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Reactions involving the central cavity of porphyrin molecules attached to self-assembled monolayers



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| ARTICLE INFO | A B S T R A C T |
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| Keywords: Surface Porphyrin Metalation Transmetalation Demetalation Self-assembled monolayer | In this work we studied the metalation, transmetalation and demetalation reactions of protoporphyrin (PPIX) molecules attached to self-assembled monolayers (SAM) grown over Au(111) surfaces at the solid/liquid interface. Using X-ray photoelectron spectroscopy we found that when the molecules attached to the SAM are immersed in Cu^{2+} or Zn^{2+} containing solutions, the degree of metalation is larger for Cu^{2+} than for Zn^{2+} . Furthermore, when ZnPPIX molecules attached to the SAM are placed in contact with a Cu^{2+} solution the partial exchange of Zn ions with Cu ions at the porphyrin central cavity is observed. This suggests that insertion of Cu^{2+} to form CuPPIX is both kinetically and thermodynamically favored over the insertion of Zn^{2+} in agreement with the solution chemistry of the molecules. Finally, unlike the behavior in solution, Zn and CuPPIX molecules attached to the SAMs are more stable against demetalation in acidic conditions. We attribute |

1. Introduction

Porphyrin molecules are heterocyclic compounds composed of 4 pyrrolic units connected via methine bridges. The molecules have a very strong UV–vis absorption, excellent photostability and a central cavity where a great diversity of transition metal ions can fit. Thus, the chemical reactivity as well as the electronic, optical and magnetic properties can be easily tuned providing diverse applications in sensors [1], catalysis [2], dye-sensitized solar cells [3], and in organic light emitting [4] and photoelectrochemical devices [5]. Chemical reactions that result in the insertion, exchange or removal of the metal atom from the central cavity are important since the identity of the metal center strongly influences the properties of the molecule.

The metalation of free-base porphyrin molecules involves the exchange of two pyrrole hydrogen atoms from the central cavity of the molecule with a metal ion. Although metalation on surfaces has been known for many years [6], it was observed recently at the molecular level under controlled conditions [7]. Since then, much effort has been expended to understand the factors controlling the reaction [8]. Metalation of surface porphyrins has been observed under different conditions such as metalation by metal atoms co-deposited on the surface [9], by metal atoms from the substrate [10], by ions from the oxide lattice [11], and by ions dissolved in solution [12].

this difference to the competing protonation of the amine terminal groups. Our results could be useful for the

design of molecular devices based on porphyrins that are exposed to liquid interfaces.

Metaloporphyrins adsorbed on surfaces can also undergo a transmetalation reaction, in which the central metal ion is replaced by coadsorbed metal atoms or by metal atoms from the substrate [13,14]. Insight into the on-surface transmetalation was gained with the investigation of the redox transmetalation of a monolayer of lead(II)tetraphenylporphyrin with copper from a Cu(111) surface [15]. Recently, the exchange of Zn^{2+} ions in the macrocycle by Cu^{2+} ions from solution on Zn porphyrins adsorbed on Au(111) surfaces was informed [16]. Although there are a few reports on the transmetalation of adsorbed porphyrins [13–17] there are still open questions regarding the mechanism governing this reaction, including the role of the surface.

Finally, the central metal ion can be removed from the porphyrin molecule central cavity and replaced by two protons in a reaction known as demetalation. This reaction has been observed under reducing conditions for porphyrin molecules adsorbed on metal electrodes [6,18]. Recently we have found that Zn and Cd porphyrin multilayer films adsorbed on Au(111) surfaces are less susceptible to losing their metal center when exposed to acidic solutions than dissolved molecules [19].

In this work we studied the metalation, transmetalation and

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Fig. 1. (a) Molecular structure of protoporphyrin IX (PPIX) and (b) steps followed to covalently attach PPIX molecules to a 16-amino-1-hexadecanethiol self-assembled monolayers on Au(111) (see reference 20 for a detailed description).

demetalation reactions of porphyrin molecules attached to selfassembled monolayers (SAM) at the solid/liquid interface. Protoporphyrin IX (PPIX, see Fig. 1a) molecules were attached to a SAM of 16amino-1-hexadecanethiol grown on a Au(111) surface through the formation of an amide bond following the procedure we used successfully in the past (see Fig. 1b) [20]. In this system the porphyrin molecules are separated from the Au(111) metal surface by the SAM layer uncoupling the influence of the metal surface from the molecular reactivity.

2. Experimental section

2.1. Materials

All the experiments were carried out using a Au(111) single crystal (MaTeck GmbH). Protoporphyrin IX (PPIX), Protoporphyrin IX zinc (II) (ZnPPIX), 16-amino-1-hexadecanethiol hydrochloride, 1-ethyl-3-(3-dimethylamino-propyl) carbodiimide (EDC), *N*-hydroxysuccinimide (NHS), zinc acetate, and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich and used as received.

2.2. Sample preparation

The Au(111) single crystal was cleaned by sputtering-annealing cycles until no impurity signals were observed by XPS. All the experiments were carried out in a liquid cell attached to the UHV chamber under an Ar atmosphere (fully described elsewhere) [21]. The PPIX/SAM/Au(111) system was prepared by placing the clean Au crystal in contact with a 1 mM 16-amino-1-hexadecanethiol ethanolic solution for 4 h at room temperature. Afterwards, the Au crystal was removed from the solution, rinsed with 25 ml of ethanol and dried in an Ar stream. In the meantime, a 0.3 mM PPIX, 8 mM EDC and 4 mM NHS solution in DMSO:H₂O (1:1) was incubated for 1 h to activate the carboxylic group for the amidation reaction. In a second step, the functionalized SAM surface was immersed overnight in the PPIX solution. Subsequently, the sample was removed from solution, rinsed with 25 ml of DMSO, and dried in an Ar stream. The same procedure was followed to prepare the ZnPPIX/SAM/Au(111) system. Formation of PPIX multilayers was



Fig. 2. N 1 s XP spectra corresponding to the SAM-functionalized Au(111) surface, to PPIX molecules bound to the SAM-functionalized surface, to multilayers of PPIX deposited on the Au(111) surface, and to a monolayer of ZnPPIX deposited on the Au(111) surface.

possible by impregnating the Au crystal with a PPIX solution and allowing the solvent to evaporate, since attempts to deposit PPIX molecules on the Au(111) surface by evaporation resulted in molecular fragments.

2.3. X-ray photoelectron spectroscopy

XPS measurements were performed in a UHV chamber (base pressure below 5×10^{-10} mbar) equipped with a 150 mm hemispherical SPECS electron energy analyzer and a nine channeltron detector. All XP spectra were acquired using a monochromatic Al K α (1486.6 eV) X-ray source operated at 15 kV and 20 mA with a detection angle of 20° with respect to the surface normal. The binding energies were corrected by referring them to the aliphatic carbon emission at 285 eV.

3. Results and discussion

Fig. 2 shows the N 1 s XP spectra corresponding to two different stages in the surface functionalization: (i) after the formation of the 16amino-1-hexadecanethiol (NH2C16) SAM, and (ii) after binding PPIX molecules to the SAM. The N 1 s region also shows the reference spectrum corresponding to multilayers of PPIX deposited on the Au(111) surface in the absence of the SAM and to a monolayer of ZnPPIX molecules also deposited directly on the Au(111) surface. Note that the bottom 3 spectra correspond to the experiments reported in our previous investigation [20]. The spectrum corresponding to the NH₂C₁₆ SAM shows a broad signal with two important contributions: one at \sim 400 eV due to the amino group (–NH₂) and another at ${\sim}402$ eV due to the protonation of the amino group (-NH₃⁺) [22]. Amino groups could be protonated when the surface is rinsed with protic solvents after the functionalization or reaction steps. When PPIX molecules bind to the NH₂C₁₆ SAM a change in the shape of the XPS spectrum is observed. The most evident change is the appearance of a new contribution at \sim 397.7 eV due to the two iminic nitrogen atoms (=N-) in the porphyrin



Fig. 3. N 1 s and Zn $2p_{3/2}$ XP spectra before and after placing the PPIX/SAM/Au(111) surface (top spectra) and the SAM/Au(111) surface (bottom spectra) in contact with a 0.01 M Zn²⁺ solution in acetonitrile (AcCN) at room temperature for 1 h.

molecules [23]. The contribution of the two amine (–NH-) atoms in PPIX is expected at ~ 399.9 eV, overlapping with the –NH₂ signal of the underlying SAM as shown by the spectrum corresponding to the PPIX multilayers. This is considered by fitting a peak at ~399.9 eV with the same area as the iminic nitrogen atom peak. In addition, a small contribution at ~400.8 eV due to the amide bond (–NC=O) [24] formed once the molecules are bound to the SAM is expected. The reference spectrum of a monolayer of ZnPPIX molecules deposited on the Au(111) surface shows a single peak at 398.5 eV due to the four equivalent nitrogen atoms (*N*-Zn). There is 1 PPIX molecule covalently bonded to the surface every approximately 10 amine/protonated amine functional groups as estimated from the N 1 s XPS signals.

Fig. 3 shows the N 1 s and Zn $2p_{3/2}$ XP spectra before and after placing the PPIX/ SAM/Au(111) surface in contact with a 0.01 M Zn²⁺ solution in acetonitrile (AcCN) at room temperature for 1 h. Fig. 3 also shows the spectra before and after a SAM/Au(111) surface, ie. without

the attached PPIX molecules, is placed in contact with the Zn²⁺ solution under the same conditions. Contacting the SAM/Au(111) surface with a Zn²⁺ containing solution does not produce any significant changes in the XP spectra in either the N 1 s or the Zn $2p_{3/2}$ region. Furthermore, the absence of Zn^{2+} indicates that rinsing after extracting the surface from the solution removes all the Zn^{2+} cations that could be interacting with the terminal amino groups when the amino terminated SAM was in contact with the solution. However, exposure of the PPIX/SAM/Au (111) surface to the Zn^{2+} solution results in the presence of Zn on the surface even after copious rinsing. The amount of Zn remaining on the surface corresponds to a metalation of around 70 % of the PPIX molecules bound to the SAM. Moreover, the N 1 s spectrum measured after placing the system in contact with the Zn^{2+} solution could be adjusted by adding a new contribution at \sim 398.2 eV that corresponds to metalated porphyrin (N-Zn) molecules (see Fig. 2) with a peak area corresponding to 70% metalation. Previously we showed that when the



Fig. 4. N 1 s and Cu $2p_{3/2}$ XP spectra before and after placing the PPIX/SAM/Au(111) surface (top spectra) and the SAM/Au(111) surface (bottom spectra) in contact with a 0.01 M Cu²⁺ aqueous solution at room temperature for 1 h.

reaction is carried out using water instead of acetonitrile as a solvent only 20% of the porphyrin molecules attached to the SAM were metalated at room temperature [20]. The degree of protonated amine groups in the SAM should be higher if water is used as a solvent instead of acetonitrile hence providing increased repulsion to the positively charged Zn ions resulting in a lower degree of metalation.

The metalation reaction was also carried out using Cu^{2+} ions. For this purpose, the PPIX/SAM/Au(111) surface was placed in contact with a 0.01 M Cu^{2+} aqueous solution for 1 h at room temperature. Fig. 4 shows the N 1 s and Cu $2p_{3/2}$ XP spectra before and after the reaction. In the N 1 s region the component corresponding to the iminic nitrogen atoms of PPIX disappears after exposure to Cu^{2+} and a new component corresponding to four equivalent nitrogen atoms appears. This indicates that metalation to form CuPPIX is complete. Thus, metalation of PPIX molecules covalently attached to self-assembled monolayers with Cu^{2+} ions is more favorable than metalation with Zn^{2+} ions. This is the same behavior observed when molecules are metalated in solution [25]. Given that using the less effective solvent resulted already in complete metalation with Cu^{2+} , no further studies were undertaken using acetonitrile as a solvent, where complete metalation is also expected. In the $Cu 2p_{3/2}$ region, two peaks appear after exposure, one centered at 934.6 eV, corresponding to the Cu^{2+} ions of the metalated CuPPIX molecules, and the other at 932.0 eV, indicating the presence of Cu on the gold surface [14,26]. Although the Au(111) surface is covered with a monolayer of aminothiols that should prevent Cu ions from reaching the surface, previous work has shown that copper is able to penetrate the SAM layer [27]. In fact, placing the SAM in contact with the Cu^{2+} solution under identical conditions results in the presence of the same Cu $2p_{3/2}$ XPS peak at 932.0 eV as shown in the bottom spectra of Fig. 4.

The 70% metalated ZnPPIX/SAM/Au(111) surface (see Fig. 3) was placed in contact with a 0.01 M aqueous solution of Cu^{2+} initially for 1 h and then for an additional 4 h. The N 1 s, Zn $2p_{3/2}$ and Cu $2p_{3/2}$ XPS spectra are shown in Fig. 5. The N 1 s spectra shows that complete metalation of the PPIX molecules is achieved after 1 h. This is



Fig. 5. XP spectra of the N 1 s (a), Zn $2p_{3/2}$ (b) and Cu $2p_{3/2}$ (c) regions corresponding to PPIX molecules bound to the SAM before and after immersion in a 0.01 M solution of Zn(AcO)₂ in acetonitrile at room temperature and subsequently in a 0.01 M aqueous solution of CuSO₄ for 1 h and 5 h. (d) Zn $2p_{3/2}$ peak area and Cu $2p_{3/2}$ porphyrin-related peak area as a function of immersion time.

accompanied by a decrease in the Zn^{2+} signal and an increase in the Cu^{2+} signal related to the porphyrin molecules (934.6 eV component). Increasing the time in solution results in a further decrease in the Zn^{2+} signal along with an increase in the Cu^{2+} component at 934.6 eV. Fig. 5d shows the peak areas (corrected by their respective sensitivity factors) of the Zn^{2+} and Cu^{2+} XPS signals as a function of time in the Cu^{2+} solution. In the case of the Cu $2p_{3/2}$ region, only the porphyrin-related peak at 934.6 eV was considered. These results indicate that part of the Zn^{2+} in the porphyrin ring is replaced by Cu^{2+} ions and that the amount of replaced Zn^{2+} increases as the exposure time to the Cu^{2+} solution increases. This suggests that metalation of protoporphyrin IX with Cu^{2+} over Zn^{2+} is not only favored kinetically but also thermodynamically, i. e. there is a higher energy gain upon complexation with Cu^{2+} .

Finally, the stability of Zn- and CuPPIX molecules against demetalation was studied. Fig. 6 shows the N 1 s and Zn $2p_{3/2}$ XP spectra before and after exposing the ZnPPIX/SAM/Au(111) surface to a pH = 4 solution at room temperature for 1 h. Note that the pH values chosen correspond to complete demetalation in solution [19]. Initially, only one N 1 s peak associated with the Zn PPIX molecules is observed at 398.0 eV accompanied by a single peak at 1021.4 eV in the Zn 2p_{3/2} region. After exposing the system to the acidic solution for 1 h, minor changes are observed. The area of the Zn peak decreased by 23 %, suggesting that 23% of the ZnPPIX molecules lost their metal center. In good agreement with this change, the area of the nitrogen peak corresponding to the metalated molecules also decreased in the same proportion and two new peaks appear at 397.7 eV and 399.7 eV due to the free-base porphyrin molecules formed. A very small peak at 403.8 eV probably due to the adsorption of impurities from the acidic solution is barely visible. Given that at this pH conditions complete demetalation in solution is observed [19], we conclude that attaching the molecule to the amino containing SAM decreases the degree of demetalation. This is probably due to the competing protonation of the amino groups that should prevent a higher



Fig. 6. XP spectra for the N 1 s and Zn $2p_{3/2}$ regions before and after placing the PPIX/ SAM/Au(111) surface in contact with a pH = 4 aqueous solution at room temperature for 1 h.



Fig. 7. XP spectra for the N 1 s and Cu $2p_{3/2}$ regions before and after putting in contact the PPIX/SAM/Au(111) surface with a pH = 2.5 aqueous solution at room temperature for 1 h.

degree of demetalation.

The case of CuPPIX demetalation is different. Fig. 7 shows the N 1 s and Cu $2p_{3/2}$ XP spectra before and after exposing a CuPPIX/SAM/Au (111) surface to a pH = 2.5 solution at room temperature for 1 h. Exposure to the acidic solution results in no observable changes in both the N 1 s and Cu $2p_{3/2}$ XP spectra. Moreover, the area of the Cu peak at 934.6 eV associated with the porphyrin molecules remains constant. The only noticeable change is a decrease in the amount of Cu in contact with the Au surface (932.1 eV), probably due to partial diffusion into the solution. This indicates that under these conditions CuPPIX molecules attach to amino SAMs do not suffer demetalation. This suggests that the activation barrier for demetalation of Cu porphyrin molecules is larger than that of Zn porphyrins.

4. Conclusions

Free-base protoporphyrin IX molecules were attached to amino terminated self-assembled monolayers grown on Au(111) surfaces via an amidation reaction. Exposing the molecules attached to the SAM to Zn^{2+} solutions result in partial metalation, whereas exposure to Cu^{2+} solutions result in complete metalation. Furthermore, when ZnPPIX molecules attached to the SAM are exposed the Cu^{2+} solutions the partial exchange of Zn ions with Cu ions at the molecule central cavity is observed. This suggests that insertion of Cu^{2+} to form CuPPIX is favored over the insertion of Zn^{2+} in agreement with the solution chemistry of the molecules. Finally, unlike the behavior in solution Zn and CuPPIX molecules attached to the amino terminated SAMs are more stable against demetalation in acidic conditions. We attribute this difference to

the competing protonation of the amine terminal groups. Our results shed new light into reactions involving the metal center in surface porphyrins and are therefore relevant in the design of molecular devices based on porphyrins.

CRediT authorship contribution statement

Cynthia C. Fernández: Investigation, Formal analysis, Writing – original draft. **Federico J. Williams:** Funding acquisition, Project administration, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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