

Surface-Enhanced Raman Scattering and Surface-Enhanced Infrared Absorption Spectroscopic Studies of a Metalloporphyrin Monolayer Film Formed on Pyridine Self-Assembled Monolayer-Modified Gold

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A self-assembled monolayer film (SAM) of 2,3,7,8,12,13,17,18-octaethylporphinatozinc formed on a gold surface premodified with a SAM of 4-pyridinethiol was studied by means of surface-enhanced Raman scattering (SERS), surface-enhanced infrared absorption (SEIRA), and ultraviolet–visible (UV–vis) spectroscopies. The SERS spectrum of the porphyrin monolayer on the pyridine-modified Au surface shows bands only from the underlying pyridine group. The frequency shift and change in the relative intensity of the bands due to the pyridine group in the SERS spectra imply indirectly the binding of the metalloporphyrin to the pyridine group in the SAM. This is further supported by the SEIRA spectra of the porphyrin–pyridine SAM, in which vibrational bands arising from both the porphyrin moiety and the pyridyl group appear clearly. In addition, the UV–vis spectra also suggest the formation of the porphyrin–pyridine SAM and the weak porphyrin–porphyrin interactions in the SAM.

Introduction

Axial ligation of metalloporphyrin derivatives to a ligand-modified metal or oxide surface to form a monolayer or multilayer films is of ever-increasing interest^{1–10} due to the following advantages of the method. One is that self-assembled monolayer (SAM) films of metalloporphyrins can be formed readily under ambient conditions by simply immersing a SAM of ligand on a surface into a solution of a metalloporphyrin. The second merit is its versatility in preparing ultrathin solid films of various porphyrins and the related compounds. The arrangement of each component in the molecular architecture is essentially important for their practical applications. The frequently used surface analytical techniques such as X-ray photoelectron spectroscopy (XPS), infrared reflec-

tion–absorption spectroscopy (IRAS), and ultraviolet–visible (UV–vis) spectroscopy provide only partial structural information of layered assemblies and, therefore, are far from enough for exploring the detailed structure–function relationship.

There are some works on structural characterization of molecules adsorbed on metal surfaces investigated by combination of IR, Raman, and other techniques.^{11–15} To provide new insight into the chemical mechanism operating in surface-enhanced Raman scattering (SERS) of a SAM of *p*-aminothiophenol on Ag island films, Osawa et al.¹¹ employed surface-enhanced infrared absorption spectroscopy (SEIRAS). Since measuring IR and Raman spectra of the same sample yields complementary and reliable information on the structure of the adsorbed molecules, they could obtain new and unique information about the vibrational properties and molecular orientation in the SAM. Han and his colleagues¹⁵ investigated the structure of a SAM of 1,4-phenylene diisocyanide on a Ag island film. The conclusions drawn from their IR results, including SEIRAS data, were strongly supported by the SERS spectra of the SAM. These investigations have demonstrated that the combined use of SERS and SEIRAS is powerful for structural characterization of well-ordered monolayer films on a metal surface fabricated by SAM and/or Langmuir–Blodgett (LB) techniques. There are still, however, very limited reports on this area, and further

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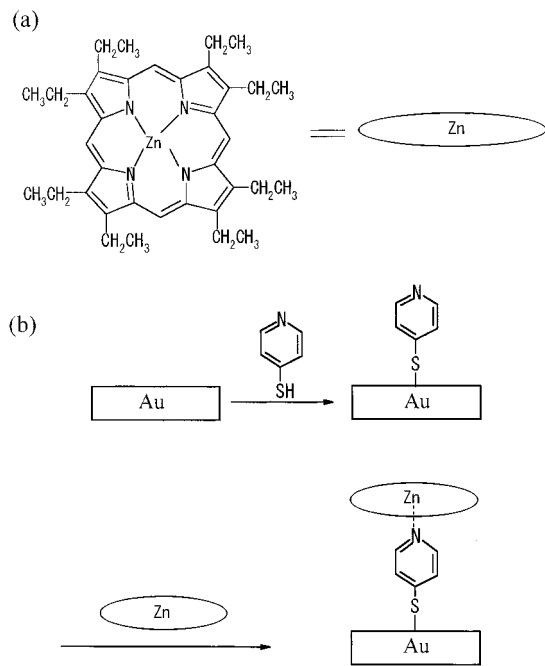


Figure 1. (a) Structure of 2,3,7,8,12,13,17,18-octaethylporphinatozinc and (b) procedure for the preparation of a monolayer film of ZnOEP on a 4-pyridinethiol SAM-modified Au substrate.

investigations are highly desired for taking advantage of the complementary utility of SERS and SEIRAS in surface analysis.

In this paper we report a normal Raman scattering and SERS, normal IRA and SEIRA, and UV-vis spectroscopic investigation of a SAM of 2,3,7,8,12,13,17,18-octaethylporphinatozinc (ZnOEP) on a gold island film precoated with a SAM of 4-pyridinethiol (PySH). The structure of ZnOEP and a simplified approach to formation of the porphyrin monolayer are shown in Figure 1. In this method, the SAM of PySH is formed on the Au island film in advance, which serves as an axial ligand for coordination bonding of the metal center of the porphyrin to it. The present work demonstrates that the combination of SERS and SEIRA techniques enables us to obtain selectively structural information from the porphyrin or the pyridyl moiety, or both, in the composite film consisting of a SAM of ZnOEP and a SAM of PySH on a Au island film. Such work is especially important for structural investigation of multilayer films consisting of different components.²⁻⁶

Experimental Section

Chemicals. The samples ZnOEP and PySH were purchased from Aldrich and used as received. Other reagents used in the experiment were all commercially available and in analytical grade.

Au Substrates. The 10 nm thick Au island films used as SERS- and SEIRA-active substrates were prepared by thermal vapor evaporation onto flat glass slides in a vacuum chamber at a pressure of about 10^{-6} Torr.¹⁶ The thickness and deposition rate were monitored with a quartz crystal oscillator. The deposition rate was kept at 0.1 Å/s throughout the deposition process. Thick Au films (200 nm in thickness) evaporated on glass with a 150 nm chromium film as an adhesion layer were used to form the pyridine and porphyrin SAMs for the normal Raman and normal IRA spectral measurements. Prior to the formation of the SAMs, the thick Au substrates were treated with "piranha solution" to remove organic contaminants physisorbed on the surface.⁷

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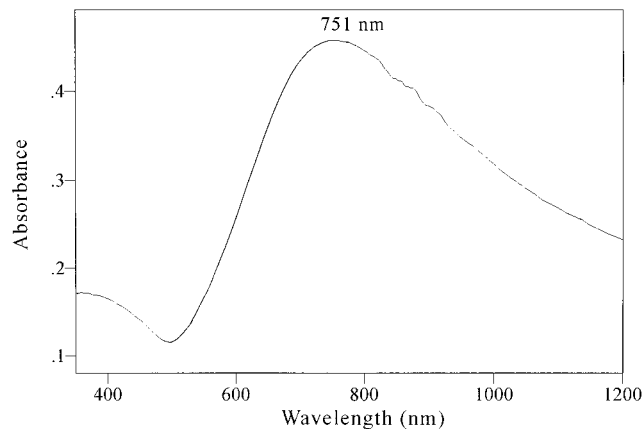


Figure 2. UV-vis-near-IR transmission spectrum of a Au island film (10 nm in thickness).

SAM Formation. Procedures for preparing SAMs of PySH and then formation of a metalloporphyrin monolayer film by axial ligation to it have been described previously.^{6,10} Briefly, a SAM of PySH was fabricated by soaking a freshly prepared (or cleaned) Au island film (or thick Au substrate) in an ethanol solution of PySH (1×10^{-3} M) for 3 min at room temperature, followed by copious rinsing with ethanol. After spectral measurement, the SAM-coated substrate was then immersed into an ethanol solution of ZnOEP (5×10^{-4} M) for 24 h under ambient conditions to form a monolayer film of ZnOEP. Followed by thorough rinsing, spectra were taken again. Care must be taken during the washing and handling processes to avoid peeling off or scratching the Au island film.

Instruments. (1) *Electronic Absorption Spectra.* UV-vis (or UV-vis-near-IR) transmission spectra were recorded on a Shimadzu UV-2200 (or 3101PC UV-vis-near-IR) spectrophotometer. A blank Au island film on glass was always used as a reference to obtain absorption spectra of the bare Au island film or the porphyrin SAM.

(2) *Raman Spectra.* Near-infrared FT-Raman spectra were measured using a JEOL JRS 6500N FT-Raman spectrometer equipped with an InGaAs detector. The spectra were collected at a 4 cm^{-1} resolution, and 2000 scans were co-added to ensure a good signal-to-noise ratio. The laser power used was 200 mW.

(3) *IR Spectra.* Infrared spectral measurements were carried out with a Bio-Rad FTS 575C FT-IR spectrometer equipped with a liquid nitrogen cooled MCT detector. All spectra were acquired with 1024 scans at a 4 cm^{-1} resolution. IR spectra of all SAMs formed on the metal surface were measured in reflection-absorption modes using a Harrick reflectance attachment with an incidence angle of 75° . A spectrum of the bare Au substrate measured as a single beam before the formation of the SAM was usually used as the reference except as noted otherwise.

Results and Discussion

UV-Vis Spectra. A UV-vis transmission spectrum of a bare Au island film with a thickness of 10 nm is shown in Figure 2. A strong and broad band appears in the visible region, extending further to the near-IR and mid-IR regions. This band results from excitation of the surface plasmon mode of the Au island film that is responsible for the observed SERS and SEIRA effects.¹⁷

Figure 3 presents UV-vis spectra of ZnOEP (a) in a chloroform solution and (b) in a SAM formed on the Au island film precoated with a SAM of PySH. The solution exhibits a strong band (the Soret band) at 406 nm. In the case of the porphyrin monolayer film, the Soret band

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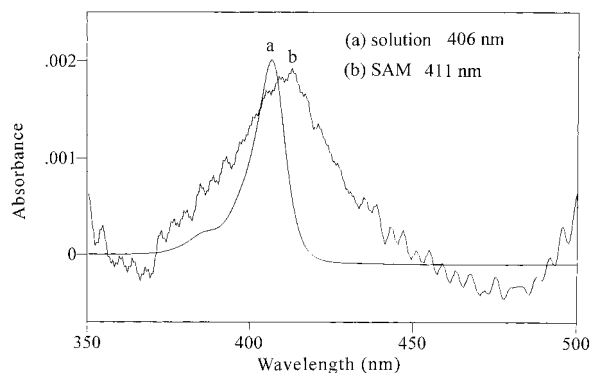


Figure 3. UV-vis transmission spectra of ZnOEP (a) in an ethanol solution (au) and (b) as a monolayer film on a pyridine SAM-modified Au island film.

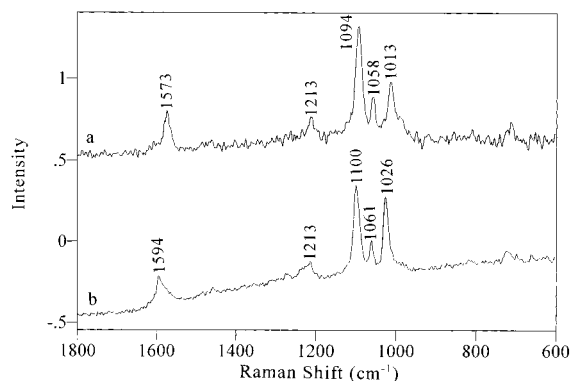


Figure 4. Near-infrared SERS spectra of a SAM of 4-pyridinethiol on a Au island film (a) before and (b) after the formation of a monolayer film of ZnOEP.

appears at 411 nm, which is 5 nm red-shifted and broadened in comparison with the solution profile. This suggests successful formation of a porphyrin SAM on the Au island film. The red shift and broadening of the Soret band reflect the influence of binding of the porphyrin to the pyridine and the difference in chromophore-chromophore interactions in the film environment and in solution.¹ The small red shift by 5 nm and broadening of the Soret band in the present case indicate rather weak interaction of the porphyrin molecules in the film.

Raman Spectra. Raman spectra were measured using near-infrared excitation at 1064 nm to avoid problems caused by strong fluorescence and undesired photoreaction of chromophoric groups of the adsorbed molecules,¹³ which often occur during Raman measurement of porphyrin and its related compounds. It is also well-known that near-infrared excitation is very suitable for SERS of thin films on Au substrates.¹³ In the present work, Raman spectra of the SAM of PySH on a 200 nm thick Au substrate and that of the monolayer of ZnOEP formed on the PySH-modified thick Au substrates were measured using an excitation wavelength of 1064 nm, but no signals from the adsorbed molecules were detected due to low sensitivity of the normal Raman spectra for monolayer films (data not shown). The corresponding SAMs of the PySH on the Au island film and ZnOEP on PySH-modified Au island films, however, give rise to distinct bands due to the adsorbed pyridine species in the Raman spectra.

Figure 4 gives SERS spectra of a SAM of PySH on the Au island film (a) before and (b) after the reaction with ZnOEP solution. It was found that there is no substantial change in the spectral profiles for the SAM of PySH on the Au island film before and after the formation of the

ZnOEP monolayer film. That is, the bands due to vibration modes of the porphyrin moiety were not detected. A similar phenomenon was also observed previously by other researchers.^{18–20} The phenomenon was explained in terms of a lack of resonance- and distance-dependent SERS effects.²⁰

In the present experiment, since the surface plasmon band of the 10 nm Au island film is located at 751 nm (Figure 2), whereas the strong Soret band of ZnOEP appears at about 410 nm (Figure 3), it is difficult to induce surface-enhanced resonance Raman scattering (SERRS) effects. Zhang et al.⁶ previously investigated formation of a SAM of cobalt(II) 5,10,15,20-tetrakis-phenylporphyrin formed on a PySH SAM on a Au surface. They obtained successfully SERS spectra of the porphyrin SAM, on which a monolayer of Au nanoparticles encompassed by an adsorbed layer of citric acid^{21,22} was deposited as a SERS-active substrate. Their work suggests that distance-dependent SERS effects are not important. Therefore, a conclusion could be drawn for the present case; that is, failure to observe SERS of ZnOEP is mainly due to a lack of resonance Raman effects rather than the distance between the ZnOEP molecule and the Au island film.

It is, however, interesting to point out that the SERS bands arising from the SAM of PySH on the Au island film before and after binding ZnOEP do show significant changes in frequency and relative intensity. The band at 1573 cm^{-1} due to a stretching mode of the pyridyl ring shifted to 1594 cm^{-1} after the formation of the ZnOEP monolayer. Changes were also observed for three bands in the 1000–1100 cm^{-1} region. Yamada and Yamamoto²³ observed substantial spectral changes in the same region in the Raman spectra of pyridine adsorbed on a metal oxide surface and assigned these changes to different binding types of the pyridine on the metal oxide surface. Therefore, our observation of changes for the three bands in the 1000–1100 cm^{-1} region implies binding of the metal ion of the porphyrin to the nitrogen atom of the pyridyl group.

IR Spectra. As in the case of Raman spectra, we measured normal IRAS and SEIRAS of the pyridine and ZnOEP SAMs formed on a thick Au surface and on a Au island film, respectively. The SEIRAS of PySH before and after binding ZnOEP are shown in spectra a and b, respectively, of Figure 5. A normal IRAS spectrum of ZnOEP bound to a SAM of PySH on a thick Au surface is also presented in Figure 5c. Both the IRAS and SEIRAS of the ZnOEP monolayer in Figure 5 were measured taking bare Au as the background. The IR spectrum for the same porphyrin monolayer was also recorded with the SAM of PySH on the Au island film as the background, which is shown in Figure 6a. A spectrum of ZnOEP solid dispersed in a KBr pellet is also presented in Figure 6b. To facilitate further structural analysis, the band assignment for ZnOEP as a SAM and in the solid state is given in Table 1, on the basis of previous literature.^{24–26}

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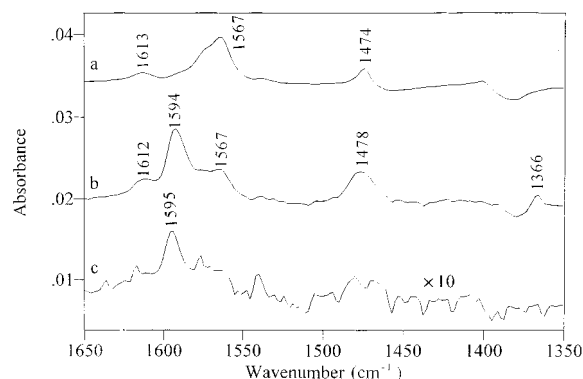


Figure 5. IR spectra of a SAM of 4-pyridinethiol on a Au island film (a) before and (b) after the formation of a monolayer film of ZnOEP. For comparison purposes, an IR spectrum of a ZnOEP SAM formed on a 4-pyridinethiol SAM on a thick Au surface is added as spectrum c.

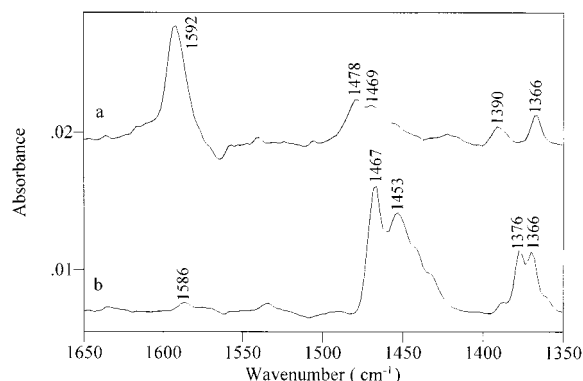


Figure 6. IR spectra of (a) a SAM of ZnOEP obtained with a Au island film precoated with a SAM of PySH as the background and (b) ZnOEP dispersed in a KBr pellet (au).

Table 1. Frequencies (cm⁻¹) and Assignment for the IR Bands of ZnOEP in the Solid State and a SAM

solid	SAM ^a	assignment ^b	solid	SAM ^a	assignment ^b
1586	1592	$\nu(\text{C}_\beta\text{C}_\beta)$	1453	d	ethyl
^c 1478		$\nu(\text{C}_\alpha\text{C}_m)$	1376	1390	$\nu(\text{C}_\alpha\text{C}_\beta)$, $\nu(\text{C}_\beta\text{C}_s)$
1467	1469	ethyl	1366	1366	ethyl

^a The IR data for a SAM of ZnOEP refer to spectrum a in Figure 6. ^b The designations C_α and C_β refer to the carbon atoms adjacent to the nitrogen atom and at the β -pyrrole position, respectively. C_m and C_s denote the methine bridge and the substituent, respectively. The symbol ν refers to the stretching mode. ^c Overlapped with the band at 1467 cm^{-1} .²⁴ ^d As a shoulder in the lower frequency side of the band at 1469 cm^{-1} .

There are two notable features in the IR spectra shown in Figure 5. One is that compared with the SAMs formed on a thick Au surface, the SAMs on Au island films do give distinctly enhanced IR absorption of the pyridine and some new bands corresponding to the ZnOEP moiety. For a SAM of PySH, the band at 1567 cm^{-1} due to the 8b vibration mode of the pyridyl group is 15 times stronger than the corresponding bands in IRAS of the same SAM (data not shown). As for the ZnOEP bounded to the SAM of PySH, the band at 1594 cm^{-1} due to the ZnOEP skeletal mode is 12 times stronger than the corresponding band in IRAS. Several peaks that were not detectable in the IRAS appear clearly in the SEIRAS, for example, bands at 1612 , 1567 , 1478 , and 1366 cm^{-1} .

The second interesting point is that, for ZnOEP bound to a SAM of PySH, the SEIRAS shows bands from both porphyrin and pyridine moieties, in contrast to the SERS of the same sample discussed above. As is shown in Figure

5b, the SAM of ZnOEP formed on the top of the SAM of PySH exhibits two new bands at 1594 and 1366 cm^{-1} due to the porphyrin, as well as three bands at 1613 , 1567 , and 1474 cm^{-1} due to the 8a, 8b, and 19a stretching modes of the pyridyl group.^{16,27}

It is interesting to mention that the SEIRAS of the ZnOEP–PySH composite film shown in Figure 5b was obtained with the bare Au island film as the background, and therefore, the bands due to the ZnOEP moiety as well as the pyridyl group appear simultaneously. The bands due to the pyridyl part can be eliminated when the IR spectrum of the composite film is measured by using the Au island film coated with the SAM of PySH as the background, as shown in Figure 6a. A strong band at 1592 cm^{-1} clearly results from the presence of ZnOEP, rather than the pyridyl moiety. The weak appearance of this band in the solid spectrum and the intensive presence in the SEIRAS and IRAS may be for two reasons: One is the structural change in the ZnOEP molecule caused by axial coordination reaction with the pyridine. The other may be associated with the surface selection rule in the SEIRAS and IRAS.^{11,12,17a}

The coupled bands at $1478/1469$ and $1390/1366\text{ cm}^{-1}$ in spectrum a correspond to bands at $1467/1453$ and $1376/1366\text{ cm}^{-1}$ in spectrum b of the ZnOEP solid, respectively. Interestingly, the bands at 1467 and 1376 cm^{-1} associated with the porphyrin core vibration modes are shifted significantly from the bulk to the SAM state, while those due to the ethyl substituent remain unchanged. The reason may be that binding of the metalloporphyrin to the pyridyl group alters the electronic state of the porphyrin molecule and thus the vibration modes of the porphyrin core while the binding imposes less effect on the vibration modes due to the ethyl substituent.

Combination of the SERS and SEIRAS results in the present study leads to a better understanding of the surface reaction of the metalloporphyrin with the pyridine, as we discussed above. Such a study also provides new insight into differences of the mechanisms operating in SERS and SEIRAS. It was originally expected that some vibrational modes of the porphyrin moiety appear in the SERS, like in the SEIRAS, of the same sample, since the two surface-enhanced vibrational spectroscopies share similar mechanisms.¹⁷ The absence of bands due to the porphyrin molecule in the SERS spectrum of the ZnOEP monolayer on the pyridine SAM-modified Au island surface, apparently, does not result from the distance of the porphyrin moiety from the Au island surface, which is only ca. 0.5 nm (thickness of a SAM of PySH). According to electromagnetic theory in SERS and SEIRAS, the enhancement can extend up to 5 nm from the metal surface.²⁸ The resonance Raman effect may be important in observed SERS of the porphyrin monolayer on the Au island surface separated by a layer of PySH, but it is still possible to observe enhanced Raman scattering of the ZnOEP with a lack of resonance effects, because the electromagnetic mechanism seems to play a dominant role in both SERS and SEIRAS. Clearly, observation of the bands due to the porphyrin in the SEIRAS but not in the SERS in the present case implies that the mechanisms for SERS and SEIRAS may not be completely the same.

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More theoretical and experimental work is desired for further understanding the origins responsible for SERS and SEIRAS.

Conclusions

We presented here a spectroscopic study on the formation of a ZnOEP monolayer film on a thick Au surface and on a Au island film with a SAM of PySH as the coupling layer. The main conclusions drawn from this study include the following: (1) On the basis of the SERS spectral results, it is concluded that the lack of resonance Raman effects is mainly responsible for failure to observe bands due to vibration modes from the porphyrin moiety. However, observations in the changes of the frequency and relative intensity of the bands due to the pyridyl group do suggest binding of the pyridyl group to the ZnOEP molecule. (2) In contrast to the SERS, the SEIRA spectra measured before and after exposure of the pyridine SAM to the

porphyrin solution exhibit rather different spectral features. The bands due to the vibrational modes of the porphyrin part appear clearly in the SEIRA spectrum. When ratioed to different background spectra, the SEIRA spectra obtained show bands due to vibrational modes of the porphyrin and the pyridyl groups, or those of the porphyrin moiety only. (3) Comparison between the SEIRA and SERS spectra of the porphyrin monolayer film formed on a pyridine SAM also provides mechanisms operating in SEIRA and SERS. Clearly, more work is desired for exploring the differences of the mechanisms for SERS and SEIRAS.

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