CsMnBr₃: Lead-Free Nanocrystals with High Photoluminescence Quantum Yield and Picosecond Radiative Lifetime

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ABSTRACT: Lead halide compounds, including lead halide perovskite nanocrystals (NCs), have attracted the interest of researchers in optoelectronics and photonics because of their high photoluminescence quantum yields (PLQYs) coupled with relatively short PL lifetimes (on the order of a few nanoseconds). However, lead-free metal halides of high PLQY, including double perovskites and their doped NCs, typically possess long PL lifetimes (up to microseconds) that limit their application space. Here, we introduce CsMnBr₃ NCs, which are lead-free and red-emitting, that combine a high PLQY with an exceptionally short radiative lifetime (on the order of picoseconds). We find that the octahedral coordination of Mn²⁺ in CsMnBr₃ induces a red emission centered at ∼643 nm with a PLQY of ∼54% and a fast radiative decay rate. Femtosecond transient absorption and transient PL spectroscopies reveal the existence of a low-lying excited state of Mn²⁺ that relaxes to the ground state within around 605 ps by emitting light at around 643 nm. At greater excitation energies, higher excited states of Mn²⁺ relax in the sub-nanosecond time scale to this low-lying excited state of Mn²⁺ that relaxes to the ground state within around 605 ps by emitting light at around 643 nm. At greater excitation energies, higher excited states of Mn²⁺ relax in the sub-nanosecond time scale to this low-lying excited state. A similarly positioned PL peak with a short picosecond scale PL lifetime and a PLQY of ∼6.7% was also detected in bulk CsMnBr₃ single crystals reported in this study—a relatively high quantum yield for a bulk material. Our experimental results and density functional theory modelling show that the crystal structure and the strong coupling among Mn²⁺ ions govern those luminescence properties of CsMnBr₃ NCs and single crystals. These findings pave the way for new lead-free materials that combine high PLQY and ultrafast luminescence.

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56 materials in the literature that exhibit a very broad range of PL lifetimes, suggesting a strong structural-dependence of the PL decay kinetics. These materials usually have a relatively high PLQY and either green or red emissions from the d-d transition of Mn$^{2+}$ ions in the tetrahedral and octahedral coordination, respectively. However, the PL lifetime of the Mn-emission can vary from a few nanoseconds to milliseconds depending upon the structure, type of halide ions, the local environment of Mn$^{2+}$, and most crucially, the shortest Mn−Mn distance. For example, Rodriguez and co-workers found that the PL lifetime of the Mn$^{2+}$ emission in [(CH$_3$)$_4$N]$_2$MnBr$_4$ decreases by two orders of magnitude when the structure changes to [(CH$_3$)$_4$N]MnBr$_3$. The authors ascribed the shorter PL decay lifetime to the relatively shorter Mn−Mn distance of 3.25 Å in [(CH$_3$)$_4$N]MnBr$_3$ compared to 7.89 Å in [(CH$_3$)$_4$N]$_2$MnBr$_4$. Moreover, a recent work on [C$_6$H$_{10}$N]$_2$MnBr$_4$ with a Mn−Mn distance of 3.38 Å showed a PL peak at ~628 nm with a fast radiative decay (~1.4 ns) and a high PLQY (46%). However, the nanosecond PL lifetime was attributed to emission originating from Mn clusters facilitated by the arrangement of pyrrolidine molecules. The origin of the unusually short lifetimes of Mn$^{2+}$ in compounds with short Mn−Mn distances is still far from being understood but presents an opportunity to design lead-free NC emitters that simultaneously exhibit high quantum yield and ultrafast radiative decay. Unfortunately, organic-inorganic manganese-based halides suffer from poor crystallinity and thermal instability, which make it difficult to conceive colloidal NCs out of them. Thus, we reasoned that moving to an all-inorganic system, which also exhibits short Mn−Mn distances, would enable the synthesis of NCs with high PLQY and short radiative lifetimes.

Here, we report the colloidal synthesis of all-inorganic CsMnBr$_3$ NCs and studied their structural and optical properties. These NCs show an intense red emission at ~643 nm with a high PLQY ~54% and an unprecedently ultrashort PL lifetime, on the order of several hundreds of picoseconds. Structural studies confirmed the octahedral coordination of Mn$^{2+}$ and the strong Mn−Mn coupling in CsMnBr$_3$ NCs. Steady-state optical absorption and PL excitation (PLE) spectra of CsMnBr$_3$ NCs revealed the well-defined peaks of d−d transitions of the Mn$^{2+}$ units. Transient absorption spectroscopy and DFT studies were carried out to investigate the photophysics and the electronic band structure of the material. To investigate whether the surface of NCs plays any role in the unusual photophysics, we synthesized CsMnBr$_3$ single crystals, and we observed a similar red PL emission and a fast luminescence decay, consistent with our findings on NCs. To the best of our knowledge, the CsMnBr$_3$ NCs reported herein exhibit the shortest PL lifetime of any highly luminescent inorganic NCs. These findings open a new avenue for realizing ultrafast luminescence-based devices and a future of luminescent materials beyond lead-based perovskites.

The colloidal synthesis of CsMnBr$_3$ NCs is complicated by energetically similar competing phases that form in the CsBr-MnBr$_2$ phase diagram. Therefore, the tolerance range of reaction parameters, such as reactants concentration and temperature, to achieve phase-pure CsMnBr$_3$ NCs is narrower than that usually observed in lead halide perovskite NCs. Here, we prepared CsMnBr$_3$ NCs using a separate bromide precursor like in previous reports for lead-free metal halide NCs. Typically, manganese acetate and cesium acetate are dissolved in octadecene using oleic acid and oleylamine ligands degassed at 130 °C, followed by the injection of benzoyl bromide precursor at 170 °C. We carefully optimized the precursor concentration and temperature to achieve phase-pure CsMnBr$_3$ NCs.

![Figure 1. Structural characterizations of CsMnBr$_3$ NCs. (a) Schematic of the CsMnBr$_3$ crystal structure presenting the octahedral coordination of Mn$^{2+}$. (b) Crystal structure along the c-axis. (c) XRD pattern of NCs film synthesized in this work (black) and the calculated reference pattern (red). (d) TEM and (e) HRTEM images of NCs featuring a hexagonal morphology. (f) FFT pattern of a single CsMnBr$_3$ NC obtained from image e. (g) Size distribution histogram of NCs with an average size ~25.4 ± 4.8 nm. (h) EPR spectrum of CsMnBr$_3$ NCs powder.](image)
Figure 2. Optical properties of CsMnBr$_3$ NCs. (a) PLE and absorption spectra with the assigned d–d transitions in the octahedrally coordinated Mn$^{2+}$, (b) Tanabe–Sugano diagram showing five low-lying excited states of Mn$^{2+}$ in the presence of ligand crystal field. The dashed line represents the $\Delta/B$ ratio calculated from the experimental data of the d-orbitals in Figure 2a. (c) PL spectrum of CsMnBr$_3$ NCs upon illumination at 450 nm. Inset: photograph of colloidal CsMnBr$_3$ NCs before (left) and after excitation with UV light (right). (d) Energy level diagram for d–d transitions and the PL emission from the free and octahedrally coordinated Mn$^{2+}$ ions in CsMnBr$_3$ NCs. (e) PLQY of the red emission for different [Cs:Mn] molar ratios along with the PLQY stability of the colloidal NCs. (f) Intrinsic absorption coefficient of NCs with a typical molar absorption coefficient of 83.6 M$^{-1}$ cm$^{-1}$ at 544 nm, assuming NCs with an average size $\sim$25 nm.

The crystal structure of CsMnBr$_3$ consists of one-dimensional (1D) chains of distorted face-sharing octahedra along the c-axis that are bridged by Cs ions as depicted in Figure 1a and b. Interestingly, the Mn–Mn distance is very short $\sim$2.7 Å, along the c-axis leading to strongly-coupled optical transitions, as we will discuss later. The phase purity of CsMnBr$_3$ NCs was investigated by powder X-ray diffraction (PXRD), revealing a hexagonal crystal structure and a P6$_3$/mmc space group consistent with the literature on bulk CsMnBr$_3$ (Figure 1c). Transmission electron microscopy (TEM) images of CsMnBr$_3$ NCs show a hexagonal morphology (Figure 1d), matching the hexagonal crystal structure of CsMnBr$_3$ with a mean size $\sim$25 ± 4.8 nm, along the elongated hexagon (Figure 1g); see more TEM images in Figure S1. We also synthesized smaller ($\sim$9.5 nm) CsMnBr$_3$ NCs by performing the colloidal synthesis at a relatively lower temperature of 120 °C (see details in the experimental section in the Supporting Information). A maximum weight of 50 mg of CsMnBr$_3$ NCs can be dispersed in 1 mL of toluene. The high-resolution TEM (HRTEM) image in Figure 1e displays NC lattice planes with an interplanar distance of 0.30 nm assigned to the (021), (011), and (010) planes, respectively. We then studied the local environment around the Mn$^{2+}$ ions in CsMnBr$_3$ NCs through electron paramagnetic resonance (EPR) spectroscopy. The broad EPR signal from the Mn$^{2+}$ centers and the absence of the sextet hyperfine splitting pattern (usually obtained for five unpaired electrons of isolated Mn$^{2+}$) indicated a strong Mn–Mn interaction (Figure 1h) compared to doped Mn$^{2+}$ ions in semiconductor NCs. Thermogravimetric analysis (TGA) in Figure S2 suggested a 21% weight loss between 200–300 °C, which is due to the decomposition of the organic ligands present on the surface of NCs. Above 300 °C, we observed no further loss up to 590 °C, highlighting the inorganic part's thermal stability in CsMnBr$_3$ NCs. Finally, ligands on the surface of NCs after several washes were verified via Fourier transform infrared (FTIR) spectroscopy (Figure S3).

It is worth mentioning that the CsMnBr$_3$ phase has the highest dimensionality in the CsBr-MnBr$_2$ phase diagram when compared to the other known phases, Cs$_2$MnBr$_4$ and Cs$_4$MnBr$_6$, wherein the [MnBr$_4$]$^{2–}$ tetrahedra are isolated in the zero-dimensional crystal structure. Therefore, the CsMnBr$_3$ phase is expected to have unique optical properties induced by the crystal structure and the local environment of the Mn$^{2+}$ ions.

To elucidate the optical properties of CsMnBr$_3$ NCs, we recorded the steady-state absorption spectrum of CsMnBr$_3$ NCs dispersed in hexane. The spectrum in Figure 2a shows five structured peaks at 364, 378, 432, 455, and 544 nm. The overlaid photoluminescence excitation (PLE) spectrum in Figure 2a also shows similar peaks after monitoring the PL onset at 650 nm. These peaks typically arise from the d–d transitions present in the tetrahedrally coordinated Mn$^{2+}$ ions. The assignment of these peaks is based on the crystal
field theory (CFT) and Tanabe–Sugano (T-S) diagram. The
T-S diagram shown in Figure 2b was calculated based on two
parameters: the crystal field splitting energy (\(\Delta\)), which
measures the degree of splitting in d-orbitals, and Racah’s
parameter (B), which measures the metal–ligand bond
strength.33,34 The splitting of the five low-lying excited states
in Mn\(^{2+}\) is shown in the T-S diagram in Figure 2b. The
experimental optical d–d transitions of Mn\(^{2+}\) in CsMnBr\(_3\) NCs
are represented by the dashed line determined from the ratio
between the lowest two transitions at 544 and 455 nm.
Therefore, the B and \(\Delta\) were found to be 760 and 8494 cm\(^{-1}\),
respectively (Table 1). The assignments of the five peaks in the
absorption and PLE spectra are depicted in Figure 2a and
summarized in Table 1.

### Table 1. Assignment of Mn\(^{2+}\) Based d–d Transitions in the PLE and Absorption Spectra of CsMnBr\(_3\) NCs along with the Crystal Field Splitting Energy and Racah’s Parameter

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavenumber (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6^A_1 \rightarrow 4^T_1(G))</td>
<td>18518</td>
</tr>
<tr>
<td>(6^A_1 \rightarrow 4^T_2(G))</td>
<td>22222</td>
</tr>
<tr>
<td>(6^A_1 \rightarrow 4^A_2(E))</td>
<td>23095</td>
</tr>
<tr>
<td>(6^A_1 \rightarrow 4^E(D))</td>
<td>26316</td>
</tr>
<tr>
<td>(6^A_1 \rightarrow 4^T_2(D))</td>
<td>27473</td>
</tr>
<tr>
<td>(\Delta/B)</td>
<td>11.18</td>
</tr>
<tr>
<td>(B)</td>
<td>760</td>
</tr>
<tr>
<td>(\Delta)</td>
<td>8494</td>
</tr>
<tr>
<td>Emission (4^T_1 \rightarrow 6^A_1)</td>
<td>15552</td>
</tr>
</tbody>
</table>

Interestingly, CsMnBr\(_3\) NCs show bright red photo-
luminescence (PL) spectrum centered at 643 nm with a full-
width at half-maximum (FWHM) \(\sim 78\) nm (Figure 2c). The
red PL spectrum is identical at the three different excitation
wavelengths selected from the PLE spectrum (Figure S4a).
Therefore, we attribute the red PL emission to the relaxation
from the low-energy excited state to the ground state of Mn\(^{2+}\).
(\(4^T_1 \rightarrow 6^A_1\)) as illustrated in Figure 2d, in agreement with the
assignment of the red emission in the octahedrally coordinated
Mn\(^{2+}\) in the literature.33,34 The PLQY was then measured
using an integrating sphere. Our optimized conditions of
[Cs:Mn] molar ratio of \([0.5:1]\) showed a maximum PLQY \(\sim
1.05\) \(\%\) (Figure 2e) with a batch-to-batch reproducibility.
The colloidal NCs retained more than 70\% of their initial PLQY
upon storage inside the fume hood for 20 days (Figure 2e).
When we used higher Cs concentration to synthesize CsMnBr\(_3\),
NCs, the maximum PLQY dropped to \(\sim 40\%\) for \([1:1]\) molar
ratio of [Cs:Mn], and we detected impurities and undesired
phases. For comparison, ligand-passivated and lead-based
CsPbI\(_3\) quantum dots have near-unity PLQY, but with a
deep red emission peak \(\sim 680\) nm.11 The lead-free PEA\(_2\)SnI\(_4\)
films have a pure red emission centered at 630 nm but with a
relatively low PLQY \(\sim 7\%\).36,37 We, therefore, calculated the
intrinsic absorption coefficient of CsMnBr\(_3\) NCs using the
equation \(\mu_l = \frac{\ln(10) \times A}{l}\), where \(A\) = absorbance, \(l\) = path length
(cm), \(\mu_l\) = intrinsic absorption coefficient (in units of cm\(^{-1}\)),
and \(f = \) volume fraction of NCs, as reported in the
literature.38,39 We obtained the concentration and volume
fraction of NCs following a methodology explained else-
where.40 The intrinsic absorption coefficient in Figure 2 was
then used to calculate the molar absorption coefficient \((\varepsilon)\)
through the equation \(\varepsilon = \frac{\mu_l \times f}{\ln(10) \times c}\), where \(c\) is the concent-
ration of NCs.39 The \(\varepsilon\) value at 544 nm is 83.6 M\(^{-1}\) cm\(^{-1}\)
(assuming NCs with an average size \(\sim 25\) nm), which is
relatively high for spin and Laporte forbidden d–d transition of
Mn\(^{2+}\). The relatively high absorption coefficient may originate
from the large \(\Delta \sim 1.05\) eV (8494 cm\(^{-1}\) from Table 1) and the
strong intrachain Mn–Mn coupling in the CsMnBr\(_3\) structure
(1.05 eV and \(1.05\) eV).38,39

The time-resolved PL (TRPL) spectrum was measured by
probing the PL at 643 nm at the three different excitation
wavelengths corresponding to the Mn\(^{2+}\) d–d transitions in the
PLE spectrum (Figures 2a and 3a). Unlike the PL peak
the PL decay dynamics strongly depend on the
excitation wavelength, similar to a prior report on [(CH\(_3\))\(_4\)N]
MnBr\(_3\).25 The experimental TRPL decay upon excitation at
450 and 380 nm were fitted with a tri-exponential decay
function with two nanoseconds and one picosecond
components for each excitation (see Figure 3a and Table S2
for fitting parameters). However, the PL decay obtained upon
excitation at 540 nm showed only a single component \(\sim 605 \pm
56\) ps after fitting with a mono-exponential decay function. The
fast PL decay in the order of a few nanoseconds to several
hundreds of picoseconds and its excitation dependence in
CsMnBr\(_3\) NCs is unexpected given that the d–d transitions in
the octahedrally coordinated Mn\(^{2+}\) are typically spin and parity
forbidden. The origin of such ultrafast PL decay dynamics in
NCs will be discussed later. We then studied the temporal
dynamics of the excited states in NCs and their dependence on
the excitation wavelength using femtosecond transient
absorption spectroscopy. The excited state of NCs upon
excitation at 380 nm (Figure 3b) was short-lived and decayed
260 ps to the ground state within \((5.2\) ps and \(1.14\) ns) when probed at \(550\) nm (Figure S5), in agreement with the TRPL decay
dynamics of CsMnBr\(_3\) NCs discussed earlier. However, when \(\varepsilon\)
the excitation wavelength was between 450 and 500 nm, the
excited state dynamics of NCs revealed some interesting
photophysics. We discuss here the 480 nm excitation data
(probe was at 580 nm) shown in Figure 3c. Initially, the
excited state of NCs decayed very quickly within the time
constants of $50 \pm 2$ ps, followed by repopulation of the excited
state in $400 \pm 15$ ps time. One possible explanation for such
observation is that the higher energy excited state transferred
the excess energy to the low lying excited state of Mn$^{2+}$ (Figure
3d). In other words, there is a delay in populating the low
energy excited state of Mn$^{2+}$ before it returns to the ground
state. The final low-lying excited state, $^4T_1$ of Mn$^{2+}$, then
decayed to ground state in $600 \pm 24$ ps (Figure 3d), which is
matching to TRPL decay lifetime of $605 \pm 56$ ps obtained at
540 nm excitation (Figure 3a). Therefore, excitation depend-
ence of PL lifetime and additional components observed at
higher excitation energies (lower excitation wavelengths)
originates from the delay in the relaxation of the higher excited
states of Mn$^{2+}$ to the low-lying excited state. The actual PL
time of red emission in CsMnBr$_3$ NCs is, thus, concluded as
$605 \pm 56$ ps.

To confirm that surface defects in CsMnBr$_3$ NCs do not
play a major role in our hypothesis of the ultrafast PL decay,
we successfully synthesized CsMnBr$_3$ single crystal and
compared the optical and structural properties. Single-crystal
XRD data confirmed the coordination and space group of
CsMnBr$_3$ single crystal (Table S1), consistent with the crystal
structure adopted by CsMnBr$_3$ NCs (Figure 1c). Further, CsMnBr$_3$ single crystals and NCs share the same red emission
and the picosecond PL decay dynamics of excited states of
Mn$^{2+}$ along with a two nanosecond component (Figure S6).
The CsMnBr$_3$ single crystals have a PLQY of $\sim 6.7\%$, a
relatively high PLQY for a bulk material. In single crystals, the
fast PL decay component is $\sim 550$ ps, close to the $605$ ps PL
time of CsMnBr$_3$ NCs for the same red emission.

Previous studies showed that the PL lifetime of the d–d
transitions in Mn$^{2+}$ could vary significantly and is sensitive to
the surrounding halide ions, local coordination, and especially
to the adjacent Mn–Mn distances.24,25,27,41 Thus, to under-
stand the role of the Mn–Mn distances on the electronic band
structure that governs the optical properties in CsMnBr$_3$, we
performed density functional theory (DFT) calculations on
three known phases with different Mn–Mn distances; CsMnBr$_3$, Cs$_2$MnBr$_4$, and Cs$_3$MnBr$_5$. The spin-polarized calculations at the Generalized Gradient
Approximation (GGA) and Perdew–Burke–Ernzerhof (PBE)
Figure 4(see Figure S7 for the probed Brillion dynamics, single-crystal synthesis, and optical properties NCs, such as TEM images, TGA, FTIR, TRPL picoseconds PL lifetimes. The short PL decay lifetime and the short Mn–Mn distance of 2.7 Å in CsMnBr3 may be correlated through 300 energy transfer along the 1D chains, superexchange interaction or bimolecular recombination. Further investigation into the underlying mechanisms will follow in future work. We also note that a few reports in the literature suggested that the short Mn–Mn distance of 3.38 to 3.6 Å in organic–inorganic manganese bromides lead to a red emission with a few nanoseconds PL lifetimes. However, the Mn–Mn distance of 3.38 Å is slightly greater than the 2.7 Å realized in the CsMnBr3 structure, which could explain the much faster PL lifetime of 605 ps observed in our NCs.

In conclusion, we successfully synthesized red-emitting phase-pure CsMnBr3 NCs with a relatively high PLQY (~54%) and an ultrashort PL lifetime (~605 ps). Surprisingly, the PL decay lifetime of the red emission exhibited a strong dependency on the excitation wavelengths. Our transient absorption studies suggest that upon excitation with lower pump wavelengths in the range of 450–500 nm, relaxation of the higher excited states of Mn5+ to the low-lying excited state occurs in a sub-nanosecond time scale. This relaxation time becomes evident in the TRPL decay dynamics, especially at lower excitation wavelengths. The red emission and the picosecond PL lifetime are also observed in CsMnBr3 single crystals, suggesting that the ultrafast excited state dynamics stem from bulk properties rather than surface defects. DFT modelling indicates a strong Mn–Mn coupling in the ground state of the CsMnBr3 phase leading to a metallic-like electronic band structure; in contrast to the other phases, Cs2MnBr4 and Cs3MnBr5 show well-defined band gaps. Our findings on the remarkable luminescent properties of CsMnBr3 NCs and Cs2MnBr4 and Cs3MnBr5 phases, respectively (Figure 4). The shorter Mn–Mn distance in the CsMnBr3 structure leads to the strong coupling of adjacent Mn5+ atoms; hence, the metallic like band structure in Figure 4. On the other hand, the absence of the Mn–Mn coupling in Cs2MnBr4 and Cs3MnBr5 structures leads to a semiconducting electronic band structure with well-defined band gaps. This new finding highlights the significance of the Mn–Mn distance on the nature of the host materials’ electronic band structure and optical behavior.

Similarly, we can conclude that the ‘T1’ excited states of coordinated Mn5+ ions are also coupled along the 1D chains in the CsMnBr3 structure, leading to ultrafast picosecond PL lifetimes.

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