Peripheral substituent and solvent effects on the aggregation and photochemical properties of copper(II)phthalocyanine and copper(II)phthalocyanine-3,4′,4″,4‴-tetrasulfonic anion*

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Abstract: The role played by the peripheral substituent and the solvent on the aggregation and photochemical properties of copper(II)phthalocyanine and copper(II)phthalocyanine-3,4′,4″,4‴-tetrasulfonic anion $[Cu(tsPc)^{-4}]$ in aqueous solution has been studied by resonance Raman spectroscopy (RRS). The vibrational mode v_4 (1530 cm^{-1}) and the symmetric and antisymmetric stretching modes of water have been used as a probe of interactions and aggregation in resonance Raman measurements. It has been shown that the $Cu(tsPc)^{-4}$ molecules have a tremendous influence on water properties in solutions. In contrast, the influence of water on the $Cu(tsPc)^{-4}$ properties appears to be weak.

INTRODUCTION

Photochemistry of phthalocyanines has been the subject of intensive studies over many decades [1]. Phthalocyanines have many well-established and potential applications such as: green and blue dyes and pigments, sensing elements in chemical sensors, catalyzers in oxydase- and catalyse-like reactions, photovoltaic cell elements, red-sensitive photocopying applications, electronic display devices, liquid crystal color display devices, conducting polymers, and many others applications. In recent years, interest in phthalocyanine derivatives has been stimulated by a promising photochemical activity that can be applied in photodynamic therapy of cancer (PDT) and other medical applications [2–3].

The photodynamic activity of photosensitizer depends on photochemical mechanisms of photooxidation. On the other hand, the photochemical mechanisms of photooxidation depend on the degree of aggregation as one of the main features of photodynamic sensitizers is the ability to generate singlet oxygen that is expected to be different for monomers and dimers since the rate of deactivation by internal conversion to the ground state is suggested to be much greater for dimer.

The degree of aggregation strongly depends on the metal inside the ring, and the peripheral substitution at the benzo group has a tremendous influence on the aggregation [4–5].

In this paper, we wish to concentrate on the role played by the peripheral substituent and the solvent on the aggregation and photochemical properties of copper(II)phthalocyanine-3,4′,4″,4‴-tetrasulfonic anion $[Cu(tsPc)^{-4}]$ (Fig. 1) in aqueous solution by resonance Raman spectroscopy. We have measured the resonance Raman spectra at 294 K in the range 200–6000 cm^{-1} as a function of concentration for $Cu(tsPc)^{-4}$ in aqueous solutions and for $Cu(tsPc)^{-4}$ in the solid phase as well as the resonance

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Raman spectra for copper(II)phthalocyanine without any peripheral substitution (CuPc). The vibrational normal mode ν_4 of $Cu(tsPc)^{-4}$ and (CuPc) as well as the symmetric and antisymmetric stretching modes of water have been used as a physical probe of interactions and aggregation in resonance Raman measurements.

EXPERIMENTAL

Copper(II)phthalocyanine and copper(II)phthalocyanine-3,4′,4″,4‴-tetrasulfonic acid, tetrasodium salt were purchased from Aldrich. They were used without further purification. Water was distillated before preparing the solutions.

Raman spectra were recorded with Ramanor U1000 (Jobin Yvon) and Spectra Physics 2017-04S argon ion laser operating at 514 nm at power of 125 mW at 294 K. The spectral slit width was 6 cm^{-1} in the full temperature range, which corresponds to the 500-μm mechanical slit of the spectrometer. A λ/4 wave plate was used to change the linear polarization into the circular one to avoid the different sensitivity of the gratings to the polarization. The interference filter was used to purify the laser line by removing additional natural emission lines that interfere with the Raman lines, especially in the case of the solid samples.

RESULTS AND DISCUSSION

Figure 1 shows the structure of phthalocyanines, copper(II)phthalocyanine-3,4′,4″,4‴-tetrasulfonic anion.
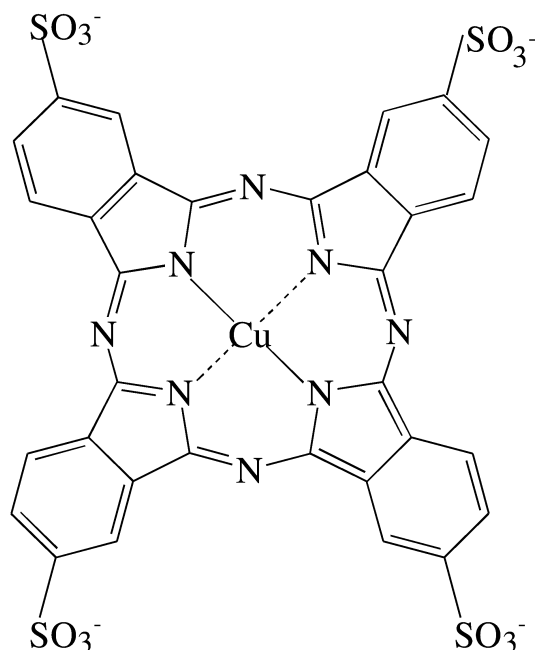
Fig. 1 Structure of phthalocyanines, copper(II)phthalocyanine-3,4′,4″,4‴-tetrasulfonic anion.

Figure 2 shows the resonance Raman spectra of the ν_4 vibrational normal mode for copper(II)phthalocyanine and copper(II)phthalocyanine-3,4′,4″,4‴-tetrasulfonic anion in solid phases and in aqueous solution. Most phthalocyanines including CuPc are not soluble in water, but the substitution of CuPc with hydrophylic groups like sulfonic groups $[Cu(tsPc)^{-4}]$ makes them soluble in aque-
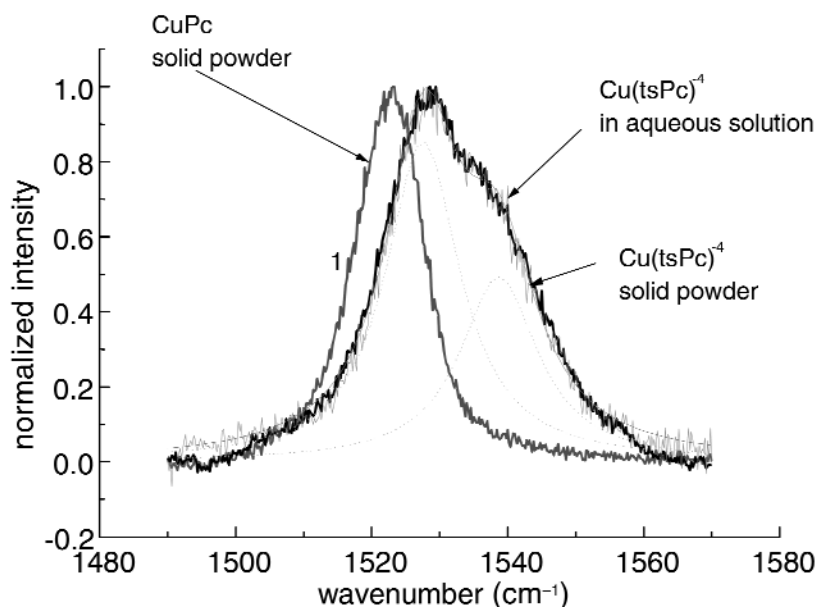
Fig. 2 The Raman spectrum of the ν_4 vibrational normal mode in copper(II)phthalocyanine (CuPc) in solid phase and copper(II)phthalocyanine-3,4′,4″,4‴-tetrasulfonic anion in aqueous solution Cu(tsPc)$^{-4}$ (c = 0.01 mol/dm^3) and in solid phase at 294 K.

ous solutions. One can see from Fig. 2 that both the band shape and the band maximum position differ significantly for nonsubstituted (CuPc) and substituted by sulfonic groups [Cu(tsPc)$^{-4}$] phthalocyanines. The frequency of the ν_4 vibrational normal mode in CuPc is significantly red-shifted by about 10 cm^{-1} with respect to the tetrasulfonated phthalocyanine. Moreover, the band shape of the ν_4 mode for CuPc is symmetric and purely Lorentzian in contrast to Cu(tsPc)$^{-4}$ for which the band consists of two overlapping bands: at 1527 cm^{-1} and 1538 cm^{-1}. We have shown [6] that the band at 1527 cm^{-1} corresponds to monomer, whereas the band at 1538 cm^{-1} corresponds to dimer.

It is worth noticing that the band shape of the ν_4 mode for tetrasulfonated phthalocyanine Cu(tsPc)$^{-4}$ in aqueous solution is identical to the band shape in the solid phase of pure Cu(tsPc)$^{-4}$ at 294 K. It indicates that at high concentrations of Cu(tsPc)$^{-4}$ (c = 10^{-2} mol/dm^3) the aggregation in liquid aqueous solution is very similar to that observed in the solid phase of tetrasulfonated copper(II)phthalocyanine. In contrast, nonsubstituted copper(II)phthalocyanine molecules does not form dimers even in the solid phase.

In view of these results, it is obvious that the hydrophylic groups at the benzo group must play a crucial role in the aggregation. It was reported [5,7] that copper(II)phthalocyanines as many other phthalocyanines form ring-stacked aggregates along the axis perpendicular to the plane of the molecule macrocycle. It was suggested [7] that the π–π interactions between the adjacent molecule rings stabilize columnar aggregates. However, our results presented in Fig. 2 provide strong evidence that copper(II)phthalocyanine molecules without peripheral substitution by hydrophylic groups do not form columnar aggregates and exist almost entirely as monomers even in the solid phase. It indicates that the π–π interactions that are present both in CuPc and in Cu(tsPc)$^{-4}$ are not the main factor in dimer or polymer stabilization and the peripheral groups play a crucial role in stabilization of ring-stacked dimers. Our results provide a strong evidence that the interaction between the adjacent molecules of Cu(tsPc)$^{-4}$ is strongly enhanced by the substitution with the sulfonic groups.

It is generally assumed that the character of aggregation in phthalocyanines is hydrophobic. Indeed, we have shown [6] that Cu(tsPc)$^{-4}$ dimerizes readily in aqueous solutions and tends to aggre-

gate even at 10^{-5} mol/dm^3 indicating that water does not perturb significantly the intermolecular interactions between the adjacent rings of the Cu(tsPc)$^{-4}$ molecules.

It would be interesting to learn more about the origin of the interactions between water and Cu(tsPc)$^{-4}$ molecules monitoring the properties of water in the phthalocyanine aqueous solutions.

Figure 3 shows resonance Raman spectra of Cu(tsPc)$^{-4}$ in aqueous solutions at 294 K as a function of Cu(tsPc)$^{-4}$ concentration in the solution. The narrow peaks in the region 200–2000 cm^{-1} correspond to the vibrational normal modes of Cu(tsPc)$^{-4}$, the broad band between 3000–3600 cm^{-1} corresponds the stretching (symmetric and asymmetric) modes of water. For the concentration between 10^{-3} mol/dm^3 to 10^{-4} mol/dm^3 we observe the broadband emission in the range between 200–3000 cm^{-1} that disappears at lower concentrations. The emission is not also observed at concentrations higher than 10^{-3} mol/dm^3. The origin of this emission has been discussed in our recent paper [8].

Striking behavior reveals when we compare the intensities of the stretching modes of water at different concentration of Cu(tsPc)$^{-4}$. Taking into account that the concentration of Cu(tsPc)$^{-4}$ is much lower than the concentration of water in the solutions, which is approximately constant and equal to 55.5 mol/dm^3, we should expect the similar intensities of the water bands at all concentrations. In contrast, the intensity of the stretching mode of water significantly depends on the Cu(tsPc)$^{-4}$ concentration. Indeed, for concentrations higher than 10^{-3} mol/dm^3, the intensity of the band of water is negligible. It increases significantly when the concentration of Cu(tsPc)$^{-4}$ falls below 10^{-4} mol/dm^3 and strongly depends on the concentration of Cu(tsPc)$^{-4}$ although the concentration of water is practically
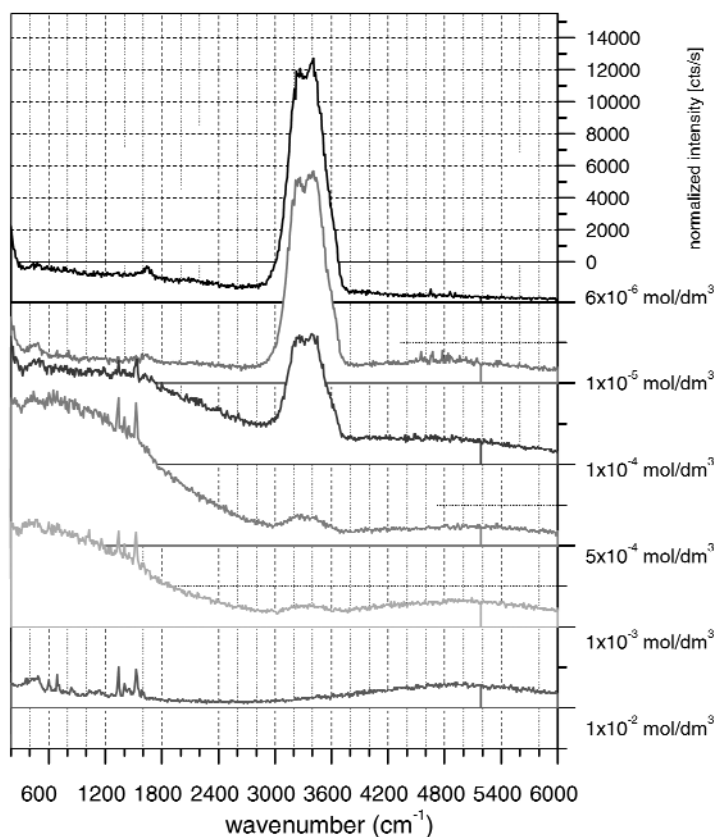
Fig. 3 Resonance Raman spectrum of Cu(tsPc)$^{-4}$ in aqueous solutions at 294 K as a function of Cu(tsPc)$^{-4}$ concentration.

the same. We may suspect that this pattern of behavior comes from the preresonance Raman conditions. Indeed, the emission between 200–3000 cm^{-1} reflects the presence of the electronic transitions in this spectral range with the stretching modes of water at around 3000–3600 cm^{-1} laying on the wings of this emissive state. However, we can see from Fig. 3 that for the concentrations between 10^{-3} mol/dm^3 and 5×10^{-4} mol/dm^3 for which the emission is very strong and the preresonance conditions should be the most effective, the intensity of the band of water at 3000–3600 cm^{-1} is very weak. Even if we assume that the mechanisms of deactivation of the excited electronic states change from radiative to radiationless processes with Cu(tsPc)$^{-4}$ concentration, the preresonance electronic transitions should influence more the intensity of water band at higher concentrations of Cu(tsPc)$^{-4}$ rather than for lower concentrations, which is in contrast to the experimental results in Fig. 3. So, this quite unusual behavior of water cannot be related to the preresonance Raman conditions.

In the view of the results presented in Fig. 3, we can state that Cu(tsPc)$^{-4}$ molecules have a tremendous influence on water properties in solutions. In contrast, the influence of water on the Cu(tsPc)$^{-4}$ properties shown in Fig. 2 appears to be weak. It is evident that Cu(tsPc)$^{-4}$ molecules modify the transient dipole moments of water molecules that are responsible for the intensity of Raman scattering. The interactions may origin from H-bond interactions between the sulfonic groups of Cu(tsPc)$^{-4}$ and water molecules. However, taking into account the relative concentrations of water and Cu(tsPc)$^{-4}$, the effect is much larger than expected as there are still many non-H-bonded species that should give a contribution to the Raman band intensity of the stretching modes of water. Further studies are necessary to establish the reason of unusual behavior of water in aqueous solutions of Cu(tsPc)$^{-4}$.

ACKNOWLEDGMENTS

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