Electric Field Driven Dual-Functional Molecular Switches in Tunnel Junctions

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Electrically driven switches are one of the most elementary components in electrical circuitry, but new types of multifunctional molecular scale switches are needed to, e.g., reduce the footprint of devices, decrease power consumption in nanoelectronic circuitry and enable new functionalities in, for instance, soft robotics and neuromorphic computing¹⁻⁶, which are stable, reversible, writable, and addressable in the solid state. For example, to avoid cross-talk and suppress leakage currents in next generation resistive random access memory (RRAM), two types of switches are combined in series (a resistive switch and a current rectifier (a diode), *i.e.*, one diode—one resistor (1D-1R) RRAM), but this increases the operating voltage (and associated power consumption) as the potential drops over two consecutive junctions, which complicates the design and increases the footprint considerably⁷. Hence, there is a need for switching elements with dual functionality, but so far, it has been challenging to switch molecules efficiently in the solid state by electrical means⁸⁻¹². Here we report a molecular tunnel junction with a new type of molecular switch where the molecules provide an unprecedented dual functionality of diode and variable resistor resulting in molecular-scale 1D-1R RRAM with excellent device properties of current rectification ratio = 2.5×10^4 and resistive on/off ratio = 6.7×10^3 , and a low drive voltage of 0.89 V (compared with 2 to 6 V for other devices) as the potential only drops over one junction, see Section S1. Our results indicate that switching relies on dimerization of redox units resulting in hybridization of molecular orbitals accompanied by directional ion migration. This new type of electric field driven molecular switch operating in the tunneling regime enables a new class of molecular devices where multiple electronic functions are preprogrammed inside a single molecular layer with a thickness of only 2 nm (10 to 500 times smaller than other devices, Table S1).

Molecular switches for memory applications with large on/off ratios (10^2-10^3) reported so far require external stimuli, *e.g.*, light, magnetic fields, ion binding, or changes in

2

pH, to switch the tunnel junction between two stable conductance states^{8,9,13,14}, but these approaches do not give access to non-volatile memory and cannot be used in applications that require all-electrically driven circuit components. The challenge in obtaining stable and efficient electric field driven switchable molecular junctions is to fine-tune stabilization of charge on the molecule under bias in extremely high electric fields on the order of GV/m: unstable on and off states will switch back due to thermal relaxation but overly stable states will result in impractical slow switching speeds. In solution, mechanisms to stabilize on and off states are available *via* conformational changes of the molecules, formation/breaking of chemical bonds, or change in redox state¹⁵⁻¹⁸. Such mechanisms are not available in molecular tunnel junctions (stable light-switchable molecular junctions were demonstrated only recently¹⁹) and so they suffer to date from small on/off ratios <10 (ref.¹⁰), low reproducibility and low stability^{11,12} rendering them unsuitable for memory applications.

Figure 1a shows a schematic of the junctions with Ag bottom-electrode, selfassembled monolayer (SAM) of S(CH₂)₁₁MV²⁺X⁻₂ and GaO_x/EGaIn top-electrode where MV is methylviologen and X⁻ is counterion (Sections S2-6). MV has three oxidation states: dicationic MV²⁺ ground state, radical cation MV⁺⁺, and fully reduced neutral form MV⁰ (ref.²⁰). MV⁺⁺ dimerizes to form stable dimer complex [MV⁺⁺]₂ driven by π - π stacking and pairing of the electron spins of each MV⁺⁺ (ref.²¹). Dimerization and migration of counterions is sketched in Figure 1b and provides charge stabilization required for resistive bistability. Figure 1b inset shows the equivalent circuit of the junction which is the same of that of 1D-1R RRAM. Here, the diode rectifies current, with high current rectification ratios, $I_{RR}=J(V)/|J(-V)|(J=$ current density for a given voltage V) achieved by asymmetric placement of MV²⁺ units inside the junction. This diode is in series with a variable resistor where high on/off ratios, $R_{2/1}=R_2/R_1$, between the high, R_2 , and low, R_1 , conductance states of the junction are provided by formation of [MV^{*+}]₂. To form $[MV^{*+}]_2$ efficiently, the MV^{2+} units must be pre-organized which requires densely-packed, high quality SAMs^{21,22}. To demonstrate that our SAMs fulfill these requirements, we recorded both angle resolved X-ray photoelectron spectroscopy (AR-XPS) and cyclic voltammograms (CVs) of SAMs of S(CH₂)₁₁MV²⁺X⁻₂ on Ag and Au (Sections S7 and S8) which demonstrate that our SAMs are densely packed and well organized. The CV for X⁻ = Cl⁻ given in Fig. 1c shows two successive reduction waves associated with $MV^{2+} \leftrightarrow MV^{*+}$ and $MV^{*+} \leftrightarrow MV^0$. The first redox-wave consists of two components, one broad $(E_{fwhm} = 121 \text{ mV})$ and the other narrow $(E_{fwhm} = 73 \text{ mV})$ and considerably smaller than 90 mV for an ideal one-electron redox formation of $[MV^{*+}]_2^{22}$. Formation of $[MV^{*+}]_2$ was also confirmed with density functional theory (DFT) electronic structure calculations (Fig. 1d, Section S9). Calculations of the periodic SAM indicate that the dense SAM environment stabilizes $[MV^{*+}]_2$ formation by 0.93±0.19 eV (Fig. S7). These results demonstrate that our SAMs are pre-organized and facilitate formation of $[MV^{*+}]_2$. Dimer is always formed irrespective of the nature of X⁻, but below we show that switching behavior of the junctions depends critically on counterion size.



Fig. 1. (a) Schematic illustration of Ag-S(CH₂)₁₁MV²⁺X⁻2//GaO_x/EGaIn junctions (X⁻ = I⁻, Br⁻, Cl⁻, F⁻, ClO₄⁻ and PF₆⁻) at positive applied bias and (b) at negative applied bias when MV²⁺ is reduced and [MV⁺⁺]₂ forms. The blue shades indicate dimer formation. The black arrow indicates ion migration. The equivalent 1D-1R (1 diode and 1 variable resistor) circuit of the junction is shown on the right. (c) Cyclic voltammogram (black line) of S(CH₂)₁₁MV²⁺Cl⁻₂ SAM on Au in 0.1 M NaCl at a scan rate of 0.2 V/s with Ag/AgCl as reference electrode. The first redox-wave is split into two components associated with reduction of MV²⁺ to MV⁺⁺ (blue line) and [MV⁺⁺]₂ formation (green line); orange line is sum

of blue and green lines. (d) HOMO and LUMO of [MV *+]₂ I⁻₂ computed using Gaussian16 with dispersion-corrected B97D functional (Section S9).

We measured statistically large numbers of J(V) curves and constructed Gaussian logaverage values of J, $\langle \log | J |_G \rangle$, vs. V curves following previously reported methods (Section S10). Figure 2 shows that all junctions have large unipolar hysteresis only at negative bias which strongly depends on X⁻. The largest on/off ratio $R_{2/1}$ of 6.7×10^3 was obtained for junctions with X⁻=I⁻ (Fig. 2i shows how $R_{2/1}$ and I_{RR} are extracted from the J(V) curves), but $R_{2/1}$ decreases steadily with shrinking of the counterion across the halogen series (Table S5). The switching speed of the junction is 0.10 ms for an applied bias of 1.6 V, and 1.8 ms at 1.0 V (Section S11). Junctions with halide counterions all have large I_{RR} of $>10^3$ at ± 1 V, with highest $I_{\rm RR}$ of 2.5 × 10⁴ for X⁻=I⁻ (Table S5) – amongst the highest values recorded for molecular junctions²³. Figure S24 shows the SET voltage (V_{set}) – the voltage at which the junction changes from the low to the high conductance state – decreases with increasing counter ion size from -1.12 V for X = F to -0.89 V for X = I (Section S12). This V_{set} value is very low because in our devices the potential drops over only one junction rather than over two separate junctions (i.e., the diode and memory element) in series (Table S1) which would require large V_{set} values of 2-6 V. This measurement is in agreement with the observation from the DFT calculations that both dimerization and ion binding to the dimers weakens as the diameter of the ion increases so the large ion is more mobile in the SAM (so lower V_{set}) as shown in Figures. S9 and S10. Junction performance is poor when X⁻ is too bulky for X⁻ = ClO_4^{-} or PF₆ (Figs. S14-17). As a control, we also recorded characteristics of junctions with counterions but lacking MV²⁺ units, *i.e.*, SAMs of S(CH₂)₁₁NH₃Cl or S(CH₂)₁₁COONa; these junctions did not switch or rectify (Figs. S14-17). We note that EGaIn junctions with redox

units only show a marginal hysteresis with $R_{2/1}$ of 2-3 since such junctions lack a mechanism to stabilize the injected charge on the molecule²⁴.

To demonstrate 1D-1R non-volatile memory, we recorded write-read-erase-read (WRER) cycles (Section S13) from a typical junction with X⁻=I⁻ (Fig. 2i) using write voltage of -1.0V, read voltage -0.3V, and erase voltage +1.0V, as input (Fig. 2j). Figure 2k shows junctions switching 80 times from high conductance (R_2) to low conductance (R_1) states with cycling time of 11 s. For junctions with the EGaIn top-electrode stabilized in microchannels, we demonstrated excellent stabilities against voltage cycling over ± 1.5 V for 2.0 $\times 10^{6}$ voltage sweeps. Figure 2l shows junctions in on and off states for 3.6×10^3 s (Section S13) for junctions with cone-shaped EGaIn tips, which could be extended to 1.2×10^4 s for junctions with stabilized EGaIn top electrodes (Section S13). The junction was continuously in operation and exposed to high electric fields (~0.5 GV/m at 1 V), yet the molecules inside the junctions retain their charge over prolonged periods of time. Although stability against voltage cycling has been reported before^{10,23,25}, stable information retention with such large values of $R_{2/1}$ has not been demonstrated before in molecular tunnel junctions. The stable response of junctions against bias stressing also rules out the possibility of electrochemical reactions involving the electrode surfaces (e.g., involving oxidation of GaO_x) as such (side) reactions result in time-dependent changes in EGaIn junctions and may only become apparent at much larger drive voltages than used in this study^{26,27}.



Fig. 2. Heat maps of $\log_{10}|J|$ vs. (V) curves (a-d) and $\log_{10}R_{2/1}$ vs. (V) (e-h) for Ag-S(CH₂)₁₁MV²⁺X⁻₂//GaO_x/EGaIn junctions [X⁻=I⁻ (a,e), Br⁻ (b,f), Cl⁻ (c,g) and F⁻ (d,h)]. Black solid lines are Gaussian log-averages. (i) Representative J(V) curve of Ag-S(CH₂)₁₁MV²⁺I⁻ $_2$ //GaO_x/EGaIn junction with low conductance (R_1) and high conductance (R_2) states labelled together with write, read and erase voltages. The red solid line is a fit to a single level

tunneling model (Section S20). The black arrows indicate the scan direction and are numbered accordingly. (j) Read-write-read-erase pulse sequence with $V_W = -1V$, $V_E = +1V$, $V_R = -0.3V$ and (k) corresponding output where red data points indicate R_1 , blue indicate R_2 , black indicate W and gray indicate E. (l) Current retention in the on (blue) and off (red) state of a Ag-S(CH₂)₁₁MV²⁺I⁻₂//GaO_x/EGaIn junction. Additional data are provided in Figures. S25, 26 and 27.

To study the operating mechanism in detail, we performed electronic structure calculations of the isolated dimers and SAMs. The computed complexes confirm that [MV^{*+}]₂ forms tightly-bound complexes (Fig. 3a) with dimerization energies in the range of -1.6 to -2.2 eV for different counterions driven by π - π interactions and electron spin pairing (Fig. 1d and Fig. S7). Upon dimerization, the HOMO-LUMO gap reduced significantly for all halides (Section S14), which, in part, explains increase in conductance upon dimerization. Reduction of the HOMO-LUMO gap is confirmed experimentally by UV-Vis-NIR absorption measurements of $[MV^{+}]_2$ (Figs. S28 and 29). The calculations also explain the dependence of the value of $R_{2/1}$ on the counterion. Smaller ions bind too tightly to the dimer, resulting in poor reversibility of the dimerization and low $R_{2/1}$ (Fig. S9 and Table S5). Larger counterions weaken both dimerization and ion binding and can move more freely in the SAMs; calculated structures show migration of excess counterions toward the bottom-electrode, resulting in reversible switching and high $R_{2/1}$. Thus, the calculations point to a two-step switching mechanism involving charging followed by dimerization and ion migration which is clearly visible in the individual J(V) curves (Fig. 2i, Section S15). Fig. 3b shows the linear relationship between experimentally determined $R_{2/1}$ and $\Delta_{\text{dimer}}/\delta E_{\text{HOMO}}$ (where Δ_{dimer} is difference in calculated dimerization energy in on vs. off states and δE_{HOMO} is experimentally determined energy offset between the HOMO and electrode Fermi-level (Section S16 and

Table S3) for the halide series proving that strong counterion binding degrades performance of the junctions. The calculations indicate that ClO_4^- and PF_6^- result in poor reversibility of conductance switching due to too strong counterion— $[MV^{*+}]_2$ interactions, but experimental results show the junctions always in the on-state (Fig. S14 and S15). Likely migration of these large molecular counterions disrupts SAM packing, generating large leakage currents that diminish diode functionality and, consequently, device performance (Table S5). Therefore, optimal balance between stabilization of the dimer and counterion migration is needed to maximize junction performance.

Fig. 3c and 3d summarizes the operating mechanism of the junctions based on experimentally obtained LUMO and HOMO levels which follow the same trends as those obtained from DFT (Sections S17-18). The LUMO is separated from the bottom-electrode by the long alkyl chain and therefore coupled to the top-electrode. Large current rectification is observed because the LUMO can only enter the bias window at negative bias (confirmed with normalized differential conductance (NDC) analysis, Section S19). Once the LUMO enters, an electron can be injected from the top-electrode resulting in formation of MV⁺⁺ and increase in conductance (first step) followed by dimerization and migration of excess counterions to the positively-charged bottom-electrode (second step), also confirmed with NDC analysis. The HOMO-LUMO gap of $[MV^{*+}]_2$ is smaller than that of MV^{2+} and the HOMO of $[MV^{*+}]_2$ can enter the conduction window at negative bias resulting in sharp increase in conductance of the junction. This involvement of the HOMO in the resistive switching mechanism explains the linear relationship between $R_{2/1}$ and $\Delta_{\text{dimer}}/\delta E_{\text{HOMO}}$ in Fig. 3b (Section S16). To confirm the latter, we modelled the I(V) characteristics using a single level model based on the Landauer formalism which allows us to use the parameters obtained from spectroscopy for modelling, confirming the robustness of our approach (Section S20). The solid red line in Fig. 2i is a fit to this model (see Figure S37 for more details) and shows the model fully

reproduces our experimental I(V) curves. This agreement between experiment and theory firmly establishes the mechanism of charge transport across our junctions.



Fig. 3. (a) Periodic DFT calculations of $[MV^{*+}]_2$ SAM (on state) and MeV²⁺ SAM (off state) on Au. (b) Experimentally-determined maximum $R_{2/1}$ for Ag-S(CH₂)₁₁MV²⁺X⁻₂//GaO_x/EGaIn junctions (X⁻ = I⁻, Br⁻, Cl⁻ and F⁻) as a function of $\Delta_{dimer}/\delta E_{HOMO}$. The error bars represent 95% confidence intervals. The black dashed line is a linear fit with a coefficient of determination $R^2 = 0.99$. (c) Energy-level diagrams of Ag-S(CH₂)₁₁MV²⁺X⁻₂//GaO_x/EGaIn junction at -1V and (d) +1V, where black arrows indicate electron transport and the blue arrow ion-migration, and Φ_1 and Φ_2 are the work functions of the bottom and top electrode.

We have demonstrated a new class of electric field driven molecular switches enabling junctions with dual functionality with large resistive on/off and rectification ratios. The benefits of having dual-functionality within a single molecular layer (rather than having the diode and memory functionalities in separated junctions or layers connected in series) are the low drive voltage V_{set} of <1.0 V, small molecular dimension (our molecular layer is only 2 nm thick), and simplification of the device structure and associated fabrication (Table S1). The key design principles are to fine-tune the balance between stability and switchability of the system, which was achieved here by optimizing the size of the counterion, and to preorganize the molecules such that dimerization is efficient. In principle, our findings can be extended to other types of redox systems coupled to (supramolecular) chemical reactions, large conformational changes, or dimerization, exemplifying the potential and scope of our findings. Interestingly, our junctions switch to the on state in two distinct steps associated with charging and then dimerization coupled with directional migration of excess negativelycharged counterions to the positively-charged electrode. Although redox processes have been studied in electrochemical memory and thin (polymer) film devices^{28,29,30}, we show here that its effects result in novel function and can be stabilized by ion motion migration in molecular tunnel junctions. The exact mechanism of counterion migration (which also has been observed in tunnel junctions with 1-10 nm long molecular wires³¹, and may depend on the relative humidity of the environment^{32,33}) and the corresponding dynamic electrostatic potential profile of solid state molecular junctions are important to address in future experiments (e.g., by studying junctions with small lateral dimensions with extremely high cut-off frequencies³⁴) and need new quantum-based methods to map the coupled electronic and molecular motions of these field driven processes which typically occur over pico- to nanosecond^{35,36} time scales.

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