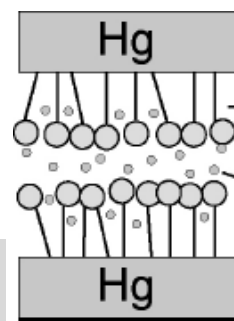


DOI: 10.1002/adma.200502412

# Experimental Approaches for Controlling Current Flowing through Metal–Molecules–Metal Junctions\*\*

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Two experimental approaches that enable control of current flow through metal–molecules–metal junctions are described. A number of studies using two-electrode metal–molecules–metal junctions have shown that the current between the electrodes depends on the structures of the incorporated molecules. When a tunneling mechanism dominates electron transport through organic molecules, the molecules behave similar to resistors with resistivities that can be controlled by changing the structure. Incorporation of molecules with increasing conjugation into Hg-based junctions increases the current flow dramatically. Alternatively, by using four-electrode electrochemical junctions that allow the potential of the electrodes to be controlled with respect to the energy levels of the incorporated molecules, it is possible to change the mechanism of electron transfer and produce abrupt increases in the current flow. These signals, analogous to solid-state diodes, are particularly significant for molecular electronics. Electrochemical junctions also permit prediction of the value of the applied potential at which the current will start taking off and to identify the mechanism of charge transport. New and recently published results obtained using junctions based on Hg electrodes in an “electrochemical” mode show that two junctions incorporating redox centers by different interactions behave as current switches, with the current flow dominated by different charge-transport mechanisms.

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[\*\*] We acknowledge funding by NSF (CHE-0518055) (USA), by EU Projects GRD1-2001-40772 (MWFM) and IST-2001-35503 (LIMM), and by FIRB-RBNE019H9K.

## 1. Introduction

Electron-transfer processes through molecular systems have attracted much attention over the past fifty years. The traditional experimental approach for studying these processes is based on measuring the electron-transfer rate in D–B–A supramolecular systems between electron donor (D) and acceptor (A) units that are covalently linked through a molecular bridge (B).<sup>[1]</sup> In the late 1990s, a combination of nanotechnology, scanning probe microscopy, and methods to form functional connections to metal surfaces, triggered the fabrication of different kinds of metal–molecule(s)–metal junctions and opened the door to a new experimental approach to measure electron-transfer processes through molecules as current flowing between two electrodes.<sup>[2]</sup> By using a combination of sophisticated and expensive techniques, dif-

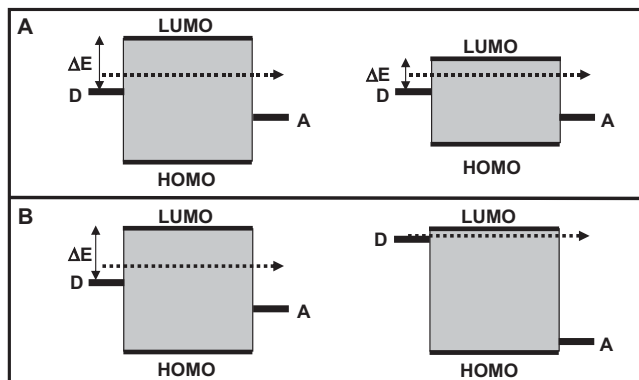
ferent kinds of molecular junctions have been assembled. Significantly, all these studies show that the features of the measured current–voltage ( $I$ – $V$ ) curves and the behavior of the resulting device are related to the structure of the incorporated molecules regardless of the junction geometry. Based on these results, and following the trend of miniaturization of electronic circuits, the integration of molecular components into electronic circuits is starting to be explored. Several critical features of organic and organometallic molecules make them as attractive alternatives to solid-state materials at the nanometer scale, including the ease of tuning their electronic structure and their potential for self-assembly on metal surfaces.

The key function of traditional electronic elements, such as resistors, diodes, and transistors, is the control of the current flow. The traditional experimental approach for studying electron-transfer processes between electron donor and acceptor units, through molecular bridges, had already made clear the role of the chemical structure of the bridge in facilitating electron transfer.<sup>[1]</sup> By using metal–molecule–metal junctions, both pioneering and more-recent studies<sup>[2–4]</sup> have demonstrated that there is a correlation between the electron-transfer rate and the molecular structure, similar to that widely investigated by using a molecular-donor–bridge–acceptor geometry.

The results obtained by both experimental approaches,<sup>[1–5]</sup> supported by theoretical studies,<sup>[6]</sup> show that the relevant factor in determining the electron-transfer rate and the control of the current flow is the energy gap ( $\Delta E$ ) between the energy states of the molecular bridge and the energy level of the donor and acceptor units.

Figure 1 represents two ways to change  $\Delta E$  and therefore to control the current flow. For the sake of simplicity, the electron-transfer processes are drawn schematically regardless of the nature of the electron/acceptor units, which can be either molecular systems or electrodes, and without discussing the mechanism and the kinetics of electron-transfer processes in detail. Hole-transfer processes are also excluded for simplicity.

When the molecular orbitals are high in energy with respect to the energy levels of the donor and acceptor (large  $\Delta E$ ), the electron-transfer process will be dominated by a “through-bond” non-resonant tunneling mechanism, and the electron-



**Figure 1.** Energy diagrams for D–M–A systems. D and A represent electron-donor or electron-acceptor units regardless of their nature (molecules or electrodes). A) A system where  $\Delta E$  is changed by changing the electronic structure of the molecular bridge. B) A system where  $\Delta E$  is changed by changing the energy levels of the donor or acceptor units. HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital.

transfer rate will exhibit a negative exponential decay with the length of the molecule ( $d$ ) according to  $I = I_0 e^{-\beta d}$ , where  $\beta$  is the decay factor. The correlation of  $\beta$  with the energy gap  $\Delta E$  is described by different theories.<sup>[6]</sup>

In particular, Figure 1A represents two cases where molecules of different electronic structures are incorporated in a junction, and  $\Delta E$  decreases by decreasing the separation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The electron-transfer rate through molecules is then higher for molecules with lower values of  $\Delta E$ . Organic molecules that “conduct” by tunneling are, in general, poor electron conductors. On this basis, molecules with different HOMO–LUMO separations can behave as circuit elements with different resistivity. Therefore, organic molecules can be considered as the equivalent of electronic resistors with a resistance that can be changed by modifying their electronic structure.

Alternatively, when the energies of the molecular orbitals and the donor/acceptor units are almost isoenergetic, the electron-transfer process will take place according to a resonant tunneling or a hopping mechanism, and the electron transfer rate will exhibit a “shallow” dependence on  $d$ .<sup>[6]</sup> Figure 1B



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represents a change in  $\Delta E$  obtained by tuning the energy of the donor/acceptor units with respect to the energy of the molecular orbitals. In particular, by bringing the energy of the Fermi levels of the electrodes in resonance with the energy of the LUMO/HOMO of the molecular bridge, a change in the mechanism of the electron-transfer process is induced.<sup>[7]</sup> The change from a non-resonant to resonant tunneling (or hopping) is expected to result in an abrupt increase in current, and the measured  $I$ - $V$  curves will show negative differential resistance (NDR) characteristics.<sup>[8]</sup> This phenomenon is equivalent to the function performed by traditional solid-state transistors, and the ability to control current flow is one of the most interesting features of molecular electronic devices.

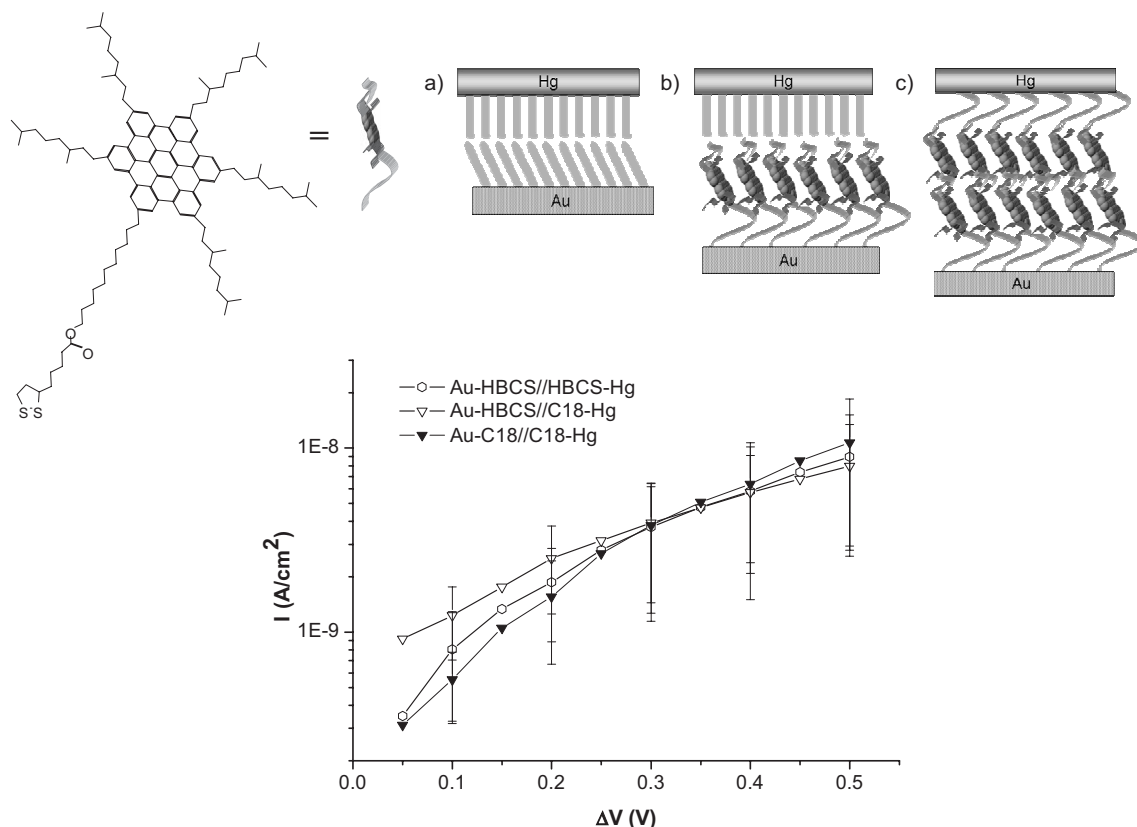
## 2. Molecules as Tunable Resistors

Quantitative evaluation of the resistivity of molecules of different structures is still an unsolved problem.<sup>[3]</sup> Comparisons of the resistivity of molecules with the same structure but obtained by different authors, and using different junctions, show large discrepancies.<sup>[3]</sup> In attempts to obtain information on the electrical characteristics of specific molecules by excluding effects related to the metal–molecule contacts and the

geometry of the junctions, few studies<sup>[2c,4,9,10]</sup> have measured and compared the current flow for a series of homologous molecules of increasing  $d$  by using the relationship  $I = I_0 e^{-\beta d}$ . These studies have been carried out using scanning tunneling microscopy, Hg-based electrodes, and conducting atomic force microscopy. Significantly, the results of these works agree in showing that the decay factor value  $\beta$  is smaller for phenyl-derived molecules ( $\beta = 0.6 \pm 0.1 \text{ \AA}^{-1}$ ) than for aliphatic chains ( $\beta = 0.98 \pm 0.1 \text{ \AA}^{-1}$ ).<sup>[3]</sup> In practical terms, this difference in the  $\beta$  values indicates that the resistivity of the molecules decreases by a few orders of magnitude upon increasing the electronic conjugation of the molecular bridge.

On the basis of these results, we have recently incorporated nanographene molecules in a series of Hg-based junctions, Hg/SAM//SAM/Au (Fig. 2 top; SAM: self-assembled monolayer), and measured the current flow under applied voltage.

These molecules, which are formed by a large number of condensed phenyl rings in a planar core and are similar to a sheet of graphite, are expected to have a very small HOMO–LUMO gap.<sup>[11]</sup> The SAMs incorporated between the electrodes were formed by the compound 2-(5-[1,2]dithiolan-3-yl-pentanoic acid dodecyl ester)-5,8,11,14,17-(3,7-dimethyloctanyl) hexa-*peri*-hexabenzocoronene (HBC) (Fig. 2, top left). The  $I$ - $V$  curves shown in Figure 2 measured for three junc-



**Figure 2.** Top left: Molecular structure of 2-(5-[1,2]dithiolan-3-yl-pentanoic acid dodecyl ester)-5,8,11,14,17-(3,7-dimethyloctanyl) hexa-*peri*-hexabenzocoronene (HBC) in the extended configuration. Top right: Illustrations of the assembled junctions: junction a, Au-C<sub>18</sub>//C<sub>18</sub>-Hg; junction b, Au-HBCS//C<sub>18</sub>-Hg (where HBCS denotes a SAM of HBC); junction c, Au-HBCS//HBCS-Hg. Bottom:  $I$ - $\Delta V$  curves measured for junction a ( $\blacktriangledown$ ), b ( $\nabla$ ), and c ( $\circ$ ). The error bars result from 40 measurements for each junction.

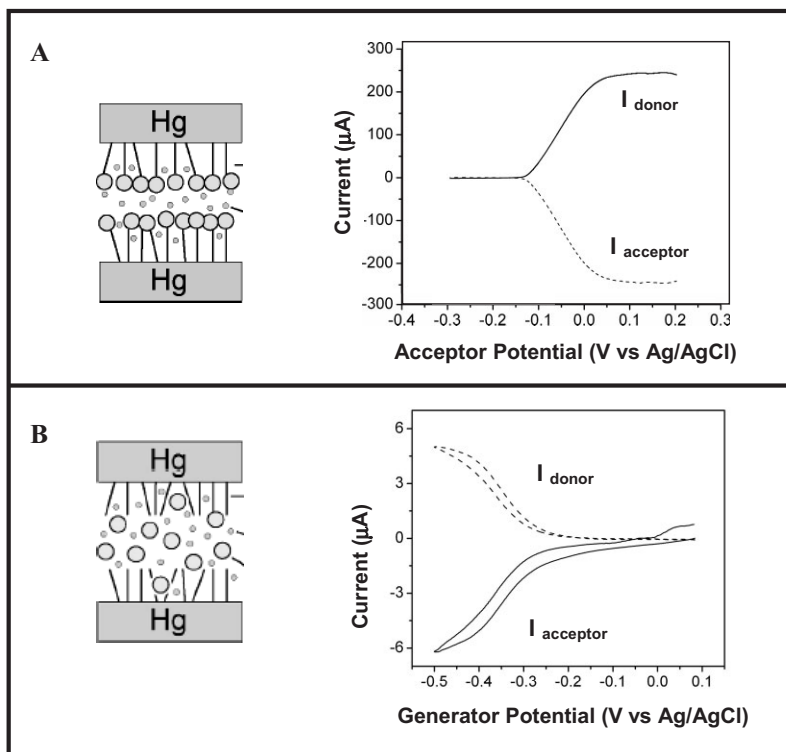
tions, junction a, Au- $C_{18}$ // $C_{18}$ -Hg (where  $C_{18}$  represents a SAM formed by octadecanethiol); junction b, Au-HBCS// $C_{18}$ -Hg (where HBCS denotes a SAM of HBC), and junction c, Au-HBCS//HBCS-Hg demonstrate that the current densities flowing across these three junctions are similar (the  $I$ - $V$  curves are the average of 40 measurements for each junction). These results lead to the conclusion that the HBC units are transparent to electrons relative to the aliphatic chains.<sup>[10]</sup>

The question of whether the mechanism of charge transport is ballistic or tunneling through a very small barrier cannot be answered in the present case because the electron-transfer rate is dominated by the tunneling barrier of the aliphatic chains, but the results clearly show that it is possible to dramatically tune the resistivity of the molecules by changing the electronic structure.

### 3. Molecules as Active Elements of Transistors

In pioneering studies, Tao<sup>[12]</sup> and Lindsay and co-workers<sup>[13]</sup> measured current flow through porphyrins incorporating different metal ions and reported  $I$ - $V$  curves with features that show NDR effects.<sup>[11,12]</sup> Since then, a number of authors<sup>[7,14–16]</sup> have reported NDR effects by using different types of junctions. According to the strategy depicted in Figure 1B, these junctions incorporate molecules with low-lying orbitals, such as those of well-defined and readily accessible redox states. It is worth noting that in some cases, particularly when a change of the molecular configuration is involved,<sup>[7a,13]</sup> the interpretation of the NDR signals is under discussion. In addition, we<sup>[17]</sup> have observed NDR features in junctions incorporating simple alkane chains. On the other hand, the literature data indicate that the most reproducible and clearly interpreted NDR results are those obtained in electrochemical junctions.<sup>[11,14–16]</sup> In fact, only by using an electrochemical junction is it possible to control the Fermi level of the electrodes with respect to the energy of the molecular orbitals (Fig. 1B). The potential of the electrodes is linked to the redox potential ( $E^\circ$ ) of the incorporated redox center (R) via the reference electrode.

By using Hg-based junctions (Hg-SAM//SAM-Hg) where the Hg electrodes are placed solution together with a Ag/AgCl reference electrode and a platinum counter electrode in an electrolyte solution and connected to a bipotentiostat, we achieved independent control of the potentials of each electrode. Figure 3 schematically shows the interfaces of two junctions: Hg-SAM-R//R-SAM-Hg and Hg-SAM//R//SAM-Hg, where redox sites, based on ruthenium metal complexes, are incorporated between the electrodes by using *different kinds*



**Figure 3.** A) Schematic of the interface of a Hg-SAM-R//R-SAM-Hg junction (left) and the current curves (right) measured as a function of applied acceptor potential. B) Schematic of the interface of a Hg-SAM//R//SAM-Hg junction (left) and the current curves (right) measured as a function of applied donor potential. The two junction behaves as diodes.

of interactions. In one case, the redox active sites are tethered to the Hg electrode surface (Fig. 3A, left); in the second case, they are trapped at the interface by electrostatic interactions (Fig. 3B, left). In both junctions the current flowing between the electrodes can be controlled by keeping the potential of one electrode constant and sweeping the potential of the other electrode across the  $E^\circ$  of the  $\text{Ru}^{\text{II/III}}$  couple.

Figure 3A (left) depicts the interface of the junction Hg-SAM-R//R-SAM-Hg.<sup>[18]</sup> The junction consists of two mercury-drop electrodes, both of which are coated with a SAM of the Ru-terminated thiol  $\text{HS}(\text{CH}_2)_{10}\text{CONHCH}_2\text{pyRu}(\text{NH}_3)_5$  (py: pyridyl). The  $E^\circ$  of the  $\text{Ru}^{\text{II/III}}$  couple in the SAMs of  $\text{HS}(\text{CH}_2)_{10}\text{CONHCH}_2\text{pyRu}(\text{NH}_3)_5$  is  $-0.04$  V. The potential of the electron-donor electrode ( $V_D$ ) is fixed at a constant voltage of  $V_D = +0.10$  V in order to keep the Ru species in the  $\text{Ru}^{\text{II}}$  form, and the potential of the electron-acceptor electrode ( $V_A$ ) is swept across the values of  $E^\circ$ . The current flowing through the junction shows the behavior reported in Figure 3A (right).

For  $V_A \leq E_0$ , the junction is non-conducting. For  $V_A$  close to  $E_0$ , the currents increase to a plateau with a half-wave potential of  $-0.04$  V, the formal potential  $E^\circ$ , and a current density of  $0.1 \text{ A cm}^{-2}$ . The key steps of the charge transport through the junction are i) the oxidation of  $\text{Ru}^{\text{II}}$  to  $\text{Ru}^{\text{III}}$  at the acceptor electrode, ii) electron exchange between  $\text{Ru}^{\text{III}}$  at the donor and  $\text{Ru}^{\text{II}}$ , and iii) reduction of  $\text{Ru}^{\text{III}}$  back to  $\text{Ru}^{\text{II}}$  at the donor electrode.

Figure 3B (left) depicts the interface of the junction Hg-SAM//R//SAM-Hg, where the redox sites are incorporated between the electrodes via electrostatic interactions at the SAMs formed on each electrode. The SAMs are formed by mercaptoundecanoic acid, and at  $\text{pH} > 4$  the  $\text{COO}^-$  head groups attract the positively charged  $\text{Ru}(\text{NH}_3)_6^{3+}$  ions at the interface. The  $E^\circ$  of the  $\text{Ru}^{\text{II/III}}$  couple at one Hg electrode covered by  $\text{COO}^-$  terminating SAMs is  $-0.21$  V. The potential of the acceptor electrode is held at  $+0.10$  V vs. Ag/AgCl in order to keep the Ru species in the  $\text{Ru}^{\text{III}}$  form, and the potential of the donor is swept past  $E^\circ$  for the reaction  $\text{Ru}(\text{NH}_3)_6^{3+} \rightarrow \text{Ru}(\text{NH}_3)_6^{2+}$ . Figure 3B (right) shows that only when the potential is swept past  $E^\circ = -0.21$  V does the current increase and become sigmoidal, reaching steady-state values with a current density of  $0.5 \times 10^{-2} \text{ A cm}^{-2}$ .<sup>[19]</sup> The current in this case is generated via a redox-cycling mechanism whereby the electroactive species diffuse between the closely spaced electrodes (separated by a few nanometers) to be alternatively reduced and oxidized.<sup>[20]</sup>

In both junctions, Hg-SAM-R//R-SAM-Hg and Hg-SAM//R//SAM-Hg, the current flows only when the potentials of the mercury electrodes are driven in such a way that one electrode (cathode) acts as the electron donor and the other one (anode) as the electron acceptor. The junctions switch from an “off” to an “on” state when the electronic states of the redox centers on the two monolayers falls between the Fermi levels of the electrodes, showing diodelike characteristics, analogous to those of solid-state devices. Significantly, the current flow is generated in these two junctions by different mechanisms. In junction Hg-SAM-R//R-SAM-Hg, the intensity of the current depends on the rates of i) the electron tunneling between the mercury electrodes and the surface-bound  $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$  centers and ii) the electron hopping between the adjacent  $\text{Ru}^{\text{II}}$  and  $\text{Ru}^{\text{III}}$  centers. In junction Hg-SAM//R//SAM-Hg, the current is dominated by a redox-cycling mechanism, and the intensity of the current depends on the inter-electrode gap.

#### 4. Concluding Remarks

We have described two fundamental strategies for tuning the current flow between electrodes, which summarize the studies reported in the literature on electron-transfer processes via molecular junctions.

The concept of using molecules as wires to supply a directional pathway to electron flow was already clear in the early studies of electron transfer in D–B–A supramolecular systems, and the consequent equivalence of molecules to electronic elements of a resistor was implicit. In contrast, the NDR effects that indicate that molecules can act as active components of nanometer-scale transistors were observed only with the study of molecular junctions. The possibility of tuning the potential applied at the electrodes permits one to switch the mechanism of electron transfer, with a consequent abrupt increase in current flow.

Many of the open problems in using molecules as active elements in electronic circuits, such as the mobility of molecules on the metal surface and the role played by the molecule–metal contacts, will be addressed because of the improved ability to fabricate sophisticated junctions with a relatively high degree of reproducibility. Hg-based junctions have the advantages of easy assembly and high versatility, and they can be fabricated both as two- and four-electrode junctions. In spite of their poor suitability for applications, they remain an excellent test bed for molecular electronics. We present here some results obtained using Hg-based junctions in the two modes, electrical and electrochemical. Two electrochemical junctions that incorporate redox sites by different interactions switch from an “off” to an “on” state at a predictable applied potential via charge-transport processes dominated by different mechanisms.

The results presented here indicate clearly that electrochemical junctions are the most suitable systems for i) providing precise control of the current flow, ii) accurately predicting the value of the applied potential at which the NDR signal will take off, and iii) identifying the charge-transport mechanisms.

Received: November 10, 2005

Final version: March 21, 2006

- [1] *Electron Transfer in Chemistry* (Ed: V. Balzani), Wiley-VCH, Weinheim, Germany **2001**.
- [2] a) M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour, *Science* **1997**, 278, 253. b) J. Chen, M. A. Reed, A. M. Rawlett, J. M. Tour, *Science* **1999**, 286, 1551. c) R. E. Holmlin, R. F. Ismagilow, R. Haag, V. Mujica, M. A. Ratner, M. A. Rampi, G. M. Whitesides, *Angew. Chem. Int. Ed.* **2001**, 40, 2316.
- [3] A. Salomon, D. Cahen, S. Lindsay, J. Tomfohr, V. B. Engelkes, C. D. Frisbie, *Adv. Mater.* **2003**, 15, 1883.
- [4] a) D. J. Wold, R. Haag, M. A. Rampi, C. D. Frisbie, *J. Phys. Chem. B* **2002**, 106, 2813. b) E. P. A. M. Bakkers, A. W. Marsman, L. W. Jenneskens, D. Vanmaekelbergh, *Angew. Chem. Int. Ed.* **2000**, 39, 13. c) R. E. Holmlin, R. Haag, M. L. Chabiny, R. F. Ismagilow, A. E. Cohen, A. Terfort, M. A. Rampi, G. M. Whitesides, *J. Am. Chem. Soc.* **2001**, 123, 5075.
- [5] a) W. B. Davis, W. A. Svec, M. A. Ratner, M. R. Wasiliewski, *Nature* **1998**, 60, 396. b) M. N. Paddon-Row, *Aust. J. Chem.* **2003**, 56, 729.
- [6] a) M. D. Newton, *Chem. Rev.* **1991**, 91, 767. b) D. Segal, A. Nitzan, M. A. Ratner, W. B. Davis, *J. Phys. Chem. B* **2000**, 104, 2790.
- [7] E. Tran, C. Grave, G. M. Whitesides, M. A. Rampi, *Electrochim. Acta* **2005**, 50, 4850.
- [8] a) D. K. James, J. M. Tour, *Top. Curr. Chem.* **2005**, 257, 33. b) R. A. Wassel, G. M. Credo, R. R. Fuieler, D. L. Feldheim, C. B. Gorman, *J. Am. Chem. Soc.* **2004**, 126, 295.
- [9] L. A. Bumm, J. J. Arnold, T. D. Dunbar, D. L. Allara, P. S. Weiss, *J. Phys. Chem. B* **1999**, 103, 8122.
- [10] K. Slowinski, H. K. Y Fong, M. Majda, *J. Am. Chem. Soc.* **1999**, 103, 7257.
- [11] M. Duati, C. Grave, N. Tcbeborateva, J. Wu, K. Müllen, A. Shaporenko, M. Zharnikov, J. K. Kriebel, G. M. Whitesides, M. A. Rampi, *Adv. Mater.* **2006**, 18, 329.
- [12] N. J. Tao, *Phys. Rev. Lett.* **1996**, 76, 4066.

- [13] W. Han, E. N. Durantini, A. L. Moore, D. Gust, P. Rez, G. Leatherman, G. R. Sealey, N. J. Tao, S. M. Lindsay, *J. Phys. Chem. B* **1997**, *101*, 10 719.
- [14] A. H. Flood, J. F. Stoddart, D. W. Steuerman, J. R. Heath, *Science* **2004**, *306*, 2055.
- [15] R. Rinaldi, A. Biasco, G. Maruccio, R. Cingolani, D. Alliata, L. Andolfi, P. Facci, F. De Rienzo, R. Di Felice, E. Molinari, *Adv. Mat.* **2002**, *14*, 1449.
- [16] a) D. I. Gittins, D. Bethell, D. J. Schiffrin, R. J. Nichols, *Nature* **2000**, *408*, 67. b) W. Haiss, H. van Zalinge, S. J. Higgins, D. Bethell, H. Hohenreich, D. J. Schiffrin, R. J. Nichols, *J. Am. Chem. Soc.* **2003**, *125*, 15 294.
- [17] M. A. Rampi, unpublished.
- [18] E. Tran, M. A. Rampi, G. M. Whitesides, *Angew. Chem. Int. Ed.* **2004**, *43*, 3835.
- [19] E. Tran, R. Murray, M. A. Rampi, G. M. Whitesides, unpublished.
- [20] A. J. Bard, J. A. Crayston, G. P. Kittlesen, T. V. Shea, M. S. Wrighton, *Anal. Chem.* **1986**, *58*, 2321.
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