

Supporting information for:
Transfer of Cl ligands between adsorbed
Fe-Tetraphenylporphyrin molecules

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S1: Theoretical method and models

All calculations were performed using DFT implemented in the Vienna Ab-initio Simulation Package VASP 5.2.11.^{S1} Classical plane waves pseudo-potentials generated with Projector Augmented Wave (PAW) method^{S2} were used to describe the electron-ion interaction and the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation^{S3} was applied for the exchange-correlation functionals. In order to reproduce the experimental spin state of the central Fe in both its II and III oxidation states, a simplified Dudarev's approach of DFT+U^{S4} was used as implemented in VASP. U and J represent the repulsion and exchange terms, respectively, in the effective Hubbard parameter ($U_{eff} = U + J$), which takes into account the d -electron correlation at the iron center.

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Periodic boundary conditions were used with super-cells of $1.48 \times 1.53 \times 2.75 \text{ nm}^3$ to investigate a closed packed molecular layer on Au(111). The Au(111) substrate was modeled with a 4-layer slab of 120 atoms. Due to the large size of these systems, only the $\bar{\Gamma}$ point of the surface Brillouin zone was considered. The cut-off energy for plane waves was 410 eV. Electronic self-consistency was converged within 0.1 meV. All atoms except for 2 bottom Au layers were fully relaxed. Atomic position were relaxed until the forces on all atoms were smaller than $10 \text{ meV}/\text{\AA}$. Four adsorption sites with Fe at atop, bridge, fcc and hcp positions were considered for calculations.

Different possible spin states of Fe(II) and Fe(III) are depicted in Figure S1. The ground state of FeTPP calculated with DFT+GGA has a spin ($S = 1$) –usually denoted ‘intermediate spin’– and is consistent with experimental data. However, DFT+GGA fails for FeTPPCL, where the calculated $S = 1/2$ (low spin) state does not match the experimental data of $S = 5/2$ (high spin). This problem was corrected by employing the DFT+U method, which does reproduce the high spin ground state of FeTPPCL.^{S5,S6} The ground states of both FeTPP and FeTPPCL were calculated with same set of parameters. From a series of DFT+U calculations with U between 1 and 8 eV we chose $U = 4 \text{ eV}$ and $J = 1 \text{ eV}$ to achieve the correct spin multiplicity. These values are in reasonable agreement with those of similar calculations.^{S5,S6}

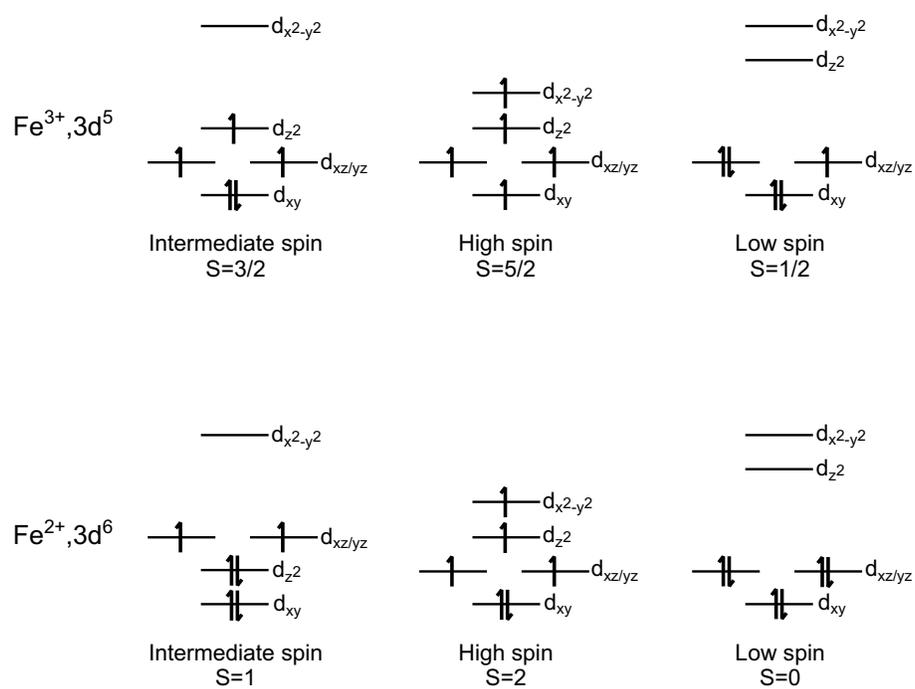


Figure S1: Molecular orbital schemes of spin states of Fe(II) and Fe(III).^{S7}

S2. STM images at different voltage polarities

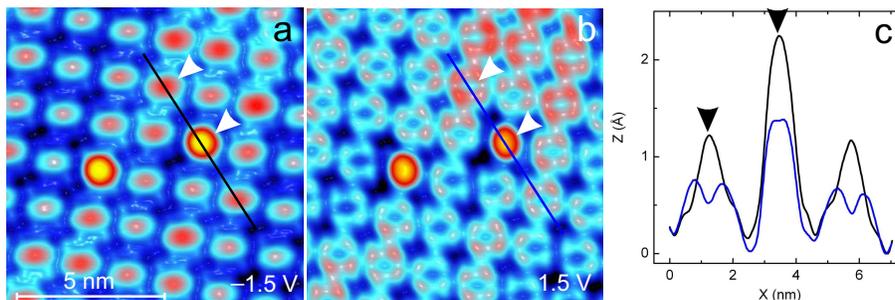


Figure S2: STM images of a layer of FeTPP and FeTPPcI (bright protrusions) at (a) negative and (b) positive sample voltage. c) Line profile through molecules in (a) and (b). The center of FeTPP appears 0.7 \AA higher at negative sample voltage. At positive bias FeTPP appears as four lobed feature with a depression at the middle and at negative bias molecules appear as a long feature (two fold symmetric) with a bright center and additional four small lobes at negative bias, which is consistent with the literature.^{S8,S9} At negative bias FeTPPcI appears $\approx 1.0 \text{ \AA}$ higher compared to that at positive bias is consistent with its calculated DOS, where a strong p -state of Cl is present below the Fermi energy. Above the Fermi energy, only d -states of Fe are accessible. The adsorption geometry of similar molecules (CoTPP) have been understood in a greater deal in the literature, where the reduced symmetry is argued due to the bending of porphyrin ring along one of the molecular axis away from surface and the intense lobe like features (especially seen at positive sample bias) are attributed to the tilted phenyl rings.^{S9,S10}

S3: pDOS of FeTPP and FeTPPCL with Fe at atop, bridge, hcp and fcc sites of Au(111)

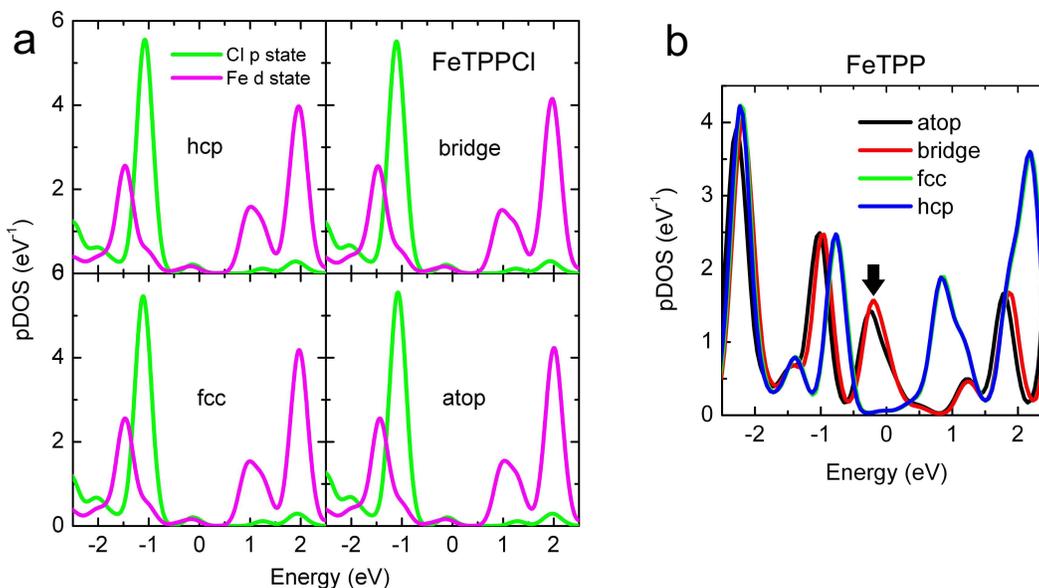


Figure S3: The pDOS of FeTPPCL (a) and FeTPP (b) with Fe at atop, bridge, hcp and fcc sites of Au(111). For FeTPPCL pDOS (Fe *d* and Cl *p*-states) is similar at all adsorption sites. Cl ligand reduces the interaction of Fe with Au and therefore the pDOS is independent of adsorption sites. For FeTPP, pDOS (Fe *d*-state) is significantly different at hcp/fcc and atop/bridge. pDOS at hcp/fcc sites shows a depletion around the Fermi energy and is comparable with tunneling spectrum. For atop/bridge site a strong interface state is appearing close to the Fermi energy (marked with arrow head) indicating a stronger interaction of Fe with Au at these sites. The interface state is mainly of d_{z^2} nature.

S4: dI/dV spectra along a row of molecule

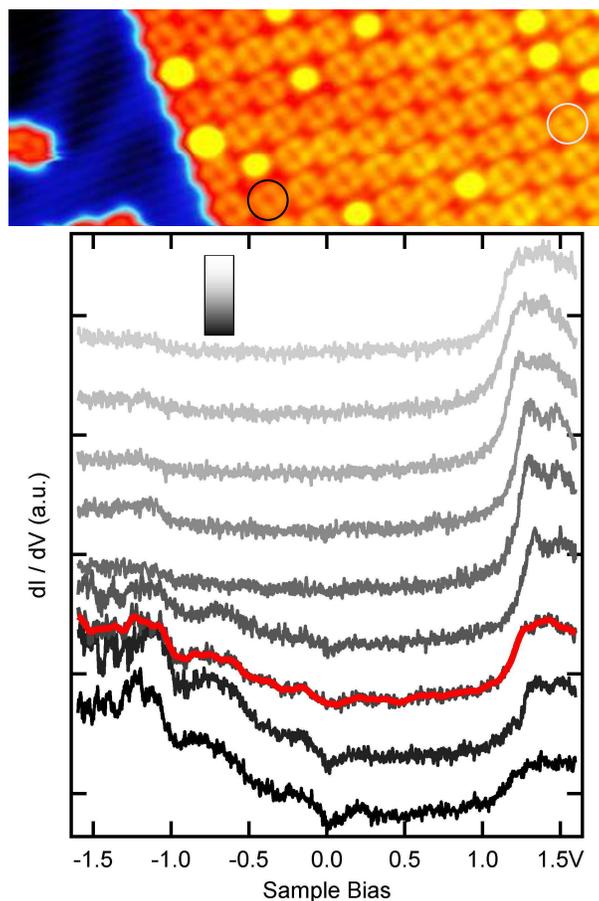


Figure S4: Top: STM constant current topography of mixed FeTPP and FeTPPCl adlayer. Bottom: dI/dV along one row of FeTPP molecules. Black spectrum is acquired at the center of molecule marked with black circle. Other spectra are acquired along the same row until the light-gray encircled molecule. The feature at ≈ -1.1 eV and 1.3 eV are prominent in all curves. In addition there is a shoulder like feature at ≈ -0.8 eV for few molecules in the row (lower four spectra). Comparing with the calculations this feature may tentatively be attributed to molecules adsorbed at top sites. Unfortunately the adsorption sites cannot be determined from our experimental data alone. Red spectrum is representative for FeTPP, which shows the prominent features and similar to dI/dV presented in the manuscript.

S5: Oxidation states of FeTPP and FeTPPCL

The partial charge of each atom in the molecule was extracted from the total charge density using a Bader charge analysis.^{S11–S13} To check the neutrality of the molecule, partial charges and the sum of partial charges from a group of similar atoms were calculated as shown in Table S5. q_{Fe} , q_{Cl} , are the partial charges on Fe and Cl; $\sum q_N$, $\sum q_C$, $\sum q_H$ are the sums of partial charges from all nitrogen, carbon and hydrogen atoms; $\sum q_{tot}$ is the net charge of the molecule. For free molecules (without substrate) neutrality is achieved ($\sum q_{tot} = 0$).

Table S1: Atomic partial charges of elements in FeTPPCL and FeTPP in free molecules and molecules adsorbed at atop and hcp sites of Au(111). The last column displays averaged Fe–N distances.

	q_{Fe}	q_{Cl}	$\sum q_N$	$\sum q_C$	$\sum q_H$	$\sum q_{tot}$	$d_{Fe-N}(\text{\AA})$
FeTPPCL	+1.36	−0.59	−4.64	+1.41	+2.47	0	2.092
FeTPP	+1.10	/	−4.59	+1.02	+2.47	0	2.001
FeTPPCL/Au(111) atop	+1.34	−0.56	−4.62	+1.39	+2.54	+0.06	2.023
FeTPPCL/Au(111) hcp	+1.35	−0.58	−4.53	+1.28	+2.55	+0.09	2.018
FeTPP/Au(111) atop	+1.13	/	−4.66	+1.31	+2.43	+0.20	2.004
FeTPP/Au(111) hcp	+1.17	/	−4.67	+1.14	+2.55	+0.19	2.005

In free molecules, Fe(II) in FeTPP and Fe(III) in FeTPPCL carry charges of +1.10e and +1.36e, respectively. The deviations from the formal charges (+2e and +3e) are due to the delocalized distribution of excess positive charge over the porphyrin macrocycle. The ratio of the sum of q_{Fe} and $\sum q_C$ between FeTPP and FeTPPCL, $(q_{Fe}^{FeTPP} + \sum q_C^{FeTPP}) / (q_{Fe}^{FeTPPCL} + \sum q_C^{FeTPPCL}) = 0.8$, is consistent with values found for similar oxidized and reduced Fe-porphyrin.^{S14} The molecules adsorbed on Au(111) surface show an excess of net charge ($\sum q_{tot}$) due to molecule–surface interaction. The larger net charge of FeTPP is consistent with its stronger interaction with the substrate. The ratio of the sums of q_{Fe} and $\sum q_C$ between FeTPP and FeTPPCL adsorbed on Au(111), $(q_{Fe}^{FeTPP} + \sum q_C^{FeTPP}) / (q_{Fe}^{FeTPPCL} + \sum q_C^{FeTPPCL}) = 0.87$, shows that the oxidation state of Fe is still higher in FeTPPCL than in FeTPP.

The calculated average distance between Fe and N, d_{Fe-N} , is larger in free FeTPPCL compared to FeTPP. This indicates a weakening of the Fe–N interaction caused by the Cl ligand. d_{Fe-N} is

relatively shorter for molecules on Au(111), however, the tendency is similar to the observation as in free molecules.

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