

# Electron Transport and Redox Reactions in Molecular Electronic Junctions

Richard L. McCreery\*<sup>[a]</sup>

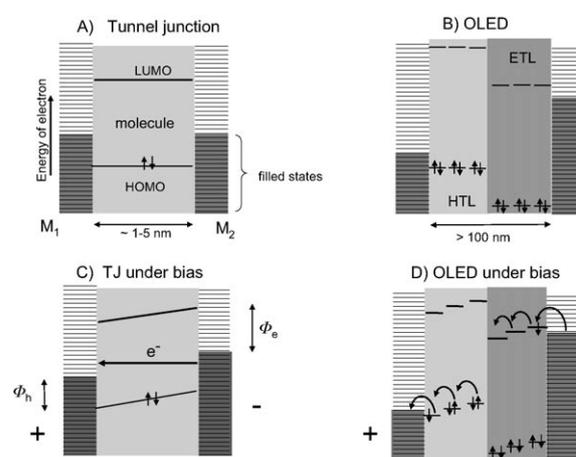
Electron transport through single molecules or collections of molecules oriented in parallel can occur by several mechanisms, including coherent tunneling, activated transfer between potential wells, various "hopping" modes, etc. Given suitable energy levels and sufficiently long charge transport times, reduction or oxidation with accompanying nuclear reor-

ganization can occur to generate "polarons", that is, localized redox centers in the molecule or monolayer. Redox events in molecular junctions are amenable to spectroscopic monitoring in working devices, and can have major effects on the electronic behavior of the junction. Several examples are presented, along with a possible application to molecular memory.

## 1. Introduction

The prospect of incorporating molecules in microelectronics as circuit elements has driven a large research effort to understand how molecules interact electronically with conventional conductors and semiconductors. The term "molecular electronics" is generally applied to paradigms involving a single molecule or a single layer of molecules oriented in parallel between two conductors (or "contacts"), with the critical dimension between contacts in the range of one to a few tens of nm. Potential applications of molecular circuit components are widespread, and exploit the small size and great variety of available molecules to increase device density and incorporate new functions into existing microelectronic devices. A variety of interesting phenomena involving molecules in electronic circuits have been reported to date, including electron transport by tunneling and various hopping mechanisms, conductance switching, photo-induced conductance changes, and bistability appropriate for molecular memory. A "molecular junction" generally refers to a two-terminal device consisting of two contacts with a monolayer of molecules oriented between them, although there are several examples of three-terminal devices resembling field effect transistors. Several diverse experimental paradigms have been investigated and reviewed,<sup>[1-6]</sup> and it is clear that a number of physical and structural factors control charge transport in molecular junctions. An example of high yield, massively parallel fabrication of molecular junctions has been reported recently,<sup>[7]</sup> as has high-density molecular memory.<sup>[8]</sup> We consider herein the interactions of two fundamental physical processes in molecular junctions: electron transport and redox reactions. In particular, what are the circumstances which promote redox activity in a molecular junction, and what are the consequences of such reactions to electronic behavior?

To provide context for the relevance of redox reactions to electron transport, consider two existing devices, the tunnel junction and the organic light emitting diode (OLED), which are shown schematically in Figures 1A and B. If the two contacts of a tunnel junction are close enough for their wavefunc-



**Figure 1.** Schematic energy levels for a tunnel junction (A, C) and an organic light emitting diode (B, D).  $M_1$  and  $M_2$  refer to metallic contacts, with the shaded areas indicating filled electronic states,  $\Phi_e$  and  $\Phi_h$  indicate the electron and hole injection (or tunneling) barriers, and ETL and HTL designate electron and hole transport layers. Curved arrows indicate electron transport under an applied bias.

tions to overlap, electrons can tunnel across the gap whether or not it contains molecules. The tunneling current is a strong function of gap spacing, and is generally negligible for gaps greater than a few nm. A significant fraction of the published work in molecular electronics involves the effect of oriented molecules on the tunneling current in such gaps, in particular how molecular structure and energy levels control the magnitude of electron (or hole) tunneling. A tunneling junction under bias is shown in Figure 1C, with the effective barriers for

[a] Prof. R. L. McCreery  
 Department of Chemistry  
 National Institute for Nanotechnology  
 University of Alberta, Edmonton, Alberta, T6G 2A1 (Canada)  
 Fax: (+1) 780 641 1601  
 E-mail: richard.mccreery@ualberta.ca

electron ( $\Phi_e$ ) or hole ( $\Phi_h$ ) tunneling indicated. In the simplest case, tunneling is coherent and controlled by the barrier height and the gap spacing, but there are numerous modifications to the simple model to account for various experimental observations. In the limit of a coherent tunnel junction, no redox reactions occur and the current is independent of temperature. Today's OLEDs have much thicker molecular layers (~100 nm) of organic semiconductors, as shown in Figure 1B. The contacts are sites for electron and hole injection, both of which are redox processes which result in reduction and oxidation of components in the OLED, respectively. The negatively biased electrode is generally a metal with a low work function (e.g. Ca, Al), and injection is accomplished by electron transfer into a LUMO (lowest unoccupied molecular orbital) of the acceptor, possibly activated by thermal motion. Transport through the acceptor layer is accomplished by a series of redox reactions (i.e. "redox exchange") until the electron reaches the donor/acceptor interface and light is produced by electron/hole recombination. Redox exchange is activated and temperature dependent, incoherent, and can transport electrons (or holes) over much greater distances than coherent tunneling. Reported cases of redox reactions occurring in molecular junctions a few tens of nm thick include metal filament formation,<sup>[9,10]</sup> conformational changes in rotaxanes<sup>[8,11]</sup>, and dynamic doping of conducting polymers.<sup>[12]</sup>

We consider here several cases between the limits of a tunnel junction and a ~100 nm "thick" junction in which coherent tunneling cannot occur. As the molecular layer becomes too thick for tunneling, or the tunneling rate is slow enough, redox reactions are possible with likely significant effects on the electronic behavior of the junction. After considering some fundamental issues controlling the interplay between tunneling and redox events, we will apply those principles to several examples from the recent literature. The conclusions will be supported by spectroscopic probes of working junctions to establish unequivocally the existence of bias-induced redox events.

## 2. Underlying principles

The most commonly applied equation for predicting the tunneling current in a molecular junction is the Simmons relation derived in 1971, based on a rectangular barrier between two planar contact surfaces.<sup>[13]</sup> Equation (1) is the first term of the Simmons relation, which correctly predicts an exponentially decreasing current with the gap between contacts ( $d$ ) and a strong dependence on the height of the tunneling barrier ( $\Phi_T$ ).

$$j_T = V \left( \frac{q^2 (2m\Phi_T)^{1/2}}{h^2 d} \right) \exp \left[ \frac{-4\pi (2m\Phi_T)^{1/2}}{h} d \right] + \dots \quad (1)$$

Experimental tunnel junctions generally show significant quantitative deviations from the current/voltage behavior predicted by the Simmons expression, and various phenomena have been proposed to account for the difference, including superexchange, non-rectangular barriers, a "tight-binding" model, and field emission to name a few. All of these variations

are temperature independent, and predict a strong dependence on gap dimension. Tunneling mechanisms generally assume that the nuclear positions of all atoms in the device are fixed on the timescale of the electron transfer, although this assumption is most valid at temperatures approaching absolute zero.

A useful parameter relevant to considerations of interactions between a tunneling electron and its surroundings is the tunneling time ( $\tau_o$ ) proposed originally by Buttiker and Landauer<sup>[14]</sup> and discussed more recently by Ratner, et al.<sup>[15,16]</sup>  $\tau_o$  is an estimate of the time spent by the electron "under" the tunneling barrier, and therefore the time during which it might interact with molecular vibrations. If a "characteristic frequency",  $\Omega_M$ , is defined to describe the dynamics of the molecular layer, then the product  $\Omega_M \tau_o$  provides an indication of the relative timescales of tunneling and molecular vibrations.<sup>[15]</sup> For  $\Omega_M \tau_o \ll 1$ , the medium is essentially static during the tunneling event, while for  $\Omega_M \tau_o \gg 1$ , the medium can react to the presence of the electron, possibly undergoing a redox reaction (as described below). For example, a typical molecular vibration of  $1000 \text{ cm}^{-1}$  corresponds to  $3 \times 10^{13} \text{ Hz}$ , so a tunneling time of 1 ps yields  $\Omega_M \tau_o = 30$ , while  $\tau_o = 10 \text{ fs}$  yields  $\Omega_M \tau_o = 0.3$ . Stated differently, 30 such vibrations can occur during a 1 ps transit time, but only 0.3 during 10 fs. After briefly considering conventional redox processes, we will consider how such events can occur in molecular junctions when  $\Omega_M \tau_o$  significantly exceeds unity.

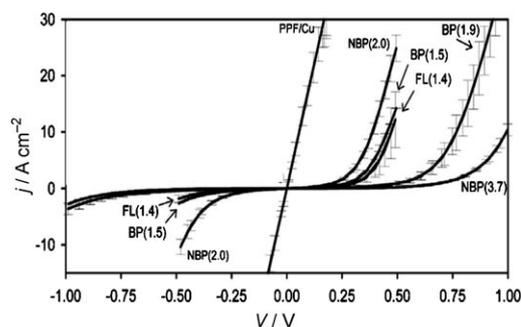
Returning to the OLED example in the introduction, consider the events associated with electron transfer through a relatively thick film of organic semiconductor. Electron "injection" from the negatively biased contact occurs into the LUMO of the semiconductor, most often accompanied by reorganization of the nuclei into the configuration of the resulting anion. Organic semiconductors are classified as electron transport layers when their LUMO energy is sufficiently low that electrons may be injected from the negatively biased contact, while hole transport layers have a HOMO (highest occupied molecular orbital) energy close to the work function of the positively biased electrode. Classical Marcus theory predicts that the activation barrier for reduction is related to the reorganization energy,  $\lambda$ , and in the simplest case equals  $\lambda/4$ .<sup>[17]</sup> Since reorganization requires nuclear motion, the requirement that  $\Omega_M \tau_o \gg 1$  must apply for a redox process to occur. In thick films, electrons are transported by a sequence of redox exchange events, and a small  $\lambda$  promotes more rapid exchange and higher electron mobility. Redox exchange is sometimes referred to as hopping, but the latter term is also applied to a sequence of tunneling events between potential wells. The important distinction is the temperature dependence, in that redox exchange will slow significantly or stop at low temperature, while certain hopping mechanisms can continue. A related phenomenon is electron transport by a series of activated transfers between traps, often referred to as Poole-Frenkel transport.<sup>[18]</sup> While the microscopic steps and sites may differ, Poole-Frenkel transport resembles redox exchange in its temperature dependence and ability to extend over long distances compared to coherent tunneling.

Considering molecular junctions with 1–10 nm thickness in the context of organic semiconductors, the question arises of what factors make a redox process likely during electron transport. As just noted, the transit time must be long enough to permit reorganization. For junctions with  $\sim 1$  nm thickness or less, coherent tunneling is rapid, and the requirement that  $\Omega_M \tau_o \gg 1$  is unlikely to be met. A second requirement is that either the HOMO (for oxidation) or LUMO (for reduction) be close enough (usually within  $kT$ ) to the Fermi level of the relevant contact (+ for oxidation, – for reduction) to occur. This requirement may be assisted by thermal fluctuations and is therefore dependent on both temperature and reorganization energy. A third factor is the possibility of a space charge generated in the molecular layer under bias, which can subsequently participate in the redox process.<sup>[19]</sup> The situation for a given molecular junction is between the two limits of a tunnel junction with a thickness of at most a few nm and a “thick” organic semiconductor. The crossover thickness between tunneling and redox exchange or another activated mechanism depends on the energy levels of the molecules involved, the electronic coupling to the contacts and between molecules, and, of course, molecular structure. The temperature dependence of the conductance provides an important indicator for distinguishing mechanisms in a given junction structure.

### 3. Examples of Redox Reactions in Molecular Junctions

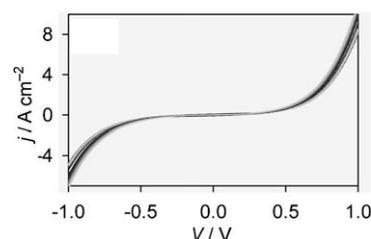
Several examples from the literature will be considered in this section, chosen to illustrate the range of junction behaviors between a tunnel junction with no known redox activity and devices which exhibit signatures of redox reactions. Where applicable, spectroscopic probes of junction structure are presented to confirm structural changes associated with redox activity. Junction notation includes the materials and their thicknesses (in nm); for example, Au/NAB(1.8)/TiO<sub>2</sub>(10)/Au indicates Au contacts, with 1.8 nm thick nitroazobenzene and 10 nm TiO<sub>2</sub> layers in the junction interior. Pyrolyzed photoresist film (PPF) is the substrate commonly used in the author’s laboratory, and is a disordered graphitic conductor (resistivity  $\sim 0.006 \Omega \text{ cm}$ ),<sup>[20,21]</sup> with a very flat surface (rms  $< 0.5$  nm) suitable for covalent bonding to the molecular layer. In addition to NAB, abbreviations include BP (biphenyl), FL (fluorene), and NBP (nitrobiphenyl), and all molecular layers were prepared by diazonium reduction, with their thickness confirmed by AFM. The original papers should be consulted for fabrication details and properties of PPF/molecule/metal molecular junctions.<sup>[19,22–26]</sup> All current/voltage curves are presented as  $J$  ( $\text{A cm}^{-2}$ ) vs  $V$  (substrate relative to top contact), with a positive current representing electron flow from the top contact through the molecular layer to the substrate (usually PPF).

Current/voltage curves for PPF/molecule/Cu junctions are shown in Figure 2, for several molecules and thicknesses. The curves show no hysteresis, are independent of scan rate (from 1 to 1000  $\text{V sec}^{-1}$ ), and may be repeated thousands of scans without observable change. Note that the observed current densities are large by the usual levels expected for redox



**Figure 2.** Current density/voltage curves obtained at 1000  $\text{V sec}^{-1}$  for PPF/molecule/Cu molecular junctions. Error bars indicate  $\pm$  standard deviation for at least 3 junctions, and number in parentheses in labels is the AFM-determined molecular layer thickness (typ.  $\pm 0.3$  nm). Adapted with permission from ref. [22], copyright The Royal Society.

events, with  $10 \text{ A cm}^{-2}$  corresponding to  $> 10^5 \text{ e molecule}^{-1} \text{ sec}^{-1}$ . An important clue to the electron transport mechanism is the nearly temperature independent behavior below  $\sim 200$  K, where plots of  $\ln J$  vs  $1/T$  yielded Arrhenius slopes of  $< 1$  meV between 80 and 200 K for all four molecules examined. A notable case is PPF/NAB(4.5 nm)/Cu/Au, for which  $J$ - $V$  curves are shown over the range of 100–400 K in Figure 3. The Arrhenius slope above 250 K is  $0.03 \pm$



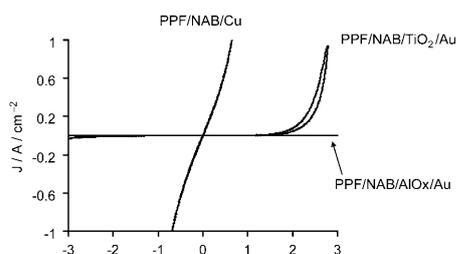
**Figure 3.** Superimposed current density/voltage curves for a PPF/NAB(4.5 nm)/Cu junction as a function of temperature in the range 100–400 K, all obtained at 1000  $\text{V sec}^{-1}$ . Adapted with permission from ref. [22], copyright The Royal Society.

0.01 eV, while that below 200 K is less than 1 meV. Recent results for the temperature range of 5 K to 100 K exhibit Arrhenius slopes of 1.4  $\mu\text{eV}$  for NAB(3.3), 10.4  $\mu\text{eV}$  for FL(1.8), and 32.4  $\mu\text{eV}$  for BP(1.4), all between PPF and Cu contacts. As reported elsewhere, these PPF/molecule/Cu devices all show an activated region above  $\sim 250$  K, with Arrhenius slopes of 0.02–0.17  $\text{eV}$ <sup>[22]</sup>.

The near-zero Arrhenius slopes below 200 K for PPF/molecule/Cu junctions rule out redox exchange as well as Schottky emission and other activated processes as the mechanism of electron transport. The results are qualitatively consistent with a tunneling mechanism, possibly modified to include field emission or other effects, as noted earlier. The absence of hysteresis and the negligible Arrhenius slope at low temperature imply minimal structural changes on the timescale of the voltage scans, and that atomic nuclei are effectively static during electron transport. It is surprising that relatively thick films

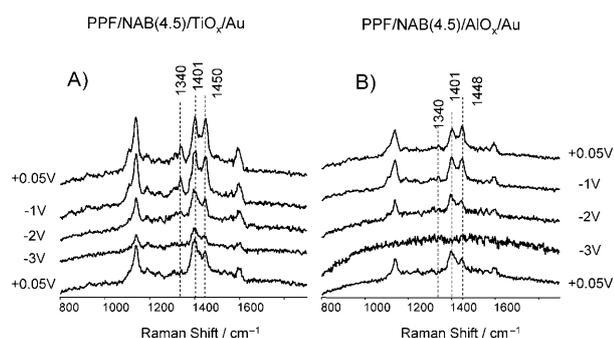
(4.5 nm) exhibit  $T$ -independence, although a recent report has attributed similar observations to a modified form of Simmons tunneling.<sup>[27]</sup> Whatever mechanism is proposed for tunneling through molecular layers with thicknesses of 1.4–4.5 nm, there is no evidence for the involvement of redox reactions for the conductor/molecule/metal devices shown in Figures 2 and 3.

We now consider addition of a thin insulating layer of  $\text{SiO}_2$ ,  $\text{TiO}_2$  or  $\text{Al}_2\text{O}_3$  to the PPF/NAB(4.5)/metal device to make a "molecular heterojunction" such as PPF/NAB(4.5)/ $\text{TiO}_2$ (10)/Au. As shown in Figure 4, the oxides greatly reduce the observed cur-



**Figure 4.** PPF/NAB(4.5) junctions with three types of top contacts, as indicated. Adapted with permission from ref. [24], copyright The American Chemical Society.

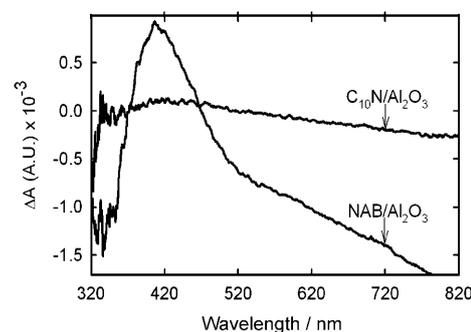
rent density compared to the same device lacking the oxide. In the case of  $\text{TiO}_2$  hysteresis is observed, with a persistent increase in current observed when the Au is biased negatively.<sup>[24,25]</sup> Unlike the case without the oxide layer, the JV behavior for the PPF/NAB(4.5)/ $\text{TiO}_2$ /Au heterojunction is strongly scan-rate dependent, with higher current and greater hysteresis for slower scan rates. For molecule/ $\text{TiO}_2$  junctions containing either NAB or FL, the hysteresis was absent at low temperature, and was absent in devices containing very low residual  $\text{H}_2\text{O}$ .<sup>[28]</sup> Figure 5 shows Raman spectra of NAB heterojunctions



**Figure 5.** Raman spectra acquired in NAB junctions containing  $\text{TiO}_2$  (A) or  $\text{AlO}_x$  (B) after 30 sec bias pulses to the indicated voltages, then held at  $V=0$  during spectrum acquisition. Spectra progressed chronologically from top to bottom. Adapted with permission from ref. [24] and [25], copyright the American Chemical Society.

containing  $\text{TiO}_x$  (5A) and  $\text{AlO}_x$  (5B), obtained in working junctions as a function of applied bias. The change in the 1401/1450  $\text{cm}^{-1}$  intensity ratio for the N=N stretch, and the decrease in the 1340  $\text{cm}^{-1}$  is a clear signature for electrochemical reduc-

tion of NAB, as established previously in solution.<sup>[29]</sup> Further support for reduction of NAB is provided by UV/Vis absorption spectroscopy through partially transparent carbon/NAB/ $\text{Al}_2\text{O}_3$ /Pt junctions,<sup>[30]</sup> shown in Figure 6. A  $-4$  V, 100 msec bias pulse



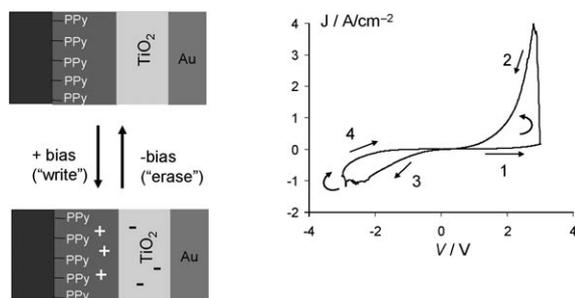
**Figure 6.** Change in absorbance ( $\Delta A$ ) of a partially transparent carbon/molecule/ $\text{Al}_2\text{O}_3$ /Pt junction containing either NAB or a redox-inactive  $\text{C}_{10}\text{H}_{21}\text{N}$  alkane, in response to a 100 msec,  $-4$  V pulse (carbon relative to Pt). Adapted with permission from ref. [30] copyright the American Chemical Society.

causes an increase in absorbance at 420 nm, corresponding to formation of the "quinoid" form of the NAB anion. A similar response was observed for carbon/NAB/ $\text{SiO}_2$ /Pt junctions, but not for analogous devices containing a  $\text{C}_8\text{H}_{17}\text{N}$  alkane instead of NAB.<sup>[24,25,30]</sup>

The spectroscopic results of Figures 5 and 6 strongly support the conclusion that NAB is reduced by an applied bias in NAB/oxide heterojunctions, and similar Raman changes were not observed in the absence of the oxide. As discussed in some detail for fluorene/ $\text{TiO}_2$  devices,<sup>[19]</sup> the observations are consistent with reduction of NAB by electrons injected by a negative bias. A bias can initially generate a negative space charge in the NAB, which has the effect of raising the Fermi energy of the NAB. This process is analogous to electrostatic doping in thin film transistors, in which a bias to the gate creates a charged layer at the interface of an organic semiconductor and the gate oxide. If the layer containing the space charge is itself reducible, it can reorganize to form an organic anion, for example,  $\text{NAB}^-$  in the current case. The elementary steps of electron injection, space charge formation, and reorganization may be complex, but the process is certainly activated and therefore exhibits temperature dependence. A simple qualitative picture of the process considers the oxide to form a barrier to electron transfer, which "traps" electrons in the NAB layer, shifts the Fermi energy, and causes reduction. In terms of the tunneling model discussed in the introduction, the electron transport is too fast to cause reduction without the oxide present, whereas any of the three oxides (Ti, Al, Si) prevent rapid tunneling and cause reduction. As shown in Figure 4A, an  $\text{Al}_2\text{O}_3$  layer blocks electron transport through the junction, even though reduction of NAB can still occur.  $\text{TiO}_2$  is itself reducible to a more conductive  $\text{Ti}^{\text{III}}$  or  $\text{Ti}^{\text{II}}$  oxide, thus causing a persistent change in junction conductivity. We have discussed the possibility of using  $\text{TiO}_2$  reduction as the basis of a memory element, with an applied bias causing redox reactions

which change the conductivity of the TiO<sub>2</sub> layer.<sup>[19,28]</sup> However, the performance of such devices is modest compared to commercial microelectronic memory, with write/erase times in the millisecond range, retention of ~30 min, and cycle life of several hundred read/write/read/erase cycles.

The conductance changes in molecule/TiO<sub>2</sub> heterojunctions is an example of conductance switching, which has received significant attention in molecular electronics since the early memory devices based on rotaxane.<sup>[4,8,31]</sup> The term refers to a junction with two or more metastable states having different conductance. Various mechanisms have been proposed for conductance switching, but several involve redox reactions, as in the case of NAB/TiO<sub>2</sub>.<sup>[19,25]</sup> A dramatic example of redox-based conductance switching is shown in Figure 7, for the



**Figure 7.** JV curve for a PPF/polypyrrole(25)/TiO<sub>2</sub>(10)/Au junction at 1000 V sec<sup>-1</sup>, starting from V=0 and scanned in the order indicated. Diagram at left is a schematic of a redox-mediated conductance change induced by the applied bias. Adapted with permission from ref. [31], copyright the American Chemical Society.

case of PPF/polypyrrole(25)/TiO<sub>2</sub>(10)/Au devices with ~35 nm thick active regions. The conductivity of polypyrrole (PPy) increases by ~10 orders of magnitude when the polymer is oxidized, while the TiO<sub>2</sub> conductivity increases by a similar factor when it is reduced. The JV curve of Figure 7B shows that when the PPF is biased positive there is a major increase in junction conductance, while a negative bias returns the conductance to its original state. Conductance changes occur in a few μs, persist for >7 days, and can be repeated thousands of r/w/e/r cycles.<sup>[31]</sup> One could argue that the PPy/TiO<sub>2</sub> heterojunction amounts to a very thin electrochemical cell, with two redox couples (PPy/PPy<sup>+</sup> and Ti<sup>IV</sup>/Ti<sup>III</sup>) that can be “charged” and “discharged” by voltage pulses. Unlike a conventional battery, however, the electronic conductance of the junction changes with the charge state, and the main charge carriers are electrons and holes rather than mobile ions. Redox based conductance switching is clearly distinguishable from tunneling, in that it has an activation barrier, involves nuclear reorganization, and can result in bistability of possible value in memory applications.

#### 4. Conclusions

The experimental evidence is very strong that redox reactions can occur in molecular junctions with thicknesses in the 10–

30 nm range, and that such reactions can significantly alter the junction conductance. Redox reactions become more likely when there are molecular orbitals close to the Fermi level of the contacts and when the transit time becomes long enough to permit molecular reorganization. A large fraction of the molecular junctions studied to date involve alkane monolayers or single molecules, in which the orbitals are distant from the Fermi level and the dimensions are short enough to favor coherent tunneling. Junctions based on conjugated organic molecules and organic semiconductors have appropriate energy levels to undergo redox reactions, and such reactions are likely, particularly for devices with thicknesses greater than a few nm.

**Keywords:** electron transport • molecular electronics • molecular junctions • redox reactions

- [1] F. Anariba, J. Steach, R. McCreery, *J. Phys. Chem. B* **2005**, *109*, 11163.
- [2] F. Anariba, R. L. McCreery, *J. Phys. Chem. B* **2002**, *106*, 10355.
- [3] R. McCreery, *Chem. Mater.* **2004**, *16*, 4477.
- [4] A. J. Bergren, R. McCreery, *Adv. Mater.* **2009**, unpublished results.
- [5] S. M. Lindsay, M. A. Ratner, *Adv. Mater.* **2007**, *19*, 23.
- [6] A. Salomon, D. Cahen, S. Lindsay, J. Tomfohr, V. B. Engelkes, C. D. Frisbie, *Adv. Mater.* **2003**, *15*, 1881.
- [7] P. A. Van Hal, E. C. P. Smits, T. C. T. Geuns, H. B. Akkerman, B. C. De Brito, S. Perissinotto, G. Lanzani, A. J. Kronemeijer, V. Geskin, J. Cornil, P. W. M. Blom, B. De Boer, D. M. De Leeuw, *Nat. Nanotechnol.* **2008**, *3*, 749.
- [8] J. E. Green, J. Wook Choi, A. Boukai, Y. Bunimovich, E. Johnston-Halperin, E. Delonno, Y. Luo, B. A. Sheriff, K. Xu, Y. Shik Shin, H.-R. Tseng, J. F. Stoddart, J. R. Heath, *Nature* **2007**, *445*, 414.
- [9] S. Ssenyange, H. Yan, R. L. McCreery, *Langmuir* **2006**, *22*, 10689.
- [10] M. N. Kozicki, M. Park, M. Mitkova, *IEEE Trans. Nanotechnol.* **2005**, *4*, 331.
- [11] A. R. Pease, J. O. Jeppesen, J. F. Stoddart, Y. Luo, C. P. Collier, J. R. Heath, *Acc. Chem. Res.* **2001**, *34*, 433.
- [12] Q. Lai, Z. Zhu, Y. Chen, S. Patil, F. Wudl, *Appl. Phys. Lett.* **2006**, *88*, 133515.
- [13] J. G. Simmons, *DC Conduction in Thin Films*, Mills and Boon, London, **1971**.
- [14] M. Buttiker, R. Landauer, *Phys. Rev. Lett.* **1982**, *49*, 1739.
- [15] A. L. Burin, Y. A. Berlin, M. A. Ratner, *J. Phys. Chem. A* **2001**, *105*, 2652.
- [16] S. Yeganeh, M. Galperin, M. A. Ratner, *J. Am. Chem. Soc.* **2007**, *129*, 13313.
- [17] A. J. Bard, L. R. Faulkner, *Electrochemical Methods*, 2nd ed., Wiley, New York, **2001**.
- [18] D. K. Aswal, S. Lenfant, D. Guerin, J. V. Yakhmi, D. Vuillaume, *Anal. Chim. Acta* **2006**, *568*, 84.
- [19] J. Wu, K. Mobley, R. McCreery, *J. Chem. Phys.* **2007**, *126*, 24704.
- [20] S. Ranganathan, R. L. McCreery, *Anal. Chem.* **2001**, *73*, 893.
- [21] S. Ranganathan, R. L. McCreery, S. M. Majji, M. Madou, *J. Electrochem. Soc.* **2000**, *147*, 277.
- [22] A. J. Bergren, K. D. Harris, F. Deng, R. McCreery, *J. Phys. Condens. Matter* **2008**, *20*, 374117.
- [23] R. McCreery, J. Wu, R. J. Kalakodimi, *Phys. Chem. Chem. Phys.* **2006**, *8*, 2572.
- [24] R. P. Kalakodimi, A. Nowak, R. L. McCreery, *Chem. Mater.* **2005**, *17*, 4939.
- [25] A. Nowak, R. McCreery, *J. Am. Chem. Soc.* **2004**, *126*, 16621.
- [26] R. L. McCreery, J. Dieringer, A. O. Solak, B. Snyder, A. Nowak, W. R. McGovern, S. DuVall, *J. Am. Chem. Soc.* **2003**, *125*, 10748.
- [27] S. A. DiBenedetto, A. Facchetti, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **2009**, *131*, 7158.
- [28] J. Wu, R. L. McCreery, *J. Electrochem. Soc.* **2009**, *156*, P29.
- [29] T. Itoh, R. L. McCreery, *J. Am. Chem. Soc.* **2002**, *124*, 10894.
- [30] A. P. Bonifas, R. L. McCreery, *Chem. Mater.* **2008**, *20*, 3849.
- [31] S. Barman, F. Deng, R. McCreery, *J. Am. Chem. Soc.* **2008**, *130*, 11073.

Received: May 28, 2009

Published online on August 7, 2009