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Published in:
ACS Applied Nano Materials

DOI:
[10.1021/acsanm.2c04342](https://doi.org/10.1021/acsanm.2c04342)

Published: 01/01/2023

Document Version
Final published version

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Please cite the original version:

Matuhina, A., Grandhi, G. K., Pan, F., Liu, M., Ali-Löytty, H., Ayedh, H. M., Tukiainen, A., Smått, J.-H., Vähänissi, V., Savin, H., Li, J., Rinke, P., & Vivo, P. (2023). Role of CsMnCl₃ Nanocrystal Structure on Its Luminescence Properties. *ACS Applied Nano Materials*, 6(2), 953–965. <https://doi.org/10.1021/acsanm.2c04342>

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Role of CsMnCl₃ Nanocrystal Structure on Its Luminescence Properties

Anastasia Matuhina, G. Krishnamurthy Grandhi,* Fang Pan, Maning Liu, Harri Ali-Löyty, Hussein M. Ayedh, Antti Tukiainen, Jan-Henrik Småt, Ville Vähänissi, Hele Savin, Jingrui Li, Patrick Rinke, and Paola Vivo*



Cite This: *ACS Appl. Nano Mater.* 2023, 6, 953–965



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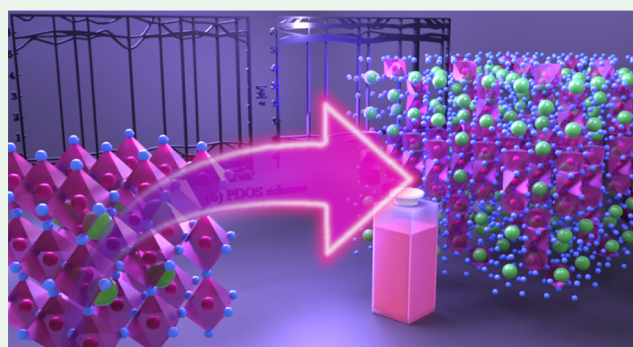
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Supporting Information

ABSTRACT: Cesium manganese chloride (CsMnCl₃) nanocrystals (NCs) have recently been recognized as potential lead-free perovskite candidates for red emission. To ascertain how the luminescence properties depend on the NC structures formed under different synthesis conditions, we synthesized CsMnCl₃ NCs in two polymorphic structures, namely, cubic (c-CsMnCl₃) and rhombohedral (r-CsMnCl₃), by tuning the reaction temperature of a hot injection route. c-CsMnCl₃ NCs are found to be nonemissive, whereas r-CsMnCl₃ NCs exhibit red emission at 670 nm with a photoluminescence quantum yield of 40%. Density functional theory calculations reveal an indirect band gap for c-CsMnCl₃—the electronic transitions between valence and conduction band edges are prohibited by orbital symmetry and spin. Conversely, r-CsMnCl₃ NCs possess a direct band gap. Further, transient absorption measurements suggest self-trapped exciton formation in r-CsMnCl₃ NCs, which contributes to their emission characteristics. Our proof-of-concept demonstration of photocurrent generated from the emitting r-CsMnCl₃ NCs indicates their suitability for luminescent solar concentrator applications. The findings of this work highlight the importance of understanding structure-luminescence relationship of emerging lead-free perovskites providing design criteria for red-emitting materials.

KEYWORDS: lead-free perovskite, nanocrystals, CsMnCl₃, density functional theory, self-trapped exciton, structure–property relationship, luminescent solar concentrators



INTRODUCTION

Three-dimensional (3D) lead-halide perovskite (LHP) nanocrystals (NCs) are promising for photonic and light-emitting applications due to their broad-range absorption, tunable emission energies within a wide range of colors, and high color purity [narrow emission full width at half-maximum (fwhm)].¹ Near-unity photoluminescence (PL) quantum yield (QY) has been achieved in blue, green, and red spectral regions for all-inorganic CsPbX₃ (X = Cl, Br, or I) NCs.² However, red-emissive CsPbI₃ NCs (emission maximum ~620–690 nm)³ have proven to be inherently phase unstable. Moreover, the toxicity of water-soluble Pb²⁺ in LHP NCs has recently triggered the search and subsequent discovery of Pb-free metal-halide NCs, typically based on Bi, Sb, and Cu, with a maximum PLQY of 97% for Cs₃Cu₂I₅ in the deep-blue spectral region.^{4,5} Nevertheless, none of the reported Pb-free NCs have so far simultaneously exhibited high PLQY and stable red emission beyond 650 nm.

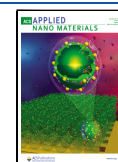
Cesium manganese halides (CsMnBr₃ and CsMnCl₃) with one-dimensional (1D) Mn–Cl chains in their structure are an interesting family of emerging Pb-free NCs displaying high

absorption coefficients, Stokes-shifted and tunable emission, and PLQYs up to ~50%.^{6–8} In particular, CsMnCl₃ NCs are intriguing as contradictory emission properties have been outlined so far. While the initial works by Gao et al.⁹ and Feng et al.¹⁰ reported nonemissive properties, Guan et al. and Hao et al. demonstrated CsMnCl₃ NCs with red emission centered at 654–660 nm.^{8,11} Guan and co-workers synthesized CsMnCl₃ NCs with emission at 660 nm and a PLQY of 0.7% through a modified hot injection approach.¹¹ The authors indicated a deviation from the 1:1:3 stoichiometry, which might explain the low PLQY. Hao and colleagues synthesized CsMnCl₃ NCs through the benzoyl chloride injection route and doped them with Zn²⁺ ions to improve their PLQY from

Received: October 3, 2022

Accepted: December 28, 2022

Published: January 5, 2023



56 to 77%.⁸ The inconsistency in the emission properties of CsMnCl₃ NCs (being emissive and nonemissive) needs to be yet clarified.

Variations in the crystal phase or the local lattice symmetry^{9,10} may explain the contradicting luminescence behavior reported for CsMnCl₃ NCs. Examples in the literature for both Pb-based and Pb-free perovskites support this argument.^{12–14} The electronic structures of LHPs can be altered by both intrinsic (e.g., defects) and extrinsic (such as temperature, pressure, and light) factors that promote transition between different crystal phases (such as cubic, tetragonal, orthorhombic, and hexagonal).^{12,13} For instance, complete PL quenching of CsPbBr₃ NCs is observed upon applying high pressure, which tilts the lead bromide octahedra and changes the band gap from direct to indirect.¹³ For Pb-free Cs₂AgInCl₆, Luo et al. demonstrated that breaking its crystal inversion symmetry facilitates radiative recombination, resulting in bright white light emission.¹⁴ These examples highlight the importance of thoroughly identifying the structure-luminescence relationships^{15,16} to discover unexpected properties of halide perovskites and promote new optoelectronic applications. However, being an emerging family of materials, only few structure-luminescence studies exist for Pb-free perovskites, thus explaining the still limited understanding of their electronic band structures.¹⁷

To elucidate the dependence of the luminescence properties of CsMnCl₃ NCs on the structural parameters, we report the synthesis of these Pb-free NCs in two different crystal phases produced via the hot injection route, which is a well-known approach for the phase control of NCs.^{18–21} The formation of cubic (c-) and rhombohedral (r-) phases of CsMnCl₃ NCs is demonstrated by the structural refinement of their X-ray diffraction (XRD) patterns. The two phases exhibit striking differences in luminescence properties, which are rationalized through the study of their electronic band structures by density functional theory (DFT) calculations. The high exciton binding energy of r-CsMnCl₃ NCs ensures a relatively bright emission (PLQY = 40%) with a maximum at 670 nm, which is highly Stokes-shifted from their band gap. In addition, transient absorption (TA) measurements reveal the ultrafast relaxation dynamics of the NCs in their excited state, which influences their emission properties. Furthermore, we study the applicability of the r-CsMnCl₃ NCs possessing the Stokes-shifted emission and the excellent phase stability for energy harvesting in proof-of-concept luminescent solar concentrators (LSCs). Overall, by establishing a structure-luminescence relationship for the emerging class of manganese chloride compounds, this work may contribute to the understanding of the emission properties of other metal-based Pb-free halide perovskites and inspire the design of new highly luminescent materials.

EXPERIMENTAL SECTION

Materials. Cesium carbonate (Cs₂CO₃, 99.9%), octadecene (ODE, 90%), oleic acid (OA, 90%), oleylamine (OLAm, technical grade, 70%), Mn (II) chloride (MnCl₂, 99%), hexane (≥95%), and methyl acetate (MeOAc, ≥98%) were purchased from Sigma-Aldrich. A conventional distillation process was carried out to obtain anhydrous MeOAc. All other chemicals were used without further purification.

Preparation of Cs-Oleate. Cs₂CO₃ (407 mg) was loaded into a 50 mL three-neck flask along with ODE (18 mL). The solution was degassed for 1 h at 120 °C. Dry OA (1.74 mL) was then injected under argon (Ar) upon an additional 15 min of degassing. At this

point, the temperature was increased to 150 °C to dissolve Cs₂CO₃ and form a fully transparent Cs-oleate solution.

The Cs-oleate precursor was cooled down to room temperature and stored under vacuum for further use. Before the injection, Cs-oleate solution was degassed for at least 30 min at 120 °C and heated up to 150 °C under Ar.

Synthesis of CsMnCl₃ NCs. CsMnCl₃ NCs were synthesized following a modified protocol.²² Anhydrous MnCl₂ (156 mg) was loaded into a 25 mL three-neck flask along with dry ODE (10 mL), dry OA (2 mL), and dry OLAm (2 mL). The scaling and handling were carried out in an inert atmosphere. The halide precursor solution was degassed under vacuum for 1.5 h at 120 °C. During the heating and degassing processes, the solution gradually turns color from reddish-brown to transparent yellow (Figure S1a). The temperature of the reaction flask was increased to the desired values (e.g., 150, 180, and 200 °C) under Ar gas, and Cs-oleate solution (i.e., 2, 3, and 4 mL which corresponds to 0.7, 0.5 and 0.35 Mn to Cs ratio) was swiftly injected into the flask under vigorous stirring. There was no obvious color change observed after the injection. The reaction was kept at the injection temperature for 5 s and then quickly quenched by an ice-water bath (Figure S1b). The crude solution was purified by centrifugation at 8550 rpm for 5 min without any antisolvent. The as-obtained white-pinkish precipitate (Figure S1c) emitted strong pink-red light under the UV lamp. After discarding the supernatant, the vials with the remaining NC precipitate were dried in a vacuum desiccator (typically overnight) to remove the excess solvent. The dry NC precipitate was redispersed in hexane for further use. All NC suspensions displayed high colloidal stability. Importantly, the nonpurified CsMnCl₃ NCs were degrading quickly and changing color to black (Figure S1d).

Purification of CsMnCl₃ NCs. To efficiently isolate the NCs from the solution and remove the excess of the ligands on their surface, different purification methods were tested. For example, after the first purification step described above, the NCs dispersed in 2 mL of hexane were centrifuged with varying speeds ranging from 8600 to 14,000 rpm. However, no visible precipitation of the NCs was observed.

A series of antisolvents were also tested. The crude solution was divided into equal parts and one portion of anhydrous isopropanol or anhydrous ethyl acetate was added to two portions of the NC dispersion. However, the resultant precipitate did not show any visible PL emission. Nevertheless, adding anhydrous MeOAc in 1:1 volume ratio to prepurified NC suspension, followed by centrifugation at 12,000 rpm, resulted in the formation of a white-pinkish NC precipitate with structural and optical properties similar to the one obtained after the first purification step.

Characterization Techniques. XRD patterns were recorded by a Malvern Panalytical Empyrean Alpha 1 diffractometer in the powder diffraction mode using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) and a cathode voltage and current of 45 kV and 40 mA, respectively. High-resolution XRD patterns were obtained for all samples under identical measurement settings (4–62° range, 0.0262° step size, and 17 s per step). Samples were prepared by drop-casting from the as-synthesized dispersions on precleaned microscopy cover glasses (20 × 20 mm). To ensure a proper comparison between the samples while guaranteeing a reasonable signal-to-noise ratio, a similar thickness was used for all samples. The structural information was derived from Rietveld refinement using Malvern Panalytical's HighScore software. A three-dimensional visualization system for electronic and structural analysis (VESTA) was used to draw the crystal structures.²³

Transmission electron microscope (TEM) images were taken using a JEM-F200 microscope (200 kV). 20 μL of the NC dispersion in hexane (the absorbance at 280 nm was set to 0.2) was drop-casted on the carbon-coated Cu grids. Ultraviolet–visible (UV–vis) absorption spectra were recorded using a Shimadzu UV-3600 UV–vis–NIR spectrophotometer. Steady-state PL, absolute PLQYs, and time-resolved PL (TRPL) decays were measured using an FLS1000 spectrofluorometer (Edinburgh Instruments, UK) comprising a mountable integrating sphere and a microflash lamp (frequency 100 Hz). The stability of the optical properties was monitored using the

same diluted NC dispersions stored under ambient conditions (RH \sim 40% $T = 25$ °C) in the dark.

Ultrafast TA measurements were conducted with a home-built TA spectrometer. The NC dispersion samples in a 2 mm thick quartz cuvette were excited by laser pulses at 300 nm (Libra F, Coherent Inc., coupled with Topas C, Light Conversion Ltd.), while a white continuum generator (heavy water) was employed to generate the probe beam. The TA responses (time resolution: \sim 150 fs) were recorded using an ExciPro TA spectrometer (CDP, Inc.) equipped with a CCD array.

Inductively coupled plasma mass spectroscopy (ICP-MS) measurements were conducted with Thermo Scientific iCAP RQ equipment. After purification, NC precipitate samples were dissolved in concentrated HNO_3 followed by dilution and measurement in 2% HNO_3 matrix. Ionic standard solutions with a concentration range of 0.001–1000 $\mu\text{g}/\text{L}$ for Cs and Mn were prepared in 2% HNO_3 using super-pure chemicals (Romil-SpA) and applied to measure calibration curves. Ultrapure H_2O (18.2 M Ω cm, Merck Milli-Q) was used for sample dilutions.

For low-temperature PL (LTPL) measurements of CsMnCl_3 NCs deposited on a silica substrate, the measurements were conducted in a cryostat (CTI CCS-150) at 20 K intervals from 30 to 293 K. The samples were excited by a 380 nm light-emitting diode (pE-4000—CoolLED) at 380 nm.

DFT Calculations. DFT calculations were carried out based on the measured crystal and atomic structure of both *c*- and *r*- CsMnCl_3 models. We first identified the most stable magnetic state of both structures. Then, we calculated the band structure based on the primitive cell models of these states. Specifically, the most stable magnetic state of *c*- CsMnCl_3 is the G-type antiferromagnetic one, in which the spin-up and -down Mn^{2+} ions adopt a face-centered cubic alignment with space group $Pm\bar{3}m$. The most stable magnetic state of *r*- CsMnCl_3 has the $R\bar{3}m$ symmetry.

To accurately calculate the electronic structure, we used the hybrid Heyd-Scuseria-Ernzerhof (HSE06) exchange–correlation functional in combination with the zero-order regular approximation to account for the scalar relativistic effects. For *c*- CsMnCl_3 ($Pm\bar{3}m$) and *r*- CsMnCl_3 ($R\bar{3}m$), we used Γ -centered $6 \times 6 \times 6$ and $3 \times 3 \times 3$ *k*-point meshes for the Brillouin-zone sampling, respectively.

LSC Setup. To explore the potential of CsMnCl_3 NCs in LSC devices, a dedicated experimental setup was built. The schematic illustration of our experimental setup including the proof-of-concept device is presented in the relevant chapter. The proof-of-concept device consists of a thin film of NCs deposited on top of a glass plate. The edge of this miniature window (~ 2 cm \times 0.15 cm) is placed directly on top of a silicon pn-junction photodiode (2×2 cm 2). An opaque cover is placed on top of the surrounding photodiode area. To eliminate the possible effect of background light, the photodiode is placed in a dark box. While in the box, a light beam with a spectrum similar to a warm white light-emitting diode (400–700 nm) collimated by a lens producing a spotlight with a diameter of ~ 1.6 cm and a power of ~ 9.5 mW is directed perpendicularly to the middle of the glass. The NCs on the glass surface absorb and re-emit some of the light that will reach the photodiode, where it will be absorbed and transformed into a photocurrent. The resulting *I*–*V* characteristics of the photodiode for an applied bias between -5 and 0.5 V were measured. Since the measured photodiode current is directly proportional to the intensity of the incident light, the configuration provides information on the intensity of the arriving light (i.e., light emitted by the NCs).

RESULTS AND DISCUSSION

CsMnCl_3 NCs were synthesized through conventional hot injection of Cs-oleate into a MnCl_2 precursor solution (see Experimental Section, Figures 1 and S1 for complete details).¹⁰ To characterize the as-synthesized NCs, we purified and dispersed them in hexane. The injection temperature and the Mn/Cs precursor molar ratio were tailored in the range of 150–200 °C and 0.35–0.7, respectively. The selected injection

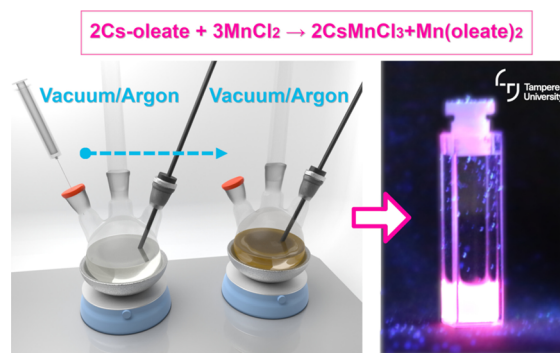


Figure 1. Schematic illustration of the NC synthesis via conventional hot injection method through the Cs-oleate route.

temperature range (150–200 °C) for the CsMnCl_3 NCs falls within the typical injection temperature range of the perovskite NCs of 120–250 °C. The injection temperature below the lower boundary of 150 °C resulted in no formation of the NCs in our synthesis. On the other hand, the NCs formed at 200 °C show significantly lower PLQY compared to the ones synthesized at 180 °C. The NCs synthesized at 150, 180, and 200 °C are hereafter referred to as 150@NCs, 180@NCs, and 200@NCs, respectively. Also, at the fixed injection temperature of 180 °C, the samples with varying Mn/Cs molar ratios (loading ratio) are labeled as 180@NCs//0.7, 180@NCs//0.5, and 180@NCs//0.35. The Mn/Cs ratio for 150@NCs and 200@NCs was fixed at 0.7.

Structural and Morphological Analysis of CsMnCl_3 NCs. The XRD patterns of all CsMnCl_3 NCs were recorded in ambient conditions (RH \sim 40%, $T = 25$ °C) to study the effect of injection temperature and Mn/Cs ratio on their crystal structure, as shown in Figure 2. To interpret the distinct XRD pattern of 150@NCs, which is different from that of the other samples, we performed Rietveld refinement on all XRD patterns (Figure 2b–e,i). The very low values of goodness-of-fit (χ^2) and residual weighting factor (R_{wp}) confirm the reliability of the refined structural parameters (see Tables S1 and S2 for the refinement parameters). The 150@NC sample adopts a 3D cubic CsMnCl_3 perovskite phase with $Pm\bar{3}m$ space group. In the perovskite structure of CsMnCl_3 , Cs^+ ions fill the voids created by the corner-shared MnCl_6 octahedra in all three crystal dimensions, as shown in Figure 2f. This crystal structure is identical to the perovskite structure of cubic CsPbCl_3 . The perovskite phase of bulk CsMnCl_3 has earlier only been successfully synthesized at high pressures, in agreement with the CsMnCl_3 phase-temperature diagram.²⁴ We, however, obtained the cubic phase of CsMnCl_3 (*c*- CsMnCl_3) at the nanoscale at ambient pressures and at a low temperature of 150 °C. We hypothesize that the high surface energy associated with the small *c*- CsMnCl_3 NCs compared to their bulk counterparts (feature size of NCs is only 3.9 nm) balances the overall energy necessary to favor the formation of the perovskite structure at ambient pressure. In other words, *c*- CsMnCl_3 crystallizes in a kinetically trapped high-pressure structure.²⁵ While metal halides based on ions other than Pb^{2+} , Sn^{2+} , and Ge^{2+} usually do not crystallize in the 3D perovskite structure,²⁶ CsMnCl_3 can form a 3D structure even at ambient pressure. This emphasizes the versatility of manganese colloidal chemistry due to the unique size of Mn^{2+} (0.67–0.83 Å depending on the high- or low-spin coordination) with respect to Cl^- (1.81 Å) ions that enables the formation of both

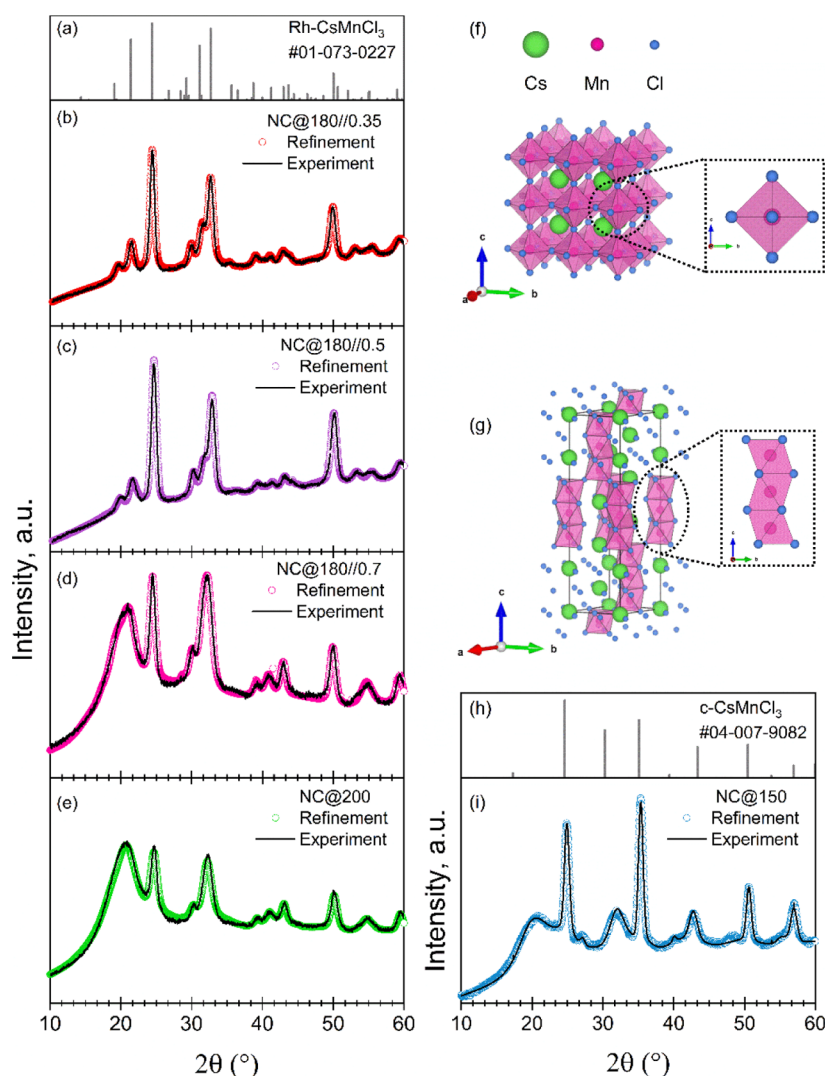


Figure 2. (a,h) Reference XRD patterns of *c*-CsMnCl₃ and *r*-CsMnCl₃ with reference codes 04-007-9082 and 01-073-02227, respectively. (b–e,i) Experimental (solid lines) and refined (open circles) profiles obtained after the full-pattern Rietveld refinement of the XRD patterns of 180@NCs//0.35, 180@NCs//0.5, 180@NCs//0.7, 200@NCs, and 150@NCs samples. The refined crystal structures of (f) *c*-CsMnCl₃ NCs and (g) *r*-CsMnCl₃ NCs. The corresponding insets display the repeating manganese iodide polyhedral unit of the structures.

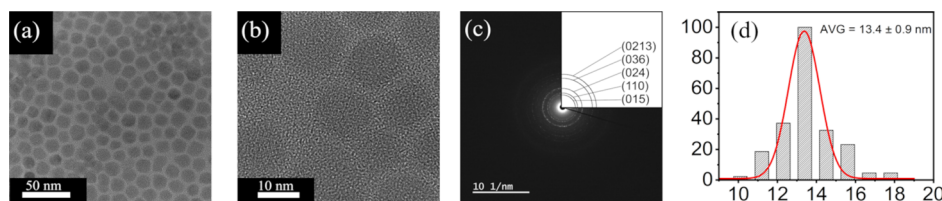


Figure 3. (a,b) TEM images of NCs@180//0.5 sample. (c) SAED pattern with assigned reflections. (d) Size distribution, determined as the diameter of the pentagons of NCs@180//0.5 sample.

perovskite and nonperovskite structures.²⁴ CsMnCl₃ NCs crystallize in a pure rhombohedral (nonperovskite) phase when the injection temperature is equal to or higher than 180 °C (Figure 2b–e). The space group of $R\bar{3}m$ of these NCs is the same as for the reported bulk CsMnCl₃.²⁷ In the crystal structure of *r*-CsMnCl₃ (Figure 2g), three face-sharing MnCl₆ octahedra form a 1D chain; these Mn₃Cl₁₂ chains are further interconnected into a 3D framework via corner-sharing; the negatively charged framework binds the Cs⁺ ions along the *c*-axis. The formation of *r*-CsMnCl₃ NCs instead of *c*-CsMnCl₃ NCs at higher injection temperatures is similar to the

formation of the hexagonal structure of bulk CsMnCl₃ after heating its cubic structure at 300 °C for a few hours.²⁴ Similar injection temperature-dependent phase control has already been achieved in the case of Pb-based perovskite NCs.^{19–21} The anticipated 1:1 Cs/Mn ratio of all NCs was further confirmed by ICP–MS (see Table S3).

The morphological evolution and size distribution of the synthesized NCs were studied by TEM, as shown in Figures 3, S2, and S3. The 150@NC sample exhibits a mixed morphology, with most of the particles having a rodlike shape. The morphology of the particles is dependent on the

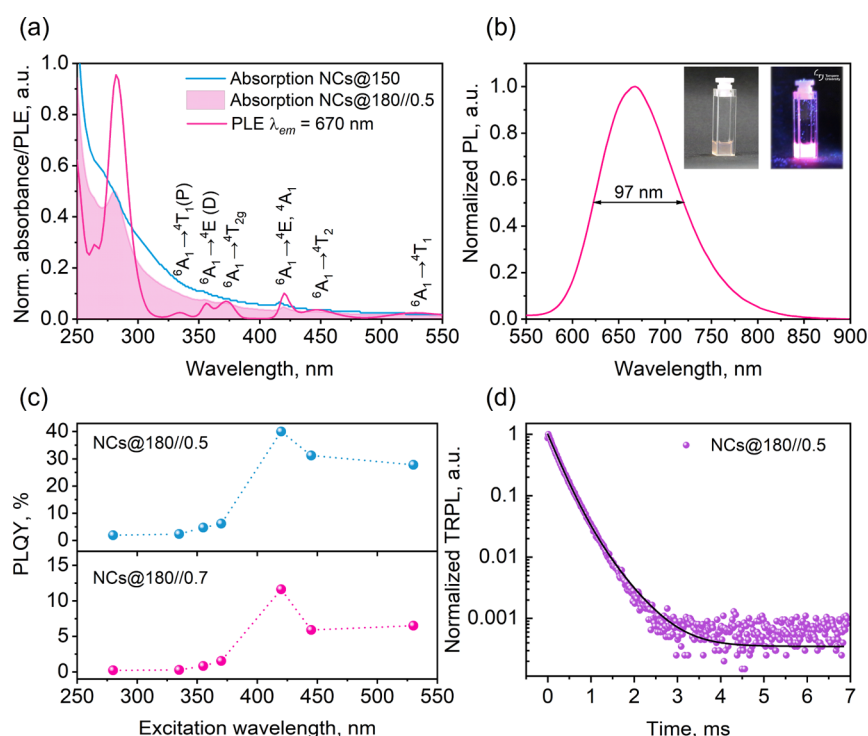


Figure 4. (a) Normalized absorption spectra of 150@NCs (c-CsMnCl₃) and 180@NCs//0.5 (r-CsMnCl₃) NCs along with the PLE spectrum of r-CsMnCl₃ NCs. (b) Normalized PL spectrum of r-CsMnCl₃ NCs. Inset: photos of the NCs in hexane under room (left) and UV ($\lambda = 365$ nm) lights (right). (c) Excitation wavelength-dependent PLQY of r-CsMnCl₃ NCs for two different Cs/Mn ratios. (d) TRPL decay of r-CsMnCl₃ NCs.

precursor ratio in the case of the 180@NC samples. Truncated sphere-shaped particles are obtained when the Mn/Cs ratio is 0.7 (Figure S2c). When decreasing the Mn/Cs ratio, the edges of the particles gradually become more defined and finally convert into hexagons when the ratio is 0.35. The average diameter of the hexagon- or sphere-like shaped particles varies from 10.8 ± 0.8 nm to 13.4 ± 1.0 nm, and the nanorods (150@NCs sample) are 3.9 ± 0.9 nm in length (see Figures 3 and S3).

Optical Properties and Electronic Band Structure from DFT.

The key optical properties of the as-synthesized CsMnCl₃ NCs are presented in Figure 4a–d. The c-CsMnCl₃ and r-CsMnCl₃ NCs strongly absorb at 275 and 280 nm (Figure 4a), respectively. The c-CsMnCl₃ NCs (150@NCs) are nonemissive. On the contrary, the r-CsMnCl₃ NCs exhibit red emission centered at 670 nm (Figure 4b) with a PLQY of 40%. The corresponding Stokes shift between absorption and PL is 2.6 eV. The emission wavelength of 670 nm is the longest ever reported for these NCs. Guan and co-workers show the PL for the CsMnCl₃ NCs centered at 660 nm with a very low PLQY of 0.7%,¹¹ which can be partially attributed to the surface traps. Hao et al. synthesized the NCs through benzoyl chloride injection and achieved an improved PLQY of 56.3%,⁸ which is the consequence of the excess chloride ions provided by the benzoyl chloride.^{28,29} Nevertheless, the Cs-oleate injection route employed in this work might be preferable over the one involving hazardous benzoyl chloride when aiming at eco-friendly alternatives to LHP NCs. Further, the fwhm value of the NCs is 97 nm (Figure 4b), that is, comparable to the value reported in a previous study on these NCs.¹¹

Absorption and PL excitation (PLE) spectra in the above-mentioned works are also depicted in a shorter wavelength range compared to our work. The corresponding optical band

gap values for c-CsMnCl₃ and r-CsMnCl₃ NCs are 4.8 and 5.0 eV, respectively (see Figure S4b and Table S4 for Tauc plot analysis). The very large band gaps of the NCs are supported by their electronic band structures obtained from DFT calculations (see Figure 5).

The MnCl₆ octahedra in the case of the rhombohedral structure are slightly distorted, whereas the cubic one consists of undistorted octahedra. The octahedral distortion can be

quantified using $D = \frac{1}{6} \sum_{i=1}^{i=6} \left(\frac{|l_i - l_{\text{avg}}|}{l_{\text{avg}}} \right)$,³⁰ where l_i is the bond

lengths between Mn²⁺ and six Cl⁻ and l_{avg} is the average bond length. The octahedra in the rhombohedral structure are 7.8% distorted compared to the cubic structure. The local symmetry breaking, driven by dimensional reduction, may lead to the difference in the electronic structure of the two crystal phases of CsMnCl₃.³¹

To gain insight into the electronic structure of CsMnCl₃, we carried out first-principles DFT calculations based on the experimental structures of both 180@NCs//0.5 (rhombohedral structure, space group: $R\bar{3}m$) and 150@NCs (cubic structure, space group: $Pm\bar{3}m$). We used the hybrid HSE06 exchange–correlation functional³² implemented in the all-electron numeric-atom-centered orbital code FHI-aims.^{33–36} The default amount of 25% screened Hartree-Fock exchange in HSE06 facilitates a more accurate description of the materials' electronic structure including the on-site Coulomb interaction between the Mn 3d electrons.

Test calculations indicate that the G-type antiferromagnetic (AFM) state of c-CsMnCl₃ is the most stable, and similarly, r-CsMnCl₃ adopts an AFM configuration, in which the unpaired 3d⁵ electrons of nearest-neighbor Mn²⁺ cations have opposite spins. Figure 5a,b shows the band structures and projected densities-of-states (PDOS) of these two AFM structures.

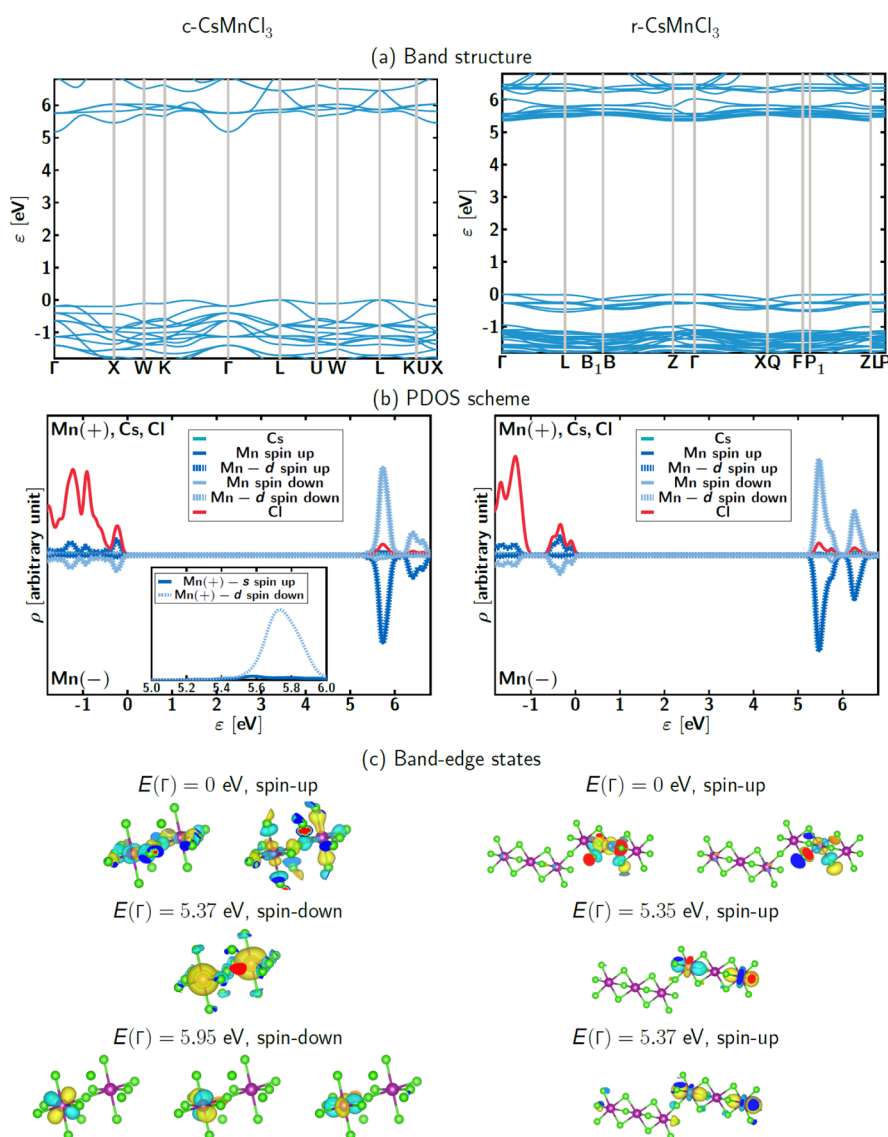


Figure 5. DFT-calculated electronic structure of AFM *c*-CsMnCl₃ (left column) and *r*-CsMnCl₃ (right column): (a) band structures, (b) PDOS schemes, and (c) wave functions of selected band-edge states at Γ . The VB maximum is shifted to 0 eV. In (a), only spin-up bands are shown as spin-down components exhibit the same structure. In (b), the spin-up DOS (identical to the spin-down counterparts) projected on both Cs and Cl species are colored in turquoise and red, respectively. Both spin-up (+) and spin-down (−) components (in blue and light blue, respectively) from a set of Mn²⁺ cations denoted by Mn(+) are shown in the upper panel, while the lower panel shows the Mn PDOS contributed by Mn(−) cations, the nearest neighbors of Mn(+). The d components of Mn PDOS are highlighted in dashed lines. In (c), the positive and negative parts of the wave functions are colored in cyan and yellow, respectively. Mn²⁺ and Cl[−] ions are given in purple and light green, respectively, while the Cs⁺ ions are not depicted for clarity.

These two polymorphs exhibit similar band gaps and similar valence band characters that consist of Cl-3p and Mn-3d orbitals. Figure 5c shows the wave functions for selected states. The plots of the valence band (VB) top at $E(\Gamma) = 0$ eV show two degenerate bands: one with mainly Mn-3d_{x²-y²} character and the other with Mn-3d_{z²}.

Unlike in their VBs, *c*-CsMnCl₃ and *r*-CsMnCl₃ differ in their CBs (conduction bands). The CB minimum of *c*-CsMnCl₃ has a pronounced 4s character, which is highly dispersed (see Figure 5a left) and extends over a large energy range (see the inset of Figure 5b left). This results in an indirect band gap of 5.18 eV, which is noticeably smaller than the direct band gap (5.37 eV). More importantly, the electronic transitions between the d-type VB-top states and the s-type CB-bottom states are unfavorable. This agrees with

the nonemissive behavior of the *c*-CsMnCl₃ NCs. Above this s-type band, we find three unoccupied bands with 3d_{xy}, 3d_{yz}, and 3d_{xz} character. However, on-site transitions between these and the VB-top states are suppressed because of the opposite spins. In contrast, *r*-CsMnCl₃ is a direct band gap material, and its CB edge states are mainly contributed by d-orbitals. Specifically, these unoccupied orbitals and the VB-top 3d orbitals are centered at the nearest-neighboring Mn²⁺ cations and have the same spin. This would establish a charge-transfer electronic-transition channel that involves two nearest-neighboring Mn²⁺ ions. It is similar to the case of emissive CsMnBr₃ which has a similar crystal structure as *r*-CsMnCl₃, whose band edges are primarily composed of Mn d orbitals.³⁷ The d–d electronic excitations in the AFM *r*-CsMnCl₃ between the band edges are spin-allowed (as both are spin-

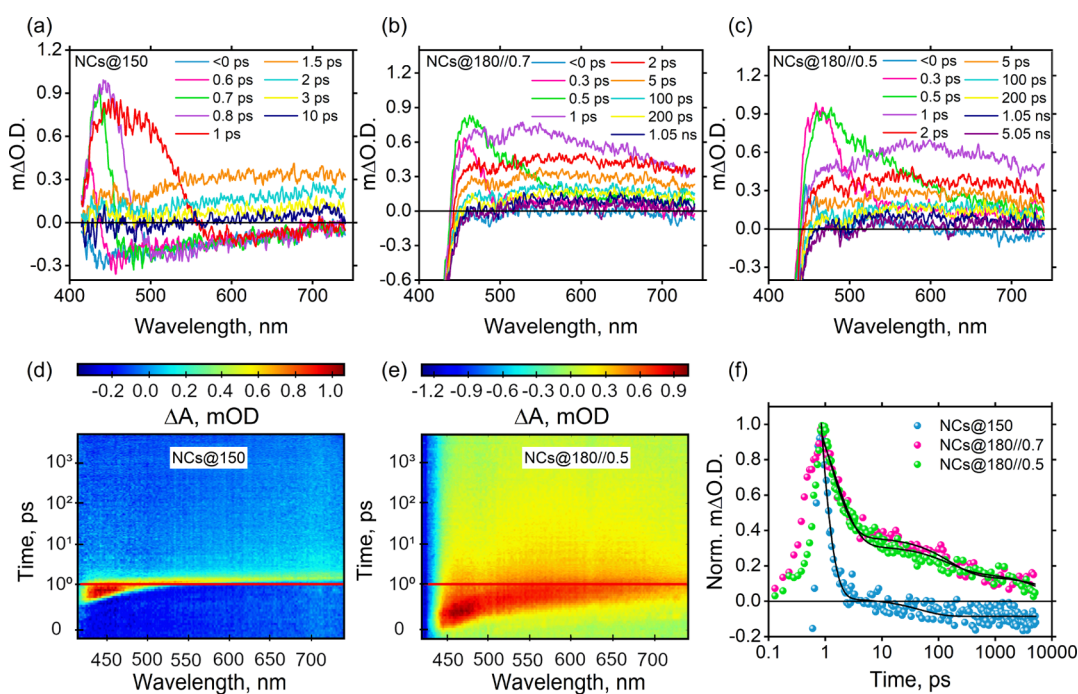


Figure 6. Ultrafast TA spectra of CsMnCl₃ (a) 150@NCs, (b) 180@NCs//0.7, and (c) 180@NCs//0.5 excited at 300 nm with an excitation power of 80 μW. TA mapping images of CsMnCl₃ (d) 150@NCs and (e) 180@NCs//0.5. (f) TA decays of CsMnCl₃ NCs monitored at 445 nm for 150@NCs and 550 nm for 180@NCs//0.7 and 180@NCs//0.5. Solid lines present the fitting results with a triexponential function:

$\Delta O. D. = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right)$ for 180@NCs//0.7 and 180@NCs//0.5 and with a bi-exponential function: $\Delta O. D. = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$ for 150@NCs, respectively, $\Delta O. D.$ is the change of optical density.

up orbitals), and the local symmetry breaking partially relaxes the Laporte forbidden nature of the transitions.

Electronic transitions between VB and CB edge states of *c*-CsMnCl₃ are prohibited by orbital symmetry and spin. Spin does not prohibit the VB maximum to CB minimum transition in *r*-CsMnCl₃. However, the DFT-HSE band gap of *r*-CsMnCl₃ is larger than the experimentally observed emission energy and the experimentally measured onset of absorption. We speculate that the involvement of defects, exciton self-trapping, or an as of now unresolved mechanism is responsible for the experimentally observed redshift in the emission spectrum. We can, however, provide further insight into the characteristics of the emissive feature by investigating the PLE spectrum of the NCs monitored at the emission maximum of 670 nm. It features six peaks at 335, 355, 370, 420, 450, and 530 nm, in addition to the 280 nm band gap feature (Figure 4a). Transitions corresponding to these six peaks might be of *d* orbital nature.^{6,38} We assigned these peaks with the help of the crystal field theory and Tanabe-Sugano (T-S) diagram.³⁸ The Racah's Parameter (*B*) (which measures the Mn–Cl bond strength) and the crystal field splitting energy (Δ) (which quantifies the strength of the crystal field and hence the degree of splitting of the *d*-energy levels) were determined from the lowest *d*–*d* transitions at 450 and 530 nm and were found to be 770 cm⁻¹ (0.095 eV) and 8601 cm⁻¹ (1.06 eV), respectively. These values are in the range typically found for the electronic transitions in octahedrally coordinated manganese compounds.^{6,38} The assignment of all peaks of the PLE spectrum is depicted in Figure 4a and summarized in Table S5. The calculated values of the *B* and Δ parameters are given in Table S5. Also, the PL spectra collected at different excitation wavelengths exhibit the same shape and the peak wavelength,

which suggests that the emission occurs from the relaxation of the same excited state regardless of the excitation energy (Figure S5a). Further electronic-structure theory calculations, which are beyond the scope of this work, can utilize our PLE analysis to identify the source of the red emission.

The emission maximum and the fwhm values of the *r*-CsMnCl₃ NCs are identical (see Table S4) regardless of the injection temperature (180 or 200 °C) or the Mn/Cs ratio. This indicates that the changes in the average size (10.8–15.5 nm) of the emissive NCs have no effect on the position and shape of the emission. The optimized Mn/Cs molar ratio of 0.5 (180@NCs//0.5) leads to the highest PLQY of 40%, while the PLQY of 180@NCs//0.7 is around 12%, and an excess amount of injected Cs-oleate results in a lower PLQY of 24% (180@NCs//0.35). We observe that 180@NCs//0.5 exhibits the longest Mn–Mn distance of 3.52 Å, larger than 3.13 and 3.17 Å for 180@NCs//0.7 and 180@NCs//0.35 samples, respectively, precisely following their PLQY trend. The PLQY dependency on the separation between metal polyhedra was also observed in other low-dimensional Pb-free perovskites.³⁹ Additionally, the influence of surface traps on the PLQY of the NCs cannot be ignored. Hao et al. showed that the passivation of surface traps by chloride ions is necessary to improve the PLQY of the CsMnCl₃ NCs.⁸ Subsequently, the radiative recombination is improved as observed from the TRPL decay of the NCs. Furthermore, the PLQY of the *r*-CsMnCl₃ NCs is dependent on the excitation wavelength (Figure 4c). The wavelength dependence of PLQY follows the *d*–*d* peak intensity variation in the PLE spectrum (Figure 4a), that is, the excitation wavelength corresponding to the most intense *d*–*d* peak (420 nm) leads to the highest PLQY. The relative PLE intensity of the *d*–*d* peaks typically indicates the relative

strength of the corresponding transitions, in turn, suggesting that the PLQY is maximum through the excitation of most prominent d–d transition of the system, similar to the case of other manganese halides.⁴⁰

The TRPL decay profile of r-CsMnCl₃ NCs was fitted with a biexponential function as shown in Figure 4d. The average PL lifetime of the NCs is around 240 μs, which is in the same order of magnitude as the bulk CsMnCl₃²⁷ and the NCs reported earlier.^{8,11} Interestingly, Bakr and co-workers demonstrated picosecond PL lifetime for the CsMnBr₃ NCs in contrast to microsecond lifetime observed for the same NCs in another report.^{6,7} The variation in the PL lifetime can be correlated with the variation in the Mn–Mn distance—the shorter the distance, the faster the PL decay.^{6,27} The Mn–Mn distance of our r-CsMnCl₃ NCs varies between 3.12 and 3.52 Å, and the corresponding PL lifetime is a few hundred microseconds. By contrast, organic–inorganic manganese halides with a similar Mn–Mn distance of 3.38 Å exhibited a PL lifetime of only a few nanoseconds.⁴¹ Owing to high electron-phonon coupling in low-dimensional metal halides,⁴² we anticipate that an intermediate electronic excited state, such as a self-trapped exciton (STE) state, causes the extension of the excited-state decay time in the case of r-CsMnCl₃ NCs.⁷

STE Formation in r-CsMnCl₃ NCs. To verify the formation of STE in the excited state of r-CsMnCl₃ NCs, ultrafast TA measurements were conducted on as-synthesized CsMnCl₃ NC dispersions. Figure 6a–c shows the TA spectra of c-CsMnCl₃ NCs (150@NCs) and r-CsMnCl₃ NCs (180@NCs//0.7 and 180@NCs//0.5) excited at 300 nm. A broad positive photoinduced absorption (PIA) band with a long tail toward 750 nm is detected for both 180@NCs//0.7 and 180@NCs//0.5 compared to the narrow PIA band with a short tail up to about 560 nm detected for 150@NCs (Figure S6). We assign this broad PIA band to the STE state, as observed for other Pb-free halide perovskite NCs involving STEs.^{43,44} The evolution of the signal in the 2D TA mapping image (Figure 6e) of 180@NCs//0.5 shows a clear redshift, particularly after 1.5 ps, unlike the 150@NCs case. The comparison between the cubic and rhombohedral cases (Figure 6d) further clarifies an STE effect in the r-CsMnCl₃ NCs. Figure 6f compares the TA decays monitored at 445 nm for 150@NCs and 550 nm for 180@NCs//0.7 and 180@NCs//0.5, which were fitted well with biexponential and triexponential functions, respectively (see Table 1). We assign the two fast components ($\tau_1 < 2$ ps

Table 1. Summary of Fitting Results of TA Decay Curves of CsMnCl₃ NCs

sample	A ₁ (%)	τ ₁ (ps)	A ₂ (%)	τ ₂ (ps)	A ₃ (%)	τ ₃ (ps)
150@NCs	95.8	0.4	4.2	47.1		
180@NCs//0.7	70.9	1.5	10.6	152.7	18.5	8026.8
180@NCs//0.5	71.8	1.1	11.2	161.7	17.0	8525.1

and $\tau_2 < 200$ ps) to the carrier-trapping process and energy-transfer process, respectively, and the slow component ($\tau_3 > 8$ ns) to the STE-related radiative recombination.⁴⁵ On the other hand, the TA decay of c-CsMnCl₃ NCs (150@NCs) shows a negligible slow component instead, presenting a negative signal. The r-CsMnCl₃ NCs (180@NCs//0.7 and 180@NCs//0.5) show a similar long decay lifetime (>8 ns) corresponding to the STE state. Therefore, the structural transition from the cubic phase to the rhombohedral phase induced by the increase of the injection temperature indeed

triggers the facile distortion of MnCl₆ octahedra in the excited state, which results in the observed STE effect. This is consistent with the ultrafast exciton self-trapping observed in low-dimensional metal halides (1D r-CsMnCl₃ NCs in this case) as the potential barrier that exists for the distortion of metal halide polyhedra is much lower than for 3D metal halides (c-CsMnCl₃ NCs in this case).⁴² We thus speculate that the STE states for r-CsMnCl₃ form in the excited state, eventually enhancing the observed red emission, similar to Mn-doped Pb-free double-perovskite NCs.⁴⁶ It should be noted here that STE generation does not take place when excited with 370 or 420 nm, that is, below the band gap of the NCs (see Figure S6). It is consistent with the fact that excitation energy a little higher than the band gap is necessary to pump the electrons into the free-carrier or free-exciton state to cause the carrier self-trapping.

To estimate the exciton binding energy of r-CsMnCl₃ NCs, we performed a LTPL characterization on the strongly emitting sample (180@NCs//0.5). PL maximum of the sample gradually red-shifted from 655 nm at room temperature to ~680 nm at nearly 110 K (Figure 7a). The blue-shifted emission at high temperatures can be ascribed to the lattice expansion. This trend is similar to that of LHP NCs and bulk CsMnCl₃ thin films but opposite to that of conventional semiconductors.^{27,47} However, the PL maximum of the sample undergoes a small blueshift to 673 nm when cooled below 100 K. Such spinodal nature of the PL peak position with decreasing temperature has been ascribed to Mn–Mn magnetic coupling.¹¹ As expected, the PL intensity increases as the temperature decreases up to 100 K owing to the emission thermal quenching effect (Figure 7b,c).⁴⁸ Below 100 K, the intensity drops slightly.

The temperature-dependent PL quenching of the r-CsMnCl₃ NCs (100–300 K) can be expressed via the following equation

$$I(T) = \frac{I_0}{1 + A e^{-E_b/k_B T}}$$

where $I(T)$ and I_0 are the PL intensities at temperatures T and 0 K, respectively, E_b is the exciton binding energy, and k_B is the Boltzmann constant. By fitting the PL quenching data using the above equation, an exciton binding energy (E_b) value of 100 ± 18 meV is extracted (Figure 7b), which closely matches the earlier reported value (81.36 meV).⁸ The binding energy of 100 meV is higher than that of 3D LHPs and comparable to those of all-inorganic 1D lead-free halide perovskites or quasi-2D organic–inorganic hybrid perovskites.^{49–51} A high E_b value indicates strong confinement of the excitons in the r-CsMnCl₃ NCs, which might explain its high PLQY. The fwhm of the emission decreases from 69 to 52 meV when the sample cools down from 293 to 50 K (Figure S7), consistent with the earlier studies on the NCs.^{8,11} The gradual drop in the fwhm of the NCs with decreasing temperature suggests reduced exciton phonon coupling strength (lattice vibrations), which contributes to the increased integrated PL intensity (Figure 7c).^{8,11}

Structural and Emission Stabilities of CsMnCl₃ NCs.

We assessed the structural stability of the CsMnCl₃ NCs in a film form and their PL stability in hexane dispersions. The XRD patterns of c- and r-CsMnCl₃ NCs films stored and measured in the ambient conditions (in darkness, RH ~ 40%, $T = 25$ °C) were collected as a function of time (Figure 8a). The r-CsMnCl₃ NCs display the same XRD pattern before and after 3 months, suggesting the long-term structural stability in

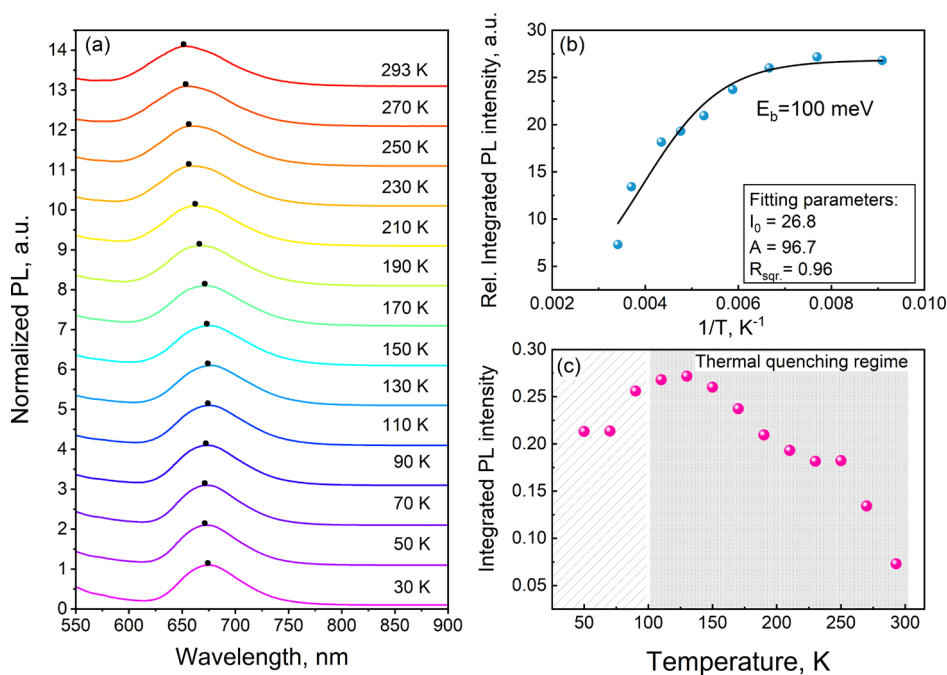


Figure 7. (a) Normalized LTPL spectra of r-CsMnCl₃ NCs excited at 380 nm. The sample was initially cooled down up to 30 K, followed by a gradual increase of the temperature toward room temperature with 20 K ramp. The PL maxima are marked with black dots to guide the eye. (b,c) Variation of the integrated PL intensity of r-CsMnCl₃ NCs as a function of temperature and determination of the exciton binding energy.

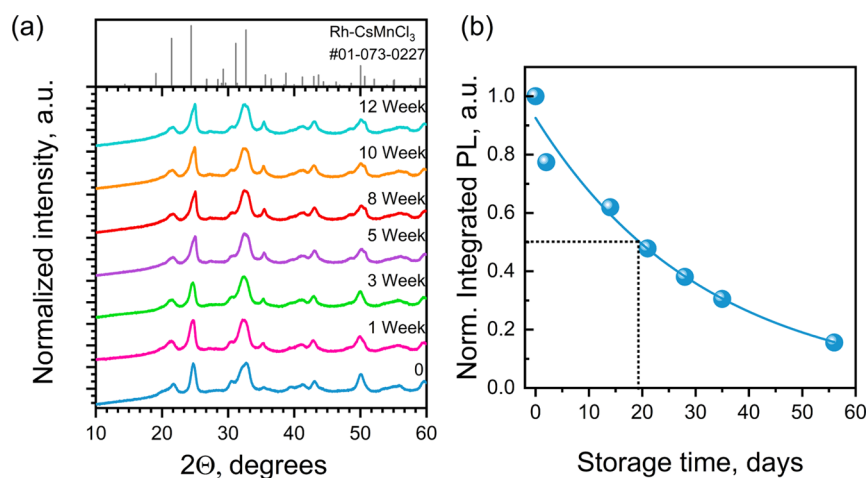


Figure 8. (a) Storage time-dependent XRD patterns of r-CsMnCl₃ NCs. (b) Relative integrated PL intensity of the NCs (solid line is to guide the eye, and dashed lines represent drop till 50% from the initial value).

ambient conditions of the r-CsMnCl₃ NCs without additional treatments or encapsulation, unlike the red-emissive CsPbI₃ NCs.^{3,52,53} On the other hand, nonemissive c-CsMnCl₃ NCs (150@NCs) do not retain their original XRD pattern already after 9 weeks of storage in air (Figure S8). The Rietveld refinement performed on the aged 150@NCs pattern shows that most of c-CsMnCl₃ decomposes into CsCl (Figure S8). Hence, the rhombohedral structure of CsMnCl₃ NCs is energetically more favorable than their cubic structure, as supported by our DFT calculations as well as previous studies.²⁴ Notably, the r-CsMnCl₃ NCs retain >70% of their original PLQY after a week in the air (Figure 8b), demonstrating improved luminescence stability compared to the reported CsMnCl₃ and Zn-doped CsMnCl₃ NCs (which preserved only 10.1 and 51.7% of their initial PLQY, respectively).⁸ However, the PL efficiency of the r-CsMnCl₃

NCs gradually decreases and reaches 50 and 5% of its initial value in the air after 20 and 55 days, respectively. The TEM images of the aged sample show a partial agglomeration of the NCs (Figure S9). This introduces new surface and structural defects that can act as additional recombination channels and possibly cause or contribute to the luminescence quenching. This may be attributed to the stripping of the protective ligand shells from the NC surface.⁵⁴ Consequently, ligand engineering may tackle this issue and prolong the PL stability of the NCs through improved surface passivation. A dedicated follow-up study could focus on this direction.

CsMnCl₃ NCs for LSC Applications: A Proof-of-Concept Demonstration. Recent advances in the building-integrated photovoltaics demonstrated a new possible way of sunlight harvesting, namely LSCs. The main idea of this concept is to encapsulate the luminescent material in a

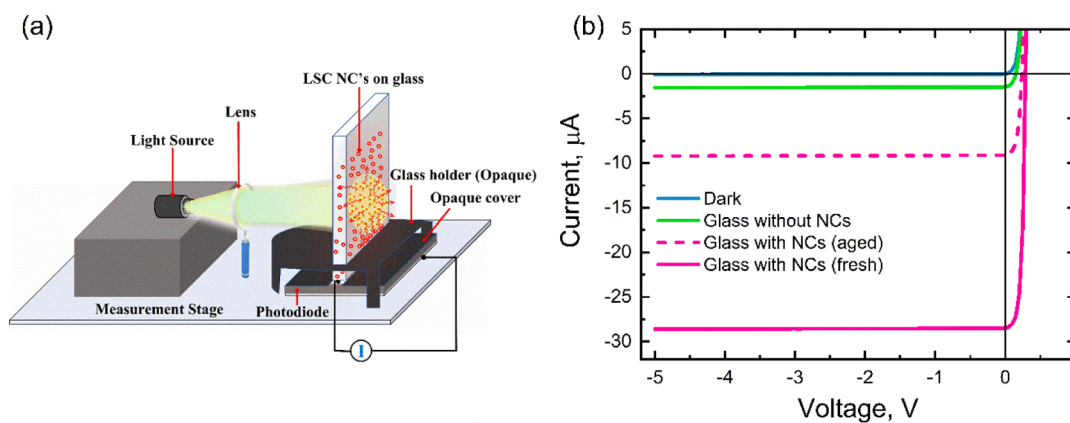


Figure 9. (a) Schematic illustration of the experimental setup. The proof-of-concept device consists of a silicon photodiode that is placed directly under the edge of a miniature glass window with embedded NCs. (b) I – V characteristics of the Si photodiode with different glass configurations including an aged (11 weeks) NC film. Dark current is a few nA.

polymer composite or glass and embed it in the window. The deployed LSC will absorb part of the sun light arriving at the window and then re-emit it at a longer wavelength. Higher than air refractive index glass will act as a waveguide and direct most of the emitted light to the edges, where the light is converted into electricity via solar cells. The high PLQY of the LHP NCs is appealing for this application. However, apart from the lead toxicity and poor stability in ambient conditions, LHP NCs typically exhibit small Stokes shifts leading to reabsorption effects, which are detrimental for LSCs and limit their scalability. To our knowledge, only Bi-doped $\text{Cs}_2\text{Ag}_{0.4}\text{Na}_{0.6}\text{InCl}_6$ NCs were found to be efficient emitters in LSCs due to their PLQY of 38%, broad emission, and low reabsorption.⁵⁵

The above-discussed properties of CsMnCl_3 NCs, namely, the Stokes-shifted luminescence in the visible region with a 40% QY and fairly good stability in the air, suggest that they could have potential as active material in LSC devices. To explore this, a dedicated experimental setup presented in Figure 9a was constructed. The details of the setup are described in the Experimental section. Figure 9b shows the measured I – V characteristics of the photodiode (i) in the dark (blue curve), (ii) under illumination with a standard glass (green curve), and (iii) under illumination with an NC-coated glass (red curve). In the dark, the photodiode exhibits rectifying characteristics with a very low current of a few nA. The benefit from the PL of the NC film is evident as the photocurrent for an NC thin film-coated glass is an order of magnitude higher than for a glass without NCs (and approximately 4 orders of magnitude higher than the dark current). This result demonstrates the potential of the CsMnCl_3 NCs to produce electricity when coupled in an actual LSC device.

Additionally, we examined how the aging of the CsMnCl_3 NC film affects the photocurrent by measuring the same film after 11 weeks of aging in air (Figure 9b). Evidently, due to the degradation of the PL properties of the NCs (Figure 8b), the measured photocurrent is nearly 3 times lower than the initial value (but still higher than the reference). This experiment provides additional confirmation that the observed photocurrent is caused by the luminescence of the NCs instead of mere light scattering by the film components that in turn should not be affected by the stability of the NCs. It should be noted that the NC films were completely unencapsulated here;

therefore, LSCs evidentially demonstrate a drop in the performance. However, even in these conditions, the photocurrent was still generated, which allows us to speculate that considerably longer stability is expected for the NCs integrated into a protective matrix. Therefore, we believe that CsMnCl_3 NCs is a promising candidate for LSC applications among other lead-free NCs.⁵⁵

CONCLUSIONS

In summary, we have successfully synthesized 3D and 1D CsMnCl_3 NCs, namely, cubic and rhombohedral phases, by tuning the temperature of a hot injection colloidal synthesis. The DFT-calculated electronic band structures of *c*- CsMnCl_3 and *r*- CsMnCl_3 NCs demonstrate that they have indirect and direct band gaps, respectively. This may explain their distinct PL properties; *c*- CsMnCl_3 NCs are nonemissive, while *r*- CsMnCl_3 NCs that possess allowed electronic transitions between the VB and CB edge states display bright red luminescence centered at 670 nm. Furthermore, the luminescence stability of the NCs in the air is improved compared to earlier reports. However, much higher stability is essential to realize optoelectronic devices, like the proof-of-concept example of LSCs. We suggest that ligand engineering, with capping ligands that reduce the surface defects while strongly binding to the NC surface, could be a promising future approach to simultaneously improve the PLQY and luminescence stability.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnm.2c04342>.

Photographs of the NCs; TEM images and size distribution of the NCs; Rietveld refinement parameters of CsMnCl_3 NCs; Tauc plots; injection temperature-dependent absorption and PL spectra and TRPL decay curves; excitation wavelength-dependent PL spectra; excitation wavelength-dependent TA spectra and decay curves; temperature-dependent fwhm variation; and stability studies of CsMnCl_3 NCs (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Dr. Mari Honkanen and Tampere Microscopy Center are gratefully acknowledged for the TEM images. This work is part of the Academy of Finland Flagship Programme, Photonics

Research and Innovation (PREIN), decision No 320165. P.V. acknowledges the support of Jane & Aatos Erkkö foundation (project "SOL-TECH"). M.L. thanks the Finnish Cultural Foundation (00210670) for funding. H.M.A. and V.V. acknowledge the financial support of the Academy of Finland (#331313). H.M.A., V.V., and H.S. acknowledge the provision of facilities and technical support by Micronova Nanofabrication Centre and Nanomicroscopy Centre in Espoo, Finland within the OtaNano research infrastructure at Aalto University. The assistance provided by Dr. Diao Li regarding the optical components and their setup for the proof-of-concept photodiode I - V measurements is highly appreciated.

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