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Charge transfer excited states of zinc(II) derivatives of β-substituted dinitrotetraphenylporphyrin

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Abstract

The photophysical properties of the zinc(II) derivatives of five isomers of dinitrotetraphenylporphyrin were investigated in seven different solvents of varying polarity. The red shift of the optical absorption band and the enhanced oscillator strength of the Q(0,0) transition are highly specific of the nature of the isomers. The solvatochromic effect on the emission data of the isomers reveals large structural changes on excitation. The excited state geometries of the isomers involve the partial rotation of the nitro groups about the plane of the porphyrin. The multiexponential decay of the excited singlet state of these isomers suggests a broad angular distribution of the emitting state. The magnitude of the excited state dipole moment and the low value of the transition moment of the isomers point to the possible existence of twisted intramolecular charge transfer in the excited singlet state.

Keywords: Solvatochromic effect; Five isomers of Zn(II) derivatives of β-substituted dinitro tetraphenylporphyrin

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1. Introduction

The investigation of intramolecular charge transfer (ICT) in the photoexcited states of porphyrin systems bearing acceptor groups in the peripheral positions is of contemporary research interest and relevant to the understanding of the primary reactions of photosynthesis. The good π-acceptor properties of nitro groups make the nitro-substituted porphyrins an interesting system for the study of photophysical properties. Of the various peripheral positions of the porphyrin at which substitution is possible, the covalent attachment of nitro groups at the pyrrole carbons is most desirable in view of the proximity of the acceptor group to the donor π-ring. Recent studies [1,2] on the steady state absorption and emission spectroscopy of β-substituted mononitrotetraphenylporphyrin and its zinc(II) derivative reveal the existence of ICT in the lowest excited singlet state. Although the nature of the geometrical structure of the emitting charge transfer state is not very clear, the excited state properties closely resemble those of a twisted intramolecular charge transfer (TICT) state [3]. The TICT state is often characterized in systems in which the orientation of the donor and acceptor entities is mutually perpendicular, thereby confirming the minimum overlap rule. The inclusion of interaction with the solvents in the TICT model has been proposed whenever the donor/acceptor involved is a large π-system [4].

The present work is concerned with the elucidation of the photophysical properties of the zinc(II) derivatives of five isomers of β-substituted dinitrotetraphenylporphyrin (Fig. 1). We focus on the effects of the solvent on the charge transfer fluorescence maxima, halfwidths, quantum yields, lifetime of the excited states and radiative rate constants to obtain information on the nature of the excited states. The relative ease of rotation

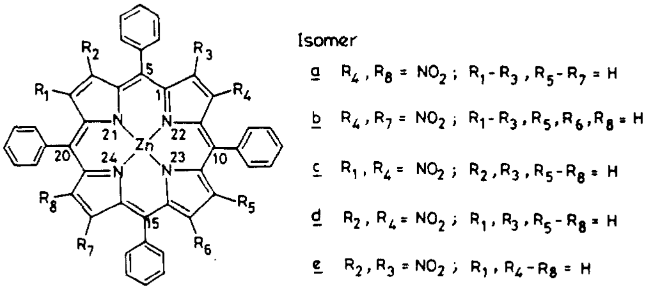

Fig. 1. Structure of zinc(II) derivatives of five isomers of dinitrotetraphenylporphyrin.

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of the nitro groups about the single bond (with pyrrole carbons) permits a large number of geometrical conformations and these constitute variables in the study of the geometrical structure of the excited states. The isomer-specific photophysical properties can be used to evaluate the thermodynamics of photoinduced charge separation processes in these systems.

2. Experimental details

The free-base porphyrins were prepared by the nitration of the copper(II) derivative of mesotetraphenylporphyrin (CuTPP) with fuming nitric acid followed by demetallation. The isomers were separated by thin layer chromatography (TLC) and the R_f values of the isomers **a** : **b** : **c** : **d** : **e** were 1.00 : 0.94 : 0.84 : 0.78 : 0.69. The different isomers were characterized by dynamic proton nuclear magnetic resonance (^{1}H NMR) [5]. The structure of one of the isomers (**b**) determined by single crystal studies has provided support for the characterization of the isomers [6]. The zinc(II) derivatives were prepared according to the method described in the literature [7]. Recrystallized zinc(II) acetate tetrahydrate and free-base porphyrin in a molar ratio of 2 : 1 were dissolved in a minimum amount of a mixture of CH_3OH and $CHCl_3$ (1 : 1, v/v). The mixture was stirred at 60 °C for 15 min and the metallated product was purified by TLC. The zinc(II) derivatives of the various isomers of dinitrotetraphenylporphyrins were found to be spectroscopically pure. ^{1}H NMR (270 MHz) in $CDCl_3$ ppm (J, Hz): **Zna**: 9.16 (s, 2), 8.94–8.92 (d, 2, $J=4.9$), 8.88–8.85 (d, 2, $J=4.9$), 8.19–8.14 (m, 8), 7.78–7.51 (m, 12); **Znb**: 9.16 (s, 2), 8.88, 8.87 (2s, 4), 8.19–8.14 (m, 8), 7.79–7.69 (m, 12); **Znc**: 9.14 (s, 2), 8.91–8.90 (d, 2, $J=4.8$), 8.83–8.81 (d, 2, $J=4.8$), 8.16–8.14 (m, 8), 7.65–7.81 (m, 12); **Znd**: 9.14 (s, 1), 9.12 (s, 1), 8.93–8.81 (m, 4), 8.36–8.12 (m, 8), 7.78–7.52 (m, 12); **Zne**: 9.09 (s, 2), 8.87–8.86 (d, 2, $J=4.9$), 8.84–8.83 (d, 2, $J=4.9$), 8.15–7.94 (m, 8), 7.78–7.51 (m, 12).

The optical absorption spectra were obtained using a Hitachi U-3400 spectrophotometer with a pair of matched quartz cells (path length, 10 mm). The fluorescence spectra were measured using a Hitachi 650-60 fluorescence spectrometer. The right angle detection method was employed. The steady state quantum yields of fluorescence (ϕ_f) of the isomers were calculated using the methods described previously [8]. The singlet excited state decay measurements were carried out using a picosecond laser excitation, time-correlated, single-photon counting method with the experimental apparatus described in Ref. [9]. The analysis of the fluorescence decay data to fit a single or multiexponential function was carried out by the non-linear least-squares method using iterative reconvolution and Marquardt's procedure for the optimization of parameters.

All the solvents used in this study were of Fluka Puriss grade and were distilled and dried before use. The solution for optical studies was prepared under a blanket of argon and protected from light. The concentrations of the solutions employed in this study were well within the range of no detectable intramolecular interaction. The solvents showed no luminescence at the sensitivity used.

The optimized geometries of the various isomers were obtained using MMX calculations [10]. The output of these calculations was used for AM1 calculations [11]. The energies of the states of the various zinc(II) derivatives obtained from these studies were used in a discussion of the experimental results.

3. Results

The optical absorption spectra of the zinc(II) derivatives of two representative isomers in different solvents are shown in Fig. 2. The optical absorption data in solvents of different polarity are given in Table 1. The oscillator strengths of the transitions were calculated using the expression [12]

$$f=4.33\times10^{-9}\epsilon\nu_{1/2} \qquad (1)$$

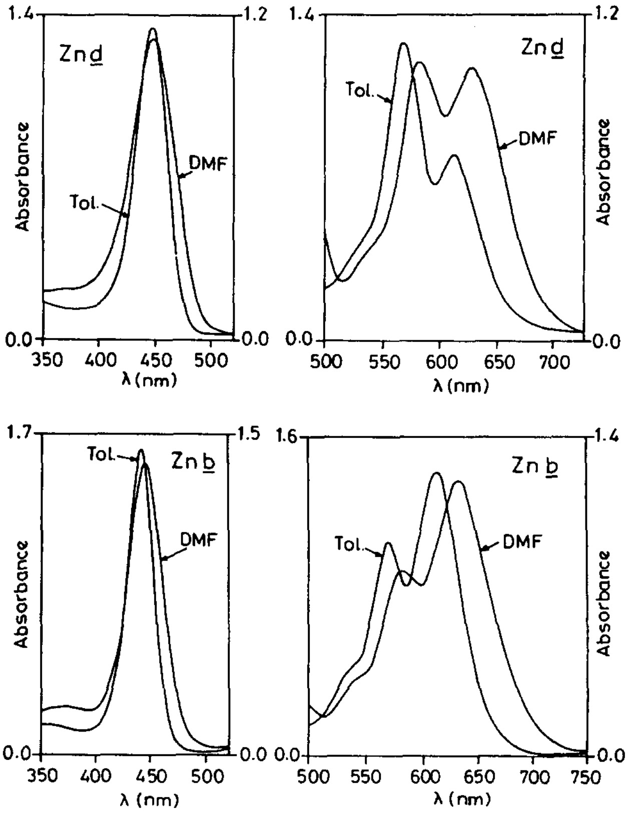

Fig. 2. Optical absorption data of **Znb** and **Znd** in N,N- dimethylformamide (DMF) and toluene (Tol) at 300 K.

Table 1
Optical absorption data of the zinc(II) derivatives of the five isomers of dinitrotetraphenylporphyrin in different solvents at 300 K

Isomer	Solvent	λ_{max} (log ϵ)			B(0,0)	Q(0,0)
		B(0,0)	Q(1,0)	Q(0,0)	$\nu_{1/2}$ (cm^{-1})	f
Zna	Toluene	439.5 (5.33)	569.5 (3.96)	631.9 (4.14)	1400	0.074
	CH_2Cl_2	437.0 (5.25)	565.0 (3.95)	613.0 (4.13)	1700	0.079
	DMF	443.0 (5.12)	581.0 (3.86)	630.2 (4.06)	1840	0.086
Znb	Toluene	441.3 (5.39)	569.4 (3.98)	615.3 (4.10)	1420	0.073
	CH_2Cl_2	437.4 (5.29)	567.6 (4.00)	613.1 (4.14)	1780	0.077
	DMF	445.1 (5.13)	582.3 (3.92)	632.7 (4.08)	1880	0.084
Znc	Toluene	444.0 (5.26)	568.3 (4.17)	617.8 (3.95)	1420	0.042
	CH_2Cl_2	440.0 (5.20)	565.9 (4.18)	614.4 (3.97)	1710	0.056
	DMF	445.6 (5.16)	579.5 (4.07)	631.2 (4.04)	2020	0.074
Znd	Toluene	446.3 (5.30)	570.8 (4.12)	616.6 (3.94)	1610	0.049
	CH_2Cl_2	443.1 (5.26)	568.2 (4.13)	616.4 (3.94)	2000	0.063
	DMF	449.4 (5.19	582.8 (4.03)	628.2 (4.02)	2340	0.077
Zne	Toluene	446.0 (5.22)	570.2 (4.07)	618.2 (3.93)	1460	0.044
	CH_2Cl_2	442.1 (5.16)	567.8 (4.03)	616.3 (3.92)	1850	0.052
	DMF	451.5 (5.08)	581.5 (3.93)	636.9 (3.98)	2180	0.069

DMF, *N*,*N*-dimethylformamide.

where ϵ is the molar absorption coefficient (dm^3 mol^{-1}) and $\nu_{1/2}$ is the full width at half-maximum (cm^{-1}). It can be seen that the zinc(II) derivatives of the five isomers of dinitrotetraphenylporphyrin exhibit typical porphyrin spectra with the appearance of an intense Soret band (B) followed by Q transitions [13]. The B and Q bands of the isomers are considerably red shifted relative to that observed for unsubstituted zinc tetraphenylporphyrin (ZnTPP) and its mononitro derivative $ZnTPPNO_2$ [2]. Moreover, the substitution of the nitro groups results in the broadening of the B(0,0) and Q(0,0) bands accompanied by a large increase in the oscillator strength of the Q(0,0) band; the longest wavelength transition exhibits a relatively larger f value (approximately 1.5 times) for isomers **Zna** and **Znb** than for **Znc**, **Znd** and **Zne**. The difference in the f values observed for the various isomers clearly demonstrates the importance of the position of substitution of the nitro groups in modulating the transition probability of the Q bands.

We then examined the effect of the solvent polarity on the optical absorption bands of the isomers. The B and Q bands of the porphyrins exhibit a red shift with increasing polarity of the solvent. The magnitude of the red shift of the Q bands depends on the nature of the solvent as: DMF > toluene > CH_2Cl_2. The red shift of the Q(0,0) bands is 4–5 times larger than that of the B(0,0) band. Both the B(0,0) and Q(0,0) bands become progressively broadened with increasing polarity of the solvent; however, the B(0,0) band exhibits only a small change in the f value, whereas the Q(0,0) band displays a larger increase in f value with increasing polarity of the solvent. It is interesting to note that the effect of the polarity of the solvent on the f value of the Q transition is larger for **Znc**, **Znd** and **Zne** relative to that observed for isomers **Zna** and **Znb**. This leads to the suggestion that **Znc**, **Znd** and **Zne** are more polar, thereby exhibiting greater interaction with the solvent. As shown later the polar nature is directly related to the relative arrangement of the nitro groups in the isomers. It is known that strongly polar solvents, such as DMF, can interact with zinc(II) derivatives to form axially coordinated complexes [14]. The existence of the complexes is often revealed by a red shift of the absorption bands and a change in intensity of the transitions. All the zinc(II) derivatives of the isomers exhibit red-shifted B and Q bands with significant changes in intensity of the transitions, indicating possible solvation/coordination of the solvent.

The corrected fluorescence spectra of the isomers in toluene are shown in Fig. 3. All the isomers exhibit a red- shifted, broad, featureless emission with a small quantum yield. It is of interest to note that, of the isomers, **Zna** and **Znb** show a larger red shift (669–673 nm) than **Znc**, **Znd** and **Zne** (approximately 659 nm). A variation in the excitation wavelength does not result in a significant change in the emission profile, which indicates the presence of only one conformer in the ground state or a fast equilibrium between the different conformers arising from the different orientations of the nitro groups [15]. The excitation spectra are identical with the optical absorption spectra at the concentration used (10^{-6} M or less). The large Stokes shift observed for all the isomers suggests that the potential surface of the emitting state is considerably different from that of the ground state. The emission spectra of a representative isomer in various solvents are shown in Fig. 4. The emission spectra of the isomers are highly sensitive to the polarity of the solvent. The emission data are presented in Table 2. In a highly polar solvent, such as CH_3CN, only isomers **Zna** and **Znb** exhibit a very weak fluorescence around 730 nm with a negligible quantum yield. An increase in the solvent polarity shifts the emission maximum to the red, accompanied by a large decrease in the intensity, with isomers **Zna** and **Znb** exhibiting a larger effect of the solvent. The

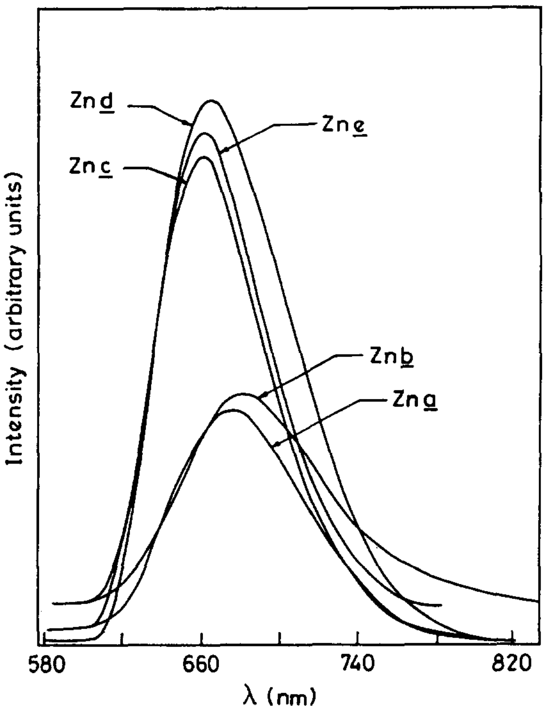

Fig. 3. Fluorescence spectra of zinc(II) derivatives of five isomers of dinitrotetraphenylporphyrin in toluene at 300 K. The excitation wavelength is 560 nm.

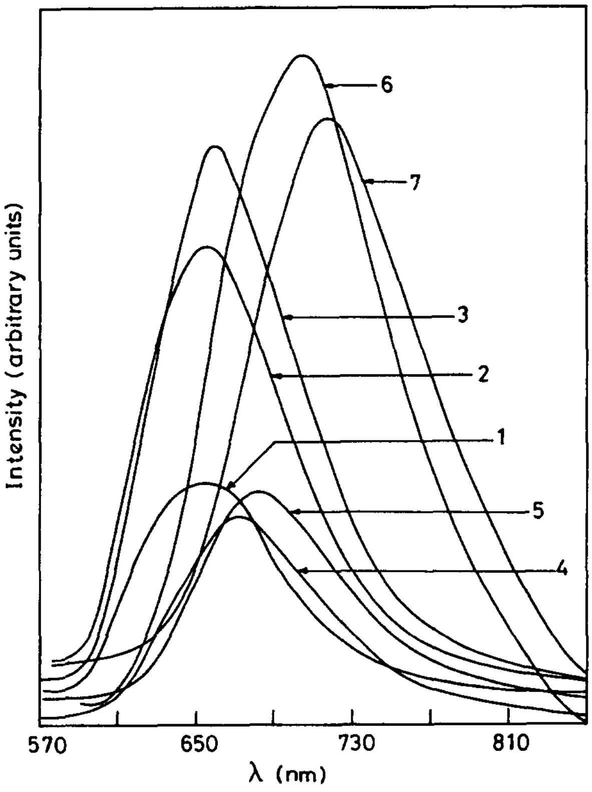

Fig. 4. Fluorescence spectra of **Znb** in seven different solvents: 1, hexane; 2, heptane; 3, cyclohexane; 4, carbon tetrachloride; 5, toluene; 6, dichloromethane; 7, tetrahydrofuran.

magnitude of the Stokes shift increases with increasing polarity of the solvent, indicating that the excited state must be polar in nature and is progressively stabilized in more polar solvents. The results indicate that all the isomers must possess a considerable fraction of charge transfer in the excited state.

The large solvatochromic shift observed for the emission maxima of the isomers can be used to calculate the excited state dipole moment on the basis of Onsager's theory of the reaction field [16]. Assuming a point dipole located at the centre of a spherical cavity, neglecting the ground state dipole moment and assuming a mean solute polarizability ($\alpha \cong \alpha_e \cong \alpha_g = 0$) involved with the state during the transition, we can relate the fluorescence maximum in solution (ν_{max}) as [17]

$$hc\bar{\nu}_{max} = hc\bar{\nu}_{max(0)} - \left(\frac{2\mu_e^2}{a_0^3}\right)\left[\frac{\epsilon-1}{2\epsilon+1} - \frac{1}{2}\frac{(n^2-1)}{2n^2+1)}\right] \qquad (2)$$

where $hc\nu_{max(0)}$ is the gas phase charge transfer fluorescence maximum, μ_e is the excited state dipole moment and a_0 is the effective radius of the Onsager cavity ($a_0 = 7.53$ Å was taken from the crystal structure parameter of one of the isomers). For systems in which polarizability effects on the reaction field are more significant ($\alpha \cong \alpha_e \cong \alpha_g \cong 0.5$), Eq. (2) is modified as [18]

$$hc\bar{\nu}_{max} = hc\bar{\nu}_{max(0)} - \left(\frac{2\mu_e^2}{a_0^3}\right)\left[\frac{\epsilon-1}{\epsilon+2} - \frac{1}{2}\frac{(n^2-1)}{(n^2+2)}\right] \qquad (3)$$

Plots of ν_{max} vs. the solvent polarity function of Eqs. (2) and (3) exhibit reasonably good straight lines with a linear correlation coefficient $r > 0.99$ in most cases. A representative plot is shown in Fig. 5. The inclusion of polar solvents, such as CH_2Cl_2 and tetrahydrofuran (THF), results in a plot with a poor r value and these were excluded from the graph. The excited state dipole moments calculated from the plots using Eqs. (2) and (3) are given in Table 3. The μ_e values obtained using Eq. (3) are smaller in magnitude than those obtained using Eq. (2). This indicates that the latter values include the induced dipole moment and are thus larger than those corresponding to the dipole moment of the free molecule. This observation is similar to that observed for the aryl derivatives of aromatic amines [18].

The singlet lifetimes of the isomers were measured in different solvents and a representative decay curve is shown in Fig. 6. In most cases, the decay curves can be satisfactorily fitted to a biexponential expression with good χ^2 values (1.05–1.40). Isomers **Znd** and **Zne** in toluene exhibit a monoexponential decay ($\chi^2 = 1.14$ and 1.35), while isomer **Zna** in cyclohexane shows a triexponential decay with $\chi^2 = 1.22$. In general, the short-lived component of the isomers has a larger amplitude than the long-lived component. The multiexponential decay observed for the isomers can arise as a result of two different emitting species or due to a broad

Table 2
Emission data of the zinc(II) derivatives of the five isomers of dinitrotetraphenylporphyrin in different solvents at 300 K

Isomer	Parameter	Solvent [a]						
		1	2	3	4	5	6	7
Zna	λ_{em} (nm)	653	653	658	669	675	702	714
	$\nu_{1/2}$ (cm^{-1})	1800	1820	1856	1900	1668	2069	1811
	$\bar{\nu}_a - \bar{\nu}_f$	1360	1360	1450	1636	1605	2060	2056
	ϕ_f	0.017	0.018	0.020	0.023	0.018	0.0083	[b]
Znb	λ_{em} (nm)	656	656	661	673	680	708	716
	$\nu_{1/2}$ (cm^{-1})	1892	1850	1942	2011	1820	2110	2071
	$\bar{\nu}_a - \bar{\nu}_f$	1410	1410	1497	1648	1554	2022	1994
	ϕ_f	0.018	0.017	0.017	0.021	0.017	0.008	[b]
Znc	λ_{ec} (nm)	647	647	651	659	663	677	689
	$\nu_{1/2}$ (cm^{-1})	1889	1836	1682	1507	1512	1922	1752
	$\bar{\nu}_a - \bar{\nu}_f$	696	696	1045	1139	1183	1484	1499
	ϕ_f	0.014	0.014	0.021	0.0135	0.0106	0.0051	[b]
Znd	λ_{em} (nm)	649	649	653	660	665	695	704
	$\nu_{1/2}$ (cm^{-1})	2100	2072	1693	1750	1692	2195	2109
	$\bar{\nu}_a - \bar{\nu}_f$	747	747	1201	1323	1180	1998	1778
	ϕ_f	0.015	0.015	0.026	0.026	0.0307	0.0056	[b]
Zne	λ_{em} (nm)	646	646	649	658	663	692	700
	$\nu_{1/2}$ (cm^{-1})	1972	1860	1651	1576	1507	1915	1745
	$\bar{\nu}_a - \bar{\nu}_f$	701	701	1129	1124	1116	1630	1608
	ϕ_f	0.016	0.017	0.027	0.031	0.032	0.0016	[b]

[a] 1, hexane; 2, heptane; 3, cyclohexane; 4, carbon tetrachloride; 5, toluene; 6, dichloromethane; 7, tetrahydrofuran.
[b] The quantum yield is <0.001.

angular distribution of the emitting state [19]. The singlet lifetime data and quantum yield permit the evaluation of the radiative rate constant (k_f), non-radiative rate constant (k_{nr}) and transition dipole moment (M) in different solvents. They were obtained according to the following expressions [20]

$$k_f = \frac{\phi_f}{\tau_f} \tag{4}$$

$$k_{nr} = \frac{1-\phi_f}{\tau_f} \tag{5}$$

$$|M|^2 = \frac{3hk_f}{64\pi^3 n^3 \nu_f^3} \tag{6}$$

The average value of τ_f was used in the case of multiexponential decays and was calculated from the following expression

$$\bar{\tau}_f = \frac{\tau_1 A_1 + \ldots + \tau_n A_n}{A_1 + \ldots + A_n} \tag{7}$$

The values of k_f, k_{nr} and M of the isomers are given in Table 3. It is observed that the k_f and M values of the isomers decrease with increasing polarity of the solvent.

4. Discussion

The zinc(II) derivatives of the different isomers exhibit optical absorption and emission properties highly specific of the nature of the isomers, with the nitro groups located at different peripheral positions of the porphyrin. The MMX optimized geometry of one of the isomers (**b**) agrees well with the X-ray crystal structure, thereby validating the usefulness of the calculation. The relative energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in different isomers, obtained from AM1 calculations, are found to be a sensitive function of the position of the nitro groups at the periphery of the porphyrin ring. There is a general agreement between the optical absorption bands and the energy difference between the HOMO and LUMO levels calculated for the isomers.

It is fruitful to compare the excited state dipole moments μ_e obtained from the solvent-dependent emission data. The μ_e values of the isomers **Zna** and **Znb** are found to be larger than those observed for **Znc**, **Znd** and **Zne**, indicating that the isomers **Zna** and **Znb** possess considerable charge transfer in the excited state. The magnitudes of the μ_e values are essentially dictated by the radius of the Onsager cavity and the charge separation distance. The isomers differ only in terms of the relative arrangement of the nitro groups in the

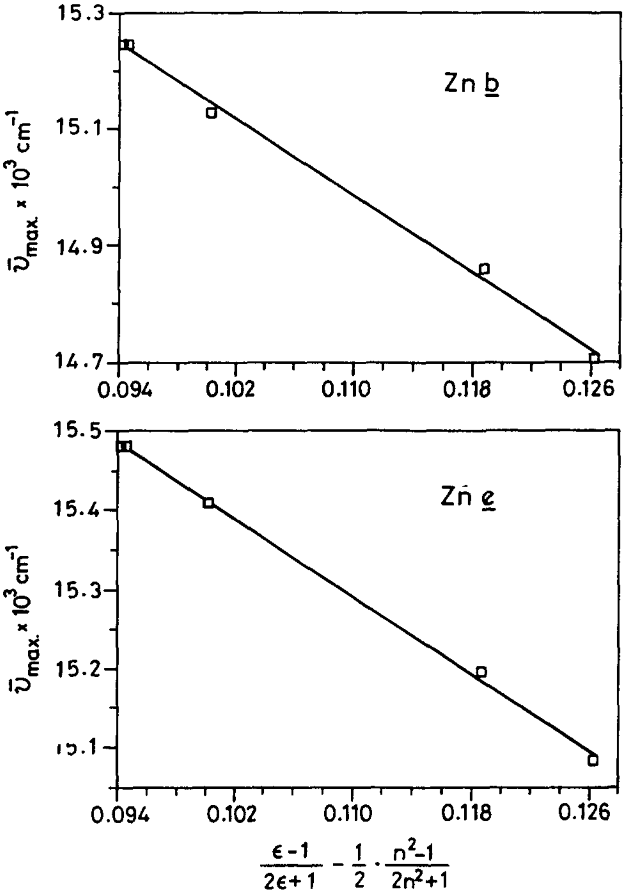

Fig. 5. Plots of fluorescence maxima of **Znb** and **Zne** vs. the solvent polarity parameter.

β-pyrrole positions of the porphyrin macrocycle and hence the Onsager cavity radius and charge separation distance must be of the same magnitude in all the isomers. This suggests that the different magnitudes of charge transfer in the excited state of the isomers arise from the different excited state geometries. It is relevant to compare the μ_g and μ_e values in different isomers, since these provide an estimate of the increase in polarity on excitation to the relaxed excited singlet state. It is possible to obtain the μ_g and μ_e values of the various isomers from the absorption and emission data in various solvents. The data were analysed, in solvents which do not possess a permanent dipole moment, using the following expressions [21]

$$\bar{\nu}_a - \bar{\nu}_f = \frac{2(\mu_e-\mu_g)^2}{a_0^3hc}\left[\frac{\epsilon-1}{2\epsilon+1} - \frac{(n^2-1)}{(2n^2+1)}\right] + (\bar{\nu}_a^0 - \bar{\nu}_f^0) \qquad (8)$$

$$\bar{\nu}_a + \bar{\nu}_f = -\frac{2(\mu_e^2-\mu_g^2)}{a_0^3hc}\left[\frac{\epsilon-1}{2\epsilon+1} + \frac{(n^2-1)}{(2n^2+1)}\right] + (\bar{\nu}_a^0 + \bar{\nu}_f^0) \qquad (9)$$

where ν_a^0 and ν_f^0 represent the unperturbed absorption and emission maxima. Plots of $\nu_a - \nu_f$ and $\nu_a + \nu_f$ vs. the respective polarity function are linear with $r > 0.98$. The values of μ_g and μ_e for the various isomers have been obtained from these plots. The μ_g values are in the range 0.8–3.0 D, whereas the μ_e values lie in the range 17.4–18.1 D for the different isomers. The low μ_g values obtained from these studies validate the assumption of negligible μ_g values in deriving Eqs. (3) and (4). The magnitudes of the μ_e values are in close agreement with those obtained using Eq. (3). It is of interest to note that the isomers **Zna** and **Znb** exhibit a larger change in dipole moment on excitation as revealed by the magnitude of $(\mu_e - \mu_g)$. This suggests that these isomers undergo considerable structural rearrangement in the excited state.

The radiative (k_f) and non-radiative (k_{nr}) rate constants represent the dynamics of the charge separation and charge recombination processes, which in turn are dependent on the solvent reorganization energies [22]. The decrease in k_f values with increasing polarity of the solvent indicates the stabilization of the relaxed charge transfer state in all the isomers. The k_{nr} values are two orders of magnitude greater than the k_f values. The magnitudes of the k_{nr} values are representative of both the k_{isc} and k_{ic} processes. It has been shown previously that the substitution of nitro groups at the meso position of porphine increases the probability of non-radiative deactivation to the ground state [23]. We believe that the enhanced k_{nr} values observed in these isomers are due to fast k_{ic} from the relaxed excited singlet state S_1 to the ground state. The excited state dynamics of the isomers can be interpreted in terms of two different mechanisms: (1) the dependence of the charge transfer emission on the structural change in the excited state, which involves torsion between the donor and acceptor parts of the molecule, resulting in an orthogonal conformation of the donor and acceptor groups; this mechanism is commonly known as the TICT mechanism [3]; (2) a solvent-assisted relaxation process involving solute–solvent dipole–dipole interaction; in strongly coupled donor–acceptor pairs, the adiabatic excited state results from the mixing of diabatic locally excited and charge transfer configurations induced by the orientational polarization of the solvent; this mechanism was proposed by Barbara and coworkers [24].

It is worth considering the transition moment *M* values of the various isomers in the different solvents. The *M* values decrease with increasing polarity of the solvent, and this can be interpreted in terms of a change in the electronic structure of the emitting state due to interactions with the solvent. The small value of *M* in polar solvents is suggestive of the forbidden nature of the transition arising from the rotation of the nitro groups leading to a perpendicular orientation to the plane of the macrocycle. Isomers **Zna** and **Znb** exhibit

Table 3
Photophysical properties of the zinc(II) derivatives of the five isomers of dinitrotetraphenylporphyrin in different solvents at 300 K

Isomer	Solvent	τ_1 [a] (ns)	τ_2 [a] (ns)	μ_c [b] (D)	μ_e [c] (D)	$\tilde{\nu}_{max}$ (cm^{-1})	k_f (10^6 s^{-1})	k_{nr} (10^8 s^{-1})	$\|M\|$ (D)
Zna	Cyclohexane	2.9(7.4) 0.26(31)	1.18(61.6)				19.6	9.61	2.48
	Toluene	2.06(39.7)	1.11(60.3)	25.47	19.9	16750	12.1	6.89	1.88
	CH_2Cl_2	1.47					5.65	6.75	1.47
Znb	Cyclohexane	2.35(8.54)	0.83(91.5)				21.9	10.2	2.63
	Toluene	2.9(8.1)	1.24(91.9)	26.39	20.66	16790	12.4	7.12	1.93
	CH_2CL_2	2.56(7.4)	1.06(92.6)				6.84	8.48	1.63
Znc	Cyclohexane	2.76(48.6)	1.06(51.4)			16530	11.1	5.18	1.80
	Toluene	2.65(81.2)	0.93(18.8)	22.03	17.26		5.79	4.25	1.26
	CH_2Cl_2	1.49(80.3)	0.68(19.7)				3.83	7.48	1.15
Znd	Cyclohexane	2.09(23.1)	1.33(76.9)				14.6	11.0	2.10
	Toluene	2.41		21.97	17.19	16470	12.7	4.02	1.88
	CH_2Cl_2	1.17(48.4)	0.60(51.6)				6.40	6.59	1.55
Zne	Cyclohexane	1.81(24)	0.84(76)				25.4	9.09	2.79
	Toluene	1.49		22.76	17.81	16630	21.3	6.50	2.42
	CH_2Cl_2	1.19(81.1)	0.38(18.9)				15.9	9.46	2.34

[a] Amplitude of the components in parentheses.
[b] Values obtained using Eq. (2).
[c] Values obtained using Eq. (3).

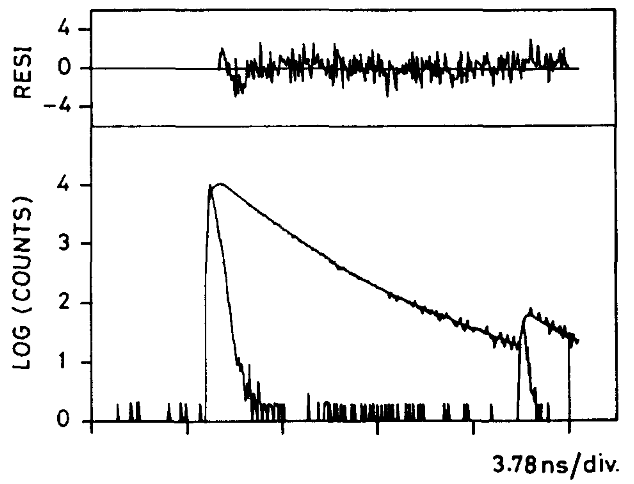

Fig. 6. Decay curve of **Znb** in toluene.

a larger decrease in *M* values than **Znc**, **Znd** and **Zne**. This implies that isomers **Zna** and **Znb** undergo a large structural rearrangement in the excited state. The difference in behaviour amongst the isomers can be related to the restricted rotation of the nitro groups. In the isomer **Zne**, the phenyl rings interposed between the two nitro groups should exert steric constraint on the rotation leading to a restricted variation in geometry. It is anticipated that this isomer should exhibit a smaller change in *M* value with increasing polarity of the solvent relative to that obtained for the other isomers. The observed change in *M* value of **Zne** with increasing polarity of the solvent is small (16%), thereby suggesting the importance of the rotation of the nitro groups in influencing the excited state dynamics with the possible existence of a TICT state. On the other hand, if solvent interaction is the dominant factor in governing the excited state dynamics, we would expect a larger change in *M* value of **Zne** with increasing polarity of the solvent. This is not the case, although **Zne** exhibits a higher magnitude of μ_e relative to **Znc** and **Znd**. As pointed out earlier, the nitro groups located at different positions of the pyrrole carbons experience restricted rotation imposed by the presence of bulky phenyl groups at the meso positions. The rotation of the nitro groups to a nearly perpendicular conformation would lead to negligible *M* values. However, the significant *M* values observed in this study suggest that the nitro groups may not be fully orthogonal and/or mixing with the LE state must be present. Although a solvent-assisted relaxation mechanism cannot be ruled out completely, it is more probable that the rotation of the nitro groups is the dominant factor in governing the excited state dynamics.

The importance of this study lies in the determination of isomer-specific photophysical properties, which are relevant to the design of non-linear optics materials and to an understanding of the charge separation events in photosynthesis.

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