Theoretical Study of the Electronic and Optical Properties of Photochromic Dithienylethene Derivatives Connected to Small Gold Clusters

Aurélie Perrier,* François Maurel, and Jean Aubard

Université Paris Diderot—Paris 7, ITODYS, UMR CNRS 7086, 1 Rue Guy de la Brosse, 75005 Paris, France

Received: May 5, 2007; In Final Form: July 5, 2007

In the course of developing electronic devices on a molecular scale, dithienylethenes photochromic molecules constitute promising candidates for optoelectronic applications such as memories and switches. There is thus a great interest to understand and control the switching behavior of photochromic compounds deposited on metallic surfaces or nanoparticles. Within the framework of the density functional theory, we studied the effect of small gold clusters (Au_3 and Au_9) on the electronic structure and absorption spectrum of a model dithienylethene molecule. The molecular orbital interactions between the photochromic molecule and the gold cluster made it possible to rationalize some experimental findings (Dulic, D.; van der Molen, S. J.; Kudernac, T.; Jonkman, H. T.; de Jong, J. J. D.; Bowden, T. N.; van Esch, J.; Feringa, B. L.; van Wees, B. J. *Phys. Rev. Lett.* **2003**, *91*, 207402). For the closed-ring isomer, grafting a photochromic molecule on a small gold cluster does not change the characteristics of the electronic transition involved in the ring-opening reaction. On the opposite, the absorption spectrum of the photochromic open-ring isomer is strongly modified by the inclusion of the metallic cluster. In agreement with experimental results, our study thus showed that the cycloreversion reaction which involves the closed-ring isomer should be still possible, whereas the ring-closure reaction which involves the open-ring isomer should be inhibited. Connecting a dithienylethene molecule to a small gold cluster hence provides a qualitative comprehension of the photochromic activities of dithienylethenes connected to a gold surface.

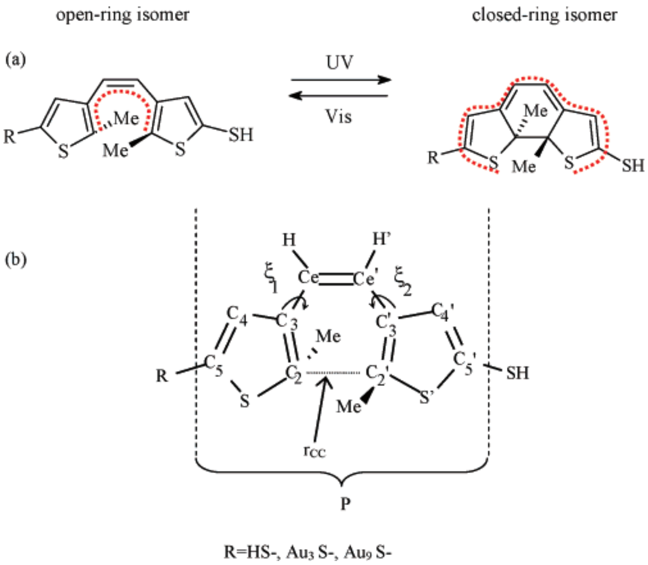
I. Introduction

Dithienylethenes with heterocyclic aryl groups show photochromism, which is defined as the photoreversible transformation between two isomers having different absorption spectra.[1] Dithienylethenes undergo a ring-closure reaction (cyclization) under UV irradiation, whereas a ring-opening reaction (cycloreversion) occurs under visible light irradiation (see Scheme 1). These molecules are fatigue resistant and thermally stable photochromic compounds[2] since both isomers require light for isomerization.

The high thermal- and photostabilities as well as the reversibility make the dithienylethenes promising candidates for optoelectronic applications such as memories and switches.[2,3] Implementation of this type of molecule in an electronic device would both miniaturize it and add the commutation property. It was also demonstrated that these compounds can be used to modulate different properties such as electric currents or surface plasmon resonances of metallic nanoparticles.[4]

In order to use these photochromic compounds within an active electronic device, it is necessary to ensure that their commutation properties are preserved when they are in contact with metallic surfaces. There is thus a great interest to understand and control the switching behavior of photochromic compounds deposited on metallic surfaces or nanoparticles. Photochromic molecular switches made of dithienylethene derivatives self-assembled on gold have been recently studied.[5−8] Both the electronic transport and spectroscopic properties of these molecular devices have been investigated by using break junction experiments and UV−vis spectroscopy. It was demonstrated that the photochromic properties of dithienylethene switches between two gold electrodes can be dramatically affected. Hence, the authors have shown that the cyclization mechanism depends on the nature of the spacer linking the switching molecule to the metal surface.[6,7] For example, in the

SCHEME 1: (a) Open and Closed Forms of the Free Photochome Molecule and (b) Atom Numberings[a,b]



[a] The dashed lines depict the π-electron conjugation path from inspection of the HOMO and LUMO. [b] r_{cc} is the distance between the two reactive carbons, 2 and 2′; ξ_1 and ξ_2 are, respectively, defined as −4−3−e−H and −4′−3′−e′−H′; P corresponds to the photochromic unit.

---

* Corresponding author. E-mail: perrier@itodys.jussieu.fr.

10.1021/jp073436a CCC: $37.00

case of diarylethenes with a phenyl group spacer grafted on Au(111), the optoelectronic properties of the photochromic molecules are preserved. On the opposite, a thienyl linker inhibits the ring-closure process of the photochromic moiety.

Therefore, using dithienylethenes molecules in these different devices requires a fine comprehension of the optical and electronic properties of molecules attached to metallic surfaces. In this work, we are interested in studying the effect of small gold clusters (Au_3 and Au_9) on the electronic structure and absorption spectrum of a model dithienylethene molecule. This photochromic molecule is grafted on the metallic cluster through a thiol group (see Scheme 1, R = SH). The aim of our present study is to obtain a qualitative description of the switching properties of photochromic molecules interacting with small metallic gold clusters. To correctly reproduce the experimental issues, a metal surface should be used instead of a small cluster. Nevertheless, both scanning tunneling microscope measurements[9,10] and theoretical calculations[11] have shown that the contact between the metal and the molecule corresponds to a single localized Au−S bond. Our work should thus provide a good modeling of the contact between the metal and the molecule and then lead to a satisfying understanding of the influence of the metals on the electronic properties of the molecule.

The paper is organized as follows. In section II, we present the computational details. Results concerning the reference molecule are given in section III. The modification of the electronic and optical properties induced by Au_3 and Au_9 clusters on both closed-ring and open-ring isomers is also discussed in section III. We conclude in section IV.

II. Computational Details

All the calculations described in this work were carried out with the Gaussian 03[12] software package. Geometry optimizations have been performed under density functional theory (DFT) using the hybrid B3LYP exchange-correlation functional.[13,14] 6-31 G basis set was used for H, C, and S atoms. The B3LYP/6-31G level has previously been used by Goldberg et al.[15] to determine the geometrical parameters of a series of diarylethenes. Calculated results were found to be in good agreement with X-ray data. In particular, the most important geometrical parameter, the reaction distance (r_{cc}, see Scheme 1), is nicely reproduced by calculations at this level of theory (1% error between experimental and calculated values). The relativistic Los Alamos National Laboratory effective core potential (ECP) with a double-ζ valence (LANL2DZ) was used for Au atoms.[16] This ECP treats explicitly the 5s, 5p, 5d, and 6s electrons of Au.

The absorption spectra of free and metal−molecule systems were calculated by using time-dependent density functional theory (TD−DFT) calculations with the same level of calculations. TD−DFT was shown to be an efficient method to evaluate spectroscopic properties of large conjugated molecules[6,17−21] such as organic dyes[21] or dithienylethenes.[22−29] In the case of dithienylethenes,[24] the calculated absorption maximum of a series of closed-ring isomers was found to be in good agreement with experimental values (2% of average error between experimental and theoretical values). Although a more extended basis set is needed to achieve high accuracy in excitation energies,[29] it was shown that the 6-31 G basis set provides a reasonable compromise between computational time and accuracy of the results.[30] Moreover, the aim of the present study is to provide a qualitative, rather than quantitative, understanding of the optical properties of the "gold cluster−photochrome" system.

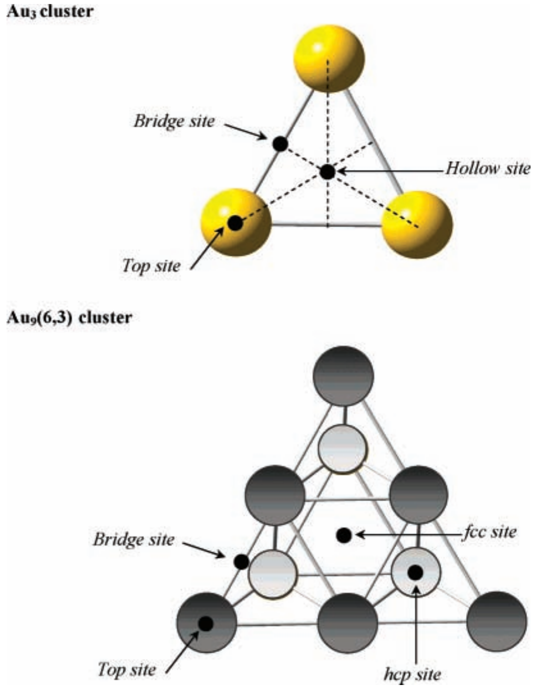


Figure 1. Representation of the Au_3 and Au_9 cluster models. The different adsorption sites are represented: top, bridge, hollow, "fcc" (face-centered cubic), and "hcp" (hexagonal closed packet). For the Au_9 cluster, the six dark atoms are on the first layer, the three other atoms are on the second layer.

We will now detail how the geometry and electronic properties of gold−dithienylethene systems have been obtained. Hereafter, the photochromic part of the molecule will be referred as P (see Scheme 1). The free photochrome molecule will thus correspond to the acronym "HS−P−SH" and the "cluster−molecule" systems will be denoted as "Au_nS−P−SH" ($n = 3$, 9).

The considered free photochrome presents a terminal thiol group to favor the adsorption of the molecule on the metallic cluster. On the basis of experimental issues on self-assembled monolayers, it is generally accepted that hydrogen atoms are generally dissociated upon adsorption to surfaces.[31−33] The adsorption reaction can proceed either by a ionic dissociation of the thiol or by a "homolytic" reaction leading to radical formation:[34]

$$\mathrm{RSH} + \mathrm{Au} \rightarrow \mathrm{RSAu}^- + \mathrm{H}^+ \qquad (1)$$

$$\mathrm{RSH} + \mathrm{Au} \rightarrow \mathrm{RSAu} + \mathrm{H}^\bullet \qquad (2)$$

where R is an organic group. On the basis of available electrochemical evidence as well as conductometric data, reaction 2 is favored significantly over reaction 1 for self-assembled monolayers.[34] We assume that reaction 2 should also be favored for thiol-terminated photochromes, and we thus only consider the formation of neutral Au_3 and Au_9 dithienylethene clusters. One must notice that, in order to study closed-shell "gold cluster−molecule" systems, we have only considered clusters with an odd number of Au atoms.

For Au_3 clusters, we have considered three different adsorption sites, "top", "bridge", and "hollow", which are represented in Figure 1. The Au_3 initial geometry parameters have been chosen to represent the Au(111) surface: the Au(111) surface is constructed using the bulk lattice constant of 4.078 Å[35] which leads to a Au−Au bond distance of 2.885 Å.

For each adsorption site (top, bridge, and hollow), full geometry optimization of the system has been performed

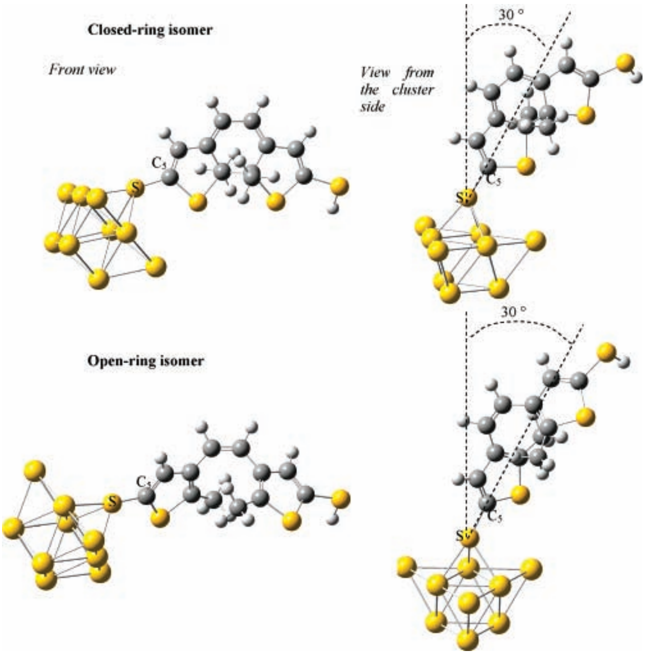


Figure 2. Au$_9$S−P−SH closed-ring and open-ring isomers.

according to the following procedure: (i) we first optimize the Au$_3$SH molecule with symmetry constraints (top site, C_{2v} symmetry; bridge, C_{2v} symmetry; hollow, C_{3v} symmetry), (ii) we remove the symmetry constraints and the geometry of Au$_3$SH system is reoptimized, (iii) we replace the hydrogen atom of the Au$_3$SH system with the photochromic unit "P−SH", and the geometry optimization is performed with constraints (the geometry of the Au$_3$S subunit is fixed), and (iv) all the constraints are removed.

For computation time reasons, we could not perform a geometry optimization of the Au$_9$S−P−SH system. We considered a Au$_9$ (6, 3) cluster model (i.e., six atoms in the first layer and three atoms in the second layer as depicted in Figure 1) to represent the Au(111) surface. As in the Au$_3$ initial geometry, the Au(111) surface is constructed using the bulk lattice constant which leads to a Au−Au bond distance of 2.885 Å. For the Au$_9$ system, there are four sites of adsorption represented in Figure 1: the top site, the bridge site, and two threefold hollow sites which correspond to the "fcc" site (face-centered cubic) and the "hcp" site (hexagonal closed packet). The "hcp" site lies above a subsurface atom, whereas the "fcc" site does not. DFT calculations have previously shown that the hollow fcc site is the energetically preferred site.[36] The distance between the surface and the linking S atom was chosen as 2.04 Å[37] which corresponds to a Au−S distance equals to 2.66 Å. We then assume that the photochromic molecule is tilted 30° as this is the case in alkane self-assembled monolayer.[38] This angle corresponds to the angle between the normal to the gold surface and the S−C$_5$ bond (Figure 2 and Scheme 1). The geometry of both open-ring and closed-ring molecules corresponds to the optimized geometry of the molecule within the Au$_3$S−P−SH system.

III. Results and Discussion

III.1. Geometry, Electronic Structure, and Absorption Spectrum of the Free Molecule. The key geometrical parameters are summarized in Table 1, where r_{cc} is the reaction distance between the two reactive carbons and ξ_1 and ξ_2 are the dihedral angles depicted in Scheme 1. The overall optimized structures of both the open-ring and closed-ring isomers are depicted in the Supporting Information.

TABLE 1: Closed-Ring and Open-Ring Isomers: Calculated HOMO and LUMO Levels, HLGs (HOMO and LUMO Gaps), Bond Lengths and Angles for the Free Molecule (HS−P−SH) and for Molecules Connected with a Au$_n$ Cluster (n = 3, 9)[a]

	compound	HOMO (eV)	LUMO (eV)	HLG (eV)	d_{S-Au} (Å)	r_{cc} (Å)	∠C5−S−H or ∠C5−S−Au
closed-ring isomer	HS−P−SH	−5.04	−2.02	3.02		1.539	96.8
	Au$_3$S−P−SH (top)	−4.88	−4.08	0.80	2.406	1.539	104.4
	Au$_3$S−P−SH (bridge)	−5.06	−3.69	1.37	2.631	1.540	104.5
	Au$_3$S−P−SH (hollow)	−4.94	−3.71	1.23	2.861	1.540	144.0
open-ring isomer	HS−P−SH	−5.95	−1.24	4.71		3.626	97.9
	Au$_3$S−P−SH (top)	−5.52	−4.34	1.18	2.394	3.613	104.2
	Au$_3$S−P−SH (bridge)	−5.76	−3.74	2.01	2.631	3.615	110.2
	Au$_3$S−P−SH (hollow)	−5.62	−3.80	1.82	2.861	3.614	145.8

[a] The letter P in the molecule names corresponds to the photochrome central unit (see Scheme 1).

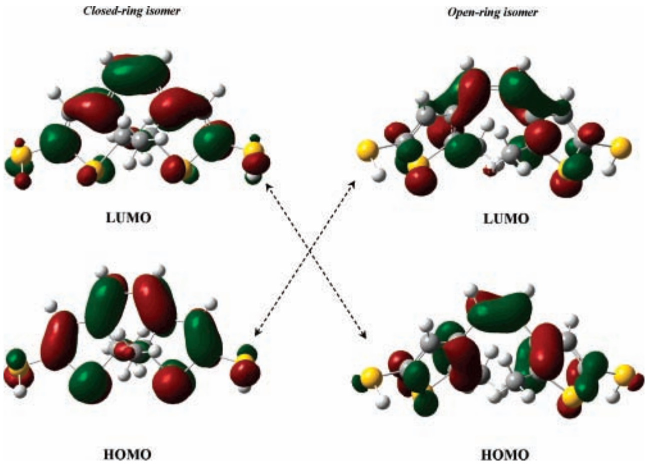


Figure 3. HOMO and LUMO orbitals of the free photochrome molecule (isodensity = 0.04 au).

The size and signs of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of both open-ring and closed-ring isomers are illustrated in Figure 3. The frontier HOMO and LUMO are distributed along the π-conjugation chains shown in Scheme 1. In the open-ring isomer, the π-path has severe distortion along the hexatriene center (between the 2 and 2′ positions) due to the nonplanar geometry. The frontier orbitals are mainly delocalized between the 2 and 2′ positions. In the closed-ring isomer, the frontier orbitals are more extended and coplanar along the polyene chain shown in Scheme 1: the HOMO and LUMO are delocalized between the 5 and 5′ positions.

The HOMO of the open-ring isomer and the LUMO of the closed-ring form present a bonding character between the C_e and $C_{e'}$ atoms. On the opposite, the LUMO of the open-ring form and the HOMO of the closed-ring isomer are bonding between C_3−C_e and $C_{3'}$−$C_{e'}$ positions. Therefore, one can notice that the HOMO (respectively, the LUMO) of the open-ring isomer correlates with the LUMO (respectively, the HOMO) of the closed-ring isomer. According to Woodward−Hoffmann rules,[39] the ground state cyclization and cycloreversion are forbidden. From now on, the designation "photochromic orbitals" will correspond to the orbitals involved in the cyclization/

TABLE 2: Relative Energies (in kcal·mol^{-1}) of the Closed-Ring (CF) and Open-Ring (OF) Isomers for the Free Photochrome Molecule and the "Au$_3$−Molecule" System

	E(CF)	E(OF)	E(CF) − E(OF)
HS−P−SH[a]	0.0	−4.0	4.0
Au$_3$S−P−SH (top)[b]	0.0	1.5	−1.5
Au$_3$S−P−SH (bridge)[b]	9.9	9.0	0.9
Au$_3$S−P−SH (hollow)[b]	31.0	30.1	0.9

[a] Reference: closed-ring isomer. [b] Reference: closed-ring top isomer.

TABLE 3: Closed-Ring and Open-Ring Isomers: Transition Corresponding to the Electronic Excitation within the Photochrome Unit, Corresponding Wavelength, and Oscillator Strength

	compound	λmax (nm)	description	oscillator strength
closed-ring isomer	HS−P−SH	462	HOMO → LUMO	0.259
	Au$_3$−P−SH (top)	492	HOMO → LUMO + 2	0.237
	Au$_9$−P−SH (hollow)	491	HOMO → LUMO + 5	0.366
open-ring isomer	HS−P−SH	292	HOMO → LUMO	0.112
	Au$_3$−P−SH (top)	319	HOMO → LUMO + 3	0.027
	Au$_9$−P−SH (hollow)	332	HOMO → LUMO + 6	0.002

cycloreversion reactions, that is to say, to the orbitals delocalized over the hexatriene system.

The excitation energies of both open-ring and closed-ring isomers are given in Table 3. For both the open-ring and the closed-ring isomers, the TD−DFT absorption spectrum shows that the transition with the highest oscillator strength corresponds to the HOMO → LUMO ($\pi \rightarrow \pi^*$) single excitation, that is to say, to the excitation from the 1A to 1B state under C_2 symmetry. This is in agreement with previous CASSCF calculations[15,40,41] which have shown that this electronic excitation is the first step of both the cyclization and cycloreversion reactions.

III.2. Effect of a Small Cluster on the Photochrome Optical Properties: Au$_3$−Dithienylethene System. Geometrical and energetic parameters of the Au$_3$S−P−SH systems (top, bridge, and hollow) are summarized in Tables 1 and 2. The results show that the hollow position is unstable and that the top position is energetically more stable than the bridge position by 9.9 kcal·mol^{-1} for the closed-ring isomer and 7.5 kcal·mol^{-1} for the open-ring isomer (Table 2). Therefore, in the following, we will focus on the results obtained for the Au$_3$S−P−SH top system. One can also notice that the interaction with the metallic cluster decreases the energy difference between the closed-ring and open-ring isomers compared to the free photochrome (Table 2). For the top position, the closed-ring isomer becomes more stable than its open-ring counterpart, suggesting that the molecule−cluster interaction is stronger in this position.

III.2.1. Closed-Ring Isomer. III.2.1.1. Geometrical Parameters. The main characteristics of the optimized structure of Au$_3$S−P−SH closed-ring isomer are given in Table 1 (see also the Supporting Information). The Au−S−C angle is 104.4° as compared to 96.8° for the H−S−C angle in the free photochrome, and the distance between Au and S atoms is 2.406 Å. Linking the photochrome molecules to the Au$_3$ cluster leads to a decrease of the bond length between the terminal sulfur and the nearest carbon C_5 in the thiophene ring (1.819 to 1.788 Å). At the same time, there is an increase of both the C_5−C_4 bond (+0.016 Å) and the C_3−C_e bond (+0.010 Å), while the C_4−C_3 and C_e−$C_{e'}$ bonds decrease (respectively, −0.015 and −0.010 Å). The other bond lengths in the thiophene ring close to the Au atom (S−C_2, C_2−C_3, C_5−S) are slightly modified, while the value of the reaction coordinate r_{cc} does not change.

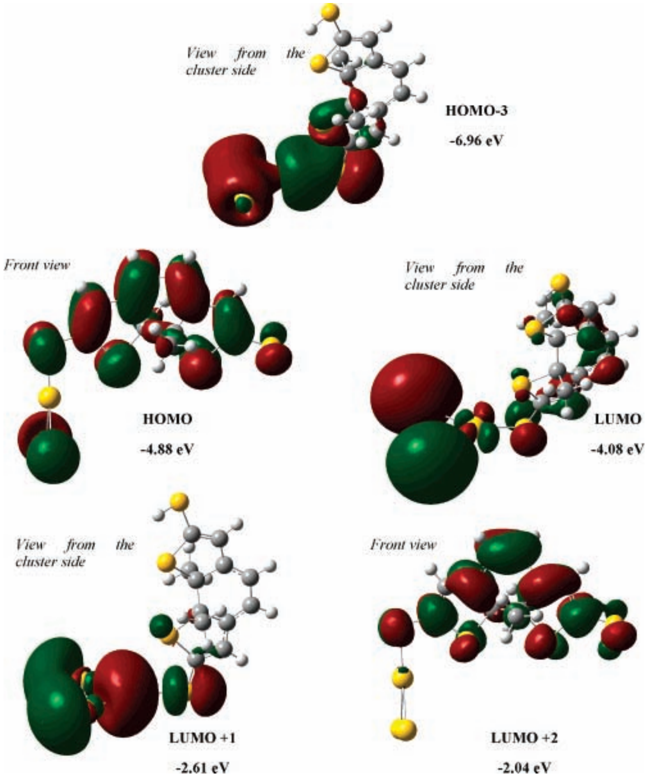


Figure 4. Reference photochromic molecule connected to a Au$_3$ cluster (top position). Closed-ring isomer: representation of some characteristic orbitals (isodensity = 0.02 au).

III.2.1.2. Molecular Orbitals. The HOMO of the Au$_3$−photochrome unit corresponds to the HOMO of the free photochrome with some minor contributions of the Au$_3$ 6s orbitals (Figure 4). These contributions lead to a destabilization of the HOMO orbital compared to the free molecule (Table 1).

The LUMO and LUMO + 1 orbitals are mainly of Au$_3$ character (Figure 4): the LUMO corresponds to an antibonding interaction between the 6s orbitals of the two Au atoms not linked to the sulfur atom, whereas the LUMO + 1 orbital presents an antibonding interaction between the 5d Au orbitals. These two cluster antibonding orbitals are inserted between the HOMO and LUMO of the free photochrome molecule. This thus leads to a strong decrease of HOMO−LUMO energy gap (HLG) of the Au$_3$−photochrome unit compared to the free molecule (Table 1).

The LUMO + 2 orbital corresponds to the first unoccupied orbital of the free molecule. The energy level of the LUMO + 2 orbital is −2.04 eV for the closed-ring isomer as compared to −2.02 eV for the LUMO of the free molecule. Therefore, grafting the photochrome molecule to a Au$_3$ cluster neither changes the shape nor the energetics of the LUMO located on the organic moiety, i.e., of the LUMO of the "photochromic" system.

III.2.1.3. Absorption Spectrum. To get an absorption spectrum covering the IR and UV regions, we had to calculate 25 states. Information concerning the most intense transitions is given in Table 4. The transition corresponding to the electronic excitation within the photochrome unit corresponds to the HOMO → LUMO + 2 transition. Hereafter, this electronic excitation will

TABLE 4: Au3−P−SH Closed-Ring and Open-Ring Isomers Absorption Spectra: Calculated Wavelength, Oscillator Strength, and Major Contributions (Only the Most Intense Transitions Are Given)

	wavelength (nm)	oscillator strength	description
closed-ring isomer	1426	0.199	HOMO → LUMO
	492	0.237	HOMO → LUMO + 2
	324	0.248	HOMO − 3 → LUMO + 1, HOMO − 2 → LUMO + 2
open-ring isomer	1276	0.080	HOMO → LUMO
	582	0.073	HOMO → LUMO + 1
	353	0.126	HOMO − 3 → LUMO + 1, HOMO → LUMO + 2
	319	0.027	HOMO → LUMO + 3
	309	0.113	HOMO − 6 → LUMO + 1

be denoted as the “photochromic” transition. In comparison to the photochromic transition of the gas-phase photochrome, Table 3 still shows a large oscillator strength and a 30 nm red-shift due to the introduction of the Au_3 cluster.

The absorption spectrum (Table 4) is also dominated by a transition lying in the infrared domain which corresponds to a HOMO → LUMO electronic excitation. An inspection of the frontier orbitals shows that this transition corresponds to a charge transfer from the photochromic unit to the metallic cluster. The 324 nm transition is also particularly intense: it arises from the HOMO − 3 → LUMO + 1 transition, that is to say, from a Au_3 localized excitation.

Thus, the strongest allowed photochromic localized transition of the closed-ring free photochrome is not strongly modified by the inclusion of the Au_3 cluster. The corresponding excitation wavelength shows a 30 nm bathochromic shift compared with the free molecule (Table 3), indicating the perturbation of the electronic structure of the closed-ring isomer due to the Au_3 cluster. As a matter of fact, the destabilization of the HOMO orbital leads to a decrease of the gap between the photochromic last occupied and first unoccupied orbitals (respectively, the HOMO and LUMO + 2). Since there is a strong correlation between the energy gap of the photochromic frontier orbitals and the maximum absorption wavelength,[30] the strongest allowed photochromic localized transition shifts to larger wavelength. Although the molecule under investigation is a model system, one can notice that this bathochromic shift is also observed experimentally in the case of diarylethenes with a phenyl group spacer grafted on Au(111).[8] Besides, when the complete absorption spectrum is examined, an infrared absorption band corresponding to a charge transfer from the photochromic unit to the Au_3 cluster (e.g., a ligand metal charge-transfer band) and a UV absorption band corresponding to a transition localized on the metallic cluster appear.

III.2.2. Open-Ring Isomer. III.2.2.1. Geometrical Parameters. The optimized geometry of the photochrome open-ring isomer bonded to a Au_3 cluster is given in Table 1 (see also the Supporting Information). The Au−S−C angle is 104.2° as compared to 97.9° for the H−S−C angle in the free photochrome, and the distance between Au and S atoms is 2.394 Å. Linking the photochrome molecules to the Au_3 cluster leads to a decrease of the bond length between the terminal sulfur and the nearest carbon C_5 in the thiophene ring (1.807 to 1.792 Å). Unlike the closed-ring isomer, the geometry of the thiophene ring close to the Au atom is not modified. Besides, in comparison to the free molecule, the reaction coordinate r_{cc} does not change (Table 1) and there is a small decrease of the value of the dihedral angles ξ. Then, the metallic cluster does not influence the geometry of the open-ring isomer.

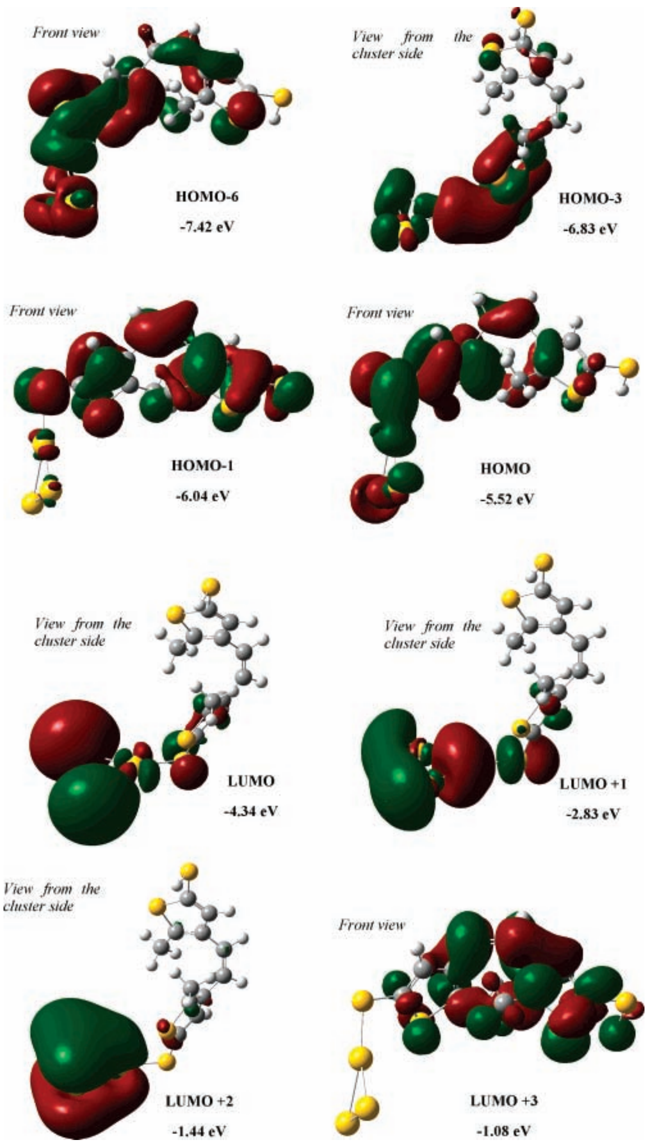


Figure 5. Reference photochromic molecule connected to a Au_3 cluster (top position). Open-ring isomer: representation of some characteristic orbitals (isodensity = 0.02 au).

III.2.2.2. Molecular Orbitals. The HOMO (Figure 5) presents a significant contribution on the Au_3 cluster, on the linking sulfur atom, and on the thiophene ring close to the metallic cluster. The contribution on the thiophene ring opposite to the Au_3 cluster is much smaller. Therefore, the HOMO orbital is modified as compared to the last occupied orbital of the free photochrome (Figure 3). Since the antibonding character of the HOMO orbital increases due to the antibonding interaction between the linking S atom and the thiophene ring, the energy of this orbital increases (Table 1).

The LUMO and LUMO + 1 orbitals of the cluster−molecule system correspond to cluster antibonding orbitals. The LUMO + 2 orbital arises from a π-bonding interaction between the three Au atoms and is then an unoccupied cluster bonding orbital.

The LUMO + 3 orbital is equivalent to the LUMO of the free photochrome and thus corresponds to the first unoccupied photochromic orbital. The energy level of the LUMO + 3 orbital is −1.08 eV compared to −1.24 eV for the LUMO of the free molecule. Therefore, grafting the photochrome molecule to a

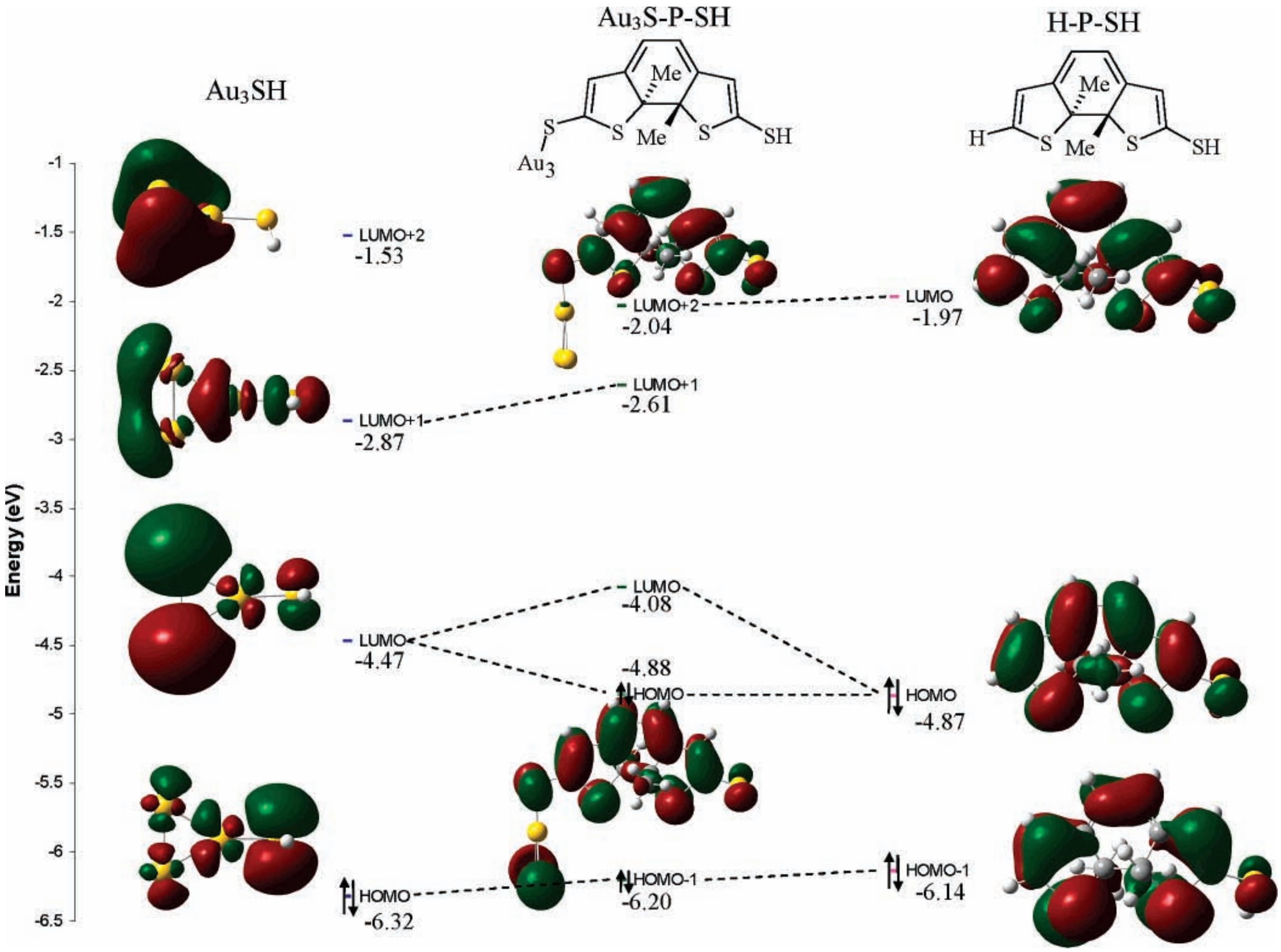


Figure 6. Molecular electronic orbitals diagram of Au_3SH and of the closed-ring forms of $Au_3S-P-SH$ and $H-P-SH$ (energies are in eV).

Au_3 cluster leads to a destabilization of the LUMO of the free photochrome molecule.

III.2.2.3. Absorption Spectrum. The most intense transitions of the absorption spectrum are given in Table 4. One can notice that the absorption spectrum of the free photochrome is strongly modified by the inclusion of the Au_3 cluster. This spectrum is dominated by two transitions corresponding to charge transfer from the photochrome unit to the Au_3 cluster. These transitions correspond to electronic excitations from the following:

(i) The HOMO to the LUMO (1276 nm). Since the HOMO orbital is partly delocalized over the Au_3 cluster, this transition has a nonnegligible oscillator strength.

(ii) The HOMO to the LUMO + 1 (582 nm).

The absorption spectrum is also dominated by two bands corresponding to charge transfer from the thiophene rings to the Au_3 cluster. The corresponding electronic excitations are as follows:

(i) A combination between the HOMO → LUMO + 2 and the HOMO − 3 → LUMO + 1 excitations (353 nm). The HOMO − 3 orbital is delocalized on the Au_3 cluster and on the thiophene ring close to the metallic cluster (Figure 5).

(ii) HOMO − 6 → LUMO + 1 (309 nm) where the HOMO − 6 orbital is delocalized on the Au_3 cluster and on the thiophene ring close to the metallic cluster.

An inspection of the molecular orbitals in Figure 5 shows that these four transitions correspond to a charge transfer from the photochromic unit of the molecule to the metallic cluster. The transition involved in the cyclization reaction corresponds to the HOMO → LUMO + 3 electronic excitation. Since the HOMO and LUMO + 3 orbitals are not localized on the same part of the molecule, the oscillator strength is weak. Besides, the destabilization of the HOMO orbital leads to a bathochromic effect: the wavelength of the photochromic transition is 319 nm, whereas the maximum absorption band of the free molecule is 292 nm (Table 3).

Thus, the inclusion of the Au_3 cluster strongly modifies the absorption spectrum of the free photochrome. The HOMO orbital is delocalized over the metallic cluster, and there is a destabilization of both the last occupied and first unoccupied photochromic orbitals (respectively, the HOMO and LUMO + 3 orbitals for the open-ring $Au_3S-P-SH$ system). The destabilization of the HOMO being the major effect, the photochromic HOMO−LUMO gap decreases and the photochromic transition is red-shifted (+27 nm). At the same time, the value of the oscillator strength decreases. This transition is surrounded by 10 electronic excitations in the 300−340 nm region presenting strong oscillator strength and corresponding to charge transfer from the photochromic unit (or from the thiophene unit) to the metallic cluster. Other mechanisms proceeding through these electronic excitations may thus occur, and the cyclization reaction, which involves an electronic excitation from the last occupied to the first unoccupied photochromic orbitals, may be strongly affected by these competitive pathways. Since the photochromic reactivity of the open-ring isomer also depends

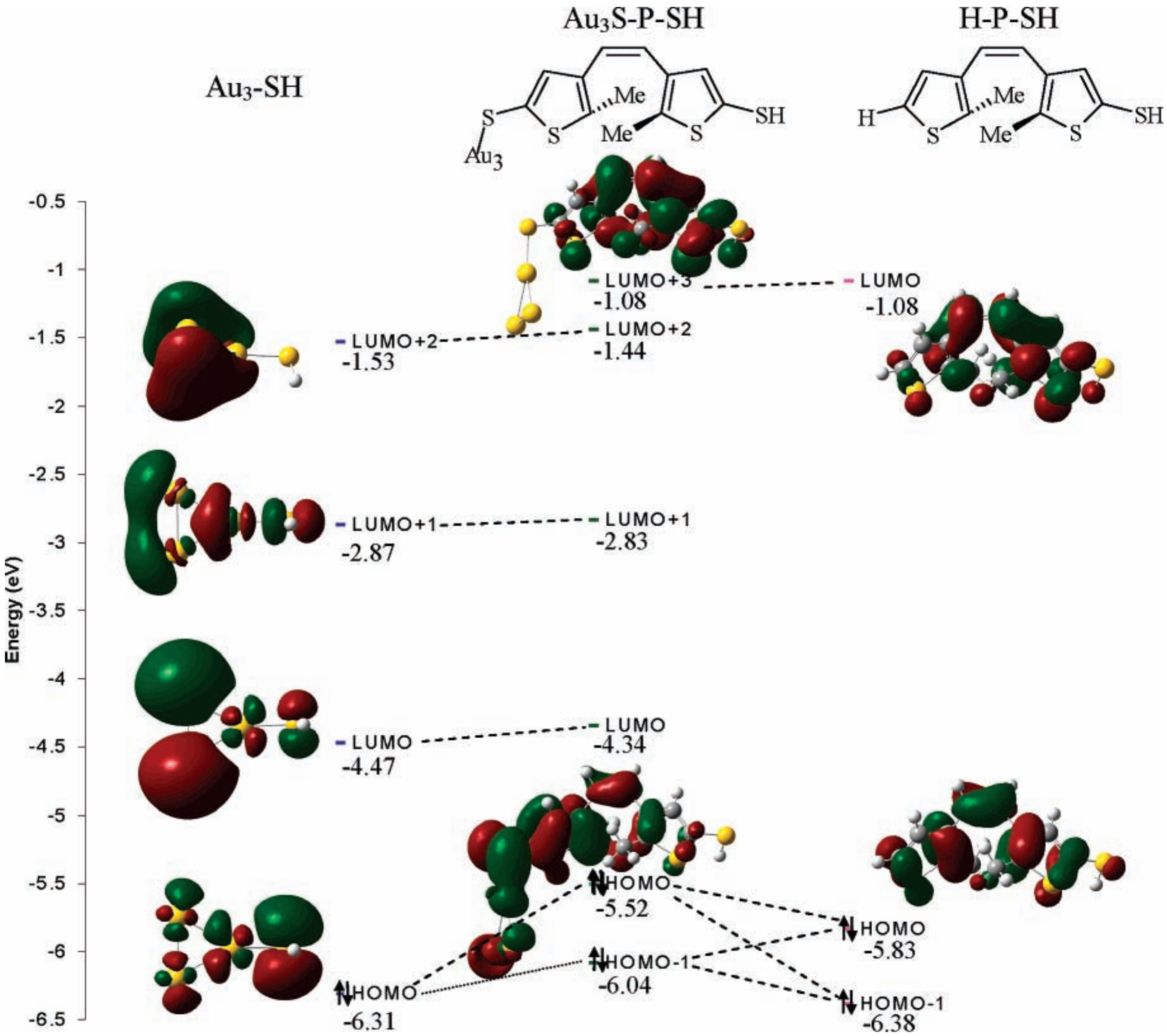


Figure 7. Molecular electronic orbitals diagram of Au$_3$SH and of the open-ring forms of Au$_3$S$-$P$-$SH and H$-$P$-$SH (energies are in eV).

on the potential energy surfaces (PES) of the excited states, the careful investigation of the cyclization reaction of the Au$_3$S$-$P$-$SH system would require the computation of the first excited states PES.[15,40]

III.2.3. Orbital Fragments Interactions Analysis. Comparison of both photochromic isomers shows that the open-ring isomer absorption spectrum is much more modified than the closed-ring one. In order to understand these differences, we have studied, for both isomers, the Au$_{3-}$molecule system (Au$_3$S$-$P$-$SH) orbital diagram in terms of orbital fragments interactions. We have considered that the Au$_{3-}$molecule system was formed from two fragments, Au$_3$SH and H$-$P$-$SH. As a matter of fact, we have built the Au$_3$S$-$P$-$SH molecules from these fragments (see section II). In Figure 6 (respectively, Figure 7), the molecular orbitals of Au$_3$SH and of the closed-ring (respectively, open-ring) H$-$P$-$SH moieties constituting the complex are correlated to the orbitals of the closed-ring (respectively, open-ring) Au$_3$S$-$P$-$SH molecule. This correlation was done by comparing the shape and energies of the Au$_3$S$-$P$-$SH molecule orbitals with those of the fragments.

For the closed-ring isomer, due to the weak overlap between the first unoccupied orbital of the Au$_3$SH fragment and the HOMO of the H$-$P$-$SH photochromic fragment, there is a small interaction between these two orbitals although they are close in energy. Therefore, the photochromic HOMO orbital and the cluster LUMO orbital are slightly modified. One can notice that, since the HOMO orbital of the Au$_3$S$-$P$-$SH system has some contributions on the metallic cluster, the HOMO → LUMO electronic transition has a nonnegligible oscillator strength. Besides, the LUMO + 1 and LUMO + 2 orbitals of the Au$_3$SH fragment and the LUMO of the H$-$P$-$SH moiety do not interact significantly for energetic and symmetrical reasons. As a consequence and as previously seen, both the photochromic last occupied and first unoccupied orbitals of the closed-ring isomer mainly keep their identity and the photochromic transition is not strongly modified.

For the open-ring isomer, in comparison to the closed-ring isomer, we both have a stabilization of the HOMO and a destabilization of the LUMO of the H$-$P$-$SH fragment (Figure 7). The destabilization of the LUMO mainly comes from the strong antibonding interaction between positions C$_e$ and C$_{e'}$. For the HOMO, along the π-electron conjugation path of the open-ring isomer, between positions 2 and 2′, there are two antibonding interactions, whereas for the closed-ring isomer, the π-electron conjugation path presents three nodes between positions 5 and 5′. Due to this energetic stabilization, the HOMO of the H$-$P$-$SH photochromic fragment now interacts strongly with the HOMO and HOMO $-$ 1 of the Au$_3$SH fragment. This results in a delocalization of the HOMO of the Au$_3$S$-$P$-$SH molecule on the Au atoms and on the thiophene ring close to the metallic cluster. Both the identity of the HOMO photochromic orbital and the nature of the photochromic transition are thus completely lost. Furthermore, since the HOMO orbital has some important contributions on the Au atoms, strong transitions from the HOMO to the first unoccupied metallic orbital (LUMO, LUMO + 1, LUMO + 2) appear. The absorption spectrum of the photochromic open-ring isomer is thus strongly modified by the inclusion of the Au$_3$ cluster, and this may lead to important consequences on the ring-closure reaction.

Hence, our results concerning a model dithienylethene molecule grafted on a small gold cluster provides a simple explanation of the experimental results of Dulic et al.[5] They have shown that the cycloreversion reaction which involves the closed-ring isomer is still possible, whereas the ring-closure reaction which involves the open-ring isomer is inhibited. This can be explained by the strong mixing of the metallic and the photochromic orbitals within the open-ring isomer. We have also found the same conclusions as other theoretical studies.[36,42,43] Contrary to the present work, these studies have used large gold clusters to model the gold surface. For instance, Li et al.[36] have used a (3 × 3) periodic lattice made up of eight ideal Au(111) layers. They attributed the inhibition of the ring-closure process to the overlapping of the HOMO photochromic orbital with the Au d band which has a high density of states. Therefore, our study has shown that connecting dithienylethene molecule to a small Au$_3$ cluster can give qualitative information about its photochromic activity. On the other hand, the small size of the cluster may lead to proper effects on the electronic structure and absorption spectrum of the gold−molecule system. To analyze this size effect, the Au$_9$S−P−SH system is studied and compared to the Au$_3$S−P−SH molecule.

III.3. Effect of the Cluster Size on the Optical Properties: Au$_9$−Dithienylethene System. *III.3.1. Closed-Ring Isomer.* For the closed-ring isomer, the photochromic last occupied orbital corresponds to the HOMO of the Au$_9$S−P−SH system, whereas the photochromic first unoccupied orbital corresponds to the LUMO + 5 orbital of the complex (Figure 8). For the HOMO orbital of the Au$_9$S−P−SH molecule, the contributions on the gold cluster are small, whereas there are totally negligible for the LUMO + 5 orbital. A comparison of the frontier orbital of HS−P−SH, Au$_3$S−P−SH, and Au$_9$S−P−SH (Figures 3, 4, and 8) shows that the shape of the photochromic last occupied and first unoccupied orbitals is not modified when this molecule is grafted to a Au$_3$ or Au$_9$ cluster. Besides, when the size of the cluster is increased, the energies of the two photochromic orbitals are slightly modified: the energy level of the last occupied orbital is −4.88 eV for the Au$_3$S−P−SH system and −4.81 eV for the Au$_9$S−P−SH molecule. In the same way, the energy level of the photochromic first unoccupied orbital is −2.04 eV for Au$_3$S−P−SH and −1.92 eV for Au$_9$S−P−SH.

The photochromic transition corresponds to the HOMO → LUMO + 5 electronic excitation. As given in Table 3, the corresponding wavelength (491 nm) is really close to the photochromic excitation wavelength in the Au$_3$S−P−SH system (492 nm). This result is consistent with the weak contribution of the gold cluster in the orbitals involved in this transition (HOMO and LUMO + 5). Interestingly, Table 3 also shows that the photochromic transition in Au$_9$S−P−SH is much more intense than in the free photochromic molecule or in the Au$_3$S−P−SH system.

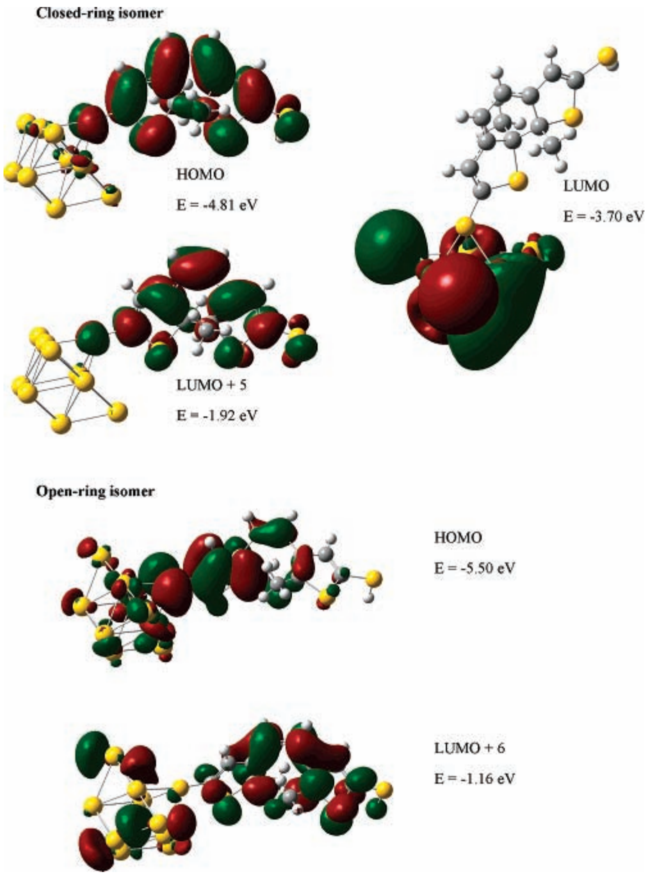


Figure 8. Characteristic orbitals of the Au$_9$S−P−SH isomers (isodensity = 0.02 au).

Figure 9 depicts the complete absorption spectra of the free molecule HS−P−SH, the Au$_3$S−P−SH system, and the Au$_9$S−P−SH complex within the 400−2000 nm range. These spectra have been obtained by fitting the TD−DFT calculated transitions with a Gaussian distribution. Information concerning the photochromic transition can be found in the 400−600 nm region. For the Au$_9$S−P−SH molecule, there is a transition in the infrared region (1694 nm). Like the infrared absorption band of Au$_3$S−P−SH, this transition arises from a HOMO → LUMO electronic excitation. Since the LUMO of the Au$_9$S−P−SH molecule is delocalized on the metallic cluster, this transition corresponds to a molecule to cluster charge transfer. Figure 9 shows that from Au$_3$S−P−SH to Au$_9$S−P−SH, the oscillator strength of the HOMO → LUMO excitation strongly decreases. For Au$_3$S−P−SH, the transition is intense because the photochromic HOMO has some contributions on the Au atoms. There is a nonnegligible overlap between the HOMO and LUMO of the cluster−molecule system. On the opposite, for Au$_9$S−P−SH, the HOMO has some small contributions on the Au atoms close to the linking sulfur. The orbital is not delocalized on the overall cluster, and the overlap between the HOMO and the LUMO is small. Therefore, the oscillator strength decreases. It then appears that the charge-transfer transition is a consequence of the small size of the gold cluster, and most probably, this band should disappear for a system made of a molecule grafted on an infinite gold surface.

III.3.2. Electronic and Spectroscopic Properties of the Open-Ring Isomer. For the open-ring isomer, the photochromic highest occupied orbital corresponds to the HOMO of the Au$_9$S−P−SH system, whereas the photochromic first unoccupied orbital corresponds to the LUMO + 6 orbital of the complex (Figure 8). Like the Au$_3$S−P−SH system, the identity of the last occupied photochromic orbital is completely lost: this orbital has some important contributions on the cluster, on the linking S atom, and on the neighbor thiophene ring. This orbital is similar to the HOMO of Au$_3$S−P−SH system which tends to prove that we have a strong interaction between the last occupied orbital of the cluster and the HOMO of the molecule. Besides, when the size of the cluster is increased, the energies of the last occupied and first unoccupied photochromic orbitals are

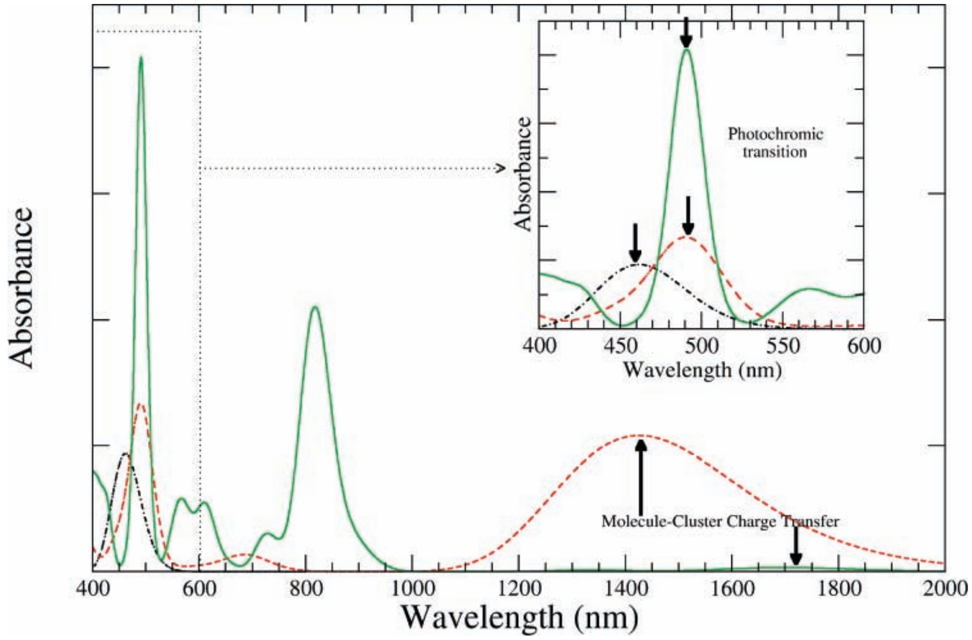


Figure 9. Closed-ring isomers: absorption spectra of the free photochromic molecule HS−P−SH (dotted-dashed line), Au_3S−P−SH (dashed line), and Au_9S−P−SH (solid line).

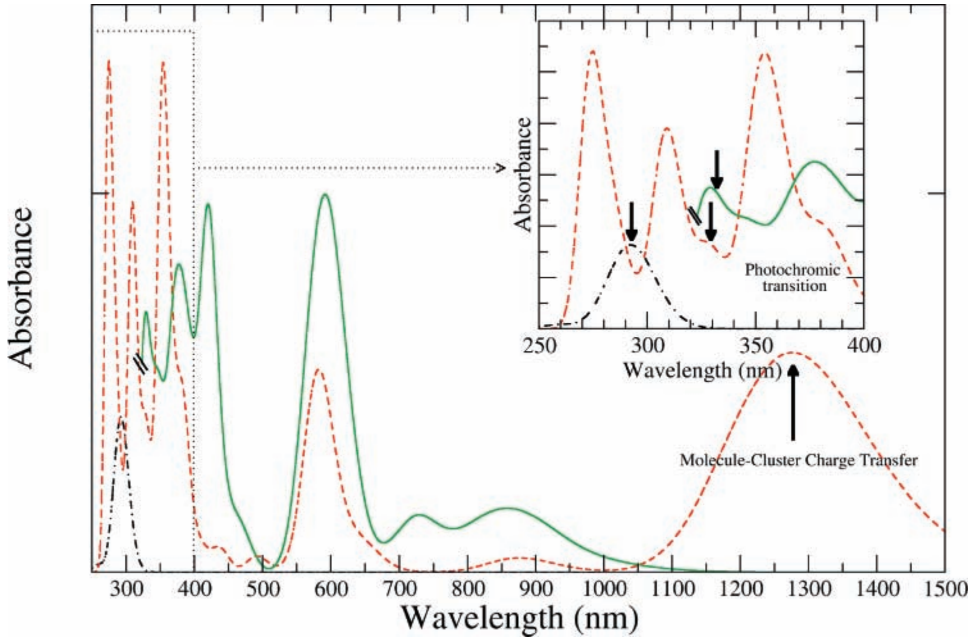


Figure 10. Open-ring isomers: absorption spectra of the free photochromic molecule HS−P−SH (dotted-dashed line), Au_3S−P−SH (dashed line), and Au_9S−P−SH (solid line).

not strongly modified: the energy level of the photochromic last occupied orbital (respectively, the photochromic first unoccupied orbital) is −5.52 eV (respectively, −1.08 eV) for the Au_3S−P−SH system and −5.50 eV (respectively, −1.16 eV) for the Au_9S−P−SH molecule.

Since the Au_9S−P−SH density of states is large in a small energy domain, it has been necessary to calculate 80 excited states to obtain the information concerning the photochromic transition. The latter transition corresponds to the HOMO → LUMO + 6 electronic excitation. As shown by Table 3, the corresponding absorption band (332 nm) is red-shifted in comparison with the Au_3S−P−SH open-ring isomer (319 nm). Table 3 also shows that the photochromic transition in Au_9S−P−SH is less intense than in the free photochromic molecule or in the Au_3S−P−SH system. Indeed, in the Au_9S−P−SH system, the photochromic transition is surrounded by electronic excitations presenting strong oscillator strength and corresponding to cluster localized electronic excitations. Hence, one can draw the same conclusions as the Au_3S−P−SH open-ring isomer: the cyclization reaction which proceeds though the HOMO → LUMO + 6 electronic excitation may be strongly affected.

Figure 10 depicts the complete absorption spectra of HS−P−SH, Au_3S−P−SH, and Au_9S−P−SH within the 250−1500 nm range. For the Au_9S−P−SH system, the absorption spectrum has been calculated from 320−1500 nm. Information concerning the photochromic transition can be found in the 250−400 nm region. For the Au_3S−P−SH molecule, there is a strong transition in the infrared region (1276 nm, Table 4). As previously seen, this transition arises from a HOMO → LUMO electronic excitation which corresponds to a molecule to cluster charge transfer. For the Au_9S−P−SH molecule, the HOMO →

LUMO excitation is blue-shifted ($\lambda \approx 1000$ nm) and nonoptically active. As a matter of fact, from $Au_3S-P-SH$ to $Au_9S-P-SH$, the oscillator strength of the HOMO → LUMO excitation strongly decreases. Like the closed-ring isomer, for $Au_3S-P-SH$, the strong charge-transfer transition found in the infrared region is an artifact due to the small size of the gold cluster.

IV. Conclusion

There is currently a great interest in the development of electronic devices on a molecular scale. Within this framework, the diarylethene photochromic molecules are candidates of choice since they can be activated under an external stimulus, like an electromagnetic irradiation, and thus carry out a function at the molecular level. However, in order to use these photochromic compounds within an active electronic device, it is necessary to have a fine comprehension of the optical properties of molecules attached to metallic surfaces. Within the framework of the DFT, we have thus studied model dithienylethene molecules grafted on small gold clusters (Au_3, Au_9) through thiol groups. Particular attention was paid to the effect of gold clusters on the electronic structure and absorption spectrum of photochromic molecules.

For the closed-ring isomer, we have found that grafting a photochromic molecule on a Au_3 cluster slightly changes the characteristics of the electronic transition involved in the ring-opening reaction. On the opposite, the absorption spectrum of the photochromic open-ring isomer is strongly modified by the inclusion of the Au_3 cluster. As demonstrated by an orbital fragment interaction analysis, in the open-ring isomer, there is a strong interaction between the last occupied orbitals of the cluster and the molecule. Both the identity of the last occupied photochromic orbital and the nature of the photochromic transition are completely lost, which may lead to important consequences on the ring-closure reaction. Our results concerning a model dithienylethene molecule grafted on a small gold cluster thus provide a simple explanation of the experimental results of Dulic et al.:[5] they have shown that the cycloreversion reaction which involves the closed-ring isomer is still possible, whereas the ring-closure reaction which involves the open-ring isomer is inhibited.

To analyze the cluster size effect, we have compared the $Au_3S-P-SH$ and $Au_9S-P-SH$ molecules. For the $Au_9S-P-SH$ system, we have obtained the same conclusions concerning the photochromic activity of the dithienylethene moiety. We have also found that the molecule−cluster charge transfer observed in the IR domain for the $Au_3S-P-SH$ system is an artifact arising from a size effect which should not be seen experimentally. One can then use a small Au_3 cluster to study the influence of metals on the electronic excitations involved in the ring-opening/ring-closure reactions but should consider with precaution the overall absorption spectrum.

As a conclusion, our study shows that grafting a dithienylethene molecule to a small Au_3 cluster gives a qualitative comprehension of the photochromic activities of dithienylethenes connected to a gold surface. By considering small clusters, we can still use DFT calculations with atomic orbitals basis sets, that is to say, we can still analyze the electronic and spectroscopic properties of the molecule from a “chemical” point of view. This tool should thus be used to study the electronic properties of larger dithienylethene molecules (with thiophene and phenyl linkers) grafted on a gold surface.

Supporting Information Available: Geometrical parameters of the closed-ring and open-ring gas-phase isomers, geometrical parameters of the closed-ring Au_3−dithienylethene system, and geometrical parameters of the open-ring Au_3−dithienylethene system. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Dürr, H.; Bouas-Laurent, H. *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, 1990.

(2) Irie, M. *Chem. Rev.* **2000**, *100*, 1715.

(3) Feringa, B. L. *Molecular Switches*; Wiley-VCH: Weinheim, Germany, 2001.

(4) Masson, J.-F.; Liddell, P. A.; Banerji, S.; Battaglia, T. M.; Gust, D.; Booksh, K. S. *Langmuir* **2005**, *21*, 7413.

(5) Dulic, D.; van der Molen, S. J.; Kudernac, T.; Jonkman, H. T.; de Jong, J. J. D.; Bowden, T. N.; van Esch, J.; Feringa, B. L.; van Wees, B. J. *Phys. Rev. Lett.* **2003**, *91*, 207402.

(6) Kudernac, T.; Molen, S. J. V. D.; Wees, B. J. V.; Feringa, B. L. *Chem. Commun.* **2006**, 3597.

(7) Katsonis, N.; Kudernac, T.; Walko, M.; van der Molen, S. J.; van Wees, B. J.; Feringa, B. L. *Adv. Mater.* **2006**, *18*, 1397.

(8) Ikeda, M.; Tanifuji, N.; Yamaguchi, H.; Irie, M.; Matsuda, K. *Chem. Commun.* **2007**, 1355.

(9) Majumder, C.; Briere, T.; Mizuseki, H.; Kawazoa, Y. *J. Chem. Phys.* **2002**, *117*, 7669.

(10) Reed, M. A.; Zhou, C.; Muller, C. J.; Burgin, T. P.; Tour, J. M. *Science* **1997**, *278*, 252.

(11) Xue, Y.; Dutta, S.; Ratner, M. *J. Chem. Phys.* **2001**, *115*, 4292.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision D.01 ed.; Gaussian, Inc.: Wallingford, CT, 2004.

(13) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(14) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(15) Goldberg, A.; Murakami, A.; Kanda, K.; Kobayashi, T.; Nakamura, S.; Uchida, K.; Sekiya, H.; Fukaminato, T.; Kawai, T.; Kobatake, S.; Irie, M. *J. Phys. Chem. A* **2003**, *107*, 4982.

(16) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(17) Jacquemin, D.; Preat, J.; Wathelet, V.; Fontaine, M.; Perpete, E. A. *J. Am. Chem. Soc.* **2006**, *128*, 2072.

(18) Maurel, F.; Aubard, J.; Millie, P.; Dognon, J. P.; Rajzmann, M.; Guglielmetti, R.; Samat, A. *J. Phys. Chem. A* **2006**, *110*, 4759.

(19) Jacquemin, D.; Preat, J.; Wathelet, V.; Perpete, E. A. *J. Mol. Struct. (THEOCHEM)* **2005**, *731*, 67.

(20) Jacquemin, D.; Preat, J.; Perpete, E. A. *Chem. Phys. Lett.* **2005**, *410*, 254.

(21) Guillaumont, D.; Nakamura, S. *Dyes Pigm.* **2000**, *46*, 85.

(22) Majumdar, D.; Han Myoung Lee, J. K.; Kim, K. S.; Byung Jin, M. *J. Chem. Phys.* **1999**, *111*, 5866.

(23) Giraud, M.; Leaustic, A.; Charlot, M.-F.; Yu, P.; Cesario, M.; Philouze, C.; Pansu, R.; Nakatani, K.; Ishow, E. *New J. Chem.* **2005**, *29*, 439.

(24) Higashiguchi, K.; Matsuda, K.; Asano, Y.; Murakami, A.; Nakamura, S.; Irie, M. *Eur. J. Org. Chem.* **2005**, 91.

(25) Chen, D.-Z.; Wang, Z.; Zhao, X.; Hao, Z. *J. Mol. Struct. (THEOCHEM)* **2006**, *774*, 77.

(26) Clark, A. E. *J. Phys. Chem. A* **2006**, *110*, 3790.

(27) Jacquemin, D.; Perpete, E. A. *Chem. Phys. Lett.* **2006**, *429*, 147.

(28) Yokojima, S.; Matsuda, K.; Irie, M.; Murakami, A.; Kobayashi, T.; Nakamura, S. *J. Phys. Chem. A* **2006**, *110*, 8137.

(29) Perpete, E. A.; Jacquemin, D. *J. Photochem. Photobiol., A* **2007**, *187*, 40.

(30) Perrier, A.; Maurel, F.; Aubard, J. *J. Photochem. Photobiol., A* **2007**, *189*, 167.

(31) Vondrak, T.; Cramer, J. C.; Zhu, X.-Y. *J. Phys. Chem. B* **1999**, *103*, 8915.
(32) Grönbeck, H.; Curioni, A.; Andreoni, W. *J. Am. Chem. Soc.* **2000**, *122*, 3839.
(33) Hasan, M.; Bethell, D.; Brust, M. *J. Am. Chem. Soc.* **2002**, *124*, 1132.
(34) Karpovitch, D. S.; Schessler, H. M.; Blanchard, G. J. The Kinetics and Thermodynamics of Monolayer Formation. In *Thin Films*; Ulman, A., Ed.; Academic Press: New York, 1998; Vol. 24.
(35) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 79th ed.; CRC Press: Boca Raton, FL, 1998.
(36) Li, J.; Speyer, G.; Sankey, O. F. *Phys. Rev. Lett.* **2004**, *93*, 248302.
(37) Gottschalck, J.; Hammer, B. *J. Chem. Phys.* **2002**, *116*, 784.
(38) Ramachandran, G. K.; Tomfohr, J. K.; Li, J.; Sankey, O. F.; Zarate, X.; Primak, A.; Terazono, Y.; Moore, T. A.; Moore, A. L.; Gust, D.; Nagahara, L. A.; Lindsay, S. M. *J. Phys. Chem. B* **2003**, *107*, 6162.
(39) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, Germany, 1970.
(40) Guillaumont, D.; Kobayashi, T.; Kanda, K.; Miyasaka, H.; Uchida, K.; Kobatake, S.; Shibata, K.; Nakamura, S.; Irie, M. *J. Phys. Chem. A* **2002**, *106*, 7222.
(41) Uchida, K.; Tsuchida, E.; Aoi, Y.; Nakamura, S.; Irie, M. *Chem. Lett.* **1999**, 63.
(42) Speyer, G.; Li, J.; Sankey, O. J. *Phys. Status Solidi B* **2004**, *241*, 2326.
(43) Zhuang, M.; Ernzerhof, M. *Phys. Rev. B* **2005**, *72*, 073104.