

Electrons Are Transported through Phenylene–Ethyne Oligomer Monolayers via Localized Molecular Orbitals

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Abstract: We report excellent correlations between the first negative threshold potentials (V_{THS}) for electric conduction, electrochemical potentials, and computed lowest unoccupied molecular orbital energies in a series of phenylene–ethyne oligomers bearing a sulfur-based anchoring unit and different electroactive substituents on the central benzene ring. The theoretical and electrochemical results strongly suggest that the peaks observed in the i – V curves have a true molecular origin and are associated with distinct unoccupied molecular levels of the compounds that are strongly localized on the central ring (except for compound I). This localization might account for the existence of a long-lived radical–anion state that permits lateral electron hopping and leads to charge trapping and storage.

For molecular electronic devices to come to fruition, it is necessary to understand the electrical properties of molecules and how these correlate with the molecular structure and device characteristics. Recently, we reported very sharp peaks in the i – V curves taken with a number of substituted oligo(phenylene ethyne)s and oligophenylenes self-assembled on a gold surface when contacted by a Pt tip.¹ Here, from a joint experimental and theoretical study, we establish that these current peaks have a true molecular origin and depend on the specificity of the molecular orbitals of the compounds themselves; they result from resonances between the discrete electronic levels of the molecule and the very narrow density of states around the Fermi energy of the sharp metal tip.² The present work thus opens the way toward fine chemical tuning of molecular devices.

The emergence of the field of molecular electronics has brought up many fundamental questions dealing with, for instance, the mechanism of charge conduction through molecules, the structural rearrangements on charge transfer, the existence of localized charge and charge trapping, or the nature of the current–voltage (i – V) characteristics. A number of

electrode (and contact) arrangements and techniques for measuring the i – V characteristics of self-assembled monolayers (SAMs) of molecular compounds have been reported, e.g., break junctions,³ crossed wires,⁴ conducting probe atomic force microscopy (CPAFM),^{5,6} mercury drop contacts,⁷ scanning tunneling microscopy (STM),⁸ and electrochemical methods.⁹ In some cases, the i – V curves are characterized by a peak-shaped current–voltage curve or so-called negative differential resistance (NDR) behavior.¹⁰ Such a peak profile has been proposed as the basis of molecular electronic switches for memory circuits.¹¹ Several explanations have been proposed for the observed sharp current peaks at low voltage bias, e.g., a sudden change in the conformation of a molecule induced by

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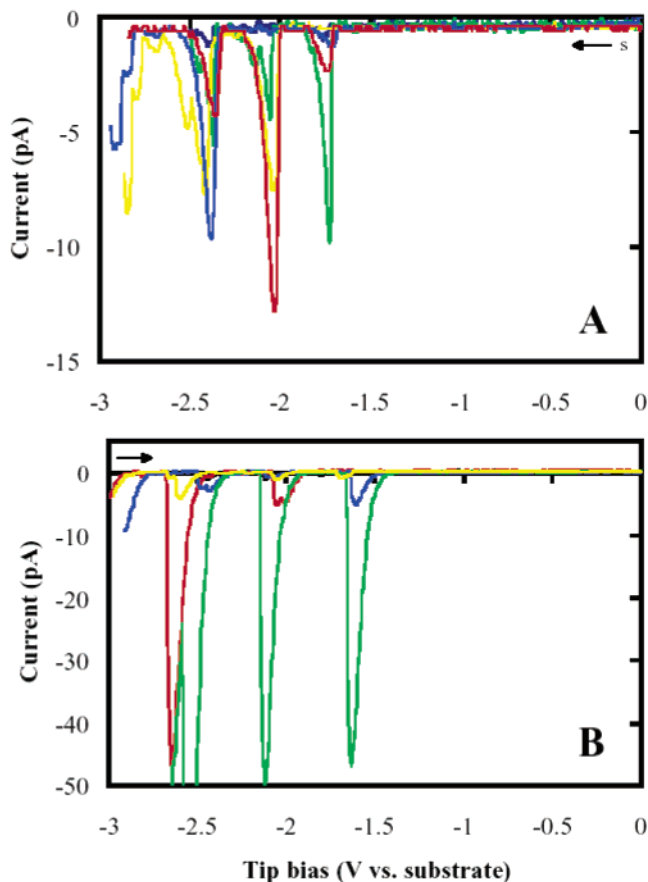


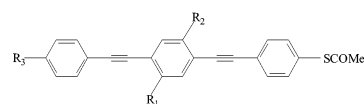
Figure 1. Ten i - V curves of a SAM of compound **IV** in the negative tip bias region at a Pt tip: (A) Five forward scans (black, yellow, blue, red, and green); (B) Five reverse scans (black, yellow, blue, red, and green). The curves represent scans at five different locations on two different samples.

the interaction between the electric field and the permanent dipole of the substituted molecule;^{11,12} a doping mechanism involving a change in molecular conductivity, associated with the extent of delocalization of the molecular orbitals (MOs) with a change in the charge state of the molecule;¹³ or the existence of a twisted conjugated backbone acting as a barrier for electron transfer that is electric field-strength dependent.¹⁴

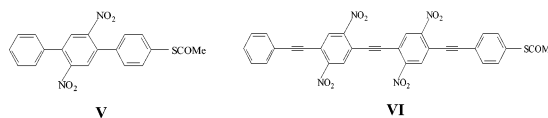
We recently studied substituted oligo(phenylene ethynylene)s (OPEs) and oligophenylenes (OPs) self-assembled on a gold surface.¹ When contacting the molecules by a Pt tip, very sharp peaks were observed in the i - V curves. The location (voltage) at which the peaks appear was essentially constant for a given compound (Figure 1), not random, and depended reproducibly on molecular structure (see also Supporting Information), although it has been difficult to demonstrate that these current peaks have a true molecular origin.¹ Note that such peaks are different from the stochastic ones that are sometimes observed and are based on effects not inherent in the molecule, e.g., surface bonding rearrangements at the molecule/metal contact (i.e., a sulfur atom changing its hybridization state or slightly shifting its bonding arrangements to the gold atoms on the surface)⁸ or breaking the molecule/metal contact¹⁵ that are

sometimes also described as “NDR-effects”. To understand how the various observed features are associated with molecular levels, we have now carried out electrochemical (EC) measurements for these compounds in solution to determine their redox potentials and also performed electronic structure calculations. We focus here on a series of OPE and OP compounds substituted by a single sulfur-based anchoring unit (unless otherwise noted) and bearing different electroactive substituents on the central rings; see below for the chemical structures.

We report here that a negative tip bias probes unoccupied levels of these molecules and that there is a good linear correlation between the lowest negative threshold peak voltage (V_{TH}) of the experimental i - V curves of a number of SAMs in the Ar environment and the first EC half-wave reduction potential ($E_{1/2}$) or peak potential (E_p) in a nonaqueous solution. Moreover, the energy of the lowest unoccupied level calculated for the various compounds by means of the Hartree–Fock semiempirical INDO (intermediate neglect of differential overlap) method also scales linearly with V_{TH} . Here, we focus our discussion only on unoccupied levels of molecules, since we are unable to reliably assign the positive V_{TH} values to the occupied levels of these molecules that are difficult to oxidize. We do see anodic peaks in the charge storage process¹ after scans to the negative bias regime, but those discharge peaks do not correlate with the calculated values of the HOMO energies (not shown).



I: $R_1 = \text{H}, R_2 = \text{Et}, R_3 = \text{H}$ **II:** $R_1 = \text{H}, R_2 = \text{NO}_2, R_3 = \text{H}$ **III:** $R_1 = \text{NO}_2, R_2 = \text{H}, R_3 = \text{H}$ **IV:** $R_1 = \text{NO}_2, R_2 = \text{NO}_2, R_3 = \text{H}$ **VII:** $R_1 = \text{NO}_2, R_2 = \text{NH}_2, R_3 = \text{H}$ **VIII:** $R_1 = \text{O}, R_2 = \text{O}, R_3 = \text{H}$



A sharply etched Pt tip attached to a tuning fork in a scanning probe microscope was used to locate and contact the surface of a SAM¹⁶ and for i - V measurements (scan rate, 6 V/s) at room temperature.¹ The surfaces were never scanned in an X - Y direction during the measurements. The i - V characteristics of various SAMs of this series of compounds on Au substrates in an Ar atmosphere are molecule-specific and have been reported previously.¹ Generally, peak-shaped i - V curves were obtained at different locations for the nitro-based OPE SAMs studied here. These peaked i - V curves were found at about the same location during a negative and reverse scan and can be used to define a threshold tip bias (V_{TH}) for electric conduction. For instance, for compound **IV** (the dinitrophenyl OPE), three peaks (at -1.75 , -2.10 , and -2.50 V) could be clearly identified in the negative tip voltage (vs substrate) scan in the voltage range between -1.5 and -3.0 V (see Figure 1), although the current amplitudes among different scans show more significant varia-

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Table 1. Experimental Values of the Negative Peak Potentials (V_{TH}) in the Current–Voltage Curves of SAMs and the Electrochemical Reduction Half-Wave Potentials ($E_{1/2}$) or Peak Potentials (E_{p}) of Several Compounds under Study Together with the INDO-Calculated LUMO Energies^a

compound	V_{TH} (V) ^b	$E_{1/2}$ or E_{p} (V vs $E_{1/2}$ of Fc^+/Fc) ^c	LUMO energy (LUMO+1) energy (LUMO+2) energy (LUMO+3) energy	
I	−2.79	−2.31, E_{p}	−0.34	
II	−2.25	−1.38	−1.42	
		(−0.57)	(−0.81)	(0.80)
	−2.82	−2.19, E_{p}	−0.62	
III	−2.56	−1.40	−1.40	
		(−0.28)	(−0.81)	(0.77)
	−2.84	−2.21, E_{p}	−0.63	
IV	−1.75	−0.97	−2.12	
		(−0.73)	(−0.20)	(0.75)
	−2.10	−1.17	−1.37	
		(−0.40)	(−1.13)	(0.39)
	−2.50	−2.30	−0.98	
V	−2.24	−1.16	−1.46	
		(−0.34)	(−0.13)	(0.09)
	−2.58	−1.29	−1.37	
		(−0.35)	(−1.21)	(0.19)
	−2.82	−2.38, E_{p}	−1.18	
VI	−1.74	−0.95, E_{p}	−2.36	
		(−0.35)	(−0.09)	(0.27)
	−2.09	−1.04, E_{p}	−2.09	
		(−0.43)		(0.67)
	−2.52	d	−1.42	
		(−0.26)		(0.14)
	−2.78	d	−1.28	
VII ^e	−2.09	−1.67, E_{p}	−1.27	
			(−0.75)	(0.72)
	na	−2.23, E_{p}	−0.55	
VIII ^f	−1.58	−0.69	−2.15	
			(−0.71)	(1.70)
	na	−1.40	−0.45	
			(−1.28)	
		−2.68		

^a The second, third, and fourth V_{TH} and $E_{1/2}$ (or E_{p}) values and (LUMO+1), (LUMO+2), and (LUMO+3) energies are also given, if available. The data in parentheses are the separations between the given V_{TH} , $E_{1/2}$, or E_{p} , and LUMO levels for the compounds. ^b Values taken from ref 1 and are the tip potentials vs the Au substrate. ^c $E_{1/2}$, except for an irreversible redox process, where E_{p} , the peak potential, is given. ^d Ill-defined wave. ^e The corresponding compound of compound **VII** for i - V study is the amino-nitrothioacetate, instead of monothioacetate. ^f The corresponding compound of compound **VIII** for CV study has no thioacetate linkage at either end.

tion, perhaps due to the gap variation during a scan or in different scans. Note that at a constant tip bias, e.g., −2.8 V, the current recorded for a few seconds (much longer than the time required to traverse a peak in a voltage scan) at the same location fluctuated somewhat but did not decrease rapidly with time to the noise level as observed for the current peaks in the i - V curve.¹ This indicates that the current peak is associated with a potential-dependent process rather than being a purely time-dependent transient. However, it is difficult to maintain a fixed tip/substrate distance with the feedback circuit off for extended time periods because of thermal drift. Note also that the peaks (e.g., the one near −2.5 V) in reverse scan direction are significantly different from those taken in the forward scan direction, perhaps because of a charging effect¹⁷ of the molecule due to the addition of electrons to localized molecular orbitals (see the following discussion). In Table 1 we summarize the V_{TH} values in the negative tip bias region of the compounds listed above. Note that several negative peaks were observed in the i - V curves for compounds **II**, **III**, **IV**, **V**, and **VI**; while compound **I** showed only one (see also the Supporting Information). As shown in Figure 1 (and also Figures S1 and S2 in the Supporting Information), those peaks are rather narrow (widths

of ca. 0.1 V) as compared with those normally observed in charge-transfer waves in electrochemistry in solution (e.g., the cyclic voltammograms shown here), where a large number of molecules in solution are studied. Thus, the very sharp NDR peaks we observed (and observed by others, e.g., ref 10) may reflect that a small group of molecules is probed and the molecules are in the gas phase. Further broadening of a peak by vibronic coupling to the electron transfer process is possible; however, the width of the vibronic envelope depends on the energy of the vibrational modes coupled to the electron transfer, which still cannot be readily addressed in this report.

The EC properties of the compounds dissolved in nonaqueous solvents were measured at an inlaid Pt disk in an inert-atmosphere drybox.¹⁸ Representative cyclic voltammograms (CVs) of compounds **II**, **IV**, and **V** in acetonitrile (MeCN) solution containing 0.1 M tetra-*n*-butylammonium hexafluoro-

(18) General experiments for electrochemistry such as cyclic voltammetry were carried out as follows: A cylindrical Pyrex vial 1.2 cm in diameter was used as an EC cell, where an inlaid Pt disk (1.5–2.0 mm diameter), Pt coil, and silver wire served as working, counter, and quasi reference electrodes, respectively. All potentials were calibrated vs an aqueous saturated calomel electrode (SCE) by the addition of ferrocene as an internal standard taking $E^{\circ}(\text{Fc}^+/\text{Fc}) = 0.424$ V vs SCE. The supporting electrolyte, TBAPF₆, was recrystallized twice and dried in a vacuum oven at 100 °C prior to transferring it into an inert-atmosphere drybox, where the EC measurements were carried out. Anhydrous MeCN or mixed MeCN/benzene was used as the solvents.

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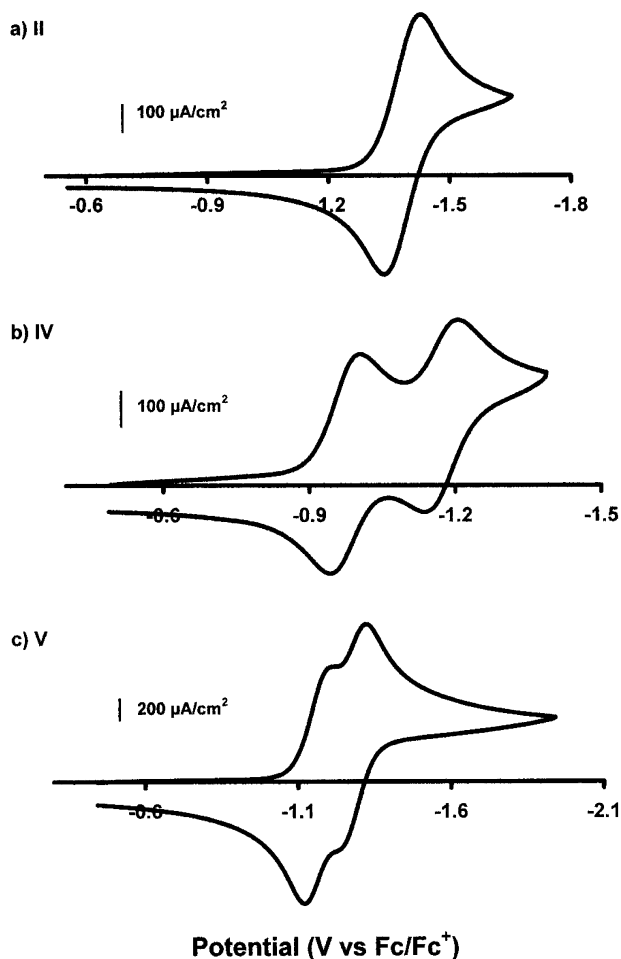


Figure 2. Cyclic voltammograms of 1 mM solutions of (a) **II**, (b) **IV**, and (c) **V** in 0.1 M TBAPF₆ in MeCN at an inlaid platinum disk electrode. Potential scan rate = 200 mV/s. E° of Fc/Fc⁺ is taken as 0.424 V vs an aqueous saturated calomel electrode (SCE).

phosphate (TBAPF₆) as the supporting electrolyte are shown in Figure 2. Compound **II** (2'-nitrophenyl OPE) showed one reversible one-electron reduction wave at $E_{1/2} = -1.38$ V vs ferrocene/ferrocenium (Fc/Fc⁺), as well as two other irreversible peaks at $E_p = -2.19$ and -2.59 V, while **IV** showed two consecutive reversible one-electron reduction waves at $E_{1/2} = -0.97$ and -1.17 V and one quasi-reversible multielectron reduction wave at $E_{1/2} = -2.30$ V. For compound **V** (dinitrophenyl OP), two very closely spaced reversible one-electron reduction waves were observed at $E_{1/2} = -1.16$ and -1.29 V, with the two waves nearly merged, with a third irreversible reduction at $E_p = -2.50$ V. Note that the OP backbone makes the first and third reductions of **V** more difficult as compared with those of **IV** which has an OPE backbone. The reduction potentials of these and the other compounds are summarized in Table 1.

In the theoretical computations, we initially made the working hypothesis that most of the voltage drop occurs at the tip/molecule interface and the gold substrate in the current measurements behaves as a quasi-reference electrode (see the discussion in the last section). In this situation, the application of a voltage will simply move the Fermi energy of the tip while keeping constant the relative position of the molecular levels with respect to the Fermi energy of the larger electrode; resonances are then created by matching the Fermi energy of

the tip with discrete electronic levels.² Within this framework, our theoretical approach is validated by recent experiments showing that the electronic structure of molecular wires is weakly perturbed upon adsorption on a gold surface by means of a sulfur atom.¹⁹ The geometries of the oligomers were optimized using the semiempirical Hartree–Fock AM1 method.²⁰ All the phenylene–ethynylene-based oligomers were found to be planar.²¹ This is also the case for compound **V**, where the nitro groups are rotated by 90° out of the plane defined by the benzene rings. The electronic structures of the oligomers were computed by the semiempirical Hartree–Fock INDO technique, as developed by Zerner and co-workers;²² the reason for this choice is that INDO calculations have provided a very good simulation of the inverse photoemission peaks in a series of π -conjugated molecules.²³ The INDO results indicate that the OPE compounds **II**, **III**, **IV**, **VI**, **VII**, and **VIII** show unoccupied levels ((LUMO+1) for **II**, **III**, **VII**, and **VIII**, (LUMO+2) for **IV**, and (LUMO+3) for **VI**) that presents the same bonding–antibonding pattern as the LUMO level of compound **I**; there is a new molecular orbital appearing at lower energy in compounds **II** and **III**, while two new levels are observed for compounds **IV** and **V** and three for compound **VI**. It is important to point out that all of these new levels, except the last ones, are mainly localized on the nitro groups attached to the central benzene ring.

We find remarkably good linear relationships between the INDO-calculated energies of the lowest LUMO levels of the compounds and the experimental voltages of the first negative peak (V_{TH}) as well as the corresponding EC reduction potentials ($E_{1/2}$ or E_p) for **I** to **VI** (Figure 3). Similar correlations between electrochemical potentials and orbital-mediated resonance tunneling data was also recently observed for metal phthalocyanine or porphyrin thin films in metal–insulator–metal tunnel junctions or with STM.²⁴ In the correlations reported here, the change in V_{TH} from compound **II** to **III** is larger than the changes in the calculated LUMO energies and in the experimental $E_{1/2}$ values, suggesting that the orientation of molecules relative to the surface of the substrate or the tip might have a subtle effect on the electric properties of the SAMs. As summarized in Table 1, we also find a very good correlation between the theoretical values of the (LUMO+1) energies of the compounds and the

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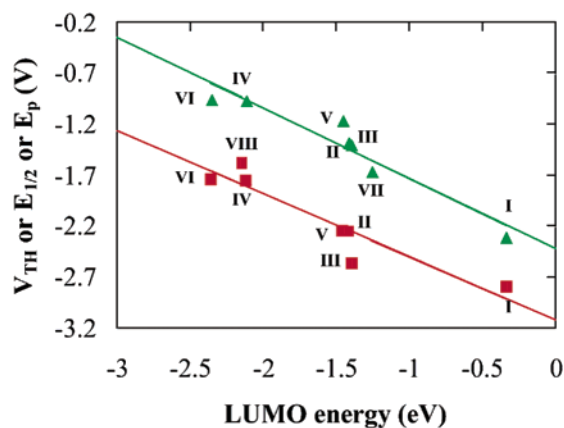


Figure 3. Linear relationships between first negative V_{TH} (red squares for experimental data and red line for linear regression fit with slope = -0.62 and intercept = -3.12), the corresponding $E_{1/2}$ or E_p (green triangles for experimental data and green line for linear regression fit with slope = -0.69 and intercept = -2.43), and theoretical LUMO energy of a series of OPEs or OP.

experimental values of the second negative peak ($V_{\text{TH},2}$). As expected, the theoretical (LUMO+1) energies do not correlate with the EC second reduction E value, since this involves transfer of a second electron into the lowest LUMO. Compound **VIII**, with a quinone group, shows a negative peak at much lower voltage than compound **I**, in good agreement with the experimental results (both V_{TH} and $E_{1/2}$). The calculations also point to the existence of a second unoccupied level in **VIII** that is delocalized over the molecular backbone, which was not reported in the i - V measurements of SAMs but is observed in the EC measurements. Note that the energies of the unoccupied levels given by theoretical calculations are based on isolated gas-phase molecules rather than molecules in a solvent or in condensed thin film, and thus the correlations have to be discussed on a relative basis rather than on an absolute scale; this can lead to nonunity slopes for these linear relationships due to changes in the electrostatic interactions within SAMs or in solutions when going from one compound to another. Similar effects in correlations have been seen in aromatic hydrocarbons.²⁵

For **I**, **II**, **III**, **IV**, **V**, and **VI**, there is a one-to-one correspondence between the number of negative peaks in the i - V curves and the number of low-lying unoccupied molecular orbitals. There is also a good quantitative agreement for the energy spacing between the calculated LUMOs and the measured V_{TH} values. The most negative V_{TH} occurred at about -2.8 V for all of these compounds and can therefore be attributed to a level having the same characteristics as the LUMO level of compound **I**. That these experimental V_{TH} peaks appear at nearly the same potential (-2.8 V) does not correlate well with the evolution of the highest LUMO levels (from -0.34 eV for **I** to -1.18 eV for **V**). Thus, the most negative V_{TH} peaks seem to be associated with a delocalized level for the last V_{TH} .

In summary, the theoretical and EC results strongly suggest that the peaks (NDR) observed in the i - V curves are associated with distinct unoccupied molecular levels of the compounds. One can schematically picture the electron transport through the molecules as shown in Figure 4, which contrasts a single

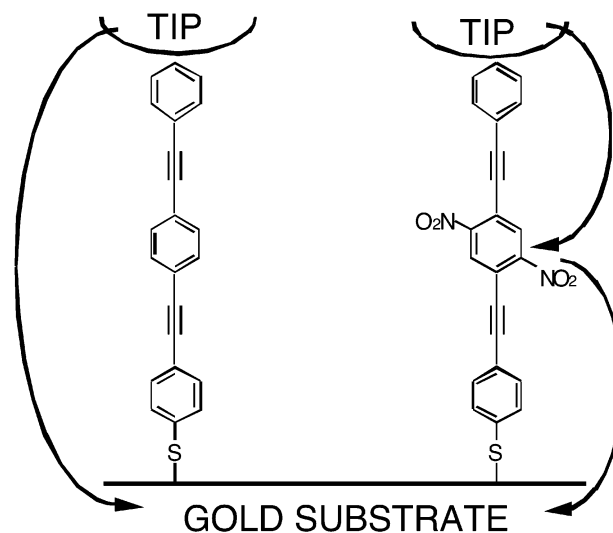


Figure 4. Schematic representation of proposed model for electron transfer through monolayers. (Left) Tunneling from tip to substrate via molecule. (Right) Tunneling via an intermediate molecular orbital on central benzene ring.

step tunneling to one via an intermediate molecular orbital which, except for **I**, is strongly localized on the central ring. This mechanism contrasts with a belief that only delocalized levels lead to significant conduction and current in the i - V curves.^{13,26} Other treatments describe circumstances where electrons on bridge sites are important.²⁷ This localization might also account for the existence of a long-lived radical-anion state that permits lateral electron hopping and leads to the charge trapping and storage process demonstrated earlier.^{1,28}

The good correlation between the tip measurements of the monolayers in the gas phase and electrochemical potentials in solution also suggests that the gold substrate in the tip measurements behaves as a quasi-reference electrode, just as the mercury pool did in early polarography experiments.²⁹ This same approach has been suggested in STM of redox-active species.³⁰ The approach described here, using electrochemical measurements and theoretical energy levels to make predictions about molecular conductivity and electrical behavior, can be extended to probe other molecules, such as those having strong electron-donating (oxidizable) substituent groups with the same molecular backbones or those having different redox moieties, where HOMO levels can be probed; these will be reported elsewhere.

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Supporting Information Available: Two figures demonstrating the reproducibility of the i - V scans with SAMs of **I** and

III (Figures S1 and S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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