

## Recording the birth of a AIE crystal

Z. Zhang,<sup>1,\*</sup> E. Tedoldi<sup>2</sup> J.F. Audibert,<sup>1</sup> A. Spasojevic<sup>2</sup> and R.B. Pansu<sup>1</sup>.

<sup>1</sup> Univ. Paris-Saclay, CNRS, ENS Paris-Saclay, CentraleSupélec, LuMIn, Gif-sur-Yvette, 91190

<sup>2</sup> Univ. Paris-Saclay, CNRS, CentraleSupélec, SMPS, Gif-sur-Yvette, 91190 France

\*E-mail: zhengyu.zhang@ens-paris-saclay.fr

90% of the chemicals are purified by precipitation. But the nucleation mechanism is unknown and “crystal growth and design” remains a domain of recipes and know how. To discover the mechanism of the nucleation, we use the possibility to induce, by a laser shot, the nucleation of crystals (NPLIN).<sup>[1]</sup> With NPLIN, we know when (ns) and where ( $\mu\text{m}$ ) the crystal will be produced. AIE crystals are fluorescent solids formed from non-fluorescent solutions. This allows to detect and characterize the smallest fluorescent aggregate. From the fluorescence signal, we can identify the polymorphs, measure the nucleation rate, the growth rate, the density of defects in the crystals. We use microfluidic channels under a microscope. The flow allows a constant renewal of the solution for the collection of nucleation events with a high statistic. With microfluidic we can prepare flows with controlled metastable supersaturations by the mixing of a solvent and an antisolvent.<sup>[2]</sup>

Two examples will be presented. The NPLIN nucleation of DBDCS, an organic AIE molecule, is performed during an anti-solvent precipitation. We show that the spontaneous nucleation and the NPLIN produce the same distribution of polymorphs. Thus, NPLIN trigs the nucleation but does not change the mechanism. We also show that the polymorph dominant at the nucleation spot is not the one that escapes and grows. The mechanism of NPLIN is not known but optical tweezer effects can be observed when focusing the laser in solvent flows. In contrast the NPLIN nucleation of MAPbBr<sub>3</sub> - a hybrid lead halide perovskite - occurs even below the saturation.<sup>[3]</sup> MAPbBr<sub>3</sub> presents a retrograde solubility in DMF and crystalizes at high temperature. We see a thermal lensing effect during the nucleation. Thus, NPLIN could be due in the case of MAPbBr<sub>3</sub> to a heating of the solution by the laser.

In both cases, we observe that the nucleation is preceded by the formation of the super-cooled liquid phase of the solute. This nucleation mechanism has been called two steps nucleation.<sup>[4]</sup> We shall discuss this mechanism in the frame of the thermodynamic of solutions.

### References

- [1] Bošnjaković-Pavlović N, Clair B, Ikni A et al. Acta Crystallographica Section A.;77:C256-C (2021).
- [2] Tran VL, Génot V, Audibert J-F, Prokazov Y, Turbin E, Zusratter W, et al. New J Chem.; 40:4601-5 (2016).
- [3] Islam MJ, Yuyama K-i, Takahashi K, Nakamura T, Konishi K, Biju V. NPG Asia Materials. 11(1) (2019).
- [4] Loh ND, Sen S, Bosman M, Tan SF, Zhong J, Nijhuis CA, et al. Nat Chem. 9(1):77-82 (2017).