10th International Conference on Molecular Electronics
November 29 - December 2, 2021

Theoretical Design of Multi-State Multi-Addressable Multi-Functional Molecular Switches

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Abstract:

This paper illustrates how theoretical chemistry methods are developed and enacted to help designing multi-state (more than 2), multi-addressable (more than one stimuli; *e.g.* light irradiation, pH/redox potential changes), multi-functional (linear and nonlinear optical properties) molecular switches. The targeted molecules are built from benzazolooxazolidine (BOX) units, which are combined with 1°) different kinds of organic/organometallic donor units, with 2°) other switchable units like diarylethene, or simply 3°) linked together to create diBOX or triBOX derivatives. To study these switches in solution as well as in the form of self-assembled monolayers, the theoretical chemistry methods encompass 1°) quantum chemistry approaches, mostly density functional theory (DFT) and time-dependent DFT, of which the reliability has been substantiated by comparison with high-level wavefunction methods and 2°) molecular dynamics simulations using re-parameterized force fields to describe the π-conjugated frameworks because the optical properties are much sensitive to the molecular geometry. Our work focuses on those molecular switches presenting contrasts of second harmonic generation (SHG), a second-order nonlinear optical (NLO) phenomenon that is probed in solution by using the hyper-Rayleigh scattering technique. From an application perspective, NLO molecular switches present the "read without erase" advantage while the SHG response is much sensitive than the linear ones.

This paper shows how large SHG contrasts can be achieved and how they are related to structural changes as well as to the corresponding linear optical responses (usually analyzed by UV/vis absorption spectroscopy so that the SHG response is analyzed within few-state models). Besides the molecular properties (including also the change of free enthalpy upon (de)protonation/redox reactions), the presentation discusses the role of the surrounding (solvent, monolayer) and how it can be modelled (polarizable continuum model *versus* explicit solvation; polarization and local field effects).

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