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Structure–Property Relationships in Redox-Gated Single Molecule Junctions – A Comparison of Pyrrolo-Tetrathiafulvalene and Viologen Redox Groups

Edmund Leary,[†] Simon J. Higgins,^{*,†} Harm van Zalinge,[†] Wolfgang Haiss,[†] Richard J. Nichols,[†] Sune Nygaard,[‡] Jan Oskar Jeppesen,^{*,‡} and Jens Ulstrup[§]*Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, U.K., Department of Physics and Chemistry, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark, Department of Chemistry and NanoDTU, Technical University of Denmark, DK2800 Kgs. Lyngby, Denmark*

Received March 6, 2008; E-mail: shiggins@liv.ac.uk; joj@ifk.sdu.dk

There is a growing realization of the important role that electrochemistry plays in molecular and organic electronics and of the potential for creating new electronic devices which use electrochemistry to control an electrical response. Electrochemical processes have been implicated in controlling the electrical behavior of a number of molecular devices such as rotaxane based switches and negative differential resistance (NDR)¹ devices, although it is not always straightforward to ascertain the mechanism. It has recently been demonstrated that the electrical properties of single molecules incorporating redox groups (e.g., viologens,^{2,3} oligophenyleneethynylenes,⁴ perylene tetracarboxylic diimides (PTCDI),⁵ and oligo-anilines⁶) can be characterized as they are electrochemically switched between redox states, opening the possibility to examine directly the link between redox state and conductance of individual molecules.² Such experiments typically use a scanning tunneling microscope (STM), with individual redox active molecules tethered via Au–S bonds between a gold substrate and tip, under potential control.

There is a clear analogy in these experiments to a molecular transistor, with the tip and surface acting as source and drain, I_{SD} being the current flow between these two electrodes, while the counter electrode acts as a “gate”. It has been shown in several instances that electrochemically gated conductance increases occur concomitantly with redox changes.^{2–6} The following questions now arise: can other device characteristics be controlled by the structural, chemical or electronic properties of the redox group, and can structure–property relationships be derived? Here, we show that the nature of the I_{SD} vs electrochemical gating potential (E_{Gate}) profile can be controlled by the nature of the redox group: the pyrrolo-tetrathiafulvalene (PTTF) molecular bridge 6PTTF6 (Figure 1) exhibits a sharp off–on–off transition as E_{Gate} is swept through the redox transition, while the viologen 6V6 exhibits a much broader off–on switching profile. We discuss possible reasons for these observations.

The two molecular bridges shown in Figure 1 (left) only differ in the central redox moiety. In this configuration, the redox groups are electronically “decoupled” from the enclosing metal contacts by the $-(CH_2)_6SH$ arms, giving double tunneling barriers. It has been previously shown² that the conductance of 6V6 increases as the potential is swept negative, but no peak is observed in the conductance–overpotential relation around the $V^{2+}/V^{•+}$ equilibrium potential. Instead, a broad rise occurs across the redox wave, which does not level off within the attainable negative potential limit. This unusual behavior has been attributed to configurational fluctuations

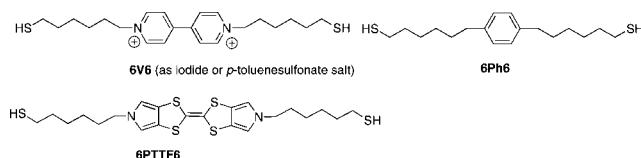


Figure 1. Structures of redox-active double tunneling barriers 6V6 and 6PTTF6 (left) and redox-inactive control 6Ph6⁷ (right).

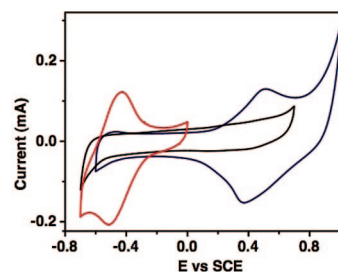


Figure 2. Cyclic voltammograms of 6PTTF6 (blue), 6V6 monolayer (red), and 6Ph6 (black) monolayers on Au(111) single crystal electrodes, recorded in 10 mM Na_2HPO_4/NaH_2PO_4 , pH 6.8 at $1 V s^{-1}$. The irreversible oxidation at $>+0.8 V$ seen for 6PTTF6 is due to oxidative desorption of Au–S.

of the flexible polymethylene chains.^{2b} This process leads to a “soft gating” of superexchange-based electron transport across 6V6, as the molecular bridge attains configurations in which tunneling is more facile by preorganization of the nuclear coordinates and environment.

We next examined structurally related molecules, to test whether “soft gating” is a general phenomenon. Tetrathiafulvalene (TTF) derivatives have already served as π -electron donors in molecular and supramolecular systems designed for molecular electronics.⁸ We chose the PTTF redox moiety (Figure 1) since (i) possible complications arising from cis and trans mixtures for “symmetrically” disubstituted TTFs⁹ are obviated¹⁰ and (ii) PTTFs are particularly electron-rich and show two fully reversible, one-electron oxidations, the first of which lies well within the potential range where Au–S bonds are stable in aqueous electrolyte. Compound 6PTTF6 was synthesized and fully characterized¹¹ (see Supporting Information (SI)).

Figure 2 shows cyclic voltammograms of monolayers of 6PTTF6, 6V6, and 6Ph6 on Au(111) in aqueous buffer, and Figure 3 shows single molecule conductance data for each molecule as a function of the overpotential (redox active molecules) or electrode potential (6Ph6). For 6PTTF6, the data show a conductance rise from ~ 0.5 nS in its neutral state to a maximum of 2.5 nS, which falls again to the “off” conductance value of ~ 0.5 nS at positive overpotentials. The width of the conductance peak is $\sim 0.2 V$, in the range

[†] University of Liverpool.[‡] University of Southern Denmark.[§] Technical University of Denmark.

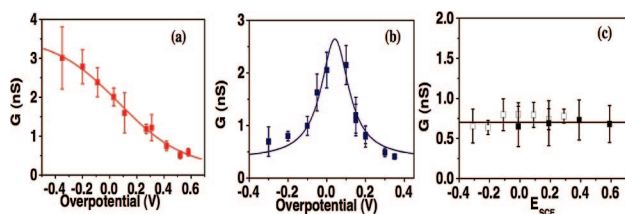


Figure 3. Single molecule conductance of (a) 6V6 (red), (b) 6PTTF6 (blue), and (c) 6Ph6 (black), versus the overpotential (η) for the redox molecules and the electrode potential for 6Ph6. Data for filled symbols obtained using I(s) method; for open symbols using I(t) method (see SI).

expected¹² for the tip-to-sample bias voltage of 0.2 V employed in these experiments. The conductance of the redox-inactive 6Ph6⁷ is similar to that of the “off” states of 6V6 and 6PTTF6 but does not change as a function of potential; the frontier π -orbitals of the benzene ring are too far from the Fermi energy of Au to be brought into resonance by gate potentials accessible in these experiments. The “classical” behavior of the gold|6PTTF6|gold single molecule junction, with a symmetrical peak close to the first oxidation potential for PTTF, can be rationalized in terms of both two-step (hopping) mechanisms and superexchange (tunneling) modes. In the hopping mechanism the oxidized (PTTF⁺) and reduced (PTTF⁰) forms would contribute comparably at the equilibrium redox potential to the tunneling current across the molecular junction.¹³ A maximum would then result in the conductance vs overpotential relationship, as is experimentally observed. A maximum is also expected in the tunneling or superexchange mechanisms when the two redox states of PTTF are comparably populated at the reversible potential.^{13a} The question is why does the PTTF moiety behave classically, while the viologen moiety does not?

The conductance of both 6V6 and 6PTTF6 in the “off” state and the factor by which the conductance changes on reduction (6V6) or oxidation (6PTTF6) are similar. The difference clearly must lie in the properties of the central redox moiety, because the flexible alkyl spacers are present in all three molecules. Both the neutral PTTF moiety¹⁴ and structurally characterized TTF⁺ derivatives¹⁶ are planar in the solid state. DFT calculations¹⁵ show that the PTTF core of an isolated molecule (as found in metal–molecule–metal junctions) is also planar for both states. Viologen dications can be planar or twisted about the inter-ring C–C bond, depending upon the anion, suggesting that inter-ring twisting is a low-energy process.¹⁷ Strong π – π interactions in the solid state mean that the sole crystal structure of a V²⁺ salt¹⁸ can tell us little about the likely configuration of an isolated molecule, but greater coplanarization upon reduction and increased inter-ring C–C double bond character is predicted.^{15,19} There are therefore significant configurational differences between V²⁺ and V^{•+} that are not apparent in the PTTF system.²⁰ We suggest that these are the likely cause of the differences in the two systems and that the tunneling factor depends upon the instantaneous nuclear configuration of the twisting mode for the viologen, giving the different form of the current/overpotential relation.

In summary, we have shown that well-defined redox switching can be obtained in gold|6PTTF6|gold single molecule junctions. We have achieved off–on–off switching (in accord with theoretical expectations and the simplest view of the two-step process^{13b}) in these junctions, controlled by the redox electrochemistry of the

PTTF group. Differences between the conductance–overpotential behavior of 6V6 and 6PTTF6 are rationalized in terms of conformational dynamics of the respective systems.

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Supporting Information Available: Details of the synthesis and characterization of 6PTTF6, molecular conductance determinations, and SPARTAN calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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