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Transfer of Cl Ligands between Adsorbed Iron Tetraphenylporphyrin Molecules

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Supporting Information

ABSTRACT: Iron tetraphenylporphyrin chloride (FeTPPCl) adsorbed on a Au(111) substrate is investigated using low-temperature scanning tunneling microscopy. Cl is controllably transferred between the Fe center of a selected molecule and the tip of the microscope without disrupting the surrounding molecular pattern. Cl abstraction from FeTPPCl is triggered by removing an electron from the highest occupied molecular orbital. Density functional calculations suggest that the reaction involves a change in the oxidation state of the Fe ion.

Reduction–oxidation (redox) reactions are used in electrovoltaic cells, galvanization, and catalysis.[1] They are key chemical reactions in biological systems, a prominent example being the transport of oxygen and carbon dioxide by iron-porphyrin in hemoglobin.[2,3] A change in oxidation state of a metal porphyrin is usually associated with a chemical modification of metal atoms, namely the addition or removal of ligands. Concomitantly, a major change of the molecular electronic properties takes place.[4−8] The oxidation state may also affect the spin state as demonstrated for reactions in solution, bulk,[9,10] and ultrathin films.[11,12] To manipulate the redox state of a single organometallic complex, it is of interest to controllably coordinate/de-coordinate a ligand to/from a metal center. An important step toward reversible coordination/de-coordination was reported in ref 13, where lateral motion of CO between adjacent prophyrine molecules was induced with the tip of a scanning tunneling microscope (STM). This lateral motion of the ligand likely involves several steps of binding and unbinding. An alternative approach is to transfer a ligand to the STM tip and then redeposit at another molecule. In this case the molecule for deposition may be arbitrarily selected. Moreover, the process may offer some control of the binding site of the ligand to the molecule. While the vertical transfer of an atom or molecule between an STM tip and a crystal surface has been achieved in a number of cases,[14−23] coordination and de-coordination of a ligand to a molecule using this process has not been reported. It should be noted that electron induced bond breaking, which serves as an initial step of vertical transfer, has been observed for various adsorbed molecules.[24−31]

Here, we show controlled de-coordination and coordination of Cl from/to the Fe center of chlorinated Fe-tetraphenylporphyrin (FeTPPCl). Scanning tunneling spectroscopy of the differential conductance of the Fe center shows strong changes in electronic structure upon removal/addition of the Cl ligand. Density functional theory (DFT) calculations indicate that the Cl transfer is accompanied by a change of the oxidation state of FeTPP.

The STM experiments were performed with a home-built STM operated in ultrahigh vacuum at 5.2 K. FeTPPCl was repeatedly degassed close to its sublimation temperature (~400 °C) prior to deposition. After degassing, the molecules were deposited from a tantalum crucible onto a clean Au(111) surface kept at room temperature. The Au(111) surface and etched tungsten tips were cleaned by Ar^+ sputtering and annealing. For further preparation the tips were indented into the Au(111) surface. Separation of Cl upon heating was previously reported for a related compound, Mn(III)Cl porphyrin.[32] Therefore, a similar effect may be expected during sublimation of FeTPPCl. Differential conductance (dI/dV) spectroscopy was performed by superimposing a modulation (7 kHz, 5−10 mV_{rms}) onto the sample voltage V and measuring the first harmonic of the current response with a lock-in amplifier. All voltages indicated with STM images and spectra are with respect to the sample. Calculations were performed using DFT as implemented in the Vienna Ab inito Simulation Package (VASP).[33] To obtain the spin configurations of the central Fe in its II and III oxidation states as reported from previous theoretical[9] and experimental (crystalline powder)[3] work,[34] a simplification of Dudarev's approach of DFT+U was used.[35] Further details of the calculations may be found in Supporting Information (SI) S1.

In a monolayer of FeTPPCl on Au(111) the molecules arrange in a rectangular lattice (Figure 1a, rectangle).[36] A majority of them exhibit four lobes (two examples are indicated with flowers in Figure 1a), which is typical of metalloporphyrins. Only a quarter of the molecules are imaged as a round protrusion (circle in Figure 1a). They appear ~1 Å higher than the four-lobed molecules and are found in random positions of the rectangular lattice. We attribute only these round, high features to FeTPPCl whereas the four-lobed patterns are due to FeTPP. This interpretation is based on the Cl-transfer experiments and dI/dV spectroscopy presented below, which show that FeTPPCl can be transformed to FeTPP and vice versa. The symmetry of FeTPP indicates a flat

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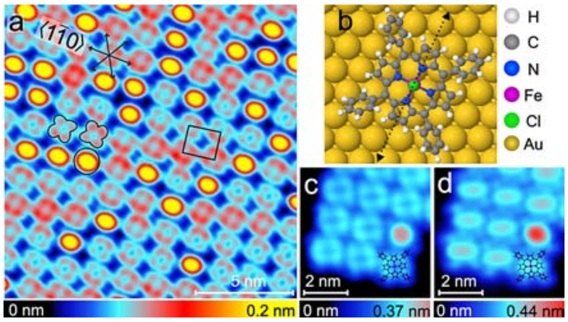

Figure 1. (a) Constant current topography (1.50 V, 100 pA) of a mixed monolayer of FeTPPCl (example indicated with a circle) and FeTPP (indicated with flowers) on a Au(111) surface. A rectangle indicates the unit cell of the adlayer. (b) Top view of the optimized geometry of FeTPPCl with Fe adsorbed on the hcp site of Au(111). A dashed line depicts one of the molecular axes which encloses an angle of 4.6° with one of the compact directions of Au(111). Constant current topography (|1.50| V, 100 pA) of edge of an island with FeTPPCl (bright protrusion) and FeTPP at positive (c) and negative (d) sample voltage.

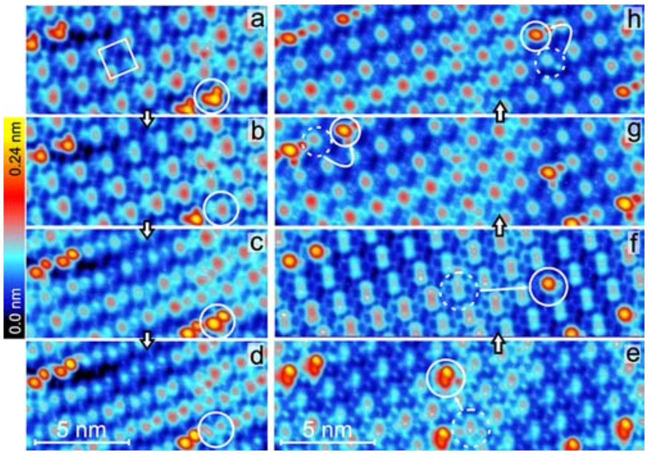

Figure 2. Series of constant-current STM images (−1.5 V, 100 pA) of a monolayer of FeTPPCl (bright) and FeTPP (dim) on Au(111). A white rectangle in (a) depicts the unit cell of adlayer. Cl removal and addition are demonstrated for the molecule indicated with a white circle. To remove the Cl ion the tip was positively biased, positioned above the center of the indicated FeTPPCl molecule, and the tunneling current was increased (1 nA for ~1 s). To transfer Cl from tip back to the molecule the tip polarity was reversed at elevated current (1 nA). Cl removed from one location (dashed circle) is attached to another location (full circle) to illustrate that the tip assisted reaction can be performed independent of the position of FeTPP within the layer (e−h). The transfer of Cl between the tip and the sample changes the tip apex and thus modifies the image contrast between consecutive images. For example, (a) reflects an asymmetric tip, and (c) is affected by a multiple tip apex.

adsorption geometry similar to earlier reports from various metal porphyrins.[37−39] Figure 1c,d shows an edge of a molecular island at positive and negative sample bias polarities, respectively. At positive bias, molecules appear as a four-lobed feature with a central depression, whereas, at negative bias, an elongated feature with a bright center is observed along with four additional small lobes in agreement with prior results.[39,40] The overlaid structure shows a tentative molecular geometry. Further details are included in SI S2. Closer inspection reveals small variations of the image contrast between different FeTPP molecules (cf. two flowers in Figure 1a), which we tentatively attribute to different adsorption sites due to the incommensurable molecular network on the Au(111) substrate.

Figure 1b shows the optimized geometry of FeTPPCl on Au(111). One of the molecular axes (dashed double headed line) is rotated by 4.6° with respect to one of the compact directions of Au(111). The calculated dihedral angle of the four phenyl rings with respect to the planar porphyrin ring is ~74° for gas phase FeTPP/FeTPPCl. According to the calculations this angle decreases to ~57° upon adsorption on Au(111). In addition the porphyrin ring becomes nonplanar and the phenyl groups are slightly pushed away from the surface. This geometry implies that the electronic coupling of the metal center with the substrate is decreased.[41]

Single-molecule chemistry is demonstrated in a sequence of STM images (Figure 2). Figure 2a shows an array of FeTPPCl and FeTPP molecules imaged at negative sample bias. Modified image contrasts compared to Figure 1d result from the transfer of Cl between the tip and the sample and are usually absent when no Cl transfer is attempted. Despite these detailed changes FeTPPCl and FeTPP may still conveniently be discerned. After recording Figure 2a, the tip (positively biased) was placed above the molecule marked with a white circle, and the current was increased to 1 nA. Over a time interval of ~1 s, a sudden drop of the current occurred signaling a change of the tunneling junction. The image recorded subsequently at low current (Figure 2b) shows that Cl was removed from the molecule. A change of the tip apex is evident from the modified submolecular contrast suggesting that Cl has been transferred to the tip apex. Next, the Cl at the tip apex is used to oxidize the Fe center again. To this end the Cl tip was placed above the encircled molecule, the current was raised to 1 nA, and the bias polarity was inverted (negative tip). This lead to redeposition of Cl at the FeTPP molecule as shown in Figure 2c. Finally, Figure 2d shows another transfer process from the same molecule, which was achieved by again reversing the bias polarity (tip positive) above the molecule. We have reproduced the reversible transfer of Cl from various, randomly chosen molecules (examples are shown in Figure 2e−h). This shows that the reaction is independent of the detailed adsorption site of FeTPP. The removal of Cl, which was monitored by the tunneling current, has a success rate close to one. Redeposition of Cl to a molecule was less reproducible (success with ~15% of the Cl tips). This is not surprising as Cl may presumably adsorb to various sites at the tip, which leads to a corresponding variability of the redeposition process.

The STM-induced reaction appears to be closely related to the well-known one-electron redox process of Fe complex molecules where chlorine removal or addition involves a change of the oxidation state of Fe between II and III.[42,43] Below additional experimental and theoretical results are presented which provide some insight into the mechanism of the Cl transfer and the concomitant changes of the electronic states.

dI/dV spectra acquired at the center of FeTPPCl and FeTPP are shown in Figure 3a. While FeTPPCl shows sharp peaks at both negative (~−0.85 V) and positive (~1.26 V) sample bias, FeTPP shows only broad resonances (~−1.1 and 1.3 eV). Moreover, FeTPP shows a small but reproducible feature close to the Fermi energy ($V = 0$ V), which may be due to a Kondo effect.

As to the Cl removal process, the data show a clear influence of the sample bias. Figure 3b shows a series of dI/dV spectra of FeTPPCl, which were taken at different vertical distances of the

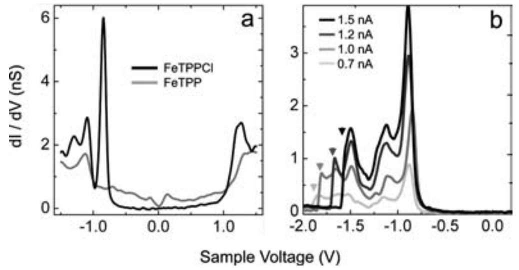

Figure 3. (a) Constant-height dI/dV spectra acquired from the center of FeTPPCl (black) and FeTPP (gray) molecules. 1.5 V, 0.5 nA were used to set the tip−sample distance before disabling the STM feedback loop. (b) dI/dV spectra acquired from the center of FeTPPCl at different set currents. A sharp drop of the differential conductance (indicated by arrows) signals the transfer of chlorine to the tip.

tip from the Fe center. The distance was controlled via the current set before opening the current feedback loop, which is indicated in Figure 3b. While the spectra reproduce the low-bias features of Figure 3a, a rapid decrease of the conductance (marked with triangles) is observed in each spectrum at elevated bias. This jump, which signals the removal of Cl, occurs at lower sample bias as the set current increases. Repeated experiments showed that the minimum voltage required to break the Cl−Fe bond is ∼0.85 V. This voltage corresponds to the onset of the positive ion resonance detected in Figure 3a and indicates that the extraction of an electron from the highest occupied molecular orbital provokes the transfer of Cl to the tip. The time required to remove Cl at a given bias is approximately inversely proportional to the current. This is consistent with a one-electron process and also indicates that the electric field alone is not decisive for breaking the Fe−Cl bond. Whether Cl is transferred as a Cl^- ion or as a neutral atom is not clear from the experimental data. Nevertheless, the directions of the transfer and the electric field are consistent with Cl being negatively charged. The associated charge of FeTPP may transfer to the metal substrate. Unfortunately, we did not succeed in obtaining a similarly reproducible influence of the tunneling parameters on the Cl addition. This might have been expected since the Cl ion may attach to various adsorption sites at the tip which leads to a corresponding variability of the addition process.

The experimental data directly show Cl transfer between the tip and the adsorbed molecules and also suggest a mechanism for the Cl removal. Nevertheless, it is interesting to further analyze the main observed spectral features using density of states (DOS) calculations. Figure 4a shows a side view of the optimized geometry of FeTPPCl adsorbed on Au(111) with Fe at the hcp site. An overview of the corresponding total DOS along with contributions from different states is displayed in Figure 4b. The experimental spectra of FeTPPCl were recorded with the tip above the molecular center, i.e., closest to the Cl and Fe atoms. We therefore use the partial DOS (pDOS) of Fe d- and Cl p-states (Figure 4c) for comparison. The experimental resonances at ∼−0.85 V and ∼1.26 V are assigned to the Cl p-state (∼−1.1 eV) and the Fe d-state (∼1.2 eV), respectively. The change of the apparent height of Cl, high protrusion at negative sample voltage and lower protrusion with a small dip at positive sample voltage (see SI S2), is consistent with the pDOS of Cl p-states below and above the Fermi energy. The pDOS of Fe d- and Cl p-states shows no major contributions around the Fermi energy, which is in agreement with the low differential conductance between

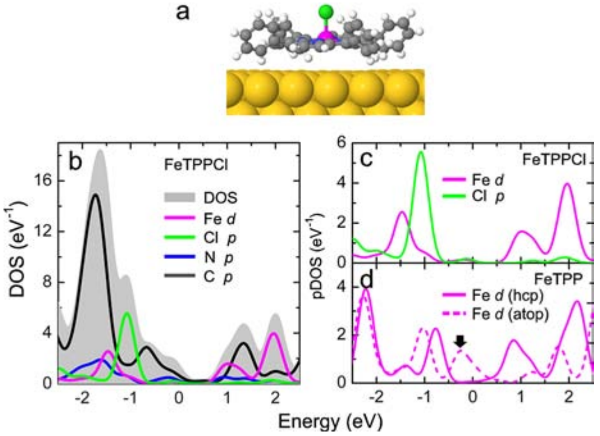

Figure 4. Side view of the optimized geometry (a) and DOS per unit cell at the molecular plane (b) of FeTPPCl with Fe adsorbed at hcp site of Au(111). The contributions of particular states are shown by solid lines. A shaded area indicates the total DOS. (c) Partial DOS from Fe d- and Cl p-states of FeTPPCl at its equilibrium position on hcp site of Au(111). (d) Partial DOS from Fe d-states of FeTPP with Fe on atop (dashed line) and hcp (full line) sites of Au(111). Thick arrowhead indicates the interface state, which is mainly of d_{z^2} nature.

the resonances at negative and positive bias. Rather limited variations are observed in the pDOS of FeTPPCl adsorbed to different sites of the substrate (hcp, atop, bridge, and fcc positions; see SI S3). This may be attributed to electronic decoupling of Fe from the metal surface due to axial Cl ligand, which was achieved previously by self-decoupling molecules[44] and multilayers on metal surfaces.[45] In the case of FeTPP, the pDOS of Fe d-states does exhibit clear differences between different sites. Molecules adsorbed at hcp (Figure 4d, solid line) or fcc sites show a depletion around the Fermi energy and clear resonances at ∼−0.9 and ∼1 V. In contrast the pDOS at atop (Figure 4d, dashed line) or bridge positions shows a state (thick arrow) close to the Fermi energy. dI/dV spectra recorded along a row of molecules (see SI S4) show differences; especially from certain molecules an additional shoulder-like feature is observed below the Fermi energy. This indicates that FeTPP molecules along a row are presumably adsorbed at different adsorption sites.

A Bader charge analysis was carried out to address the oxidation state of Fe (see SI S5 for details). In the free molecules, the calculated charges of Fe in FeTPP and FeTPPCl are $+1.10e$ and $+1.36e$, respectively. The amount of deviation from the formal charges ($+2e$ and $+3e$) is due to the delocalization of excess positive charge at the porphyrin macrocycle. This effect and its order of magnitude are characteristic of metal−ligand coordination complexes.[12,46] As excess positive charge is delocalized over the porphyrin macrocycle, we use the sums of the partial charges of Fe (q_{Fe}) and all carbon atoms ($\sum q_{\mathrm{C}}$) to estimate the total positive charge. The ratio of $q_{\mathrm{Fe}} + \sum q_{\mathrm{C}}$ between FeTPP and FeTPPCl is 0.8, which is consistent with the reported oxidation states of II in FeTPP and III in FeTPPCl.[46,47] When the molecules are adsorbed on Au(111) this ratio is increased to 0.87. This increase is attributed to charge transfer between Fe and Au(111) (see SI S5 for details). However, the ratio indicates that FeTPPCl is still in a higher oxidation state than FeTPP. Additionally the calculated spin configuration of FeTPP and FeTPPCl on Au(111) was evaluated. The density of states projected onto Fe d-states shows that the center Fe exhibits an intermediate spin configuration with $S = 3/2$ for FeTPPCl and $S = 1$ for FeTPP. A related change of the spin ($S = 1$ to $3/2$) was reported for the Fe porphyrin upon addition of a fifth ligand.[3,9]

In summary, tip-induced removal/addition of Cl from/to FeTPP on Au(111) has been demonstrated. The reaction is similar to the redox reaction of free Cl and FeTPP molecules. The redox reaction does not change the geometry of the adlayer demonstrating its stability. DFT calculations suggest that the reaction switches the oxidation state of the Fe ion and also modifies the magnetic moments of the adsorbed molecule. Similar controllable switching on different organometallic molecules with different metallic centers and different kind of ligands could be used as alternative options, thus openning a potential field in geometrically stable electronic and magnetic switch at a single molecule scale on surfaces.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

S1, details of the theoretical method and models; S2, STM images at different voltage polarity; S3, pDOS of FeTPP and FeTPPCl with Fe at atop, bridge, hcp, and fcc sites of Au(111); S4, d*I*/d*V* spectra along a row of FeTPP molecules; S5, oxidation states of FeTPP/FeTPPCl on Au(111). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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