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Reversible Color Switching in Dual-Emitting Mn(II)-Doped $CsPbBr_3$ Perovskite Nanorods: Dilution versus Evaporation

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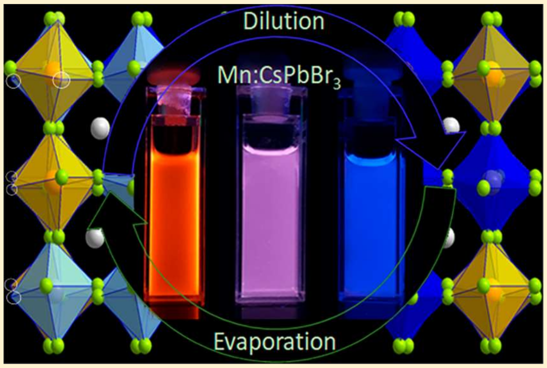
Supporting Information

ABSTRACT: Postsynthesis halide treatment can brighten perovskite nanocrystals. While this has been recently explored for undoped nanocrystals having only the exciton emission, herein, the impact of halide-enriched and -deficient environments was studied for dual-emitting Mn(II)-doped $CsPbBr_3$ nanorods. This was performed by adopting a self-regulated approach where the nanorod solution reversibly switched the color brightness from blue to orange and vice versa by dilution and evaporation, respectively. With control experiments, it was established that the color switching was not due to a change in the rate of the exciton energy transfer from host to dopant energy states; rather, it was related to self-regulated fulfilling and again creating halide vacancies observed with variation of nanorod concentration. Being that the halide vacancy was established as one of the key factors for controlling the brightness of these nanocrystals, this reversible switching in doped $CsPbBr_3$ adds new fundamental insight into controlling the photoluminescence of these emerging nanocrystals.



Light-emitting perovskite nanocrystals recently emerged as one of the most demanding energy materials for optoelectronic applications.[1−4] Enormous efforts have been put forward to understand the photophysics and stabilize their intense emissions.[5−14] It has been recently established that halide deficiency in lead halide perovskite nanocrystals remained as a key feature for dominating their photoluminescence quantum yields (PLQYs).[15−19] Introduction of excess halides was found to successfully brighten the high-energy-emitting $CsPbCl_3$ and platelets of $CsPbBr_3$ nanocrystals.[18,20,21] This multifold enhancement of the emission intensity in halide-rich systems was related to suppression of defect states in halide-deficient perovskite nanocrystals.[16,19] Beyond the excitonic emission, recently, intense dopant emission for these high-energy-absorbing Mn(II)-doped perovskite nanocrystals was also established.[22−26] In most cases, a halide-rich system was adopted to facilitate the Mn(II) doping, where more Mn(II) ion insertion or brightening of the d-state emission was expected with excess halide ions.[24,27−29] This limits the understanding of the impact of halide concentration on dispersed doped nanocrystals. Moreover, Mn(II) doping was extensively studied for the host $CsPbCl_3$, which has ideal band positions for efficient energy transfer and also ionic size compatibility to retain inside of the host crystal.[22−24,30] Among others, even though quantum-confined $CsPbBr_3$ nanocrystals retain their blue emission,[24,31,32] but doping in these nanostructures is limited. Hence, with doping in the $CsPbBr_3$ system and creating halide-deficient and halide-rich environments, understanding their impact in both dopant and host emissions remained challenging and needed to be explored.

Keeping these in mind, herein, doping Mn(II) in blue-emitting $CsPbBr_3$ nanorods is reported. Adopting a unique approach, the system was allowed to self-regulate in tuning the brightness of host and dopant emission as a function of dilution and evaporation of the dispersed solvent. The as-synthesized orange-emitting doped nanorods showed unprecedented enhancement of the host excitonic blue emission with dilution, and again, this was rapidly quenched, bringing back the original orange emission during evaporation. The visible change from blue to orange color under irradiation and

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