Reversible conductance and surface polarity switching with synthetic molecular switches

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SPIROPYRAN SWITCHES IN MOLECULAR TUNNELING JUNCTIONS

This chapter describes the photo-induced switching of conductance in tunneling junctions comprising self-assembled monolayers of a spiropyran moiety using eutectic Ga-In top contacts. The magnitude of switching of hexanethiol mixed-monolayers was higher than that of pure spiropyran monolayers. The first switching event recovers 100% of the initial value of $J$ and, in the mixed-monolayers, subsequent dampening is not the result of degradation of the monolayer. The observation of increased conductivity is supported by zero-bias DFT calculations showing a change in the localization of the density of states near the Fermi level as well as by simulated transmission spectra revealing positive resonances that broaden and shift towards the Fermi level in the open form.

This chapter is based on Sumit Kumar, Jochem T. van Herpt, Regis Y. N. Gengler, Ben L. Feringa, Petra Rudolf, and Ryan C. Chiechi, "Maximizing Conductance Switching by Photoisomerization of Spiropyrans at the Molecule-Electrode Interface in Tunneling Junctions with EGaIn Top Contacts using Mixed Monolayers", *J. Am. Chem. Soc.* 2016, 138, 38, 12519 – 12526
3. SPIROPYRAN SWITCHES IN MOLECULAR TUNNELING JUNCTIONS

3.1. INTRODUCTION

There are two complementary goals in the study of charge transport in molecular junctions: understanding the underlying physical phenomena and extracting useful functionality, i.e., constructing devices. Break-junctions, and other methods for capturing single molecules between electrodes, are powerful tools for studying the physics of tunneling transport,[1] but they are limited either to sampling molecules from a population via the formation of transient junctions or proof-of-principle studies on short-lived and low-yielding devices.[2] Bottom-up tools, in which the smallest dimensions of a device are defined by the molecules in a junction,[3, 4] are better suited for investigating functionality because they are long-lived (physically stable) and yield a high number of working devices.[5–7] Eutectic Ga-In (EGaIn) has proven to be a useful tool for investigating bottom-up junctions[8] to understand structure-property relationships,[9–12, 12–17] to construct devices,[18] and to produce useful functionality.[19, 20] However, thus far the functionality has been limited to passive properties of molecules in a self-assembled monolayer (SAM). In this work, we demonstrate control over the conductance of EGaIn/Ga$_2$O$_3$//SAM/Au$^{TS}$ junctions with light (where “//” denotes an interface involving physisorptive bonds, “/” denotes an interface involving chemisorptive bonds and Au$^{TS}$ refers to template-stripped[21] Au.) Junctions comprising SAMs of a spiropyran moiety (SP) were irradiated with either broadband visible (> 520 nm) or monochromatic UV (365 nm) light to convert SP between the “open” merocyanine (SP-open) and “closed” spiropyran (SP-closed) forms shown in Figure 3.1.

The photochemical switching of SP on Au surfaces has been investigated in detail; it is robust and reversible.[22] Importantly, the electrochemical-induced switching is well-characterized as an irreversible dimerization pathway that can compete with reversible switching,[23] which allows us to exclude these phenomena as possible sources of conductance switching using X-Ray photoelectron spectroscopy (XPS).

![Figure 3.1 A schematic of the SAMs of SP in EGaIn/Ga$_2$O$_3$//SAM/Au$^{TS}$ junctions in their open and closed forms. The distances are from DFT minimized structures (the exact orientation with respect to the substrate is not known). The thickness of SAMs of the closed (left) form estimated by XPS is 15.4 ± 2 Å.](image-url)
3.2. RESULTS AND DISCUSSION

Ring-opening of the spiropyran form (SP-closed) to the zwitterionic, merocyanine form (SP-open) is typically accomplished by irradiation with UV light. This form will revert back to SP spontaneously, but it is accelerated by irradiation with visible light.

Conductance switching, in which the conductance of molecules spanning two electrodes is modulated by (photo)chemically converting molecules in-place, has been shown, for example, using azobenzenes with Hg top-contacts,[24] diarylethanes with PEDOT:PSS top-contacts,[25] dihydroazulenes using reduced graphene oxide top-contacts,[26] azobenzenes covalently attached to graphene[27] and conjugated oligomers covalently attached to carbon nanotubes.[28] Due to the lengths of the molecules involved, transport in the latter two systems is probably not dominated by tunneling, making them difficult to compare to our work. The other systems rely either on a change in tunneling distance (i.e., the cis/trans isomerization of azobenzene units) or a change in conjugation patterns (i.e., the rearrangement of bonds.) The switching of SP induces a change in the conjugation pattern and the distribution of charge, but causes a negligible change in tunneling distance (approximately 2 Å). The long aliphatic chain is what sets SP apart; in the aforementioned systems, the π-system is directly coupled to both electrodes, making them sensitive to small perturbations in the π-framework. The electronic structure of SP is more similar to bipyridyl- and ferrocene-terminated alkanethiols,[20, 29] in which the conjugated portion is confined to the EGaIn interface and separated from the bottom electrode by a σ framework constituting a large tunneling barrier. Thus, the effects of switching SP are confined to the EGaIn interface (which is insensitive to a wide array of functional groups[30, 31]) and are, in the absence of a pronounced change in distance, expected to be either very subtle or nonexistent; rigorous characterization of the switching process is particularly important.

A common problem to virtually all molecular junctions is that characterization is limited to the ex situ investigation of the chemical compounds, SAMs, and gaps; interrogating molecules either in situ or post factum is hindered by the small dimensions and quantities of compounds participating in transport. The rheological properties of EGaIn[32] enable both the facile formation and disassembly of junctions, allowing the interrogation of a SAM before and after both switching and applying a bias. This trait is particularly important for the study of conductance switching because virtually all switches (including SP) show fatigue after only a few switching cycles.[33] The reasons for this fatigue can be ascribed to desorption [34], disorder [35], side-reactions [36], but only by disassembling a junction and interrogating the SAM spectroscopically can we experimentally rule out these specific effects.

3.2. RESULTS AND DISCUSSION

3.2.1. FORMATION OF SELF-ASSEMBLED MONOLAYERS

We initially based the conditions for the formation of SAMs of SP on previous studies on roughened Au and Au-on-mica that used $10^{-4}$ M solutions in CH$_2$Cl$_2$.[22] However, AuTS substrates do not tolerate CH$_2$Cl$_2$ because it swells the optical adhesive backing. Fortunately SP is sufficiently soluble in EtOH to allow the formation of dense SAMs from $10^{-4}$ M solutions. Junctions comprising these SAMs were robust enough to produce
current-density versus voltage ($J/V$) data and to show conductance switching, however, the XPS data revealed unbound or physisorbed sulfur, in addition to the desired covalent Au-S species, indicating that not all of the disulfide (or thiolate) groups are attached to the Au substrate. Thus, we formed SAMs from $10^{-5}$ M solutions, significantly reducing the unbound/physisorbed sulfur signal and producing more robust junctions (i.e., fewer shorts). Junctions comprising these SAMs were about a factor of 10 less conductive (at 0.5 V) than those formed from $10^{-4}$ M solutions, but the ratio of $J$ between SP-open and SP-closed was nearly identical. The area of the nitrogen 1s peak in the XPS data also did not differ between the two SAMs, suggesting that the difference in $J$ is unrelated to the densities of the SAMs and may simply be a reflection of the better coupling of covalently-bound sulfur, an interesting proposition given the insensitivity of EGaIn junctions to the identity of anchoring groups.[31, 37, 38] The XPS and $J/V$ data for SAMs formed on AuTS at $10^{-4}$ M are shown in the Figure 3.2. Unless otherwise mentioned, all data are for SAMs formed from $10^{-5}$ M solutions of SP-closed in EtOH.

**Figure 3.2** X-ray photoemission spectra of the N 1s (left) and S 2p (right) core level regions of a SAM formed under different concentrations ($10^{-5}$ M and $10^{-4}$ M) on AuTS. In the N 1s core level region (left) top curve (black) only spiropyran contributions were observed, namely the indoline nitrogen contribution at 399.6 eV and the nitro peak at 406.2 eV. After exposure to UV light a new component at 400.9 eV was observed (green and blue) originating from the indoline part of the ring-opened merocyanine form in different concentrations at $10^{-4}$ and $10^{-5}$ M ($UV - 10^{-4}$ and $UV - 10^{-5}$). The S 2p core level region (right) contains two doublets, one with maximum at 161.8 eV, which is indicative of a chemisorbed species and one with a maximum at 163.6 eV, which is characteristic of dimerized or physisorbed species.
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Figure 3.3 Current-density versus voltage plots of EGaIn/GaO$_2$/SP/Au$^{TS}$ junctions in the open (green) and closed (red) forms. Open and closed symbols correspond to SAMs formed from $10^{-4}$ and $10^{-5}$ M respectively. Each data point is the peak of a Gaussian fit of log-normal plots of $|J|$ for that voltage $\mu_{\log}$. The error bars are the standard deviation of the Gaussian fit $\sigma_{\log}$. The data for SAMs formed at $10^{-4}$ M were computed from 535 and 178 $J/V$ traces for SP-closed and SP-open, respectively. The data for SAMs formed at $10^{-4}$ were computed from 420 $J/V$ traces for both SP-open and SP-closed.

3.2.2. CONDUCTANCE SWITCHING

Tunneling junctions formed by making contact to a large (compared to the size of a molecule) area of a SAM, rely on statistical analyses to characterize effects because small variations in the SAM (i.e., defects) have an exponential influence on the magnitude of $J$, leading to data that are distributed log-normal.[11, 39] This approach is particularly important for conductance switching in SAMs because the observable is often a change in $J$ that is comparable to the junction-to-junction variation[26] due to incomplete photochemical conversion when confined to a surface.[25] There are systems that show cooperative switching, which (partially) mitigates this problem, however, they are the exception.[40] While cooperative switching can lead to changes in $J$ of a factor of 25,[24] from the quantitative analysis of XPS spectra, we estimate the percentage of switching to SP-open from SAMs of SP-closed to be 38% and, therefore, expect smaller changes irrespective of the mechanism. To measure the effect of photochemically switching SP from the closed to open states on tunneling transport, we grew SAMs of SP-closed on Au$^{TS}$ substrates and then measured the conductance through the SAMs by contacting them in various locations with tips of EGaIn and sweeping the potential from $-1.0$ to $1.0$ V to produce a histogram of log $|J|$ for each value of $V$ comprising data from at least 40 junctions across at least three substrates. We then irradiated each substrate with 365 nm light for 30 min immediately before performing another conductance measurement.

It is known that the roughness of the electrode supporting a SAM can strongly influence the $J/V$ characteristics. [41, 42] Of particular relevance to SP is the sensitivity of the packing of relatively bulky head-groups in alkane-based SAMs.[16] The driving force to form a complete thiolate monolayer competes with favorable packing of the
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Figure 3.4 Switching ratio (black line) and intensity of N 1s photoemission peak at 399.6 eV corresponding to the indoline N (blue line) versus immersion time of SAMs of pure SP in solutions of hexanethiol. Longer immersion times increase the fraction of hexanethiolate in, SP-mixed, the mixed monolayers of SP and hexanethiolate, as can be seen by the decreasing intensity of the indoline N signal. The switching ratio goes through a maximum at 24 hours, which is the time used to prepare the SP-mixed SAMs shown in the main text.

Spiropyran moieties, leading to over-crowding of the latter and incomplete coverage of the former. This steric congestion then inhibits ring-opening in the densely-packed regions of the SAMs; on roughened Au beads there is sufficient disorder to affect complete switching in one direction, but apparently not the reverse.[22] To test this hypothesis we prepared mixed-SAMs (SP-mixed) by incubating SAMs of SP in a solution of hexanethiol for 24 hours, at which the magnitude of switching goes through a maximum (Figure 3.4).

The switching of SP between the closed and open forms has been shown to be reversible for at least six cycles following a “burn-in” after the first exposure to 365 nm light by integrating the area under Raman bands associated with those forms.[22] Those SAMs were formed from CH$_2$Cl$_2$ at $10^{-4}$ M on roughened Au, which is not compatible with conductance measurements (and surface-enhanced Raman spectroscopy is incompatible with Au$^{TS}$). While subtle differences in packing may affect the reversibility of the switching process on Au$^{TS}$ substrates, we used SAMs formed from ethanol at $10^{-4}$ M to recreate those conditions as closely as experimentally possible. We measured $J$ at 0.8 V for SP-closed from which we calculated $\Delta \log |J|$ as the SAM was cycled between the open and closed forms by subsequent exposure to 365 and > 520 nm light. These data are shown in Figure 3.5 (black squares.)

For the first open-closed cycle, $\Delta \log |J| \approx 0.8$ recovers completely, but the overall conductance decreases and then rapidly dampens; by the second open-closed cycle $\Delta \log |J| \approx 0.2$. Nonetheless, the conductance switching is demonstrably reversible. The switching of SP-mixed (Figure 3.5, blue circles) shows considerably less fatigue. While the values of $\Delta \log |J|$ for SP and SP-mixed overlap exactly in the closed form, the values for SP-mixed
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Figure 3.5 A plots of $\Delta \log |J|$ at 0.8 V for SAMs of SP (black squares) and SP-mixed (blue circles) on Au$^{\text{TMS}}$ as they are switched between the open and closed forms by irradiation with 365 and > 520 nm light, respectively. The lines are to guide the eyes. The differences in $\log |J|$ are compared to the initial measurements of SP-closed, thus the negative value reflects a downward trend in conductivity of both SP and SP-mixed after the first cycle in addition to the gradual loss of the conductance switching effect (i.e., fatigue.)

in the open form are considerably higher and show less fatigue. This result implies that synthetic modifications, e.g., that affect the packing of the chromophore and junction optimizations, e.g., changing the contacts,[43] may extend switching past five-to-seven cycles.

To gain some insight into the differences in fatigue between SP and SP-mixed, we obtained XPS spectra of SP-closed for both before and after repeated switching (i.e., the first and last data points of Figure 3.5.) These data are summarized in Figure 3.6. The two main peaks in the N 1s core-level region (Figures 3.6A and C) originate from the indoline nitrogen (at a binding energy of 399.6 eV) and the NO$_2$ group (405.9 eV to 406.1 eV.) The area under this peak is about 30% smaller for SP-mixed compared to SP. After irradiation of SP-closed with 365 nm light for 20 min, a new N$^+$ component appears at 408.0 eV (SP-mixed) or 401.1 eV (SP) corresponding to the merocyanine moiety in SP-open.[23] The absence of this peak in Figure 3.6A confirms a lack of merocyanine in the SAMs of SP before switching. After the switching cycles, however, this peak is prominent in SP, but comprises only 5% of the spectrum of SP-mixed, indicating an incomplete return to SP-closed for the pure SAMs. Figures 3.6B and D show the S 2p core-level region of the X-ray photoemission spectra (XPS). The doublet peaked at 161.8 eV corresponds to chemisorbed SP (bound to the substrate through Au-S bonds).[44] The additional doublet peaked at 163.6 eV that is present only in the pure SAMs of SP corresponds to dimerized or physisorbed thiol,[45] indicating that not all of the SP molecules are attached to the substrate covalently. Thus, the hexanethiol was able to penetrate the SAM of SP and fill vacancies by displacing (presumably) weakly-bound molecules, resulting in the exclusive formation of S-Au bonds and a complete return to SP-closed after the switching cycles.
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Figure 3.6 X-ray photoemission spectra of pristine SAMs of SP-closed and mixed monolayers of SP-closed and hexanethiol (SP-mixed) before and after cycling between the open and closed forms. A and B show the spectra of SP-closed before cycling. A: The N 1s core-level region showing no change to the nitrogen signals corresponding to the spiropyran moieties between SP and SP-mixed. B: The S 2p core-level region showing a single S-Au species in the mixed monolayer SP-mixed. C and D show the same spectra after the switching cycles shown in Figure 3.5. C: The spectrum of the pure SAM SP shows the appearance of an additional component in the N 1s core-level region at 401.1 eV that is absent in SP-mixed. D: The S 2p core-level region of SP shows an additional doublet peaked at 167.1 eV; the spectrum of SP-mixed is unchanged from the initial spectrum shown in the top of panel B.

The most significant difference between SP and SP-mixed after the switching cycles is the appearance of a new N 1s component at 398.5 eV in SP, which we ascribe to CNH$_2$.[46] While the other peaks—unbound thiols and residual N$^+$—can be attributed to structural differences in the SAMs, this peak is evidence of an unexpected side reaction causing an irreversible chemical change. The appearance of a new, more stable nitrogen species indicates that the dampening of SP in Figure 3.5 is at least partially due to damage to the SAMs of SP that is not present in SP-mixed (i.e., the component at 398.5 eV is absent in SP-mixed.) The S 2p core-level region shows a peak at 167.1 eV for SP after the switching cycles (Figure 3.6D) corresponding to oxidized sulfur species that are completely absent in SP-mixed. Based on the XPS and conductivity data from cycling the switches, we suggest the following mechanism: the relatively large head-groups of the SP molecules lead to disordered SAMs containing a significant fraction of defects. When immersed in a solution of hexanethiol, weakly-bound SP molecules at these
3.2. Results and Discussion

Figure 3.7 Current-density versus voltage plots of EGaIn/Ga$_2$O$_3$/SP/Au$_{TS}$ junctions in the open (green) and closed (red) forms. Top panel: data from pristine SAMs (SP). Bottom panel: data from mixed monolayers of hexanethiol and SP (SP-mixed). Each data point is the peak of a Gaussian fit of log-normal plots of $|J|$ for that voltage. The error bars are the standard deviation of the Gaussian fit.

defect sites are readily displaced, followed by a retarded, steady replacement of SP by hexanethiolate. Approximately 10 hours after the retarded replacement begins, a SAM (SP-mixed) has formed for which the switching ratio of $J$ goes through a maximum (Figure 3.4). This maximum corresponds to a SAM in which the bulky head-groups are optimally packed, such that they are not sterically hindered, not in proximity of the metal substrate and are separated by densely-packed regions of hexanethiolate, preventing side-reactions and maximizing the return to the closed form after each switching cycle.

Optically switching SAMs of SP-mixed does not induce any (experimentally resolvable) side reactions, but there is a well characterized electrochemical dimerization pathway for SP. [23][47] To show that $J/V$ cycling with EGaIn does not induce that or any other irreversible processes, we acquired XPS data for the N 1s core-level of SAMs of SP before and after five sweeps at ±1.0 V (Figure 3.8). This measurement is possible because the average area of the junctions formed by EGaIn (tens of microns in diameter) is on the same order as the spot-size of the XPS instrument. Thus, we marked a region of the SAM, acquired an XPS spectrum, formed a junction, swept the voltage and then acquired another XPS spectrum post factum. We found no change (the XPS data look identical to Figure 3.8) before and after the $J/V$ sweeps. We observed no significant
changes in the S 2p core-levels; the area of the doublet peaked at 163.6 eV changes by at most 1%. This result indicates both that the $J/V$ sweeps alone do not trigger the electrochemical dimerization pathway and that the XPS does not damage the SAMs sufficiently to induce shorts. Thus, the switching between low/high conductance states and any changes present by XPS after cycling the switches can be ascribed entirely to the photochemical switching process.

**Figure 3.8** X-ray photoemission spectra of the N 1s (a) and S 2p (b) core level regions of SAMs of SP on AuTS formed from $10^{-4}$ M ethanol solutions before (1) and after (2) $J/V$ measurements with EGaIn top contacts. These spectra are both for SP-closed before any exposure to UV light. The N 1s spectra are identical before and after the $J/V$ sweeps, indicating that no electrochemically-induced dimerization takes place. The change in the area of the S 2p peaks is within error; the spectra otherwise indicate no change to the Au-S anchoring groups. Taken together, these data show that $J/V$ sweeps (at least up to ±1.0 V) have no measurable impact on the structure or composition of the SAMs.

**Table 3.1:** Comparison of switching ratios of SP

<table>
<thead>
<tr>
<th>SAM</th>
<th>%N⁺</th>
<th>%N_{SP}</th>
<th>Rel. %N⁺</th>
<th>Rel. %N_{SP}</th>
<th>$N_{+}^{\text{rel}}/N_{\text{SP}}$</th>
<th>$J_{\text{open}}/J_{\text{closed}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP-mixed</td>
<td>28 ± 3</td>
<td>22 ± 6</td>
<td>56</td>
<td>44</td>
<td>1.27 ± 0.35</td>
<td>34.5</td>
</tr>
<tr>
<td>SP</td>
<td>22 ± 4</td>
<td>36 ± 6</td>
<td>38</td>
<td>62</td>
<td>0.61 ± 0.14</td>
<td>7.4</td>
</tr>
<tr>
<td>SP-Ref. 22</td>
<td>19 32</td>
<td>37</td>
<td>n/d</td>
<td>n/d</td>
<td>0.59b</td>
<td>n/a</td>
</tr>
</tbody>
</table>

*Note:*

- a: from the data in Figure 3.7 at 1 V
- b: calculated by us from the data in Ref. 22

We measured $J/V$ curves for SAMs of SP-mixed-closed and SP-mixed-open under identical conditions as those used to acquire the $J/V$ data in Figure 3.5. These curves are shown in Figure 3.7, revealing both lower values of $J$ for SP-closed and higher values for SP-open. The magnitude of $J$ at 1.0 V in SAMs of SP increased from $10^{-3.1}$ A cm⁻² in the closed form to $10^{-2.2}$ A cm⁻² in the open form, a ratio of $J$ of approximately 8. The magnitude of $J$ at 1.0 V in SAMs of SP-mixed increased from $10^{-3.4}$ A cm⁻² in the
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Figure 3.9 Conductance heatmap plots of mixed monolayers of SP and hexanethiolate, SP-mixed, in the open and closed form binned to $\log|dJ/dV|$ (conductance, Y-axis) versus potential (in V, X-axis). The colors correspond to the frequencies of the histograms; lighter colors indicate higher frequencies. The uniform, positive curvature of these plots is an indication that the mechanism of charge transport is non-resonant tunneling and that is not mediated by defects or other artifacts.

closed form to $10^{-1.8}$ A cm$^{-2}$ in the open form, a ratio of $J$ of approximately 35. Together with the XPS data, these results support the hypothesis that the mixed SAM allows both for a more densely packed SAM containing the less conductive SP-closed form and for a more favorable packing of the spiropyran groups, leading to a higher degree of switching (to the more conductive SP-open). These data are summarized in Table 3.1. It is also possible that there is sufficient disorder in the SAMs of pure SP that some SP molecules are lying flat or folded (with unbound disulfides or physisorbed sulfur species); in either case, the mixed SAMs perform better than the pure SAMs.

3.2.3. MECHANISM OF SWITCHING

With the phenomenon of conductance switching unambiguously established, the key question is the mechanism by which the (partial) conversion of a spiropyran moiety to its merocyanine form affects $J$. Molecules of SP are anchored to the surface through two thiolates attached to an ethyl octanoate linker; i.e., the equivalent of a nine-carbon alkyl chain (Figure 3.1), thus, the entirety of the photochemical transformation is confined to a $\sim 3$ Å layer at the EGaIn/Ga$_2$O$_3$ interface—roughly 20% of the total thickness of the monolayer. Combined with the fact that only $\sim 38\%$ of SP-closed actually switches to SP-open in the pure SAM, an observable change in conductance, let alone an increase by factor of 35 in SP-mixed is remarkable and suggests a strong effect at the molecular level. Ideally, we would establish the mechanism of charge-transport as non-resonant tunneling by variable-temperature measurements, but obtaining reliable results from light-sensitive mixed-monolayers is presently unfeasible experimentally. However, the room temperature data are perfectly symmetric and differential conductance plots (Figure 3.9) are smooth and U-shaped, both of which strongly suggest non-resonant tunneling. Hopping processes arising from strong coupling to localized $\pi$-states and defects cause asymmetry[48] and negative curvature,[49] respectively.

The most obvious source of conductance switching in SP is a change in tunneling distance, i.e., a change in thickness of the SAM in the open and closed forms. We determined the thickness of SAMs of SP-closed to be $15.4 \pm 2$ Å by XPS,[50–52] however,
the thickness of the SAM after switching to SP-open cannot be determined because the XPS signal is averaged over the spot-size and only a fraction of the molecules in the SAM switch, which would give an average height of SP-open and SP-closed. Since tunneling currents are dominated by the most conductive element of the mixed SAM,[11] the relevant value is the end-to-end length of SP-open. Thus, we turned to DFT calculations to help understand the changes in geometry that are associated with switching. The thicknesses shown in Figure 3.1 correspond to distances in the DFT optimized structures. The only geometry that corresponds to the XPS thickness of SP-closed is the one depicted (with the spiropyran moiety more-or-less parallel to the substrate) with a height of 15.4 Å, it agrees perfectly. That distance in the optimized geometry of SP-open is 13.3 Å, corresponding to a decrease in thickness of 2 Å upon switching with light. Any change in orientation, for example, if the merocyanine moiety rotates away from parallel, yields an increase in thickness, which would predict a lower conductance for SP-open. If we assume that the effect is entirely distance-dependent, we can estimate the maximum expected change in \( J \) from the Simmons equation: \( J = J_0 e^{-\beta d} \), where \( J_0 = 10^{3.4} \text{ A cm}^{-2} \) and \( \beta = 0.75 \text{ Å} \) for alkanes.[14] This estimate predicts a ratio of \( J \) of 2.0, a factor of 17.5 lower than the (maximum) experimentally observed value. For this estimate to agree with that observation, \( \beta \) would have to increase, meaning that SAMs of SP have a higher tunneling decay coefficient (\( \beta \)) than alkanes, which is incredibly unlikely given that \( \beta \approx 0.2 \text{ Å} \) for \( \pi \)-conjugated systems.[53] It is, therefore, highly unlikely that the slight decrease in the tunneling distance is responsible for the observed increase in \( J \) in SP-open as compared to SP-closed.

Another possible mechanism of conductance switching is the change in the dipole moment perpendicular to the substrate, \( \mu_\perp \). The collective action of \( \mu_\perp \) in a SAM shifts the electrostatic energy (vacuum level), changing the effective work function \( \Phi \) of the AuTS electrode regardless of its position relative to the electrode.[54] When sufficiently close to a semiconductor interface, these dipole moments can also induce the formation of charge carriers, modulating conductivity.[55] This mechanism is unlikely because, although bulk Ga\(_2\)O\(_3\) is a semiconductor, it is sufficiently thin (0.7 nm) that charges can tunnel directly to the bulk Ga-In.[56] While the effect on conductance is difficult to separate from other changes (e.g., in the orbital structure), such changes in \( \mu_\perp \) correlate to changes in \( V_{\text{trans}} \) (the minimum of plots of \( \ln (J \ V^{-2}) \ vs. \ V^{-1} \)).[12, 57] Thus, by comparing \( V_{\text{trans}} \) in SP-open and SP-closed, we can at least determine if the transport properties are sensitive to the difference in \( \mu_\perp \). Table 3.2 summarizes the DFT-calculated HOMO energies, \( V_{\text{trans}} \) the shift in \( \Phi \) with respect to bare AuTS (\( \Delta \Phi \)) as determined

### Table 3.2: Comparison of energies of HOMOs, shifts in work function, and \( V_{\text{trans}} \) of SP.

<table>
<thead>
<tr>
<th>SP SAM</th>
<th>HOMO(^a) (eV)</th>
<th>( \Delta \Phi )(^b) (eV)</th>
<th>( V_{\text{trans}}^+ ) (V)</th>
<th>( V_{\text{trans}}^- ) (V)</th>
<th>( \mu_\perp ) (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Closed</td>
<td>-5.20</td>
<td>1.0 ± 0.1</td>
<td>0.29 ± 0.04</td>
<td>-0.24 ± 0.05</td>
<td>8.60</td>
</tr>
<tr>
<td>Open</td>
<td>-5.31</td>
<td>1.0 ± 0.1</td>
<td>0.25 ± 0.03</td>
<td>-0.23 ± 0.04</td>
<td>8.85</td>
</tr>
</tbody>
</table>

\(^a\) Gas-phase B3LYP/TZV(2d/sp) with alkyl tails removed.  
\(^b\) Measured by UPS.
from the secondary electron emission cutoff in Ultraviolet photoelectron spectroscopy (UPS) data and $\mu_\perp$. Surprisingly, despite the formation of a zwitterion, $\mu_\perp$ changes by only 0.25 D. In theory that will induce a shift in $V_{\text{trans}}$ of the same magnitude as the commensurate shift in vacuum level, but in practice the value is influenced by the offset of the Fermi level of Au and the energy of the HOMO of SP.$^{[58]}$ The data are consistent; $\Delta \Delta \Phi \approx \Delta V_{\text{trans}} \approx 0$. There is almost no difference in $\Phi$ before and after switching. Although there is a shift in $V_{\text{trans}}^+ \approx 0.3$ eV (and a calculated shift in the HOMO of approximately 0.1 eV) the values are within one standard deviation and there is no change to $V_{\text{trans}}^-$ (Figure 3.10). We can conclude only that the change in $\mu_\perp$ has either little or no effect on $V_{\text{trans}}$ and, therefore, likely no effect on $J$.

The changes in tunneling distance and $\mu_\perp$ are probably too subtle to explain the relatively large change in $\log |J|$ that accompanies switching between SP-open and SP-closed. The last parameter likely to have an influence on conductance

![Histograms of $V_{\text{trans}}$ at positive (top) and negative (bottom) bias for EGaIn/Ga$_2$O$_3$/SAM/Au$^{\text{TS}}$ junctions comprising SAMs of SP in the open (green) and closed (red) forms. The solid lines are Gaussian fits of the histograms. The p-values for $V_{\text{trans}}$ are 0.03 and 0.12 for the top and bottom plots, respectively; i.e., there is no difference at the 99% confidence level.](image)

**Figure 3.10**
Figure 3.11 A: A schematic of a model junction comprising the optimized geometry of the SP fragment that would be in contact with the EGaIn electrode and the distribution of the DOS derived from the vacuum HOMO of SP-open (left) and SP-closed (right). The two nitrogen atoms in each isomer are indicated with arrows for clarity. The DOS is localized on the electrode for SP-closed, but spans the entire junction for SP-open. B: Simulated transmission curves of the model junctions at zero bias with $E_f$ set to $-4.5$ eV. The x-axis is the energy offset of the molecular states with respect to $E_f$ and is not related to the experimental applied bias. The shift in electron density is reflected in these curves, which show resonances shifting closer to the center of the bias window. This effect is particularly evident around 1.0 eV, where a broad resonance appears for SP-open.

is the distribution and relative energies of the density of states (DOS) near the energy of the Fermi level, $E_f$. Figure 3.11A is a schematic of a model junction comprising the spiropyran and merocyanine portions of single molecules of SP including DFT-minimized geometries and the spatial distribution of the DOS derived from the vacuum HOMO. The alkyl anchors were truncated to two Carbon atoms.
CONCLUSIONS

In this chapter, we have demonstrated conductance switching based on the photo-isomerization of spiropyran moieties supported by long alkyl chains that is not accompanied by an appreciable change in distance. We observed an increase in the magnitude of conductance-switching from a factor of 8 in pristine SAMs to 35 in mixed SAMs, accompanied by a decrease in fatigue with repeated switching. We ascribe this to simulate the isolation of the spiropyran moiety from the thiol without having to minimize the entire alkyl chain. The DOS that is localized to the bottom electrode (i.e., the S-Au contact) in SP-closed delocalizes across the molecule in SP-open. While there are deeper orbitals in SP-closed that do span the electrode, transport is dominated by the orbitals nearest in energy to \( E_f \). A similar situation occurring very near resonance manifests as rectification\(^{[59, 60]} \) rather than \( \Delta J \), but the principle is the same; delocalized states near \( E_f \) affect the rate of tunneling.

These calculations are not models of an EGaIn junction, which would have to include the (unknown) details of the SAM//Ga\(_2\)O\(_3\) interface, the packing of SP (and SP-mixed) on Au\(^{TS}\) and the broadening and electrostatic effects of the SAM on the level alignment. Rather, they are model junctions showing the zero-bias transmission spectra of single molecules between clusters of Au meant to examine electronic effects intrinsic to the structure of SP-open and SP-closed; it is reasonable to assume these effects would manifest in the commensurate Au\(^{TS}/\)SAM//EGaIn junction. A qualitative description of the switching mechanism based on these electronic effects can be thought of as a molecular analog of a mercury switch; in the open form, the \( p \)-nitrophenol moiety rotates, becoming coplanar with the indoline moiety and molecular orbitals spread (like mercury flowing in a switch) to the electrode interface, ‘closing the contact’ and increasing the total conductance. The plot in Figure 3.11B is a more quantitative description, showing simulated zero-bias transmission curves for SP-open and SP-closed. We set \( E_f \) to \(-4.5 \text{ eV}\), which is approximately the average of Ga, In and Au. (This choice is somewhat arbitrary as the plots would not change if referenced to the vacuum level since both junctions have the same molecular formula.) As is depicted in Figure 3.11A, we approximate the electrodes with 9- or 10-atom clusters of Au. These curves show the qualitative description of the switching effect in detail; SP-closed shows two sharp resonances more than 1.5 \text{ eV} above/below \( E_f \). In SP-open, these peaks broaden and shift closer to \( E_f \)—and into the bias window—particularly above \( E_f \) where a broad resonance dips below 1.0 \text{ eV}.

Given the non-covalent EGaIn/SP interface and the long alkyl spacer at the Au electrode it is reasonable to assume\(^{[61]} \) that, regardless of the true value of \( E_f \), the Fermi level lies in the frontier orbital gap of SP and the transmission calculation predicts that one or both frontier orbitals will shift towards it and broaden. Thus, SP-open will likely exhibit higher values of \( J \) than SP-closed under bias. While we cannot know for certain what effect an applied bias will have on the transmission features in a real EGaIn junction, the movement of the resonant peaks closer to \( E_f \) and within the range of applied bias supports the experimental observation that SP-open is more conductive than SP-closed. We used a similar analysis to describe a photo-gating effect by considering the effective change in distance when DOS appears on a chromophore attached to an alkyl tail under irradiation.\(^{[43]} \)

3.3. CONCLUSIONS

In this chapter, we have demonstrated conductance switching based on the photo-isomerization of spiropyran moieties supported by long alkyl chains that is not accompanied by an appreciable change in distance. We observed an increase in the magnitude of conductance-switching from a factor of 8 in pristine SAMs to 35 in mixed SAMs, accompanied by a decrease in fatigue with repeated switching. We ascribe
the superior performance of the mixed SAMs to optimized packing of the spiropyrans at the electrode interface. The direction of switching—*i.e.*, that SP-open is the more conductive form—is supported by DFT calculations showing that the DOS is localized on the AuTS electrode in the closed form, but that it delocalizes in the open form. Simulated transmission spectra confirm that this delocalization shifts positive resonances closer to $E_f$ and broadens them, leading to higher conductivity.

An important consideration concerning phenomena in molecular electronics that are ostensibly targeted at (not very near) future applications is that the observations take place in static devices that do not damage the molecules under investigation. In this study, the first switching event is completely reversible, followed by a dampening that is not the result of electrochemical degradation. The fact that cycling EGaIn junctions does not (substantially) damage the SAMs leaves open the possibility of further optimization. These results also provide additional evidence that simulated transmission curves on single-molecules placed between clusters of Au are useful models for experimentally observed trends in large-area junctions such as those formed with EGaIn.[9]
BIBLIOGRAPHY


