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Photoactive forms of donor–acceptor complex formed by associated porphyrin molecules

Alexander V. Udal'tsov[a,*], Lev A. Kazarin[b]

[a]*Faculty of Biology, Moscow State University, Moscow 119899, Russia*

[b]*Faculty of Chemistry, Moscow State University, Moscow 119899, Russia*

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Abstract

Associated forms of *meso*-tetra(*p*-aminophenyl)porphine covalently bound with hydrophobic–hydrophilic copolymer and dimeric forms of *meso*-tetraphenylporphine mimicking the interaction between porphyrin macrocycles of neighboring molecules of the former were studied by absorption spectroscopy. Two types of dimeric forms of *meso*-tetra(*p*-aminophenyl)porphine bound with the copolymer, which are involved in photoactivation of donor–acceptor complex, were found. These photoactivation processes proceed under photoinduced electron transfer in the three-component system with triethylamine and benzylviologen. With respect to spectral properties, these dimeric forms of *meso*-tetra(*p*-aminophenyl)porphine bound with the copolymer were found to be similar to singly protonated dimeric forms of *meso*-tetraphenylporphine and close to the corresponding singly protonated forms of *meso*-tetra(*p*-aminophenyl)porphine bound with the copolymer.

Keywords: Photoactive species; Donor–acceptor complexes; Dimers of porphyrin; Absorption spectroscopy

1. Introduction

Electron transfer to viologen in the presence of a photosensitizer and an electron donor was studied by the methods of kinetic spectroscopy [1–3] and under steady-state illumination with accumulation of the reduced viologen form [4–7]. The mechanisms of the sensitized photoreduction of electron acceptor and the processes of reversible and irreversible decay of an electron donor, when reversible or irreversible (so-called sacrificial) electron donor was utilized, have been studied for such systems. Among the three-component systems, special attention was focused on the system with rather unusual phenomenon, which was interpreted as a photoactivation of donor–acceptor complex based on dimeric or associated molecules of porphyrin [8]. In this case, photoactivation increases the rate of accumulation of the reduced viologen and is accompanied by irreversible changes in the corresponding absorption spectrum of the three-component system, which are likely to be associated with structural re-arrangements in the complex of pigments.

Unusual behavior of this three-component system is likely to be related to the formation of donor–acceptor complexes between dimeric or associated porphyrin molecules [9]. These speculations were invoked to explain the principle features of sensitized photoreduction of viologen. However, further studies of electron transfer to viologen revealed new facts, which did not receive their adequate explanation. These facts may be explained in the results of studying physicochemical fundamentals of the formation of intermolecular donor–acceptor complexes since the associated forms of aminoporphyrin, which is able to form donor–acceptor complexes, were used as a photosensitizer. In connection with this, further studies concerning a spontaneous association and aggregation of porphyrin will allow one to obtain a new information in order to simulate the interactions of the corresponding radical cation in the donor–acceptor complex.

In this work, we studied the associated forms of *meso*-tetra(*p*-aminophenyl)porphine bound with the hydrophobic–hydrophilic copolymer, which are able to form intermolecular donor–acceptor complexes, and dimeric forms of *meso*-tetraphenylporphine obtained by a spontaneous association in aqueous-organic solutions.

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*Corresponding author.

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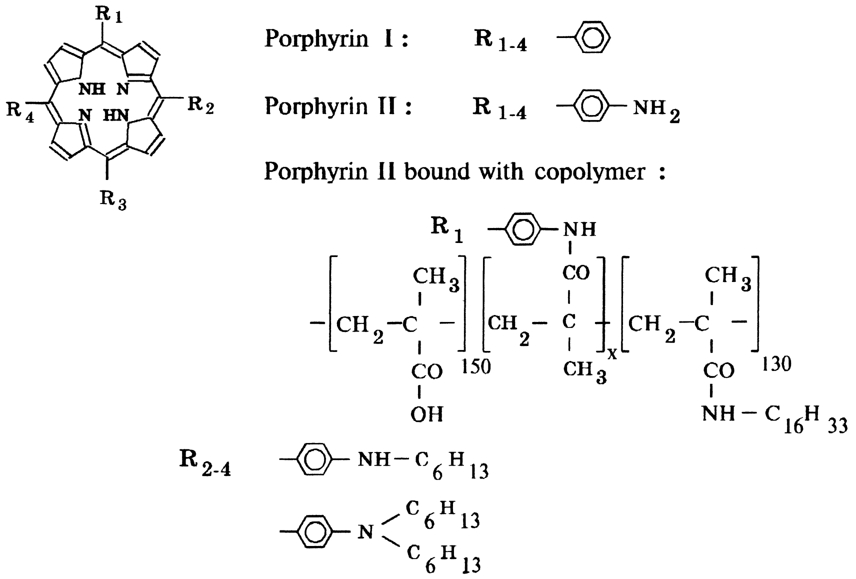
2. Experimental

Synthesis of the compounds presented in the scheme is described elsewhere [10–12]. Dimethylformamide (DMF) and other organic solvents were additionally purified according to standard procedures [13]. Organic solvent were dried using 4A molecular sieves. Chemical oxidation of porphyrin was carried out under argon atmosphere [14]. To prepare aqueous-organic solutions, distilled or twice distilled water was used.



Absorption spectra, the kinetics of absorption, and differential spectra were obtained with a Specord M-40 spectrophotometer. Absorption spectra of the frozen porphyrin solutions in 95% methanol were recorded at 77 K using a Hitachi-557 spectrophotometer. The kinetics of absorption was studied immediately after illumination of porphyrin solution with a 150 W halogen lamp. Electron transfer in the three-component systems with the accumulation of the reduced viologen were studied in the presence of the sacrificial electron donor, i.e. triethylamine (TEA), with a concentration of 2×10^{-2} mol l^{-1} and benzyl violgen chloride with a concentration of 3.5×10^{-4} mol l^{-1}. Photochemical reaction was carried out in the solutions of copolymer or porphyrin in DMF/ethanol/water = (1/1/1 (v/v)) without any buffer solution. However, the solution of the photosensitizer was titrated with caustic potash solution to pH $\sim$ 10. Before illumination, the three-component solutions were bubbled with argon for 40 min. The kinetics of accumulation of viologen radical cation ($BV^{\bullet +}$) in the three-component systems was investigated by recording the absorption spectra in the spectral regions with maxima at 402 nm and 607 nm immediately after each illumination dose. The formation of viologen radical cation was observed neither in two-component nor in one-component systems. To calculate the concentration of $BV^{\bullet +}$, extinction coefficient was taken to be equal to 1.2×10^4 mol^{-1} cm^{-1} at a wavelength of 607 nm.

3. Results

The absorption spectra presented in Fig. 1 show the photochemical reduction of viologen sensitized by the associates of porphyrin bound with hydrophobic–hydrophilic copolymer. In the case of the three-component system composed of triethylamine, benzylviologen, and porphyrin II bound with the copolymer, illumination of this system with visible light leads to an effective accumulation of viologen radical cation (curve 2). This three-component system show a peculiar feature, namely photoinduced activation of donor–acceptor complex based on dimeric or associated porphyrin molecules [8]. The photoinduced activation is most likely to be accompanied by structural rearrangements of this donor–acceptor complex. In contrast, when porphyrin II is used as a low-molecular weight photosensitizer, no photoactivation was observed. However, in this case, a spontaneous aggregation of the porphyrin takes place. This aggregation is likely to be due to the formation of radical cation of porphyrin II in DMF which was observed under illumination of the solution in the absence of electron donor and acceptor. At room temperature, the radical cation is accumulated as the dication [15] or in the case of the three-component system, where the low-molecular weight photosensitizer was used, the radical cation serves as an aggregation site.

Differential absorption spectrum (spectrum of the solution of porphyrin II after 20 min visible light illumination minus the spectrum of the same solution before illumination) is presented on Fig. 2, curve 1. The spectrum of associated porphyrin II bound with the copolymer also shows irreversible changes induced by illumination with

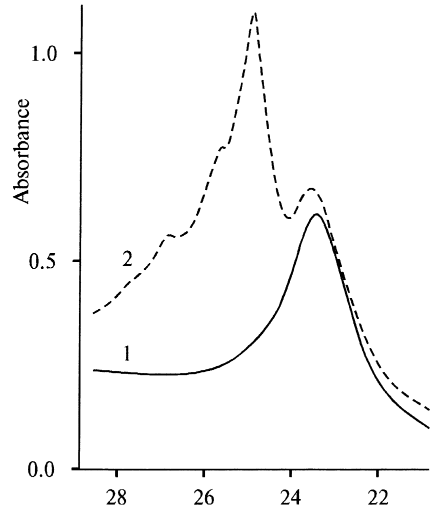


Fig. 1. Absorption spectra of the three-component system including benzyl viologen, triethylamine, and porphyrin II bound with hydrophobic–bydrophilic copolymer as a photosensitizer in 0.2 cm cuvette: before illumination, (1); after 7 min-illumination, (2).

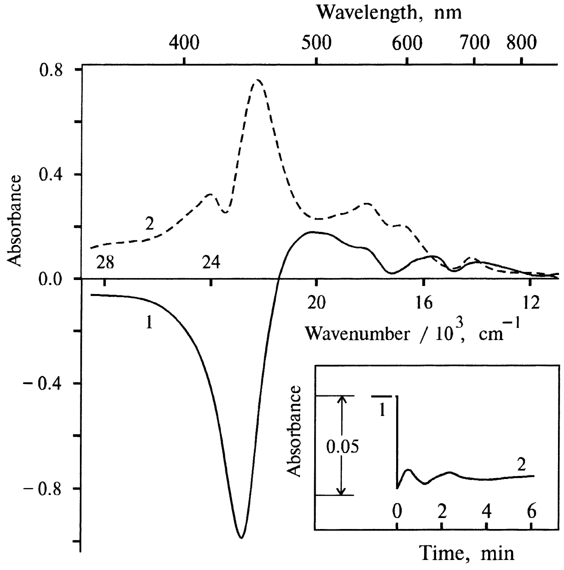


Fig. 2. Differential spectra of porphyrin II in DMF, (1); and porphyrin II bound with hydrophobic–hydrophilic copolymer in DMF-water (90 : 10, v/v), (2); (see explanation in the text), light pathway is 1 cm. The inset shows kinetics of absorption of porphyrin II in DMF measured at 435 nm in 0.2 cm cuvette.

the visible light. Fig. 2, curve 2 shows the corresponding differential spectrum (spectrum of the solution before illumination minus the spectrum of the same solution after 22 min illumination). It is found that after the preliminary illumination, the solution of this porphyrin bound with the copolymer did not show its ability for photoactivation in the three-component system in the presence of the same electron donor and acceptor. As a result, no accumulation of viologen radical cation in such three-component system is observed. Hence, the corresponding differential spectrum (curve 2) suggests destruction or 'burn-off' of the photoactive forms of this porphyrin.

The burn-off of the associated forms of porphyrin II bound with the copolymer (curve 2) is irreversible because a prolonged stay of the illuminated solution in darkness does not lead to the recovery of these forms. An irreversible character of this photochemical reaction may be associated with the dissociation of the donor–acceptor complex and formation of irreversible products. This conclusion is likely to be supported by studying the analogous low-molecular weight porphyrin II. In the latter case, the kinetics of photoinduced absorption exhibits an oscillating character of absorption in a minute time scale (Fig. 2, the inset). This behavior suggests the occurrence of dark process, which is likely to involve a product of the illumination. After 4–5 min visible light illumination, maximum oscillation amplitude is equal to 16–20% of absorption decrease at $\lambda = 435$ nm. When the kinetics of absorption is recorded at $\lambda = 500$ nm quite similar oscillation character is observed in the same time interval (these results are not presented in this work). Hence, in the case of the low-molecular weight system based on porphyrin II, dark directed reactions are likely to take place. These reactions yield stable products. One of products is the dication located in associated molecules of this porphyrin.

Hence, this evidence shows that photoactivation is a complicated process, which is likely to involve different forms of dimeric or associated porphyrin. According to the differential spectrum, the formation of photoactive donor–acceptor complex is based on the forms of the porphyrin, which burn off under steady-state illumination of the associated porphyrin II bound with hydrophobic–hydrophilic copolymer in the absence of electron donor and acceptor. As a result, this effect does not allow the photoactivation processes to occur.

This burn-off in the absorption spectrum (Fig. 2, curve 2) is likely to be related to the generation of radical ions in associates of porphyrin II. But in the case of porphyrin II bound with the copolymer, dark process yields some other products as compared with the system in the presence of electron donor and acceptor. Below, we will show a real possibility of an alternative process different from the photoactivation which concerns participation of dimeric form of radical monocation at the initial stages of water oxidation. Standard oxidation potential of molecular bromine in liquid state is equal to 1.065 V, whereas the corresponding value for radical cation of monomeric porphyrin I is equal to 1.1 V on average [7]. The presence of lateral amino groups in phenyl rings favours an easier oxidation of porphyrin II as compared with porphyrin I. Fig. 3 presents the absorption spectra recorded during oxidative titration of porphyrin II with molecular bromine. Titration is accompanied by a decrease in the Soret band with maximum at 423 nm and by a concomitant increase in absorption bands with maxima at 464 nm and about 720 nm (curves 1 and 2).

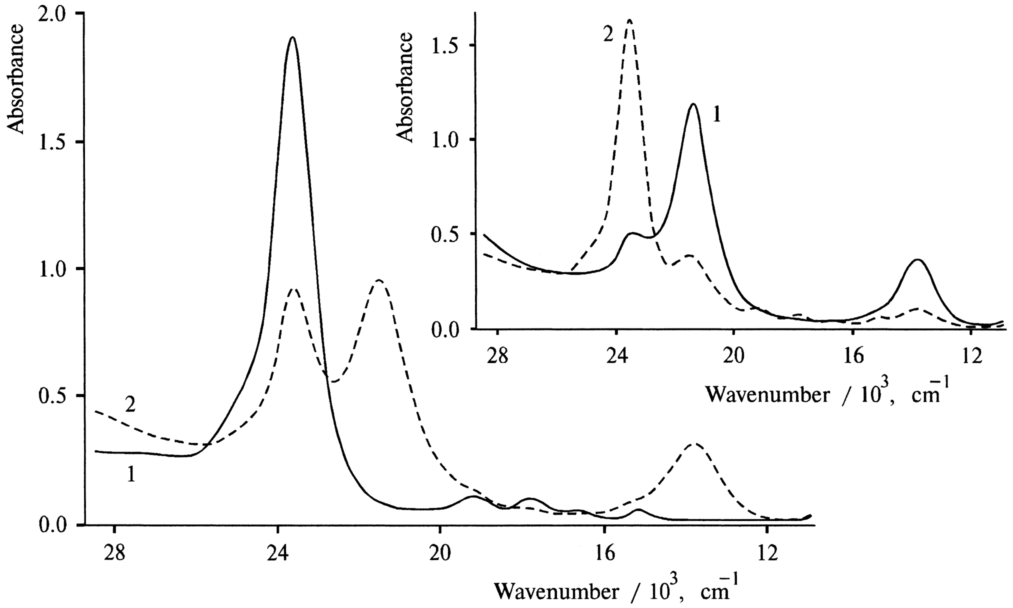


Fig. 3. Absorption spectra of porphyrin II in solution of ethyl alcohol and ethyl ether (1 : 1, v/v) in the course of oxidative titration of the porphyrin with liquid bromine: before titration, (1); in the presence of 0.7×10^{-3} mol l^{-1} Br_2, (2). The inset shows absorption spectra of porphyrin II in the same solution in the presence of 1.4×10^{-3} mol l^{-1} Br_2, (1); and after adding of water to the solution, (2).

In this case, the typical structure of quasi-allowed transitions of dimeric porphyrin II gradually vanishes, the initial spectrum with five bands (including the Soret band) finally contains only two bands. The characteristics of the latter spectrum are very similar to those of the spectrum of the singly protonated dimer of porphyrin II bound with a copolymer [8]. The addition of water to the solution of radical monocation of porphyrin II obtained by oxidation with bromine leads to dramatic changes in the corresponding spectrum (Fig. 3, the inset). Absorption of the band with maximum at 464 nm abruptly decreases, whereas absorption of the band with maximum at 423 nm increases in proportion to a decrease in the concentration of radical monocation (the inset, curve 2).

This evidence shows that radical cation of porphyrin II in its dimeric state is likely to be reduced by addition of water. This behavior suggests that radical monocation of the dimeric porphyrin has unique properties, which are possibly able to provide early stages of oxidation of water. Hence, in addition to dimerization of radicals monocation of the associated porphyrin in the solution and formation of dication, one may expect the occurrence of other processes, which yield other irreversible products, in particular, when porphyrin is bound with hydrophobic–hydrophilic copolymer and dimerization of its radical cation is markedly hindered. These irreversible processes are likely to provide an alternative pathway for radiationless deactivation of excitation, whose occurrence prevents further events of photoactivation in the three-component system including electron donor and acceptor.

The effect of the local macromolecular surrounding on photoactivation of donor–acceptor complex is shown in Fig. 4, which presents the kinetics of accumulation of viologen radical cation at different degrees of ionization of carboxyl groups of the copolymer. As follows from Fig. 4, the higher the degree of ionization, the higher efficiency of accumulation of viologen radical cation is observed. For comparison, this figure shows the kinetics of accumulation of viologen radical cation under sensitization of electron transfer by porphyrin II in the solution. In the case, the associated forms of porphyrin are freely accessible for viologen in contrast to the porphyrin, which is bound with hydrophobic–hydrophilic copolymer and is likely to exist in a local hydrophobic surrounding. In the case of porphyrin II in solution, a delay in accumulation of the reduced viologen in the initial stage of kinetic curve is much less pronounced (curve 4) as compared with the case of sensitization by porphyrin II bound with the copolymer (curves 2 and 3). Photoactivation processes are more effective when

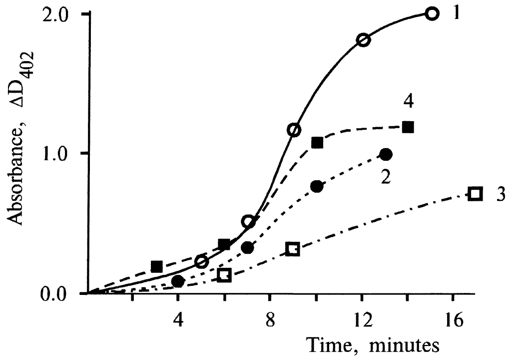


Fig. 4. Kinetics of accumulation of benzyl viologen radical cation in the system with porphyrin II bound with hydrophobic–hydrophilic copolymer as photosensitizer and triethylamine as electron donor with extent of dissociation of polymeric carboxyl groups equaled (1–3): 95% (1); 60% (2); 10% (3) and porphyrin II in solution as photosensitizer (4).

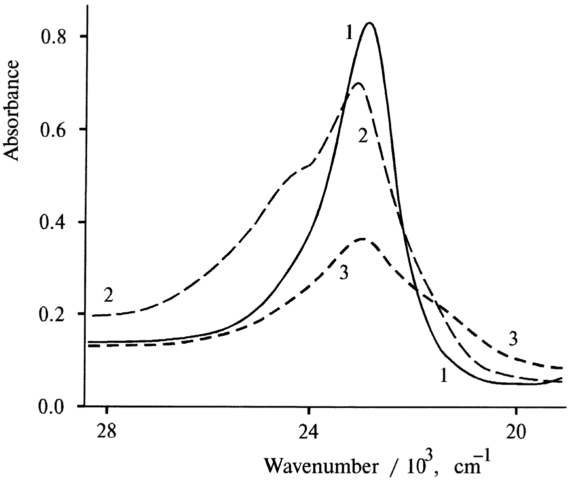


Fig. 5. Absorption spectra of the three-component system including benzyl viologen, triethylamine, and porphyrin II in solution as a photosensitizer (1, 2): before illumination (1); after 20-min illumination and deactivation of $BV^{+\bullet}$ accumulated (2); and two-component system including benzyl viologen and porphyrin II in solution after 12-min illumination (3).

porphyrin II bound with the copolymer is easily accessible for electron donor and acceptor molecules (curve 1), i.e. at almost complete ionization of the carboxyl groups.

It seems interesting to study the light-induced irreversible changes in spectra of porphyrin II in solution, i.e. under a free access for viologen to porphyrin associates in different molecular systems. Fig. 5 (curve 2) shows the absorption spectrum for the three-component system (viologen, triethylamine, porphyrin II) after illumination and subsequent deactivation of the reduced viologen, i.e. when the spectrum with the characteristics corresponding to the viologen radical cation completely vanishes. As compared with porphyrin II bound with a copolymer [8], absorption of the Soret band decreases (compare curves 1 and 2) that is accompanied by the increase of absorption around the Soret band. In the absence of triethylamine in the solution, one may observe only an increase in absorption in the red region of the Soret band and a more dramatic decrease in absorption at maximum of the Soret band (curve 3). As was mentioned, no accumulation of viologen radical cation was observed in this system.

Hence, this evidence and earlier results [8] suggest that in the case of the accumulation of viologen radical cation, photoactive intermolecular complexes are formed under involving of triethylamine, viologen and likely different forms of dimeric or associated porphyrin II bound with copolymer.

The formation of different dimeric forms may be mimicked by using a simpler porphyrin, i.e. *meso*-tetraphenylporphine, which contains no amino groups in phenyl rings. Spectral properties of monomeric this porphyrin in its protonated state are similar to those of the corresponding radical cation. The difference between these two dimeric porphyrin systems is that, the molecules may be freely oriented with respect to each other under dimerization of porphyrin I. Whereas, orientation of the molecules of porphyrin II is controlled by amino groups in phenyl rings because the presence of these groups produces a well-pronounced association of these porphyrin molecules both in solution and under covalent binding with copolymers [9]. Dimeric singly and doubly protonated forms of tetraphenylporphine were obtained under the competition between protonation reaction and aggregation of the porphyrin [16]. Fig. 6 shows the absorption spectra of dimeric forms of porphyrin I in aqueous-organic solutions in the presence of 0.4 N hydrochloric acid. This evidence shows that the appearance of the spectra is rather controlled by specific features of interactions of dimeric forms of porphyrin with a solvent and possible additions of mixtures in it than by concentration of porphyrin. This conclusion is also proved by the fact that the ratio between the three forms with maxima in the region of the Soret band at 403, 437, and 465 nm may be controlled by varying the organic component of aqueous-organic solution. In the red spectral region, these three forms show absorption bands with maxima at 638, 654, and 694 nm, respectively. These forms were identified as the doubly protonated state with $\lambda_{max} =$ 437 nm and two singly protonated states of dimeric porphyrin ($\lambda_{max} = 403$ and 465 nm), which have different orientation of molecules in dimer. According to the presented spectra, both solutions contain only three main dimeric forms in different from the earlier spectra [16].

Similar forms were also observed for the protonated porphyrin II bound with the copolymer. Fig. 7 shows the spectra for this sample in 95% methanol when the degree of association of porphyrin is close to dimeric state (curve 1). As a result of addition of hydrochloric acid, associated porphyrin is transformed into singly protonated state (curve 2) according to the spectral characteristics [16]. This state is stable in a wide range of pH values. As temperature is decreased, reaction of reversible protonation of porphyrin is shifted towards the formation of protonated product because this reaction is exothermic [17]. Fig. 7 (curve 3) shows the spectrum of the protonated porphyrin II bound with the copolymer at 77 K. This spectrum also reveals, at least, three forms. The form with the maximum at 438 nm, which is also likely to be assigned to doubly protonated dimer, appears to prevail as compared with the low- and high-energy singly protonated dimeric forms of the porphyrin.

Dimeric forms of porphyrin II bound with the copolymer are better seen in the spectrum obtained by subtraction of the spectrum of doubly protonated porphyrin dimer from the initial spectrum (Fig. 7, curve 3). The resultant spectrum is presented in Fig. 8 (curve 1). Analysis of this spectrum shows two minor forms with maxima at about 400 and 480 nm in the region of the Soret band in addition to the bands with maxima at 423 and 446 nm. Also this figure shows the differential spectrum of the forms of porphyrin (curve 2), which are involved in the photoactivation processes and also shown in Fig. 2, (curve 2). Principal characteristics of this spectrum are similar to the characteristics of the spectrum presented in Fig. 8 (curve 1). The difference

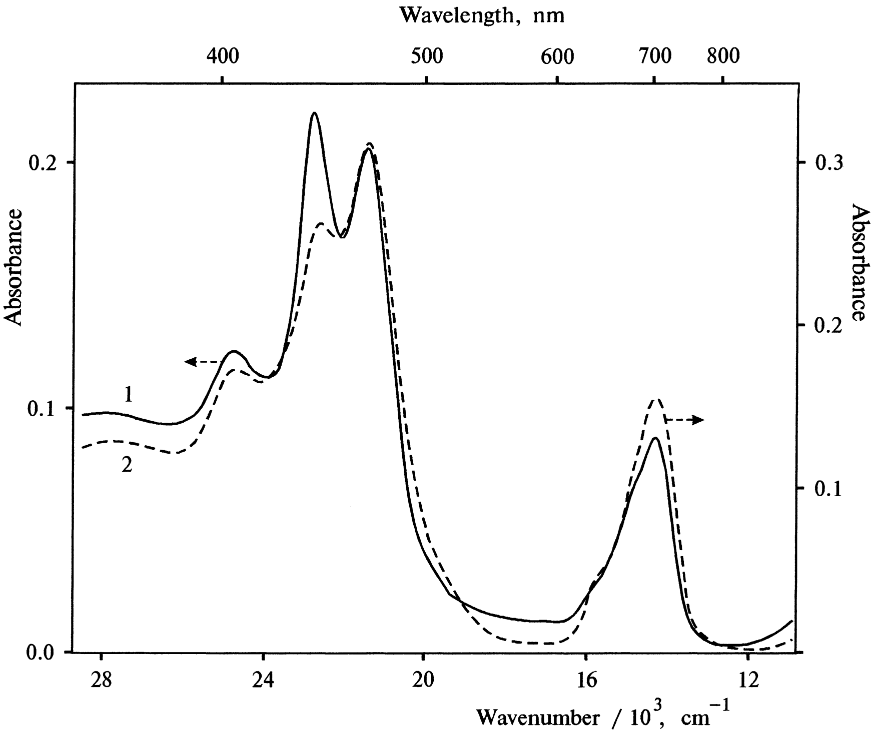


Fig. 6. Absorption spectra of porphyrin I in solutions in the presence of 0.4 N hydrochloric acid: in water–acetone–dioxane (90 : 5 : 5) (v/v) (1) and in water–glycerol–tetrahydrofuran solution (86.5 : 10 : 3.5) (v/v), (2).

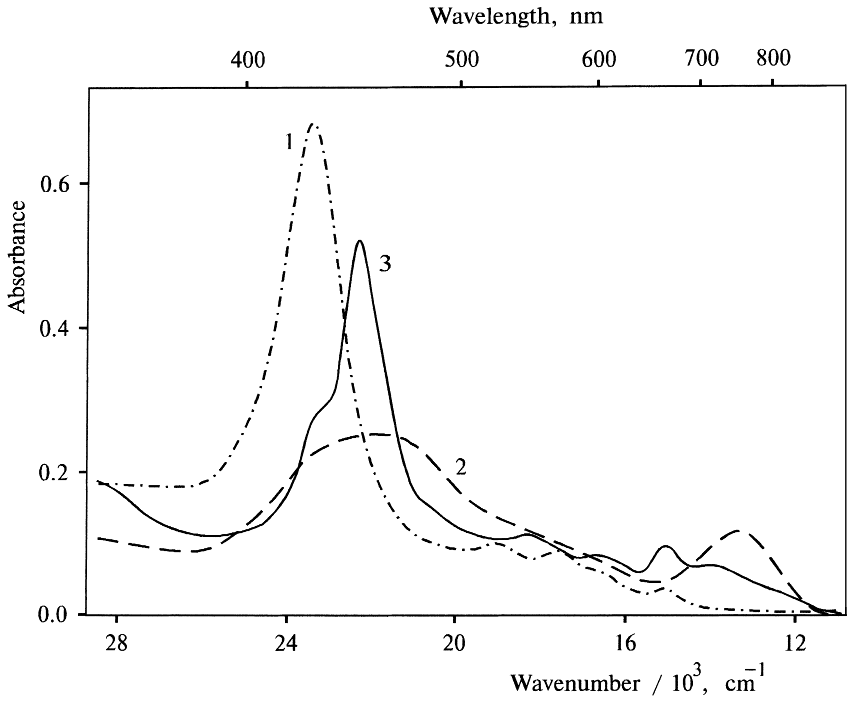


Fig. 7. Absorption spectra of porphyrin II bound with hydrophobic–hydrophilic copolymer in 95% methanol: initial spectrum (1); and the presence of 2 mN hydrochloric acid at 298 K (2); and at 77 K (3).

between these spectra are likely to be due to unidentical states of the associated forms of porphyrin. Hence, similar appearance of these spectra suggests similar structure of the singly protonated dimeric forms and the forms of porphyrin, which are involved in photoactivation processes of donor–acceptor complex.

Hence, main photoactive forms of the donor–acceptor complex based on the associated porphyrin II bound with

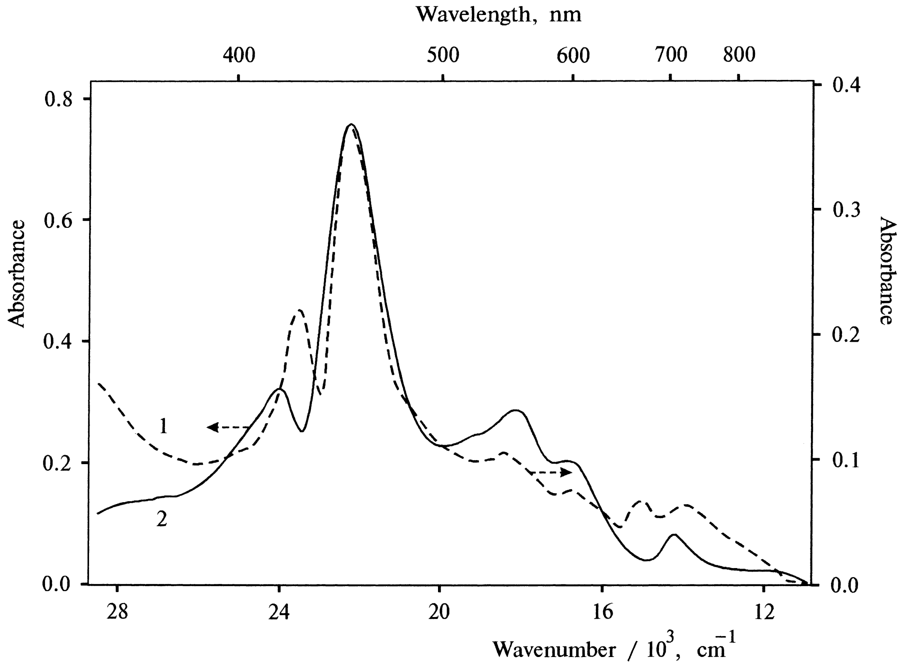


Fig. 8. Differential spectra, the spectrum of protonated porphyrin II bound with hydrophobic–hydrophilic copolymer at 77 K minus that of doubly protonated porphyrin I, (1) and the spectrum of porphyrin II bound with the copolymer in DMF-water (90 : 10, v/v) before illumination minus the same solution after 22 min-illumination with visible light, (2).

hydrophobic–hydrophilic copolymer are similar on the spectral properties to the forms of singly protonated porphyrin dimers.

4. Discussion

The above evidence shows that photoactivation, which accompanies electron transfer to viologen under steady-state illumination in the presence of triethylamine and dimeric or associated porphyrin II bound with hydrophobic–hydrophilic copolymer, appears to be far more complicated process as was anticipated initially [8]. Irreversible changes in the absorption spectrum suggest the occurrence of the light-induced structural rearrangements in the donor–acceptor complex. These changes are accompanied by an increase in the rate of accumulation of the reduced viologen. As was mentioned earlier, this phenomenon is absent when the solution of porphyrin bound with the copolymer was pre-illuminated for 20–30 min in the absence of electron donor and acceptor. In this case, absorption spectra of the burnt-off forms appear to be similar to the corresponding spectra of the singly protonated dimeric forms of the porphyrin. Spectral characteristics of one of such dimeric form with maximum at 465 nm are similar to those of the dimeric radical monocation of porphyrin II. As compared with the associated form of porphyrin II dication (Fig. 2, curve 1), which is accumulated during illumination, the singly protonated forms of the porphyrin bound with copolymer can be produced in the excited state as a result of interaction with carboxyl groups of the copolymer [8,9].

Taking into account the above evidence, one may advance a plausible explanation for an extremely fast deactivation of viologen radical cation, which was accumulated under steady-state illumination, when deactivation is carried out by a simple mixing of the solution by turning over the cuvette with solution. Deactivation is completed within one turn-over: when a small bubble from the surface of solution reaches the bottom and then returns back to the surface, blue color of viologen radical cation completely disappears. The above specific features may hardly be explained by generation of a singlet oxygen or deactivation of the radical cation on intermolecular donor–acceptor complexes. After deactivation, absorption spectrum of the donor–acceptor complex shows a weak band with maximum at 476 nm which was built up in the photoactivated complex [8]. However, concentration of this complex is, at least, by two orders of magnitude lower than the concentration of viologen radical cation accumulated during illumination. At the same time, triethylamine is known as an sacrificial electron donor [7], hence, the reduction of the oxidized triethylamine is impossible in this system. Also it should be noted that under prolonged illumination (of about 30 min), the corresponding kinetic curve shows a maximum, i.e. at a certain moment of time illumination decreases the concentration of viologen radical cation in the solution. But this effect is absent in the case of a marked increase in viscosity of the solution upon addition of glycerol. Furthermore, in the presence of glycerol, accumulation of viologen radical cation is observed without any preliminary bubbling with argon. Hence, with increasing the viscosity of the solution, the rate of diffusion of the photoreaction products decreases in the solution as a result of which an effective deactivation of viologen radical cation is prevented.

Taking into consideration the above reasons, these specific features may be explained as follows. In addition to accumulation of viologen radical cation according to the absorption spectra, also this system generates an oxidizing agent. So far, there is no evidence which intermediate serves as an oxidizing agent for the reduced viologen. However, there are some other indirect facts. The reduction of radical monocation of dimeric porphyrin II upon the addition of water (Fig. 3, the insert) suggests the possible occurrence of initial stages of oxidation of water. At the same time, participation of, at least, two different dimeric forms of porphyrin II bound with copolymer in photoactivation of donor–acceptor complex (Fig. 8, curve 2) may produce an intermediate oxidizing agent. Also acidification of the solution of one of aminoporphyrins under illumination with visible light in electrochemical cell, which is accompanied by a decrease in absorption of the broad band with maximum at 736 nm [18], suggest a real possibility of the occurrence of initial stages of oxidation of water in such systems. This fact seems to be a very plausible argument if a dimeric form of porphyrin interacting with carboxyl groups of copolymer serves as a proton interface in the photoreaction.

5. Conclusion

Similar structure of electron transitions of dimeric forms of *meso*-tetra(*p*-aminophenyl)porphine which burn off under steady state illumination and protonated dimeric forms of this porphyrin at 77 K suggests that in the three-component system, photoactivation processes of intermolecular donor–acceptor complex involve two different types of dimeric forms of the porphyrin bound with the copolymer. In this case, only dimers, whose spectral properties are similar to those of singly protonated dimeric forms of the porphyrin bound with the copolymer, are photoactive. Doubly protonated dimers of the porphyrin are likely not to be involved in the photoactivation processes. In the case of analogous low-molecular weight system in the absence of electron donor and acceptor, illumination of the associated *meso*-tetra(*p*-aminophenyl)porphine with the visible light leads to the formation of radical ion products.

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References

[1] H. Ohtani, T. Kobayashi, T. Ohno, S. Kato, T. Tanno, A. Yamada, Nanosecond spectroscopy on the mechanism of the reduction of methylviologen sensitized by metallophthalocyanine, J. Phys. Chem. 88 (1984) 4431.

[2] M.D. Yanuck, R.H. Schmehl, Effect of non-electrolyte polymers on photoinduced electron transfer reactions. Influence of aqueous poly(vinylalcohol) on quenching of tetraanionic porphyrins by methyl viologen, Chem. Phys. Lett. 122 (1985) 133.

[3] J.W. Otvos, T.E. Casti, M. Calvin, Polyelectrolytes as interfaces for retarding backreaction in photoinduced electron transfer reactions, Sci. Papers I.P.C.R. 78 (1984) 129.

[4] N. Carnieri, A. Harriman, Photochemistry of manganese porphyrins V. The photoreduction of methyl viologen, J. Photochem. 15 (1981) 341.

[5] M. Rougee, T. Ebbesen, F. Ghetti, R.V. Bensasson, Kinetics and mechanism of porphyrin-photosensitized reduction of methylviologen, J. Phys. Chem. 86 (1982) 4404.

[6] M.-C. Richoux, A. Harriman, Influence of electrostatic forces upon the efficiency of charge separation for the Zinc porphyrin/methyl viologen system, J. Chem. Soc., Faraday Trans. I 78 (1982) 1873.

[7] J.R. Darwent, P. Douglas, A. Harriman, G. Porter, M.-C. Richoux, Metal phthalocyanines and porphyrins as photosensitizers for reduction of water to hydrogen, Coord. Chem. Rev. 44 (1982) 83.

[8] A.V. Udal'tsov, Characteristics of donor–acceptor complexes formed in porphyrin–polymer systems and their photoactivation in electron transfer photoreaction, J. Photochem. Photobiol. B: Biol. 37 (1997) 31.

[9] A.V. Udal'tsov, V.Z. Paschenko, A.A. Churin, V.B. Tusov, V.S. Pshezhetskii, Donor–acceptor interactions in porphyrin associates immobilized in biplilic copolymer, J. Photochem. Photobiol. B: Biol. 21 (1993) 87.

[10] A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour, L. Korsakoff, A simplified synthesis for *meso*-tetraphenylporphine, J. Org. Chem. 32 (1967) 476.

[11] J.-H. Fuhrhop, K.M. Smith, Laboratory methods, in: K.M. Smith (Ed.), Porphyrins and Metalloporphyrins, Elsevier, Amsterdam, 1975, pp. 757.

[12] V.S. Pshezhetskii, A.V. Udal'tsov, Influence of modified poly(-methacrylic acid) covalently bound to porphyrin on its acid–base properties, Vysokomol. Soedin. Ser. A. (in Russian) 30 (1988) 1470.

[13] A. Gordon, R. Ford, Sputnik Khimika (in Russian), Mir, Moscow 1976, p. 437.

[14] J. Fajer, D.C. Borg, A. Forman, D. Dolphin, R.H. Felton, π-Cation radicals and dications of metalloporphyrins, J. Am. Chem. Soc. 92 (1970) 3451.

[15] A.V. Udal'tsov, A.A. Churin, Photochemical properties of donor–acceptor complexes formed by associated forms of porphyrin, Internet Photochem. Photobiol. (1998), http://www.photobiology.-com./v1/udaltsov/udaltsov.htm.

[16] A.V. Udal'tsov, Absorption and luminescence spectroscopy of restrictively protonated dimeric forms of porphyrins (Moscow), Biochemistry 62 (1997) 1026.

[17] B.D. Berezin, N.S. Enikolonjan, Coordinative properties of porphyrins, in: N.S. Enikolonjan (Ed.), Porphyrins: Structure, Properties, Synthesis (in Russian), Nauka, Moscow 1985, pp. 49.

[18] A.V. Udal'tsov, et al., unpublished results.