

The photophysical and metal coordination properties of the N-CH₃ substituted porphyrins: H(N-CH₃)TPP vs H(N-CH₃)OEP

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ABSTRACT: The effect of N-methyl substitution on photophysical and metal coordination properties of the respective derivatives of octaethylporphyrin (H₂OEP) and tetraphenylporphyrin (H₂TPP) was studied by means of steady-state and time-resolved optical spectroscopies combined with semi-empirical quantum-chemical calculations and coordination chemistry methods. In case of H₂TPP, the insertion of the methyl substituent into the center of the porphyrin macrocycle leads to noticeable nonplanar distortions of the molecule and is accompanied by changes of its photophysical and physicochemical properties towards those manifested by “classical” nonplanar porphyrins. Contrasting to that, N-methyl substituted H₂OEP does not undergo significant nonplanar distortions and possesses photophysical characteristics mainly similar to unsubstituted H₂OEP, except for the long-wavelength shift of the absorption and emission bands. The Zn coordination/Zn complex dissociation and macrocycle thermal stability parameters were also determined for both N-methyl substituted and parent unsubstituted macrocycles, which correlate well with a higher degree of nonplanarity of the N-methyl substituted H₂TPP as compared to H₂OEP. Basing on the results of this study the conclusion postulated is that N-methyl substitution has a different effect on the photophysical and coordination properties of H₂TPP vs. H₂OEP. Copyright © 2005 Society of Porphyrins & Phthalocyanines.

KEYWORDS: porphyrin, photophysics, excited states, nonplanar distortion, N-methyl substitution, OEP, TPP.

INTRODUCTION

The N-substituted porphyrins are found *in vivo* where they are formed upon interaction of some drugs (for instance, alkyl- or arylhydrazines) with hemoproteins that results in severe metabolic defects (hemoprotein deactivation) [1, 2]. The products of such interaction cause inhibition of ferrochelatase

and heme oxygenase, which are responsible for iron enzymatic incorporation in the process of hemoglobin biosynthesis [2-3].

The N-substituted free-base porphyrins exhibit high reactivity towards metal coordination and acid-base interactions, whereas their metallocomplexes demonstrate low stability toward demetallation [2]. Furthermore, the N-substituted porphyrins can stabilize metal ions in uncommon oxidation states, including Co(II), Fe(II) and Fe(IV) [2, 4], and form organometallic σ -complexes capable of reversible

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migration of an alkyl- or aryl-substituent from the metal to the nitrogen atom [5].

The N-substitution is an efficient structural as well as electronic factor. It has been suggested on the basis of X-ray and electronic absorption data, as well as of the data on the chemical reactivity of N-substituted porphyrins, that N-substitution leads to complete or partial $sp^2 \rightarrow p^3$ re-hybridization of the substituted nitrogen atom [2, 6-7]. The re-hybridization is, likely, partial for N-substituted porphyrins and complete for their metallocomplexes [7]. The latter is evidenced, for example, (i) by characteristic changes of the bond lengths and valence angles observed for the substituted nitrogen atoms, and (ii) by a change of the type of the electronic absorption spectra of the metalloporphyrinic macrocycle upon N-substitution being indicative of the change of the π -electron conjugation contour.

In addition to the re-hybridization, N-substitution can potentially lead to another obvious structural and electronic effect, namely to nonplanar distortions of the porphyrin macrocycle. It is well established in the literature that, for the porphyrins possessing highly nonplanar structures due to bulky peripheral substituents or/and additional protonation of the porphyrin core in acidic media [8-12], such nonplanar distortions cause severe perturbations of spectral properties for both ground and excited states.

The aim of this work was to clarify whether the two N-methyl substituted porphyrins studied, H(N-CH₃)TPP and H(N-CH₃)OEP, really possess nonplanar distortions of the macrocycle and how these distortions, if available, influence photophysical and complex formation / complex dissociation properties of the porphyrins. To answer the above questions, both steady-state and time-resolved absorption and fluorescence spectroscopies were applied combined with physicochemical studies. Additionally, the semi-empirical quantum-chemical methods were used for optimization of the molecular structures and evaluation of their macrocycle nonplanarity.

MATERIALS AND METHODS

N-methyl-5,10,15,20-tetraphenylporphyrin and N-methyl-2,3,7,8,12,13,17,18-octaethylporphyrin (H(N-CH₃)TPP and H(N-CH₃)OEP, respectively) (shown in Fig. 1) were synthesized as described previously [2, 13].

Optical spectroscopy experiments were performed in a set of solvents of different polarity (*n*-hexane, toluene, acetone, DMF = dimethyl formamide) at room temperature and in the solvent mixture THF/diethyl ether (1:1) at 77 K (THF = tetrahydrofuran). Solvents utilized in fluorescence experiments were checked before use for the lack of background

fluorescence.

Steady-state fluorescence and fluorescence excitation measurements were carried out on the spectrofluorimeter SDL-2 (LOMO production, USSR). The detection channel was oriented at a right angle with respect to excitation. The xenon arc lamp DKsSh-120 was used as the light source. The fluorescence as well as fluorescence excitation spectra were corrected for the wavelength dependence of the photomultiplier response and for the spectral distribution of the exciting light, respectively. The steady-state absorption was measured utilizing a Cary-500 Scan spectrophotometer (VARIAN). For all steady-state emission and absorption experiments 10×10 mm quartz cells were used.

Time-resolved emission experiments were performed using the time-correlated single photon counting instrument of the Wageningen University and Research Center, described previously in reference 14. The laser pulses of 4 ps FWHM were used as the source of exciting light, the pump pulse energy was ≤ 100 pJ, and the excitation position was tunable over vis and near UV spectral regions. The light polarization in the detection channel was set at the "magic" angle (54.7°) relative to the polarization of the exciting beam, the detection direction was organized at the right angle relative to the direction of excitation. The time resolution of the overall instrument is estimated as ~ 50 ps.

For the time-resolved emission experiments, 4×10 mm quartz cells (Hellma) were used. All emission decay experiments were carried out in the presence of dissolved oxygen of air. The experimentally obtained emission decay curves were fitted by the least-squares method to the double-exponential function:

$$I(t) = A_1 \cdot \exp(-t/\tau_1) + A_2 \cdot \exp(-t/\tau_2)$$

The solvents used in physicochemical studies were subjected to additional purification [15]. Acetic acid of the reagent grade was frozen several times,

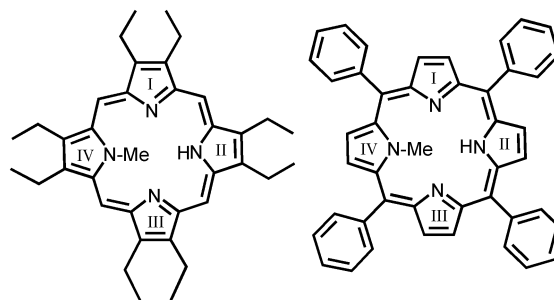


Fig. 1. Molecular structures of N-methyl-octaethylporphyrin (H(N-CH₃)OEP, left) and N-methyl-tetraphenylporphyrin (H(N-CH₃)TPP, right). The numbering of the quadrants referred to in Table 2 is shown within pyrrole rings

boiled with a matched amount of acetic anhydride and distilled, accepting the fraction with the boiling temperature 117.5 °C. Dimethylsulfoxide (reagent grade) was treated with calcinated CaO and distilled in vacuum ($t < 90$ °C).

Thermogravimetric studies were carried out using a derivatograph 1000D by MOM, Hungary. The accuracy of the temperature measurements (± 0.5 °C) in the temperature interval of interest was controlled by characteristic temperatures of the reference compounds. The accuracy of the mass measurements was within ± 0.2 mg.

Kinetic control of the metal coordination reaction with a free-base porphyrin and of metal dissociation from the respective zinc complexes was performed spectrophotometrically in a 10×10 mm quartz cell. The solutions of the studied compounds were inserted into a thermostabilized sample chamber of the Hitachi U2000 spectrophotometer, and the progress of a reaction was monitored by the optical density changes.

Quantum-chemical calculations of the H(N-CH₃)TPP and H(N-CH₃)OEP macrocycle atom deviations from the mean macrocycle plane were carried out with the semi-empirical PM3 method incorporated into the HyperChem™ suit.

RESULTS

Steady-state absorption and emission data

Absorption spectra of H(N-CH₃)TPP and H(N-CH₃)OEP in toluene at room temperature are shown in Fig. 2A,B (solid lines). Both compounds demonstrate the intense Soret absorption band in the near UV (~ 400 -430 nm) typical for all porphyrins. In the vis region there is a set of less intense Q absorption bands (450-770 nm) ($Q_x(0,0)$ and $Q_y(0,0)$ bands and respective vibronic overtones).

Relative to the absorption spectrum of the parent unsubstituted H₂TPP, H(N-CH₃)TPP manifests considerable shifts of the absorption bands to the longer wavelength (Fig. 2A): the Soret band is shifted by 15 nm, and the Q-bands are shifted by 20-30 nm to the red comparing to H₂TPP. Besides the long wavelength shift, the intensity ratio of the $Q_y(0,0)$ (at 570 nm) and $Q_x(1,0)$ (at 532 nm) absorption bands of H(N-CH₃)TPP is altered, so that this ratio is reversed comparing to the parent H₂TPP [11-12]. The absorption bands of H(N-CH₃)OEP are also shifted, by ~ 20 nm, to the red with respect to the parent H₂OEP (Fig. 2B) [11].

Fluorescence spectra of H(N-CH₃)TPP and H(N-CH₃)OEP (in toluene at room temperature) are presented on Fig. 2A,B in dashed lines. The emission spectra of H(N-CH₃)TPP and H(N-CH₃)OEP consist

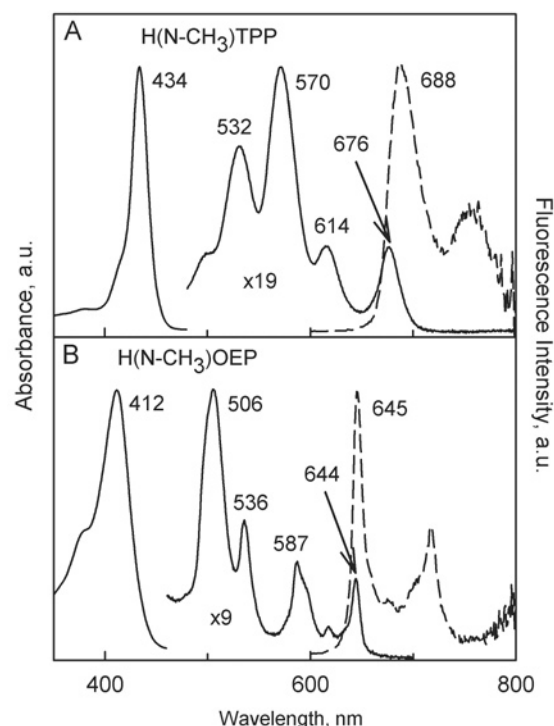


Fig. 2. Ground-state absorption spectra (solid lines) and fluorescence spectra (dashed lines) for H(N-CH₃)TPP (A) and H(N-CH₃)OEP (B) in toluene at room temperature. The numbers indicate the positions of corresponding absorption and emission maxima. For the means of presentation the visible region of the absorption spectra was scaled by the factors indicated

of two bands, $Q(0,0)$ and its vibronic overtone $Q(0,1)$, that is typical for the porphyrins. The Stokes shift is increased for H(N-CH₃)TPP as compared to H₂TPP (260 and 140 cm⁻¹, respectively) but does not change for H(N-CH₃)OEP as compared to H₂OEP (50 cm⁻¹).

Time-resolved emission data

The time-resolved fluorescence data, obtained by the time-correlated single photon counting technique [16], is presented in Fig. 3A,B for H(N-CH₃)TPP and in Fig. 4A,B for H(N-CH₃)OEP. The upper panels of both figures show the emission decay traces (along with the fitting curves) measured at different temperatures, and the bottom panels of these figures demonstrate the results of the measurements in solvents of different polarity (*i.e.* with different dielectric constant ϵ).

The H(N-CH₃)TPP fluorescence decay kinetics were measured at 675 or 688 nm, and in case of H(N-CH₃)OEP the broadband detection was applied covering the range 625-680 nm. In all cases the experimental traces were well fitted by the double-exponential function, with the longest-lived component τ_2 dominating in the kinetics. The numerical results of the time-resolved emission experiments for both porphyrins are collected in Table 1.

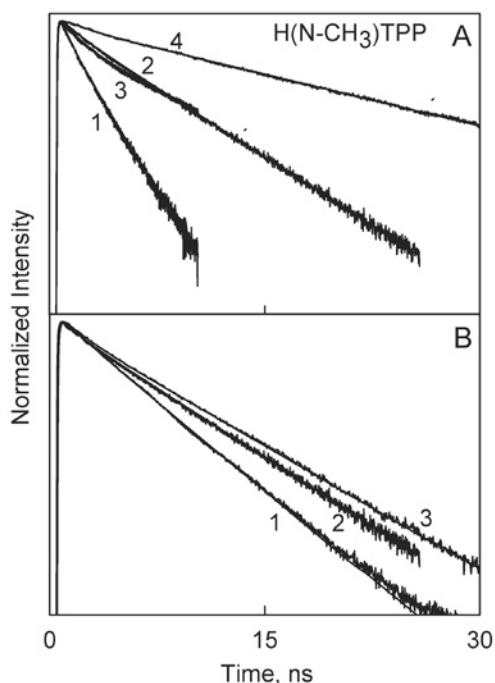


Fig. 3. Emission decay traces (in semi-logarithmic scale) for H(N-CH₃)TPP. Panel A: at number of temperature settings (1, 2, and 3: in toluene at 343 K, 300 K, and 276 K respectively, 4: in THF/diethyl ether mixture at 77 K). Panel B: at 300 K in the selected solvents of different polarity (1: in DMF, 2: in toluene, 3: in *n*-hexane). See Table 1 for the lifetimes. On both panels, the experimental traces are presented along with the corresponding fitting curves

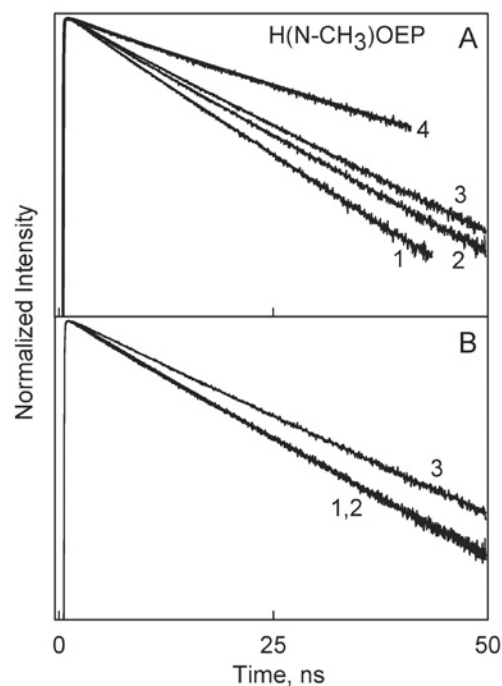


Fig. 4. Emission decay traces for H(N-CH₃)OEP. Panel A: all the same as for Fig. 3A. Panel B: at 300 K in the selected solvents of different polarity (1: in toluene, 2: in acetone, 3: in DMF). The rest is the same as for Fig. 3

Table 1. Emission decay data for H(N-CH₃)TPP and H(N-CH₃)OEP in solvents of different polarity and at different temperatures of media

Compound	Solvent	$E_T^{N^a}$	Temperature, K	τ_1 , ns (A_1) ^b	τ_2 , ns (A_2) ^c
H(N-CH ₃)TPP	<i>n</i> -hexane	0.009	300	1.35 (24%)	5.10 (76%)
	toluene	–	276	1.16 (43%)	5.73 (57%)
		0.099	300	1.02 (20%)	4.61 (80%)
	DMF	–	343	0.60 (33%)	1.80 (67%)
		0.404	300	1.10 (16%)	3.54 (84%)
THF/diethyl ether	–	77	1.38 (21%)	12.24 (79%)	
H(N-CH ₃)OEP	toluene	–	276	2.98 (15%)	10.01 (85%)
		0.099	300	2.85 (13%)	9.06 (87%)
		–	343	3.02 (12%)	7.71 (88%)
	acetone	0.355	300	4.80 (9%)	8.96 (91%)
		0.404	300	5.83 (10%)	11.04 (90%)
	THF/diethyl ether	–	77	4.88 (14%)	16.50 (86%)

^a Normalized empirical parameter of solvent polarity [17]. ^b Short-lived (minor) emission decay component lifetime with weighted contribution in parentheses. ^c Long-lived (dominating) emission decay component lifetime with weighted contribution in parentheses.

For H(N-CH₃)TPP in toluene the emission decay proved to be significantly faster (judging on the major decay component of ~5 ns, Table 1) than for parent unsubstituted H₂TPP (~9-10 ns in presence of the dissolved molecular oxygen [11]), the weighted contribution of dominating longer-lived component being 60-80%. Additionally, for H(N-CH₃)TPP in toluene considerable shortening of the emission decay kinetics with the temperature rise was detected: with temperature changes from 276 K to 343 K, the lifetime of the dominating (longer-lived) decay component decreases from 5.73 ns to 1.80 ns, the weighted contribution of this component into decay kinetics does not show any systematic dependence on temperature (Fig. 3A and Table 1). Such temperature dependence of the longer-lived component of the S₁ state decay corresponds, assuming Arrhenius-type dependence, to the activation energy of ~3.3 kcal/mol. As concerns the shorter-lived (minor) decay component, its lifetime also decreases somewhat, from 1.16 ns at 276 K down to 0.60 ns at 343 K, with rise of temperature. A change of solvent from non-polar *n*-hexane or toluene to polar DMF leads to a decrease of lifetime of the major (longer-lived) emission decay component from 5.10 - 4.61 ns to 3.54 ns without considerable changes of the weighted magnitude (Fig. 3B and Table 1). At the same time, the lifetime of the minor decay component does not change within experimental error.

The H(N-CH₃)OEP emission lifetime proved to be considerably longer than that for H(N-CH₃)TPP, reaching values typical for unsubstituted planar porphyrins. For H(N-CH₃)OEP in toluene the dominating (longer-lived) emission decay component has the lifetime of ~9 ns with the weighted magnitude up to 90% (Table 1). When the temperature of the media was changed, the longer-lived decay component demonstrated comparatively weaker reduction of the lifetime, from 10.01 ns at 276 K to 7.71 ns at 343 K, with practically constant relative magnitude (Fig. 4A, Table 1). The weighted magnitude and lifetime of the shorter-lived component were practically unchanged when the temperature was varied. The change of solvent from non-polar toluene to polar acetone and DMF did not lead to any shortening of

the emission lifetime with increase of media polarity, but rather an opposite effect was observed, when the major decay component in polar DMF manifested a somewhat longer lifetime comparing to non-polar toluene (11.04 and 9.06 ns respectively, Fig. 4B and Table 1).

Quantum-chemical calculations

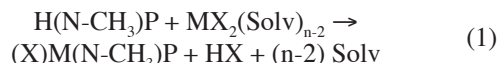
The optimization of H(N-CH₃)TPP and H(N-CH₃)OEP molecular structure, performed by the semi-empirical quantum-chemical methods, demonstrated considerable distinctions between these two molecules with respect to the magnitude of nonplanar distortions induced by the N-methyl group.

The values of deviation of the β carbon atoms of the pyrrole rings from the mean macrocycle plane are collected in Table 2. The structures of both molecules undergo non-symmetrical saddle-type distortions, and, as illustrated by Table 2, for both H(N-CH₃)TPP and H(N-CH₃)OEP, the pyrrole ring bearing the N-methyl substituent possesses the biggest deviation from planarity. However, the magnitude of the β carbon atoms deviation is much bigger for H(N-CH₃)TPP than for H(N-CH₃)OEP: 0.9 and 0.5 Å for the maximum and average out-of-plane deviation, respectively, in the former case and 0.4 and 0.1 Å in the latter.

Metal complexation/metallocomplex dissociation and thermal stability experiments

The following chemical parameters were studied for H(N-CH₃)TPP in comparison with H(N-CH₃)OEP (see Table 3):

(i) the rate constants of the metal M (M = Zn and X = Ac⁻ in our case) complexation according to Equation 1:



(ii) the rate constants of the metallocomplex dissociation according to the Equation 2:

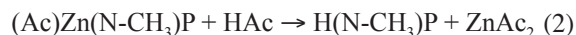


Table 2. Deviations of C_β atoms from the mean macrocycle plane (in Å). Quadrant numbering is shown on Fig. 1

Compound	Quadrant I		Quadrant II		Quadrant III		Quadrant IV		Four-quadrant average
	Actual	Average	Actual	Average	Actual	Average	Actual	Average	
H(N-CH ₃)TPP	-0.304	0.344	0.399	0.403	-0.298	0.345	0.881	0.885	0.494
	-0.383		0.407		-0.393		0.888		
H(N-CH ₃)OEP	0.047	0.027	-0.032	0.032	-0.007	0.023	-0.363	0.372	0.113
	-0.007		-0.032		0.040		-0.380		

Table 3. Characteristics of oxidative thermodestruction, porphyrin ligands (H₂P) coordination and their Zn-complexes (ZnP) solvoprotolytic dissociation^a

Compound	T _{init} , K ^b	k _v , l.mol ⁻¹ .s ⁻¹ ^c	k _{eff} × 10 ³ , s ⁻¹ ^d
H ₂ TPP	680	-	-
ZnTPP	613	very slow	0.26 ± 0.02
H(N-CH ₃)OEP	583	-	-
H(N-CH ₃)TPP	533	-	-
(Ac)Zn(N-CH ₃)OEP	485	0.55 ± 0.01	1.87 ± 0.09
(Ac)Zn(N-CH ₃)TPP	503	6.14 ± 0.15	26.65 ± 0.39

^a The characteristics are calculated according to [18]; in more detail the data of this table will be discussed elsewhere. ^b Initial temperature of thermodestruction. ^c Conditional H₂P complexation rate constant; DMSO, ZnAc₂, 298 K. ^d Effective ZnP dissociation constant; HAc, 298 K.

(iii) the temperature T_{init} of an initiation of the compound's thermodestruction (obtained in thermogravimetric experiments in the presence of air).

The rate constants of Zn complexation obtained for the N-substituted porphyrins are several orders of magnitude higher than those measured for the non-substituted (planar) analogs. On the other hand, the rate constant of Zn complexation found for H(N-CH₃)OEP is about one order of magnitude lower compared to H(N-CH₃)TPP.

The values of the effective rate constants (k_{eff}) for the metal dissociation process (2) (see Table 3), obtained in the glacial acetic acid (HAc), demonstrate that (Ac)Zn(N-CH₃)OEP dissociation is about 15 times slower comparing to more distorted (Ac)Zn(N-CH₃)TPP, but still is 7-fold faster relative to unsubstituted ZnTPP.

The temperature of the thermodestruction initiation is found to be maximum for planar H₂TPP and is reduced when going to nonplanar H(N-CH₃)OEP and H(N-CH₃)TPP by 97 and 147 degrees, respectively.

DISCUSSION

Porphyrin molecules with nonplanar distortion of the π-conjugated macrocycle have attracted considerable interest with respect of studying their chemical, spectral and photophysical properties. The number of works appeared within last decade demonstrating that the nonplanarity of the porphyrin macrocycle causes lowering of the S₁ state energy, shortening of the fluorescence lifetime and decrease of the fluorescence quantum yield due to enhancement of the internal conversion (IC) and intersystem crossing (ISC) radiationless deactivation channels [8-12].

In photophysical studies of nonplanar porphyrins performed so far only two approaches of the nonplanar

distortion generation were considered: (i) attaching bulky substituents on the porphyrin macrocycle periphery [8-10, 12], and (ii) insertion of two additional protons into the porphyrin core (*i.e.* a generation of the porphyrin diacids) [11]. The first way allowed studies of the nonplanarity influence on the properties of the free-base porphyrins as well as of the respective metallocomplexes, but at the expense of the possible (undesirable) electronic influence of numerous peripheral substituents onto the electronic properties of the macrocycle itself. At the same time, although the nonplanar porphyrin diacids are free of such electronic influence of the peripheral substituents, they are subjected to the influence of the attached acid residues, which are not completely "neutral" and probably can participate in excited state deactivation [19].

In the present study we investigated another, not so common type of nonplanar porphyrin molecules, which are distorted from planarity by means of chemical substitution at one of the nitrogen atoms in the center of the porphyrin macrocycle.

Double-exponential character of the fluorescence decay

As seen from Table 1, for both molecules studied the double-exponential decay is observed when the dominating (longer-lived) emission decay component is accompanied by the minor component having a smaller lifetime. The origin of double-exponentiality is not clear at this moment, and most likely it is caused by the presence of two conformations of the distorted porphyrins in the lowest excited singlet S₁ state, the two conformations having somewhat different deactivation rates to the ground state. Regarding the conformational landscape of the ground state, the steady-state emission and emission excitation experiments carried out for both molecules studied showed no evidence of any additional spectrally distinguishable ground state conformations.

It should be noted that similar double-exponential character of the emission decay was also found in previous studies of nonplanar porphyrin diacids of H₂TPP and H₂OEP [11] and for the set of nonplanar β-ethyl substituted derivatives of tetraphenylporphyrin [12]. It was suggested that such complex behavior of the emission decay was due to the conformational inhomogeneity of the S₁ state of the molecules studied [11-12]. Taking into account a minor contribution of the shorter-lived decay component, in the discussion below we shall consider only the dominating (longer-lived) emission decay component.

H(N-CH₃)TPP

The results of this study indicate that the influence of the N-methyl substitution on the porphyrin structure and photophysics is different for tetraphenylporphyrin as compared to octaethylporphyrin. The quantum-chemical calculations indicated that the presence of the methyl group in the center of the porphyrin core of H(N-CH₃)TPP produces a considerable nonplanar distortion of this molecule. Despite the fact that the methyl group is bound only to one of the four pyrrole rings, all of them demonstrate marked out-of-plane displacements (see Table 2). As follows from the data of Table 2, the minimal deviation of the β carbon atoms from the mean macrocycle plane is about 0.3 Å, and the maximum deviation, observed for the β carbons of the pyrrole ring actually bearing the methyl group is about 1 Å. This value is comparable to the length of C-C bond and is quite typical for severely distorted nonplanar porphyrins like H₂OETPP [20] or H₂DPP [21]. It is, therefore, reasonable to expect that photophysical properties of H(N-CH₃)TPP should resemble those of other nonplanar porphyrins studied to date, and that was actually found. The considerable bathochromic shift of absorption and emission, which was observed here for H(N-CH₃)TPP, is common for nonplanar porphyrins. The values of the long-wavelength shift of absorption bands of ~30-50 nm (and even more) are quite typical for nonplanar peripherally substituted porphyrins [8-10, 12]. In the case of H(N-CH₃)TPP, the absorption and emission bands are less shifted to the red (15-30 nm) as compared to "classical" nonplanar porphyrins that correlates well with smaller average nonplanarity of the former (0.5 Å for H(N-CH₃)TPP as compared to ~1.0 Å for peripherally substituted porphyrins such as H₂OETPP and H₂DPP [8-10, 12]).

The increased Stokes shift of the fluorescence spectrum found for H(N-CH₃)TPP (up to 260 cm⁻¹) relative to parent H₂TPP (140 cm⁻¹) is also quite typical for nonplanar porphyrins. The spectral interval between the maxima of emission and longest-wavelength absorption band can reach 1000 cm⁻¹ for nonplanar porphyrins bearing multiple peripheral substituents, and this is considered as the evidence of high flexibility of nonplanar porphyrins relative to planar analogs and is a manifestation of the conformational relaxation taking place in the S₁ state [11-12]. However, the most prominent feature of the nonplanar porphyrins is a considerable reduction of the S₁ state lifetime. As was shown previously, the nonplanar macrocycle distortions lead to an increase of the emission decay by an order of magnitude, and in some instances even by two-three orders of magnitude [8-10]. This effect originates from the considerable increase of rate (and efficiency) of

radiationless deactivation – both internal conversion and intersystem crossing, and, in addition to increasing of the S₁ state decay, provides a decrease of the fluorescence quantum yield [8-10]. Such a feature, although not so prominent, was observed in the present work for H(N-CH₃)TPP: the emission for this molecule in toluene decays twice as fast as for the parent unsubstituted H₂TPP. The S₁ state lifetime for H(N-CH₃)TPP decreases even further with increase of the temperature of media and when more polar solvents are used (like DMF, see Fig. 3 A,B and Table 1). These findings resemble the temperature and solvent polarity dependence of the emission decay rates observed earlier for nonplanar porphyrin diacids and a number of nonplanar peripherally substituted porphyrins [11-12]. The reduction of the S₁ state lifetime with increase of temperature is supposed to reflect some barrier crossing in the course of excited state deactivation, and the barrier height estimate obtained for H(N-CH₃)TPP (assuming Arrhenius-type reaction) as 3.3 kcal/mol is of the same order as that measured in reference 11 for nonplanar diacids of H₂TPP and H₂OEP (3.7-4.0 kcal/mol) and two-three times bigger than the value obtained in reference 12 for the set of nonplanar β -ethyl substituted derivatives of tetraphenylporphyrin (0.6-1.5 kcal/mol in toluene).

The finding that the emission lifetime of H(N-CH₃)TPP is subjected to further decrease in the solvents of higher polarity could be easily explained in the framework of the model suggested in reference 12. The idea is that the nonplanar macrocycle distortions of certain types and symmetry (*e.g.* saddle-type nonplanarity) provide the molecules with considerable static dipole moment (~1-2 D) approximately perpendicular to the mean macrocycle plane. Use of solvents of high polarity stimulates enhancement of the dipole moment that proceeds via an increase of nonplanar macrocycle distortions of the molecule. In turn, the increase of molecular nonplanarity causes a further shortening of the S₁ state lifetime.

It is worth noting that the described strong dependence of S₁ state deactivation rate on surrounding medium temperature and polarity is characteristic of namely nonplanar porphyrins and is not regularly observed for their planar analogs.

H(N-CH₃)OEP

The geometry optimization calculations performed for H(N-CH₃)OEP demonstrated that in this case the methyl group introduced into the porphyrin core provides relatively small average deviation of the macrocycle from planarity. As is illustrated in Table 2 for H(N-CH₃)OEP, the average value of the β carbons deviation from the mean macrocycle plane is quite small, ~0.1 Å. Some "classical" porphyrins like H₂TPP

are considered planar but possess nonplanar deviation of the macrocycle carbons of comparable value [22]. Therefore, based only on the average nonplanar distortion, the H(N-CH₃)OEP molecule could be similarly assigned to the planar type of molecules. The detailed examination of the calculated structural parameters presented in Table 2 indicates that one of the pyrrole rings, actually bearing the methyl group, undergoes noticeable structural perturbation with β carbons displacement of ~ 0.4 Å. It seems unlikely that this relatively modest distortion of one of the pyrrole rings, while the average distortion magnitude being really weak, could alter the photophysics of H(N-CH₃)OEP towards what is documented for highly nonplanar porphyrins. Indeed, basing on the conclusions of an earlier publication [12], one could expect the photophysical properties of sterically constrained porphyrins to be governed by the average degree of nonplanarity rather than the peak values. Though not completely but for H(N-CH₃)OEP this expectation proved to be correct (*vide supra*).

As was evidenced by the steady-state absorption and emission data obtained for H(N-CH₃)OEP, this molecule shows a considerable (~ 5 –20 nm) bathochromic shift of absorption and emission bands as a result of N-methyl substitution. Although it is accepted in the literature that nonplanar macrocycle distortions of the porphyrins result in a large bathochromic shift of absorption and emission bands, the opposite statement does not necessarily take place. Therefore, generally speaking, it is not always possible to conclude that there is considerable nonplanar distortions basing only on the red-shifted absorption and emission bands. The good example of such situation is the present case of H(N-CH₃)OEP, because this molecule manifests no photophysical features typical for nonplanar sterically constrained porphyrins other than the red shift of absorption and emission. For instance, in contrast to majority of nonplanar porphyrins studied so far, H(N-CH₃)OEP shows no increase of the Stokes shift comparing to parent H₂OEP. Next, the time-resolved emission experiments discovered quite a long emission lifetime of H(N-CH₃)OEP (~ 9 ns) that is of similar magnitude as that for parent unsubstituted H₂OEP [11]. That means that the N-substituted derivative of octaethylporphyrin does not possess the most remarkable photophysical feature of nonplanar porphyrins, *i.e.* considerable shortening of the S₁ state lifetime relative to planar porphyrins. This prompts us to conclude that the bathochromic shift of electronic spectra of H(N-CH₃)OEP originates from some specific electronic effect of N-methyl substitution but not from the macrocycle nonplanarity. Therefore, despite the large red shift of the absorption and emission bands, the number of photophysical parameters does not allow H(N-CH₃)OEP to enter the class of nonplanar

porphyrins, and such a conclusion agrees well with the above-mentioned results of semi-empirical calculations.

Supporting the idea of principal distinctions of photophysics of H(N-CH₃)OEP from the properties of typical nonplanar porphyrins, H(N-CH₃)OEP does not display any increase of the S₁ state deactivation rate in more polar media and shows no such striking emission lifetime reduction with rise of temperature as found here for H(N-CH₃)TPP (see Table 1), for nonplanar diacids of H₂TPP and H₂OEP [11], and for the set of nonplanar β -ethyl substituted derivatives of TPP [12]. The weak decrease of the emission lifetime still seen for H(N-CH₃)OEP in toluene when the temperature is increased is of the same origin as for planar H₂TPP and is caused by differences in concentration/diffusion rate of molecular oxygen present in the sample at different temperatures. As we found in our experiments with H₂TPP, the major emission decay component (comprises 95% of the decay) for this compound in toluene manifests a slight lifetime shortening with rise of temperature, from 10.22 ns at 276 K to 8.83 ns at 343 K, which we associate with change in the rate of S₁ state quenching by molecular oxygen (data not published).

Metal coordination/metallocomplex dissociation and thermal stability experiments

The results of reactivity studies of the two N-substituted porphyrins investigated, *i.e.* the metal coordination ability of the free-base porphyrins and stability of the respective metallocomplexes in protic media, as well as a stability for thermooxydation of both free-base and metalloporphyrins serve as an indirect support of distinction between H(N-CH₃)TPP and H(N-CH₃)OEP in the degree of their macrocycle nonplanarity (see Table 3).

The fact that the rate of the Zn complex formation following reaction 1 is approximately an order of magnitude slower for H(N-CH₃)OEP relative to H(N-CH₃)TPP provides reasons to expect the structure of the former compound to be more planar. Compared to planar not-substituted porphyrins, both N-substituted free-base porphyrins demonstrate a considerable increase of the rate of Zn coordination.

Additional evidence of substantial nonplanarity of H(N-CH₃)TPP is given by the high value of the dissociation rate of its Zn complex in protic solvents. As was already mentioned, the effective rate constant (k_{eff}) of the process 2 obtained in glacial acetic acid for (Ac)Zn(N-CH₃)OEP is ~ 15 times lower than for more distorted (Ac)Zn(N-CH₃)TPP but still 7-fold faster than for planar ZnTPP, *i.e.* the stability of the metallocomplexes in protic media is in good qualitative agreement with the degree of macrocycle planarity in the series ZnTPP > (Ac)Zn(N-CH₃)OEP

> (Ac)Zn(N-CH₃)TPP, expected from other data obtained.

The thermal stability of the π -system serves as an indirect criterion of its aromaticity, which in turn is closely related to the planarity of the macrocycle. In this regard one can judge that the temperatures of destruction initiation T_{init} , obtained by the thermogravimetric method for H(N-CH₃)OEP, H(N-CH₃)TPP, as well as H₂TPP and the corresponding Zn(II)-complexes (see Table 3) indicate larger nonplanarity of H(N-CH₃)TPP in comparison to H(N-CH₃)OEP. In the case of the zinc complexes of N-substituted porphyrins the thermodestruction of a molecule starts not by breakdown of the conjugated π -system, but, instead, by a release of the N-substituent. Therefore, for zinc complexes of N-substituted porphyrins a value of T_{init} is predominantly determined by the basicity of the substituted nitrogen atom, which is higher for (Ac)Zn(N-CH₃)OEP compared to (Ac)Zn(N-CH₃)TPP [2].

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