Oral presentation

Polymorphism in lead halide hybrids comprising methylhydrazinium cation

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The unique characteristics of lead halide hybrid organic-inorganic compounds (specifically 3D and 2D hybrid perovskites (HOIPs) of the ABX_3 and A_2BX_4 formula, respectively [1]) arise directly from molecular-level interactions and are strictly contingent on the constituents within the structure. Thus, altering the chemical composition is essential for comprehending and modifying their properties. The primary strategy for elemental modification involves *A- and X-site engineering*, entailing the substitution of organic cations and halides, respectively. This method has demonstrated its usefulness in 3D HOIPs of the $MHyPbX_3$ formula (MHy = methylhydrazinium, X = Br, Cl), resulting in new crystal polymorphs with heavily distorted perovskite substructures adopting noncentrosymmetric alignment [2, 3]. Halide exchange directly influences the strength of hydrogen bonding, affecting the atomic arrangement and contributing to shifts in the bandgap, PL color, excitonic absorption bands, and more across a broad spectrum. Another proposed path is the *A- and X-site alloying* (two constituents at a single site). This approach was incorporated into MHy-based 3D hybrids of the $MHyPbBr_xCl_{3-x}$ formula [4]. Here the halide-mixing directly impacts the intermolecular interactions, enabling the stabilization of both high-temperature (HT) polymorphs of single-halide analogs ($Pm\text{-}3m$ and $Pb2_1m$ for Br^- and Cl^- counterparts, respectively) for a specific compositional area ($x \geq 1.33$). The changes on a molecular level are manifested in tuned energy bandgap, PL color and bandwidth, ionic conductivity and intensity of non-linear optical effects. The coexistence of two organic cations in $IMMHyPbBr_4$ (IMPB) and $IMMHyPbCl_4$ (IMPC) 2D HOIPs (IM = imidazolium) leads to crystallization in rarely observed structural class, namely Alternating Cation in the Interlayer space (ACI) 2D perovskites with (110)-oriented layers (derivatives of 3D parental structures created by ‘slicing’ along the (110) plane). The MHy^+ moieties, placed within the intralayer space, violate the coordination spheres of Pb, inducing the heaviest out-of-plane tilting of the inorganic substructure ever reported within this class of compounds. Owing to the synergistic effect of unusual atomic alignment and large distortion, both materials demonstrate broad PL with large Stokes shifts and the change of PL emission color, including *white-light emission* for IMPB observed at 200 K [5].

Herein, the combination of X-ray diffraction with Raman and optical spectroscopy is employed to understand and deeply characterize the structure-property relationships in the emerging subclass of hybrid organic-inorganic materials – lead halides comprising MHy^+. Thus far, this organic moiety fulfilled the strict geometric limitations of fitting into the 3D perovskite structure [2-4], served as a ‘spacer’ in layered counterparts of Ruddlesden-Popper and ACI types [5, 6], and contributed to other structural forms, such as 1D chain phase and 0D with isolated octahedra [7, 8]. The selected structural characteristics of the aforementioned $MHyPbBr_xCl_{3-x}$ and $IMMHyPbCl_4$ perovskites, as well as MHy-based hybrids of lower dimensionality, will be presented, highlighting the implications for bulk physicochemical properties.

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