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DFT-Based Methods in the Design of Two-Photon Operated Molecular Switches

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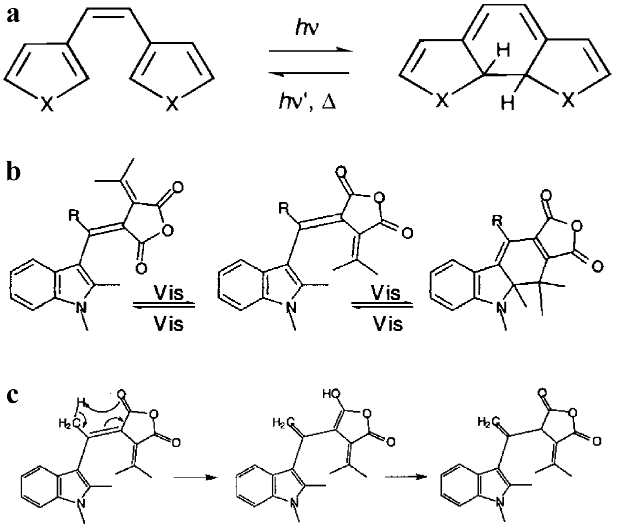
Conjugated organic molecules with photochromic properties are being extensively studied as prospective optical switching and data storage materials. Among different photochromic compounds, diarylethenes demonstrate thermal stability, fatigue resistance, and high quantum yield. The mechanism of photoswitching in diarylethenes involves a symmetry-allowed conrotatory electrocyclic reaction, initiated by UV light. Replacement of one UV photon with two near-IR ones would offer a number of practical advantages, including drastic increase in storage capacity via three-dimensional multilayer design. For this purpose we designed a prototype molecule with a two-photon absorbing (2PA) pendant substituent, attached to the photochromic diarylethene moiety. However, this molecule was experimentally shown to have lost the photoswitching properties. We analyze reasons for this loss using quantum chemistry tools. Analysis of the nodal structure of the frontier Kohn−Sham orbitals, allowed us to trace the route of the problem to the lone pair orbital of the 2PA substituent falling within the HOMO−LUMO (highest occupied molecular orbital−lowest unoccupied molecular orbital) gap of the photoreactive diarylethene moiety. We suggest a chemical modification of the 2PA substituent in order to restore the order of the orbitals. Potential energy plots along the reaction coordinate at the M05-2X/6-31G* theory level for the prototype 2PA photochromic molecule before and after the modification confirm the predictive capability of the proposed orbital approach. The Slater transition state method was used to obtain geometries along the reaction pathway by the constrained optimization of excited states, whereas potential energy curves were plotted using the recently proposed (Mikhailov, I. A.; Tafur, S.; Masunov, A. E. *Phys. Rev. A* **2008**, *77* (1), 012510) a posteriori Tamm−Dancoff approximation to the time-dependent density functional theory in second order of the external field. We show that this combination is able to produce accurate potential surfaces for 1B and 2A excited states, as compared to available experimental data and results of high-level multireference wave function theory methods.

1. Introduction

Exponential growth in the information technology industry generates ever-increasing amounts of data. Thus, the recording density of the storage media is crucially important, prompting the development of optical solutions as an alternative to traditional magnetic storage devices. Optical data storage refers to systems that use light for recording information as well as for readout. Most optical memory systems available on the market currently utilize inorganic materials and are based on magneto-optical[1,2] and phase-change[3] effects. Both effects are utilized in heat-mode recording, where light energy is converted into heat. This induces a magnetic or structural phase transition, altering the physical properties of the medium.

SCHEME 1: (a) Diarylethene Photoswitching, X = O, S; (b) Indolylfulgide Photoswitching; (c) Indolylfulgide Photodegradation Pathway



Until recently, organic materials have not been considered as viable candidates because of insufficient reliability. However, the situation changed after the recordable compact disk (CD-R) technology was introduced, which was based on organic dyes as the memory medium. This technology uses polymers, doped with the photochromophores (molecules, which undergo a reversible photoinduced isomerization or photochromism).[4−6] Examples of photochromophores include diarylethene compounds, shown in Scheme 1a. They undergo photochromic processes (isomerization), involving the photoinduced conrotatory opening and closing of the central bond, and fulfill requirements needed for material applications, namely, thermal

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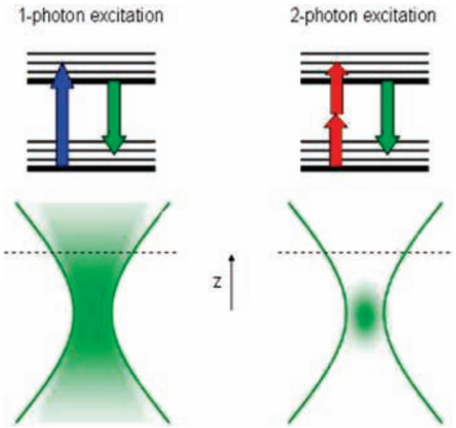


Figure 1. 1PA (blue) and 2PA (red) transitions between molecular energy levels. Regions that are appreciably excited are shown in green. 2PA-related processes are more localized in space.

stability and resistance to linear optical photofatigue.[7] Other examples include indolfulgides (Scheme 1b),[8] which demonstrate lower fatigue resistance due to moderate photodegradation (Scheme 1c).

Photochromic materials are now considered to be promising candidates for next generation erasable memory media.[6] Another important property of photochromic materials is an ultrafast isomerization upon irradiation. Photochromic compounds with ultrafast switching capabilities can be also useful for optical communication, signal processing, interconnection and as components of various photonic devices, such as optical switches, variable frequency filters, attenuators, and phase shifters.

Besides reversibility and ultrafast switching, photochromic storage materials realize recording in the photon mode (as opposed to heat-mode ones) which leads to another important advantage. They offer a possibility of data recording using individually addressable three-dimensional (3D) arrays of bits. The 3D design provides an opportunity of using hundreds of layers beneath an optical disk surface, thus increasing storage capacity by at least 2 orders of magnitude. In order to increase storage density one needs to reduce cross-talk between the recording layers; to this end Parthenopoulos and Rentzepis suggested using two-photon absorption of light.[9]

Two-photon absorption (2PA) is a nonlinear optical process in which chromophores that would normally be excited by a single photon of ultraviolet or visible light are excited by two photons of near-infrared wavelength radiation (Figure 1). The probability of 2PA is quadratically dependent on intensity of the incident radiation, affording spatial localization. The use of longer wavelength light provides better penetration in absorbing or scattering media, whereas the quadratic dependence of absorption probability on light intensity allows for high 3D spatial selectivity through the use of a tightly focused laser beam. Under tight focusing conditions, the absorption is confined at the focus to a volume of order λ^3 (where λ is the laser wavelength), and any subsequent process, such as fluorescence or photoinduced chemical reactions, is localized in this small volume.

A number of molecular structures were designed as candidates for 2PA-initiated photochromic materials[10] but were found to have insufficient 2PA cross sections. A functioning 2PA-based 3D optical storage system was reported recently.[11] It offered an interlayer separation of 5 μm and depth of up to 600 μm. However, the diode laser commonly used in DVD (digital video disc) devices was not able to provide sufficient intensity to record information, and a higher-power solid-state laser was used for recording. Thus, design of photochromic dyes with higher 2PA cross sections and quantum yields is vitally important for practical applications. The engineering of such materials is in need of rational strategies able to guide progress in materials design.

Herein, we report a molecular prototype for a 2PA photochromic switch and analyze reasons for its poor performance. In order to improve the molecular chromophore design, we propose to use the Kohn−Sham orbital analysis and validate it using minimum energy pathways. We also propose modification of the prototype molecule by means of fluorination and predict its photoswitching ability using orbital diagrams and potential energy surfaces.

2. Theory

Computational chemistry offers a number of theoretical methods for investigation of photochemical reaction mechanisms. Unlike thermally activated chemical reactions, that take place in the ground electronic state (S_0), a photochemical process involves an electronically excited state (S_1). During this process, the reactive system is promoted from S_0 to S_1, and after some evolution on the upper potential energy surfaces (PES) decays back to the ground state to either the product or reactant basin. This decay may proceed via light emission, vibronic energy dissipation, or pass through or near a conical intersection (CIX).[12] In the case of electrocyclic reactions, the CIX is often accessible to the system with no potential energy barrier, resulting in ultrafast (ca. 10 fs) decay.

The simplest example of an electrocyclic reaction is the cyclohexadiene/hexatriene (CHD/HT) isomerization. Dynamics of cycloreversion in the CHD/HT system has been repeatedly studied using time-resolved ultrafast spectroscopy techniques.[13,14] The results are summarized in ref 15. Although a solvent can stabilize the ionic 1B state compared to the covalent 2A and 1A states, this does not have an appreciable effect on the CHD/HT conversion rate, although it slows down conformational isomerization of HT considerably.[16] To describe the detailed mechanism of this photoprocess, it is convenient to consider state correlation diagrams, briefly described below.

The CHD/HT system presents a textbook case of an electrocyclic reaction, considered in the very first publication of orbital symmetry conservation rules by Woodward and Hoffmann.[17] Their short communication stated that in order for the HT → CHD transition to have a low activation barrier in the ground state (be thermally allowed), the highest occupied molecular orbital (HOMO) should have bonding character with respect to the C1−C6 interaction, closing the ring. This condition is satisfied when the HOMO lobes localized on C1 and C6 atoms overlap in phase during the disrotatory motion of terminal CH_2 groups. Thus, HOMO symmetry controls the stereochemistry of the thermal reaction product when substituents are present. Promotion of an electron to the lowest unoccupied molecular orbital (LUMO) in the photoinduced process inverts the symmetry of the wave function. In this case, the conrotatory motion of HT (or CHD in the cycloreversion reaction) is necessary for lobes on the C1 and C6 atoms to overlap in phase (Figure 2, bottom) and create no potential barrier along the reaction pathway (making the reaction photochemically allowed).

Longuet-Higgins and Abrahamson reformulated the rule in terms of state correlation diagrams[18] (Figure 2, center). These diagrams consider three electronic states of the HT/CHD system, classified as symmetric (1A, 2A) or antisymmetric (1B) with

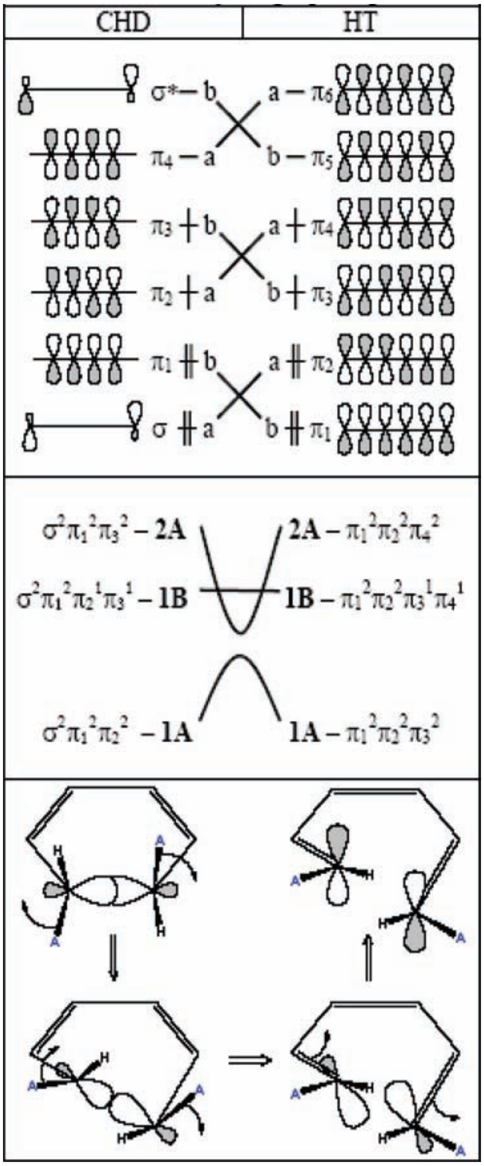


Figure 2. Orbital (top) and state (center) correlation diagrams for photoinitiated electrocyclic conversion of CHD to HT (bottom). Lines connect the orbitals as they continuously transform along the C_2-symmetric reaction path. Different orbital occupations give rise to different electronic states. Doubly excited state 2A of CHD correlates with the ground state of HT and vice versa; when their energies approach each other, the states strongly mix and avoid crossing; true CIX occurs away from the symmetric coordinate.

respect to the axis C_2, conserved along the conrotatory cyclization pathway. State 2A is the doubly excited state of the reactant (two electrons in the LUMO, zero electrons in the HOMO). It correlates with the ground state of the product, that has the same symmetry (1A), whereas the singly excited state of the reactant (1B) correlates with the singly excited state of the product (HOMO and LUMO occupied with one electron each). It is important to note that selection rules allow 1A → 1B transitions in the 1PA regime and 1A → 2A transitions in the 2PA regime. Along the reaction pathway, 1A rises and 2A drops in energy. When approaching degeneracy, 1A and 2A mix to form an avoided crossing. This region forms a potential barrier on the ground-state surface and the so-called pericyclic minimum on the doubly excited state (2A) surface. Even though energy diagrams are drawn along the C_2-symmetric coordinate, and clearly present an oversimplification, qualitative diagrams based on semiempirical molecular orbital calculations served as useful guidance for the rational design of thermally irreversible photochromic molecules.[7]

It is worth noting that the σ and σ^* orbitals of CHD, involved in the bond breaking process (Figure 2), are not frontier orbitals (HOMO and LUMO), unless the bond is elongated enough. As was stressed by Michl,[19] the photochemical transformations are controlled by essential orbitals, which often do not coincide with frontier orbitals. This means that a photochemically excited state (usually the lowest singlet state of essentially HOMO → LUMO character) may increase in energy along the reaction pathway before it can proceed down to the pericyclic minimum. This may lead to an activation barrier which will slow down or prohibit the photochemical process. Thus, even simple orbital considerations can be used for semiquantitative prediction of the photochemical kinetics.

More accurate quantitative calculations, on the other hand, involve plotting realistic PESs that, until recently, required the use of ab initio multireference-based quantum chemistry methods. The pioneering complete active space (CAS) study of HT/CHD system was published by Robb, Olivucci, and coworkers.[20−22] They found that 2A and 1A surfaces touch at a molecular conformation of tetraradical character, located away from the C_2-symmetric coordinate and including C1···C6 and C2···C6 partial bonds. They also found that accounting for dynamic electron correlation is essential to predict correctly relative energies of the 1B and 2A states. Despite the fact that 2A/1A and 1B/2A CIXs complicate the energy landscape by adding an extra dimension, the qualitative interpretation given by the state correlation diagram along the symmetric coordinate still holds. It was further confirmed at a high level (CAS second-order perturbation theory and multireference configuration interaction) by building ab initio PESs[14] and performing two-dimensional quantum dynamics[23,24] on these PESs. A barrierless descent on the excited-state PES was found to determine ultrafast photoconversion between CHD and HT, and the quantum yield of this process was primarily determined by the location of the 2A/1A CIX.

Semiempirical Hamiltonian INDO/S in combination with Coupled Electronic Oscillator (CEO) formalism was used by Tretiak, Mukamel, and others to study the excited state dynamics for electrocyclic reactions in diarylethene derivatives.[25,26] They were able to explain the slow conversion by the presence of the potential barrier, separating this minimum from the conical intersection to the ground state.[27]

In this paper, we also consider dithienylethene (Scheme 1a with X = S) as the simplest homologue of diarylethenes, a potentially important class of compounds for photoswitching applications. In the closed conformation, its thiophene rings are joined through the central bond to form a conjugated π-electron system. In the open form, the π-conjugation between the rings is disrupted by large dihedral twists. The one-photon initiated photochemistry of dithienylethene upon one-photon irradiation was studied in ref 12 using the molecular mechanics−valence bond computation. The dynamics was simulated on a hydrocarbon model system having the same PES topology as dithienylethene. The critical points were obtained at the CAS(10,10) theory level with 6-31G and 6-31G* basis sets.

Dynamics were found to be essential to explain the observed photochemical behavior qualitatively. The authors claim[12] that the reaction path alone is insufficient for that purpose, as the initial relaxation for this system was not directed toward CIX. However, the shape of the first excited-state PES was found to be useful in the interpretation of the ultrafast ring closure and relatively low quantum yield observed for the ring-opening reaction. The stepwise multiphoton processes in dithienylethene were studied in ref 28. The minimum energy pathways of several lowest singlet excited states were calculated at CAS(10,10)/6-31G and CAS(12,14)/6-31G theory levels. In all three of the excited states reported, the potential surfaces had a barrier to cycloreversion, located between the closed-ring conformation and the pericyclic minimum. Although the crossover between excited states was not found in that study (presumably, due to neglect of dynamic electron correlation), the height of the barrier was found to be much lower in higher-lying states. This fact was used to explain the experimentally observed sequential two-photon photoinduction (via excited-state absorption) in this system.

Although accurate quantum dynamics calculations[29−31] for triatomic systems with CIX have been performed, large molecules of practical interest necessitate the semiclassical[31,32] approach. In this approach, adiabatic surfaces are treated classically, whereas transitions between the surfaces are estimated using quantum mechanics. Another approximation involves reducing dimensionality of the system to two degrees of freedom and treating the resulting two-dimensional problem using wave packets.[33] Further simplification is called the pathway approach.[34] Instead of the entire PES, it considers a minimum energy path,[35] which is followed by the center of the wavepacket.[15] This approach is focused on local properties of the PES, such as minima, barriers, and slopes. In the pathway approach, the CIX serves as a funnel, delivering the excited-state intermediate to the ground-state reactant or product so that the quantum yield is largely determined there.[36] It has been found to be very useful for qualitative analysis of reaction mechanisms, prediction of photoproducts, and rationalization of experimental excited-state lifetimes, quantum yields, along with absorption and emission spectra.[13,37]

A number of computational tools have been developed to predict the PES.[36,38,39] Most of them are based on the CAS method, where molecular orbitals are determined self-consistently within the multiconfigurational ansatz (full configuration interactions in a limited orbital space). Although this method yields acceptable molecular geometries, accounting for dynamic electron correlation is required for accurate energy predictions and is typically accomplished by the multireference configuration interaction or perturbation theory treatment. These methods are computationally expensive and impractical for PES exploration in large molecular systems.

Formalisms based on density functional theory (DFT) are being considered among the most affordable alternatives. One of the approaches to treat excited states with DFT is Δ-self consistent field (ΔSCF), where an electron is transferred from one of the occupied to one of the unoccupied orbitals, and orbital relaxation with the SCF procedure is repeated. In general, ΔSCF is possible if the orbitals in this pair belong to different irreducible representations. This limitation is avoided in the restricted open-shell Kohn−Sham method,[40] which is based on the Ziegler sum rule,[41] stating that a single Kohn−Sham determinant with two orbitals occupied by unpaired electrons of the opposite spin is a 50/50 mix of pure singlet and triplet states and, therefore, has energy which is an average between the two. This method was shown able to describe geometry and perform molecular dynamics of the open-shell singlet excited state, calculate nonadiabatic coupling,[42] and include S_0−S_1 surface hopping into molecular dynamics simulations.[43]

An alternative approach to study PESs of electronically excited systems is based on the time-dependent (TD) or, more precisely, linear response DFT formalism. Instead of orbital relaxation, TD-DFT uses an equivalent procedure where the Kohn−Sham (KS) wave function is expanded in terms of Slater determinants singly excited with respect to the reference state. The rigorous formulation of TD-DFT[44] demonstrates that this description is, in principle, exact, given that the frequency-dependent exchange-correlation functional is known. In most practical applications, however, this frequency dependence is ignored (so-called adiabatic TD-DFT). This method was often reported to predict accurately electronic spectra and excited-state geometries. However, TD-DFT was found to be somewhat less successful in description of PESs in the vicinity of a CIX[45] In this paper, we show that these difficulties may be rooted in the failure of the restricted KS formalism for the reference ground state near the pericyclic energy minimum and introduce a possible solution.

The KS formalism of DFT was developed for nondegenerate cases; it breaks down for systems with strong diradical character and degeneracy of the electronic levels, such as CIX geometries. However, the static (also known as left−right) electron correlation can be taken into account by using different orbitals for different spin. This approach, known as the unrestricted KS formalism was found to yield a qualitatively correct description of bond breaking.[46] Alternatives to the broken spin-symmetry KS solution exist, including multireference DFT,[47] local Hartree−Fock method,[48] and ensemble KS approach.[49] These new approaches, however, require development of new exchange-correlation functionals to obtain accurate numerical results.

Excited states, on the other hand, require the restricted formalism to avoid heavy mixing of the higher spin states into description of the excited singlet. Although TD-DFT was suggested in the unrestricted KS reference,[50] this is considered to be incorrect according to rigorous theory.[51] One possible approach to PESs of the excited states can be formulated by adding excitation energies obtained in the restricted TD-DFT formalism to the ground-state energies calculated with the unrestricted KS method. Hereafter, we will refer to this approach as to RTD-UDFT. Although, for the photoswitching systems that we consider, the difference in the ground-state energies obtained with restricted and unrestricted KS formalisms are close to being within 20 kcal/mol or less, we will numerically show that this difference is sufficient to bring excited-state PES into agreement with results obtained at a higher theory level, when available.

At first glance, the combination RTD-UDFT may appear contradictory. Let us consider that the KS approximation to the DFT is semiempirical by virtue of the exchange-correlation potential used, including frequency (in)dependence of this functional to describe the excited states. The broken symmetry KS formalism compensates for the deficiency of the electron correlation description at the expense of spin contamination. The symmetry dilemma (broken symmetry or restricted) presents a choice of the lesser evil, and this choice need not be the same for the ground and excited states. Although spin contamination is moderate and tolerable for the ground state, we found it to be excessive for excited states.

Another theoretical development, necessary to describe the region of CIX, is related to the double excited states, missing in the adiabatic linear response TD-DFT approximation.[52] Mixing of the double excited states into the linear response TD-DFT states through the so-called "dressed TD" was introduced recently by Cave et al.[53] as a result of the particular frequency dependence for the exchange-correlation potential. However, a much more conceptually simple solution exists in the coupled electronic oscillator formalism,[54−56] where doubly excited states appear in second order as simple products of the excitations obtained at the linear response level. We recently used this to propose the a posteriori Tamm–Dancoff approximation (ATDA) and demonstrated its accuracy for linear polyenes in their ground-state geometry.[57] For excited states that appear in linear response TD-DFT, the ATDA yields identical excitation energies and transition dipoles from the ground state, although permanent dipoles and state-to-state transition dipoles differ. According to ATDA, the double excited state is too high in energy around the Franck–Condon region to affect the experimentally observed 2PA absorption spectrum. The double excited state, however, approaches the ground state near the pericyclic minimum.

Since analytical gradients in the ATDA-UDFT approach are not yet implemented in computer codes, in our studies we use the Slater transition state (STS) method to optimize geometry of the excited states. In this method, half an electron is promoted from the HOMO to the LUMO, and self-consistency is achieved with these fractional orbital occupations.[58] STS is known to be a good approximation to the corresponding ΔSCF excitation energy.[59,60] It can be further extended to the modified linear response DFT method,[61] which yields considerable improvement in the description of the charge-transfer and Rydberg states, compared to the linear response TD-DFT approach. A practical advantage of STS is easier SCF convergence, particularly compared to excited-state SCF convergence, which often presents a major problem.[62]

3. Computational Details

All calculations were performed using the Gaussian 2003, rev. E1 suite of programs.[63] We used the hybrid meta-GGA exchange-correlation functional M05-2X from Truhlar's group,[64] designed for accurate descriptions of both equilibrium geometries and transition states. Relaxed energy scans (RES) were constructed by means of a constrained optimization technique and used as approximations to the true minimum energy pathways.[65] The pericyclic C–C bond (reaction coordinate) was fixed in the range from 1.4 to 3.6 Å with 0.1 Å step size. The ground singlet state 1A was optimized at UM05-2X/6-31G level of theory, whereas single 1B and double 2A excited singlet state geometries were optimized with the STS method. The STS method was implemented using equal fractional occupation numbers for the HOMO and LUMO in the α-set only [to approximate the geometry of the single excited state 1B, IOp(5/75 = 1, 76 = 2)], and both α and β sets to approximate the geometry of the double excited state 2A [IOp(5/75 = 1, 76 = 2, 77 = 1, 78 = 2)]. Although the STS-UM05-2X/6-31G theory level gave reasonable estimates for molecular geometries, the SCF energies obtained at this level were found to have insufficient accuracy for our purposes. Instead, the excitation energies were taken from single-point calculations at the corresponding optimized geometry in the ATDA for the lowest single excited state 1B and the lowest double excited state 2A. The excitation energies, thus obtained at the ATDA-M05-2X/6-31G level, were added to the ground-state energies obtained at the UM05-2X/6-31G level of theory. The resulting ATDA-UM05-2X/6-31G//STS-UM05-2X/6-31G energies are plotted in Figures 3, 5, 6, and 7. The KS orbitals in Figure 8 were generated using the VRML option in the Molden graphical visualization package.[66]

The 2PA absorption spectra were obtained in the sum-over-states (SOS) formalism from the ground-state geometry optimized in restricted DFT with the M05-2X functional and the 6-31G* basis set. An empirical line width of 0.1 eV was used to stimulate the 1PA and 2PA. The dipole moments and excitation energies were calculated at the ATDA-M05-2X/6-31G* level. In the ATDA approach, the ground-to-excited-state dipoles as well as excitation energies were identical to those in conventional TD-DFT, whereas excited-to-excited-state dipoles (including permanent dipoles for excited states) may be different. Further details will be published elsewhere.

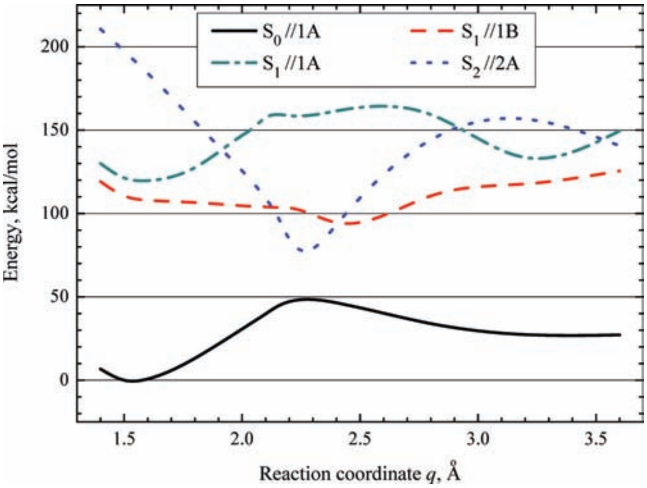


Figure 3. Relaxed potential energy scans for the ground (S_0, 1A—solid line), single excited (S_1, 1B—long dashes), and double excited states (S_2, 2A—short dashes) along the reaction pathway of the ring-closing C–C bond in the CHD/HT system, predicted at the ATDA-UDFT/6-31G*//STS-DFT/6-31G* theory level, using the M05-2X exchange-correlation functional. Absence of an appreciable energy barrier on the pathway from the 1B state of CHD in the Franck–Condon geometry (left) to the minimum on the 2A surface is consistent with an ultrafast rate of the photoinitiated cycloreversion reaction CHD → HT. The dashed-dotted line corresponds to the vertical single excitation at the optimized ground-state geometry (S_1, 1A).

4. Results and Discussion

In the discussion below we assume the following mechanism for the photochromic transformation. The molecule is first excited (in either 1PA or 2PA regime) to a higher electronic state, then undergoes internal conversion to the lowest-lying excited state by means of vibronic relaxation. After evolving on the potential surface of the lowest excited state to the pericyclic minimum, it finally relaxing to the ground electronic state by passing through or near a CIX. A potential barrier on the reaction pathway may slow down this evolution and lead to premature relaxation to the ground state without isomerization. This mechanism is essentially an application of the Vavilov–Kasha rule.[67] In support of this mechanism, mounting experimental evidence indicates that, in the case of diarylethene derivatives, isomerization quantum yields remain nearly constant over a wide range of wavelengths, covering several absorption maxima and thus populating different excited states; the quantum yields are also similar for both one- and two-photon absorption photochemistry.[68–71] A rapid internal conversion to the lowest excited state was observed in supersonic free jet experiments.[72] One may envision the case where photoisomerization is proceeding faster than internal conversion. However, description of this mechanism would require nonadiabatic dynamics simulations of the excited states, which extends beyond the scope of this paper.

4.1. Hexatriene. Relaxed potential energy scans obtained in this study for the HT/CHD system are plotted in Figure 3. They are in surprisingly good agreement with high-level ab initio results. As the C1···C6 reaction coordinate contracts from

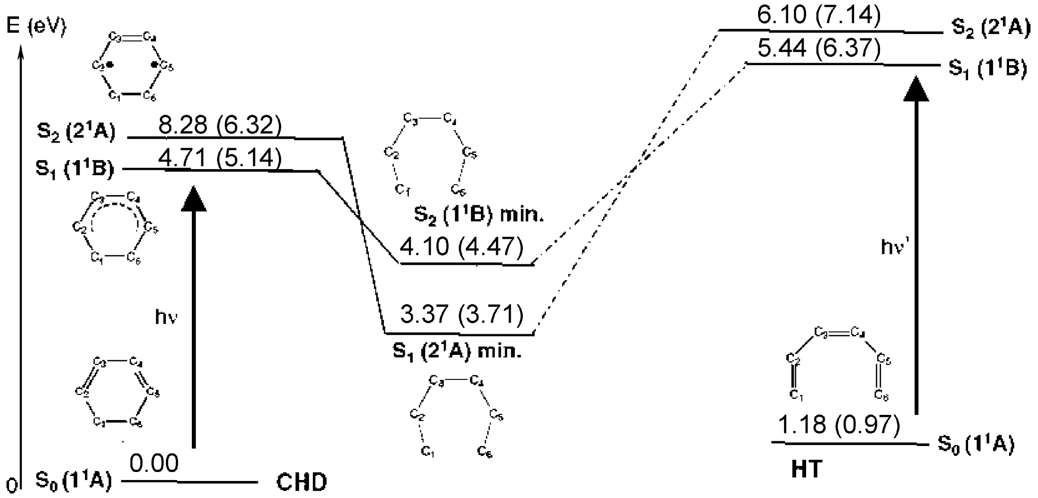


Figure 4. Relative state energies (in eV) for the ground and two lowest singlet excited states in the CHD/HT system, obtained at the ATDA-UDFT/6-31G*//STS-DFT/6-31G* theory level, using the M05-2X exchange-correlation functional. The results of high-level ab initio calculations from ref 23 (multiconfigurational quasi-degenerated perturbation theory) are shown for comparison in parentheses.

nonbonding distance to the normal covalent bond, the bright 1B state (characterized by the large transition dipole from the ground state) is monotonically stabilized in energy, descending toward the pericyclic minimum. At the same time the dark 2A state (with a negligibly small transition dipole from the ground state) is stabilized even faster, crosses the 1B state surface, and forms the bottom of the pericyclic minimum.

It is worth noting that the geometry of the ground state does not approximate the excited-state geometry accurately enough to produce a reasonable RES. The vertical excitation energy curve, plotted in Figure 3 representing the energy of the 1B excited state at the ground-state geometry, displays a maximum instead of the pericyclic minimum and contradicts both high-level ab initio data and the more accurate relaxed ATDA-UDFT data.

Qualitative comparison between our ATDA-DFT results and a state-of-the-art wave function method (multireference second-order perturbation theory) for the CHD/HT system is presented in Figure 4. Four important points were considered: equilibrium geometries for closed and open isomers (CHD and HT), corresponding to the Franck−Condon geometries of the ground states, and excited states 1B and 2A, optimized into the respective pericyclic minima. As one can see, ATDA-UDFT//STS-DFT at the M05-2X/6-31G* theory level, adopted in this work, almost uniformly overstabilizes both excited states by 0.4−1.0 eV but retains the correct order of the excited states, as compared to the multireference perturbation theory results. To the best of our knowledge, this is the first report of the correct state ordering in this system obtained from a DFT-based approach.

4.2. Dithienylethene. Our calculations for dithienylethene (Scheme 1a with X = S) produced the minimum energy pathways for the ground and two lowest excited states, plotted in Figure 5. One can see that the RES of the 1B state has a minimum in the closed form and monotonically rises to the Franck−Condon region of the open form. The doubly excited 2A state, on the other hand, forms the pericyclic minimum and crosses below the 1B state in the vicinity of the CIX. Therefore, an excitation of the open form is followed by ultrafast barrierless relaxation into the pericyclic minimum along 1B and then 2A PES, whereas excitation of the closed form will populate the potential minimum on the excited-state surface. Conversion of the excited closed form into the pericyclic minimum must first overcome a small potential energy barrier (ca. 5 kcal/mol), leading to relatively slow cycloreversion. Excited-state absorption will then bring the system from the 1B to the 2A state, followed by barrierless relaxation toward CIX. Thus, RESs explain both slow cycloreversion and ultrafast photoswitching upon sequential two-photon absorption.

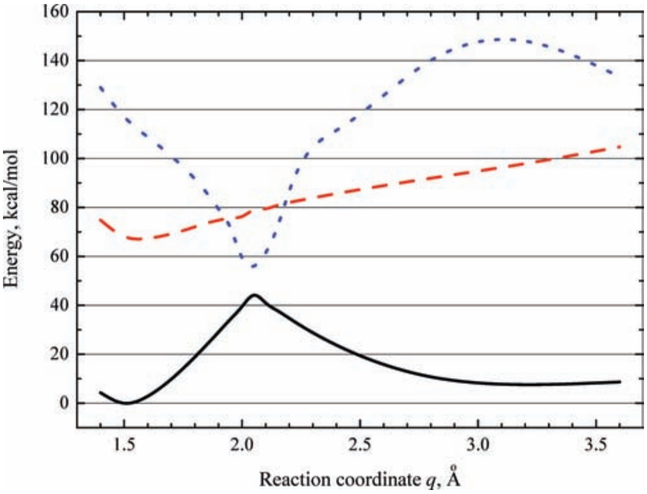
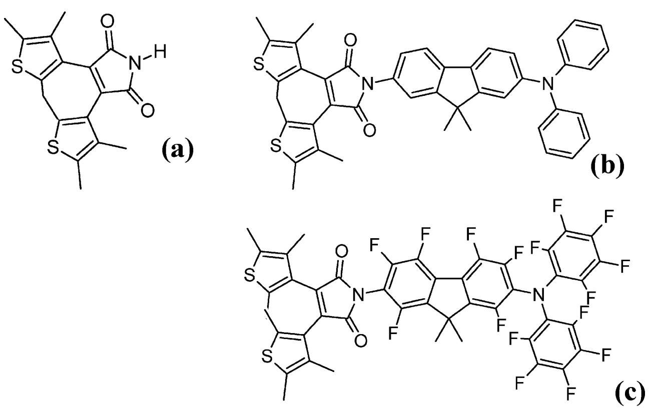


Figure 5. Relaxed energy scan for the ground (S$_0$, 1A), single excited (S$_1$, 1B), and double excited states (S$_2$, 2A) along the reaction pathway of the ring-closing C−C bond in the dithioarylethene system, predicted at the ATDA-UDFT/6-31G*//STS-DFT/6-31G* theory level, using the M05-2X exchange-correlation functional. The legend is the same as in Figure 3.

4.3. Photoswitching Prototype Molecule Designed to Function in the 2PA Regime. Compound **2b** (Scheme 2b) was recently synthesized by Belfield's lab.[71] The diphenylamino-fluorene moiety was covalently attached to the commercially available compound **2a**. RESs for **2a** are plotted in Figure 6 and indicate that the excited state of the open form relaxes barrierlessly to the pericyclic minimum, whereas the closed form in its lowest excited state is separated from the pericyclic minimum by a sizable potential energy barrier. Therefore, our method predicts **2a** to undergo ultrafast photochemical cyclization, whereas the cycloreversion is expected to be slow, in agreement with experimental data.[73] In the experiment, compound **2a** was incorporated into polymer matrixes (poly(vinyl carbazol) and poly(methyl methacrylate)). In either case, the rate constant of the color-forming process (cyclization) was

SCHEME 2: Open Forms of Diarylethene Compounds



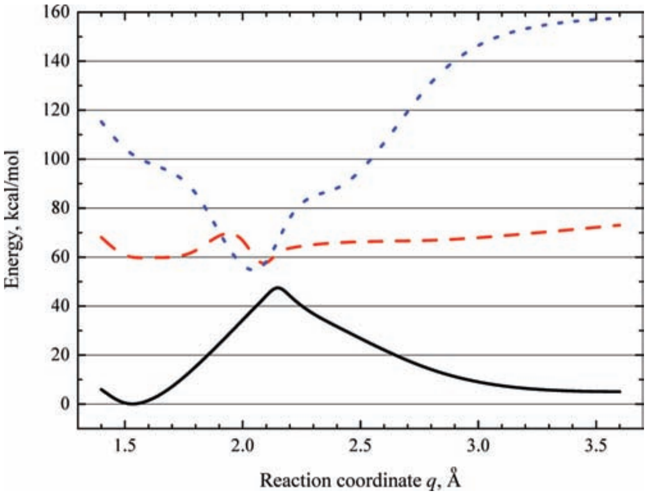


Figure 6. Relaxed energy scan for the ground state and the lowest single and double excited states in compound **2a** (Scheme 2a). The legend is the same as in Figure 3. There is no barrier along the single excited state from the open-ring Franck−Condon region toward the pericyclic minimum. Experimentally, this compound is photoreactive in the both closed and open forms, though the rate of the coloring process (cyclization) is higher than the rate of bleaching (cycloreversion).

found to be more than twice as fast as the rate of the bleaching process (cycloreversion). The absorption spectrum of diarylethene **2a** in the closed form has two absorption bands (470−550 and 360−390 nm). Our TD-DFT calculations in the gas phase gave a blue shift when compared to the experiment. We obtained the lowest vertical singlet excitations at 423 and 324 nm for the closed-ring geometry. Upon irradiation with visible light in the experiment, the first band disappeared while the second one was considerably reduced in intensity. This was reproduced by TD-DFT calculations. The first singlet excited state for the open form **2a** was at 386 nm, but the first excitation with sufficient oscillator strength was at 216 nm.

The diphenylaminofluorene substituent was designed to be similar to other fluorene-based donor−fluorene−donor and donor−fluorene−acceptor chromophores, previously shown to have a large 2PA cross section.[74,75] Its attachment to the photoswitching core **2a** (Scheme 2a) was expected to produce an enhanced photochromic compound, designed to work as a photoswitch in the 2PA regime.

Although compound **2a** was experimentally found to be photoreactive, the molecule **2b** did not display photochromic properties in either the 1PA nor 2PA regime. We applied our ATDA-UDFT//STS-DFT approach, verified in sections 4.1 and 4.2, to predict the RESs in molecule **2b**. The resulting curves are reported in Figure 7a. As one can see, the RES of the lowest excited state forms minima for both the open and closed forms, separated from the pericyclic minimum by potential energy barriers of 4.7 and 8.0 kcal/mol, respectively. We have shown in the previous sections that the barrier for the closed form is typical for other diarylethene derivatives. However, the barrier for the open form is unexpected and is responsible for the loss of photoswitching properties.

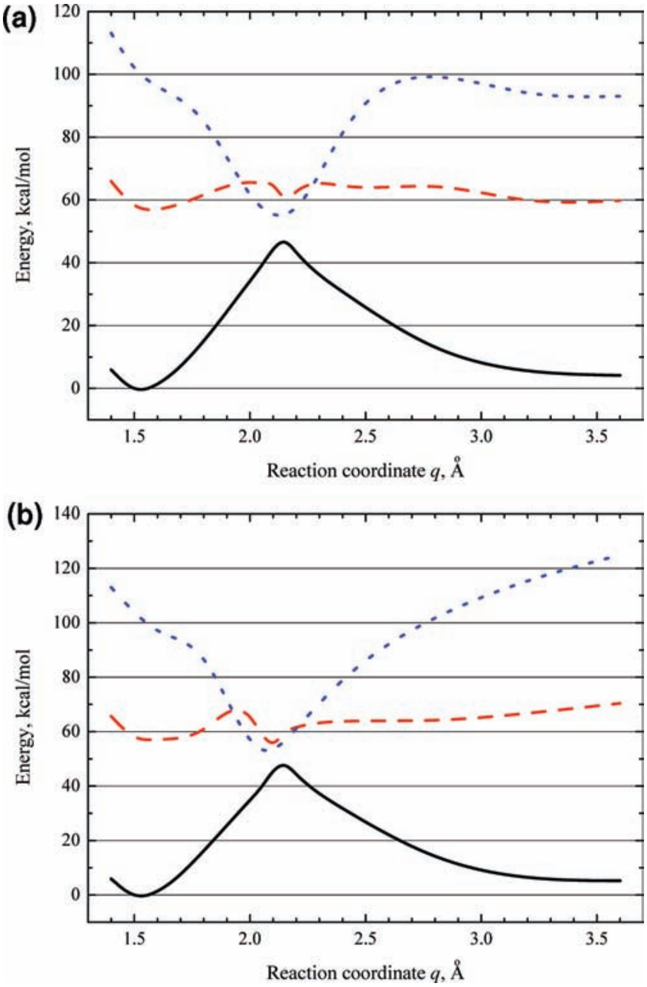


Figure 7. Relaxed energy scan for photocyclization in molecules **2b** (a, top) and **2c** (b, bottom), according to our results at the ATDA-UDFT//STS-DFT, M05-2X/6-31G level of theory. The legend is the same as in Figure 3. Whereas for **2b** both excited states exhibit potential energy barriers from the open isomer to the pericyclic minimum (a, top), there is no such a barrier in case of **2c** (b, bottom). This indicates that ultrafast photoconversion is expected for **2c**.

In order to determine the nature of this barrier, we analyzed the KS orbitals in these molecules and found that, whereas the essential orbitals (antibonding and bonding with respect to forming the new C−C bond) are, respectively, HOMO and LUMO in molecule **2a**, they are HOMO−1 and LUMO for molecule **2b**. At the same time the HOMO in molecule **2b** is primarily the lone pair of the nitrogen atom and is localized on the diphenylaminofluorene pendant group (Figure 8), designed to increase the 2PA cross section. In molecule **2a**, the HOMO to LUMO excitation reduces an antibonding effect and creates a bonding one. This increases the bond order between carbon atoms closing the ring from −1 to 0 and allows the descent toward the pericyclic minimum on the excited-state PES. On the other hand, in molecule **2b** the change in HOMO occupation

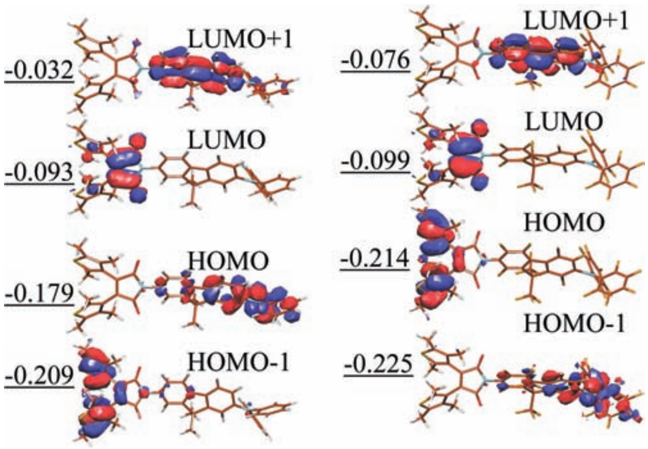


Figure 8. Kohn−Sham energy levels (au) and orbital plots for open forms of compounds **2b** (left) and **2c** (right) at the M05-2X/6-31G level of theory. Whereas the orbitals essential for the ring closure are the HOMO−1 and LUMO in **2b**, they are the HOMO and LUMO in **2c**. This is the reason why the lowest excited state of **2c** is photoreactive.

has no pronounced effect on the ring closure. The antibonding electrons are kept on the HOMO−1 upon the excitation. The placement of an electron into the LUMO increases the bond order from −1 to −1/2 with the net antibonding effect remaining, which is apparently insufficient for initiation of the ring closure reaction. Therefore, the lowest excited state is no longer photoreactive and has substituent-to-core charge-transfer character. Not surprisingly, its energy increases along the reaction coordinate connecting the Franck−Condon region and the pericyclic minimum. This is consistent with what we observed on the RES plotted in Figure 7a.

Apparently, in order to restore photoreactivity in the prototype molecule, one needs to stabilize the lone pair of the donor substituent. This can be accomplished by chemical modification of the pendant group with an electronegative substituent. If this stabilization is sufficient, the donor orbital will have lower energy than both of the essential orbitals, and they become the HOMO−LUMO pair once again. Among various alternatives considered, we found that perfluorination of the pendant group yields sufficient stabilization of the substituent lone pair. The modified prototype (molecule **2c**) is shown in Scheme 2c. Comparison of the energy levels in molecules **2b** and **2c** is presented in Figure 8. Although perfluorination of the pendant group lowers the energy for all the orbitals considered, the stabilization is the greatest for the lone pair orbital, localized primarily on this fragment. The plot of the RESs for the excited states in molecule **2c** (Figure 7b) indeed confirms these simple orbital considerations. The energy of the lowest excited state monotonically descends from the Franck−Condon region of the open form to the pericyclic minimum with no barrier. Thus, the electronic structure of the reactant can be used to predict the nature of the lowest excited state of the molecule, PES of this excited state, and the photochemical kinetics of electrocyclization.

The calculated 2PA spectrum (Figure 9, top) predicts a high 2PA cross section (ca. 30 GM) for molecule **2c**. Although the lowest excited state is somewhat populated in both one- and two-photon absorption regimes, both 1PA and 2PA result in excitation to the higher states. According to the Vavilov−Kasha rule, any electronically excited molecules in higher states quickly reach the lowest excited state via internal conversion. Therefore, if the lowest excited state is photoreactive, the molecule is photoswitchable, regardless whether the 1PA or 2PA excited states are photoreactive or not. Thus, in this paper we demonstrated, theoretically, the photoreactivity of the perfluorinated prototype molecule **2c**.

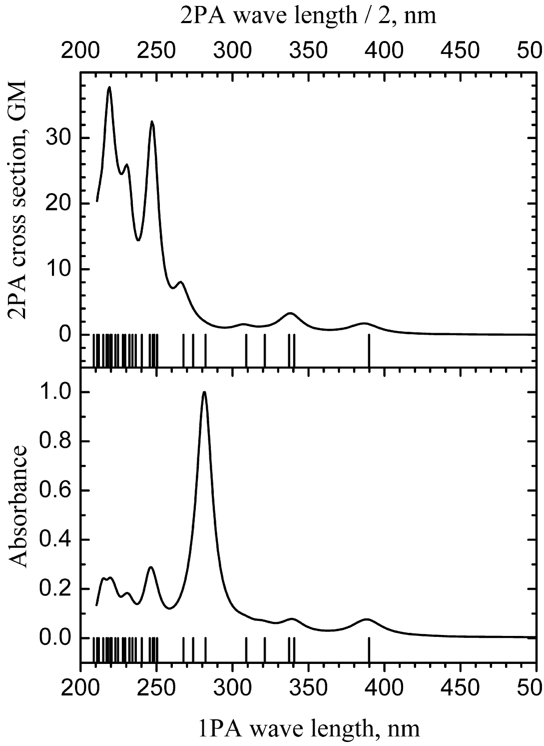


Figure 9. 2PA (top) and 1PA (bottom) profiles for the open form of molecule **2c**. Vertical lines correspond to calculated energies of excited states. Calculations were performed at the ATDA-M05-2X/6-31G* level of theory.

We can therefore formulate a principle for assisting in the design of photochromic molecules: substituents should not introduce any electronic energy levels within the HOMO−LUMO gap between the essential orbitals.

5. Conclusions

A new method to build potential energy surfaces of the excited states, based on the DFT is presented. The approach includes both single and double excitations appearing in first- and second-order TD-DFT in the coupled electronic oscillator formalism (dubbed the *a posteriori* Tamm−Dancoff approximation, ATDA-DFT). The unphysical spikes on these surfaces close to the pericyclic minima were traced to the failure of the restricted KS formalism to describe partial bond breaking in the ground states. The spikes were eliminated by replacing the ground-state energy component of the excited state with the one obtained in the unrestricted broken symmetry KS formalism (termed here ATDA-UDFT). The importance of excited-state geometry optimization (as opposed to the habitual use of unrelaxed ground-state geometries) in accurate prediction of these PESs was confirmed. Because of the lack of analytical derivatives at ATDA-UDFT theory level, the lowest single and double excited-state geometry was approximated using the Slater transition state method (STS-DFT). Compared with high-level multireference perturbation theory, the combined ATDA-UDFT//STS-DFT approach was shown to slightly underestimate energies of both excited states. However, it correctly reproduced the state ordering and the energy crossovers. The approach was also able to explain experimentally observed slow photochemical cycloreversion rates and fast excited-state absorption initiated cycloreversion in model dithioarylethenes.

After this validation, the ATDA-UDFT//STS-DFT approach was used to explain the loss of photochromic reactivity in a newly designed 2PA photoswitch. The nature of the effect was traced to the presence of a barrier on the PES of the lowest excited state. The KS orbital analysis revealed this barrier to be the result of the lone pair orbital of the donor chromophore group appearing within the HOMO−LUMO gap of the essential orbitals in the photoswitching molecular core. This changed the character of the lowest excited state from photoreactive to charge transfer. In order to restore the photoreactivity, the stabilization of the lone pair orbital to an energy below the HOMO orbital energy was suggested. As a proof of principle, perfluorination of the 2PA chromophore pendant group was proposed. This substitution was found to restore the order of the essential orbitals and eliminate the energy barrier on the excited-state potential surface, suggesting restoration of the photochromic reactivity. On the basis of these findings, an essential design principle for new photochromic molecules was formulated: substituents should not introduce any electron energy levels within the HOMO−LUMO gap of the photoreactive fragment. This principle will assist in future development of materials for 3D optical data storage devices with unprecedented storage capacity for advanced applications in information technology.

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