Supporting information for:

Analyzing and Tuning the Energetic

Landscape of H_2Pc Tautomerization

Jens Kügel,[*,†] Lucas Klein,[†] Markus Leisegang,[†] and Matthias Bode[†,‡]

†*Physikalisches Institut, Experimentelle Physik II, Universität Würzburg, Am Hubland,*
97074 Würzburg, Germany

‡*Wilhelm Conrad Röntgen-Center for Complex Material Systems (RCCM), Universität*
Würzburg, Am Hubland, D-97074 Würzburg, Germany

E-mail: jens.kuegel@physik.uni-wuerzburg.de;

Analysis of the switching rate

The switching rate can be determined in two different ways:[S1] either by dividing the number of switching events by the total amount of time or by binning the dwell time, fitting this data points with an exponential fit to extract the lifetime [cf. Fig. S1(a)] and taking the reciprocal value of this lifetime. The results of both methods are plotted for the vibrational analysis of the pristine H_2Pc molecule in Fig. S1(b). In the case of the first method an average switching rate is plotted, whereas the other analysis shows two separated switching rates for the stable and the metastable state. Because of the symmetry mismatch between substrate and molecule,[S2] the switching rate of the proton bound to the metastable arm is much higher as compared to the stable arm. Furthermore, the tip was always positioned at the metastable arm, which further decreases the lifetime of this state due to a bending of the energy landscape.[S3] As the switching rate of the metastable state is much higher, an average switching rate, which can be determined by the first method, essentially follows the data points of the stable arm multiplied by a factor of 2 [cf. Fig. S1(b)], due to counting both directions of the switching. Thus, the average switching rate can be used to describe the switching from the stable to the metastable position. In our analysis we used the first
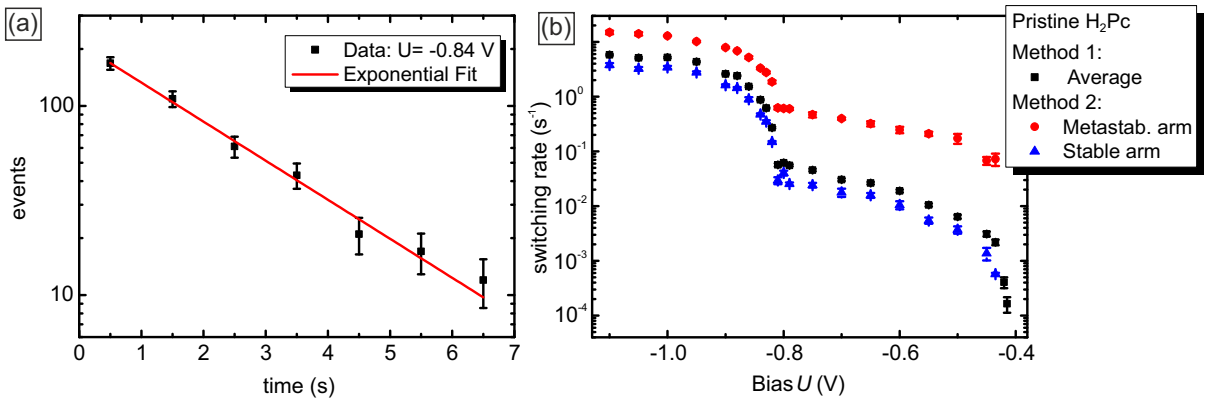
Figure S1: (a) Histogram of the dwell time to extract the lifetime for the stable arm at a bias voltage $U = -0.84$V. (b) Switching rate determined by dividing the switching events by the total amount of time (black data points) or by fitting the dwell time (blue and red data points).

method, as the statistical analysis of the dwell time can only be used for an relatively high amount of switching events. For example, at switching rates $10^{-3}\,s^{-1}$ or lower one would need to measure more than 11 days to get a suitable statistic of 1000 events, which is impracticable in a real experiment. Since the data points at low switching rates are particularly important for analyzing the threshold of the action spectroscopy, we used the first method to analyze the switching rates.

Atom manipulation and analysis of the manipulated molecules

The lateral manipulation of silver atoms was achieved in constant height mode with a bias voltage of $U = 20\,\text{mV}$ and a tunneling of about $I \approx 1.3\,\mu\text{A}$ stabilized on top of a silver atom. With the same method also the atom manipulation of the molecules was achieved: After activating the constant height mode on top of the silver atom, the tip was directly moved to the intended silver adsorption site, i.e., the center of the deprotonated H_2Pc molecule to produce HPc(Ag) or to an arm of the intact H_2Pc molecule to create H_2Pc(Ag-S) or H_2Pc(Ag-M). In the case of the HPc molecule this atom manipulation has a success rate of nearly $100\,\%$, which indicates that it is energetically favorable for the silver atom to stay at this particular position. In contrast, the success rate for H_2Pc(Ag-S/M) molecules is much lower. This is ascribed to the existence of many almost degenerate Ag adsorption sites with respect to the molecular frame.

This difference is further supported by moving the different types of manipulated molecules, as it is shown in Fig. S2. In the case of the HPc(Ag) molecule [cf. Fig. S2(a)-(c)], the silver atom always stays in the center of the molecule even if the molecule is moved many nanometers. In contrast, the silver atom in the case of H_2Pc(Ag-M) [cf. Fig. S2(d)] changes the position with respect to the molecule when the molecule is moved [cf. Fig. S2(e) and (f)], indicating a weaker bonding between atom and molecule. Therefore, the silver
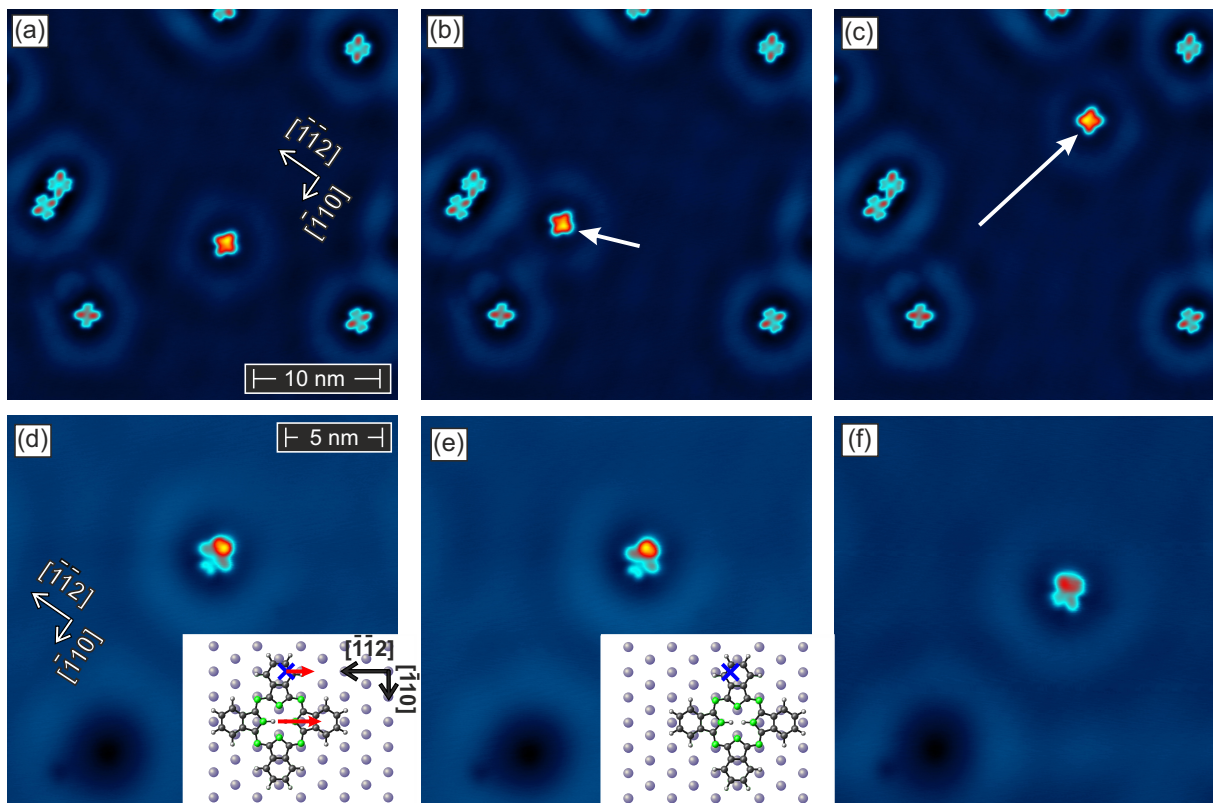
Figure S2: Movement Series of manipulated H_2Pc molecules: (a)-(c) Topography showing a HPc(Ag), which was moved (white arrow) to different locations. (d) Topography of H_2Pc(Ag-M) with a model showing a possible adsorption site of the silver atom (blue cross). This molecule was moved to the next adsorption site in the $[11\bar{2}]$-direction indicated by the red arrow in the center of the molecule. (e) Topographic image of this molecule after the movement. (f) After moving the molecule a second time, the silver atom changed again the position with respect to the molecule indicated by the different topographic appearance.

atom most likely does not sit on top of the molecule but on the silver substrate. This interpretation is further supported by the symmetry reduction observed in the topography. As the topography of the H_2Pc(Ag-M) is not axisymmetric anymore, an adsorption position on top of the molecule is unlikely, as these points (e.g. center of the benzene ring) lie on the high symmetry axis and therefore would not brake this symmetry.

The topographic height of the H_2Pc(Ag-M) is roughly three times larger than the height of a H_2Pc and almost three times larger than the height of a single silver atom, which indicates that there is a strong interaction between atom and molecule. Thus, the silver atom should be very close to the molecule. The silver atom most likely sits underneath the
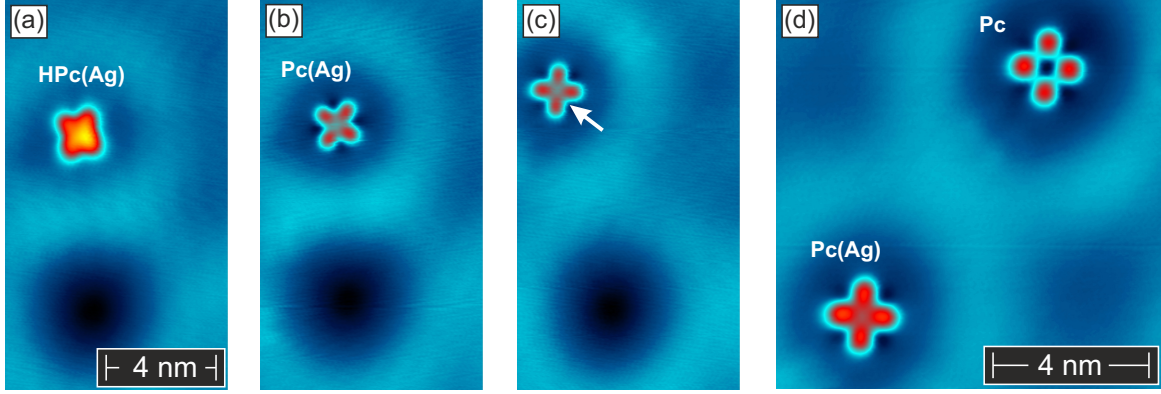
Figure S3: (a) Topography of a HPc(Ag) molecule. (b) Topography of the same molecule after the removal of the second proton. (c) This Pc(Ag) molecule can be moved (white arrow) without altering the topographic appearance. For comparison, a H_2Pc, where both protons removed, was positioned next to the Pc(Ag) molecule.

molecule, thereby bending the benzene ring upwards, which would explain the very high topographic height. To enhance the precision of the adsorption site model, the differences between Fig. S2(d) and (e) were analyzed. We find that the molecule is shifted by 0.5 nm in the $[11\bar{2}]$-direction, which agrees to a jump of the molecule to the next adsorption site indicated by the red arrow in the inset in Fig. S2(d). By this movement, a mirror image of the former molecule is created with the highest topography being located at the same absolute position. The manipulation of CuPc/Ag(100) by Li atoms[S4] shows a very similar topographic image of the molecule in the case of a Li atom sitting under the benzene ring. All of these findings are in line with the adsorption site of the silver atom marked by the blue cross in Fig. S2(d).

To further analyze the HPc(Ag) molecule, the topography of which is shown Fig. S3(a), also the second proton was removed by moving the tip to the center of the molecule and applying a bias voltage of $U = 2.9$ V. A jump in the topographic height indicates the removal of the second proton. The topography of the double-deprotonated molecule is shown in Fig. S3(b). It is also possible to move this Pc(Ag) molecule without altering its topographic shape as can be seen in Fig. S3(c). For comparison, another H_2Pc molecule was moved closer to the Pc(Ag) molecule and the inner two protons were removed. As can be seen in Fig. S3(c)

the topographic shape of both molecules is very different, indicating that the silver atom is still in the center of the molecule. Furthermore, the topography of these to molecules is in excellent agreement with the topography of AgPc and Pc molecule, which was measured by Sperl *et al.*[S5] Even though our analysis indicates, that the Ag atom is very close to the center of the molecule, we can only speculate about details of the bonding of the Ag atom. In this respect, we refer to a recent publication on a related material system, i.e., H2TPP/Au(111), for which Au–N bonds have been identified for the singly deprotonated molecule.[S6]

References

(S1) Koch, M.; Pagan, M.; Persson, M.; Gawinkowski, S.; Waluk, J.; Kumagai, T. Direct Observation of Double Hydrogen Transfer via Quantum Tunneling in a Single Porphycene Molecule on a Ag(110) Surface. *J. Am. Chem. Soc.* **2017**, *139*, 12681–12687.

(S2) Kügel, J.; Sixta, A.; Böhme, M.; Krönlein, A.; Bode, M. Breaking Degeneracy of Tautomerization-Metastability from Days to Seconds. *ACS Nano* **2016**, *10*, 11058–11065.

(S3) Kumagai, T.; Hanke, F.; Gawinkowski, S.; Sharp, J.; Kotsis, K.; Waluk, J.; Persson, M.; Grill, L. Controlling Intramolecular Hydrogen Transfer in a Porphycene Molecule with Single Atoms or Molecules Located Nearby. *Nat. Chem.* **2014**, *6*, 41–46.

(S4) Krull, C.; Robles, R.; Mugarza, A.; Gambardella, P. Site-and Orbital-Dependent Charge Donation and Spin Manipulation in Electron-Doped Metal Phthalocyanines. *Nat. Mater.* **2013**, *12*, 337–343.

(S5) Sperl, A.; Kröger, J.; Berndt, R. Controlled Metalation of a Single Adsorbed Phthalocyanine. *Angew. Chem., Int. Ed.* **2011**, *50*, 5294–5297.

(S6) Pham, V. D.; Repain, V.; Chacon, C.; Bellec, A.; Girard, Y.; Rousset, S.; Abad, E.; Dappe, Y. J.; Smogunov, A.; Lagoute, J. Tuning the Electronic and Dynamical Prop-

erties of a Molecule by Atom Trapping Chemistry. *ACS nano* **2017**, DOI: 10.1021/ac-snano.7b05235.