

## Direct Determination of the Energy Required to Operate a Single Molecule Switch

Ch. Loppacher,<sup>1,\*</sup> M. Guggisberg,<sup>1</sup> O. Pfeiffer,<sup>1</sup> E. Meyer,<sup>1</sup> M. Bammerlin,<sup>2</sup> R. Lüthi,<sup>2</sup> R. Schlittler,<sup>2</sup>  
J. K. Gimzewski,<sup>2,†</sup> H. Tang,<sup>3</sup> and C. Joachim<sup>3</sup>

<sup>1</sup>*Institute of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland*

<sup>2</sup>*IBM Research Division, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland*

<sup>3</sup>*CEMES/CNRS, 29, rue Jeanne Marvig, 31055-Toulouse Cedex, France*

(Received 11 October 2002; published 14 February 2003)

Using a noncontact atomic-force and scanning-tunneling microscope in ultrahigh vacuum, we have measured the switching energy of a single molecule switch based on the rotation of a di-butyl-phenyl leg in a Cu-tetra-3,5 di-tertiary-butyl-phenyl porphyrin. The mechanics and intramolecular conformation of the switched leg is controlled by the tip apex of the noncontact atomic-force microscope. The comparison between experimental and calculated force curves shows that the rotation of the leg requires an energy less than  $100 \times 10^{-21}$  J, which is 4 orders of magnitude lower than state-of-the-art transistors.

DOI: 10.1103/PhysRevLett.90.066107

PACS numbers: 82.37.Gk, 34.20.Gj, 68.37.Ps

The very low “ON-OFF” switching energy of nano-scale switches fabricated using a single molecule is often argued to present a major advantage of molecular electronics [1]. If true, this will offer a drastic reduction of the power dissipated by a molecular electronic circuit compared to the actual solid state integrated circuits. The power consumption of today’s processor chips such as the Pentium 4 is in the order of 30 W, which is already a problem for the application in notebooks where the extra power needed for heat removal drastically reduces the run time by battery. Currently, a solid state transistor can be switched with less than a femtojoule of energy. At room temperature, this is 5 orders of magnitude larger than the thermodynamic limit  $kT \log 2$  [2] and 4 orders larger than the energy required to isomerize a single molecule. The electrical characteristics of mechanical [3–6], electromechanical [7], and field-effect [8] molecular switches have recently become a topic of great interest. Using noncontact AFM/STM (atomic-force microscopy and scanning-tunneling microscopy) in ultrahigh vacuum (UHV), we report here the first direct measurement of the switching energy of a selective intramolecular rotation in a porphyrin-based molecular switch.

The single molecule switch is based on the rotation of a di-butyl-phenyl (DBP) leg of a Cu-tetra-3,5 di-tertiary-butyl-phenyl porphyrin (Cu-TBPP) [Fig. 1(a)] placed in a tunnel junction. The electronic characteristics of such a hybrid nanoswitch have been studied with STM [10]. In its “ON” state, the axis of a DBP leg was manipulated by the STM tip to be perpendicular to the copper surface. In its “OFF” state, the orientation was parallel, resulting in a low tunneling current through this leg. In this Letter, we control the state of this switch by using the tip apex of an AFM to push and therefore rotate one of the four legs of the Cu-TBPP while recording force-distance  $F(z)$  characteristics. This has permitted us to uniquely identify the forces and energies required to rotate a single (C-C)  $\sigma$  bond in the molecule.

The experiments were performed using a custom-built combined AFM/STM [11,12] which operates under UHV conditions ( $p < 10^{-10}$  mbar) at room temperature. *n*-doped silicon cantilevers were used to acquire the data in a dynamic mode. In this mode, the cantilever is excited at its resonance frequency with a constant amplitude using an oscillation feedback controller. A tunneling current  $I_t$  feedback was used for the distance regulation.

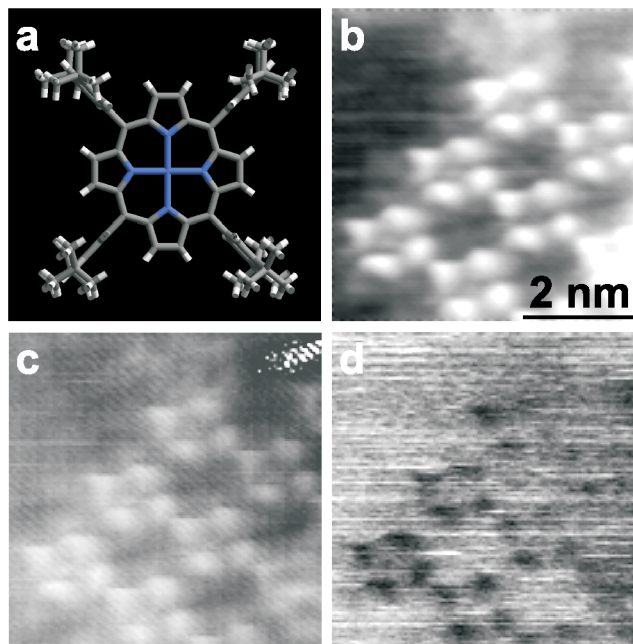


FIG. 1 (color online). (a) Chemical structure of the di-tertiary-butyl-phenyl porphyrin molecule (Cu-TBPP). (b) Topography of six Cu-TBPP molecules close to a step operating in constant mean tunneling current mode;  $I_{t,\text{mean}} = 3.8$  nA  $\rightarrow$   $I_t = 50$  nA,  $A_0 = 4.4$  nm,  $U_{\text{sample}} = 1.75$  V. (c) Frequency shift with a mean value of  $\Delta f = -320$  Hz and a corrugation of 1.8 Hz. (d)  $A_{\text{exc}}$  corresponding to the dissipated power  $P = 2.7 \times 10^{-14}$  W with a corrugation of  $\Delta P = 9.0 \times 10^{-16}$  W [9].

As the cantilever is vibrating,  $I_t$  is recorded during only a small fraction of the oscillation cycle when the tip is in tunneling proximity to the surface [13]. Consequently, the mean tunneling current  $I_{t\text{-mean}}$  was used as a feedback signal.

Approximately 0.5 monolayers of Cu-TBPP molecules were sublimated onto an atomically clean Cu(100) surface [14]. Typically, the sample displayed terraces several tens of nanometers in size, which were covered by small ordered islands and isolated molecules at the monatomic steps.

Figure 1(b) shows the topography of an island with six molecules recorded using a mean tunnel current  $I_{t\text{-mean}} = 3.8$  nA which corresponds to a value of  $I_t$  settled at the closest point of the oscillation cycle of 50 nA [13]. Although this value of  $I_t$  is high, the applied sample bias voltage of 1.75 V provides a tunneling resistance of  $R_t = 35$  M $\Omega$  which is in good agreement with conventional STM experiments where the molecules were imaged [15]. We assume that with these imaging parameters the molecules do not undergo a conformational change. Figures 1(c) and 1(d) show the simultaneously recorded frequency shift  $\Delta f$  and excitation amplitude  $A_{\text{exc}}$  while imaging at constant  $I_{t\text{-mean}}$ .  $A_{\text{exc}}$  is the amplitude provided by the oscillation feedback controller in order to keep the preset oscillation of 4.4 nm constant.  $A_{\text{exc}}$  is proportional to the dissipated power [9]. Both  $A_{\text{exc}}$  and  $\Delta f$  display a clear fine structure above individual legs which we mainly ascribe to long-range interactions between the tip apex (estimated radius of 10 nm) and the substrate [16]. When scanning above the molecules, the mean distance between the tip-apex end and the substrate increases by 0.2 nm.

Across a rectangular shaped island of  $4 \times 5$  Cu-TBPP molecules, we recorded 20 curves of frequency versus distance  $\Delta f(z)$ . Here the tip was retracted 27 nm from the surface and then reapproached until a fixed set point of  $I_{t\text{-mean}}$  was reached. This value of  $I_{t\text{-mean}}$  was chosen higher than the value used for imaging. Extreme care was taken in order to minimize lateral drift which was less than 5 nm/h. After each series of distance curves, the probed area of the surface was reimaged to be sure that the sample was undamaged and to assess for possible lateral drift of the tip in relationship to the molecular array.

Figure 2(a) shows seven approach curves (solid) recorded above the clean Cu(100) substrate and two curves (dashed) recorded above the DBP legs of a Cu-TBPP molecule. A subtraction of the two curves was used to obtain the short-range interaction  $\Delta f_{\text{chem}}$  [Fig. 2(b)] between the tip apex and a DBP leg of the molecule. The background force of the long-range interaction is eliminated by this procedure.

Several methods have been proposed [18–21] to extract the interaction forces  $F(z)$  between an oscillating tip and the sample from experimental  $\Delta f(z)$  curves where  $\Delta f(z)$

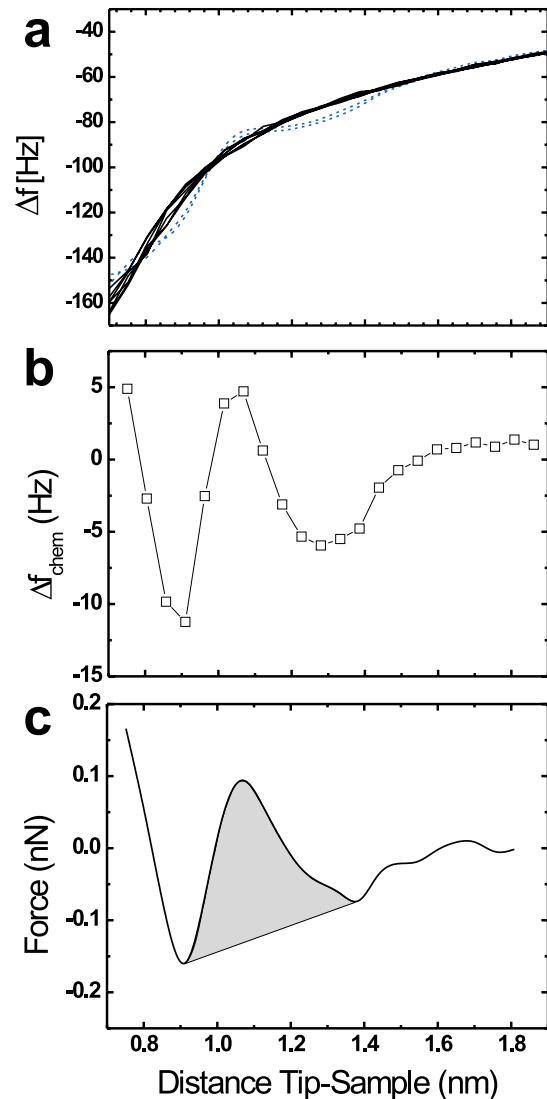


FIG. 2 (color online). (a) Frequency-distance curves recorded on the pure substrate (solid curves) and above the legs of individual molecules (dashed curves). The data contains short- and long-range interactions. (b) A subtraction of the two kinds of curves (solid and dashed) reveals the short-range interaction between the tip-apex end and the molecule leg. (c) An algorithm developed by Giessibl [17] was used to directly extract the short-range tip-molecule force  $F(z)$  out of the data in (b) whose calculated version is presented in Fig. 3(a). The grey area gives the experimental work produced by the tip apex (47 zJ).

have to be integrated over the whole oscillation cycle which was 4.4 nm in this experiment. Here we used a direct method to obtain the results shown in Fig. 2(c) using the experimental data [17]. The spring constant and resonance frequency of the cantilever are  $k = 30$  N/m and  $f = 147$  kHz, respectively. The absolute zero of the tip to surface distance was calibrated 5 Å from the onset of the tunneling current which also corresponds to the onset of short-range  $A_{\text{exc}}$ . The short-range  $F(z)$  part has two minima: one at  $z = 1.4$  nm and a

second one at  $z = 0.9$  nm [Fig. 2(c)]. An evaluation of the energy dissipated between these two minima reveals a switching energy of 47 zJ (zeptojoule,  $10^{-21}$  J). Using this value to calculate a dissipated power assuming that switching occurs in every approach of the oscillation cycle and no energy is gained back on retraction reveals a power consumption of 7 fW. This value is smaller than the intrinsic damping of the cantilever (27 fW) but, for example, about an order of magnitude larger than the difference in power dissipation obtained above different atomic sites on the Si(111)  $7 \times 7$  surface [9]. As we think that only a small fraction of the switching energy really is dissipated, we conclude that in the acquired  $A_{\text{exc}}$  signal other dissipation channels than the switching dominate.

To identify these minima, details of the rotation of the DBP leg under the tip-apex constraints and its energetics were calculated using a combined approach that accounts for both the long-range as well as the short-range interactions between the tip and surface or the tip molecule and surface. Molecular mechanics calculations (MM2) were used with a jellium description of the mesoscopic part of the AFM tip apex and of the surface [22]. We computed  $F(z)$  during a full tip-surface approach of the tip apex on one DBP leg down to the point where significant deformations of the central porphyrin occurred. The complete surface-molecule-tip mechanical junction is described atom by atom for the Cu-TBPP molecule, the Cu(100) surface (two-layer slab with a dimension of 1.8 nm by 1.8 nm embedded in a metallic jellium [22]) and the tip apex (a 100-oriented five-layer cluster supported by a 100 nm in diameter jellium sphere). For each tip-apex altitude  $z$ , the molecule geometry under the tip was optimized using MM2. In Fig. 3(a), the calculated short-range  $F(z)$  component reproduces well the two experimental minima, one (A) at  $z = 1.5$  nm and the second one (B) at  $z = 1.1$  nm, providing a high level of confidence that we can use the theoretical results to interpret the experimental force curve. The variation of the total  $F(z)$  force during a complete approach sequence is presented in the Fig. 3(a) inset together in Fig. 3(b) with a three-dimensional visualization selected Cu-TBPP conformation based on the molecular coordinates optimized to get the Fig. 3(a) curve.

The mechanical switching events in the molecule triggered by the tip-apex approach can now be described in detail. Starting with the tip apex distant from the top of a given DBP leg in a short- and long-range attractive regime, the first minimum (A) in  $F(z)$  occurs, where the DBP leg finds a new equilibrium conformation in the AFM junction but is still perpendicular to the porphyrin core. This corresponds to the ON state of the switch. A first rotation barrier is met while approaching where the tip apex starts to rotate the DBP leg. Here the total energy of the deformed molecule is larger than the first equilibrium conformation (A). Once this rotation barrier is overcome, an attractive regime is reestablished (B). The total

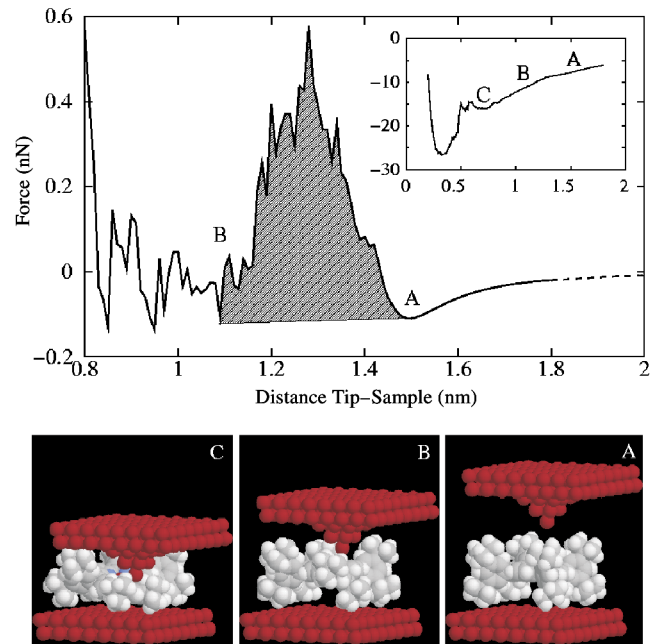


FIG. 3 (color online). (a)  $F(z)$  vertical force vs tip-sample  $z$  distance curve calculated considering only the short range interaction between the very end of the tip apex and the molecule. The grey area gives the work produced by the tip apex (83 zJ). The inset curve is the same force vs distance curve, but calculated with both a local atomic of the tip apex and a mesoscopic description of the surface and tip apex of the AFM. (b) Images presenting the conformation changes of the porphyrin molecule at different selected tip-sample distances.

energy of the molecule is then similar to the minimum (A), and this new conformation (B) is metastable on the Cu(100) surface and will be stable on a Cu(111) surface. Note that many local minima exist in (B) corresponding to small deformations of the other legs and of the central porphyrin. (B) then corresponds to the OFF state of the switch [4]. When the tip apex approaches still further, a second much higher barrier than the initial (A)-(B) barrier is encountered. Here a strong repulsive regime prevails which corresponds to deformations of the whole molecule by the tip apex. In this regime, all of the DBP legs begin to rotate to reach a third minimum (C) [inset in Fig. 3(a)]. In the calculations, continuing the approach even further causes the tip apex to interact directly with the surface, finally reaching a strong, repulsive regime where lateral molecular motion occurs.

In our experiments, the molecular switch was operated only between stages (A) and (B). The molecule is adsorbed on a metal surface which plays the role of a reservoir. Therefore, the mechanical behavior of the switch is semiclassical. The switching energy of our single molecule switch is simply obtained by calculating the work of the short-range force produced by the tip apex in passing from conformation (A) to conformation (B) on a single DBP leg. The corresponding switching energy is

83 zJ using the curve of Fig. 3(a) and 47 zJ using the Fig. 2(c) experimental curve. We note that the work expended by the long-range forces in passing from the (A) to (B) distance  $z$  is essentially the same with or without a molecule in the junction. Theoretical and experimental values are close to NMR data for the energy rotation barrier of a DBP leg in the free state of molecules in solution: 21 kcal/mol (or 145 zJ) [23]. Our calculated value is lower than the NMR experimental one because the deformation of the porphyrin core starts before the full rotation of the leg. This lowers the leg rotation barrier. The changes introduced by the tip apex on the full molecular conformation is an additional factor in our electromechanical conformational switch not accountable by NMR. Interestingly, our switching energy is also lower than the estimated 1 aJ (attojoule,  $10^{-18}$  J) switching energy of a C<sub>60</sub> single molecular electromechanical amplifier [24] and of the minimum 550 zJ required to trans-cis isomerize a single azobenzene monomer in a polyazobenzene peptide [25]. Our observation suggests a method to approach the thermodynamic limit of switching by designing “optimized” molecular switches based on internal bond rotation.

In conclusion, we have shown that the intramolecular conformation of an individual molecule can be switched through the forced rotation of a single C-C bond and its mechanics quantitatively determined using noncontact AFM. We find excellent agreement between theory and experiment on both the absolute values and the vertical position of the force minima. Comparison between experimental and calculated force curves shows that the rotation of a di-phenyl-butyl leg requires an energy less than 100 zJ, which is 4 orders of magnitude lower than state-of-the-art field effect transistors. In a machine made of an assembly of  $10^{12}$  interconnected molecular nanodevices working together at a frequency of 1 GHz, using a molecular bottom-up approach, our results suggest that the power consumption of such a full system could be less than 100 W.

Financial support from the Swiss NCCR “Nanoscale Science” program, from the Assembler Tool for Molecular Structures (ATOMS), and from the IST-FET “Bottom-up Nanomachine (BUN)” project are gratefully acknowledged.

---

\*Corresponding author.

Present address: Institute of Applied Photophysics, TU-Dresden, 01062 Dresden.

Email address: Loppacher@iapp.de

†Present address: UCLA, Department of Chemistry, 607 Charles E. Young Dr., East, Los Angeles, CA 90095.

- [1] C. Joachim, J.K. Gimzewski, and A. Aviram, *Nature (London)* **408**, 541 (2000).
- [2] R. Landauer and S. Lloyd, *Nature (London)* **400**, 720 (1999).
- [3] C. Joachim and J.K. Gimzewski, *Chem. Phys. Lett.* **265**, 353 (1997).
- [4] F. Moresco, G. Meyer, K.-H. Rieder, H. Tang, A. Gourdon, and C. Joachim, *Phys. Rev. Lett.* **86**, 672 (2001).
- [5] Z. Donhauser *et al.*, *Science* **292**, 2303 (2001).
- [6] C. Loppacher, M. Bammerlin, M. Guggisberg, E. Meyer, H.-J. Güntherodt, R. Lüthi, R. Schlittler, and J.K. Gimzewski, *Appl. Phys. A* **72**, S105 (2001).
- [7] C. Joachim, J.K. Gimzewski, R.R. Schlittler, and C. Chavy, *Phys. Rev. Lett.* **74**, 2102 (1995).
- [8] M. Di Ventra, S.T. Pantelides, and N.D. Lang, *Appl. Phys. Lett.* **76**, 3448 (2000).
- [9] C. Loppacher, R. Bennowitz, O. Pfeiffer, M. Guggisberg, M. Bammerlin, S. Schär, V. Barwich, A. Baratoff, and E. Meyer, *Phys. Rev. B* **62**, 13 674 (2000).
- [10] F. Moresco, G. Meyer, K.-H. Rieder, H. Tang, A. Gourdon, and C. Joachim, *Phys. Rev. Lett.* **87**, 088302 (2001).
- [11] G. Binnig and H. Rohrer, *Helv. Phys. Acta* **55**, 726 (1982).
- [12] G. Binnig, C. F. Quate, and C. Gerber, *Phys. Rev. Lett.* **56**, 930 (1986).
- [13] F.J. Giessibl and H. Bielefeldt, *Phys. Rev. B* **61**, 9968 (2000).
- [14] The authors thank T. Takami for providing the molecules.
- [15] J.K. Gimzewski, T.A. Jung, M.T. Cuberes, and R.R. Schlittler, *Surf. Sci.* **386**, 101 (1997).
- [16] M. Guggisberg, M. Bammerlin, C. Loppacher, O. Pfeiffer, A. Abdurixit, V. Barwich, R. Bennowitz, A. Baratoff, E. Meyer, and H.-J. Güntherodt, *Phys. Rev. B* **61**, 11 151 (2000).
- [17] F.J. Giessibl, *Appl. Phys. Lett.* **78**, 123 (2001).
- [18] F.J. Giessibl, *Phys. Rev. B* **56**, 16 010 (1997).
- [19] H. Hölscher, W. Allers, U.D. Schwarz, A. Schwarz, and R. Wiesendanger, *Phys. Rev. Lett.* **83**, 4780 (1999).
- [20] B. Gotsmann, B. Anczykowski, C. Seidel, and H. Fuchs, *Appl. Surf. Sci.* **140**, 314 (1999).
- [21] U. Dürig, *Appl. Phys. Lett.* **76**, 1203 (2000).
- [22] H. Tang, C. Joachim, and J. Devillers, *Europhys. Lett.* **30**, 289 (1996).
- [23] S. Eaton and G. Eaton, *J. Am. Chem. Soc.* **97**, 3660 (1975).
- [24] C. Joachim, J.K. Gimzewski, and H. Tang, *Phys. Rev. B* **58**, 16 407 (1998).
- [25] T. Hugel, N. Holland, A. Cattani, L. Moroder, M. Seitz, and H. Gaub, *Science* **296**, 1103 (2002).