Spectroscopic properties of meso-thienylporphyrins with different porphyrin cores

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Abstract

The absorption and fluorescence properties of a series of meso-thienylporphyrins with different porphyrin cores (N4, N3O, N3S and N2S2 cores) were studied and compared with the corresponding meso-tetraarylporphyrins. The replacement of six-membered phenyl groups with five-membered thienyl groups at meso-positions resulted in red shifts and broadening of absorption and emission bands, low quantum yields and decreased S1 state lifetimes and the maximum effects were observed for meso-tetra thienylporphyrin with N2S2 porphyrin core. Similar observations were noted for the dications of meso-thienylporphyrins compared to the dications of the corresponding meso-tetraarylporphyrins. These results suggest that the replacement of six-membered aryl group with five-membered thienyl groups at meso-positions, the electronic properties of the porphyrin were altered significantly.

Keywords: Heteroporphyrins; Spectroscopic properties; meso-Thienylporphyrins

1. Introduction

The meso-tetraarylporphyrins are model compounds used extensively for various applications owing to their ease of synthesis and facile functionalization [1]. The properties of the porphyrin macrocycle can be modulated at will by introducing suitable substituents at meso- and β-positions. There are several reports on β-substituted porphyrins having both electron withdrawing and electron donating substituents have been shown as a robust catalysts for the oxidation of organic substrates [2]. Furthermore, the β-substituted porphyrins with electron withdrawing substituents have been shown as a robust catalysts for the oxidation of organic substrates [3]. However, the reports on porphyrins having meso-substituents as five-membered heterocycles such as pyrrole, thiophene furan [4], etc. are scarce. In recent times, there have been a few reports on meso-tetra thienylporphyrins [5,6]. Effenberger et al. [5a] synthesized anthryloligothienylporphyrins containing the anthracene donor, the porphyrin acceptor and a conjugated oligothiophene bridge. This system showed an efficient energy transfer from anthracene to porphyrin unit mediated by the oligothiophenebridge. The oligomeric thienyl porphyrins also showed film forming and efficient conductivity behaviour [5l]. It was also shown recently that by introducing the five-membered thienyl groups in place of six-membered aryl groups at meso-carbon atoms, the electronic properties were altered dramatically using optical, redox and axial ligand studies [5d]. The interesting properties exhibited by the meso-thienylporphyrins suggest that these porphyrins can be used as a substitute for meso-tetraarylporphyrins for various applications. We recently reported[6] the synthesis of various meso-thienylporphyrins having heteroatom substituted porphyrin cores such as N4, N3S and N2S2 cores. A perusal of literature reveal that there are no systematic studies on absorption and emission properties of meso-thienylporphyrins to compare with various meso-aryl heteroatom substituted porphyrins. In general, the reports on photophysical properties of heteroatom substituted porphyrins are very few. In this paper, we explored the absorption and emission properties of meso-thienylporphyrins with different porphyrin cores and their dications and compared the properties with
those of corresponding meso-arylporphyrins and their dications. We studied the absorption and fluorescence properties of meso-thienylporphyrins (Fig. 1) by varying the (1) the number of meso-thienyl groups and (2) the change of the porphyrin core from N₄ to heteroatom substituted cores (N₃S, N₃O and N₂S₂) and compared with the corresponding meso-tetraarylporphyrins. The study clearly indicated that the replacement of six-membered aryl groups with five-membered thienyl groups alter the electronic properties of the porphyrin ring considerably.

2. Experimental

The meso-tetraarylporphyrins with heteroatom substituted porphyrin cores used in the present study were synthesized as described in our earlier work [6]. The meso-tetraarylporphyrin with different porphyrin cores [7a,b] and 5,10,15,20-meso-tetraarylporphyrin [5] and its Zn²⁺ derivative were synthesized by following the literature procedures [5d]. The dications were generated by adding a drop of trifluoroacetic acid to a dilute solutions of porphyrins in toluene. All the experiments were performed at room temperature in AnalaR grade toluene. Absorption and emission spectra were recorded in Perkin-Elmer Lambda-35 UV–vis spectrometer and Perkin-Elmer LS-55 Luminescence spectrometer, respectively. The fluorescence quantum yields ($\phi_f$) of meso-thienylporphyrins and dications were estimated from the emission and absorption spectra by comparative method [8] using the following equation

$$\phi_f = \frac{\int F(\text{sample}) \, d\lambda}{\int F(\text{standard}) \, d\lambda} \, \phi_f (\text{standard})$$

where $\int F(\text{sample})$ and $\int F(\text{standard})$ are the integrated fluorescence intensities of the meso-thienylporphyrins or their dications and the standard $[A(\text{sample})]$ and $[A(\text{standard})]$ represents the quantum yield of the standard sample. Free base tetraphenylporphyrin ($\phi_f = 0.11$) was used as the standard for free base porphyrins and their dications, and zinc (II) tetraphenylporphyrin ($\phi_f = 0.033$ and $\phi_f = 0.00039$) for the Zn²⁺ derivative of meso-tetraarylporphyrin (ZnS5) [9]. The time resolved fluorescence decay measurements [10] were carried out at magic angle using a picosecond diode laser based time correlated single photon counting (TCSPC) fluorescence spectrometer from IBH, UK. All the decays were fitted to single exponential equation given by

$$I(t) = A \exp \left( -\frac{t}{\tau} \right)$$

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 [11] by following equations

$$\sum k = \frac{1}{\tau_f}$$

$$k_r = \frac{\phi_f}{k}$$

$$k_{nr} = k - k_r$$

3. Results and discussion

3.1. Absorption Properties

The absorption spectra of meso-thienyl substituted 21-thiaporphyrins 1–4 are shown in Fig. 2 and the absorption data of 1–4 along with 5,10,15,20 tetraphenyl-21-thiaporphyrin

\[ R_1 = \begin{array}{c}
\text{S} \\
\text{S}
\end{array} ; \quad R_2 = \begin{array}{c}
\text{S} \\
\text{S}
\end{array} \]

\[ X = Y = \text{NH} \quad : \text{5} \]

\[ R_1 = \begin{array}{c}
\text{S} \\
\text{S}
\end{array} ; \quad R_2 = \begin{array}{c}
\text{S} \\
\text{S}
\end{array} \]

\[ X = \text{NH} ; \quad Y = \text{O} \quad : \text{6} \]

\[ R_2 = \begin{array}{c}
\text{S} \\
\text{S}
\end{array} ; \quad R_3 = \begin{array}{c}
\text{S} \\
\text{S}
\end{array} \]

\[ X = Y = \text{S} \quad : \text{7} \]
The absorption and emission properties were also studied for meso-tetraphenylporphyrins having different porphyrin cores such as N4, 5, N4S 4, N2O 6 and N2S2 7 cores and compared the properties with those of corresponding meso-tetraphenyl analogues H2TPP, STPPH, OTPPH and S2TIPP respectively [12]. The absorption spectra of six-membered phenyl groups with five-membered thienyl groups, the electronic properties of the porphyrins were altered significantly. This may be attributed to smaller thienyl groups, the electronic properties of the porphyrins.

The absorption spectra of dications of meso-thienyl-21-thiaporphyrins 1–4 showed characteristic I–IV Q-bands and one strong Soret-band similar to STPPH [12]. The following observations were noted for 1–4 compared to STPPH: (1) red shift and broadening of both Soret- and Q-bands; (2) considerable alteration of extinction coefficients of Soret- and Q-bands; (3) the magnitude of red shifts, broadening and alteration in extinction coefficients were dependent on the number of thienyl groups at meso-positions and maximum effects were observed for meso-tetra(thienyl)porphyrin 4. These observations indicate that the replacement of six-membered phenyl groups with five-membered thienyl groups, the electronic properties of the porphyrins were altered significantly. This may be attributed to smaller ring size of meso-thienyl groups which may become more coplanar with the porphyrin plane and facilitate the delocalization of π-electrons of the porphyrin into the meso-thienyl groups by resonance interaction. The X-ray structure solved earlier for one of the meso-thienyl substituted N4S porphyrin with two meso-thienyl and two meso-tolyl groups [6] showed that the porphyrin structure has become more planar compared to slightly saddle shaped structure of STPPH [12] supporting the greater resonance interaction between porphyrin and meso-substituents.

The absorption spectra of dications of meso-thienyl-21-thiaporphyrins 1H2, 2H2, 3H2, 4H2, and 4H4 recorded in toluene are shown in Fig. 2 (inset) and data are tabulated in Table 2 along with dication of meso-tetraphenyl-21-thiaporphyrin STPPH32+ [13]. The dications were generated by adding trifluoroacetic acid to porphyrins 1–4 in toluene. It is clear from Fig. 2 (inset) that the dications shows one strong Soret-band and a broad single Q-band. Also the absorption bands of dications were considerably red shifted compared to their corresponding neutral analogues (Table 2) in agreement with the previously observed for STPPH32+, the dication derivative of STPPH. It was explained [14] that, on protocation, the free base tetraarylporphyrins undergo a structural change by releasing the repulsive interaction between the ortho-hydrogens of the meso-phenyl rings and the adjacent pyrrole protons. This results in the phenyl rings becoming more coplanar with the porphyrin plane, enhancing the delocalization of π-electrons into the phenyl rings by resonance interaction leading to large red shifts of the Soret- and Q-bands. As clear from the table that the dications of 1–4 exhibited more red shifts and broadening compared to STPPH32+ suggests that the meso-thienyl groups were more in coplanar with the porphyrin ring and providing a greater π-delocalisation of the porphyrin macrocycle extended to the meso-thienyl groups.

The absorption and emission properties were also studied for meso-tetraphenylporphyrins having different porphyrin cores such as N4, 5, N4S 4, N2O 6 and N2S2 7 cores and compared the properties with those of corresponding meso-tetraphenyl analogues H2TPP, STPPH, OTPPH and S2TIPP respectively [12]. The absorption spectra of

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>Soret-band λ (nm) (ε × 104)</th>
<th>Q-bands λ (nm) (ε × 104)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STPPH</td>
<td>429 (18.7)</td>
<td>513 (17.1) 547 (4.4) 618 (1.9) 675 (3.0)</td>
</tr>
<tr>
<td>1</td>
<td>433 (15.4)</td>
<td>517 (21.4) 553 (9.6) 620 (3.3) 679 (4.5)</td>
</tr>
<tr>
<td>2</td>
<td>456 (29.3)</td>
<td>520 (20.6) 557 (9.4) 622 (3.1) 684 (3.4)</td>
</tr>
<tr>
<td>3</td>
<td>457 (23.9)</td>
<td>521 (17.5) 557 (9.4) 624 (2.6) 687 (3.2)</td>
</tr>
<tr>
<td>4</td>
<td>460 (13.7)</td>
<td>523 (22.7) 562 (11.3) 627 (3.8) 692 (3.6)</td>
</tr>
</tbody>
</table>
meso-tetra-thienyl-2-thiaporphyrins 4, 5 and 7 recorded in toluene are presented in Fig. 3 and the data are listed in Table 3. As evident from the Table 3 the absorption bands of meso-tetra-thienylporphyrins 4-7 experienced red shifts and peak broadening as porphyrin core changes from N4 to N3 S2 and maximum effects were observed for meso-tetra-thienylporphyrins having N2 S2 core. In general, among tetraphenyl heteroporphyrins, the thiaporphyrins show larger red shifts in absorption bands compared to normal and oxaporphyrins. This can be explained on the basis of iterative extended huckel (IEH) calculations [15a] and electrochemical studies [15b] which suggested that the drain of π-electron density from the porphyrin π-system is more effective in thiaporphyrins to promote bonding interactions between the heteroatoms because of the reduced core size resulted in the reduction of the HOMO–LUMO gap. This effect is not expected in the case of oxaporphyrins since the core size is not altered much upon substitution of oxygen in place of nitrogen because of the similar sizes of N and O[16]. Thus, qualitatively the absorption maxima of the oxaporphyrins are expected to be closer to the parent H2TPP[16]. Furthermore, the tetra-thienylporphyrins 4-7 showed red shifts in both Soret- and Q-bands, broadening and significantly altered extinction coefficients compared to their corresponding tetraphenylporphyrins supported the alteration of electronic properties of porphyrin on introduction of thiényl groups in place of phenyl groups at meso-positions. The X-ray structure solved [6] previously for 7 also indicated that 7 is very planar compared to its corresponding phenyl analogue S1 TPP supporting the maximum shifts in the absorption bands observed for 7.

The absorption spectral properties were studied for meso-tetra-thienylporphyrins with N2 S2 core by varying the S-group from 2- to 3-position on the thienyl groups as well as for Zn5+-derivative of 8. The N2 S2 porphyrin with 3 thienyl groups at meso-position showed less shifts in the Soret- and Q-bands compared to N2 S2 porphyrin with 2-thienyl groups at meso-position 7 indicating the 2-thienyl groups alter the electronic properties more effectively than 3-thienyl groups at meso-positions [5d] (Table 3). Interestingly, the Zn5 showed negligible effects in absorption peak maxima although the peaks were much broadened compared to ZnTPP [5d].

The absorption spectra of dications of porphyrins with different cores 4H22+, 5H22+, 6H22+, 7H22+ and 8H22+ exhibited one broad Q-band and one strong Soret-band (Fig. 3, inset) and experienced large red shifts compared to the dications of their corresponding tetraphenylporphyrin analogues [13,14,16] (Table 2). The magnitude of red shifts depend on the kind of porphyrin core and the position of thiényl group attached to porphyrin. As evident from the Table 3, the maximum shifts were noted for 7H22+ which has N2 S2 core having 2-thienyl groups at meso-position.

### 3.2. Fluorescence properties

In order to understand the effect of meso-thiényl groups on electronic properties of porphyrins in singlet excited state, the fluorescence properties were studied by both steady state and time resolved techniques. Fig. 4 shows a comparison of the fluorescence spectra of 2-thiaporphyrins containing one, two, three and four thiényl groups at meso-positions 1-4 and the fluorescence data are listed in Table 4. In particular, the

Table 3: Absorption data of meso-thiényl and meso-arylporphyrins in toluene

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>Soret-band λ (nm) (ε × 10^4)</th>
<th>Q-bands λ (nm) (ε × 10^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2TPP</td>
<td>419 (46.4)</td>
<td>515 (18.7)</td>
</tr>
<tr>
<td>5</td>
<td>426 (38.9)</td>
<td>523 (19.9)</td>
</tr>
<tr>
<td>Zn5</td>
<td>422 (61.7)</td>
<td>553 (25.7)</td>
</tr>
<tr>
<td>STPP</td>
<td>427 (46.6)</td>
<td>555 (25.1)</td>
</tr>
<tr>
<td>OTPPH</td>
<td>429 (18.7)</td>
<td>513 (17.1)</td>
</tr>
<tr>
<td>6</td>
<td>440 (33.7)</td>
<td>523 (22.7)</td>
</tr>
<tr>
<td>S1 TPP</td>
<td>430 (10.1)</td>
<td>536 (5.5)</td>
</tr>
<tr>
<td>7</td>
<td>435 (25.0)</td>
<td>547 (7.0)</td>
</tr>
<tr>
<td>8</td>
<td>440 (15.4)</td>
<td>554 (6.6)</td>
</tr>
</tbody>
</table>

Fig. 3. Comparison of Soret- and Q-band absorption spectra of meso-tetra-thienyl-2-thiaporphyrins 4, 5 and 7 recorded in toluene. The concentrations used were 3 × 10^-6 M.
following spectral changes were observed on replacement of phenyl groups with thienyl groups at meso-positions: (1) the fluorescence bands of 1–4 were shifted to higher wavelengths compared to STPPH; (2) the absorption/fluorescence shifts (Stokes shifts) increases with the increase of number of thienyl groups at meso-position; (3) broadening of the emission bands with significant quenching of fluorescence intensity leading to a decrease in the quantum yields relative to STPPH; (4) the magnitude of red shifts and reduction in the fluorescence yields were dependent on number of thienyl groups present at the meso-position and maximum effects were observed for 21-thiaporphyrin having four meso-thienyl groups 4. These results were in parallel with absorption spectral studies. The red shifts in fluorescence peak maxima were due to increased resonance interaction between the porphyrin and meso-thienyl groups in the singlet excited state. The Stokes shift data indicated that the structure of excited state is different compared to ground state and the maximum structural change in the excited state was occurred for 4. The decreased quantum yields of 1–4 compared to STPPH was attributed in particular to the heavy sulfur atoms of meso-thienyl groups 17.

The time-resolved fluorescence studies carried out on 1–4 supports these observations. The porphyrins 1–4 were excited at 406 nm and emissions were detected at emission wavelengths depending on the emission peak positions of the porphyrins. The fluorescence decays of 1–4 along with STPPH are shown in Fig. 5 and the data of lifetime $\tau$, rate of radiative decay $k_r$ and the rate of non-radiative decay $k_{nr}$ are presented in Table 5. The fluorescence decays of 1–4 were fitted to single exponential. An inspection of Table 5 reveal the following changes upon the replacement of phenyl groups with thienyl groups at meso-positions: (1) the lifetimes $\tau$ of meso-thienyl-21-thiaporphyrins 1–4 were decreased compared to STPPH; (2) the rates of radiative $k_r$ and non-radiative $k_{nr}$ decay of 1–4 decreased and increased respectively compared to those of STPPH; (3) the maximum effects were observed for porphyrin with four meso-thienyl groups 4. The low lifetimes of meso-thienyl-21-thiaporphyrins 1–4 and decreased and increased of $k_r$ and $k_{nr}$, respectively supported the observed low fluorescence yields resulted due to the presence of heavy sulfur atoms 18 of the meso-thienyl groups. The heavier sulfur has empty d-orbitals which have an appropriate symmetry for better coupling with the $\pi$-system of porphyrin.

### Table 4

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>$Q(0.0)\lambda_{em}$ (nm)</th>
<th>$Q(0.1)\lambda_{em}$ (nm)</th>
<th>$\phi$</th>
<th>Absorption/emission shift (cm$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>STPPH</td>
<td>678</td>
<td>750 (sh)</td>
<td>0.0168</td>
<td>66</td>
</tr>
<tr>
<td>1</td>
<td>683</td>
<td>761 (sh)</td>
<td>0.0061</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>699</td>
<td>765 (sh)</td>
<td>0.0024</td>
<td>314</td>
</tr>
<tr>
<td>3</td>
<td>691</td>
<td>765 (sh)</td>
<td>0.0026</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>700</td>
<td>–</td>
<td>0.0012</td>
<td>346</td>
</tr>
<tr>
<td>H$_2$TPP</td>
<td>652</td>
<td>718 (sh)</td>
<td>0.110</td>
<td>118</td>
</tr>
<tr>
<td>5</td>
<td>650</td>
<td>727 (sh)</td>
<td>0.0046</td>
<td>203</td>
</tr>
<tr>
<td>6</td>
<td>650</td>
<td>–</td>
<td>0.0046</td>
<td>170</td>
</tr>
<tr>
<td>S$_2$TPP</td>
<td>706</td>
<td>781 (sh)</td>
<td>0.0076</td>
<td>245</td>
</tr>
<tr>
<td>7</td>
<td>738</td>
<td>–</td>
<td>0.0022</td>
<td>475</td>
</tr>
<tr>
<td>8</td>
<td>717</td>
<td>–</td>
<td>0.0193</td>
<td>257</td>
</tr>
</tbody>
</table>
resulting in the decrease of $S_1$ state lifetimes. The $S_1$ state lifetimes mainly depend on the increase of $S_1 \rightarrow T_1$ intersystem crossing and increase of $S_1 \rightarrow S_0$ internal conversion rates. The increase in internal conversion rate can be attributed to the enhancement of the Franck-Condon factor associated with structural reorganization in the excited state [19] and the increase in the intersystem crossing rate can be attributed to the enhancement of the spin-orbit coupling caused by the heavy sulfur atom [17] of meso-thienyl groups. The emission spectra of dications $H_2^{2+}$, $H_3^{2+}$, $H_4^{2+}$, and $H_5^{2+}$ are shown in Fig. 4 (inset) and the data are tabulated in Table 6. The emission spectra of dications showed one or two bands and the peak maxima were shifted to longer wavelengths as the number of meso-thienyl groups increases.

The maximum effects observed for the dication of meso-tetraphenylporphyrin, $meso$-tetraphenylporphyrin, were noted for $H_3^{2+}$ and $H_5^{2+}$. $meso$-tetraphenylporphyrins correspond to their corresponding $meso$-tetraphenylporphyrins; (3) the quantum yields of $meso$-tetraphenylporphyrins were very low compared to corresponding $meso$-tetraphenylporphyrins; (4) the maximum red shifts of fluorescence bands and reduction in quantum yields were observed for $meso$-tetraphenylporphyrin with $N_2S_2$ core.[16] (5) The comparison of emission spectra of $meso$-tetraphenylporphyrins with $N_2$ core 5, $N_2S$ core 4 and $N_2S_2$ core 7 are presented in Fig. 6 and the data calculated from the emission spectra of $4-7$ are presented in Table 4.

Some important observations from the emission data are: (1) the emission bands of $meso$-thienylporphyrins $4-7$ were broadened and red shifted compared to their corresponding $meso$-tetraphenyl analogues [17]; (2) larger Stokes shifts were found for $meso$-tetraphenylporphyrins compared to corresponding $meso$-tetraphenylporphyrins; (3) the quantum yields of $meso$-tetraphenylporphyrins were very low compared to corresponding $meso$-tetraphenylporphyrins. The time-resolved fluorescence studies carried out on $4-7$ supported these observations. The Fig. 7 shows the fluorescence decay profiles and weighted residuals of $4-7$ and the data are tabulated in Table 5. The fluorescence decays of $4-7$ were fitted to single exponential. The lifetimes of $meso$-tetraphenylporphyrins with different cores $4-7$ were low compared to their corresponding $meso$-tetraphenylporphyrins. The decreased lifetimes $\tau_f$ for $4-7$ was supported by the increased $k_{isc}$ and decreased of $k_t$ for all $meso$-tetraphenylporphyrins compared to the corresponding $meso$-tetraphenylporphyrins. The comparison of $meso$-tetraphenyl-21,23-dithioporphyrins with 2-thienyl groups 7 and 3-thienyl groups 8 at $meso$-positions shown in Fig. 6 (inset) indicate that the emission bands of $7$ were more red shifted with reduction in quantum yield and singlet state lifetime $\tau_f$ compared to $8$. These observations were in agreement with the ground state absorption studies [5d] and suggest a greater resonance interaction between the porphyrin and $meso$-thienyl groups in $7$ compared to $8$. The dications of $meso$-tetraphenylporphyrins with different porphyrin cores $4H_4^{2+}$, $5H_5^{2+}$, $6H_6^{2+}$, $7H_7^{2+}$.
Fig. 7. Fluorescence decay profiles of meso-thienyl-21-thiaporphyrins 4, 5, 7 and the weighted residual distribution fits of fluorescence decays of 4, 5 and 7 in toluene. The excitation wavelength was 406 nm and emissions were detected at different wavelengths depending on the emission peak positions of the porphyrines.

SII$^{2+}$ showed red shifted fluorescence bands with low fluorescence yields compared to the corresponding neutral porphyrins (Table 6).

The emission properties of Zn5 were studied by both steady state and time resolved fluorescence techniques. Similar to ZnTPP, the Zn5 showed emission from both the S1 and S2 excited states [20]. The comparison of S1 and S2 emission spectra of Zn5 and ZnTPP are shown in Fig. 8. The salient features of this study are: (1) a red shift in both the S1 ($\lambda_{em} = 620, 656$ (sh)) and S2 ($\lambda_{em} = 445$) emission maxima of Zn5 relative to ZnTPP S1 ($\lambda_{em} = 598, 645$ (sh)) and S2 ($\lambda_{em} = 435$); (2) a reduction in the S1 ($\phi_f = 0.0054$) and S2 ($\phi_f = 3.8 \times 10^{-5}$) fluorescence yields of Zn5 relative to ZnTPP S1 ($\phi_f = 0.033$) and S2 ($\phi_f = 0.00039$); (3) the lifetime of Zn5 ($\tau_f = 0.617$ ns) was reduced compared to ZnTPP ($\tau_f = 1.98$ ns). These results were in agreement with the free base meso-thienyl/porphyrins indicating that the replacement of phenyl groups by thienyl groups at meso-positions alter the electronic properties significantly.

4. Conclusions

The absorption and fluorescence studies revealed that the electronic properties were considerably altered on replacement of six-membered phenyl groups with five-membered thienyl groups at meso-positions of porphyrin macrocycle. By substituting the six-membered aryl groups with five-membered thienyl groups at meso-positions resulted in large red shifts and peak broadening of absorption and emission bands, low fluorescence yields and reduction in excited state lifetimes supports the alteration of electronic properties by greater π-delocalization in meso-thienyl/porphyrins due to the stronger resonance interaction between porphyrin and meso-thienyl groups.

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