

## Fluorescence properties of meso-tetrafurylporphyrins

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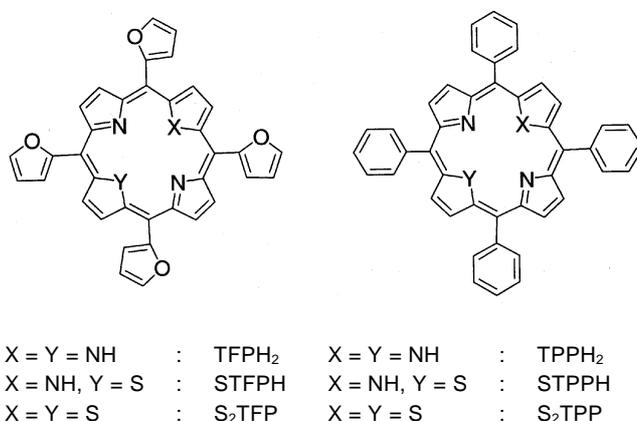
**Abstract.** Fluorescence properties of meso-tetrafurylporphyrins with  $N_4$ ,  $N_3S$  and  $N_2S_2$  porphyrin cores are studied by both steady-state and time-resolved fluorescence techniques and compared with the corresponding meso-tetraarylporphyrins. The study shows that the replacement of six-membered aryl groups with five-membered furyl groups at meso-positions alter the fluorescence properties considerably, as reflected in the large red shifts and broadening of fluorescence bands with reduction in quantum yields and singlet excited-state lifetimes. However, zinc(II) derivatives of meso-tetrafurylporphyrin and meso-tetraarylporphyrin did not show significant differences in their emission properties.

**Keywords.** Tetrafurylporphyrins; fluorescence; core-modification; diacations.

### 1. Introduction

Electronic properties of porphyrins can be modulated at will by introducing suitable substituents at meso- and **b**-positions. Meso-tetraarylporphyrins are the most widely studied model compounds owing to their ease of synthesis and functionalization.<sup>1</sup> Most of the studies carried out on meso-tetraarylporphyrins involve introducing substituents either at **b**-positions or on the meso-aryl groups. Introduction of substituents at the **b**-positions alters the electronic properties tremendously as the substituents are in direct conjugation with the porphyrin.<sup>2</sup> However, substituents on the meso-aryl groups do not significantly alter the electronic properties of the porphyrin, since they are not in direct conjugation with the porphyrin macrocycle. Recently, it has been shown by optical and electrochemical studies that with replacement of six-membered aryl groups with five-membered thienyl groups, the electronic properties of the porphyrin change considerably.<sup>3</sup> However, reports on porphyrins having five-membered heterocycles such as pyrrole, thiophene, furan, etc. as meso-substituents are very few.<sup>4</sup> We have recently reported the synthesis and characterization of a series of meso-furyl porphyrins with different porphyrin cores.<sup>5</sup> Our investigations show that the presence of furyl groups instead of phenyl groups at the meso-positions alter the electronic properties significantly. Interestingly except our two reports,<sup>5</sup> to the best of our knowledge, there

is no report on the meso-tetrafurylporphyrins to investigate their physico-chemical properties. In this paper, we extend the study of the effect of meso-furyl groups on the electronic properties of the porphyrins. We explored the fluorescence properties of meso-tetrafurylporphyrins with three different porphyrin cores (figure 1); meso-tetrafurylporphyrin (TFPH<sub>2</sub>,  $N_4$  core), meso-tetrafuryl-21-monothiaporphyrin (STFPH,  $N_3S$  core) and meso-tetrafuryl-21,23-dithiaporphyrin ( $S_2$ TFP,  $N_2S_2$  core). The fluorescence properties of meso-tetrafurylporphyrins were compared with their corresponding meso-tetraarylporphyrins (figure 1); meso-tetraphenylporphyrin (TPPH<sub>2</sub>,  $N_4$  core), meso-tetraphenyl-21-monothiaporphyrin (STPPH,  $N_3S$  core) and meso-tetraphenyl-21,23-dithiaporphyrin ( $S_2$ TPP,  $N_2S_2$  core). The study



**Figure 1.** Structures of meso-tetrafuryl and meso-tetraarylporphyrins.

Dedicated to the memory of the late Professor Bhaskar G Maiya

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clearly indicates that the fluorescence properties of the porphyrin are significantly altered by the presence of five-membered furyl groups in place of the six-membered aryl groups at meso-positions.

## 2. Experimental section

The meso-tetrafurylporphyrins with different porphyrin cores used in the present study were synthesized as described in our earlier work.<sup>5</sup> The meso-tetraarylporphyrins with different porphyrin cores were synthesized by following the literature procedures.<sup>6</sup> The dications were generated by adding a drop of trifluoroacetic acid to a dilute solution of porphyrins in toluene. All the experiments were performed at room temperature in AnalaR grade toluene. Emission spectra were recorded on a Perkin–Elmer LS-55 luminescence spectrometer. The fluorescence quantum yields ( $f_f$ ) of meso-tetrafurylporphyrins were estimated from the emission and absorption spectra by a comparative method<sup>7</sup> using the following equation,

$$f_f = \frac{[F(\text{sample})][A(\text{standard})]/[F(\text{standard})][A(\text{sample})]}{f_f(\text{standard})} \quad (1)$$

where  $[F(\text{sample})]$  and  $[F(\text{standard})]$  are the integrated fluorescence intensities of the meso-tetrafurylporphyrins and the standard,  $[A(\text{sample})]$  and  $[A(\text{standard})]$  the absorbances of meso-tetrafurylporphyrins and the standard at the excitation wavelength and  $f_f$  (standard) the quantum yield of the standard sample. Free-base tetraphenylporphyrin ( $\text{H}_2\text{TPP}$ ,  $f_f = 0.11$ ) was used as the standard for free-base porphyrins, and zinc(II) tetraphenylporphyrin<sup>8</sup> ( $\text{ZnTPP}$ ) was used as the standard ( $f_f^{\text{S}_1} = 0.033$  and  $f_f^{\text{S}_2} = 0.00039$ ) for the  $\text{Zn}^{2+}$  derivative of meso-tetrafurylporphyrin ( $\text{ZnTFP}$ ).

Time-resolved fluorescence decay measurements were carried out at the magic angle of  $54.5^\circ$  using a picosecond diode laser-based time correlated single photon counting (TCSPC) fluorescence spectrometer from IBH, UK. All the decays were fitted to a single exponential equation given by

$$I(t) = A \exp(-t/\tau_f). \quad (2)$$

The good-fit criteria were low chi-square (1.0) and random distributions of residuals. The radiative and non-radiative rate constants,  $k_r$  and  $k_{nr}$ , were calculated<sup>7</sup> by following equations

$$\Sigma k = 1/\tau_f, \quad (3)$$

$$k_r = f_f \times k, \quad (4)$$

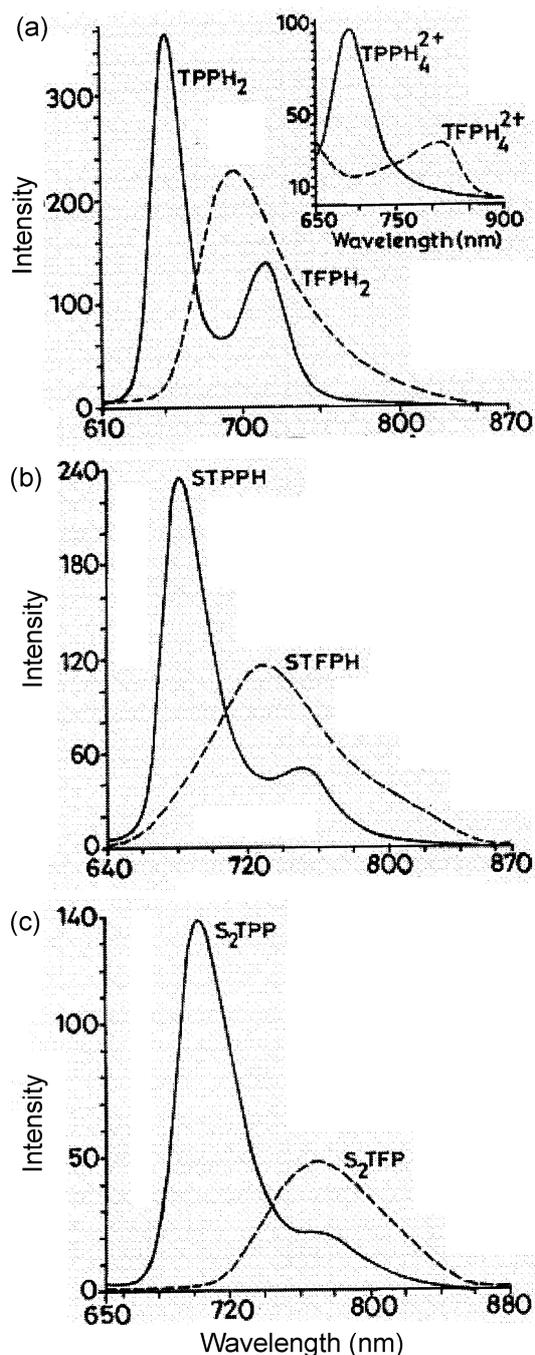
$$k_{nr} = k - k_r. \quad (5)$$

## 3. Results and discussion

Comparison of the fluorescence spectra of meso-tetrafurylporphyrins  $\text{TFPH}_2$ ,  $\text{STFPH}$  and  $\text{S}_2\text{TFP}$  along with their corresponding meso-tetraarylporphyrin analogues  $\text{TPPH}_2$ ,  $\text{STPPH}$  and  $\text{S}_2\text{TPP}$  respectively are presented in figures 2a–c and the fluorescence data are given in table 1. An inspection of figure 2 and table 1 reveals the following: (1) broadening and red shifts of fluorescence bands of meso-tetrafurylporphyrins relative to corresponding meso-tetraarylporphyrins;<sup>9</sup> (2) significant absorption/fluorescence shifts (Stokes shifts) in meso-tetrafurylporphyrins as compared to that of the meso-tetraarylporphyrins;<sup>10</sup> (3) quantum yields,  $f_f$ , are considerably reduced on replacement of phenyl groups with furyl groups at meso-positions of porphyrins; (4) among meso-tetrafurylporphyrins studied, maximum red shifts and

**Table 1.** Steady state emission data of meso-tetrafurylporphyrins and meso-tetraarylporphyrins recorded in toluene.

Porphyrin	Q (0,0)			
	Absorption I (nm)	Fluorescence I (nm)	Quantum yield $f_f$	Stokes shift ( $\text{cm}^{-1}$ )
$\text{TPPH}_2$	647	652	0.110	118
$\text{TFPH}_2$	670	697	0.0109 ( $\pm 0.0005$ )	578
$\text{STPPH}$	675	678	0.0168	066
$\text{STFPH}$	705	729	0.0021 ( $\pm 0.0001$ )	467
$\text{S}_2\text{TPP}$	696	706	0.0076	243
$\text{S}_2\text{TFP}$	740	773	0.0017 ( $\pm 0.0008$ )	577



**Figure 2.** Comparison of fluorescence spectra of (a) TFPPh<sub>2</sub> and TPPH<sub>2</sub> (the inset shows the comparison of fluorescence spectra of TFPPh<sub>4</sub><sup>2+</sup> and TPPH<sub>4</sub><sup>2+</sup>); (b) STFPPh and STPPH; (c) S<sub>2</sub>TFP and S<sub>2</sub>TPP in toluene. Concentration =  $3 \times 10^{-6}$  M;  $I_{\text{ex}} = 450$  nm.

broadening of fluorescence bands with reduction in fluorescence intensities are observed for porphyrin with N<sub>2</sub>S<sub>2</sub> core (S<sub>2</sub>TFP). Similar conclusions were drawn earlier from the ground state absorption studies of meso-tetrafurylporphyrins.<sup>5</sup> The absorption spectra

of meso-tetrafurylporphyrins are quite different from that of meso-tetraarylporphyrins. Unlike meso-tetraarylporphyrins which shows four defined Q-bands, the meso-tetrafurylporphyrins showed two or three Q-bands. Furthermore, the absorption bands of meso-tetrafurylporphyrins are significantly red-shifted with reduction in absorption coefficients compared to those of meso-tetraarylporphyrins.<sup>5</sup> Thus, the absorption and fluorescence studies indicate that with the replacement of phenyl groups with furyl groups at the meso-positions, the electronic properties of the porphyrin are altered considerably.

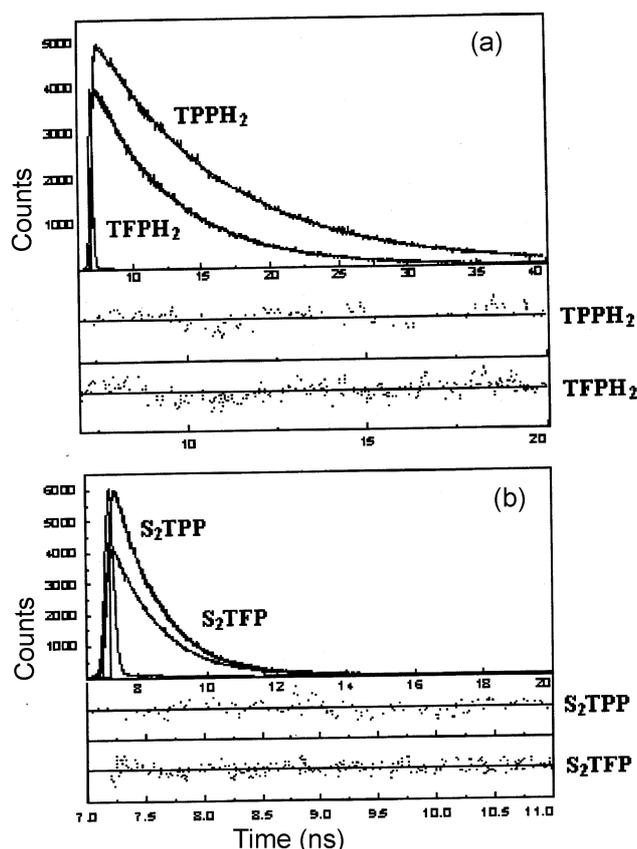
The four-orbital model developed by Gouterman<sup>11</sup> best describes the absorption and emission characteristics of free-base porphyrins. This model focuses on transitions from the highest occupied porphyrin molecular orbitals (HOMOs) to the lowest unoccupied molecular orbitals (LUMOs). The energies of these orbitals are very sensitive to the structure of the porphyrin ring. Thus, one can modulate the energies of HOMOs and LUMOs by peripheral substitution, change of central metal ions, and change of axial ligand. The absorption and fluorescence study of meso-tetrafurylporphyrins indicates that the presence of furyl groups at the meso-positions alters the energy levels of HOMO and LUMO and reduces the energy gap between them, resulting in significant changes in ground and excited-state properties. The large Stokes shifts observed for meso-tetrafuryl porphyrins (table 1) suggest that the structure of the porphyrin in the excited state is different from that in the ground state. This observation is in contrast with that for the meso-tetraarylporphyrins which show small Stokes shifts implying that the porphyrin in the excited state may have the same structure as that of the ground state.<sup>10</sup> Thus, the Stokes-shift data indicate that the meso-tetrafurylporphyrins undergo structural reorganization in the excited state.<sup>12</sup> Furthermore, all meso-tetrafurylporphyrins are weakly fluorescent compared to the corresponding meso-tetraarylporphyrins (table 1). The weak fluorescence behaviour of meso-tetrafurylporphyrins may be due to the orientation of meso-furyl groups with respect to the porphyrin plane and the decay of the singlet excited state through internal conversion. Generally the internal conversion accounts for about 20% decay of porphyrins.<sup>11</sup>

Time-resolved fluorescence studies were carried out on meso-tetrafurylporphyrins to understand their fluorescence properties in detail. Fluorescence decays of TFPPh<sub>2</sub> along with TPPH<sub>2</sub>, as well as S<sub>2</sub>TFP

along with  $S_2$ TPP are shown in figure 3. Data on lifetime  $t_f$ , rate of radiative decay  $k_r$  and rate of non-radiative decay  $k_{nr}$  of meso-tetrafurylporphyrins, and of the corresponding meso-tetraarylporphyrins are presented in table 2. As evident from table 2, lifetimes  $t_f$  of meso-tetrafurylporphyrins are shorter than those of meso-tetraarylporphyrins. The decrease in

$k_r$  and increase in  $k_{nr}$  are in agreement with the shorter lifetimes of meso-tetrafurylporphyrins compared to meso-tetraarylporphyrins. Thus, the low fluorescent yields,  $f_f$  observed for meso-tetrafurylporphyrins may be due to the decreased  $S_1$  state lifetimes and possibly to increased  $S_1 \rightarrow T_1$  intersystem crossing and increased  $S_1 \rightarrow S_0$  internal conversion rates.<sup>12</sup> The large Stokes shifts noted for meso-tetrafurylporphyrins support the enhancement of the Franck–Condon factor due to substantial structural reorganization in the excited state resulting in the increased non-radiative decay rates.<sup>12</sup>

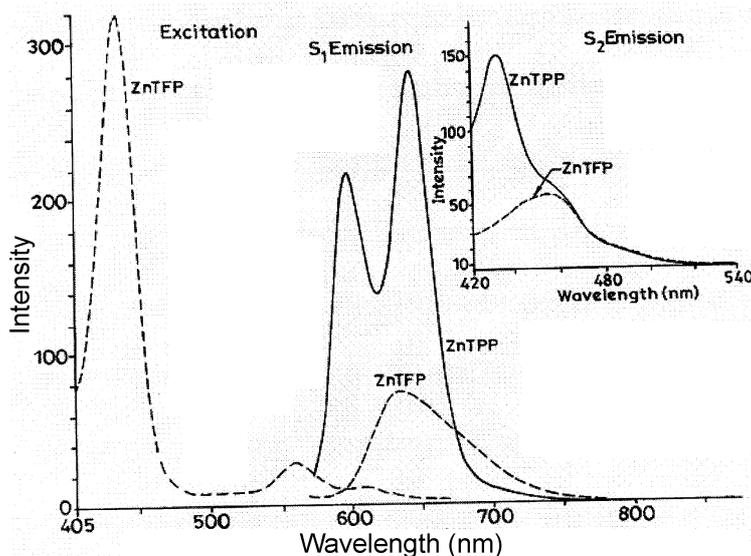
We attempted to study the fluorescence properties of dications of meso-tetrafurylporphyrins,  $TFPH_4^{2+}$ ,  $STFPH_3^{2+}$  and  $S_2TFPH_2^{2+}$ . The dications were generated by addition of a few drops of acid to the porphyrin solution. The optical properties of dications of meso-tetraarylporphyrin are well documented in literature.<sup>13</sup> Generally, it was observed that the dications possess very low fluorescence compound to neutral porphyrins. However, the porphyrins exhibit interesting structural changes upon dication formation which reflects in large red-shifts in absorption and emission bands. It was shown by Stone and Fleischer<sup>13</sup> that the protonation of meso-arylporphyrins is expected to release the repulsive interaction by tilting the pyrrole rings out of the porphyrin plane inducing significant non-planarity and thus making the phenyl rings more co-planar with the porphyrin plane. This would facilitate the delocalization of *p*-electrons into the aryl rings by a resonance interaction. The greater resonance interaction between the porphyrin and the meso-aryl groups in porphyrin dications results in large red-shifts of absorption and emission bands compared to neutral porphyrins. Unfortunately, the dications of meso-tetrafurylporphyrins are very weakly fluorescent compared to the corresponding dications of meso-tetraarylporphyrins  $TPPH_4^{2+}$ ,  $STPPH_3^{2+}$  and  $S_2TPPH_2^{2+}$ . Figure 2 (inset) shows the comparison of the emission spectra of the  $TFPH_4^{2+}$  and  $TPPH_4^{2+}$ , and data for all dications are presented in table 3. The spectra of  $TFPH_4^{2+}$  and  $STFPH_3^{2+}$  exhibit single broad structureless emission with very low quantum yields, while  $S_2TFPH_2^{2+}$  does not show any emission. However, the emission bands of dications of meso-tetrafurylporphyrins experience red-shifts relative to neutral derivatives, which are in agreement with the changes observed upon dication formation of meso-tetraarylporphyrins. Furthermore, comparison of the emission properties of the dications of meso-tetrafurylporphyrins with those of di-



**Figure 3.** Fluorescence decay profiles and weighted residual distribution fits of (a)  $TFPH_2$  and  $TPPH_2$ ; (b)  $S_2TFP$  and  $S_2TPP$ . The excitation wavelength used was 406 nm and emissions were detected at different wavelengths depending on the emission peak positions of the porphyrins.

**Table 2.** Photophysical data of meso-tetrafurylporphyrins and meso-tetraarylporphyrins in toluene.

Porphyrin	$t_f$ (ns)	$k_r \times 10^{-8}$ ( $s^{-1}$ )	$k_{nr} \times 10^{-8}$ ( $s^{-1}$ )
$TPPH_2$	9.32	0.1180	0.9549
$TFPH_2$	5.77	0.0343	1.6987
$STPPH$	1.77	0.0949	5.5548
$STFPH$	1.06	0.0199	9.4140
$S_2TTP$	1.34	0.0567	7.4059
$S_2TFP$	1.20	0.0141	8.3193



**Figure 4.** Comparison of  $S_1$  fluorescence spectra of ZnTFP and ZnTPP and excitation spectrum of ZnTFP. Emission spectra were recorded using  $I_{\text{ex}} = 550$  nm and the excitation spectrum was recorded using  $I_{\text{em}} = 700$  nm. The inset shows a comparison of  $S_2$  emission spectra of ZnTFP and ZnTPP ( $I_{\text{ex}} = 405$  nm). Concentrations used for  $S_1$  and  $S_2$  emissions were  $3 \times 10^{-6}$  M.

**Table 3.** Steady state emission data of dications of meso-tetrafurylporphyrins and meso-tetraarylporphyrins in toluene.

Porphyrin	$Q(0,0)$	
	$\lambda$ (nm)	$f_f$
TPPH <sub>4</sub> <sup>2+</sup>	700	0.0166
TFPH <sub>4</sub> <sup>2+</sup>	809	$<10^{-5}$
STPH <sub>3</sub> <sup>2+</sup>	748	0.0044
STFPH <sub>3</sub> <sup>2+</sup>	816	$<10^{-5}$
S <sub>2</sub> TPPH <sub>2</sub> <sup>2+</sup>	771	0.0066
S <sub>2</sub> TFPH <sub>2</sub> <sup>2+</sup>	—	—

cations of meso-tetraarylporphyrins indicate that the emission bands of dications of meso-tetrafurylporphyrins are more red-shifted with drastic reduction in intensity compared to the dications of meso-tetraarylporphyrins. This suggests increased resonance interaction between the meso-furyl groups and the porphyrin macrocycle in dications of meso-tetrafurylporphyrins.

In order to understand the effects of the presence of metal ion on the fluorescence properties of meso-tetrafurylporphyrins, steady-state and time-resolved fluorescence studies were carried out on ZnTFP. Comparison of  $S_1$  emission spectra of ZnTFP and ZnTPP is shown in figure 4. Unlike ZnTPP, which shows two well-defined  $S_1$  emission bands, ( $I_{\text{em}} =$

596 nm, 645 nm),<sup>11</sup> ZnTFP shows a single broad emission ( $I_{\text{em}} = 637$  nm). The excitation spectrum of ZnTFP recorded by setting the wavelength at the emission maxima matches its absorption spectra, confirming the emission (figure 4). Interestingly, the fluorescence yield ( $f_f = 0.028$ ) and the life time ( $t_f = 2.31$  ns) of ZnTFP do not differ much from that of ZnTPP ( $f_f = 0.033$ ,  $t_f = 1.98$  ns).<sup>11</sup> However, compared to freebase H<sub>2</sub>TFP, the fluorescence yield of ZnTFP is greater, which is surprising at first since the heavy metal insertion into porphyrin is expected to result in diminished emission because of increased intersystem crossing yields. The observed increase in the fluorescence yield of ZnTFP compared to H<sub>2</sub>TFP is attributed tentatively to the increased rigidity of the meso-tetrafurylporphyrin structure on Zn(II) insertion, which is expected to decrease the intersystem crossing yields. Further work is needed to understand this unusual fluorescent behaviour of ZnTFP.

It is well established that ZnTPP shows emission from  $S_2$  state in addition to  $S_1$  emission on excitation only at the Soret band.<sup>8</sup>  $S_2$  emission is not observed on excitation of Q-bands, thus ruling out the possibility of any thermal repopulation of the  $S_2$  state from  $S_1$  state.  $S_2$  emission properties of ZnTFP are studied by exciting at 405 nm. Comparison of  $S_2$  fluorescence spectra of ZnTFP and ZnTPP is shown in figure 4 (inset). As evident from the figure, the  $S_2$  emission

of ZnTFP is broad and red-shifted ( $I_{em} = 456$  nm) compared to that of ZnTPP ( $I_{em} = 435$  nm), and the quantum yield of ZnTFP ( $f_f = 0.00023$ ) is slightly lower than that of ZnTPP ( $f_f = 0.00039$ ).<sup>8</sup> Thus, fluorescence study of the Zn<sup>2+</sup> derivatives of meso-tetrafurlylporphyrin indicates that their emission properties are not changed significantly compared to ZnTPP, unlike for their corresponding free-base analogues which show considerable differences in their emission properties.

#### 4. Conclusions

In conclusion, we studied the emission properties of meso-tetrafurlylporphyrins with N<sub>4</sub>, N<sub>3</sub>S and N<sub>2</sub>S<sub>2</sub> porphyrin cores and compared them with those of the corresponding meso-tetrarylporphyrins. It has been shown that on replacement of phenyl groups with furyl groups at the meso-positions of porphyrins, their emission properties are significantly altered, indicating considerable changes in the electronic properties of the porphyrin macrocycle. However, on the introduction of Zn<sup>2+</sup> into meso-tetrafurlylporphyrin, the emission properties are nearly similar to that of ZnTPP. To understand the differences in fluorescence properties of metallated and metal free meso-tetrafurlylporphyrins, one must await the X-ray structural studies of these compounds.

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