Single-Molecule Switches

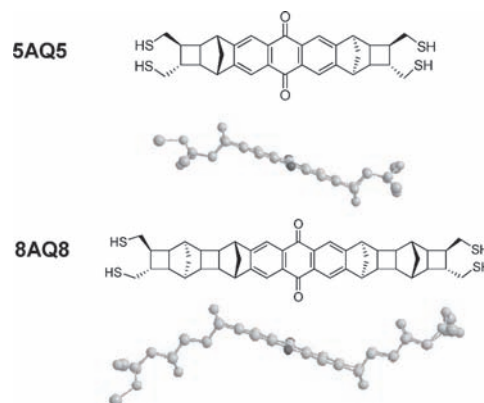# Observation of Electrochemically Controlled Quantum Interference in a Single Anthraquinone-Based Norbornylogous Bridge Molecule**

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There is considerable ongoing interest in understanding the electrical properties of single molecules both from a fundamental point of view and for potential applications in single-molecule technologies.[1–4] An important goal in molecular electronics is the ability to switch, by means of electrochemical gating, the conductance through a single molecule and, in this context, the anthraquinone/hydroanthraquinone, AQ/H_2AQ, redox couple has been proposed as a suitable candidate for study.[5] Indeed, calculations[6] predict that electrochemical gating of conductance in AQ-based molecular switches should be strong, with conductance on(H_2AQ)/off(AQ) ratios of several orders of magnitude. The switching mechanism is due to the presence of destructive quantum interference (QI) between various conductance channels in the cross-conjugated AQ, which is absent in the linear-conjugated H_2AQ, thereby resulting in lower conductance in AQ, compared to H_2AQ. Recently, Fracasso et al.[7] have experimentally confirmed the operation of QI in bulk conductance studies of self-assembled monolayers (SAMs) of arylethynylene thiolates (aryl = anthracene, AQ, 9,10-dihydroanthracene).[7]

We now report the first experimental evidence for the operation of electrochemically controlled QI in a novel AQ-based norbornylogous bridge tetrathiol, **5AQ5** (Scheme 1), from single-molecule conductance measurements using the scanning tunneling microscopy (STM) break junction technique.[8] We show that the AQ moiety in **5AQ5** can be electrochemically and reversibly switched in situ between the

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Scheme 1. Molecular structure of the compounds used in this study. The **5AQ5** molecule possesses five bonds on each side and an AQ moiety in the center. **8AQ8** possesses eight bonds on each side and an AQ moiety in the center. The detailed experimental procedures for the synthesis of compounds **5AQ5** and **8AQ8** along with analytical and spectral information can be found in the Supporting Information.

high-conducting H_2AQ form and the low-conducting AQ system. Further, we demonstrate that the potential range of the conductance enhancement can be shifted using different pH values. This pH dependency of the AQ/H_2AQ redox reaction constitutes an extra degree of freedom that can control single-molecule conductivity.

A key design feature of **5AQ5** is the cementing of the AQ group into a rigid, structurally well-defined norbornylogous (NB) unit bearing two pairs of thiol groups at each end, thereby conferring additional stability to SAMs derived therefrom. The 19.8 Å length of **5AQ5** is much greater than the gate thickness, that is, the electrochemical double layer that relates to the diameter of the ions used in the electrolyte, thereby ensuring that the field screening effect due to the proximity of the source and drain electrodes is negligible.[9]

Norbornylogous bridges have played pivotal roles in investigating many fundamental aspects of electron-transfer (ET) processes,[10,11] including those involving SAMs derived therefrom.[12–16] In particular, NB bridges are very efficient mediators of ET by the superexchange mechanism and it was hoped that the NB bridge would likewise facilitate coherent charge transport in **5AQ5**, which is a prerequisite for QI to be operative. This issue was first investigated by determining the magnitude and distance dependence of the single-molecule conductivity in **5AQ5** and its longer cognate, **8AQ8**. X-ray photoelectron spectroscopy (XPS) and STM studies on SAMs formed from **5AQ5** and **8AQ8** on gold surfaces confirmed that the **5AQ5** and **8AQ8** molecules stand upright on the gold surface, anchored by a pair of thiolates at one end and a pair

of free thiols at the distal end that is easily accessible to the gold STM tip (see the Supporting Information). Single-molecule conductance measurements were determined using the STM break junction method with a two-electrode setup.[8] Conductance histograms were built using several hundred current–transient curves for **5AQ5** and **8AQ8** (see the Experimental Section for details). The conductance values (G_o) for **5AQ5** and **8AQ8** are $(2.7 \pm 1.1) \times 10^{-4}\ G_o$ and $(1.7 \pm 1.0) \times 10^{-5}\ G_o$, respectively (Figure 1). These values are significantly larger than those obtained previously for completely saturated NB tetrathiolates of comparable length.[14] For example, the conductance of **5AQ5**, with a bridge length of 16 bonds, is more than two orders of magnitude greater than that measured for a completely saturated 15-bond NB bridge molecule $(1.6 \times 10^{-6}\ G_o)$.[14] The distance dependence attenuation factor,[*] β, for the conductance of **5AQ5** and **8AQ8** is (0.46 ± 0.17) bond^{-1}. This value is smaller than that obtained for saturated NB bridge systems (around 1 bond^{-1}).[2] The enhanced conductance and smaller β values for **5AQ5** and **8AQ8**, compared to saturated NB bridges, signifies that the charge transport in these molecules is occurring through superexchange-mediated coherent (i.e. tunneling) charge transport involving virtual ionic states of the AQ group. An incoherent, ohmic scattering mechanism is ruled out on the grounds that the conductance would show a linear dependence on the bridge length resulting in a conductance ratio for **5AQ5:8AQ8** of around 1.4, instead of the observed value of 15.9.

Electrochemical gating of **5AQ5** was performed using a four-electrode setup in which a counter electrode, controlled through a reference electrode, acts as the "gate" for the tunneling process. The other two electrodes (the STM tip and the gold surface) act as contacts to the molecules and can be thought of as the source or the drain of a single molecular device.

The AQ moiety in **5AQ5** undergoes a proton-coupled redox reaction in aqueous solution and the redox couple can be switched between the oxidized AQ form and the reduced H_2AQ form.[17] This is confirmed by cyclic voltammograms (CVs) of a SAM formed from **5AQ5** on an Au(111) surface in
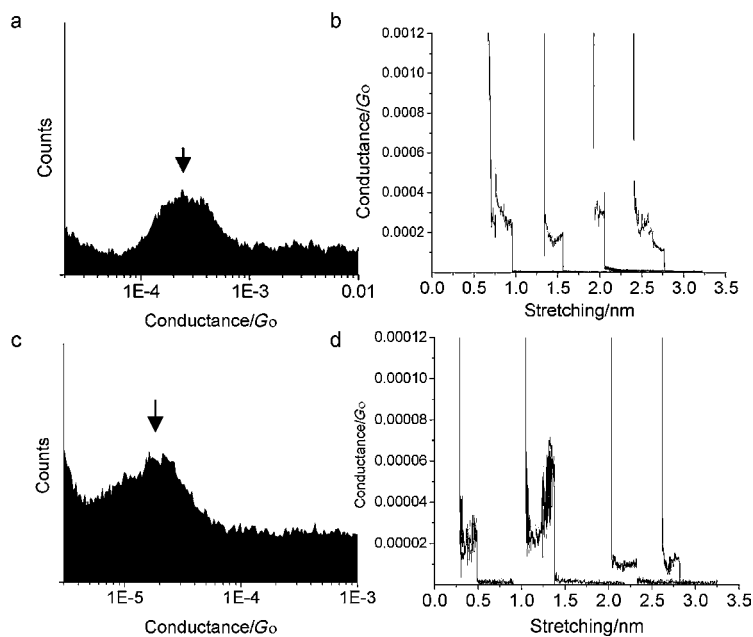
Figure 1. a) Conductance histogram of **5AQ5**. b) Typical individual current–transient curves of **5AQ5**. c) Conductance histogram of **8AQ8**. d) Typical individual current–transient curves of **8AQ8**. The histograms were built from around 750 individual transient curves by counting the number of times each step occurs and weighting that number by the time duration of the step.

0.5 M phosphate buffer at two different pH values (pH 3 and 8). The CVs show reduction/reoxidation peaks corresponding to a two-electron redox switching of the AQ redox center (Figure 2a). The half-wave potential ($E_{1/2}$) of the redox
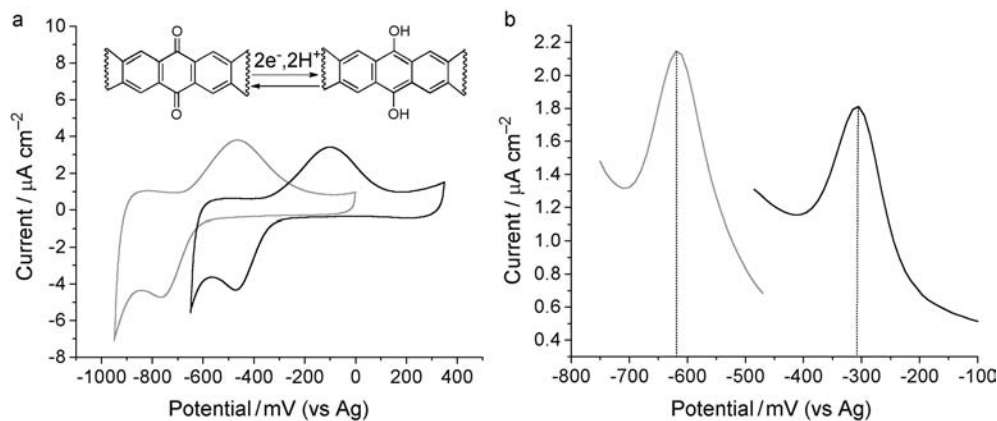

Figure 2. a) Cyclic voltammetry at 50 mVs^{-1} vs. Ag of an Au(111) surface modified with a SAM of **5AQ5** in 0.5 M phosphate buffer, pH 3 (black line) and pH 8 (grey line). The inset is the redox reaction of the AQ moiety to an H_2AQ moiety. b) ACVs at pH 3 (black line) and pH 8 (grey line). Data was obtained at a frequency of 1 Hz and an AC amplitude of 15 mV.

reaction was found to shift more cathodic by around 315 mV when the buffer used is changed from pH 3 to 8. The values of $E_{1/2}$ were obtained from the peak maximum in alternating current voltammograms (ACVs) at low frequency of 1 Hz (Figure 2b). The shift of $E_{1/2}$ with pH is consistent with a $2e^-/2H^+$ redox reaction which is widely reported on

[*] Conductance is given by $G = G_c e^{-\beta L}$ where G_c is the contact conductance, β is the tunneling decay constant, and L is the length of the molecule.

AQ SAMs in this pH range.[17–19] The anodic and the cathodic waves in the CVs scaled linearly with the scan rate indicating a surface-related redox process. Plots showing the dependence of the peak current and the peak potential on the scan rate are presented in the Supporting Information.

Figure 3 shows the corresponding dependence of the single-molecule conductance on the electrochemical potential of **5AQ5** at pH 3 and 8. The conductance measurements were performed at a constant tip–surface bias of $+100$ mV. At a surface potential of $+300$ mV (vs. Ag), where the AQ is in its oxidized form, the single-molecular conductance of **5AQ5** is $(2.4 \pm 1.2) \times 10^{-4}$ G_o which is close to that obtained with the two electrode systems, $(2.7 \times \pm 1.1) \times 10^{-4}$ G_o.
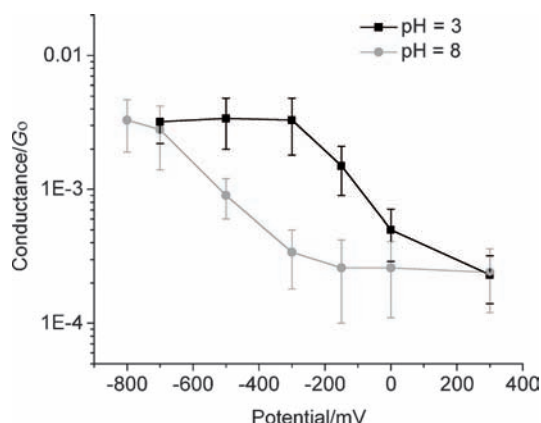
Figure 3. Evolution of the conductance of **5AQ5** with a gate potential at pH 3 (black line) and pH 8 (grey line). Each data point is the peak maximum in the histograms. Error bars are calculated from the full width at half maximum (fwhm) of the histogram peaks. Each data point is obtained at a fixed gate potential vs. Ag. The conductance value plateaus at around -300 mV for pH 3 and around -700 mV for pH 8. Typical individual curves along with histograms at different gate potentials are presented in the Supporting Infomation.

As the potential of the surface is shifted more cathodic, the conductance histogram shifts to higher values and reach a maximum value of $(3 \pm 1.4) \times 10^{-3}$ G_o. Thus, the conductance is increased by more than an order of magnitude at potentials more cathodic than the $E_{1/2}$ of the redox reaction. When the pH of the electrolyte was changed from 3 to 8, the increase in the conductance is shifted to more cathodic values. The conductance value reaches a maximum value at around -300 mV for pH 3 and around -700 mV for pH 8. These values are close to the $E_{1/2}$ values obtained at pH 3 (-305 mV) and pH 8 (-620 mV) in the CVs and ACVs. Once the potential is shifted back to $+300$ mV the conductance value was found to restore its original value of $(2.5 \pm 1.0) \times 10^{-4}$ G_o, which indicates that the switching system is reversible.

As a control experiment, we found that a SAM constructed using a NB bridge (11-NB) that lacked the AQ moiety (Figure 4, inset) displayed no dependence of the conductivity on the electrochemical potential over the same potential window that was used for **5AQ5** at pH 3 (Figure 4). This finding confirms that the increase in the conductance of
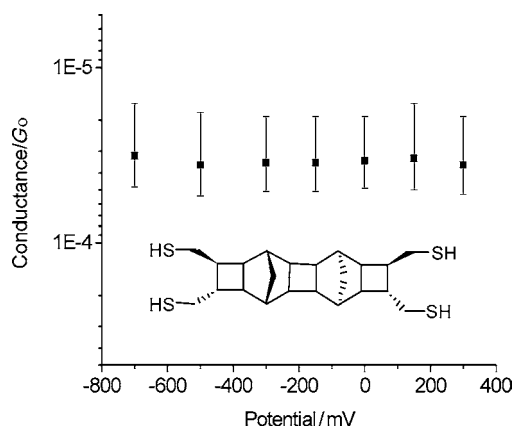
Figure 4. Evolution of the conductance of 11-NB that lacks the AQ moiety, with a gate potential at pH 3. The inset is the structure of 11-NB. Typical individual curves along with histograms at different gate potentials are presented in the Supporting Information.

5AQ5 at the $E_{1/2}$ value is due to the redox switch from the AQ to the more conducting H$_2$AQ moiety.

The conductance of 11-NB is $(3.5 \pm 1.2) \times 10^{-5}$ G_o. This value is significantly lower than the conductance of **5AQ5** in the oxidized form, $(2.7 \pm 1.1) \times 10^{-4}$ G_o, despite the **5AQ5** being five bonds longer than 11-NB. The high conductance of **5AQ5** and **8AQ8** opens up the possibility to design partially conjugated NB bridges that incorporate two or more AQ moieties thus achieving very long molecules that are chemically stable, rigid, and can be electrochemically switched to a higher conductance state by reducing the AQ moieties.

In summary, we have shown the successful operation of a single-molecule switch in an AQ-NB system with a conductance on/off ratio of an order of magnitude. This magnitude, which is attributed to destructive QI effects operating in the AQ form,[*] is smaller than that predicted from simple theoretical calculations,[6] but is similar to the experimentally found magnitude from bulk conductance studies across SAMs.[7] The AQ moiety can be electrochemically switched in situ between the high-conducting H$_2$AQ system and the low-conducting AQ system. Further, it is shown that the potential range of the conductance enhancement can be shifted using different pH values. Therefore, such systems could potentially be used as single-molecule pH-gated transistors.

[*] Evidence that the observed electrochemical switching in **5AQ5/** 5 H$_2$AQ5, is due to QI, rather than to incoherent processes is: 1) For relatively short molecules, such as **5AQ5**, the time-scale for the electrons is expected to be fast compared to the time-scale of vibrations or solvent polarization, so the transport should be coherent. 2) Theoretical work in ref. [7] confirms the presence of QI in a related system. 3) The conductance vs. potential plot (Figure 3) shows a plateau at negative potentials, rather than a drop as would be predicted for an incoherent process, which further confirms that the molecule is either in AQ or H$_2$AQ form.

Experimental Section

Sample preparation: Gold substrates were prepared by thermally evaporating around 100 nm of gold (99.999% Alfa Aesar) on freshly cleaved mica slides (Ted Pella, Inc.) in an ultrahigh-vacuum chamber (around 5×10^{-8} torr). Prior to each experiment, the substrate was briefly annealed in a hydrogen flame to remove possible contamination and to form an atomically flat surface and then it was immediately immersed into a 10 μm NB bridge solution in dichloromethane (DCM). The substrate was left in the modification solution for three hours after which it was removed, washed thoroughly with DCM and used for the measurements.

Electrochemistry: The redox electrochemistry of SAMs formed on freshly annealed Au(111) substrates of compound **5AQ5** were studied by cyclic voltammetry using a BAS 100B electrochemical analyzer. The counter electrode was a platinum mesh and the reference electrode was a silver wire. The electrolyte used was 0.5 m phosphate buffer using Na_2HPO_4/NaH_2PO_4 for pH 8 and NaH_2PO_4/H_3PO4 for pH 3. The same setup was used to record the ACVs with a Solartron Impedance/Gain-Phase Analyzer. The alternating current (AC) amplitude was 15 mV. Data analysis was carried out using the program Z view by Scribner Associates Inc.

Conductance measurements: The STM break junction setup was a modified Pico-STM (Molecular Imaging) using a Nanoscope IIIa controller. The setup and method have been described in details elsewhere.[8] The SAM modified Au (111) substrate was placed in a Teflon STM cell and the surface was covered with toluene. The molecular conductance was measured by repeatedly forming and breaking Au point contacts using an STM gold tip (99.998% Alfa Aesar). The first step was to image the substrate in the regular STM mode. Images showing clear and sharp atomic steps are good indication of a clean substrate and a sharp tip. After surveying the substrate and confirming the tip condition, the tip was fixed at the center of an atomically flat terrace and the STM feedback loop was turned off. Consequently, a Lab View program was used to move the tip into and out of contact with the substrate at a typical rate of 40 nms^{-1}. During the contact process, molecules can bridge between the tip and the molecules on the surface through the thiol linkers at the distal end of the molecules. After reaching a preset current value, the tip was pulled back until the current drops to zero. This process was repeated automatically thousands of times. Typically 3000 curves were collected for each experiment. Transient curves that are either noisy or that showed smooth exponential decay because of the absence of a bridging molecule were all rejected when building the histograms. The percentage decay curves that showed clear molecular steps were typically between (20–40)% and were all selected for building the histograms.

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