Low-Dimensional Functionalized Hybrid Inorganic-Organic Perovskites: A new class of versatile semiconductors for opto-electronic applications?

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Three-dimensional (3D) hybrid organic-inorganic perovskites (HOIPs) based on lead iodide octahedra as building blocks are drawing significant interest due to their potential use in different optoelectronic applications, especially but not limited to photovoltaic devices. On the other hand, low-dimensional and especially two-dimensional (2D) HOIPs draw a growing interest as they allow for a larger structural degree of freedom to incorporate a broad range of smaller and larger organic cations. Mostly, these organic ammonium cations are simple in structure in the sense that they do not possess a specific functionality or can contribute directly to the opto-electronic properties of the 2D HOIP. Over the last few years, we have studied the incorporation in low-dimensional HOIPs of ammonium cations decorated with larger aromatic conjugated systems inspired by structures familiar from the research field of organic semiconductors. For example, recently, we incorporated a benzothieno[3,2-b]benzothiophene (BTBT) alkylammonium cation into the organic layer of a 2D layered lead iodide perovskite. The formation and degradation under thermal stress will be discussed. The use of a solvent vapor annealing method significantly enhances the absorption, emission, and crystallinity of these 2D HOIP films compared to regular thermal annealing. Especially the solvent vapor annealed films show markedly higher photoconductivity. Besides BTBT cations, also bi-, ter- and quarter-thiophene oligomers were studied. Said systems show a more diverse phase behavior giving rise to other low-dimensional HOIPs depending on the processing conditions and on their thermal history. A systematic study was performed in which a series of 2D layered HOIPs (Bit-C3)₂PbX₄ (with X= Cl, Br, and I) containing a 2,2'-bithiophene chromophore functionalized with a propylammonium tethering chain was used. The crystal structure and phase behavior of the 2D HOIPs were studied and suggest that *via* halide substitution from iodide to bromide and chloride, the molecular degrees of freedom of the Bit-C3 ammonium cations are reduced by spatial confinement of a smaller inorganic framework. Therefore, limiting the formation of lower-dimensional hybrids besides the targeted 2D HOIP. Finally, the complexity of structures can be further extended by intercalating an additional organic compound via secondary interactions. In this way, organic charge-transfer complexes were incorporated into the organic layer of 2D HOIPs.