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Photoinduced self-organization of donor–acceptor complex intended for oxidative splitting of water

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Abstract

The ground and excited states of complexes combined on the base of associated forms of *meso*-tetra(*p*-aminophenyl)porphine (TAPP) and donor–acceptor complex formed between triethylamine and manganese(II), in which manganese(II) moiety of the complex possessing ΔH_{pp}=70 mT was preliminary transformed into the EPR-silent form, are investigated by absorption and luminescence spectroscopy. According to absorption and fluorescence spectra dramatic photoinduced transformation of the combined complex in the presence of $NaHCO_3$ is found under illumination with a non-stop change of exciting light wavelength from red to ultraviolet. Absorption spectrum (before the transformation) had a broad Soret band with the maximum at 433 nm, where the associated state of the porphyrin is preliminary estimated as a trimer. The complex obtained after the transformation has the components of monomeric porphyrin with the maximum of Soret band at 418 nm in the spectrum and porphyrin dimer coordinated with the manganese ions. The dimer has a broad Soret band with λ_{max}=467 nm and a broad red band with the maximum at ca. 780 nm in the absorption spectrum, although none of these bands are observed in the spectrum before the illumination. Selective excitation into these Soret bands and the intermediate region, reveals well-known fluorescence of monomeric porphyrin, which is similar to that of tetraphenylporphine, and a strong IR emission with the maximum at 875–880 nm. The relationship between the fluorescence of the monomeric porphyrin and the IR emission depends on the wavelength of excitation. The results of the study of the combined complexes allow to conclude that the photoprocess of water oxidation takes place in the combined complex formed between associates of TAPP and EPR-silent manganese–triethylamine complex.

Keywords: Dimers; Associates; Porphyrins; Donor–acceptor complexes; Photoinduced self-organization; Assembled manganese(II) ions; Near IR emission

1. Introduction

The processes of photooxidative splitting of water taking place in photosystem II and mimicking artificial systems, attract the attention of many researchers in connection with the problem of solar energy conversion [1–7]. Our approach to the development of the system of artificial photosynthesis is based on experimental data, the main peculiarities of which are the capability of a donor–acceptor system to photoactivation under illumination with the visible light [8], and photoinduced irreversible changes in the absorption spectra of an aminoporphyrin derivative. In combination with other results these irreversible changes rather denote some initial steps towards water splitting in the aminoporphyrin associates involving water in the structure of the complex [9]. As a matter of fact, the capability of a donor–acceptor complex to photoactivation is its inner property of self-organization of the structure of the components in the complex under light action. This property makes the artificial system to be somewhat similar to the corresponding biological system. From our point of view, this peculiarity of the self-organizing complex provides the preference of these model systems as compared to synthetic covalently bound pigments used for the mimicking of similar processes. At the same time, note that the presence of donor–acceptor interactions in the complex of associated porphyrins [10] can be utilized as a background for assembly of a combined complex with higher organization of it's structure. The results of this investigation of donor–acceptor complexes formed between aliphatic amines and manganese(II) ions [11] allowed us to test the ability of a simple system to the self-organization of its own structure, when the components of the system were associates of *meso*-tetra(*p*-aminophenyl)porphine and the complex of aliphatic amine with manganese(II) ions. It should be noted that the simplicity of the system provides the possibility to utilize simple means of spectroscopy to study the ground and excited states of porphyrin.

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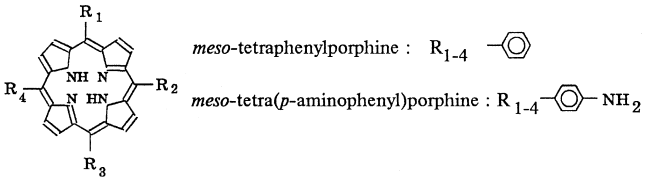
Compounds



Scheme 1.

In this connection, in the present work results of the formation of porphyrin–manganese–amine complex under steady-state illumination and spectral properties of the ground and excited states of the combined complexes investigated by absorption and luminescence spectroscopy are reported.

2. Experimental

Synthesis of *meso*-tetraphenylporphine (TPP) and *meso*-tetra(*p*-aminophenyl)porphine (TAPP) (Scheme 1.) were carried out according to the procedures described elsewhere [12,13]. Dimethylformamide (DMF) and other organic solvents used were additionally purified by conventional methods [14]. For the preparation of aqueous–organic solutions, distilled water was used.

Two manners of illumination were applied for the study of self-organization of the combined complexes, i.e. the complexes formed between associates of porphyrin and aliphatic amine–manganese(II) complex. The first manner of steady-state illumination was provided with a 60-W incandescent lamp. In contrast, the second was carried out with a non-stop change of wavelength of excitation from 700 to 300 nm by monochromatic light separated from 400-W xenon lamp. At this point, we propose that the second specific manner of illumination somewhat mimics the conditions as the sun light illumination when it rises in the morning, i.e. when red light prevails in the solar energy spectrum. Therefore, in the case of the second manner of illumination, the situation with the compose of the light had a rough mimicking of a natural sunrise. Procedure of preparation of manganese(II)–aliphatic amine complexes is described earlier [11] but spectral characteristics of the manganese–amine complex utilized in this work are presented below in Section 3. The fresh-prepared manganese–amine complex has a wide EPR signal which usually decreases with time. Therefore, the EPR-silent manganese–amine complex can be obtained as a result of its staying at room temperature.

UV–VIS spectra of porphyrin solutions were recorded with a Specord M-40 spectrophotometer. Fluorescence spectra were obtained with the setup described elsewhere [15]. The measurements were carried out under the same conditions as described earlier [10] except for the excitation. The excitation in the region of Soret band, was provided by monochromatic light with a half-width of 12 nm separated from a xenon lamp with the use of monochromator. Fluorescence spectra were completely calibrated using the known spectral sensitivity of the equipment. All measurements were carried out at 298 K.

3. Results

Photophysical bases for the assembly of high-structured complexes with the use of porphyrin pigments can be demonstrated with restrictively protonated dimeric forms of *meso*-tetraphenylporphine (TPP). Absorption spectra of the protonated TPP dimeric forms in water–organic solutions are presented in Fig. 1. The spectrum of the forms in water–ethanol solution exhibits small and medium Soret bands with the maxima at 403 and 465 nm, respectively, as compared to the band with the maximum at 437 nm (panel A, curve 1). The decrease of the absorption of the 465 nm band in the spectrum (curve 1) as compared to the similar band in the spectrum (curve 2) produces the corresponding decrease of the 694 nm band. The latter leads to the appearance of the pronounced 654 nm band which corre-

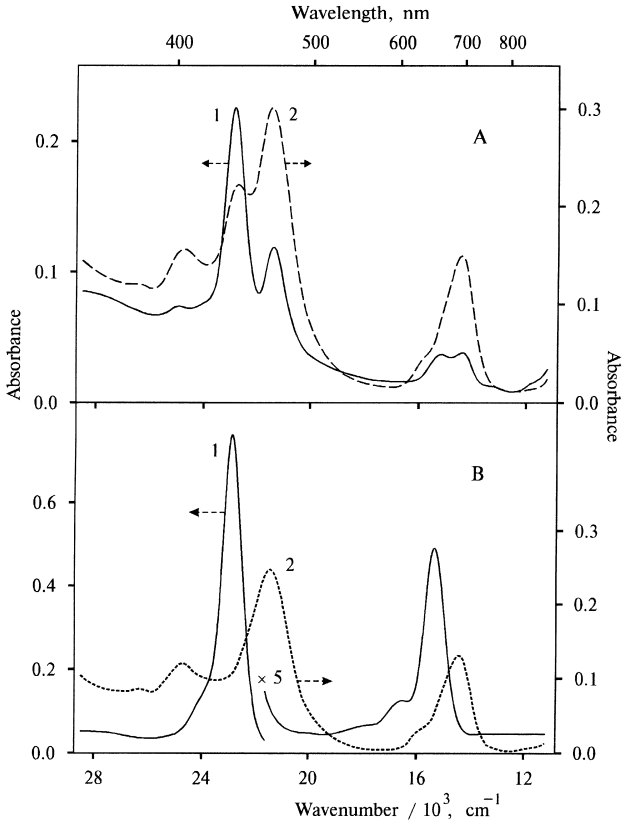


Fig. 1. Absorption spectra of TPP, panel A: in water–ethanol solution (91:9) in the presence of 0.4N hydrochloric acid, 1; and in water–glycerol–tetrahydrofuran solution (86.5:10:3.5) in the presence of 0.4N hydrochloric acid, 2; and panel B: in 50% (v/v) aqueous solution of dioxane in the presence of 0.2N hydrochloric acid, 1; and differential spectrum, 2 (see explanation in the text).

sponds to doubly protonated TPP dimer as well as 437 nm band [16]. In contrast, the spectrum of the protonated TPP dimeric forms in water–tetrahydrofuran–glycerol solution (curve 2) exhibits three well-resolved Soret bands but the corresponding red bands of the dimers are strongly overlapped. The spectrum of doubly protonated TPP dimer is shown in Fig. 1, panel B (curve 1), where the maxima of the main absorption bands are located at 437 and 654 nm. The differential spectrum (the spectrum Fig. 1, panel A, curve 2 minus the spectrum, curve 1 normalized on a coefficient to remove the spectrum of the doubly protonated dimer) is also presented in this figure, panel B, curve 2. It is obvious that the bands in the spectrum (panel B, curve 2) especially in the Soret band region are considerably broadened as compared to that of doubly protonated TPP dimer (curve 1).

The fluorescence spectra of the solutions of these forms are proved to be strongly different. Fluorescence spectra of protonated TPP dimeric forms in water–tetrahydrofuran–glycerol solution presented in Fig. 2, panel A are changed with the change of wavelength of excitation. Selective excitation (λ_{ex}=403 or λ_{ex}=437 nm) reveals the main emission band with the maximum at 693 nm and a shoulder in the 700–760 nm region in the spectra (curves 1 and 2). However, the spectrum with λ_{ex}=465 nm exhibits the band with the maximum at 730 nm and a shoulder at 693 nm (curve 3). This spectrum strongly differs as from those obtained under the above excitations of the protonated TPP dimers as well as from the spectrum of TAPP associated in DMF (curve 4). In contrast, the fluorescence spectra of these dimeric forms in water–ethanol solution under the same selective excitation (λ_{ex}=403, 437 or 465 nm) are very similar, Fig. 2, panel B. The spectra with λ_{ex}=403 and 437 nm are practically identical (curves 1 and 2). Although the spectrum on excitation at 465 nm exhibits a slightly broadened emission band, the maximum of which is red shifted by 4–5 nm (curve 3) as compared to that of the other spectra presented in this figure. It is interesting that in the case of water–ethanol solution, the spectrum (curve 2) coincides completely with the fluorescence spectrum of doubly protonated TPP dimer (curve 4). These results denote that there is the competition between ethanol and water for hydrogen bonds formation with porphyrin dimer. Ethanol has the properties somewhat similar to those of methanol, which can produce isoporphyrins under interaction with porphyrin cations [17]. Therefore, ethanol affect on the protonated TPP dimers is somewhat similar to the action of methanol on similar compounds. In contrast, interaction of water with protonated porphyrin dimers produces alternative products, namely, water–porphyrin dimeric complexes [18]. In this case the bands with the different maxima at 693 and 730 nm observed on the selective excitation in the spectra (Fig. 2, panel A) are rather related to different fluorescent states of the protonated dimeric forms of porphyrin.

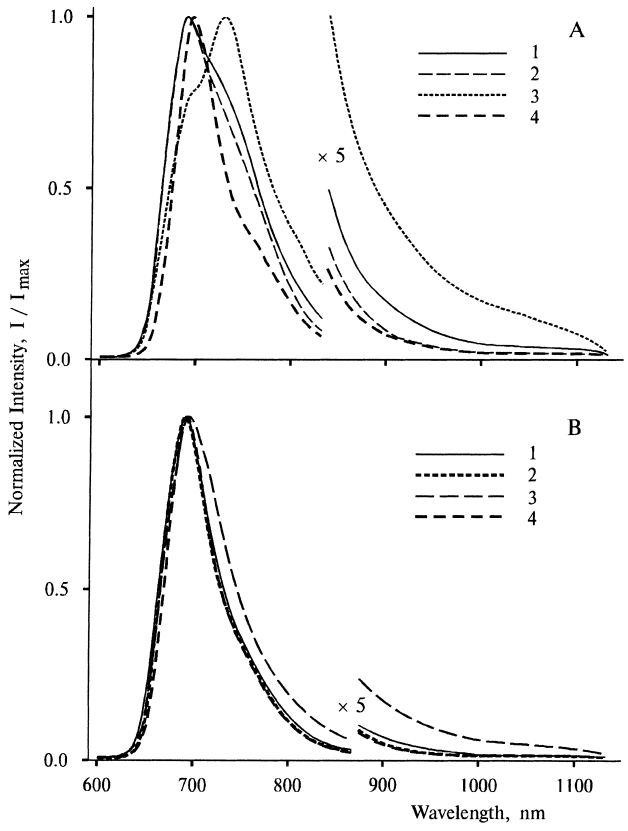


Fig. 2. Fluorescence spectra of TPP, panel A: in water–glycerol–tetrahydrofuran solution (86:10:4) in the presence of 0.4N hydrochloric acid on excitation at 403 nm, 1; 437 nm, 2; and 465 nm, 3; and TAPP in DMF on the excitation into Soret band, 4; panel B: in water–ethanol solution (91:9) in the presence of 0.4N hydrochloric acid on excitation at 403 nm, 1; 437 nm, 2; and 465 nm, 3; and in 50% (v/v) aqueous solution of dioxane in the presence of 0.2N hydrochloric acid, 4. The spectra are normalized on the intensity of the main emission band.

Hence, these results show that the three different protonated TPP dimers observed in the ground state reveal only two different dimers under transition in the excited state. The appearance of the shoulder with the maximum at ca. 730 nm in the spectra on the excitation at 403 or 437 nm, suggests that the fluorescence with the maximum at 693 nm can be effectively absorbed by the red band of low-energy dimeric form of porphyrin, the absorption maximum of which is located at ca. 694 nm. No similar properties were found for the associates of *meso*-tetra(*p*-aminophenyl)porphine (TAPP). The spectra are observed unchanged independent from similar different excitation and exhibit the main emission band only at ca. 700 nm, so that these spectra coincide to those observed earlier [10]. Note that unusual properties of TAPP associates are to be due to donor–acceptor interactions between aminoporphyrin molecules having aminogroups in the phenyl rings. Peculiarities of coordination of the TPP dimers and TAPP associates with manganese(II) ions proved to be different [19]. At the same time, it was shown that the low-energy dimeric TPP form (λ_{max}=465 nm) is only coordinated with Mn^{2+}, however, the complex between Mn^{2+} and the protonated TPP dimer was found to be unstable.

Hence, in the case of donor–acceptor interactions induced by coordination of TPP dimer with exogenous proton, a

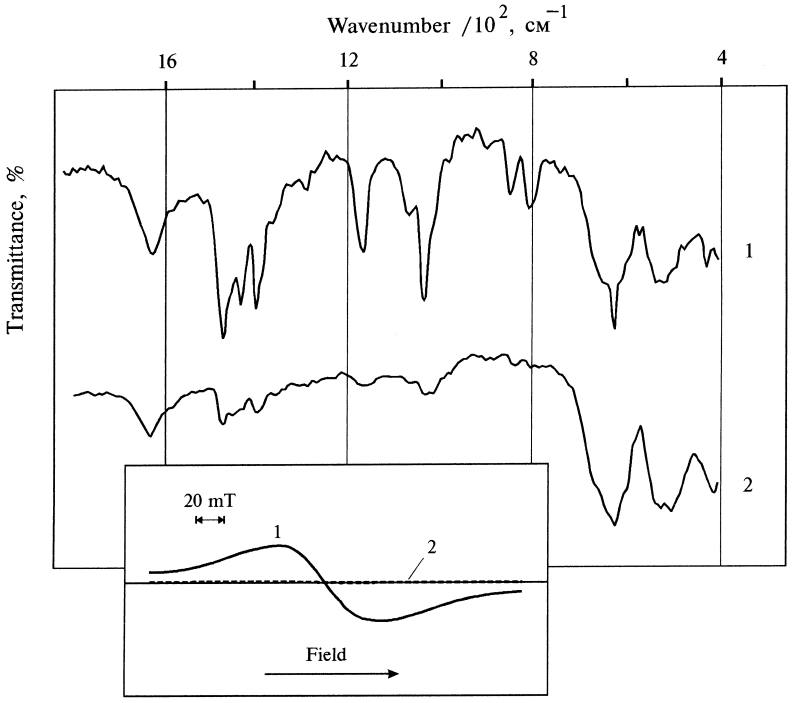
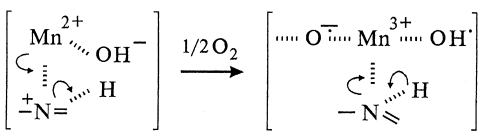


Fig. 3. Infrared spectra of fresh prepared complex between Mn^{2+} and TEA in KBr, 1; and the corresponding EPR-silent complex formed between the manganese and TEA, 2. The inset shows the corresponding EPR spectra of the fresh prepared complex, 1; and the EPR-silent complex, 2.

distance interaction between configurationally different porphyrin dimers occurs in the solution. This conclusion follows from fluorescence spectra obtained on selective excitations (Fig. 2, panel A). Although, some additional aggregation of the protonated TPP dimers can not be excluded according to absorption spectra (Fig. 1, panel A, curve 2 and panel B, curve 2). In contrast, the presence of ethanol in the solution prevents involving of water into donor–acceptor interaction with the porphyrin dimers. Nevertheless, the different absorption and fluorescence properties of the TPP dimers and TAPP associates, we observed a similar character of interaction between porphyrin macrocycle and water involved in the complex of associated porphyrin molecules [18,20]. This main peculiarity can be useful for the assembly of combined donor–acceptor complexes.

The above results provide the basis for assembly of the combined complex based on associates of the aminoporphyrin and the complex formed by triethylamine and manganese(II). Fig. 3 shows IR spectra of complexes formed between triethylamine and manganese(II) ions, one of which (curve 1) has a wide signal in EPR spectrum with *g*-factor of free electron and width, ΔH_{pp}, equalled to 70 mT (Fig. 3, the inset, curve 1). The other complex formed by triethylamine and manganese(II) ions, which has no EPR signal (the inset, curve 2), has strongly changed the corresponding IR spectrum (Fig. 3, curve 2). The changes observed in the spectrum (curve 1) suggest direct participation of nitrogen atom of aliphatic amine in the complex [11], as compared to the spectrum of the amine (the latter is not presented here). The strong decrease of the intensity of the bands in the IR spectrum of EPR-silent complex (curve 2) as compared with the intensity of those in the spectrum of fresh-prepared Mn^{2+}–amine complex (curve 1) suggests the decrease of polarity in the EPR-silent complex. This decrease of polarity can be related to the amine moiety of the complex and, therefore, suggests some change of its structure associated with transformation of the valance state of the manganese involved in the complex. The EPR-silent complex (curve 2) apparently has manganese with the other valence, i.e. probably manganese(III) because of the spin properties of manganese(III) complexes [21]. It should be noted that involving coordinated dioxygen in the transformation process as an oxidizer is very likely because of brown color of the final complex that indicates some sort of MnO(OH) species [3]. Hence, the transformation of manganese involved in the complex can be accompanied by hypothetical redox process depicted in the Scheme 2.. This simplified scheme does not show the assembled state of the manganese ions although one can assume that the state is dimeric or higher. According to the scheme and the IR spectrum (Fig. 3, curve 2), bonds of the amine moiety in the final complex to not have to be strongly polarized.



Scheme 2.

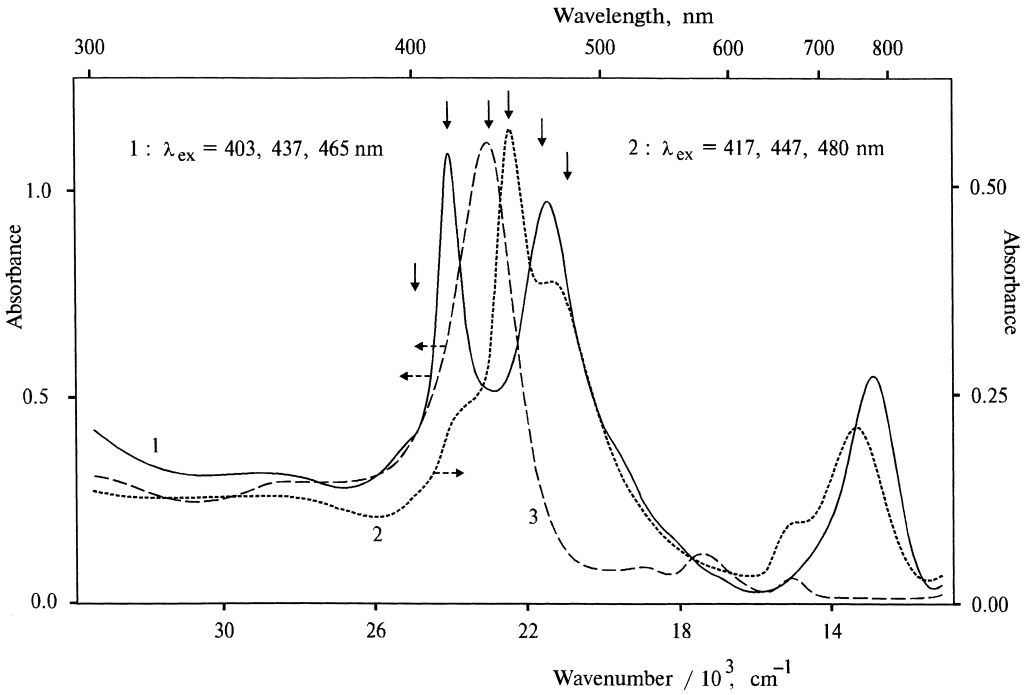


Fig. 4. Absorption spectra of the complex between of TAPP and the EPR-silent manganese–amine complex in DMF containing 1–2% (v/v) of water preliminary treated with $NaHCO_3$ after 20-min illumination with a non-stop change of the wavelength, 1; the mixture of the same solution of the illuminated porphyrin with EPR-silent manganese–amine complex and not illuminated solution of TAPP, 2 (see details in the text); and TAPP in DMF containing 1–2% (v/v) of water, 3. The points of excitation are marked by the solid arrow.

On the other hand, the main frequency characteristics of the IR spectrum are kept the same. This peculiarity gives the hope that the manganese involved in the complex with aliphatic amine, can be utilized in the reversible redox process for photochemical splitting of water. From this point of view, this triethylamine–manganese EPR-silent complex was utilized for the preparation of the combined complex as described below.

Absorption spectrum of TAPP in DMF in the presence of 1–2% (v/v) of water and the TEA–manganese EPR-silent complex preliminary treated with $NaHCO_3$ after illumination with non-stop change of the wavelength (see details in Section 2) is presented in Fig. 4, curve 1. The broad Soret band with the maximum at 433 nm, which characterizes TAPP associated in DMF (curve 3), is splitted into the two bands with the maxima at 418 and 467 nm after the illumination of the solution (curve 1). A broad band with maximum at 778 nm, which is comparable with the corresponding Soret band, is observed in the red region of the spectrum of the illuminated solution. However, if the same illuminated solution of the same compounds is mixed with the initial solution, in this case the resultant spectrum of the mixture is strongly changed (curve 2) as compared to that of the previous complex (curve 1). This fact looks like so that no illuminated porphyrin of the initial solution becomes doubly protonated dimer after the mixing, since Soret band of the porphyrin, where λ_{max}=447 nm in the spectrum (curve 2), is somewhat similar to Soret band of doubly protonated TPP dimer (Fig. 1, panel B, curve 1). Although, the corresponding narrow Soret band in the spectrum (Fig. 4, curve 2) is red shifted by 10 nm as compared to that band in the spectrum of the doubly protonated TPP dimer. Besides, the bands with the maxima at 418 and 467 nm are considerably decreased in magnitude in the spectrum of the complex (curve 2) and are rather noted in the spectrum as two shoulders. Also, this spectrum exhibits a similar broad red band with the maximum at 755 nm and an additional shoulder at ca. 666 nm. The latter denotes that no illuminated TAPP is involved in the complex, but rather as a protonated species since other structure of associated TAPP in the region of quasi-allowed electron transition disappears, in particular, the quite strong band with the maximum at 574 nm is not observed in the spectrum (curve 2). Therefore, the state of no illuminated TAPP involved in the complex is strongly different from that of associated TAPP in solution. Meanwhile as the strong and broad red band in the 650–900 nm region denotes out-of-plane coordination of porphyrin dimers with the manganese ions involved in the complex. Similar out-of-plane coordination of protonated TPP dimers and TAPP associates with transition metal ions have been found recently [19,20]. But in this case the out-of-plane coordination occurs as a result of a photoreaction.

The excited state of these porphyrin–manganese–amine complexes obtained in the result of illumination were studied under similar selective excitation of fluorescence. Out-of-plane coordination of singly protonated TPP dimer with Mn^{2+} produces new absorption in the spectrum at ca. 480 nm [19] so that is why the combined complexes

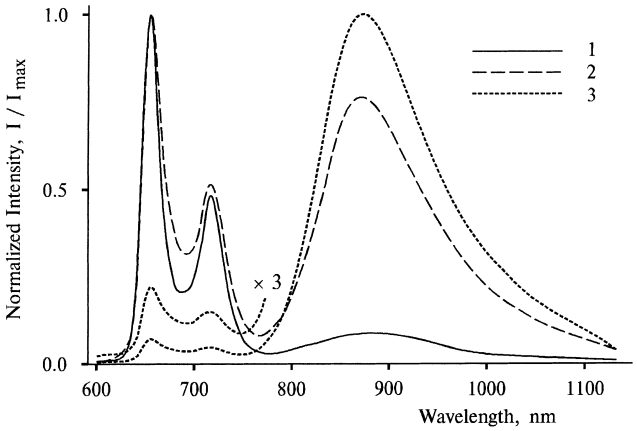


Fig. 5. Fluorescence spectra of the complex between of TAPP and the EPR-silent manganese–amine complex formed after the definite illumination on excitation at 403 nm, 1; 437 nm, 2; and 465 nm, 3. The spectra are normalized on the intensity of main emission band. The experimental conditions are the same as indicated in the caption of Fig. 4, curve 1.

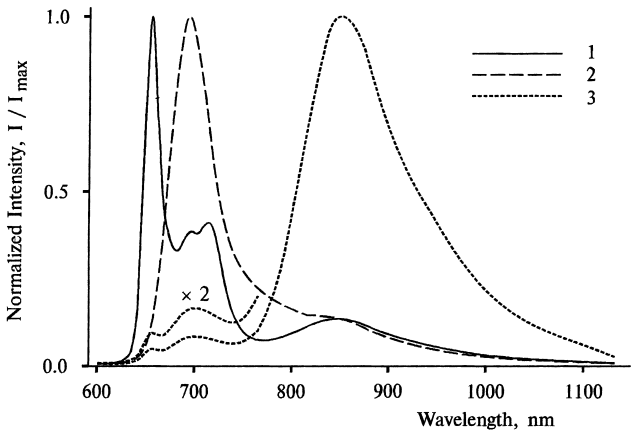


Fig. 6. Fluorescence spectra of the mixture of the illuminated solution of TAPP with EPR-silent manganese–amine complex and not illuminated solution of TAPP on excitation at 417 nm, 1; 447 nm, 2; and 480 nm, 3. The spectra are normalized on the intensity of main emission band. The experimental conditions are the same as indicated in the caption of Fig. 4, curve 2.

were studied including the latter wavelength of excitation. The fluorescence spectra of the first complex (see absorption spectrum in Fig. 4, curve 1) are proved to be strongly changed on dependence from wavelength of excitation, Fig. 5. The spectrum on the excitation at 403 nm exhibits main emission band with the maximum at 655 nm, vibrational satellite of this band with the maximum at 720 nm and near IR emission with the maximum at 880 nm (curve 1). It is easy to recognize two former bands in this spectrum as monomeric porphyrin which is similar to the fluorescence spectrum of TPP monomer [10]. In contrast, other selective excitations (λ_{ex}=437 and 465 nm) produce the strong increase of the near IR emission with the maximum at 875 nm (curves 2 and 3). This high near IR emission in the fluorescence spectra suggests a very effective trapping of the excitation energy by the combined complex. The self-organization of the complex is most probably initiated by illumination of red light since donor–acceptor complex between water and TAPP associates has absorption band in this region of the spectrum [22]. It is interesting that as a result of the restructuring of TAPP associates, the spectrum of monomeric porphyrin with the maxima at 655 and 720 nm is also revealed. This means that TAPP associate in DMF preliminary estimated as a trimer according to absorption spectrum (Fig. 4, curve 3) undergoes crucial restructuring into porphyrin monomer and dimer. At this point the latter is involved in out-of-plane coordination with EPR-silent manganese presented in the state of the complex with amine.

In the case of the second combined complex, i.e. the mixture of the illuminated and not illuminated solutions (see Fig. 4, curve 2), similar selective excitation results in the different fluorescence spectra too, Fig. 6. The spectrum on the excitation at 417 nm exhibits similar fluorescence of porphyrin monomer, i.e. the emission bands with the maxima at 655 and 720 nm, near IR broad band with the maximum at 845 nm and new small maximum at 693 nm (Fig. 6, curve 1). In contrast, on excitation at 447 nm the emission band with the maximum at 693 nm only and the near IR emission as a long tail are observed in the spectrum (curve 2). Whilst, the spectrum with λ_{ex}=480 nm exhibits small shoulder at 655 nm, appreciable band with the maximum at 693 nm and the very large near IR emission band with the maximum at 845 nm (curve 3). Hence, the narrow band with the maximum at 693 nm is observed in the spectrum (Fig. 6, curve 2) instead of a broad band with maximum at ca. 700 nm in the fluorescence spectrum of TAPP associates (Fig. 2, panel A, curve 4), i.e. the porphyrin which was added in the case of the second complex. Therefore, the same band with the maximum at 693 nm is also noted in the spectra (Fig. 6, curves 1 and 3). Similar band but without analogous large IR emission tail is observed in the fluorescence spectrum of doubly protonated TPP dimer (Fig. 2, panel B, curve 4). Hence, these results indicate that doubly protonated porphyrin dimer is the product of the interaction between molecules of TAPP, which was added to the solution of the illuminated TAPP in the presence of the triethylamine–manganese complex and $NaHCO_3$.

It is important to note that the effect of self-organization of porphyrin–manganese–amine complex observed under above steady-state illumination in the presence of bicarbonate ions is absent under other procedure of illumination. In the case of addition of solid triethylamine–manganese complex and $NaHCO_3$ to the solution of TAPP in DMF containing 1–2% (v/v) of water, the illumination with 60-W incandescent lamp results in very small non-specific changes in the corresponding absorption spectrum, Fig. 7 (curve 2), compare with the spectrum (curve 1). Fluorescence spectra on similar selective excitations (λ_{ex}=417, 447 or 465 nm) of the illuminated solution (curve 2) are proved to be identical to each other independent from the wavelength of excitation. The spectra exhibit the broad band with the maximum

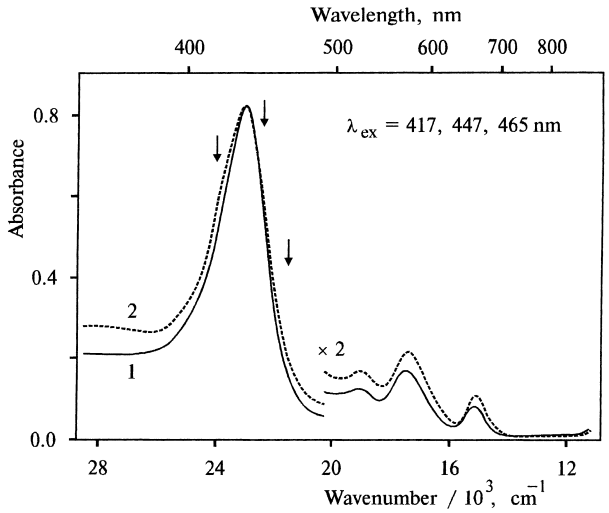


Fig. 7. Absorption spectra of TAPP in DMF containing 1–2% (v/v) of water, 1; and the mixture of TAPP in DMF containing 1–2% (v/v) of water, EPR-silent manganese–amine complex, and $NaHCO_3$ added to the porphyrin solution in the solid state after 30-min illumination with 60-W incandescent lamp, 2. The points of excitation are marked by the solid arrow.

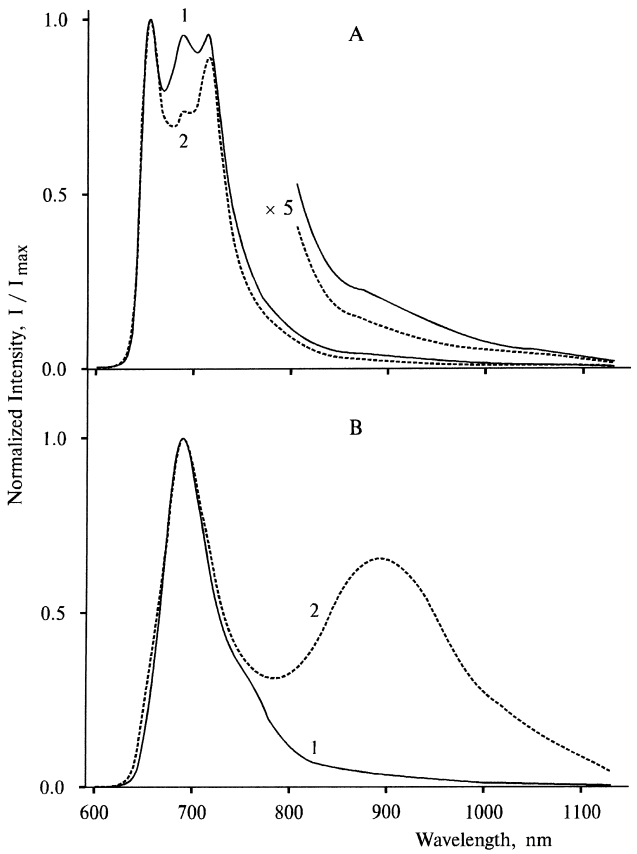


Fig. 8. Fluorescence spectra of the complex between of TAPP and the EPR-silent manganese–amine complex formed after the definite illumination, in the presence 10% of glycerol (v/v) in DMF containing 1–2% (v/v) of water on excitation at panel A: 403 nm, 1; 417 nm, 2; panel B: 437 nm, 1; and 480 nm, 2. The spectra are normalized on the intensity of main emission band.

at ca. 700 nm (results are not presented), i.e. the spectra are very similar to that of TAPP in DMF (Fig. 2, panel A, curve 4). Although, the fluorescence spectrum on the excitation at 417 nm exhibits an additional small shoulder which can be assigned to the band with the maximum at 655 nm (results are not presented). Therefore, specific conditions of the above illumination plays a key role in the self-organization of the combined complex. At the same time, we propose that the presence of bicarbonate ion is needed to stabilize or renew the EPR-silent state of manganese ions involved in the complex.

Hence, processes of the self-organization of the porphyrin–manganese–amine complex under light action show unusual behavior of these systems, for stabilization of which bicarbonate ions are needed. As known, bicarbonate ions are direct participants in the processes of photooxidative splitting of water in plants and algae [23,24].

It should also be noted that the illuminated solutions (see Fig. 4, curve 1) can be kept in the dark during several days without changes in the spectrum after that some change apparently indicating the reverse reaction takes place (results are not presented). Similar destabilization of the porphyrin–manganese–amine complex perhaps proceeds in the result of a considerable increase of the viscosity and/or presence of alcohol groups when glycerol is added to the solution. In this case, similar selective excitation gives some different results. Fluorescence spectra on the excitation at 403 and 417 nm presented in Fig. 8, panel A, exhibit main emission bands with the maxima at 655 and 693 nm and unusual strong band of the vibrational satellite with the maximum at 720 nm corresponding to monomeric porphyrin. But no similar near IR emission band is observed in the spectra except for a long IR tail. The spectra (panel A, curves 1 and 2) are alike each other although the intensity of the corresponding bands with the maxima at 693 and 720 nm is somewhat different. In contrast, the spectrum on the excitation at 447 nm exhibits the main emission band with the maximum at 693 nm and a small shoulder in the 730–780 nm region, Fig. 8, panel B, curve 1. The spectrum with λ_{ex}=480 nm also exhibits the band with the maximum at 693 nm and a broad near IR emission band with the maximum at 890 nm (panel B, curve 2). However, the latter is strongly quenched as compared with the corresponding near IR band in the spectrum (Fig. 5, curve 3). Let us consider some final states after a long staying of the solutions in the dark when reverse transformation of the absorption spectra takes place. It is interesting that the band with the maximum at ca. 780 nm disappears completely in the spectrum of the porphyrin–manganese–amine complex in the presence of 10% (v/v) of glycerol after several days of being kept in the dark, Fig. 9, curve 2. While this band in the spectrum of the same solution but without glycerol is partly retained (curve 1). Also, note that in the case of the mixture of the illuminated and not illuminated solutions (see Fig. 4,

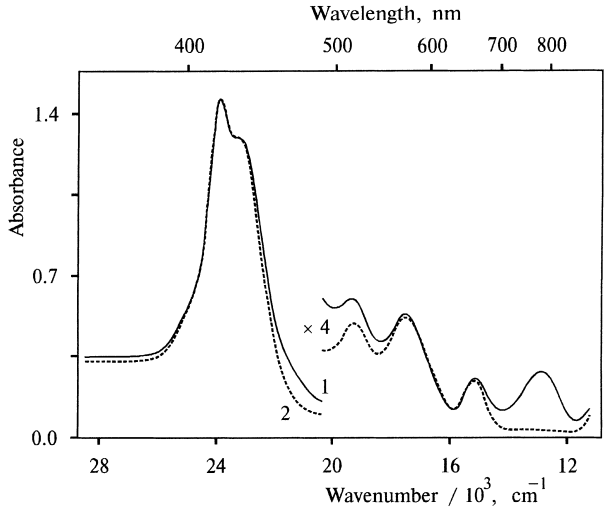


Fig. 9. Absorption spectra of the complex between of TAPP and EPR-silent manganese–amine complex formed after the definite illumination, in several days of keeping in the dark, 1; and the same complex but in the presence 10% (v/v) of glycerol, 2. The experimental conditions of the complex preparation were the same as indicated in the caption of Fig. 4, curve 1.

curve 2), the spectrum of the porphyrin–manganese–amine complex is proved to be stable for a longer time.

Hence, in the course of the reverse transformation of absorption spectrum of the combined complex, there is an intermediate state, selective excitation of which reveals new fluorescence behavoir. Namely, when the IR emission is strongly decreased and its maximum is red shifted under similar selective excitation as earlier, the fluorescence intensity of the vibrational satellite of the monomeric porphyrin with the maximum at 720 nm is strongly increased and apparently the band with the maximum at 693 nm too (compare the spectra in Fig. 8 with those in Figs. 5 and 6). Without a doubt, this behavior of fluorescence under selective excitation is to be due to structural damage of the combined porphyrin–manganese–amine complex in the dark. According to the absorption spectra (Fig. 9), addition of glycerol to the solution of the porphyrin–manganese–amine complex accelerates the damage of the complex.

Hence, processes of self-organization of the porphyrin–manganese–amine donor–acceptor complex induced by light of 300–700 nm region depend on the composition of the components in the solution, where participation of bicarbonate ions is most probably needed for stabilization or renewal of the EPR-silent state of manganese ions in the complex. At the same time, the increase of the viscosity of solution and/or presence of hydroxyl groups brings about destabilization of the porphyrin–manganese–amine complex.

4. Discussion

Usually π-electron structure of porphyrin monocation is unstable [25] but the electron structure can be stabilized in the ground state in the case of dimeric form by coordination of the neighboring porphyrin molecule with the formation of water–porphyrin dimeric complex via hydrogen bonds of two water molecules involved in the complex [18]. In the excited state, this stabilization of the singly protonated porphyrin dimer leads to the strengthening of water–porphyrin interaction. Therefore, under transition in the excited state π-electron structure of one configuration of the singly protonated porphyrin dimer is stabilized as the result of proton lending by water molecule bound with the dimer that leads to the formation of doubly protonated state of the dimer. Whereas water molecule bound in the other configuration of the mono-protonated dimer lends an electron to the dimer. The different configurations of the dimer are proposed to be *cis* and *trans* NH-tautomers, respectively. With this consideration, the singly protonated TPP dimer with the maximum of the main emission band at 693 nm was assigned to the configuration, π-electron structure of which is stabilized in the excited state in the result of proton lending by water molecule bound with the porphyrin dimer. This is high-energy singly protonated TPP dimer with the maximum of Soret band at 403 nm. Therefore, this form is present in the excited state as the doubly protonated dimer. Its fluorescence characteristics are identical to those of doubly protonated TPP dimer which is observed in the ground state (Fig. 2, panel B, curve 4). Whereas, the other singly protonated dimeric form of porphyrin with the maximum of the emission band at 730 nm is stabilized in the result of the lending of an electron by water molecule bound in the water–porphyrin dimeric complex. This fluorescence band is observed on the excitation at 465 nm, i.e. the corresponding band of the low-energy TPP dimeric form (λ_{max}=465 nm). It should be noted that in the terms of this consideration, close value of the energy of exciton interactions between these different dimers [26] and the energy of water deformations, suggests interaction between different high- and low-energy dimeric forms of porphyrin involving the dynamics of liquid water structure.

It was shown that the interaction between the different dimers of porphyrin are most probably responsible for electron transfer in the case of protonated TPP dimers and also irreversible electron transfer between different dimeric (associated) forms of aminoporphyrin [9]. The results presented above show that similar interaction in the excited state between high-energy monomer and low-energy dimer and similar electron transfer between them can be responsible for irreversible self-organization of the porphyrin–manganese–amine complex. If photoinduced dissociation of water–porphyrin donor–acceptor complex is the initial step of the photoprocess under red light action then in this case the porphyrin monomer and dimer can be formed from the porphyrin trimer. As mentioned above, preliminary estimation of the extent of TAPP association in DMF (Fig. 4, curve 3) shows trimeric state of the porphyrin. At the same time, involvement of the EPR-silent manganese–amine complex leads to out-of-plane coordination of the manganese

ions. The products of the photoreaction are long-living intermediates as in the case of associates of another aminoporphyrin [9], that is why protonation of TAPP added after the photoreaction takes place. In this case only water can be a source of these protons. Therefore, the combined complex can be used for photooxidative splitting of water. There is a high probability that bicarbonate ions, whose participation is needed for the positive effect of the steady-state illumination (see Fig. 4, curve 1), are necessary for the renewal of the manganese intermediates produced during the photoreaction and recovering of the EPR-silent state. According to the fluorescence spectrum (Fig. 6, curve 2), protons are some sort of intermediate products of the photoreaction. The presence of the main emission band with the maximum at 693 nm suggests that not illuminated TAPP added after completion of the illumination accepts two protons produced by the photoreaction. As a result, the whole complex (Fig. 4, curve 2) are highly stable since protons are proved to be bound with the porphyrin dimers. It should be noted that not perturbed doubly protonated TPP dimer has Soret band with the maximum at 437 nm in the absorption spectrum [16]. While Soret band of the doubly protonated TAPP dimer bound in the complex has maximum at 447 nm in the spectrum (Fig. 4, curve 2). Note that similar location of the maximum at 446 nm has been found in the absorption spectra of photoactive dimeric forms of TAPP covalently bound with copolymer after photoactivation of donor–acceptor complex in the electron transfer reaction to viologen [27].

Now what can we said about hypothetical structures of the complexes investigated in this work. It is obvious that the manganese–amine complex is directly involved in the structure of associated porphyrin so that the trimer of the porphyrin is divided on the monomer and dimer. The latter is coordinated with the manganese–amine complex, most probably, by the same way as in the case of polymer-bound porphyrin associates [20]. Hence, out-of-plane coordination of manganese ions by *trans* isomer of mono-protonated porphyrin dimer is the peculiarity of the combined complex. On the other hand, electron transfer photoreaction and as a consequence the next structural reordering of the complex is initiated by illumination into red band of water–porphyrin donor–acceptor complex. That suggests unique coordination of water with the aminoporphyrin molecules in the associates. Unfortunately, the structure of the aminoporphyrin donor–acceptor complex is still undefined. From our point of view, coordination and hydrogen bonds between components of the combined complex including the intermediates of the photoreaction are responsible for the structure of the complex. However, available results do not enable us to suggest a hypothetical structure of the combined complex which meets the most important criteria. This matter is complicated by that the formation of the whole complex of porphyrin pigments as an integral part mimicking the corresponding apparatus of photosystem I and II is highly possible for these self-organizing complexes.

As mentioned above, the bands with the maxima at 655 and 720 in the spectrum (Fig. 5) are fluorescence of monomeric TAPP since the spectrum in this region is very similar to that of monomeric TPP [10]. In the case of decomposition of the porphyrin–manganese–amine complex after a long staying, the increase of the fluorescence intensity of the satellite band at 720 nm is accompanied by a decrease of the IR emission, so that the maximum of the IR band is some red shifted as compared with that of the initial complex. This fact suggests that the electron-vibrational states of the monomer and dimer of TAPP are involved in the process of the excitation energy degradation in the combined complex. This means a good combination of these two complexes, the aliphatic amine–manganese complex coordinated with porphyrin macrocycle and the complex of associated TAPP molecules which involves water in its structure.

Hence, the results suggest that protons of water molecules are produced by the photoreaction in the case of definite conditions of illumination of the TAPP associates and EPR-silent manganese–triethylamine complex preliminary activated with $NaHCO_3$. This way of assembly of self-organizing donor–acceptor complex is a real tool for the mimicking of the photosynthetic splitting of water.

5. Conclusion

The results presented above show the way of involving of the complex formed between triethylamine and EPR-silent manganese, apparently manganese(III), into donor–acceptor complex with associated aminoporphyrin. The resultant porphyrin–manganese–amine complex of unique structure has the strong near IR emission band with the maximum within 845–890 nm depending from the composition or state of the complex. It is established that bicarbonate ions are needed for the positive effect and involved in the renewal or stabilization of the complex or intermediate products of the photoreaction. It is proposed that self-organization of the porphyrin–manganese–amine complex proceeds in the result of electron transfer reaction in TAPP associates, where molecules have similar orientations as two different high- and low-energy TPP dimers. But the self-organization of the complex has to be initiated by dissociation of the donor–acceptor complex formed between water molecules and TAPP associates according to definite conditions of the illumination. As a consequence, these water molecules bound with the porphyrin can be used as the sacrificial electron donor in the photoreaction. Hence, the above features of the photoreaction demonstrate some photochemical bases for the photosynthetic splitting of water in artificial system.

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