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Surface Enhanced Raman Spectroscopic Studies on Zn(II) and Mn(III) Tetrakis (4–N–Methyl Pyridyl) Porphyrins

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The surface enhanced Raman scatterings of Zn(II) tetrakis (4–N–methyl pyridyl) porphyrins were studied in silver sol. Zn(II) tetrakis (4–N–methyl pyridyl) porphyrin was found to be adsorbed on silver surface *via* flat-on geometry with some inhomogeneous distribution in the orientation of pyridyl groups. Both the selective enhancement of Raman modes depending on the mode character and the theoretical arguments of SERS are utilized to support the above conclusion. The surface induced substitution reaction of Mn(III) tetrakis (4–N–methyl pyridyl) porphyrin chloride to Ag(II) tetrakis (4–N–methyl pyridyl) porphyrin was detected *via* surface enhanced Raman spectrum.

Introduction

Surface enhanced Raman scattering (SERS) spectroscopy has proven to be a very powerful method for investigating the structures of the molecules adsorbed on metal surface.[1,2] Not only the application of this distinct phenomena to molecular systems but also the elucidation of the strong Raman signal enhancement mechanism has attracted a great attention. In addition, SERS spectroscopy has been utilized to study the surface chemical reaction induced by the surface and/or the laser beam because the reaction provides direct changes in SERS spectra of the adsorbed molecule.[1] Indeed, some observations of a surface reaction *via* SERS spectra have been reported on small molecules.[3]

Some applications of SERS to hemoproteins revealed that a change in molecular structure or conformation may occur when they are adsorbed on a silver surface.[4,5] More specifically, the adsorption of hemoproteins on the silver surface can facilitate the separation of the porphyrin macrocycle from the hemoprotein into the μ–oxo–bridged iron porphyrin dimer as a decomposition product from either thermally denatured or autooxidized hemoglobin.[4,5] For model compounds, Itoh *et al.*[6] reported that SERS on free-base TMPyP(4)H$_2$ in silver and copper mixed sol follows the formation of either Cu(II)TMPyP(4) or Ag(II)TMPy(4) through the metal insertion into the porphyrin core, depending on the ratio of the mixed sol and its pH.

In this paper, we examine the SERS of Zn(II)TMPyP(4) and Mn(III)TMPyP(4)Cl in silver sol to address the interaction between the metal surface and the adsorbed molecules. We found that no surface chemical reaction has occurred in

the SERS of Zn(II)TMPyP(4). However, in Mn(III)TMPyP (4)Cl, the surface induced substitution reaction has occurred and the formation of Ag(II)TMPyP(4) was observed by the SERS spectra.

Experimental

Silver sols were prepared according to the literature. The distilled and purified water was used here. A 10 m*l* volume of silver nitrate solution (6×10^{-4} mol/*l*) was added dropwise slowly to a 30 m*l* sodium borohydride solution (1.5×10^{-3} mol/*l*) with continuous stirring. All the solutions were chilled in an ice-water during the preparation. The yellowish silver sol produced was stable at room temperature. After the addition of a small amount of Zn(II)TMPyP(4) and Mn(III) TMPyP(4)Cl (Porphyrin Product, Logan, UT, USA) into the silver sol, the color changed to red–orange and finally to blue–grey. The details of the Raman measurement system were described elsewhere.[7] Briefly, a sample solution was circulated at 2 m*l*/min with a peristaltic pump through a quartz capillary of 1.4 mm i.d. to avoid possible degradation. A 90° scattering geometry was employed. A Spectra-Physics 165 Ar$^+$ ion laser was used for sample excitation. A 1 m Jobin-Yvon Raman U–1000 double monochromator, a Hamamatsu R943–02 photomultiplier with a PMT cooler and a Hamamatsu C1230 photon counter/discriminator were used. For the intensity ratio measurement of SERS bands, two separate spectra were acquired, using scanning in both forward and backward directions with a fresh sample, keeping all the other conditions same. The two separate spectra were added to compensate the intensity
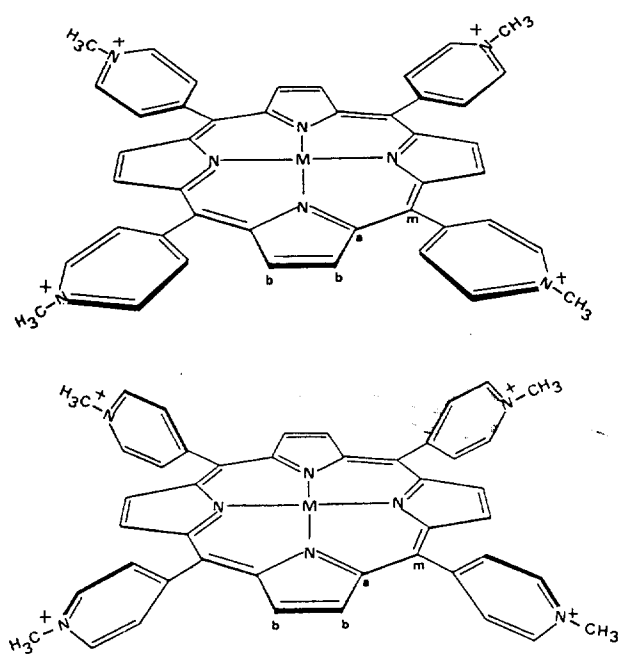
Figure 1. The structural diagram of Metallo–TMPyP(4) (bottom) and the proposed structural diagram of Metallo–TMPyP(4) when adsorbed on silver surface (top). a, b and m denote different carbon positions on Metallo–TMPyP(4).

variations during the measurement.

Results and Discussion

It is inferred from the structure of metallo–TMPyP(4) shown in Figure 1 and the previous SERS studies on small molecules that the binding to the silver surface is probably through the electron backdonation from the silver to the pyridyl nitrogen LUMO's. In this case, there is a possibility that the pyridyl ring antibonding electrons are involved in the binding process. The other possible binding sites could be the pyrrole nitrogens on rings. These seem unlikely as metallo–TSPP(4) does not adsorb on a silver surface even though this molecule has a structure (and hence steric hindrance) similar to metallo–TMPyP(4).[8] And the binding to the metal surface via four pyridyl groups presumably results in laying the porphyrin macrocycle plane parallel to the metal surface if all four pyridyl groups are involved simultaneously in the binding process. In this case, one major change in the geometry expected in the adsorption process is the rotation of the pyridyl groups in favor of binding through pyridyl groups because it is a well–known fact that four pyridyl groups are vertical to the porphyrin macrocycle plane in the ground state.[9]

For the RR spectroscopy of metalloporphyrins, the selective enhancement pattern has been established through numerous investigations utilizing various excitation wavelengths.[10] To summarize, the excitation in the neighborhood of the strongly allowed B band mainly enhances totally symmetric modes of the porphyrin ring which have appreciable Franck–Condon overlaps with the excited state via A term scattering. While the excitation is in resonance with the quasi–forbidden Q band, the vibronic scattering (B term) dominates the enhancement mechanism; non–totally sym-
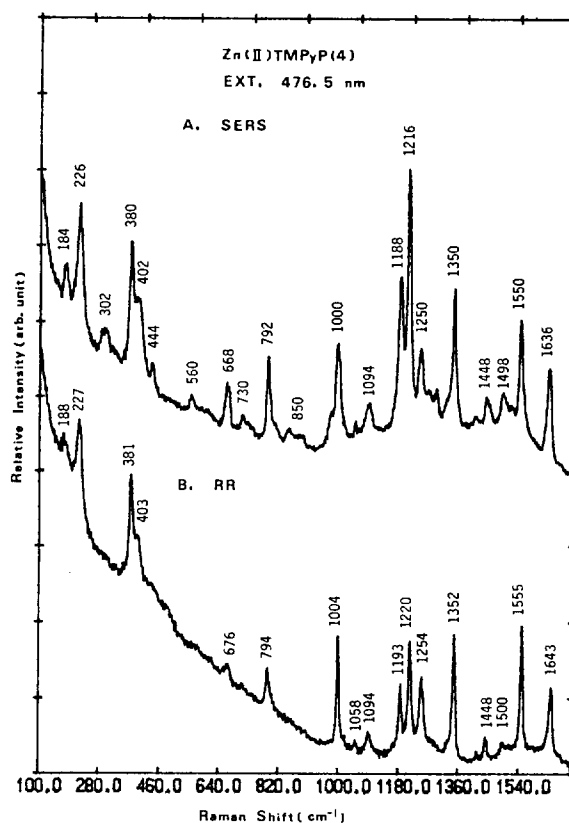
Figure 2. RR and SERS spectra of Zn(II)TMPyP(4). SERS spectrum: 1.2 μM sample concentration, 30 mV laser power, 0.5 cm^{-1} resolution, 2 cm^{-1}/s scan speed. RR spectrum: 0.2 mM sample concentration, 60 mW laser power. The other conditions are the same as in SERS.

metric modes which are effective in Q–B mixing are dominated by this excitation. In the idealized D_{4h} symmetry, these modes have B_{1g}, B_{2g} and A_{2g} symmetry, with depolarization ratio of three–fourth (B_{1g}, B_{2g}) or greater (A_{2g}). However, this general rule is no longer effective for SERS because of the possibility of a perturbation in the electronic state and the geometry when metalloporphyrins adsorb on metal surface. In addition, in SERS the bands are all depolarized probably due to the multiple scattering effects at the roughened surface and the polarization measurements are not effective in assigning the mode symmetry.[1(a)]

Figure 2 shows the RR and SERS spectra of Zn(II) TMPyP(4). The spectral comparison of the RR and SERS spectra shows the distinct differences: the strong Raman signal enhancement in the SERS spectrum even though the concentration used for SERS measurement is significantly lower; and the different enhancement patterns of some modes in RR and SERS spectra. In SERS spectrum, all the modes regardless of their symmetry groups are enhanced with some variations in the degree of the enhancement depending on the mode character. The frequencies and band assignments are given in Table 1. Some frequency shifts were observed depending on the mode but the SERS frequencies are quite different from those of Ag(II)TMPyP(4) particularly for ν_2 and ν_4 (Table 1).[11] This indicates that the formation of Ag(II) TMPyP(4) has not occurred when adsorbed on the silver surface. More significantly, the broaden-

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Table 1. RR and SERS Frequencies and the Average Relative Enhancement Factors for Various metallo-TMPyP(4)

Mode Assignment[a]	Zn(II)TMPyP(4)		I_{SERS}/I_{RR}	Mn(III)TMPyP(4)Cl		Ag(II)TMPyP(4)[c]
	RR	SERS		RR	SERS	SERS
δ(Pyridyl)	1643^m	1636^m	2.2	1646^{vw}	1638^w	1643^m
ν_2: $\nu(C_b-C_b)$	1555^s	1550^s	1.0	1566^m	1540^m	1546^s
ν_{19}: $\nu(C_a-C_m)$asym	—	1530^w	—	—	—	—
ν_{11}: $\nu(C_b-C_b)$	1500^w	1498^w	1.0	1462^w	1492^w	1493^{vw}
$\nu_3\nu_{28}$: $\nu(C_a-C_m)$sym	1448^w	1448^w	1.4	—	—	1457^{vw}
ν_4: ν(Pyr. half-ring)sym	1352^s	1350^s	1.1	1363^s	1342^s	1344^s
δ (C$_m$-Pyridyl)	1254^m	1250^m	1.4	1254^w	1246^s	1254^m
δ (Pyridyl)	1220^m	1216^s	2.6	—	1214^s	1220^m
δ (Pyridyl) + ν(N$^+$-CH$_3$)	1193^m	1188^s	2.4	1184^w	1190^m	1191^m
ν_9: δ(C$_b$H)sym	1094^w	1094^w	1.4	1090^{vw}	—	1098^m
ν_{17}: δ(C$_b$H)sym	1058^{vw}	1054^{vw}	—	—	1054^m	1050^m
ν_6: ν(Pyr. breathing)	1004^s	1000^s	1.3	1014^m	1002^s	1003^m
$\nu_7\nu_{16}$: δ(Pyr. def.)Sym	—	850^{vw}	—	908^m	904^m	906^m
Pyridyl ν(C-C) + ν(N$^+$-CH$_3$)	794^{vw}	792^{vw}	1.3	790^s	794^m	793^m
Pyr. folding	—	730^{vw}	—	—	—	—
δ(Pyridyl) + δ(C-N$^+$-CH$_3$)	676^{vw}	668^{vw}	1.9	640^{vw}	650^w	—
Pyr. folding	—	560^{vw}	—	580^{vw}	—	—
δ(por) + δ(pyridyl)	403^m	402^m	2.0	394^s	396^m	398^s
ν_8 δ(C$_b$H)	381^m	380^m	1.2	—	374^m	380^m
(C$_m$C$_a$)def.	—	302^{vw}	—	314^{vw}	310^{vw}	308^{vw}
Pyr. tilting	227^m	226^s	2.4	234^w	228^w	230^{vw}
δ(por) + ν(C$_m$-Pyr)	188^w	184^w	1.4	—	190^w	—

[a] Mode assignment is based on ref. 12(d). [b] 457.9 nm, 476.5 nm and 488.0 nm spectra were averaged in this calculation. [c] SERS frequencies are based on ref. [6].

Abbreviations used here: Pyr.: Pyrrole, por: porphyrin ring, ν: stretching, δ: bending, def.: deformation, s: strong, m: medium, w: weak, vw: very weak.

ing of some modes (4 ~ 8 cm^{-1} broader in FWHM) was observed especially at 1000, 1188, 1216, 1250 and 1636 cm^{-1} which are contributed by pyridyl ring stretching/bending modes.[12] In contrast, the broadening of in-plane porphyrin skeletal modes is relatively less significant especially at 1550 and 1350 cm^{-1} (2 cm^{-1} broader in FWHM). These observations imply that the binding to silver metal involves the pyridyl groups. In addition, the broadening of the modes contributed by pyridyl groups indicates that heterogeneity on the binding site through pyridyl groups possibly occurs.

From the previous investigations on the excited triplet state RR spectra of Zn(II), Mg(II) and Pd(II)TPP's,[13] a particulary interesting question is raised about the fate of phenyl modes, several of which have been identified in RR spectra, although these substituents are known to be oriented at nearly right angle to the porphyrin ring and the conjugation is not significant in the ground state.[12] It was suggested that the resonance enhancement of the phenyl modes reflect an increase in conjugation in the excited state through the rotation of the phenyl groups against the porphyrin ring. The appreciable broadening of the phenyl modes suggest an interesting possibility of an inhomogeneous distribution in the phenyl orientations with respect to the porphyrin ring plane with a broad range of vibrational frequencies as indicated in the triplet state RR spectra of Zn(II), Pd(II) and Pt(II)TPP's. Hence, in SERS of Zn(II) TMPyP(4), the broadening of pyridyl models is probably due to the inhomogeneous distribution of pyridyl orientations caused by the steric hindrance from the

nonbonded interaction between the protons at the ortho positions of the pyridyl groups and these at the outer pyrrole carbon atoms. Nevertheless, the vibrational frequencies are expected to be sensitive to the torsion angle between the pyridyl groups and the porphyrin ring plane because of the effect of conjugation.[12] The relatively less significant broadening of porphyrin in-plane skeletal modes might be justified since the electronic influence is spread over a large ring. Additionally, the metal itself is supposed to contribute to the broadening of these by providing an extra vibrational relaxation channel.[1]

Spiro et al.[14] demonstrated, as confirmed by other groups,[15,16] the appearance of out-of-plane modes below 1000 cm^{-1} for metalloporphyrins, even though these modes are not expected to be enhanced via either Q or B band excitation. As shown in Figure 2 and Table 1, the Raman modes which are not observed in RR spectrum have gained intensities in SERS spectrum especially at 850, 730, 560, 444 and 302 cm^{-1} which are mainly caused by out-of-plane modes of porphyrin macrocycle based on previous normal mode analysis on Ni(II)TPP.[11,12]

To have further insight into the orientation of the adsorbed molecule, the peak height for each mode was calculated and normalized with respect to the ν_2 mode for each RR and SERS spectrum. The choice of ν_2 mode can be justified since this mode is in-plane skeletal mode and consequently less sensitive to the geometry and the environment of adsorbed molecule. The averaged values of the SERS and RR intensity

ratios for each mode obtained *via* three Ar$^+$ ion laser lines (457.9 476.5 and 488.0 nm) are given in Table 1. Small variations were observed depending on the excitation wavelengths, but there is a general enhancement pattern which shows that the out-of-plane porphyrin modes and the pyridyl modes are more strongly enhanced than in-plane porphyrin skeletal modes. However, it is noteworthy that the relatively small enhancement ratios compared to small molecules are probably attributable to the fact that most of porphyrin modes are mixed with other vibrational modes[12] because of the complicate vibrational characters. Also the imperfect flat-on adsorption supported by pyridyl mode broadening seems to contribute to this effect. An attempt was made to investigate the selective enhancement of the CH vibration of the pyridyl rings around at 3000 cm^{-1}. The selective enhancement on CH vibration of pyridyl groups in SERS spectrum is not significant (not shown) because of the overtone and mixed Raman bands (induced by many strong bands between 1400 ~1600 cm^{-1}), the contribution by C_bH vibrations and the possible inhomogeneous distribution of the pyridyl groups on the silver surface.

The correlation between the geometry of an adsorbed molecule and the selection rule in conjunction with the electromagnetic field enhancement model has been investigated by several groups.[17-20] Regardless of some inconsistences, there is one common feature; if a molecule is adsorbed face-on to the metal surface, the out-of-plane mode would be strongly enhanced relative to the in-plane modes. On the other hand, if adsorbed edge-on to the silver surface, the situation would be reverse. From the previous investigations on the SERS of Cu(II) chlorophyllin a,[21] (Fe(III)PP)$_2$O[22] and Fe(III)PPDME(Cl),[23] these molecules were found to adsorb tilted on the silver surface because these molecules have non-symmetric binding sites through the propionate functional groups and the enhancement pattern for each mode simply follows the absorption profile of these molecules. Hence this behavior was explained by the simple electromagnetic enhancement of the SERS.[20] Considering all the observations of Zn(II)TMPyP(4) and the theoretical arguments mentioned above, this molecule seems to be adsorbed on the silver surface *via* flat-on geometry with inhomogeneity in the pyridyl orientations.

The RR and SERS spectra of Mn(III)TMPyP(4)Cl are presented in Figure 3. The comparison between these two spectra represents different characteristics in Raman frequencies and intensity patterns. In overall, the SERS frequencies of Mn(III)TMPyP(4)Cl are very close to those of Ag(II)TMPyP(4) particulary for 1190, 1214, 1246, 1342, 1492 and 1540 cm^{-1}. Among these, 1342 cm^{-1} band has been established as the metal oxidation state sensitive band and 1540 cm^{-1} band as the porphyrin core size sensitive marker band from the previous investigations.[10] These observations indeed indicate that the substitution reaction by the silver has occurred when adsorbed on the silver surface. These also provide indirect evidences that this molecule adsorb on the silver surface *via* flat-on geometry in favor of the substitution reaction. We also investigated whether this surface induced reaction is assisted by the laser beam. The acquisition of SERS spectra was limited to the ν_4 band which is quite different between Mn(III)TMPyP(4)Cl and Ag(II) TMPyP(4). As we increase the laser power, the simple
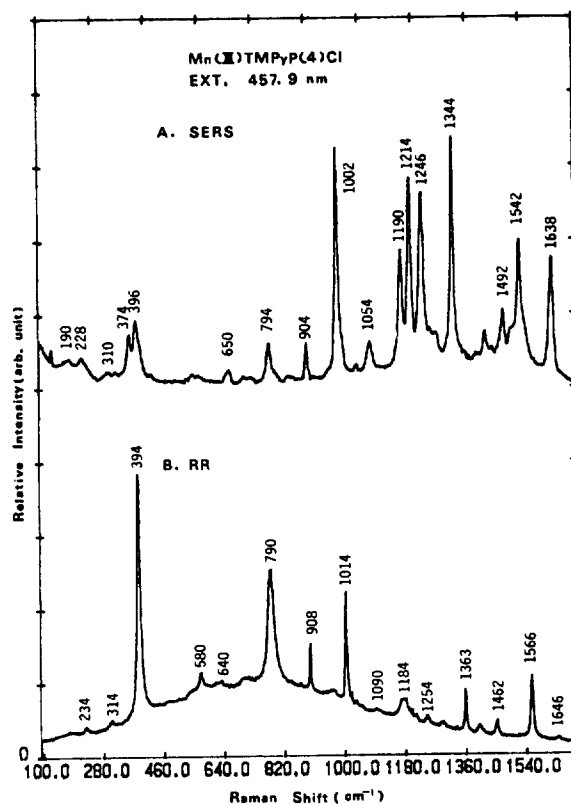

Figure 3. RR and SERS spectra of Mn(III)TMPyP(4) Cl. SERS spectrum: the conditions are the same as in Figure 2. RR spectrum: the conditions are the same as in Figure 2.
1643^m (N$^+$-CH$_3$) 794^{vw}

decrease of Raman signal was observed owing to the decomposition of the adsorbed molecule. The decrease in laser power reduces the Raman signal without any changes in frequency. These observations suggest that the substitution reaction on silver surface is mainly caused by the surface itself and is not assisted by photon. The changes in the excitation wavelength (457.9, 476.5, 488.0 and 514.5 nm) do not show any significant differences. We also examined the time dependence of the evolution of Ag(II)TMPyP(4) SERS signals. We changed the time interval between the addition of the Mn(III)TMPyP(4)Cl into the silver sol and the acquisition of the ν_4 Raman band. The SERS spectrum acquired even at the shortest time interval (in our case around 1 min) shows no trace of Mn(III)TMPyP(4)Cl SERS ν_4 band in SERS spectrum, indicating that the surface induced substitution reaction occurs very fast. The substitution reaction on Mn(III)TMPyP(4)Cl is probably due to the relatively weak bonding of Mn(III) metal to the pyrrole nitrogens compared with that in Zn(II)TMPyP(4).[23] The relatively high pH value of silver sol (around~9) seems not to have any effect on this reaction, since Mn(III)TMPyP(4)Cl was known to be stable even at pH 14.[24]

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Low Energy Ion–Surface Reactor

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Ion-surface collision studies at low kinetic energies (1–100 eV) provide a unique opportunity for investigating reactions and collision dynamics at surfaces. A special ion optics system for generating an energy- and mass-selected ion beam of this energy is designed and constructed. An ultrahigh vacuum (UHV) reaction chamber, in which the ions generated from the beamline collide with a solid surface, is equipped with Auger electron spectroscopy (AES) and thermal desorption spectrometry (TDS) as *in- situ* surface analytical tools. The resulting beam from the system has the following characteristics: ion current of 5–50 nA, energy spread <2 eV, current stability within $\pm 5\%$, and unit mass resolution below 20 amu. The performance of the instrument is illustrated with data representing the implantation behavior of Ar^+ into a graphite (0001) surface.

Introduction

The dynamics of atomic and molecular collisions on solid surfaces is a newly developing area where new experimental data, interpretations, and model calculations are constantly emerging. Especially, the interaction with surfaces in the low