Electronic Supplementary Information
for
Following the steps of a reaction by direct imaging of many individual molecules
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All experiments as well as the sample preparation are performed in an ultrahigh vacuum system. The Cu(111) surface is prepared by several cycles of sputtering by Ar+ ions at a kinetic energy of 2.5 keV (45 min at ≈15 μA/cm²) and annealing to 880 K for 90 min. The preparation is checked by low energy electron diffraction (LEED). The 2,3,7,8,12,13,17,18-octaethylporphyrin Fe(III) chloride (FeOEP-Cl) used in our experiments has a purity of 98% according to the retailer Porphyrin Systems. The molecules are thermally evaporated from a tiny oven with a quartz crucible heated by a tungsten filament to a temperature of 500 K. Prior to the experiments, the oven was carefully outgassed. The flow of molecules is checked by a quadrupole mass spectrometer (QMS) covering the range from 1 to 1028 amu. Three QMS spectra with different electron energies used to ionize the molecules are presented in Fig. S 1. With increasing ionization energy, the number of dechlorinated molecules in the QMS rises. Therefore, only a lower limit of at least 60% chlorinated molecules out of all sublimated molecules can be given. More information about the ratio of chlorinated to dechlorinated molecules after adsorption can be found in an earlier publication.1 Here a submonolayer is deposited onto the copper surface at room temperature. Previous experiments showed that depending on the sample temperature during preparation two different species - chlorinated and dechlorinated species - are observed. Beside these, no further species or fragments are found on the surface.
The STM images are obtained using a home-built low-temperature scanning tunneling microscope (STM) in ultra-high vacuum at $T = 80$ K. The tunneling tips are electrochemically etched from a tungsten wire with a diameter of 100 μm. They are further prepared in situ by field emission in front of a Au(111) surface. The data are acquired using the GxSM\textsuperscript{2} software and further processed by the WSxM\textsuperscript{3} software.