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both substrates (and to the relatively weak substrate-adsorbate bond strength for the methyl surface), neither material acts as a good template for the formation of ordered water overlayers.

Acknowledgment. We thank Prof. D. L. Allara for calculating

the spectra plotted in Figure 1 and for many useful discussions regarding the interpretation of these data.

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The Role of Triton X-100 as an Adsorbate and a Molecular Spacer on the Surface of Silver Colloid: A Surface-Enhanced Raman Scattering Study

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The ability of the nonionic surfactant Triton X-100 [*p*-(1,1,3,3-tetramethylbutyl)phenylpoly(oxyethylene)] to act as a molecular spacer between the surface of Ag colloid and an adsorbate [free base 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin = TPPC₄] is investigated by surface-enhanced Raman scattering (SERS) spectroscopy. SERS spectra of Triton X-100 and of poly(ethylene glycol) (PEG) 400 (poly(oxyethylene)) adsorbed on Ag colloid are reported. The identity of both spectra indicates that Triton X-100 is adsorbed on the surface via its hydrophilic (poly(oxyethylene)) part. SERS spectra of Ag colloid/Triton X-100/TPPC₄ and of Ag colloid/PEG 400/TPPC₄ systems are also reported. A good-quality SERS spectrum of free base TPPC₄ was obtained for the former system, in contrast to the latter one. The role of the hydrophobic part of the Triton X-100 molecule in prevention of the porphyrin metalation as well as in its attraction to the vicinity of the surface is thus demonstrated.

Introduction

Silver colloids as active surfaces for surface-enhanced Raman scattering (SERS) spectroscopy possess several distinct features as compared to e.g. silver electrodes and films. It is now well-known that the surface enhancement of Raman scattering works most effectively for aggregated colloids.¹⁻⁵ Aggregation is induced either by the adsorbate itself or by a preaggregation agent.^{6,7} The conditions under which the aggregation of the colloid occurs (the preparation protocol of the colloid, the "age" of the colloid at the moment of adsorbate addition, the concentration, the volume and the chemical nature of the adsorbate added, the temperature and the presence or absence of the preaggregating agent) have, in many cases, to be tailored for each particular adsorbate. The aggregation process can be easily monitored by UV/vis absorption spectroscopy via the changes in the surface plasmon absorption of the colloid induced by aggregation.^{1,3-5} A substantial amount of information about the relationship between the state of aggregation and SERS activity of the Ag colloid/adsorbate system can thus be obtained.

One of the characteristics of the SERS-active silver surfaces, the colloids in particular, is the presence of reactive Ag_n⁺ species (*n* > 1) which is responsible for strong chemical interaction of many types of adsorbates with the surface.^{1,4,5,8-11} The SERS spectrum of such an adsorbate provides valuable structural information about the Ag_n⁺-adsorbate surface complex. On the other hand, information about the adsorbate itself is distorted, as both the geometrical and the electronic structures of the adsorbate are altered by its interaction with the surface. This fact is a serious drawback for studies of biomolecules on Ag colloidal surfaces, as information about the native, unaltered form of the

adsorbate is required in this particular case.^{12,13}

In this paper we propose a possible way to overcome this problem by designing a molecular spacer which would (i) prevent direct chemical interaction of the adsorbate with the surface and (ii) ensure the fixation of the adsorbate onto the spacer-modified Ag surface in such a way that the adsorbate could be positioned sufficiently close to the metal surface to experience the surface enhancement of Raman scattering. A similar approach has been adopted in ref 14 where a phospholipid spacer between the Ag

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surface and the analyte was investigated.

In the present study, we have focused our attention on surfactants as possible candidates for this type of molecular spacer. The choice is motivated by the unique molecular structure of surfactants which is formed by combining a hydrophilic and a hydrophobic moiety into one molecule. Our idea is that, while one part of the surfactant molecule could interact with the Ag surface, the other one could be exposed to the interaction with adsorbate studied. As a model for the surfactant-based spacer, we selected the nonionic surfactant Triton X-100, which consists of the hydrophilic poly(oxyethylene) chain and the *p*-(1,1,3,3-tetramethylbutyl)phenyl group forming the hydrophobic moiety.

Our choice has also been supported by the results of a SERS spectroscopic study of several cationic, anionic, and nonionic surfactants on a Ag electrode.¹⁵ The dependence of the SERS spectra on the electrode potential for these substances has shown that, at slightly negative potentials (−0.5 V), the surface of the Ag electrode attracts the hydrophilic parts of the surfactant molecules. At more negative potentials (−1.3 V), the electrode surface becomes apparently more hydrophobic as the manifestation of the hydrophobic parts of the surfactant molecules is more pronounced in the SERS spectrum.¹⁵ The SERS spectrum of Triton X-100 on Ag electrode has been measured and discussed in ref 16. At the electrode potential −1.0 V, the surface enhancement of bands originating from both the hydrophilic poly(oxyethylene) part of the surfactant and the hydrophobic *p*-(1,1,3,3-tetramethylbutyl)phenyl moiety have been observed simultaneously.¹⁶

Recently, preparation of Ag colloid by reduction of AgNO₃ by sodium citrate in the presence of surfactants and polymers (Triton X-100, sodium dodecyl sulfate, poly(vinyl alcohol)) has been reported.¹⁷ The intensity increase of the SERS spectrum of crystal violet dye adsorbed onto this modified Ag colloid has been ascribed to the difference in the size and shape of the aggregates which are formed after the addition of adsorbate to the surfactant containing colloid as compared to the nonpretreated Ag colloid/crystal violet system.¹⁷ In accordance with the philosophy described above, we have adopted a different approach to the modification of the Ag colloid by the surfactant. Besides the Ag colloid/Triton X-100 SERS-active system, we have prepared an analogous system with poly(ethylene glycol) (PEG) 400, which represents a model of the hydrophilic moiety of Triton X-100. The comparison of the resulting SERS spectra allowed us to interpret the observed Raman bands in both systems and to determine the role of hydrophobic and hydrophilic parts of Triton X-100 in its interaction with Ag colloid surface.

For the investigation of the ability of Triton X-100 to form an efficient molecular spacer between the surface of Ag colloid and an adsorbate, we have selected the water-soluble, free base 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (TPPC₄) as a model adsorbate. Free base TPPC₄ has been shown previously¹⁸ to become completely metalated upon adsorption on the surface of Ag colloid, i.e., to form the Ag^{II}TPPC₄ surface complex. TPPC₄ thus represents a good example of adsorbates strongly interacting with the metal surface. Moreover, both the free base and the metalated forms of the porphyrin manifest themselves by the characteristic and distinct patterns of Raman bands.^{11,18} The molecular structure of TPPC₄ also allows for both the hydrophobic (via aromatic tetrapyrrole macrocycle or peripheral phenyl groups) and the hydrophilic (via COOH groups) interactions.

Experimental Section

Materials. Analytical grade chemicals and redistilled deionized water were used for all sample preparations. Triton X-100 (for scintillation technique, SERVA, Feinbiochemica) and poly-

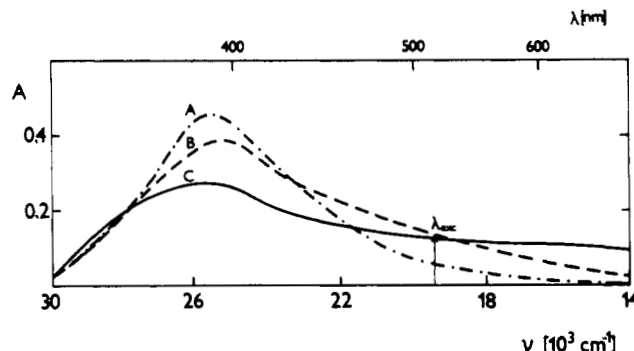


Figure 1. Absorption spectra of (A) freshly prepared Ag colloid, (B) Ag colloid (4 mL)/Triton X-100 (40 μ L of 10^{-2} M aqueous solution) SERS-active system, and (C) Ag colloid (4 mL)/poly(ethylene glycol) 400 (40 μ L of 10^{-2} M aqueous solution) SERS-active system. The position of the Raman excitation line at 514.5 nm is indicated by an arrow.

(ethylene glycol) 400 (for gas chromatography, Merck) were characterized by the mass spectrum and used without further purification. The 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin was synthesized according to ref 19. Freshly prepared 10^{-4} M solutions of the porphyrin in 2×10^{-2} M phosphate buffer (pH = 7.3) were used for preparation of the SERS-active system.

Preparation Procedures. Ag colloid was prepared by reduction of AgNO₃ by NaBH₄ following the preparation protocol described in ref 20. The analogous Ag colloid was prepared using D₂O (99.88% Sovchimeksport) as the solvent. In this preparation procedure, the temperature of the NaBH₄ solution upon addition of AgNO₃ had to be changed from 4 °C (see ref 20) to 7 °C.

Preparation of Ag Colloid/Triton X-100 and Ag Colloid/PEG 400 Systems. To 4 mL of Ag colloid was added 40 μ L of 10^{-2} M aqueous solution of Triton X-100 or PEG 400 2 h after the Ag colloid preparation. The SERS-active system with Triton X-100 was formed for 3 days, and that with PEG 400 for 1 day, at laboratory temperature (20 °C). Equimolar concentrations of Triton X-100 and PEG 400 used for preparation of the SERS-active systems ensured the same number of PEG moieties to be present in both systems. Both these systems were also prepared using D₂O instead of H₂O for preparation of the Ag colloid as well as of the Triton X-100 and PEG 400 solutions.

Preparation of Ag Colloid/Triton X-100/TPPC₄ (Free Base) and Ag Colloid/PEG 400/TPPC₄ (Free Base) Systems. To Ag colloid (4 mL)/Triton X-100 (40 μ L, 10^{-2} M) or Ag colloid (4 mL)/PEG 400 (40 μ L, 10^{-2} M) SERS-active systems was added 40 μ L of a 10^{-4} M solution of TPPC₄ in 2×10^{-2} M phosphate buffer. The concentration of TPPC₄ in both SERS-active systems was 10^{-6} M. SERS spectra were measured at least 2 h after preparation of the system. No spectral features of the phosphate buffer appeared in the SERS spectra.

Instrumentation. Raman spectra were measured using a modular spectrometer²¹ consisting of a high-resolution monochromator (THR 1500, Jobin-Yvon), an additional compact 1/8-m monochromator (Oriel), a photon counting system assembled from NIM modules (Tennelec and Ortec) and a personal computer compatible with an IBM AT. The spectra were accumulated step by step with a spectral slit width of 6 cm^{−1} (for SERS measurements) and 3 cm^{−1} (for Raman spectra of liquids), a wave-number step of 1 cm^{−1}, and an accumulation time of about 1 s per spectral point. Excitation was provided with the 514.5-nm line of an argon ion laser (ILA 120, Carl Zeiss Jena) with the laser power at the sample 120 mW. All samples were studied in quartz cells. UV/vis absorption spectra were recorded on a Specord M 40 (Carl Zeiss Jena) spectrometer using 0.2-cm quartz cells. GC-MS analyses were carried out using chemical ionization

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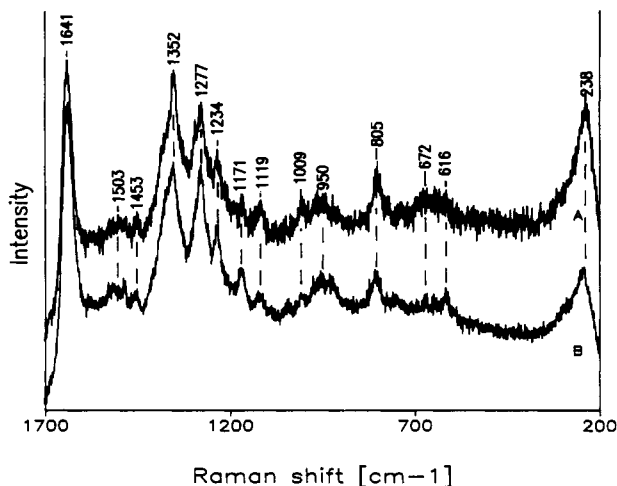


Figure 2. SERS spectra of (A) Ag colloid (4 mL)/Triton X-100 (40 μ L of 10^{-2} M aqueous solution) system and (B) Ag colloid (4 mL)/poly(ethylene glycol) 400 (40 μ L of 10^{-2} M aqueous solution) system.

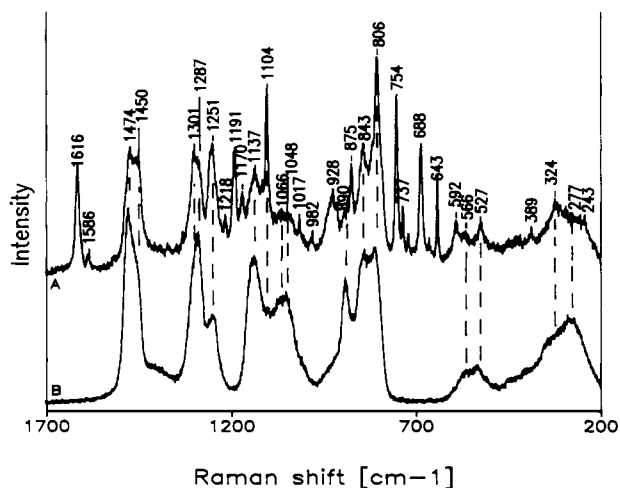


Figure 3. Raman spectra of pure liquids: (A) Triton X-100 and (B) poly(ethylene glycol) 400.

and a Varian 3400 with Inco 50 mass spectrometer and Data General 10/SP data station.

Results and Discussion

Adsorption of Triton X-100 on the Surface of Ag Colloid. The SERS spectra of Ag colloid/Triton X-100 and Ag colloid/PEG 400 systems were measured 3 days after preparation. The SERS-active system formation was achieved by a spontaneous aggregation of Ag colloid by the adsorbate, i.e., without any preaggregation either by addition of an aggregating agent or by aging the colloid. Absorption spectra of both systems are shown in Figure 1. The surface plasmon absorption curves of the Ag colloid/Triton X-100 (curve B) and Ag colloid/PEG 400 (curve C) systems in comparison to that of the freshly prepared Ag colloid (curve A) reflect the state of Ag colloid aggregation in each of these SERS-active systems as is further discussed below.

The SERS spectra of Ag colloid/Triton X-100 (curve A) and Ag colloid/PEG 400 (curve B) are presented in Figure 2. Both the positions and relative intensities of bands in the SERS spectrum of Triton X-100 (A) are virtually identical to those found in the SERS spectrum of PEG 400. This means that only the vibrations of the hydrophilic (PEG-like) part of the Triton X-100 molecule experience the surface enhancement in our system. This observation is in contrast to a comparison of the normal Raman spectra of the pure liquid Triton X-100 and PEG 400 presented in Figure 3. Although the bands of the PEG 400 can be easily identified in the normal Raman spectrum of Triton X-100, they are supplemented with the additional bands ascribed to the phenyl ring and the 1,1,3,3-methylbutyl group of the hydrophobic part of

TABLE I: Comparison between the Vibrational Frequencies (cm^{-1}) (a) of the Free PEG Moiety in the Normal Raman Spectrum of PEG 400 and (b) of the Adsorbed PEG Moiety in the SERS Spectra of Triton X-100 and PEG 400

Raman shift, cm^{-1}		assignment ²³⁻²⁵
PEG 400 liquid ^a	PEG 400 adsorbed ^b	
	238	$\nu(\text{Ag}^+-\text{O})$
277		$\delta(\text{C}-\text{O}-\text{C})$
527	616	$\delta(\text{C}-\text{C}-\text{O})?$, $\delta(\text{C}-\text{O}-\text{C})?$
566	672	
806	805	CH_2 rocking
843		CH_2 rocking
890		CH_2 rocking
1048	950	$\nu(\text{C}-\text{O})$, $\nu(\text{C}-\text{C})$
1066	1009	
	1119	$\nu(\text{C}-\text{O})$, $\nu(\text{C}-\text{C})$
1137	1171	
1251	1234	$\nu(\text{C}-\text{C})$, $\nu(\text{C}-\text{O})$
1287	1277	
	1352	CH_2 twisting
	1453	CH_2 twisting
1450	1482	CH_2 wagging
1474	1482	CH_2 scissoring
	1641	CH_2 scissoring
		$\delta(\text{H}_2\text{O})$

Triton X-100.²² By inspection of Figure 2, one can confirm that none of the bands belonging to the hydrophobic moiety have been observed in the SERS spectrum of Triton X-100 adsorbed on Ag colloid (see also ref 30).

The SERS spectrum of Triton X-100 on Ag colloid (Figure 2, spectrum A) thus differs substantially from that on Ag electrode,¹⁶ in which the bands of both parts of the Triton X-100 molecule have been observed. This difference indicates that both the surface potential and the surface morphology influence the mode of interaction of the surfactant with the surface.

Our interpretation of the SERS spectra of Triton X-100 and PEG 400 is based on the comparison with the ordinary Raman spectrum of PEG 400 (Table I). The Raman spectrum of PEG 400 (Figure 3, spectrum B) is in a good agreement with that of the molten high molecular weight PEG reported in refs 23 and 24. For the normal Raman spectrum of PEG 400 we have therefore adopted the band assignment as published in refs 23-25.

The most remarkable feature of the SERS spectra of the Triton X-100 and PEG 400 adsorbed on Ag colloid (Figure 2) is the appearance of new strong bands at 1641, 1352, and 238 cm^{-1} , which do not have counterparts in the ordinary Raman spectrum of liquid PEG 400 (Figure 3, spectrum B). The band at 238 cm^{-1} is tentatively attributed to the stretching vibrational mode of the Ag_n^+-O (etheric oxygen) bond. The frequency of this mode is comparable to that of $\text{Ag}_n^+-\text{Cl}^-$ (240 cm^{-1}) and Ag_n^+-N (pyridine, 228 cm^{-1}).¹ The 1352- cm^{-1} band has a rather weak counterpart in the spectrum of molten high molecular PEG assigned to the CH_2 wagging mode.²³

However, hardly any vibrational mode of the PEG unit can be attributed to the 1641- cm^{-1} band. On the other hand, the position of this band is typical for a $\text{H}-\text{O}-\text{H}$ deformation mode of H_2O . To investigate this possibility, we have measured the SERS spectra of Ag colloid/Triton X-100 and Ag colloid/PEG 400 systems prepared with D_2O . The results are shown in Figure 4 (spectrum A, system with Triton X-100; spectrum B, system with PEG 400). In both SERS spectra, the 1641- cm^{-1} band shows a typical deuteration shift to 1210 cm^{-1} and can thus be unambiguously attributed to the $\delta(\text{H}-\text{O}-\text{H})$ mode of H_2O . However, observation of a residual band at 1631 cm^{-1} in both spectra A and B in Figure 4 signifies that, besides the D_2O molecules responsible for the 1210- cm^{-1} band, H_2O molecules are also still present in both systems. This indicates that the SERS bands discussed above originate from those H_2O molecules associated with the PEG

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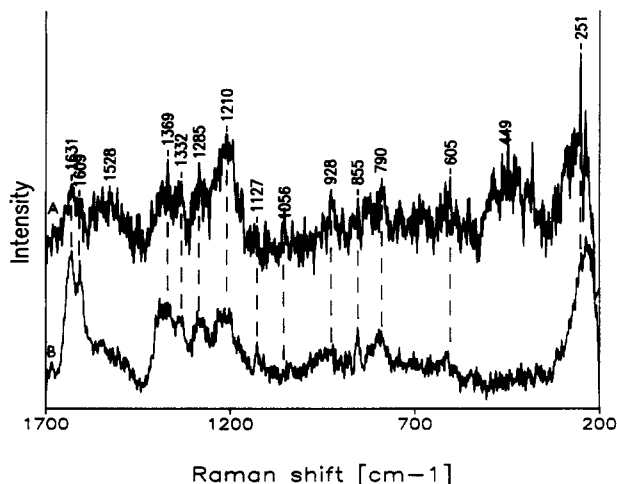


Figure 4. SERS spectra of systems prepared with D_2O as the solvent: (A) Ag colloid (in D_2O , 4 mL)/Triton X-100 (40 μL of 10^{-2} M D_2O solution) system; (B) Ag colloid (4 mL)/poly(ethylene glycol) 400 (40 μL of 10^{-2} M D_2O solution) system.

chains in both Triton X-100 and PEG 400 samples. Association of H_2O molecules with the PEG chain and their partial immobilization was proved e.g. by NMR spectra (ref 22 and references therein). Observation of both H_2O and D_2O bending modes in the systems with D_2O thus appears to be a consequence of a partial exchange of these H_2O molecules with bulk D_2O . Furthermore, some of the spectral features of the PEG chains are slightly but still noticeably modified in systems with D_2O (Figure 4) with respect to those observed in the H_2O -based systems (Figure 2). This indicates that replacement of H_2O by D_2O does somewhat influence the vibrational frequencies of the poly(oxyethylene) chain in both Triton X-100 and PEG 400.

Combining these two observations, we can conclude that the intense band of the H-O-H deformation vibration observed at 1641 cm^{-1} in the SERS spectra of Triton X-100 and PEG 400 originates from those H_2O molecules which are in an interaction with PEG chains adsorbed on the surface. We believe to be observing the phenomenon similar to that described in ref 26 where SERS from H_2O molecules forming the hydration shell of bovine serum albumin was observed.

Another characteristic feature of the SERS spectra of PEG 400 (Triton X-100) on Ag colloid is the disappearance of two "satellite" bands at 843 and 890 cm^{-1} (843 and 875 cm^{-1}) which accompany the band at 806 cm^{-1} in the normal Raman spectra of liquid samples. All three bands are attributed to the CH_2 rocking mode of the chain in different conformations (Table I). The SERS enhancement of only one of these CH_2 rocking modes indicates that the PEG chain adopts probably only one preferred conformation on the Ag surface.

Additional differences appear in the $900\text{--}1200\text{ cm}^{-1}$ region of the Raman spectra which, for liquid PEG, are dominated by two strong bands at 1137 and 1048 cm^{-1} attributed to coupled C-O and C-C stretching modes (Table I). In the SERS spectra, two groups of weaker bands at 1171 , 1119 and at 1009 , 950 cm^{-1} newly appear. This observation can be explained by decoupling of C-O and C-C modes due to the weakening of C-O bond which is a consequence of strong electron donation from oxygen to silver upon PEG chain chemisorption in the preferred conformation.

In conclusion, the interpretation of the SERS spectrum of Triton X-100 adsorbed on Ag colloid shows that (i) the hydrophobic part of the Triton X-100 surfactant is not in direct contact with the Ag surface, which is indicated by the absence of surface enhancement of hydrophobic moiety vibrations, (ii) Triton X-100 is adsorbed on the Ag colloid surface via the hydrophilic, i.e. PEG moiety, and (iii) the SERS spectrum of the adsorbed PEG moiety shows substantial differences with respect to the Raman spectrum of liquid PEG. Conclusions ii and iii indicate that both Triton

X-100 and PEG 400 are strongly and similarly chemisorbed on the Ag colloid surface.

The spectral changes which occur upon chemisorption of both species are attributed to coordination (via lone electron pair donation) of the etheric oxygen atoms of PEG units to Ag_n^+ ($n \geq 1$) species present on the surface of Ag colloid. This type of coordination reduces the PEG chain flexibility and can be the reason for a single preferential conformation adopted by the PEG chains on the surface.

There is experimental evidence supporting the above explanation: Poly(ethylene glycol) is known to form complexes with metal halides, e.g., those of Ca^{2+} and Mg^{2+} ²⁵ and of Hg^{2+} .²⁷ Vibrational spectra of these complexes show two spectral features similar to those observed upon chemisorption of PEG on the Ag surface (see Table I): (i) splitting of bands in the $950\text{--}1200\text{ cm}^{-1}$ region and (ii) shifts of $\delta(C-C-O)$ and $\delta(C-O-C)$ bending modes in the $500\text{--}600\text{ cm}^{-1}$ region to somewhat higher frequencies. The frequency shifts are smaller than in our systems; however, a more quantitative agreement can hardly be expected as (i) the PEG chain should adopt a different conformation when interacting with the isolated metal ions and with the surface (e.g., fixation of the PEG chain to the surface can seriously affect the frequencies of the bending modes, as shown in Table I) and (ii) the strength of coordination bonding generally differs for different metal ions.

Although the SERS spectra of Triton X-100 and PEG 400 are identical, there is an experimentally observable difference between the Ag colloid/Triton X-100 and Ag colloid/PEG SERS-active systems in their absorption spectra (see Figure 1, curves B and C). As the surface plasmon absorption of a SERS-active system is related to the state of aggregation of Ag colloid, we can interpret this difference in terms of a different size distribution of aggregates in both systems discussed. Aggregation of Ag colloid by Triton X-100 leads to a preferential formation of small aggregates, while upon aggregation by PEG 400, bigger aggregates are also formed. Moreover, the kinetics of aggregation also differs for both systems: while the SERS-active system Ag colloid/PEG 400 is formed within 1 day, formation of the Ag colloid/Triton X-100 system is slower (3 days). Considering that aggregation is induced by adsorption of the adsorbate via destruction of the original surface dielectric bilayer stabilizing the isolated colloidal particles, we can expect the rate of aggregation to be influenced by the rate of adsorption. In our case, the presence of the hydrophobic part in the Triton X-100 molecule can be the factor slowing down the penetration of this molecule into the hydrophilic interface, thus reducing the rate of its adsorption. Consequently, the rate of the SERS-active system formation will also be reduced. Examination of other types of SERS-active systems²⁸ assured us that slower aggregation generally produces smaller aggregates, as observed here for Triton X-100. However, it is worth noting that, under the conditions of our experiment, i.e. 514.5 nm excitation, the intensities of the SERS spectra of Triton X-100 and PEG 400 are comparable. The difference in the aggregate size distribution thus does not severely influence the SERS intensities. This can be explained by the fact that the extinction coefficients of surface plasmon absorption at 514.5 nm are similar for both systems (Figure 1).

Triton X-100 as a Molecular Spacer in the Ag Colloid/Triton X-100/TPPC₄ System. Finally, the SERS spectra of free base TPPC₄/Triton X-100/Ag colloid system were measured to test the ability of Triton X-100 to suppress the chemical interaction between the porphyrin and the Ag surface (i.e., porphyrin metalation)¹⁸ while maintaining the surface enhancement of Raman scattering by the porphyrin. Furthermore, to elucidate which part of the surfactant molecule is responsible for this effect, we have investigated the SERS spectrum of TPPC₄ in the Ag colloid/PEG 400/TPPC₄ system, too. The following spectral characteristics are important for this investigation:^{11,18} The metalated form of

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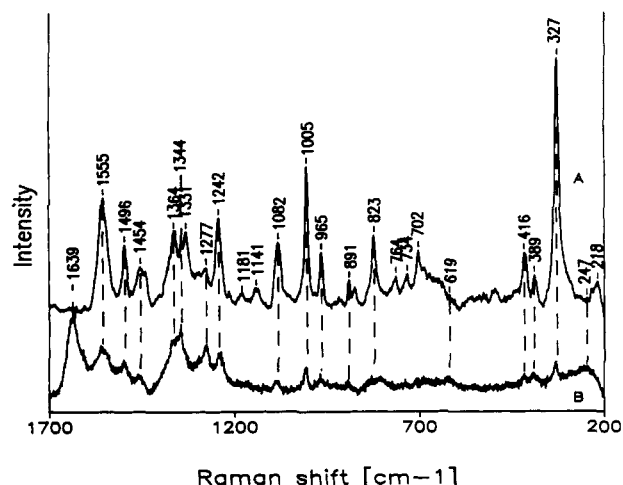


Figure 5. SERS spectra of (A) Ag colloid (4 mL)/Triton X-100 (40 μ L, 10^{-2} M)/TPPC₄ (40 μ L, 10^{-4} M) system and (B) Ag colloid (4 mL)/PEG 400 (40 μ L, 10^{-2} M)/TPPC₄ (40 μ L, 10^{-4} M) system.

the porphyrin, i.e., Ag^{II}TPPC₄ surface complex, is characterized by a marker band at 390 cm^{-1} . On the other hand, the 327- cm^{-1} band is typical for a native, free base form of the porphyrin. These two forms of TPPC₄ can thus be easily distinguished in the SERS spectra.

Furthermore, it is necessary to emphasize that, under the conditions of our experiment, the resonance enhancement will occur in addition to the surface enhancement of Raman scattering of the free base form of the porphyrin, as the excitation wavelength 514.5 nm is nearly coincident with the first maximum of the Q electronic absorption band at 516 nm. The resonance enhancement contribution is smaller for the metalated form of the porphyrin, for which the maximum of the electronic absorption is shifted to 542 nm.

Surface plasmon absorption spectra of the Ag colloid/Triton X-100/TPPC₄ and of Ag colloid/PEG 400/TPPC₄ SERS-active systems (not shown) are virtually identical to those of the corresponding systems prior to addition of the porphyrin (shown in Figure 1).

The SERS spectra of the systems obtained 2 h after addition of the porphyrin are compared on the identical intensity scale in Figure 5: spectrum A, Ag colloid/Triton X-100/TPPC₄; spectrum B, Ag colloid/PEG 400/TPPC₄. Comparison of the band position/intensity pattern of spectrum A with those of free base and metalated TPPC₄^{11,18} confirms that the majority of the adsorbed porphyrin molecules are in the free base form. This is most apparently demonstrated by the intense marker band of the free base form of the porphyrin at 327 cm^{-1} . The pretreatment of Ag colloid by Triton X-100 thus effectively prevents the metalation of the porphyrin.

In contrast, spectrum B differs from spectrum A in four main features: (i) The intensity of the porphyrin bands is substantially higher in spectrum B than in spectrum A although the same amount of porphyrin molecules is present in both systems. (ii) Spectrum A is dominated by the bands of free base TPPC₄ while the observable spectral features of hydrophilic (PEG-like) moiety of Triton X-100 are limited to two bands at 1277 and 1344 cm^{-1} . On the other hand, in spectrum B, the PEG bands are stronger relative to those of porphyrin. (iii) In contrast to the spectrum B, the band at 1641 cm^{-1} attributed to SERS of H₂O interacting with PEG moiety is completely absent in spectrum A. (iv) Marker bands of the free base as well as of the metalated form appear in both spectrum A and B. However, there is a pronounced difference both in their absolute intensities and in their mutual intensity ratio between spectra A and B (Figure 5). The marker band of the free base form is more than 10 times as intense in spectrum A than in spectrum B. The intensity of the 390- cm^{-1} marker band of the metalated form is about twice as high in spectrum A than in spectrum B. The intensity ratio of the 327- cm^{-1} (free base) to the 390- cm^{-1} (metalated) marker band is 10

for spectrum A and 2 for spectrum B.

The most important conclusion of this comparison is that the signal from the free base form of the porphyrin is 10 times more intense in system with Triton X-100 than in that with PEG 400. Moreover, neither the bands of Triton X-100 nor those of the Ag^{II}TPPC₄ surface complex interfere seriously with those of free base TPPC₄. Triton X-100 thus proves to be an effective molecular spacer for SERS of TPPC₄.

Considering the reasons for an order of magnitude increase of the SERS signal of the free base TPPC₄ in the system with Triton X-100 in comparison to that with PEG 400 (note the identical concentration of TPPC₄ in both systems: 10^{-6} M), there are basically two factors: (i) the enhancement factor and (ii) the concentration (number) of TPPC₄ molecules which experience the surface enhancement. Both the enhancement via the electromagnetic mechanism of SERS and the resonance enhancement of Raman scattering contribute to the overall SERS intensity of free base TPPC₄. Unfortunately, we cannot comment on the relative contributions of the two mechanisms, as we did not succeed in obtaining the resonance Raman spectrum of free base TPPC₄ in solution, neither for the 10^{-6} M nor for a higher concentration. The resonance contribution should be identical for both systems as it originates from the same species, i.e. free base TPPC₄.

Considering the electromagnetic mechanism of SERS, it is necessary to decide whether or not the difference in the aggregate size distribution between the system with Triton X-100 and PEG 400 may influence the SERS enhancement factor of TPPC₄. The difference in aggregate size distribution between the initial systems with Triton X-100 and PEG 400 has not changed upon addition of TPPC₄ into these initial systems (see above). Furthermore, it has been already shown that this difference did not affect the intensity of SERS of the PEG chain in the initial systems, probably due to the similar surface plasmon absorption at 514.5 nm. As the surface plasmon absorption remained the same upon addition of the porphyrin, we suppose that the SERS enhancement of TPPC₄ is also not affected by the different aggregate size distribution in both systems.

There is, however, a difference between the Ag colloid/Triton X-100/TPPC₄ and the Ag colloid/PEG 400/TPPC₄ systems in the SERS-active system structure on a molecular or, possibly, supramolecular²⁹ level. This difference follows from the difference in the molecular structure of Triton X-100 and PEG 400, i.e., from the presence of the hydrophobic part of Triton X-100. Up to now we do not have evidence that the special molecular (or supramolecular) structure of the Ag colloid/Triton X-100/TPPC₄ system could cause the increase of the enhancement factor of SERS of TPPC₄. Therefore, we present here a more obvious explanation of the role of the hydrophobic part of Triton X-100 in the SERS-active system with free base TPPC₄ based on a hydrophobic interaction between the porphyrin and the hydrophobic Triton X-100 moiety which (i) attracts a sufficient amount of porphyrin molecules to a location in the vicinity of the Ag colloid surface (and in this way substitutes for the direct adsorption of the porphyrin on the Ag surface) and (ii) simultaneously disables the porphyrin in competition with the PEG chains in the adsorption to the Ag colloidal surface being thus responsible (either in an energetic or a kinetic sense) for the surfactant shielding effect. Furthermore, the rejection of H₂O molecules from the vicinity of PEG chains adsorbed on Ag surface is apparently caused by the near-surface location of TPPC₄ mediated by the hydrophobic part of Triton X-100.

The general properties of Triton X-100 as a molecular spacer in systems with Ag colloid and porphyrins as well as other types of adsorbates are currently investigated in our group. In particular, a thorough comparison of SER(R)S of free base TPPC₄ and its Ag(II) complex adsorbed on Ag colloid both directly and via a

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(30) SERS spectra of Triton X-100 and PEG 400 have also been compared in the 2600–3600- cm^{-1} region (not shown here). A weak spectral feature appears at 2930 cm^{-1} in both spectra, together with two broad bands with maxima at 3240 and 3350 cm^{-1} and a shoulder at 3400 cm^{-1} attributable to O–H stretching modes of water.

molecular spacer is the subject of our forthcoming paper.²⁸

Conclusions

(i) The nonionic surfactant Triton X-100 aggregates spontaneously the Ag colloid to form the SERS-active system. Only the vibrational frequencies of the hydrophilic part of Triton X-100 molecule are active in the SERS spectrum of the system.

(ii) The surfactant molecules are adsorbed on the surface of Ag colloid via their hydrophilic (PEG) moiety with the hydrophobic part exposed to possible interaction with other molecules studied.

(iii) Upon addition of free base TPPC₄ to the Ag colloid/Triton X-100 SERS-active system, the surfactant acts as an effective

molecular spacer between the porphyrin and Ag colloid. Its hydrophobic part represents an "affine group" capable of hydrophobic interaction with the porphyrin macrocycle.

(iv) According to our experience, the surfactant-covered silver surface currently represents the only possibility for obtaining the SERS spectrum of an unaltered free base porphyrin in the system with Ag colloid.

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Registry No. PEG, 25322-68-3; TPPC, 14609-54-2; Ag, 7440-22-4; Triton X-100, 9002-93-1.

Improvement of Photoelectrochemical Properties of Chloroaluminum Phthalocyanine Thin Films by Controlled Crystallization and Molecular Orientation

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An orientation-controlled thin film of AlPcCl was prepared by vacuum deposition on a (001) surface of a KCl substrate. In the epitaxially grown film on KCl AlPcCl molecules stack cofacially, staggering around the Al-Cl-Al bonds and holding the molecular planes parallel to the KCl surface. At a low substrate temperature the deposit was a uniform and closely oriented thin film. As the substrate temperature increased, the film became rugged and cracked due to growth of a large size of crystallites. The photovoltaic properties of the oriented AlPcCl film were measured in a photoelectrochemical cell of ITO/AlPcCl/I₃⁻/I⁻/Pt. The oriented AlPcCl films showed good rectifying *I-V* curves of p-type conductance and cathodic photocurrents under illumination of white light. As compared to amorphous or polycrystalline AlPcCl films, photovoltaic efficiency was improved especially in increase of *I_{sc}* by the epitaxial orientation. The photocurrent quantum yield of the uniform thin film with epitaxial orientation was 25 times as high as that of the rugged and cracked polycrystalline film with large crystallites. The epitaxial AlPcCl film showed an intense peak at 830 nm in the photocurrent action spectrum, which could be attributed to carrier generation from charge-transfer excitons of the cofacially stacked molecules. It was concluded that the reason for the improvement of the photovoltaic properties was that exciton diffusion and charge carrier mobility were larger through the molecular column in the epitaxial film, while exciton trapping and recombination of carriers were probably caused in grain boundaries between crystallites in the polycrystalline film.

I. Introduction

Solar energy conversion is the most important technology for a future energy source because solar energy is pollution-free and inexhaustible. The energy conversion efficiency of silicon semiconductors has been more than 10%; however, electrical energy obtained with these cells is expensive. On the other hand, colored molecular organic semiconductors may be good candidates for materials of future solar cells due to their cheapness, low processing costs of thin films, and nearly unlimited variability.² The conversion efficiency of stable organic solar cells has barely come up to 1% in a pn-junction configuration with phthalocyanines and perylene derivatives, which are known as p- and n-type semiconductors, respectively.¹⁻³ Since the solar energy conversion system in nature, photosynthesis, functions with chlorophyll in which the interior ligand is in structural analogy with phthalocyanines, synthetic organic molecules could be tailored for a biomimetic approach. The chlorophyll molecules are integrated in a crystallographically ordered biological system to give a high

efficiency of carrier generation and electron transport.^{4,5} Therefore, for improvement of the conversion efficiency, especially the photocurrent, of organic solar cells, it is very important to control the crystal growth and the molecular orientation in a thin film. Porphyrins^{6,7} and phthalocyanines⁸⁻¹¹ exhibit an epitaxial growth in vacuum-deposited thin films onto a cleavage surface of alkali metal halides. Their crystal structure and molecular orientation have been examined by high-resolution electron microscopy and electron diffraction.⁶⁻¹² The vacuum-deposited

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