

Demetalation of a Single Organometallic Complex

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S Supporting Information

ABSTRACT: Single lead-phthalocyanine molecules adsorbed to ultrathin lead islands on Ag(111) are demetalized by transferring the lead atom of the inner macrocycle to the tip of a scanning tunneling microscope. Reactants and products are discriminated by their images and spectroscopic fingerprints.

Phthalocyanine (*Pc*) molecules are planar organometallic complexes with extended π -conjugation. They provide, along with their stability and availability,¹ a wide range of functions such as chemical reactivity, optoelectronic conductance, and optical absorbance, and they act as electron donors or acceptors.^{1,2} The central metal ion of *Pc* molecules has recently attracted particular interest. It has been shown that the spin state of FePc molecules on Au(111) can be controlled by ligand attachment to the Fe atom.³ Further, the reversible vertical movement of the central metal ion through the molecular plane of a *Pc* molecule has been considered as a single-molecule switch.^{4,5} Metal-free H₂Pc molecules have been metalized by exposing preadsorbed H₂Pc to metal atoms to understand the chemical reactivity of the central metal ion and its influence on the electronic structure of the molecule.^{6–10} The controlled metalation of a single H₂Pc molecule using the tip of an STM has recently been reported.¹¹

Here, we show the preparation of a demetalized *Pc* at the single-molecule level. The central metal ion of PbPc molecules adsorbed on ultrathin Pb films on Ag(111) has been transferred from the inner macrocycle to the apex of the tip of a scanning tunneling microscope (STM). The increased length of the tip and the spectroscopic fingerprints of reactants and products provide clear evidence for the demetalation process.

Demetalation of a metal-*Pc* requires breaking of chemical bonds between the central metal ion and the four N atoms of the inner macrocycle (Figure 1a). PbPc molecules are favorable candidates for this process as the molecule adopts a domed geometry (Figure 1b) with the central Pb atom weakly bonded to the *Pc*. According to density-functional calculations for the gas phase molecule using Gaussian 03 with a B3LYP/LANL2DZ basis set, the Pb ion is positively charged. On the surface the molecule may be found in two configurations, PbPc[↑] and PbPc[↓], in which the Pb atom is located above or below the molecular plane.¹²

The proposed demetalation process is schematically depicted in Figure 2a. The tip approaches the central Pb atom of PbPc[↑] at elevated negative tip voltage. At small distances the Pb cation is detached from the macrocycle and transferred to the tip apex while the remaining empty *Pc* adopts a flat geometry.

Figure 2b shows six molecules of a PbPc[↑] array on Pb on Ag(111). To demetalize a PbPc[↑] molecule at the island edge the

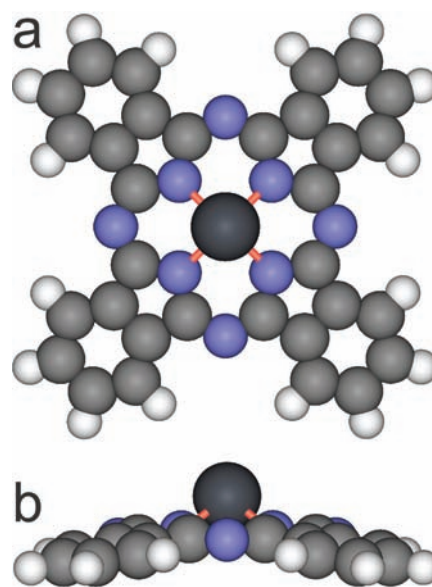


Figure 1. (a) Top and (b) side views of optimized structures of PbPc in the gas phase. Calculations were performed using Gaussian 03 with a B3LYP/LANL2DZ basis set. Demetalation of the PbPc requires breaking of the red indicated bonds of the Pb ion and the four N atoms of the inner macrocycle.

tip approached the center of the molecule marked by a black cross at a sample voltage of +2 V. During the approach the simultaneously recorded current suddenly dropped, which, as will be discussed below, signals the demetalation process. Next, the tip was retracted and an STM image of the demetalized molecule (Figure 2c) was recorded. The central protrusion of the original PbPc has been converted into a depression. The apparent height (with respect to the metal substrate) of the center after demetalation is ~ 120 pm compared to ~ 270 pm for PbPc[↑]. Simultaneously, the additional atom at the tip apex leads to a retraction of the tip above the metal surface from Figure 2b to Figure 2c of $\Delta h \approx 110$ pm.

To demonstrate the reproducibility of the demetalation process, the procedure was repeated on the PbPc[↑] molecules marked with red crosses in Figure 2c. The measured retraction of the tip was $\Delta h = 60–120$ pm per transferred Pb atom. Negative values of Δh were not observed. Demetalation is accompanied by lateral translation of the molecule (270–350 pm) from its original position (Figure 2b–d). Moreover, some rotation occurs. Demetalation of

Received: April 7, 2011

Published: June 24, 2011

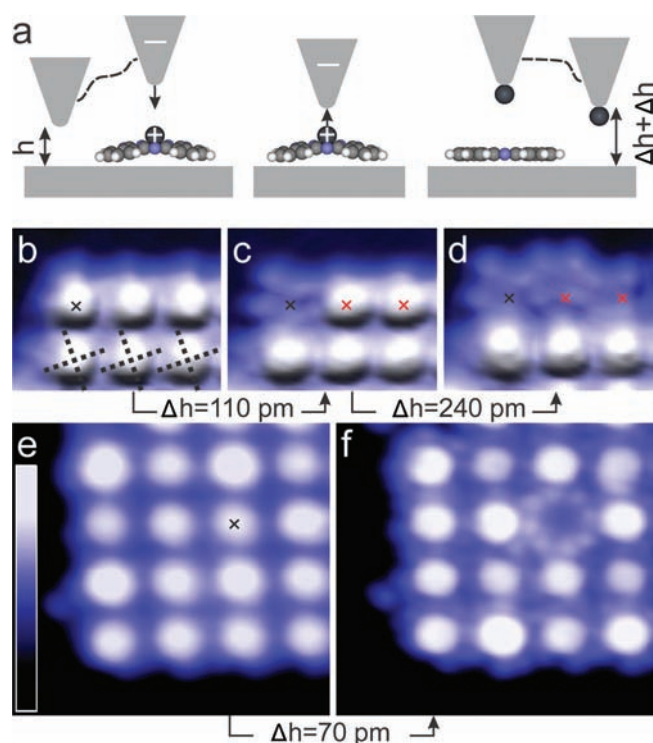


Figure 2. (a) Schematics of the demetalation of a PbPc molecule. From its initial position above the metal substrate, with a tip height h , the tip is moved to the center of PbPc, approaching the Pb ion. Next, transfer of the Pb atom to the tip apex occurs. Subsequent imaging reveals a modified molecular geometry and an increase of the tip height above the substrate, Δh . (b–d) Pseudo-three-dimensional representations of constant-current STM images of PbPc† islands on 3 ML of Pb on Ag(111) ($4.4 \text{ nm} \times 3.5 \text{ nm}$, 0.1 V , 0.1 nA) (b) before and (c) after demetalation of the molecules marked by black and red crosses. In (b) the orientation of individual molecules in the island is indicated by dashed crosses. From (b) to (c) and (c) to (d) the tip retracted by $\Delta h = 110$ pm and $\Delta h = 240$ pm, respectively. (e, f) Constant-current STM images of PbPc† islands (3 ML of Pb on Ag(111), $12.4 \text{ nm} \times 5.7 \text{ nm}$, 0.1 V , 0.1 nA) (e) prior to and (f) after demetalation of the indicated molecule. The lobes of the remaining *Pc* appear higher in STM than those of demetalized molecules at the edges of PbPc arrays. In contrast to other molecules, it exhibits clear submolecular features. The color scale applies to (b)–(f) and covers apparent heights from 0 (black) to 280 pm (white).

molecules within dense arrays is feasible, too (Figure 2e,f). STM images of such molecules exhibit submolecular resolution of the ligands, in contrast to the less feature-rich images of molecules at island edges (Figure 2c,d). Moreover, demetalized molecules appear higher (height ≈ 190 pm) within arrays than at edges. Lateral translation or rotation do not occur.

The experimental observations are consistent with the process of Figure 2a. The conversion of the central protrusion into a depression may safely be attributed to the transfer of the Pb ion to the tip apex as it leads to stepwise retraction of the tip upon each demetalation process. Demetalation of free PbPc changes the molecular geometry from shuttlecock-shaped to flat. Adsorbed to a surface, flat *Pc* is expected to require more space than PbPc.¹³ Indeed, molecules at edges laterally move and rotate upon demetalation. Within arrays, where neighboring molecules constrain lateral motion, demetalized *Pc* is apparently lifted from the substrate. The STM images indicate that the ligands of the

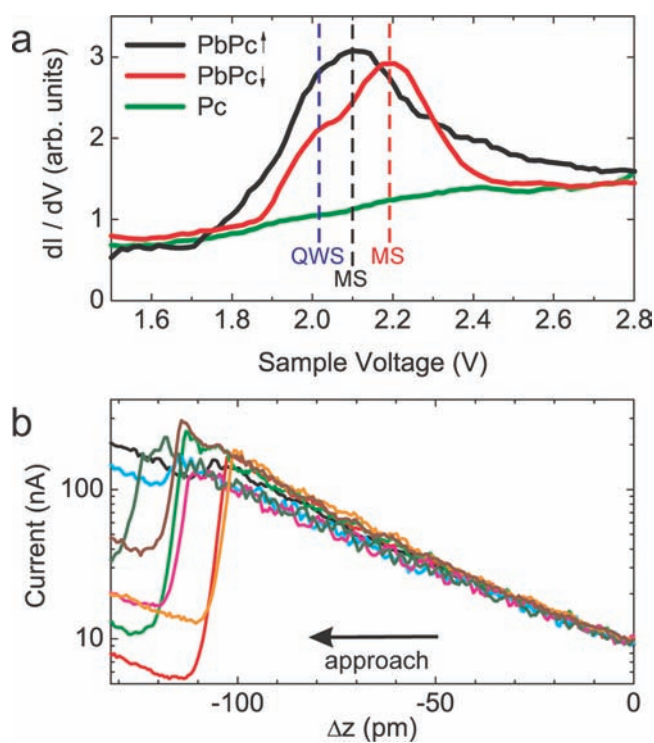


Figure 3. (a) Constant-current dI/dV spectra of PbPc† (black) and its demetalized product, *Pc* (green), in an ordered array on 3 ML of Pb. For comparison the spectrum of PbPc↓ (red) on the same Pb island is shown. An unoccupied molecular state (MS) gives rise to a broad peak in the spectra of PbPc† (~ 2.1 V) and PbPc↓ (~ 2.2 V). A quantum well state (QWS) of the Pb film appears as a weak shoulder in both spectra at ~ 2 V.¹² The spectrum of demetalized *Pc* is featureless in this range. (b) Evolution of the current with tip displacement, Δz , toward the center of PbPc† molecules. Different colors show measurements from molecules on Pb islands with thicknesses of 3 and 8 ML ($\Delta z = 0$ corresponds to the tip-molecule distance at 10 nA and 2 V).

demetalized molecule reside on ligands of adjacent molecules, which act as a spacer between the demetalized molecule and the Pb film. The submolecular resolution achieved is typical of partial electronic decoupling from the metal substrate.^{14–17} The increased apparent height compared to demetalized molecules at island edges in STM images is a supplementary indication.

In principle, the procedure described in Figure 2a may convert a PbPc† into a PbPc↓ molecule, which likewise appears with a central depression in STM images.¹² However, in the voltage range from 1.5 to 2.8 V dI/dV spectra of PbPc†, PbPc↓, and demetalized *Pc* molecules are distinctly different (Figure 3a). The spectrum of PbPc† (black) exhibits a broad feature due to an unoccupied molecular state centered at ~ 2.1 V.¹² For PbPc↓ (red) this feature is slightly shifted to ~ 2.2 V. Calculations of the frontier orbitals of a similar system, PbPc on Ag(111), show that the lowest unoccupied molecular orbital exhibits some spectral weight at the Pb site, which may be the case here, too.¹⁸ The spectrum of demetalized *Pc* (green) from Figure 2f, however, is virtually featureless. Moreover, the spectra of PbPc† and PbPc↓ exhibit an additional shoulder at ~ 2 V (blue dashed line), which is due to a quantum well state of the Pb film.¹⁹ The absence of this state from the spectrum of demetalized *Pc* is consistent with the suggested partial decoupling of the molecule from the substrate. Overall, these differences are further evidence for demetalation.

We note that demetalation of PbPc[†] did not occur at low bias voltage (0.1 V) but was successful at elevated positive sample bias. This may indicate that the demetalation involves injection of electrons into the unoccupied molecular state ~ 2.2 V along with vibrational excitation.^{20,21} Moreover, the orientation of the electric field in the junction favors transfer of the Pb ion to the tip.

The demetalation process exhibits some variability, which is most clearly seen in repeated measurements of the evolution of the current, I , with the displacement of the tip, Δz , toward the central Pb atom (Figure 3b). Starting from the tunneling range ($0 > \Delta z > -100$ pm) I increases approximately exponentially until a drastic order-of-magnitude drop occurs.²² Beyond this point, I again grows exponentially at a rate which is similar to that of the tunneling range. The tip displacement where the drop takes place and the magnitude of the current show some scatter. In all cases, however, images recorded after the current drop occurred showed a demetalized molecule whereas smaller tip displacements left the PbPc intact. The current decrease is, therefore, a clear signal of the demetalation of the molecule. While a detailed interpretation of the current drop requires atomistic modeling, the experimental data indicate the relevant factors. The transfer of the Pb atom from the molecule to the tip alone would not necessarily reduce the conductance; however it has two side effects. First, the spectroscopic signature of the molecular orbital at ~ 2 V disappears. Second, the geometry of the molecule is expected to change from domed to flat. Both factors are likely to contribute to the conductance decrease. A possibly related observation was reported from C₆₀ on Cu(110), which is irreversibly changed at elevated currents.²¹ In Figure 3b, small deviations from a purely exponential variation of I with Δz may be discerned. They most likely reflect relaxations of the junction, which result from attractive forces between the tip and the molecule.

A single organometallic complex adsorbed to a metal surface has been demetalized with the tip of a scanning tunneling microscope. Demetalation is evidenced by a combination of imaging, the transfer of the metal ion to the tip, and the spectroscopic fingerprint of the demetalized molecule. It will be interesting to use this reaction as a first step for subsequent metalation with atoms in order to tailor electronic or magnetic properties. Time-resolved measurements of the demetalation process may provide more details about breaking the chemical bonds between the central metal atom and the molecule.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental setup and procedures are included in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

Financial support by the Deutsche Forschungsgemeinschaft through SFB 677 and discussions with W. A. Hofer, University of

Liverpool, and R. Herges, Christian-Albrechts-Universität zu Kiel, are acknowledged.

■ REFERENCES

- (1) Leznoff, C. C.; Lever, A. B. P. *Phthalocyanines: Properties and Applications*; VCH: Weinheim, 1989.
- (2) Khadis, K. M.; Smith, K. M.; Guillard, R. *The Porphyrin Handbook*; Academic Press: Boston, 1999.
- (3) Isvoranu, C.; Wang, B.; Schulte, K.; Ataman, E.; Knudsen, J.; Andersen, J. N.; Bocquet, M. L.; Schnadt, J. *J. Phys.: Condens. Matter* **2010**, *22*, 472001.
- (4) Strohmaier, R.; Ludwig, C.; Petersen, J.; Gompf, B.; Eisenmenger, W. *J. Vac. Sci. Technol. B* **1996**, *14*, 1079.
- (5) Wang, Y.; Kröger, J.; Berndt, R.; Hofer, W. A. *J. Am. Chem. Soc.* **2009**, *131*, 3639.
- (6) Lukaszcyk, T.; Flechtner, K.; Merte, L. R.; Jux, N.; Maier, F.; Gottfried, J. M.; Steinrück, H.-P. *J. Phys. Chem. C* **2007**, *111*, 3090.
- (7) Flechtner, K.; Kretschmann, A.; Bradshaw, L. R.; Walz, M.-M.; Steinrück, H.-P.; Gottfried, J. M. *J. Phys. Chem. C* **2007**, *111*, 5821.
- (8) Bai, Y.; Buchner, F.; Wendahl, M. T.; Kellner, I.; Bayer, A.; Steinrück, H.-P.; Marbach, H.; Gottfried, J. M. *J. Phys. Chem. C* **2008**, *112*, 6087.
- (9) Gottfried, J. M.; Marbach, H. *Z. Phys. Chem.* **2009**, *223*, 53.
- (10) Song, C.-L.; Wang, Y.-L.; Ning, Y.-X.; Jia, J.-F.; Chen, X.; Sun, B.; Zhang, P.; Xue, Q.-K.; Ma, X. *J. Am. Chem. Soc.* **2010**, *132*, 1456.
- (11) Sperl, A.; Kröger, J.; Berndt, R. *Angew. Chem., Int. Ed.* **2011**, *50*, 5294.
- (12) Sperl, A.; Kröger, J.; Berndt, R. *J. Phys. Chem. A* **2011**, *115*, 6973.
- (13) The intermolecular distance of ~ 1.2 nm in PbPc islands is significantly smaller than that observed from other metal-phthalocyanines.^{8,10,17,23,24}
- (14) Repp, J.; Meyer, G.; Stojković, S. M.; Gourdon, A.; Joachim, C. *Phys. Rev. Lett.* **2005**, *94*, 026803.
- (15) Liljeroth, P.; Repp, J.; Meyer, G. *Science* **2007**, *317*, 1203.
- (16) Lin, X.; Nilius, N. *J. Phys. Chem. C* **2008**, *112*, 15325.
- (17) Wang, Y.; Kröger, J.; Berndt, R.; Hofer, W. *Angew. Chem., Int. Ed.* **2009**, *48*, 1261.
- (18) Baran, J. D.; Larsson, J. A.; Woolley, R. A. J.; Cong, Y.; Moriarty, P. J.; Cafolla, A. A.; Schulte, K.; Dhanak, V. R. *Phys. Rev. B* **2010**, *81*, 075413.
- (19) Becker, M.; Berndt, R. *Phys. Rev. B* **2010**, *81*, 205438.
- (20) Pecchia, A.; Romano, G.; Di Carlo, A. *Phys. Rev. B* **2007**, *75*, 035401.
- (21) Schulze, G.; Franke, K. J.; Gagliardi, A.; Romano, G.; Lin, C. S.; Rosa, A. L.; Niehus, T. A.; Frauenheim, Th.; Di Carlo, A.; Pecchia, A.; Pascual, J. I. *Phys. Rev. Lett.* **2008**, *100*, 136801.
- (22) The width of the drop appears broadened due to a low-pass filter (-3 dB at 10 kHz) at the feedback loop input.
- (23) Kröger, J.; Jensen, H.; Neél, N.; Berndt, R. *Surf. Sci.* **2007**, *601*, 4180.
- (24) Wang, Y.; Ge, X.; Manzano, C.; Kröger, J.; Berndt, R.; Hofer, W. A.; Tang, H.; Cerda, J. *J. Am. Chem. Soc.* **2009**, *131*, 10400.