

SIMULATION OF ULTRAFAST PHOTOSWITCHING MATERIALS AND THEORETICAL PRINCIPLES OF THEIR DESIGN

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Method Development

We developed two new methods for theoretical design of organic photoswitching molecules: (i) ATDA: *a posteriori* Tamm-Dancoff approximation to the second order time-dependent density functional theory (TD-DFT), that allows one to account for double excitations and to predict permanent and state-to-state transition dipole moments, and (ii) RTD-UDFT//STS: a combination of spin restricted TD-DFT for excitation energy, unrestricted DFT for the ground state energy, both calculated on a geometry obtained using the Slater transition state (STS) method. The ATDA was validated for short linear polyenes [1] and para-nitroaniline. It was also validated in predicting two-photon absorption (2PA) spectra for several conjugated organic molecules (see an example in Fig. 1) of practical interest [2-6].

We used a combination of these methods to predict potential energy surfaces for the excited states, and to study structure-property relationships, including absorption spectra [7], thermal stability [8], fatigue resistance [9], and photoreactivity [10, 11], for optical switching molecules. We then apply these methods to explain lack of photoswitching activity in the *de novo* designed prototype molecular 2PA photoswitch [10]. We also formulate and validate a rational design principle for new molecular photoswitches.

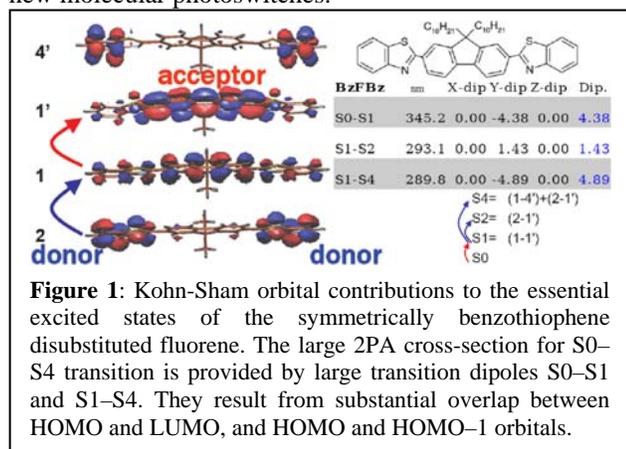


Figure 1: Kohn-Sham orbital contributions to the essential excited states of the symmetrically benzothiophene disubstituted fluorene. The large 2PA cross-section for S0-S4 transition is provided by large transition dipoles S0-S1 and S1-S4. They result from substantial overlap between HOMO and LUMO, and HOMO and HOMO-1 orbitals.

Method Applications

We simulated absorption spectra for closed and open isomers of diarylethene photochromic compounds with

several DFT functionals. We recommend the TD-M05/6-31G*/PCM//M05-2X/6-31G* theory level for prediction of structure and spectral parameters, where solvent effects are described by the polarizable continuum model (PCM). This theory level gives quantitative agreement with experimentally measured geometric parameters and absorption spectra shown in Fig. 2 [7, 9].

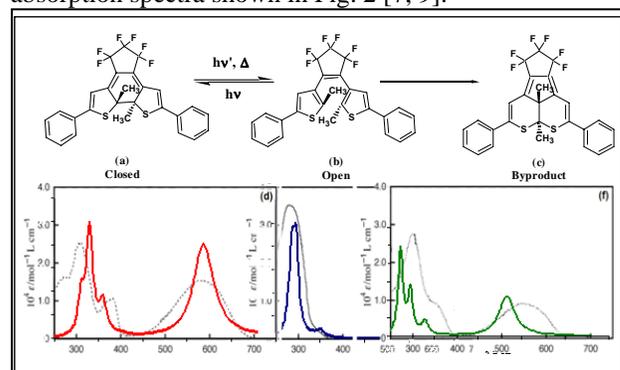
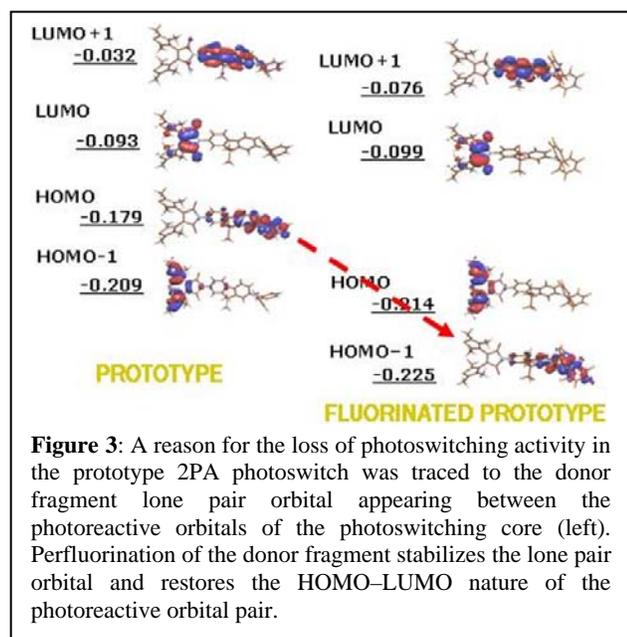


Figure 3: The TD-M05/6-31G*/PCM//M05-2X/6-31G* theory level predicts linear absorption spectra for both closed (red line), open (blue) and byproduct (green) isomers in excellent agreement with experiment (black dots).

We studied kinetics of cycloreversion and photofatigue resistance [9]. We investigated a mechanism of byproduct formation in 3 different compounds to predict their photofatigue. We found the activation energy, leading to byproduct from the bicyclohexyl intermediate, to be 5 kcal/mol higher for the methylated derivative, and used this fact to explain its higher fatigue resistance. We analyzed the orbital structure of five lowest excited states in open, closed, and byproduct forms of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene [9]. The optical transition proceeds to the state with the brightest optical band. This brightest band does not necessarily have to be the lowest excited state. Apparently, some vibrational relaxation from the higher-lying photoabsorbing state to the lowest photoreactive state has to occur before the photocyclic transformation. The established principle can be used in computational design of new photoswitching materials [8].

A prototype molecule was investigated, where a two-photon absorbing fragment was combined with an ultrafast photoswitching fragment. Surprisingly, this compound was experimentally found to be photochemically inactive. The loss of photoswitching

activity was explained by presence of a barrier on the potential energy surface of the lowest excited state. The Kohn-Sham orbital analysis revealed the nature of this barrier. A chemical modification was suggested to restore the photoswitching activity (Fig. 3).



A design principle for new molecular photoswitches was formulated. It states that the substituent should not introduce any electron energy levels within the HOMO–LUMO gap of the photoreactive fragment.

The above work was extended to other classes of compounds of practical interest as organic NLO and plastic photovoltaic materials. We studied the mechanism of symmetry breaking in a series of cationic streptocyanines with different conjugated length, including polymethines and squarenes [12, 13]. The calculations show that a minimum number of vinylene groups in the conjugated chain necessary to break the symmetry in streptocyanines is eight in the gas phase and six in cyclohexane. We also predicted hyperpolarizability for molecules and aggregates [14].

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