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Fluorescence study of some deformed zinc(II) porphyrins

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Abstract

The effect of deformation in the porphyrin ring on the emission properties of a series of zinc(II) derivatives of basket handle porphyrins is reported. Emission from the upper excited S_2 state is observed in all zinc(II) deformed porphyrins. The porphyrin ring deformation results in red shifts of both the S_1 and S_2 emission bands and perturbed lifetimes of the S_1 state. Decreased quantum yields and increased intersystem crossing rates are also caused by porphyrin ring deformation. The decrease in the S_1 fluorescence yields can be interpreted in terms of an enhancement of the non-radiative rate, whereas a reduction in the energy gap between the S_2 and S_1 states results in low S_2 quantum yields relative to planar derivatives.

Keywords: Deformation; Fluorescence; Zinc(II) porphyrins

1. Introduction

Interest in the role played by conformational distortion of porphyrins in the function of many biomolecules has prompted the synthesis of many substituted porphyrins in which deformation from planarity is induced by several methods [1]. Recently, we have synthesized a series of deformed basket handle porphyrins by covalent attachment of a short bridging chain across the periphery [2,3]. Detailed studies of the electronic structure have indicated that the properties can be significantly altered by permanent distortion of the porphyrin ring [4,5]. It has also been observed that structural perturbations of porphyrin macrocycles alter the rates and yields of the fundamental excited state deactivation processes [6,7]. However, studies on the effect of non-planarity on the fluorescence properties of porphyrins are still very rare. Studies on the photophysical properties of basket handle porphyrins have suggested that deformation influences significantly the fluorescence peak maxima, quantum yields and lifetimes [8,9]. In this report, we extend our study of the effect of porphyrin ring deformation to a series of Zn(II) derivatives of basket handle porphyrins. Fluorescence originating from the S_2 level of the porphyrin ring (in addition to the S_1 level) is observed in all the porphyrins described here (Fig. 1). The red shifts of the emission bands and the reduction in the quantum yields and lifetimes are linearly correlated with the degree of porphyrin ring deformation.

2. Experimental details

The synthesis of zinc(II) derivatives of basket handle porphyrins has been described previously [2,10,11]. The synthesis of β-halogenated porphyrins will be reported elsewhere [12]. The solvent was toluene which was used as supplied (A.R. grade). All the experiments were performed without degassing the solvent. Steady state fluorescence measurements were performed using a Shimadzu RF-540 fluorometer. The fluorescence quantum yields ϕ_f of various zinc(II) basket handle porphyrins were estimated from the emission and absorption spectra by a comparative method [13] using the equation

$$\phi_f = \frac{[F(\text{ZnBHP})]\,[A(\text{ZnTPP})]}{[F(\text{ZnTPP})]\,[A(\text{ZnBHP})]} \times \phi_f(\text{ZnTPP}) \qquad (1)$$

where $[F(\text{ZnBHP})]$ and $[F(\text{ZnTPP})]$ are the integrated fluorescence intensities of the corresponding zinc(II) basket handle porphyrin and zinc(II) tetraphenylporphyrin respectively, $[A(\text{ZnBHP})]$ and $[A(\text{ZnTPP})]$ are the absorbances of ZnBHP and ZnTPP respectively at the excitation wavelength and $\phi_f(\text{ZnTPP})$ is the quantum yield of ZnTPP. $\phi_f(\text{ZnTPP})$ for S_1 emission was 0.033 and for S_2 emission was 0.00039 [14].

The time-resolved fluorescence decay measurements were carried out using the experimental set-up described previously [15]. The light source was a rhodamine 6G dye laser (pulse width, 6–10 ps; tunability, 570–630 nm; cavity-dumped repetition rate, 800 kHz) derived from a continuous

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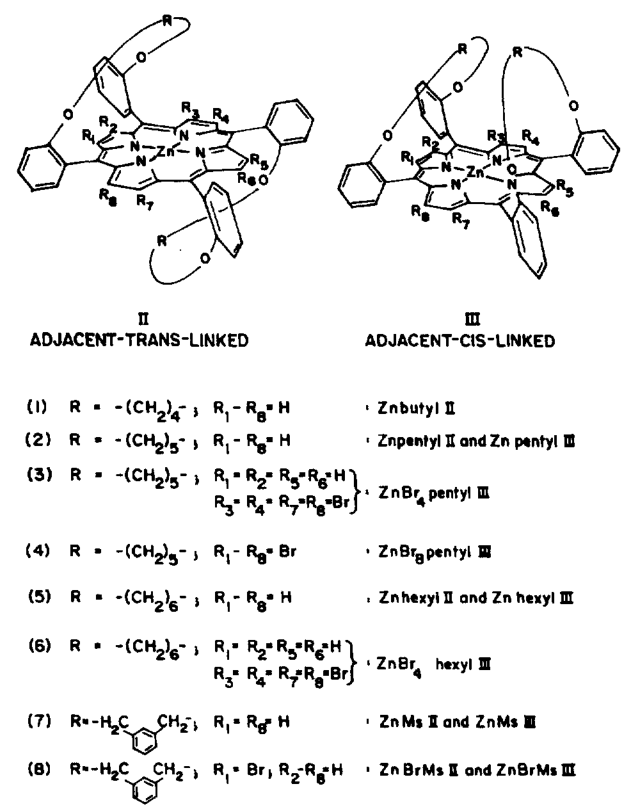

Fig. 1. Structures of various Zn^{2+} basket handle porphyrins.

wave (CW), mode-locked, frequency-doubled Nd:YAG laser. The full width at half-maximum (FWHM) of the instrument response function was typically 80–100 ps using a microchannel photomultiplier (Hamamatsu R2809). Fluorescence decays were obtained at the magic angle (54.7°). The porphyrins were excited at 600 nm and emission was detected at different emission wavelengths depending on the emission peak positions of the porphyrins. All the decays were adequately fitted to single exponential equations. The decays were convoluted by the instrument response function using a non-linear, least-squares method described previously [16].

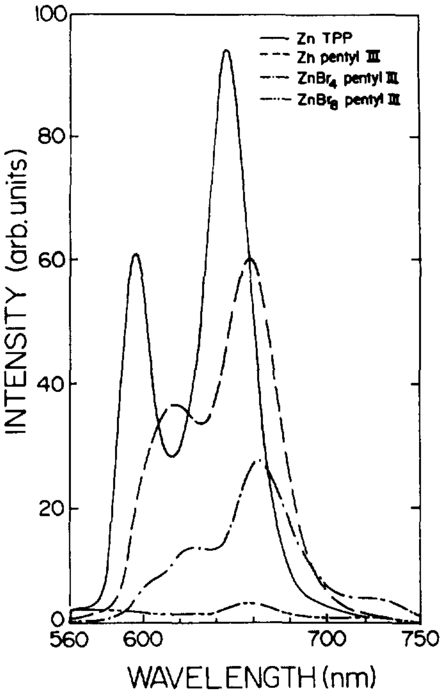

Fig. 2. Comparison of steady state S_1 fluorescence emission spectra of various Zn^{2+} basket handle porphyrins with ZnTPP in toluene. All the spectra were recorded at 25 °C at an excitation wavelength of 430 nm.

3. Results and discussion

3.1. S_1 fluorescence

In order to understand the effect of porphyrin ring deformation on the emission properties, the fluorescence spectra of various zinc(II) basket handle porphyrins and planar ZnTPP are displayed in Fig. 2 and the emission data are given in Table 1. It is clear from Fig. 2 that the fluorescence bands of zinc(II) basket handle porphyrins are red shifted compared with those of planar ZnTPP. Inspection of Table 1 reveals that the red shifts are linearly related to the degree of deformation. Earlier spectral and electrochemical studies have indicated that the introduction of a short bridging chain across

Table 1
Emission data of Zn^{2+} basket handle porphyrins in toluene ($T=25$ °C)

Porphyrin	$B_{(0,0)}$ λ_{max} (nm)	$\phi_f(S_2)$ ($\times 10^4$)	$Q_{(0,0)}$ λ_{max} (nm)	$Q_{(0,1)}$ λ_{max} (nm)	$\phi_f(S_1)$ [a]	$\Delta E(S_2$–S_1 ($\times 10^{-3}$ cm^{-1})
ZnTPP	433	3.9	598	647	0.033	6.69
Znbutyl II	448	3.2	626	–	0.019	6.35
Znpentyl II	440	3.5	613	653	0.023	6.23
Znpentyl III	442	3.6	609	652	0.024	6.15
$ZnBr_4$pentyl III	442	0.34	623	663	0.001	6.57
$ZnBr_8$pentyl III	440	<0.2	618	655	<0.001	6.54
Znhexyl II	436	3.7	599	647	0.028	6.28
Znhexyl III	437	3.1	603	647	0.024	6.30
$ZnBr_4$hexyl III	441	0.50	601	655	0.0026	6.04
ZnMS II	443	3.4	618	660	0.022	6.39
ZnBrMS II	442	0.63	610	662	0.002	6.23
ZnMS III	444	–	610	660	–	6.13
ZnBrMS III	441	–	605	662	–	6.14

[a] Error bar for $\phi_f(S_1) = \pm 0.001$.

the porphyrin periphery induces significant distortion in the porphyrin skeleton, making the porphyrin core non-planar; shorter chains induce larger non-planarity [2,10]. The introduction of bromines at the β carbons of basket handle porphyrins further enhances the degree of deformation [3]. The observed red shifts are in line with this. The largest red shifts are observed for the most distorted halogenated derivatives. Furthermore, it is well established from theoretical calculations on a variety of distorted metalloporphyrins, as well as from earlier experimental data on a series of non-planar porphyrins, that the non-planarity in the porphyrin ring reduces the energy gap between the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs), which is spectroscopically manifested in a red shift of the emission bands relative to the corresponding planar porphyrins [17,18].

All zinc(II) basket handle porphyrins are weakly fluorescent compared with ZnTPP. The quantum yields are very low for β-substituted porphyrins. Reduced quantum yields have also been observed recently for sterically crowded non-planar porphyrins [6]. It was concluded that the reduced quantum yields of sterically perturbed porphyrins are due to the decreased S_1 state lifetime. The decrease in the S_1 state lifetime mainly depends on increased $S_1 \rightarrow T_1$ intersystem crossing and increased $S_1 \rightarrow S_0$ internal conversion rates. The increased internal conversion rate has been attributed to the enhancement of the Franck–Condon factor associated with structural reorganization in the excited state, and the increased intersystem crossing rate has been assigned to the enhancement of the spin–orbit coupling caused by the non-planarity of the porphyrin macrocycle [6,7]. To understand these effects in our zinc(II) basket handle porphyrins, we have carried out time-resolved studies. The fluorescence decays of all the porphyrins were fitted to a single exponential. The fluorescence decay of Znbutyl II is shown in Fig. 3 and the lifetime data are presented in Table 2. The rate of radiative decay k_r and the rate of intersystem crossing k_{nr} were calculated using the following equations

$$\tau_0 = \tau_f / \phi_f \qquad (2)$$

$$k_r = 1/\tau_0 \qquad (3)$$

$$k_{nr} = k_r[(1-\phi_f)/\phi_f] \qquad (4)$$

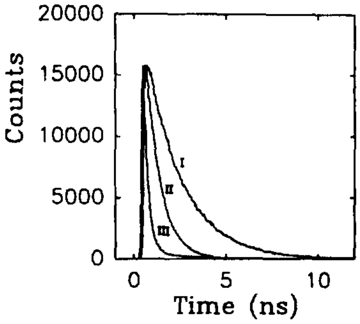

Fig. 3. Fluorescence decay profiles of ZnTPP (I), Znbutyl II (II) and ZnBrMS II (III) in toluene. The excitation wavelength was 580 nm and the emission wavelength was 625 nm. The fluorescence decay was detected at the magic angle (54.7°).

Table 2
Analysis of photophysical data of various Zn^{2+} basket handle porphyrins in toluene

Porphyrin	τ_f^a (ns)	$k_r \times 10^{-7}$ (s^{-1})	$k_{nr} \times 10^{-7}$ (s^{-1})
ZnTPP	1.96	1.68	49.17
Znbutyl II	0.73	2.59	133.72
Znpentyl II	2.21	1.04	44.17
Znpentyl III	1.04	2.31	93.94
$ZnBr_4$pentyl III	0.13	1.00	768.23
$ZnBr_8$pentyl III	<0.05	<1.0	$>10^3$
Znhexyl II	2.24	1.25	43.39
Znhexyl III	1.95	1.23	50.06
$ZnBr_4$hexyl III	0.17	1.50	574.42
ZnMS II	1.11	1.99	88.46
ZnBrMS II	0.19	1.25	522
ZnMS III	1.00	–	–
ZnBrMS III	0.39	–	–

[a] In a few cases, the decay was fitted to a two exponential function. The minor component, which has a contribution of less than 5%, is neglected assuming that it is due to impurities.

Table 2 reveals that the deformation in the porphyrin ring reduces the lifetimes significantly. The decrease in the fluorescence decay rate k_r and the increase in the rate of non-radiative decay k_{nr} are also due to deformation effects. The maximum effects are observed for β-halogenated derivatives. Generally, internal conversion accounts for about 20% of the decay of the S_1 state in porphyrins. Therefore the decrease in the quantum yields is due to the decreased S_1 state lifetimes and, possibly, to increased $S_1 \rightarrow T_1$ intersystem crossing rates. Intersystem crossing in porphyrins depends on the wavefunction overlap involving the central nitrogens of the macrocycle, and this may be facilitated by out-of-plane distortions in S_1, T_1 or both, enhancing spin–orbit coupling in non-planar porphyrins. In β-halogenated porphyrins, the much lower quantum yields are due to a further increase in spin–orbit coupling, caused by the heavy halogens, resulting in higher intersystem crossing rates. Thus the low quantum yields of deformed porphyrins are due to the combined effects of increased rates of internal conversion and intersystem crossing.

3.2. S_2 fluorescence

In addition to fluorescence from the S_1 state, all zinc(II) basket handle porphyrins emit from the second excited singlet state $S_2 \rightarrow S_0$. A comparison of the S_2 fluorescence of zinc(II) basket handle porphyrins with that of ZnTPP is shown in Fig. 4. The inset shows the mirror image relationship between the Soret fluorescence and the Soret absorption for ZnBrMS II.

Although S_2 fluorescence has been observed in a number of cases [19–21], the conditions under which a molecule emits from the higher level S_2 state are not very clear. The detection of Soret fluorescence is very difficult because of the scattered incident light and the re-absorption by the intense Soret band. These problems can be overcome by

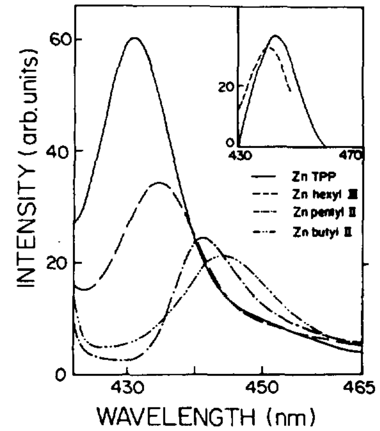

Fig. 4. S_2 fluorescence spectra of Zn^{2+} basket handle porphyrins and ZnTPP in toluene. The excitation wavelength was 415 nm. The inset shows the emission (———) ($\lambda_{ex}=415$ nm) and excitation (- - -) ($\lambda_{em}=442$ nm) spectra of ZnBrMS II.

excitation at wavelengths considerably shorter than the Soret absorption maximum and by the use of very dilute solutions. All porphyrins in the present study were excited at 415 nm, approximately 25 nm below the Soret absorption maximum. The S_2 emission was observed only on excitation at the Soret absorption. This indicates that it is not due to thermal repopulation of S_2 from S_1. Furthermore, the ability of deformed porphyrins to emit from the Soret band level suggests the following: (1) the two common (π,π^*) excited state configurations ($^1(a_{1u}e_g)$ and $^1(a_{2u}e_g)$) are accidentally degenerate and the energy surfaces of the S_1 and S_2 excited states are parallel; this retards $S_2 \rightarrow S_1$ intramolecular relaxation; (2) there is no triplet excited state between S_1 and S_2 excited states [22].

The effect of deformation is also reflected in the S_2 emission properties. The S_2 emission band is red shifted and the quantum yields are reduced in zinc(II) deformed porphyrins relative to ZnTPP. The magnitude of the red shift and the decrease in the fluorescence yield depend on the degree of deformation, and the maximum effects are observed for the most deformed β-halogenated porphyrins. The reduced quantum yields can be accounted for in terms of the reduction in the energy gap ΔE between S_2 and S_1 in distorted zinc(II) porphyrins compared with ZnTPP (Table 2). Earlier workers arrived at the conclusion that the ratio of $S_2 \rightarrow S_1$ internal conversion, which is the main source of decay from the S_2 state, is linearly related to the energy gap between the S_2 and S_1 excited states [19]. Thus the decrease in the energy gap between the S_1 and S_2 states in the distorted zinc(II) porphyrins raises the possibility of a faster rate of $S_2 \rightarrow S_1$ internal conversion which, in turn, results in lower quantum yields.

4. Conclusions

Emission from the upper excited S_2 state is observed in addition to the usual S_1 emission in deformed zinc(II) porphyrins. Deformation in the porphyrin ring results in a red shift of the emission bands due to the reduction in the energy gap between HOMO and LUMO relative to the planar derivative. The reduction in the quantum yields of both S_1 and S_2 state emissions is due to the non-planarity in the porphyrin macrocycle.

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