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Activity boost of a biomimetic oxidation catalyst by immobilization onto a gold surface

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Abstract

Thiol-functionalized cobalt porphyrins were used as a model system for investigating catalytic activity in homogeneous and heterogeneous oxidation catalysis. Self-assembled monolayers of thiol-functionalized cobalt porphyrins were prepared on a gold surface and served as heterogeneous catalysts. These immobilized molecules prevented the strong inactivation observed for their homogeneous congener. As a result, the turnover number per molecule in heterogeneous catalysis was at least 100 times higher than that of the corresponding homogeneous catalyst. It is atypical for a heterogenized catalyst to outperform its homogeneous congener. The properties of the molecular layers were characterized on the molecular level by means of X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). The results demonstrate that the performance of these biomimetic catalysts can be dramatically improved if the catalyst arrangement can be controlled on the molecular level.

Keywords: Biomimetic; Catalysis; Thiol-functionalized porphyrin; Gold surface; Immobilization; X-ray photoelectron spectroscopy; Scanning tunneling microscopy; Self-assembled monolayers

1. Introduction

The need for efficient chemical processes with both low energy consumption and low environmental impact has stimulated the quest for improved catalytic systems. One example is the development of oxidation reactions that use molecular oxygen and a metal catalyst at room temperature. These reactions replace more conventional oxidation methods that require harsher conditions and stoichiometric amounts of oxidant and produce the reduced oxidant as waste material instead of just water [1,2]. For industrial applications, the development of heterogeneous catalysts is crucial for overcoming some of the limitations of homogeneous catalysts, such as the need to separate the product from the catalyst and the incompatibility with flow reactors. Although a heterogeneous catalyst can be developed from a homogeneous catalyst in various ways, in many cases this "heterogenization" results in inferior catalyst performance; therefore, such catalysts are currently used in only a few cases [3,4].

Recent insight into catalytic processes on the molecular level has improved inorganic catalysts and advanced the design and development of new types of catalysts [5–7]. In addition, for organic catalysts, the impact of immobilization and ordering on catalytic activity has been investigated in different cases, providing increased insight into the processes involved [8,9]. Metal porphyrins have been used as homogeneous catalysts in various oxidation reactions [10–13]. Supported porphyrin molecules have been used in heterogeneous oxidation catalysis where even an increased activity on immobilization was observed [14,15]. Different self-assembled thiol-functionalized cobalt porphyrin layers have been prepared on gold surfaces, and electrocatalytic reduction of O_2 has been demonstrated [16,17].

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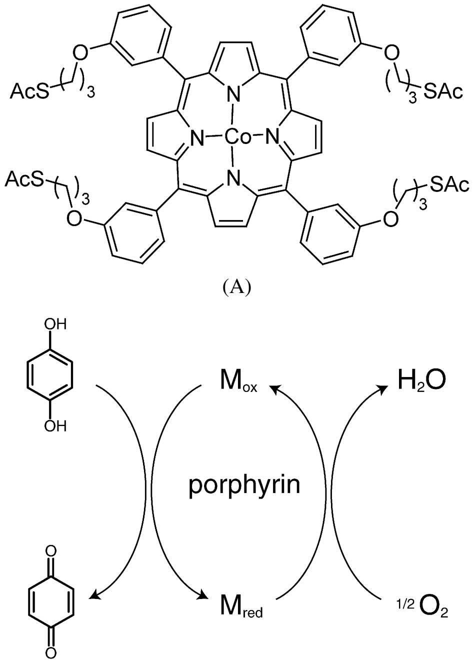

(A)

(B)

Fig. 1. (A) Chemical structure of the cobalt porphyrin (**1**) with the four thiol-linkers (Ac = $COCH_3$). (B) Porphyrin-catalyzed biomimetic oxidation of hydroquinone (HQ) to *p*-benzoquinone (BQ) with molecular oxygen.

We report on catalysis experiments of a thiol-functionalized cobalt porphyrin in homogeneous and heterogeneous catalysis immobilized onto a gold surface. This system was chosen as a model system to investigate the effect of catalyst immobilization on the catalytic performance. We combine the catalytic study with a detailed molecular-level characterization of the immobilized catalyst by means of surface science techniques (XPS and STM) and thus obtain information on the activity on the molecular level.

The molecular structure of the catalyst is shown in Fig. 1A [18]. The thiol groups were acetylated to prevent disulfide formation between molecules. The catalyst was tested in the aerobic oxidation of hydroquinone (HQ) to the corresponding *p*-benzoquinone (BQ) as shown in Fig. 1B:

$$\underset{\text{HQ}}{C_6H_4(OH)_2} + (1/2)O_2 \xrightarrow[\text{acetic acid}]{\text{Co-porphyrin}} \underset{\text{BQ}}{C_6H_4(O)_2} + H_2O.$$

This reaction, also involving related quinones and metal macrocyclic systems, is of importance and occurs in many biomimetic oxidation systems [12,13,19] as well as biological oxidation systems (i.e. the aerobic chain) [20,21]. It constitutes a “clean” reaction, because water is the only byproduct. Furthermore, it proceeds at room temperature and ambient pressure.

2. Experimental

2.1. Homogeneous catalysis

The homogeneous catalysis was conducted in acetic acid solution for a series of catalyst concentrations (1 mg/ml, 200 µg/ml, 40 µg/ml, 4 µg/ml, 0.4 µg/ml of porphyrin **1** in a total volume of 5 ml, containing 25 mg/ml hydroquinone). This corresponds to a total amount of porphyrin between 1.7 nmol (lowest concentration) and 4.2 µmol (highest concentration). The two highest concentrations (1 mg/ml and 200 µg/ml) of porphyrin in acetic acid were not completely soluble. Reactions were performed in vessels exposed to an oxygen atmosphere (1 atm).

Solid products were formed during the reaction for the highest porphyrin concentration (1 mg/ml). These black crystals were identified as quinhydrone (1:1 complex of HQ and BQ).

2.2. Heterogeneous catalysis

The heterogeneous catalyst was prepared by self-assembled cobalt-porphyrin monolayers on gold surfaces. Polycrystalline gold films on Si(100) were prepared by thermal evaporation of a Cr adhesion layer (about 10 nm), followed by thermal evaporation of about 150 nm of gold. The gold coating was added on both sides of a polished Si(100) wafer with a diameter of 10 cm. These surfaces were cleaned in piranha solution (H_2SO_4:H_2O_2 30%, (v/v) 2:1) and rinsed with ultra-pure water. Finally, the surfaces were blown dry with argon.

Co-porphyrin layers were immobilized on these gold surfaces. A 0.1 mM solution of functionalized porphyrin **1** (120 µg/ml) in *N*,*N*-dimethylformamide (DMF) was prepared, and the freshly cleaned Au surface was immersed in the solution for about 2.5 h. Subsequently, the samples were thoroughly rinsed in DMF, then ultra-pure water, to remove any nonspecifically bonded porphyrin molecules. Finally, the sample was blown dry in argon.

The heterogeneous catalysis experiments were performed on a total volume of 25–30 ml of acetic acid solution, containing 25 mg/ml of hydroquinone.

2.3. ^{1}H NMR spectroscopy

NMR spectroscopy was chosen as a nonevasive technique to monitor the reactions. ^{1}H NMR spectra were recorded at 500 MHz on a Varian Unity Inova spectrometer for solutions in acetic acid (HOAc) with addition of 5% HOAc-d_4 for locking, and suppression of the CH_3COOH peak by presaturation. The conversion of HQ to BQ was determined by quantification of their relative amounts from line shape deconvolution of their ^{1}H NMR signals.

2.4. X-ray photoelectron spectroscopy

The XPS measurements were performed in a Scienta ESCA-300 spectrometer using monochromatic AlK_α radiation with a photon energy of 1487 eV [22]. All spectra are referenced to the Au4$f_{7/2}$ core level at a binding energy of 84.0 eV. Spectra were recorded at 90° take-off angle (TOA) (normal emission) and at 10° TOA (grazing emission). The surface sensitivity of XPS is given by the short mean free path of the photoelectrons in the material analyzed. Measurements at 10° TOA lead to increased surface sensitivity compared with 90° TOA due to the longer path of the photoelectrons in the material until they leave the surface. Thus, information about the spatial depth distribution is obtained by comparing spectra recorded at 10° TOA and 90° TOA.

2.5. *Scanning tunneling microscopy*

The STM experiments of the molecular arrangements on the atomically flat Au(111)/mica surfaces were performed in ultrahigh vacuum with a Omicron variable-temperature AFM/STM. All STM images were obtained at room temperature in the constant-current mode by recording the vertical tip movement. Pt/Ir tips were used for these experiments.

2.6. *Molecular coverage*

The coverage of the porphyrin monolayers on the gold surface was estimated based on XPS and STM data. For XPS, the coverage was calculated using standard cross-sections by comparing the intensity of the N1s signal to the intensity of the Au4f signal at normal emission according to [23]. A footprint size of 1.5 nm^2 per molecule was obtained following this procedure. For STM, individual molecules were counted in high-resolution images. This analysis resulted in a footprint size of 10 nm^2 per molecule. However, contamination of the surface leads to an overestimation of the coverage on XPS. On the other hand, recognizing all of the molecules in the STM images is difficult, and thus STM leads to underestimation of coverage.

As a result, the footprint size per molecule is estimated to be 5 nm^2 (coverage, 0.2 molecule/nm^2), comparable to the lateral size of a single molecule. The total surface area of the Au surface (two-sided coated 10-cm wafer) was about 150 cm^2, because some small pieces were cut from the wafer for the XPS characterization and were not used in the catalysis experiment. Thus, the total number of porphyrins on the surface in the heterogeneous catalysis experiments was estimated to 3×10^{15}, which corresponds to 5 nmol. However, the uncertainty in the total number of molecules is large due to the uncertainty in the calculated coverage. A factor of 2–3 is considered a reasonable error in the calculated number of molecules to account for the discrepancy in the coverage of the XPS and STM data.

3. Results and discussion

The results for the homogeneous catalysis for a series of catalyst concentrations using porphyrin **1** are shown in Figs. 2A and 2B. The turnover number of BQ is plotted for different experimental runs and different porphyrin concentrations. In the case of the two lowest concentrations tested (4 and 0.4 µg/ml), the amount of BQ produced was too low to be measured accurately by ^{1}H NMR spectroscopy (relative amount of BQ:HQ < 0.001; total amount of BQ < 0.13 mg), and thus the results are consistent with BQ ≈ 0. For the three higher concentrations, BQ was produced and increased with the concentration of porphyrin catalyst, with a similar turnover number for all

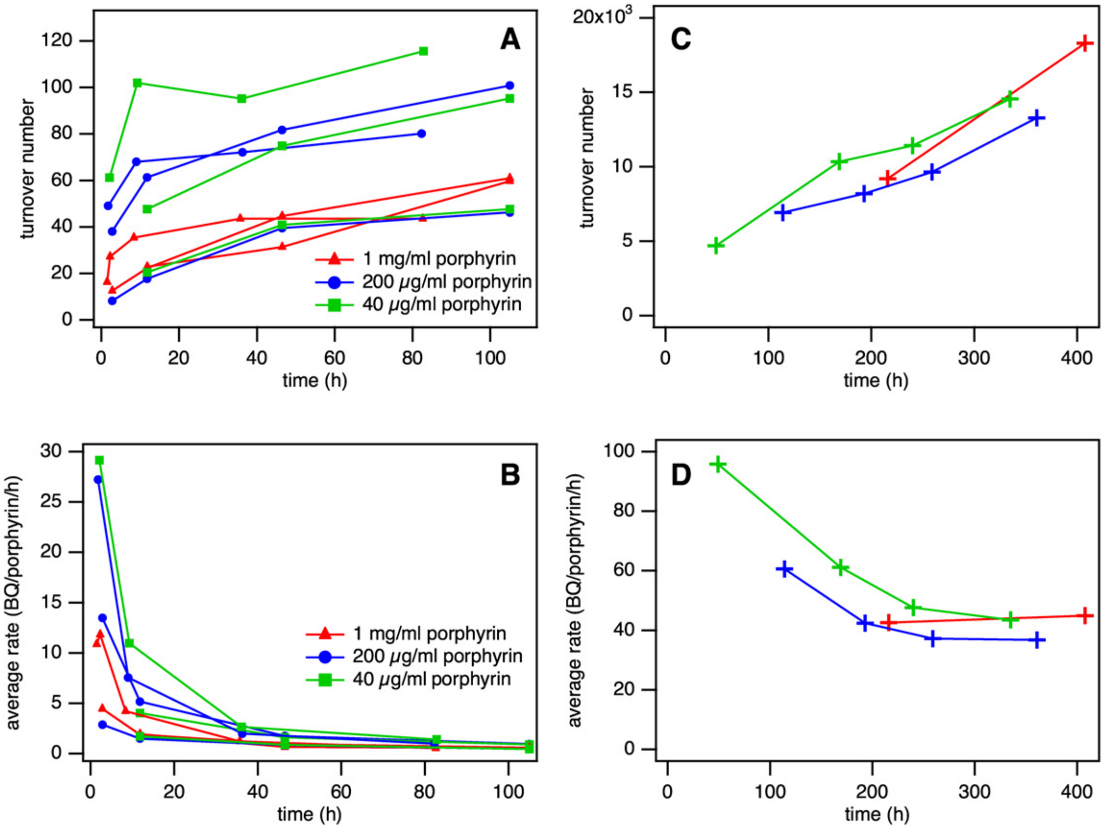

Fig. 2. Activity of the porphyrin molecule (**1**) in homogeneous ((A) and (B)) and heterogeneous ((C) and (D)) catalysis. (A) Turnover number per porphyrin, homogeneous system. (B) Average rate of BQ formation, homogeneous system. Inactivation of the catalyst is observed after about 10 h. (C) Turnover number per porphyrin, heterogeneous system. (D) Average rate of BQ formation, heterogeneous system. No inactivation is observed after a run time of more than 300 h.

concentrations (Fig. 2A). The activity of the catalyst dropped dramatically after an initial reaction time of about 10 h. During this period, each porphyrin molecule transformed <100 HQ into BQ. The declining turnover number is a strong indication of catalyst inactivation. One possible reason for this may be the formation of oxygen complexes of the metal porphyrin, followed by dimerization to form peroxo- and μ-oxo complexes [24].

The heterogeneous catalyst was prepared by self-assembled cobalt-porphyrin monolayers on gold surfaces. The characterization of the porphyrin layers is discussed below. Figs. 2C and 2D show the catalytic performance of the porphyrin molecules immobilized on the gold surface for different experimental runs. Each porphyrin molecule produced more than 10,000 BQ molecules during the duration of the experiment (about 350 h). The turnover number did not level out, but continued to increase. Consequently, the turnover number of the heterogeneous catalyst was at least 100 times higher than that of its homogeneous congener. The catalyst lifetime increased dramatically on heterogenization, with essentially no inactivation of the porphyrin molecules observed. Notably, the total number of porphyrin molecules on the surface (5 nmol) was about the same as for the two lowest concentration solutions of porphyrin molecules used for homogeneous catalysis. At these low concentrations of homogeneous catalyst, no detectable amount of BQ was formed. In summary, these results conclusively show the improved performance of the porphyrin catalyst by immobilization onto the gold surface.

Two different control experiments were performed. After the heterogeneous catalyst was removed from the reaction solution, the experiment was continued for typically another 180 h, at which point there was no observed increase in BQ concentration. In addition, the reaction was repeated using bare gold-coated wafers; 0.6 mg of BQ (BQ:HQ ≈ 0.001) was detected after 335 h. This is significantly less than the amount of BQ produced by the immobilized porphyrin layer after the same reaction time (about 7 mg). This small amount of BQ produced during the control experiment might be due to auto oxidation of HQ [25].

The combined X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM) studies provide a detailed insight in the geometric and electronic structure of the Co-porphyrin layers prepared on gold. XPS reveals insight in the electronic structure of the molecular layer on the gold surface. Different chemical environments of an adsorbate, or a species in general, lead to slightly different binding energies of the atomic core levels. This energy difference in the binding energy is called a “chemical shift” [26]. The XPS experiments are complemented by STM images, which provide a real-space map of topographic and electronic features reflected to the molecular layer, thus allowing determination of the lateral arrangement of the molecules.

Self-saturating layers of the thiol-functionalized porphyrin on the Au surface are obtained; that is, the growth stops after an initial layer [18]. Our XPS and STM results confirm the presence of porphyrin monolayers, as reported previously by others [16,17]. The self-assembled monolayers were obtained by the formation of bonds between the thiol linkers and the gold surface. Fig. 3 shows the XPS spectra of the S2p core level, which appears as a doublet because of the spin-orbit coupling. The doublet in Fig. 3 with the $2p_{3/2}$ component at a binding energy of 161.9 eV (red) is attributed to thiolate formation (i.e., bonding between the thiol linker and the gold surface), whereas the doublet with the $2p_{3/2}$ component located at a binding energy of 163.4 eV (blue) is attributed to S not bonded to Au [16,27]. In case of the nonbonded linkers, it is not clear whether the protective acetyl group is still present or if the linkers are present as “free” thiols. On average, about 60% of the thiol linkers are bound to the Au surface; this represents a mean value averaged over many molecules due to the large lateral area measured by XPS.

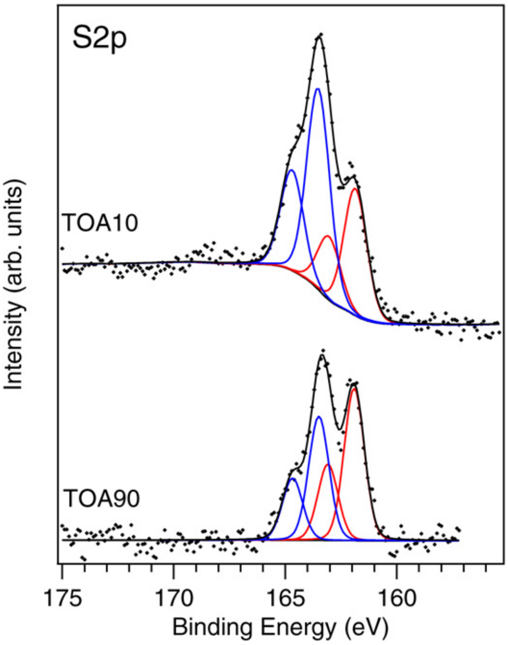

Fig. 3. XPS spectra at different take-off-angles of the S2p core level and corresponding fitted curves for a self-assembled porphyrin layer on gold. Two chemically different states of the sulfur are observed. The red doublet with the $2p_{3/2}$ component at a binding energy of 161.9 eV is attributed to thiolate formation while the blue doublet with the $2p_{3/2}$ component located at a binding energy of 163.4 eV is attributed to S not bonded to Au. The unbound sulfur is within the outermost part of the surface, since the signal of this component is enhanced in the more surface sensitive measurement at 10° TOA. The step-like function in the background of the spectrum at 10° TOA is due to the higher amount of inelastically scattered photoelectrons compared to 90° TOA.

The spatial height distribution of the thiol-linkers was studied by measuring the electron photoemission at different TOAs relative to the surface plane. Comparison of highly surface sensitive measurements at 10° TOA to the more bulk sensitive measurements at 90° TOA gives information about the spatial height distribution of the linkers. At 10° TOA, the intensity in the spectrum due to nonbonded linkers is dominant, whereas at 90° TOA, the intensity contribution from the bonded linkers dominates (Fig. 3). Consequently, the nonbonded linkers are located in the outermost part of the porphyrin layer. This analysis of the S2p spectra suggests that the porphyrin molecules are adsorbed on the gold surface with the porphyrin core not completely parallel but rather tilted relative to the surface.

However, it is also possible that the porphyrin core is oriented coplanar to the surface and that the nonbonded linkers are sticking away from the surface. As stated above, XPS is integrating over many molecules, and most likely various individual adsorption geometries are present.

XPS spectra on the Co2p core level revealed the presence of the central Co ion in the porphyrin molecule. The calculated amount of Co is slightly lower than the stoichiometric value of the molecule, but fits within the error of the limited statistics (low amount of Co on the surface). In summary, the Co ion is present in most of the porphyrin molecules and is potentially released only in a minority. The binding energy of the $Co2p_{3/2}$ core level was measured at 780.0 eV (compare supplementary information), significantly higher than the value of 778.3 eV for clean Co metal [28]. Thus, we assume that the Co ion is present as Co^{2+} as in the free molecule.

Ultra-high-vacuum STM experiments were conducted on porphyrin layers immobilized on atomically flat Au(111)/mica. The STM experiments revealed the formation of a complete monolayer where the molecules are arranged in a disordered pattern (Fig. 4). Step edges of the buried Au(111) surface are visible (Fig. 4A) and indicate a rather "smooth" molecular layer. Individual molecules are resolved and imaged with a height of about 0.5–1.0 nm at a bias voltage of 1.7 V. The different heights of individual molecules may be due to slightly different adsorption geometries of the porphyrin molecules immobilized on the gold surface. Spots are present in the STM images that have a higher apparent height compared with the residual area of the image. These spots are possibly due to porphyrins clustering in a second layer. Subsequent STM images revealed that individual molecules did not exhibit mobility, demonstrating that the molecules were effectively immobilized on the Au surface via the linker–gold bonds. The adsorption behavior was dominated by molecule–substrate interactions, whereas intermolecular interactions were suppressed, as concluded from the formation of the disordered pattern. These findings would also be expected to be valid in the case of porphyrins immobilized on the polycrystalline Au/Si used in the catalysis experiments. The greater number of defects on the polycrystalline surface results in preferred adsorption sites and thus stronger immobilization [29]; consequently, the porphyrins would be expected to form a disordered pattern on the Au/Si and not exhibit mobility.

4. Conclusion

The present work demonstrates that the catalytic functionality of thiol-functionalized cobalt porphyrins was completely preserved when the molecules were immobilized on a gold surface. Furthermore, the strong inactivation of the porphyrin molecules observed in the homogeneous catalysis experiments was circumvented by immobilization. Intermolecular inactivation processes, such as dimerization, are suppressed by the immobilization of the catalysts and could possibly lead to the improved activity. In the present study, the lifetime and the turnover number increased significantly; a 100-fold increase in turnover number was observed for heterogeneous catalysis compared with homogeneous catalysis. Characterization of the immobilized layers revealed that the molecules formed a disordered monolayer, with nonbonded linkers located in the outermost part of the layer. Our findings demonstrate that the lifetime and thus the efficiency of biomimetic catalysts can be dramatically enhanced if the processes on the molecular level can be controlled. The approach of using "large-area" model surfaces allows for the study of functionality and structural properties on the same surface, thus providing information on functionality at the molecular level.

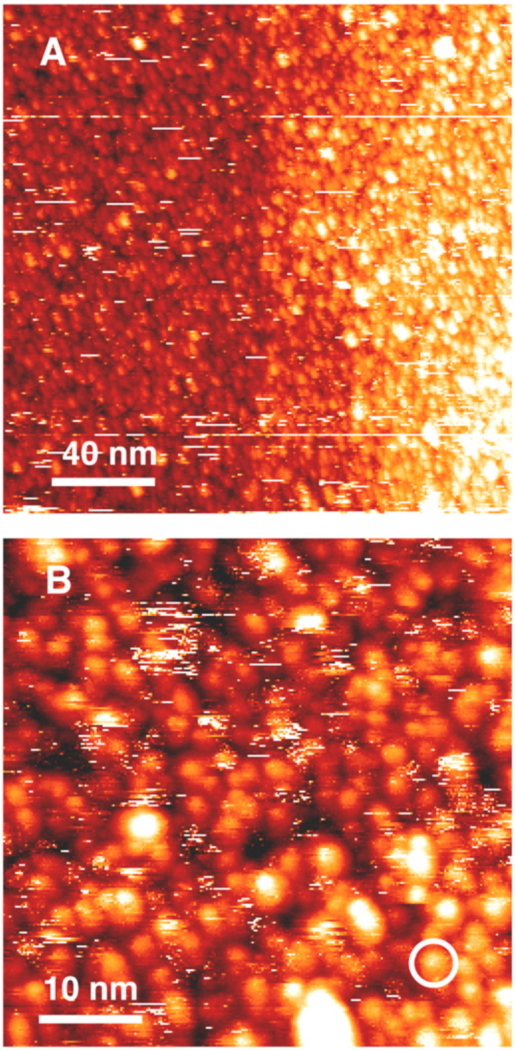

Fig. 4. Constant current STM images of the porphyrin layer on Au(111)/mica taken with a bias voltage of $U = 1.7$ V and a tunneling current of $I = 1.5$ pA. (A) Large-area survey image. Step edges of the Au(111) surface running across the image can be seen. A disordered porphyrin layer is formed. (B) High-resolution image. The white circle highlights a single porphyrin molecule.

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Supplementary information

The online version of this article contains additional supplementary material.

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