

Second Harmonic Responses of Azobenzene-based Self-Assembled Monolayers: A Computational Approach

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Light-responsive nonlinear optical (NLO) materials have attracted a great deal of interest in the recent decades for the development of photonic devices such as all-optical molecular-scale memories. In particular, the use of second harmonic generation (SHG) responses to probe the system state gives the devices non-destructive readout capability (Figure 1). The suitability of a material for practical use in a photo-responsive NLO device is mainly conditioned by two requirements. First, the molecular building blocks must show a large first hyperpolarizability in one of their forms, as well as large contrast upon photoconversion. The second requirement concerns the spatial orientation of the molecular photoswitches in the material, where centrosymmetric stacking must be avoided. By constraining the alignment of the molecular units within controlled concentrations, surface functionalization with self-assembled monolayers (SAMs) constitutes the most effective strategy for introducing NLO chromophores into a device in view of maximizing its macroscopic second-order optical susceptibility (the macroscopic equivalent of the first hyperpolarizability).

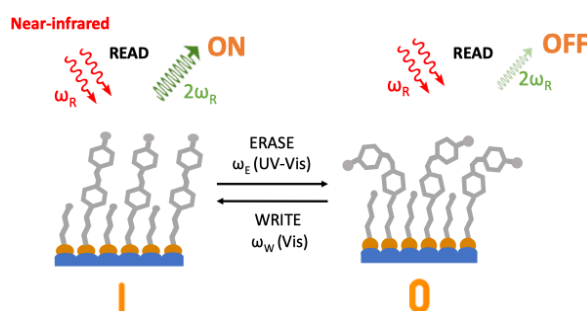


Figure 1: Schematic representation of an optical memory device based on information storage using UV and visible light, and whose reading process exploits the phenomenon of second harmonic generation.

In complement to surface engineering and spectroscopic characterizations, the rational design of new NLO devices and optimization of their performances calls for the development of computational strategies that provide a fundamental understanding of the relationships linking the interfacial molecular organization to the NLO responses of the material. In this context, a mixed quantum/classical computational methodology combining molecular dynamic simulations (MD) and Density Functional theory (DFT) calculations has been developed to characterize the NLO responses of SAMs functionalized with azobenzene derivatives. This approach allows to capture the effects of the conformational dynamics of the individual fragments, constrained by steric interactions, and has proved reliable for rationalizing the amplitude of the NLO responses of the SAMs, as well as their contrast upon commutation.