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Large Amplitude Conductance Gating in a Wired Redox Molecule

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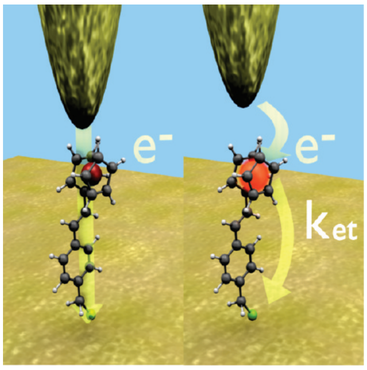
ABSTRACT Further developments in the field of molecular electronics will require an understanding of the key relationships between chemical composition and subsequently observed electron transport characteristics. Although the relationship between redox activity and conductance gating has emerged in recent years, our ability to chemically engineer these characteristics (such as "on−off" switching magnitudes) is only now emerging. The report herein describes, to our knowledge, the first example of gated conductance in a single wired redox molecule in which a 3 orders of magnitude "on/off" switching ratio is observed. This switching magnitude significantly exceeds that observed with molecules weakly coupled to the supporting electrode and correlates directly with both electrochemical switching and an in situ determined heterogeneous electron transfer rate constant.

SECTION Electron Transport, Optical and Electronic Devices, Hard Matter



In any proposed "bottom up" nanofabrication route, the spontaneous self-assembly of organic molecules onto metallic surfaces is of considerable benefit. By applying the "vertical electrode configuration" of an appropriately configured scanning probe microscope, the conductance characteristics of pre-imaged molecular wire candidates can be examined in a statistically meaningful manner with relative ease and spatial and load control. Scanning tunnelling microscopy (STM) enables routine imaging of single molecules with angstrom-level lateral resolution, conductance measurement, and current−voltage spectroscopy. In an appropriate electrolytic environment, tunnelling conductance analyses can, additionally, be carried out with contact electrodes at potentials fixed to a reference point where molecules of interest are both solvated and enjoy access to counterions. It has previously been shown that, in the absence of any directly accessible orbitals, transport through many adsorbates (including alkyl thiols, pi-delocalized systems, and biological molecules) can be treated as that through a structureless dielectric of some defined barrier height and length.[1−4] The presence of a redox site (orbital states accessible at certain incident electron energies) means that this simple model fails at certain voltages; specifically, the availability of accessible metal states facilitates a "surge" in current at specific incident electron energies.[5−12] This electrochemical conductance gating is powerfully probed in a four-electrode configuration and is analogous to transistor behavior at the single-molecule level. Although the relationship between redox activity and conductance gating has emerged in recent years, our ability to chemically engineer these characteristics (such as "on−off" switching magnitudes) is yet to be explored. We report here a comparison of the single molecule electrochemical gating magnitudes, as determined in equivalent tunnelling environments observable with iron redox sites strongly and weakly coupled to their supporting electrode surface.

We initially consider a molecule in which redox site-electrode coupling is characteristically weak a metalloprotein. Figure 1 is a tunnelling image of horse heart cytochrome *c* (HHCC) molecules physisorbed on a 11-mercaptoundecanoic acid-modified Au(111) surface. These molecules, in which the redox site is accessible only through the protein and saturated alkyl dielectrics, exhibit comparatively slow heterogeneous electron transfer kinetics (electron transfer rate, k_{et} 10 ± 1 s^{-1}) and nanoSiemens-level conductance that can be tuned across less than an order of magnitude (see below), an observation broadly consistent with previous metalloprotein analyses.[14−16]

In bridging the separation between a redox active iron moiety and an underlying electrode with a π-delocalized molecular wire [electronic distance decay parameters of oligo-phenylenevinylene (OPV), alkyl and a protein fold are ∼0.1−0.6, 0.9−1.2 and ∼1.4 $Å^{-1}$ respectively[17−19]], coupling between the two, as detectable through electrochemically determined k_{et}, is greatly increased (*vide infra*).[20] To rigorously analyze single molecule conductance in a well-defined surface conformation, **1** was assembled by insertion into the point defects presented by a preassembled crystalline

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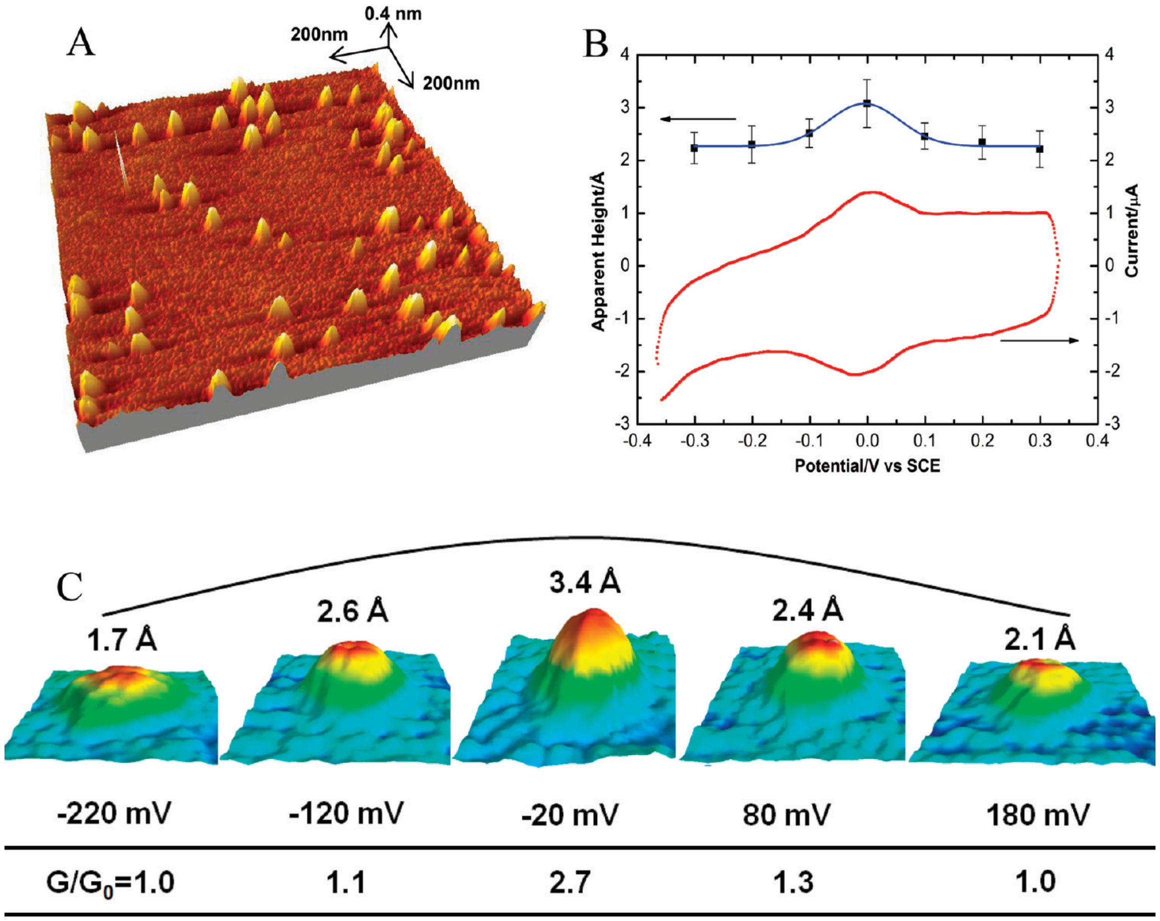

Figure 1. (A) In situ fluid tunnelling image of the HHCC adlayer (200 nm × 200 nm). The low apparent molecular height (2−4 Å) is reflective of the protein fold conductance.[13] (B) Comparative plots of tuned molecular height (qualitatively equivalent to molecular conductance and averaged across 24 molecules) and monolayer voltammetric response ($E_{1/2}$ −19 ± 3 mV vs SCE). (C) Three-dimensional (3D) representation of the modulation of measured STM apparent height of a HHCC molecule on a 11-mercaptoundecanoic acid self-assembled monolayer (SAM) as a function of applied substrate potential (vs SCE). The modulation is attributed to the tuning of the available redox energy level relative to the Fermi energies of the two electrodes (tip and substrate). The difference between on- (−0.02 V vs SCE) and off-resonance (−0.22 V vs SCE) measured heights of 1.0 Å corresponds to an increased conductance of 2.7-fold (values here generated by averaging over 24 single molecules). The black line is an aid to the eye.

monolayer (Figure 2), a protocol that has been usefully applied to conductance analyses in alkyldithiols,[21] and a number of nanoparticle-tagged molecular wires including oligophenylene ethynylenes (OPEs), OPVs,[22,23] oligo-thiophenes,[24] viologen dithiols,[25] and porphyrins.[3]

The ferrocene wires are imaged 4.5 ± 0.8 Å higher than the surrounding decanethiol matrix (at underlying substrate potentials far from resonance; see below), despite their expected equivalent molecular height (Figure 2).[27] This high contrast is expected with molecules of high relative conductance,[22] and specifically equates to a conductance enhancement of ∼31000 times using a tunnelling decay constant of 2.3 Å^{-1} for the inert atmosphere junction between the tip and the molecule.[28,29] These films exhibit close to ideal voltammetric behavior (Figure 3A) and a half wave potential of 313 ± 2 mV versus saturated calomel electrode (SCE), averaged over 90 different sweep rates (between 1 V s^{-1} and 240 V s^{-1}). An in situ chronoamperometric analysis of the kinetics of redox electron transfer (within equipment bandwidth limitations) suggests a rate, k_{et}, exceeding 10^4 s^{-1}, as expected based on published indirect laser-induced temperature jump analyses of ferrocene linked by an OPV bridge with similar length.[17]

As with the cytochrome junction, only considerably more so, tunnelling current was observed to be sensitively dependent on the underlying substrate potential (Figure 3B,C). Using a model introduced previously,[33] the relative conductance of the "on" and "off" states of a redox tunable molecule may be topographically estimated (conductance increase being reflected by piezo driven tip withdrawal from the molecule and an increase in apparent molecular height, Δh). Specifically, in making the reasonable assumptions that neither molecular height nor buffer solution tunnelling barrier are affected by surface potential (the tip bias is fixed), the relative conductance of the two states is given by[33] G_1/G_2 = $\exp(\beta\Delta h)$, where β is the decay constant of the buffer solution, determined in situ above the adlayers to be 1 ± 0.1 Å^{-1} (see Supporting Information).[34] For the weakly coupled cytochrome conductance is modulated by a factor of

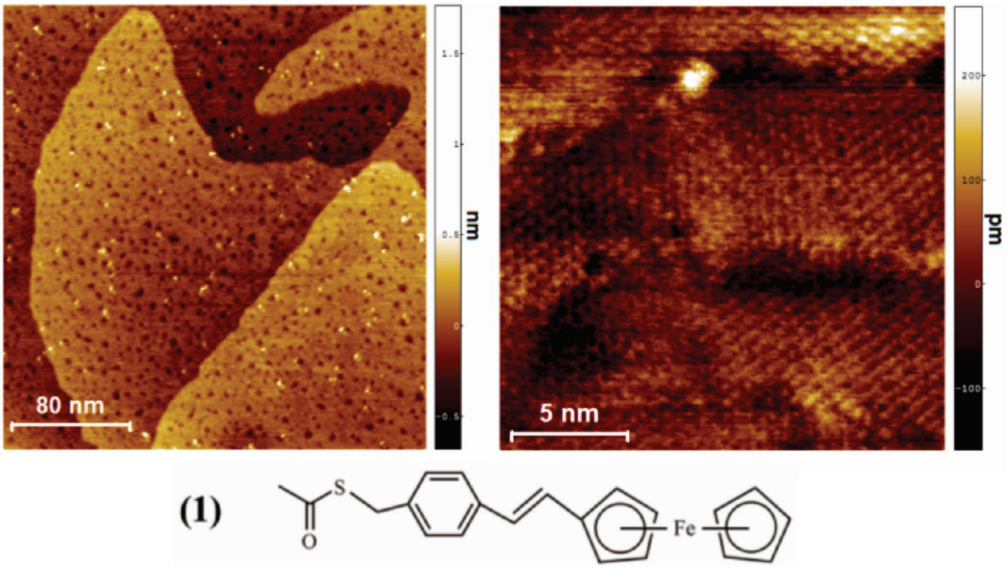

Figure 2. Constant-current STM images (0.2 V, 25 pA) of the ferrocene-terminated wire **1** embedded in a decanethiol monolayer by postassembly. The dark spots evident are pinhole SAM defects well-known to be resolved in such imaging. A comparison of charge transfer under reductive stripping and Faradaic analysis estimates that the ferrocene wire constitutes typically ∼0.4% of the monolayer film (a coverage broadly consistent with imaging analyses). Vertically orientated molecules of **1** are estimated (Chem 3D/Gaussian 2.1) to be approximately the same as the host film thickness, 1.4−1.5 nm (as determined by ellipsometry).[26]

approximately 2−3. For the ferrocene wire **1**, the 7−8 Å piezo movement corresponds to an on/off conductance ratio of *up to 3000* (see Figure 4). Analyses under equivalent experimental conditions of either the saturated decanethiol matrix or a nonferrocene appended form of **1** confirm the absence of any gating effects. Gated imaging analyses (conductance analysis through image contrast change as a function of the gate voltage) of all molecules were carried out under conditions of comparable ionic strength (10−20 mM phosphate buffer, pH 7.0) and 1−1.5 GΩ tunnelling ($1.2-1.3 \times 10^{-5}$ G_0, where G_0 is the conductance quantum) resistance (from which we rule out significantly variant tip−molecule electronic coupling).

An in situ determination of the electrochemical reorganization energy associated with **1** (with the tunnelling probe withdrawn) gives a value of 1.18 ± 0.04 eV, broadly consistent with prior reports on with molecules of this type[17,31] (see Supporting Information). Within the analysis of its conductance gating we have not neglected potential changes in this parameter with surface potential (tunnelling probe position); in considering the relative radii of the probe apex and terminal ferrocene group (∼10 Å and 6.6 Å[35] respectively), and the weak mechanical coupling between them off-resonance,[5,11] a 7−8 Å increase in separation would correspond to a reorganization energy (λ) increase of much less than 0.1 eV,[10] a modulation that will not impact the conclusion of a 3 order of magnitude gating. In the models developed by Schmickler,[36] and Kuznetsov,[10,12] these λ values also define the relationship between conductance maximum and electrochemically determined half wave potential. A one-step resonance tunnelling model predicts a maximum molecular conductance when the surface potential E_{surface} is displaced from the redox site midpoint potential E_0 according to: $E_{\text{surface}} = E_0 - \lambda - V/2$ where V is the applied bias.[9] (Predictions within a coherent two-step tunnelling process[10] are equivalent). The experimentally observed conductance maxima for HHCC and **1** are displaced from corresponding midpoint potentials by 50 ± 2 mV and 14 ± 3 mV, respectively. This observation of positive offset lies contrary to the predictions of coherent tunnelling and is consistent with sequential two step tunnelling being dominant in both cases. Within such a theoretical framework, in the limit of adiabatic coupling to both electrodes, the width of the switching peak has been related to the junction field asymmetry.[11]

In summary, on moving a redox active iron center into the strongly coupled adiabatic regime, gated molecular conductance can be modulated dramatically by the supporting electrode potential. In any tunnelling configuration, measured conductance is a sensitive function of the ability of incident electrons to utilize a potentially accessible density of states (at least partially controllable through the Fermi window spanned by the electrodes). This in turn is tunable by absolute electrode potential to a degree that is dependent on the strength of molecule−electrode electronic coupling, the parameter qualitatively reflected by electrochemically determined electron transfer kinetics. Whether (mechanistically) transport proceeds via a one-step resonance process or a two-step redox process (the latter more consistent with observations we report here), redox site-electrode coupling is likely to make a significant (or indeed limiting) contribution to current. Since the first example of potential modulated molecular conductance by Tao,[6] subsequent work with transition metal complexes or metalloproteins has been associated with redox sites electrochemically decoupled from supporting electrodes, and comparable degrees of gating (2−15-fold) have been demonstrated.[7,33,37−39] In many cases, the relationship between gated conductance and electrochemistry is unclear. The report herein describes, to our knowledge, the first

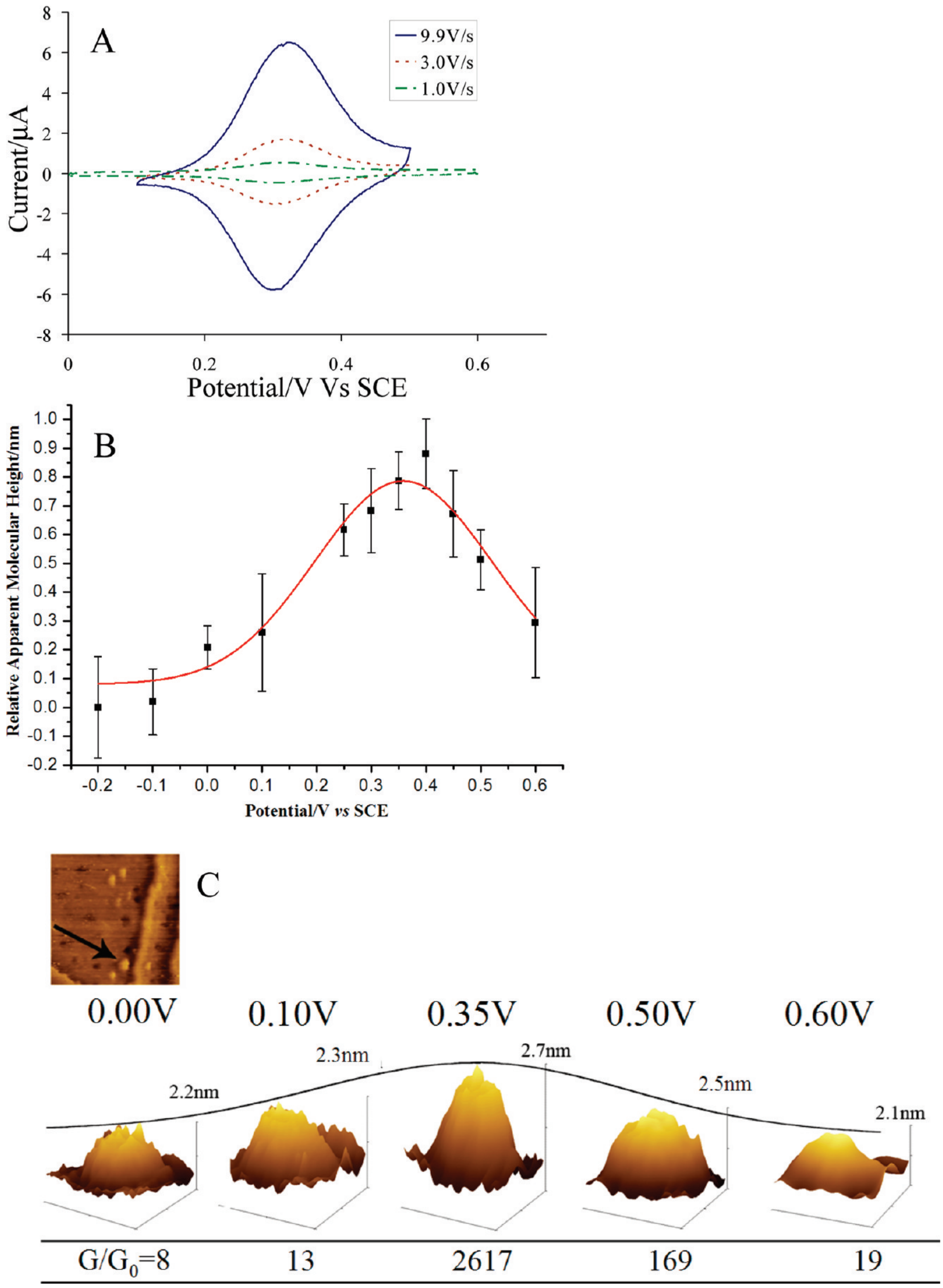

Figure 3. (A) Cyclic voltammograms of a mixed ferrocene wire/dodecanethiol monolayer, obtained in 100 mM phosphate buffer, pH 7.0. The peak separation remains small even at high scan rates, and the full width at half-maximum of 125 mV at 1 V s^{-1} is close to the theoretical minimum. The half wave potentials of ferrocene-appended monolayers are known to be sensitive to chain length (image charge effects), local environment, and the linker.[17,30,31] The half wave potential reported here is 50−100 mV more anodic than previous reports of ferrocene-terminated alkyl or OPV layers but in line with OPE equivalents. (B) Ferrocene-wire **1** apparent electrochemical STM (EC-STM) height modulation (black squares with a Gaussian best fit) at varying substrate potential, obtained in 10 mM phosphate buffer, pH 7.0; current set-point 0.2 nA, tip−substrate bias 0.2 V. Normalized molecular conductance is tuned by applied potential, reaching a maximum near the half-wave potential. The Gaussian fit shows a maximum at 0.36 V/SCE, 0.05 V positive relative to E_0. (C) 3D representation of the conductance gating of a single molecule of **1** (the arrowed high contrast feature in the inset; the "dark holes" are pinhole defects in the SAM[32]). As with the cytochrome buried iron tunnelling current increases to a maximum close to the electrochemical midpoint potential ($E_{1/2}$), falling off at potentials either side of this. The black line is an aid to the eye. These contrast changes can be used to calculate the relative conductance (G) of states compared to the "off-resonance" height observed at potentials far from $E_{1/2}$. In defining the latter as G_0 (taken in this case to be the measured height at −0.2 V vs SCE), G/G_0 then corresponds to the magnitude of conductance switching (values here generated by averaging over 37 single molecules).

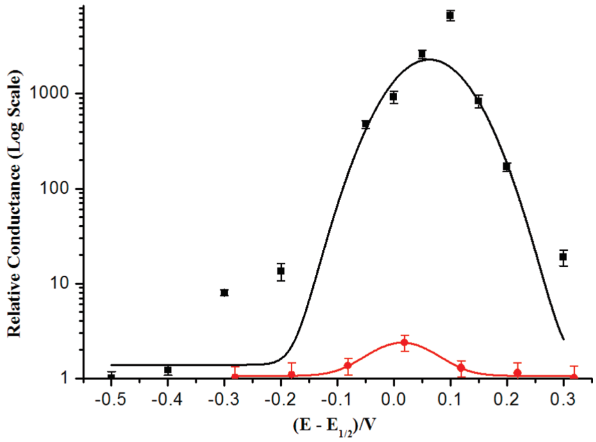

Figure 4. Comparison of calculated relative conductance change for **1** (black squares) and HHCC (red circles). The solid lines are a guide to the eye and depict the best Gaussian fits. The redox active wire **1** is seen to exhibit a far higher conductance modulation between the on- and off-resonance states. In both cases, conductance is maximized close to the respective half-wave potential.

example of gated conductance in a single wired redox molecule in which a 3 orders of magnitude "on/off" switching ratio is observed and correlated directly with both electrochemical switching and an in situ determined heterogeneous electron transfer rate constant.

SUPPORTING INFORMATION AVAILABLE Synthesis of **1**, electroanalyses, Gaussian fits to EC-STM height modulation, and tunnelling data for in situ determination of the distance decay parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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