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Complexes produced by associated forms of porphyrin bound with hydrophobic–hydrophilic copolymer and transition metal ions

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Abstract

Properties of protonated dimeric forms of *meso*-tetraphenylporphine (TPP) and *meso*-tetra(*p*-aminophenyl)porphine (TAPP) bound with copolymer and also complexes produced by associated TAPP bound with copolymer, Mn^{2+}, and Fe^{3+} are investigated by absorption, luminescence, and Raman spectroscopy. According to absorption spectra of protonated dimers of TPP, three dimeric forms of the porphyrin are observed in the ground state. However, selective excitation of these forms according to the fluorescence spectra reveals only two dimeric forms in the excited state. In contrast, similar selective excitation of TAPP bound with copolymer in aqueous–dioxane solution results in weak changes in the fluorescence spectra, nevertheless, there is strong interaction between porphyrin and macromolecular carboxyl groups in the ground state. In the case of the formation of the complexes between associated TAPP bound with copolymer, Mn^{2+} and Fe^{3+}, a new band in the near IR region with a maximum at 840 nm is built up in the fluorescence spectrum. However, this near IR emission is completely quenched when new strong vibrational bands at approximately 1800 and 1900 cm^{-1} are revealed in the resonance Raman spectra of the complexes. The observed effects are explained in terms of direct participation of water molecules involved in the water–porphyrin dimeric complex in the processes of transformation of excitation energy. The involvement of water in this dimeric complex can lead to redistribution of flows of the energy degradation when transition metal ions play a role of the agent which enhances the trapping properties of the porphyrin–metal-ions complexes. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Dimers; Associates; Porphyrins; Donor–acceptor complexes; Transition metal ions; Near IR emission

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1. Introduction

Interaction between porphyrin pigments and water or porphyrin and transition metal ions is of interest to many researchers in connection with mimicking of events of the photosynthetic conversion of light energy and, in particular, properties of manganese-containing biological complexes [1–6]. Mimicking of properties of the pigment complex of photosystem II with the use of assembled manganese ions or model complexes produced by manganese ions and pigments is the most extensive investigation of photosynthetic events in artificial systems [5–7]. At the same time, crucial features of interaction between water and donor–acceptor complexes involving porphyrin pigments are still not established. Note that the important condition for investigation of the interaction between water and porphyrins on their spectral properties is the ability of dimeric or associated porphyrin species to coordinate water with the formation of donor–acceptor complexes [8]. The latter is the prerequisite for assembly of the systems with more high complexity.

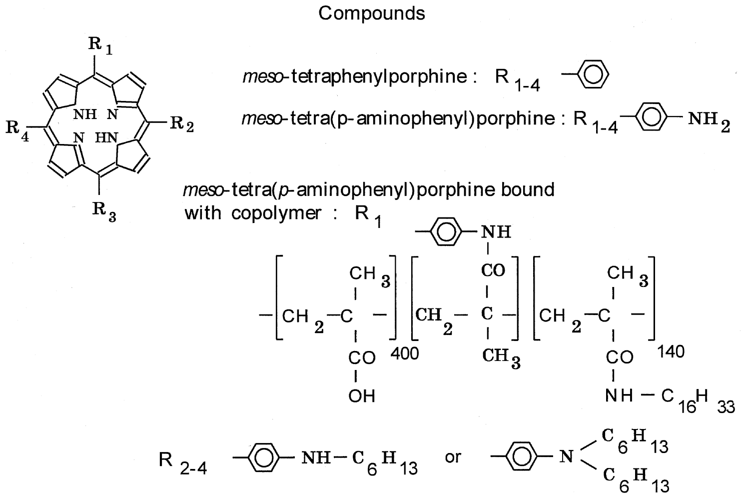
On the other hand, there is the gradation of separate steps on the rates in the events in photosynthetic apparatus of living organisms, i.e. from very fast reactions at the primary stages of photosynthesis to several orders of magnitude slower for the reactions on the late stages of photosynthesis. This peculiarity of biological photosynthesis is due to features of light energy conversion in living cells and as a consequence there are many different components in the photosynthetic apparatus. Many of the components serve intermediate electron acceptors to prevent backward electron transfer. Meanwhile, a study of relationships between porphyrin pigments in photosystems I and II meets difficulties in the multi-component system. Hence, a strong simplification of the whole system is required or selection of a suitable model system to elucidate whether interaction between photosystems II and I can be the driving force of the photosynthesis. We have selected dimeric and associated porphyrins to try and mimic these interactions. Porphyrin dimers are formed as a result of spontaneous association that was found under investigation of protonated forms of *meso*-tetraphenylporphine in aqueous–organic solutions [9]. It is important to note that these dimeric and associated porphyrins can be coordinated with water. At the same time, the involvement of water into donor–acceptor interactions in associated forms of *meso*-tetra(*p*-aminophenyl)porphine or its derivatives is a necessary base for production of different complexes with transition metal ions. It is proposed that the investigation of these complexes can help find an approach to study the specificity of the interactions between different dimeric forms of porphyrin, when water plays an active role in the interactions with porphyrin molecules [10]. Additionally, some properties of the structure of the biological reaction center (for instance, the binding of transition metal ions) are proposed to mimic the hydrophobic–hydrophilic environment of the copolymer. In this connection, the subject of the work was the study of the properties of the porphyrin-based donor–acceptor system under coordination of hydrogen ions or transition metal ions with a dimeric (associated) porphyrin.

Absorption, luminescence, and vibrational properties of dimeric forms of *meso*-tetraphenylporphine coordinating water and associated *meso*-tetra(*p*-aminophenyl)porphine bound with copolymer were investigated in this work under interaction with hydrogen ions or manganese (II) and iron (III) ions in solutions.

2. Experimental

Synthesis of the compounds presented in scheme 1 was carried out according to the procedures described elsewhere [11,12]. Dimethylformamide (DMF) and other organic solvents were additionally purified by conventional methods [13]. For the preparation of aqueous–organic solutions distilled water was used.

UV-visible spectra of porphyrin solutions were recorded with a Specord M-40 spectrophotometer. Fluorescence spectra were obtained with the setup described elsewhere [14]. The measurements were carried out under the same conditions as earlier [15] except for the excitation. The excitation in the region of the Soret band was



Scheme 1.

provided by monochromatic light with a half-width of 12 nm separated from the xenon lamp with the use of a monochromator. Fluorescence spectra were completely calibrated using the known spectral sensitivity of the equipment. Raman spectra of porphyrin solutions were obtained to an accuracy of ± 3–4 cm^{-1} using the setup described by Gadgiev et al. [16]. Excitation was provided by a He–Cd laser into the Soret band ($\lambda_{ex} = 441.6$ nm). A spectral slit width of 4 cm^{-1} was used for registration. The concentration of porphyrin in solution under measurements of Raman spectra did not exceed 3.0×10^{-5} mol l^{-1}. All measurements were carried out at 298 K. The equilibrium constants of complexes formed between porphyrin bound with copolymer, Mn^{2+}, and Fe^{3+} were estimated as described earlier [17].

3. Results

Fig. 1 shows absorption spectra of singly and doubly protonated dimeric forms of *meso*-tetraphenylporphine (TPP) and associated *meso*-tetra(*p*-aminophenyl)porphine (TAPP) bound with a hydrophilic–hydrophobic copolymer. Dimeric forms of TPP have been identified as doubly protonated ($\lambda_{max} = 437$ nm) and two singly protonated dimers of porphyrin ($\lambda_{max} = 403$ and 465 nm) with the different orientation of neighboring molecules in the dimer [9]. The change of the composition of organic solvents leads to some changes in the spectrum (curve 1). In this case the bands of doubly protonated dimers and the low-energy form of singly protonated dimers ($\lambda_{max} =$ 465 nm) are red shifted by 2–4 nm. As a result the maxima in the Soret band region are noted at 403, 439, and 467 nm, but in the red region the

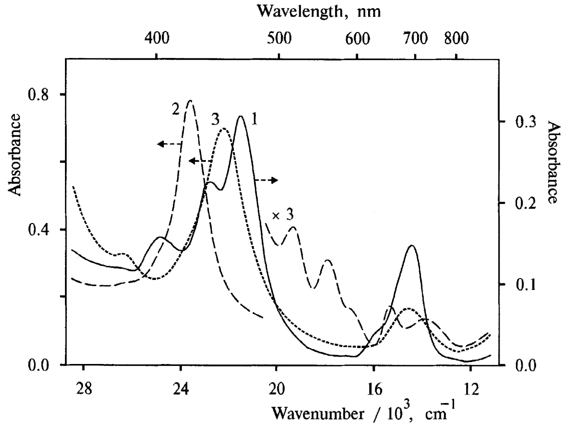


Fig. 1. Absorption spectra of *meso*-tetraphenylporphine in water–glycerol–tetrahydrofuran solution (86:10:4) in the presence of 0.4 N hydrochloric acid, 1; and *meso*-tetra(*p*-aminophenyl)porphine bound with the hydrophobic–hydrophilic copolymer in 30% water (v/v) in dioxane, 2, and in the presence of 0.1 N hydrochloric acid, 3.

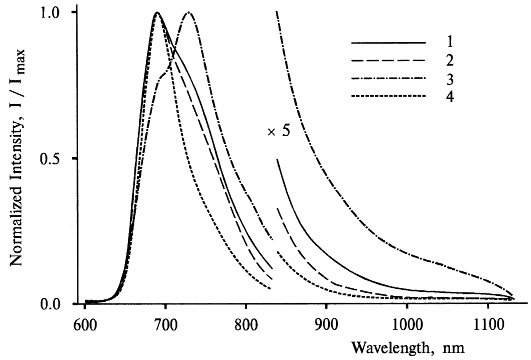


Fig. 2. Fluorescence spectra of *meso*-tetraphenylporphine in water–glycerol–tetrahydrofuran solution (86:10:4) in the presence of 0.4 N hydrochloric acid on excitation at: 403 nm, 1; 437 nm, 2; 465 nm, 3; and *meso*-tetraphenylporphine in 50% (v/v) aqueous acetone in the presence of 0.4 N hydrochloric acid, 4.

bands are strongly overlapped and noted as a shoulder at 638 nm and broad band with the maximum at 698 nm. In the spectrum of TAPP bound with copolymer, different dimeric forms of porphyrin are not pronounced in general that is why there is only one Soret band with the maximum at 425 nm (curve 2), which is red shifted and considerably broadened after protonation of porphyrin (curve 3). The state of porphyrin in the spectrum (curve 2) is close to the spectral characteristics of the dimer and in the region of quasi-allowed transitions, the absorption bands produce the characteristic picture due to donor–acceptor interaction between porphyrin molecules in dimers. At the same time, the presence of the band with the maximum at 725–728 nm denotes the interaction between porphyrin and carboxyl groups of the polymer when approximately 30% of water (v/v) is present in the solution [18]. Addition of hydrochloric acid to this porphyrin bound with copolymer leads to protonation of porphyrin and transformation of the absorption spectrum, and as a result of this, the maxima of the Soret band and another one are noted at 450 and 688 nm, respectively (curve 3).

Hence, interaction of proton with dimers of porphyrins results in separate Soret bands in the case of TPP dimeric forms but a lone Soret band in the case of associated TAPP bound with hydrophilic–hydrophobic copolymer.

Fluorescence spectra of protonated dimeric forms of TPP presented in Fig. 2 are appreciably changed with the change of excitation wavelength. On selective excitation (λ_{ex} = 403 and 437 nm) the maximum of the main emission is observed at 693 nm and a shoulder in the 700–760-nm region is noted too (curves 1 and 2). However, the spectrum with λ_{ex} = 465 nm exhibits the maximum at 730 nm and a shoulder at 693 nm (curve 3). In contrast, in the case of only doubly protonated dimer of TPP in solution, the narrower band of the main emission with the maximum at 693 nm as compared with the previous emission spectra is observed in the fluorescence spectrum (curve 4). Note that all spectra have the near IR-emission tail, among which singly protonated dimeric forms of porphyrin exhibit more intense emission in the near IR region.

Hence, according to the fluorescence spectra, different protonated dimeric forms of TPP exhibit different fluorescent states, which depend apparently on the configuration of the dimer.

In the fluorescence spectrum of TAPP bound with copolymer in 30% of water (v/v) in dioxane, the maximum of the main emission is observed at 674–675 nm on selective excitation (λ_{ex} = 403 and 437 nm) (Fig. 3, curves 1 and 2). However, in the case of the spectrum with λ_{ex} = 465 nm (curve 3), the maximum of the main emission is slightly red shifted and noted at 678 nm. At the same time, the intensity of the near IR emission in-

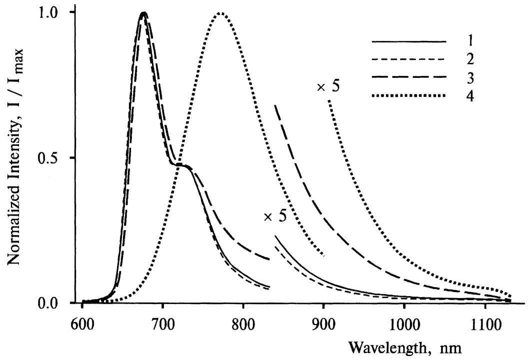


Fig. 3. Fluorescence spectra of *meso*-tetra(*p*-aminophenyl)porphine bound with the hydrophobic–hydrophilic copolymer in 30% water (v/v) in dioxane on excitation at: 403 nm, 1; 425 nm, 2; 465 nm, 3; and in the presence of 0.1 N hydrochloric acid, 4.

creases as compared with that in the spectra (curves 1 and 2). This behavior is similar to that observed in the spectra of protonated dimeric forms of TPP. In the case of TAPP bound with copolymer in the presence of hydrochloric acid, the fluorescence spectrum is strongly changed (curve 4) as well as the absorption spectrum. In this case, the band of the main emission is proved to be very broad and the maximum of the band is located at 770 nm.

Hence, in the case of TAPP bound with hydrophobic–hydrophilic copolymer, similar different fluorescent states as in the case of dimeric forms of TPP are not found, although the corresponding absorption spectra indicate the presence of porphyrins with the different character of interactions. But at the same time, selective excitation results in similar behavior of the near IR emission as in the case of protonated dimeric forms of TPP. A very large Stokes shift, equal to 1550 cm^{-1}, is found in the case of protonated TAPP bound with the copolymer.

Resonance Raman spectra of these dimeric and associated forms of porphyrins demonstrate unusual features. Fig. 4 shows spectra of singly and doubly protonated dimeric forms of TPP (curve 1) and TAPP bound with copolymer (curve 2) on excitation at 441.6 nm. The doublet formed by 1025 and 1000 cm^{-1} bands and several doublets in the region of translational and librational vibrations of water with the same frequency interval equaled 25 ± 2 cm^{-1} are revealed in the spectrum of dimeric forms of TPP. The former was assigned to proton transitions in hydrogen-bonded molecules of water and hydroxonium ions, respectively [19]. These species of water interact with porphyrin as a result of which the water molecules are involved in donor–acceptor interaction with the dimer of the porphyrin. A new 1608 cm^{-1} band characterizing these interactions arises in the spectrum. The doublet with the 218 and 245 cm^{-1} bands (± 2 cm^{-1}) was assigned to translational vibrations of neutral water molecules bound in the water–porphyrin dimeric complex, whereas the doublets formed by 328, 354 cm^{-1} bands and 423, 447 cm^{-1} bands (± 2 cm^{-1}) characterized vibrations of water molecules involved in donor–acceptor interactions with aminoporphyrin [10]. Note that the latter doublet in the region of librational vibrations of water is almost inappreciable in the noise in the spectrum (curve 1). The new 1302, 1325, and 1347 cm^{-1} bands are found in the spectrum of TAPP bound with copolymer in the presence of a large amount of water (curve 2). These bands are not observed in the spectrum of the same sample but in DMF in the presence of water traces [10]. It is quite possible that burn-off of photoactive forms of porphyrin observed at 10% of water (v/v) or at higher contents of water in organic solvent [20], is responsible for the new bands in the spectrum (curve 2). Also note that in the region of translational and librational vibrations of water in this spectrum, the broad 327 and 450 cm^{-1} bands are noted instead of two corresponding doublets.

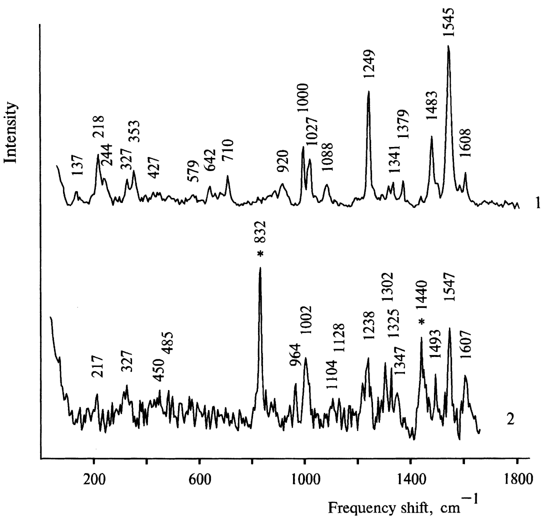


Fig. 4. Resonance Raman spectra of *meso*-tetraphenylporphine in water–glycerol–tetrahydrofuran solution (86:10:4) in the presence of 0.4 N hydrochloric acid, 1; and *meso*-tetra(*p*-aminophenyl)porphine bound with the hydrophobic–hydrophilic copolymer in 30% water (v/v) in dioxane, 2. An asterisk marks the most intense bands of dioxane.

Hence, the results of resonance Raman spectroscopy of protonated dimeric forms of TPP and associated TAPP bound with copolymer demonstrate thin vibrational structure in the low-frequency region of dimeric forms of the former and the corresponding broad bands in the spectrum of associated forms of the latter.

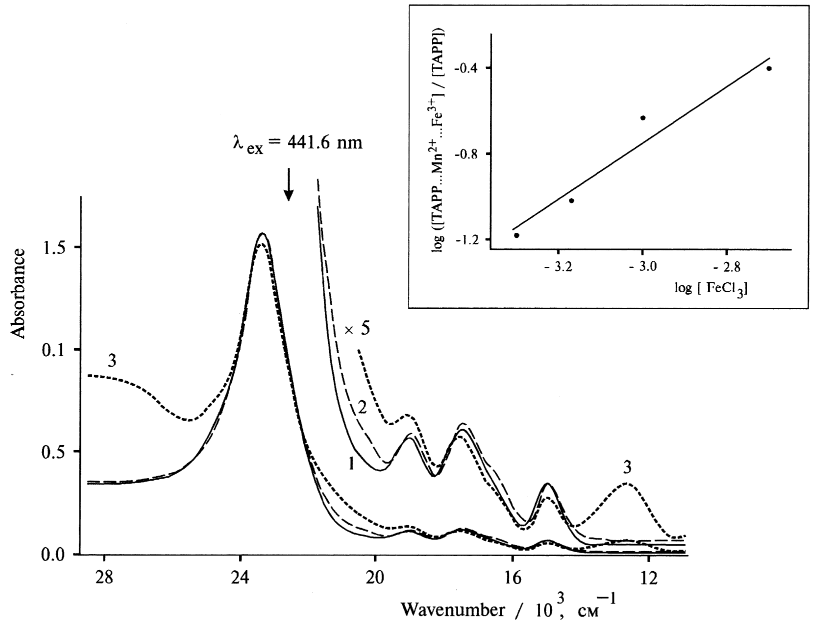


Fig. 5. Absorption spectra of *meso*-tetra(*p*-aminophenyl)porphine bound with the hydrophobic–hydrophilic copolymer in dimethylformamide containing 1–2% of water, 1; in the presence of 1.2×10^{-3} mol l^{-1} $MnCl_2$, 2; and in the presence of 1.2×10^{-3} mol l^{-1} $MnCl_2$ and 0.7×10^{-3} mol l^{-1} $FeCl_3$, 3; (optical pathway is 0.2 cm). The inset shows the plot of log ([(TAPP...Mn^{2+})...Fe^{3+}]/[TAPP]) vs. log [$FeCl_3$] at the constant value of $MnCl_2$ concentration equaled 5.0×10^{-4} mol l^{-1}.

The peculiarities of proton coordination by dimeric and associated forms of porphyrins have similar expression under interaction between these porphyrins and transition metal ions. In the spectrum of TAPP bound with copolymer, a small absorption in the 450–500-nm region is noted in the presence of $MnCl_2$ in the solution (Fig. 5, curve 2, compare with curve 1). However, a broad absorption band in the 660–900-nm region with the maximum at 760 nm and a high extinction coefficient is observed in the spectrum of TAPP bound with copolymer in the presence of $MnCl_2$ and $FeCl_3$ in the solution (curve 3). In this case we can see the appreciable absorption in the 450–530-nm region too. The constant of the formation of the complex between TAPP bound with copolymer, Mn^{2+}, and Fe^{3+} is proved to be quite high (Fig. 5, inset), $K_{\mathrm{dac}} = (3.9 \pm 0.6) \times 10^6$ l mol^{-1}. Note that the addition of $FeCl_3$ to the similar solution of TAPP bound with copolymer but in the absence of $MnCl_2$ does not result in a similar effect.

Fig. 6 shows absorption and fluorescence spectra of the complexes formed between TAPP bound with copolymer, Mn^{2+}, and Fe^{3+} at the different concentrations of porphyrin (panels A and B). As we can see from the figure (panel A), fluorescence spectra is somewhat changed with the change of wavelength of excitation. On excitation at the Soret band ($\lambda_{ex} = 425$ nm), the maximum of the main emission is observed at 668 nm and the maximum of the vibrational satellite of this electron transition is located at 720 nm (curve 2). However, on excitation at 480 nm the band of the main emission is broadened and the maximum of the band is red shifted by 17–18 nm (curve 3). As a result of this, the band of the vibrational satellite is almost masked and noted in the spectrum as a shoulder. With an approximately fourfold decrease of the concentration of porphyrin bound with copolymer as compared with the previous concentration (panel A), the absorption band with the maximum at 760 nm is proved to be considerably less in magnitude (panel B, curve 1, compare with panel A, curve 1). In this case on excitation at the maximum of the Soret band, the characteristics of the fluorescence spectrum are kept the same (panel B, curve 2). However, a broad emis-

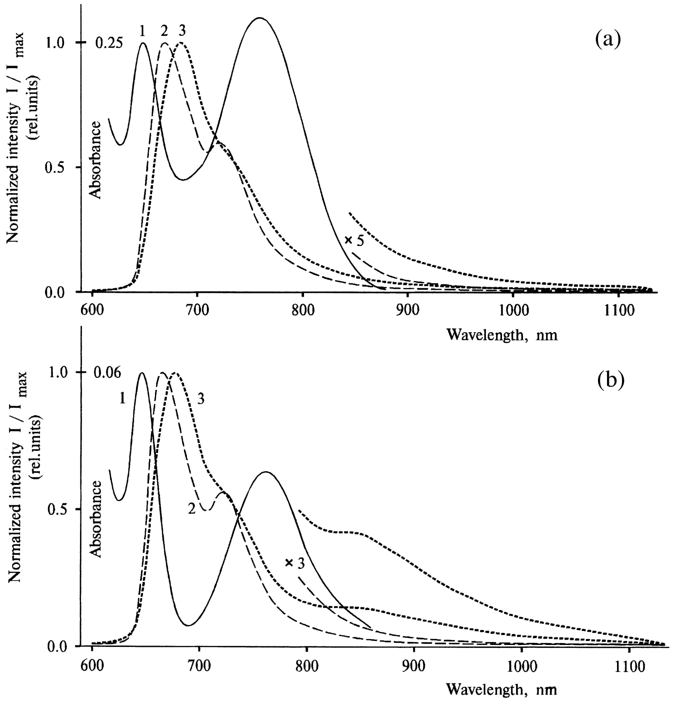


Fig. 6. Absorption (panel A, 1, and panel B, 1) and fluorescence spectra (panel A, 2 and 3, panel B, 2 and 3) of *meso*-tetra(*p*-aminophenyl)porphine bound with the hydrophobic–hydrophilic copolymer in DMF containing 1–2% of water in the presence of 1.2×10^{-3} mol l^{-1} $MnCl_2$ and 0.7×10^{-3} mol l^{-1} $FeCl_3$, panel A: on excitation at 425 nm, 2; and 480 nm, 3; and in the presence of 2.0×10^{-3} mol l^{-1} $MnCl_2$ and 1.0×10^{-3} mol l^{-1} $FeCl_3$, panel B: on excitation at 425 nm, 2; and 480 nm, 3; the concentration of porphyrin in this case is approximately fourfold lower as compared with that in the case of panel A.

sion band with the maximum at 840 nm is revealed in the spectrum on excitation at 480 nm (panel B, curve 3). This emission is most probably the fluorescence of the complex formed between TAPP bound with copolymer, Mn^{2+}, and Fe^{3+} which has the broad band with the maximum at 760 nm in the absorption spectrum. At the same time, this fluorescence spectrum (curve 3) exhibits similar broadening and shift of the main emission band.

Hence, fluorescence of the three-component complex formed between TAPP bound with copolymer, Mn^{2+}, and Fe^{3+} is found at small concentrations of the porphyrin, i.e. when the distance between different dimeric forms of porphyrin is strongly increased. This suggests that the probability of interaction between different dimeric forms of porphyrin falls substantially. Although in the first case (panel A), the band with the maximum at 760 nm is larger in magnitude than in the second case (panel B), but no fluorescence with the maximum at 840 nm is observed in the first case.

Fig. 7 shows resonance Raman spectra of the complexes formed between TAPP bound with copolymer and the transition metal ions. In the case of a small concentration of porphyrin, i.e. when the near IR emission with the maximum at 840 nm is present in the fluorescence spectrum of the three-component complex, a new 1810 cm^{-1} band is noted in the Raman spectrum (curve 1). In contrast, this band is absent in the spectrum of TAPP bound with copolymer in DMF (results not presented). In the case of an approximately fourfold concentration of porphyrin as compared to the small concentration, a new intense 1895 cm^{-1} band is observed in the spectrum of the two-component complex formed between TAPP bound

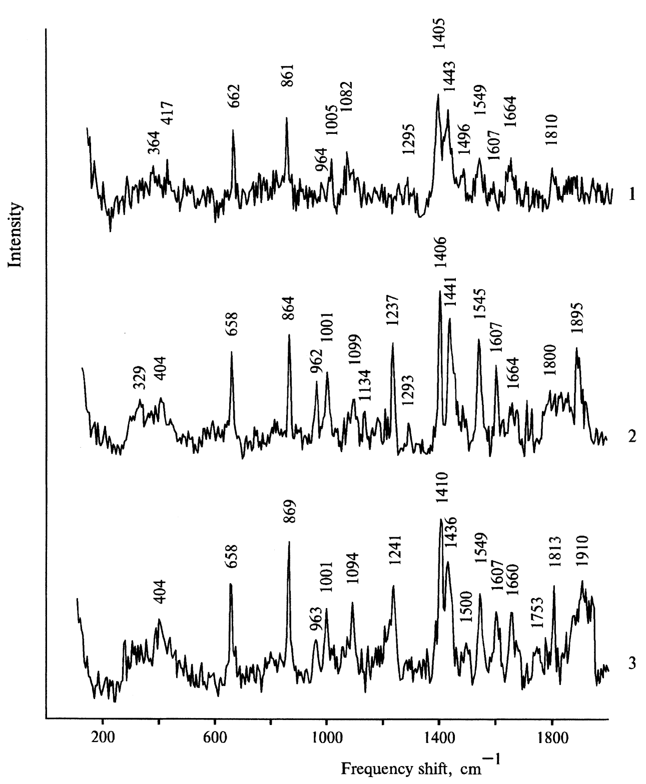


Fig. 7. Raman spectra of *meso*-tetra(*p*-aminophenyl)porphine bound with the hydrophobic–hydrophilic copolymer in DMF containing 1–2% of water at a small concentration of porphyrin ($\sim 0.6 \times 10^{-5}$ mol l^{-1}) in the presence of 2.0×10^{-3} mol l^{-1} $MnCl_2$ and 2.0×10^{-3} mol l^{-1} $FeCl_3$, 1; and at approximately fourfold concentration of porphyrin ($\sim 2.6 \times 10^{-5}$ mol l^{-1}) in the presence of 1.2×10^{-3} mol l^{-1} $MnCl_2$, 2; and in the presence of 1.2×10^{-3} mol l^{-1} $MnCl_2$ and 0.7×10^{-3} mol l^{-1} $FeCl_3$, 3.

with copolymer and Mn^{2+} (curve 2). However, in the case of the three-component complex formed between TAPP bound with copolymer, Mn^{2+}, and Fe^{3+}, several new bands are revealed in the spectrum (curve 3), among which it should be noted a new 1753 cm^{-1} band, the intense 1813 cm^{-1} band, and broad and intense 1910 cm^{-1} band. Regarding the other vibrational characteristics, note that all three spectra are quite similar and some changes in the bands of small intensity can be due to a moderate value of the noise.

Hence, the appearance of new bands at approximately 1810 and 1900 cm^{-1}, and apparently a 1750 cm^{-1} band in the resonance Raman spectra of the three-component complex formed between TAPP bound with copolymer, Mn^{2+}, and Fe^{3+} most probably suggests a direct relationship with the quenching of the near IR emission with the maximum at 840 nm in the fluorescence spectrum. The fact is that the presence of the near IR emission in the fluorescence spectrum is accompanied by a disappearance of the intense bands in the region higher than the band of deformational vibrations of water (1662 ± 2 cm^{-1}) in the corresponding Raman spectrum. This means that, on excitation of associated forms of TAPP bound with copolymer in the state of the three-component complex with the transition metal ions, there is a channel of deactivation of the excitation energy which competes with the near IR emission at a high efficiency.

4. Discussion

The results presented above show similarity of the properties of protonated dimeric forms of TPP and associated forms of TAPP bound with copolymer in the state of the complex with transition metal ions. The presence of a protonated nitrogen atom in the singly protonated dimeric forms of TPP, when the neighboring porphyrin macrocycle is coordinated via two water molecules, brings about donor–acceptor interactions in the dimer [19]. The 1608 cm^{-1} band in the Raman spectrum (Fig. 4, curve 1) just indicates donor–acceptor interactions in these dimers. In contrast, in the case of TAPP bound with copolymer, donor–acceptor interactions are realized due to lateral amino groups on phenyl rings. However, in this case water molecules are also involved in donor–acceptor interactions with porphyrin [8,15]. The substantial increase of intensity of the 1607 cm^{-1} band in the Raman spectrum (curve 2) as compared with that in the spectrum (curve 1) shows evidence of strong donor–acceptor interaction between porphyrin and water bound with the porphyrin.

In the difference from absorption spectra of protonated dimeric forms of TPP, where three dimeric forms are observed in the ground state, only two dimeric forms with the different maxima of the main emission (λ_{max} = 693 and 730 nm) are revealed according to fluorescence spectra. It is interesting that Stokes shifts for doubly protonated and low-energy singly protonated dimeric forms are proved to be close, i.e. 770 and 630 cm^{-1}, respectively. While Stokes' shift for the high-energy singly protonated dimeric form (λ_{max} = 403 nm in the Soret band region of the absorption spectrum) is 1245 cm^{-1}. In contrast, in the case of TAPP bound with copolymer in DMF, the maximum of the main emission is noted at 668 nm and Stokes shift equals to 270 cm^{-1} (results not presented). However, when this porphyrin strongly interacts with carboxyl groups of the copolymer in the ground state, i.e. in the case of TAPP bound with copolymer in water–dioxane solution (Fig. 3, curves 1–3), the fluorescence spectra exhibits a maximum of the main emission at 674–678 nm and Stokes' shifts within 420–490 cm^{-1} independent from wavelength of excitation. However, if this porphyrin is present in the protonated state, Stokes' shift increases to 1550 cm^{-1}.

Hence, the difference between properties of protonated dimeric forms of TPP and TAPP bound with copolymer is due to the presence of a nitrogen atom of the porphyrin macrocycle in the protonated state. As a result, the properties of the singly protonated dimers of TPP in the ground state depend on the orientation of the dipole transition moments in the porphyrin dimer. While, in the difference from the protonated dimeric forms of TPP, selective excitation of TAPP bound with copolymer in water–dioxane solution results in small changes of the corresponding fluorescence spectra.

Under interactions between TAPP bound with copolymer, Mn^{2+}, and Fe^{3+}, the formation of a donor–acceptor complex takes place according to the absorption spectrum (Fig. 5, curve 3). The spectrum exhibits a new electron transition, i.e. the broad band with the maximum at 760 nm and a high extinction coefficient. The appearance of the broad band in the red and near IR region is accompanied by the increase of the absorption in the 450–530-nm region in the spectrum. Excitation at this region (λ_{ex} = 480 nm) results in appreciable changes in the fluorescence spectrum as compared with that in the case of excitation at the maximum of the Soret band (Fig. 6). In this case, the most strong changes are noted at a small concentration of porphyrin (panel B, curve 3), when an apparent interaction between different dimeric (or associated) forms of porphyrin according to the Raman spectrum is strongly weakened (Fig. 7, curve 1, compare with curve 3). Note that one would speak about radiative deactivation of the complexes formed between TAPP bound with copolymer and the transition metal ions in the case of increase of the near IR emission with the maximum at 840 nm with the increase in magnitude of the absorption band with the maximum at 760 nm. However, since this is not the case, the situation is more complicated. There is the reverse situation, i.e. the quenching of the near IR emission with the increase in magnitude of the near IR absorption band that in combination with the appearance of the 1753, 1813, and 1910 cm^{-1} bands in the Raman spectrum suggests a new way of deactivating excitation energy. This is observed only in the case of the three-component complex formed between associated TAPP bound with copolymer, Mn^{2+}, and Fe^{3+}. The new way of the excited state deactivation can compete with a high efficiency as with the radiative deactivation according to the above results as well as the dissociation into radical ions of the donor–acceptor complex formed by aminoporphyrin [21]. It is proposed that this three-component complex of associated forms of TAPP bound with hydrophobic–hydrophilic copolymer, Mn^{2+}, and Fe^{3+} actually mimic the relationship between porphyrinic pigments in photosystem I and II.

The main question was how two porphyrin pigment systems can be modeling a relationship between those in photosystems I and II, i.e. what factor can be a cause for interaction between two porphyrin dimers. We assume that interaction between two different porphyrin dimers can be enhanced similar that way as the electron-transfer chain in the photosynthetic apparatus is organized due to non-valence interactions. From this point of view, out-plane coordination of transition metal ions with porphyrin dimers (or associates) was applied to enhance the interactions between different porphyrin dimers (or associates). In a simple system of TPP protonated dimers a similar interaction between different forms of the dimeric porphyrin was found according to fluorescence spectra when parallel and anti-parallel transition moments in the porphyrin dimers produce two different Soret bands with the maxima at 403 and 465 nm, respectively. Moreover, it has been found recently that Mn^{2+} is coordinated to the anti-parallel configuration of the porphyrin dimer only, which has the maximum at 465 nm in the absorption spectrum [17]. As a result of the coordination a new absorption band with the maximum at 480 nm is built up in the spectrum. On the other hand, our results show an apparent reduction of protons bound in the complex with the manganese(II) ion–porphyrin dimer under visible light illumination in water–dioxane or water–dimethylformamide solution. These data suggest that water molecules can be utilized as the electron donor for the photoreduction of the protons bound to the porphyrin dimers–manganese(II) complex. It should be noted that our model systems are strongly simplified as compared to the biological system. As a consequence these model systems demonstrate unusual features presented in this and other papers [10,17,21]. The unique properties of these dimeric systems appear to be associated not only with exciton interaction in porphyrin dimers but with interaction with hydrogen bond-network of water too. The energy of the exciton interactions in singly protonated porphyrin dimers was proved to be close to the energy of deformational vibrations of water in the tetrahedral network, i.e. equal to 1650 cm^{-1} [21]. Therefore, water can take active participation in the processes of the excitation energy or electron transfer between two different porphyrin dimers with the parallel and anti-parallel configurations. Furthermore, the interaction between two different porphyrin dimers serves apparently as an organizing factor in photoreaction when a suitable electron donor and acceptor can be incorporated into the structure of the complex of associated porphyrin bound to copolymer with the formation of a local electron transfer chain [18]. Hence, our porphyrin–polymer systems possess some properties similar to biological photosynthetic apparatus and on dependence from the composition of the donor–acceptor complex the artificial system can be a model of separate steps of photosynthetic events.

The other porphyrin dimer with parallel transition moments is probably coordinated with Fe^{3+}. This out-plane coordination results in a strong and broad absorption band with a maximum at 760 nm which denotes formation of a new donor–acceptor complex in the porphyrin–polymer system where Mn^{2+} is also involved. In this case our system is proposed to mimic the situation when an electron from a water molecule in the Mn-complex in photosystem II is transferred to photosystem I. The main evidence for the electron transfer in the porphyrin–polymer system is that the increase of the broad band with the maximum at 760 nm is accompanied by the quenching of the emission of the complex with the maximum at 840 nm. Meanwhile, as new intense 1810, and 1910 cm^{-1} bands denote somewhat stable intermediates of the proposed electron transfer photoreaction. Therefore, this transfer of the electron from water molecules can initiate the whole photoprocess of photosynthesis and makes it irreversible. Hence, from this point of view the step can generate photosynthesis. On the other hand, the photoreaction between two different configurations of porphyrin dimer should be related to the field of photo-adaptation of the photosynthetic reaction center to the visible light, since the photoreaction is sensitive to the light and is possibly responsible for the photoactivation phenomenon revealed earlier [18]. The further study of similar porphyrin–polymer systems can help in understanding the photochemistry of photo-adaptation of the photosynthetic reaction center.

5. Conclusions

Hence, the features of coordination of protons and transition metal ions by dimeric or associated forms of porphyrins suggest some similarity of the structure of the complexes formed in the solutions. The results demonstrate that processes of vibrational deactivation in the donor–acceptor complex formed between TAPP bound with copolymer, Mn^{2+}, and Fe^{3+} can compete with a high efficiency in the case of selective excitation with the radiative deactivation of excitation energy. The effective competing of vibrational processes leads to a decrease of near IR emission with the maximum at 840 nm observed in the fluorescence spectrum and the emission disappears completely when the intense 1810, and 1910 cm^{-1} bands (± 2–3 cm^{-1}) are observed in the corresponding Raman spectrum of the complex. We propose that the fluorescence quenching is due to the interaction between different forms of porphyrin dimers (or associates), which have axially coordinated Mn^{2+} or Fe^{3+}, respectively, since the increase of porphyrin concentration can lead to the increase of the probability of interaction between the porphyrin complexes. Hence, these data appear to be evidence that the interaction between different porphyrin dimers in the state of the complex mimic the interactions between photosystems I and II and therefore, the interactions can be the driving force of directed electron transfer in the electron transfer chain in photosynthesis. At the same time out-plane coordination of Mn^{2+} with dimeric porphyrin pigments produce the complex which is apparently capable of reducing protons bound with the complex and, as a consequence, activate water molecules by seizing their electrons. The other dimeric form of porphyrin apparently coordinating with Fe^{3+} in the porphyrin–polymer system under the out-plane coordination with transition metal ions can serve as the electron acceptor in this model system. The complete disappearance of the near IR emission with the maximum at 840 nm suggests the leaving of the electron in the excited state from electron vibrational levels. Hence, the electron vibrational nature of the process between the different forms of porphyrin dimers under selective excitation means that the electron transfer processes can proceed very quickly on the late steps of light energy conversion too as in artificial as well as in biological photosynthetic apparatus. Although in the latter, the rate of slow reactions apparently limits the overall process. The model system presented in this work represents an approach in the investigation of water utilization for the photosynthetic pathway of solar energy conversion in artificial systems. These artificial systems are geared towards been capable of photo-adaptation under light, which is peculiar to biological systems.

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