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## Photophysics of Soret-excited free base tetraphenylporphyrin and its zinc analog in solution



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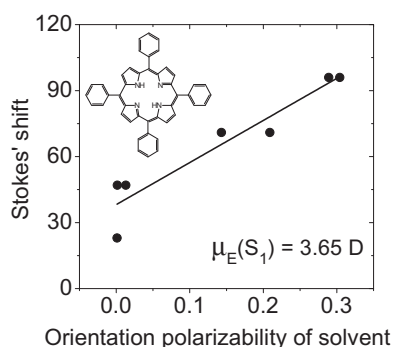
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### HIGHLIGHTS

- Spectral characteristics of porphyrins are affected by solvent polarizability.
- Ground state dipole moments of porphyrins are found to be very low.
- Solvatochromic Stokes' shift method is used to find excited state dipole moment.
- The first excited singlet state of porphyrins possesses moderate dipole moments.
- Other properties of porphyrins are nearly insensitive to solvent polarity.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Photophysical properties of free base tetraphenylporphyrin and its zinc analog are investigated in detail in solvents of varying polarity by using steady state and time-resolved techniques. Both the porphyrins are excited at the Soret band to have better signal-to-noise ratio. Also, the fluorescence emission measurements are carried out by using dilute solutions ( $\sim 10^{-7}$  mol/L) of the fluorophores in order to minimize the self-quenching effect. It is observed that the steady state absorption and emission characteristics of the porphyrin molecules are mainly affected by polarizability (via refractive index) rather than polarity (via dielectric constant) of the moderate to highly polar solvents. As the molecules are highly symmetric in the ground state, the associated dipole moments are found to be very low from quantum chemical calculations performed by density functional theory method by using Gaussian 03 package. The dipole moments associated with the first excited singlet state of the porphyrins are computed by applying solvatochromic Stokes' shift method. To the best of our knowledge, this is the first attempt to calculate the excited state dipole moments of the porphyrins used in the present investigations. Also, fluorescence quantum yield, fluorescence lifetime of the first excited singlet state, radiative and non-radiative rate constants of the porphyrins are reported in solvents of varying polarity.

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### Introduction

Various porphyrin compounds play important roles in biophysics [1], solar energy harvesting and artificial photosynthesis [2–12], industrial processes as catalysts [13–20], photodynamic

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therapy [21–23], anticancer pharmaceutical drugs [24] and photodynamic destruction of viruses [25,26]. Therefore, spectroscopic characteristics and photophysics of porphyrins have been extensively studied by many research groups for the last few decades [27–68]. Porphyrins are cyclic molecules composed of four smaller 5-membered heterocycles, called pyrroles, each one containing one nitrogen and four carbon atoms. The electronic absorption spectra of a free base porphyrin consist of an intense band at about 400 nm, called Soret band (or B band) and four weaker bands in the visible region (about 500–650 nm), called Q bands. The former originates because of  $\pi, \pi^*$  transition from the ground singlet state to the second excited singlet state ( $S_0 \rightarrow S_2$ ), while the latter are attributed to  $\pi, \pi^*$  transitions from the ground singlet state to the first excited singlet state ( $S_0 \rightarrow S_1$ ). When free base porphyrin is metalated, the molecule becomes more symmetrical and this leads to the four Q bands in the absorption spectra to collapse into two. Martin Gouterman and co-workers first proposed the four-orbital model in the 1960s to explain the Q and B bands in the absorption spectra of porphyrins and metalloporphyrins [27,28,35]. The internal conversion from  $S_2$  to  $S_1$  is rapid and hence fluorescence is usually observed from the  $S_1$  state in accordance with Kasha's rule. The fluorescence from the  $S_1$  state is quite weak (quantum yield  $\sim 10^{-2}$ ) [33]. Moreover, very weak fluorescence is observed from the  $S_2$  state of porphyrins (quantum yield  $\sim 10^{-4}$ ) [61].

It is known that the UV–visible spectroscopic characteristics of a fluorophore molecule are influenced by its immediate environment, especially the nature of solvent. A change of solvent is accompanied by a change in polarity, dielectric constant and polarizability of the surrounding medium of the fluorophore. Thus, a change of solvent affects the electron distribution in the ground and excited states of the fluorophore to different extents, thereby changing the dipole moments of these states. In the present work, two porphyrin derivatives are used as fluorophores, viz., free base tetraphenylporphyrin (5,10,15,20-tetraphenyl-21H,23H-porphine, TPhP) and zinc tetraphenylporphyrin (5,10,15,20-tetraphenyl-21H,23H-porphine zinc, ZnTPhP) (Fig. 1). Detail steady state and time-resolved spectroscopic measurements are carried out on these porphyrins in different solvents of varying polarity at the ambient temperature (300 K). An attempt is made to compute the dipole moments associated with the first excited singlet state of the porphyrins by applying solvatochromic Stokes' shift method. To the best of our knowledge, this is the first report on the excited state dipole moments of the aforementioned porphyrins. Also, we report the effect of solvent polarity on the fluorescence quantum yield, fluorescence lifetime of the first excited singlet state, radiative rate constant and non-radiative rate constant of the two porphyrin molecules in detail.

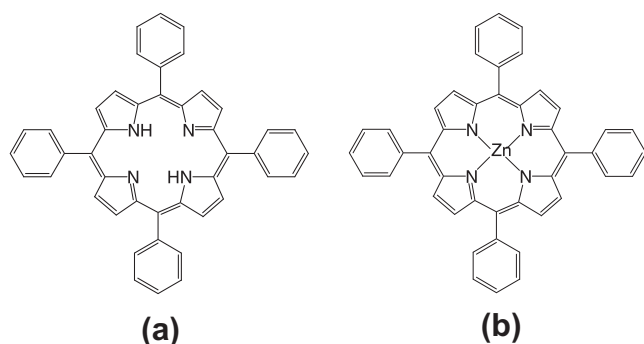


Fig. 1. Molecular structures of (a) TPhP and (b) ZnTPhP.

## Experimental

### Chemicals

The samples TPhP and ZnTPhP were used as supplied by Sigma–Aldrich. The solvents acetonitrile (ACN), ethanol, tetrahydrofuran (THF), chlorobenzene (CB), toluene, benzene and hexane of spectroscopic grade were purchased from Sigma–Aldrich and were tested before use for the absence of any impurity emission in the wavelength region studied.

### Spectroscopic apparatus

The steady state electronic absorption spectra of the samples were recorded at the ambient temperature (300 K) using 1 cm pathlength rectangular quartz cuvette by means of JASCO V-650 absorption spectrophotometer. Steady state fluorescence spectra of the samples were recorded by JASCO FP-6500 fluorescence spectrometer at 300 K. Emission was detected at right angles to the direction of excitation light in order to avoid stray light. The fluorescence emission spectra were measured by exciting at the Soret band to have better signal-to-noise ratio. Also, all the fluorescence emission measurements were carried out by using dilute solutions ( $\sim 10^{-7}$  mol/L) of the samples in order to minimize the self-quenching effect, which is known to deform the emission spectra in shape as well as peak energy positions [69].

The time-resolved fluorescence measurements were carried out using a time correlated single photon counting (TCSPC) spectrometer from IBH (UK). The sample was excited with 405 nm light from a diode laser with 1 MHz repetition rate. A PMT based detector (TBX4, IBH) was used for detection of the emitted photons through a monochromator. The instrument response of the TCSPC set-up was measured by collecting the scattered light from a  $\text{TiO}_2$  suspension in water. The instrument response function thus measured was  $\sim 200$  ps. The decays were analyzed using IBH DAS-6 analysis software. The reduced  $\chi^2$  and residuals were used to judge the goodness of the fit.

## Results and discussion

### Quantum chemical calculations

The quantum chemical calculations for the porphyrin molecules are performed by density functional theory (DFT) method by using Gaussian 03 package [70]. The ground state geometries of the molecules are fully optimized at the B3LYP/6-31G(d,p) level and the structures are shown in Fig. 2. Both the porphyrin molecules are highly symmetric in the ground singlet state. The calculated Zn–N distance in ZnTPhP is 2.043 Å. It is to be mentioned that the

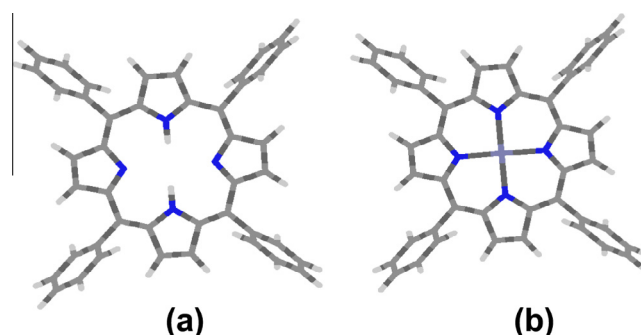
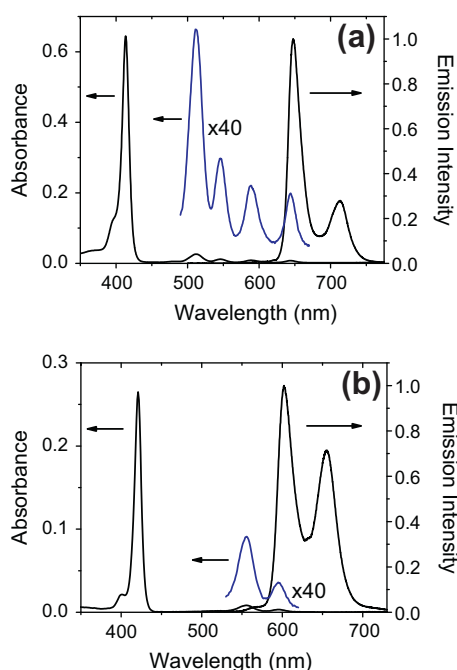


Fig. 2. Geometric structures for the ground state of (a) TPhP and (b) ZnTPhP, fully optimized at the B3LYP/6-31G(d,p) level.

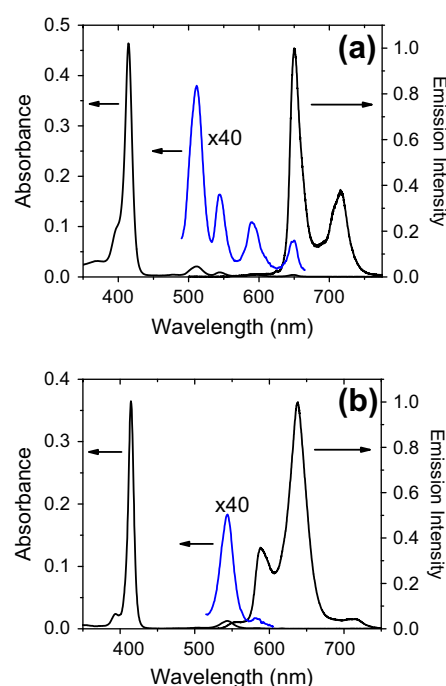
reported value of the Zn–N distance in ZnTPhP is 2.037 Å (experimental, crystal data) [71] and 2.055 Å (theoretical, by using DFT-B3LYP calculations) [55]. Thus, our calculated Zn–N distance in ZnTPhP is very close to the literature data. The largest diameter for TPhP and ZnTPhP is calculated to be 17.63 Å and 17.60 Å, respectively. As the molecules are highly symmetric in the ground singlet state, the associated dipole moment is likely to be very low. The calculated ground state dipole moment of TPhP and ZnTPhP in the gas phase is 0.04 D and 0.01 D, respectively. Earlier, Sazanovich et al. [72] reported from semiempirical calculations that TPhP molecule shows practically a complete absence of any ground state dipole moment. This is in agreement with our theoretical prediction about the ground state dipole moments of the presently used porphyrins.

#### Steady state absorption and emission spectra

Figs. 3 and 4 show the steady state absorption and fluorescence emission spectra of TPhP and ZnTPhP in polar solvent ACN (dielectric constant,  $\epsilon = 37.5$ ) and non-polar solvent hexane ( $\epsilon = 1.9$ ), respectively, at the ambient temperature (300 K). The absorption and emission peaks of the samples are given in Table 1, measured in a series of solvents ACN, ethanol, THF, CB, toluene, benzene and hexane of varying polarity. All the absorption spectra consist of a highly intense Soret band in the blue side of the spectra and very weak Q-bands in the red side of the spectra. The Q-bands in the absorption spectra of the free base porphyrin (TPhP) show four peak positions, while those of the metalloporphyrin (ZnTPhP) show only two peak positions. The fluorescence emission spectra originate from the  $S_1$  state of the porphyrins. The generic features of the absorption and emission spectra of the presently used porphyrins are in good accord with the literature data [28,33,35,36,40,49,52,56,59,60,69].



**Fig. 3.** Steady state absorption spectra ( $l = 1$  cm) and fluorescence emission spectra in ACN at 300 K of (a) TPhP (absorption spectra: concentration =  $1.6 \times 10^{-6}$  mol/L; emission spectra: concentration =  $7.5 \times 10^{-8}$  mol/L, excitation wavelength = 413 nm) and (b) ZnTPhP (absorption spectra: concentration =  $5.1 \times 10^{-6}$  mol/L; emission spectra: concentration =  $5.0 \times 10^{-7}$  mol/L, excitation wavelength = 421 nm).



**Fig. 4.** Steady state absorption spectra ( $l = 1$  cm) and fluorescence emission spectra in hexane at 300 K of (a) TPhP (absorption spectra: concentration =  $1.5 \times 10^{-6}$  mol/L; emission spectra: concentration =  $5.0 \times 10^{-8}$  mol/L, excitation wavelength = 415 nm) and (b) ZnTPhP (absorption spectra: concentration =  $2.2 \times 10^{-6}$  mol/L; emission spectra: concentration =  $1.3 \times 10^{-7}$  mol/L, excitation wavelength = 415 nm).

In general, as the polarity of the solvent is increased, the Soret band ( $S_0 \rightarrow S_2$ ) peak position in the absorption spectra of the presently used porphyrins is moderately red-shifted (bathochromic shift) in non-polar solvents, but slightly blue-shifted (hypsochromic shift) in medium to highly polar solvents (Fig. 5). The effect of solvent polarity on the  $S_0 \rightarrow S_2$  transition of the porphyrins, presently used, is quite unusual in nature as it shows bathochromic as well as hypsochromic shifts in different polarity regions of the solvents.

The transitions between the ground state ( $S_0$ ) and first excited singlet state ( $S_1$ ) for the two porphyrin molecules are found to be affected somewhat differently (compared to  $S_0 \rightarrow S_2$  transition) by the solvent polarity (Fig. 6). The  $S_0 \rightarrow S_1$  transition (steady state absorption) follows a hypsochromic shift with increase in solvent polarity over the entire polarity region of the solvents (non-polar hexane to polar ACN) for the free base porphyrin (TPhP). However, for the  $S_1 \rightarrow S_0$  transition (steady state emission) of TPhP, we observe a slight bathochromic shift initially in non-polar solvents, followed by the hypsochromic shift in medium to highly polar solvents. On the other hand, for the corresponding zinc analog (ZnTPhP), both  $S_0 \rightarrow S_1$  and  $S_1 \rightarrow S_0$  transitions suffer a moderate bathochromic shift with increase in solvent polarity in non-polar solvents, but remain almost unaffected by the solvent polarity in medium to highly polar solvents.

It is well-known that the solvent molecules tend to align themselves around the fluorophore molecule so as to stabilize the fluorophore. As the presently used porphyrins do not possess any significant dipole moment in the ground state ( $S_0$ ), the solute–solvent stabilization is effective only for the excited states ( $S_1$  and  $S_2$ ) of the porphyrins. Both the porphyrins are found to possess moderate dipole moments associated with the first excited singlet state (vide infra). Therefore, as the polarity of the solvent is increased, the excited singlet states of the porphyrins are expected to be stabilized more, resulting in a gradual bathochromic shift in the

**Table 1**

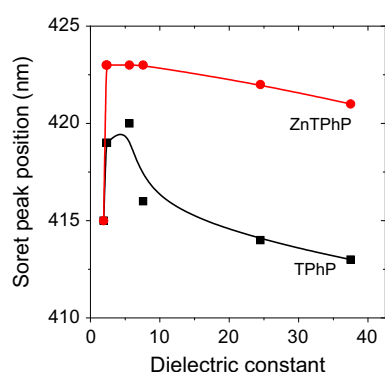
Steady state spectral data, orientation polarizability ( $\Delta f$ ), Stokes' shift ( $\bar{\nu}_a - \bar{\nu}_f$ ), dipole moment ( $\mu_G$ ) of the ground singlet state and dipole moment ( $\mu_E$ ) of the first excited singlet state for TPhP and ZnTPhP in different solvents.

Sample	Solvent	Absorption peak (nm)		Emission peak (nm)	$\Delta f^a$	$\bar{\nu}_a - \bar{\nu}_f$ (cm <sup>-1</sup> )	$\mu_G^b$ (D)	$\mu_E^c$ (D)
		Soret band	Q-band					
TPhP	ACN	413	512, 546, 589, 644	648, 713	0.304	96	0.04	3.65
	Ethanol	414	512, 546, 589, 645	649, 714	0.289	96		
	THF	416	513, 547, 591, 648	651, 717	0.209	71		
	CB	420	515, 550, 592, 649	652, 718	0.143	71		
	Toluene	419	514, 549, 592, 649	651, 718	0.013	47		
	Benzene	419	514, 549, 591, 649	651, 717	0.0015	47		
	Hexane	415	511, 545, 592, 649	650, 716	0.0012	23		
ZnTPhP	ACN	421	556, 595	603, 655	0.304	223	0.01	3.34
	Ethanol	422	557, 596	603, 655	0.289	194		
	THF	423	556, 595	602, 654	0.209	196		
	CB	423	550, 589	596, 647	0.143	200		
	Toluene	423	549, 590	596, 647	0.013	170		
	Benzene	423	550, 590	596, 647	0.0015	170		
	Hexane	415	544, 583	588, 638	0.0012	146		

<sup>a</sup>  $\Delta f$  was calculated by using Eq. (2) (see text). Dielectric constant for ACN, ethanol, THF, CB, toluene, benzene and hexane was taken as 37.5, 24.5, 7.58, 5.62, 2.38, 2.27 and 1.9, respectively. Refractive index for ACN, ethanol, THF, CB, toluene, benzene and hexane was taken as 1.344, 1.361, 1.406, 1.525, 1.497, 1.501 and 1.375, respectively.

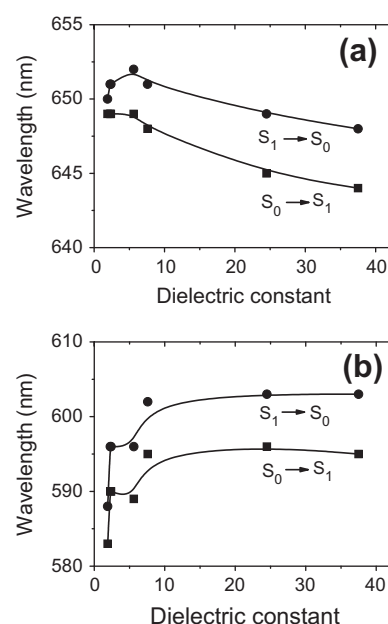
<sup>b</sup>  $\mu_G$  was calculated by using DFT method under B3LYP/6-31G(d,p) level (see text).

<sup>c</sup>  $\mu_E$  was calculated by using Lippert–Mataga Eq. (1) (see text).



**Fig. 5.** The Soret band peak position of the steady state absorption ( $S_0 \rightarrow S_2$ ) versus dielectric constant of the solvent for (a) TPhP (black solid square) and (b) ZnTPhP (red solid circle). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

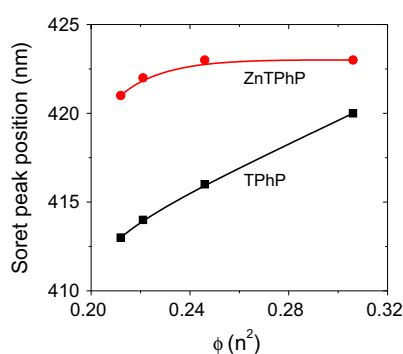
absorption as well as emission spectra. However, this feature is observed only in non-polar solvents (solvents of low polarity). In moderate to highly polar solvents, a gradual hypsochromic shift is found for the free base porphyrin (TPhP) with increase in solvent polarity, while almost no solvatochromic shift is observed for the metalloporphyrin (ZnTPhP). This type of unusual feature was reported by Renge [39,41] on free base tetraphenylporphyrins. Earlier, porphyrin band energies have been found to respond to the polarizability of the solvent [39,41] via a function of the refractive index ( $n$ ) and, to a limited extent, the polarity of the solvent [34,36,37] via dielectric constant. The Lorentz–Lorentz function,  $\phi(n^2) = (n^2 - 1)/(n^2 + 2)$ , is one of the most commonly used functions relating solvent refractive index to polarizability. Akers et al. [58] investigated the UV–visible absorption spectra of several porphyrins in binary mixtures of solvents with similar polarities and dissimilar refractive indices. They reported that the Soret bands are red-shifted on the increase of  $\phi(n^2)$  due to the dispersive stabilization of the excited state. Figs. 7 and 8 show the absorption ( $S_0 \rightarrow S_2$ ,  $S_0 \rightarrow S_1$ ) and emission ( $S_1 \rightarrow S_0$ ) peaks versus Lorentz–Lorentz function for the presently used porphyrins in moderate to highly polar solvents. The value of  $\phi(n^2)$  is equal to 0.212, 0.221, 0.246 and 0.306 for ACN, ethanol, THF and CB, respectively.



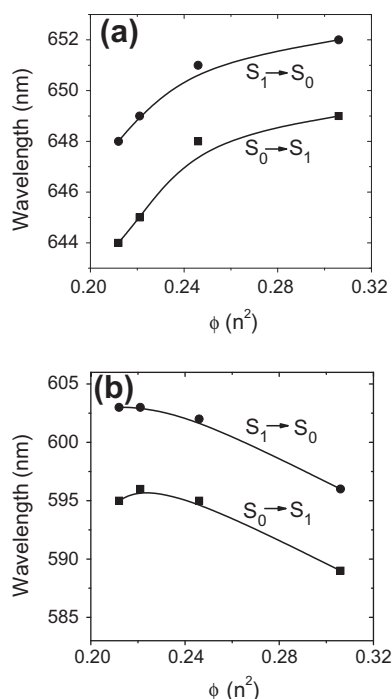
**Fig. 6.** The (0,0) peak positions of the steady state absorption ( $S_0 \rightarrow S_1$ ) (solid square) and emission ( $S_1 \rightarrow S_0$ ) (solid circle) versus dielectric constant of the solvent for (a) TPhP and (b) ZnTPhP.

The absorption and emission peaks show bathochromic shifts on the increase of  $\phi(n^2)$  for TPhP (Figs. 7 and 8). This seemingly indicates that the steady state absorption and emission characteristics of the free base porphyrin molecule are mainly affected by polarizability rather than polarity of the solvents (moderate to highly polar) used in the present investigations. For ZnTPhP, the  $S_0 \rightarrow S_2$  transition (Soret absorption band) shows a weak bathochromic shift on the increase of  $\phi(n^2)$  (Fig. 7). Thus, the  $S_0 \rightarrow S_2$  transition for ZnTPhP seems to be affected by polarizability rather than polarity of the solvents (moderate to highly polar), though the solvent polarizability effect is quite weak. On the contrary, unusual hypsochromic shifts are observed for the  $S_0 \rightarrow S_1$  (steady state absorption) and  $S_1 \rightarrow S_0$  (steady state emission) transitions on the increase of  $\phi(n^2)$  for ZnTPhP (Fig. 8b). However, Fig. 6b shows that



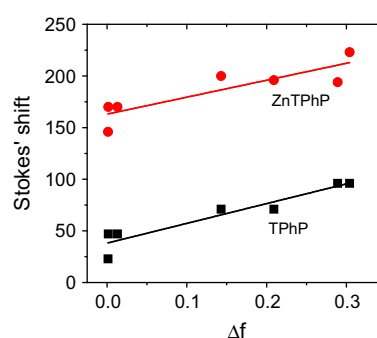


**Fig. 7.** The Soret band peak position of the steady state absorption ( $S_0 \rightarrow S_2$ ) versus Lorentz-Lorentz function of the solvent for (a) TPhP (black solid square) and (b) ZnTPhP (red solid circle). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 8.** The (0,0) peak positions of the steady state absorption ( $S_0 \rightarrow S_1$ ) (solid square) and emission ( $S_1 \rightarrow S_0$ ) (solid circle) versus Lorentz-Lorentz function of the solvent for (a) TPhP and (b) ZnTPhP.

the transitions involving  $S_0$  and  $S_1$  states of ZnTPhP suffer almost no solvatochromic shifts with the increase of the polarity of the solvents (moderate to highly polar). Therefore, we may conclude that the transitions involving  $S_0$  and  $S_1$  states of ZnTPhP are affected by polarity rather than polarizability of the solvents (moderate to highly polar), though the solvent polarity effect is quite insignificant. Therefore, the  $S_1$  and  $S_2$  states of ZnTPhP remain almost unaffected by the solvent medium via either solvent polarity or solvent polarizability of the moderate to highly polar solvents. This is expected keeping in view that the metalloporphyrin is more symmetrical in nature than the free base porphyrin and hence the former molecule is supposed to possess lower excited state dipole moment than the free base one. However, the difference in the calculated values of the excited state ( $S_1$ ) dipole moments of the presently used porphyrins (vide infra) may not fully explain the different spectroscopic natures of the two porphyrin molecules in solvents of varying polarity.



**Fig. 9.** Lippert-Mataga plots for TPhP (black solid square) and ZnTPhP (red solid circle). The solid lines show the linear fits (TPhP: black solid line, ZnTPhP: red solid line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Clearly, proper theoretical models need to be developed in future so as to address these quite unusual features of the presently used porphyrins regarding the nature and extent of stabilizations of the excited singlet states ( $S_1$  and  $S_2$ ) by various solvent parameters, viz., polarity, polarizability, etc.

#### Excited state dipole moment

The relationship between solvatochromic Stokes' shift and solvent polarity is usually given by Lippert-Mataga equation (Eq. (1)) [73–78]. It is based on the Onsager's reaction field theory, which assumes that the fluorophore is a point dipole residing in the centre of a spherical cavity in a homogeneous and isotropic dielectric medium.

$$\bar{\nu}_a - \bar{\nu}_f = \frac{2(\mu_E - \mu_G)^2}{hca^3} \Delta f + \text{constant} \quad (1)$$

Here,  $(\bar{\nu}_a - \bar{\nu}_f)$  is the Stokes' shift being equal to the difference between the (0,0) peak positions of the steady state absorption ( $S_0 \rightarrow S_1$ ) and emission ( $S_1 \rightarrow S_0$ );  $\mu_G$  and  $\mu_E$  are the dipole moments of the ground singlet state and first excited singlet state, respectively; 'a' is the Onsager cavity radius;  $\Delta f$  is the orientation polarizability; other symbols have their usual meanings. The value of 'a' is taken as the radius of the fluorophore molecule, calculated by using DFT method under B3LYP/6-31G(d,p) level (vide supra). The orientation polarizability ( $\Delta f$ ) of the solvent is given by the following equation.

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (2)$$

Table 1 shows a gradual increase in the Stokes' shift with increase in the polarity of the solvents as a generic nature of both the porphyrins, presently used. Lippert-Mataga plots (Stokes' shift versus orientation polarizability), by using Eq. (1), are shown in Fig. 9 for the two porphyrin molecules. From the slopes of the linear plots, values of  $(\mu_E - \mu_G)$  are calculated. Hence,  $\mu_E$  is calculated as  $\mu_G$  is already known from quantum chemical calculations (Table 1). It is noteworthy that both the presently used porphyrins possess very low values of  $\mu_G$  in the gas phase obtained from quantum chemical calculations, as the molecules are highly symmetric in the ground state. Therefore, solute-solvent stabilization interactions are expected to be negligible in the ground state of the fluorophore molecules. Hence, the values of  $\mu_G$  of the two porphyrins in the gas phase should remain practically unaltered in the solution phase. The computed values of the dipole moments associated with the first excited singlet state ( $S_1$ ) of the porphyrins are given in Table 1. Clearly, the  $S_1$  state of each of the two porphyrins possesses

**Table 2**

Fluorescence quantum yield ( $\phi_f$ ), fluorescence lifetime ( $\tau_f$ ) of the first excited singlet state, radiative rate constant ( $k_r$ ) and non-radiative rate constant ( $k_{nr}$ ) for TPhP and ZnTPhP in different solvents.

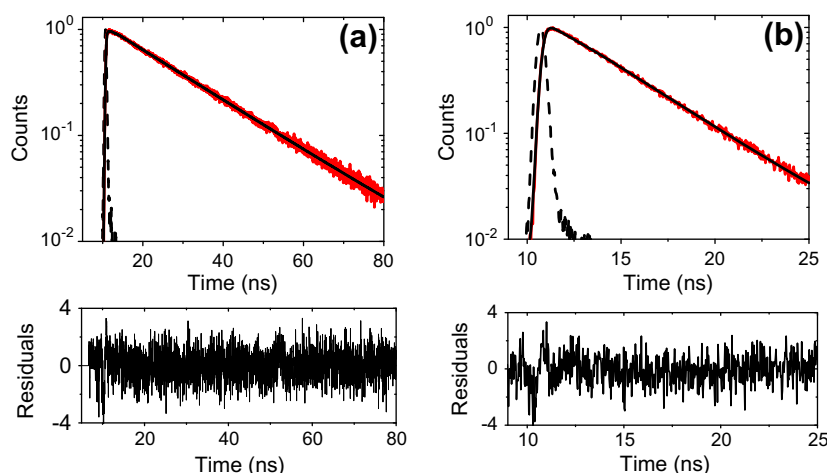
Sample	Solvent	$\phi_f^a$	$\tau_f^b$ (ns) ( $\pm 0.1$ ns)	$k_r \times 10^{-7c}$ ( $s^{-1}$ )	$k_{nr} \times 10^{-7d}$ ( $s^{-1}$ )
TPhP	ACN	0.061	9.2 (648)	0.7	10.2
	Ethanol	0.052	10.1 (649)	0.5	9.4
	THF	0.052	10.0 (651)	0.5	9.5
	CB	0.051	9.6 (652)	0.5	9.9
	Toluene	0.048	9.3 (651)	0.5	10.2
	Benzene	0.054	10.0 (651)	0.5	9.5
	Hexane	0.041	8.6 (650)	0.5	11.1
ZnTPhP	ACN	0.032	1.9 (603)	1.7	50.9
	Ethanol	0.031	2.0 (603)	1.6	48.4
	THF	0.035	1.8 (602)	1.9	53.6
	CB	0.045	1.9 (597)	2.4	50.3
	Toluene	0.037	2.0 (597)	1.9	48.1
	Benzene	0.033	1.9 (596)	1.7	50.9
	Hexane	0.054	2.1 (588)	2.6	45.0

<sup>a</sup>  $\phi_f$  was calculated by using Eq. (3) (see text).

<sup>b</sup>  $\tau_f$  was measured at the emission wavelength given in parenthesis in nm. Excitation wavelength for lifetime measurement was 405 nm.

<sup>c</sup>  $k_r$  was calculated by using Eq. (4) (see text).

<sup>d</sup>  $k_{nr}$  was calculated by using Eq. (5) (see text).



**Fig. 10.** Normalised fluorescence decay curves in ACN at 300 K of (a) TPhP (concentration =  $6.5 \times 10^{-7}$  mol/L) at an emission wavelength of 648 nm and (b) ZnTPhP (concentration =  $2.1 \times 10^{-6}$  mol/L) at an emission wavelength of 603 nm. All the measurements were carried out at an excitation wavelength of 405 nm. Solid line: fitted decay curve; red line: original decay curve; dashed line: instrument response profile. Lower panels show the respective residuals for fitting. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

moderate dipolar character. Also, the value of  $\mu_E$  is lower for ZnTPhP ( $\mu_E = 3.34$  D) compared to that for TPhP ( $\mu_E = 3.65$  D). This is attributed to the more symmetric nature of the metalloporphyrin compared to the free base porphyrin.

#### Other photophysical parameters

Fluorescence quantum yield ( $\phi_f$ ) of an unknown sample is calculated by using Eq. (3) [78].

$$\phi_f = \phi_f^R \frac{I_f}{I_f^R} \frac{A^R}{A} \left( \frac{n}{n^R} \right)^2 \quad (3)$$

Here,  $\phi_f^R$  is the known fluorescence quantum yield of the reference sample (referred by the superscript 'R');  $I_f$  and  $I_f^R$  are the integrated fluorescence intensities of the unknown sample and reference sample, respectively;  $A$  and  $A^R$  are the absorbances of the unknown sample and reference sample, respectively;  $n$  and  $n^R$  are the refractive indices of the solvents for the unknown sample and reference sample, respectively. The unknown sample and reference sample are excited at the same wavelength for measuring  $I_f$  and  $I_f^R$ ,

respectively. The fluorescence quantum yield of the samples are measured at 300 K relative to that of ZnTPhP in benzene solution ( $\phi_f^R = 0.033$  at 30 °C) [33].

The calculated values of the fluorescence quantum yield of the presently used porphyrins in different solvents of varying polarity are given in Table 2. Clearly, for both the porphyrins,  $\phi_f$  is nearly independent of the solvent polarity in moderate to highly polar solvents. However, in general, the values of  $\phi_f$  are lower for the metalloporphyrin than those for the free base porphyrin in different solvents. Again, observed fluorescence lifetime ( $\tau_f$ ) of the first excited singlet state of each of the two porphyrins is found to be single-exponential (Fig. 10, some representative plots) and nearly independent of the solvent polarity (Table 2). However,  $S_1$  fluorescence lifetime of the metalloporphyrin (ZnTPhP) is significantly shortened compared to that of the free base one (TPhP).

The radiative and non-radiative rate constants associated with the decay of the first excited singlet state ( $S_1$ ) of the porphyrin molecules in various solvents are calculated by using Eqs. (4) and (5), respectively [78].

$$k_r = \phi_f / \tau_f \quad (4)$$



$$k_{nr} = (1 - \varphi_f)/\tau_f \quad (5)$$

Both radiative and non-radiative rates for the two porphyrins, presently used, are found to be nearly insensitive to the polarity of the solvent medium (Table 2). The non-radiative rates are one order of magnitude higher than the corresponding radiative rates for each of the two porphyrins in different solvents of varying polarity. However, both the radiative and non-radiative rates are nearly 3–5 times higher for the zinc porphyrin (ZnTPHP) compared to those for the free base porphyrin (TPHP).

## Conclusion

Steady state absorption and emission characteristics of free base tetraphenylporphyrin and its zinc analog are found to be mainly affected by solvent polarizability (dispersive stabilization) rather than solvent polarity (dielectric stabilization) in moderate to highly polar solvents. Quantum chemical calculations by using density functional theory method show that the ground state dipole moments of the porphyrins are very low due to their highly symmetric structures. The first excited singlet state of the porphyrins possesses moderate dipole moments, calculated by using Lippert–Mataga equation (solvatochromic Stokes' shift method). Other photophysical properties, viz., fluorescence quantum yield, fluorescence lifetime of the first excited singlet state, radiative and non-radiative rate constants are found to be nearly insensitive to the solvent polarity, especially in moderate to highly polar solvents. All these findings are expected to shed better light into the complex photophysics of the porphyrins, used in the present investigations, in liquid medium and consequently to develop proper techniques in various applications such as artificial photosynthesis, and organic solar photovoltaic cells.

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