

# Challenges for Incorporating Optical Switchability in Organic-Based Electronic Devices

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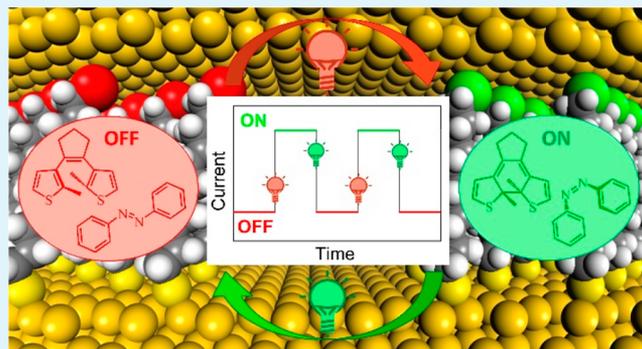
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**ABSTRACT:** Transistors operate by controlling the current flowing from a source to a drain electrode via a third electrode (gate), thus giving access to a binary treatment (ON/OFF or 0/1) of the signal currently exploited in microelectronics. Introducing a second independent lever to modulate the current would allow for more complex logic functions amenable to a single electronic component and hence to new opportunities for advanced electrical signal processing. One avenue is to add this second dimension with light by incorporating photochromic molecules in current organic-based electronic devices. In this Spotlight, we describe different concepts that have been implemented in organic thin films and in molecular junctions as well as some pitfalls that have been highlighted thanks to theoretical modeling.

**KEYWORDS:** *molecular switches, azobenzene, diarylethene, self-assembled monolayers, molecular junctions*



## 1. INTRODUCTION

Photochromic molecules have been developed a long time ago in several research areas to trigger changes in electronic and optical properties via photoinduced isomerization processes generating at least two bistable states.<sup>1–4</sup> They have been initially extensively used to modulate optical properties, as they do naturally to govern the mechanisms of vision, and were shown to be able to tune the transmittance and reflectance of thin films, with interesting outcomes for optical data storage.<sup>5</sup> The switching can also modulate the fluorescence properties of single molecules or that of blends by changing the efficiency of energy transfer processes as a function of the state of the switch.<sup>6</sup> Such molecular switches have also deeply impacted the field of supramolecular chemistry at the nanoscale, leading, in particular, to the design of molecular machines awarded by the Nobel Prize in Chemistry in 2016.<sup>7,8</sup> Although a plethora of photochromic chemical compounds have been synthesized over the years,<sup>9</sup> we will focus here on two representative examples involved in most recent studies in the field of organic and molecular electronics.

The first type of molecular switch under scrutiny, still the most studied in literature, is based on the azobenzene core.<sup>10</sup> This molecule is made of two phenylene rings connected by a double N–N bond (i.e., the azo group) and adopts two different isomers (*cis* vs *trans*). The *trans* form can be converted into the metastable *cis* form (less stable by ~50 kJ/mol compared to the *trans* form) under an illumination in the UV range, while the back conversion can be induced by an

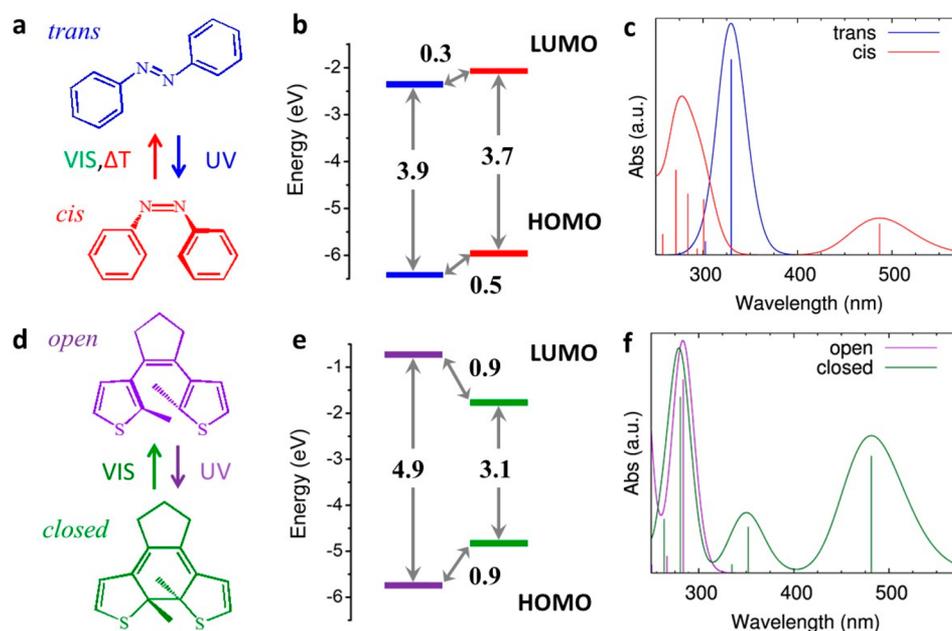
illumination in the visible or upon heating (Figure 1a).<sup>11</sup> The dynamics of the isomerization processes<sup>12</sup> as well as the stability (and hence lifetime) of the metastable *cis* form<sup>13,14</sup> can be modulated by functionalizing the azobenzene core. These derivatives undergo severe structural changes upon isomerization, since the length of the molecule evolves from 9 Å down to 5.5 Å going from the *trans* to the *cis* form; a strong loss of planarity also takes place in the *cis* form in order to limit the steric hindrance between the two adjacent phenylene rings. In turn, these structural changes strongly impact the electronic and optical properties of the molecule. Figure 1b,c illustrates the evolution of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) level energies together with the changes in the optical absorption spectrum between the two forms, as calculated at the Time-Dependent Density Functional Theory (TD-DFT) level. In close similarity with the typical experimental trends,<sup>12</sup> the *trans* form exhibits an intense optical band around 350 nm, which disappears in the *cis* form to yield a smaller band at higher energy and a weak absorption band around 450 nm assigned to an  $n \rightarrow \pi^*$  transition; note

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**Figure 1.** Chemical structures (a, d), one-electron energy diagram (b, e), and simulated absorption spectra (c, f) for the two isomeric forms of azobenzene and diarylethene molecules, respectively. The (TD)-DFT calculations were performed at the B3LYP/6-311G(d) level<sup>24</sup> of theory within the Gaussian 16 package.<sup>25</sup>

that this transition between orbitals lying in perpendicular planes is forbidden in the *trans* geometry (see Figure 1c). Interestingly, the electronic (HOMO–LUMO) gap is moderately increased by  $\sim 0.2$  eV (with a larger stabilization for the HOMO level of 0.5 eV compared to that of the LUMO level amounting to 0.3 eV) when moving from the *cis* to *trans* form, as illustrated in Figure 1b. Several azobenzene moieties can also be coupled within the same molecule, yielding many complex architectures owing to multiple (more than two) stationary states.<sup>15–17</sup> One illustrative example of such multiazobenzene architectures is the C3-symmetric star-shaped compounds, where three azobenzene branches are connected to a central phenyl core via a *meta* substitution.<sup>18–23</sup>

Ultrafast spectroscopy measurements proved very useful to shed light on the photoisomerization kinetics of photochromic molecules and the role of their surrounding environment. For instance, azobenzenes immersed in a tight packing configuration such as in a polymer matrix exhibited excited-state lifetimes that are  $\sim 20$  times larger with respect to the values reported in solution.<sup>26</sup> In contrast, when they are attached to gold nanoparticles and, thus, embedded in a less dense environment, they displayed a dynamics similar to that in solution.<sup>27</sup> In this regard, a recent study reported a large decay of the photoisomerization kinetics when moving from isolated to two-dimensional (2D) and three-dimensional (3D) geometries, yielding excited-state lifetimes that range from a few picoseconds for the azobenzenes in solution to tens of minutes when they are assembled in 3D crystals.<sup>28</sup>

The second family of widely studied molecules relies on a diarylethene (DAE) core involving typically two phenylene or thiophene rings connected by a double C–C bond,<sup>29</sup> see Figure 1d. The isomerization proceeds here via a ring-closure reaction from an *open* form to a metastable *closed* form. The structural changes are rather minimal, keeping unaffected the length of the molecule; however, they do strongly impact the electronic properties by creating a fully conjugated path in the

*closed* form, while only the three central C–C double bonds are conjugated in the *open* form. As a result, the HOMO [LUMO] level of the *open* form is stabilized [destabilized] by as much as 0.9 eV compared to the *closed* form, leading to an increase in the electronic gap by 1.8 eV (see Figure 1e). In addition to a minimal structural relaxation, another advantage of the DAE core is the ease of modulation of the energy of the frontier electronic levels by a chemical derivatization.<sup>30,31</sup> In absorption spectra, the lowest intense optical band around 300 nm characteristic of the *open* form is replaced by a new intense band around 550 nm in the *closed* form, see DFT results in Figure 1f. The design of molecular switches for practical applications requires extensive studies to find the best candidates, which should maximize the stability and lifetime of the metastable form and the cyclability of the isomerization process (also referred to as the fatigue resistance) by limiting the amount of byproducts formed.<sup>32,33</sup> An attractive feature of DAE and azobenzene derivatives is their high fatigue resistance, since they can survive up to  $10^4$  switching cycles in solution and crystalline phases.<sup>1,34,35</sup> Such optimization and selection procedures have not been yet fully achieved for optoelectronic device applications typically exploiting so far well-characterized prototypical molecules.

In the next Sections, we will describe different strategies to translate an optical stimulus into measurable changes in device electrical properties by encompassing switches in the bulk of organic layers, at interfaces, or when inserted in molecular junctions. We do not intend here to provide a comprehensive description of the domain but rather to highlight some representative studies.

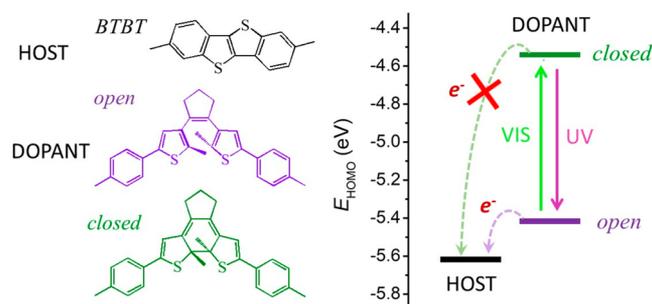
## 2. MOLECULAR SWITCHES IN THE BULK

Changes upon illumination in the electrical conductivity of organic layers made of photochromic molecules or molecular structures containing a switchable building block<sup>36</sup> have been reported both in diode and transistor configurations. This

switching is triggered by changes in the delocalization and energy of the frontier electronic levels, impacting in turn the charge injection and charge transport processes.<sup>37,38</sup> If the lifetime of the metastable state is long, the devices can also be used as memory elements, since information (the current amplitude) can be written by selecting a specific conformer, read in a given state (with stability over one week reported), and erased by converting the molecules into their other isomeric form;<sup>39</sup> the advantage here is that the reading process is not expected to change the state of the switch, as might happen with optical storage and readout. Thin films made of photochromic layers have been used as transducing layers in light-emitting devices to tune the current density flowing across the device and hence the intensity of the light emitted.<sup>40</sup> The photoconversion of the neutral spiropyrane into the charge-separated merocyanine form has also been exploited in the dielectric layer of a transistor as a remote control to tune the current flowing in the channel via electrostatic gating;<sup>41</sup> a similar effect was observed with an intermediate layer of azobenzene derivatives on top of the dielectric layer.<sup>42</sup>

Although an increase by several orders of magnitude of the electrical conductivity has been reported upon the illumination of organic layers containing photochromic molecules, it must be realized that the conductivity values involved are often very low, especially with highly twisted mesomeric forms typically behaving as a quasi-insulating layer ( $\sigma < 10^{-7}$  S/cm in ref 36 involving chromene as molecular switch) for both states of the switch. Optimizing charge transport in layers made of photochromic molecules actually proves very challenging in view of the intrinsic contradiction that high charge mobilities require a high degree of order and a high packing density to promote close contacts between molecules,<sup>43</sup> whereas photochromic molecules typically need space to switch from one mesomeric form to another.

This has motivated the idea of introducing the photochromic molecules as dopants in a matrix with good transport properties or by attaching them covalently to a conjugated backbone.<sup>44</sup> A possible role of such a dopant is to increase the amount of energetic disorder in a reversible way, as achieved via electrostatic effects by using the neutral spiropyrane-zwitterionic merocyanine couple.<sup>45,46</sup> Alternatively, one can find the best matching partners so that the HOMO of the host lies ideally between the HOMO characteristic of the two isomeric forms of the switch. When the HOMO of the dopant lies above that of the matrix, it acts as a trap for hole carriers. On the one hand, such traps are going to reduce the density of holes available for transport and are also expected to lower the hole mobility; indeed, it is more challenging for a hole to find a percolation pathway in a medium filled with fixed electrostatically repulsive charges. Note that the LUMO level of one of the dopant isomeric forms can act as well as trap for electron carriers.<sup>47</sup> On the other hand, the impact of the dopant is much more limited when its HOMO level lies below that of the matrix; in that case, the dopant acts as a scattering center (since there is an energy barrier to occupy the HOMO of the dopant) that can be easily circumvented by finding another transport path, provided that the transport is not strictly one-dimensional (1D). The same principle holds true when the HOMO level of the dopant acts as a shallow trap in one form and as a deep trap in the other form, see Figure 2. This concept is illustrated by studies in which neutral photochromic molecules have been dispersed in a conjugated polymer matrix, leading to a variation in the current density (i.e., ON/OFF



**Figure 2.** Chemical structures (left) and HOMO trapping mechanism (right) for a system consisting of 2,7-dialkyl-benzothieno(3,2-b)benzothiophene (BTBT) molecules acting as a host matrix and a DAE molecule used as switching dopant, as investigated in ref 54. The dopant promotes here shallow traps in the *open* form and deep traps in the *closed* form.<sup>54</sup> The HOMO energies of the isolated molecules have been estimated in the gas phase by means of DFT calculations performed at the B3LYP/6-311G(d) level,<sup>24</sup> as implemented in the Gaussian 16 suite package.<sup>25</sup>

ratio) of  $\sim 2$  orders of magnitude;<sup>48–50</sup> compared to layers made only of photochromic molecules, the ON/OFF ratio thus appears to be significantly reduced when the molecular switches are incorporated in a matrix with good transport properties in the pristine state, although we can now switch between two different conducting states. However, there is room for improvement, since several factors can be responsible for the limited variations: (i) some isomers in their metastable state can be converted back thermally in the operating device; (ii) some photochromic molecules do not have simply enough space to isomerize in the solid state; for the sake of illustration, it was estimated in ref 48 dealing with spiro-based switches dispersed in a conjugated polymer matrix that one over 1500 dopant was actually active in switching the current density; and (iii) there is a poor dispersion of the dopants in the matrix and the formation of clusters, thus resulting in phase-segregated regions.<sup>51</sup> Note also that the pristine conductivity values can be already lowered by the introduction of the dopants due to a perturbation of the host packing, which scales with the rate of loading; interestingly, in partly crystalline polymer samples, the dopants do not perturb significantly charge transport by concentrating principally in the amorphous region<sup>49</sup> or by lying in the regions formed by saturated chains of polymers instead of being inserted between conjugated cores.<sup>46</sup> A deep analysis of the complex interplay between energy landscape and film microstructure has recently opened the way to ON/OFF ratio up to  $10^3$  combined with high hole mobility in the pristine state for polymers doped with DAE-based compounds.<sup>52</sup> We emphasize before concluding this section that dopants can also be introduced in matrices to modulate the photoconductive properties of transistors under continuous illumination, such as the rise time and relaxation time of the photogenerated charge carriers.<sup>53</sup>

### 3. PHOTOCROMIC MOLECULES AT INTERFACES

Instead of diluting the photochromic compounds into a matrix, another possibility is to use them in an interfacial layer to modulate the efficiency of charge injection from metallic contacts into active layers. This can be achieved by introducing a thin layer made of photochromic molecules next to an electrode in which charges are first injected and relaxed into polarons.<sup>38</sup> The current density can be amplified upon

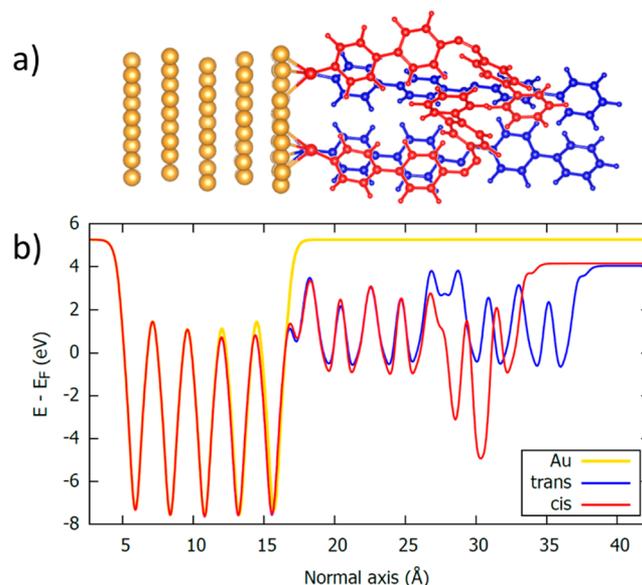
illumination with DAE molecules by switching *open* forms into *closed* ones, which reduce the barriers for charge injection due to their lower electronic gap; however, a small degree of isomerization can prove detrimental to the device by making the *closed* forms act as traps within a matrix dominated by the *open* forms. Another elegant strategy onto which we will dwell more hereafter is to tune the efficiency of a charge carrier injection by changing in a reversible way the work function of the metal by depositing a switchable self-assembled monolayer (SAM) through which charges tunnel from the electrode to the active organic layer with an efficiency depending on the thickness of the tunnel barrier and the availability of electronic levels of the SAM-forming molecules close to the Fermi level of the electrodes.

SAMs are made of a two-dimensional array of closely packed molecules chemisorbed on a metallic or oxide substrate via proper anchoring groups and thus stand upright to favor intermolecular interactions.<sup>55,56</sup> They are widely exploited in transistors to modulate the work function of metallic electrodes in order to minimize the charge injection barriers (defined as the energy difference between the work function and the HOMO [LUMO] level of the molecules in the organic layer for hole [electron] injection).<sup>57,58</sup> The shift of the work function is triggered by the introduction of a dipole moment at the interface, built from two quasi-independent contributions: (i) the dipole supported by the SAM-forming molecules; and (ii) the dipole resulting from the grafting of the anchoring group on the surface (also referred to as the bond dipole).<sup>59</sup> In turn, the bond dipole can be casted down in two contributions originating from (i) the modification of the surface dipole intrinsic to any bare metallic surface upon deposition of the SAMs (the so-called pillow effect)<sup>60</sup> and (ii) the electronic reorganization at the metal/organic interface upon chemisorption, which does not necessarily imply a net charge transfer between the two components. A third possible term arises from the reconstruction of the surface upon an SAM deposition, which is generally small for metals but can be more pronounced for metal oxide surfaces.<sup>61</sup> According to the classical Helmholtz equation, the total work function shift can be expressed as

$$\Delta\phi = \frac{\mu_{\perp}}{\epsilon_0 S} \quad (1)$$

with  $\mu_{\perp}$  being the dipole moment perpendicular to the surface associated with one molecule and  $S$  being the surface occupied by this molecule. The total work function shift can be readily measured by ultraviolet photoelectron spectroscopy (UPS)<sup>62</sup> and can also be routinely calculated at the density functional theory (DFT) level using a slab approach (i.e., a unit cell made of a few layers replicated in two dimensions, as depicted in Figure 3a).<sup>63,64</sup> It is worth stressing that the dipole appearing in eq 1 includes the contributions of both the molecule (SAM) and associated bond dipole. The molecular contribution does not readily correspond to the dipole that could be computed for a molecule in the gas phase; indeed, the charge distribution of a given polar molecule is always significantly perturbed by the presence of adjacent molecules, leading typically to a pronounced decrease in the individual dipole moment from the gas phase to the SAM (typically referred to as depolarization effects).<sup>65–67</sup>

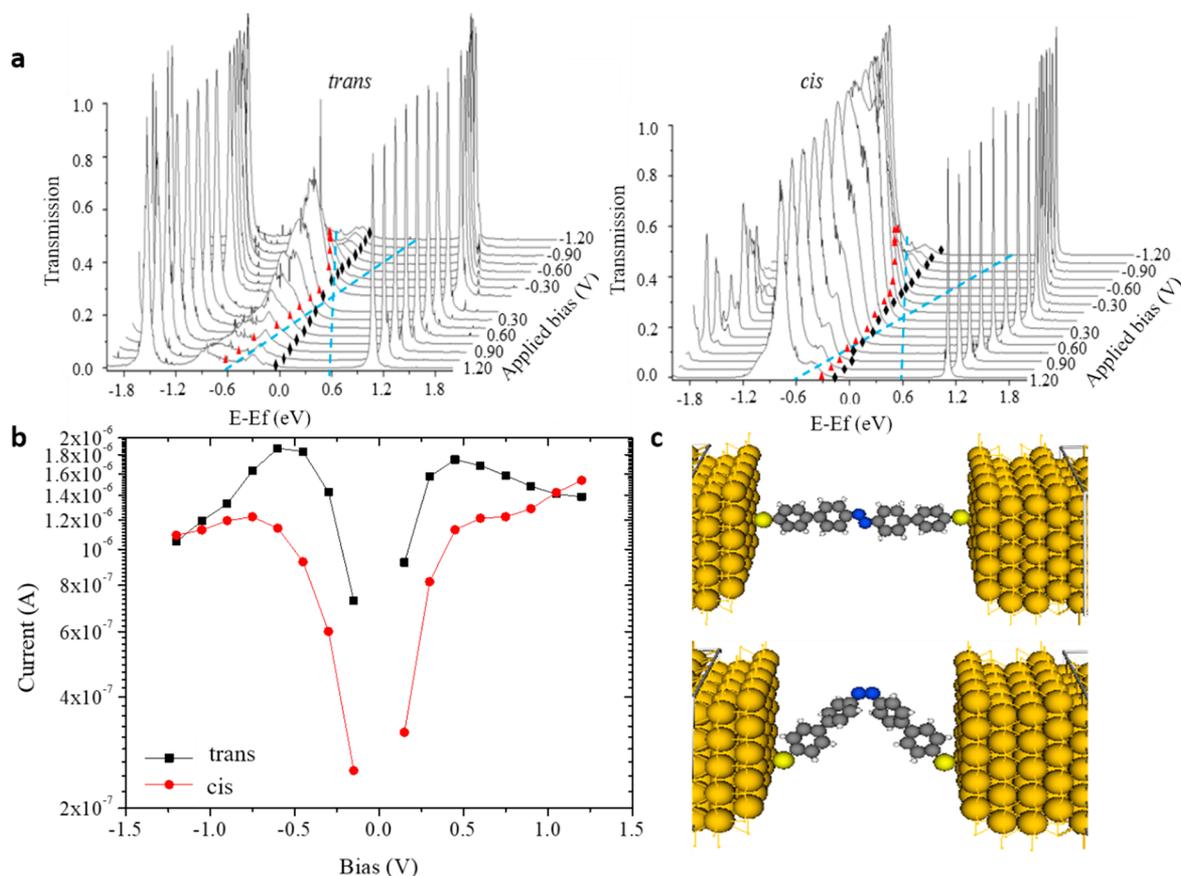
Since the work function shift is intimately connected to the surface dipole, there is an interest here to deposit SAMs based on photochromic molecules in order to promote a dynamical



**Figure 3.** (a) Lateral view of the slab models employed to compute the electronic properties of the biphenyl azobenzene SAMs attached to the Au(111) surface; and (b) corresponding plane-averaged potential profiles along the normal direction to the surface for the Au slab (yellow) and Au-SAMs in both *trans* (blue) and *cis* (red) forms. All details related with the slab models and computational parameters can be found in ref 70.

control by light of charge injection barriers in devices. The prerequisite is to find switches whose isomeric forms exhibit significantly different dipole moments. Another constraint is to make sure that a large fraction of molecules can switch in the SAMs; note that the switching can also be facilitated by forming mixed SAMs containing the azobenzene moieties and saturated chains.<sup>68</sup> Azobenzene derivatives appear to be good candidates fulfilling these requirements. As a matter of fact, the dipole of azobenzene in the gas phase is calculated at the DFT level (B3LYP/6-31G\*\*) to be 5.30 D in the *trans* form and 2.81 D in the *cis* form. Moreover, it has been shown by scanning tunneling microscopy (STM) imaging that entire crystalline domains made of azobenzene derivatives can be switched on a surface due to collective effects, with photoisomerization yields approaching 100%.<sup>69</sup> This has stimulated a series of recent studies to probe by UPS or kelvin probe force microscopy (KPFM) the change in the work function of a gold electrode covered by an SAM made of azobenzene derivatives upon illumination.<sup>70–73</sup> Rather disappointingly, these measurements pointed to moderate changes in the work function (typically between 100 and 200 meV) rationalized theoretically by the fact that the dipole moment of the two forms is depolarized by a different extent, leading finally to similar values in the SAM (see values of the averaged potential at the right side of Figure 3b); in other words, the larger the dipole moment, the larger the amplitude of the depolarization effects leading to a global compensation.<sup>74,75</sup> Similarly, a moderate work function modification upon irradiation (50 meV) was measured in the case of DAE-based SAMs grafted to a gold surface.<sup>76</sup>

Switchable SAMs based on azobenzene derivatives were successfully used in transistors to modulate the source-drain current and the threshold voltage. The better device performance obtained with the *cis* form is, however, not attributed to



**Figure 4.** (a) Voltage-dependent transmission spectra for a biphenyl azobenzene molecular junction, for both *trans* (left) and *cis* (right) forms. Black diamonds (red triangles) depict the evolution of the HOMO (HOMO–1) energy; (b) corresponding  $I/V$  curves and (c) structures of the junctions. For a detailed description of the computational methodology, see ref 94.

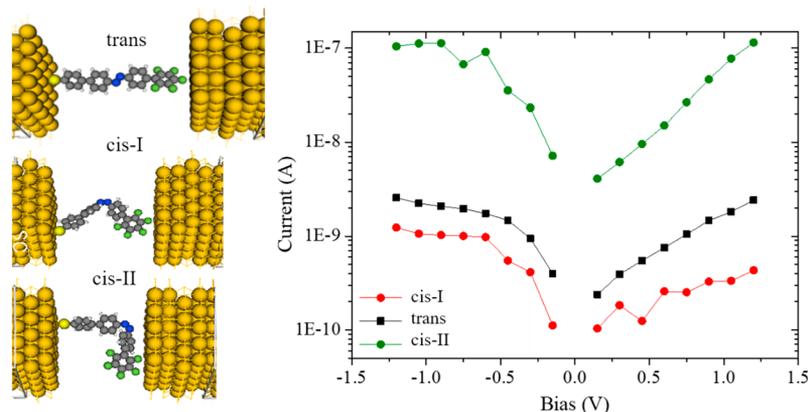
the change in the metal work function upon illumination but rather to the change in the SAM thickness and, hence, in the tunneling resistance associated with charge injection,<sup>77</sup> as further supported by STM measurements.<sup>78</sup> The same concept was exploited by the dispersion in a polythiophene matrix of gold nanoparticles decorated with azobenzene moieties; the latter act as switchable traps as a function of the isomeric form of the molecular switch by dictating the tunneling barrier into the nanoparticles.<sup>79</sup> Along the same vein, optical switching was also reported for a two-dimensional lattice made of gold nanoparticles connected by diarylethene switches.<sup>80</sup> The device characteristics can also be switched by using hybrid dielectric layers made of a photoactive SAM grafted on an oxide layer.<sup>81</sup> An optical switch in the charge carrier density has also been reported in a transistor based on a graphene sheet chemically functionalized by azobenzene groups.<sup>82</sup>

All switchable interfaces discussed so far consist of photochromic molecules covalently bonded to a substrate that is acting as electrode. However, molecular switches can be also adsorbed flat on a given surface via noncovalent forces (via a physisorption driven by electrostatic,  $\pi$ – $\pi$ , and van der Waals interactions). Although the switchable assemblies are less stable under working conditions with respect to the covalently bound structures, this strategy is of particular interest in the case of 2D materials (such as graphene, transition-metal dichalcogenides, etc.), since they offer the advantage of preserving the crystalline structure of the underlying material and its unique optoelectronic properties.<sup>83</sup> In this respect, both

azobenzene<sup>84</sup> and diarylethene<sup>85</sup> molecules have been successfully employed to modulate the current density of 2D materials upon illumination in devices via such as nonbonded photochromic interfaces. Interestingly, the use of switchable multichromophoric compounds has recently given access to the dynamic control of molecular pattern on surfaces, which could be exploited for light-triggered host–guest interactions.<sup>22,86</sup>

#### 4. PHOTOCROMIC MOLECULES IN JUNCTIONS

The field of molecular electronics aims at inserting between two electrodes single molecules or, more realistically for applications, self-assembled monolayers in order to define an electrical function. The simplest is to use the molecules as a conducting wire by a proper tailoring of the molecular topology and size in order to minimize the charge injection barriers and hence maximize the transmission probability across the junction. There is of course an interest to go beyond<sup>87</sup> and introduce other functionalities, such as diode behavior with a high rectification ratio (defined as  $R = I(V)/I(-V)$ ) and a large current when a forward bias is applied. To do so, many strategies rely on the asymmetrization of the interfacial contacts (by promoting, for instance, a chemisorption on one side and a van der Waals contact on the other side), typically accompanied by the drop in the current density compared to junctions featuring a covalent anchoring of the molecule at the two interfaces.<sup>88</sup> Switching of the current can be achieved by fabricating transistors at the molecular scale.<sup>89</sup>



**Figure 5.**  $I/V$  curves for a fluorinated azobenzene junction. Two different *cis* orientations were considered: *cis*-I with the anchored segment tilted with respect to the plane of the gold electrode planes and *cis*-II where it lies perpendicular to the electrode. The computational parameters employed for these calculations are collected in ref 94.

Another strategy is to introduce photochromic molecules in two-terminal devices to switch the amplitude of the current upon illumination<sup>90</sup> or electrochemical triggering.<sup>91</sup> Instead of switching fast the current, the light input could also be used to store information for memory applications.<sup>92</sup> We will describe in the following the recent advances made by introducing azobenzene- and DAE-based molecules in optically addressable junctions.

Many experimental studies have been performed on junctions containing azobenzene units, although these are not the most ideal candidates. Indeed, as mentioned before, the photoisomerization is accompanied by a pronounced shrinking of the molecular size, thus requiring in turn a reduction of the nanogap to maintain the interfacial contacts; the introduction of a flexible saturated spacer between the molecule and the electrodes can help to cope with such deep structural variations.<sup>93</sup> Assessing whether the *cis* or *trans* form yields the larger current led to very contradictory results in the literature.<sup>94</sup> For instance, two separate studies showed by conducting atomic force microscopy (AFM) that a larger conductance is found for the *cis* isomer when the molecules are physisorbed on one gold electrode and attached by a sulfur atom at the other,<sup>95,96</sup> in contrast to the theoretical prediction made with chemisorbed contacts.<sup>97</sup> This demonstrates that the  $I/V$  characteristics are highly sensitive to the nature of the interfacial contact (chemisorption vs physisorption) and the nature of the contact geometry (such as the actual tilt angle of the molecule with respect to the surface that controls the hybridization between the orbitals of the two components); note that the actual conformation of the molecule in the junction is also a tributary of the degree of coverage of the surface.

Theory can prove here very useful to shed light on this issue by modeling the  $I/V$  curves of geometrically well-defined junctions. Such simulations are now done routinely at the DFT level (coupled with a Non-Equilibrium Green's Function (NEGF) formalism) in a coherent regime implying an absence of nuclear relaxation when the charge transits over the molecular backbone. Nevertheless, one must be aware that these calculations are not expected to depict the  $I/V$  curves in absolute values due to the inherent limitations of the approach but do provide reliable trends to help in the interpretation of experimental data; moreover, this formalism fails in the presence of long chains when charge (incoherent) hopping

becomes the main transport mechanism across the junction.<sup>98</sup> For the sake of illustration, Figure 4 displays the voltage-dependent transmission spectra of a junction containing a biphenyl azobenzene molecule, in the *trans* versus *cis* form, attached covalently by a sulfur atom to two gold electrodes; the corresponding  $I/V$  curves are also reported.

In both cases, there is an intense transmission peak close to the Fermi level originating from occupied levels, thus indicating that electron transmission occurs through the tail of the hybridized molecular HOMO level. A striking difference is that the tail of this transmission peak quickly enters into the bias window with an increasing voltage for the *trans* form, while this effect is delayed to higher voltages for the *cis* form. As a result, the *trans* form is much more conductive than the *cis* form for a given bias, leading to an ON/OFF ratio of  $\sim 1$  order of magnitude. When a van der Waals contact is promoted at one side of the junction, we systematically find a significant drop in the current density and an ON/OFF ratio that is strongly dependent on the actual layout of the molecule in the junction. This is theoretically exemplified in Figure 5 for a fluorinated azobenzene derivative featuring a current for the *cis* form intimately linked to the configuration assumed for the molecule. Interestingly, the current calculated for the *cis* form is larger than that of the *trans* form for configuration II minimizing the size of the nanogap, as rationalized by the fact that the current decays exponentially with distance in the coherent regime.

Another interesting design reported in ref 99 is to have the azobenzene unit lying transversely to the conjugated backbone in single-molecule junction and to exploit the photoisomerization as an optical gating effect.<sup>99</sup> Along the same line, a photomechanical switch was designed by clipping an azobenzene core to an oligothiophene-based molecular backbone; the idea is here to modulate the current by disrupting the conjugation of the molecular wire via a photoisomerisation of the attached azobenzene unit.<sup>100</sup> All previous considerations deal with molecules stretched along the nanogap in order to connect the two metallic tips in single-molecule junctions or to favor intermolecular interactions in SAMs. In contrast, the azobenzene molecules are expected to lie flat on a substrate at low degree of coverage. This does not prevent switching events to be observed, as reported in a recent study contacting the deposited molecules by an STM tip.<sup>101</sup>

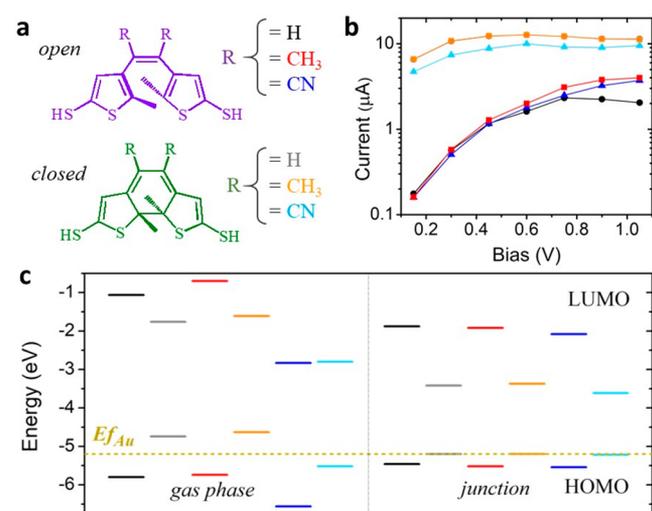
A major hurdle when attaching the molecular switch covalently to the two electrodes is the competition between the photoisomerization process and the quenching of the excitation by the metal contacts. This is the reason for which the initial experimental studies on DAE showed a *closed* to *open* conversion but not the reverse process.<sup>102</sup> This can be circumvented by introducing on each side a short conjugated linker with a meta connection to break the conjugation and decouple the DAE core from the electrodes.<sup>103</sup> Nevertheless, the measured ON/OFF ratio (i.e., the ratio of the current between the *closed* vs *open* form) turned out to be relatively small ( $\sim 3$ – $4$ ); a similar concept has also been exploited in single-molecule junctions.<sup>104</sup> A photomodulable transport was also reported for a conjugated organometallic wire incorporating a central DAE unit, with a reversible ON/OFF ratio of  $\sim 1$  order of magnitude.<sup>105</sup> Another strategy is to introduce a short saturated spacer, as achieved in single-molecule junctions including a DAE core connected to two graphene electrodes and yielding an ON/OFF ratio close to 100 and good cyclability.<sup>106</sup>

Intuitively, one could expect modulating the ON/OFF ratio by modifying the electronic structure of the DAE core, for instance, by attaching electroactive substituents on the central double bond. When checking this hypothesis at the theoretical level for a bare dithienylethene core, we do observe a strong variation in the energy of the HOMO and LUMO levels of the isolated molecular switch upon substitution. Surprisingly, when all these derivatives are inserted into a single-molecule junction, we end up with the same energy-level alignment of the molecular orbitals with respect to the Fermi level of the electrodes, and hence to similar  $I/V$  curves and ON/OFF ratio, as it has been represented in Figure 6.<sup>107</sup> This points to a pronounced Fermi level pinning, which can wipe out a design strategy elaborated in solution. When a single molecule is inserted into the junction, the pinning effect originates from a change in the amplitude of the interface dipole at both

electrodes as a function of the energy of the HOMO level of the isolated molecule; the deeper the HOMO level, the larger the interface dipole. This originates from the strong hybridization between the molecular HOMO level and the orbitals of the electrodes, leading to a significant broadening of the HOMO level. To reach an equilibrium via an equalization of the chemical potentials of the molecule and of the electrodes, a charge reorganization process occurs at the metal-molecule interfaces, leading to interface dipoles. Those dipoles shift the electrostatic potential in the molecular region until they accommodate the energy shifts observed in the gas phase upon substitution. In turn, the HOMO energy level is pinned inside the junction and thus becomes rather insensitive to chemical derivatization (see Figure 6c). This pinning effect can be strongly weakened by the introduction of a spacer allowing to decouple electronically the two components (for instance, with a saturated chain or a conjugated spacer with a meta connection), though always at the expense of the current density.<sup>108</sup>

Interestingly, when SAMs made of the same molecules are sandwiched between the two electrodes, there is no change in the interfacial dipole strength as a function of the chemical substitution. Collective electrostatic effects linked to the presence of many local dipoles come into play here, making the vacuum levels defined on each side of the layers inherently different from the isolated molecule scenario; the impact of substituents can be completely screened versus one or each of those vacuum levels.<sup>109</sup> This makes again the energy-level alignment almost unaffected. Note that the same behavior is observed for dense SAMs made of small conjugated oligomers, with a given conjugated core decorated by different electroactive substituents.<sup>63</sup> Decoupling between the metal and the photochromic molecules can also be exploited in SAMs to promote the same evolution of the electronic structure upon photoisomerization in solution or upon grafting on a substrate, as exemplified for DAE-based molecules grafted on ZnO<sup>61</sup> and indium tin oxide (ITO)<sup>110</sup> with a methylene unit as spacer or attached to Au substrates by means of a phenylene bridge.<sup>111</sup>

In most of the experimental studies, the ON/OFF ratio does not exceed a typical factor of 100. A new avenue recently explored is to increase the number of layers between the two electrodes and investigate the electronic properties of thin layers of  $\sim 10$  nm in thickness. In doing so, an ON/OFF ratio of up to 400 was recently obtained for diarylethene oligomers.<sup>112</sup>



**Figure 6.** (a) Chemical structures of substituted DAE molecules for both *open* and *closed* forms; (b) simulated  $I/V$  curves for these systems sandwiched between two Au(111) electrodes; and (c) corresponding frontier molecular orbital energies in the gas phase (left) and in the Au/DAE/Au junction (right). The Au electrode Fermi level energy is depicted by a horizontal dashed line. More technical details about the calculations are given in ref 107.

## 5. CONCLUSIONS AND PERSPECTIVES

Using light as an external stimulus to trigger changes in electrical currents in organic-based devices is an avenue of high technological interest toward multifunctional logic devices. However, this road is paved with many hurdles to reach the significant current variations needed for practical applications. In condensed media, the first requirement is structural in nature and is to make sure that the molecules have enough space to switch; promisingly, domino-like collective switching is known to occur in ordered monolayers. When used as dopants in a matrix or when using mixed SAMs, the clustering of the molecules must be avoided. Besides these morphological considerations, detrimental electronic phenomena often intervene to limit the switching efficiency. Among them, we have illustrated the role of (i) depolarization effects that tend to reduce the amplitude of permanent dipoles when going from isolated molecules to a dense SAM and hence limit the

exploitation of the change in dipole moment between two photoisomers; the extent of depolarization can be limited by a molecular design inducing a larger intermolecular separation or by diluting the photochromic units in a matrix made of SAM-forming molecules; (ii) pinning effects that, when operative, make the interfacial energy-level alignment insensitive to many chemical designs typically applied to isolated compounds; and (iii) excitation quenching effects that impede photoisomerization processes close to metallic electrodes. The best strategy to fight against pinning and quenching effects is to decouple electronically the molecules from the electrodes; in molecular junctions, this is, however, most often achieved at the expense of the current density, and/or the ON/OFF ratio. The field is thus in search of new clever strategies to obtain high and reversible ON/OFF ratios coupled to good device properties in the ON state. For the sake of illustration, the incorporation of saturated spacers in the chemical design of molecular switches prevents the close contact between switching molecules, thus facilitating the isomerization process and hampering undesired depolarization effects.

Another path of investigation would be to add a supplementary dimension into the logical processing of the information via a new orthogonal stimulus.<sup>113</sup> For SAM-based electronic devices, a very attractive route is to sandwich the monolayer between two ferromagnetic electrodes in order to trigger a change in the spin-polarized current flowing across the junction through a modulation of the relative magnetization of the two electrodes in order to generate a magnetoresistance. This concept of spin valve is at the heart of the emerging field of molecular spintronics that is also awaiting profound developments.<sup>114–119</sup>

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### Notes

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