Surface Chemistry

DOI: 10.1002/ange.201100950

Controlled Metalation of a Single Adsorbed Phthalocyanine**

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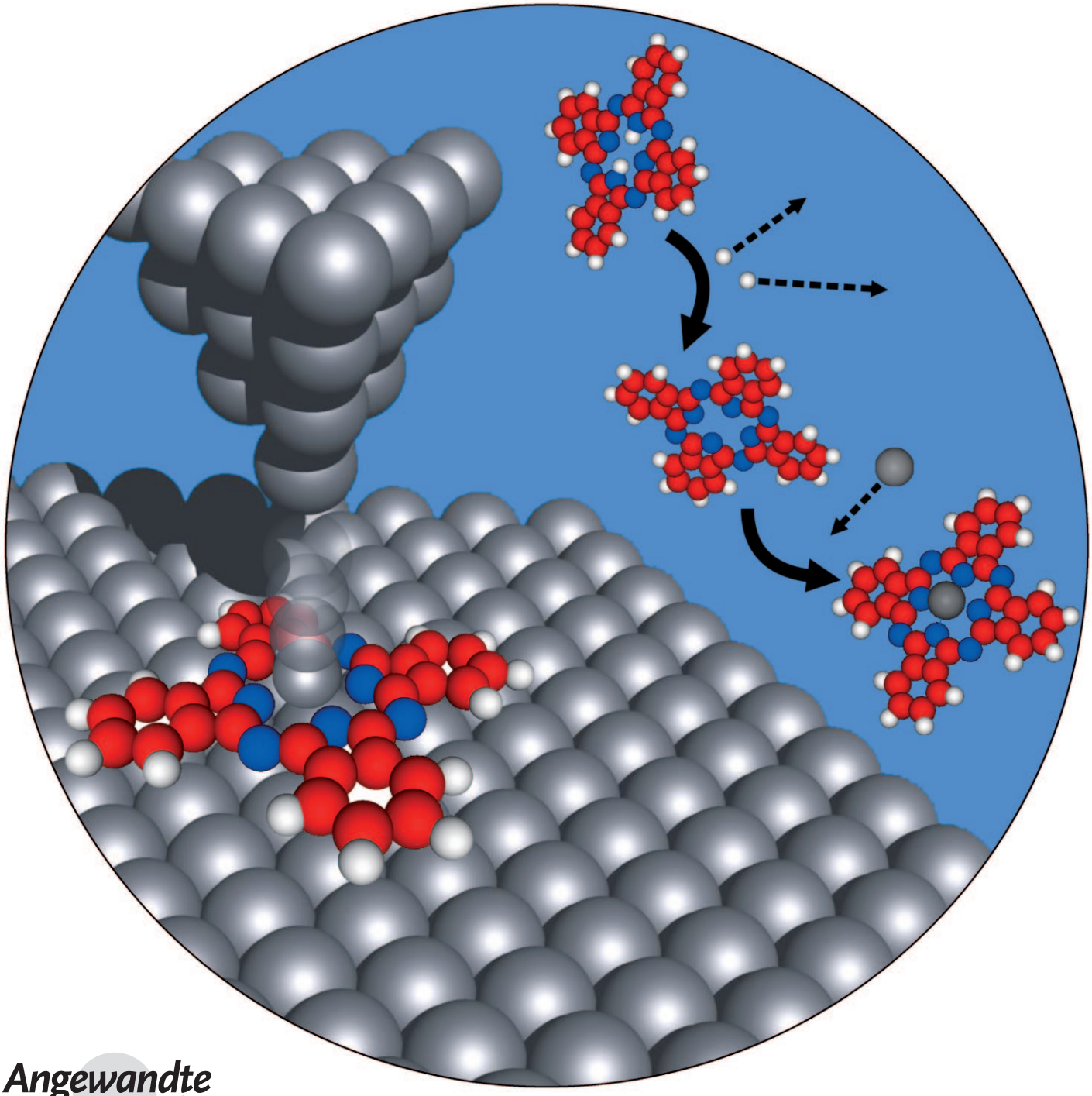

Phthalocyanine (Pc) molecules exhibit an intriguing variety of functional properties in biological and artificial systems.[1] Owing to their electronic and optical properties, they are perceived as promising building blocks for nanotechnology.[2] The phthalocyanine macrocycle can host two hydrogen atoms (H_2Pc) or a metal ion (MPc; Figure 1 a,b). Metalation of H_2Pc and porphyrins on surfaces has been achieved for molecular layers at elevated temperatures by either evaporating metal atoms onto a previously formed molecular layer[3–7] or by depositing molecules onto a substrate that had been precovered with metal atoms.[5,8] These approaches lead to a statistical distribution of MPc, as observed with scanning tunneling microscopy (STM).[4,7] Herein, we demonstrate the controlled metalation of single H_2Pc molecules to AgPc using low-temperature STM. The reaction requires several steps, namely stepwise dehydrogenation of the inner macrocycle and subsequent implantation of a silver ion. Direct metalation of H_2Pc was not observed in this type of experiment. Along with the metalation process, hydrogen tautomerization of H_2Pc and hopping of a single hydrogen in the inner macrocycle of HPc were induced by electron injection from the STM tip. After each reaction step, the electronic fingerprint of the product was determined by scanning tunneling spectroscopy (STS).

STM images of single H_2Pc molecules adsorbed on a Ag(111) surface exhibit a two-fold symmetry (Figure 1 c). The ligands which are oriented along a crystallographic $\langle 1\bar{1}0\rangle$ direction appear lower. Density functional calculations indicate that the reduced symmetry involves a saddle-shaped distortion of the molecule[9] that is similar to CoPc on Cu(111).[10] Similar reduced symmetry was observed from some other adsorbed phthalocyanines (CuPc, CoPc, and FePc on Cu(111),[9,11–14] and SnPc on Ag(111)[15,16]). Hopping of the hydrogen atoms at the pyrrolic nitrogen atoms of the inner macrocycle may be induced by positioning the tip over the center of the molecule and pulsing the sample voltage from 0.16 V above a threshold of 1.6 V (Figure 1 c–e). The changes observed in STM images cannot be due to a rotation of the molecule, as rotations to other orientations along equivalent $\langle 1\bar{1}0\rangle$ directions were never observed in repeated experiments despite the hexagonal symmetry of the surface layer. A similar tautomerization reaction has recently been reported for phthalocyanine and naphthalocyanine adsorbed on a variety of insulating films (NaCl, RbI, and Xe).[17]

A single hydrogen atom can be removed from the inner macrocycle by applying a voltage above a threshold of 3.0 V,

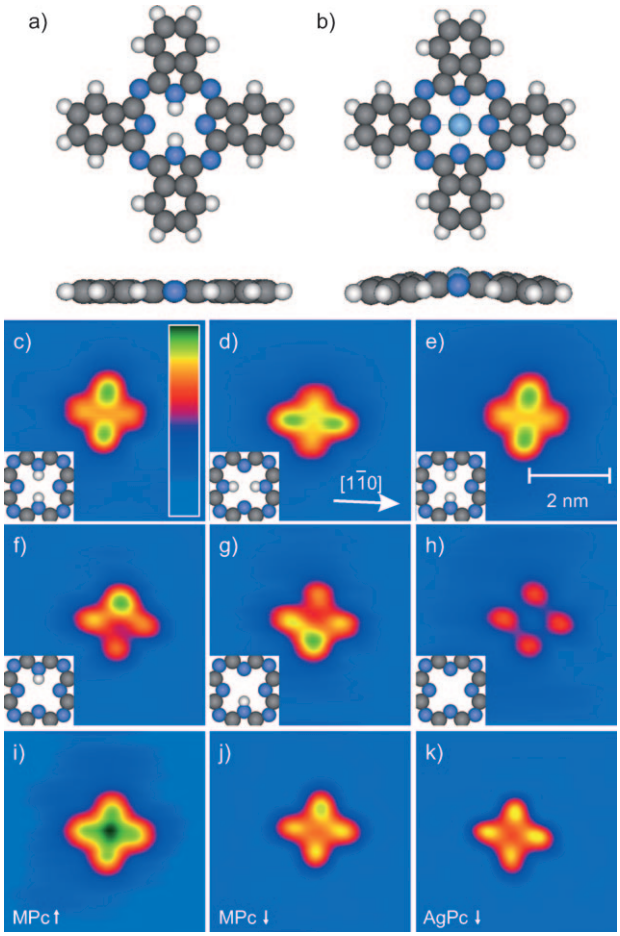

Figure 1. a,b) Orthogonal views of optimized structures of a) H_2Pc and b) AgPc in the gas phase. Calculations were performed using Gaussian 03 with the ROHF/LANL2DZ basis set. c–j) Constant-current STM images (0.1 nA, 0.1 V) of H_2Pc and derived molecules. The color scale covers apparent heights from 0 (blue) to 77 pm (green). Inferred molecular structures of the central part of the Pc molecules are shown as insets. c–e) Tautomerization of H_2Pc, which was induced by voltage pulses of 1.6 V. f,g) STM images of HPc obtained after removal of one pyrrolic hydrogen atom from H_2Pc by a voltage pulse of 3.0 V. Hopping of the remaining pyrrolic hydrogen atom was induced by voltage pulses of 2.5 V. h) Pc molecule fabricated by pulsing the voltage to 3.5 V. i) After approach of the Ag tip to the center of the Pc, MPc↑ is formed. j) A voltage pulse of 3.0 V leads to an interconversion of MPc↑ into MPc↓. By comparison with the image of AgPc on Ag(111) prepared by sublimation from a heated crucible (k), the molecule in (j) is identified as AgPc, with the Ag atom between the surface and the molecular plane (AgPc↓).

which is similar to the breaking of a C–H bond in a single acetylene molecule.[18] In STM images of dehydrogenated molecules (Figure 1 f), the apparent height of one of the lobes, which was originally higher, is reduced below the height of the low lobes oriented along $\langle 1\bar{1}0\rangle$. This effect cannot be attributed to a change of the STM tip, as the height of the other ligands is virtually not affected. It may be due to a N–Ag bond, which forms upon detaching the hydrogen atom. A related reduction of the apparent height was reported from Co and Sn phthalocyanine molecules in which the peripheral hydrogen atoms were removed. According to first principles

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[**] Financial support by the Schleswig-Holstein Fonds and the Deutsche Forschungsgemeinschaft through SFB 677 is acknowledged.

calculations, bending of the ligands towards the metal substrate and the formation of bonds occurs in those cases.[19,20]

Hopping of the remaining central hydrogen between two opposite positions was induced by applying a voltage above a threshold of 2.5 V. The resulting molecule can be imaged at voltages below the threshold for inducing hydrogen motion (Figure 1 f,g). Switching of the hydrogen atom to any of the other two positions (at ligands along $\langle 1\bar{1}0\rangle$) was not observed.

The second central hydrogen atom was removed by applying a voltage exceeding 3.5 V. In STM images of the remaining Pc (Figure 1 h), the molecular ligands appear with very similar heights (ca. 45 pm), which makes the molecule almost four-fold symmetric. This height is reduced compared to STM images of H_2Pc acquired at the same voltage (ca. 55 pm and ca. 70 pm parallel and perpendicular to $\langle 1\bar{1}0\rangle$), which reflects a modified bonding of the molecule to the surface mediated by the unsaturated nitrogen atoms.

The final step of the metalation reaction is the insertion of a metal ion into the completely dehydrogenated inner macrocycle. Previously, the transfer of single atoms from the tip to metal surfaces has been observed and attributed to strong adhesive forces.[21–24] Although the Pc molecule is adsorbed on a metal substrate, the dehydrogenated molecular center may be expected to be rather reactive towards an atom at the apex of an STM tip. Therefore, the tip was approached to the molecular center at low voltage (0.1 V). Figure 2 a displays the evolution of the current I with the displacement Δz of the tip (the direction of the tip approach is from right to left). Starting from the tunneling range, the current rises exponentially as expected. At $\Delta z \approx -30$ pm, an abrupt increase of the current from about 0.15 μA to 0.26 μA occurs, which signals the formation of a tip–molecule contact. In repeated experiments using a sample voltage $V = 0.1$ V, the conductance I/V of the single molecule contact exhibited some variability over the range 0.009···0.036 G_0, where $G_0 = 2e^2h^{-1}$ is the quantum of conductance.

For tip displacements up to about 80 pm beyond contact formation, no modifications of the molecule were observed in STM images that were subsequently recorded. Further approach of the tip to $\Delta z \approx -120$ pm results in a second abrupt increase of the current from about 0.95 μA to about 1.5 μA. Subsequent imaging in the tunneling range (Figure 1 i) reveals a drastic change of the molecular structure. The central depression of the empty inner macrocycle (Figure 1 h) has turned into a protrusion with an apparent height of about 77 pm (Figure 1 i). The STM image suggests that an atom has been transferred from the tip to form a metalated Pc (MPc).[25,26] The intermediate product molecule can be laterally moved by the tip at an elevated tunneling current ($I = 400$ nA, $V = 0.1$ V), thus indicating its stability. As will become clear below, the new molecule is most likely AgPc with the Ag atom located at the vacuum side of the molecule (AgPc↑).

The injection of electrons at elevated voltages (> 3 V) at the center of the MPc↑ leads to a molecule with a central depression (Figure 1 j; MPc↓).[27] A similar interconversion from a ↑ to ↓ configuration was reported for SnPc on Ag(111).[16] With its four-fold symmetry, the STM image of

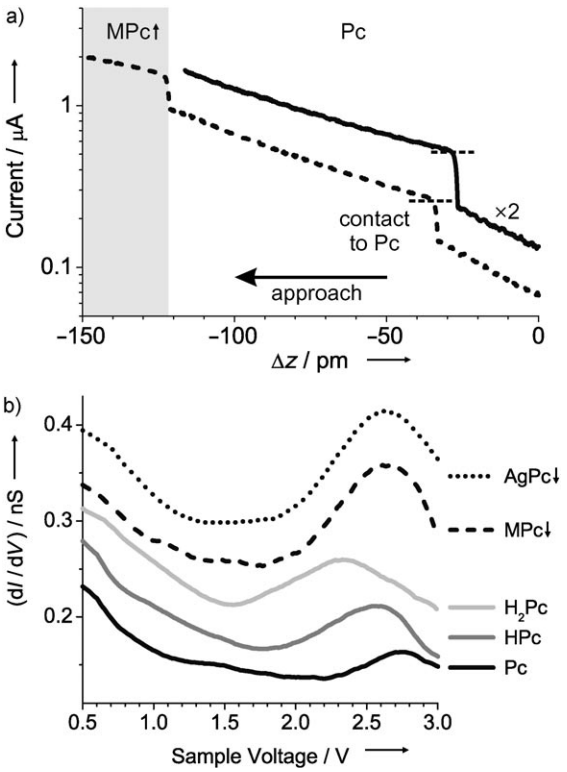

Figure 2. a) Evolution of current upon approaching (from right to left) the tip to the center of a Pc molecule with the dehydrogenated inner macrocycle. Zero displacement ($\Delta z = 0$) corresponds to the tip–molecule distance at 0.1 V and 67 nA. No irreversible changes of the molecular structure occur as long as $\Delta z > -120$ pm (solid line). At contact (indicated by horizontal dashed lines), the conductance is about 0.034 G_0. Further approach leads to a second abrupt rise of the current (dashed), signaling the transfer of an atom from the tip to the molecule (Figure 1 i). (b) Constant-current dI/dV spectra of the molecules presented in Figure 1. Spectra are vertically offset relative to Pc for clarity in 0.05 nS steps. The broad peak at about 2.5 V is attributed to the lowest unoccupied molecular orbital. While systematic differences exist between Pc (black), HPc (gray) , H_2Pc (light gray), and MPc↓ (dashed), the spectra of MPc↓ and sublimated AgPc (dotted) are identical within the experimental uncertainty.

MPc↓ is similar to STM images of Pc but can be easily discriminated by its different apparent height, namely about 60 pm for MPc↓ compared to about 45 pm for Pc. The STM image of MPc↓ is virtually identical to the image of AgPc molecules that were sublimated onto Ag(111) at ambient temperature (Figure 1 k). Sublimated AgPc molecules exclusively appear with a central depression in constant-current STM images, which is consistent with a position of the central Ag ion below the molecular plane (AgPc↓). It is therefore tempting to identify MPc↓ as AgPc↓. As a consequence, the MPc↑ configuration generated by the manipulation sequence presented above turns out to be metastable.

To further test the chemical identity of the synthesized MPc↓ molecule, spectra of dI/dV were recorded at positive sample voltages to probe its lowest unoccupied molecular orbitals close to the Fermi energy level (Figure 2 b). The fingerprint of MPc↓ (blue line) is clearly different from those of H_2Pc (light gray), HPc (gray), and Pc (black). However, it is

virtually identical to the data from sublimated AgPc (red), which further confirms the interpretation of Figure 1 i,j in terms of ↑ and ↓ configurations of AgPc. Furthermore, the spectra provide a hint to the mechanism driving the interconversion from the ↑ to the ↓ configuration. Spectra of AgPc↓ exhibit a broad unoccupied orbital centered at about 2.6 V. The threshold voltage for interconversion of about 3 V is consistent with the injection of electrons into this orbital along with coupling to vibrational degrees of freedom of the molecule. The efficiency of such processes was previously studied theoretically[28] and in contact experiments with C_{60}.[29] This type of mechanism appears to be at work in removing the second hydrogen atom from the inner macrocycle of HPc, too. Its threshold is higher than for the removal of hydrogen from H_2Pc, in agreement with the different positions of the lowest unoccupied orbital (Figure 2 b, black and gray lines).

In summary, we have presented a stepwise single-molecule synthesis of AgPc on Ag(111) from H_2Pc. One may speculate with some confidence that this experimental approach will be feasible for a variety of metal ions and may be extended to other related molecules. It will be interesting to use these possibilities to tailor arrays of such molecules and probe their mutual coupling and properties.

Experimental Section

Experiments were performed with a homemade scanning tunneling microscope operated at 7 K and in ultrahigh vacuum with a base pressure of 10^{-9} Pa. Ag(111) surfaces and chemically etched tungsten tips were cleaned by argon ion bombardment and annealing. Tips were indented into the substrate in vacuo. This treatment resulted in the tip apices being covered with silver from the substrate. H_2Pc (Figure 1 a) and AgPc molecules (Figure 1 b) were deposited from a heated tantalum crucible onto the surface at ambient temperature. To induce chemical reactions such as tautomerization or successive dehydrogenation of the inner macrocycle of H_2Pc, rectangular voltage pulses were applied to the sample for sub-second time intervals with the feedback enabled. Spectroscopy of the differential conductance dI/dV, which is related to the local density of electronic states, was performed by adding a sinusoidal voltage (20 mV_{rms}, 1.9 kHz) to the sample bias V and measuring the first harmonic of the current response with a lock-in amplifier.

Received: February 7, 2011
Published online: May 4, 2011

Keywords: metalation · phthalocyanines · scanning probe microscopy · silver · surface chemistry

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[25] An alternative explanation, namely capture of a substrate atom, appears unlikely. At the cryogenic temperature of the experiments, diffusing adatoms are not available. The extraction of surface atoms upon contact is energetically less favorable than the abstraction of an atom from the tip.[23] Moreover, the STM images of the fabricated AgPc↓ and deposited AgPc are virtually identical. This appears to be inconsistent with a substrate atom missing underneath the fabricated molecule.
[26] We monitored the tip status by comparing the apparent height of the substrate before and after the metalation procedure. In six out of eleven metalation processes, no change of the tip (defined as changes below 30 pm) was detected. In three cases, the tip length increased by 1, 0.50, and 0.50 nm. In two cases, the tip length decreased by 0.10 nm and 0.24 nm. These values cannot directly be interpreted in terms of added or removed single atoms. We attribute them to rearrangements of the atomic structure of a larger apex region.
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