Change of the Magnetic Coupling of a Metal−Organic Complex with the Substrate by a Stepwise Ligand Reaction

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ABSTRACT: The surface-assisted intramolecular ligand reaction of a porphyrin molecule adsorbed on Au(111) is studied by scanning tunneling microscopy and spectroscopy. The temperature-induced stepwise transformation of iron octaethylporphyrin proceeds via a concentric electrocyclic ring closure, with the final product iron tetrabenzoporphyrin being identified by its characteristic Kondo resonance. Along with the transformation of the organic ligand, changes in the magnetic fingerprint are observed, indicating an increasing coupling of the iron spin with the substrate electrons.
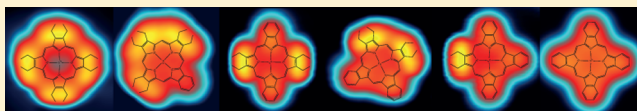
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Metal−organic complexes are promising candidates for building blocks in spintronic devices. While the transition metal atoms provide the spin, the organic ligand fulfills a manifold function: it determines the interaction with the surroundings,[1−6] provides the zero-field splitting of the spin eigenstates,[7] and allows for connecting several transition metal atoms in molecular magnets.[8] Furthermore, the spin state can be altered by the adsorption of additional ligands, thus changing the oxidation and spin state and/or the magnetic anisotropy.[9−14] The magnetism of metal−organic molecules is influenced by subtle details in the atomic-scale environment.[3,5,6] Changes of the organic ligand can drastically affect the magnetism of the complex.[1,2] Recently, *on-surface* intramolecular reactions have been observed by scanning tunneling microscopy (STM) on a single-molecule level,[15−17] and intermediate products were identified with intramolecular resolution by noncontact atomic force microscopy.[17] However, it remains unclear how such a reaction alters the magnetic interaction with the surface.

A simple system to resolve this consists of a single transition metal atom coordinated by a well-defined organic ligand, which can undergo a chemical reaction. Iron octaethylporphyrin chloride (FeOEP-Cl) is a porphin derivate with two ethyl groups attached to each pyrole unit of the porphin macrocyle. The Fe atom, coordinated in the center, holds an additional axial Cl ligand, which increases the Fe oxidation state to +3. We investigate the stepwise thermal transformation of FeOEP-Cl into tetrabenzoporphyrin (FeTBP) as tracked by scanning tunneling microscopy (STM) and spectroscopy (STS). FeOEP-Cl adsorbed on a Au(111) surface is heated to temperatures above 500 K. Annealing first leads to desorption of the axial Cl ligand and is followed by the surface-assisted electrocyclic ring closure (ECRC) of the ethyl groups of the ligands. This reaction transforms the octaethylporphyrin into a tetrabenzo-porphyrin. We can unambiguously identify the reaction product by its characteristic Kondo resonance in STS. Furthermore, we show how the stepwise modification at the periphery of the macrocycle changes the interaction of the central iron spin with the Au substrate. These results emphasize the role of the organic ligand for the interaction of a metal−organic spin with a metallic substrate.

Throughout the experiments, a home-built STM operating at a base temperature of 4.5 K under ultrahigh vacuum (UHV) conditions was used. FeOEP-Cl was evaporated at 490 K onto the clean, precooled Au(111) surface ($T_{sample} \approx$ 130 K), followed by annealing to 240 K for 3 min to enable self-assembling. Spectra of the differential conductance dI/d$V(V)$, where V is the sample bias with respect to the tip, were recorded via conventional lock-in detection (f = 733 Hz; V_{rms} = 0.86 μV, if not noted differently). A chemically etched W-tip was treated in vacuo, first by field emission at +100 V sample bias, followed by soft indentations into the clean gold surface until it showed a flat dI/d$V(V)$ spectrum on the bare gold surface. All measurements were repeated with various tips.

The FeOEP-Cl molecules self-assemble in densely packed quasi-hexagonal islands on Au(111) (Figure 1a). The herringbone reconstruction remains unperturbed upon the adsorption, suggesting that FeOEP-Cl is physisorbed rather than chemisorbed on Au(111). The molecules are imaged as 4-fold structures with a dim ring around the bright protrusion of the Cl ligand in the center of the molecule; that is, the porphyrin macrocycle adsorbs parallel to the surface, and the axial ligand points toward the vacuum. Only a few molecules
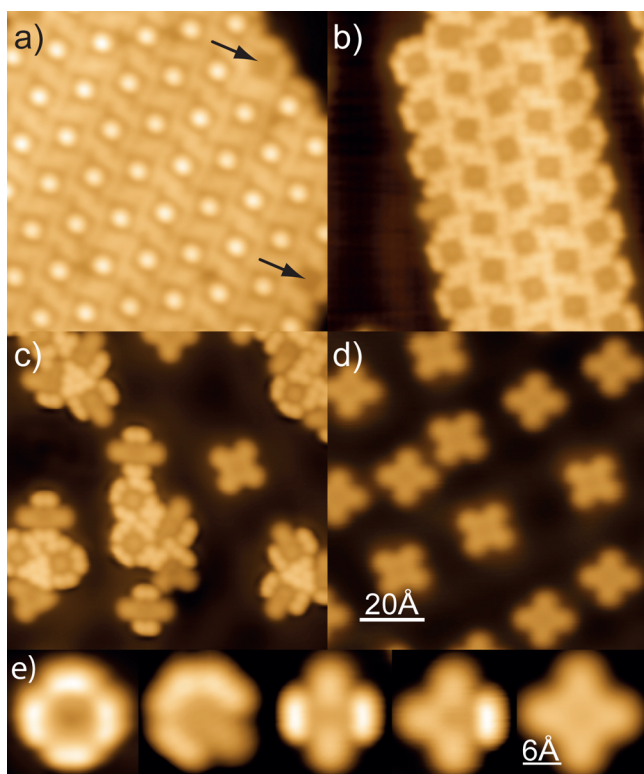
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Figure 1. STM topographs of iron porphyrins on Au(111). (a) FeOEP-Cl after deposition onto Au(111) and annealing to 240 K. (b–d) Iron porphyrins on Au(111) after annealing to 520 K, 530 K, and 550 K, respectively. Annealing alters the molecular structure as well as the self-assembling. (e) High-resolution images of different molecular species produced via annealing.

(<10%, in the following referred to as FeOEP) appear with a dim center, indicating the loss of the Cl ligand upon evaporation/deposition (indicated by arrows in Figure 1a).

Stepwise annealing of the sample induces changes of the chemical structure as visualized in the STM topographs. Figure 1b shows the sample after annealing to 520 K. The bright protrusion in the center of the molecules, that is, the Cl ligand, is now absent on all molecules, while the organic macrocycle remains unperturbed. The removal of the Cl ligand changes the nominal oxidation state of the central Fe ion from +3 to +2.[18]

Further annealing to 530 K yields different molecular structures as can be distinguished in the STM topograph (see Figure 1c). The new species are only partially arranged in islands, the unperturbed parts of the macrocycle facing each other. Finally, annealing to 550 K leads to one single, cross-shaped species all over the Au(111) surface, resembling phthalocyanine molecules as observed in ref 16. All molecules now avoid close distances (see Figure 1d).[19] Starting from the chemical structure of FeOEP, we propose the following mechanism for the formation of a benzopyrrole unit:
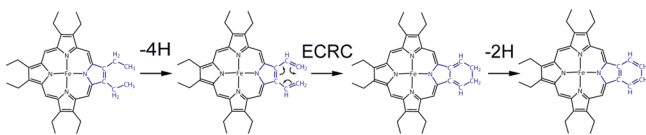
The activation of the reaction cycle happens via the dehydrogenation of two neighboring ethyl groups. The dehydrogenation might be enabled by Au adatoms, present on the gold surface at the reaction temperature similar to ref 21.

The desorption of molecular hydrogen from the surface under UHV conditions removes hydrogen out of the equilibrium reaction, blocking the back reaction. In a concerted electrocyclic ring closure (ECRC), two ethylene groups now form a six-membered carbon ring.

This intramolecular coupling is possible due to the high probability to bring the two terminal C atoms of neighboring ethyl groups in the right position for coupling and to the low ring strain for six-membered rings. Furthermore, instead of the double bond in the pyrrole ring, the nitrogen lone pair can temporarily complete the delocalized 18-electron-π-system, thereby stabilizing the intermediate species. At last, a second dehydrogenation step completes the reaction to a benzopyrrole unit. This fully reestablishes the aromaticity of the macrocycle. Depending on how often this reaction cycle takes place, one of the five different species shown in Figure 1e is observed.

To prove that the final reaction product is indeed a tetrabenzoporphyrin (TBP), that is, a porphyrin with four benzopyrrole units, we use its characteristic dI/dV spectrum around the Fermi level (E_F) (dotted line in Figure 2b). For
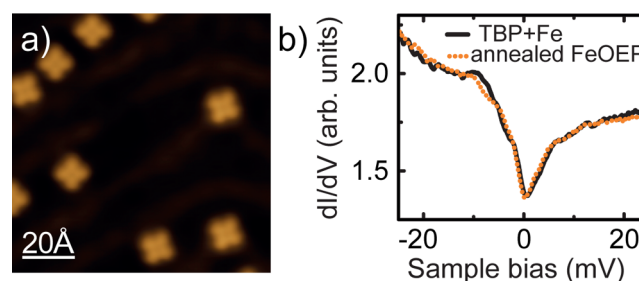

Figure 2. Metalation of H_2TBP with iron. (a) Topograph of the Au(111) surface after metalation of H_2TBP with Fe at room temperature. (b) dI/dV spectra acquired over the center of FeTBP produced via *on-surface* annealing of FeOEP (dotted line) and metalation (full line), respectively.

comparison, we co-deposit iron and free-base tetrabenzoporphyrin (H_2TBP) in a stoichiometric ratio onto Au(111) at room temperature. The *in situ* metalation[22,23] yields FeTBP (see topograph in Figure 2a).[24] We compare dI/dV spectra acquired over the center of these molecules with spectra measured over the final annealing product (see Figure 2b). An identical and characteristic dip-feature at E_F is observed for the two species, which is linked to a Kondo resonance as we will discuss below. It is an unambiguous fingerprint of FeTBP. These spectra differ significantly in width and shape from the spectra of all other species investigated (cf. Figure 3). We are now able to attribute a specific chemical structure to each of the species observed in the STM topographs (shown next to the STM topographs in Figure 3).

Although we cannot determine any absolute value for the activation barriers of the different reactions, we can draw some conclusions on the energy landscape of the reaction from the STM topographs. First, the two adjacent ethyl groups on a pyrrole are either both unperturbed or reacted toward a benzopyrrole. Only occasionally (<2%), we observe molecules with single ethyl groups modified. We conclude that the initial removal of hydrogen reduces the activation barrier for dehydrogenation at an adjacent ethyl group and is the rate-determining step of the cycle. Second, we observe all species shown in Figure 1e on the very same sample, that is, after the same annealing procedure (cf. Figure 1c). This suggests that
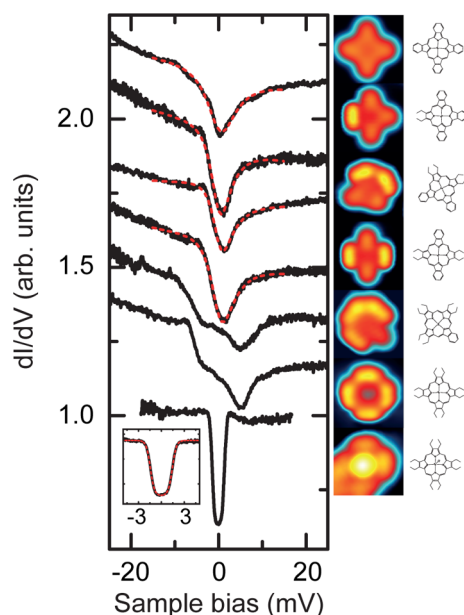
Figure 3. Tunneling spectra of iron porphyrins on Au(111). The dI/dV spectra acquired over the center of the different porphyrin species, which were produced via surface-assisted reactions, are offset for clarity. The inset shows a spectrum of FeOEP-Cl acquired at 2.1 K with V_{rms} = 0.43 μV (full black line) and its fit with symmetric step functions (dashed red line). The steps at $|eV|$ = 1.44 ± 0.05 meV are signatures of the opening of an inelastic tunneling channel. The upper four spectra are fitted with a single Fano line shape yielding a Kondo temperature of T_K = 45/29/28/34 ± 5 K (from top to bottom).

each benzopyrrole formation step has a similar activation barrier, independently of the number of previous transformations the molecule has undergone. Furthermore, a statistical analysis of the products with two benzopyrrole units yields a distribution of 62:176 for molecules with benzopyrrole units at opposing and at neighboring sites, respectively. The benzopyrrole formation is only slightly favored at neighboring sites, as a purely statistic ratio would be 1:2 (one opposite versus two neighboring sites). In conclusion, we observe only minor effects of already established benzopyrrole units on the activation barrier of further reaction cycles.

In the following, we show that the chemical modification of the organic ligand alters the magnetic properties of the molecule. Figure 3 shows the characteristic dI/dV spectra acquired over the Fe ion of each of the species.[27] At the bottom, the spectrum acquired on FeOEP-Cl is shown. A stepwise increase of the dI/dV signal occurs at $|eV|$ = 1.44 ± 0.05 meV symmetric with respect to E_F (see inset). These steps in the differential conductance are the spectroscopic manifestation of the opening of an inelastic tunneling channel at the energy of the step.[28] The low energy value together with the large change in conductance suggests inelastic spin flip excitations[29] as origin and rules out vibrational excitations here. Recently, we demonstrated that the spin state of FeOEP-Cl adsorbed on Pb(111) is S = 5/2,[30] which is also the spin state in the bulk phase.[31] The zero-field splitting due to magnetic anisotropy leads to excitations at $|eV|$ = 1.4 meV, which is related to an axial anisotropy parameter[7] D = 0.7 meV. The similar energy and intensity of the inelastic excitation observed here indicate the same spin state and similar anisotropy as for the adsorption on Pb(111).[30] Despite the

degenerate spin ground state of S_z = ±1/2, no sign of Kondo screening is observed down to 2.1 K. We assign the absence of Kondo screening to the increased Fe−surface distance compared to individual adatoms[32,33] or planar metal−organic molecules.[2,3] On the one hand, the axial Cl ligand slightly lifts the Fe atom out of the macrocycle plane.[18] On the other hand, the sp^3 hybridized ethyl ligands attached to the porphyrin core increase the porphyrin−surface distance due to steric repulsion of the hydrogen atoms at the ethyl groups and the surface Au atoms.

The removal of the Cl ligand now changes the magnetic state of the Fe ion and its manifestation in dI/dV spectroscopy. Besides a reduction of the nominal oxidation state of the Fe to +2, the Fe atom also relaxes into the molecular plane, thereby decreasing the Fe−surface distance. In the dI/dV spectrum, the low-energy excitation disappears, and rounded steps appear at $|eV|$ = 6 meV. The line shape is no longer completely symmetric to E_F. We interpret this deviation as an indication of stronger hybridization with the substrate. This leads to a competition between the magnetic anisotropy of the molecule and the Kondo scattering with the conduction electrons. This effect is indeed expected for magnetic centers with spin states S > 1/2 in an anisotropic environment, where the anisotropy energy is similar to the energy scale of the Kondo effect k_bT_K with k_b the Boltzmann constant and T_K the Kondo temperature.[34] In this case the ratio of D and T_K determines the properties of the many body ground state and its appearance in tunneling spectra.

The first transformation of two ethyl groups into one benzopyrrole does not change the overall character of the asymmetric spectrum but smears out the line shape and increases the step energy to $|eV|$ = 7 meV. This hints toward a decrease in lifetime of the spin state due to an increased scattering with the substrate's electrons and a rising T_K.

With an increasing number of benzopyrrole units, the spectrum develops into a Fano-shaped dip, as typically observed for S = 1/2 Kondo systems.[33,32] In a simplified approach, we can neglect the influence of the magnetic anisotropy. We treat the spectroscopic line shapes as Kondo resonances, with their widths reflecting the strength of the Kondo screening energy. For two and three benzopyrroles, the molecules exhibit very similar Kondo temperatures between 28 and 34 ± 5 K. For FeTBP, however, T_K increases to 45 ± 5 K. We attribute this to an increased interaction due to the absence of steric hindrance of the ethyl groups and the increased size of the aromatic system, which pulls the macrocycle closer to the surface, thus increasing the hybridization with the substrate.

In summary, we used STM and STS to track a surface-assisted intramolecular reaction of a metal−organic complex. The Kondo resonance observed in STS helps to unambiguously identify the reaction product. Furthermore, we show how the change in the structure of the organic ligand influences the magnetic properties, a result of the altered interaction with the surface. Our results highlight the importance of chemical synthesis for controlling the magnetism of single molecules on surfaces.

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