

Molecular Switch Controlled by Pulsed Bias Voltages

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Recent experiments have shown that the current–voltage characteristics (I – V) of BPDN-DT (bipyridyl-dinitro oligophenylene-ethynylene dithiol) can be switched in a very controlled manner between “on” and “off” traces by applying a pulse in a bias voltage, V_{bias} . Here, the polaron formation energies are calculated to check a frequently held belief, namely, that the polaron formation can explain the observed bistability. These results are not consistent with such a mechanism. Instead, a conformational reorientation is proposed. The molecule carries an intrinsic dipole moment, which couples to V_{bias} . Ramping V_{bias} exerts a force on the dipole that can reorient (“rotate”) the molecule from the ground state (“off”) into a metastable configuration (“on”) and back. By elaborated electronic structure calculations, a specific path for this rotation is identified through the molecule’s conformational phase space. It is shown that this path has sufficiently high barriers to inhibit thermal instability but that the molecule can still be switched in the voltage range of the junction stability. The theoretical I – V s qualitatively reproduce the key experimental observations. A proposal for the experimental verification of the alternative mechanism of conductance switching is presented.

Keywords:

- density functional calculations
- molecular electronics
- molecular mechanics
- molecular switches
- molecular wires

1. Introduction

During the past few years, experiments in the field of molecular electronics have experienced significant improvements. This has made possible the observation of Coulomb blockade^[1] and Kondo effects^[2] in molecular transistor geometry. Improved statistical methods for accessing the conductance of molecular junctions have been developed.^[3,4] A spectacular manifestation of molecular low energy excitations has been detected in inelastic current spectroscopy.^[5] Concerning potential applications, molecular electronics has the potential for the realization of functional devices like memory elements, switches, transistors, and so on by designing

suitable molecular complexes. For this reason, a considerable effort has been made to design and test molecular systems with a controlled switching behavior.^[6,7] The challenge is ubiquitous in the field of nanotechnology, namely, how can a device or material be built and manipulated with full control down to the atomic level. Therefore, one may expect that a solution in one subfield will result in exciting developments in many others.

The proposed prototypes for single-molecule memory elements can be sorted according to which physical degree of freedom underlies the switching bistability. The three principle categories are: i) switches with different (meta)stable charge configurations;^[8–13] ii) conformational switches with molecules exhibiting different stable isomers;^[14–17] iii) conformational switches with molecular reorientations against the contact atoms.^[18] Once it is known how to operate a single molecule, arrays of molecules can be addressed as well, which eventually may result in the formation of an entirely new class of molecular hybrid materials.

It is very encouraging that switching has recently been successfully demonstrated by Blum et al.,^[19] Keane et al.,^[20] and Lörtscher and Riel.^[21] These researchers have been using a molecular wire of the “Tour-type,” that is, bipyridyl-dinitro oligophenylene-ethynylene dithiol (BPDN-DT) (Figure 1),

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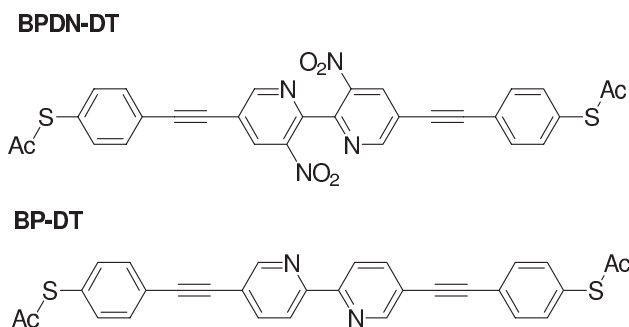


Figure 1. Upper panel: The BPDN-DT molecule that shows switching in single molecule transport experiments.^[20,21,23] The protection groups, Ac, are released when the molecule forms a chemical bond with the Au surface. Lower panel: a reference molecule that does not switch.^[20,21]

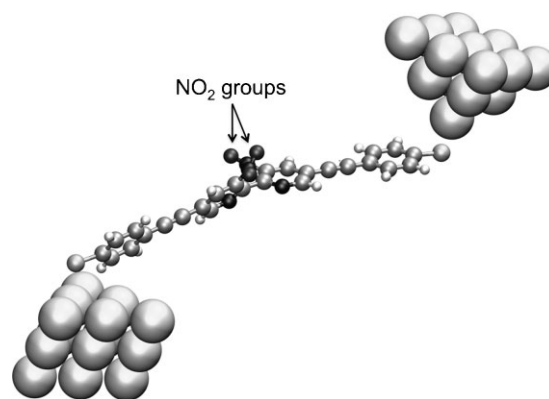


Figure 2. Extended molecule used for the DFT calculations. The NO₂ groups (indicated by the arrow) introduce a dipole moment perpendicular to the wire direction. In addition, their steric interaction drives the wire out of the planar conformation.

which was investigated in several experimental and theoretical works before.^[18,22,23] This particular set of experiments has two intriguing features: first, switching is established in a two-terminal device by employing a pulse in the bias voltage, and second, the effect is very stable, so much so that it has even been observed at room temperature. Specifically, the BPDN-DT wire shows a characteristic experimental behavior:^[21] with a very slow (adiabatic) change of the bias, V_{bias} , the current-voltage characteristic (I - V) is fully reversible for up-sweeping and down-sweeping. However, with a faster sweeping rate the adiabatic regime is left and a hysteretic behavior is seen in the I - V if V_{bias} is tuned beyond ≈ 1 V. The new I - V curve signals the existence of a second (meta)stable state of the molecular junction. One returns to the original curve only by repeating the procedure with inverted bias.

The physical origin of bistability in these experiments has not yet been identified. He et al.^[23] attribute it in their experiment in an electrochemical environment to a change in the oxidation state of the molecule. A polaron-caused bistability was also put forward by Galperin et al.^[24] as a possible explanation of switching observed in the break-junction experiment by Lörtscher et al.^[21] who investigated a freely suspended molecular bridge. On the other hand, Keane et al.^[20] argue that the formation of a polaron is not a likely occurrence in their electromigrated break-junction experiment. They suspect rather that a bias-driven modification of the contacts may be responsible.

Identifying a possible switching mechanism operating for Tour-type molecules is the aim of this work. Our calculations suggest the following picture: the BPDN-DT molecule in vacuum or in between two contacts (Figure 2), is not susceptible to charging. Unless it is stabilized by counter charges that are located very close to the bipyridine unit, any excess charge recombines with its images on the

electrodes (Figure 3). This makes polaron formation (class I) unlikely in the experiments,^[19,20,21] which is in support of an earlier claim.^[20]

However as we shall demonstrate, the key property for switching (bistability), can originate from a rotational degree of freedom associated with BPDN-DT molecules contacted to electrodes. The inertia driving the rotation results from the action of the electrical field (associated with V_{bias}) on the dipole moment of the dressed bipyridine unit. Two stable configurations can be reached by a double axis p-rotation (Figure 4) (classes II and III). Our calculations suggest that the rotation can be performed in such a way that the rotational barrier is high enough — so both states are stable against temperature — but at the same time low enough so that one state rotates into the other under bias voltages of ≈ 1 V (Figure 5). The theoretical I - V curves (Figure 6) that one obtains for either state closely resemble the experimental findings.^[19,20,21]

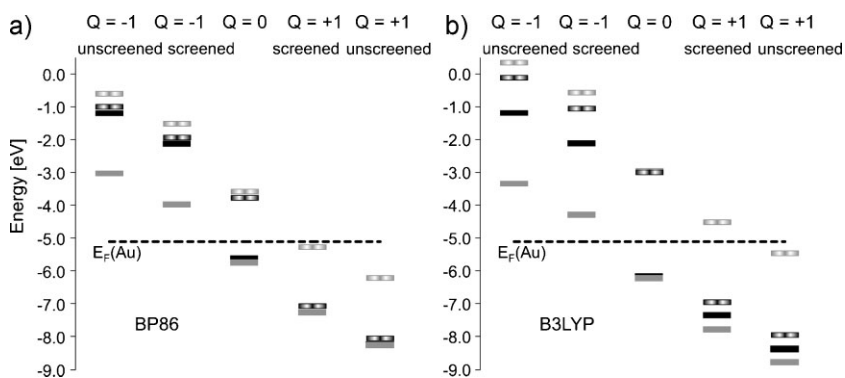


Figure 3. Energies of the HOMO (dark solid) and the LUMO (dark dashed) for the molecular wire depicted in Figure 1 (with the replacement Ac \rightarrow H). Also neighboring orbitals, HOMO-1 (light solid) and LUMO+1 (light dashed), are shown. For the molecule with excess charge, $Q = \pm 1$, orbitals have been obtained with (“screened”) and without (“unscreened”) image charges; this models screening in the vicinity of metallic (Au) electrodes. Fermi energy of Au face-centered-cubic (fcc) clusters are $E_{\text{Fermi}} \approx -5.05$ eV, with BP functional ($E_{\text{Fermi}} = -5.65$, -5.55 , and -5.42 eV for Au(111), Au(100), and Au(110) with local density approximation (LDA), respectively).^[31] The plot on the left (a) shows results obtained within the BP86^[28, 29] exchange correlation functional, while the plot on the right (b) shows corresponding results for the B3LYP functional.^[30] No qualitative difference in level positions is observed indicating that self-interaction errors do not interfere.

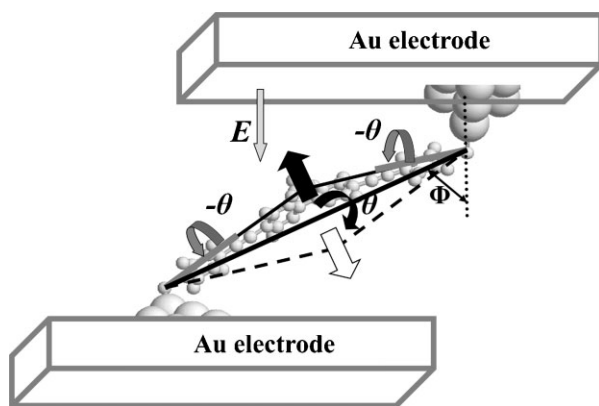


Figure 4. Schematics indicating the two-axis rotation, which connects the two bistable states realizing the molecular switch. The black arrow indicates the NO_2 groups, thin black lines the carbon backbone (Figure 2). The first step is rotation of the whole molecule by θ about the thick black axis connecting the two S atoms, which flips the NO_2 groups represented by the white arrow. The second step is (back) rotation of the connecting phenyl ring only about the grey axis with angle $-\theta$. Back rotation partly eliminates the energy cost associated with the contact modification. The pale grey arrow indicates the direction of the external electric field.

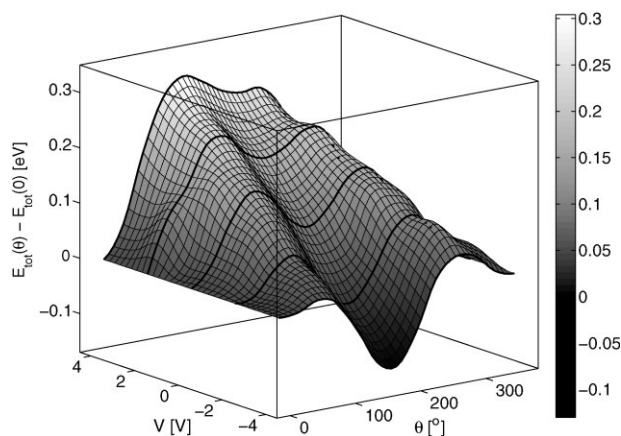


Figure 5. Dependency of the total ground state (DFT) energy, $\Delta E_{\text{tot}}(\theta)$, of the extended molecule (Au_{14} clusters) on the rotation angle θ and an inter-electrode electric potential drop, V , with homogeneous gradient $\mathbf{E} = -\nabla V$ (Figure 4). (The simulation angle is $\Phi = 70^\circ$; full geometry relaxation has been done for $V = 0\text{ V}$ at $\theta = 0^\circ$).

2. Model and Method

The model setup used for the density functional theory (DFT) transport calculations is depicted in Figure 2. The Au_{14} -clusters mimic the electrodes. Computations based on the DFT have been performed with the real-space based package TURBOMOLE.^[25] Optimized basis sets of triple- ζ quality including polarization functions have been used (exception: I - V with a split-valence basis set of double- ζ quality).^[26,27] The exchange correlation (XC) functional BP86^[28,29] was employed. Charging analysis and relaxations were checked against a hybrid functional, B3LYP.^[30]

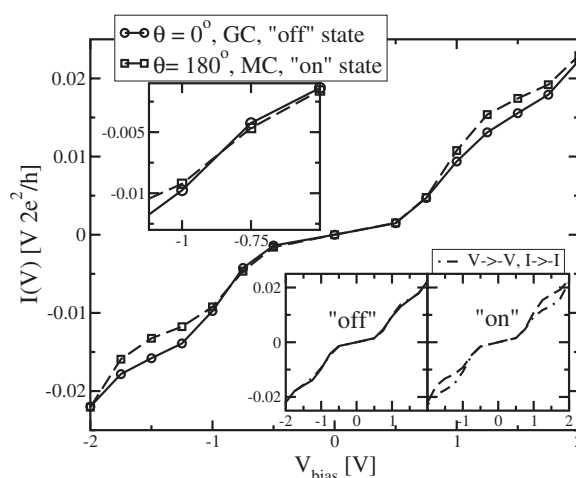


Figure 6. Current voltage trace for the BPDN-DT molecule at $\Phi \approx 70^\circ$ for the ground-state configuration, GC (\circ , solid line), as well as for the metastable one, MC (\square , dashed line). Inset upper left: blow-up of main plot near small negative V_{bias} . Inset lower right: behavior of I - V curves under the transformation $V_{\text{bias}} \rightarrow -V_{\text{bias}}$, $I \rightarrow -I$, dashed-dotted line (left "off", right "on").

3. Absence of Polarons

In order to investigate the possibility of polaron formation, we have considered the core region of the molecule only, replacing the Au_{14} cluster by a H atom. We compared the electronic structure for the uncharged ($Q = 0$) and the charged species ($Q = \pm 1$ in units of the electron charge $|e|$). Energies for the highest occupied (lowest unoccupied) molecular level, HOMO (LUMO), are given in Figure 3. We first discuss the molecule in the gas phase (free molecule). The data indicate that the LUMO of the positively charged ion ($Q = +1$) has energy, $E_{\text{LUMO}}(Q = +1)$, of approximately -8.1 eV . Upon approaching a metal surface, $E_{\text{LUMO}}(Q = +1)$ will increase due to the interaction with the image charge. Assuming that the excess charge distribution is arranged about the center of the molecule with an extension much smaller than the molecule length, one can give an estimate of the energy change by employing an image charge analysis. We obtained $E_{\text{LUMO}}(Q = +1) \approx -7.2\text{ eV}$ for the LUMO after screening. Since it is certain that the workfunction of any uncharged Au surface is above 6 eV and below 5 eV ,^[31] one can conclude that the positively charged ion will be neutralized as soon as it makes contact with a Au surface. By a completely analogous argument for the HOMO of the anion (Figure 3), we deduce that also the molecule with $Q = -1$ is unstable near a Au surface.

All calculations have been performed with a fully relaxed molecular structure; the charged molecule undergoes a conformational change, which mostly affects the NO_2 groups. However, our calculations do not give any indication that a geometrical deformation could stabilize the ion in the vicinity of the electrodes (Figure 3). More precisely, the energy change of the anion's HOMO (cation's LUMO) upon structure relaxation is not sufficient in order to induce a level crossing with the Fermi energy. This implies that the contacted BPDN molecule does not exhibit a polaron inside a trivial vacuum bounded by

the two electrode plates. This is the case in the break-junction experiments.^[20,21] Our conclusion does not necessarily apply to experiments in an electrochemical environment^[23] if this has a sufficiently large dielectric response.

4. Rotations and Bistability

After dismissing charge degrees of freedom as a likely origin for bistability, we now turn our attention to mechanisms related to charge-neutral conformational changes. Since the control molecule (Figure 1) did not show hysteresis,^[19,21] bistability should involve a (charge-neutral) conformational modification of the BPDN functional unit. An important second requirement is that an external electric field (realized via V_{bias}) must be able to address the putative degree of freedom. Since the monopole moment of the functional unit remains zero, it should be the force on its dipole moment, p_0 , generated by the NO_2 groups that pushes one configuration into the other and back. According to our calculations (employing BP functional) $p_0 \approx 3.0$ Debye. Unlike BPDN-DT, the reference molecule (BP-DT) enjoys the inversion symmetry and, therefore, has a vanishing intrinsic dipole moment. We take this as an explanation for why its I - V does not exhibit hysteretic behavior.

By this reasoning, one is led to look for rotations that take either the entire molecule or at least its BPDN unit over from a stable ground-state configuration (GC, “off”) to another (meta)stable one (MC, “on”). Any such rotation corresponds to a path in the atomic configuration space of the (extended) molecule. Apart from bistability, the optimal path has to satisfy a number of constraints, as follows, in order to be a viable candidate for realizing a molecular switch. i) The energy barrier between GC and MC, ΔE^* , should exceed temperature ($\Delta E^* \gg T$) to avoid uncontrolled thermal switching. ii) In external fields the optimal path should have a continuous deformation so that GC at forward bias and MC at reverse bias become unstable in the sense that $\Delta E^* \lesssim T$. The instability should be reachable at switching voltages, V_{on} , still tolerable for the molecular junction (in experiments $V_{\text{on}} \approx 1$ V). iii) GC and MC should have two I - V curves, I_{on} and I_{off} , which can be discriminated from each other.

Given typical switching voltages $V_{\text{on}} \approx 1$ V, one can estimate the energy barrier ΔE^* separating two states at zero bias. Assuming that the molecule (length $d \approx 25$ Å) forms an angle $\approx 45^\circ$ with the bias electric field, we have $E_{\text{on}} \approx \sqrt{2}V_{\text{on}}/d$. Once a dipole, p_0 , is flipped in the bias field, the system’s energy gain is $\Delta E_{\text{dipole}} \approx 2\rho_0 E_{\text{on}}/\sqrt{2}$, which should be of order ΔE^* if the energy mismatch between GC and MC is small compared to ΔE^* . Using $p_0 \approx 3$ Debye, one arrives to an estimate of $\Delta E^* \approx \Delta_{\text{dipole}}$ at 50 meV.

After an extensive search, we have found a family of paths best described as a consecutive one parameter (angle θ) rotation about two axes (Figure 4). The family parameter is the (average) angle, Φ , that is formed between the longitudinal axis of the molecular wire and the (hypothetical) surface normal of the electrode. Consider a variation of ground state energy of the system, $\Delta E_{\text{tot}}(\theta)$, with rotation angle θ . As may be inferred from Figure 5 (trace 0 V), the example path with $\Phi \approx 70^\circ$ satisfies condition (i) since the barrier between GC ($\theta = 0$) and MC

($\theta \approx \pi$) is $\Delta E^* \approx \Delta E_{\text{tot}}(\pi/2) \approx 100 \text{ meV} \approx 1160 \text{ K}$, which is in rough agreement with the above estimate. (Notice that the double axis rotation is crucial to obtain consistent energies. Unbalanced single rotations, for example about the S–S axis or the C–C axis near the functional unit, give much higher barriers, (≈ 200 meV) and thus are ruled out.) Furthermore, the evolution of the traces depicted in Figure 5 under the applied homogeneous electric field, E_{h} , shows that for a path with $\Phi \approx 70^\circ$ condition (ii) is also met: the value of E_{h} at which either GC or MC becomes unstable corresponds to an effective voltage $|V_{\text{on}}| \approx 2$ –4 V. Finally, we can show that condition (iii) is also fulfilled. To this end we have determined the I - V curves for the situations GC and MC, again at $\Phi \approx 70^\circ$, with our homemade transport package employing the non-equilibrium Green’s function method.^[32]

5. I - V Characteristics

The theoretical I - V curves (Figure 6) clearly display two different I - V traces that allow reading of the state (“on” or “off”) of the molecular piece. They exhibit the following key feature. a) A step-like increase in the current is observed (near 1 V). It is mainly due to the molecular orbital HOMO entering the voltage window. b) Under the transformation

$$\mathbf{I}: V_{\text{bias}} \rightarrow -V_{\text{bias}}, I \rightarrow -I \quad (1)$$

both I - V s are nearly invariant (Figure 6, insets). Equation (1) implies that dI/dV is an even function of V_{bias} . Generally speaking, \mathbf{I} invariance is an exact property of non-interacting (i.e., non-polarizable) electron systems.^[33] In interacting systems, charge localized on the molecule is redistributed as a response to V_{bias} . The polarization produces a change in the effective potential that feeds back into the current carrying orbitals, thus giving rise to second order effects, V_{bias}^2 , on the current. Details of the redistribution depend strongly on contacts and the orientation of the molecule in the bias-induced E -field (in particular its sign). In the present case the molecular junction has an approximate inversion symmetry (Figure 4) and therefore violation of \mathbf{I} is weak. c) It is important for understanding the theoretical I - V to notice that symmetry violation is stronger with “on” than with the “off” trace (Figure 6, inset), so that $I_{\text{on}} > I_{\text{off}}$ at positive V_{bias} but $|I_{\text{on}}| < |I_{\text{off}}|$ at sufficiently large reverse biases $|V_{\text{bias}}| > V_{\text{c}}$ (the dashed trace in Figure 6 is always above the black one). For the θ rotations (Figure 4), the difference relates to a slightly modified contact geometry. d) The contact difference between “on” and “off” states also manifests itself in the zero bias conductance. According to our calculations $G_{\text{off}} = 0.0016$ and $G_{\text{on}} = 0.00175$, so $G_{\text{off}} \lesssim G_{\text{on}}$. Together with (c), the inequality implies that there must be an intersection of the I - V s at a voltage V_{c} , which is a detail observed in our data (Figure 6, upper inset).

6. θ -Invariance of Φ -junctions and I - V

For a more general class of molecular Φ junctions, which do not share the (approximate) symmetries of the extended molecule (Figure 4) \mathbf{I} -invariance can be strongly broken if

polarization effects become large. In this case the hysteretic features of the I - V will be even more pronounced. Indeed, there is an intrinsic residual symmetry of any Φ junction,

$$I_{\text{on}}(V_{\text{bias}}) = -I_{\text{off}}(-V_{\text{bias}}), \quad (2)$$

which in reality will be violated but only due to contacts. If the impact of contacts is not too strong, then the approximate validity of Equation (2) ensures that the junction's I - V curves closely resemble the switching characteristic of Figure 6 (main plot) in the sense that there is a well-defined upper ("on") and a lower ("off") curve.

7. Discussion

The theoretical I - V (Figure 6) shares all essential qualitative features with the experimental result.^[21] For three reasons, a detailed quantitative comparison of absolute values for currents and the characteristic voltages, V_c and V_{on} , appears quite difficult. 1) Our theoretical analysis implies that the angle Φ determines the switching voltage, V_{on} , since it controls the effective force ($\approx \sin \Phi$) that acts on the intrinsic BPDN dipole moment facilitating the molecular rotation. Since details of the atomic conformation of the molecular junction realized in experiments are not known, Φ remains largely unspecified. In fact, our atomistic modeling of the contact (Figure 2), can be only a crude caricature of experimental reality and therefore parameters like Φ are not necessarily very well defined. In addition, their statistics may fluctuate between different experiments.^[19,20,21] 2) Another uncertainty relates to the fact that in experiments the molecule may not be in a fully relaxed conformation. Our preliminary calculations show that depending on whether or not molecular geometries are relaxed, the $E_{\text{tot}}(\theta)$ traces depicted in Figure 5 vary, if only in a quantitative way. Moreover, our switching path, (Figure 4), is a particularly simple, one-parameter species and there is no reason to expect that it is already optimal. Rather, paths realized in experiments will most likely be somewhat different, that is, some (smooth) deviations of it. 3) It is a well-known fact that due to the local approximations in the exchange correlation functionals (XC), DFT calculations do not usually give precise quantitative results for conductances^[32] or molecular polarizabilities.^[34] For this reason, our theoretical results have an intrinsic quantitative uncertainty.

We believe, that in view of points (1–3) it is not surprising that our estimate for the switching value $V_{\text{on}} \approx 2$ – 4 V does not very precisely reproduce the experimental result of ≈ 1 V.^[19,21]

8. Predictions

We close with offering two qualitative predictions that follow from our theoretical analysis. p1) The "easy axis" rotational degree of freedom of BPDN around the carbon triple bonds (Figure 1) is crucial for θ rotations. If easy rotation is blocked, for example, by molecular design, then the rotational barriers become much higher, switching is more difficult, and hysteresis should be suppressed. p2) The switching voltage, V_{on} , can be modified by dressing the BP unit (Figure 1) with other redox groups, for example carboxyl groups, instead of NO_2 . We

expect that the switching voltage decreases when the intrinsic dipole moment of the BP complex becomes larger. (Here, we have assumed that the change in molecular conformation, which accompanies the exchange of the redox groups, is less important.)

Summarizing, we have identified a two-axis rotation that takes a four-type molecular junction (BPDN-DT) from its ground-state conformation ("off") into a metastable one ("on"). The energy barrier for this process is larger than temperature, but can be controlled by applying a bias voltage. At sufficiently large biases, the molecule undergoes the transition from "off" to "on" and reverse, so that it can realize a molecular switch. Our theoretical analysis may explain the pronounced switching behavior observed in recent experiments.^[19,20,21]

Acknowledgements

We gratefully acknowledge helpful discussions with K. Fink, H. Fliegl, M. Mayor, M. Ruben, F. Schramm, and Th. Wandlowski. Our particular gratitude belongs to our colleagues at IBM Zurich, E. Lörtscher and H. Riel, for inspiring discussions and for generously sharing unpublished material. This work was supported by the Center of Functional Nanostructures at Karlsruhe University.

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Received: December 12, 2008
Published online: June 18, 2009