Impact of derivatization on electron transmission through dithienylethene-based photoswitches in molecular junctions†

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We report a combined Non-Equilibrium Green’s Function – Density Functional Theory study of molecular junctions made of photochromic diarylenes between gold electrodes. The impact of derivatization of the molecule on the transmission spectrum is assessed by introducing: (i) substituents on the diarylethene core; and (ii) linker substituents between the gold surface and the diarylethene. We illustrate that substituents on the core shift considerably the HOMO/LUMO level energies in gas phase but do not change the I–V characteristics of the molecular junctions; this behaviour has been rationalized by establishing links between the transmission spectrum and interfacial electronic reorganization upon chemisorption. In contrast, the different linker substituents under study modulate the conductivity of the junction by changing the degree of orbital hybridization with the metallic electrodes and the degree of orbital polarization.

A. Introduction

Since the first concept of a molecular rectifier, published by Aviram and Ratner in the seventies,1 the field of molecular electronics has kept challenging researchers at both the applied and fundamental levels.2–5 The last few decades have experienced the development of experimental setups to measure the electrical conductivity of devices at the molecular scale and of theoretical tools to predict I–V characteristics of molecular junctions. This endeavor stems from the prospects of moving microelectronics to the realm of nanoelectronics. Another key feature in dealing with molecules is the ability to tune the I–V characteristics by exploiting the huge versatility of chemical synthesis.

The idea of introducing molecular photoswitches between electrodes to generate functional molecular junctions recently emerged.6,7 Prototypical molecules are diarylethene derivatives that can adopt two different structures, i.e. a closed and open isomer, interconverting under the action of light at different wavelengths (see Fig. 1). The two isomers have comparable sizes but differ in the length of their conjugation paths (longer for the closed isomer), which promote different electronic gaps and transmission properties, and hence electrical conductivities. Moreover, their thermal stability makes them attractive candidates in the
field of molecular electronics. Recent experimental studies based on dithienylethenes chemisorbed either on gold or carbon nanotube electrodes have demonstrated a switching effect and its reproducibility. However, further improvements in the reversibility of the photochromic effect in the junction and in the current ratios between closed and open isomers are required. This motivates theoretical studies aiming at a molecular description of the switching effect and at the definition of the key parameters governing the current ratios. Theory further allows for a fundamental understanding of I-V characteristics on well-defined molecular architectures in contrast to many experimental measurements lacking details about the exact contact geometry or the number of molecules in the junction.

Several theoretical papers have previously studied dithienylethene-based molecular junctions, most often with gold electrodes, addressing in particular the origin of conductivity switching and the ratio between the closed and open isomers, as well as the reversibility of the photoswitching associated with quenching processes by the electrodes. All these transport studies are based on the coherent Landauer’s picture of conductivity (described by transmission probabilities) and the Non-Equilibrium Green’s Function (NEGF) method combined with Density Functional Theory (DFT) or a tight-binding approximation.

Earlier studies were either limited to equilibrium (zero bias, no I-V curves) or to a bias applied not self-consistently, that is, the electronic structure of the entire junction is not re-optimized for every applied voltage. However, they pinpointed the principal differences between the two forms in the junction: closer alignment to the Fermi level of the electrodes and a higher delocalization of the HOMO level in the closed isomer thus yielding a better conductivity. Maximum current ratios around 22 have been reported for the unsubstituted dithienylethene core with the sulfur atom of the thiol group anchored on a top position over the Au(111) surface; an increase up to 57 has been obtained by attaching laterally a thiénylthiol unit.

More recently, fully self-consistent studies with gold, silver and nickel metal electrodes appeared, leading to improved I-V curves. Generally confirming the previous findings, they showed in particular that the polarization of the orbitals by the electric field is a key ingredient to be also taken into account. This polarization effect has been demonstrated by examining the shape of the molecular orbitals of isolated molecules under the influence of an electric field (without coupling to open electrodes) and via a Projected Density Of States (PDOS) analysis that does not allow for the visualization of the orbitals within the junctions. It has been suggested that the orbitals of the open isomer are more polarizable under bias than those of the closed form, leading to a decrease in the transmission probability of the former with increasing bias.

The photoreversibility critically depends on the nature of the lateral anchoring group (R’ in Fig. 1) attached to the photochromic core and on the nature of the electrodes (such as gold, carbon nanotubes, silver, or nickel). The switching mechanism is, however, not affected by the anchoring groups or the electrodes. For gold electrodes, the irreversibility of the switching event has been attributed to a strong hybridization of the molecular orbitals with the gold orbitals. In the case of carbon nanotubes and graphene electrodes, this coupling has been shown to reduce the excited-state lifetime and hence the efficiency of the photoswitching.

In a study connecting the molecule to finite gold clusters, the width of the transmission peak at the Fermi level has been correlated to the amount of mixing between the HOMO level and the gold orbitals, thus supporting the role of the orbital hybridization in the quenching process.

In the present study, we report a comprehensive fully self-consistent analysis of the transport properties of several dithienylethene derivatives, in their closed and open forms, inserted between two gold electrodes in well-defined geometries. Our results further allow us also to speculate on the reversibility of photoswitching between the two forms in the junction. We analyze separately and systematically the impact of different substituents on the ethylene bridge (R) and of different linker connections (R’) on the calculated I-V characteristics (see Fig. 1). Six different substitution patterns of the photochromic core have been considered in order to modulate the gap and the absolute energies of the electronic levels via inductive/mesomer effects or changes in the amplitude of the torsion angles for the open isomer. The three lateral thiolated linkers involved in our study (a thiophene ring and a benzene ring with meta and para connections) are those extensively found in the literature. The large set of substituents allows us to compare the evolution of the electronic properties of the photochromic core in the isolated state and within the junctions and to assess the nature of the linker which optimally protects the central responsive unit by reducing the amount of hybridization with the gold electrodes. A critical comparison is made with corresponding experimental data indicating that the switching process is reversible with a meta- or para-phenylene linker and irreversible with a thiophene moiety. Moreover, in order to link the electronic structure of the compounds in the junctions to the calculated transmission spectra, we visualize the molecular orbitals of the contacted molecules using the Molecular Projected Self-consistent Hamiltonian (MPSH) approach. The MPSH approach illustrates that some orbitals get strongly polarized in a molecular junction under bias and that the orbital shape plays a crucial role in defining the I-V characteristics. Moreover, we find here that the degree of polarization depends on the nature of the R’ linker substituent. Interestingly, in spite of large variations in the HOMO energy of the different compounds substituted on their central photochromic core, the HOMO is aligned similarly with respect to the Fermi level of the gold electrodes for all compounds, thus pointing to a Fermi level pinning. This teaches us that designing the alignment of electronic levels in molecular junctions by the mere consideration of isolated molecular units could prove highly misleading due to the neglect of the interfacial electronic processes.

The paper is structured as follows: after a brief presentation of the theoretical methodology in Section B, we discuss the properties of the isolated molecules and of the junctions at equilibrium and under bias in Section C. For the sake of clarity,
we distinguish between the impact of $R$ or $R'$ substitutions in each section. Conclusions and perspectives are outlined in Section D.

**B. Computational methods**

We have first optimized the ground-state geometry of each compound in its two isomeric forms at the DFT level using the widely used B3LYP hybrid functional and a 6-31G** basis set, as previously done with organic compounds especially diarylethanes. The calculations have been performed with the Gaussian03 package. The electronic structure and transmission spectrum of the gold–molecule junctions have been calculated using the Non-Equilibrium Green’s Function formalism based on the DFT method, as implemented in the ATK2008.10 package. The exchange–correlation is treated with the GGA.repeatPBE functional. 

In all junctions, the anchoring geometry was fixed, with the sulfur atoms anchored on the top position on the gold surface with an Au–S distance fixed at 2.42 Å, as suggested experimentally and theoretically, in order to focus on the impact of the molecular internal structure on conductivity. More computational details can be found in the ESL.[1]

The electronic structure of the molecules within the junction has been characterized by MPSH analysis, which consists in diagonalizing the Hamiltonian of the scattering region in an LCAO basis restricted to a chosen set of atoms of the central region. The MPSH spectrum provides valuable information about the alignment of the molecular levels with respect to the Fermi level of the electrodes and helps to rationalize the nature and intensity of the peaks in the transmission spectra. The charge transfer occurring upon covalent bonding to the gold surface has been estimated by computing the $z$-averaged density profiles of three subsystems: the total system without the molecule, the gold surface has been estimated by computing the electronic reorganization due to the gold–molecule interactions. On that basis, we can also build-up the density arising from the gold–molecule–gold interactions. On that basis, we can also build-up the density arising from the gold–molecule–gold interactions.

The thiolated linkers introduce an additional thiophene ring or as hydrogenated or fluorinated saturated five-carbon rings. Atoms, cyano and methyl groups on the central double bond as lateral substituents on the electronic structure of the photochromic core, as calculated at the B3LYP level. The torsion angle characterizing the loss of coplanarity of the thiophene rings in the open isomer is defined from the vectors connecting atoms 1–3, 3–4, and 4–6 in Fig. 1. The C1–C6 is the distance between atoms 1 and 6. The bond angle involves atoms 2, 3, and 4 of the ethylene bridge (see labelling in Fig. 1), thus translating into a torsion angle increased by about 10 degrees.

The B3LYP shapes of the HOMO acting as a transport channel in the junction [plotted with an isovalue = 0.02] and frontier orbital energies are reported in ESL† (Fig. S2). We observe that the pattern of the HOMO remains unchanged upon derivatization of the photochromic core or by changing the torsion angle ($R=\text{CH}_3$). We can directly relate the pattern of the HOMO level to that of octatetraene and hexatriene for the closed and open isomers which are displayed in Fig. 2. We also observe that HOMOs do not bear a significant weight on the substituents. While the substituents do not modify the shape of the HOMOs, they significantly alter the absolute energies of the frontier molecular orbitals and the HOMO–LUMO energy gap (see Table 1 and Fig. 2). When taking the $R=\text{H}$ compound as reference, the introduction of fluorine atoms stabilizes the frontier electronic levels for both isomers, with a more pronounced effect for the Fcyclo. This stabilization usually dominates transmission and the chemical potential of the molecules, defined as the energy at midgap. In the junction, the alignment of the molecular electronic levels with the Fermi level of the electrodes will be driven by an evolution towards equalization of the chemical potentials of the two components. However, this equalization is apparently not necessarily achieved at equilibrium depending on the actual density of states available. We will show that the changes due to derivatization can be considerable and will discuss the corresponding energy level alignment in the following sections. The actual position of the frontier electronic levels of the closed and open isomers in gas phase was speculated to be a key parameter defining the properties of dithiynylethene-based molecular memory devices.

**Core substituents.** The DFT calculations show that the backbone of all closed isomers is planar, in agreement with previous studies. In contrast, the open isomers exhibit a significant dihedral angle between the planes of the two thiophene rings, varying as a function of the nature of the core substituent (Table 1). In comparison to $R=\text{H}$, the largest distortion is observed for $R=\text{CH}_3$, where the steric hindrance cannot be accommodated by a strong reduction of the bond angle associated with the carbon atoms 2, 3, and 4 of the ethylene bridge (see labelling in Fig. 1), thus translating into a torsion angle increased by about 10 degrees.

### Table 1: Geometric parameters of the open isomer substituted on the photochromic core, as calculated at the B3LYP level.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Torsion angle</th>
<th>C1–C6 (Å)</th>
<th>Bond angle</th>
<th>Closed HOMO (eV)</th>
<th>Closed LUMO (eV)</th>
<th>Open HOMO (eV)</th>
<th>Open LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>46</td>
<td>3.6</td>
<td>130</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>47</td>
<td>3.7</td>
<td>131</td>
<td>–0.22</td>
<td>–0.22</td>
<td>–0.14</td>
<td>–0.28</td>
</tr>
<tr>
<td>CN</td>
<td>51</td>
<td>3.6</td>
<td>127</td>
<td>–0.78</td>
<td>–1.04</td>
<td>–0.76</td>
<td>–1.77</td>
</tr>
<tr>
<td>CH₃</td>
<td>57</td>
<td>3.8</td>
<td>123</td>
<td>–0.11</td>
<td>+0.15</td>
<td>+0.06</td>
<td>+0.36</td>
</tr>
<tr>
<td>Fcyclo</td>
<td>50</td>
<td>3.7</td>
<td>130</td>
<td>–0.52</td>
<td>–0.78</td>
<td>–0.62</td>
<td>–0.84</td>
</tr>
<tr>
<td>Hcyclo</td>
<td>48</td>
<td>3.7</td>
<td>129</td>
<td>+0.14</td>
<td>+0.07</td>
<td>+0.14</td>
<td>+0.16</td>
</tr>
</tbody>
</table>

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is further enhanced in the presence of cyano substituents yielding shifts as large as 0.76–0.78 eV for the HOMO levels. The CH₃ and Hcycle substitutions induce a little destabilization of the HOMO level; the larger destabilization is 0.14 eV in both the open and closed isomers for the Hcycle substitution. As expected, the HOMO–LUMO gaps are systematically smaller in the closed isomers due to the larger delocalization of the conjugated pathway. The band gap is further modulated by the introduction of the substituents. Using H-substitution as reference, the gap for the closed and open CH₃-substituted compounds is increased by 0.04–0.30 eV, respectively, while a decrease by 0.26–1.01 eV is observed for the closed and open CN-substituted isomers.

The chemical potential also varies significantly upon derivatization. The values lie in between −4.16 eV and −3.12 eV for the closed form and −4.70 eV and −3.22 eV for the open form. Lower values are obtained for fluorinated and CN-substituted compounds. For a given structure, the chemical potential is always lower for the open isomer.

**Lateral linkers.** The introduction of the linkers does not affect the geometry of the central core. The core is still characterized by torsion angles between the thiophene rings around 45° and a C1–C6 distance of 3.6 Å in the open isomer. The dihedral angles between the linkers and the thiophene rings of the photochromic core are reasonably small, up to 27° for the meta-phenylene linker. This is expected to ensure a good delocalization between the linker and the core and hence a significant conductance across the molecular junctions.¹¹ The HOMO–LUMO gap is reduced by 0.50–0.72 eV for the closed form and 0.41–0.85 eV for the open form upon introduction of the linkers due to the increase in the size of the conjugated pathway. The range of chemical potentials is much less extended than for the core substitution, varying between −3.32 eV and −3.55 eV for the closed isomer and between −3.21 eV and −3.50 eV for the open form. The shape of the HOMO orbitals displayed in ESI† confirms the good delocalization of this level. Interestingly, with the meta-phenylene linker, the closed HOMO level has no electronic density on the external C–S bonds that will be attached to the gold surface in the junction due to the breaking of the electronic communication introduced by the meta connection. The meta linkers are thus expected to strongly reduce the coherent transmission through the molecule due to a poor electronic coupling between gold and the molecule.⁵⁵–⁵⁸

**b Junctions at equilibrium**

The fundamental property of a junction in the coherent transport regime is the transmission probability for an electron to cross it. In this section, we firstly analyze the way the transmission spectrum at zero bias, that is at the Fermi level and in the absence of electric field, is affected by the core and lateral substituents.

**Core substituents.** Fig. 3a shows that the transmission curves are practically identical in the vicinity of the Fermi level for all substituted molecules in both closed and open forms, in spite of the significant differences in the frontier orbital energies in the isolated molecules. Both isomers are characterized by a wide and intense transmission peak in the vicinity of the Fermi level. The HOMO peak is perfectly aligned with the Fermi level in the closed form whereas the transmission peak of the open isomer is shifted to lower energy such that only its tail is aligned with the Fermi level. The high transmission intensity (on the order of 1⁰⁻¹) and the considerable width of the transmission peak of the open form are hardly compatible with a simplistic view of this isomer as a non-conjugated unit; the conjugated pathway might be affected by cross-conjugation effects. For comparison, NEGF-DFT calculations on saturated C8 and C12 alkanedithiol self-assembled monolayers (SAMs) (with a thickness similar to the length of the photochromic cores) between gold electrodes yield a transmission raising up to 1⁰⁻³ at the Fermi level.⁵⁹

In order to get a deeper insight into the transmission spectra, we start by performing the MPSH analysis. The open R=H isomer is displayed in Fig. 3b. Many MPSH levels are states concentrated only on gold atoms that do not offer a pathway for transmission. The relevant levels are those delocalized over the molecular part that we can identify from the shape of the orbitals computed for the isolated molecules. The MPSH level associated with the transmission peak of the closed-H form is very reminiscent of the HOMO level of the isolated molecule (and will be referred in the following as the MPSH HOMO). This level acts as the conducting channel in agreement with previous studies²⁹–³⁴ and exhibits a significant electron density on all atoms connecting the two electrodes, thus explaining the high transmission probability. The MPSH open-H HOMO has a smaller density on the central two carbon atoms than the MPSH open-H LUMO, which translates into a higher transmission probability for the latter. Generating an intense peak of transmission thus requires a good delocalization on all atomic p_orbitals along the conjugated pathway. On the other hand, a good hybridization between the orbitals of gold and of the external sulfur atoms is observed in the closed-H and open-H HOMO levels whereas no electronic density is...
found at the interfacial region in LUMO open-H. This translates into a much larger width of the HOMO transmission peak compared to the LUMO peak in Fig. 3b. A small hybridization will not yield high conductivities since hybridization plays a major role in broadening the resonant transmission peaks and thus in increasing the current upon integration.

The larger hybridization between the gold and molecular orbitals for the open isomer is consistent with the fact that the switching process operates only from the closed to open geometry at the experimental level for dithienyl derivatives since the excited-state lifetime is expected to be reduced in the open form due to the strong coupling with the metal. The large width of the open-H HOMO transmission peak thus generates a high conductance signal and yields irreversibility of the photochromic process. In this respect, the lateral linkers might act as anti-quenching groups by reducing the extent of hybridization and could further increase the ON/OFF ratio of the molecular junction. The strong hybridization between the gold and molecular orbitals also promotes a Fermi level pinning, as reflected by the fact that the energy difference between the HOMO level and the Fermi level is almost the same for all derivatives, i.e. 0.13–0.14 eV for the closed isomers and 0.19–0.25 eV for the open isomers. This pinning originates from charge-transfer processes between the molecule and the electrodes and implies that the amount of charge transferred varies with the nature of the substituents.

In order to visualize the charge transfer, we have computed the $\rho$ profiles for several closed isomers, according to the procedure described in the methodology section, together with the charge integrated over the molecular part, see Fig. 4. The charge transfer primarily occurs at the interface. The surface gold layers lose a significant fraction of electrons, as evidenced by the dip in the density between the first two reference lines, whereas the sulfur gains some negative charge though less than the neighboring carbon atom in comparison to the biradical. This reflects that the charge transfer from the carbon to the sulfur within the C–S bonds of the biradical is partially cancelled upon creation of the gold–sulfur bond. The charge distribution in the central molecular part is similar for all closed isomers. The molecular backbone as a whole gains electrons, with the excess charge integrated between the two external carbon atoms on the order of 0.10–0.14 e. The results

\[ \text{MPSH closed-H HOMO} \]
\[ \text{MPSH open-H HOMO} \]
\[ \text{MPSH open-H LUMO} \]

**Fig. 3** (a) Transmission spectra (in log scale) of each photochromic core around the Fermi level (set to zero for convenience) for the closed (left) and open (right) isomers; (b) transmission spectrum of the open-H isomer in a linear scale. The MPSH spectrum is superimposed in red to highlight the good match between the transmission peaks and MPSH levels. MPSH orbitals of closed-H HOMO, open-H HOMO, and open-H LUMO are also displayed from top to bottom (iso-value = 0.04).
demonstrate that the Fermi level pinning is established by the creation of interface dipoles whose amplitude varies with the nature of the substituent. The two bond dipoles create an upward shift of the electrostatic potential at the interfaces.\textsuperscript{54} The electronic density localized over the central molecular backbone experiences this shift, leading to a destabilization of the HOMO level with a shift depending on the strength of the dipoles balancing the variation of the chemical potential among the derivatives (see the scheme in Fig. 4).

Strictly speaking, the chemical potentials of the neutral molecules cannot be directly confronted to the chemical potential of gold (5.26 eV at both the experimental and theoretical levels\textsuperscript{50,60} since the corresponding value for the biradical (without the terminal H atoms) coupled to the gold surface matters in the junction.\textsuperscript{61} Still, it is reasonable to assume that the relative values of the chemical potentials will be similar for the isolated molecules and for biradicals hybridized systematically in the same way with the gold surface. A similar scenario prevails for the open isomers. It should be noted that the amplitude of the interface dipole might also be affected by the anchoring position of the sulfur atom on the gold surface. This is, however, beyond the scope of the present paper focusing on the amplitude of the ON/OFF ratios of photoisomers in the same contact geometry. The calculated interface dipole does depend on core substitution: it grows along the same order CN > F-cycle > H (Fig. 4) as the chemical potentials calculated for the isolated molecules (Section C.a: 4.16 eV for closed-CN > 3.90 eV for closed-F-cycle > 3.25 eV for closed-H).

Larger interface dipoles for the molecules with lower lying frontier MOs lead to increased destabilization of these levels in the junction, thus counteracting the initial level positioning. This mechanism dominates the metal–molecule level alignment and is responsible for the similar alignment of the series of molecules with different frontier MO energies.

**Lateral linkers.** We analyze here the impact of introducing three aromatic linkers between the photochrome and the anchoring thiol unit on the properties discussed in the previous section. The transmission spectra of the linker-substituted photochromic cores are reported in Fig. 6a. The *meta*-phenylene linker has clearly a distinct behaviour, yielding an extremely narrow transmission peak at the Fermi level for the closed isomer, in agreement with previous theoretical studies on benzene-dithiol junctions.\textsuperscript{53–58} The narrowness of this peak originates from the lack of hybridization between the gold and the frontier molecular $\pi$ orbitals and gives rise to a negligible current across the junction. For the other two linkers, the transmission peaks at the Fermi level are quite similar to closed-H. The linker substitution modifies significantly the intensity of the transmission peak of the open-H isomers: for the *para*-phenylene and thiophenyl linkers, the intensity decreases while it increases in the presence of the *meta*-phenylene linker. In the latter case, the changes can be detrimental for the current switching performance if the intense peak enters in the transmission window under bias. For all linker-substituted derivatives, we also observe a second intense transmission peak due to the reduction in the energy difference between the HOMO and LUMO – 1 levels of the isolated molecules following the increase in the length of the conjugated path. This second peak is not expected to contribute to the $I$–$V$ curve since it lies far away from the Fermi level (more than 0.5 eV).

The MPSH spectra confirm that it is again the HOMO level of the three compounds which is aligned with the Fermi level. For the closed isomers, the introduction of the *para*-phenylene and thiophenyl linkers preserves the alignment of the HOMO level, lying at $-0.13$ eV below the Fermi level. As seen in Fig. 6b, these levels are well delocalized throughout the backbone, with a significant weight on the terminal sulfur atoms and the gold surface. This description is similar to that prevailing for the compounds without linkers and explains the little changes in the transmission spectra at the Fermi level. For the open isomers, the thiophenyl and *para*-phenylene linkers exhibit a HOMO aligned in the same range of energy compared to the results obtained in the previous section ($-0.22$ eV and $-0.28$ eV below the Fermi level, respectively). The alignment energy at exactly the same value for the reference $R$–$H$ compound and that featuring a thiophene-based linker is rationalized by the fact that the interfacial hybridization and charge reorganization are expected to be very similar in both cases due to the identical anchoring groups.

Since the charge transfer between the gold surface and the molecule was found in the previous section to mostly occur at the interface, it is likely that the anti-quenching groups will act as a shield against electronic reorganization in the photochromic core. When plotting the plane-averaged profile of $\delta p$ (see Fig. 5), we do observe a reduction in the amplitude of the oscillations over the central core, thus pointing to a limited electronic reorganization. The excess charge on the photochromic core is about 0.05–0.07|e| after integration with the thiophenyl and *para*-phenylene linkers and is lower compared to the unsubstituted photochromic core (0.10–0.14|e|). The amplitude of the interface dipole does not correlate with the chemical potential of the isolated molecules since each linker hybridizes in a different way with the gold surface. As expected from the identical nature of the anchoring group.
The degree of hybridization and coupling between the molecule and gold can be indirectly assessed from the widths of the transmission peaks: the larger the width, the larger the degree of coupling, and hence the smaller the lifetime of the excited state on the molecular backbone. In turn, a reduced lifetime will lower the probability for the geometric reorganization in the excited state to occur. The Full Width at Half Maximum is directly connected to the interfacial coupling strength for a simple model based on a single resonant transport level. FWHM of the transmission peaks reported in Fig. 6 is collected in Table 2. The determined FWHM values demonstrate that the nature of the linker strongly influences the width of both the HOMO and LUMO transmission peaks. These peaks are the most relevant since the lowest optical transition in diarylthene compounds primarily involves an electronic transition between the HOMO and LUMO levels. The LUMO peak of the open form is always rather narrow with or without linkers. In contrast, the width of the LUMO peak in the closed form is strongly reduced with linkers, which are thus expected to facilitate the closed to open switch in the junction by increasing the lifetime of the excited state. All together, we conclude that the meta-phenylene linker is the best candidate among the three to ensure the reversibility of the mechanism of photoswitching.

### Junctions under bias

Having considered the properties of our junctions at zero bias in the previous section, we will now study them under bias, which opens the way to the simulation of $I$–$V$ curves. We are now interested in the transmission probability for an electron to cross the junction within a transmission energy window (defined by the applied bias) around the Fermi level. For the calculation of the full $I$–$V$ characteristics, it is often considered that the transmission spectrum calculated at equilibrium (zero bias) remains in first approximation unaltered when a bias is applied. Therefore, only this single transmission spectrum is integrated for different transmission windows to obtain the $I$–$V$ curve of a junction. This approach is generally too simplistic since the polarization of orbitals induced by the applied bias can significantly modify the electronic properties of the junction, as it will be shown below. Moreover, the pinning of the molecular orbitals with the most stable Fermi level under bias cannot be grasped without a self-consistent treatment. In this section, we discuss the transmission spectra calculated under bias from 0 V to 1.05 V by steps of 0.15 V, and integrated to obtain the current flowing across the molecular junctions.

#### Core substituents

The transmission spectra calculated at 0.90 V are shown in Fig. 7a for both the closed and open isomers together with the transmission window at 0 K characterized by Fermi–Dirac step-like statistics. The HOMO transmission peaks of the closed isomers responsible for the current keep their shape and intensity. In contrast, the HOMO peak of the open isomers under bias experiences a significant

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**Fig. 5** Plane averaged profiles of $\Delta \rho$ due to the electronic reorganization upon adsorption for the closed (up) and open (down) isomers. The two vertical reference lines correspond to the position of the interfacial gold layer and the chemisorbed sulfur atom. The photochromic core part extending between the carbon atoms bonded to the linkers is highlighted in red.

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unit, the electronic reorganization upon adsorption is similar for the reference R=H compound and upon introduction of the thiényl linker.

In the presence of the meta-phenylene linker, the MPSH HOMO of the closed form does not bear a weight on the sulfur atoms and is aligned differently with the Fermi level (at $-0.06$ eV). The first observation readily explains why the transmission peak is so narrow and indicates that the linker hybridizes in a different way with the gold surface. For the same reason, the open isomer with the meta-phenylene linker also aligns differently, i.e. at $-0.38$ eV below the Fermi level. It is, however, surprising that the meta-phenylene linker promotes an efficient transmission peak in the open form. This is, however, coherent with the shape of the MPSH orbital showing a significant weight on the sulfur atoms and delocalization throughout the conjugated pathway. Fortunately for the switch, this peak is quite low in energy and is not likely to enter the transmission window and contributes to a significant current for the open form. The meta-phenylene linker is the best shield to protect the central core, as evidenced by lower fluctuations of the charge density wave over the central part. The excess charge transferred to the central core delimited by the two carbon atoms connected to the linkers is $0.05|e|$ and $0.02|e|$ for the closed and open isomers, respectively. This transfer is equivalent to that occurring with the other linkers for the closed isomer but is reduced among the open forms.
decrease in intensity down to half the value at equilibrium. Moreover, a fraction of this broad peak is shifted outside the transmission window due to the pinning of the HOMO level of the open isomer to the lower Fermi level (i.e., the positive electrode). As a result, the current through the open isomers under bias is much lower than through their closed equivalents and significantly lower than what could have been expected from their zero-bias transmission spectra. This has a positive impact on the closed/open current ratio.

In order to shed light on the different behaviour of the isomers, we also report in Fig. 7b the MPSH orbitals associated with the main transmission peaks at 0.90 V. The shape of the MPSH HOMO orbital of the closed form is very reminiscent of that found at equilibrium and is therefore hardly modified by the electric field. Strikingly, the MPSH HOMO orbital of the open form is completely polarized towards one side of the junction. The loss of delocalization of this orbital explains the significant drop in intensity of the transmission peak. Furthermore, the strong confinement on one side of the junction promotes a larger hybridization with the gold surface which preserves the energy difference between the MPSH HOMO orbital and the most stable Fermi level under bias (Fermi pinning). These results clearly demonstrate that a fully self-consistent treatment is essential to provide a reliable description of the \( I-V \) characteristics.

The simulated \( I-V \) curves for the different photochromic cores are reported in Fig. 7c. As already discussed for the junctions at equilibrium, the different substitution patterns have nearly no impact on the shape of the \( I-V \) curves and hence on the current ratios. This is due to both: (i) the similar shape of the conducting HOMO orbital at equilibrium or under bias when varying the nature of the electroactive substituents or torsion angles in the closed and open isomers; and (ii) the Fermi pinning effect which makes the alignment insensitive to changes in the chemical potential of the compounds. Different \( I-V \) traces would be obtained by modulating in a stronger way the shape of the HOMO orbital or by changing the chemistry at the molecule–gold interface as a linker does. The current ratio decreases with a growing bias because the transmission peak of the closed form is quickly fully incorporated in the transmission

<table>
<thead>
<tr>
<th>Peak</th>
<th>H</th>
<th>( m )-Phenylene</th>
<th>( p )-Phenylene</th>
<th>Thiényl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Closed HOMO</td>
<td>180</td>
<td>&lt;3</td>
<td>147</td>
<td>189</td>
</tr>
<tr>
<td>Closed LUMO</td>
<td>177</td>
<td>12</td>
<td>66</td>
<td>72</td>
</tr>
<tr>
<td>Open HOMO</td>
<td>333</td>
<td>114</td>
<td>255</td>
<td>228</td>
</tr>
<tr>
<td>Open LUMO</td>
<td>&lt;12</td>
<td>24</td>
<td>42</td>
<td>51</td>
</tr>
</tbody>
</table>
window, leading to saturation of the current, in contrast to the broader transmission peak associated with the open form. As a consequence, we predict that the low bias regime yields a higher switching ratio for all photochromic cores without any linker. However, the strong interfacial hybridization might preclude the observation of the switching effect, thus motivating the introduction of linkers at the experimental level.

**Lateral linkers.** Fig. 8a shows the transmission spectra of the three linker-substituted derivatives under a bias of 0.90 V. The closed isomers with the para-phenylene and thienyl linkers behave like the isolated photochromic core, with a small shift of the transmission peaks associated with the different hybridization of the phenylthiol with the gold surface. The shift away from the center of the transmission window is expected to reduce the current at low bias. The transmission peaks are always governed by the HOMO level which does not polarize under bias. For the corresponding open isomers, there is a strong polarization of the HOMO level under bias which shifts the level at quite the same energies as for the isolated photochromic cores albeit with a drop in intensity. This picture is fully corroborated by the MPSH orbitals reported in Fig. 8b. The decrease in the transmission of the open isomer under bias and the conservation of a strong transmission for the closed form thus guarantee a high current ratio.

The situation is radically different for the meta-phenylene linker. The transmission peak of the HOMO level of the closed form is extremely narrow, as rationalized in the previous section, and lies outside the transmission window at 0.90 V. This translates into a very small current across the junction. The transmission peak of the open form is also centred outside the transmission window. In contrast to the other two linkers, the polarization effects are softened. A high intensity of the transmission peaks is observed, which is fully supported by the MPSH analysis that features an orbital still delocalized over both sides of the junction. The meta-phenylene linker is thus acting as a shield against charge reorganization due to interfacial hybridization effects and against polarization effects under bias. However, this linker is not an attractive candidate for molecular switches since: (i) it creates a large contact resistance, hence smaller current, by reducing hybridization...
effects at the interface and; (ii) it reduces the polarization effects that are favourable for high current ratios.

The previous considerations allow us to readily understand the $I-V$ curves and $I-V$ ratios plotted in Fig. 8c. The calculated current for a para-phenylene or thienyl linker is about the same as that of the reference compound for the closed isomer, whereas the amplitude is reduced by one order of magnitude for the open isomers. This translates into ON/OFF ratios of order 10$^2$ that are one order of magnitude larger than for the photochromic core without a linker. On the other hand, the meta-phenylene linker generates a current two to three orders of magnitude lower for both isomers with similar performance compared to the reference photochromic core. Since the HOMO level is outside the transmission window with the meta-phenylene linker, the switching mechanism does not rely on different shapes of the HOMO orbital under bias but rather on subtle difference in the energy level alignment. The energy alignment might be further affected by the nature of the anchoring site and by the choice of the theoretical approach which is expected to modulate less the extent of polarization effects. Moreover, the poor performance predicted in the coherent regime and the strong decoupling might open the way to other charge transport mechanisms, for instance a Coulomb blockade regime.

Some experimental results have been published for the linker-substituted isomers involved in our theoretical study.$^{11,12,18}$ In mechanical break junctions based on gold electrodes, the thienyl-based compound gave a ratio one order of magnitude higher than in our calculations due to a smaller measured current in the open form. A similar ratio (≈ 10$^2$) is obtained theoretically and experimentally for the para-phenylene linker anchored on a gold surface and probed by a gold STM tip, although the calculated current is two orders of magnitude higher. The meta-phenylene linker has been used in large area junctions with a gold-dithienylethene–PEDOT/PSS–gold architecture, leading to a switching ratio of one order of magnitude. The nature of the interface with the PEDOT–PSS layer is, however, far from being understood$^{62}$ and the number of bad contacts and non-switching molecules in the junction is difficult to estimate. The lack of a unique experimental protocol and the ill-defined nature of fabricated junctions make it very difficult to critically compare theory and experiment at this stage. This further motivates theoretical calculations on well-defined architectures to better assist the interpretation of the experimental curves as well as measurements on several functional compounds using strictly the same experimental protocol. However, it is worth stressing that the experimental and calculated current ratios are generally in good quantitative agreement.
agreement and that the calculations do shed light on the (ir)reversibility of the switching observed experimentally.

D. Concluding remarks

We have reported transmission spectra and I–V characteristics calculated at a fully self-consistent level for a series of molecular junctions incorporating dithienylethene photochromic cores. We have modified the central part by substituents or the lateral linkers in search of design rules for reversible molecular switches with a high ON/OFF ratio.

Interestingly, it is the HOMO level that aligns in the same way in the vicinity of the Fermi level of the electrodes, irrespective of the chemical potential of the core-substituted isolated molecules that can be quite different, hence pointing to Fermi level pinning. Consequently, derivatization does not alter the shape of the transmission peak responsible for conductivity since the shape of the HOMO is not modified by the electroactive substituents.

The pinning effect is established via an interfacial charge transfer from the electrode to the adjacent S–C bond. The amplitude of charge transfer correlates with the chemical potential of the isolated molecules. Two bond dipoles are actually created on each side of the junction shifting up the central electrostatic potential between the contacts and dictating the final alignment of the molecular levels with the Fermi level of the electrodes. Larger interface dipoles for molecules with lowering MOs are responsible for the similar energy level alignment of a series of molecules with different frontier MO energies. On the other hand, different alignments of the HOMO transmission peak can be triggered by changing the electronic reorganization at the interface, for instance by introducing a phenyl-thiol unit in a linker instead of a thienylthiol unit. The present results thus demonstrate that the design of molecules for the fabrication of functional molecular junctions cannot be limited to the sole consideration of the isolated molecules.

An intense transmission peak requires both good hybridization between the anchoring part of the molecule and the gold surface and a well delocalized orbital with a significant electronic density all along the backbone (as revealed by MPSH analysis). These two conditions do not necessarily go hand in hand: the degree of hybridization of the HOMO was found to be systematically higher for the lower conducting open isomers.

The introduction of linkers limits the extent of electronic reorganization over the central photochromic core upon adsorption. In addition, the meta-phenylene linker breaks the communication between the core and the gold electrodes, which is of interest for the reversibility of the switching process but not beneficial for a high current across the junction.

We suggest that a sensible way to further improve the current ratio performance of the photoswitches is to modulate the nature of the linker and the anchoring group or to vary in a more significant way the molecular topology of the central core to yield HOMO levels with a distinctively new orbital pattern.

Under bias, the HOMO transmission peaks of the closed and open isomers behave in a very different way for most of the derivatives under study. A strong electronic polarization of the HOMO takes place in the open form, as evidenced by the MPSH analysis, and drastically reduces the intensity of the transmission peak. On the other hand, the shape of the HOMO level and hence the intensity of the transmission peak are preserved in the closed form. This polarization effect is crucial for the actual ON/OFF current ratio of the junction and cannot be properly taken into account in calculations that are not fully self-consistent. The introduction of thiényl or para-phenylene linkers generates a drop in the intensity of the HOMO transmission peak by one order of magnitude in the open form leading to a large exaltation of the ON/OFF ratio (~10^2). A meta-phenylene linker, in contrast, shields the open isomer against polarization and promotes both very small currents and low ON/OFF ratios. In contrast to the pronounced linker effect, all substitutions considered for the central photochromic core yield identical I–V characteristics.

The invariability of the electrical behaviour of the junction upon chemical modifications of the photochromic molecule provides freedom to improve properties such as stability or fatigue resistance without changing the ON/OFF ratios for the devices.

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Notes and references

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