

Electrochemically active supramolecular entities in layered hybrid halide perovskites

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Halide perovskites are remarkable, unconventional semiconductors as they have high optical absorption coefficients, long charge carrier diffusion lengths, intense photoluminescence, and slow rates of non-radiative charge recombination [1]. Furthermore, layered hybrid halide perovskites ($A^I_2M^{II}X_4$ or $A^{II}M^{II}X_4$ (A=monovalent or bivalent cation, M=bivalent p-block metal, X=halide anion), consist of anionic sheets of corner-sharing metal-halide octahedra, selectively “partitioned” by organic cations to form crystallographically ordered nanoscale sheets. This arrangement generates natural multiple quantum wells that exhibit stable excitonic features with intense photoluminescence (PL) characteristics observable already at room temperature.

Some of the exotic properties of halide perovskites is also revealed in this class of materials since a handful of them exhibit broadband optical emission, generating white light as a result of the self-trapped exciton mechanism [2]. Understanding this type of trap-activated behavior requires careful design of the materials involving a variety of organic spacers that can potentially trigger or suppress this effect.

In this work, we have designed and synthesized a series of layered perovskites with electrochemically-active spacers, where the electrochemical state of the spacer can influence the optical emission of the bulk material. Concomitantly, the installation of a functional group in the spacer cation, further enhances the structural

complexity by engaging in weak supramolecular interactions which can use as “perturbation probes” to interrogate the optical response of the materials as a function of the electrochemical state of the spacer cation. Towards this end we have synthesized two sister A_2PbBr_4 compounds ($A^+=2,3$ dihydroxyphenylethylammonium((HO)₂-PEA) and 2-(3-aminoethyl)benzoic acid (HO₂C-PEA)) as a redox-active and redox-inert pair of compound with a similar supramolecular interaction environment. Interestingly, the redox-active compound spontaneously crystallizes in its partially oxidized semiquinone form undergoing a one-electron oxidation during the synthesis. In this form, the compound exhibits similar photoluminescence characteristics (strong blue-light emission at 400nm) with those of the redox-inert compound, suggesting that the chemically reactive radical has been quenched during the reaction. Ongoing work on the electrocatalytic reaction mechanism using cyclic voltammetry suggest that both the fully reduced form ((HO)₂-PEA)₂PbBr₄ and the fully oxidized ((O=C)₂-PEA)₂PbBr₄ are present in the solution, prompting further optical and structural characterization of these metastable halide perovskite species.

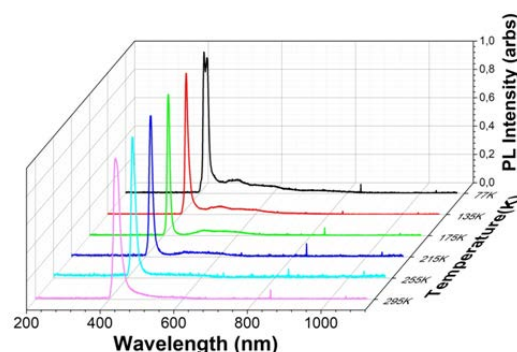


Figure 1: Temperature Dependent Photoluminescence of structure ((3,4-dihydroxy)PEA)₂PbBr₄.

References

- [1] C.C Stoumpos and M.G. Kanatzidis, Adv.Mater.**28**, 5778 (2016).
- [2] M. D. Smith and H. I. Karunadasa, Acc. Chem. Res.**51**, 619 (2018).