

Micro-Raman Spectroscopy of *meso*-Tetrakis(*p*-sulfonatophenyl)porphine at Electrode Surfaces

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Micro-Raman techniques are used to acquire Raman spectra of a water-soluble porphyrin (*meso*-tetrakis(*p*-sulfonatophenyl)porphine) adsorbed onto smooth and roughened Ag electrodes. We combine such Raman studies with cyclic voltammetric measurements conducted for the porphyrin adsorbed onto smooth, polished Ag and Pt electrodes (both as functions of pH and electrode potential) and gain insight into the mechanism for protonation of monomeric porphyrin and formation of aggregates. It is deduced that variation in the Raman spectrum, induced by potential and pH changes, is related to the interfacial proton concentration. Electrochemical reduction of water and not the release of hydrogen from a coadsorbed porphyrin leads to the formation of the diacid that then is incorporated into aggregates. Another finding is that electrochemically induced protonation and the concomitant aggregation of TSPP are reversible on a time scale defined by the diffusion of H₂ into bulk solution.

I. Introduction

Self-assembled molecular aggregates have particular promise as molecular electronic devices and as models of antenna systems that function to transfer energy and electrons in biomembranes.^{1,2} Only recently have Raman measurements for aggregated molecule systems been reported that have the vibrational resolution requisite for highly detailed information about the structure of the constituent molecules and the specific intramolecular, structural effects associated with intermolecular interactions between the molecules.^{3–7}

We concern ourselves here with aggregated porphyrins, which, especially for porphyrin ensembles embedded into natural as well as artificial matrices, have attracted sustained scientific attention for decades. In general the ambiguous nature of the matrix has made it impossible to unequivocally attribute any spectral or temporal response of the system (that accompanies excitation) to its various components. The primary reason for this analysis shortfall often is the low concentration of porphyrin chromophores in the matrix. Resonance Raman (RR) scattering has been one technique for attempting to compensate for low porphyrin concentration and has been successfully used, for example, to acquire Raman spectra of tetrakis(4-(1-alkyloxy)phenyl)porphines and their Cu complexes in an LB film.³ But dynamical changes in the matrix are undoubtedly crucial in defining the important interactions that dictate the direction and speed of energy and electron transfer.^{8,9} Hence, a valid assessment of the mechanism of energy and charge movement within the system demands insight into structural changes both in the ensemble and in the host matrix; the lack of Raman resonance effects in the latter has hindered progress in extracting host structural change information.

In this paper, we investigate idealized systems in which the surfaces of smooth and roughened electrodes play the roles of

the hosts in which the porphyrin is “dissolved” and resonance Raman scattering is used to acquire structural information for the adsorbate; additionally, for the roughened surface, surface-enhanced resonance Raman scattering (SERRS) occurs. For these types of systems, changes in the matrix are mimicked (or modeled) by changes in surface potential.

We utilize a water-soluble porphyrin (specifically, *meso*-tetrakis(*p*-sulfonatophenyl)porphine; hereinafter referred to as TSPP) that self-aggregates. Earlier studies in this laboratory have revealed that aggregation enhancement of Raman scattering (AERS) occurs for such a system, and, more generally, prerequisites for self-aggregation in a homogeneous solution phase have been shown to be zwitterionic character and planar conformation of constituent monomers.^{4,5} It is to be noted that requirements for aggregation that we have found for porphyrins also have been shown to apply for aggregates of cyanine dyes that form in homogeneous aqueous solution¹⁰ as well as on the surface of a phospholipid.¹¹

We exploit all three resonance enhancement processes (mentioned above) in this work (specifically, RR, SERRS, and AERS). Furthermore we use confocal micro-Raman techniques to detect surface as well as homogeneous phase scattering from TSPP, to distinguish scattering spectra of the porphyrin in the two environments. We combine such Raman studies with cyclic voltammetric measurements conducted for TSPP adsorbed onto smooth, polished Ag and Pt electrodes (as functions of both pH and electrode potential) and gain insight into the mechanism for protonating adsorbed porphyrin molecules.

As regards earlier studies dealing with water-soluble porphyrins adsorbed onto an electrode (vide infra),^{12–17} it is to be noted that several researchers have applied Raman scattering (specifically, SERRS) to porphyrins adsorbed onto metal substrates. In particular, SERRS studies have been used to characterize TSPP adsorbed onto various substrates. One such study by Itoh et al.¹⁶ has been interpreted as indicating, by the presence of Raman bands at 983 and 1535 cm⁻¹ in SERRS experiments involving TSPP on an anodized Ag electrode, with

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potentials ranging from 0.0 to -0.3 V (vs SCE) in 0.05 M aqueous H_2SO_4 solution, that the diacid ($\text{H}_4^{2+}\text{TSPP}^{4-}$) is formed. Additionally, the existence of Raman bands at 314 and 420 cm^{-1} has been interpreted as indicating the presence of adsorbed, aggregated TSPP. Further, the vanishing of the above bands upon sweeping the electrode potential more negatively to -0.4 V has been associated with deprotonation of TSPP diacid, resulting in TSPP monomers in the free-base form ($\text{H}_2\text{TSPP}^{4-}$), which, in turn, are involved in a Ag incorporation reaction.

Ag incorporation of TSPP was first invoked by Cotton et al.¹² to assign bands at 355, 425, and 1346 cm^{-1} , in the SERRS spectrum of TSPP adsorbed onto a silver electrode in basic 0.1 M Na_2SO_4 solution, to the Ag metalloporphyrin—on the basis of the presence of the bands in the Raman spectrum of Ag^{II} -TSPP and their absence in the Raman spectrum of TSPP in bulk solution.

Diacid formation and Ag incorporation of TSPP have also been proposed from SERRS studies involving Ag/Ag Cl colloids.¹⁴ The diacid formation was assumed to result from protonation of the two imine nitrogen atoms of one TSPP by protons released during Ag incorporation into a neighboring adsorbed TSPP molecule. It was further suggested that the diacid species was incorporated into aggregate structures on the colloidal particles, as revealed by Raman bands at 238, 318, and 702 cm^{-1} attributed to the aggregate. The above steps implicitly represent a mechanism for aggregation of TSPP.

In this paper, our principal finding concerns the mechanism for diacid and aggregate formations. We combine electrochemical and potential-dependent Raman measurements and deduce a mechanism for formation of the aggregated TSPP on a silver electrode different from that proposed by others.^{14–16}

Experimental Section

Materials and Procedures. TSPP was purchased as the sodium salt from Porphyrin Products, Inc., and used without further purification. Redistilled, deionized water was used to prepare solutions; pH was adjusted with either 0.1 M HClO_4 or 0.1 M NaOH, and measured using a Marrison Science, Inc., model 90 pH/temperature meter.

The preparation of the electrode and the setup of the spectroelectrochemical cell have been described in detail elsewhere.¹⁸ Briefly, Ag and Pt disks of 99.999 and 99.99% purity, respectively, with geometric areas of 0.1 cm^2 were embedded in a Teflon shroud, polished successively with 1 and $0.05\text{ }\mu\text{m}$ alumina powder, and cleaned by sonication in deionized water. A Pt ring and saturated calomel electrode (SCE) were used for the counter and reference electrodes, respectively.

Roughening was accomplished in an aqueous 1.0 M NaClO_4 solution by switching the applied potential from -0.60 V to $+0.55$ V for 5 s, and then the potential was set at -0.10 V (all vs SCE) to allow the optimization of roughness features; subsequently the potential was set at -0.60 V. The electrode was then transferred to a fresh solution containing appropriate concentrations of electrolyte and dye.

Films of TSPP on polished, mirror-finish Ag or Pt electrode surfaces were prepared by immersing the electrodes into a solution containing TSPP of concentration $(1\text{--}2) \times 10^{-5}$ M, followed by slow extraction of the electrode—while an approximately vertical relative orientation of the electrode's surface to the surface of the solution was maintained. The coated electrode was then inserted into the electrochemical cell containing only solvent and supporting electrolyte (0.05 M H_2SO_4). Such films were used to acquire Raman spectra and to

examine the response time of the thin film, aggregated TSPP to potential change.

The chemical character of TSPP (free base, diacid, or aggregate) in the aqueous solution at different pH values was identified by distinctive Soret absorption bands; e.g., the absorption bands at 412, 432, and 490 nm are attributed to free base, diacid, and aggregate, respectively.³ The chemical character of TSPP adsorbed on the electrode surface was assessed by comparing Raman bands with the bands that are found to occur at different pHs in solution; in effect, local pH values in the adsorbed thin film are deduced through the existence of Raman bands that are characteristic of the various forms of the porphyrin.

Instrumentation. Absorption spectra of TSPP in solution were acquired using a Perkin-Elmer Lambda 18 UV/vis spectrophotometer.

Raman spectra of a TSPP monolayer on a metallic (Ag and Pt) electrode was acquired using a confocal micro-Raman probe instrument in which Raman scattering was excited with 488 nm radiation from a Spex 2000 argon ion laser. The exciting radiation was directed through an Olympus BH-2 microscope, and the diffraction-limited spot was focused onto the sample via a $\times 50$ microscopic objective of 8 mm working distance. The sample holder could be micropositioned both vertically and horizontally with spatial resolutions of 1 and $10\text{ }\mu\text{m}$, respectively. Raman scattering was collected in a backscattering configuration, using the same microscope objective, and directed through a THR-1000 (JY) spectrograph, equipped with a 1200 groove/mm grating and a holographic notch filter, to a Spex-View 2D CCD detector controlled by Spectromax software. Microcal's Origin 4.1 software was used for background subtraction and data processing. Raman spectra bandwidths are estimated to be $\pm 1.0\text{ cm}^{-1}$.

Cyclic voltammograms were recorded with a CHI660 electrochemical workstation (CH Instruments, Inc.), and applied electrode potentials were controlled by a BAS CV-27 potentiostat.

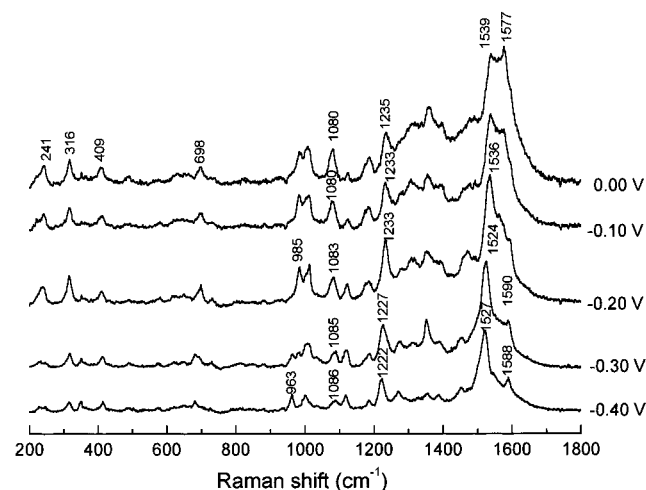
Results

TSPP Adsorbed onto a Roughened Ag Surface. Raman scattering was not observed for TSPP in 0.1 M NaClO_4 aqueous solution when the incident radiation was focused about $60\text{ }\mu\text{m}$ or more off the surface (geometrically, above) of a roughened Ag electrode, but it was observed when the focus was at the surface. Thus, Raman scattering is confirmed by the confocal microscope system as emanating from adsorbed TSPP.

Table 1 provides band positions and relative intensities for the data contained in Figures 1 and 2 (pertaining to pH values of 7.0 and 3.5, respectively); additionally, for the data in Table 1, excitation was with 488 nm radiation and TSPP was adsorbed from an aqueous solution whose TSPP concentration was ca. 10^{-5} M. The data (in Table 1) reveal regular band intensity change with electrode potential change from 0.00 V toward more negative potentials, with the most significant change (for both pH 7.0 and pH 3.5) occurring in the potential region -0.20 to -0.30 V vs SCE for the two low-frequency bands at ca. 242 and 318 cm^{-1} . In fact, for pH 3.5 data, one finds that a substantial enhancement of two low-frequency bands at 234 and 318 cm^{-1} is evidenced in the spectrum of TSPP (adsorbed onto a Ag electrode in a 0.1 M NaClO_4 solution and excited by 488 nm radiation) for electrode potentials more positive than -0.20 V. These bands, however, exhibit relative intensities that decrease as the potential is made more negative; concurrently, a Raman band at ca. 964 cm^{-1} exhibits a relative growth in

TABLE 1: Raman Scattering (cm^{-1}) by TSPP (1×10^{-5} M) on a Ag Electrode (Key: (A) Cotton et al.;¹² (B) Itabashi et al.;¹³ (C) Mou et al.¹⁴)

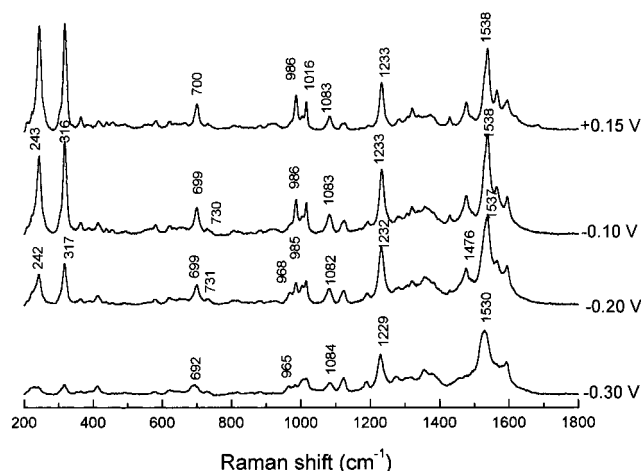
pH 7.0						pH 3.5				A	B	C
0.00 V	−0.10 V	−0.20 V	−0.30 V	−0.40 V	0.15 V	−0.10 V	−0.20 V	−0.30 V				
241 (0.74)	241 (0.42)	234 (0.36)			243 (2.34)	243 (1.39)	243 (0.59)	242 (0.18)	216 m		204 w	
316 (1.06)	316 (0.64)	316 (0.61)	317 (0.42)	316 (0.34)	318 (2.38)	317 (1.61)	317 (0.82)	317 (0.35)	313 s		242 s	238
			351 (0.16)	349 (0.36)	364 (0.33)	363 (0.16)	363 (0.09)		355 m (Ag)		316 s	318
409 (0.52)	409 (0.32)	410 (0.24)	413 (0.25)	413 (0.34)	415 (0.24)	413 (0.17)	413 (0.16)	413 (0.24)	425 m (Ag)		360 w	350
					439 (0.12)							416
488 (0.26)					491 (0.18)							
											490?	
					582 (0.17)	580 (0.06)	579 (0.27)				554	
					621 (0.12)	621 (0.11)	621 (0.09)	621 (0.10)			582	
698 (0.52)	698 (0.32)	698 (0.39)	683 (0.40)	681 (0.29)	700 (0.51)	699 (0.44)	699 (0.33)	692 (0.28)			620	
		731 (0.12)	728 (0.13)		731 (0.04)	731 (0.09)	731 (0.08)	731 (0.10)			699 m	702
								818 (0.06)	807		804	
					881 (0.08)	881 (0.07)	881 (0.06)	881 (0.13)	886		880	810
					917 (0.11)						915	
			963 (0.19)	963 (0.59)		968 (0.44)	968 (0.13)	965 (0.18)	965 m			964
986 (0.70)	985 (0.57)	985 (0.46)	982 (0.12)		986 (0.70)		985 (0.23)	985 (0.10)			983 m	990
1008 (0.78)	1008 (0.57)		1007 (0.51)	1002 (0.49)	1004 (0.08)			1003 (0.19)	1008 m			
		1012 (0.49)			1016 (0.46)	1016 (0.37)	1016 (0.23)	1016 (0.19)			1012 m	1014
1080 (1.22)	1080 (0.82)	1083 (0.46)	1085 (0.35)	1086 (0.35)	1083 (0.31)	1083 (0.32)	1082 (0.33)	1084 (0.27)	1080		1080	1090
1124 (0.35)	1123 (0.32)	1122 (0.32)	1119 (0.48)	1119 (0.50)	1124 (0.16)	1124 (0.20)	1123 (0.27)	1122 (0.46)	1127		1120	1130
1184 (0.78)	1184 (0.57)	1184 (0.32)		1186 (0.25)	1195 (0.07)	1193 (0.11)	1190 (0.14)	1189 (0.23)	1185			1194
1235 (1.00)	1233 (1.00)	1233 (1.00)	1225 (1.00)	1222 (1.00)	1233 (1.00)	1233 (1.00)	1232 (1.00)	1229 (1.00)	1232 s		1227 m	1238
			1278 (0.29)	1270 (0.37)	1282 (0.11)	1282 (0.08)	1278 (0.07)	1274 (0.21)	1295		1280	
	1311 (0.36)				1321 (0.23)	1320 (0.15)	1320 (0.12)				1314	1324
1360 (0.96)	1356 (0.50)	1353 (0.32)	1353 (0.78)	1353 (0.26)		1356 (0.10)	1356 (0.15)	1356 (0.26)	1346 (Ag)	1352	1380	1376
					1429 (0.20)	1429 (0.15)	1429 (0.08)		1362		1426	1432
		1467 (0.34)	1453 (0.23)	1452 (0.25)					1456 vw		1472 m	1480
					1477 (0.51)	1476 (0.42)	1476 (0.35)		1503			
	1538 (2.27)	1534 (1.44)	1524 (2.06)	1527 (2.20)	1538 (1.39)	1537 (1.26)	1537 (1.08)	1530 (0.94)			1535 s	1540
1577 (2.96)	1574 (0.57)	1563 sh			1565 (0.36)	1564 (0.22)	1564 (0.18)		1565 m		1560	1564
		1597 sh	1588 (0.26)	1588 (0.49)	1595 (0.26)	1595 (0.26)	1594 (0.30)	1593 (0.45)	1597		1590	1598

**Figure 1.** Surface-enhanced Raman spectra of TSPP on a Ag electrode at various potentials (vs SCE): 1×10^{-5} M TSPP aqueous solution of pH 7.0 with 0.1 M NaClO_4 as supporting electrolyte; excitation wavelength 488 nm. Spectra were acquired sequentially, from 0.00 V to more negative potentials, with time to collect a single spectrum of ca. 1 min and total time to collect spectra on the order of $1/2$ h.

intensity, while bands at ca. 700 and 988 cm^{-1} exhibit a relative decrease in intensity, and the band at ca. 1534 cm^{-1} experiences a downshift.

One also deduces from the data in Table 1 that when the potential is -0.3 V or lower, the Raman spectra for TSPP are essentially the same regardless of the pH of the solution.

We have found that potential-dependent Raman spectra are essentially unchanged with rapid cycling of the applied potential; but spectral intensities are found to gradually weaken as the

**Figure 2.** Surface-enhanced Raman spectra of TSPP on a Ag electrode at various potentials (vs SCE): 1×10^{-5} M TSPP aqueous solution of pH 3.5 with 0.1 M NaClO_4 as supporting electrolyte; excitation wavelength 488 nm. Spectra were acquired sequentially, from high to low potentials, with time to collect a single spectrum of ca. 1 min and total time to collect spectra on the order of $1/2$ h.

number of sweeping cycles is increased. Also, the potential region -0.20 to -0.30 V is apparently a threshold beyond which more negative potentials lead to substantial changes in the properties of the adsorbed TSPP.

TSPP Adsorbed onto Polished Ag and Pt Electrodes. Raman spectra of a TSPP adsorbed onto smooth surfaces of Ag or Pt electrodes in 0.05 M H_2SO_4 solution are displayed in Figures 3 and 4, respectively. It is immediately clear that the general features of the Raman spectra are similar, though the spectra for the Ag-electrode systems have higher intensities than

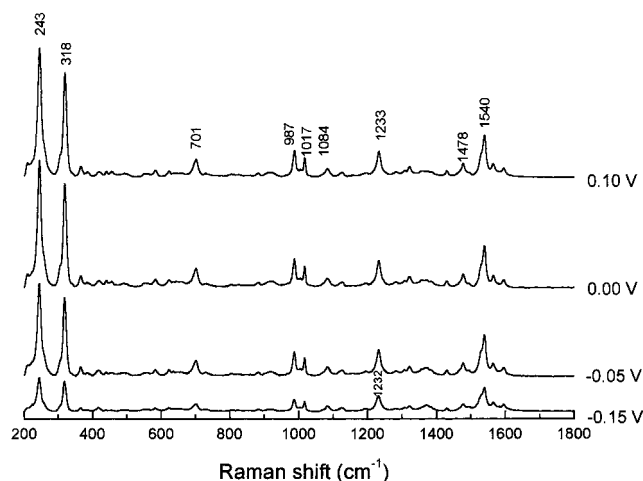


Figure 3. Raman spectra of a TSPP adsorbed from a 1×10^{-5} M bulk solution onto the smooth surface of a Ag electrode at various potentials in 0.5 M aqueous H_2SO_4 solution; excitation wavelength 488 nm and spectral acquisition sequence from high to low potential. Temporal collection of the spectra was the same as that for Figure 1.

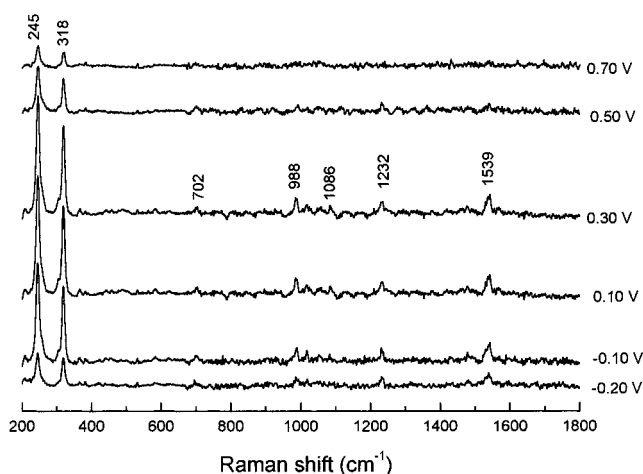


Figure 4. Raman spectra of a TSPP adsorbed from a 1×10^{-5} M bulk solution onto the smooth surface of a Pt electrode at various potentials in 0.5 M aqueous H_2SO_4 solution; excitation wavelength 488 nm and spectral acquisition sequence from high to low potential. Temporal collection of spectra was the same as that for Figure 1.

those for the Pt-electrode system. Moreover, these Raman spectra, particularly regarding the presence of intense low-frequency bands at 243 and 318 cm^{-1} , are similar to SERRS spectra for TSPP adsorbed onto a roughened Ag electrode in electrolytic solution of pH 7.0 (see Figure 1) when the electrode potentials are kept above the threshold value around -0.20 V. In particular, for both cases, the intensities of the 243- and 318- cm^{-1} Raman bands, relative to other bands in the spectra, increase with electrode potential changes from -0.20 to 0.0 V and diminish when the potential is swept to more positive values; this diminution occurs when the potential is ca. $+0.50$ V in the case of the Pt-electrode study. Such a potential dependence is similar to that mentioned above for the SERRS spectra of TSPP on a roughened Ag electrode in an acidic electrolytic solution; however, for the smooth-surface systems (both Ag and Pt), SERRS is not applicable, and a different enhancement mechanism is operative.¹⁰

Visible Absorption Spectra of TSPP in Solutions of Different pHs. To elucidate the chemical nature of TSPP at electrode surfaces, electronic absorption spectra of TSPP (in the form of its sodium salt) dissolved in aqueous solution were

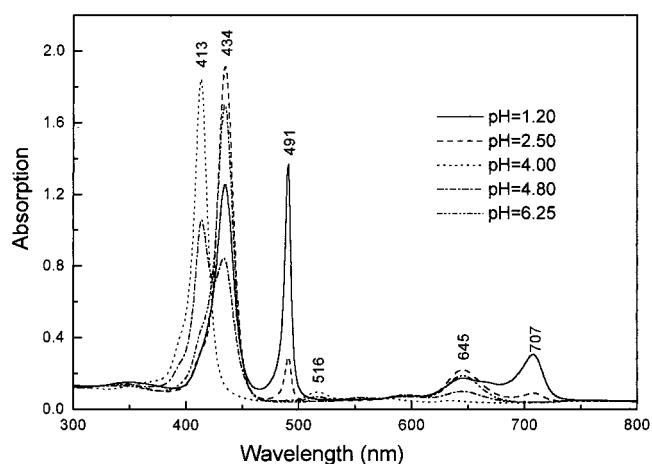


Figure 5. Absorption spectra of TSPP in solutions of 1×10^{-5} M TSPP + 0.1 M NaClO_4 of various pHs.

recorded at different pH values; see Figure 5, where spectra are identical to those reported elsewhere.³ From our earlier study, the absorption bands at 413, 434, and 491 nm are attributed to free-base, diacid, and aggregated TSPP, respectively.

Cyclic Voltammetric Measurements. Cyclic voltammograms for a Pt electrode in 0.5 M H_2SO_4 , in the absence and presence of TSPP solute, are displayed in Figure 6A, parts a and b, respectively. These curves indicate that, upon sweeping the Pt electrode's potential from the "double-layer region" (at which no electrochemical process takes place), a hydrogen adsorption process occurs near $+0.05$ V, while for a potential near -0.20 V a fast hydrogen evolution process is evident.

Similar applied-potential-dependent behaviors are observed for the voltammetry of an Ag electrode in diluted H_2SO_4 solution (see Figure 6B): no electrochemical events occur in this case for potentials more positive than -0.1 V, and hydrogen evolution is the dominant electrochemical process when the potential is more negative than -0.35 V.

The mechanism or mechanisms of the electrochemical processes at intermediate potentials are not completely clear for either the Pt or the Ag systems, but a discussion in terms of reactions that lead to hydrogen adsorption or evolution has been presented.¹⁹

It is apparent that the applied potentials at which hydrogen adsorption and evolution take place are essentially identical to the potentials where the Raman spectra of adsorbed TSPP exhibit major changes. Hence, one might expect the electrochemistry of TSPP to provide clues to the mechanism for formation of active species in the Raman scattering spectra. This issue is addressed in the next section.

Discussion

Solution phase protonation and aggregation of TSPP and the spectral characterization of different molecular forms of TSPP have been discussed in prior publications.⁴⁻⁶ Briefly, the TSPP diacid formed by protonation of the two central imine nitrogen atoms is characterized by (1) an electronic absorption band at 432 nm, (2) a structural change from a propeller-like geometry for the free base to a nearly planar conformation for the diacid, (3) the symmetric positioning of four protons in the central core of the macrocycle, and (4) a distortion of the porphyrin macrocycle plane to a ruffled structure (in which alternate pyrrole hydrogens are positioned above and below the central plane of the macrocycle).

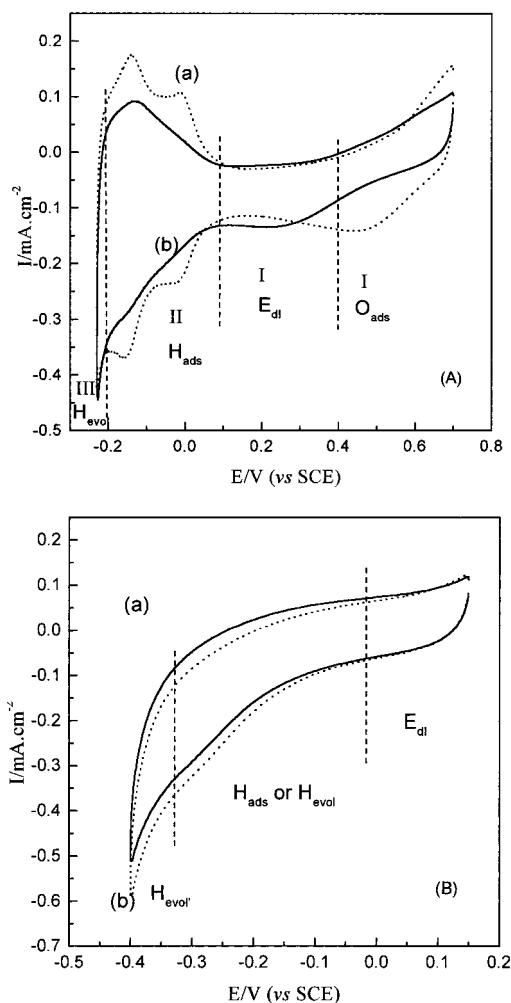


Figure 6. Cyclic voltammograms of Pt (A) and Ag (B) in 0.5 M aqueous H_2SO_4 solution without (a) and with (b) adsorbed TSPP films.

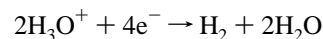
In terms of vibration band shifts, we have found that protonation results in an upshift of the Raman band at 964 cm^{-1} to 988 cm^{-1} , a downshift of the band attributed to outer $\text{C}_b=\text{C}_b$ double bond stretching, and a shifting in opposite directions for Raman bands at 1080 and 1233 cm^{-1} , which are respectively associated with stretching of the bond between the peripheral aryl substituents relative to the *meso* carbon $\text{C}_m-\Phi$ and to the outer C_b-H bond bending. Furthermore, only slight changes in the spectral patterns for bands at frequencies greater than 1000 cm^{-1} (essentially associated with the skeletal vibrations of the porphinato macrocycle) are observed.⁴⁻⁶

Moreover, because of Coulomb attraction between the oppositely charged sites in the two adjacent molecules, protonated TSPP monomers are assumed to cofacially stack in a stairlike arrangement.⁴ Aggregation results in the formation of a sharp excitonic absorption peaking at 490 nm and a dramatic enhancement of Raman intensity for bands at 240 and 314 cm^{-1} .⁴

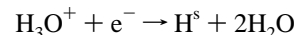
The characteristics of the Raman spectra discussed above when protonation is induced suggest that the bands present in SERRS spectra of TSPP adsorbed at a Ag-electrode surface, with applied potential more negative than -0.2 V , are predominantly associated with the free base. This free-base form is apparently present regardless of whether the electrolytic solution is basic or acidic. The observation that a Raman band at 987 cm^{-1} is present when the electrode potential is held in the range -0.10 to $+0.15\text{ V}$ in acidic or -0.20 to 0.00 V in neutral solution and its intensity increases as that of the 964-cm^{-1} band

decreases (vide supra) indicates that adsorbed TSPP exists in the protonated form, even for neutral electrolytic solution. Moreover, the observation of intense bands at 238 and 316 cm^{-1} for acidic electrolytic solution is convincing evidence for the presence of aggregated TSPP adsorbed onto the surface. The presence of these same bands for TSPP adsorbed onto smooth Ag- and Pt-electrode surfaces provides evidence in support of the aggregation enhancement effect, which has been described theoretically²⁰ and verified for systems composed of TSPP^{4,6} and cyanine dyes.¹⁰

The mechanism for protonation of adsorbed free-base TSPP and the apparent deprotonation of the diacid that occurs when the applied potential is set to the "transition region" described earlier (at which the spectrum dramatically changes) is next addressed. An explanation for the protonation of TSPP adsorbed onto a metal substrate is suggested by the observation of the potential-dependent electrochemical behavior. Specifically, hydrogen adsorption and evolution at the electrolyte-electrode interface, which can be elucidated from cyclic voltammetry measurements, are shown to occur (Figure 6A) in the same potential region that effects dramatic changes in the Raman spectra. It has been well documented that both hydrogen adsorption and evolution are directly related to the change in proton concentration within the molecular monolayer in contact with the electrode surface, in accord with the electrochemical reactions



(hydrogen evolution from acidic solution)



(adsorbed hydrogen, H^s , in acidic solution)

The first process above leads to an absolute decrease in the interfacial proton concentration in the molecular monolayer. The second process leads to a reduction in proton concentration to a value slightly lower than that in bulk solution yet higher than that present when the potential region is one where the hydrogen evolution process dominates. Interestingly, the sharp but reversible change in Raman spectral pattern for TSPP adsorbed onto a smooth Pt electrode (Figure 4), upon repeated potential sweeps across a narrow potential region around -0.20 V , occurs for just the potential region where the proton concentration in the interfacial monolayer is expected to undergo substantial change. We thus deduce that variation in the Raman spectral pattern is directly related to the interfacial proton concentration, which determines whether adsorbed TSPP is protonated: if the potential is more negative than ca. -0.2 V vs SCE, hydrogen evolution occurs and TSPP is deprotonated; for a potential more positive than ca. -0.2 V , TSPP is protonated and leads to formation of the aggregate. Such a conclusion is consistent with the observation of Raman spectra of TSPP in acidic and basic homogeneous solutions.³⁻⁵

We have made the further observation that a reversible change in the Raman spectral pattern of adsorbed TSPP is observed only if the speed of the potential sweep across the "transition region" is above some threshold rate. This determination suggests that the potential-dependent spectral change is governed solely by the protonation-deprotonation of interfacial TSPP. As a result, it can be concluded that the molecular state of TSPP (specifically, monomer, aggregate, or diacid) adsorbed onto the electrode surface is controllable by adjusting the interfacial proton concentration via surface electrochemical redox reactions.

For our system, as opposed to those mentioned earlier,¹²⁻¹⁴ it is of interest to note that 355- , 425- , and 1346-cm^{-1} Raman

bands, suggested as signaling Ag incorporation into TSPP, were not observed for either pH 7 or pH 3.5 systems. The lack of Ag incorporation in our case would appear to be associated with the counterion (i.e., ClO_4^-) used. This anion has been reported to cause demetalation of metalloporphyrins.²¹ But the more likely effect is simply the dominance of protonation over metal incorporation. The latter issue will be more fully discussed elsewhere.²²

In summary, we have ascertained that the principal factor that affects TSPP protonation and aggregation on an electrode surface is the same as that for the homogeneous solution, i.e., the pH. We deduce, however, that electrochemical reduction of water, not the release of hydrogen from a coadsorbed porphyrin as found for the colloidal system,⁹ leads to the formation of the diacid that then is incorporated into aggregates—as we have earlier shown to occur in homogeneous solutions.^{3–5} An additional important finding is that electrochemically induced protonation and the concomitant aggregation of TSPP are reversible on a time scale defined by the diffusion of H_2 into bulk solution.

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References and Notes

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