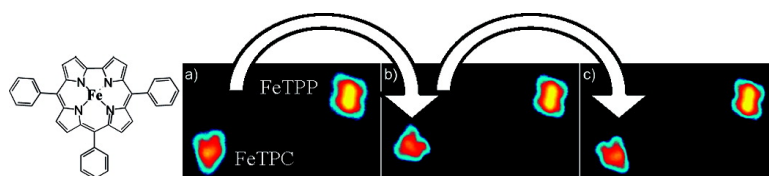## Communication

"Naked" Iron-5,10,15-triphenylcorrole on Cu(111): Observation of Chirality on a Surface and Manipulation of Multiple Conformational States by STM

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"Naked" Iron-5,10,15-triphenylcorrole on Cu(111): Observation of Chirality on a Surface and Manipulation of Multiple Conformational States by STM

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The observation and manipulation of nanoobjects on metallic surfaces by scanning tunneling microscopy (STM) have reached an amazing level of sophistication.[1] Among the different classes of molecules studied as individuals on surfaces, metalloporphyrins and phthalocyanines have proven the most successful due to their nanoscale size and peripheral as well as electronic variability.[2] Properties like mobility, magnetism, conformation, and intramolecular interaction can be imprinted on the molecular level by synthetic means and then used directly in nanoscience. In particular, molecular sensors and actuators, conformational switches, self-assembled nanostructures, and artificial aggregates have successfully been built by design from metalloporphyrins and could be investigated and modeled down to atomic resolution.[3] In addition, the high stability and easy accessibility of metalloporphyrins and phthalocyanines have contributed significantly to the success of this class of functional molecules.

A new member of the metalloporphyrinoid class, the one-carbon short corrole, has been developed in the past decade to be a very accessible, easily tunable compound with many potential applications in material science and catalysis.[4] Corroles differ from the parent porphyrin mainly by their lower inherent symmetry and the smaller cavity. In addition, the fully deprotonated macrocycle is formally trisanionic as opposed to only dianionic porphyrin ligands. The latter feature leads to more intense metal−ligand interactions in metal chelates and to interesting electronic structures. In a pilot study we have now established the suitability of the simple iron complexes of 5,10,15-triphenylcorrole (FeTPC)[5] for vapor deposition under ultrahigh vacuum conditions and were able to study individual iron triarylcorrole molecules on a Cu(111) surface by low-temperature STM.

Other than for the structurally related Fe^II porphyrins,[6] all attempts to prepare and study "naked" FeTPC molecules, i.e., without attached axial ligands, in bulk have failed. Here, we demonstrate the stabilization of FeTPC as adsorbates on a surface. Figure 1 shows STM images of isolated FeTPC molecules adsorbed on Cu(111) as sublimed from different starting materials. The appearances of the molecules vary slightly with the (unknown) tip shape, but indications for variations of molecular structures were not observed. Instead, when molecules from different starting materials were prepared in parallel on the same surface, molecules were indistinguishable. We interpret these molecules as intact "naked" FeTPC molecules. Therefore, in the following we will simply denote molecules as FeTPC molecules independent of the originating source.

Figure 2a presents a high-resolution image of an isolated FeTPC molecule on a Cu(111) surface. FeTPC appears without any
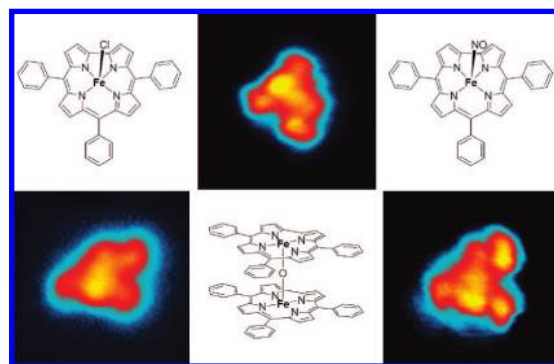
Figure 1. Iron(III) triphenylcorroles with different axial ligands employed in this study along with their appearances in STM images (all, 3 × 3 nm², −1000 mV, 100 pA).
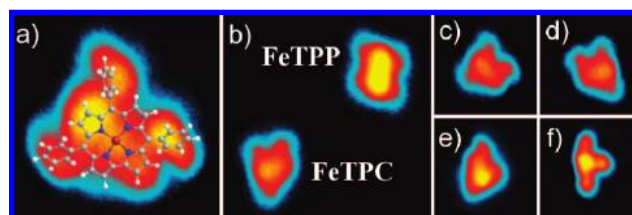

Figure 2. (a) High resolution topographic image of an individual FeTPC molecule adsorbed on a Cu(111) surface. The overlaid model is scaled to the image size and illustrates the proposed saddle conformation of the corrole macrocycle with twisted phenyl legs (2 × 2 nm², −1000 mV, 100 pA). (b) FeTPC and FeTPP molecules on Cu(111) (6 × 6 nm², −1000 mV, 300 pA). (c) After manipulation with the STM tip, the FeTPC molecule in (b) turned by 60° clockwise. (d) Another manipulation step led to a turn of only 30° and exchange of upward and downward bend axes, a change of chirality. (e and f) Manipulation of an FeTPC molecule into a mirror symmetric conformation (3 × 3 nm², −1000 mV, 300 pA).

symmetry. Each molecule has three dominant outer and elongated protrusions at its opposite ends which represent the phenyl legs and one unoccupied end which breaks mirror symmetry. For the corrole center, we find an accentuated backbone in a cigar shape with one side highlighted (see also blue/green sketch in Figure 3). This side is located between two outer protrusions. The interpretation of the adsorption geometry follows in a natural way the observed symmetry. The corrole macrocycle is deformed into a saddle conformation, and all three phenyl legs are twisted relative to the surface normal. The accentuated backbone reflects the upward bend pyrrolic units of the corrole macrocycle, whereas the other pyrrolic units show toward the surface plane. Additionally, the macrocycle is slightly tilted relative to the plane of the substrate due to the asymmetry of the phenyl legs with one side lifted by the supporting phenyl legs. This interpretation is demonstrated by the overlaid structure of FeTPC and is in line with the interpretation

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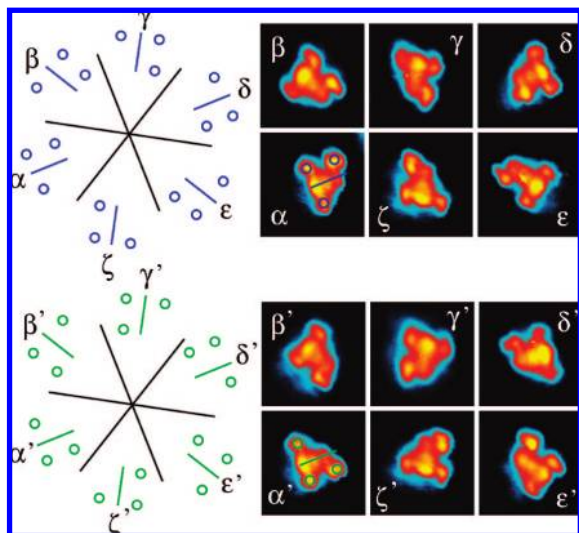
Figure 3. Representation of the different orientations and conformations of FeTPC on Cu(111) in STM images. For orientation, all 12 geometries (6 enantiomeric pairs shown in blue and green, respectively) are schematically indicated by the backbones (line) and phenyl legs (circles) along the crystalline axes of the Cu(111) substrate (black, see Figure S1) (all STM images 3×3 nm^2, -1000 mV, 100 pA).

of the adsorption of a related class of molecules, the tetra-phenyl porphyrins (TPPs).[7] Both FeTPC and FeTPP appear in similar shapes (Figure 2b) but with one phenyl leg less for FeTPC due to the exchange of the porphyrin against a corrole core.

A major consequence of the proposed bending of the macrocycle and twisting of phenyl legs is surface supported chirality.[8] The experimental manifestation is demonstrated in Figure 3. Exactly 12 different orientations and conformations are identified for the adsorption of FeTPC on Cu(111). Six different orientations of the backbone and two mirror symmetric conformations of phenyl legs for each orientation are found. The backbones of the macrocycle are perpendicular to the closed packed rows of the underlying substrate (as previously determined by atomic resolution data), and the pyrrolic units which are bent toward the substrate are parallel to one of the crystallographic axes of the substrate. Whereas the six orientations reflect the symmetry of the substrate (α, β, ...), the two different conformations reflect chirality (α vs α' etc.).

Using the STM tip as a manipulation tool,[9] it is possible to switch iron corrole molecules between different conformations and orientations. An exemplary series of manipulation steps is depicted in Figure 2b–d where we use an FeTPP molecule as a topological marker on the surface. In the starting configuration (Figure 2b), the FeTPC molecule is adsorbed in an orientation previously denoted as α. Then, the STM tip is precisely positioned above the center of the molecule and lowered toward the adsorbed molecule ($\Delta z = 0.8 \pm 0.2$ Å). Under reduction of the tip–sample distance the molecule starts interacting with the tip and rotates from orientation α by 60° into orientation β. Additional increase of tip–molecule interaction by further lowering the tip ($\Delta z = 1.0 \pm 0.2$ Å) can even induce a change of chirality, here from orientation β into δ' without any destruction of the molecule itself.

With a different method for manipulation, it is possible to switch molecules into an alternative conformation. The starting geometry of the molecule is shown in Figure 2e. Again, the tip is positioned over the center of the molecule, and now, the voltage is ramped up to $+4$ V. After manipulation, the molecule exhibits mirror symmetry

(see Figure 2f) with the phenyl groups being fully symmetric. The exact conformation stays speculative and cannot be determined by STM; however the symmetry and the apparent size of the imaged FeTPC give an indication; the corrole macrocycle is in either a planar geometry or a so-called "dome" conformation with all pyrrolic units bent downward. The reduced apparent size of FeTPC can be interpreted in the direction of the latter case with the electron cloud above the molecule lowered at the edges toward the surface. In both cases, steric interaction between hydrogen atoms of the phenyl groups and the pyrrolic units will favor a more perpendicular orientation of phenyl legs than for a saddle conformation.

In summary, the vapor deposition of iron triphenylcorrole as reported here proceeds without decomposition of the compound and provides a prerequisite for the opportunity to implement the restricted symmetry and the special molecular electronics of metallocorroles in functionalized surfaces at the nanoscale. On this basis we could demonstrate how an individual molecule with low symmetry can be switched and encoded in multiple configurations and were able to employ the feature of molecular chirality for this purpose for the first time.

Supporting Information Available: Experimental methods, atomically resolved Cu(111) surface, details on orientation and manipulation. This material is available free of charge via the Internet at http://pubs.acs.org.

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