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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.11–16 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, ion binding, heat, or changes in pH or electrochemical potential to toggle between two, or more, states.13,16–20 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 bulk 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 10^2–10^3 s–1,23–30 apart from a few exceptions in which stochastic switching remains an issue.21,22 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. Figure 1 shows two possible ways to induce large conductance switching in junctions by changing the tunneling barrier height and the molecule–electrode coupling, \( \Gamma \). In this example, the highest occupied molecular orbital, HOMO, is lower in energy than the Fermi-level, \( E_F \) of the electrodes, as indicated by \( \delta_{\text{EM,off}} \), but a similar reasoning applies to junctions where the lowest unoccupied molecular orbital, LUMO, is shifted above \( E_F \). The tunneling barrier height is given by \( \delta_{\text{EM}} \) and the coupling strength of the molecular orbital with the left (l) and right (r) electrodes are given by \( \Gamma = \Gamma_l + \Gamma_r \). In the Landauer framework for coherent tunneling, the current across the junction, \( I \), is given by

\[
I = \frac{2e}{h} \int_{-\infty}^{\infty} T(E) [f_l(E) - f_r(E)] dE,
\]

with

\[
T = \frac{4\Gamma_l \Gamma_r}{(E - \varepsilon)^2 + [\Gamma_l + \Gamma_r]^2}
\]

and

\[
\varepsilon = \mu_r(V) + \delta_{\text{ME}} + \eta eV.
\]

where \( \varepsilon \) is the charge of the electron, \( h \) is Planck’s constant, \( T(E) \) is the transmission function as a function of energy \( E \), \( f_l(E) \) is the Fermi distribution function, \( \mu_r(V) \) is the electrochemical potential of the right 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 where 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 \( \delta_{\text{EM,off}} \) and weak molecule–electrode interaction \( \Gamma_{\text{off}} \) 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 \( \delta_{\text{EM,off}} < \delta_{\text{EM,on}} \) and (ii) the molecule–electrode coupling strength increases \( \Gamma_{\text{on}} > \Gamma_{\text{off}} \) (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 \( \Gamma_l \) or \( \Gamma_r \) as the closest coupling limits the conductance, without resulting in a measurable change of the level width (which is determined by \( \Gamma_l + \Gamma_r \)). In principle, the relative values of \( \Gamma_l \) 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 \( \delta_{\text{EM}} \) and \( \Gamma \) can be used to obtain dual-functional switches through two 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 \( \text{S(CH}_3)_2\text{FeC} = \text{CFc} \) (Fc = ferrocene) that behaves as a molecular diode [Fig. 2(b)] in series with an electrostatic on/off switch.
and Table I summarizes the operating parameters. The long alkyl spacer ensures that the FcC/C17/CfC (in shorthand, Fc2) functionality is decoupled from Ef, so it follows the changes in Ef,F 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 [black arrows in Figs. 2(c) and 2(d)] results in typical rectification ratios RR = 100–500 which are very close to the maximum values of RR of 103, expected 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.

FIG. 2. (a) Schematic illustration of S(CH15)Fc2 inside a junction along with circuit symbols to indicate that this junction behaves as a diode in series with an electrostatic on/off switch. (b) The average J(V) curve along with the predicted J(V) curve based on a single-level Landauer model (dashed line) and a fit to a modified Landauer model (solid red line) to account for electrostatic switching. Energy level diagrams of the off-state (c) and on-state (d) illustrating the operating mechanism as explained in the text (the filled states of the electrodes are indicated with the yellow rectangles) and the black arrows indicate change in the mechanism of charge transport. The green and blue arcs indicate Γ1 and ΓF and the increase in Γ1 results in broadening in the molecular level (red bar). Molecular dynamics simulations (e) showing electrostatic switching due to bias-induced electrostatic repulsion between the Fc2 units and electrostatic attraction between the positively charged Fc2 units and the negatively charged top electrode (represented by the red oxygen atom spheres). Panels (b) and (e) are reproduced with permission from Chen et al., Nat. Nanotechnol. 12, 797 (2017). Copyright 2017 Nature Springer.
TABLE I. Operating mechanisms of the dual-functional switches.

| Junction        | Function                        | Conduction mechanism | Change in | Diode mechanism | Change in parameters |
|-----------------|---------------------------------|----------------------|-----------|-----------------|----------------------|
| M-(CH2)11(MV2+) | Diode and on/off switch         | Charge tunneling to hopping | $\Gamma_{on} \gg \Gamma_{off}$ | Asymmetric voltage drop | $\eta = \frac{I_{on}}{I_{off}}$ |
| M-(CH2)11(MV2+) | Diode and memory                 | Charge tunneling to hopping | $\Gamma_{on} \gg \Gamma_{off}$ | Asymmetric voltage drop | $\eta = \frac{I_{on}}{I_{off}}$ |

$M$ is the metal electrode, “–” indicates covalent contact, and “//” indicates physisorbed contact.

$I_{on}$ and $I_{off}$ are the currents in the on and off states, respectively.

$\eta$ is the rectification ratio, defined as $\eta = \frac{I_{on}}{I_{off}}$.

$\delta$EM is the energy barrier for electrostatic interactions.

$X$ is the counterion, typically a halide.

$d$ is the distance between the electrodes.

$E_0$ is the Fermi level.

$\phi$ is the work function.

$\phi_D$ is the vacuum level.

$\phi_M$ is the metal work function.

$\phi_{left}$ is the Fermi level of the left electrode.

$\phi_{right}$ is the Fermi level of the right electrode.

$\phi_{D(right)}$ is the vacuum level of the right electrode.

$\phi_{M(left)}$ is the metal work function of the left electrode.

$\phi_{D(left)}$ is the vacuum level of the left electrode.

$\phi_{M(right)}$ is the metal work function of the right electrode.

$\phi_{D(right)}$ is the vacuum level of the right electrode.

$\phi_{D(left)}$ is the vacuum level of the left electrode.

$\phi_{M(right)}$ is the metal work function of the right electrode.

$\phi_{D(left)}$ is the metal work function of the left electrode.

$\phi_{D(right)}$ is the vacuum level of the right electrode.
in the dicationic $\text{MV}^{2+}$ 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 $[\text{MV}^{2+}]_2$ 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 $X$ 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, $I_{\text{on}}/I_{\text{off}}$, 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 $1.0\, \text{V}$, read voltage of $0.3\, \text{V}$ to read out the on, $V_{R,\text{on}}$, and off, $V_{R,\text{off}}$ voltages for each cycle. The output of 80 read–write–read–erase pulses (with $V_W = -1\, \text{V}$, $V_R = +1\, \text{V}$, $V_E = -0.3\, \text{V}$) with $R_1$ (red), $R_2$ (blue), $W$ (black), and $E$ (grey) as a function of the number of cycles. Panels (a), (b), (e), and (f) are adapted from Han et al., Nat. Mater. (published online, 2020). Copyright 2020 Nature Springer.
and, 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 × 10^8 voltage sweeps) and the junction retained the charge in the on and off states for 1.2 × 10^6 s (see Ref. 56). From these results, we conclude that the on/off states are stable during operation in high electric fields (∼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, FeC-based diodes show only very marginal conductance switching with a small hysteresis in the I(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 FeC 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 sypipryran which converts under the influence of light reversibly into the open-ring merocyanine isomer. At room temperature, merocyanine switches back to a sypipryran. By exposing the monolayer to acidic conditions, the merocyanine is protonated and stable enabling non-volatile memory; hence, the on-state (with 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 θ_{RM} and Γ, 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-functionality. 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(CH2)11MV2\(\mathrm{X}^-\) switch has tested retention times of up to 1.2 × 10^4 s and an endurance of 2.0 × 10^8 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. (cf. criterion i). 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 hydrde 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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