

PHOTODESTRUCTION OF ZINC COMPLEXES OF TETRABENZOPORPHYRINS IN A POLYMERIC MATRIX AND PHOTSENSITIVE MATERIALS BASED ON THEM

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At room temperature, a high-efficiency photochromogenic reaction of destruction of Zn-tetra(4-tert-butylbenzo)porphin molecules in a polyvinylbutyral matrix has been revealed. The linear dependence of the photobleaching rate of porphyrin on the irradiation power density is indicative of a single-photon character of the reaction. The influence of pyridine and ethyl iodide additives as well as of intermolecular oxygen on the photodissociation rate of pigment molecules has been investigated. The most probable mechanism of transformation of the porphyrin compound is its photodestruction involving free radicals. We suggest using the composition as a photosensitive material, and we have determined its photosensitivity experimentally ($S = 0.4 \cdot 10^3 \text{ cm}^2/\text{J}$).

Keywords: metal complex of porphyrin, polymeric matrix, photodestruction, free radical, photosensitive material, optical data recording.

Introduction. One of the key problems of optical data recording is the problem of choosing photosensitive materials with definite characteristics. Many modern methods of optical data recording (based on frequency-selective spectral hole burning [1, 2], holographic data recording [3], compact-disc recording, etc.) use recording materials with an organic dye as the main component of the photosensitive composition. In this connection, the search for ways of increasing the efficiency of phototransformations of particular dyes as well as for new high-efficiency photochemical reactions with their participation is important in solving the above-mentioned problems.

Of the variety of porphyrin-like molecules, free bases have been considered until recently to be the most attractive for the purposes of optical data recording. This is due to the presence, for the metal-free porphyrins, of effective photo-induced intramolecular NH-restructuring [4] leading to marked spectral changes in the arising NH-isomers, which is promising for their use in various methods of data recording [2]. As to the metalloporphyrins, the use of metallophthalocyanines and metallonaphthalocyanines in the photosensitive layer of a recording material sensitive to heating by IR irradiation is known [5]. Photochemical reactions involving metalloporphyrins were revealed in polymeric matrices containing a specific electron acceptor (halogenomethanes, aromatic cyanides, etc.) as well as a tetrapyrrole donor — in most cases, this is a zinc complex of derivative tetrabenzoporphin (ZnTBP) or tetraphenylporphin (ZnTPP) [6–11]. In these reactions, donor-acceptor electron transfer from the T_n state of the donor populated under two-photon excitation (with different wavelengths) to the acceptor molecule takes place. As a result, a porphyrin monocation that does not absorb at one of the excitation waves is formed, which just leads, at helium temperatures, to the formation of

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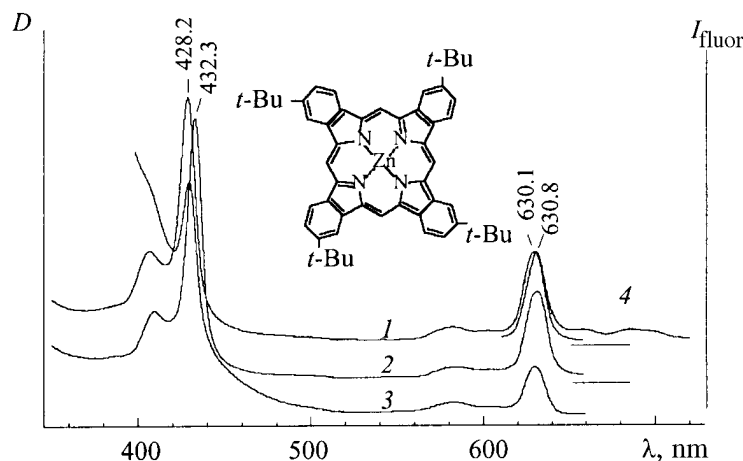


Fig. 1. The spectra of ZnTBP^{tBu} absorption in PVB (1), PVB + pyridine (2), and PVB + C₂H₅J (3) films, and of ZnTBP^{tBu} fluorescence in the PVB film (4) at 300 K.

a spectral hole in the 0–0 band of $S_1 \leftarrow S_0$ absorption. The irreversible photochemical reactions of porphyrin metal complexes in halogenomethane solutions at room temperature are described in [12, 13]. In this system, there occurs electron transfer from the S_1 state of porphyrin to CCl₄ with the formation of a pigment cation-radical leading to a marked change in the absorption spectrum, as well as an interaction of the metalloporphyrin with the reactive products of the photodissociation of halogenomethane followed by its destruction. In [14], the results of the investigation of the photochromic thermoreversible reaction of the ZnTBP derivative in a polymethylmethacrylate matrix containing a small acceptor additive are presented. Despite the fact that in the latter case there occurs donor-acceptor electron transfer and a ZnTBP cation-radical is formed, the reaction has a single-quantum character as opposed to the data of [6–11]. The foregoing points to the diversity of routes of photochemical reactions with the participation of metal complexes of porphyrins. In this connection, the search for new conditions providing a high rate of photochemical changes in metalloporphyrins is topical.

This work presents the results of the investigation of the phototransformations of ZnTBP and Zn-tetra(4-tert-butylbenzo)porphin (ZnTBP^{tBu}) in polyvinylbutyral (PVB) at room and nitrogen temperatures. Although primary consideration is given to particular porphyrins in a certain polymeric matrix, it may be suggested that in the general case the proposed mechanism of photoinduced transformations will also be applicable to other combinations of metal porphyrins and organic polymers. Moreover, the aim of this work is to explore the possibility of using the ZnTBP^{tBu}/PVB composition as a photosensitive material for optical data recording. Tentative results of these investigations are given briefly in [15, 16].

Objects of Investigation and Experimental Procedure. The zinc complexes of porphyrins were obtained by known techniques: ZnTBP — by the technique of [17] and ZnTBP^{tBu} — by the technique of [14]. The structural formula of ZnTBP^{tBu} is given in Fig. 1. To prepare polymeric films, we used monodispersed PVB powder which was preliminarily dissolved in ethanol. An ethanol additive of metalloporphyrin was introduced into such a viscous solution of PVB. The polymeric films were obtained traditionally: a porphyrin-colored ethanol solution of PVB with a thickness of up to 1 mm was put on a glass or quartz substrate and dried in air at 20°C for 24 hours. The content of metalloporphyrins in the films provided an optical density in the $S_1 \leftarrow S_0$ absorption band of no more than 0.2.

The kinetic curves of photoinduced transformations of porphyrins were obtained as dependences of the fluorescence intensity of the films at $\lambda_{\text{reg}} = 630$ nm on the time of photoirradiation by a light having a

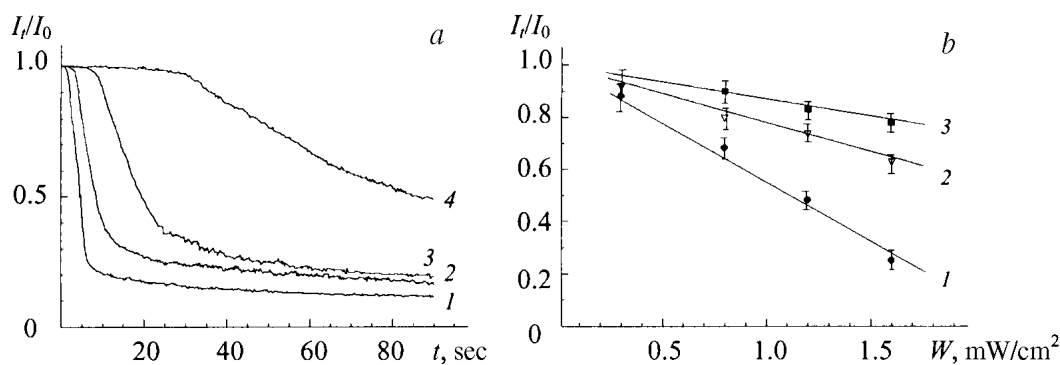


Fig. 2. Dependences of the relative fluorescence intensity of $\text{ZnTBP}^{\text{tBu}}$: a) on time at a photoirradiation power density of $W_{\text{exc}} = 1.6$ (1), 1.2 (2), 0.8 (3), and 0.3 mW/cm^2 (4) in the PVB + pyridine film; b) on the photoirradiation power density at $t = 5$ sec in the PVB + pyridine (1), PVB (2), and PVB + $\text{C}_2\text{H}_5\text{J}$ (3) films.

certain spectral composition and power density. An SVDSH-500 mercury lamp served as the light source. Combinations of color and neutral glass filters permitted us to separate the radiation of a particular spectral range (for photoirradiation in the region of the Soret band (350–450 nm) and $S_1 \leftarrow S_0$ absorption bands (570–640 nm)) and regulate its power density within the 0–1.6 mW/cm^2 range.

Results and Discussion. The PVB matrices colored by ZnTBP and $\text{ZnTBP}^{\text{tBu}}$ molecules have absorption and fluorescence spectra that are characteristic of metal complexes of tetrabenzoporphyrins (Fig. 1). The experiment has shown that on excitation of these systems in the UV region of the absorption spectrum the zinc-porphyrin molecules undergo photochromogenic (irreversible) transformations. The red light (570–640 nm) has the same effect, but the efficiency of the photoprocess thereby is two orders of magnitude lower than under UV irradiation. It has been found that the presence of a small pyridine additive in the initial ethanol mixture of ZnTBP/PVB promotes the photochromogenic reaction, whereas the methyl iodide ($\text{C}_2\text{H}_5\text{J}$) additive appreciably retards the process. It has also been noted that the addition of volume tert-butyl groups to the ZnTBP molecules increases the rate of phototransformations. As an example, Fig. 2 shows the relative fluorescence intensity at 630 nm in the polymeric composition $\text{ZnTBP}^{\text{tBu}}$ /PVB + pyridine as a function of the photoexcitation time in the 350–450-nm range at various power densities. Practically on all curves, three portions can be separated. It is not excluded that in the first (initial) portion, as the intensity decreases slightly with time, there appears a filtering effect that is due to the fact that the light is only absorbed by the outer layers of the films (in the Soret band the optical density reaches 0.4–0.5), although other causes are more probable (see below). Then the fluorescence intensity of $\text{ZnTBP}^{\text{tBu}}$ rapidly decreases, which is shown in the second portion of the curves of Fig. 2a. The third portion, where the curves practically go to a plateau, corresponds mainly to the luminescence of $\text{ZnTBP}^{\text{tBu}}$ molecules, which for some reason are not subjected to phototransformations.

The efficiency of the photochemical transformations of metalloporphyrins in the PVB matrices was estimated by the methods of [19], i.e., by the inclination of the tangent drawn to the origin of the second portion of the kinetic curve. We thereby determined for each curve the relative fluorescence intensity of $\text{ZnTBP}^{\text{tBu}}$ after the sample photoirradiation during $\Delta t = 5$ sec and thus obtained the dependence of the $\text{ZnTBP}^{\text{tBu}}$ transformation rate on the irradiation power density for samples differing in chemical composition (Fig. 2b). As is seen, the obtained dependences are linear. Since, under the action of photoirradiation, the absorption bands of the starting molecules completely disappear and new ones do not appear, it may be ar-

gued that the process of irreversible destruction of $\text{ZnTBP}^{\text{tBu}}$ with the formation of colorless products that are subsequently incapable of reversible reconstruction of the starting molecule is proceeding. It is important to note that the characteristic absorption bands of cation (anion) radicals of metalloporphyrins do not appear either. For example, in [7] it is shown that in a medium favoring the formation of ionic forms of *meso*-substituted MgTBP a change in the optical density of the initial $S_1 \leftarrow S_0$ absorption band by $\Delta D \approx 0.3$ leads to the appearance of the absorption band at ~ 440 nm ($D \approx 0.10\text{--}0.15$) of its monocation. According to [20], the linear dependence of the destruction rate of the dye on the irradiation power density points to the participation of the medium molecules in the photochemical expansion. The set of experimental data obtained permits the conclusion that the $\text{ZnTBP}^{\text{tBu}}$ molecules are destroyed under the action of the medium radicals.

One source of free radicals R^\bullet in the system under consideration is the molecules of the PVB matrix itself (possibly the molecules of the polymerization initiator residues), which, when irradiated by UV light, undergo photolysis. Moreover, the molecules of this ethyl alcohol used for preparing PVB films effectively participate in the chain of radical reactions that follow, thus increasing the R^\bullet concentration. Lying in close proximity to the porphyrin molecules and interacting with them (formation of labile contact porphyrin-radical pairs), these radicals or active products of their transformations lead to the destruction of the $\text{ZnTBP}^{\text{tBu}}$ molecule. In this case, there is no need for translational diffusion of such reaction-active particles from other areas of a solid polymeric matrix.

Proof, although indirect, of the radical mechanism of $\text{ZnTBP}^{\text{tBu}}$ destruction is a change in its rate upon additional introduction into the system of pyridine or ethyl iodide. The addition of nitrogen-containing strongly coordinating pyridine molecules into the ethanol solution of PVB leads to an extracoordination of the central metal atom of $\text{ZnTBP}^{\text{tBu}}$ molecules, which is evidenced by the small bathochromic shift of the absorption spectrum (Fig. 1, curve 2). Most probably, the pyridine molecules, being an additional ligand of $\text{ZnTBP}^{\text{tBu}}$, i.e., lying in close proximity to the porphyrin macrocycle and participating actively in the chain of radical reactions, encourage an increase in the dissociation of pyridine into simple products (Fig. 2b, curve 1). But the ethyl iodide molecules are characterized by the fact that they are readily subjected to photolysis with the formation of highly mobile radicals J^\bullet which can effectively participate in the sequence of reactions with the radicals of the starting polymeric mixture components (see above). Recombination of the medium radicals by means of labile radicals J^\bullet can lead to a break of the chain of radical reactions (which is equivalent to the inhibition of the free radicals of the starting medium components) and, consequently, to a retardation of the process of photodissociation of $\text{ZnTBP}^{\text{tBu}}$ molecules (Fig. 2b, curve 3). When the colored polymeric matrix is cooled to nitrogen temperature (77 K) the process of $\text{ZnTBP}^{\text{tBu}}$ destruction is completely terminated independent of the presence of the pyridine or $\text{C}_2\text{H}_5\text{I}$ additive. A decrease in the temperature sharply decreases the lability of the radicals, in the first place due to the "freezing" of local molecular motions.

The results of the investigation of the $\text{ZnTBP}^{\text{tBu}}$ resistance to molecular hydrogen also argue in favor of the radical mechanism of its photodestruction in the PVB matrix. Figure 3a shows the dependences of the relative fluorescence intensity of $\text{ZnTBP}^{\text{tBu}}$ /PVB at 630 nm and under photoexcitation of polymeric samples in the 350–450-nm range. It is seen that the photodestruction rate of metalloporphyrin in the polymeric film dried in a vacuum cell (the pressure was kept at $\sim 10^{-4}$ torr (curve 1)) considerably exceeds the dissociation rate of the pigment in the same dried film, but after the cell is filled with air (curve 2). In the latter case, diffusion of atmospheric gases into the polymeric matrix takes place. And the triplet (biradical) state oxygen begins to interact actively with the medium radicals R^\bullet and regenerate them or form peroxide (less active) products ROO , which just leads to an inhibition of the metalloporphyrin photodestruction. The $\text{ZnTBP}^{\text{tBu}}$ photodissociation rate in the PVB film dried in the atmosphere at normal pressure (Fig. 3a, curve 3) is also inhibited, which is not inconsistent with the above mechanism of decoloration of the polymeric composition. If the main mechanism of $\text{ZnTBP}^{\text{tBu}}$ dissociation was associated with their direct interaction with the oxygen molecules, the destruction rate of $\text{ZnTBP}^{\text{tBu}}$ /PVB in an air oxygen-containing atmosphere would, conversely, be higher than in a deoxidized medium.

As the experiment has shown, no photoinduced destruction of ZnTBP or ZnTBP^{tBu} is observed in a mixture of diethyl and petroleum ethers with isopropyl alcohol in a 5:5:2 volume ratio at both room and nitrogen temperature. This confirms the correctness of the proposed mechanism of the photochemical reaction in the polymeric composition under investigation (since the ether-alcohol mixture is incapable of effectively generating free radicals) and does not disagree with the conclusion that the molecular hydrogen does not participate in the photochemical transformations of the zinc complex of TBP.

It should be noted that the experimental data obtained do not allow us to definitely establish in which electronic state the ZnTBP^{tBu} molecules undergo destruction. If the process takes place upon excitation of the porphyrin molecule, the linear dependence of their destruction rate on the irradiation power density is indicative of simple photophysical reactions for which one single-photon act of light absorption by the ZnTBP^{tBu} molecules is enough for them to be dissociated, with a certain probability, into simple products. In this situation, the destruction occurs in the first excited (S_1 or T_1) electronic state. Upon photodissociation of the metalloporphyrin as a result of the interaction between the free radical and the molecule excited to the T_1 state, the observed inhibition of the process of ZnTBP^{tBu} destruction in the presence of ethyl iodide or molecular oxygen in the system can also be associated with the partial quenching of the ZnTBP^{tBu} T_1 state by the ethyl iodide and/or oxygen. However, one should not exclude the possibility of interaction between the free radicals of the medium and the metalloporphyrin molecules in their ground electronic S_0 state.

Our investigations of the primary photochemical processes in a particular molecular composition can also be of practical importance in developing and preparing samples of a photosensitive material containing no expensive halogenide-silver components [15, 16]. Note that in the primary photoprocesses the photosensitivity of materials based on photochemically active dyes in polymers and other media reaches values not exceeding 10^2 cm²/J (e.g., systems including spiropyrans [21]). A higher photosensitivity (up to 10^3 cm²/J) was obtained on organic photoresists and photopolymerized layers [21]; however, they require additional stages of chemical treatment of the composite.

The experimental data enabled us to determine the photosensitivity (S) of the composition ZnTBP^{tBu}/PVB + pyridine. The photosensitivity criterion is the radiant exposure $W \cdot t$ required for decreasing the optical density (in our case, the luminescence intensity) by 20%, i.e., $S_{0.2} = 1/(W \cdot t_{0.2})$. For the prepared samples, such a decrease leads to a differential optical density of absorption in the Soret band $\Delta D = 0.1$ during the photoirradiation time $t_{0.2}$, which is already quite enough for obtaining a hard image. By the experimental curves in Fig. 2, we found $S_{0.2} = (0.3-0.4) \cdot 10^3$ cm²/J, which practically is an order of magnitude higher than the known values of S for organic dyes in primary photoprocesses [21].

Despite the fact that this photosensitive material has no reversible photochromic effect, it can be used successfully for irreversible optical recording, processing, and storage of data in the form of particular images [15]. It should be noted that the process of data recording requires no subsequent chemical treatment of the material. Moreover, an additional advantage is the ease of image fixing, which is reduced to drying of the exposed polymeric layer in the dark under normal conditions. As is seen from Figs. 3b and c, with increasing drying time of the photosensitive material the form of the kinetic curves of ZnTBP^{tBu} photodestruction changes: the initial portion of the dependences is noticeably "extended" (see curves 2 and 3), the slope of the second portion gradually decreases, and in the third portion the value of the plateau, to which the kinetic curves go, increases. All these changes definitely point to an increase in the photostability of ZnTBP^{tBu} in the polymeric composition, i.e., to a decrease in the photosensitivity of the material with increasing time of its drying. This effect can be explained by the gradual evaporation from the matrix of the ethanol residue and pyridine or ethyl iodide additives. As a result, in the material, which solidifies progressively, there is a decrease in the probability of formation of reactive free radicals. In reading the recorded data, when "white" photoirradiation with a power density several orders of magnitude lower than in recording is used, practically no changes in the fluorescence intensity are observed. The thus-recorded data can be stored over a period of many years.

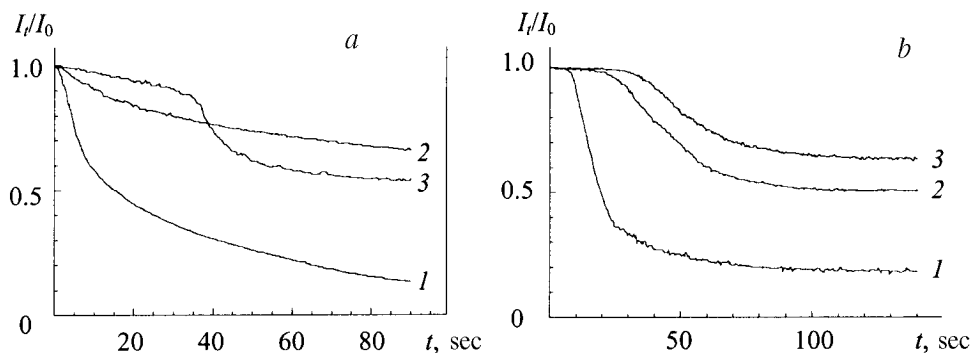


Fig. 3. Time dependences of the relative fluorescence intensity upon photoirradiation in the 350–450-nm range ($W_{\text{exc}} = 0.8 \text{ mW/cm}^2$): a) vacuum-dried ZnTBP^{tBu}/PVB film (1): film (1) placed in an atmosphere (2), and atmosphere-dried film (3); b) ZnTBP^{tBu}/PVB + pyridine film upon drying over 1 (1), 45 (2), and 90 days (3).

Note that the photosensitive material prepared by the proposed method provides data recording by obtaining a conventional visible image, i.e., by changing the absorption coefficients of the photochromogenic pigment when, on the initially green polymeric film, individual areas are decolorized under the action of light. However, a more important fact is that for the given composition it is possible to obtain a latent, luminescent image at a lower concentration of ZnTBP or ZnTBP^{tBu} (the optical density in the Soret band $D < 0.1$ and the film is practically transparent) [15]. Under these conditions, the image recorded under the photoaction can be read (visualized) by photoexciting the fluorescence whose fairly high quantum yield (for example, for ZnTBP $\phi_F \approx 0.1\text{--}0.2$ depending on the solvent [22]) provides a hard visible image of recorded data.

The spectral region of photosensitivity of the photochromogenic material is limited to the absorption spectra of zinc complexes of TBP. Photodestruction of the photosensitive pigment can be attained by activating not only the UV radiation (absorption in the Soret band) but the radiation in the 570–640-nm range as well, although in this case, as mentioned above, the photochromogenic effect is much weaker. The resolution of the material is defined by a value close to the diffraction limit because of the absence of the granular structure from the photosensitive composition.

Conclusions. The revealed and investigated high-efficiency photodestruction reaction of the zinc complex of TBP in the PVB matrix has formed the basis for developing a photosensitive composition. Such a photosensitive silver-free material can find wide application, first of all, in optical data recorders, storages, and processors. Moreover, it can be used in applied and scientific photography as well as for art and decoration purposes in order to obtain patterns and figures that are hidden under normal conditions of observation and are visualized under UV excitation.

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