

Highly Emissive Divalent Ion Doped Colloidal $\text{CsPb}_{1-x}\text{M}_x\text{Br}_3$ Perovskite Nanocrystals through Cation Exchange

Ward van der Stam,^{1§} Jaco J. Geuchies,^{1§} Thomas Altantzis,² Karel H. W. van den Bos,² Johannes D. Meeldijk,³ Sandra Van Aert,² Sara Bals,² Daniel Vanmaekelbergh¹, Celso de Mello Donega¹

¹Debye Institute for Nanomaterials Science, Utrecht University, The Netherlands

²EMAT, University of Antwerp, Belgium

³Electron Microscopy Utrecht, Utrecht University, The Netherlands

Colloidal CsPbX_3 ($X = \text{Br}, \text{Cl}, \text{I}$) perovskite nanocrystals (NCs) have emerged as promising phosphors and solar cell materials due to their remarkable optoelectronic properties. These properties can be tailored not only by controlling the size and shape of the NCs, but also by post-synthetic composition tuning through topotactic anion exchange [1,2]. In contrast, property control by cation exchange is still underdeveloped for colloidal CsPbX_3 NCs.

In this work, we developed a post-synthetic method that allows partial cation exchange in colloidal CsPbBr_3 NCs, whereby Pb^{2+} is exchanged for several isovalent cations, resulting in doped $\text{CsPb}_{1-x}\text{M}_x\text{Br}_3$ NCs ($M = \text{Sn}^{2+}, \text{Cd}^{2+}, \text{Zn}^{2+}$, $0 < x \leq 0.1$), with preservation of the original NC shape [3]. The size of the parent NCs is also preserved in the product NCs, apart from a small (a few %) contraction of the unit cells upon incorporation of the guest cations.

The partial Pb^{2+} for M^{2+} exchange leads to a blue-shift of the optical spectra, while maintaining the high photoluminescence quantum yields (>50%), sharp absorption features and narrow emission of the parent CsPbBr_3 NCs. The blue-shift is attributed to the contraction of the perovskite lattice due to the incorporation of smaller divalent guest cations ($\text{Sn}^{2+}, \text{Cd}^{2+}, \text{Zn}^{2+}$), resulting in shorter Pb-halide bonds and hence an increased interaction between Pb and Br orbitals. In contrast to what has been reported for bulk perovskite materials, we show that the blue-shifted PL energy scales linearly with the lattice vector of the doped $\text{CsPb}_{1-x}\text{M}_x\text{Br}_3$ NCs, showing that the lattice contraction induced by Pb^{2+} for M^{2+} exchange can be used to tune the PL wavelengths of perovskite NCs.

This work thus opens up new possibilities to engineer the properties of halide perovskite NCs, which are demonstrated to be the only known system to date where post-synthetic topotactic cation and anion exchange reactions can be sequentially combined while preserving the original NC shape, resulting in compositionally diverse perovskite NCs. This opens up a library of possible compositions attainable for colloidal CsPbX_3 NCs, which might possess unprecedented and unparalleled optoelectronic properties and may prove beneficial for a number of applications.

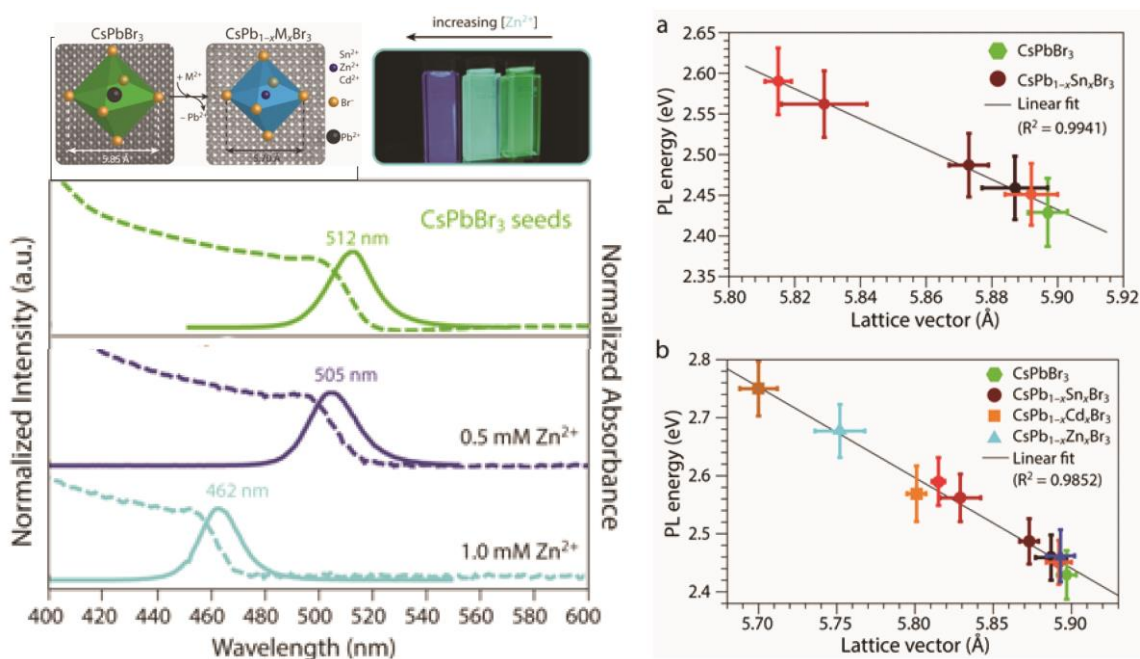


Fig. 1. **Top left:** Schematic illustration of the Pb^{2+} for M^{2+} CE reaction in CsPbBr_3 NCs. **Top center.** Photograph of colloidal suspensions under UV illumination of parent CsPbBr_3 NCs (right vial) and product NCs after reaction with different concentrations of ZnBr_2 . **Bottom Left.** PL (full lines) and absorption (dashed lines) spectra of parent NCs (green lines) and product NCs obtained after reaction with different concentrations of ZnBr_2 (blue lines). **Right.** PL energy and lattice vector correlation in $\text{CsPb}_{1-x}\text{M}_x\text{Br}_3$ perovskite NCs obtained by post-synthetic Pb^{2+} for M^{2+} cation exchange in CsPbBr_3 NCs. (a) $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ NCs (b) $\text{CsPb}_{1-x}\text{M}_x\text{Br}_3$ ($M = \text{Sn}, \text{Cd}, \text{Zn}$) NCs.

§ These authors contributed equally to this work

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