Supplementary information for

Exploiting a single intramolecular conformational switching Ni-TPP to probe charge transfer dynamics at the nanoscale on bare Si(100)-2x1

Hatem Labidi¹, Henry Pinto², Jerzy Leszczynski² and Damien Riedel^{1*}

¹ Institut des Sciences Moléculaires d'Orsay (ISMO), CNRS, Univ Paris Sud, Université Paris-Saclay, F-91405 Orsay, France

² Interdisciplinary Center for Nanotoxicity, Department of Chemistry, Jackson State University, Jackson, Mississippi 39217, USA

List of the supplementary documents:

Figure S1: Topographical description of the M1 molecular conformation Figure S2: Tunnel current traces during the electronic excitation and statistical analysis Figure S3: DFT simulation and characterization of the M1 molecular conformation Figure S4: Evolution of the energy of the M_{2d} molecular conformation while reaching the M_{2u} conformation Figure S5: Evolution of the molecular conformation from M_{2d} to M_{2u} during the switching



Figure S1: (a) $(262 \times 264 \text{ Å}^2)$ STM topography of the bare Si(100) surface (V_s = - 2.1 V, I_t = 45 pA) after the adsorption of 0.1 ML of Nickel-tetraphenyl-porphyrin molecules. The insert in (a) indicate the gas phase molecular structure with the H atoms in white, the C atoms in gray, the N atoms in light purple and the Ni atom in blue. (b), (d) and (f) (42.3 x 42.3 Å²), (38.5 x 38.5 Å²) and (27.5 x 27.5 Å²) STM topography (V_s = - 2.0 V, I_t = 50 pA) of three M₁ molecular conformations. The red dotted line indicate where the apparent height profile presented in (c), (e) and (g) are selected. (c), (e) and (g) apparent height profile acquired across M₁ as a function of the distance along the line shown in (b), (d) and (f). In (c), an isodensity profile extracted from the simulated STM image is shown for comparison.

Figure S1 Note: A comparison between the adsorption site M_1 in the larger STM topography (Fig. S1b, S1d and S1f) and the molecular structure of the NiTPP in the gas phase indicates that the initial D_{4h} symmetry of the molecule is reduced due to its interaction with the surface¹. Three height profile measured across the molecule in the M_1 conformation along the P_{1-3} lines gives additional indications about the adsorption conformation (Fig S1c, S1e and S1g). The measured average size of the adsorbed molecule (~ 14.3 ± 0.2 Å) is consistent with the one estimated in gas phase (~ 14.5 Å, insert in Fig. 1a). Furthermore, the apparent height of the molecule is estimated to be between 1 (left aryl) and 2 Å (right aryl, measured from the silicon surface) which gives supplementary indications that the NiTPP is chemisorbed on the Si(100) surface.



Figure S2: (a) Tunnel current traces acquired during the excitation of the $M_{2u/2d}$ conformations at three different sample voltages: -2.5 V, -2.2 V and -2.0 V for an average excitation current of 2.4 x 10⁻¹⁰ A. The inserts in the lower panel recall the excitation position on M_{2d} and M_{2u} with the ensuing current levels. (b) Histogram of the excitation durations distribution measured for the $M_{2d} \rightarrow M_{2u}$ movement for a sample bias of -2.5 V. The light blue curve is the exponential fit of the bin values that allows to deduce the average excitation time $\tau_{exc.}$

Figure S2 Note: Three examples of current traces recorded during the same excitation time at three different sample voltages are shown in Fig. S2d. In these examples, the STM tip is initially located at P_A on the M_{2d} conformation (Fig. 2b of the main text). Hence, the lower current level corresponds to the case where the STM tip is on top of the M_{2d} conformation and the higher current level, when the excitation is done at P_B on M_{2u} . As one can see from these current traces, the molecule has switched many times from the M_{2d} to the M_{2u} conformations (and inversely) for the excitation voltage -2.5 V while switching only a few times at -2.2 V and just one time at -2.0 V. Assuming

that the tunnel current is a succession of independent event, our results imply that the switching process is triggered via the tunnel electrons (Fig. S2b). Note that when the NiTPP molecule switches from the M_{2d} to the M_{2u} conformations or reversibly, the global position of the molecule does not move across the surface differently to what is observed for other molecular switches^{2,3,4}. Here, only the side distribution of the charge density located inside the molecule varies before and after the switch which endorses the intramolecular character of the switching device⁵.



Figure S3: (a) to (c) top and sides views of the ball and sticks structures of the Si(100) surface with the adsorbed NiTPP molecule in the M₁ conformation after DFT optimization. The red arrows in (a) indicate the positions of the chemical bonding between the molecule and the surface. The Si atoms as well as the Si-Si bond are in yellow. The C, N, Ni and H atoms are represented as dark gray, blue, purple and white balls, respectively. The insert in (a) recall the corresponding STM topography of the calculated molecular conformation. (d) Comparison between two (19.5 x 19.5 Å²) occupied and unoccupied state STM topographies (V_s = -1.8 V and +1.8 V, I_t = 45 pA) of the NiTPP molecule in the M₁ adsorption conformation with the corresponding DFT simulated images after relaxation as shown in (a).

Figure S3 Note: In order to understand the molecular dynamics of the intramolecular switching, it is crucial to describe precisely the structural changes of the adsorbed NiTPP molecule in the M_1

conformation compared to the gas phase. For that, we have performed numerical simulations that use the density functional theory (DFT) to relax the molecular structure on the Si(100) surface. The conformation presented in Fig. S3a is the one that reproduces our experimental data for the M_1 conformation. One can see that the NiTPP molecule bonds to the Si(100) surface at five positions (red arrows in Fig. S3a). The side view plotted along the [110] direction (Fig. S3b) reveals that the position of the left aryl group is bonded to the surface via the possible loss of one hydrogen atom³. This reaction would involve that the hydrogen re-adsorbed in the neighborhood of the NiTPP molecule (green arrow in Fig. S3b). This bonding has already been observed on other systems and governs the direction of the plane of the front-side aryl group to be perpendicular to the silicon surface as shown in the front view of the molecule (Fig. S3c). In our simulations, we have considered that the ejected hydrogen atom is located nearby the reacting arvl group because of the mirror symmetry observed experimentally along the A_1 axis (Fig. S1b). However, the presence or not of this hydrogen atom on the silicon surface will only slightly affect the STM topographies and the simulated STM images. As described by the computed molecular conformations in Figs. S3b and S3c, the three other aryl groups of the NiTPP molecule appear to be detached from the surface. Two of them are located along the silicon back-bond row groove of the Si(100)-2x1 surface which prevents their chemical bonding with the silicon atoms and provide a local physisorbed character to these aryl groups. Additionally, one can notice that the aryl group located at the right side of the molecule in the side view of Fig. S3b is farther from the silicon surface than the other aryl groups as it is slightly rotated and pushed upward to avoid bonding with the surface. This explains the brighter part of the molecule on the STM topography at this location (see insert in Fig. S3a) and is coherent with the height profile shown in Fig. S1c. The variation of the calculated local density of state (LDOS) of the M₁ conformation at two different energies (E-E_f) is presented in Figure 4d and compared with the corresponding STM topographies for two different biases (occupied states at -1.8 V and unoccupied states at +1.8 V). These simulated STM images reproduce correctly the experimental measurements with a very good accuracy which demonstrates that the described molecular conformations displayed in Figs. S3a to S3c correspond to the experimental conformation M_1 . Resetting the M_{2u} or M_{2d} conformations to the initial M_1 state has been observed in some few rare cases but will not be studied here since its control is not yet understood.



Figure S4: Evolution of the energy of the M_{2d} molecular configuration as a function of the angle θ that makes the front benzene radical with the plane of the silicon surface calculated with the nudged elastic band optimization method. The definition of θ is given in the upper left insert. Three ball and sticks front views molecular structures are given for three θ values (122°, 111° and 90°). The green arrows in the right upper insert ball and stick molecular structure indicate that the two front pyrrole groups are raised up when $\theta = 90^\circ$, corresponding to a saddle point of the molecular PES.

Figure S4 Note: The computational minimization of the reaction pathways and saddle points along the adiabatic minimal energy paths connecting each initial and final state of the switching Ni-TPP molecule are performed using the climbing image NEB implemented in VASP⁶. Each step is described as a function of the angle value that makes the front aryl group with a plane parallel to the surface.



Evolution of the molecular conformation during the switching

Figure S5: Evolution of the molecular conformation from M_{2d} to M_{2u} during the switching. The switching is performed through the rotation of the front side aryl group that allow at the saddle point to lift up the two front side pyrrole groups of the molecule. The second part of the switching dynamics (steps 4 to 6) is related to the stabilization of the M_{2u} confirmation: the left aryl group is kept lifted up while the right aryl group is chemically bonded to the surface.

Cited articles:

¹ Computational modeling of metalporphyrin structures and vibrational Spectra : Porphyrin ruffling in NiTPP, Rusch, T.S.; Kozlowki, P.M. et al. *J. Phys. Chem. B* **2000**, 104, 5020.

² Mastering the molecular dynamics of a bistable molecule by single atom manipulation, Martin, M.; Lastapis, M.; Riedel, D.; *Phys. Rev. Lett.* **2006**, 97, 216103.

³ Picometer-scale electronic control of molecular dynamics inside a single molecule, Lastapis, M.; Martin, M.; Riedel, D.; Hellner, L. et al. *Science* **2005**, 308, 1000.

⁴ Remotely Controlled Isomer Selective Molecular Switching, Schendel, V.; Borca, B.; Pentegov, I.; Michnowicz, T.; Kraft,U.; Klauk, H.; Wahl, P.; Schlickum, U.; Kern, K.; Nano lett., **2016**, 16, 93.

⁵ Current-Induced Hydrogen Tautomerization and Conductance Switching of Naphthalocyanine Molecules, Liljeroth, P.; Repp, J.; Meyer, G. *Science* **2007**, 317, 1203.

⁶ A climbing image nudged elastic band method for finding saddle points and minimum energy paths, G. Henkelman and H. Jónsson, *J. Chem. Phys.* **2000**, 113, 9901-9904.