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Water–porphyrin interactions and their influence on self assembly of large scale porphyrin aggregates

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Abstract

Properties of protonated *meso*-tetraphenylporphine (TPP) aggregates are investigated by absorption, circular dichroism and infra-red (IR) spectroscopic techniques. The protonated TPP aggregates were tested by scanning electron microscopy (SEM) in thin films prepared on glass plates. The aggregates with size of approximately 1 μm to several micrometers are usually observed in the films. Two maxima at 388 ± 3 nm and 465 ± 3 nm are revealed in circular dichroism spectra of protonated TPP in water–tetrahydrofuran solutions in the presence of 0.4N hydrochloric acid. The maximum at 465 nm coincides exactly with the corresponding maximum in the absorption spectrum. Both maxima in the CD spectra undergo some changes with an increase of porphyrin concentration. According to IR spectra, water is involved in the interaction with porphyrin in the aggregates. All water molecules confined in the aggregates are distributed in two groups: proton-donating and proton-accepting molecules. The bands of stretching vibrations of water and the H–O–H bending vibrations are observed in the spectra as doublets with maxima at 3512, 3457, and 1610 and 1632 cm^{-1}, respectively. A new broad band located in the 2136–2156 cm^{-1} region is revealed in the IR spectra of protonated TPP aggregates. But this broad band is absent in the spectrum of TPP amino-derivative associated in thin film. These peculiarities are due to water–porphyrin interactions in the protonated TPP aggregates, when the whole spatial structure of water is involved in the interactions to delocalize the positive charges in TPP dimers.

Keywords: Aggregates; Associates; Porphyrins; Circular dichroism; Water–porphyrin interactions; Thin films; State of water

1. Introduction

The interaction between water and porphyrinic pigments attracts the attention since water influences the properties or/and structure of dimers or associates of the pigments under their formation [1–3]. This field rather concerns biophysical aspects and relationships between porphyrin pigments, when water can play an important role in charge separation or other steps of photosynthesis [4,5]. On the other hand, suitable artificial systems show the relationships between porphyrin pigments and often mimic successfully some steps of photosynthesis [6,7]. Self-assembly of the pigments or other organic compounds is now-a-days a subject of study carried out by many researchers [8,9]. In this respect, investigation of properties of water in relation to organic solvents or compounds can give us very interesting information [10,11]. The ordered structures of porphyrinic pigments formed due to non-valence interactions, are now extensively studied but characteristics of water often remained unclear. These systems are usually complicated for detailed investigation of water–pigment interactions and meet difficulties in interpretation. In this case, compound modeling properties of the corresponding biological species can be useful. Similar situation takes place in biological photosynthesis. Appearance of charges under the transformation of light quanta at the early step of photosynthesis must lead to the crucial changes in the environment. The effect of charge appearance in the photo-system and its consequences and the corresponding characteristics of the interaction with the environment can be tested only using a model system, such as protonated porphyrin aggregates.

The finding of large scale aggregates of protonated *meso*-tetraphenylporphine (TPP) has been reported recently [12]. Formation of these aggregates in aqueous organic solutions was proposed to be due to involvement of water in the structure of TPP dimers and strong water–porphyrin interactions, so that self assembly of the aggregates can occur from the protonated porphyrin dimers. Unusual absorption and fluorescence properties of protonated TPP dimers were interpreted in terms of the aggregation. At the same time, the protonated TPP aggregates with size of 1 μm to several

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micrometers have been found by using scanning electron microscope (SEM). The main goal of this work is the study of characteristics of water involved in large scale porphyrin aggregates and water–porphyrin interaction, when we can look for the properties of water only confined in the aggregates. Also, it was interesting to compare characteristics of water–porphyrin interactions in protonated TPP aggregates with those of the interaction in associates of the other porphyrin, *meso*-tetra(*p*-aminophenyl)porphine (TAPP). The comparison can be useful for detailed characterization of both porphyrinic systems by vibrational spectroscopy and can help for an assignment of unusual vibrational bands.

In this work, properties of protonated *meso*-tetraphenylporphine in aggregates are studied by absorption, circular dichroism and infra-red (IR) spectroscopies and SEM. The results obtained are considered in comparison with the corresponding properties of associated *meso*-tetra(*p*-aminophenyl)porphine.

2. Experimental details

Synthesis of *meso*-tetraphenylporphine was carried out according to the procedures described elsewhere [13]. Tetrahydrofuran (THF), dimethylformamide (DMF) and other organic solvents were additionally purified by conventional methods [14]. For the preparation of aqueous organic solutions singly or twice distilled water was used.

UV–VIS spectra of porphyrin solutions or films were recorded with a Specord M-40 spectrophotometer. The electronic spectra of TPP solutions were obtained in the case of three ranges of the concentrations, low, medium and high. In the case of the low concentration, it was within $(0.5–2.0)\times10^{-5}$ mol l^{-1}, in the case of medium, the concentration was within $(4.0–8.0)\times10^{-5}$ mol l^{-1}, and in the case of high, it was greater than $(1.4–2.0)\times10^{-4}$ mol l^{-1}. Circular dichroism spectra of porphyrin solutions were recorded with a spectropolarimeter Jasco J-500C. IR spectra of thin films of porphyrins were obtained with a Specord M-80 spectrophotometer. Preparation of the films of associated TAPP has been described earlier in [15]. While thin films of TPP aggregates on CaF_2 plates for IR spectroscopy or on thin glass plates for electron microscopy were prepared under evaporation of the corresponding water–organic solution of TPP with a warm flux of air. At this point, the green color of the porphyrin aggregates remained unchanged.

The procedure of preparation of the TPP thin films for electron microscopy was the same as earlier [12], but the main features of this procedure are presented here again. Usually, two to three layers of the aggregates were quite sufficient for their preservation under vacuum. The manner of the powdering of a sample, i.e. the time of the powdering and the value of the current, was selected so that the thickness of the metal layer would be about 150 Å. Pictures of porphyrin aggregates were obtained with a Hitachi S-520 scanning electron microscope. All measurements were carried out at 298 K.

3. Results

3.1. Aggregation of protonated TPP forms in aqueous organic solutions and properties of the aggregates in thin films

Aggregation of protonated TPP in aqueous organic solutions has been observed recently [12], but aggregates of the porphyrin were not found earlier until quite large concentrations of porphyrin were used for the experiments. In the case of a low concentration of porphyrin the corresponding solutions were found quite stable. The absorption spectra of similar solutions are presented in Fig. 1. These spectra exhibit three Soret bands at 403, 437 and 465 nm, and one broad band at 694 nm formed by the red bands of the corresponding dimeric forms of porphyrin. These red bands of the dimers are strongly overlapped providing the interaction between the different dimers. The 437 nm band is larger as compared with the other bands in the case of low concentrations of porphyrin so that this band indicates a large concentration of di-protonated porphyrin dimer in the solutions. At the same time, broad band at 365 nm indicating the protonated state of porphyrinic macrocycle is also present in the spectra, since only protonated porphyrin forms can exist in the solutions with prevailing concentration of water [16].

An increase of porphyrin concentration usually leads to the decrease of the 437 nm band and increase of the 694, 403 and 365 nm bands (Fig. 1, curve 2). In this case, the decrease of the 437 nm band is the evidence for aggregation of porphyrin as found earlier [12]. At large concentration of porphyrin in aqueous organic solution, the 437 nm band is strongly decreased and seen in the spectrum rather as a shoulder (Fig. 2, curve 1). This concentration of porphyrin is quite sufficient for the appearance of a slight and fluffy green precipitate of protonated TPP aggregates, next day, after the preparation of the solution. The precipitate is completely dissolved after mixing of the solution but the strong opalescence indicates the presence of the aggregates. To obtain solution with higher concentration of porphyrin that is necessary for IR spectroscopy and SEM, the solution over the precipitate was carefully removed. Typical absorption spectrum of the removed solution is shown in the same figure (curve 3). This solution has some opalescence that also indicates apparently the presence of porphyrin aggregates but the solution remains stable for a long time. After removing of the solution over the precipitate and mixing of the rest, the final concentration of porphyrin usually was higher than $(1.4–2.0)\times10^{-4}$ mol l^{-1} (curve 2). Similar solutions were in use for preparation of thin films by evaporation of the solvent.

IR spectra of thin films prepared by evaporation of TPP in water–THF (93:7, v/v) in the presence of hydrochloric acid are displayed in Fig. 3. The procedure of the preparation

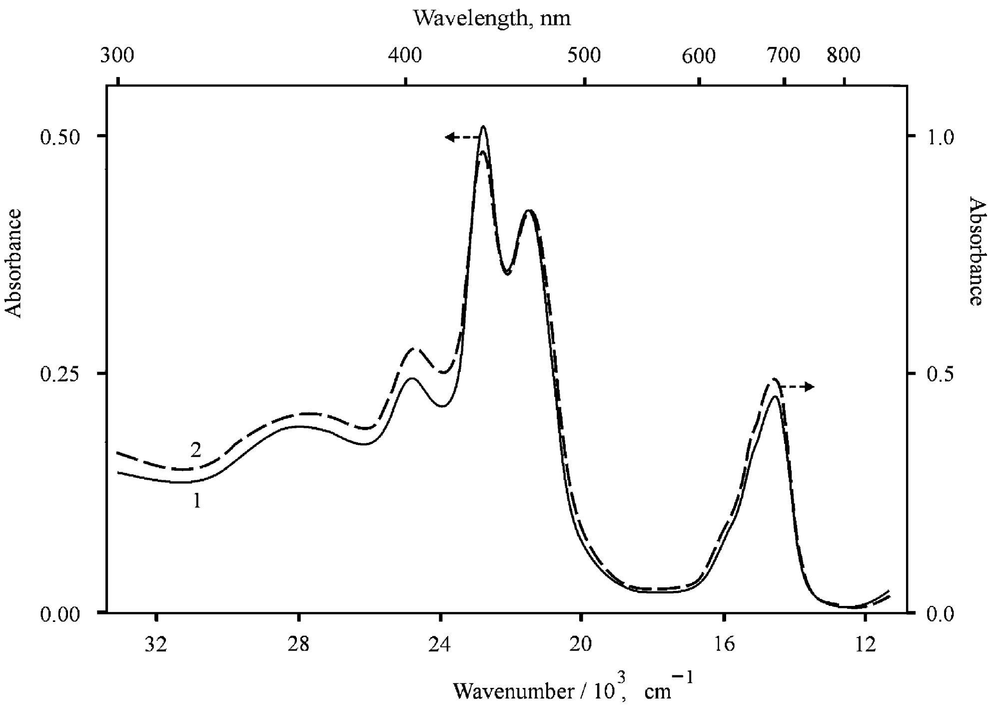


Fig. 1. Absorption spectra of TPP at a low concentration of porphyrin in the presence of 0.4N hydrochloric acid in water–tetrahydrofuran (THF) solution (97:3, v/v), curve 1; and approximately at two-fold concentration of porphyrin in similar solution (94:6, v/v), curve 2.

was standard as for the thin film, the spectrum of which is presented in this figure (curve 1), as well as for the films tested by electron microscopy. In contrast, the drying of the other thin film (curve 2) was interrupted immediately after water had disappeared from the surface of the film. Thus, this film contains some excess of bound water since the drying was not carried out to the completion. The difference between the films is clearly seen in the corresponding

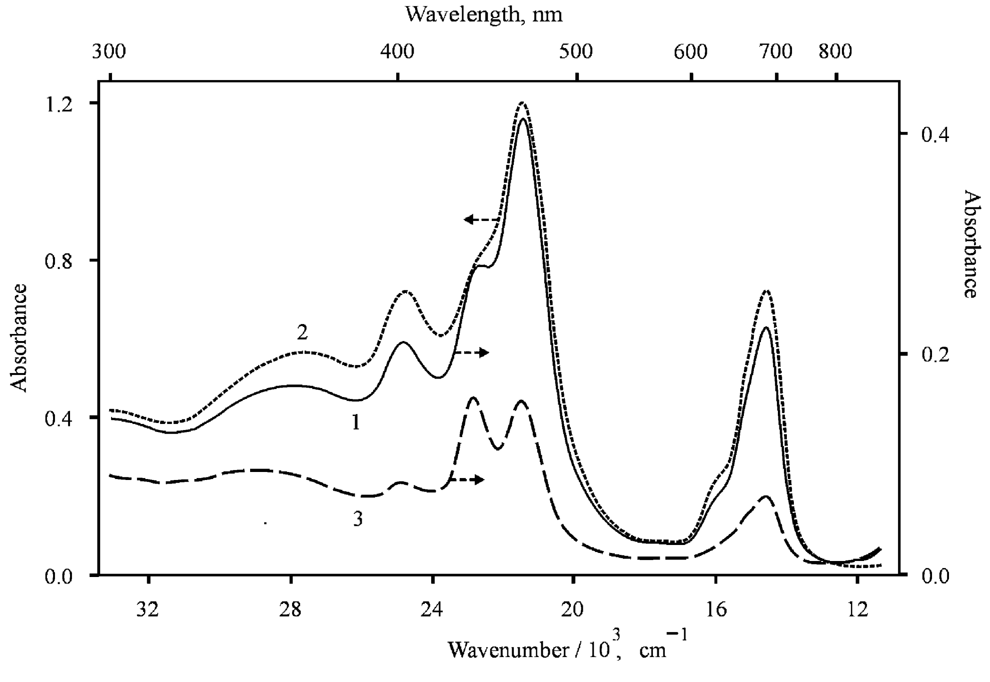


Fig. 2. Absorption spectra of TPP in water–THF solution (93:7, v/v) in the presence of 0.4N hydrochloric acid at medium concentration, curve 1; high concentration, curve 2; and low concentration of porphyrin, curve 3. The spectra were recorded next day after preparation of the solution; samples of porphyrin aggregates (curves 1 and 2) were mixed before the measurements.

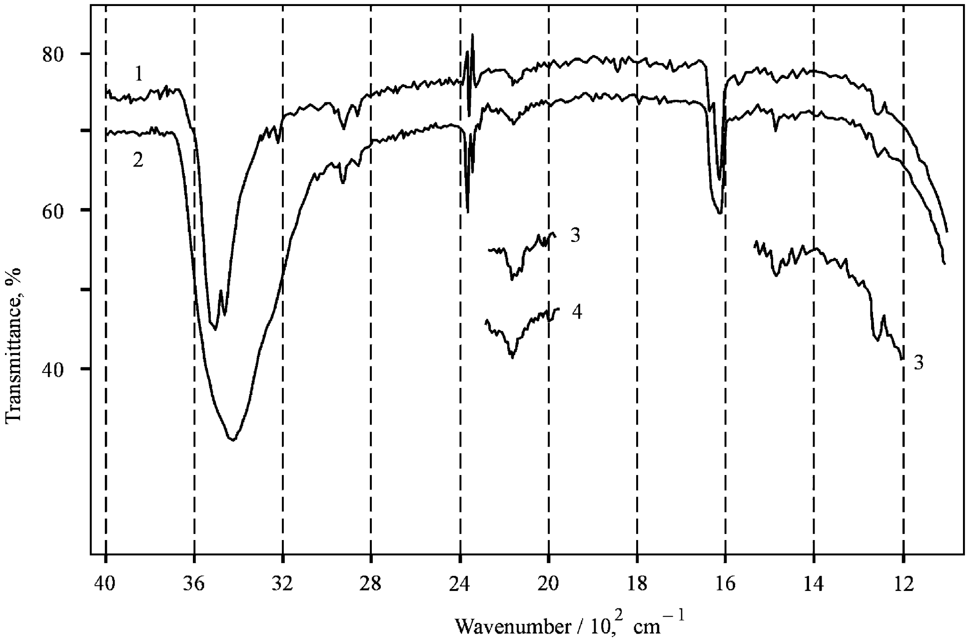


Fig. 3. IR spectra of protonated TPP aggregates in thin films prepared on CaF_2 plates by evaporation of solvent; after standard procedure, curve 1; and the procedure interrupted just after disappearance of solvent from the surface, curve 2. The spectra (curves 3 and 4) corresponding to curves (1 and 2) were recorded in 0–50% transmittance range. The experimental conditions are the same as indicated in the caption of Fig. 2, curve 2.

IR spectra. The strong and broad band of stretching vibrations of water bound in the film (curve 2) are located at 3424 cm^{-1}, while splitting of a similar band is observed in the spectrum (curve 1). In the region of the H–O–H bending vibrations, a doublet at 1612 and 1632 cm^{-1} is found in the spectrum (curve 1) but not the splitting corresponding band at 1612 cm^{-1} in the other spectrum (curve 2). In the former, the bands of stretching vibrations forming a doublet has the mirror reflection relative to the bands of the H–O–H bending vibrations, so that the larger band and the band of some less intensity are located at 3508 and 3460 cm^{-1}, respectively. Both films had green color as they were taken for measurements. According to weak bands of C–H vibrations in the 2850–2960 cm^{-1} region and the 1440 and 1483 cm^{-1} bands of porphyrin (the latter is responsible for C=N vibrations of the macrocycle), the concentration of porphyrin in the films is very low. Unusual 2156 and 2164 cm^{-1} bands are also observed in both spectra (curves 1 and 2), respectively. The thickness of the film after the standard procedure of drying (curve 1) was found to be 5.0 ± 0.4 μm for the two-layer film or 7.0 ± 0.4 μm for the three-layer film (see Fig. 10), while the thickness of similar three-layer film but not completely dried was 8.4 ± 0.5 μm.

Estimation of thickness of thin films allows to calculate some characteristics of water confined in the films. Extinction coefficient for bound water in the region of stretching vibrations (the larger component of the doublet at approximately 3500 cm^{-1}) is found to be seven times lower ($\varepsilon^{3492} = 8.9\,\mathrm{mol}^{-1}\,\mathrm{l}\,\mathrm{cm}^{-1}$ for the 5 μm thin film and $\varepsilon^{3508} = 8.2\,\mathrm{mol}^{-1}\,\mathrm{l}\,\mathrm{cm}^{-1}$ for the 7 μm thin film) as compared with that of water in liquid state ($\varepsilon^{3490} = 62.7\,\mathrm{mol}^{-1}\,\mathrm{l}\,\mathrm{cm}^{-1}$ [17]). On an average, $\varepsilon^{3500} = 8.5 \pm 0.5\ \mathrm{mol}^{-1}\,\mathrm{l}\,\mathrm{cm}^{-1}$ for the stretching vibrations of bound water in thin films after the standard procedure of the preparation. Similar extinction coefficient is found for the 3424 cm^{-1} band in the case of not completely dried thin film. It should be noted that the extinction coefficient of stretching vibrations of water in triethylamine [18] has been found similar to that of water in liquid state, $\varepsilon^{3380} = 75 \pm 4\,\mathrm{mol}^{-1}\,\mathrm{l}\,\mathrm{cm}^{-1}$ for water in TEA. The corresponding IR spectra of water–TEA system had some peculiarities, one of them was a 1690 cm^{-1} band. This band was apparently associated with proton-donating water molecules since water undergoes alkaline ionization in the presence of aliphatic amines. The latter provides appearance of many proton-donating water molecules in water–TEA mixtures. The quantitative estimations allow to calculate concentrations of water and porphyrin in thin films and as a consequence water/porphyrin ratio. The water/porphyrin ratio of 630 ± 40 is found for 5 and 7 μm thin films, while the ratio equals 760±50 for not completely dried thin film with a thickness of 8.4 μm. This means that in the former case, each porphyrin dimer has a water coat containing approximately 1200 water molecules. It is quite possible that the actual number of bound water molecules is somewhat less since water can enter in the composition of solvate film localized between porphyrin aggregates on the glass plate. Although in the case of control films, i.e. similar film but without porphyrin aggregates, the IR spectrum has completely different characteristics that suggests the other behavior of water.

Bars of irregular and regular shape with size of 1 μm to several micrometers are usually found by SEM of porphyrin aggregates in thin films prepared on glass plate (see Fig. 4).

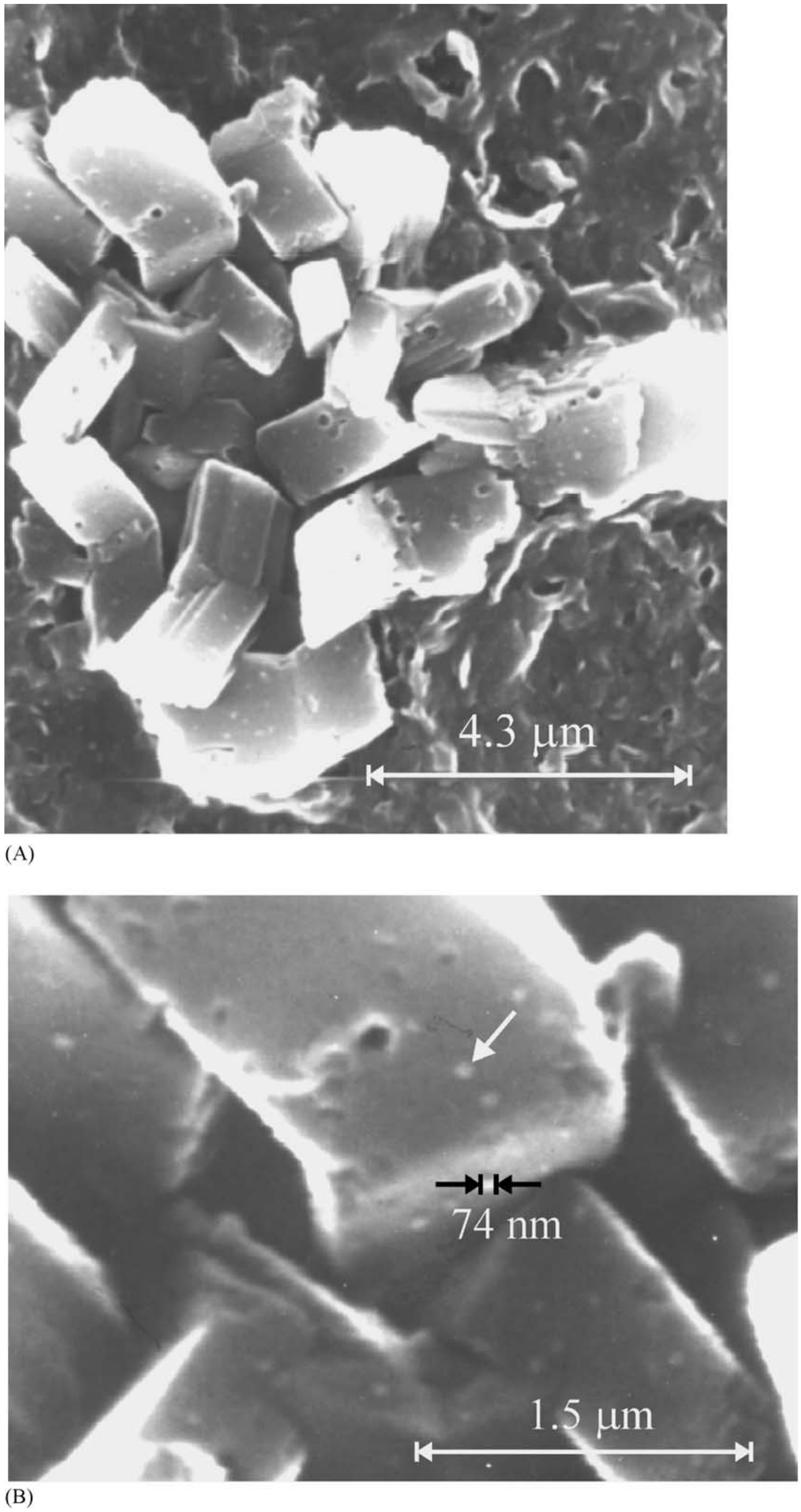


Fig. 4. Microphotographs of TPP aggregates (panels A, B, C, D) obtained on a glass plate after evaporation of water–THF solution (93:7, v/v) in the presence of 0.4N hydrochloric acid.

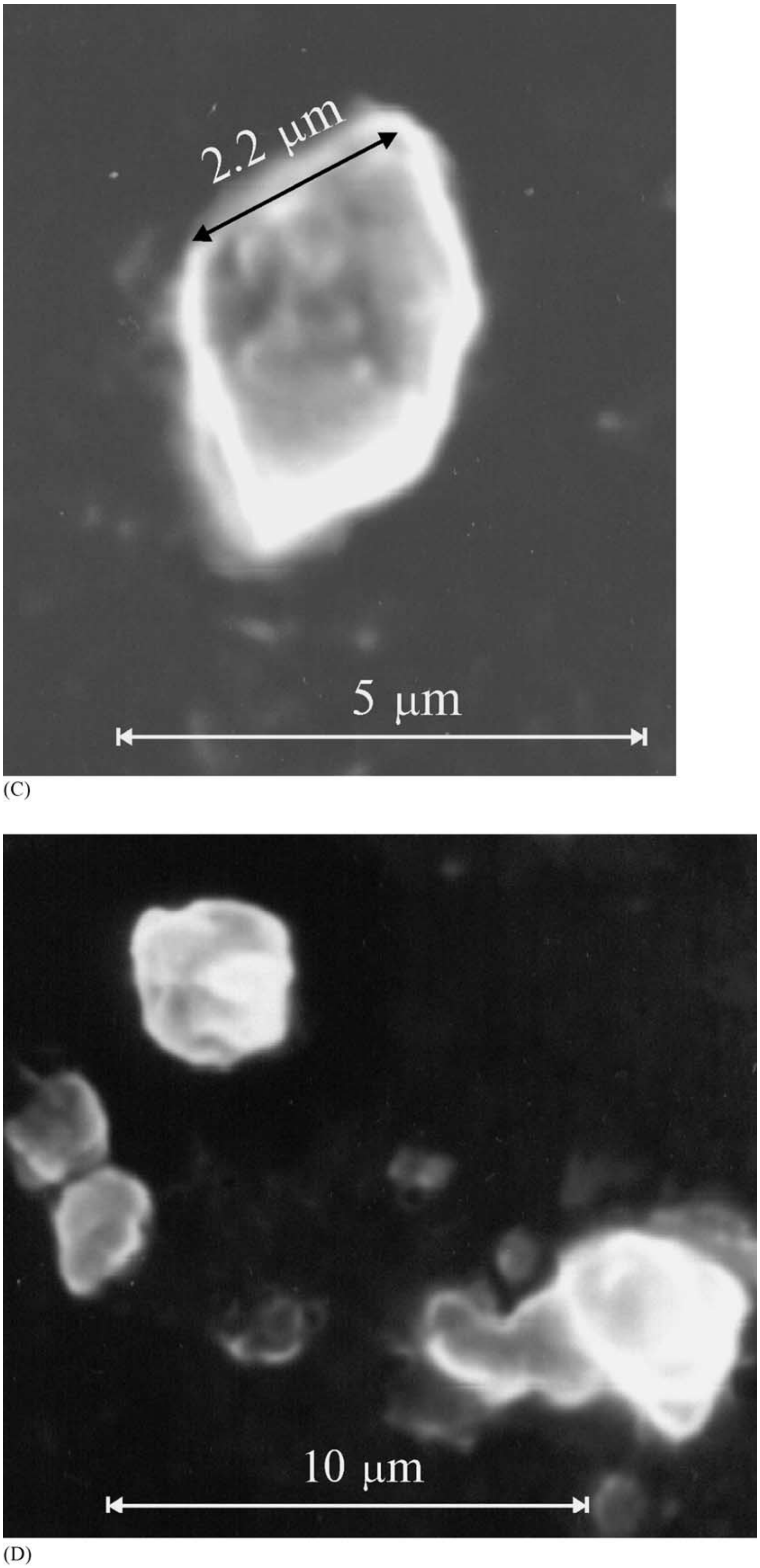


Fig. 4. (*Continued*).

The bars shown in panel A have a quite smooth surface and sharp edges. We can see a heap of the bricks of the same size in the panel. This is a rare case when the bars alike bricks are formed in a result of the falling of a very large block into pieces under the affect of warm flow of the air at the late step of drying of the film. Other large scale porphyrin aggregates presented in this figure are three-dimensional objects which often have a relief on their surface and some thickness (panels C and D). Although we cannot estimate the thickness from a microphotograph but other sizes of the aggregates estimated, are in good agreement with the average thickness of 5 μm obtained for the two-layer thin film. The microphotograph (panel A) also shows that the large scale porphyrin aggregates have on their surface dark and light small spots. The dark spots are the holes in the aggregates, but the light spots are most probably the small porphyrin aggregates, which are present in the solution over the precipitate (see absorption spectrum in Fig. 2, curve 3). We have mentioned earlier that a small volume of the solution was kept for dissolving of the precipitate. Therefore, these small aggregates giving some opalescence can be also found simultaneously with the large scale porphyrin aggregates. The small aggregates with a size of approximately 60–80 nm are displayed in panel B, where one of them is marked by light arrow. No aggregates are observed by SEM in the absence of porphyrin in similar solutions.

Absorption spectra of porphyrin aggregates in thin films exhibit the same main bands as those of the corresponding solutions, although the bands are broadened in the spectrum of the film, Fig. 5 (curve 1). This effect leads to the covering of the small 403 nm band by the broadened strong 467 nm band in the spectrum. The same location of the bands in the spectra indicate that the protonated state of porphyrin in thin films is kept nevertheless, removing of free water from the film.

Hence, the aforementioned results show that the formation of large scale porphyrin aggregates with size of 1 μm to several micrometers, i.e. self-assembly from protonated TPP forms, takes place in aqueous organic solutions. The aggregates mainly consist of two mono-protonated dimers (λ_{max} = 403 and 465 nm) differing from each other by their configurations [12]. The process of the self-assembly is accompanied by the formation of small aggregates with a size of approximately 60–80 nm, where apparently excess of the positive charges on the surface (see the corresponding spectrum in Fig. 2, curve 3) prevents the progress of self-assembly process. This is apparently the cause of their small size. Water–porphyrin interactions in large scale porphyrin aggregates in thin films demonstrate unique peculiarity which, however, depends on the amount of water bound in thin film.

3.2. Properties of TPP aggregates and water–porphyrin interactions in the aggregates in comparison with the interactions in TAPP associates

Properties of TPP aggregates in different aqueous organic solutions will be considered later in comparison with those

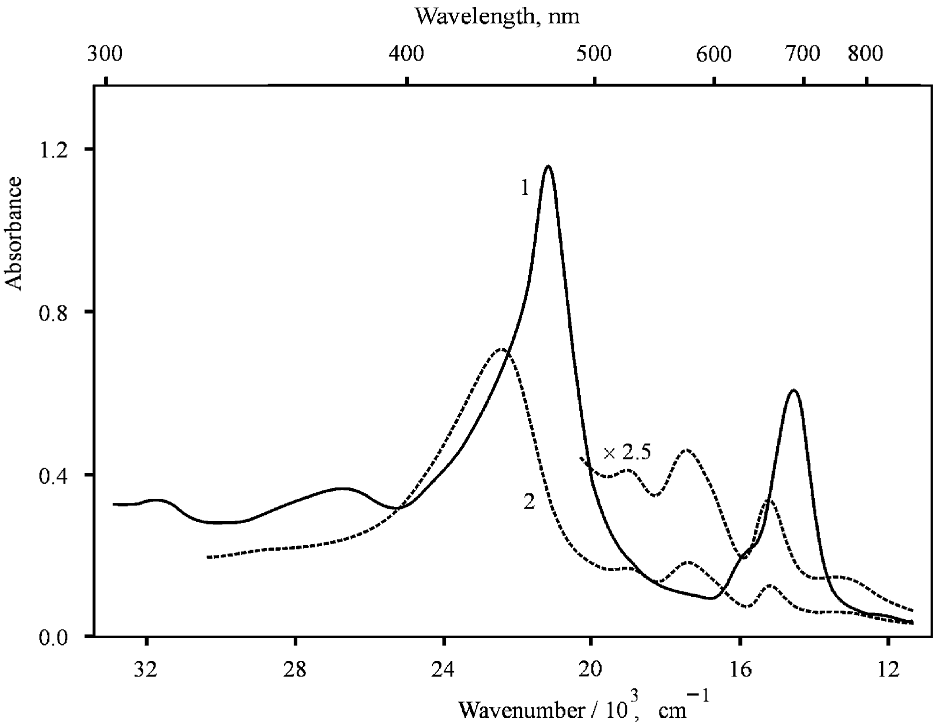


Fig. 5. Absorption spectra of protonated TPP aggregates, curve 1; and associated TAPP, curve 2; in thin films. The experimental conditions for (1) are the same as indicated in the caption of Fig. 2, curve 2. The thin film (2) was prepared by evaporation of TAPP solution in DMF containing water traces.

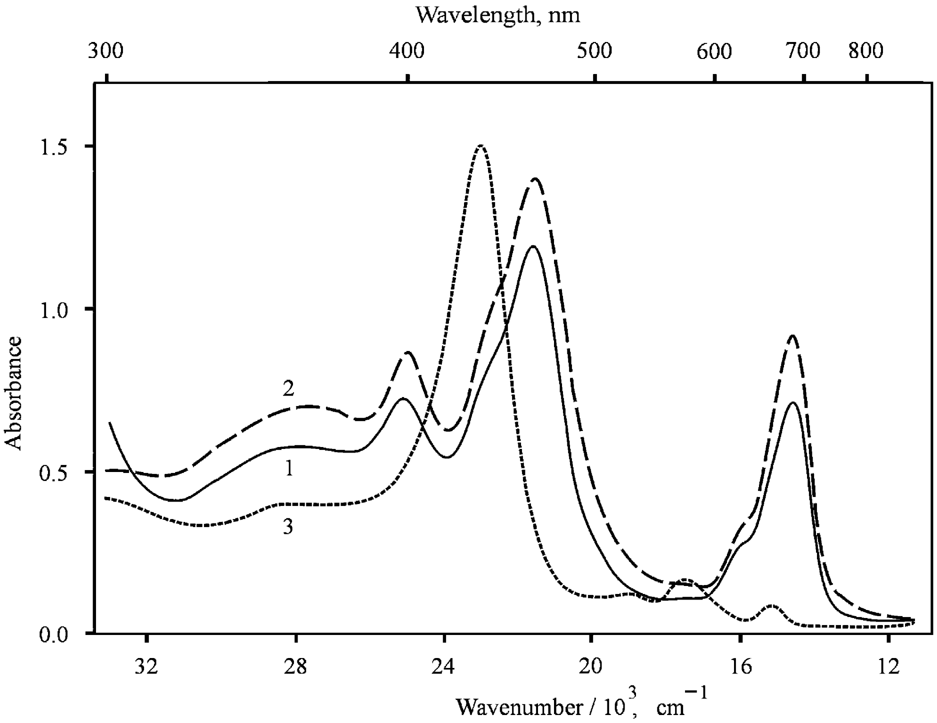


Fig. 6. Absorption spectra of TPP at a high concentration of porphyrin in the presence of 0.4N hydrochloric acid in water–acetone solution (93:7, v/v), curve 1; and in water–dioxane solution (93:7, v/v), curve 2; and TAPP in DMF containing water traces, curve 3.

of associated *meso*-tetra(*p*-aminophenyl)porphine with the aim to find resemblance and difference in the interaction of water with the porphyrins. Absorption spectra of the TPP aggregates in water–acetone and water–dioxane solutions (Fig. 6, curves 1 and 2) exhibit strong and medium bands at 465, 694 and 403 nm (±2 nm), while the spectrum of TAPP (curve 3) exhibits one strong Soret band at 435 nm. The broad band at approximately 365 nm in the spectra (curves 1 and 2) indicates protonated state of TPP in the aggregates. Very minute particles of porphyrin aggregates can be seen by eye in the first two solutions at a high concentration of porphyrin. The aminoporphyrin is not protonated and presents in associated state [19]. The solution of the porphyrin is homogeneous as compared with those of protonated TPP at high or medium concentration. The structure of quasi-allowed electron transitions of TAPP is considerably changed as compared with that of neutral TPP in monomeric state. The changes of the structure are due to donor–acceptor interactions in the associates of aminoporphyrin.

Aggregated and associated states of the porphyrins were tested by circular dichroism spectroscopy. The CD spectrum of protonated TPP forms at a low concentration of porphyrin exhibits two maxima (Fig. 7, curve 1), one of them at 465 ± 3 nm coincides with the corresponding maximum in the absorption spectrum (see Fig. 1, curve 1). But the other maximum in the CD spectrum is located at 388 ± 3 nm, i.e. between the 365 and 403 nm bands of the corresponding absorption spectrum. The 388 nm band in the CD spectrum is increased and broadened after an increase of porphyrin concentration although the position of the corresponding maximum is not changed (Fig. 7, curve 2). At the same time, the 465 nm band is red shifted by 5 nm after the increase of porphyrin concentration and somewhat masked or decreased in the CD spectrum as compared with that in the spectrum (curve 1). The changes observed in the spectrum (curve 2) can be associated with the further aggregation of porphyrin at larger concentration or with a photoreaction between different dimers in porphyrin aggregates as the fluorescence and EPR spectra evidenced [18]. A final state of this tendency of the changes is observed in the CD spectrum of TAPP associated in DMF (curve 3), where only the large band with the maximum at 395 ± 3 nm is found. We can see from the absorption spectra (Fig. 1) that aggregation of protonated TPP forms is accompanied by relative decrease of the concentration of di-protonated dimer ($\lambda_{max} = 437$ nm) and increase of that of high energy mono-protonated TPP dimer ($\lambda_{max} = 403$ nm) in the solution. Therefore, in this case the increase of the 388 nm band in the CD spectrum (Fig. 7, curve 2) is responsible for the increase of relative concentration of the high energy mono-protonated TPP dimer. From this point of view, the quite a large band at 395 nm in the CD spectrum of associated TAPP suggests that the configuration of at least two neighboring molecules in the associate is similar to the configuration of the high energy mono-protonated TPP dimer.

Porphyrin aggregates prepared in water–acetone and water–dioxane solutions can be also seen by SEM (Fig. 8). We were looking at the separate aggregates to examine their

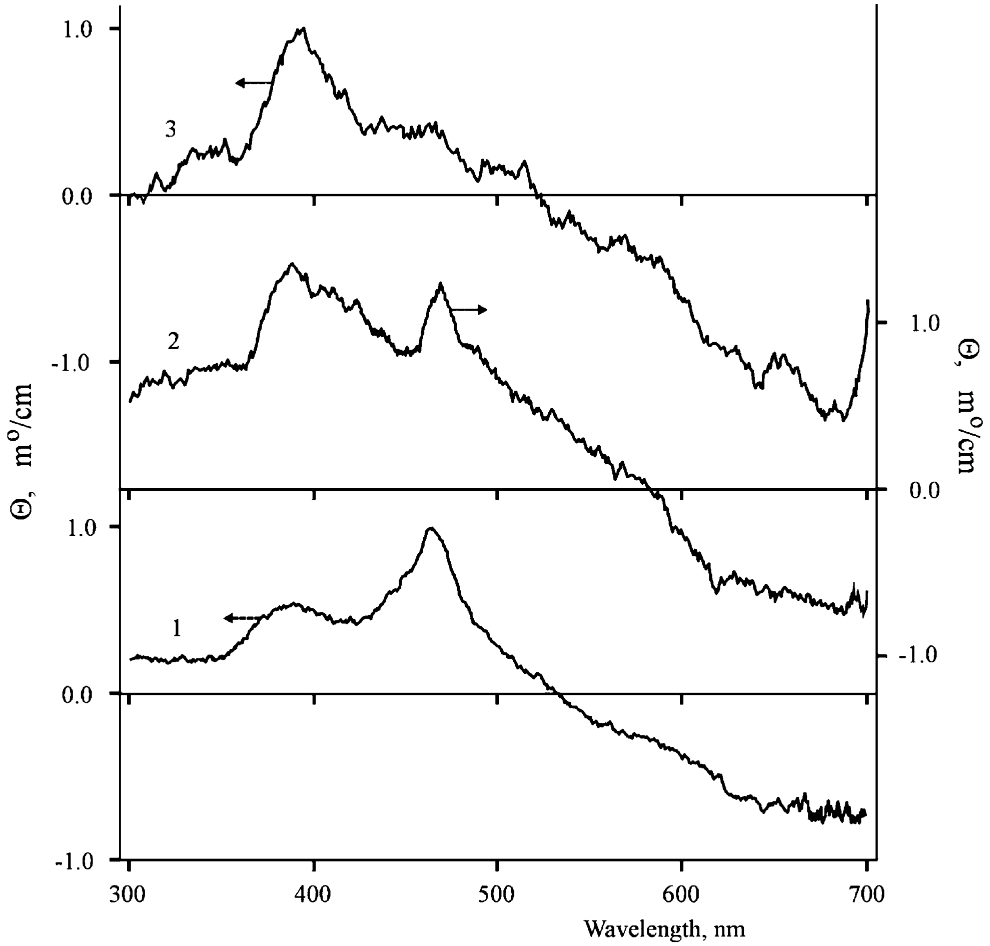
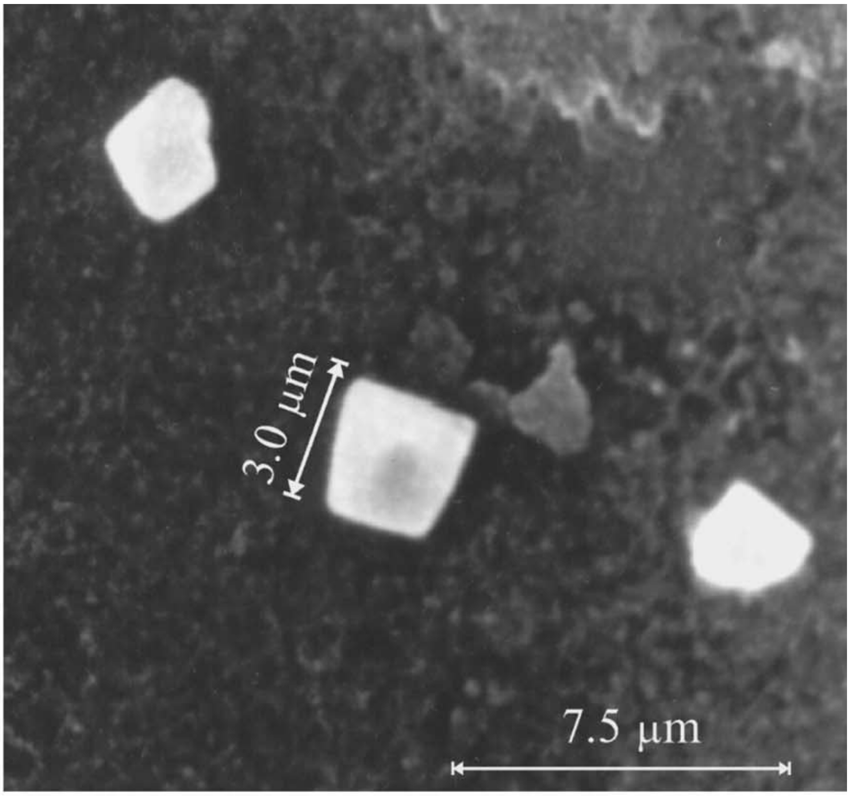


Fig. 7. Circular dichroism spectra of TPP at a low concentration, curve 1; and at two-fold concentration of porphyrin, curve 2 (the experimental conditions are the same as indicated in the caption of Fig. 1); and TAPP in DMF containing water traces, curve 3.

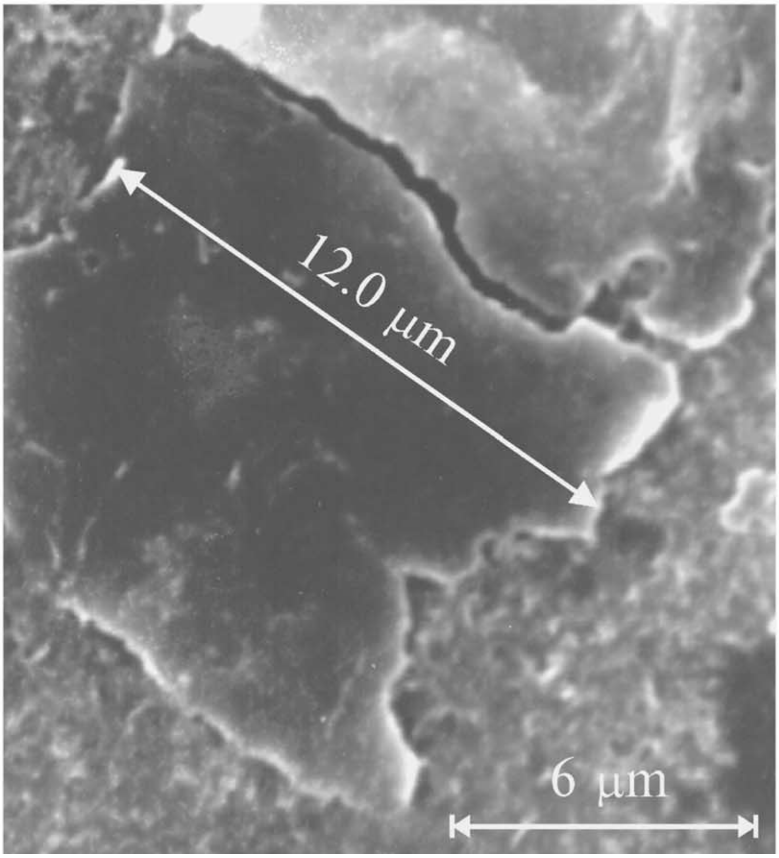
sizes and surface, since the interpretation of a picture of very large aggregates often meets difficulties for the present time. The bars of regular or irregular shape with sizes of 1 μm to several micrometers or approximately 10 μm (panel B) are displayed in the microphotographs. The larger aggregates are formed, when the procedure of mixing of the solution just before thin film preparation was not accomplished. In this case, very large porphyrin aggregates of green color were visible even by naked eye while the mixing leads to the destruction of similar large blocks. This fact suggests that the aggregates with size of 1 μm to several micrometers are smaller objects, which have been preserved under the mixing. When an aggregate of about 10 μm is deposited on the small surface of the glass plate, in this case, the aggregate can be destroyed and fallen into pieces. This situation mentioned is a rare case (see Fig. 4, panel A and the text).

It was interesting to compare IR spectra of protonated TPP forms in the large scale aggregates and associated TAPP in thin films. The corresponding electronic spectra of the thin films are displayed in Fig. 5. The spectrum of the former is mentioned in earlier sections, while features of TAPP in thin films (curve 2) have been described in detail earlier [15]. Here we only note that the donor–acceptor interactions in TAPP associates lead to the appearance of a broad absorption in the 650–900 nm region of the spectrum. This peculiarity was accompanied by some changes in the corresponding IR spectra. The IR spectrum of protonated TPP aggregates exhibits strong bands of water and very weak bands belonging to porphyrin (Fig. 9, curve 1). The 1484 cm^{-1} band is the most intense among the TPP bands and is high frequency shifted by 11 cm^{-1} as compared with the usual position of the band at 1473 cm^{-1} [20]. It is important to note that the frequency of stretching vibrations ($\nu_{\mathrm{N-H}}$) in pyrole rings of protonated TPP aggregates and in associated TAPP coincides exactly, $\nu_{\mathrm{N-H}} = 3220\,\mathrm{cm}^{-1}$ for both porphyrins. This suggests similar donor–acceptor interaction between porphyrin and water involved in the solvate cover of both porphyrins. Thus, the main characteristics of the spectra of TAPP and protonated TPP in thin films are different, while the characteristics responsible for water–porphyrin interactions are similar.

Standard procedure of preparation of thin films containing porphyrin aggregates implies complete removing of free water when only strongly bound water is preserved in the



(A)



(B)

Fig. 8. Microphotographs of TPP aggregates obtained on a glass plate after evaporation of solutions in the presence of 0.4N hydrochloric acid: water–acetone solution (93:7, v/v), panels A and B; and of water–dioxane solution (93:7, v/v), panel C.

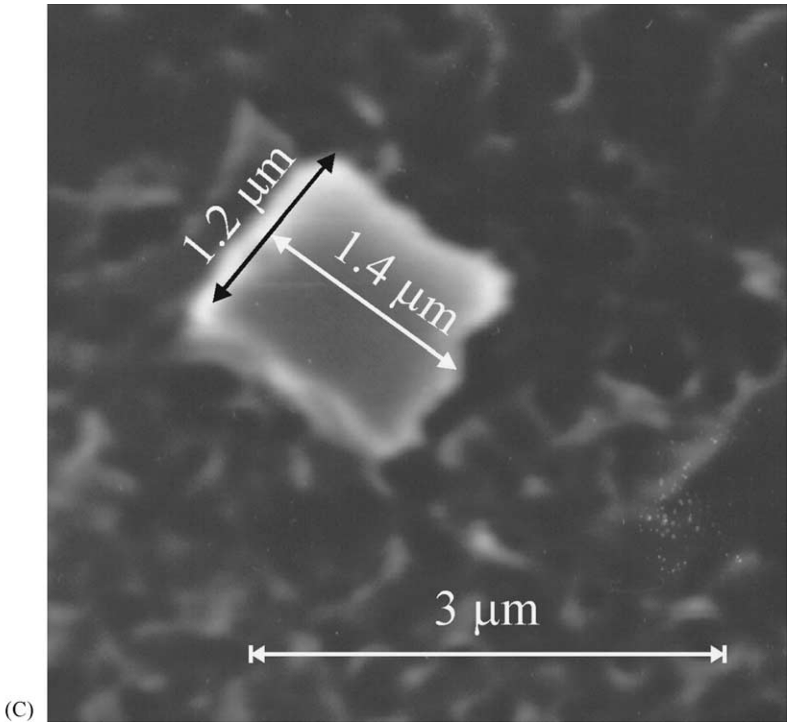


Fig. 8. (*Continued*).

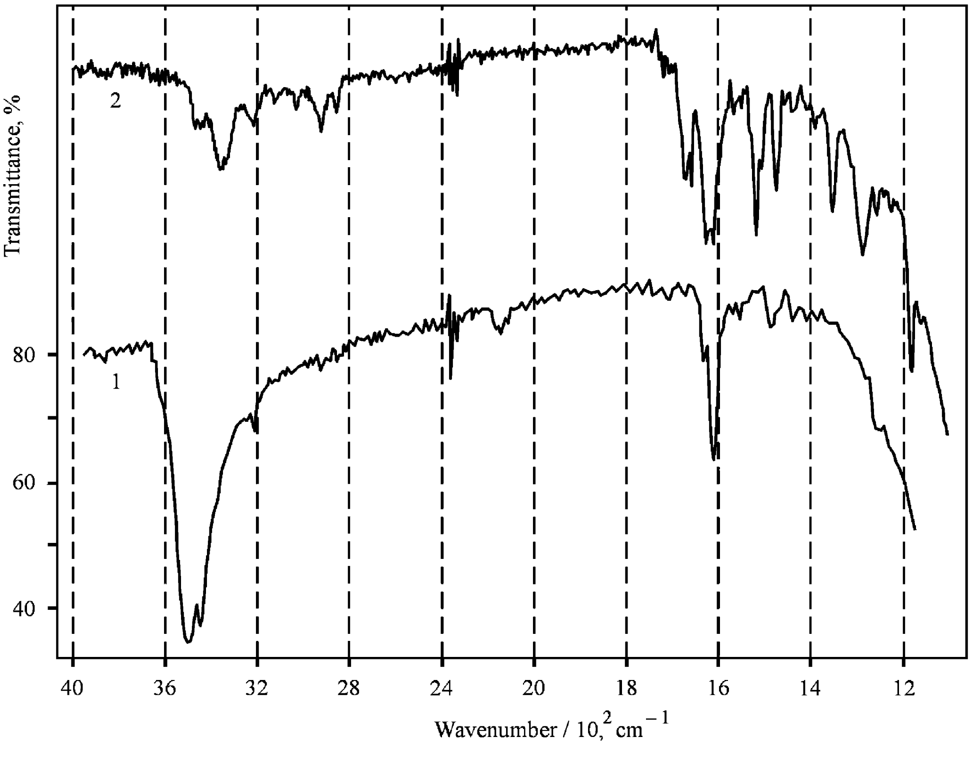


Fig. 9. IR spectra of TPP aggregates obtained on a CaF_2 plate after evaporation of water–acetone solution (93:7, v/v) in the presence of 0.4N hydrochloric acid, curve 1; and TAPP associated in thin film prepared on a CaF_2 plate by evaporation of DMF containing water traces, curve 2.

films. The doublet of the H–O–H bending vibrations (the strong 1610 cm^{-1}, and weak 1632 cm^{-1} bands, Fig. 3, curve 1 and Fig. 9, curve 1) indicate that all water molecules are bound inside the porphyrin aggregates, and a major part of the bound water is involved as the proton-acceptor because the frequency is close to the 1607 cm^{-1} whose position indicates proton-accepting water molecules [21]. In this case, the weak 1632 cm^{-1} band is rather responsible for the vibrations of proton-donating water molecules involved in the associates, since the band occupies the middle position between usual frequency of H–O–H bending vibrations (1645 ± 5 cm^{-1}) and the frequency of well-pronounced proton-donating water molecules (1618 cm^{-1}).

Hence, water–porphyrin interaction has donor–acceptor character in the large scale porphyrin aggregates, where the interactions are directed to weaken the charges located in the protonated porphyrins in the system. The deviation of the frequency for proton-accepting water molecules in this system is 2–3 cm^{-1}, while the deviation for proton-donating water molecules in the aggregates equals 14 cm^{-1}. These results show that all bound water is involved in the interactions.

The splitting observed for water bands in the IR spectra of porphyrin aggregates in thin films, allows to assign the components of the doublet of stretching vibrations. Respectively, to the H–O–H bending vibrations, strong 3512 cm^{-1} band of stretching vibrations of O–H groups is associated with proton-accepting water molecules, while the 3457 cm^{-1} band with somewhat less intensity in the magnitude is responsible for the vibrations of proton-donating water molecules involved in the system. This IR spectrum of thin film (Fig. 9, curve 1), where water is actually activated as a result of the donor–acceptor interaction with protonated TPP in the aggregates, exhibits a broad 2136 cm^{-1} band. The same characteristics of water confined in protonated TPP aggregates are observed in the IR spectra of other thin films (Fig. 10). These spectra of the films prepared by evaporation of water–tetrahydrofuran and water–dioxane solutions, exhibit similar splitting of the H–O–H bending and stretching vibrations and also broad 2156 and 2152 cm^{-1} bands, respectively. The former IR spectrum (curve 1) is very similar to the spectra presented in the previous figures (see Fig. 3, curve 1 and Fig. 9, curve 1). But the latter (Fig. 10, curve 2) exhibits some new bands. One of them is located at 1740 cm^{-1}, which has probably appeared due to enhancing donor–acceptor interaction between water and porphyrin in the presence of dioxane. This solvent has a low value of dielectric constant and perhaps is concentrated in the film because of its higher boiling point of 101 °C as compared with that of water. A similar band with stronger intensity has been observed in the IR spectra under the formation of charge-transfer complex in thin films of aminoporphyrins [15,22]. The 1740 cm^{-1} band is absent in the previous spectra of protonated TPP aggregates since other organic solvents (acetone and tetrahydrofuran) are almost completely evaporated from the corresponding thin films.

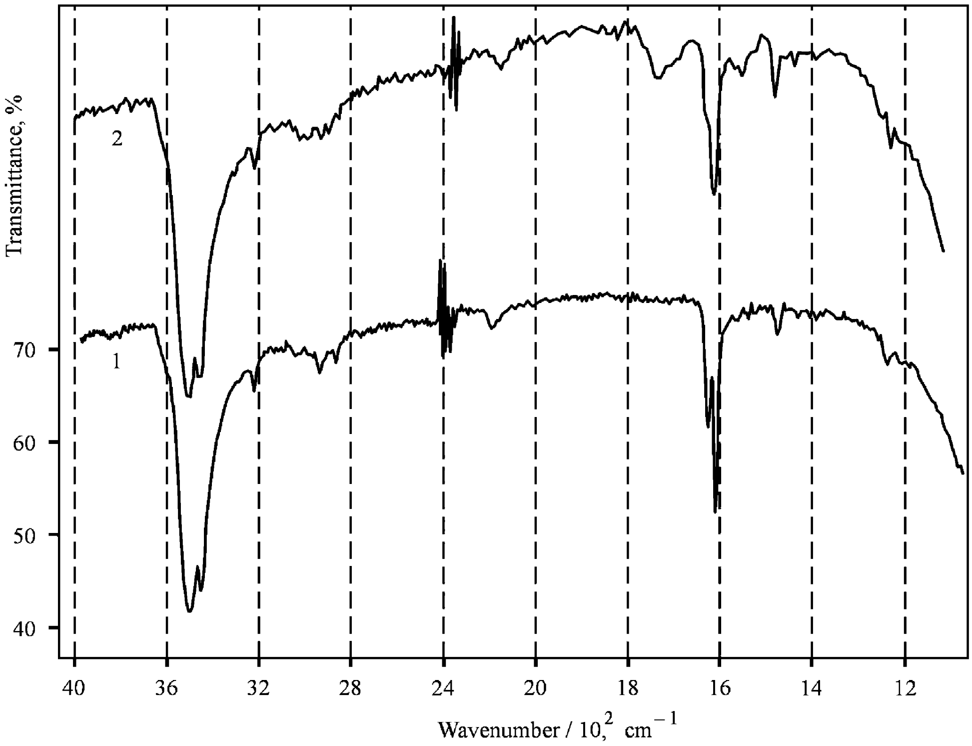


Fig. 10. IR spectra of TPP aggregates in three-layer thin films obtained on a CaF_2 plate after evaporation of water–THF solution (93:7, v/v), curve 1; and water–dioxane solution (93:7, v/v), curve 2; in the presence of 0.4N hydrochloric acid.

The other new band in the spectrum (curve 2) is located at 1538 cm^{-1} and apparently associated with porphyrin. In this spectrum, the lower component (1632 cm^{-1}) of the doublet of the H–O–H bending vibrations is seen as a shoulder.

Hence, the aforementioned results show that the increase of the 403 nm band responsible for the high energy mono-protonated TPP dimer is accompanied by the increase of the 388 nm band in the CD spectrum. In this case, the broad 365 nm band in electronic spectra associated with the protonated state of porphyrin is also increased nevertheless, the 437 nm band corresponding to di-protonated porphyrin dimer is decreased. Analogously, a quite large band at 395 nm in CD spectrum of TAPP associated in DMF is apparently due to similar configuration taking place in the associate, when the interaction between nitrogen-containing groups of neighboring aminoporphyrins occurs via water molecules. IR spectra of large scale porphyrin aggregates in thin films demonstrate that all water molecules bound in the films are distributed in two groups with proton-accepting and proton-donating characteristics. This fact implies that the relaxation of protons of water molecules occurs in the system with positive charges on porphyrins, so that the whole water–porphyrin system is involved in the donor–acceptor interactions. This behavior strongly differs from that in TAPP associates in thin films, where the donor–acceptor interactions are localized within the associates of the aminoporphyrin although water is also involved in the interactions.

4. Discussion

The study of large scale porphyrin aggregates by circular dichroism and IR spectroscopies demonstrates unusual properties. It is found using circular dichroism that the increase of TPP concentration is accompanied by increase of the ultraviolet band with the maximum at 388 nm due to further aggregation of protonated TPP forms or a photoreaction. This band is located between broad band at approximately 350 nm indicating protonated state of porphyrin and the band at 403 nm observed in the electronic spectra. The latter is the Soret band of mono-protonated TPP dimer, where one of the porphyrin macrocycles containing a bound proton is most probably present in the configuration of *cis*-NH-tautomer [12], so that the dimer is stabilized via hydrogen bonds of the bound water molecules (Fig. 11). This way, the stabilization of the mono-protonated TPP dimers allows observation of both dimers with *cis*- and *trans*-NH-tautomers in the absorption spectra with $\lambda_{max} = 403$ and 465 nm, respectively. Hence, the energy gap between the levels of the dimers is 0.4 eV. Similar value of energy gap between *cis*- and *trans*-NH-tautomers (0.35–0.4 eV) has been found theoretically earlier for porphyrin monomer [23]. But in the case of porphyrin monomer only the *trans*-NH-tautomer can be observed in absorption spectra since the electronic structure of *cis*-NH-tautomer is very unstable, while low energy monomer with *trans* configuration can be stabilized due to favorable interactions in solution. It should be noted that two water molecules localized between the planes of porphyrin macrocycles in the dimer (Fig. 11) are involved in donor–acceptor interaction with the macrocycles. It is interesting that the configuration of one of the bound water molecules in the porphyrin dimer corresponds to the state of water in the structure of ice. This configuration of the bound water molecule suggests that one proton of the molecule can be easily shifted to a porphyrin as compared with water in the dimeric complex with *trans*-NH-tautomer. As a result, the proton-transfer from the bound water molecule is utilized by the porphyrin dimer (with *cis*-NH-tautomer) for the stabilization of its structure in the excited state. This behavior takes place under selective excitation into the 403 nm band as found earlier and similar interpretation has been proposed for explanation of fluorescence spectroscopy results [18].

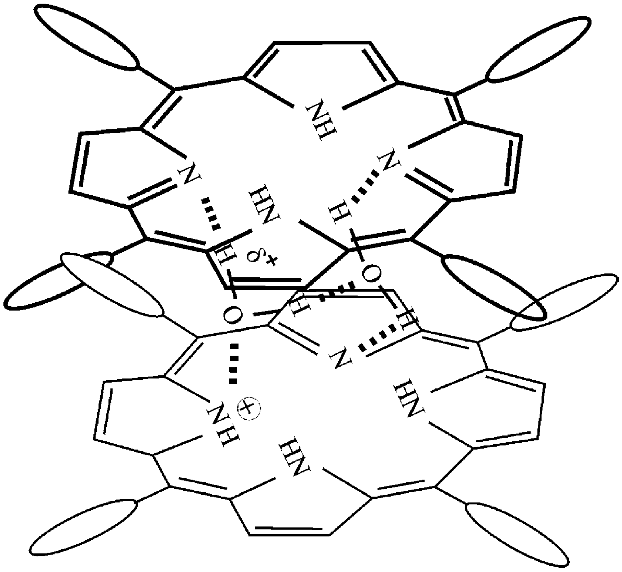


Fig. 11. The proposed structure of water–porphyrin dimeric complex containing *cis*-NH-tautomer.

The maximum of the band at 388 nm in CD spectrum coincides neither with the maximum of protonated state (at 350 nm), nor with the maximum of the Soret band of mono-protonated TPP dimer (at 403 nm) observed in the absorption spectra. We propose that this phenomenon is due to structural difference of the state of water in water–porphyrin dimeric complexes. From this point of view, the optical activity of mono-protonated TPP dimers (with Soret bands at 403 and 465 nm) is rather associated with water molecules possessing unusual configuration, in which other distribution of local charges in the water molecules changes the properties of its local environment. Some interesting facts are found by IR spectroscopy of large scale aggregates of protonated TPP in thin films. The first is that all water bound in the films are distributed in two large groups, proton-accepting and proton-donating molecules. This result suggests that the system of tetrahedral network of hydrogen bonds of water has proved very flexible, so that relaxation of protons in the whole system is directed to delocalize the positive charges presented in porphyrin dimers. This peculiarity makes the porphyrin aggregates quite stable but water molecules in the aggregates are actually proved to be in some activated state. In this case, the activation of water means the changes of its properties so that the involvement of water in electron and/or proton transfer reactions is promoted. On the other hand, the bound water confined in large scale porphyrin aggregates undergoes transformation into the solid state after complete removal of free solvent under the film preparation. This is supported by the fact that the extinction coefficients estimated for stretching vibrations of water bound in the films, are found very low as compared with the coefficient for the same vibrations of liquid state of water. It means that the large scale TPP aggregates possess quasi-crystal structure, where each porphyrin dimer has a water coat containing about 1200 molecules.

The second interesting fact is that the frequency of the stretching vibrations of N–H bonds of pyrole rings observed in the IR spectra, coincides for both protonated TPP in the aggregates and associated TAPP in thin films. The position of the corresponding peak in both cases is situated at 3220 cm^{-1}, that is low frequency shifted by 95 cm^{-1} relative to the frequency for solid TPP in KBr. This fact indicates that the interaction between water and porphyrin macrocycle of TAPP is similar to the interactions in protonated TPP dimers. Keeping this in the mind proposed structure for TPP dimer containing *cis*- and *trans*-tautomers, the following event may be possible. The positive charges on the nitrogen atom in pyrrolle rings coordinate the water molecules in which relaxation of protons of the network of hydrogen bonds concerns the whole cooperative structure of water. In the case of TAPP, there is the 1286 cm^{-1} band in the IR spectrum (Fig. 9, curve 2) indicating the presence of radical cation [24] and this band has been observed in the spectra as the thin films as well as solid TAPP in KBr [15]. It should be noted that similar band situated at approximately 1260 cm^{-1} is observed in the IR spectra of protonated TPP in thin films. But this band is small like other bands of porphyrin of the sample (2868 and 2936 cm^{-1} bands of C–H bonds and 1484 cm^{-1}). Generation of radical cation in associated TAPP is most probably due to the interaction with dioxygen and subsequent electron transfer reaction [15]. Hence, in the case of TAPP similar relaxation of protons of water molecules but in local solvate cover have to occur because of generation of the radical cation.

And the third interesting fact is that the unusual broad and small band with a maximum in 2136–2156 cm^{-1} region for various thin films being under investigation is observed in the IR spectra of large scale aggregates of protonated TPP. Although this broad band is also small like porphyrin bands but the band is associated with water vibrations. The first evidence is that the very broad band in this region is observed in similar film but without porphyrin. And the second is the following. When the band of stretching vibrations of water at 3424 cm^{-1} is broader in the spectrum (Fig. 3, curve 2) as compared with a similar band in the spectrum (curve 1), the corresponding 2156 cm^{-1} band is also broadened in the spectrum (curve 2). The broadening can be seen better when the spectra are recorded applying 0–50% transmittance range (curves 4 and 3, respectively). This broad band is usually assigned to combination vibrations of water (translation + the H–O–H bending vibration) or overtone 2α [25].

Hence, when water is organized by donor–acceptor interactions into the ordered structures like large scale porphyrin aggregates, quite appreciable band in the 2136–2156 cm^{-1} region is appeared in the corresponding IR spectra. No doubt, this peculiarity is due to unique state and structure of water in the aggregates where water has a continues microphase. In contrast, water present in thin film of associated TAPP simultaneously with the organic solvent (DMF) according to 1653 and 1670 cm^{-1} bands, respectively (Fig. 9, curve 2). Therefore, in this case, water is involved in the corresponding solvate cover but not form any continues microphase. Detailed analysis of the TAPP spectra meets difficulties because of the presence of the bands in the spectra responsible for the amino groups. Nevertheless, involvement of proton-donating water molecules (the peak at 1618 cm^{-1} in the IR spectra) in the interaction with the aminoporphyrins in similar films has been shown earlier [15].

5. Conclusion

The results presented show further evidence for self-assembly of large scale TPP aggregates due to water–porphyrin interactions in the aggregates. The self-assembly of the aggregates is apparently quite a fast process since simultaneously with the formation of the large scale porphyrin aggregates more minute porphyrin aggregates are also formed. However, the growth of these small aggregates is apparently prevented by the excess of positive charges on their surface. There is no doubt that the donor–acceptor interactions in mono-protonated TPP dimers in combination with cooperative properties of water are the organizing force of the self-assembly process. In this respect, the surprising fact is that the behavior of water confined in the porphyrin aggregates, is found specific and directed to delocalize the positive charges situated in TPP dimers. The water–porphyrin interactions in protonated TPP aggregates and associates of TAPP are found to be similar nevertheless, strong influence of lateral amino groups on the characteristics of IR of TAPP takes place.

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