

$(\text{CH}_3(\text{CH}_2)_5\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Pb}_n\text{Br}_{3n+1}$: A homologous series of 2D halide perovskites with tuneable energy gap in the blue and green visible spectrum

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Hybrid halide perovskites represent a new family of high-performance semiconductors with unconventional optoelectronic properties, thriving in photovoltaics and other aspects of optoelectronic technology^[1]. One derivative class of the materials are the dimensionally reduced two-dimensional (2D) perovskites which consists of periodic nanometer-thick layers of extended, anionic inorganic lattices separated by insulating organic cations. In this configuration, the materials behave as multiple quantum wells (MQW) naturally forming within single-crystals of the respective compounds. Because of this configuration, 2D halide perovskite form an excellent testbed for study of quantum phenomena, especially because the materials can stabilize excitons that are observable at room temperature^[2].

In this work, the $(\text{CH}_3(\text{CH}_2)_5\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ ($n = 1-5, \dots, \infty$) homologous series of 2D inorganic-organic lead-halide perovskites were investigated. Deriving from the bulk, three-dimensional (3D) lattice of the parent $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite (the $n = \infty$ end-member), a targeted synthetic approach using hexylammonium $\text{CH}_3(\text{CH}_2)_5\text{NH}_3^+$ cations as molecular scissors yields a new family of 2D perovskites with perovskite slices of quantized length, adjusted from the n -value of the chemical formula. The combination of alternating organic and inorganic layers affords both dielectric and quantum confinement in two dimensions. By controlling the number of layers in the inorganic plane, it is thus possible to tune the degree of the confinement, resulting in tuneable bandgap, in the range of 2.3-3.1 eV, and adjustable exciton binding energy of the photogenerated species. The excitons in the homologous series appear to follow the Mott-Wannier exciton series based on diffuse reflectance and photoluminescence measurements. Our results indicate that the general behavior of the bromide perovskites is analogous with that of the well-studied iodide-based perovskites family, with a notable difference that the excitonic features of the spectra persist even for the high n -value perovskites, suggesting larger exciton binding energy and a smaller exciton Bohr radius.

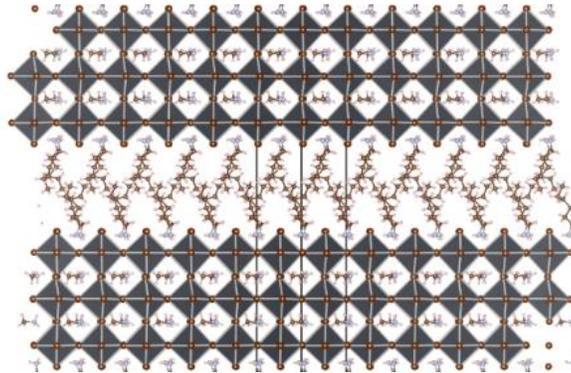


Fig. 1. The crystal structure of $(\text{CH}_3(\text{CH}_2)_5\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_2\text{Pb}_3\text{Br}_{10}$ (the $n=3$ member). The structure is comprised of 3 layers of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite sheets, separated by a bilayer of hexylammonium cations.

1. Huang L, Lambrecht WRL. Electronic band structure, phonons, and exciton binding energies of halide perovskites CsSnCl_3 , CsSnBr_3 , and CsSnI_3 . *Physical Review B* 2013;88(16).
2. Mazin II, Rashkeev SN. Effect of low symmetry on electron-phonon coupling in perovskite superconductors. *Solid State Communications* 1988;68(1).