

Deprotection, tethering and activation of a catalytically active metalloporphyrin to a chemically active metal surface: [SAc]₄P-Mn(III)Cl on Ag(100)

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ABSTRACT

The adsorption and subsequent thermal chemistry of the acetyl-protected manganese porphyrin, [SAc]₄P-Mn(III)Cl on Ag(100) have been studied by high resolution XPS and temperature programmed desorption. The de-protection event, leading to formation of the covalently bound thio-porphyrin, has been characterized and the conditions necessary for removal of the axial chlorine ligand have been determined, thus establishing a methodology for creating tethered activated species that could serve as catalytic sites for delicate oxidation reactions. Surface-mediated acetyl deprotection occurs at 298 K, at which temperature porphyrin diffusion is limited. At temperatures above ~ 425 K porphyrin desorption, diffusion and deprotection occur and at > 470 K axial chlorine ligand is removed.

Introduction

The bottom-up fabrication of systems consisting of functional molecules tethered to solid surfaces is an important research area of relevance to a wide range of applications including electrochemistry, molecular electronics and catalysis.¹ Robust, reproducible molecule-surface tethering is important and is often achieved by means of thiol linkages. However, the reactivity of thiol groups is such that they need to be protected during synthetic procedures and then deprotected to enable covalent linkage to the solid surface. Recent interest in the electrochemical and physical properties of metalloporphyrins has stimulated work on the covalent attachment these macrocycles to electroactive surfaces, an important example being the synthesis of thiol-functionalized porphyrins,²⁻¹⁰ led by the work of Lindsey *et al.*³ Our interest lies in a hitherto neglected field: the attachment of catalytically active metalloporphyrins to metal surfaces to create hybrid catalytic systems in which the characteristic chemistry of the porphyrin is harnessed to the complementary chemistry of the metal surface—for example to produce systems capable of carrying out delicate selective oxidations. We choose silver because at ambient temperature it can dissociatively adsorb dioxygen and π -adsorb alkenes, thus preparing the reactants in the desired state.

We have previously made a porphyrin-functionalized silver surface that exhibits ligand binding, unbinding and displacement reactions characteristic of the free metalloporphyrin¹¹ and have also used well-chosen ligands to dramatically alter their dynamics.¹² Such weakly bound systems are unlikely to be sufficiently robust for catalytic applications, however, especially in the presence of a solvent where resistance to leaching is an essential attribute.

Very recently, we reported the first direct observation by scanning tunneling microscopy (STM) of *spontaneous* surface-mediated deprotection of a *free base* thiol-terminated porphyrin ([SAc]₄P-H₂) on Ag(100):¹³ such tethered porphyrins possess no inherent catalytic properties, of course. Here we extend this work into the domain of chemically active metalloporphyrins that are known to catalyze oxygen transfer reactions in solution.¹⁴⁻²¹ As explained above, this is the next step towards the creation of

hybrid heterogeneous selective oxidation catalysts. Our aim was to deposit the acetyl-protected porphyrin [SAc]₄P-Mn(III)Cl (Figure 1) on Ag(100), deprotect it by removal of the acetyl groups thus enabling covalent tethering to the surface by Ag-S bonds, and finally activate it by removal of the axial chlorine ligand. The actual sequence of events was followed under well defined conditions by means of synchrotron high-resolution X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD). In regard to their homogenous chemistry, manganese porphyrins are well known for their effectiveness as selective oxidation catalysts when used in conjunction with a single-oxygen donor.¹⁴⁻²¹ In the present case, the silver surface bearing oxygen adatoms is envisaged as the entity that will act the single oxygen donor.

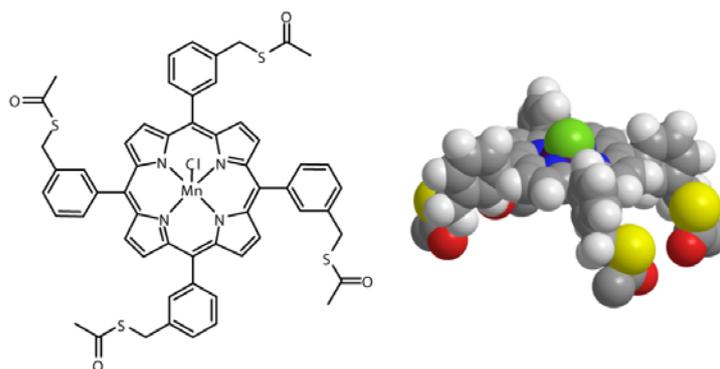


Figure 1. Molecular structure and 3D space-filling model of [SAc]₄P-Mn(III)Cl.

Experimental Methods

The free base 5,10,15,20-Tetrakis[3-(S-acetylthiomethyl)phenyl] porphyrin was synthesized using the method described by Lindsay *et. al.* in reference 3. Metallation of the free-base porphyrin was achieved in a mixture of acetic acid : acetic anhydride = 4 : 1 at 110°C using MnCl₂·4H₂O as the Manganese source. After completion of the reaction the remaining inorganic salts were filtered off leaving the pure [SAc]₄P-Mn(III)Cl porphyrin.

High resolution XPS was carried out on the SuperESCA beamline at the ELETTRA synchrotron radiation source in Trieste, Italy. Spectra were collected using a single-pass 32-channel concentric

hemispherical electron analyser and the angle between the entrance lens of the analyzer and the incoming photon beam was 70° in the horizontal plane. Experiments were performed with a photon incidence angle of 10° with respect to the surface. The Ag(100) crystal was attached to a motorised manipulator *via* a tantalum backplate fitted with a T1T2 thermocouple and could be heated resistively to 900 K or cooled to 77 K. Repeated cycles of Ar⁺ (99.999% Messer) sputtering followed by annealing at 800 K were carried out until a clean, atomically flat surface was obtained, as monitored by XPS and LEED.

Temperature programmed desorption experiments were conducted in Cambridge in an ultra-high vacuum chamber operated at a base pressure of 1×10^{-10} torr. The sample was exposed to gases by backfilling the chamber which was equipped with an Omicron 3 grid retarding field analyser for LEED/AES analysis and a VG 300 quadrupole mass spectrometer whose ionizer was positioned 5 mm from the front face of the sample. The Ag(100) single crystal could be cooled to 100 K and heated to 1400 K, monitored by a T1T2 thermocouple attached directly to the sample. The sample was cleaned by repeated cycles of Ar⁺ (99.999% Messer) sputtering followed by annealing at 700 K until a clean atomically flat surface was obtained, as observed by LEED and AES.

Porphyrins were deposited onto the Ag surface, both in Cambridge and in Trieste, by means of a resistively heated collimated evaporation source fitted with a T1T2 thermocouple. The (very small) amounts of porphyrin used were injected into the sublimation source as solutions in dichloromethane which were evaporated to dryness before mounting in the vacuum chamber.

Results and Discussion

Figure 2a shows the S 2p spectrum acquired following initial deposition of the porphyrin with the Ag(100) sample at 300 K. Three peaks are clearly evident which are due to two distinct, overlapping S 2p_{1/2,3/2} doublets. The emission at higher binding energy of 163.7 eV (red hatching) is due to thiol groups that are still acetyl protected. The component at lower binding energy, centered at 162.3 eV

(blue hatching), may be confidently assigned²² to *deprotected* thiol groups covalently bonded to the silver surface, after cleavage of the acetyl group.

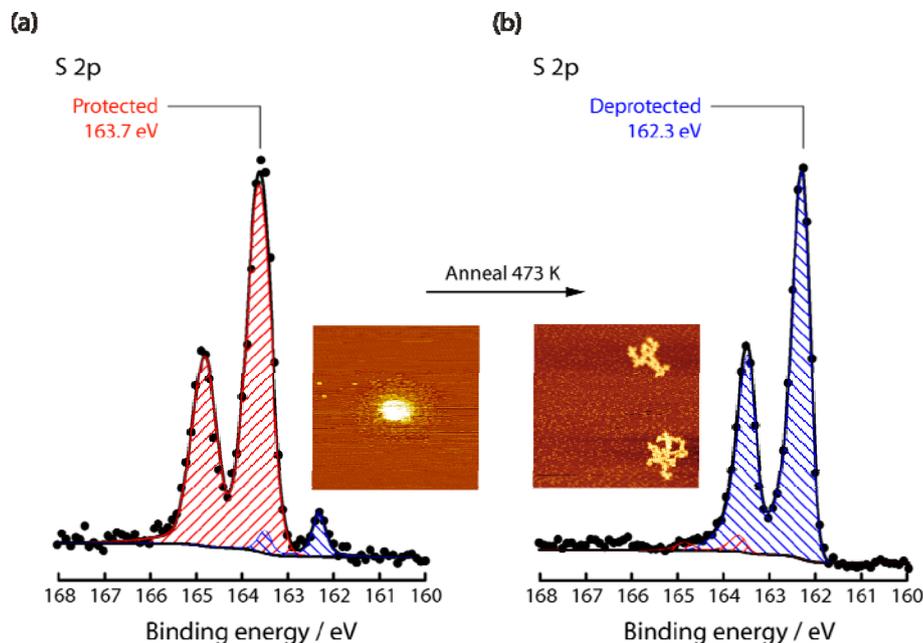


Figure 2. S 2p region of XP spectra acquired (a) immediately following porphyrin deposition and (b) after sub-sequent annealing at 473 K. As a guide, the XP spectra are overlaid with a representative STM image of a equivalent surface state for the free base porphyrin, [SAc]₄P-H₂, taken from reference 13 (left image: 900 Å × 900 Å, $V_{\text{tip}} = 1.5$ V, $I = 0.1$ nA; right image: 400 Å × 400 Å, $V_{\text{tip}} = 0.75$ V, $I = 0.05$ nA).

Annealing at 473 K for 15 minutes resulted in the XP spectrum shown in Figure 2b. Note that this procedure is the same as that used¹³ for dispersing and de-protecting the closely related *free base* porphyrin [SAc]₄P-H₂ where we were able to follow the surface processes by means of STM. For the purpose of illustration, the corresponding images taken from reference 13 are shown as insets to Figure 2. It is apparent from Figure 2b that 473 K annealing leads to essentially complete de-protection of remaining porphyrin. The presence of a single S 2p signal clearly indicates that all thiol groups are bonded to the silver surface.

Figure 3a shows the uptake of $[\text{SAc}]_4\text{P-Mn(III)Cl}$ as monitored by the S 2p emission; the right panel shows a plot of corresponding integrated intensities of the S 2p and Ag 3d emission as a function of dosing time. These data were acquired by depositing the porphyrin at room temperature followed by annealing at 473 K for 15 minutes to disperse the initially formed 2D islands and desorb any multilayer material, a process that occurred at ~ 425 K (see below): this deposition method provided a convenient way of preparing any given coverage in the submonolayer to monolayer regime. The procedure was then repeated in order to build up coverage from the submonolayer regime to that of a fully saturated covalently bonded monolayer. (No Mn 2p emission was ever observed, consistent with the small number density of Mn atoms on the surface, even at saturation coverage, and the relatively low value of the Mn photoionization cross section).

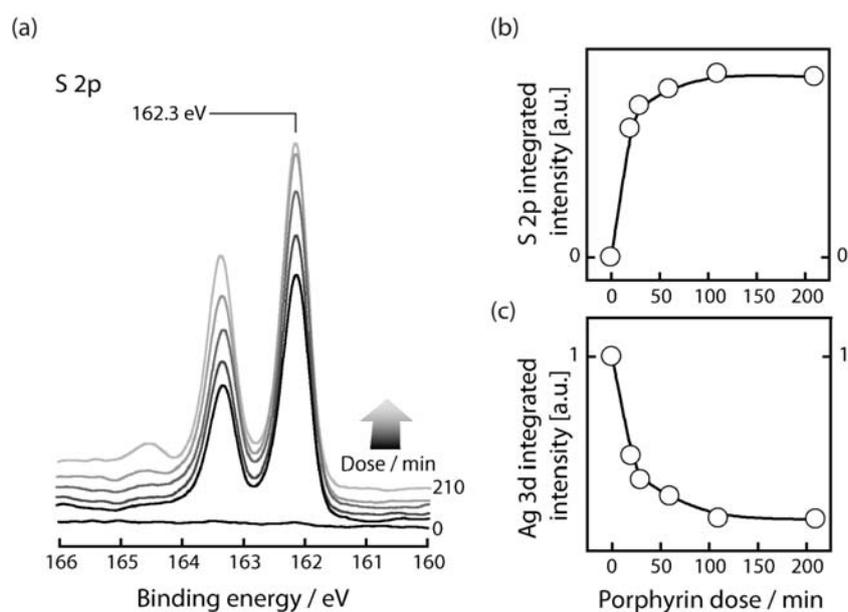


Figure 3. (a) S 2p region of XP spectra taken with increasing $[\text{SAc}]_4\text{P-Mn(III)Cl}$ porphyrin dose time. In each case the surface was annealed at 473 K for 15 min prior to recording the spectrum. (b) Integrated S 2p intensity for each curve, plotted with respect to porphyrin dose time. (c) Associated Ag 3d integrated intensities.

It is apparent from Figure 2 that at room temperature a small degree of thiol deprotection occurs immediately upon deposition. This implies that cleavage of acetyl groups is surface-mediated and that

the process is limited by the inability of most porphyrin molecules to access the surface as suggested by the inset to Figure 2a (i.e. the relevant STM image): the majority are present in large aggregates, and only those at the periphery can undergo deprotection. Elevated temperature increase porphyrin diffusion and deprotection (Figure 2), although even at room temperature, given sufficient time, a significant degree of deprotection occurs. Figure 4 illustrates an S 2p XP spectrum acquired 10 h after initial S deposition—the situation is intermediate between the two extreme cases of total protection/deprotection shown in Figure 2.

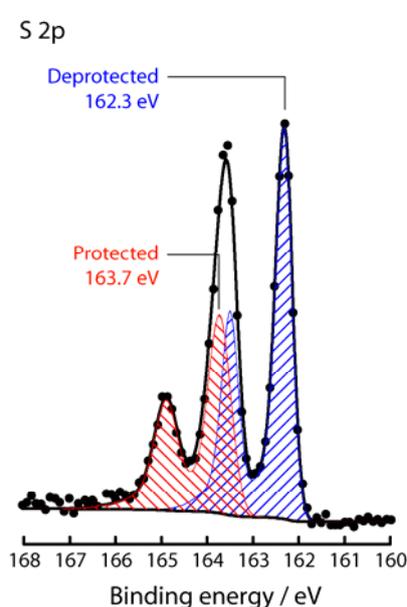


Figure 4. S 2p region of the XP spectrum acquired after initial deposition and following 10 hours left at room temperature. The protected S contribution is represented by red hatching; de-protected S is represented by blue hatching.

Figure 5a shows a series of temperature-programmed C 1s XP spectra acquired over the interval 298 K - 523 K with a ramp rate of 5 K s^{-1} , after deposition of $[\text{SAc}]_4\text{P-Mn(III)Cl}$. Upon porphyrin deposition, two C 1s signals were observed at 285.6 eV and 288.1 eV. Upon raising the temperature, the 288.1 eV component attenuated rapidly, disappearing by 523 K, at which point only the higher binding energy component remained, slightly downshifted to 285.4 eV. These two components are ascribed, respectively, to porphyrin molecules in contact with the Ag surface (285.6 eV) and molecules in the

second or higher layers (288.1 eV), the lower binding energy of the former reflecting greater final state screening of the C 1s core hole by the Ag valence electrons.²³

Figure 5b, showing the total integrated C 1s intensity as a function of temperature, is consistent with this interpretation. The initial slow decrease in the C 1s integrated intensity is principally due to evaporation of the more weakly held "multilayer" molecules, followed by a much faster decrease that sets in at 410 K due to desorption of molecules in the contact layer.

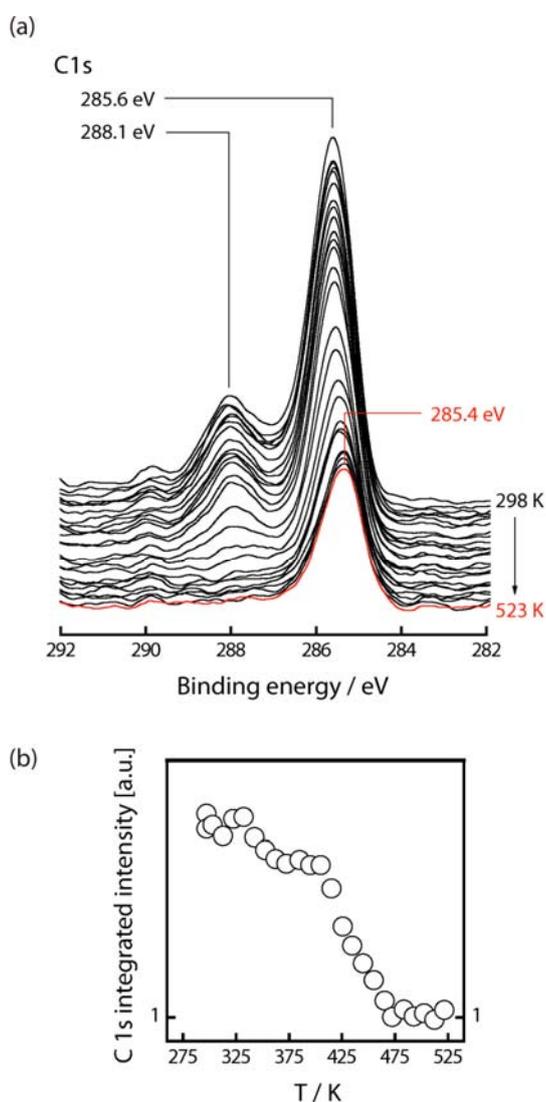


Figure 5. (a) C 1s region of the temperature-programmed XP spectrum acquired whilst applying a 5 K s⁻¹ temperature ramp from 298 K to 523 K. (b) C 1s integrated intensity of each curve plotted with respect to temperature.

Representative TPD measurements carried out after deposition of [SAc]₄P-Mn(III)Cl on Ag(100), are shown in Figure 6 for $m/z = 43$ (CH_3CO^+), $m/z = 35$ (Cl^+), $m/z = 32$ (S^+), the three data sets being acquired simultaneously; m/z values > 100 were beyond the range of the quadrupole mass spectrometer. The maximum at 425 K in the $m/z = 43$ profile is assigned to the CH_3CO^+ fragment ion due to protected porphyrin molecules desorbing from the contact layer ($m/z = 43$ was an intense signal in the mass spectrum of the porphyrin vapour from the evaporation source). This is in good agreement with the XPS results (Figure 5b) which exhibit a steep decline in C 1s intensity over the same temperature range. The TPD result also implies that upon raising the temperature some of the acetyl-protected molecules desorb intact, whereas others undergo de-protection and become strongly bound to the surface *via* S-Ag linkages. Correspondingly, the coincident feature at 425 K in the $m/z = 35$ spectrum is assigned to the Cl^+ fragment ion from intact desorbing porphyrin molecules.

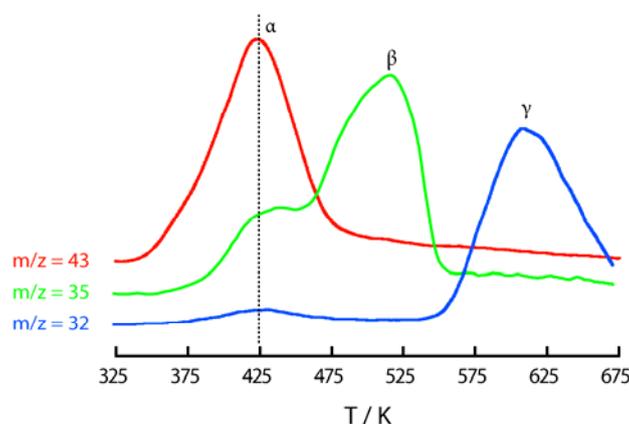


Figure 6. Temperature programmed desorption data acquired after dosing [SAc]₄P-Mn(III)Cl onto clean Ag(100). Curves correspond to: $m/z = 43$ (CH_3CO^+), $m/z = 35$ (Cl^+), $m/z = 32$ (S^+).

The Cl^+ desorption peak at ~ 515 K corresponds to loss of the manganese-bound chlorine ligand and in this connection the XPS results illustrated in Figure 7 are revealing. Examination of the Cl 2p emission before and after annealing the porphyrin layer at 473 K (onset of chlorine loss in Figure 6) for 15 minutes shows complete removal of Cl. Thus this relatively mild thermal treatment both deprotects

and immobilizes the porphyrin on the surface *and* leave the manganese metal centre in a low-coordination state, thus preparing it as a catalytically active site.

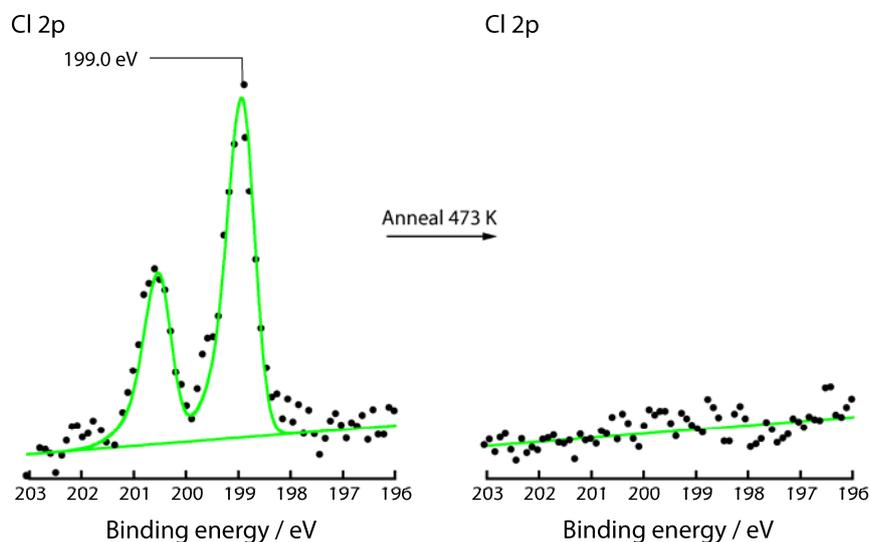


Figure 7. Cl 2p XP spectrum acquired after initial deposition of [SAc]₄P-Mn(III)Cl (left) and after subsequent annealing at 473 K for 15 min (right).

At temperatures above ~ 560 K the de-protected porphyrin molecules decompose with desorption of sulfur (Figure 6, 8) and formation of a carbonaceous residue (Figure 5(a,b)). The S 2p intensity that persists after heating to 673 K (Figure 8) is consistent with Figure 5 from which it is apparent that S desorption is incomplete at this temperature.

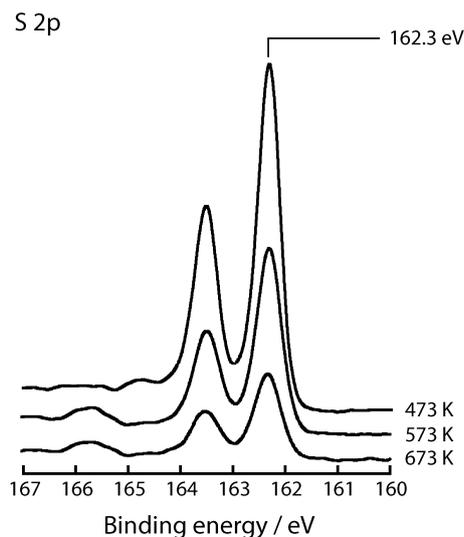


Figure 8. S 2p emission as a function of thermal treatment: spectra acquired after annealing the porphyrin-covered surface to the indicated temperature for 5 minutes.

Conclusions

The acetyl-protected manganese porphyrin, [SAc]₄P-Mn(III)Cl may be deposited on Ag(100) and subsequently deprotected leading to stable, covalently bound thioporphyrin molecules. These in turn may be de-chlorinated resulting in formation of stable, surface tethered low-coordinate Mn centers, thus establishing a methodology for creating thio-tethered activated species that could serve as catalytic sites for delicate oxidation reaction. These species appear to be stable to over 500 K which is well above the temperature range of the intended application.

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