# Reversible and Controllable Switching of a Single-Molecule Junction**

*Emanuel Lörtscher, Jacob W. Ciszek, James Tour, and Heike Riel**

Molecular electronics is aimed at the use of small ensembles or even individual molecules as functional building blocks in electronic circuits.[1] In recent years, devices applying thousands of molecules in parallel as functional elements have been presented,[2–5] revealing intriguing features such as negative differential resistance,[3,6] rectification behavior,[7] the Kondo effect,[8–11] or conductance switching.[4,12] For example, a unipolar voltage-triggered conductance switching of an ensemble of bipyridyl-dinitro oligophenylene-ethynylene dithiol (BPDN-DT) molecules was reported previously using three different techniques.[13] Another type of switching often observed is stochastic switching.[14] This phenomenon is caused by statistical fluctuations in the molecule itself or the molecule–metal contact. The lack of control over this type of switching makes it essentially undesirable for any technological application. Recent experiments aiming to identify the fundamental mechanisms responsible for voltage-induced switching in sandwich structures[12] indicate that the generic mechanism is dominated by the electrode properties or the molecule–metal interfaces, rather than behavior inherent to the molecule.[15,16] The investigation of intrinsic molecular functionality is difficult in these device architectures employing thousands of molecules in parallel, in particular because contact effects and collective phenomena can not be excluded. In this paper, we demonstrate that a single molecule connected to two symmetric leads in a simple two-terminal configuration can be reversibly and controllably switched between two stable states in response to an external voltage stimulus. In this geometry and under a very controlled environment, we can exclude the formation of metal filaments and can conclude that the observed switching has truly a molecular origin. In addition, we show that the control achieved over this effect can be used to employ a single molecule as a memory element.

Using the mechanically controllable break-junction (MCBJ) technique (Figure 1 and Experimental Section), we have investigated charge-carrier transport through single
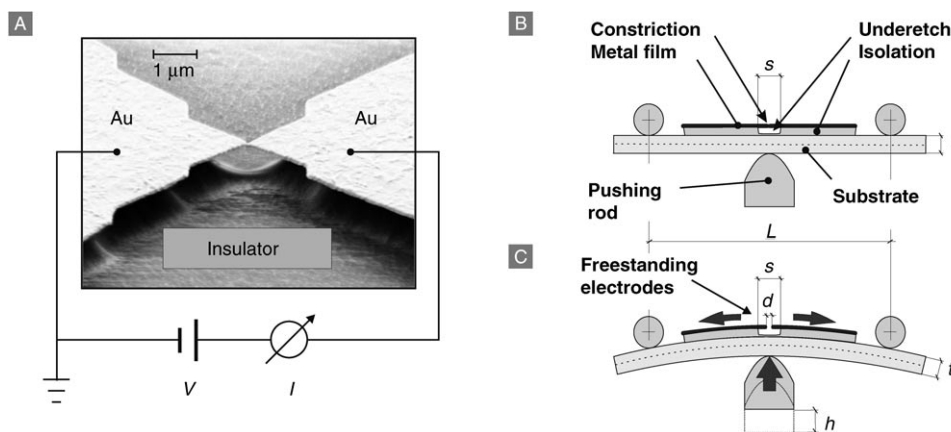


**Figure 1.** Principle of a MCBJ: A) Scanning electron microscope image of a microfabricated MCBJ sample consisting of a freestanding metal bridge with a central lateral constriction on top of a flexible isolating substrate. The electric circuit is schematically drawn. B) The MCBJ sample is mounted onto a three-point bending mechanism. C) The bending force applied to the bottom of the substrate introduces surface extension, which elongates and finally breaks the metal bridge at its smallest constriction creating two separated electrodes. The distance between the electrodes can be controlled in both the opening and closing direction with sub-picometer accuracy by bending or relaxing the sample.

[*] E. Lörtscher, Dr. H. Riel
IBM Zurich Research Laboratory
Säumerstrasse 4, 8803 Rüschlikon (Switzerland)
Fax: (+41) 44-724-8956
E-mail: hei@zurich.ibm.com
J. W. Ciszek, Prof. J. Tour
Department of Chemistry and
the Smalley Institute for Nano Science and Technology
Rice University, 6100 Main Street, Houston, Texas 77005 (USA)

BPDN-DT molecules (Figure 2A)[17] and bipyridyl oligophenylene-ethynylene dithiol (BP-DT) molecules (Figure 2B). The BP-DT molecule without nitro groups acts as a reference molecule. The rigid rodlike molecules are designed such that the BP-DT can attain a more planar arrangement due to minimal steric interactions in the central bipyridyl unit compared with the significant juxtaposed nitro interactions in BPDN-DT. The molecules are dissolved in tetrahydrofuran (THF; concentration of $10^{-4}$ mol L$^{-1}$) and the acetate moieties are removed with aqueous $NH_4OH$ during assembly to the gold leads via the free thiols.

Figure 2C displays current–voltage ($I–V$) sweeps starting from $-1.2$ V to $+1.2$ V, and back again to $-1.2$ V (double sweep) for BPDN-DT (black) and BP-DT (gray) at 100 K. All data presented are raw data and no filter was applied. Both molecules reveal a symmetric $I–V$ curve with a con-
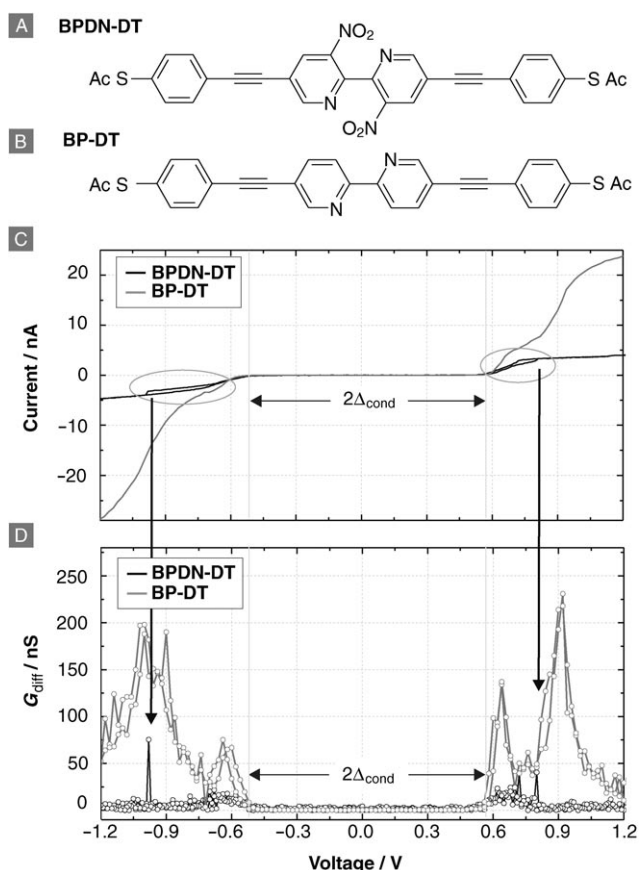
**Figure 2.** Molecular structures of the two molecules under investigation: A) Bipyridyl-dinitro oligophenylene-ethynylene dithiol (BPDN-DT), and B) bipyridyl oligophenylene-ethynylene dithiol (BP-DT). Charge-carrier transport characteristics of single BPDN-DT (black) and BP-DT (gray) molecules acquired at 100 K; C) statistically representative I–V curves (double sweep) based on several-hundred measurements. An approximately six-times higher current is observed for the BP-DT molecule compared to the BPDN-DT molecule (all raw data). A reversible hysteresis in the BPDN-DT signal is highlighted with gray rings; D) $G_{diff}$–V data reveals a similar conductance gap for both molecules. Black arrows indicate the discontinuity in the BPDN-DT curve.

The curves shown for BPDN-DT and BP-DT represent the statistically most probable characteristics out of several hundreds acquired, which all reveal the features described. For every molecule, seven different MCBJ samples have been used and several hundreds of characteristics were measured with each sample. As the molecules are deposited from a very dilute solution onto the junction, a molecule is only successfully contacted in 50% of the MCBJ samples. For all the samples with BPDN-DT applied, the measurements always reveal a hysteresis with switching. The BP-DT in contrast exhibits exclusively monotonic traces without any switching. In addition, stochastic switching[14] is absent for both molecular systems. This can be explained by the low temperatures at which the measurements have been performed. Consequently, the mechanisms causing the observed switching in BPDN-DT are obviously not stochastic in nature.

Figure 3 shows the hysteresis appearing in the I–V curve of BPDN-DT in more detail. Starting the measurement from 0 V, the current signal increases monotonically until
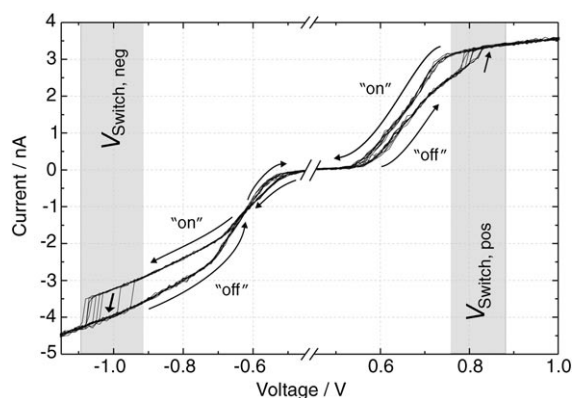
**Figure 3.** Several repeated switching cycles of the BPDN-DT: If the voltage applied to the metal–BPDN-DT–metal junction exceeds a certain positive threshold value ($V_{Switch,pos}$), the system switches from the initial "off" state to the "on" state. This state is maintained when operating only at voltages above $V_{Switch,pos}$. A negative voltage sweep or a pulse below the negative threshold value ($V_{Switch,neg}$) resets the molecule again to the initial "off" state.

ductance gap ($2\Delta_{cond}$) of approximately 1 V, where charge-carrier transport is based only on direct tunneling between the electrodes.[18] In the case of BP-DT, the current increases for voltages above 0.5 V and reaches ±20–30 nA at ±1.2 V. For BPDN-DT, the currents above +0.6 V and below −0.6 V are approximately six times lower than for BP-DT. Since the molecule–metal coupling is equal in both molecules, the lower current flow in BPDN-DT can be explained by reduced conjugation due to its more twisted molecular structure. It is noticeable that the I–V curve of BPDN-DT exhibits hysteresis at ±0.9 V, which is highlighted in Figure 2C by the gray rings. In Figure 2D, the differential conductance–voltage ($G_{diff}$–V) is plotted. The conductance of BP-DT reveals two pronounced peaks symmetrically located at around ±0.6 and ±1.0 V. These two peaks result from the maximum current flowing through the two molecular orbitals nearest to the Fermi level $E_F$.[18] For BPDN-DT, the $G_{diff}$–V plot reveals that the hysteresis exhibits a discontinuity at −1.0 V and +0.8 V.

the voltage exceeds $V_{Switch,pos}$. The current signal suddenly jumps from a low conductive curve, called the "off" trace, at approximately +0.8 V to a high current curve, called the "on" trace. For even higher voltages, the current continues to increase. Sweeping the voltage back from +1.5 to 0 V one observes a hysteresis; the current decreases monotonically without a signal jump, exhibiting higher current values than the initial upwards sweep between 0.55 and 0.8 V. In addition, the conductance gap is now slightly reduced. After this first switching sweep, when operating only at voltages above $V_{Switch,neg}$, the initial "off" state is no longer accessible and the metal–molecule–metal system remains in the higher conductive "on" state during all subsequent positive sweeps. Performing a negative voltage sweep from 0 to −1.5 V, a similar switching behavior at around −1.0 V is observed. Sweeping back from −1.5 to 0 V, the current signal again

follows a monotonous trace; details of the intersection of the two signals at $-0.62$ V are currently under investigation. This negative sweep resets the system to the "off" state, which is verified by a subsequent positive sweep that again exhibits a lower current and reveals a switching to the "on" state at approximately $+0.8$ V.

In all our samples, the "off" state is always reconfigurable by applying a negative voltage pulse below a certain threshold voltage ($< V_{Switch,neg}$). $V_{Switch,pos}$ varies between $+0.7$ V and $+1.4$ V, and $V_{Switch,neg}$ between $-0.7$ V and $-1.4$ V, respectively. We attribute this to microscopic changes in the molecule–metal coupling causing a change in the voltage drop across the molecule. As a consequence, the positive and negative threshold can be slightly asymmetric. Despite these small variations in the switching threshold, both states of the system are remarkably stable. Even after several hours of measurement and performing more than 500 positive and negative sweeps iteratively, the hysteresis effect is maintained and the system retains its ability to switch; a remarkable result for a single-molecule system. Switching can be observed at room temperature as well (see Supporting Information), however, the junction becomes unstable after measuring a few switching events and a closed metal–metal contact is finally formed. This is due to increased mobility of the gold atoms of the electrodes at elevated temperatures, which affects the stability of the junction when applying high electrical fields.

Further insight into the switching mechanism is gained by studying the temporal behavior of the switching process: Using a long current measurement integration time $t_{int,long} = 320$ ms per data point, compared to the short integration time $t_{int,short} = 0.64$ ms per data point used previously, the current signal reveals a bistable behavior in the range of approximately $+0.7$ to $+0.82$ V for increasing voltage (Figure 4A). In this particular voltage range, the system switches back and forth between the competing "on" and "off" state. For higher voltages, which in turn also means higher electrical fields across the molecule, the current signal follows a single trace, indicating that the "on" state is energetically more favorable. Upon decreasing the voltage from $+1.0$ to $0$ V (Figure 4B), the signal follows a monotonic trace and starts to switch again in the above-mentioned voltage range. Measuring with $t_{int,long}$, the "on" state is not maintained, and the molecule relaxes to the "off" state for lower voltages. Measuring with $t_{int,short}$, the system switches to the "on" state for increasing voltages and remains in the "on" state, in contrast to $t_{int,long}$ (Figure 4C). This state persists and is unaffected by successive read pulses at low positive voltages ($+0.5$ V $< V_{Read} < V_{Switch,pos}$), consequently representing a stored "bit". This nondestructive reading makes it possible to use this single-molecule system as a memory element.

As mentioned above, voltage pulses exceeding the threshold voltages can be applied to switch the system between the two discrete states in a very controlled and reversible manner. A pulse pattern consisting of write ($+1.6$ V, 50 ms length) and erase ($-1.6$ V, 50 ms length) pulses with intermediate readings ($+1.1$ V, 3 s duration) was applied to the metal–single molecule–metal system to demonstrate its
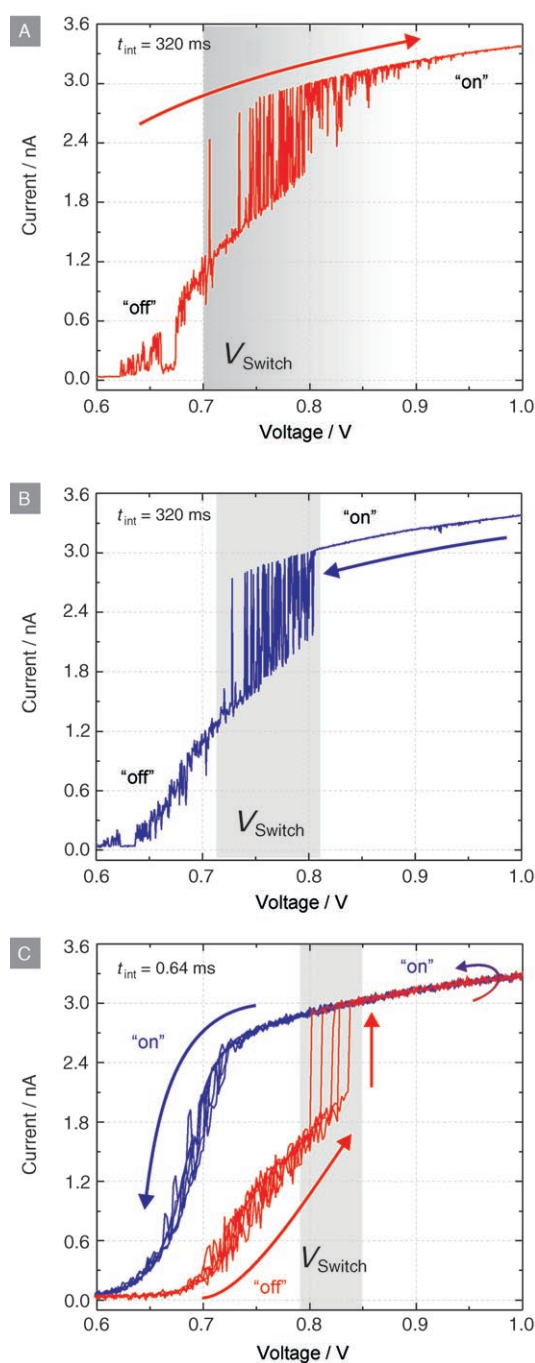


**Figure 4.** Dynamics of the switching mechanism: A) Upon increasing the current measurement integration time significantly ($t_{int,long} = 320$ ms per data point), the current signal becomes bistable for increasing voltages within a certain range, finally switching to the "on" state for higher voltages. B) When lowering the voltage with $t_{int,long}$, fluctuations can be observed in a certain voltage range, after which the "on" state finally relaxes into the "off" state for $V < V_{Switch}$. C) For short integration times ($t_{int,short} = 0.64$ ms per data point), a sudden switching to a high conductive "on" state occurs (five curves shown). The system maintains the "on" state even upon decreasing the voltage. The gray area represents the region of $V_{Switch}$.

memory operation (Figure 5A). The inset of Figure 5B shows the $I$–$V$ curve for the specific sample used. The slight difference in the hysteresis compared to the above-descri-
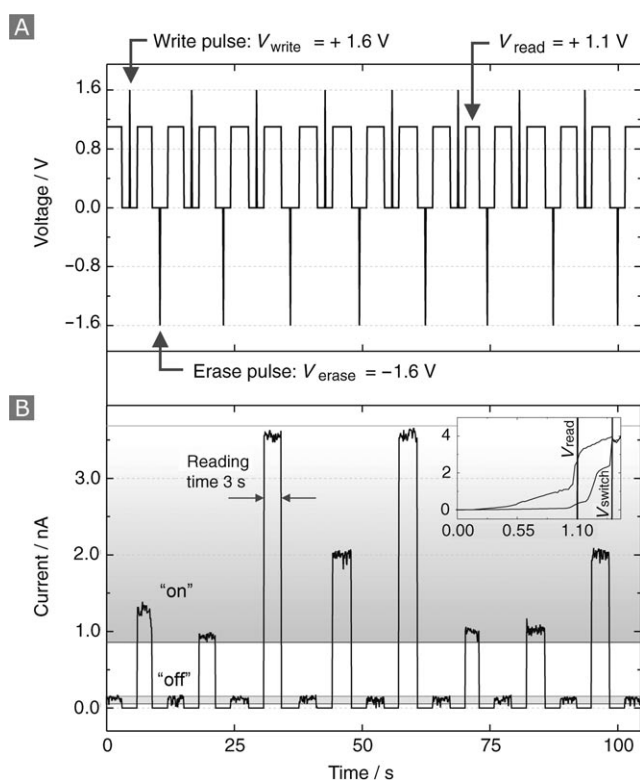
**Figure 5.** Memory operation of the BPDN-DT system: A) Write, read, and erase voltage pulse pattern applied. B) Resulting switching between "off" and "on" state: $I_{off}$ varies between 0.05 and 0.13 nA, $I_{on}$ between 0.9 and 3.6 nA. Reading times of 3 s display excellent signal stability. The inset shows the corresponding $I$–$V$ curve, indicating switching at 1.4 V and reading at 1.1 V (black lines).

bed data shows the typical variation in single-molecule junctions that occurs due to changes in the molecule–metal coupling. In this configuration, the reading voltage at $+1.1$ V is farther separated from the critical switching range ($+1.3$ to $+1.4$ V). The current through the molecule was directly probed and the data shown in Figure 5B is raw data without any further signal processing. During the reading times of 3 s, the current signals were constant and no decay of the state was observed. Even using continuous reading times of up to 30 s, the signal decreased only by 5%. The currents measured for the "off" state vary between 0.05 and 0.13 nA, and those for the "on" state between 0.9 and 3.6 nA, yielding a bit separation ($I_{on}/I_{off}$) ranging between 7 and 70. The variation in the "on"-state current can be explained by the steep increase in the $I$–$V$ signal around $+1.1$ V (inset of Figure 5B). Furthermore, periodic reading of a stored bit (i.e., no voltage applied between readings) established that this single-molecule memory is nonvolatile over a measurement time of several minutes at 100 K.

In conclusion, single BPDN-DT and BP-DT molecules have been contacted by two symmetric leads using the MCBJ technique. We have demonstrated that the metal–single BPDN-DT molecule–metal system can be controlled and reversibly switched between two distinct states using the above-described control principle. Even after performing more than 500 positive and negative sweeps iteratively,

the BPDN-DT system retained its ability to switch. In contrast, the BP-DT molecule without nitro groups did not exhibit any switching feature, not even of a stochastic type.[14] In our single-molecule measurements, collective phenomena can be excluded, therefore the switching found in BPDN-DT has a truly molecular origin. Comparing the molecular structures, it is obvious that the nitro groups of BPDN-DT cause the switching behavior. Possible reasons for switching are conformational change, trapping of charges on the molecule, or tilting.

Recently, polaronic transport[19] has been suggested to cause hysteresis effects in $I$–$V$ curves very similar to the characteristics shown in Figure 4C. The novel insight into the switching dynamics we gained via time-dependent measurements (see Figure 4) can be an important step to verify the applicability of the different theoretical models. In addition, we have demonstrated that the controlled switching behavior can be used to write, read, and erase bits by simple voltage pulses and hence employ a single-molecule as memory element. The bit separation ranged between 7 and 70 and the probed bit state is stable within reading times of 30 s. Further experimental and theoretical research is required to fully elucidate the fundamental process underlying the molecular-switching mechanism. In particular, future experimental investigations should address the bit retention times and switching dynamics as a function of temperature.

## Experimental Section

Charge-carrier transport studies were performed using a mechanically controllable break-junction (MCBJ) technique,[20] an approach which has been proven to enable charge-carrier-transport measurements through an individual molecule.[21] The principle of the MCBJ technique is shown in Figure 1. A thin metal film (e.g., gold) with a lateral constriction is fabricated on top of a flexible isolating substrate (phosphorous bronze covered with polyimide) by means of electron-beam lithography and a lift-off technique (Figure 1A). Reactive ion etching is used to create a freestanding bridge. This MCBJ sample is mounted in a three-point bending mechanism (Figure 1B) and a bending force is applied to the bottom of the sample by a pushing rod (Figure 1C). This introduces surface extension elongating the metal bridge, which finally breaks at its smallest constriction, creating two separated electrodes. The distance between the electrodes can be controlled in both the opening and closing direction with sub-picometer accuracy by bending or relaxing the sample. Owing to the high surface mobility of gold, atomically sharp tips can be formed.[22] Our MCBJ system is operated under ultrahigh-vacuum (UHV) conditions in a temperature range between 5 and 300 K. Low temperatures improve the MCBJ electrode stability due to the reduced surface mobility of gold. In the temperature range of 5–200 K, the metal–molecule–metal junction can typically endure electric fields up to approximately $10^7$ V cm$^{-1}$.

Electrical characterization was performed with a Hewlett–Packard 4156B Parameter Analyzer. Further experimental details of our setup will be published elsewhere.[23] After forming two atomically sharp electrode tips, as indicated by the observation

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

of conductance quantization at room temperature, the distance between the leads is set to be longer than the length of the particular molecules under investigation. The molecules are then deposited out of a very dilute solution onto an open junction and can thereby adsorb to one of the two electrodes. Subsequently, the system is evacuated. Upon reaching UHV conditions, the junction with molecules applied is closed stepwise and current–voltage ($I$–$V$) characteristics are measured simultaneously. The closing procedure is reversed when the resistance is smaller than 12.9 kΩ, indicating a closed metal–metal bridge. Our system is fully automated allowing the electrical transport characteristics to be acquired simultaneously during repeated closing and opening of the junction. Thereby, we observe a distinct region where the molecular transport characteristics are measured. This reversible closing/opening procedure is repeated many-hundred times for every sample and the entity of all data measured enables statistical analysis to be performed in order to determine the most probable curves and to exclude artifacts. In particular, histograms show the absence of multiple current values, indicating that only one molecule is contacted. The detailed description of our statistical approach will be published elsewhere.[23]

## Keywords:

[1] a) M. A. Ratner, A. Aviram, *Chem. Phys. Lett.* **1974**, *29*, 277; b) R. L. Carroll, C. B. Gorman, *Angew. Chem.* **2002**, *114*, 4556; *Angew. Chem. Int. Ed.* **2002**, *41*, 4378; c) J. M. Tour, *Molecular Electronics: Commercial Insights, Chemistry, Devices, Architecture and Programming*, World Scientific, New Jersey, **2003**; d) A. Nitzan, M. A. Ratner, *Science* **2003**, *300*, 1384.

[2] C. P. Collier, E. W. Wong, M. Belohradsky, F. M. Raymo, J. F. Stoddart, P. J. Kuekes, R. S. Williams, J. R. Heath, *Science* **1999**, *285*, 391.

[3] J. Chen, M. A. Reed, A. M. Rawlett, J. M. Tour, *Science* **1999**, *286*, 1550.

[4] M. A. Reed, J. Chen, A. M. Rawlett, D. W. Price, J. M. Tour, *Appl. Phys. Lett.* **2001**, *78*, 3735.

[5] Y. Luo, C. P. Collier, J. O. Jeppesen, K. A. Nielsen, E. Delonno, G. Ho, J. Perkins, H. R. Tseng, T. Yamamoto, J. F. Stoddart, J. R. Heath, *ChemPhysChem* **2002**, *3*, 519.

[6] J. Chen, W. Wang, M. A. Reed, A. M. Rawlett, D. W. Price, J. M. Tour, *Appl. Phys. Lett.* **2000**, *77*, 1224.

[7] J. G. Kushmerick, D. B. Holt, J. C. Yang, J. Naciri, M. H. Moore, R. Sashidhar, *Phys. Rev. Lett.* **2002**, *89*, 086802.

[8] H. Park, J. Park, A. K. L. Lim, E. H. Anderson, A. P. Alivisatos, P. L. McEuen, *Nature* **2000**, *407*, 57.

[9] J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abruna, P. L. McEuen, D. C. Ralph, *Nature* **2002**, *417*, 722.

[10] W. Liang, M. P. Shores, M. Bockrath, J. R. Long, H. Park, *Nature* **2002**, *417*, 725.

[11] A. N. Pasupathy, R. C. Bialczak, J. Martinek, J. E. Grose, L. A. K. Donev, P. L. McEuen, D. C. Ralph, *Science* **2004**, *306*, 86.

[12] Y. Chen, G. Y. Jung, D. A. A. Ohlberg, X. M. Li, D. R. Stewart, J. O. Jeppesen, K. A. Nielsen, J. F. Stoddart, R. S. Williams, *Nanotechnology* **2003**, *14*, 462.

[13] A. S. Blum, J. G. Kushmerick, D. P. Long, C. H. Patterson, J. C. Yang, J. C. Henderson, Y. X. Yao, J. M. Tour, R. Sashidhar, B. R. Ratna, *Nat. Mater.* **2005**, *4*, 167.

[14] a) Z. J. Donhauser, B. A. Mantooth, K. F. Kelly, L. A. Bumm, J. D. Monnell, J. J. Stapleton, D. W. Price, A. M. Rawlett, D. L. Allara, J. M. Tour, P. S. Weiss, *Science* **2001**, *292*, 2303; b) R. A. Wassel, R. R. Fuierer, N. J. Kim, C. B. Gorman, *Nano Lett.* **2003**, *3*, 1617.

[15] D. R. Stewart, D. A. A. Ohlberg, P. A. Beck, Y. Chen, R. S. Williams, J. O. Jeppesen, K. A. Nielsen, J. F. Stoddart, *Nano Lett.* **2004**, *4*, 133.

[16] C. N. Lau, D. R. Stewart, R. S. Williams, M. Bockrath, *Nano Lett.* **2004**, *4*, 569.

[17] A. K. Flatt, S. M. Dirk, J. C. Henderson, D. E. Shen, J. Su, M. A. Reed, J. M. Tour, *Tetrahedron* **2003**, *59*, 8555.

[18] M. Paulsson, F. Zahid, S. Datta, *Nanoscience, Engineering and Technology Handbook*, CRC Press, Boca Raton, **2003**.

[19] a) M. Galperin, M. A. Ratner, A. Nitzan, *Nano Lett.* **2005**, *5*, 125; b) A. Troisi, M. A. Ratner, *Small* **2006**, *2*, 172.

[20] a) C. J. Muller, J. M. van Ruitenbeek, L. J. de Jongh, *Physica C* **1992**, *191*, 485; b) J. Moreland, J. W. Elkin, *J. Appl. Phys.* **1985**, *58*, 3888; c) J. Reichert, H. B. Weber, M. Mayor, H. von Löhneysen, *Appl. Phys. Lett.* **2003**, *82*, 4137.

[21] a) H. B. Weber, J. Reichert, F. Weigend, F. Ochs, D. Beckmann, M. Mayor, R. Ahrlichs, H von Löhneysen, *Chem. Phys.* **2002**, *281*, 113; b) R. H. M. Smit, Y. Noat, C. Untiedt, N. D. Lang, M. C. van Hemert, J. M. van Ruitenbeek, *Nature* **2002**, *419*, 906.

[22] a) A. Yanson, G. Rubio Bollinger, H. E. van den Brom, N. Agrait, J. M. van Ruitenbeek, *Nature* **1998**, *395*, 783; b) H. Ohnishi, Y. Kondo, K. Takayanagi, *Nature* **1998**, *395*, 780.

[23] E. Lörtscher, H. B. Weber, H. Riel, **2006**, unpublished results.