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# Surface Enhanced Infrared Absorption and UV-Vis Spectroscopic Study of a Monolayer Film of Protoporphyrin IX Zinc (II) on Gold

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This paper describes preparation and structural characterization of a self-assembled monolayer film of protoporphyrin IX Zinc (II) by surface enhanced infrared absorption, normal infrared reflection absorption, and ultraviolet-visible spectroscopies.

## 1. INTRODUCTION

Axial ligation of metalloporphyrins to a ligand terminated self-assembled monolayer (SAM) formed on solid substrates offers a simple and effective way to prepare porphyrin monolayers [1]. It is, however, not always easy to employ surface infrared spectroscopy, due to poor S/N ratio, to probe these monolayers [1a]. Surface enhanced infrared absorption spectroscopy (SEIRAS) has recently proven to be a powerful tool in study of surface monolayer films [2]. We report herein on characterization of a SAM of protoporphyrin IX Zinc (II) (ZnPP) on an Au island film by SEIRA and ultraviolet-visible (UV-vis) spectroscopies. Two step strategy was employed to prepare the SAM of ZnPP on Au surface: formation of a SAM of 4-pyridinethiol (PySH) as a coupling layer on Au surface and then axial ligation of ZnPP to the pyridine SAM.

## 2. EXPERIMENTAL

ZnPP (Figure 1) and PySH were purchased from Aldrich and used as received. A 200 nm thick Au evaporated glass substrate was used for infrared reflection absorption spectra (IRAS) and UV-vis RAS measurements. It was

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treated with piranha solution ($H_2SO_4$: 30% $H_2O_2$ 3:1 v/v) prior to SAM formation. A 15 nm Au island film that was used for SEIRAS measurements was prepared via thermal evaporation onto a flat glass substrate in a vacuum chamber at a pressure of $10^{-6}$ Torr.

Formation of a SAM of PySH onto Au substrate was described elsewhere [3]. The SAM was then immediately immersed into an ethanol/DMF (4:1 in v/v) solution of ZnPP ($2 \times 10^{-4}$ M) and kept for 72 hours at room temperature. After withdrawal, the sample was sonicated in the ethanol/DMF mixed solvent for 1 min. (the SAM on the Au island film) or 5 min. (the SAM on the thick Au substrate). Finally, it was rinsed again with a copious amount of the mixed solvent.

UV-vis RAS were taken on a Shimadzu UV-2200 Spectrophotometer with a reflection attachment. Measurement of IR spectra in reflection mode was performed on a Bio-Rad FTS 575C FT-IR Spectrometer with a Harrick reflectance attachment at an incidence angle of 75°.

## 3. RESULTS AND DISCUSSION

### 3.1. UV-vis spectra

Figure 2 presents UV-vis (a) RAS of the porphyrin SAM on a thick Au substrate and (b) transmission spectrum (TRS) of the porphyrin SAM on the Au island film. For comparison, a UV-vis spectrum of ZnPP in ethanol/DMF (4:1 in v/v) is added as (c). The solution shows a strong band (Soret band) at 417 nm and two weak bands (Q bands) at 545 and 583 nm. For the porphyrin SAM on the Au island film, the spectrum shows the Soret band at 422 nm, suggesting formation of a SAM of ZnPP. In addition, small Soret band shift reveals weak effect of axial ligation on electronic structure of the porphyrins [3]. However, for the thick Au film, the spectrum gives rise to a strong band at 433 nm and another unresolved broad absorption band at about 480 nm occurring as a shoulder on the former band. This phenomenon was also previously observed by Zhang, one of the present authors and his colleagues [4] in a study of LB film of a long alkyl chain appended porphyrin on Au. It was confirmed now that the spectral differences between the porphyrin SAMs formed on Au island film and on thick Au surface are mainly due to spectral distortion caused by the UV-vis RAS measurement. The UV-vis results indicate successful formation of the ZnPP SAM on both kinds of Au films precoated with a SAM of PySH.



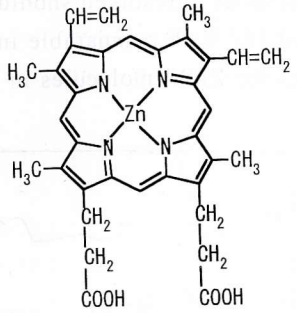


Fig. 1. Structure of ZnPP

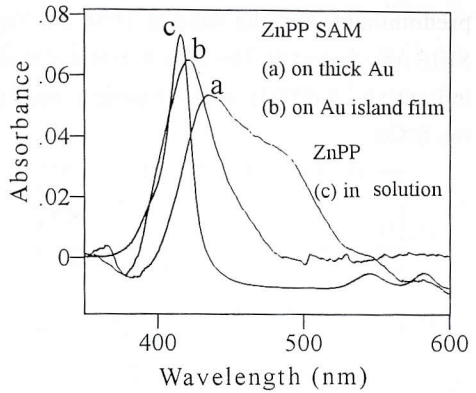


Fig. 2. UV-vis (a) RAS, (b) TRS of ZnPP SAM, and (c) TRS of ZnPP solution (a.u.)

### 3.2. IR spectra

Figure 3 exhibits (a) SEIRAS in reflection mode and (b) normal IRAS in 1700-1400 $cm^{-1}$, of a SAM of PySH on the Au island film and on the thick Au surface, respectively. The bands at 1612, 1564, and 1474 $cm^{-1}$ can be assigned to the stretching modes 8a, 8b, and 19a of the pyridyl group, respectively [3]. Compared to the normal IRAS, the three IR absorption bands in the SEIRAS show drastic enhancement of 10, 26, and 17, respectively.

Figure 4 presents (a) SEIRAS and (b) IRAS of the porphyrin SAM on the 15 nm Au island film and on the thick Au surface, respectively, precoated with the SAM of PySH, and (c) IR spectrum of ZnPP solid in KBr pellet. Two bands at 1725 $cm^{-1}$ and 1658 $cm^{-1}$ are due to C=O stretching mode of the carboxylic acid group, and the skeleton of the porphyrin molecule, respectively [5]. The band at 1576 $cm^{-1}$ is due to 8b mode of the pyridyl group. These bands are significantly enhanced in the SEIRAS, being 19, 35, and 25 times, respectively, stronger than the corresponding bands in the normal IRAS. Moreover, a weak peak at 1476 $cm^{-1}$, assignable to the 19a stretching mode of the pyridyl group, and a medium band at 1385 $cm^{-1}$, due to the C-H deformation of the alkyl part of the porphyrin molecule, either of which was not detected in the normal IRAS, are clearly seen in the SEIRAS. These facts strongly demonstrate that SEIRAS is more suitable for study of surface structures, compared with normal IRAS. It is also interesting to mention that, the band at 1576 $cm^{-1}$ in the SEIRAS of the SAM of PySH before and after the formation of the porphyrin SAM shows no noticeable alteration in band intensity, but a frequency shift by 12 $cm^{-1}$, suggesting the effect of axial ligation on the vibration mode of the pyridine. Another feature is that, in the KBr spectrum, the band at 1725 $cm^{-1}$ is

predominant, and the band at 1658 $cm^{-1}$ appears just as an unresolved shoulder. In the SEIRAS, however, the two bands are well resolved and with comparable intensities, indicative of different environment and interactions for ZnPP molecules in solid and the SAM.

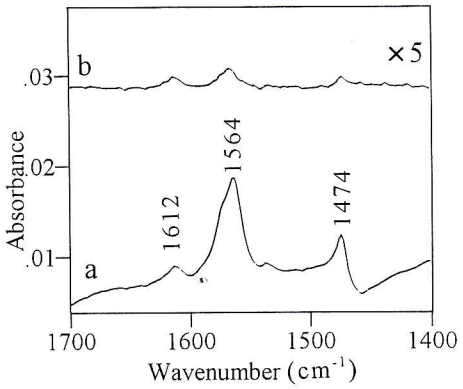


Fig. 3. (a) SEIRAS and (b) IRAS of a SAM of PySH on Au surface.

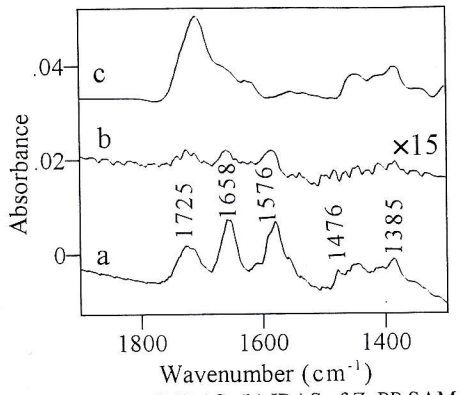


Fig. 4. (a) SEIRAS, (b) IRAS of ZnPP SAM and (c) IR TRS of ZnPP solid in KBr (a. u.).

## 4. CONCLUSIONS

Conclusions reached from this work include: (1) UV-vis spectra suggest formation of ZnPP SAM and weak interactions between ZnPP molecules in the SAM. In addition, formation of the SAM on Au island film allows us to measure UV-vis spectra in transmission mode that avoids spectral distortion occurring in the UV-vis RAS. (2) SEIRAS offers much more detailed structural information than normal IRAS in study of the porphyrin SAM.

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