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Design principles of dual-functional molecular switches in solid-state tunnel junctions

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ABSTRACT
Molecular electronics has improved tremendously over the past 20 years, but it remains challenging to develop molecular switches that operate well in two-terminal tunnel junctions. Emerging technologies demand multi-functional junctions that can switch between different operations within a single molecule or molecular monolayer. Usually the focus is placed on molecules that shift the junctions between high and low conductance states, but here we describe molecular junctions with dual-functional switching capability. We discuss the operating mechanism of such switches and present examples of “two-in-one” junctions of a diode placed in series with an additional switch, which can operate either as an electrostatic or a memory on/off switch. We propose guidelines for future designs of such dual-function molecular switches and provide an outlook for future directions of research.

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Electrically driven switches are the cornerstone of electrical circuitry, and the continued drive for device miniaturization, particularly in upcoming technologies such as neuromorphic computing and biomedical and soft electronics, motivates the development of efficient molecular switches that can reduce the footprint of devices, decrease power consumption, and enable complementary functionalities to existing solutions.1–3 While the last two decades of intense experimental and theoretical research have brought molecular electronics to the point where it is now possible to routinely measure charge transport across self-assembled monolayer and single molecule tunnel junctions,4–10 it is still challenging to address molecular switches in solid-state junctions despite the fact that solution-based (multi-functional) molecular switches are readily available.11–15 In this Perspective, we outline the design principles of dual-functional molecular switches in solid-state junctions that could greatly simplify electronic circuitry, and we identify the pitfalls and challenges in obtaining efficient switching. We show how well-crafted dual-functional molecular switches can mimic complex electronic function in solid state tunnel junctions that is otherwise only achievable with comparatively complex CMOS based architectures.

Molecular switches operate well in solutions or in the form of monolayers exposed to solutions and require external stimuli, e.g., light, magnetic field, ionic binding, heat, or changes in pH or electrochemical potential to toggle between two, or more, states.13,14,16–22 These states are usually different redox, conformational, or magnetic states, which are readily accessible in solutions and can be read out with conventional spectroscopy, electrochemical techniques, or magnetic measurements. However, these mechanisms to stabilize the different molecular states of the switches are not readily available in solid-state two-terminal junctions due to steric hindrance (which reduces conformational freedom compared to solution), absence of electrolyte (and so poor stabilization of different redox states), and increased quenching of excited states (which hampers design of solid-state light-triggered switches). Consequently, most molecular switches in molecular junctions yield low conduction on/off ratios (<10) or suffer from slow switching speeds on the order of 102–103 s−1,23–30 apart from a few exceptions in which stochastic switching remains an issue.31,32 Thus, molecular switches that are specifically designed to change the conductance of two-terminal junctions are required, so that the on and off states are stabilized.
Biological molecular evolution features a class of multi-functional proteins in which the originally selected enzymatic role becomes over time augmented with additional regulatory roles in, for example, iron regulatory protein. Inspired by this concept of multi-functionality, we seek to build additional functionality to the developed circuit elements. In the context of molecular electronics, molecular switches toggle the junction between a high (on) and low (off) current state. So far, efforts have focused on such monofunctional junctions with a variety of molecules including photo-active switches, redox-active molecules, bond topology switching, and spin switches. These approaches usually only work well at low temperatures because at room temperature the on state is not stable and the molecule thermalizes back to the original state. In this Perspective, we go one step further and introduce a dual-functional molecular switch specifically tailored to realize molecular junctions that toggle between two different functionalities at room temperature. For practical reasons, it is desirable to achieve switching in large-area molecular junctions (because of their stability) and to use differences in applied bias voltage \( V \) (rather than external stimuli) to induce switching and to read out the on and off states of the junction.

The tunneling barrier height is given by

\[ C = C \left( \frac{2}{\hbar} \right) \sum_{E} \left[ f(E) - f_c(E) \right] dE, \]  

with

\[ T = \frac{4 \Gamma_0 \Gamma_f}{(E - \epsilon)^2 + \left( \Gamma_0 + \Gamma_f \right)^2} \]  

and

where \( \epsilon \) is the charge of the electron, \( h \) is Planck’s constant, \( T(E) \) is the transmission function as a function of energy \( (E) \), \( f(E) \) is the Fermi distribution function, \( \mu_i(V) \) is the electrochemical potential of the left electrode, and \( \eta = V_L/(V_L + V_R) \) is the dimensionless voltage division parameter giving the ratio of the voltage drop between the molecule and the right electrode with respect to the total voltage drop in the junction.

Figure 1(a) shows the junction in the initial state when no external voltage bias is applied \( (V = 0 \text{ V}) \). In this situation, the junction is in the off state (low conductance state) with the HOMO energetically well below \( E_f \) as given by \( \delta_{EM,off} \) and weak molecule–electrode interaction \( \Gamma_{off} \) where off-resonant tunneling (of holes) dominates the mechanism of charge transport. Figure 1(b) shows the same junction in the on state (high conductance state) where under the action of applied bias, a hole is injected into the HOMO resulting in a semi-occupied molecular orbital (SOMO) with the following two changes yielding an increase in conduction: (i) the tunneling barrier height decreases \( \delta_{EM,off} < \delta_{EM,off} \) and (ii) the molecule–electrode coupling strength increases \( \Gamma_{on} > \Gamma_{off} \) (which results in broadening of the molecular orbital as schematically indicated). Note that the same effect would be achieved by an increase in just one of the molecule–electrode couplings \( \Gamma_f \) or \( \Gamma_r \) as the lowest coupling limits the conductance, without resulting in an measurable change of the level width (which is determined by \( \Gamma_f + \Gamma_r \)). In principle, the relative values of \( \Gamma_f \) and \( \Gamma_r \) can change upon switching, making it possible to control the asymmetry of the junction and change, e.g., diode functionality. In the following paragraphs, we discuss in detail how changes in both \( \delta_{EM} \) and \( \Gamma \) can be used to obtain dual-functional switches through examples. On a final note, charging of the molecule will likely result in other effects as well and induce, e.g., mirror charges in the electrodes (and associated renormalization of energy levels) or changes in the potentials drops across the junction. Such effects are important to consider and potentially could even be exploited to enhance electronic functionalities.

To demonstrate that this operation principle works, Fig. 2(a) shows the schematic illustration of a dual-functional junction with a monolayer of \( S(CH_3)_5FeC=CFC (Fc = ferrocene) \) that behaves as a molecular diode [Fig. 2(b)] in series with an electrostatic on/off switch.

![Energy level diagrams with a junction in the off (a) and on state (b) illustrating the operation mechanism of dual-functional molecular junctions as explained in detail in the text. The yellow rectangles indicate the filled states of the electrodes. The black arrows indicate the change in the mechanism of hole transport, the double black and green arrows indicate the change in \( \delta_{EM} \), and the black and green arcs indicate the changes in \( \Gamma \) and associated broadening of the molecular level (red bar).](image-url)
and Table I summarizes the operating parameters. The long alkyl spacer ensures that the FcC/C17 functionality is decoupled from EF, so it follows the changes in EF under applied bias because η = 0.95 (most the potential drops along the alkyl chain between the HOMO and the left electrode). Only at negative bias [Figs. 2(c) and 2(d)], the HOMO falls in the conduction window and a hole can be injected in each Fc unit. At positive bias, the HOMO falls outside the conduction window and does not participate in the mechanism of charge transport. This change in the mechanism of charge transport results in typical rectification ratios for single-level molecular junctions operating in the Landauer regime [indicated by the dashed red line in Fig. 2(b)]. These RR values, however, are orders of magnitude lower...
TABLE I. Operating mechanisms of the dual-functional switches.

<table>
<thead>
<tr>
<th>Junction</th>
<th>Function</th>
<th>Conduction mechanism</th>
<th>Diode mechanism</th>
<th>Switch mechanism</th>
<th>Change in parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-S(CH2)11(MV2+X2−)</td>
<td>Diode and memory</td>
<td>Change in hopping to hopping</td>
<td>Asymmetric voltage drop</td>
<td>Electrostatic interactions</td>
<td>( \Gamma_{on} \gg \Gamma_{off} )</td>
</tr>
<tr>
<td>M-S(CH2)11(Fc2+X2−)/M</td>
<td>Diode and on/off switch</td>
<td>Charge tunneling to hopping</td>
<td>Asymmetric voltage drop</td>
<td>Asymmetric tunneling and hopping</td>
<td>( \eta_{on} &gt; \eta_{off} )</td>
</tr>
</tbody>
</table>

\( \Gamma_{n,m} \) indicates parallel contact, and \( \eta \) indicates physisorbed contact.

All parameters are defined in Eq. (1) and Figs. 2(c), 2(d), 3(c), and 3(d).

than \( RR \) values from diodes based on Schottky barriers or pn-junctions; therefore, a mechanism to “break” the Landauer limit is needed.\textsuperscript{28} A charge can be injected in the redox-active Fc groups, but only when the HOMO falls inside the conduction window at negative bias. Therefore, the Fc–top electrode interaction changes from a relatively weak van der Waals (vdW) to a strong Coulombic interaction [green double arrow in Figs. 2(c) and 2(d)]. In addition, electrostatic repulsions between neighboring (Fc)\( _2 \)\textsuperscript{+} units result in an expansion of the monolayer as visualized and quantified with molecular dynamics simulations [Fig. 2(e)]. These two effects result in a large increase in the number of molecules contributing to conduction through the junction only in one direction of bias, enhancing the performance of the molecular diode by a factor of 1000. Accounting for this change in the number of conducting molecules inside the junctions in the Landauer model,\textsuperscript{29} a good fit with the experimental data was obtained [solid red line in Fig. 2(b)]. In this example, two functionalities were achieved as follows: (i) controlling \( \delta_{EM} \) and \( \Gamma \) ensures that charge injection occurs in only one direction of bias to achieve diode functionality, and (ii) controlling \( \Gamma \), via electrostatic interactions by changing the polarity of the applied bias to achieve an on/off switch functionality. In other words, the diode functionality was enhanced by an in-series electrostatic on/off switch as indicated schematically in Fig. 2(a).

To obtain efficient on/off current switching, it is important to stabilize the charge injected in the molecule \textit{in situ} (see the next paragraph). To “lock” the charge on the molecule and to obtain stable on and off states, we replaced the Fc with methylviologen (MV\( _2^{2+} \)) units and fabricated junctions with monolayers of S(CH2)\( _{11} \)(MV\( _2^{2+} \)X\( _2^{−} \)).\textsuperscript{30} The counterion X is typically a halide, and for this example, we used X = \( \Gamma^{−} \). Under wet electrochemical conditions, the dicationic MV\( _2^{2+} \) ground state is readily reduced to the radical cation MV\( ^{+} \) and it is well known that the MV\( ^{+} \) dimerizes to form a stable [MV\( ^{+} \)]\(_3\) complex driven by \( π−π \) stacking and electron spin pairing with the two excess counterions released into the solution.\textsuperscript{37–39} In principle, dimerization and release of counterions can stabilize the reduced form of MV in junctions resulting in large on/off conductance switching.

Figure 3(a) shows schematically the junctions with S(CH2)\( _{11} \)(MV\( _2^{2+} \)X\( _2^{−} \)) in the ground state and in the reduced form where [MV\( ^{+} \)]\(_3\) dimers formed and the excess X\( ^{−} \) migrate to the bottom electrode (Table 1 summarizes all variables). Figure 3(b) shows the density functional theory (DFT) computed monolayer structures in both states which confirm that the dimer forms and X\( ^{−} \) migrates to the bottom electrode. Figures 3(c) and 3(d) show the operating mechanism. The LUMO centered on MV\( ^{2−} \) only enters the bias window when negative bias is applied to the right electrode because the LUMO couples more strongly to \( E_{LUMO} \) as it is separated from the left electrode by the long alkyl chain. At the opposite bias, no molecular frontier orbitals enter the bias window; hence, this change in the mechanism of charge transport results in large current rectification (similar to the Fc diode explained above). Once the LUMO enters the bias window, an electron can be injected from \( E_{LUMO} \) into the LUMO, resulting in the formation of MV\( ^{+} \) followed by dimerization to [MV\( ^{+} \)]\(_3\)X\( _2^{−} \). Since the right electrode is negatively biased, the two excess ions X\( ^{−} \) readily migrate to the left electrode. This dimerization results in a reduction of the HOMO–LUMO energy gap, \( E_{LUMO} \), and \( \delta_{EM} \) [double green arrows in Figs. 3(c) and 3(d)] so that the HOMO also enters the bias window which increases the conductance of the on-state even more. The high resistive state is associated with viologen...
in the dicationic MV$^{2+}$ ground state where the mechanism of charge transport is off-resonant tunneling [black arrow in Fig. 2(c)], while the low resistive state is associated with viologen in the [MV$^{+}$]$\_2$ dimer form with a small HOMO–LUMO gap, and both the HOMO and LUMO involved in charge transport resulting in incoherent hopping [black arrows in Fig. 2(d)]. In sharp contrast to the Fc-diodes discussed in the previous paragraph, both dimerization and charge separation (by X$^-$/C$^0$ shuttling between molecule and electrode indicated with the single green arrow) provide the charge stabilization mechanisms to “lock” the molecules in two distinct resistive states, resulting in large hysteresis in the $J$(V) curves (Table I). While the alkyl chain structure below the bulky MV headgroups is sufficiently dynamic to allow small ions (X$^-$ = halide) to readily migrate across the monolayers, the device performance is adversely affected when large counterions (X$^-$ = ClO$_4^-$ or PF$_6^-$) are used.

Figure 3(e) shows a typical $J$(V) curve with large unipolar hysteresis only at negative bias. The large current on/off ratio, $I_{on/off}$, of $6.7 \times 10^3$ and large RR of $2.5 \times 10^4$ prove that this junction combines the two functionalities of diode and variable resistor. Figure 3(a) shows the corresponding equivalent circuit which is the same of that of 1D–1R RRAM (1 diode–1 resistor resistive random access memory). To demonstrate 1D–1R RRAM functionality, we recorded write–read–erase–read (WRER) cycles using write voltage, $V_w$, of $1.0\,V$, read voltage of $0.3\,V$ to read out the on, $V_{R,on}$, and off, $V_{R,off}$ voltages (V$_d$, V$_w$, V$_E$, and V$_R$).
$V_{R_{\text{on}}}$ states, and erase voltage, $V_{E_{\text{on}}}$ of +1.0 V, as input, as defined in Fig. 3(e). Figure 3(f) shows the results where a junction was switched 80 times between the high conductance (on state) and low conductance (off state) states (which could be extended to $2.0 \times 10^{6}$ voltage sweeps) and the junction retained the charge in the on and off states for $1.2 \times 10^{6}$ s (see Ref. 56). From these results, we conclude that the on/off states are stable during operation in high electric fields ($\sim 0.5$ GV/m at 1 V).

A major challenge is to stabilize the charge injected in the molecule in large electric fields of 0.1–1 GV/m that are typically required to obtain conductance switching in junctions. In 3-terminal (electrochemical) molecular junctions, the charge on the molecule can be stabilized with a gate electrode and switching can be observed, but 2-terminal junctions lack a gate and the charge has to be stabilized by alternative means. For example, Fc-based diodes show only very marginal conductance switching with a small hysteresis in the $J(V)$ curves of a factor 2–3. This small on/off ratio in the conductance between forward and backward bias sweeps is due to the lack of a charge stabilization mechanism: the charges readily hop on and off the Fc units at room temperature. Conductance switching based charge injection (or redox-events) in solid-state molecular junctions has also been observed for other types of redox groups, usually with low on/off ratios of $<5$. In general, in wet electrochemical environments, the reorganization energies and so the relative stabilities of the on and off states are larger than in solid state junctions due to counterion migration and reorganization of (many) solvent molecules. In solid-state junctions, however, these two mechanisms are usually not available and charges on the molecules are compensated by both image charges in the electrodes and inner sphere reorganization of the molecule resulting in low activation energies (which are often related to thermal broadening of the Fermi distributions of the leads). These energy differences are too small to prevent switching due to thermalization. Therefore, switching events are usually stochastic, as has been observed in junctions with, e.g., redox-active molecules or light-induced conformational switches, preventing the use of such junctions in non-volatile memory applications.

In this context, the group of Chiechi reported an interesting approach to chemically lock two different conduction states of a light-triggered molecular switch in large area junctions. They formed junctions with a sypirpyran which converts under the influence of light reversibly into the open-ring merocyanine isomer. At room temperature, merocyanine switches back to a sypirpyran. By exposing the monolayer to acidic conditions, the merocyanine is protonated and stable non-volatile memory isomer (hence, the on-state (with $10^{3}$ larger conductance than the off-state) is chemically “locked.” This ex situ switching of monolayers, however, requires temporary removal of the top electrode (although Darwish et al. showed in situ “locking” of merocyanine by adding acid to the solution used in their break junction experiments ). Others have reported the control over binary switching by mechanically changing the electrode–electrode distance. As a group, such approaches are not relevant for applications where electrodes have to be stationary.

For the dual-functional switches to work well, the following criteria have to be fulfilled. (i) The junction should operate in the intermediate/weak coupling regime. In the strong coupling regime, coherent tunneling pathways dominate the mechanism of charge transport and charges are not injected in the molecules; thus, the molecules cannot switch (apart from stochastic changes in conductance due to, e.g., inelastic effects). (ii) Charge injection should be coupled to in situ charge stabilization, i.e., charge locking mechanism, to prevent spontaneous switching back to the ground state. In other words, charge injection has to be coupled to a process that results in a switching event which, in turn, stabilizes the charged molecular state. Consequently, the mechanisms of charge transport have to be dominated by incoherent tunneling (cf. criterion i). (iii) Two states should be available with different $\alpha_{\text{EM}}$ and $T$, resulting in a large change in the conductance and large change in energy level alignment of the junction to ensure control over two different functionalities.

This overview introduces a molecular switch operable in the solid state leading to tunnel junctions with dual-functionalities. The ability to perform multiple electrical transformations within a single molecular layer potentially reduces device complexity and power consumption. For instance, 1D–1R RRAM normally requires two junctions in series, over each of which the potential drops. Consequently, operating voltages are high (2–6 V) and the fabrication of such devices typically involves complex multi-layered structures (5–7 layers), resulting in stacks with a thickness of 50–500 nm. In contrast, our junctions confine both functionalities within a single 2 nm thick molecular layer and operate <1.0 V although scaling the lateral dimensions of molecular junctions is still both a scientific and technological challenge, and industry device roadmaps vary widely between applications. For example, neuromorphic computing technologies require devices with high plasticity in sharp contrast with the highly static device requirements in CMOS-based technologies. However, device stability is always a key factor and can be gauged in terms of, e.g., on/off state retention times, switching endurance, and shelf-life. For instance, the S(CH$_2$)$_3$MV$^{2+}$X$^-$ switch has tested retention times of up to $1.2 \times 10^6$ s and an endurance of $2.0 \times 10^6$ voltage cycles, but metal–thiolate bonds oxidize over time and can, in principle, be replaced with stable covalent bonds. Demonstrations of applications of molecular junctions in upcoming technologies (e.g., synaptic, neuromorphic, or soft robotic technologies) is an important future direction to pursue, in conjunction with scaling of switchable molecular junctions in commercially viable molecular platforms.

The junctions introduced here are dynamic in nature (but this is true, at least to a certain degree, for all molecular junctions), and charge injection is coupled to conformational changes, changes in electrode–molecule interactions, image charge effects, migration of ions (if present), and associated electrostatic effects; therefore, it is important to study these kinds of dynamics in more detail to understand how they affect switching rates. Although the examples introduced in this Perspective changed from a low to a high conductance state, it would be very interesting to also design junctions that switch from a high to a low conductance state which could result, for example, in negative differential resistance. Another interesting approach would be to couple electron transport to proton transport to induce charge locking. Proton coupled electron transport is already widely studied and involves reversible addition of hydride and associated formation of molecular bonds and changes in the electronic structure. Likewise, other types of in situ chemical reactions could be explored to stabilize charges such as Bronsted or bias induced Diels–Alder chemistry. The switches introduced here also result in changes in the image charges in the electrodes, potential drops across the molecules, and interfaces (especially when migrating counterions are involved), which
currently have not been explored in detail. From the point of view of predictive modeling, it is important to develop new methods to study changes in the energy level alignment in molecular junctions induced by the dynamics of the molecules and switching events.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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