Computational Design of Surface Capping Ligands for Structurally Soft Metal Halide Nanocrystals

A. Stelmakh[1,2], V. Morad[1,2], M. Svyrydenko[1,2], L. Feld[1,2], M. Aebli[1,2], A. Baumketner[3]*, M. Kovalenko[1,2]*

[1]Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir Prelog Weg 1, CH-8093 Zürich, Switzerland, [2]Laboratory for Thin Films and Photovoltaics, Empa – Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland, [3]Institute for Condensed Matter Physics, NAS of Ukraine, 1 Svientsitsky, Lviv 79011, Ukraine

Versatile surface functionalization of highly ionic surfaces, ubiquitous among inorganic nanomaterials, remains a formidable challenge in view of inherently non-covalent surface bonding. Colloidal lead halide perovskite nanocrystals (NCs), which are of interest for classical and quantum light generation,[1,2] are a prominent example.[3] One of the reasons is a limited atomistic understanding of the NC-ligand-solvent interface. We would like to present how classical molecular dynamics simulations can be used in combination with experimental techniques to aid in understanding surface chemistry of ionic nanomaterials and to guide experimental discovery of new better capping ligands. In particular, we will present the first structural investigation of perovskite NC surfaces capped with zwitterionic phospholipid molecules. Combined computational and experimental evidence suggests that the phospholipid ligands bind to the surface of the NCs with both head-groups by displacing native ions of the perovskite. The ligand head-group affinity to the surface is primarily governed by the geometric fitness of its cationic and anionic moieties into the surface lattice sites. As a result, stable and colloidally robust nanocrystals of inherently labile hybrid perovskites – $FAPbX_3$ and $MAPbX_3$ (X – Cl, Br, I) – can be obtained for the first time using lattice-matched phosphoethanolamine head-group. Improved surface stability enables excellent optical performance of the NCs. Thoroughly purified NCs retain their stable emission with above 95% photoluminescence quantum yield in a broad concentration range, as well as in thick films. Ligand tail engineering, on the other hand, allows diverse surface functionalization of the NCs, for example control over the compatibility with solvents of diverse polarity, from hydrocarbons to acetone and alcohols.

[1] Mingming Liu, et al. *Nature Photonics*, **2021**, 15, 379-385.
[2] Gabriele Raino, et al. *Nature*, **2018**, 563, 671-675.
[3] Quinten A. Akkerman, et al. *Nature Materials*, **2018**, 17, 394-405.