

Electrochemical and Photochemical Cyclization and Cycloreversion of Diarylethenes and Diarylethene-Capped Sexithiophene Wires

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Optical switching of molecular properties are among the key focus points in the development of molecular, and in particular organic, electronics. Among the structurally diverse range of organic photochromes including fulgides, spiropyrans, overcrowded alkenes, dihydroindolizines, catenanes, *etc.*, the synthetic versatility, thermal stability, and combination of electro- and photosensitive properties place diarylethenes as a key structural unit.^{1,2} The systematic study of their spectral, physical, and electronic properties and the design and synthesis of new diarylethene molecules^{1,2} has led to the widespread application of these switches in molecular electronics,^{3–6} molecular magnetism,⁷ fine chemical synthesis,⁸ cell biology,⁹ and spectroscopy.¹ These studies over the past decade have led to the design and fabrication of molecular devices, based on diarylethenes, in which the electrical conductivity in nanojunctions can be controlled.^{3,4,10} Their synthetic versatility has proven invaluable in tuning molecular properties, enabling key problems to be solved such as the quenching of molecular switching by metallic and nanowire surfaces.^{3–6,10} The photochromic properties of diarylethenes has led to their application in molecular magnetism where they can switch the coupling strength between unpaired electrons in complex organic diradicals.^{7,11} A number of chemical reactions were reported, where switching of diarylethenes supports host–guest reaction mechanisms in organic reactions.^{1,8,12,13} Finally, the successful use of diarylethenes in labeling living cells shows a possibility for future application in novel drug design and drug discovery techniques.⁹

ABSTRACT A combined theoretical and experimental study was performed on diarylethenes and diarylethene-capped sexithiophenes aiming at an improved understanding of the electrochemical and photochemical ring-opening and ring-closing mechanisms. Theoretical calculations, based on DFT and TDDFT, suggested that the spatial distribution and the occupancy of the frontier orbitals determine and control the diarylethenes' ring-opening and ring-closing upon photoirradiation and electrochemical oxidation. Optimized geometries, potential energy surfaces, and activation energies between the open-ring and closed-ring forms were calculated for diarylethenes in the neutral ground state, excited states, and mono- and dicationic states. Analysis of the frontier orbitals was employed to understand the cyclization and cycloreversion of diarylethenes and to predict and explain the switching properties of diarylethene-capped sexithiophene molecular wires. The TDDFT data were verified with experimentally measured UV/vis spectra. The DFT calculations estimated open-shell ground states of diarylethene-capped sexithiophene dications, which were verified with EPR spectroscopy, and the broadening of the peaks in the EPR spectra were explained with the calculated singlet–triplet splitting. The good agreement of experiment and theory allows for the understanding of switching behavior of diarylethenes in solutions, in metal break junctions, in monolayers on metal surfaces, and as a part of complex organic molecular wires.

KEYWORDS: diarylethenes · photoswitching · electrochemical switching · diarylethene-capped sexithiophene wires · frontier orbitals · TDDFT

The application of diarylethenes in such a wide range of areas is as a result of the different electronic properties of two thermally stable isomeric forms: an open-ring structure and a closed-ring structure each of which has a distinct geometry, UV/vis absorption spectrum and redox properties.^{1,14,15} The switching of diarylethenes occurs through a ring cyclization (open to closed form) or ring cycloreversion (closed to open form) reaction. The ring cyclization or cycloreversion involves rearrangement of the π -bonds in the molecules between two distinct π -electron systems with different electronic properties (Scheme 1). The open-ring form is a 1,2-diaryl-substituted ethene whereas the closed-ring form can be viewed as a polyene

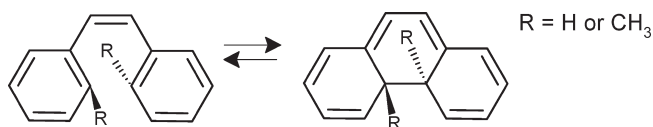
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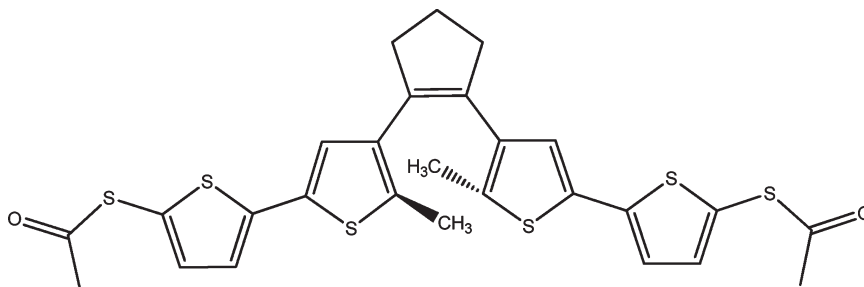
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Scheme 1



Scheme 2



(α,ω -disubstituted *bis-trans*-butadiene in more complex diarylethenes). The π -electron systems of each form are characterized by different electronic properties, *i.e.*, different HOMO–LUMO gaps, different spatial distributions of frontier orbitals, and different electron density distribution.¹⁶ The HOMO–LUMO gaps determine the spectral properties of the molecules and the spatial distribution of the frontier orbitals determines their geometry and electronic properties.¹⁶ A central feature of photochromic systems is the balance between high photostationary states and the quantum efficiency of photochemical switching between the two stable states. In the neutral ground state, the diarylethenes are characterized with a high energy barrier to the isomerization between the open-ring and closed-ring states.¹ In the electronically excited states,^{1,17–20} as well as for the cationic forms of the diarylethenes,^{14,15} the thermal barriers to photochemical and electrochemical isomerizations are much lower or are absent. These features of diarylethenes allow for their use as both photochemical and electrochemical switches.^{3,4,10,14,15} In this way, external perturbations, such as irradiation with light of different wavelengths^{3,4,10} or change of the potential at an electrode^{14,15} allows for switching of molecular properties. Switching between two stable neutral ground-state forms through an excited state or a cationic state makes the diarylethenes versatile units in the control of nanoscale processes.

Diarylethenes were used for photoswitching of electrical conductance through a single molecule³ in mechanically controllable break junction environments.²¹ The single molecule switching marks new limits in electronic devices at the edge of nanometric scale. The experiment was performed on 1,2-bis[5'-(5''-acetylsulfanylthien-2''-yl)-2'-methylthien-3'-yl]cyclopentene, shown in Scheme 2.³ However, it was reported that, as a result of surface molecule interactions, the ring cyclization reaction was quenched and only one-directional

photoswitching of conductance was observed.³ The inhibition of the normal reversibility has been overcome through design modification of the photochemical switch and its replacement with 1,2-bis[5'-phenyl-2'-methylthien-3'-yl]cyclopentene.^{4–6,10} In a different synthetic concept, introduced by Taniguchi *et al.*, long spacers were attached between the diarylethene switch and the electrodes which helped to avoid the loss in reversibility.²² These studies emphasize the importance of a detailed understanding of the photochemical reactions.

Theoretical studies have been performed on several diarylethene systems.^{23–27} Complete active space self-consistent field (CASSCF) calculations were used for smaller molecules^{17,18} while time-dependent density functional theory (TDDFT) was employed for larger molecules and for molecules attached to metal surfaces.^{19,20} TDDFT calculations have been reported recently showing highly accurate results for the UV/vis spectra and geometry of the closed- and open ring forms.²⁸ TDDFT was also used for potential energy surface (PES) scans for the cyclization/cycloreversion photochemical reactions. Those calculations were particularly useful for diarylethene molecules attached to metal surfaces for which quenching of the photoswitching was observed.^{19,20} However, the TDDFT results must be compared carefully with the experimental data and, when it is possible, with CASSCF results, due to the single reference character of the TDDFT wave function. The possibility for two-electron excitations in diarylethene molecules, especially as a result of laser irradiation, was reported in recent experimental studies.²⁹ The mechanism and the quantum yield of the photochemical reaction have attracted significant interest in the field of theory and experiment.³⁰ Recent experimental studies of the excited-state lifetime and the activation barriers on the excited-state potential energy surface

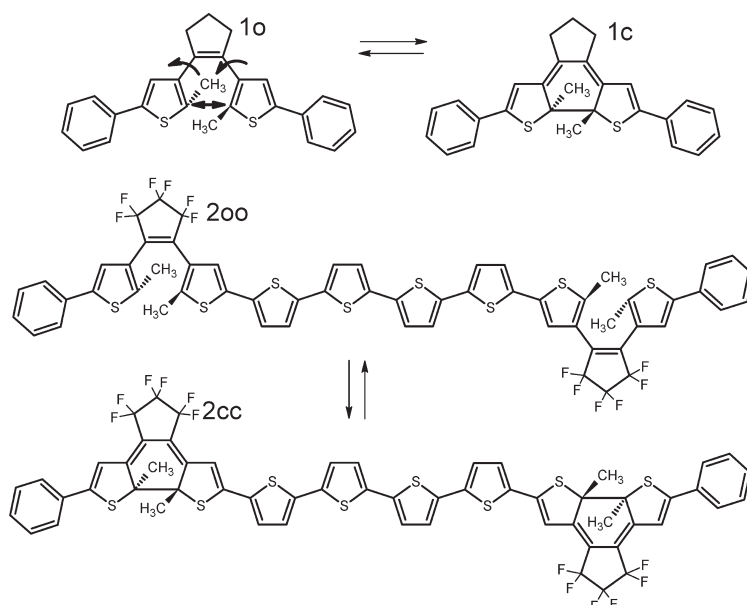


Figure 1. Investigated diarylethenes. 1,2-Bis[5'-phenyl-2'-methylthien-3'-yl]cyclopentene **1o/1c**. Diarylethene-capped sexithiophene wire **2oo/2cc**. The suffix **o** denotes the open-ring forms and with suffix **c** are denoted the closed-ring forms. In **1o**, arrows denote the possible reaction coordinates, the distance between the ring-closing carbon atoms, and the dihedral angles between the cyclopentene and thiophene rings.

have raised several questions as to our understanding of the electronic structure and behavior of this class of photochromic switch.^{29–31} A recent result concerning the occurrence of a thermal barrier to photochemically driven ring-opening and the absence of such a barrier to ring closing have provided considerable empirical evidence on which to progress our theoretical understanding of the photochemical reaction mechanism, the general profile of the excited-state PES, and importantly the correct choice of reaction coordinate.³¹

In addition to photoswitching, the diarylethenes show electrochemical ring cyclization and cycloreversion.^{14,15,32} Electrochemical studies have demonstrated switching between the closed- and open-ring forms for the dication of 1,2-bis[5'-phenyl-2'-methylthien-3'-yl]cyclopentene can occur. Importantly, the direction of the thermal reaction for the dication is dependent on the substituents with electron withdrawing groups favoring ring-opening and electron donating groups favoring ring closing. As the equilibrium favors ring closing for the perhydrocyclopentene derivatives,^{14,15} two-way switching can be achieved electrochemically when immobilized on conducting surfaces.³³ Recently, a theoretical model was proposed explaining the photochemical reversibility of diarylethenes as isolated molecules and when attached to gold surfaces.²⁰ The model was based on the analysis of the spatial distribution of frontier orbitals, PESs of the ground and the excited states, and electron excitation probabilities to those PESs. That theoretical model provided a rationalization that is in agreement with the available experimental data for the

photoswitching of diarylethenes, such as the thermal gating of the photochemical reaction,³¹ irreversible³ and reversible^{4–6} switching on gold electrodes. The electrochemical switching properties of diarylethenes suggest that a similar switching mechanism is in play.

In this contribution, we provide an intuitive explanation of the cyclization and cycloreversion reactions of diarylethenes based on the spatial distribution of frontier orbitals and the orbital overlap along the ring-closing (ring-opening) reaction coordinate. The importance of the orbital concept for the diarylethene photoswitching has been discussed in the literature.^{16,19,20,34,35} Here, we show the similarity in the optical and electrochemical switching and provide an understanding of the reaction driving force which can be useful in the further molecular design of improved nanoswitches. The theory is used to explain the switching properties of diarylethene-capped sexithiophene wires.³⁶ The computational results were verified by UV/vis spectroscopy of the investigated molecules. EPR spectroscopy of the dicationic forms and the obtained theoretical results provide important data on orbital occupancy. The complementarity of the theoretical and experimental results enhanced our understanding of the orbital analysis, electro- and photochemical switching inhibition, and EPR spectral data. The systems investigated here are shown in Figure 1. The photochemical and electrochemical cyclization and cycloreversion of 1,2-bis[5'-phenyl-2'-methylthien-3'-yl]cyclopentene, **1o** and **1c**, were studied with DFT and TDDFT methods. UV/vis measurements were performed for the open-ring and closed-ring forms. The data obtained

were used to verify the computational and experimental results for diarylethene-capped sexithiophene wires, **2oo** and **2cc**. UV/vis measurements were per-

formed for **2oo** and **2cc**, and in addition, EPR measurements were performed for the dications of **2oo** and **2cc**.

COMPUTATIONAL AND EXPERIMENTAL METHODS

The photoswitching properties of diarylethenes have been examined both experimentally and theoretically in a series of papers.^{1–18} In these reports, a wide range of diarylethenes were studied differing primarily in the aromatic substituents at the central ethene group. Although the use of “simplified” diarylethenes as a model compound has advantages in terms of the computational cost of theoretical methods, in reality the ethene moiety normally bears groups such as cyclopentene or perfluorocyclopentene, to preclude *cis–trans* isomerization around the central double bond. It should be noted, however, that the effect of such peripheral groups on the molecular properties is sufficiently large¹⁴ and that simplification reduces considerably the predictive ability of calculations. In the present study, such simplifications are not made for this reason.

DFT calculations were used to investigate the reaction mechanism of the switching of diarylethenes. Relaxed PES scans for the neutral ground state, the monocation, and dication of 1,2-bis[5′-phenyl-2′-methylthien-3′-yl]cyclopentene (**1o**) were performed. The distance between the ring closing carbon atoms was selected as the reaction coordinate. The ring-closing (ring-opening) reaction coordinate is the most important geometrical change in the diarylethene molecules for the ground state, as well as for the excited states, and the variation along it takes into account most of the important features that influence the photochemical and electrochemical reactions. A second important reaction coordinate is the dihedral angle between the thiophene ring and the cyclopentene ring; however, it is not independent of the distance between the ring-closing carbon atoms.²⁰ TDDFT was used to calculate the UV/vis spectra for the open-ring and closed-ring forms of the ground state. In the calculation of the UV/vis spectra the solvent was not included in the computational model. The PESs for the first and higher excited states were calculated with TDDFT for geometries corresponding to the ground state. The geometry of the closed-ring form in the first excited state was relaxed. Geometry optimization, UV/vis spectra, and IR spectral calculations were performed for the ground states, the monocations, and dications of the open–open (**2oo**) and closed–closed (**2cc**) forms of diarylethene-capped sexithiophene nanowires. Because of the large molecular sizes, C_1 symmetry was used during the calculations of those compounds. Triplet and singlet states were considered for the dications. Analysis of the spatial distribution of frontier orbitals was used to explain the energy profile of the PESs. EPR spectral simulations were performed for the dications of the diarylethene-capped sexithiophene nanowires.

The DFT and the fixed geometry TDDFT calculations were performed with the Firefly program package.^{37,38} Geometry optimization of the first excited state was performed with the Gaussian 09 program for which analytic gradients were implemented.³⁹ EPR simulations were performed with the Orca program package.^{40,41} PES scans of the ground states, monocations,

and dications were performed at the DFT B3LYP theory^{42–44} with the 6-31G(d) basis set.⁴⁵ In ref 46, it was reported that hybrid DFT functionals, *e.g.*, B3LYP, tend to overestimate the stability of the high-spin states while pure DFT functionals, *e.g.*, PBE, tend to overestimate the stability of the low-spin states. The TDDFT results with both functionals, B3LYP and PBE, were compared with the measured UV/vis spectra. In addition, calculations were performed with the 6-311G(2d,p) basis set. The TDDFT calculations with the B3LYP functional and the 6-31G(d) basis set were found to reproduce well the UV/vis spectra.^{20,28} We have performed calculations with both functionals, B3LYP and PBE, for structures characterized with near singlet- and triplet-state energies (Table 1). In the PES scans, the geometries were optimized for every step of the surface scan and only the reaction coordinate was kept frozen. The PES of the first and the higher excited states were performed with the TDDFT B3LYP theory. The excited-state scans were done for the same steps as the ground state scan. For the excited-state scans we performed single-point energy calculations for the corresponding optimized geometries of the ground state. The number of the excited states included in the TDDFT calculations is 20.

Calibration of the TDDFT calculations at the B3LYP and PBE levels of theory with the 6-31G(d) and 6-311(2d,p) basis sets were cross-checked with our UV/vis measurements and data from the literature.^{1,36} In the present study, the UV/vis spectra of 1,2-bis[5′-phenyl-2′-methylthien-3′-yl]cyclopentene in its closed-ring and open-ring forms have been calculated. The longest wavelength peak for the open-ring isomer in the measured spectrum is at 280 nm. The experimentally measured spectrum is shown in Figure 2A. The TDDFT calculations with the B3LYP/6-31G(d) theory show the peak at 291 nm, B3LYP/6-311G(2d, p) – 297 nm, PBE/6-31G(d) – 317 nm, and PBE/6-311G(2d,p) – 400 nm. The longest wavelength transition for the closed-ring isomer in the measured spectrum is at 550 nm. The measured spectrum is shown in Figure 2B. The TDDFT calculation with the B3LYP/6-31G(d) theory show the transition at 586 nm, B3LYP/6-311G(2d, p) – 602 nm, PBE/6-31G(d) – 720 nm, and PBE/6-311G(2d,p) – 690 nm. These calculations show that B3LYP/6-31G(d) theory reproduces well the experimental UV/vis spectra for this class of compounds. In Figure 2A and B, the measured spectra are overlaid with the spectra calculated with TDDFT B3LYP/6-31G(d) theory. The difference between the theory and the experiment for the open-ring isomer is 11 nm which corresponds to 0.167 eV photon energy or 3.85 kcal/mol. The difference between theory and experiment for the closed-ring isomer is 36 nm which corresponds to 0.138 eV photon energy or 3.18 kcal/mol.

RESULTS AND DISCUSSION

Diarylethene Switch. In this section the photochemical and electrochemical switching properties of 1,2-bis-

TABLE 1. Computational Methods Used for Geometry Optimizations and Calculations of the Electronic Properties^a

molecule	ground-state	excited-state	monocation	dication
1c	DFT B3LYP/6-31G(d)	TDDFT B3LYP/6-31G(d)	DFT uB3LYP/6-31G(d)	DFT B3LYP/6-31G(d)
1o	DFT B3LYP/6-31G(d)	TDDFT B3LYP/6-31G(d)	DFT uB3LYP/6-31G(d)	DFT B3LYP/6-31G(d)
2cc	DFT B3LYP/6-31G(d)	TDDFT B3LYP/6-31G(d)	n.a.	DFT uB3LYP/6-31G(d)
2oo	DFT B3LYP/6-31G(d)	TDDFT B3LYP/6-31G(d)	n.a.	DFT uB3LYP/6-31G(d)
2oc	DFT B3LYP/6-31G(d)	TDDFT B3LYP/6-31G(d)	n.a.	DFT B3LYP/6-31G(d)

^a uB3LYP denotes the unrestricted wave function B3LYP method.

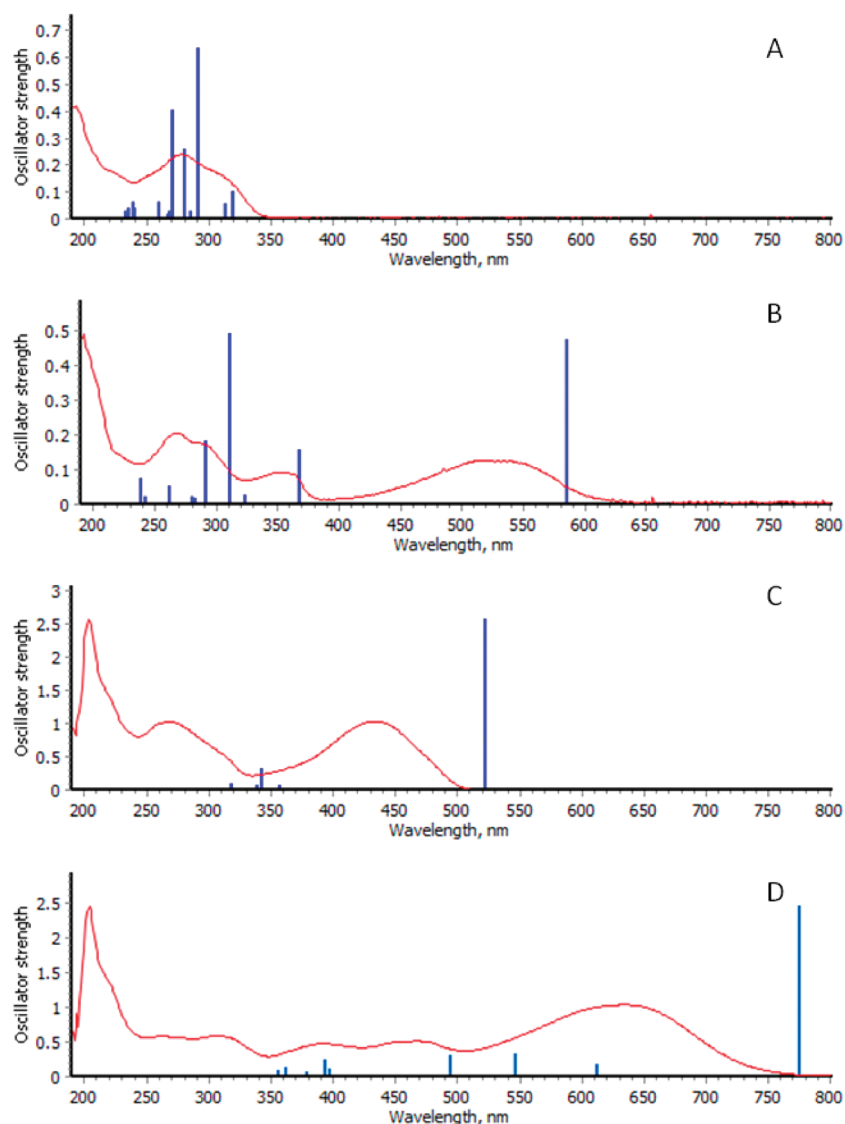


Figure 2. Experimentally measured UV/vis spectra (red lines) overlapped with theoretically calculated TDDFT spectra with B3LYP/6-31G(d) theory. (A) Diarylethene switch in its open-ring form (**1o**); (B) diarylethene switch in its closed-ring form (**1c**); (C) diarylethene-capped sexithiophene wire in its open–open ring form (**2oo**); (D) diarylethene-capped sexithiophene wire in its closed–closed ring form (**2cc**).

[5'-phenyl-2'-methylthien-3'-yl]cyclopentene, **1** (Figure 1) are discussed. This compound shows reversible electro- and photoisomerization in solution and when attached to metal surfaces.^{4–6,14,15,20} For comparison the same calculations are performed on the hexafluoro analogue, 1,2-bis[5'-phenyl-2'-methylthien-3'-yl]phexafluorocyclopentene. The geometries of the open- and the closed-ring forms, **1o** and **1c** respectively, were optimized with the B3LYP and PBE functionals with the 6-31G(d) basis set. The optimized geometries with both functionals were qualitatively similar and the results obtained with the B3LYP theory are used further here. The open-ring form has a localized double bond in the cyclopentene ring and single bonds between the cyclopentene and the thiophene rings. The torsion angles between the cyclopentene and each of the thiophene rings are 47.2°. The benzene rings are

delocalized with bond lengths close to 1.4 Å. The torsion angles between the benzene and thiophene rings are 27.9°. The optimized geometry shows that the open-ring isomer consists of a poorly delocalized π -electron system with separated cyclopentene, thiophene, and benzene subunits. The closed-ring isomer has very different π -electron conjugation. Bond length alternation is observed along the octatetraene fragment (the diarylethene subunit). The torsion angles between the “cyclopentene” and each of the “thiophene” rings are 7.5°. The π -electron system is similar to that of the polyenes. The benzene rings are again delocalized with bond lengths close to 1.4 Å. The torsion angles between the benzene and thiophene rings are 15.5°, which shows that the benzene rings are, to a larger extent than the open form, included in the conjugated π -electron system throughout the

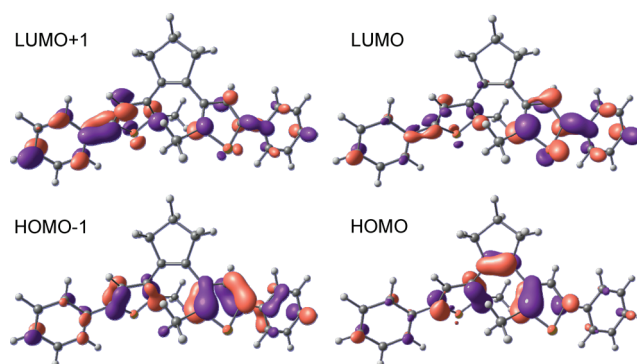


Figure 3. Spatial distribution of the frontier orbitals for the open-ring form (**1o**). The contour value is 0.05.

molecule. The optimized geometry shows that the closed-ring isomer consists of alternating bonds and polyene type π -electron system. The cyclopentene, thiophene, and benzene subunits are separated by smaller torsion angles compared to those in the open-ring isomer, which leads to better π -electron conjugation. The results of the geometry optimizations describe well the experimentally observed differences in the physical properties. The long π -electron conjugation of the closed-ring form determines its visible absorption spectrum while the fragmented π -electron system of the open-ring isomer determines its UV absorption spectrum.

Orbital Control of the Ring-Closing Reaction. Diarylethene **1** shows reversible photochemical switching in solution and in monolayers on metal surfaces, as well as, electrochemical switching as a result of oxidation on electrode surfaces.^{5,6,14,15} In a recent study, we used the spatial distribution of the frontier orbitals and the computed electronic spectra, obtained from TDDFT calculations, to understand the driving force behind the photochemical reaction.²⁰ The analysis has shown that the spatial distribution of certain molecular orbitals leads to minimization of the energy along the ring-closing reaction coordinate. That is achieved as a result of favorable spatial orientation of orbital fragments with the same phase on the ring-closing carbon atoms. When the distance between those ring-closing atoms is reduced, the energy of the molecular orbital is reduced due to the bonding interaction of the orbital fragments. The electron occupation of such orbitals leads to a ring-closing reaction.

The spatial distribution of the HOMO-1, HOMO, LUMO, and LUMO+1 of the open-ring isomer, **1o**, was calculated at the B3LYP/6-31G(d) level of theory. The orbitals are shown in Figure 3. Calculations show that the LUMOs of diarylethenes are characterized with favorable orientation of orbital fragments of the same phase on the ring-closing carbon atoms. Thus, an electron excitation to LUMO, as a result of irradiation with light, leads to ring-closing. The spatial distribution of certain molecular orbitals leads to an increase in the energy along the ring-closing reaction coordinate, due to

unfavorable spatial orientation of orbital fragments of different phase on the ring-closing carbon atoms. When the distance between those ring-closing atoms is reduced, the energy of the molecular orbital is increased, due to the antibonding interaction of the orbital fragments. The occupation of such orbitals inhibits the ring-closing reaction. Calculations show that the HOMOs and (LUMO+1)s of diarylethenes are characterized with unfavorable orientation of orbital fragments with different phase on the ring-closing carbon atoms. This is important for the thermal stability of the neutral ground state where the different phase on the ring-closing carbon atoms of the HOMO precludes spontaneous switching to the closed-ring form. An electronic excitation to LUMO+1, by irradiation with light, blocks the ring-closing. We used this model successfully to understand the irreversible photoswitching of certain diarylethenes when attached to metal surfaces.²⁰ The TDDFT calculations have shown that in the case of irreversible photoswitching the electron excitation to the diarylethene's LUMO+1 is characterized with high oscillator strength which precludes ring-closing.²⁰ The similarity in the electrochemically driven and photochemically driven ring-closing suggests similar orbital control of the reaction. Indeed, the HOMO-1 of **1o** is similar to its LUMO and shows a favorable orientation of orbital fragments with the same phase on the ring-closing carbon atoms. However, spontaneous ring closing is not observed due to the antibonding interaction within the HOMO. The oxidation of **1o** on the electrode surface to the cationic and, especially, to dicationic form will lead to an electronic configuration in which the highest occupied orbital has favorable orientation of orbital fragments with the same phase on the ring-closing carbon atoms, *i.e.*, the HOMO-1 of the neutral form. In contrast, since the dication does not have an occupied orbital characterized with unfavorable orientation of orbital fragments with different phase on the ring-closing carbon atoms, *i.e.*, the HOMO of the neutral form, it will switch to the closed-ring isomer spontaneously.^{14,15}

Orbital Control of the Ring-Opening Reaction. The photochemical ring-opening reactions can be understood

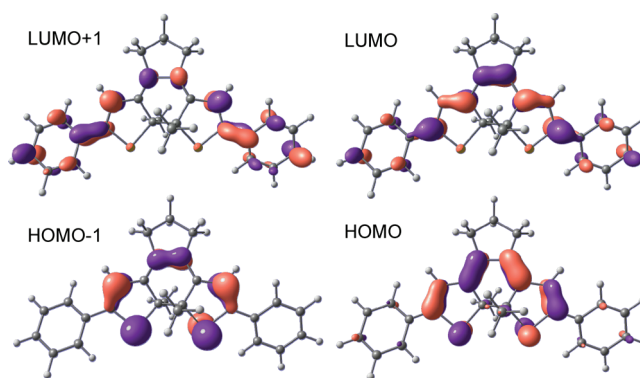


Figure 4. Spatial distribution of the frontier orbitals for the closed-ring form (1c). The contour value is 0.05.

also by inspection of the spatial distribution of the closed-ring isomer frontier orbitals. However, in the case of cycloreversion a second reaction coordinate should be considered. This coordinate is the torsion angle between the cyclopentene and thiophene subunits, shown with arrows in Figure 1, and it is important for the understanding of the cycloreversion mechanism only for geometries close to that of the closed-ring isomer. The torsion angle between the “cyclopentene” and “thiophene” subunits changes from 7.51 to 47.23° upon ring-opening and has a significant influence on the change in the type of π -electron system. Large torsion angles reduce the overlap between the $2p_z$ atomic orbitals on the carbon atoms and in this way lead to localization of the π -bonds and fragmentation of the π -electron system. The spatial distribution of the HOMO-1, HOMO, LUMO, and LUMO+1 of the closed-ring isomer was calculated at the B3LYP/6-31G(d) level of theory. The orbitals are shown in Figure 4.

The orbital phases on the connecting carbon atoms between the “cyclopentene” and “thiophene” rings lead to the same bonding interaction, *i.e.*, HOMO. Those bonding interactions tend to keep the $2p_z$ atomic orbitals on the connecting carbon atoms parallel and minimize the possibility for distortion along the torsion angles. In this way the “cyclopentene” and the “thiophene” rings remain, approximately, in the same plane. This spatial distribution of the HOMO is crucial for the thermal stability of the closed-ring form. The strong bonding interaction between the connecting atoms of the “cyclopentene” and the “thiophene” rings within the HOMO results in a short double bond for the neutral ground state closed-ring isomer. The breaking of that π -bond and a distortion along the torsion angles would involve a high energy activation barrier, which determines the thermal stability of the closed-ring isomer. Different orbital phases on the connecting carbon atoms between the “cyclopentene” and “thiophene” rings lead to antibonding interaction, *i.e.*, LUMO. Those antibonding interactions tend to orient the $2p_z$ atomic orbitals on the connecting carbon atoms perpendicular, to minimize the energy, and in this way they increase the possibility for distortions

along the torsion angles. The spatial deformation in the molecule, which is a result of the increased torsion angles, will increase the distance between the ring-closing carbon atoms and, eventually, will lead to bond breaking and ring-opening. The excitation of an electron from the HOMO to the LUMO should change the molecular geometry resulting in larger torsion angles between the “cyclopentene” and the “thiophene” rings and increased bond length between the ring-closing carbon atoms. We have performed geometry optimization of the first-excited state with the implemented analytic gradient method for TDDFT in the Gaussian 09 program. The B3LYP/6-31G(d) theory was used for this optimization. The analysis of the TDDFT calculations shows that the first-excited state is a result of the HOMO–LUMO excitation. In the optimized excited state structure the torsion angle between the “cyclopentene” and the “thiophene” rings increases from 7.5 to 13.2° and the distance between the connecting atoms of the “cyclopentene” and the “thiophene” rings increases from 1.36 to 1.41 Å. These geometrical changes indicate that the double bond character of the bond between the connecting atoms of the “cyclopentene” and the “thiophene” rings is reduced and the additional flexibility of the molecule can lead to ring-opening. Those changes could be predicted by looking at the spatial distribution of the frontier orbital. The increased torsion angles lead to elongation of the bond between the ring-opening carbon atoms. In the ground state, that bond is 1.55 Å while in the first-excited state it is 1.59 Å. A major difference between LUMO and HOMO-1 is in the orbital amplitude on the carbon atom of the “thiophene” ring, which connects to the “cyclopentene” ring. Within HOMO-1 that amplitude is very small, which will reduce the driving force for electrochemical ring-opening *via* the dication.^{14,15}

Potential Energy Surfaces. The spatial distribution of the frontier orbitals provides important insight for the driving forces of the ring cyclization and cycloreversions. However, the investigation of the PES of the neutral ground state, first-excited state, second excited state, monocationic state, and dicationic state provides additional details for the switching mechanisms. The

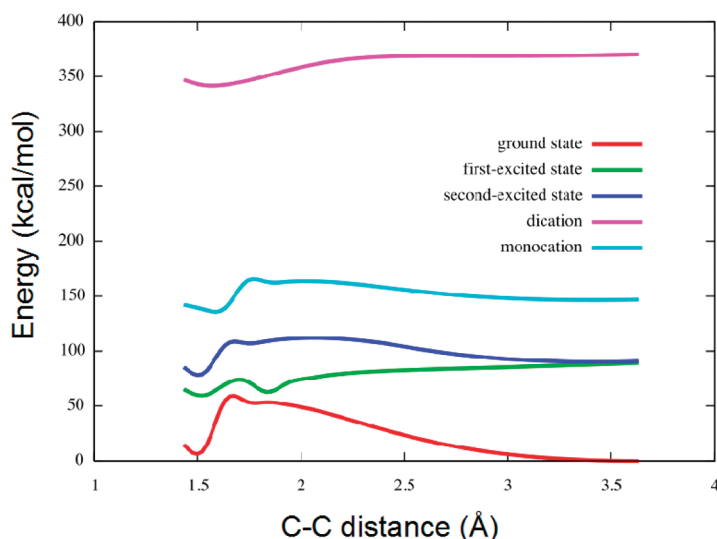


Figure 5. Profiles of the PESs for the ground state, first excited state, second excited state, monocation, and dication, of 1,2-bis[5'-phenyl-2'-methylthien-3'-yl]cyclopentene (1).

PESs are shown in Figure 5. The calculations are performed at the B3LYP/6-31G(d) level of theory. The calculations of the monocationic form were performed with the restricted-open SCF and unrestricted SCF. The calculations of the dication were performed for the closed-shell singlet form, open-shell singlet form, and the triplet form. This was performed to check for possible diradical character; however, the closed-shell singlet form showed the lowest energy. The calculations are consistent with EPR measurements, which do not show signals in the spectra of the dications. The scans for the ground state, monocationic state, and dicationic state are performed with partial optimization. For each step, the distance between the ring-closing carbon atoms, *i.e.*, the reaction coordinate, was kept frozen while all other geometry parameters were relaxed.

The reaction coordinate is varied from 1.43 to 3.63 Å with a step of 0.1 Å. Due to the high computational cost of the excited state optimization, the PES of the first excited state and second excited state are calculated as vertical excitations for the ground state geometries. Calculations of the first excited state PES of diarylethenes were reported in the literature with CASSCF,^{17,27} TDDFT,²⁰ and by changing the occupation of the frontier orbitals by promoting an electron from HOMO to LUMO.⁴⁷ Despite the conceptual differences in the level of theory and degree of approximation, the calculated excited-state PESs are qualitatively similar. Due to the possibility of two-electron excitations, the CASSCF results provide the best description of the PES especially in the region of the conical intersection. A disadvantage of CASSCF calculations is the high-computational cost and the inability to treat diarylethene molecules on metal surfaces. With CASSCF, it would be difficult to propose a unified theory treating the reversible and irreversible switching of diarylethenes on gold surfaces. Thus, we have

employed TDDFT for calculation of the excited-state PESs.²⁰

The neutral ground-state PES has two minima corresponding to the open-ring and closed-ring isomers separated by an activation barrier of 55 kcal/mol for the ring-closing reaction and 45 kcal/mol for the ring-opening reaction. The minimum corresponding to the open-ring form is located at 3.63 Å distance between the ring-closing carbon atoms, *i.e.*, the reaction coordinate. This minimum is wide and the energy slowly rises with a decrease of the reaction coordinate, due to the conformational freedom of small rotations along the thiophene-cyclopentene ring torsion angles. The closed-ring form's minimum is narrow, due to the reduced degrees of freedom. The PES profile can be easily understood by considering the occupancy of frontier orbitals. The energy of the doubly occupied HOMO of the open-ring form rises with a decrease of the distance between the ring-closing carbon atoms because of the antibonding interaction within the orbital. The antibonding interaction determines the high activation barrier of the thermal ring-closing reaction. The bonding interaction within the HOMO of the closed-ring isomer between the connecting atoms of the thiophene ring and cyclopentene ring reduces the possibility for distortions along the torsion angles and determines the high activation barrier of the ring-opening reaction. The neutral ground-state PES profile is important for the thermal stability of the open- and closed-ring isomers. The monocation PES possesses a global minimum for the closed-ring geometry and a second minimum corresponding to the open-ring geometry separated by an activation barrier of 17 kcal/mol for the ring-closing reaction and 25 kcal/mol for the ring-opening reaction. That PES is a result of the competing influences of the SOMO (*i.e.*, HOMO of the neutral form) and HOMO-1. As a result, the energy

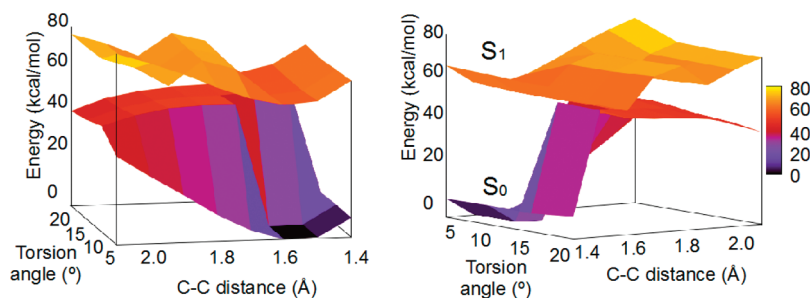


Figure 6. Two reaction coordinates PESs for the ground state, S_0 , and first excited state, S_1 , of 1,2-bis[5'-phenyl-2'-methylthien-3'-yl]cyclopentene (1). The results are plotted for geometries close to the closed-ring isomer ground-state geometry. The plot is shown from two different viewpoints to better illustrate of the conical intersection region.

barrier is significantly reduced. However, the electrochemical switching of the monocation was not achieved experimentally. The dication PES possesses one minimum corresponding to the closed-ring geometry and does not contain a minimum that corresponds to an open-ring geometry. This is a result of the bonding interaction of the ring-closing carbon atoms within the dication HOMO of the open-ring form (*i.e.*, the HOMO-1 of the neutral form). The dication PES suggests spontaneous ring closing which was observed experimentally.^{14,15} Electrochemical ring-opening was reported for the fluorinated dication. Calculations of the PES and examination of the frontier orbitals of the closed-ring form do not suggest that such a reaction is energetically favorable. It should be noted, however, that the present treatment considers only isolated molecular entities. In solution bimolecular collisions and electron transfer reactions can occur. Experimentally, ring-opening is observed due to the presence of the mono/dication, both for **1o** and its perfluorinated analogue.¹⁵ In such cases, however, the driving force for ring-opening is a difference in redox potential between the open and closed forms. This point highlights the limitations of theoretical models in predicting behavior in solution and where bimolecular reactions are possible and shows that caution should be exercised when theoretical predictions do not match experimental observations.

The TDDFT calculations show that the first-excited state is a result of the HOMO to LUMO electronic transition and the second-excited state is a result of the HOMO to LUMO+1 electronic transition. The unrelaxed PESs (vertical excitations for ground state geometries) can be understood by looking at the competitive effects of the HOMO and LUMO or LUMO+1. The bonding interaction within the ring-closing carbon atoms of the LUMO leads to energy minimization with a decrease along the reaction coordinate. A small activation barrier, of 10 kcal/mol, is calculated for the ring-closing reaction. The open-ring energy minimum of the first-excited state is at 1.83 Å along the reaction coordinate, which is significantly shorter than the ground-state energy minimum which is at 3.63 Å. The reasons for that difference are the antibonding interaction of the

ring-closing carbon atoms within the HOMO and the bonding interaction of those atoms within the LUMO. The ring-opening reaction has a lower activation barrier on the first-excited state PES, 13 kcal/mol, than on the ground-state PES. The excited-state ring-opening activation barrier was observed experimentally in the thermal gating of the photoswitching reaction.³¹ Theoretical calculations with TDDFT and CASSCF have indicated that for molecular geometries close to the closed-ring form, a second, branching, reaction coordinate plays an important role for the ring-opening.^{17,20,27,48} This is the torsion angle between the thiophene ring and the cyclopentene ring. The distortion along those torsion angles is a result of the electron occupying the LUMO in the first-excited state. This distortion significantly reduces the activation barrier of the ring-opening.

The PES of the first-excited state shown in Figure 5 indicates that the conical intersection with the ground state PES does not lie on the PESs of the chosen reaction coordinate. In order to locate the position of the conical intersection we have performed a three-dimensional PES scan for the ground state and first-excited state for geometries close to the geometry of the closed-ring isomer. The results are summarized in Figure 6. The reaction coordinates are the distance between the ring-closing carbon atoms and the torsion angle between the “thiophene” ring and the “cyclopentene” ring. The distance varies in the range from 1.4 to 2.0 Å and the angle varies in the range from 5 to 20°. As TDDFT has difficulties to locate the region of conical intersection, for the points close to it we have used the Tamm-Dancoff approximation, TDDFT-DA.⁴⁹ The results shown in Figure 6 confirm the conclusion of the importance of the branching coordinate and the role of the antibonding interaction within the LUMO for ring-opening. The conical intersection is located at larger torsion angles and at a short distance between the ring-closing carbon atoms. These results demonstrate the predictive power of the spatial distribution of frontier orbitals for the understanding of the switching mechanism of diarylethenes.

The PES of the second excited-state is similar to the ground-state PES with a high energy barrier separating the energy minima for the closed and open-ring isomers.

The ring-closing activation energy is 22 kcal/mol and the ring-opening one is 32 kcal/mol. Those barriers are too high for photochemical switching on the second-excited state PES and the two-dimensional PES scan does not suggest a conical intersection close to the geometries on the reaction coordinate. The second-excited state energy surface have contributed ions from the antibonding interactions between the ring-closing carbon atoms within the HOMO and LUMO+1, which suppresses the possibility for ring closing. The bonding interaction between the connecting atoms of the thiophene ring and the cyclopentene ring within the HOMO and LUMO+1 minimizes the possibility for distortion along the torsion angles and reduces the possibility for ring-opening. An excitation to the second-excited state PES would greatly suppress the photoswitching as was demonstrated in the irreversible switching of diarylethenes attached to gold surfaces.^{3,20}

Diarylethene-Capped Sexithiophene Wires. The unique switching properties of diarylethenes make them promising building units in materials science.⁵⁰ Diarylethenes already play an important role as current controlling elements sandwiched between metal surfaces.^{4,10} This application allowed the design of devices where a single, or a few, molecules can switch the electrical current on and off in metal nanowires.^{4,10} That design met significant difficulties in the quenching of the photochemical reaction by the metal surface which was overcome recently by means of experimental design.^{3–5} Theoretical methods employing the understanding of the frontier orbitals were used to rationalize the photochemical reaction in the environment of metal interfaces.^{19,20} A further implementation of diarylethenes is their incorporation in conducting organic polymers.³⁶ That would allow the synthesis of switchable organic wires for the needs of the fast developing field of nanoelectronics. Significant experimental efforts were made in the synthesis of diarylethene-capped sexithiophene wires which combine the conducting oligo-thiophenes with switchable diarylethene subunits.³⁶ The spectral properties of such wires and the photo- and electroswitching reactions were reported in recent studies.²⁸ Theoretical studies reported by Jacquemin *et al.* show excellent agreement between the experimentally measured UV/vis spectra and the computed electronic spectra with TDDFT and CAM-B3LYP theory.²⁸ In that study,²⁸ the geometry optimizations were carried out with the 6-311G (d,p) basis set and the authors have reported an average deviation of 0.5% from the experimentally reported bond lengths. The UV/vis absorption spectra were calculated²⁸ with the 6-311+G(2d,p) basis set. The authors²⁸ used the polarizable continuum model to include the effect of the solvent. The theoretical studies have shown that the orbitals responsible for the photo-switching of diarylethenes can be found among the frontier orbitals of diarylethene-capped sexithiophenes;

however, they are perturbed by the frontier orbitals of the thiophene wires.²⁸ While bidirectional photo-switching was reported for the diarylethene-capped sexithiophene, the electrochemical switching was suppressed in that wire. The dication of the open-ring isomer **2oo**, shown in Figure 1, loses its ability to participate spontaneously in a ring-closing reaction, while the dication of the closed-ring isomer **2cc**, shown in Figure 1, participates in a ring-opening reaction.³⁶ In the first part of this study we have shown that the mechanisms of the photo- and electrochemical switching of diarylethenes can be solely understood by looking at the spatial distribution of frontier orbitals. We have shown that perturbations to those orbitals can lead to changes and hindrance of the switching reactions. It is challenging to employ that concept in the understanding of switching properties of diarylethene-capped sexithiophene wires. We have performed geometry optimization at the B3LYP/6-31G(d) level of theory. Due to the large size of the molecules, C_i symmetry was maintained during the optimization and was used to reduce the number of molecular integrals which had to be solved during the calculation. The geometry parameters are provided in the Supporting Information of this paper and the results were previously reported in the work of Jacquemin and co-workers.²⁸ The spatial distribution of the frontier orbitals of **2oo** and **2cc** are shown in Figure 7. The HOMO and LUMO are significantly affected by the sexithiophene orbitals. However, the LUMO+1 of **2oo** and **2cc** possess spatial distribution close to those of the unperturbed diarylethenes and excitations to these orbitals would lead to photochemical switching. The LUMO of the closed-ring isomer, **2cc**, also shows spatial distribution typical for the ring-opening. We performed TDDFT calculations to simulate the electronic spectra at the B3LYP/6-31G(d) level of theory. The theoretical results were cross-checked against the UV/vis absorption spectra (shown in Figure 2C and D) and the reported spectra calculated with the CAM-B3LYP theory.²⁸ The analysis of the TDDFT excitations shows that the longest wavelength transition for **2cc**, at 775 nm (the experimental peak is at 634 nm), is a result of the HOMO to LUMO excitation. The second allowed transition with nonzero oscillator strength, at 612 nm, is the HOMO-1 to LUMO+1 excitation. These two excitations are in the visible region and are the result of excitations to orbitals with antibonding interactions on the carbon atoms connecting the thiophene- and cyclopentene-rings. Such excitations will favor the distortions along the torsion angles and will eventually lead to ring-opening. The longest wavelength excitation for **2oo** is at 522 nm (the experimental peak is at 435 nm) and corresponds to HOMO to LUMO electron transition. The line in the spectrum corresponds with the absorption spectrum of **2oo**.³⁶ The LUMO of **2oo** is not characterized with the ring-closing spatial distribution.

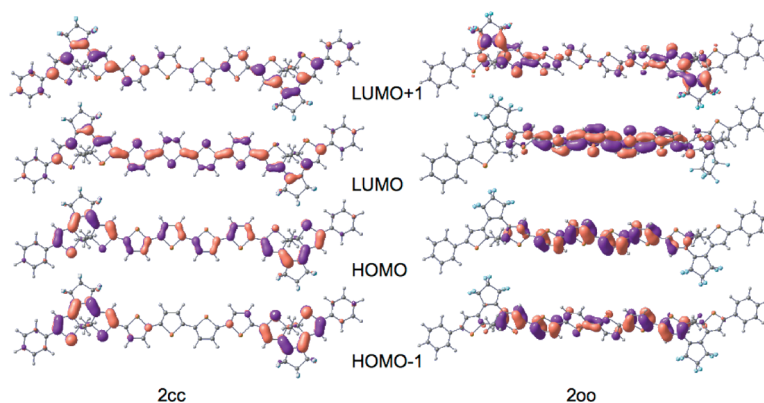


Figure 7. Spatial distribution of the frontier orbitals for the closed-ring and open-ring forms of diarylethene-capped sexithiophene nanowire.

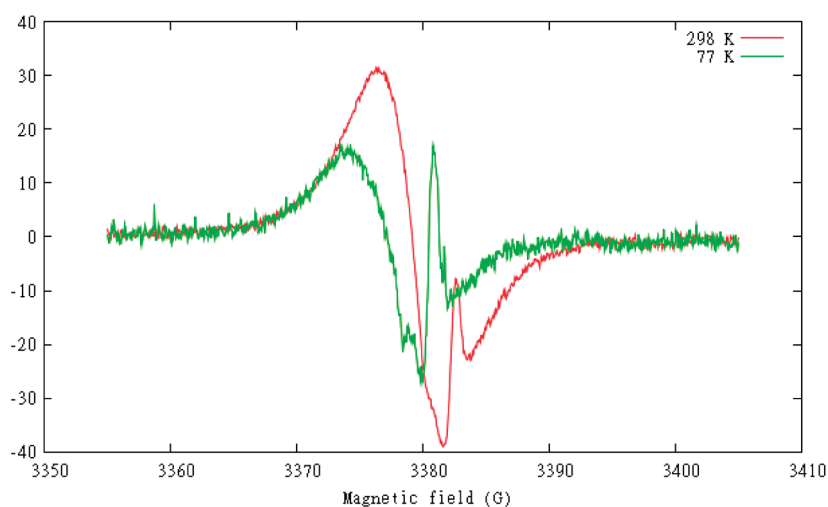


Figure 8. EPR spectra of the closed–closed isomer of diarylethene-capped sexithiophene nanowire ($2cc^{2+}/2oo^{2+}$) at 77 and 298 K.

In order to obtain photochemical ring closing an electronic excitation to the LUMO+1 is required. Such excitation is observed in the UV part of the spectrum at 357 nm, which corresponds to the experimentally observed ring cyclization at 365 nm.³⁶

The experimental study reports that as a result of the attached thiophene wire the electrochemical ring closing is blocked.³⁶ We have shown that the electrochemical ring cyclization of diarylethenes depends solely on the spatial distribution of the HOMO-1. For **2oo**, the HOMO-1 is characterized with antibonding interaction of the ring-closing carbon atoms along the reaction coordinate. Thus, the oxidation will not lead to electrochemical switching. The only part which could not be explained directly with the spatial distributions of the frontier orbitals is the electrochemical ring-opening. The ring-opening of the dication of **2cc** was also observed experimentally.³⁶ Both HOMO and HOMO-1 of **2cc** have the same phases on the atoms which connect the thiophene and cyclopentene rings. Such bonding interaction will minimize the possibilities for distortion along the torsion angles

and will block electrochemical ring-opening. The analysis of the MO energies shows that the HOMO and HOMO-1 are nearly degenerate with a difference of 0.14 eV. Thus, in the process of oxidation it is possible for each of the orbitals to donate an electron instead of only the HOMO donating the two electrons. The resulting dication of **2cc** should be a diradical. We performed calculations for the closed-shell singlet, open-shell singlet, and triplet spin multiplicities of the **2cc** dication. The calculations show nearly degenerate closed-shell and open-shell singlet states and a triplet state which is stabilized by 3.5 kcal/mol. We also performed EPR measurements of the **2cc** dication to verify the obtained computational results and indeed, signals were observed in the EPR spectra. The EPR measurements were performed at 77 and 298 K. The obtained EPR data are shown in Figure 8.

For the open-ring dication, **2oo**²⁺, the results show again that the open-shell state is more stable with 2.1 kcal/mol. However, in the case of the **2oo** dication, the triplet and open-shell singlet states are nearly degenerate with difference of only 0.3 kcal/mol. The obtained

results provide the important information that the dications of **2cc** and **2oo** are diradicals. However, for the **2cc** dication, interaction between the unpaired spins is observed, which stabilizes the high-spin triplet state, whereas for the **2oo** dication, such interaction is not observed and the triplet and open-shell singlet states are nearly degenerate. Organic molecules with a triplet ground state, even when in a dicationic state, are rarely observed and despite the good agreement between the B3LYP energy calculations and the observed EPR spectra the data ought to be analyzed with caution. Indeed, the diarylethene-capped thiophene wire can be considered as two separated diarylethene fragments and each of them donates an electron in the oxidation reaction. These two fragments are linked by the thiophene wire. It is observed that as **2cc**²⁺ converts to **2oo**²⁺ the signal intensity increases, suggesting that the triplet character of the open form is greater than that of the closed form. This is consistent with a singlet ground state of the **2cc** diradical and close lying triplet excited state. With an increase of the temperature from 77 to 298 K, the triplet excited state is more populated and results in the stronger signal. Such small difference between the singlet and triplet state can be difficult to estimate correctly by the theory and will depend strongly on the chosen computational method. For example, while the calculations with the B3LYP functional predict a triplet ground state of the **2cc** dication, the calculations with the PBE functional predict lower energy for the closed-shell singlet ground state. Nevertheless, all calculation results suggest that the triplet and singlet states are close in energy and the observed EPR spectra suggest that at room and liquid nitrogen temperatures the triplet state is populated and can potentially participate in the switching reaction.

Analysis of the EPR sample shows that it is not practical to obtain the **2cc** dication in pure form as ring-opening to form the **2oo** dication occurs within the time scale of the sample oxidation. Thus, in the EPR spectrum two distinct spectra can be seen corresponding to each of the isomers. The broader spectrum corresponds to the **2oo** dication where the unpaired spins do not interact with each other and the system behaves as two monocations while the sharp peak corresponds to the dication of **2cc** where the unpaired spins interact and stabilize the triplet state. The spatial distributions of the lowest unoccupied β -space orbitals of the triplet **2cc** dication (shown in Figure 9), the ones which donated the two electrons, are unfavorable for a ring-opening reaction. The spatial distribution of a highest occupied β -space orbital of the triplet **2cc** dication (shown in Figure 9) is favorable for a ring-opening reaction. These spatial distributions and occupancies of the frontier orbitals can explain the electrochemical ring-opening of the **2cc** dication *via* a triplet state, which is in agreement with the relatively slow rate of ring-opening observed.

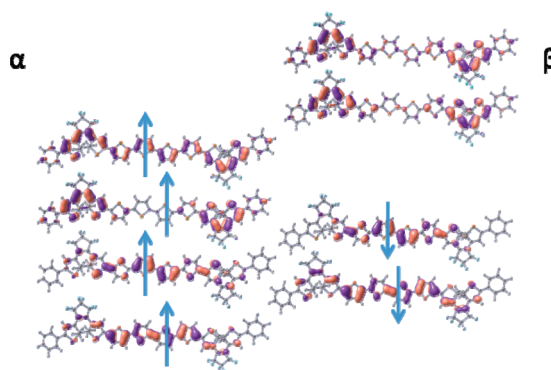


Figure 9. Frontier orbitals of the closed–closed diarylethene-capped sexithiophene isomer (**2cc**²⁺) in dicationic triplet state. The occupied α and β space orbitals are denoted with arrows.

The discussion made above is related to the synchronized reaction mechanism where the both diarylethene units are switching at the same time point. However, another reaction mechanism is possible with a reaction intermediate in which one of the diarylethene units is in its open-ring form and the other, in its closed-ring form.³⁶ The properties of that open-closed isomer can be explained with analysis of the frontier orbitals of its constituent subunits. Closed-ring diarylethenes are characterized with narrower HOMO–LUMO gaps, which result in longer wavelength absorption while open-ring diarylethenes are characterized with wide HOMO–LUMO gaps, which result in light absorption in the UV region of the spectrum. Within the diarylethene-capped thiophene wires, the diarylethene frontier orbitals are preserved although they are partially perturbed by the oligo-thiophene wire frontier orbitals. Thus, the frontier orbitals of the open-closed isomer should be those of the closed ring subunit. We performed geometry optimization of the open-closed isomer at the B3LYP/6-31G(d) level of theory. The obtained frontier orbitals are shown in Figure 10. Both, HOMO and LUMO, are the frontier orbitals of the closed-ring diarylethene subunit with small delocalization over the thiophene wire. The HOMO is characterized with bonding interaction between the cyclopentene and the thiophene rings which will minimize the possibility of thermal distortion and spontaneous ring-opening in the neutral ground state. However, in the dication that orbital will not be occupied which will favor the ring-opening. Thus, the closed–closed diarylethene-capped thiophene wire can undergo oxidative ring-opening through the open-closed isomer, which will result in the open–open dicationic state. The open–open diarylethene-capped thiophene wire cannot convert to the closed–closed wire through oxidation because the frontier orbitals of the open-closed isomer are those of the closed-ring diarylethene and the closed form tends toward ring-opening.

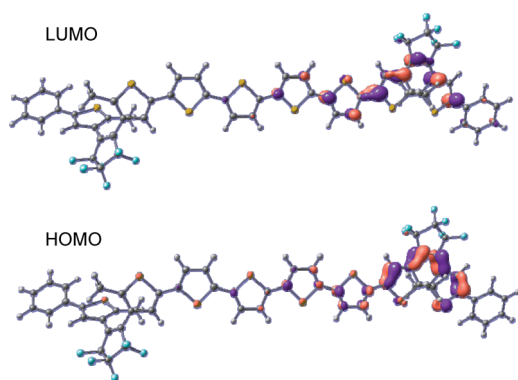


Figure 10. Frontier orbitals of the open-closed diarylethene-capped sexithiophene isomer (**20c**). The contour value is 0.05.

CONCLUSIONS

In this contribution the photochemical and electrochemical switching properties of diarylethenes were investigated to build a unified theory that rationalizes experimental data, and allows prediction of the switching properties of diarylethenes from the spatial distribution of their frontier orbitals. Both, the photochemical and electrochemical ring closing, are the result

of bonding interactions along the reaction coordinate within the LUMO and HOMO-1, respectively. The photochemical and electrochemical ring-opening results from thermal distortions along torsion angles, which are favored by the antibonding interactions within the LUMO and HOMO-1, respectively. Thus, the suitable occupation of these orbitals can lead to the desired ring cyclization and cycloreversion. On the other hand the attachment of the diarylethenes to metal surfaces or complex organic molecules alters either the spatial distribution of the frontier orbitals or the probabilities for electron excitations to the desired excited states and in this way modifies significantly the switching properties. The suggested orbital control rule for control of switching properties can be applied to complex systems such as diarylethenes in mechanically controllable break junction and diarylethenes as a part of organic oligomeric wires. In this study, we performed calculations of PES of ground, cationic, and excited states with DFT and TDDFT. The theoretical studies are calibrated and compared with experimental UV/vis and EPR spectra. We believe that our orbital rule will provide the experimentalists with additional tool for more effective molecular design of nanometric scale devices.

MATERIALS AND METHODS

Compounds **10** and **200** were available from earlier studies.^{14,36} The closed forms were generated in situ by irradiation with a UV lamp (maximum at 365 nm). UV/vis spectra were recorded on a JASCO V-570 UV/vis/NIR spectrophotometer in *n*-hexane solvent. EPR spectra were recorded at room temperature in dichloromethane and in hexane at 77 K and at room temperature in hexane using a Bruker ECS-50 X-band EPR spectrometer. The mono- and dicationic forms of **1c** and **200/2cc**, respectively were generated by addition of ferrocenium(PF₆) or CF₃CO₂H and verified by generation by bulk electrolysis as described elsewhere.¹⁶

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Supporting Information Available: Atomic Cartesian coordinates for the optimized geometries. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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