

Single Molecule Multiphotochromism with Diarylethenes

AURÉLIE PERRIER,[†] FRANÇOIS MAUREL,[†] AND
DENIS JACQUEMIN^{*,‡}

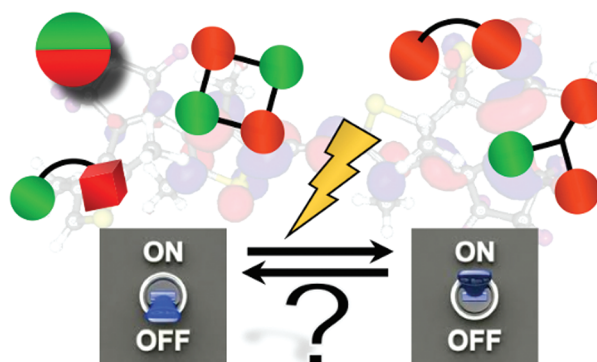
[†]Université Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR CNRS 7086,
15 rue Jean Antoine de Baïff, 75205 Paris Cedex 13, France, and

[‡]Laboratoire CEISAM - UMR CNR 6230, Université de Nantes,
2 Rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France

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CONSPECTUS

In single photochromes, the two isomers that are inter-converted in photoinduced reactions can serve as *on* and *off* states in a molecular switching device. The addition of several photochromic moieties onto a single molecule can allow the processing of more complex logical patterns. For example, an asymmetric triad could, in principle, store a byte, rather than a bit, of data. Because of the potential impact of multiphotochromic molecules in many research areas, over the past decade several groups have synthesized these coupled structures. The targets are easily addressable molecules that display increased contrast between the *on* and *off* states and in which all isomers have significantly distinguishable optical signatures.



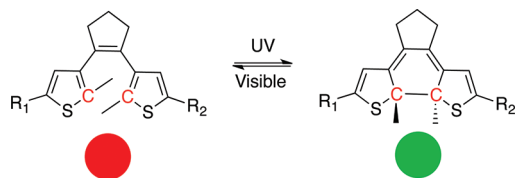
In this Account, we provide an overview of the multiswitchable molecular systems that incorporate at least one diarylethene group, which is the most successful thermally stable (P-type) organic photochrome. Up to this point, most systems have presented significant limitations. First of all, the reversibility of the processes is hindered by several side reactions more frequently than for single photochromes. Second, switching one part of the compound impedes the photoreactivity of other fragments in approximately 50% of the cases, and maximizing the electronic communication increases the probability of partial activity. In addition, most of the few synthesized operative systems only demonstrate cumulative absorption spectra rather than new features. Finally, it is impossible to selectively induce a chosen conversion because one wavelength might trigger several processes. We also emphasize the promising successes of asymmetric diarylethene dimers and trimers and molecules that combine two families of photochromes, such as diarylethene added to fulgimide or phenoxy-naphthacenequinone.

In that framework, theoretical simulations offer complementary tools to investigate these structures, both to obtain structure/property relationships and to propose paths for the design of more efficient molecules. However, due to the size of the systems, researchers can only apply semiquantitative models. The investigation of the absorption spectra of the photochromes with time-dependent density functional theory (TD-DFT), the analysis of the topology of the LUMO + n (typically $n = 1$) of the closed–open hybrid, and an estimate of the steric stress in the hypothetical (ground-state) closed–closed structure serve as a useful combination of parameters to obtain initial insights regarding the photocyclization of the different open diarylethene groups. Nevertheless, because a first-order qualitative approach does not explore the potential energy surface of the photoexcited states, it remains inadequate for the investigation of some molecules.

1. Introduction

Photochromic molecules are able to undergo a light-induced reversible transformation between two isomers characterized by specific structural and electronic features. If the properties of the two forms are significantly distinct,

photochromes can act as *on/off* switching entities. Examples of organic photoswitches include azobenzenes, phenoxy-naphthacenequinones, naphthopyrans, fulgimides, and diarylethenes (DAs, see Scheme 1). DAs have been initially proposed and developed by Irie and Lehn.¹

SCHEME 1. A Typical DA in Its *Open-Off* (Left) and *Closed-On* (Right) Forms, the Cyclopentene Ring Being the Bridging Group^a

^aThe reactive carbon atoms are displayed in red.

The most stable form of DA is a poorly conjugated open (**o**, *off*) isomer in which the two antiparallel thiophene rings are nearly orthogonal to the central bridge. The closed (**c**, *on*) isomer is strongly conjugated as the thiophene rings and central bridge become coplanar. The closure reaction is induced by UV irradiation, and the back reaction requires visible light. DAs possess several qualities required for practical applications and are one of the most intensively investigated classes of molecular switches. We redirect the readers to previous reviews for general considerations regarding DAs.^{1–4}

DAs can potentially be used in 3D optical storage devices.⁵ These systems that rely on a binary logic related to the commutation of isolated photochromes have not reached full-scale commercialization. This is due to the difficulty to secure nondestructive read-out in DA² and to the need of addressing both states via two-photon absorption. Nevertheless, the central conceptual ideas are now well established. To break the 0/1 barrier and to store more data, in a single object, multiphotochromic molecular entities, that is, compounds presenting several switchable moieties, are building blocks of choice. Indeed, an asymmetric trimer could store a byte rather than a bit of data, thanks to its eight possible isomers (2³). Several multiswitchable derivatives including at least one DA have been synthesized and characterized (see section 2.1). The quest to command and understand these complex compounds remains at the border of contemporary research, and most experimental reports have pointed out significant problems (see section 2.2). Theoretical models are useful tools to optimize the properties of coupled switches (see section 3) as it is noteworthy that the lifetimes of the excited-states in DAs are very short (ca. 5 ps).¹ This Account aims to provide a flavor of the present successes and restrictions in the field with a special focus on the understanding of the (im)possibility to obtain all expected isomers.

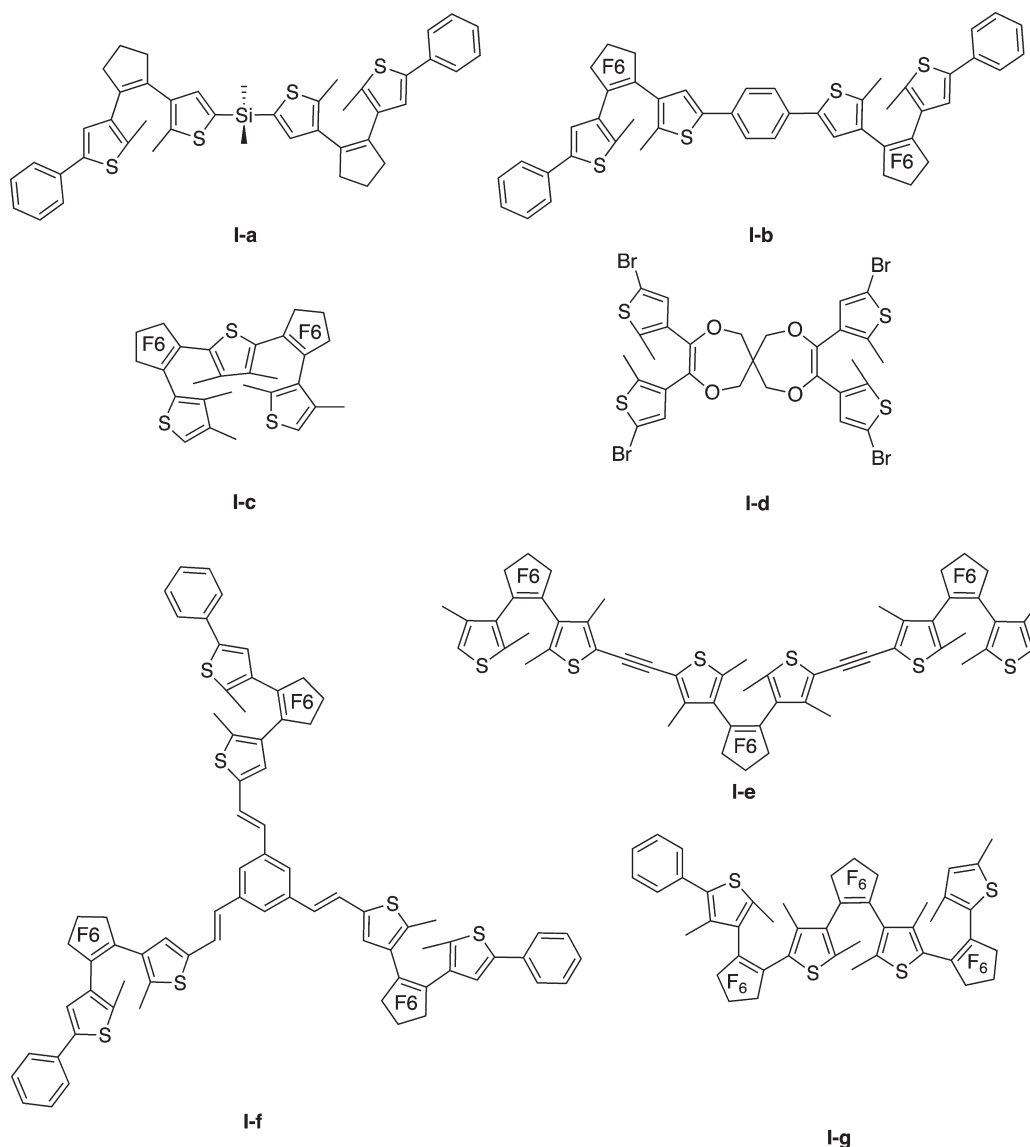
2. Synthesized Molecules

2.1. Classes of Multiphotochromes. Only a few multiphotochromic organic molecules incorporating DAs have been

synthesized. We have listed most of them in this Account, though it is not our goal to review the synthetic procedures nor to collate all spectroscopic properties. One can classify the available systems in two categories. In the first group, one finds DA-only molecules (see Scheme 2). Compounds using an organic linker to connect the DAs are gathered in Table 1,^{6–34} but organometallic structures have been synthesized as well.^{35–38} The versatility of molecular architectures is striking with DAs either bonded through the side of their thiophene rings, the bridging group, the reactive carbon atoms, or more closely overlapping; linear, star or rectangle shapes, symmetric or asymmetric systems can thus be obtained. In the second category, one finds entities constituted of two or three subunits of different photochromic classes. Specifically, compounds constituted of one DA attached to one or two hydroazulene,³⁹ phenoxynaphthacenequinone,⁴⁰ naphthopyran,^{41,42} indolinooxazolidine,⁴³ or fulgimide⁴⁴ are available (Scheme 3).

2.2. Functionalities. As can be deduced from Table 1, most available multi-DA compounds present an obvious limitation: the expected full-color (full-combination) photochromism usually remains beyond reach. Three outcomes can be observed: (1) all conceivable structures are available (e.g., **I-b**,¹³ **I-d**,²⁴ and **I-f**);²² (2) the fully closed isomer is found but the closed–open intermediate cannot be isolated (e.g., **I-a**);²⁵ (3) the fully closed structures cannot be formed (e.g., **I-c**,¹² **I-e**,¹¹ and **I-g**).²⁰ We emphasize that there is often no relationship between the nature of the linker and the observed functionality (see section 3).

For compounds displaying several active DAs, it is generally difficult to distinguish the closed–open and closed–closed forms, as well as to separate these molecules with chemical approaches (second outcome). Indeed, UV irradiation sequentially triggers both the first and the second electrocyclizations.^{24,25,32} In addition, the wavelength of the visible bands of the closed isomers are almost independent of the number of switched-*on* DA units: an intensity enhancement is observed, but no significant bathochromic shift (both first and second outcomes). Reference 32 provides a striking example: the longest wavelengths of maximal absorption (λ_{max}) are equal for the closed monomer and the fully closed hexamer. This is already an improvement for practical applications, because the disparity between the *on* and *off* states is improved, but it is disappointing that the fully closed isomers do not present specific optical features. For these systems, the symmetry and lack of electronic communications between the DAs are the two parameters limiting performance: one is stuck with a two-position switch. The asymmetric **I-c**¹² and **I-g**²⁰ designed by Irie and collaborators are

SCHEME 2. Representation of the Fully Open Isomers for Four Typical Dimers and Three Trimers^a

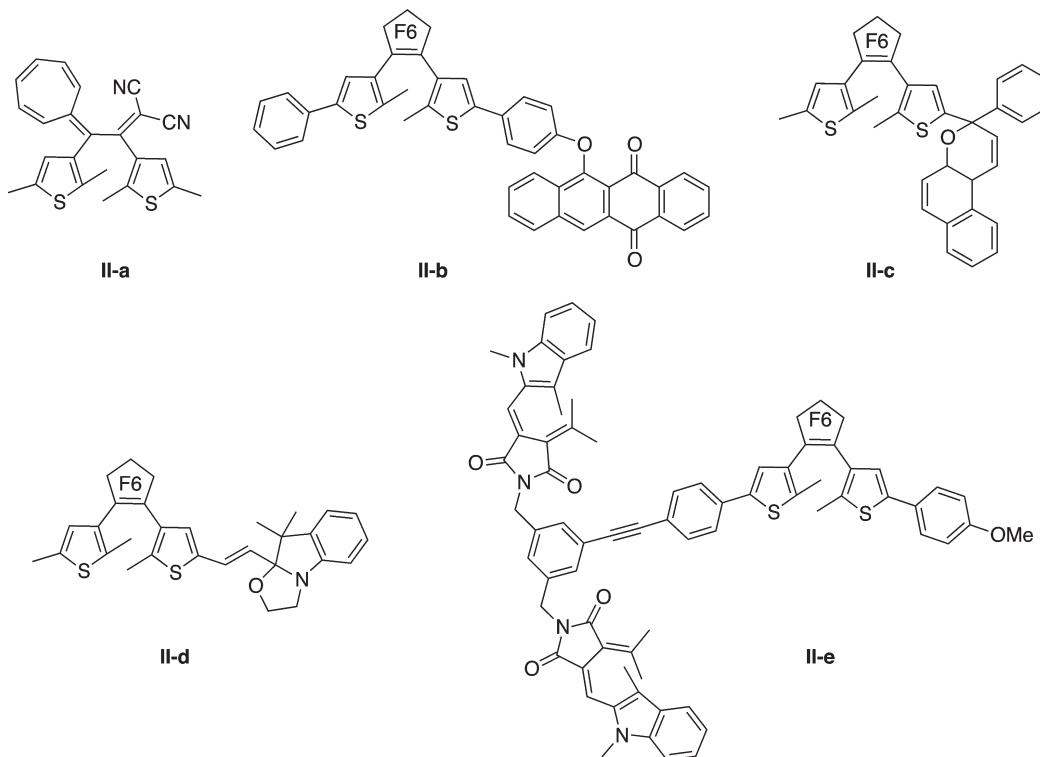
^aThe structures are from refs 25 (**I-a**), 13 (**I-b**), 12 (**I-c**), 24 (**I-d**), 11 (**I-e**), 22 (**I-f**), and 20 (**I-g**). See also Table 1.

noteworthy exceptions. In these molecules, the closed–open and open–closed isomers have distinct optical signatures. However, these compounds partially suffer from the third outcome: the fully closed isomer is out of reach.

The third outcome, observed for about half of the molecules, is troublesome: switching *on* one part of the compound impedes the photoreactivity of other subunits. Consequently, a substituted single photochrome, rather than a multiphotochromic compound, is obtained. As detailed in the next section, four considerations might explain this result: (1) the lack of an adequate excited-state centered on the open DA; (2) the instability of the putative closed product; (3) the steric hindrance in the open DA; (4) the

presence of side processes (fluorescence, parasite reactions, etc.). The first problem dominates and is consistent with the seminal explanation of partial photochromism by Irie and co-workers. Indeed, they suggested that an energy transfer occurs from the photoexcited state located on the open DA to the closed unit, preventing the electrocyclization.¹¹

For the second category encompassing mixed photochromes (Scheme 3), several isomers could be characterized experimentally: three for **II-a**³⁹ and four **II-b–e**,^{40,41,43,44} the missing closed–closed structure of **II-a** being related to steric stress.⁴⁵ These compounds emerge as interesting alternatives to DA-only structures, but several shortcomings have been pointed out. Notably for **II-c**, Frigoli and Mehl

SCHEME 3. Representation of Molecules Incorporating One DA and One or Two Other Photochromes in Their Least Conjugated Form^a

^aSee refs 39 (**II-a**, 3/4), 40 (**II-b**, 4/4), 41 (**II-c**, 4/4), 43 (**II-d**, 4/4), and 44 (**II-e**, 4/4), the number giving the functionality, as in Table 1.

determined ways to reach the four isomers but could not induce the DA ring-closure once the naphthopyran group was open.⁴¹ By contrast, Pozzo and co-workers found that the fully conjugated structure of their **II-d** hybrid is a dead-end, yielding side products.⁴³ Though the electronic communication between their photochromes is limited, **II-b**⁴⁰ and **II-c**⁴⁴ are two of the most successful systems designed to date. In both cases, four stable isomers could be identified, and (almost) all possible transformation paths are available.

3. Theoretical Analysis

3.1. Models. For isolated DA, several *ab initio* contributions have been published during the past decade, including refined multireference approaches, for example, complete active space (CAS) calculations,^{46,47} that demonstrated the importance of conical intersections. Unfortunately, these CAS schemes are not applicable to large entities. An alternative, proposed by Masunov and co-workers, relies on a DFT broken-symmetry approach and allowed them to quantify both the thermal stability and the fatigue resistance of single DA.^{48–50} In recent reports, we have proposed a more simplified approach combining time-dependent density functional theory (TD-DFT) with a molecular orbital analysis to get insights into the possibilities to close or not close the

photochromic subunits.^{51–55} Apart from the work of Staykov and co-workers,⁵⁶ who probed the S_0 and S_1 potential energy surfaces of their DA-capped wire using (TD)-DFT scans, we are not aware of other *ab initio* simulations aimed at analyzing the photochromic properties of multi-DA molecules, though several calculations of the absorption spectra are available.^{26,29,30,34} For simulating the spectral properties, we advocate the use of a PCM-TD-CAM-B3LYP/6-311+G(2d,p)//PCM-PBE0/6-311G(d,p) approach (electronic method//geometry, both obtained within the polarizable continuum model, which accounts for solvent effects). Indeed, this protocol accurately reproduces the observed absorption wavelengths of DA.^{52,55}

3.2. Discussion. As described above, the results obtained experimentally are difficult to rationalize with intuitive chemical concepts. Below, we present a series of case studies illustrating the theoretical interpretation. In a few compact systems (denoted “shared” in Table 1), the energy of the product and the distance between the reactive carbon atoms⁵⁷ should be examined (steric control). In contrast, in unconstrained coupled switches, the energetic cost associated with each ring-closure is constant and independent of the closed/open nature of the other units, whereas the distance between the reactive carbon atoms is unaffected

TABLE 1. Molecules Incorporating Several DA Bonded through a Metal-Free Linker Classified by Publication Year^a

N	architecture	linker	functionality	comments	year	ref
2	head-to-head, sym	tetrathiafulvalene	2/3	no doubly closed	1999	6
2	linear, sym	covalent bond	2/3	no doubly closed (byproduct)	2000	7
2	linear, sym	bis(phenylethynyl)-anthracene	2/3	no doubly closed	2001	8
4	tetrahedron, head-bonded, sym	spiro-bifluorene	2/6	only fully open and fully closed reported	2001	9
2	linear, sym	phenyl	3/3	nitronyl side groups	2001	10
2	linear, sym	ethynyl	2/3	no doubly closed	2002	11
3	linear, sym	ethynyl (I-e)	4/6	cannot close two neighbor DA	2002	11
4	linear, sym	ethynyl	5/10	cannot close two neighbor DA	2002	11
2	fused, nonsym	shared (I-c)	3/4	no fully closed	2002	12
2	linear, sym	phenyl (I-b)	3/3		2003	13
2	fused, nonsym	shared	3/4	no fully closed	2003	14
2	linear, sym	diethynyl	2/3	no doubly closed, strong fluorescence	2003	15
3	star, sym	triphenyl-amine	4/4		2004	16
2	bent, sym	diphenyl-fluorene	3/3		2004	17
2	linear, sym	<i>m</i> -diethynylphenyl	2/3	no doubly closed	2005	18
4	rectangle, partly sym	<i>m</i> -diethynylphenyl, ethynyl	3/7	cannot close two neighbor DA	2005	18
2	bent, head-bonded, sym	bis(phenylmethyl)-fluorene	3/3	coexistence of fully closed and closed/open	2005	19
3	fused, nonsym	shared (I-g)	5/8	cannot close two neighbor DA	2005	20
2	linear, sym	<i>p</i> -diethynyl/ethenyl-phenyl	2/3	no doubly closed, 5 related structures	2005	21
3	star, sym	triethynylphenyl	3/4	no triply closed	2006	22
3	star, sym	triethenylphenyl (I-f)	4/4		2006	22
3	star, head-bonded, sym	tricarboxylic acid-triphenyl ester	2/4	fully open and fully closed reported	2006	23
2	head-to-head, sym	saturated spiro group (I-d)	3/3		2007	24
2	bent, sym	SiMe ₂ (I-a)	2/3	fully open and fully closed reported	2007	25
2	head-to-head, sym	thienothiophene and dithienothiophene	2/3	no doubly closed	2008	26
2	linear, sym	bis(ethenyl)-bipyridine	2/3	fully open and fully closed reported	2008	27
2	rod, sym	tetrathiophene	3/3		2009	28
2	head-to-head, sym	dithienopyrrole	2/3	no doubly closed, 5 ≠ pyrrole chains	2009	29
2	face-to-face, sym	diethenyl-bipyridine	2/3	bonded by reactive carbon atoms	2010	30
2	linear, sym	benzo-bis(imidazole)	2/3	partial form not isolated, pH sensitive	2010	31
6	star, sym	hexa-diphenylbenzene	2/13	fully open and fully closed reported	2010	32
3	V-shaped, head-side	two side DA bonded to central DA	3/6	possible to close the central DA or all DA	2011	33
2	linear, sym	bis(phenoxy)-perylene	2/3	fully open and fully closed reported	2011	34

^aN gives the number of DA switches. Architecture indicates the relative positions of the DA (sym stands for symmetric, DA are bonded with the linker through their side thiophene rings except when noted by "head" when the bridging moiety is used to connect to the linker), linker is the chemical group bonding the different units ("shared" meaning that they share a part of their photochromic core, typically a common thiophene ring), functionality indicates the number of experimental forms that could be obtained/isolated out of a possible theoretical maximum.

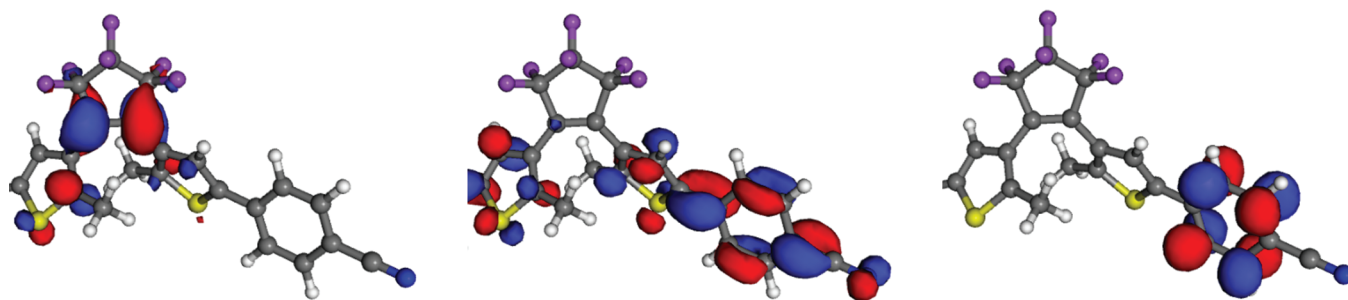


FIGURE 1. Typical molecular orbitals in DA: only the first presents a photochromic shape; the second is antibonding for the CC bond; the third is localized on the side phenyl ring with no contribution on the reactive carbon atoms.

by the state of the neighboring DA.^{52,54,55} Therefore, electronic features guide the answer in most systems. While the shape and the position of the absorption bands are generally insignificant, the nature of the states (here topology of the molecular orbitals) corresponding to the UV peaks provides insights, if one goes beyond the HOMO–LUMO approximation and analyzes higher-lying virtual orbitals.

How Does Orbital Control Work in Multi-DA? In single DA, the HOMO of the open isomer presents a shape similar

to the LUMO of the closed structure, the complementary relationship being true.⁵⁸ One can interpret this finding as an exchange between the ground (HOMO) and excited (LUMO) states of the open and closed isomers. The LUMO of the open DA possesses a significant density on the reactive carbon atom(s), as well as a bonding character for the to-be-formed CC bond. For DA presenting a conjugated bridge, the absence of such a virtual orbital having a "photochromic" shape (both bonding character and significant densities on

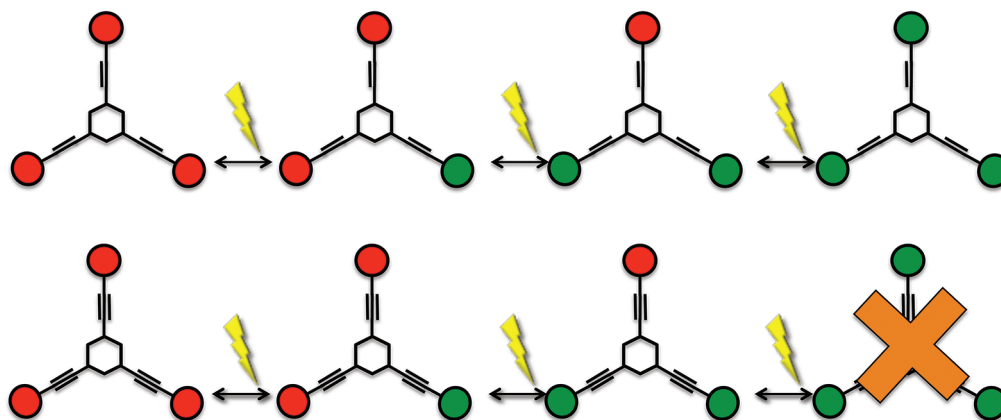


FIGURE 2. Sketch of the successive possible DA switching in **I-f** and the corresponding triply bonded star. Experimental irradiation wavelength = 365 nm.²²

the two carbons, see Figure 1) in the experimental energy range correlates with the absence of closed isomers.⁵⁹ In the closed–open (**co**) DA dimer, determining whether UV irradiation promotes the electron to a photochromic orbital centered on the open side might indicate whether the transformation toward a doubly closed structure is possible, though it remains an imperfect approximation (see section 3.3), the actual photochromic reaction involving several states. Generally the LUMO of the **co** isomers is located on the closed side, because this moiety constitutes the most conjugated part of the compound. In other words, it is the LUMO + n ($n \geq 1$) that may be helpful to study the ring-closure of the open switch in partially closed multi-DA molecules. This is also related to the presence of a visible band in **co** optical spectrum, which can be usually ascribed to a HOMO–LUMO transition able to trigger the ring-opening of the closed DA. Therefore, one needs to scrutinize the excited states in the UV range.

Why Is the Vinylic Star I-f More Effective than Its Ethynyl Counterpart (Ref 53)? This pair of triads constitutes a nontrivial case:²² only the vinylic derivative allows full cyclizations, the triple-bonded systems only yielding the **cco** and **cco** blends (see Figure 2). This experimental result is rather astonishing, if one notices, on the one hand, that the optical spectra of all available isomers are similar both experimentally²² and theoretically (see Figure 3) and, on the other hand, that the shape of the molecular orbitals are also alike for both compounds (see Figure 4). To understand the experimental trends, one needs to focus on **cco** isomers, the last common intermediates. For both ethynyl and vinylic **cco**, the visible band exclusively corresponds to a promotion from HOMO and HOMO + 1 toward LUMO and LUMO + 1. All four orbitals are located on the two closed DA and on the connecting linker but show no contribution on

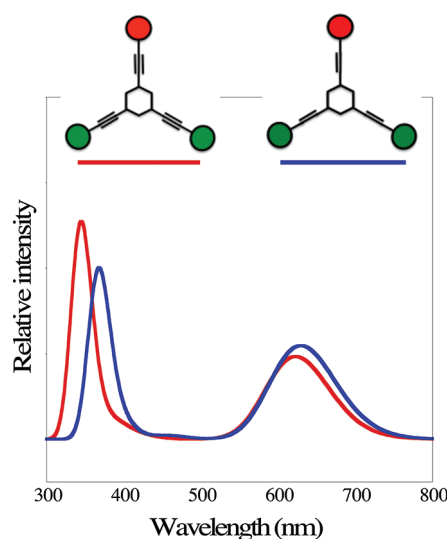


FIGURE 3. Illustration of simulated UV/vis spectra for the **cco** isomers of Figure 3. Adapted from ref 53. Note that the side phenyl rings experimentally present (see Scheme 2) have been removed in the calculation to lighten the computational burden.

the open DA (see Figure 4). This similarity is however irrelevant to predict the impact of UV irradiation (365 nm experimentally). The UV bands of Figure 3 are similar in shape and position but do not imply the same molecular orbitals. While the ethynyl UV absorption is still dominated by transitions involving the LUMO and LUMO + 1 (87%), the largest component for the vinylic compound is the LUMO + 3 (37%), which presents the photochromic shape (Figure 4). The second and third largest contributions are the LUMO + 4 and LUMO + 2, the latter also presenting the required topology. In short, the apparently similar optical characteristics of the two star-shaped isomers are related to significantly different photoexcited phenomena.

Could the Cyclization Yields of All DA Subunits Be Equivalent? Yes, if the electronic communication is

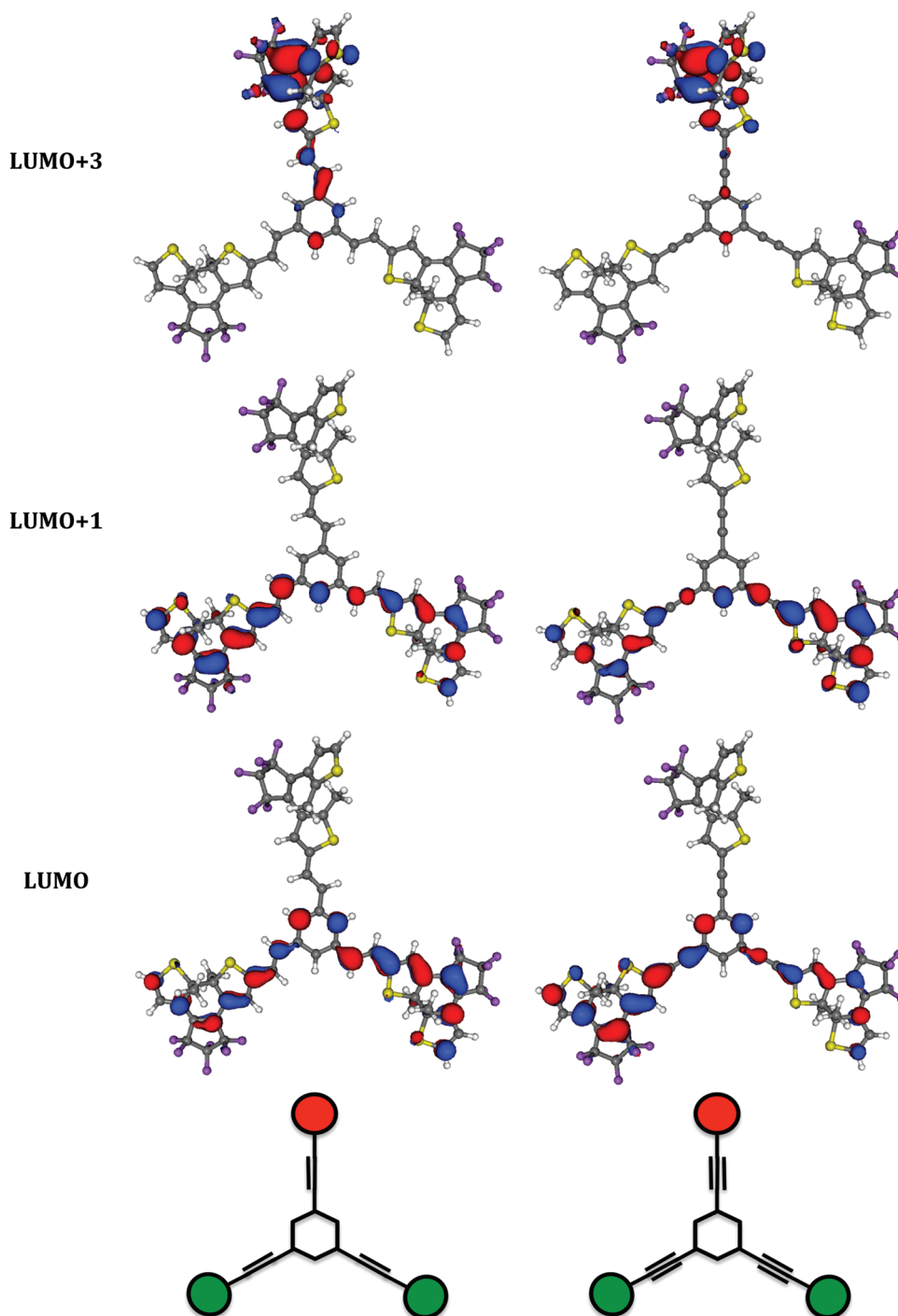


FIGURE 4. LUMO, LUMO + 1, and LUMO + 3 for the **cco** isomers of Figure 3. Adapted from ref 53.

minimal. This is illustrated by Irie's **I-d**: the two constituting DAs are essentially independent of each other and present equivalent photochromic yields.²⁴ This situation typically occurs when a nonconjugated spacer bridges the DA inhibiting the direct interaction between the photochromes and, therefore, securing full photochromism. In these cases, one notices a doubling of the on/off contrast but the

λ_{\max} remains constant (first or second outcomes in section 2.2).^{9,17,25,24} In the theoretical calculations, this is reflected by (nearly) degenerate orbitals in the doubly open isomers and the conservation of both the energy and the shape of the photochromic orbital(s) of the open DA in **co** isomer.^{52,55} This is illustrated in Figure 5 for **I-d**.

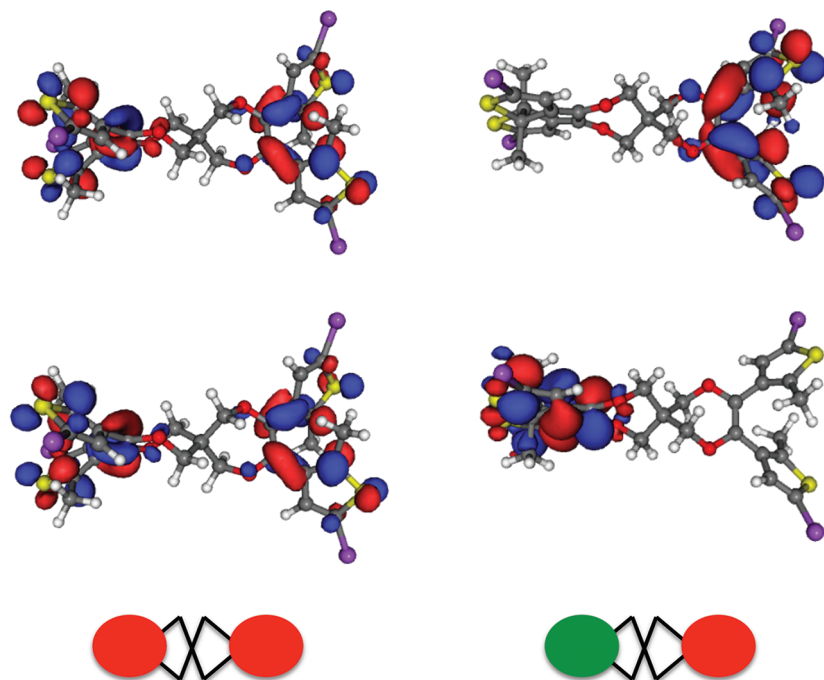


FIGURE 5. LUMO (bottom) and LUMO + 1 (top) of **I-d oo** (left) and **co** (right) isomers. One clearly notes the degenerate character in the doubly open structure and the preserved photochromic shape of the LUMO + 1 of the right open DA in **co**. Adapted from ref 55.

Why Can the Doubly Closed Form Not Be Obtained for I-c ? This is because the formation of the closed–closed isomer would exacerbate the proximity of the methyl groups (<2 Å) and produce an elongated CC σ bond (ca. 1.6 Å for the single bond formed during electrocyclization), both being clearly detrimental for the stability of the product.⁵⁵

Which Factor Limits the Trimer I-g? Examining the distances between the two reactive carbon atoms of the open DA allows us to unravel why the **coc** isomer of **I-g** cannot convert to **ccc**.²⁰ Indeed, once the two extreme DAs are closed (i.e., once all four thiophene rings are already part of a closed DA), the steric hindrance is so large that the central CC distance exceeds 5.0 Å (see Figure 6). Open DA with a separation of more than 4.2 Å between the two thiophene rings is unable to display photochromism, at least in solid-state.⁵⁷ In addition, the thiophene rings of **coc** are not properly oriented, and their rotation would imply large steric repulsions.

3.3. Limitations and Future Developments. The above theoretical analysis also fails in some cases. An expected problem is the presence of side reactions for which it does not account. Indeed, in the covalently bonded dimer of Peters and Branda,⁷ a photochromic orbital is available in the stress-free closed–open structure,⁵² which indicates a favorable case, though experimentally a competitive diatropic rearrangement takes place.⁷ One would need to explore

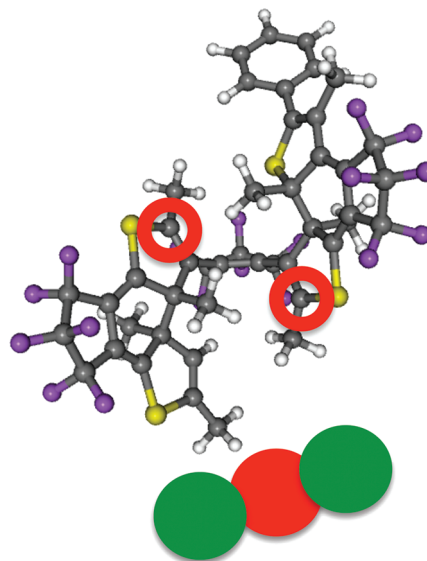


FIGURE 6. Bottom view of the optimized closed–open–closed isomer of **I-g**. The reactive carbon atoms of the central DA are red-circled and distant by 5.05 Å.

multiple transition states on both the ground and first low-lying excited states to gain more information regarding these byproducts.⁴⁸ More troublesome are the incorrect predictions made for **I-e**.⁵⁴ Starting from the **coo** isomer, the orbital analysis foresees the possibility to reach the experimentally unseen **cco** (false positive) but not **coc** that is actually obtained (false negative).¹¹

These theoretical breakdowns are related to the static approach that does not account for the electronic transfer from one DA to another nor adequately model the photochromic paths because the actual potential energy surfaces are completely unexplored beyond the minima. In short, a success rate of ca. 75% is reached by this rudimentary model,^{51–55} a result in the order of typical orbital-like (Fukui-like) schemes. In that framework, Masunov's protocol (see above)^{48–50} could be very useful for further developments of complex DA systems in a more rational way, notably for detecting parasite reactions and estimating reaction speeds. Such methods can be viewed as an extension of classical Woodward–Hoffmann rules of photocyclization to more complex cases, therefore maintaining the balance between accuracy and computational cost.

On the experimental side, two improvements would be helpful. On the one hand, most studies only apply a given wavelength to initiate all electrocyclizations, whereas the selection of different incoming rays could allow the system to reach different excited states and possibly close all DAs. On the other hand, the synthesis of less symmetric multi-DAs (e.g., push–pull structures) would help in reaching more controllable systems.

4. Conclusions

Multiphotochromes appeared 10 years ago and constitute a promising family of compounds for storing more information in a single molecule as well as building complex devices. Though industrial applications remain far from today's possibilities, several successful examples are already available, some presenting more than four distinguishable and interconvertible isomers. During this past decade, critical problems have also been identified, and solving these shortcomings still constitutes a nontrivial challenge for both experimentalists and theoreticians. Specifically, it is not straightforward to design a molecule in which an effective electronic coupling between the different switchable moieties allows one to obtain different optical signatures for all isomers, while not partially quenching photochromism. To achieve such feats, several aspects, for example, geometric constraints, relative energies, electronic energy transfer, and side reactions, should be simultaneously considered. Taking the inner track to success clearly requires joint theory and experiment studies.

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BIOGRAPHICAL INFORMATION

Aurelie Perrier was born in France in 1978; she received her Ph.D. in Physical Chemistry from the University of Bordeaux in 2005 with Prof. J. C. Rayez. After one year as a postdoctoral fellow at the University of Siena (Italy) with Prof. M. Olivucci, she joined the University of Paris Diderot as associate professor in 2007. Her interests include the modeling of the electronic and optical properties of photoactive organic molecules.

François Maurel was born in 1966 in Digne (France). He obtained a Ph.D. in theoretical chemistry from Pierre et Marie Curie University in 1995 under the direction of Professor Nguyen Trong Anh and worked as a postdoctoral Fellow at the CEA Saclay with Professor Philippe Millié. He is now a Professor of chemistry at the University Paris Diderot. His research interests include the properties of photo- and electroactive conjugated materials.

Denis Jacquemin was born in Dinant (Belgium) in 1974; he received his Ph.D. in Chemistry from the University of Namur in 1998 under the supervision of Prof. J. M. André. He then went to University of Florida for his postdoctoral stay with Prof. N. Y. Öhrn. In 2003, he was appointed Research Associate of the FNRS in Namur (Belgium), and since 2010, he has been Professor at the Université de Nantes (France). His main research interest is the modeling of phenomena related to electronically excited states in conjugated organic molecules.

FOOTNOTES

*To whom correspondence should be addressed. E-mail: Denis.Jacquemin@univ-nantes.fr. The authors declare no competing financial interest.

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