Radiative deactivation of lowest singlet and triplet excited states of water-soluble porphyrins

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RADIATIVE DEACTIVATION OF LOWEST SINGLET AND TRIPLET EXCITED STATES OF WATER-SOLUBLE PORPHYRINS

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Abstract

Radiative deactivation of lowest excited triplet and singlet states for series of free bases and Zn^{2+} -complexes of water-soluble 5,10,15,20-tetrakis-(4-sulfonatophenyl)porphyrin (H_2T4SPP); 5,10,15,20-tetrakis-(4-N-alkylpyridyl) porphyrin ($H_2T4AlkPyP$); and 5,10,15,20-tetrakis-(3-N-alkylpyridyl)porphyrin ($H_2T3AlkPyP$) was studied in solutions at 77 and 293 K. The fluorescence and phosphorescence quantum yields were found to have small but detectable differences for derivatives of the same porphyrin ligand with different counterions for the ionized aryl substituents. It was shown that these differences were due to spin-orbit coupling effects and variation of the electron donor/acceptor properties of the peripheral substituents that changed the electronic energy levels in the porphyrin-counterion system.

Keywords: *water-soluble porphyrin, phosphorescence, fluorescence.*

Introduction. Water-soluble porphyrins occupy a special place among numerous tetrapyrrole derivatives because they have great potential for practical applications in medicine, biology, and industry as drugs, catalysts, and reaction inhibitors and sensitizers [1, 2]. Water-soluble porphyrins have ionizable peripheral substituents, in contrast with their hydrophobic analogs, and can be salts of acids or bases [2–4]. The ionizable peripheral substituents carry either a negative ($\text{H}_2\text{T4SPP}$) or positive charge ($\text{H}_2\text{T4MPYP}$) that is responsible for the hydrophilic properties of the porphyrin as a whole although the tetrapyrrole macrocycle itself is hydrophobic. Therefore, solutions of the tetrapyrroles also contain counterions (sometimes protons) that can either dissociate or form ion pairs with the ionized tetrapyrrole macrocycle substituents to establish dynamic equilibrium depending on the physicochemical microenvironment [3, 4]. Intermolecular interactions of tetrapyrroles with their counterions produce noticeable changes in the electronic absorption and vibrational spectra and affect the rate constants of intramolecular transitions and intermolecular interactions [3–6]. The spectroscopic manifestations of intermolecular interactions of ionized peripheral groups with ions (including the counterions themselves) was proposed to be called halochromism of water-soluble tetrapyrroles [3, 4]. Deactivation of electronic excitation energy in water-soluble tetrapyrroles was studied several times [7–13]. Attention was paid mainly to the fluorescence properties. As a rule, studies of triplet states were limited to measurements of the quantum yield of photosensitized singlet oxygen formation [9, 11]. Population and deactivation of triplet states of water-soluble tetrapyrroles and the role of structural features (peripheral ionizable substituents and their molecular structure) were beyond the scope of the work.

The principal information source for the spectroscopic properties of the lowest triplet state is still the work of Kalyanasundaram et al. that was published over 30 years ago [7, 8]. The effect of the structural features of water-soluble tetrapyrroles on quenching of their triplet states by O_2 was studied [12]. Therefore, it seemed timely to analyze the whole database of spectroscopic properties of water-soluble tetrapyrrole triplet states taking into account their structural features.

The present work measured spectra and phosphorescence quantum yields and lifetimes of free bases of differently charged water-soluble porphyrins, i.e., anionic 5,10,15,20-tetrakis-(4-sulfonatophenyl)porphyrin (H₂T4SPP) and two cationic 5,10,15,20-tetrakis-(4-*N*-alkylpyridyl)porphyrin (H₂T4AlkPyP) and 5,10,15,20-tetrakis-(3-*N*-alkylpyridyl)porphyrin (H₂T3AlkPyP) and their Zn²⁺-complexes. In addition, the relationship between the nature of the porphyrin counterion and the measured spectroscopic properties was analyzed.

Fig. 1. Molecular structures of studied compounds; all R substituents in macrocycle *meso*- positions are identical: R = H₂TPP; H₂T4SPP; H₂T4AlkPyP; and H₂T3AlkPyP; structures are shown for the free bases; counterions are not shown.

Experimental. Halides and tosylates of cationic porphyrins H₂T4AlkPyP and H₂T3AlkPyP (Fig. 1) were synthesized by the literature methods [13]. The sodium salt of anionic H₂T4SPP was used [14]. The standard compound for the spectral and luminescence parameters was 5,10,15,20-tetraphenylporphyrin (H₂TPP). The substituents bound to the quaternized pyridyl N atom were methyl

(M, CH₃), 2'-hydroxyethyl (OE, -CH₂-CH₂-OH), and allyl (Al, -CH₂-CH=CH₂). The solvent was distilled and dried EtOH that formed a glass at 77 K. The water-soluble porphyrins were highly aggregated in aqueous solutions at 77 K. Therefore, porphyrin concentrations of $(1-2) \cdot 10^{-5}$ M were determined spectrophotometrically using known extinction coefficients [7, 8, 15]. Electronic absorption spectra were recorded on a CARY 500 Scan spectrophotometer (Varian). Experiments at 293 ± 2 K used standard quartz cuvettes (1×1 cm). Measurements at 77 K were taken by placing samples into an optical quartz Dewar flask. Weak fluorescence was isolated using a dual-disk phosphoroscope. The lifetime of the lowest triplet T_1 -state was determined from the phosphorescence decay kinetics. The excitation source was an SSh-20 pulsed Xe lamp (2- μ s pulse). Phosphorescence decay was recorded at the phosphorescence maxima of the studied compounds and stored in a C9-8 oscilloscope. Fluorescence lifetime was measured on a PRA-3000 pulsed fluorometer operating in photon-counting mode. Fluorescence and phosphorescence spectra were measured on a high-sensitivity spectrometer that was described in detail before [16].

Results and Discussion. Solutions of the water-soluble tetrapyrroles in EtOH were used to study the role of anion-cation interactions between the ionized peripheral substituents and the counterions in producing the spectroscopic properties. EtOH was chosen to model a weakly dissociating experimental medium instead of the usually used *n*-octanol for two reasons. First, it was shown earlier by us that H₂T4SPP and H₂T4MPyP in aqueous EtOH solutions with ~50 vol.% EtOH formed undissociated species, i.e., the counterions were bound to the peripheral substituents. Second, EtOH forms a glass upon freezing, in contrast with *n*-octanol. Therefore, it produces stable transparent solid solutions, which are necessary for actinometry of absorbed light to determine emission quantum yields at 77 K.

Figure 2 shows fluorescence excitation, fluorescence, and phosphorescence spectra of the free base tetraiodides and the Zn-complex of 5,10,15,20-tetrakis-(4-*N*-methylpyridyl)porphyrin (H₂T4MPyP)

in EtOH at 77 and 293 K. Table 1 presents the spectroscopic properties of the free bases and Zn-complexes of all studied compounds at 77 K that were calculated from the spectra. Before analyzing the obtained experimental results, it should be noted that the studied compounds included one anionic porphyrin and several cationic derivatives. However, the sign and size of the molecular charge ($-4e$ for H₂T4SPP or $+4e$ for H₂T4MPyP) had little effect on the measured spectroscopic and photophysical properties (Table 1) because the charge was localized on the substituents and did not affect the chromophore, i.e., the conjugated π -system of the tetrapyrrole macrocycle. Furthermore, the charge was compensated by the bound counterions in the undissociated species so that the molecule as a whole was neutral.

Counterions are situated in close proximity to the tetrapyrrole macrocycle conjugated π -system if the undissociated porphyrin species forms. Manifestation of an internal heavy-atom effect in the photophysical properties of the porphyrins analogous to that of hydrophobic halogenated tetraaryl-substituted tetrapyrroles [17] should be expected if the spin-orbit coupling constant of the counterions is large (e.g., if they are halides for cationic porphyrins). Fluorescence quantum yields Φ_{fl} of H₂T4MPyP derivatives with various counterions were measured in EtOH solutions at 293 K. The quantity Φ_{fl} did in fact decrease ($0.056 > 0.052 > 0.046 > 0.038$) in the order of counterions $\text{NO}_3^- > \text{Tos}^- > \text{Cl}^- > \text{I}^-$. The spin-orbit coupling constant ξ of the counterions increased in this order by practically an order of magnitude, from 540 to 5069 cm^{-1} . Such a clear correspondence was not observed for the fluorescence quantum yield Φ_{fl} at 77 K (Table 1).

TABLE 1. Spectral and Luminescence Characteristics of Free Bases and Zn-Complexes of Water-Soluble Porphyrins in EtOH

at 77 K

			$\Delta E(S_1-)$			
<i>Free</i>						
H ₂ TPP	645	859	386	12.0	0.67	5.6
H ₂ T4SPP/Na ⁺	641	850	384	13.5	1.6	–
H ₂ T4MPyP/I [–]	641	826	349	8.7	4.3	–
H ₂ T4MPyP/Tos [–]	641	826	349	7.4	2.6	9.9
H ₂ T4MPyP/NO [–]	640	825	349	11.5	3.1	11.0
H ₂ T4MPyP/Cl [–]	641	824	346	7.9	2.3	9.4
H ₂ T4OEPyP/Tos [–]	641	826	349	10.0	3.7	11.8
H ₂ T3OEPyP/Tos [–]	637	822	353	5.3	2.5	11.1
<i>Zn-</i>						
ZnTPP	602	782	382	3.3	3.6	25.5
ZnT4SPP/Na ⁺	596	774	386	5.6	6.5	26.0
ZnTMPyP/I [–]	607	751	310	3.2	13.0	23.4
ZnT4OEPyP/Tos [–]	608	752	315	4.7	16.0	32.0
ZnT3OEPyP/Tos [–]	597	745	333	1.5	13.0	31.0
ZnT4AlPyP/Tos [–]	611	753	309	3.3	13.0	32.5

The phosphorescence quantum yield was greatest for the derivative with an I[–] counterion, $\Phi_{\text{phos}} = 4.3 \cdot 10^{-4}$. However, the values for the studied series of compounds were not fully correlated with the spin–orbit coupling constant. The phosphorescence lifetime Φ_{phos} at 77 K was inversely proportional to the T_1-S_0 intersystem-crossing rate constant. If this quantity was mainly determined by a heavy-atom effect, then the phosphorescence lifetime should decrease with increasing spin–orbit coupling constant ξ of the counterions. However, a distinct dependence of the data for the porphyrin free bases was not observed in Table 1. The phosphorescence lifetimes of only two derivatives could be compared for the Zn-complexes. Therefore, only the trend can be discussed.

Obviously, two factors could be responsible for the lack of distinct correlations of the aforementioned quantities and the spin–orbit coupling constant. First, the molecular structure of the

porphyrin-counterion system could change in the frozen solid solution. Second, effects due to redistribution of electron density between the tetrapyrrole macrocycle and the substituents could be superimposed on the relatively small observed heavy-atom effects. These effects could also be temperature dependent because the dihedral angle between the macrocycle mean plane and the planes of the aryl fragments could change considerably on going from a liquid solution at 293 K to a solid solution at 77 K. In fact, the tetrapyrrole macrocycle π -system is not directly influenced by interaction with counterions of peripheral groups in the phenyl *para*- and *meta*-positions. Phenyl and pyridyl fragments are known to be electron-density donors so that symmetric addition of them to the porphyrin macrocycle *meso*-positions increases the energy of the a_{2u} -orbital, which has non-zero electron density on the macrocycle C_m atoms [18, 19]. It is noteworthy that the aryl fragments themselves and the ionizable groups bonded to

them in addition to the counterions are capable of redistributing electron density through σ -bonds (inductive effects) and the π -system (resonance effects). Resonance effects are highly sensitive to changes of the dihedral angle between the mean plane of the macrocycle and those of the aryl fragments. The energy of the a_{2u} -orbital of the tetrapyrrole macrocycle surely changes if one functional group in the aryl *para*-position is replaced by another. According to the literature [18], it correlates with the Hammett σ constant for the given functional group. It was shown that the donor capability of the peripheral aryl substituents

changed if their ionization state was changed. This was the basis for the halochromic effects of water-soluble tetrapyrroles [3, 4, 6]. Therefore, undissociated porphyrin species with different counterions should have different Hammett σ constants. Thus, the Hammett constants $\sigma_n = 0.23$ and 0.18 for Cl^- and I^- interacting with ionized substituents in the aryl *para*-position.

Fig. 2. Fluorescence excitation (1), fluorescence (2), and phosphorescence spectra (3) for tetraiodides of the free base (a, b) and the Zn-complex (c, d) of 5,10,15,20-tetrakis-(4-*N*-methylpyridyl)porphyrin (H₂TMPyP) in EtOH at 77 (b, d) and 293 K (a, c); portions of fluorescence excitation spectra in the visible range are expanded five times along the vertical for clarity; fluorescence excitation spectra of H₂TMPyP were measured with $\lambda_{\text{rec}} = 718/709$ nm; emission spectra, with $\lambda_{\text{ex}} = 426/425$ nm (numerators and

denominators refer to 293 and 77 K); fluorescence excitation spectra of ZnTMPyP were measured with $\lambda_{\text{rec}} = 675/751$ nm; emission spectra, with $\lambda_{\text{ex}} = 440/561$ nm.

Obviously, electronic effects are more pronounced for Cl^- , as opposed to heavy-atom effects. If resonance and inductive effects are examined separately, then the difference between these ions becomes even greater. The inductive and resonance Hammett constants $\sigma_{\text{I}} = 0.47$ and $\sigma_{\text{R}} = -0.23$ for Cl^- and 0.39 and -0.16 for I^- . Therefore, it was assumed that electronic effects due to counterions in undissociated porphyrin species are important for generating the photophysical properties of the studied porphyrins at 77 K. The fluorescence and phosphorescence quantum yields measured for porphyrins in which the macrocycle *meso*-positions were substituted by *para*- and *meta*-pyridyl fragments argued in favor of this hypothesis (Table 1). In all instances (for free bases and Zn-complexes), tosylate was the counterion. However, the fluorescence quantum yield Φ_{fl} varied by more than two times; the phosphorescence quantum yield Φ_{phos} , by almost two times. Obviously, electronic effects that differed for the *para*- and *meta*-isomers of the peripheral substituents were responsible for this.

The positions of the absorption and luminescence band maxima were also reflective of the aforementioned electronic effects. Spectral shifts were consistently observed but were less than several tens of cm^{-1} . Table 1 shows that the energy gap between the lowest singlet and triplet states $\Delta E(S_1-T_1)$ was $\sim 300\text{--}350$ cm^{-1} less for the pyridyl-substituted porphyrins than for the phenyl-substituted derivative. The differences in the position of the lowest triplet T_1 -state for these porphyrins was measured experimentally for the first time and explained differences in the literature values of the intersystem-crossing quantum yield into the triplet state of $\text{H}_2\text{T4MPyP}$ and $\text{H}_2\text{T4SPP}$ [9, 12]. The quantum yield of the former was greater than that of the latter. This agreed with the inverse dependence

of the nonradiative transition quantum yield on the energy difference of the combining states $\Delta E(S_1-T_1)$ [8]. It is noteworthy that absorption and luminescence spectra of ZnTMPyP at room temperature did not follow the mirror symmetry law (Fig. 2c). The intensity ratio of the electronic and vibronic transition bands in the fluorescence spectrum was greater than unity whereas the reverse relationship was observed in the absorption spectrum. The ratio $Q_x(0, 0)/Q_x(1, 0) < 1$ in the absorption spectrum implied that the potential surfaces of the ground S_0 and excited S_1 states were shifted relative to each other. In our opinion, the ratio $Q_x(0, 0)/Q_x(0, 1) > 1$ in the fluorescence spectrum because the porphyrins underwent conformational rearrangements during the excited-state lifetime that decreased the shift of the S_1 -state potential surface relative to that of the ground S_0 -state. The molecular conformations of these states were similar. Observance of the mirror-symmetry law by ZnTMPyP in the solid solution at 77 K argued in favor of this interpretation. The frozen solvate shell prevented the molecule from changing conformation. The intensity ratios of the electronic and vibronic transition bands in absorption and fluorescence spectra turned out to be similar.

Conclusions. It was shown that free bases and Zn-complexes of water-soluble porphyrins at 77 K could undergo radiative deactivation through both fluorescence (S_1-S_0) and phosphorescence channels (T_1-S_0). Radiative deactivation at 293 K was observed only in the S_1-S_0 channel. It was found that the spectral and photophysical properties of the studied compounds were changed by a combination of spin-orbit coupling (heavy-atom) and electronic effects of the counterions associated with the peripheral substituents. These effects were small so that radiative deactivation of the water-soluble porphyrins in general was slightly sensitive to the counterions of the peripheral substituents and was determined mainly by the molecular structure of the porphyrin ligand.

The photophysical and spectral properties of the studied compounds changed little. However, the results had indubitable practical value. The photophysical properties of porphyrins with different

counterions differed little so that a counterion could be chosen to synthesize novel porphyrin photosensitizers and their carriers considering only the sensitizer with the maximum tumor-seeking properties, which were shown to depend on the type of counterion [2]. The photodynamic efficiency of the sensitizer remained practically constant.

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