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Two-Terminal Molecular Memory via Reversible Switching of Quantum Interference Features in Tunneling Junctions

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Abstract

This paper describes large-area molecular tunneling junctions comprising self-assembled monolayers of redox-active molecules that exhibit two-terminal bias switching. The as-prepared monolayers undergo partial charge-transfer to the underlying metal substrate (Au, Pt or Ag) that converts their cores from a quinoid to hydroquinoid form. The resulting rearomatization converts the bond topology from a cross-conjugated to linearly-conjugated \( \pi \) system. The cross-conjugated form correlates to appearance of an interference feature in the transmission spectrum that vanishes in the linear-conjugated form. Due to the presence of electron-withdrawing
nitrile groups, the reduction potential and the interference feature lie close the work function and Fermi level of the metallic substrate. The relationship between conjugation patterns and quantum interference is well-studied. We exploit this relationship to create non-volatile memory in proto-devices using eutectic Ga-In as the top-contact. The underlying switching mechanism reorders bond topology without changing connectivity or altering the tunneling distance or thickness of the monolayer. These results are a proof-of-concept for switching quantum interference features on and off via \textit{in operando} redox chemistry.

**Keywords:** EGaIn, Quantum Interference, Memory, Switching, Molecular Electronics
Quantum Interference (QI) is a collection of phenomena related to Fermions whose wave functions can interfere with themselves; in molecular tunneling junctions, destructive QI can lower the transmission probability between the electrodes, significantly lowering conductance without altering the tunneling distance.\[^1\] Thus, compounds that produce destructive QI could act as molecular switches, memory devices, or transistors.\[^2,3\] Destructive QI effects have been studied both theoretically and in multiple experimental platforms. In π-conjugated molecules, they are generally ascribed to cross-conjugation,\[^4-7\] meta-substitution,\[^8,9\] or particular spatial arrangements.\[^10,11\] Of particular interest are systems capable of toggling QI effects via external inputs;\[^12-14\] however, control over QI effects is currently limited to transient, single-molecule junctions and/or comparisons of different compounds in different environments,\[^15-17\] for example, the ex operando (electro)chemical interconversion between a cross-conjugated quinone and linearly-conjugated hydroquinone.\[^18,19\] In this work we show that self-assembled monolayers (SAMs) of a cross-conjugated compound incorporating a tetracyanoquinodimethane (TCNQ) unit, \textbf{TCNAQ} (Figure 1), on different metal substrates can be switched between, and addressed in, two conductance states (ON and OFF) in a two-terminal proto-device using eutectic Ga-In (EGaIn) top-contacts. We ascribe the different conductance states to the modulation of the bond topology of the molecule; \textbf{TCNAQ}—just as TCNQ—can readily accept an electron (Figure S4) and form a stable (di)anion that converts cross-conjugated pathways to linearly-conjugated pathways, altering the transmission probability similarly to interconversion of quinones and hydroquinones (Figure 1).\[^20\] A low-lying LUMO brings the reduction potential of \textbf{TCNAQ} close to the oxidation potential of Au, Ag and Pt electrodes, eliminating the need for a third electrode or redox agents.
Figure 1: (A) A pure monolayer of TCNAQ in the cross-conjugated quinoid form is reversibly switched to a mixed-monolayer in which a fraction of the molecules are reduced to a linearly-conjugated, hydroquinoid form; (B) Difference in conjugation pathways between the cross-conjugated neutral form (top), which give rise to destructive QI, and the linearly-conjugated reduced form.

We prepared SAMs of TCNAQ on Au, Ag or Pt surfaces from the thioacetate precursor via in situ deprotection.\cite{21} X-ray photoelectron spectroscopy (XPS) spectra are consistent with upright-standing molecules attached to the surface through a single thiolate bond (Figure 2). Synchrotron measurements provide additional evidence that the nitrile groups are oriented predominantly parallel to the substrate (see Supporting Information for details). The N 1s region of the XPS spectrum of the SAM features an additional peak at lower binding energy (398.5 eV) that is not present in spectra of TCNAQ powder, which we ascribe to the spontaneous (partial) reduction of TCNAQ by the metal substrate. Similar shifts are common in monolayers of TCNQ that are spontaneously reduced by the underlying metal.\cite{22} There, TCNQ is directly adsorbed to the metal substrate while, in SAMs of TCNAQ, the redox-active core is bound through a phenylacetylene arm that is coupled to the surface through a covalent S-Au bond. Thus, charge-transfer (redox) can still occur in a geometry that is compatible with the formation of metal-molecule-metal junctions. In the XPS spectra, about 14% of TCNAQ molecules in the SAM are in a reduced state.
We investigated the electrical properties of TCNAQ in Au-on-mica/SAM//EGaIn junctions (where ‘/’ and ‘//’ denoted covalent and Van der Waals interaction respectively). EGaIn is a liquid metal that can be used to form stable, conformal, non-damaging contacts with SAMs with a diameter of about 20 µm.[23–25] This methodology enables the formation of junctions in multiple areas of a substrate rapidly and reproducibly, allowing the collection of statistically significant data and spectroscopic investigation of the SAM after J/V cycling.[26] As controls, we measured junctions comprising hexadecanethiol (C16SH) and analogs of TCNAQ bearing an anthraquinone core (AQ) or a linearly-conjugated, non-redox-active anthracene core (AC) as shown in Figure S1.

Figure 3 shows forward and reverse J/V traces for junctions comprising TCNAQ (A), AC (B), C16SH (C) and AQ (D). While the J/V traces of the latter three junctions are perfectly overlapping, TCNAQ exhibits a hysteresis loop at negative bias; i.e., after being biased at positive voltages, the conductance at negative bias decreases (OFF) and then recovers its initial conductance (ON) after reaching −1.00 V. A maximum ratio of J between
forward and reverse scan of 2.6 occurs at $-0.65 \text{ V}$. As shown in Figure 4, the hysteresis and magnitude of switching is reproducible across junctions comprising TCNAQ measured on Au-on-mica and template-stripped\cite{27} (TS) Au$^{\text{TS}}$ and Ag$^{\text{TS}}$. The effect is present but diminished on Pt$^{\text{TS}}$ (Figure S27-S28). No hysteresis or switching is present on any substrate for AC, AQ or C16SH.

Figure 3: Examples of log $|J|$ vs. $V$ of junctions comprising SAMs of TCNAQ on Au$^{\text{TS}}$ (A, black), AC (B, blue), C16SH (C, red), AQ (on Au-on-mica, D, cyan). Solid dots represent data acquired during five forward scans ranging from $-1.00 \text{ V}$ to $1.00 \text{ V}$ (in 0.05 V steps, acquired every 0.1 s), while open dots represent data acquired during five subsequent reverse scans from $1.00 \text{ V}$ to $-1.00 \text{ V}$.

Given sufficient trace/re-retrace stability, hysteresis is a form of two-terminal bias-switching,\cite{28–43} but to translate it into a memory effect, the state of a static, two-terminal junction must
Figure 4: Plot of trace over retrace ratio for junctions comprising: (A) SAMs of TCNAQ on AuTS (black), Au-on-mica (hollow), and AgTS (gray), C16SH on AgTS (red), AC on AuTS (blue), AQ on Au-on-mica (cyan). Error bars represent confidence intervals with α = 0.05 (for TCNAQ on Au-on-mica they were omitted for clarity).

be switched reversibly between at least two conductance-states in operando. To characterize the memory effects of Metal/SAM//EGaIn junctions, we performed Write operations (W) by applying a −1.50 V bias, which puts the junction in the high-conductance ON state and Erase operations (E) by applying 1.00 V, which puts it in the low-conductance OFF state. We read the state at −0.50 V, measuring current-densities $J$ of 0.10 Acm$^{-2}$ to 0.01 Acm$^{-2}$.

Figure 5A compares the resulting ON/OFF ratios for junctions comprising SAMs of TCNAQ, AC, AQ and C16SH on Au over four switching cycles. As expected, the ON/OFF ratio for the controls (AC, AQ and C16SH) is 1, indicating no effect. However, TCNAQ exhibits ratios as high as 6 ± 2. Figure 5A shows that the memory effect is identical for Au-on-mica and AuTS, but the peak switching-ratio decreases and shifts to less negative bias on AgTS. On PtTS, the peak decreases and shifts further and the hysteresis becomes noticeable only over a larger bias window (see Supporting Information for details). This trend is consistent with the proposed mechanism because the magnitude of the suppression of conductance scales with the proximity of the destructive QI feature to the Fermi level.$^{[44]}$
Figure 5: ON/OFF Ratio per $n^{th}$ Write-Erase cycle, calculated as ratio of the current after and before the $n^{th}$ Write operation for: (A) SAMs of TCNAQ on Au$^{TS}$ (black), Au-on-mica (orange), and Ag$^{TS}$ (gray), and (B) SAMs of C16SH on Ag$^{TS}$ (red), AC on Au$^{TS}$ (blue), and AQ on Au-on-mica (cyan). The error is calculated as confidence interval with $\alpha = 0.05$.

As shown in Fig. 5, the ON/OFF ratio of TCNAQ slowly decreases, approaching 2 after about 10 cycles; however, even after 30 cycles, applying a $-2.00 \text{ V}$ bias restores the initial ON/OFF ratio (Fig. S34). The conductance of TCNAQ decreases with each W-E cycle (Table S3), which is typical with repeated switching cycles in molecular tunneling junctions. For junctions comprising TCNAQ, such damping could be the result of irreversible reactions, structural modification of the SAMs or a change in the EGaIn contact. However, because the conductance remains constant during $J/V$ sweeps (Fig. 3, as opposed to R-E-W cycles, i.e., Fig. 5), the underlying phenomenon is specific to large, rapid changes in bias.

In its pristine state, a destructive QI feature is clearly present in the transmission spectrum near $E_f$ (Figure S44A). In single-molecule STM break-junctions comprising TCNAQ, this QI feature manifests as a low conductance, comparable to that of AQ, which is known to exhibit strong destructive QI effects in both single molecule and SAM-based junctions (Figure S41). However, ensemble junctions comprising SAMs of TCNAQ exhibit a relatively high conductance, comparable to the linearly-conjugated analog AC (Figure S10), which does not exhibit any QI features. We ascribe the difference between TCNAQ in SAMs and in single-molecule junctions to the presence of reduced TCNAQ in the SAM (Figure 2C). Tunneling charge-transport through SAMs is sensitive to the entire supramolecular...
structure of the monolayer, which comprises molecules in different conformations and, in the case of TCNAQ, redox states.\textsuperscript{[11,48]} Figure 1B shows the bond topology of TCNAQ in the pristine and reduced states. The addition of one or two electrons converts the cross-conjugated quinoid core into a linearly conjugated, fully aromatic hydroquinoid. (The driving force of rearomatization is the reason that TCNQ is an exceptional electron-acceptor.) Treating each molecule in a SAM as a resistor in parallel, it follows from Kirchoff’s rules that a small fraction of reduced TCNAQ molecules can dominate charge-transport through the SAM due to the exponential difference in the conductance of TCNAQ in the cross- and linearly-conjugated (quinoid/hydroquinoid) forms.\textsuperscript{[49]} Specifically, if two pathways in a SAM differ in conductance by two orders of magnitude (similar to AQ and AC at 0.50 V), the presence of only 1\% to 2\% of the more conductive pathways is sufficient to dominate the conductivity of the SAM.\textsuperscript{[50]} Thus, the hysteresis and switching phenomenon are most likely caused by a shift in the equilibrium between the low- and high-conductance states of TCNAQ; applying a bias to the junction affects the fraction of molecules in the junction that exhibit destructive QI.

If the proposed mechanism is correct, the ON state is metastable and should slowly relax to lower conductance, since the thermodynamic minimum is the neutral, low-conductance state. Indeed, the ON state current decreases in time with multiple read cycles, while the OFF state only shows small, stochastic fluctuations, which are discussed further in the Supporting Information. The initial ON/OFF ratio is restored after a new W cycle—\textit{i.e.}, applying a pulse at negative bias restores the SAM to the initial state in which a greater fraction of TCNAQ is in the reduced state. We ascribe this observation to the slow kinetics of the relaxation (re-oxidation) process. When a charge is placed in a SAM by the reduction of a molecule, the local environment in the SAM reorganizes to minimize the free energy of the system, which is a much slower process than the initial electron-transfer. After 5 min, without any applied bias, the ON/OFF ratio decreases to 70\% of its initial value; after 20 min it decreases to 60\%. 
Metal/TCNAQ//EGaIn junctions are a form of non-volatile memory; their state is retained when the power (bias) is removed. It is difficult to contextualize TCNAQ further. There are examples of memory effects in molecular tunneling junctions, each demonstrating a salient feature: some exhibit high switching ratios as single-molecules, but not in (proto-)device platforms;\textsuperscript{[37,42]} some require prohibitively complex fabrication;\textsuperscript{[35]} some only switch at low temperature;\textsuperscript{[28]} some are resistant to fatigue when switched with light, but not with bias.\textsuperscript{[51]} In simple, two-terminal proto-devices, TCNAQ exhibits reasonably high ON/OFF ratios that are stable for tens of minutes and that can be refreshed or re-written over at least dozens of cycles. The switching mechanism is phenomenologically unique, exploiting the coincidental alignment of a destructive QI feature and facile reduction with the Fermi level and work function of Au to enable the shift of a dynamic equilibrium of molecules in high-conductance states lacking QI features and low-conductance states with strong QI features near the Fermi level. The switching effect is molecular in nature, and further investigation and optimization can feasibly exploit this type of QI-based switching to achieve switching ratios of orders of magnitude.

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References


(13) Selzer, Y.; Cai, L.; Cabassi, M. A.; Yao, Y.; Tour, J. M.; Mayer, T. S.; Allara, D. L. 

(14) Jia, C. et al. 

(15) Liu, Z.; Ren, S.; Guo, X. 

(16) Yang, G. et al. 


(22) Tseng, T.-C. et al. Charge-Transfer-Induced Structural Rearrangements at Both Sides of Organic/Metal Interfaces. Nat. Chem. 2010, 2, 374–.


(24) Dickey, M. D.; Chiechi, R. C.; Larsen, R. J.; Weiss, E. A.; Weitz, D. A.; Whitesides, G. M. Eutectic Gallium-Indium (EGaIn): A Liquid Metal Alloy for the Forma-


A mixed-monolayer comprising cross- and linearly-conjugated molecules exhibit high conductance. When the linearly-conjugated species are reversibly oxidized back to cross-conjugated species, destructive quantum interference is restored and the conductance drops, causing a memory effect.