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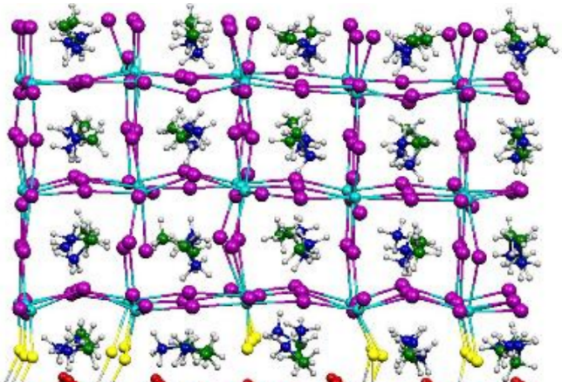
Titre de la thèse: ***Ab initio atomistic study of organic-inorganic perovskites phase diagrams***



Organic-inorganic perovskites offer a rich opportunity to develop future devices for photon-electron conversion due to their cheap fabrication process from liquid solution, their low crystallization temperature, and their excellent optoelectronic properties. In this project, we want to study the nucleation and growth of organic-inorganic perovskite based on the observation of the nucleation and growth processes at nanometer scale and *ab initio* atomistic simulations. Recent developments in the field of organic-inorganic perovskites have allowed the realization of a record external quantum efficiency of 21.6 % for LEDs[1]. To date, the micro-structure has been tuned based on trial-and-error approaches by mixing different precursors, solvents, anti-solvents and/or dopants in the liquid phase followed by post-annealing steps, resulting in devices with different optoelectronic properties and long-term stability.
In this project, we want to use a more systematic approach that allows the determination of optimal synthesis conditions for the nucleation and for the growth through *ab initio* atomistic simulations. To this end, we will use novel approaches, based on metadynamics and free-energy methods, developed at Sorbonne University by one of the proponents, with a "proof of concepts" application on the very challenging phase diagram of liquid water, amorphous and crystalline ices[2]. In a similar way, we will calculate the thermodynamically favored atomistic pathways leading amorphous perovskites into their crystalline forms, as a function of the external parameters mentioned above.
The results of the simulations will first be used to draw the phase diagrams versus the temperature for the $MAPbI_3$ and $FAPbI_3$ systems. The influence of the solvent and anti-solvent will also be mapped in a multi-dimensional phase diagram. Based on these findings, more complex systems will be simulated, such as the triple-cation perovskite systems $(A_xB_yC_{1-x-y})(Pb(I_zBr_{1-z})_3$ where A, B and C are the cations for various I/Br ratios (z). The final simulation step will be toward Ruddlesden–Popper layered perovskites. The phase diagrams and the synthesis routes predicted from the simulations will guide the project toward more stable and defect-free structures and possibly to the discovery of new organic-inorganic perovskite phases.

1. Xu, W. et al. **Nat. Photonics** (2019). doi:10.1038/s41566-019-0390-x
2. S. Pipolo et al. Ab Navigating at Will on the Water Phase Diagram, **Phys. Rev. Lett.** 119, 245701 (2017).

Techniques in use: DFT, molecular dynamics
Applicant skills: strong background in solid state and statistical physics, propensity for simulations and/or programming
Key words: theory, electronic structure, organic-inorganic perovskite, simulations