

Electrochemical reactions at a porphyrin-copper interface

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1. STM images of Cu(100) substrate covered by a well-ordered chloride layer

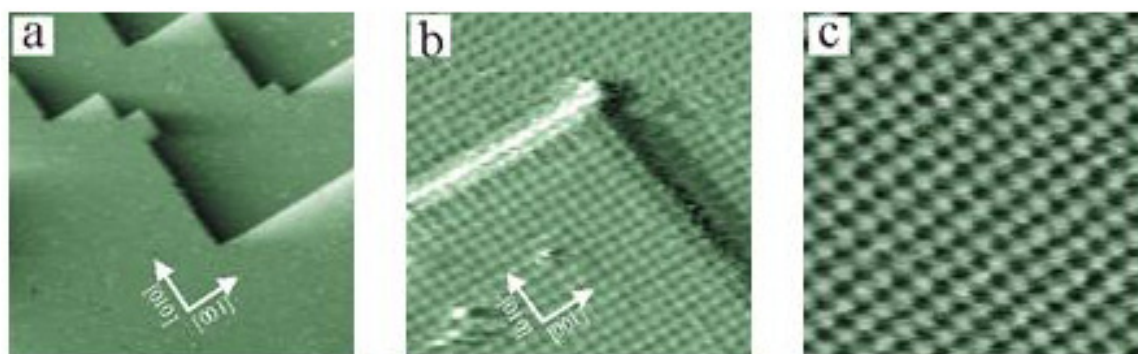


Fig. S1. $c(2\times 2)\text{Cl}/\text{Cu}(100)$, a) $69\text{ nm} \times 69\text{ nm}$, $I_t = 1\text{ nA}$, $U_b = 25\text{ mV}$, $E = -300\text{ mV}$, b) and c) close-ups of a).

2. Structural correlation between H_2TMPyP layer and the underlying chloride layer

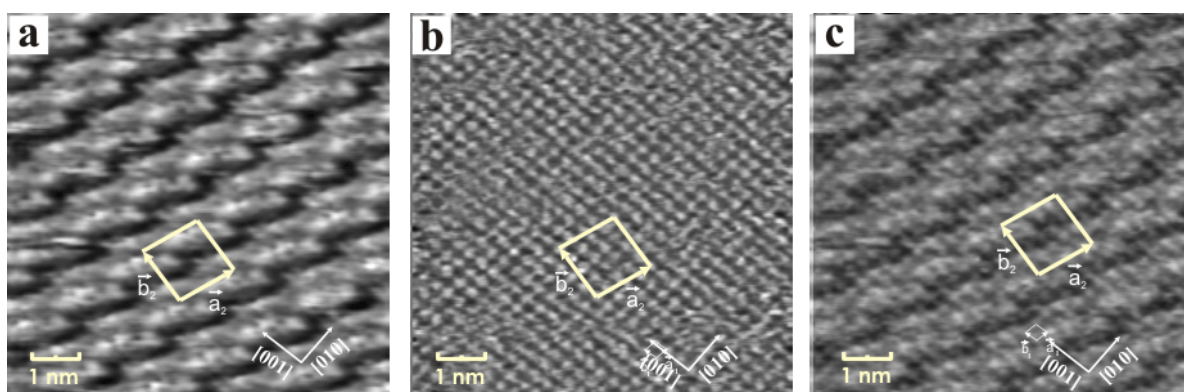


Fig. S2. Structural correlation between the H_2TMPyP layer and the underlying chloride layer, a) Porphyrin layer seen at small tunneling currents, $7.9\text{ nm} \times 7.9\text{ nm}$, $I_t = 0.38\text{ nA}$, $U_b = 256\text{ mV}$, E

= -250 mV; b) Chloride layer underneath revealed at large tunneling currents, 7.9 nm× 7.9 nm, I_t = 5 nA, U_b = 225 mV, E = -250 mV; c) Superposition of panels a and b.

Figure S2a-b represents two small STM images recorded successively at the *same* surface area with larger or smaller tip-sample distance. In the latter case the molecules are wiped away, so that both the porphyrin and the chloride lattices are clearly displayed. $(\vec{a}_1, \vec{b}_1)$ and $(\vec{a}_2, \vec{b}_2)$ are chosen to indicate the chloride and the porphyrin lattices, respectively. Superposition of these two STM images results in an image as shown in Figure S2c. From this image, the molecular lattice was found to be commensurate with the chloride lattice underneath. Thus, one unit cell containing one porphyrin molecule can be described by a matrix related to the chloride lattice: $\begin{pmatrix} 4 & -1 \\ 1 & 4 \end{pmatrix}$. Hence, it becomes clear that the molecular lattice is square.

3. UV/Vis spectroscopy in solution

Figure S3a shows the UV-Vis spectra of H_2TMPyP (1.0×10^{-5} M) and $CuTMPyP$ (1.0×10^{-5} M) in 10 mM HCl, as well as that of the porphyrin containing electrolyte surrounding the Cu(100) electrode held for 4.5 hours at $E = +300$ mV. Each spectrum is composed of two bands: the Soret band (400 – 450 nm) and the Q band (500 – 600 nm). While the Soret band is quite similar in all three spectra with a peak maximum at about 423 nm, the Q band is more characteristic for the nature of the porphyrin. The UV-Vis spectrum of H_2TMPyP is characterized by peaks in the Q bands region at 638, 585, 555, and 518 nm, which can be assigned to $[H_2TMPyP(0)]^{4+}$ [1]. The electronic absorption spectrum of $CuTMPyP$ is clearly different from that of H_2TMPyP by a large band at 548 nm and a small shoulder at 583 nm. Interestingly, the UV-Vis spectrum of the electrochemically generated porphyrin in the copper dissolution regime (at $E = +300$ for 4.5 hours) seems to be a superposition of the H_2TMPyP and $CuTMPyP$ spectra with characteristic peaks at 636, 584, 549, 519 nm, besides the Soret band (422 nm).

The spectrum of the electrochemically generated porphyrin is analyzed more closely in the region from 480 nm to 800 nm, in order to obtain the conversion ratio from H_2TMPyP to $CuTMPyP$ by the following linear sum equation:

$$\text{Absorbance} = a \times [\text{Absorbance}_{\text{H}_2\text{TMPyP}} @ 1.0 \times 10^{-5} \text{ M}] + b \times [\text{Absorbance}_{\text{CuTMPyP}} @ 1.0 \times 10^{-5} \text{ M}] \quad (1)$$

indicating that after 4.5 hours at +300 mV 33% of the H₂TMPyP in solution is converted to CuTMPyP by in-situ metallization while after 4.5 hours at +350 mV the conversion is complete, i.e. 100 %.

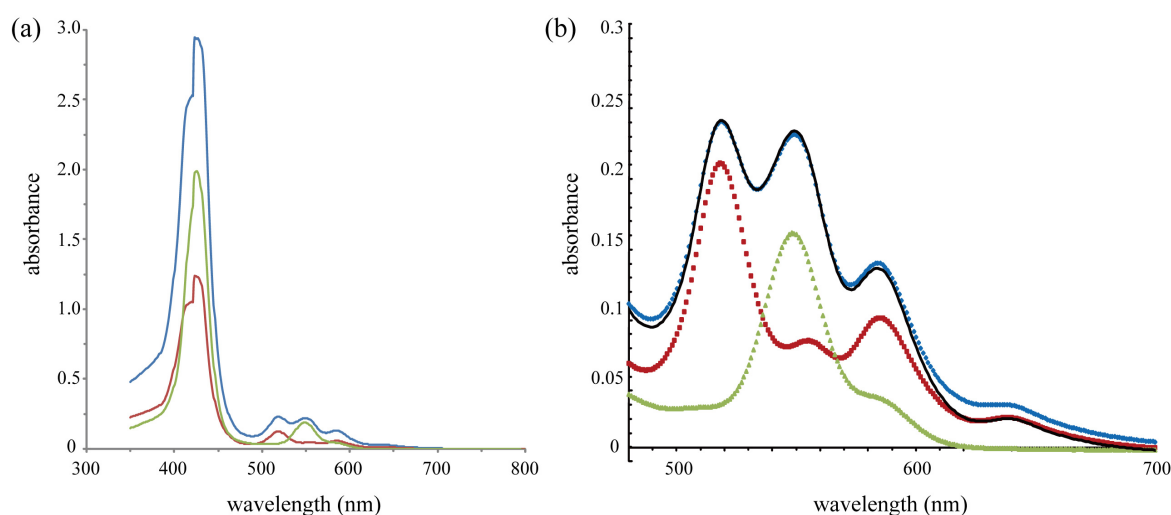


Fig. S3. a) UV-Vis spectra of the porphyrin solution being held at +300 mV vs RHE for 4.5 hours (diluted - blue line), a reference H₂TMPyP solution (1.0×10^{-5} M) (red line), and a reference CuTMPyP solution (1.0×10^{-5} M) (green line), all in 10 mM HCl; b) UV/Vis absorption spectrum of the porphyrin solution being held at +300 mV vs RHE for 4.5 hours (diluted - blue dots). Best fit according to equation (1) (black line), decomposed into the contribution of H₂TMPyP ($a = 1.6$) (red dots) and CuTMPyP ($b = 0.8$) (green dots).

[1] Untereker, D.; Bruckenstein, S., *Anal. Chem.* **1972**, 44, (6), 1009