

Dynamical Behavior and Second Harmonic Generation Responses of Molecular Switches

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Second-order nonlinear optical molecular switches are systems displaying marked variations of their second harmonic generation (SHG) responses upon external stimulation. In this article, we combine a multiscale computational method and experimental characterizations to provide a full description of the SHG responses of molecular switches built from the association of the indolino-oxazolidine unit to a bithiophene donor. In chloroform solutions [1], the addition of trifluoroacetic acid triggers the switching from a neutral closed form to a protonated open form, making an ion pair with the trifluoroacetate counterion and induces a strong enhancement of the SHG responses. The numerical simulations (i) evidence how the large and rapid thermally induced geometrical fluctuations lead to broadening the SHG responses distributions, making even difficult the determination of their sign, (ii) rationalize the variations of these responses as a function of the closure/opening of the oxazolidine ring and of the nature of its chemical substitution, and (iii) call into question common assumptions employed when analyzing the experimental SHG responses. In the case of self-assembled monolayers (SAMs) [2], the numerical simulations provide a complete atomistic picture of the morphology of the SAMs, revealing a high degree of positional disorder and an almost isotropic orientation of the chromophores. Subsequent DFT calculations, carried out to evaluate the average first hyperpolarizability of indolino-oxazolidine switches within the SAM, predict that the structural disorder does not significantly reduce the NLO contrast compared to that of the isolated molecules.

[1] K. Pielak *et al.*, *J. Phys. Chem. C* **122** (2018) 26160.

[2] C. Tonnelé *et al.*, *Phys. Chem. Chem. Phys.* **20** (2018) 21590.