Volume 30
Number 22
October 30, 1991

Inorganic Chemistry

Communications

Surface-Enhanced Raman Spectra of 5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrin/Silver Colloid System: What Information about the Porphyrin Do We Obtain?

Porphyrins, both as free bases and as metal complexes, are involved in many important biological functions (photosynthesis, metabolic redox reactions, oxygen transport, photodynamic processes, etc.). Vibrational spectroscopy of these large but highly symmetric molecules is a very sensitive probe of their structure in various types of environment. However, the generally low oscillator strengths of vibrational transitions in porphyrins make their infrared (IR) and Raman measurements at low (physiological) concentrations difficult.[1]

Surface-enhanced Raman scattering (SERS) spectroscopy overcomes this problem by the 10^4–10^6 enhancement of Raman scattering upon adsorption of the molecular species studied on a roughened surface of the particular metal.[2] Nevertheless, a specific chemical interaction of the species with the metal surface may affect the relevancy of the structural information about the species itself provided by SERS. Classification of the possible structural changes induced by adsorption of porphyrins onto the metal surface thus becomes a crucial point in the interpretation of the SERS spectra of porphyrin-containing systems. In this paper, we address this basic problem for the water-soluble free base 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (TPPC4) adsorbed on the surface of Ag colloidal particles.

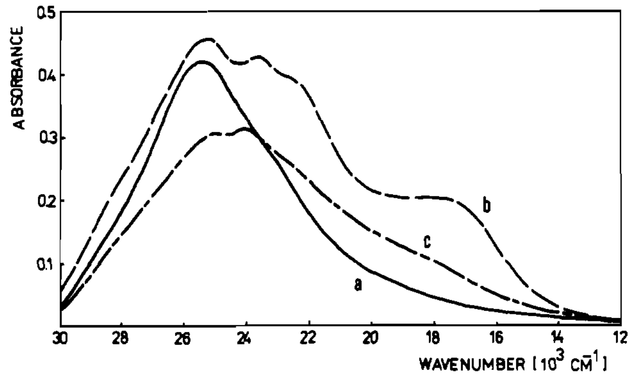


Figure 1. Electronic absorption spectra of (a) freshly prepared Ag colloid (solid curve), (b) SERS-active system I [TPPC4/Ag colloid] (dashed curve), and (c) SERS-active system II [TPPC4/Triton-X100/Ag colloid] (dot–dashed curve).

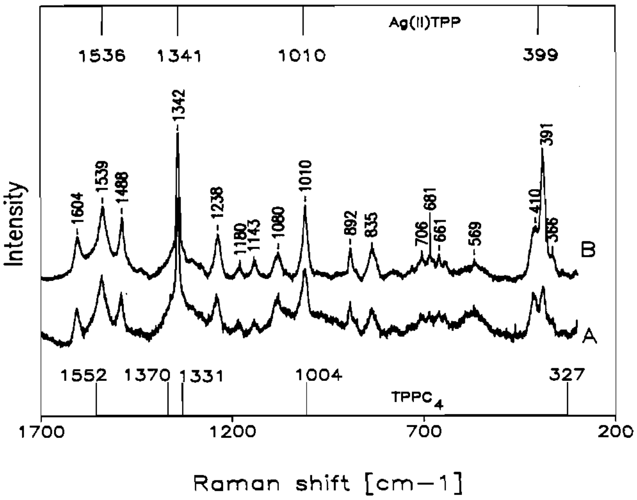


Figure 2. Curve A: SERS spectrum of system I [TPPC4 adsorbed on Ag colloid]. Curve B: SERS spectrum of system I aged for 2 months. Positions of resonance Raman bands for solid-state $Ag^{II}TPP$[7] and of those of free-base TPPC4[5] are indicated by bars on the top and bottom of the figure, respectively.

The SERS spectra were measured on a modular Raman spectrometer described elsewhere,[3] using the 514.5-nm Ar laser line for excitation. Ag colloid was prepared by reduction of silver nitrate with sodium borohydride using the procedure published in ref 4. We have found it necessary to change the original preparation procedure by using 7.5 mL of the silver nitrate instead of 9.0 mL. The electronic spectrum of the resulting Ag colloid is shown in Figure 1 (spectrum a). A 50-μL aliquot of 5×10^{-5} M TPPC4 solution in 0.02 M phosphate buffer (pH = 7.3) was added to Ag colloid aged for 1 day in the dark, and the system was shaken up for 1 h. After 18 h of formation of the SERS-active system (system I) at room temperature (22 °C) in the dark, its electronic spectrum was measured (curve b in Figure 1). The SERS spectrum of system I is curve A in Figure 2. To test the stability of the SERS-active system, the sample was stored in the dark at 4 °C for a period of 2 months. While the electronic spectrum of the aged system remained unchanged, the SERS spectrum (curve B in Figure 2) differs from that of the original sample just in two spectral features (compare spectra B and A in Figure 2): an intensity increase of the band at 391 cm^{-1} and a slight intensity decrease of the weak band at 569 cm^{-1}. The rest of the spectrum remains unaltered. Compared with the resonance Raman (RR) spectrum of solid-state TPPC4 reported in ref 5, both spectra A and B exhibit several different features. However, these differences are limited to the "marker" bands characteristic of the free-base form of the porphyrin. The 327

---

(1) Dolphin, D. *The Porphyrins*; Academic Press: New York, London, 1978; Vol. II.

(2) Jeanmarie, D. J.; Van Duyne, R. P. *J. Electroanal. Chem. Interfacial Electrochem.* **1977**, *84*, 1.

(3) Bok, J.; Praus, P.; Štěpánek, J.; Baumruk, V. *Comput. Phys. Commun.* **1988**, *50*, 225.

(4) Ahern, A. M.; Garrell, R. L. *Anal. Chem.* **1987**, *59*, 2816.

(5) Cotton, T. M.; Schultz, S. G.; Van Duyne, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 6528.

0020-1669/91/1330-4103$02.50/0 © 1991 American Chemical Society

cm^{-1} band of free-base TPPC4 is absent in the SERS spectra. At contrast, a new SERS band at 391 cm^{-1} appears. Furthermore, an intense band at 1342 cm^{-1} is found in the SERS spectra instead of the two weaker RR peaks at 1370 and 1331 cm^{-1}. Also the bands observed at 1552 and 1004 cm^{-1} in the RR spectrum of free-base TPPC4 are shifted to 1535 and 1010 cm^{-1}, respectively, in SERS. Cotton et al.[5] have reported the partial metalation of TPPC4 on an Ag electrode using the SERS technique. The metalated form of the porphyrin was characterized by bands at 380, 415, and 1365 cm^{-1}. The appearance of similar characteristic bands in our SERS spectra prompted us to compare curves A and B with the RR spectra of a structurally similar silver metalloporphyrin, solid-state silver(II) tetraphenylporphyrin ($Ag^{II}TPP$),[6] published in ref 7. SERS spectrum B exhibits all the characteristic normal vibrations of the silver-metalated tetraphenylporphyrin macrocycle, namely the strong single band at 391 cm^{-1} (compare to the 399-cm^{-1} band of $Ag^{II}TPP$), at 1342 cm^{-1} (1341 cm^{-1} for $Ag^{II}TPP$), and at 1539 cm^{-1} (1536 cm^{-1} for $Ag^{II}TPP$). We therefore conclude that the free-base $TPPC_4$ is completely metalated on the surface of the Ag colloid, thus forming the $Ag^{II}TPPC4$ surface complex. The full development of the 391-cm^{-1} band upon aging of system I (compare spectrum A and B in Figure 2) is most probably connected with positioning of the central Ag atom into the plane of the porphyrin macrocycle, which corresponds to the equilibrium geometry of the $Ag^{II}TPPC_4$ complex. Complete metalation of $TPPC_4$ on the surface of the Ag colloid contrasts with only partial metalation of the porphyrin on the Ag electrode.[5] In our opinion, it is the surface morphology rather than the surface potential that is responsible for this difference.

The comparison of the SERS spectrum of the $Ag^{II}TPPC4$ surface complex with the RR spectrum of $Ag^{II}TPP$ showed us that there are no bands attributable to either COO^- or COOH groups in our SERS spectrum. However, several minor additional bands not seen in the $Ag^{II}TPP$ solid-state RR spectrum are observed in the SERS spectra of $Ag^{II}TPPC4$. It is interesting to note that similar additional bands are reported to develop in the SERS spectrum of $Ag^{II}TPP$ in the $Ag/Ag^{II}TPP/CaF_2$ layered structure.[7] In reference to refs 8 and 9, we tentatively attribute at least two of these bands (at 569 and 681 cm^{-1}) to the out-of-plane porphyrin core vibrations. Assuming that the $Ag^{II}TPPC4$ surface complex is planar, these modes can be enhanced neither by the A term nor by the B term mechanism of resonance enhancement.[8] The surface-enhancement effect thus appears to be responsible for their activity. If this conclusion is combined with the SERS selection rules,[10] according to which the normal modes having a large α component perpendicular to the metal surface are most enhanced, a parallel geometry of the porphyrin core with respect to the Ag surface can be postulated. Moreover, only the "plane-on-Ag" orientation enables the porphyrin to be metalated via direct interaction with the Ag surface. However, it is necessary to prove that the metalation really occurs on the Ag surface and not in the solution (possibly by some residual Ag^+ ions). This is shown by the following experiments.

To prevent the chemical interaction of TPPC4 with the silver surface, we have covered the Ag colloidal particles by a surfactant prior to the adsorption of porphyrin. The following protocol for the SERS-active system preparation was used. To the Ag colloid prepared as above, 50 μL of a 10^{-2} M aqueous solution of Triton X-100 was added, and the active system was formed for 2 days in the dark at 4 °C. The SERS spectrum of the resulting system (not shown) contains the Raman bands of the surfactant, which are interpreted elsewhere.[11] Approximately 1 h before the SERS measurement, 20 μL of a 10^{-4} M buffer solution of TPPC4 was added to the Ag colloid/Triton X-100 system. The electronic spectrum of the resulting system II is presented as curve c in Figure 1; its SERS spectrum is shown in Figure 3. The bands of surfactant were found not to interfere significantly with the Raman spectrum of porphyrin due to their (10×) lower intensity. The SERS spectrum of TPPC4 exhibits all spectral characteristics of the free-base form of the porphyrin as observed in its resonance Raman spectrum.[5] This is demonstrated most evidently by the presence of the strong band at 327 cm^{-1}. Also the positions of other marker bands (the doublet at 1331, 1362 cm^{-1} and the 1555- and 1005-cm^{-1} bands) are typical for the free-base form. The almost complete lack of spectral features of $Ag^{II}TPPC4$ in the SERS spectrum of Ag colloid/Triton X-100/TPPC4 system thus excludes the possibility of metalation of free-base TPPC4 in solution prior its adsorption on the Ag colloid and proves that the metalation of TPPC4 occurs only upon direct chemisorption of porphyrin on the Ag surface.

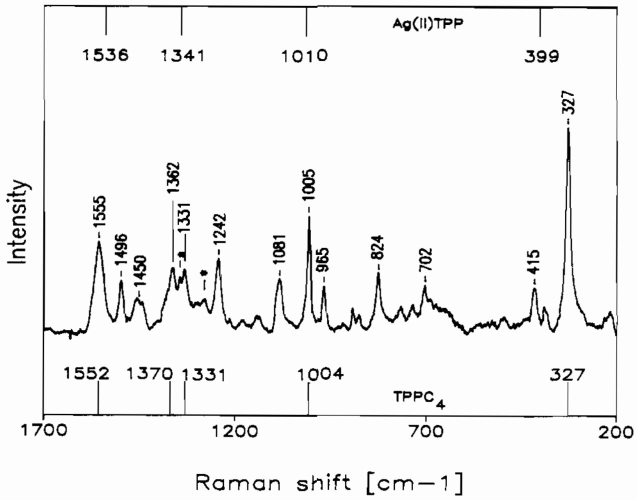


Figure 3. SERS spectrum of the Ag colloid/Triton X-100/TPPC4 system. The bands of Triton X-100 are marked by asterisks. Positions of resonance Raman bands for solid-state $Ag^{II}TPP$[7] and of those of free base TPPC4[5] are indicated by bars on the top and bottom of the figure, respectively.

Relative intensities of the metal-insensitive porphyrin core modes of TPPC4 in system II appear to be comparable to those of $Ag^{II}TPPC4$ complex in system I. We consider it as a indication that the orientation of the porphyrin macrocycle in system II is similar to that in system I, i.e. parallel to the surface.

The above experiments prompt us to discuss the mechanisms responsible for the enhancement of Raman scattering. The intensity of the SERS signal of free-base TPPC4 in the Ag colloid/Triton X-100/TPPC4 sample (system II) is practically comparable to the intensity of SERS of the $Ag^{II}TPPC4$ surface complex formed upon direct chemisorption of TPPC4 on the Ag surface (system I). It is evident that, for porphyrins, both the surface and the resonance enhancement of the Raman scattering have to be considered. In the case of surface enhancement in system I, both the electromagnetic and chemical mechanisms can contribute, while for system II only the electromagnetic enhancement mechanism is involved. Its actual magnitude will be a rather complex function of the surface–porphyrin distance (moderated by surfactant) and the intensity of plasmon resonance (at 514.5 nm). On the other hand, the contribution of the resonance enhancement is determined by specific absorption properties of the free-base and metalated porphyrins in the long-wavelength spectral region. While in the case of free-base TPPC4 (system II), the 514.5-nm excitation line is quite close to the first maximum (516 nm) of the Q electronic absorption region, the corresponding

---

(6) TPPC4 differs from tetraphenylporphyrin only by the presence of –COOH substituents in para positions of the porphyrin phenyl rings. This structural difference is assumed to have only a minor effect on the macrocycle vibrations we are studying.

(7) (a) Kobayashi, Y.; Itoh, K. *J. Phys. Chem.* **1985**, *89*, 5174. (b) Shoji, K.; Kobayashi, Y.; Itoh, K. *Chem. Phys. Lett.* **1983**, *102*, 179.

(8) (a) Li, X.-Y.; Czernusewitz, R. S.; Kincaid, J. R.; Spiro, T. G. *J. Am. Chem. Soc.* **1989**, *111*, 7012. (b) Li, X. F.; Czernuszewicz, R. S.; Kincaid, J. R.; Su, Y. O.; Spiro, T. G. *J. Phys. Chem.* **1990**, *94*, 31.

(9) Song, O.-K.; Yoon, M.-J.; Kim, D. *J. Raman Spectrosc.* **1989**, *20*, 739.

(10) (a) Creighton, J. A. *Surf. Sci.* **1983**, *124*, 209. (b) Moskovits, M.; Suh, J. S. *J. Phys. Chem.* **1984**, *88*, 5526.

(11) Matějka, P.; Vlčková, B.; Vohlídal, J.; Pančoška, P.; Baumruk, V. *J. Phys. Chem.*, in press.

absorption maximum of the $\mathrm{Ag^{II}}$TPPC4 (system I) complex (542 nm) is far removed from excitation. We can thus conclude that, in the SERS spectrum of free-base porphyrin in the colloid/Triton X-100/TPPC4 system, the relative decrease in the surface enhancement of Raman scattering is compensated for by a contribution of the resonance enhancement.

If all of the above facts are combined together, they prove that the surfactant coverage of Ag colloid particles prevents the direct chemical interaction of the porphyrin with the metal surface while the scattering enhancement remains sufficient for obtaining a good quality SERS spectrum. Moreover, our recent experiments show that the selection of the specific molecular structure of surfactant is not the only possibility and that, e.g., synthetic polypeptides can play a similar role.[12]

The results can be summarized as follows. The formation of the $\mathrm{Ag^{II}}$TPPC4 complex upon chemisorption of TPPC4 on the Ag colloid surface represents an extreme example of the metal surface influence upon molecular structure of a species studied by SERS. The disadvantage of alteration of the structural information provided by SERS (as induced by metalation of the porphyrin) is compensated for by the possibility to use this alteration to probe the porphyrin–surface geometry. For example, we took advantage of these effects to monitor porphyrin–peptide interactions.[12] On the other hand, the surfactant application can be one way to minimize the metal surface perturbational effect on the molecule studied. Our results demonstrate the advantages as well as the drawbacks of SERS spectroscopy of porphyrins and give several hints for extraction of information about the porphyrin-containing systems of biological importance from the SERS data.

Registry No. Ag, 7440-22-4; Triton X-100, 9002-93-1; TPPC4, 14609-54-2.

---

[12] Vlčková, B.; Pančoška, P.; Baumruk, V.; Čermáková, K. To be submitted for publication.

[13] To whom correspondence should be addressed.

Department of Physical and Macromolecular Chemistry
Faculty of Science
Charles University
Hlavova 2030, 128 40 Prague 2, Czechoslovakia
Blanka Vlčková*,[13]
Pavel Matějka

Department of Chemical Physics
Faculty of Mathematics and Physics
Charles University
Prague, Czechoslovakia
Petr Pančoška

Institute of Physics
Charles University
Prague, Czechoslovakia
Vladimir Baumruk

Institute of Organic Chemistry and Biochemistry
Czechoslovak Academy of Science
Prague, Czechoslovakia
Vladimir Král

Received February 8, 1991

High Oxidation State Compounds Containing Hydrazine and Hydrazido Ligands Bound to a $\mathrm{W(N\text{-}2,6\text{-}C_6H_3\text{-}\mathit{i}\text{-}Pr_2)[2,6\text{-}NC_5H_3(CH_2NTosyl)_2]}$ Core

Recently, we have found that complexes that contain the $\mathrm{MCp^*Me_3}$ core ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$; M = Mo or W,[1] Re[2]) and a variety of $\mathrm{N_2H_x}$ or $\mathrm{NH_y}$ ligands can be prepared and that the N–N bond can be cleaved in η^2-hydrazine to give ammonia, catalytically in the case of M = Mo or W in the presence of protons and a reducing agent.[1] In the belief that long-term stability of such catalysts will be limited by loss of alkane in the presence of acid, we have begun to search for related systems that do not contain metal–carbon bonds. We report examples of such complexes here.

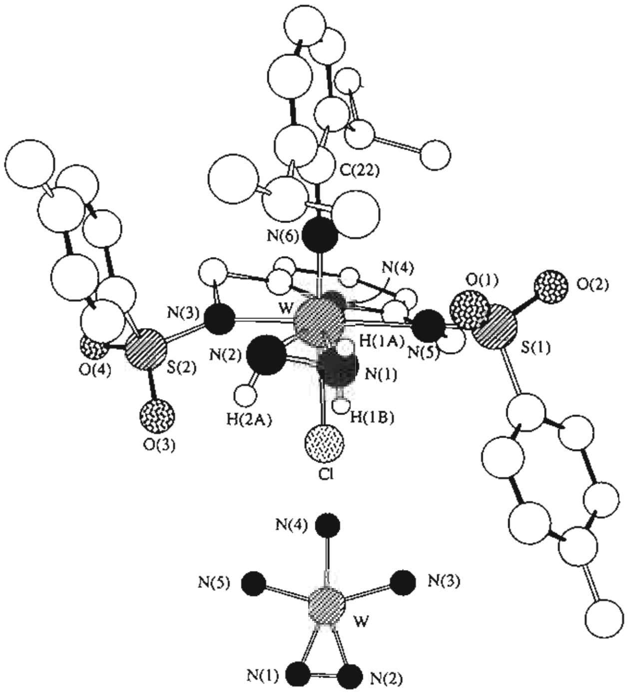
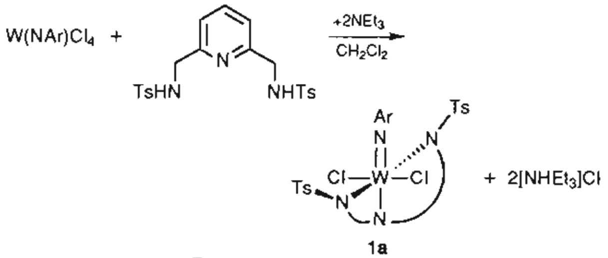


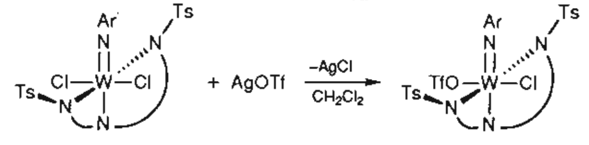
Figure 1. A view of **2** (with hydrogen atoms on the hydrazido(1–) ligand shown) and a view showing the equatorial ligands in the pentagonal arrangement.

A core of the type $\mathrm{M(NAr)[2,6\text{-}NC_5H_3(CH_2NR)_2]}$ (Ar = 2,6-$\mathrm{C_6H_3}$-*i*-$\mathrm{Pr_2}$) would be isolobal with the $\mathrm{MCp^*Me_3}$ core, *if* the imido ligand behaves as a $2\pi,1\sigma$ ligand and if square-pyramidal derivatives (pyridine donor *not* trans to the imido ligand) are favored. $\mathrm{W(NAr)Cl_4}$[3] reacts with 1 equiv of 2,6-pyridinebis(tosylmethylamine)[4] in the presence of 2 equiv of $\mathrm{NEt_3}$ to give *trans*-$\mathrm{W(NAr)[N(NTs)_2]Cl_2}$ ($\mathrm{N(NTs)_2} = 2,6\text{-}\mathrm{NC_5H_3(CH_2NTosyl)_2}$) (**1a**) in 80% yield (eq 1). The singlet at 5.48 ppm in the proton NMR spectrum for the methylene protons in the $\mathrm{N(NTs)_2}$ ligand is consistent with a C_{2v} symmetry for **1a**. Subsequent reaction of **1a** with AgOTf (OTf = triflate) gives a related molecule, W(NAr)[N(NTs)$_2$](OTf)Cl (**1b**) (eq 2), in 89% isolated yield. The proton NMR spectrum for **1b** reveals an AB



(1)

1a



(2)

1a **1b**

---

[1] Schrock, R. R.; Glassman, T. E.; Vale, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 725.

[2] Vale, M. G.; Schrock, R. R. *Organometallics* **1991**, *10*, 1661.

[3] Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L. Y.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262.

[4] Hosseini, M. W.; Comarmond, J.; Lehn, J.-M. *Helv. Chim. Acta* **1989**, *72*, 1066.

0020-1669/91/1330-4105$02.50/0