M2 INTERNSHIP POSITION: Dielectric and quantum confinements in mixed-dimensionality 2D/3D hybrid organic-inorganic perovskite

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Since 2012, the 3D hybrid organic-inorganic (3D HOP) perovskites $CH_3NH_3PbX_3$ (X: I, Br, Cl) represents a "material breakthrough" for photovoltaics: in only 3 years, the efficiency of $CH_3NH_3PbI_3$ based solar cells has progressed from 12% to 22,1%.(1) However, one of the main technological issue to overcome is the stability of the material, especially its sensitivity to moisture. The solution might come from the layered, 2D HOP and the mixed 2D/3D structures. In particular, photovoltaic devices based on the mixed 2D/3D HOP have demonstrated superior stability and a growing efficiency.(2) The 2D/3D HOP family have the following chemical formula $(RNH_3)_2(CH_3NH_3)_{m-1}Pb_mX_{3m+1}$ (R: organic group, X: halogen). The variable m corresponds to the number of inorganic layers intercalated between the organic molecules (Figure 1). For m=1, the material adopt a two-dimensional structure (2D HOP), where carriers are confined in an atomically thin inorganic layer, made of PbX_6 octahedras, and formed strongly bound excitons.(3) At the limit case of m=∞, we obtain the 3D hybrid perovskite structure AMX_3 (A: CH_3NH_3) for which the exciton binding energy is only of a few meV and the transport properties are dominated by free carriers at room temperature.(4) **From m=1 (2D) to m=∞ (3D), the dimensionality and thus the excitonic properties of HOP can be tailored.** Nevertheless, the charge carrier properties of these HOP are largely unknown for the moment. Contrary to standard quantum wells, the high contrast between the dielectric constants of the organic and inorganic part generates a dielectric confinement of the carriers, making the physics of the excitons more complex.(5–7) Besides, Coulombic interaction between the carriers and the dipole moment of the organic cation (A^+: $CH_3NH_2^+$) lead to the formation of specific polaronic states.(8)

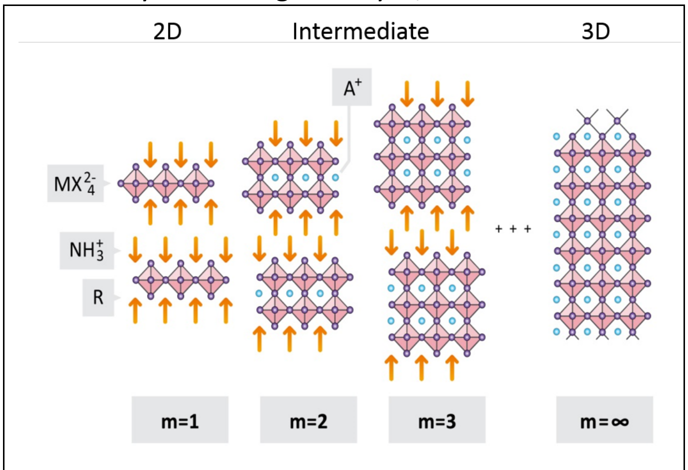

Figure 1: Family of Hybrid Halide perovskite, with 2D, 3D and intermediate 2D/3D dimensionality.

Excitonic properties of 2D and 2D/3D HOP single crystals (9) will be studied thanks to linear and non-linear optical experiments. Absorption, micro-photoluminescence (μ-PL) and PL excitation experiments as function of the temperature will give access to exciton binding energies, excitonic structure and electron-phonon coupling. The relationship between the structure, the phase transition and the optical properties will be investigated. Time-resolved spectroscopy will be used to investigate the dynamics of the carrier relaxation.

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