

Direct Observation of Surface-Mediated Thioacetyl Deprotection: Covalent Tethering of a Thiol-Terminated Porphyrin to the Ag(100) Surface

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The use of thiol (SH) groups for attachment of a wide range of molecular and supramolecular species to gold surfaces has been extensively studied, usually in connection with harnessing physical properties of the resulting self-assembled monolayers.¹ More recently, Lindsey et al.² have synthesized thiol-functionalized porphyrins to create self-assembled monolayers for potential applications in electrochemistry and molecular-based electronics.^{3,4} In all these earlier investigations, the thiolated species have been deposited from the solution phase.

Thus far, there has been essentially no work on the covalent attachment of porphyrins to catalytically active metal surfaces (such as Ag) with a view to harnessing the *chemical* properties of the macrocycle to the catalytic properties of the metal surface. We have shown that systematic chemical manipulation of metal-adsorbed noncovalently attached metalloporphyrins is possible,^{5,6} although such systems are likely to be vulnerable to degradation under practical conditions, for example, leaching by solvent. Accordingly, we aim to covalently tether metalloporphyrins to Ag surfaces to explore the potential of such hybrid systems as selective oxidation catalysts. Due to the high reactivity of free thiols, they must be protected during synthesis.⁷ Protection as the thioacetate is particularly convenient due to the ready availability of appropriate precursors required for porphyrin synthesis. Clearly, for this strategy to succeed, clean, facile deprotection upon adsorption is necessary to generate covalently tethered porphyrin molecules. Encouraged by the observation⁸ that a gold surface can spontaneously cleave a thioacetyl-terminated molecule by adsorption from solution to yield a surface-bound thiolate, we have examined the behavior of the vacuum-deposited tetra(thioacetyl) porphyrin [SAc]₄P-H₂ (Figure 1) on Ag(100).

Whether the previously reported interfacial reaction by adsorption from solution⁸ occurs directly in a single step or via hydrolysis of the thioester or its enol form by trace amounts of water is unclear.^{9,10} In the present case, vacuum deposition, the possibility of solvent effects is eliminated so that mechanistic questions may be addressed unambiguously.

Here, by means of scanning tunneling microscopy (STM), we report evidence for direct surface-activated cleavage of the acetyl group accompanied by strong binding of the porphyrin to the silver surface. Following vacuum-deposition of [SAc]₄P-H₂, imaging at 298 K revealed large aggregates of porphyrin molecules, with dimensions in the order of 200 × 200 Å (Figure 2a). This resembles the initial behavior of Zn tetrakis(3,5-di-*tert*-butylphenyl) porphyrin when vacuum deposited on Ag(100).⁵

Upon annealing to 473 K, the porphyrin agglomerates disperse to form islands of individual porphyrin molecules surrounded by a uniform sea of smaller objects likely to be acetyl groups. The individual porphyrin molecules have dimensions of ~15 × 15 Å, consistent with those expected for the macrocycle (Figure 2b and inset). The size of the smaller round features, which are ~4 Å in

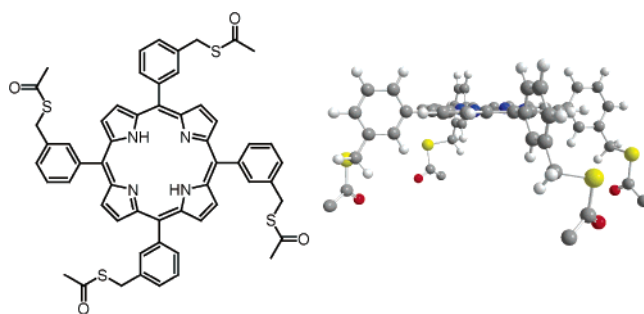


Figure 1. Structural model and three-dimensional representation of [SAc]₄P-H₂.

diameter, is indeed consistent with the expected size of the acetyl protecting group, and a magnified image of these entities is shown in Figure 2c. At this stage, although the porphyrin molecules have dispersed, they do not uniformly cover the surface but remain in clusters. This behavior is accordant with chemisorption and formation of covalent S-Ag bonds. That is, annealing results in dispersion of the initial porphyrin aggregates, and as individual molecules contact the Ag surface, the protecting groups are cleaved. The porphyrin is then strongly anchored and immobilized via four S-Ag bonds, inhibiting further migration. In contrast, the observed migration and uniform dispersal of the acetyl protecting groups indicate much weaker binding to the surface, as expected. The fact that the acetyl groups are not visible before annealing (Figure 2a) confirms the view that direct porphyrin-Ag contact, and possibly elevated temperature, are required to activate cleavage of the protecting group from the macrocycle. (In the initial aggregate, only very few porphyrin molecules are in direct contact with the silver surface itself, so only limited deprotection and subsequent acetyl migration can occur.)

We investigated the behavior of the porphyrin-functionalized silver surface under conditions relevant to oxidation catalysis. Specifically, we examined the effect of oxygen exposure and increased temperature on both the adsorbed porphyrin and the detached acetyl groups. Figure 3a shows the [SAc]₄P-H₂ covered surface (Figure 2b) imaged in the presence of 5 × 10⁻⁸ mbar O₂ at 298 K after 150 min of exposure. In marked contrast to the oxygen-free case, many porphyrin molecules (circled red) are now distributed evenly across the surface: it is clear that oxygen adsorption caused a substantial increase in room-temperature mobility of the deprotected porphyrin. (Some porphyrin aggregates remain, such as the example circled in green.) The presence of the acetyl groups on the surface can also be distinguished in the image as a sea of small features surrounding the larger and brighter porphyrins (example circled in blue). The oxygen-induced increase in room-temperature mobility could be due to oxidation of S to S^{IV} or S^{VI}, corresponding to formation of a sulfinyl or sulfonyl species, thus weakening the S-Ag surface bond.

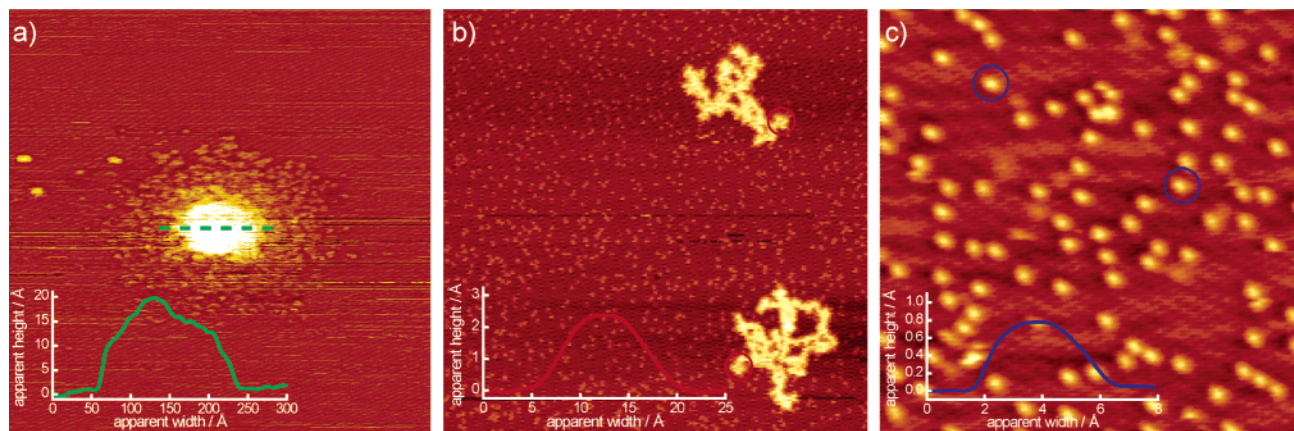


Figure 2. Room-temperature STM images and line profiles of [SAc]₄P-H₂ on Ag(100). (a) Large porphyrin aggregate formed after initial dosing, and corresponding line profile taken along the indicated green line (900 × 900 Å, $V_{\text{tip}} = 1.5$ V, $I = 0.1$ nA). (b) Surface after subsequent annealing at 473 K showing islands of individual porphyrin molecules surrounded by evenly distributed acetyl groups and corresponding characteristic height profile of features circled in red (400 × 400 Å, $V_{\text{tip}} = 0.75$ V, $I = 0.05$ nA). (c) Close-up of the acetyl groups (taken at higher surface coverage than (b) and corresponding characteristic line profile of features circled in blue (100 × 100 Å, $V_{\text{tip}} = 0.75$ V, $I = 0.05$ nA).

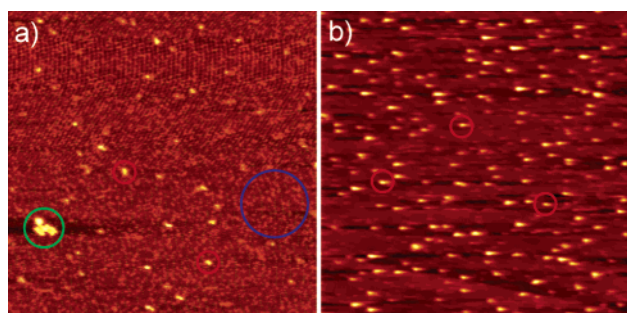


Figure 3. STM images of two different areas showing annealed [SAc]₄P-H₂ on Ag(100) taken at (a) 298 K, in the presence of 5×10^{-8} mbar O₂ (500 × 500 Å, $V_{\text{tip}} = 1.0$ V, $I = 0.1$ nA) and (b) after increasing the temperature to 325 K (750 × 750 Å, $V_{\text{tip}} = 1.0$ V, $I = 0.1$ nA).

Heating the oxygen-exposed surface to 325 K caused (i) complete dispersion of the remaining porphyrin aggregates and (ii) disappearance of the acetyl groups, as shown in Figure 3b. (The slight distortion and elongation observed in this image is due to molecular motion while scanning, confirming the increased porphyrin mobility.) Thus, the presence of oxygen results in a very large increase in porphyrin mobility and complete dispersion at a temperature ~150 K lower than that at which the molecules acquire partial mobility in the absence of oxygen (cf. Figure 2b). And at this slightly elevated temperature, the surface acetyl groups are burned off. Auger electron spectroscopy confirmed that the amount of sulfur on the surface remained constant throughout the above procedure (see Supporting Information).

Due to restricted porphyrin mobility and nonuniform coverage, a meaningful statistical comparison of the relative number densities of adsorbed acetyl and porphyrin molecules in Figure 2b is difficult (an ~4:1 ratio is expected). However, we can compare the number density of acetyls in Figure 2b with that of the porphyrins in Figure 3b imaged *after* porphyrin dispersion via exposure to O₂ and heat. The acetyl-to-porphyrin ratio on the terraces is then found to be ~7:1. The source of this apparent discrepancy is the pronounced tendency of the dispersed porphyrin molecules to aggregate at step edges, thus depleting the terraces (see figure in Supporting Information).

In summary, vacuum deposition of [SAc]₄P-H₂ on Ag(100) leads initially to the formation of aggregates. These partially disperse at higher temperature, with cleavage of the acetyl protecting groups, directly imaged in the STM, resulting in strongly adsorbed covalently tethered porphyrin molecules. The mechanism of deprotection is unambiguously surface-activated acetyl cleavage. Although this demonstration of deposition, deprotection, and protecting group elimination was conducted using porphyrins, our findings should apply to protected-thiol adsorption in general. They provide clear evidence that acetyl deprotection occurs by a direct surface-mediated mechanism, which, along with the newly discovered effects of oxygen, suggests strategies for surface functionalization, including biofunctionalization, at the gas/solid and gas/liquid interfaces.

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Supporting Information Available: Experimental procedures and supplementary STM images and AES data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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