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Paper
Статья

Protonation of *meso*−Tetraphenylporphyrin and Its β−Functionalized Derivatives by Photogenerators of Acidity in Toluene and Polymer Film

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The interaction of free-bases and Zn(II) complexes of meso-tetraphenylporphyrin, and its β-functionalized derivatives with photogenerators of acidity (PGAs, hexachloroethane or tribromoethanol) has been studied in toluene and also embedded in polymer films. The free-bases undergo fast reversible protonation during the irradiation procedure. The photoprotonation of free-bases by PGAs is accompanied by the fluorescence decay of each porphyrin substrate. The relative rates of such photoprotonation of free-base porphyrins depend to a certain extent on the porphyrin structure. The similar protonation and the fluorescence decay of the meso-tetraphenylporphyrin derivatives in the presence of PGAs also take place in a polymer film. The related Zn(II) complexes undergo photolysis under the conditions used with the fluorescence decay as well. The protonation and sharp fluorescence decay of meso-tetraphenylporphyrin derivatives during their irradiation can find application in photosensory technologies, information optical recording and antibacterial phototherapy.

Keywords: Tetraphenylporphyrin derivatives, photogenerators of acidity, protonation, fluorescence decay.

Протонирование *мезо*−тетрафенилпорфирина и его β−производных фотогенераторами кислотности в толуоле и в полимерной пленке

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Изучено взаимодействие мезо-тетрафенилпорфирина, его β-функционализированных производных и их Zn(II)-комплексов с фотогенераторами кислот (ФГК, гексахлорэтан или трибромэтанол) в толуоле и в полимерных пленках. Свободные основания подвергаются при этом быстрому и обратимому протонированию. Относи-

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тельные скорости фотопротонирования в определенной степени зависят от структуры порфирина. Фото-протонирование порфиринов сопровождается исчезновением их флуоресценции. Аналогичные протонирование и исчезновение флуоресценции производных мезо-тетрафенилпорфирина в присутствии ФГК происходят и в полимерной пленке. Zn(II)-Комплексы указанных порфиринов в названных условиях подвергаются фотолизу. Протонирование с потерей флуоресценции производных мезо-тетрафенилпорфирина при их облучении может найти применение в фотосенсорных технологиях, системах оптической записи информации и антибактериальной фотодинамической терапии.

Ключевые слова: Производные тетрафенилпорфирина, фотогенераторы кислот, протонирование, затухание флуоресценции.

Introduction

Porphyrins and related macrocycles play not only significant roles in vital biological processes (*e.g.*, respiration, photosynthesis, electron transportation and others), but also are being recognized as important partners in a wide range of applications.[1,2] The natural macrocycles and their synthetic analogues demonstrate photophysical and photochemical features for being used as possible components of molecular electronics and photonics devices,[3,4] in photovoltaic solar cells like dye-sensitized solar cells (DSSC)[5–10] and in medicine. The medicinal significance of porphyrin derivatives is due to their optical features (such as the strong light absorption and fluorescence) and so such compounds have been successfully used as photosensitizers in different contexts of photodynamic therapy (PDT) of cancer and also in image-guided theranostic processes.[11–14] It might be possible that new but still unknown potential applications can become available with further studies. Therefore, the behavior of a porphyrin and derivatives in various processes initiated by irradiation, simply in solvent or embedded in polymer films is of great interest.[15–17]

We have previously shown that the irradiation of some organic substrates in the presence of polychloroalkanes is accompanied by the generation of acidity that led to the corresponding acid-catalyzed reactions or to sensory effects.[18] Moreover, photodehydrogenation of aryl(hetaryl) pyrazolines in the presence of carbon tetrachloride or hexachloroethane has been successfully used for optical information recording.[19–21]

Under such context, we decided to evaluate the behavior of porphyrin macrocycles, in the presence of acid photogenerators in toluene or embedded in polymer films. The compounds used were of *meso*-tetraphenylporphyrin **TPP** (**1-H**), its Zn(II)-complex (**1-Zn**) and derivatives **2** and **3**. These derivatives containing respectively a formyl and an aryl(pyrazolinyl) groups as substituents at β-pyrrolic position in each case (Figure 1), could influence the expected protonation procedure. Hexachloroethane (HCE) and tribromoethanol (TBE) have been selected as the PAGs.

It has been earlier reported that the UV light irradiation of **TPP** in chlorinated solvents in the presence of silica leads to the **TPP** protonated form. The process has been explained by the photochemical decomposition of the solvent with the generation of HCl.[22] However, a systematic study of the interaction of *meso*-tetraphenylporphyrin and of its β-functionalized derivatives with photogenerators of acid in toluene and in polymer film, as far as we know, has not been reported before.

Experimental

The free base *meso*-tetraphenylporphyrin (**1-H**),[23–25] their Zn(II) complex (**1-Zn**)[26] and the 2-formyl-*meso*-tetraphenylporphyrin **2**[27] were prepared following well-established protocols reported in literature. The porphyrin-pyrazoline hybrids (**3a-d-H** and **3a-d-Zn**) were prepared by reaction of the free base 2-vinyl-5,10,15,20-tetraphenylporphyrin or its Zn(II) complexes with the appropriate nitrile imine, generated *in situ* from the adequate ethyl hydrazono-α-bromoglyoxylate as previously reported.[28] The structures of all the synthesized derivatives were confirmed by ^{1}H NMR and mass spectrometry techniques. The experimental data are in agreement with the ones described in literature. The other chemicals were supplied by Sigma-Aldrich as HPLC or spectral grade and were used without further purification.

Electronic absorption spectra were recorded on an APELPD_303UV spectrometer and fluorescent spectra – on Cary Eclipse (Varian) spectrofluorimeter. The band of excitation was 420 nm.
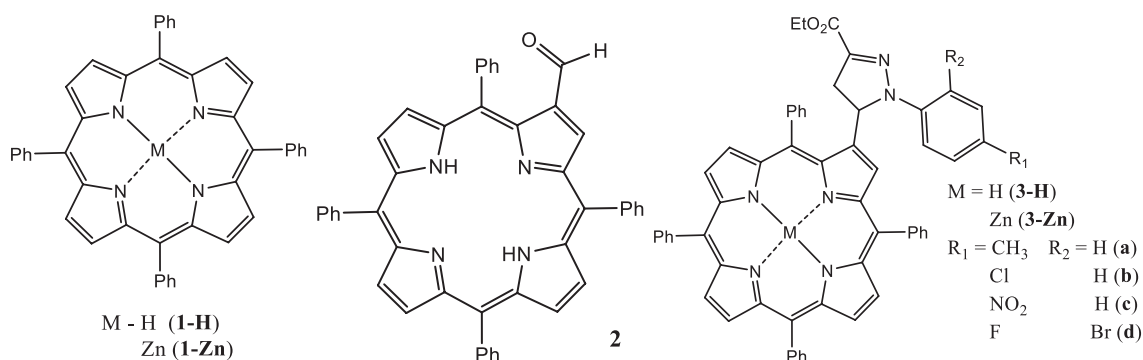

Figure 1. Structures of the studied compounds: *meso*-tetraphenylporphyrin **1-H, 1-Zn** and the β-functionalized derivatives **2** and **3a-d**.

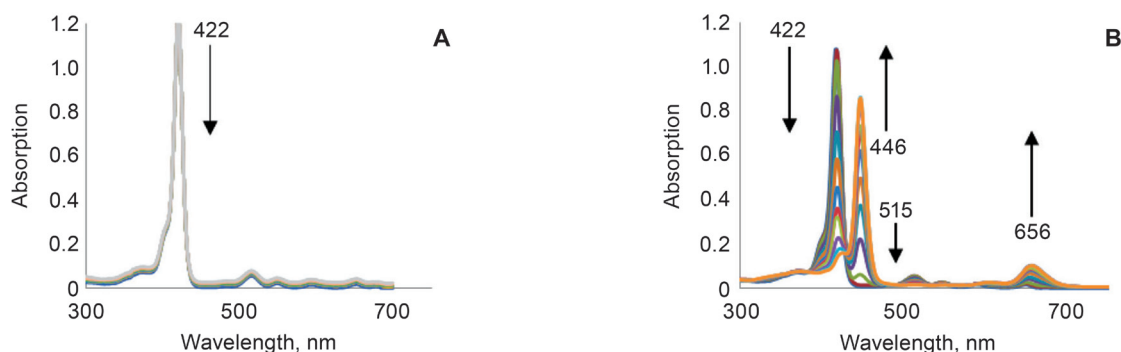**Figure 2. A)** Changes of the absorption spectra of **1-H** during irradiation in toluene; **B)** Changes of the absorption spectra of **1-H** during irradiation in toluene with addition of HCE.

The photo-irradiations were carried out using an L 5283 xenon lamp (HAMAMATZU lamp) through the light filter A-03 to select a light in the region at 240–400 nm. Rate constants of photoprotonation reactions were found by graphics method with use of linear form of the first order reaction. Changes of optical densities of the porphyrin have been used in the region of 0.2–0.8 for the rate constants calculations. The average rate constants given in Table 1 are obtained from four convergent results with accuracy 5 %.

Polymer films were fabricated using the pouring method. A solution containing copolymer methylmethacrylate-ethylacrylate, and porphyrins **1-H** or **1-Zn** as well as hexachloroethane, in a mixture dichloroethane-methylene chloride (1:4) was poured onto a horizontally placed Petri dish, afterwards the solvent was evaporated. The film (thickness around 80–100 μm) was then removed from the dish before undergoing irradiation.

Results

Interaction of meso-Tetraphenylporphyrin **1-H** with PGAs in Toluene

The irradiation of porphyrin **1-H** in the region of 240–400 nm without addition of any PGA does not lead to noticeable changes in the absorption spectra (Figure 2A). However, a slight decrease of the Soret band intensity can be mentioned. At the exposure time equal to 180 s the conversion of the **1-H** turns to be not more than 0.3 % (see Table 1 for more detail).

The addition of hexachloroethane to the solutions of **1-H** in toluene (with concentration equal to $3.9 \cdot 10^{-2}$ M) leads to the fast and definite changes in the absorption spectra of the substrate. The intense Soret band at 422 nm is decreased during the irradiation, while the new band at 446 nm of high intensity and the band at 656 nm of low intensity are proportionally increased (Figure 2B). These changes correspond to the protonation of the porphyrin core. After the exposure time equal to 8 s, the protonation of **1-H** has been found to reach 88 %. Irradiation of the porphyrin **1-H** in the presence of 2,2,2-tribromoethanol in toluene (with concentration equal to $1.8 \cdot 10^{-2}$ M) provides similar spectral changes, but the rate of protonation is higher. After the exposure time equal to 0.5 s, the protonation of **1-H** has been found to reach 84 % (Figure S1).

The photoinduced protonation of **1-H** by both HCE and TBE is a reversible process as the thermal protonation is. Addition of triethylamine at the final step of irradiation recovers the initial absorption spectra of the porphyrin freebase **1-H**. Similar changes in its absorption spectra have been recorded after addition of *p*-toluenesulphonic acid to solutions of porphyrin **1-H** in toluene.

The irradiation of the porphyrin **1-H** in the presence of PGAs leads to the fluorescence decay. For example, irradiation of the **1-H** in toluene in the presence of 2,2,2-tribromoethanol leads to a decrease in the intensity of the fluorescence maximum at 656 nm and low-intensity maximum at 720 nm. Almost complete disappearance of the fluorescent signals has been observed during irradiation for several seconds (Figure 3).

Interaction of Porphyrin **2** with HCE in Toluene

The interaction of the PAGs with the *meso*-tetraphenylporphyrins bearing additional substituent at the β-pyrrolic position were also performed in toluene. The absorption spectra of porphyrin **2** with a β-located formyl group during the irradiation without any additive are shown in Figure 4A. When compared with porphyrin **1-H**, one can see the compound **2** to be much less stable during irradiation reaching a conversion of 60 % after an irradiation time of 300 s.
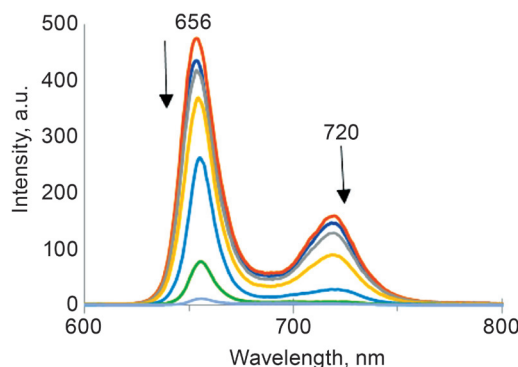

Figure 3. Changes in the fluorescence spectra of **1-H** during irradiation in toluene with the addition of 2,2,2-tribromoethanol.
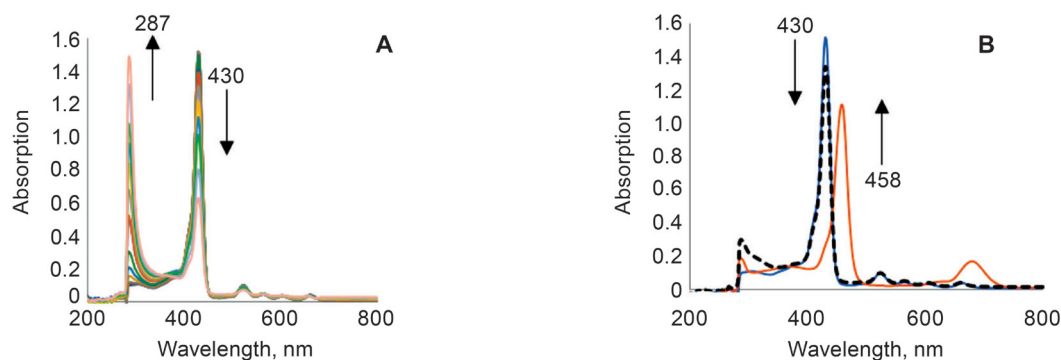
Figure 4. A) Changes in the absorption spectra of porphyrin **2** during irradiation in toluene without any PGA; B) Absorption spectra of the porphyrin **2** during its irradiation in toluene with addition of hexachloroethane for 3 s (dotted line – absorption spectrum after triethylamine addition at the end of irradiation).

Nevertheless, irradiation of the porphyrin **2** in toluene in the presence of hexachloroethane leads to fast protonation (3 s) of the porphyrin derivative. As with **1-H** protonation of **2** by PGA is a reversible process affording after the addition of triethylamine at the final step of irradiation the absorption spectrum of the free-base **2** (Figure 4B, green dotted line).

Interaction of Porphyrins *3a-d-H* with PGAs in Toluene

The insertion of an (aryl)pyrazolinyl fragment at the β-pyrrolic position of the porphyrin core leads to certain changes in the photosensitive behavior of the macrocycle. After the irradiation time equal to 300 s conversion of the **3a-H** at the same time does not exceed 25 % (Figure 5A).

The addition of hexachloroethane to **3a-H** leads to a strong increase of transformation. Irradiation of the **3a-H** in the presence of HCE provides reversible protonation of the porphyrin moiety. Addition of triethylamine at the final step recovers the initial absorption spectrum of the **3a-H** (Figure 5B). Looking at the changes in the absorption spectra, internal NH functions of porphyrin **3a-H** can be suggested as place of protonation. The presence of 2,2,2-tribromoethanol leads to a large increase in the photoprotonation rate of the porphyrin **3-H**. For example, the exposure time up to the same conversion (around 90 %) turned to be equal 0.5 s for the **3a-H**.

The behavior of the other pyrazolinylporphyrins, **3b-H**, **3c-H** and **3d-H** after being irradiated in the presence of PGAs follows the profile discussed for **3a-H** (see Supplementary Data).

Interaction of Porphyrin *1-H* with Photogenerators of Acidity in a Polymer Film

Since many photoinduced transformations of fluorescent substrates turn to have potential in sensing materials applications, we have evaluated possibility of protonation of tetraphenylporphyrin **1-H** by acid photogenerators after being incorporated in a film based in copolymer MMA-EA (methylmetacrylate-ethylacrylate). The changes of the absorption spectra of these porphyrins during their irradiation (for 120 s) in the polymer film containing tribromoethanol are shown in Figure 6A.

As it was observed in the assays performed in toluene, the protonation of porphyrin **1-H** in the presence of PGA
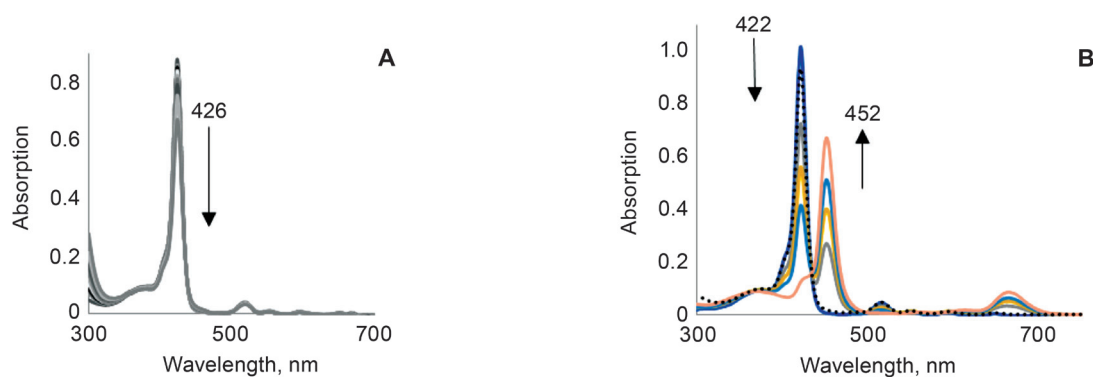

Figure 5. A) Changes in the absorption spectra of **3a-H** in toluene during irradiation; B) Changes in the absorption spectra of the porphyrins **3a-H** during irradiation in toluene in the presence of HCE (dotted line – absorption spectrum after triethylamine addition at the end of irradiation).
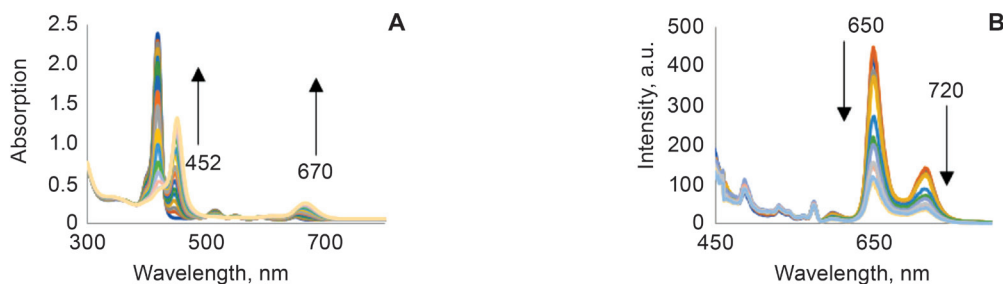
Figure 6. A) Changes in the absorption spectra of the porphyrin **1-H** during irradiation with tribromoethanol in copolymer MMA-EA; B) Emission spectra of **1-H** during irradiation with tribromoethanol in copolymer MMA-EA.

takes also place after being supported of both compounds in the polymer film but obviously with lower rates. The protonation is also accompanied by a significant fluorescence decay as it is patent in Figure 6B.

Transformations of Zn(II) Complexes of meso-Tetraphenylporphyrin and its β-Functionalized Derivatives in the Presence of Photogenerators of Acidity

The behavior of Zn-complexes of the related porphyrins **1–3** during their irradiation in the presence of PGAs turns to be much different. First of all, it should be mentioned that these Zn-complexes are much less stable at the irradiation (Figure 7A). For instance, the **1-Zn** derivative photodegradates by 33 % after 240 s of UV-light irradiation in the absence of any PGAs. No protonation can be seen during irradiation of **1-Zn** in the presence of HCE, since addition of triethylamine after irradiation does not recover spectrum of the starting substrate (Figure 7B). However, effect of PGAs on the photolysis of **1-Zn** is obvious. It undergoes much faster in the presence of HCE (see Table 2 for more detail).

The photolysis of **1-Zn** undergoes even faster in the presence of TBE. β-Functionalization of Zn-complexes increases also the rate of their photolysis. Changes of the absorption spectra of **3a-Zn** in toluene during irradiation without any additive and in the presence of HCE are compared in Figures 8A and 8B, respectively (see also Table 2 for more detail).

Either in toluene solution or when embedded in the polymer film, the fluorescence of Zn(II)-complexes decreased during irradiation in the presence of PGAs. As example, changes of emission spectra during irradiation of **1-Zn** with tribromoethanol in toluene and in polymer film are compared in Figures 9A and 9B, respectively.

Discussion

The studied transformations of *meso*-tetraphenylporphyrin and its derivatives during their irradiation in the presence of hexachloroethane or tribromoethanol lead to the protonation of the porphyrin substrate. As it is well known, porphyrins (P) are amphoteric, presenting acidic and basic properties due to the inner pyrrolic nitrogens. In the presence of a strong base, the inner protons are removed affording the anionic species, while in acidic conditions the nitrogens of imine type are able to accept extra protons affording monocation (MP) and dication (DP) species.[29–31] Monoprotonated porphyrins are known to be a highly unstable cations and in some cases seem to be difficult for detection. Accordingly to Rudine *et al.*,[31] the absorption bands at 448 nm and the 660 nm recorded in this study relate to the DP form of *meso*-tetraphenylporphyrin (Figure 2B).

We have compared the relative rates of protonation of *meso*-tetraphenylporphyrin **1-H** and its derivatives during irradiation in the presence of hexachloroethane. The comparison data are given in the Table 1. Even though, the free bases of porphyrins **1–3** undergo a photolysis in some extent
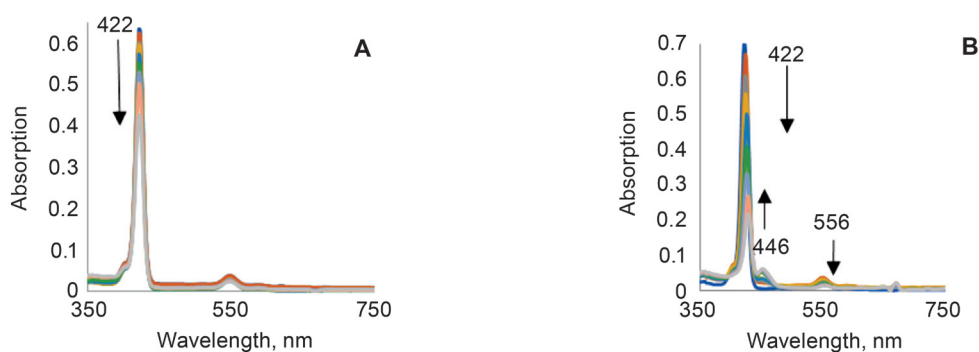

Figure 7. A) Changes in the absorption spectra of the porphyrin **1-Zn** during irradiation; B) Changes in the absorption spectra of the porphyrin **1-Zn** during irradiation in the presence of HCE.
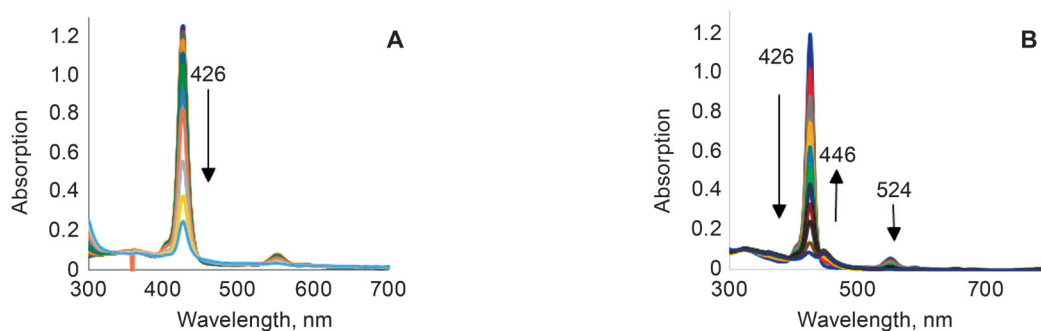
Figure 8. A) Changes of the absorption spectra of **3a-Zn** in toluene during irradiation; B) in the presence of HCE

Table 1. Relative rates of photolysis of the porphyrins **1-3** and their protonation in the presence of hexachloroethane (irradiation by L 5283 xenon lamp at 240-400 nm).

Porphyrin	λ_{max}, nm	ε, mol$^{-1}\cdot$cm^{-1}	k, s^{-1}	
			Without any PGA	With HCE
1-H	420	75700	0.000106	0.303
2	432	69200	0.00021	0.22
3a-H	426	115500	0.000364	0.192
3b-H	428	81200	0.00025	0.552
3c-H	426	120000	0.000333	0.142
3d-H	428	111500	0.000334	0.262

Table 2. Relative rates of photolysis of the Zn-complexes of porphyrins **1-3a-d** and their phototransformation in the presence of hexachloroethane (irradiation by L 5283 xenon lamp at 240-400 nm).

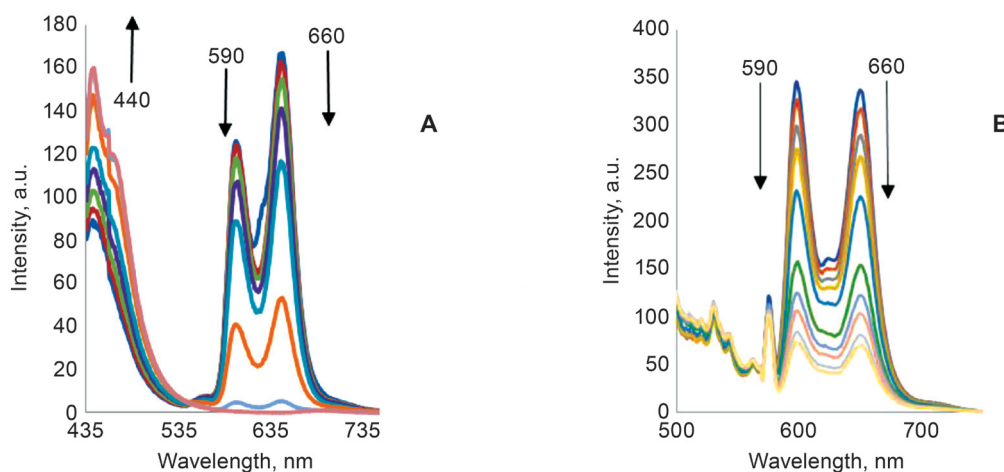| Porphyrin	λ_{max}, nm	ε, mol$^{-1}\cdot$cm^{-1}	k, s^{-1}	
			Without any PGA	With HCE
1-Zn	422	58300	0.00168	0.180
3a-Zn	424	74200	0.00275	0.101
3b-Zn	428	98800	0.00189	0.128
3c-Zn	422	110200	0.00183	0.131
3d-Zn	422	120950	0.00115	0.0709

Figure 9. A) Changes of emission spectra during irradiation of **1-Zn** with tribromoethanol in toluene (exposure time is 0.8 s); B) Changes of emission spectra during irradiation of **1-Zn** with tribromoethanol in copolymer MMA-EA (exposure time is 30 s).

under the used irradiation, their protonation by PGAs takes place much faster than their photolysis. In the case of *meso*-tetraphenylporphyrin **1-H** the rate ratio is up to $2.8 \cdot 10^3$ times. Another important point: the protonation of all the free base porphyrins **1–3** by PGAs is a reversible process. Moreover, the formed protonated forms of porphyrins **1–3** are thermally stable. They are not decomposed when the irradiation is over.

Protonation rates of H-porphyrins **1–3** in the presence of HCE are not systematically depended on the porphyrin structure. All β-functionalized derivatives of *meso*-tetraphenylporphyrin are protonated some slower than **1-H** itself. However, the compound **3b** is protonated even faster when compared with **1-H.**

The fluorescence decay that follows photoprotonation of porphyrins **1–3** by PGAs both in toluene and in polymer film should be also commented, having in mind the earlier reported results. Rudine *et al.* did not report about fluorescence changes during total thermal protonation of the **TPP**[31] Moreover, the red-shift in the emission spectra has been earlier reported. While studying the protonation of *meso*-tetraphenylporphyrin **TPP**, De Luca *et al.* noticed that the fluorescence spectrum of the initial neutral form exhibits a typical two-banded feature which undergoes a definite red-shift after protonation.[29] However, the loss of fluorescence during interaction of porphyrins with PGAs is not much surprising. First of all, the addition of a proton to the imine fragment of porphyrin leads to a violation of the flatness of its molecule. The obvious repulsion of four hydrogen atoms in the DP macrocyclic core leads to substantial tilting of the pyrrole rings, in such a way that the pairs of two opposite nitrogen atoms turn to be located at opposite sides of the macrocycle plane. Moreover, it has been earlier shown that the DP molecules can associate with counter ions (*e.g.*, halide ions) or neutral nucleophiles (*e.g.*, water). The fluorescence quenching in the DP·2A⁻˙ complexes with halides was proposed recently to be useful for the design of porphyrin molecular sensors for halides.[30]

As one can see, Zn(II) complexes of *meso*-tetraphenylporphyrin, and those of β-functionalized derivatives turned to be much less stable under the irradiation conditions selected and undergo the photolysis instead of protonation (Table 2). Moreover, in the presence of PGAs their photolysis undergoes certainly faster: for the **1-Zn** the ratio of rate constants is more than 100.

As in the case of metal-free porphyrins, photolysis of Zn(II) complexes in the presence of PGAs undergoes also with a sharp fluorescence decrease both in toluene and in polymer film.

Conclusions

meso-Tetraphenylporphyrin and its derivatives that contain a *beta*-formyl or aryl(pyrazolinyl) group as substituent undergo fast protonation when they are irradiated in the presence of photogenerators of acidity (hexachloroethane or tribromoethanol). The photoprotonation is reversible and undergoes much faster than photolysis as a sub-side transformation. In opposite to thermal process, photoprotonation by PGAs leads to fluorescence decay of the porphyrin substrate. Photoprotonation of tetraphenylporphyrin and its derivatives by PGAs that followed by the fluorescence decay undergoes also in the polymer film. The total fluorescence decay of the porphyrins **1–3a-d** during their irradiation in the presence of PGAs in polymer films can find application in photosensory technologies. It can also be useful in the design of novel media for optical information recording, since one of the trends there is the use of substrates that possess sharp fluorescence change under irradiation.[32,33] In addition, results of this study are of interest for biochemical applications, since protonated forms of porphyrins are widely studied in antibacterial photodynamic therapy.[34–36]

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