

Excitation Energy Deactivation in Monodeprotonated Porphyrin

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Spectroscopic properties of monodeprotonated form of cationic 5,10,15,20-tetrakis(4-N-methylpyridyl)porphyrin (H₂TMPyP) in solution are studied. Experimental results are interpreted according to Gouterman four-orbital model. Monodeprotonated form HTMPyP⁻ can be assigned to the D_{4h} symmetry point group, and has spectral and photophysical characteristics similar to that of the fluorescent metal complexes of H₂TMPyP with the relatively low electronegativity of chelated metal ion. The intersystem crossing with the quantum yield $\Phi_{ISC}=0.57$ is the main pathway for the excitation energy deactivation of monodeprotonated form HTMPyP⁻.

Keywords: Porphyrin, acid-base equilibria, configuration interaction, symmetry, excited states, fluorescence.

Introduction

Porphyrin molecules are amphoteric compounds having properties of both bases and acids.^[1] Basic properties are exhibited in protonation of the nitrogen atoms of the pyrroline rings when reacting with acids, and formation of monoprotonated and diprotonated forms. Acidic properties result in dissociation of the pyrrole protons during formation of metal complexes. The complete scheme for possible acid-base equilibria of porphyrin macrocycle is shown in Figure 1. While the monoprotonated and especially the doubly protonated forms of tetrapyrrolic compounds have been rather intensively studied, the monodeprotonated and doubly deprotonated molecules were out of focus of researchers. It was assumed that these forms are extremely unstable, and it is difficult to detect them experimentally.^[1,2] At the moment when we have started these studies, it was known only two experimental papers devoted to the monodeprotonated forms of two compounds: porphine (H₂P) and 5,10,15,20-tetrakis(4-N-methylpyridyl)porphyrin (H₂TMPyP),^[3,4] and one theoretical paper where a quantum chemical study was carried out for the monodeprotonated form of porphine (HP⁻).^[5]

Fluorescence spectrum has been measured for the monodeprotonated form of porphine HP⁻,^[3] but the problem of excitation energy deactivation in such proton deficient porphyrin systems has not been studied. In our recent

publication we have reported on the absorption and fluorescence spectra and have discussed molecular symmetry of monodeprotonated form H₂TMPyP (HTMPyP⁻) in the solution at room temperatures.^[6] Here we report on the intersystem crossing quantum yield Φ_{ISC} and discuss the excitation energy deactivation pathways in the monodeprotonated form HTMPyP⁻.

Experimental

Materials and Methods

5,10,15,20-Tetrakis(4-N-methylpyridyl)porphyrin tetratosylate salt (Aldrich) was used without additional purification.

Twice-distilled water or 0.2 M solution of NaOH (pH=13.5) were used to prepare the solutions. The concentration of porphyrin in solutions was determined spectrophotometrically with known extinction coefficients^[7] ($\epsilon = 226000 \text{ M}^{-1}\text{cm}^{-1}$ at 422 nm) and was $\sim 2.4 \cdot 10^{-6} \text{ M}$. The measurements were carried out in the standard quartz rectangular cells (1x1 cm, Hellma) in the air equilibrated solutions at $288 \pm 2 \text{ K}$.

Deoxygenated solutions were used for the measurements of the fluorescence quantum yield Φ_f . Deoxygenation of the solutions was performed with argon bubbling during 20 min just before measurements. The fluorescence spectra and fluorescence excitation spectra were measured with the use of spectrofluorometer SFL-1211 (Solar, Belarus). The fluorescence decay kinetics

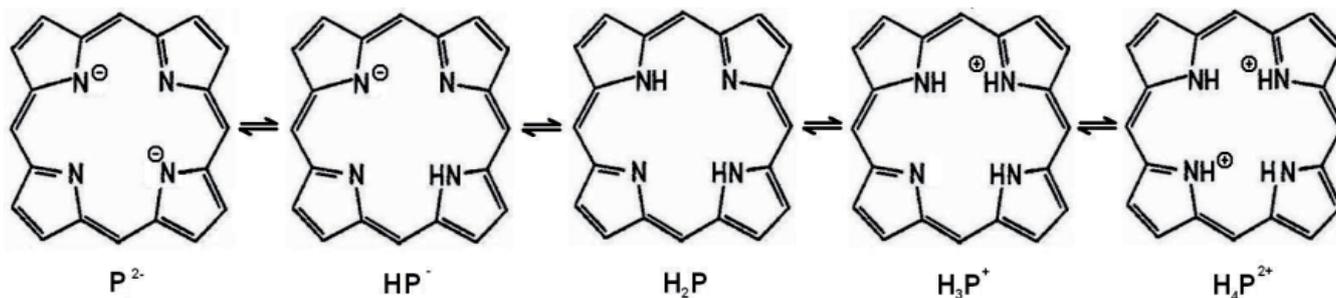


Figure 1. Acid-base equilibria of porphyrin macrocycle; P²⁻ is doubly deprotonated porphyrin, HP⁻ is monodeprotonated porphyrin, H₂P is free base porphyrin, H₃P⁺ is monoprotonated porphyrin and H₄P²⁺ is doubly protonated porphyrin.

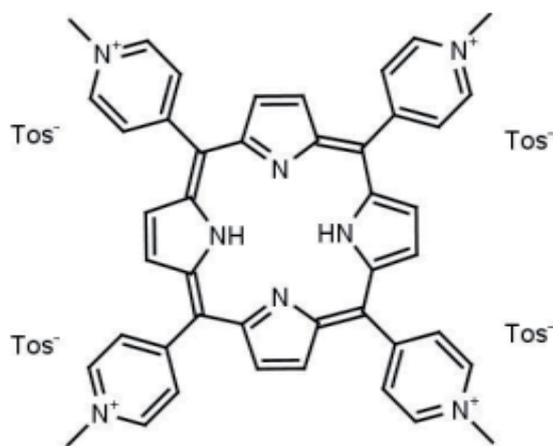


Figure 2. Structure of 5,10,15,20-tetrakis(4-*N*-methylpyridyl)porphyrin.

were measured with the use of photon counting system FLA-900 (Edinburgh Instruments, UK) which allowed to measure the decay kinetics with lifetimes down to 0.1 ns. The fluorescence quantum yield Φ_f was determined using standard sample method.^[8] The free base 5,10,15,20-tetrakis(4-*N*-methylpyridyl)porphyrin was used as a standard sample ($\Phi_f = 0.044$ ^[7,9]).

Results and Discussion

Electronic Absorption Spectra and Symmetry of Monodeprotonated Species

Electronic absorption spectra of the free base H_2 TMPyP and the monodeprotonated form HTMPyP⁻ in

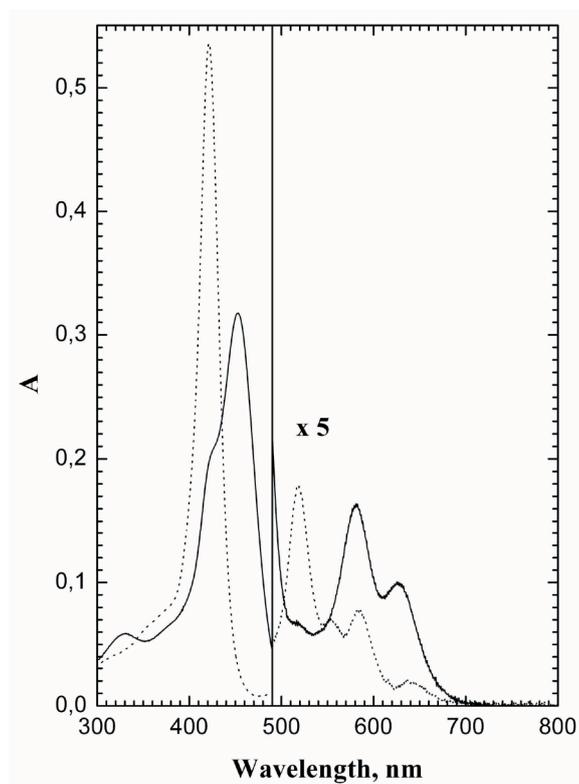


Figure 3. Absorption spectra for the monodeprotonated form HTMPyP⁻ (solid line) and the free base H_2 TMPyP (dotted line). Porphyrin concentration of each form is $2.4 \cdot 10^{-6}$ M.

equimolar concentrations are shown in Figure 3. In going from the free base to the monodeprotonated form a long-wavelength shift of the Soret band from 422 nm to 453 nm is observed (the shoulder on the short-wavelength side of the Soret band is due to trace absorption of no more than 5% of the free base species). The transformation of the shape of the spectrum in the visible region was found too: instead of the four-band spectrum of the phyllo-type with maxima at 638 nm, 584 nm, 554 nm, and 518 nm typical to the free base, we observed a two-band spectrum with maxima at 627 nm and 581 nm, the shape of which is similar to the absorption spectra of the metal complexes.

We have recently shown^[6] that the shape of the absorption spectrum for the monodeprotonated form (HTMPyP⁻) is due to the high symmetry of the molecule: it should be assigned to the D_{4h} symmetry point group rather than to C_{2v} , which could be in the case of fixed proton. We have hypothesized that such a situation was realized due to the highly effective tautomerism in the monodeprotonated porphyrin macrocycle. The proton delocalization over the porphyrin core leads to the formation of absorption spectrum like in the case of metalloporphyrins. The maximum of $Q(0,0)$ band undergoes a monotonic blue shift: $627 > 602 > 587 > 566 > 545$ nm in the series HTMPyP⁻ > ZnTMPyP > CuTMPyP > PdTMPyP > PtTMPyP. Indeed, the monoprotonated HTMPyP⁻ species are in line with metal complexes for both $Q(0,0)$ band maximum as well as for the absorbance intensity ratio $AQ(0,0)/AQ(1,0)$, indicating that in the case of the monodeprotonated form HTMPyP⁻ ${}^1E(a_{2u}, e_g) < {}^1E(a_{1u}, e_g)$.^[6] Thus, the monodeprotonated HTMPyP⁻ species can be considered as a quasimetallocomplex of H_2 TMPyP,

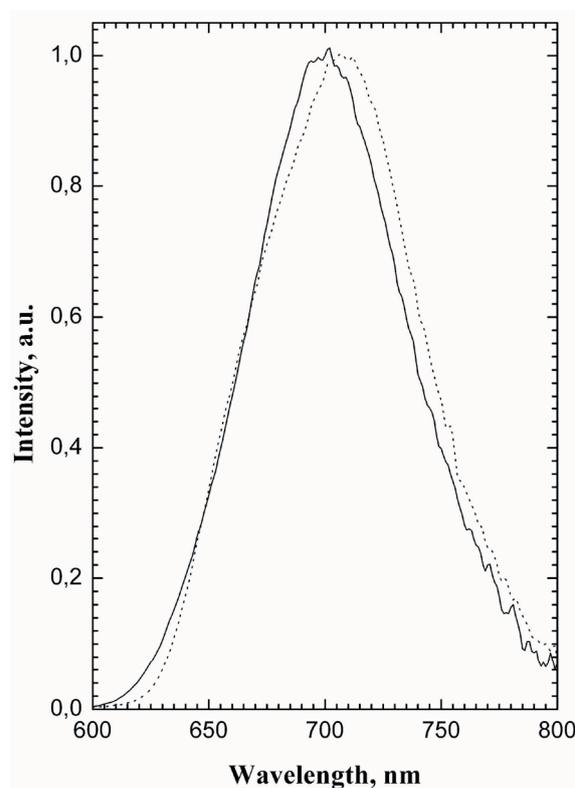


Figure 4. Fluorescence spectra for the monodeprotonated form HTMPyP⁻ (solid line) and the free base H_2 TMPyP (dotted line); $\lambda_{exc} = 580$ nm. Porphyrin concentration of each form is $2.4 \cdot 10^{-6}$ M.

Table 1. Photophysical properties of studied compounds (the methods of the deactivation rates, k_{fl} , k_{nr} , k_{ISC} and k_{SS} , determination were described earlier^[10]).

Compound	$\lambda_{\text{fl}}^{\text{max}}$, nm		τ_{fl} , ns	Φ_{fl}	k_{fl} , 10^7 s^{-1}	k_{nr} , 10^8 s^{-1}	Φ_{ISC}	k_{ISC} , 10^8 s^{-1}	k_{SS} , 10^8 s^{-1}
	$Q(0,0)$	$Q(0,1)$							
H ₂ TMPyP ^[7,9,13]	657	706	5.16	0.044	0.85	1.85	0.80	1.65	0.20
HTMPyP ⁻	655	701	1.05	0.038	3.62	9.16	0.57	5.43	3.73
ZnTMPyP ^[11,12]	626	666	1.30	0.025	1.92	7.50	0.90	6.92	0.58

in which the proton delocalized over the porphyrin cavity plays the role of chelated metal ion.

Photophysical Properties of Monodeprotonated Species

Monodeprotonated form HTMPyP⁻ fluoresces. The fluorescence spectrum consists of large band with maximum centered at 701 nm (Figure 4). Analysis of the fluorescence band shape shows that it is satisfactorily fitted by two Gaussians with maxima at 655 and 701 nm, corresponding to pure electronic $Q(0,0)$ and vibronic $Q(0,1)$ bands. The excitation spectrum for this luminescence, recorded in the region of Soret band, matches the absorption spectrum of HTMPyP⁻, which confirms our assignment of the luminescence to fluorescence of the monodeprotonated form. The fluorescence quantum yield of HTMPyP⁻ is $\Phi_{\text{fl}} = 0.038$, and is of the same order of magnitude as for the free base and the Zn complex (Table 1). The fluorescence decay kinetics ($\lambda_{\text{exc}} = 460 \text{ nm}$, $\lambda_{\text{obs}} = 710 \text{ nm}$) are monoexponential with decay time $\tau_{\text{fl}} = 1.05 \pm 0.05 \text{ ns}$.

It is known that in going from the free base porphyrins to metallocomplexes, the fluorescence quantum yield Φ_{fl} decreases by a factor of 2–5, and the probability of fluorescence k_{fl} increases by a factor of about 2.^[10] Fluorescence quantum yield of the free base H₂TMPyP is initially low ($\Phi_{\text{fl}} = 0.044$ ^[9]); the formation of Zn complex leads to almost two fold decrease in the Φ_{fl} value ($\Phi_{\text{fl}} = 0.025$ ^[11,12]), while the probability of fluorescence increases. Considering the monodeprotonated form HTMPyP⁻ as quasimetallocomplex, we should stress that the probability of HTMPyP⁻ fluorescence also follows the indicated pattern for the metallocomplexes (see Table 1). The magnitude of Φ_{fl} decreases to 0.038, while k_{fl} value increases up to $3.62 \cdot 10^7 \text{ s}^{-1}$. Obviously, the decrease in the fluorescence quantum yield Φ_{fl} for such a substantial increase in k_{fl} should be accompanied by a significant increase in the probabilities of nonradiative deactivation channels (k_{ISC} for $S_1 \rightarrow T_1$ intersystem crossing and k_{SS} for $S_1 \rightarrow S_0$ internal conversion). In fact, the overall probability of these processes $k_{\text{nr}} = k_{\text{ST}} + k_{\text{SS}}$ increases by a factor of five compared with that of the free base, and reaches $9.16 \cdot 10^8 \text{ s}^{-1}$. For ZnTMPyP molecule, the k_{nr} value also increases up to $7.50 \cdot 10^8 \text{ s}^{-1}$. Thus, deactivation of the lower excited S_1 state of HTMPyP⁻ follows the patterns for deactivation for the Zn complex of H₂TMPyP, *i.e.* the monodeprotonated form HTMPyP⁻ also behaves itself like the metallocomplex.

The lowest triplet T_1 state lifetime of the monodeprotonated form HTMPyP⁻ was found to be sufficiently long to provide the efficient quenching by molecular oxygen. The triplet state lifetime in the air-equilibrated solution τ_{T} was found to be 2.8 μs , which was close to that of 3.5 μs for

ZnTMPyP.^[14] Thus, we were able to use the singlet molecular oxygen photosensitization to determine the value of the intersystem crossing quantum yield Φ_{ISC} .^[15,16] The Φ_{ISC} value was found to be as high as 0.57 ± 0.05 . This figure is somewhat lower than those for the free base and Zn complex and results from the competition between two nonradiative deactivation channels. It must be pointed out that fraction of the $S_1 \rightarrow T_1$ intersystem crossing in nonradiative deactivation of S_1 state was found to be about 90% for both the free base and for its Zn complex,^[7,9,11] indicating the dominating role of the intersystem crossing rate k_{ISC} (Table 1). In the case of monodeprotonated form (HTMPyP⁻) nonradiative deactivation of the lowest excited S_1 state *via* the $S_1 \rightarrow S_0$ internal conversion ($k_{\text{SS}} = 3.73 \cdot 10^8 \text{ s}^{-1}$) seems to be successfully competing with the intersystem $S_1 \rightarrow T_1$ crossing ($k_{\text{ISC}} = 5.43 \cdot 10^8 \text{ s}^{-1}$). As a result, the quantum yield of the internal conversion $\Phi_{\text{SS}} = 1 - \Phi_{\text{fl}} - \Phi_{\text{ISC}}$ is as high as ~ 0.4 . Nevertheless, the intersystem crossing leading to population of the lowest triplet T_1 state remains to be the main route of the excitation energy deactivation of monodeprotonated form HTMPyP⁻ like it takes place in other metallocomplexes of H₂TMPyP porphyrin.

Conclusions

The presented results show that monodeprotonated form HTMPyP⁻ of cationic 5,10,15,20-tetrakis(4-*N*-methylpyridyl)porphyrin can be assigned to the D_{4h} symmetry point group. The electronic absorption spectrum of the monodeprotonated form can be interpreted in the framework of Gouterman's four-orbital model. It was established that monodeprotonated form HTMPyP⁻ has photophysical characteristics close to those known for the fluorescent metal complexes of H₂TMPyP with relatively low electronegativity of the chelated metal ion. The triplet T_1 state population is the main pathway for the excitation energy deactivation of the monodeprotonated form HTMPyP⁻.

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