Dynamics of the Second-Order Nonlinear Optical Responses of Organic Materials

Frédéric Castet

Univ. Bordeaux, CNRS, Bordeaux INP, ISM, UMR 5255, F-33400 Talence, France.
frederic.castet@u-bordeaux.fr

Quantum chemical calculations have been widely used during the last thirty years for rationalizing the second-order nonlinear optical (NLO) responses of small molecules or π-conjugated organic chromophores. However, most of theoretical reports assume a rigid picture of the investigated systems, the NLO responses being computed on the basis of the most stable geometry of the chromophores. Yet, recent theoretical reports combining classical molecular dynamics simulations and DFT calculations have evidenced the significant role of structural fluctuations, which may induce broad statistical distributions of the NLO responses. In this talk, we will present some case studies in which theoretical simulations have highlighted the crucial role of dynamical disorder onto the NLO responses of the investigated systems. Selected examples will include photochromic systems in solution, [1] as well as large and flexible supramolecular assemblies such as nanoparticles [2] and self-assembled monolayers [3] (Figure 1).

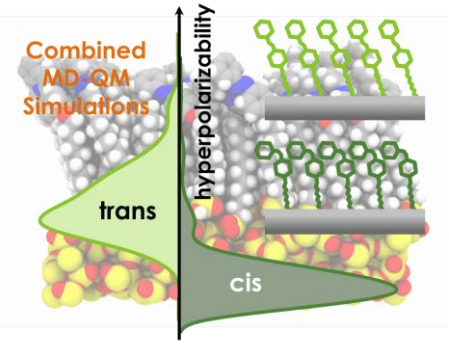

Figure 1. Illustration of the hyperpolarizability contrast upon commutation in azobenzene-based monolayers.

References:

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[3] Tonnelé, C.; Champagne, B.; Muccioli, L.; Castet F. Nonlinear Optical Contrast in Azobenzene-Based Self-assembled Monolayers *Chem. Mater*. **2019**, *31*, 6759-6769.