broad orange emission can be assigned to the $^4T_{1g} \rightarrow {}^6A_{1g}$ electronic transition of Mn^{2+} ions in the perovskite NCs.[61, 62] PL excitation (PLE) spectra of both NCs showed nearly overlapped profiles with the corresponding absorption spectra (**Figure 2a, b**), confirming an energy transfer process from the photogenerated exciton at the band edge (*i.e.,* conduction band, CB) of the NCs to the Cd^{2+} or Mn^{2+} ions in the $Cs_4M(II)Bi_2Cl_{12}$ LDP NCs. It is noteworthy that the PL peak position for the $Cs_4MnBi_2Cl_{12}$ NCs is noticeably redder than that of the Mn emission from Mn-doped $CsPbCl_3$ perovskite NCs, whose peak is typically in the range of 585~600 nm.[61, 63, 64] Such a red-shift of the Mn emission can be attributed to an inter-Mn-distance-induced Mn-Mn coupling interaction, leading to a larger d-d splitting of Mn^{2+} ion centers and correspondingly decreasing the gap of $^4T_{1g} \rightarrow {}^6A_{1g}$ transition. Similar Mn-emission redshifts were observed in Mn-doped NC samples with a high Mn concentration and/or inhomogeneous Mn distribution.[64-66] This strong Mn-Mn coupling interaction was consistent with the observed low PL QY (*i.e.,* 0.4%) and was further proved by the time-resolved PL (TR-PL) and electron paramagnetic resonance (EPR) measurements (**Figure 2e, f**). While no valid PL decay curves can be collected from the Cd-containing sample due to the low PL intensity (PL QY < 0.1%), a remarkably short PL decay lifetime of ~ 10 µs was obtained for the $Cs_4MnBi_2Cl_{12}$ NCs (**Figure 2e**). Notably, the measured PL lifetime is about two orders of magnitude faster than that of the typical Mn-dopant emission (~ 1 ms) (Table S4),[65, 67] representing one of the fastest Mn-emission dynamics reported so far.[57, 68] While the EPR silence of the $Cs_4CdBi_2Cl_{12}$ NCs is consistent with the absence of the unpaired electrons in the sample,[55] a single resonance peak (peak width: 56.4 G; *g*-value: 2.005) was observed for the $Cs_4MnBi_2Cl_{12}$ LDP NCs (**Figure 2f**). The single EPR peak signal with the absence of hyperfine splitting was attributed to the strong electron exchange interaction in the sample due to high Mn^{2+} ion concentration, consistent with the optical measurement results discussed above.[67, 69, 70] The $Cs_4M(II)Bi_2Cl_{12}$ NCs showed a relatively high shelf stability when stored in ambient conditions. The absorption spectra of both $Cs_4CdBi_2Cl_{12}$ and $Cs_4MnBi_2Cl_{12}$ LDP NCs, and the PL spectra of $Cs_4MnBi_2Cl_{12}$ NCs showed nearly no change up to 30 day (Figure S4a-c). The PL intensity of $Cs_4MnBi_2Cl_{12}$ LDP NCs showed some fluctuation with a slight increasing trend (Figure S4d), possibly caused by NC surface atom rearrangements during storage.

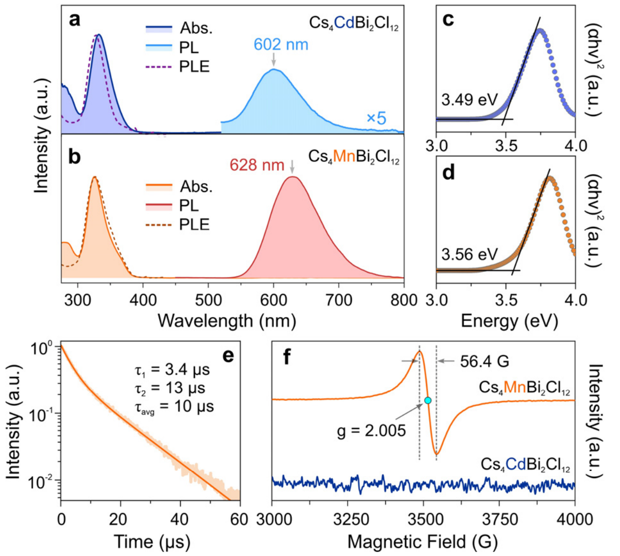

Figure 2. **(a, b)** Absorption (Abs.), PL and PLE spectra of $Cs_4CdBi_2Cl_{12}$ (a) and $Cs_4MnBi_2Cl_{12}$ (b) LDP NCs. **(c, d)** Tauc plots of $Cs_4CdBi_2Cl_{12}$ (c) and $Cs_4MnBi_2Cl_{12}$ (d) NCs. **(e)** TR-PL decay curve of the $Cs_4MnBi_2Cl_{12}$ NCs. The bi-exponential fitted curve is shown as the orange line. **(f)** EPR spectra of $Cs_4CdBi_2Cl_{12}$ (bottom) and $Cs_4MnBi_2Cl_{12}$ (top) LDP NCs. g-factor is determined using the peak center marked with the blue dot.

DFT calculation

To gain deeper understandings of the electronic structures of $Cs_4M(II)Bi_2Cl_{12}$ LDP NCs, their band structures were calculated as shown in **Figure 3** (See supporting information for calculation details).[71] For the case of $Cs_4CdBi_2Cl_{12}$, no difference in the total energy or electronic structure was found in different magnetic models due to the absence of unpaired electrons. In contrast, for the case of $Cs_4MnBi_2Cl_{12}$, both experimental results and theoretical calculations show that similar LDP systems commonly possess an intra-layer antiferromagnetic (intra-AFM) ordering due to the presence of 5 unpaired electrons of the Mn^{2+} ion (Mn^{2+}: [Ar]$3d^5$), *i.e.,* antiparallel spin alignment within each $[MnCl_6]^{4-}$ octahedral layer and parallel spin alignment between adjacent layers (Figure S5).[49, 51, 54] In addition, our calculation showed that the intra-AFM model showed the lowest energy among all magnetic ordering models (Table S5), validating the correctness of employing an intra-AFM model for the band structure calculations. The calculation results (**Figure 3a, b**) suggested that, both $Cs_4CdBi_2Cl_{12}$ and $Cs_4MnBi_2Cl_{12}$ showed direct band gaps located at the Y_2 symmetry point with band gap energies of 3.55 eV (for the Cd-containing one) and 3.48 eV (for the Mn-containing one), matching well with the experimentally determined values (*i.e.,* 3.49 eV and 3.56 eV, **Figure 2c, d**). The transitions responsible for the PL emissions in $Cs_4M(II)Bi_2Cl_{12}$ are absent in both calculated band structures, indicating their origin funneled through an energy transfer from host lattice (*i.e.,* $Cs_4M(II)Bi_2Cl_{12}$ NCs) to the M(II) ion centers,[55, 72-77] in accordance with the PLE measurements (**Figure 2a, b**). The corresponding density of states (DOS) calculations show that, for the $Cs_4CdBi_2Cl_{12}$ LDP, the conduction band minimum (CBM) mostly consists of Bi 6p, Cl 3p and Cd 5s orbitals, and its valence band maximum (VBM) is composed of Bi 6s and Cl 3p orbitals (**Figure 3c**). The CBM of $Cs_4MnBi_2Cl_{12}$ perovskites is composed of Bi 6p and Cl 3p orbitals, and the VBM contains mostly Mn 3d and Cl 3p orbitals, with a small contribution from the Bi 6s orbital. (**Figure 3d**). The forbidden transition regulated by both spin and parity spectroscopic selection rules diminish the Mn 3d orbital contribution (Mn *d-d* transitions) in electronic transitions,[78] which explains the observed similar absorption spectral profiles (contributed mainly from Bi and Cl orbitals) for both $Cs_4CdBi_2Cl_{12}$ and $Cs_4MnBi_2Cl_{12}$ LDP NCs (**Figure 2a, b**).

The electron localization function (ELF) and charge density difference for both $Cs_4CdBi_2Cl_{12}$ and $Cs_4MnBi_2Cl_{12}$ LDPs were calculated and mapped out to gain further insights about the bond characteristics and charge distributions (**Figure 3e-j**). The minimal electron density between metal cations (Bi^{3+}, Cd^{2+}, Mn^{2+}) and Cl^- anions shows the ionic bond nature of the present metal-Cl bonds. Contrasting with our recent report on $Cs_4CuSb_2Cl_{12}$ LDP NCs,[48] no distortions of the $[CdCl_6]^{4-}$ or $[MnCl_6]^{4-}$ octahedral units were observed in both $Cs_4CdBi_2Cl_{12}$ and $Cs_4MnBi_2Cl_{12}$ cases (**Figure 3e, f**). On the other hand, the $[BiCl_6]^{3-}$octahedra are distorted, such that the three Bi-Cl bonds (bridging bonds) towards the middle Cd or Mn layers are stretched to a bond length of ~ 2.90 Å, while the other three bonds (terminal bonds) towards the vacancy layers are compressed to a bond length of ~ 2.60 Å (**Figure 3g, h**). Charge density difference calculations show the electron transfer from Bi^{3+} and Cd^{2+} (or Mn^{2+}) to Cl^-, consistent with the ELF result (**Figure 3i, j**). No obvious charge redistribution occurred between the Bi and Cd (or Mn) unit (**Figure 3i, j**), again confirming the absence of Jahn-Teller distortion in the $Cs_4M(II)Bi_2Cl_{12}$ LDPs unlike the case of $Cs_4CuSb_2Cl_{12}$ LDP.[48]

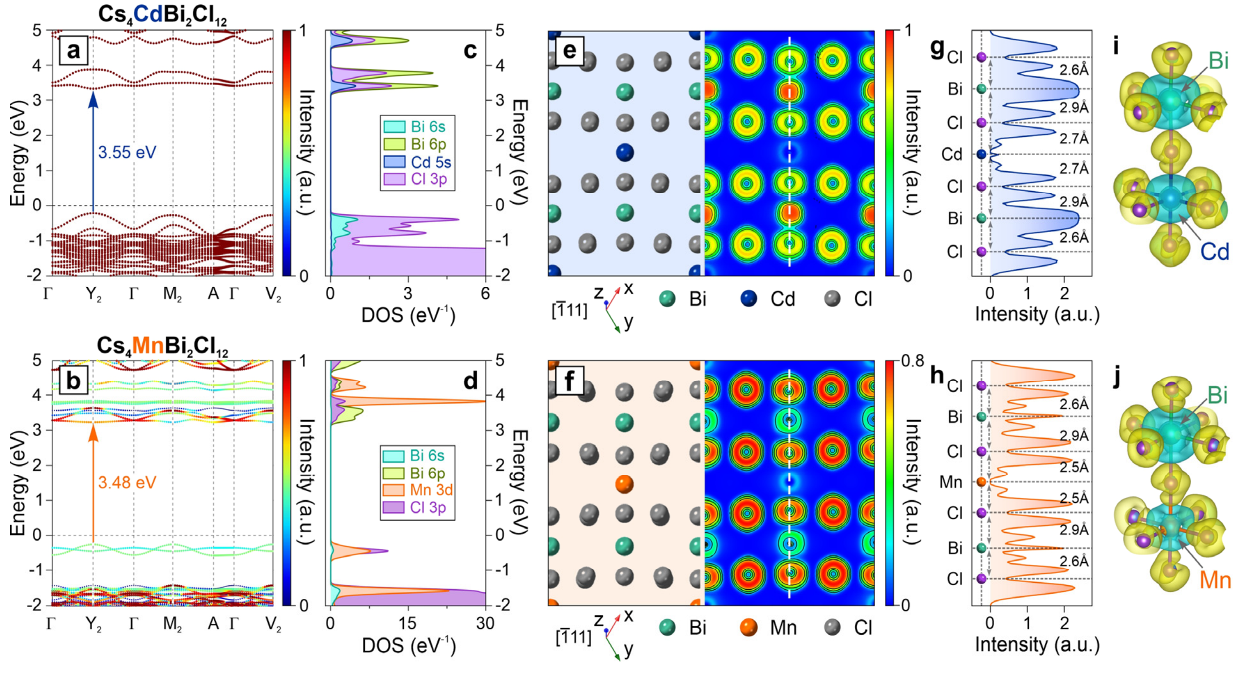

Figure 3. **(a-d)** Calculated band structure (a, b) and the corresponding projected density of states (DOS) diagram (c, d) of $Cs_4CdBi_2Cl_{12}$ (a, c) and $Cs_4MnBi_2Cl_{12}$ (b, d) LDPs. Horizonal dashed lines in (a, b) show the Fermi energy level. The colors of band structure plot represent the Bloch spectral density (spectral weight). **(e, f)** The electron localization function (ELF) of $Cs_4CdBi_2Cl_{12}$ (e) and $Cs_4MnBi_2Cl_{12}$ (f) LDPs. The atomic crystal structure viewed from the corresponding projections are shown on the left of the ELF diagrams. **(g, h)** 1D intensity profiles of the ELF along the white dashed lines in (e, f). **(i, j)** The charge density differences of $Cs_4CdBi_2Cl_{12}$ (i) and $Cs_4MnBi_2Cl_{12}$ (j) LDPs. Yellow and cyan surfaces represent charge gain and charge loss, respectively. Cs atoms are omitted in (e-j) for clear visualizations.

Controlling Mn-Mn coupling in $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ LDP NCs

The optical and EPR measurements along with the DFT calculation results suggested that the PL behavior of $Cs_4MnBi_2Cl_{12}$ LDP NCs is largely modulated by inter-Mn-center distance induced Mn-Mn coupling interaction, signified by the unique layered crystal structure. Therefore, tuning the optical property performance should be feasible through diluting the Mn concentration, thus decoupling the Mn centers inside the LDP NCs. This Mn diluting effect has been recently demonstrated in $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ solid-solution powder samples at bulk scale by both Woodward and Solis-Ibarra groups.[49, 57] Significant PL QY enhancements owing to decoupling the Mn-Mn interaction were observed.[57] To examine if similar effects can be observed at the nanoscale for the LDP particles, a series of $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ alloyed NCs were synthesized *via* mixing the Mn and Cd precursors (*i.e.*, manganese acetate and cadmium acetate) with a controlled stoichiometry ratio during the synthesis (see details in SI). The [Mn]/([Mn]+[Cd]) percentage (%) for the final products were determined to be 0%, 1.7%, 10.1%, 34.9%, 69.0%, 100% by ICP-AES measurements (Table S3). In addition, XPS measurements showed binding energy signals from both Cd 3d and Mn 2p orbitals, further confirmed the co-existence of Cd and Mn elements in the $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ NCs (Figure S6). TEM and XRD measurements of all the samples showed similar particle size and shape, as well as the same LDP crystal phase (space group: $R\overline{3}m$) as compared to the Cd- and Mn-pure LDP NCs (Figure S7 and **Figure 4a**). Careful examination of the XRD patterns revealed a continuous shift to lower 2θ angles for all the Bragg diffraction peaks upon decreasing the concentration of the Mn component (**Figure 4b**, Figure S8-S11, Table S6-S9). This result indicated a trend of lattice expansion upon replacing some Mn^{2+} ions with Cd^{2+} ions, in accordance with the relatively larger size of the Cd^{2+} ion than that of the Mn^{2+} ion. The calculated lattice parameters increased from a = 7.565 Å to 7.582 Å and from c = 37.09 Å to 37.37 Å (Table S6-S9). Correspondingly, the unit cell volume increased from 1838.3 $Å^3$ to 1860.4 $Å^3$ (**Figure 4c**). The linear relationship indicates that the unit cell volume evolution as a function of Mn/Cd ratio is on the basis of Vegard's law,[79-81] suggesting the successful formation of a solid-solution of $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ crystals with homogeneously distributed Cd^{2+} and Mn^{2+} ions in individual LDP NCs.

Based on the DFT calculation, the VBM and CBM corresponding to the observed optical transition of $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ is largely determined by the Bi or Cl components. Consistently, altering the stoichiometry ratio between Cd and Mn components resulted in similar absorption and PLE spectral profiles (**Figure 4e**). All the samples showed similar orange emission with the PL peak maximum centered in the range of 605-628 nm with different emission intensities (**Figure 4d, e**). The PL peak blue-shifted continuously upon reducing the Mn concentration from 628 nm for Mn-only sample to 605 nm for the $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ (x = 1.7%) NCs (**Figure 4d**). A slightly

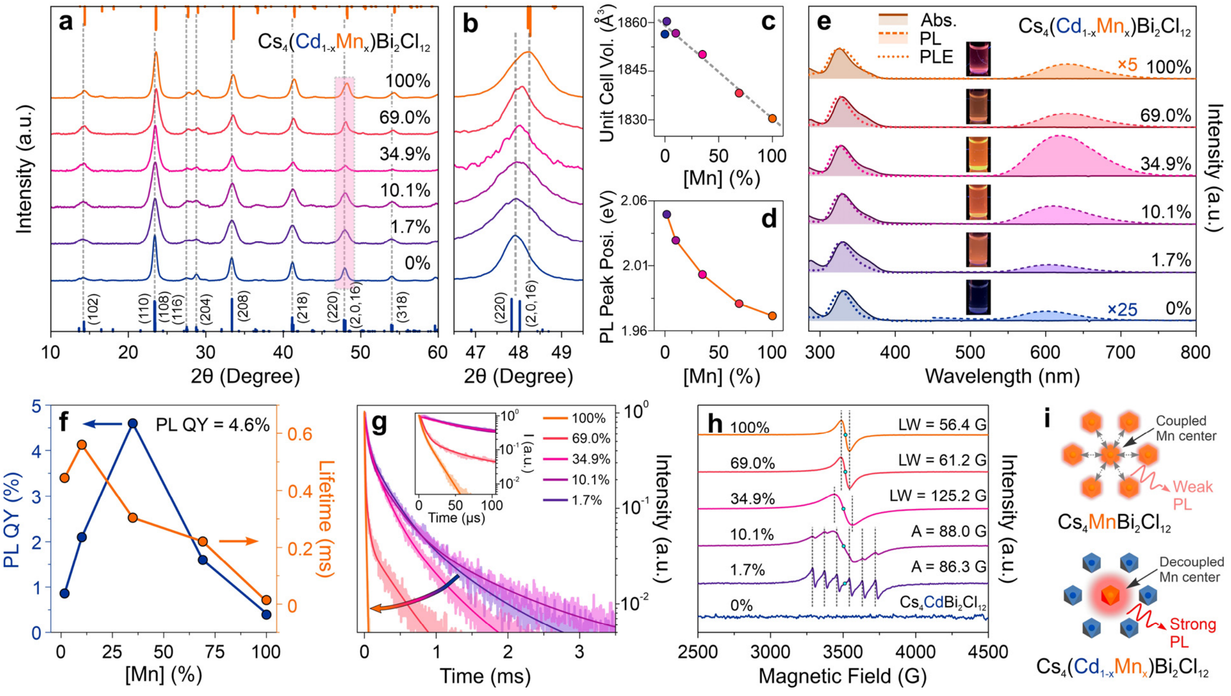

Figure 4. **(a)** XRD patterns of $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ (x = 0%, 1.7%, 10.1%, 34.9%, 69.0%, 100%) LDP NCs, and **(b)** the zoomed-in XRD patterns for the pink rectangular area labeled in (a). **(c, d)** The evolutions of unit cell volume (unit cell vol., c) and PL peak position (PL peak posi., d) of $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ NCs as a function of Mn concentration ([Mn]%: the percentage of [Mn]/([Cd]+[Mn])). **(e)** Absorption (Abs.), PL and PLE spectra of $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ LDP NCs. Inset: photographs of the corresponding NCs dispersed in toluene under UV light. **(f)** The PL QY (blue) and average PL lifetime (orange) changes as a function of Mn concentration. **(g)** TR-PL decay curves of the $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ LDP NCs. Inset: the zoomed-in area to show the fast lifetime decay curves. **(h)** The evolution of EPR spectra of $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ LDP NCs. **(i)** Schematic illustration of the Mn-Mn coupling interaction and the PL quenching phenomenon in $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ crystal lattices.

redder PL peak compared to typical dilute Mn-doped perovskites (~585~600 nm) was likely due to the shorter Mn-Cl bond in the $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ LDP lattice than that in the cubic $CsPbCl_3$ perovskite lattice (2.65 Å *vs.* 2.80 Å), which led to a larger d-d splitting energy with reduced energy difference between the $^4T_{1g}$ and $^6A_{1g}$ states of Mn^{2+} ions.[64-66] In addition to the PL peak blue-shift, a significant PL QY alteration of the NCs was measured (**Figure 4f**). An increase in PL QY was observed upon diluting Mn with Cd, reaching the highest PL QY of 4.6% for the $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ (x = 34.9%) NCs, an order of magnitude enhancement compared to the $Cs_4MnBi_2Cl_{12}$ NCs (**Figure 4f**). Further diluting Mn concentration resulted in a decrease in PL QYs (**Figure 4f**). In addition, the PL lifetimes of $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ NCs increased from 10 µs to 440 µs with decreasing Mn concentration from x = 100% to x = 1.7% (**Figure 4f, g** and Table S4).[82] This PL lifetime prolongation revealed that the symmetry-orientated spin-exchange interaction, in addition to the Mn-Mn dipole-dipole interaction, were co-responsible for the optical behavior of the $Cs_4MnBi_2Cl_{12}$ NCs.[65, 68, 72] Together, the PL peak blue-shifting, PL QY variation and PL lifetime prolongation all revealed a Mn^{2+} ion diluting effect with increased number of isolated $[MnCl_6]^{4-}$ octahedral units in the crystal lattice. This $[MnCl_6]^{4-}$ octahedral isolation can result in pseudo-0D structure with decoupled $[MnCl_6]^{4-}$ octahedral units, which impede the energy transfer/loss to adjacent $[MnCl_6]^{4-}$ units, and energy loss through crystalline or surface defect sites of the NCs (**Figure 4i**).[68, 83, 84] Such electronic isolation and magnetic decoupling effects of the $[MnCl_6]^{4-}$ octahedral units were further validated by the EPR measurements,[85] in which gradual appearance of a six-fold hyperfine splitting EPR pattern was observed for the $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ sample with $x \leq 10.1\%$ (**Figure 4h**).[67] A measured hyperfine splitting constant of 86.3 G for the $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ (x = 1.7%) sample was consistent with previous reports on octahedrally coordinated Mn species in a perovskite lattice environment.[63, 72, 86] Furthermore, the experimental results of diluting Mn in LDP NCs shown above were in good agreement with recent reports,[49, 57] as well as our experimental data on the bulk scale Cd/Mn LDP systems (Figure S12-S15, Table S10-S14). However, the relatively low PL QYs as compared to the corresponding bulk counterparts indicated the presence of other fast non-radiative energy relaxation pathways likely induced from the surface sites of the LDP NC samples.[85, 87, 88]

To further investigate the Mn-Mn coupling effect and optical performance of the $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ LDP NCs, low temperature steady-state and TR-PL measurements were conducted. When the temperature was decreased to 80 K, the PL peak of all the $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ (x = 0%, 1.7%, 10.1%, 34.9%, 69.0%, 100%) NCs red-shifted to longer wavelengths because of the thermal lattice contraction (**Figure 5a, b**).[57, 89] In general, the NCs with higher Mn concentrations showed larger PL peak red-shifts as compared to the samples with lower Mn concentrations (*e.g.,* ΔE = 64 meV for $Cs_4MnBi_2Cl_{12}$ NCs, and ΔE = 49 meV for $Cs_4(Cd_{0.98}Mn_{0.02})Bi_2Cl_{12}$ NCs). A similar trend has been observed in the bulk $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ powder samples as well.[57] A universal PL peak narrowing effect (24%-29% narrowing in FWHM) was also observed for all the samples at 80 K (Figure S16), which was induced by diminishing the electron-photon coupling (mainly electron-longitudinal optical phonon coupling) upon lowering temperature.[89, 90] This suppression of electron-phonon coupling was further confirmed by the significant enhancement for the PL intensities of the samples (~ 13-98 fold increase, **Figure 5a**, and Figure S17), which was likely co-induced by the elimination of some non-radiative recombination channels,[57, 87] in line with the prolonged PL lifetimes at a low temperature of 80 K (**Figure 5b, c**, Table S15). We also noted that all samples showed similar average PL lifetimes (0.7-1.2 ms) at 80 K, which could be ascribed to a competing effect between the suppression of the fast non-radiative channel (*i.e.,* prolonging PL lifetime) and the Mn-Mn interaction (*i.e.,* shortening PL lifetime).

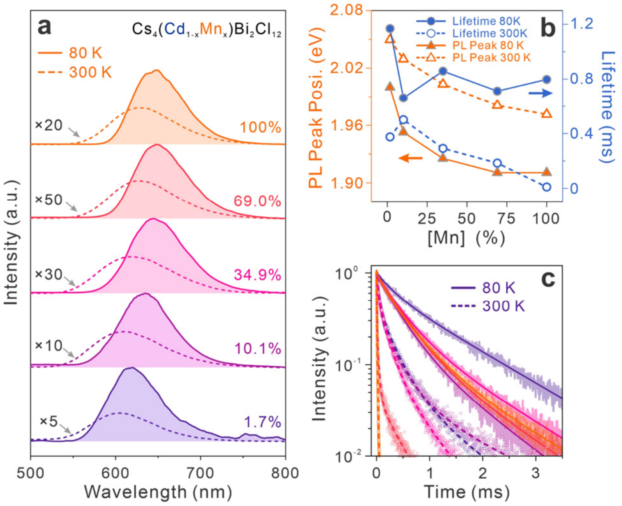

Figure 5. (a) PL spectra of $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ (x = 0%, 1.7%, 10.1%, 34.9%, 69.0%, 100%) LDP NCs at low temperature (at 80K, solid lines) and room temperature (dashed line). **(b)** The evolutions of the PL peak position (PL peak posi., orange) and average PL lifetime (blue) with different Mn concentrations. Solid circles and triangles represent the data obtained at low temperature (*i.e.,* 80K), and open circles and triangles represent the data obtained at room-temperature. **(c)** TR-PL decay curves of the $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ LDP NCs measured at low temperature (solid lines) and room temperature (dashed lines).

Conclusions

To conclude, we present the first example of the colloidal syntheses of $Cs_4M(II)Bi_2Cl_{12}$ (M(II) = Cd, Mn) LDP NCs. Both types of NC samples possess a spherical-like shape with a trigonal LDP crystal structure. DFT calculations reveal wide and direct band gap structures for both LDPs with no octahedral distortions for $[M(II)Cl_6]^{4-}$ units. Due to the high Mn concentration dictated by the stoichiometry and layered octahedral lattice feature of the crystal structure, the $Cs_4MnBi_2Cl_{12}$ NCs exhibit strong Mn-Mn interaction-dictated optical and magnetic properties. By forming a series of $Cs_4(Cd_{1-x}Mn_x)Bi_2Cl_{12}$ ($0 < x < 1$) cationic alloyed LDP NCs, the Mn-Mn coupling interaction can be effectively reduced, resulting in more isolated $[MnCl_6]^{4-}$ octahedral units inside the crystal lattice. Consistent with the studies in bulk scale materials, such a Mn component diluting effect induced electronic and magnetic decoupling process leads to significantly enhanced PL QYs with the highest value of 4.6% and prolonged PL lifetimes of the LDP NCs. Such a family of colloidal NC materials hold potentials to be developed as a new generation of optical and optoelectronic materials with solution processability. The inclusion of toxic Cd element may hinder their future application implementations. More efforts in searching non-toxic replacements and developing the corresponding synthetic chemistries are still in a pressing need.

Conflicts of interest

There are no conflicts to declare.

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