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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 (N_4, N_3O, N_3S and N_2S_2 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 S_1 state lifetimes and the maximum effects were observed for *meso*-tetrathienylporphyrin with N_2S_2 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 and explored their physico–chemical properties in detail [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*-tetrathienylporphyrins [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 [5f]. 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 ligation 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 N_3O, N_3S and N_2S_2 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

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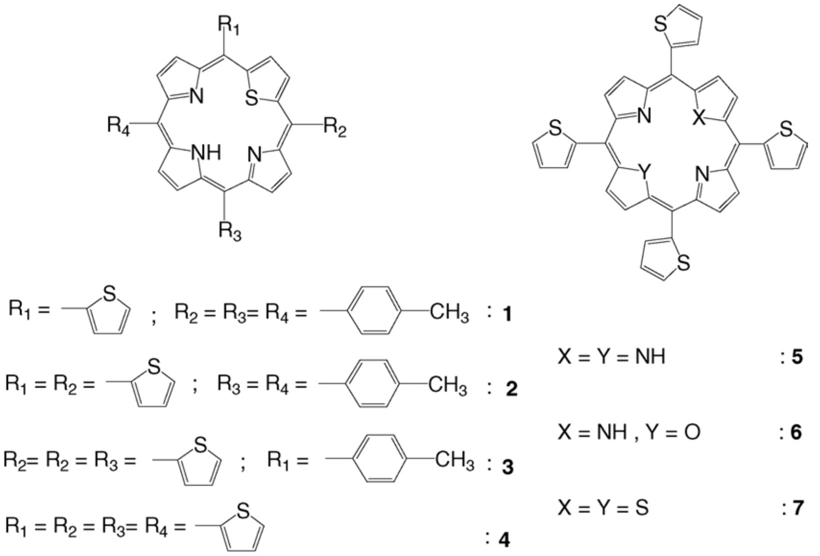

Fig. 1. Structures of various *meso*-thienylporphyrns.

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 N_4 to heteroatom substituted cores (N_3S, N_3O and N_2S_2) 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*-tetrathienylporphyrins with heteroatom substituted porphyrin cores used in the present study were synthesized as described in our earlier work [6]. The *meso*-tetraphenylporphyrins with different porphyrin cores [7a,b] and 5,10,15,20-*meso*-tetrathienylporphyrin [5] and its Zn^{2+} 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 (ϕ_f) of *meso*-thienylporphyrins and dications were estimated from the emission and absorption spectra by comparative method [8] using the following equation

$$\phi_f = \left(\frac{[F(\text{sample})]\,[A(\text{standard})]}{[F(\text{standard})]\,[A(\text{sample})]}\right)\phi_f(\text{standard}) \tag{1}$$

where [*F* (sample)] and [*F* (standard)] are the integrated fluorescence intensities of the *meso*-thienylporphyrins or their dications and the standard [*A* (sample)] and [*A* (standard)] are the absorbances of *meso*-thienylporphyrins or dications and the standard at the excitation wavelength and ϕ_f (standard) represents the quantum yield of the standard sample. Free base tetraphenylporphyrin [9] (H_2TPP, $\phi_f = 0.11$) was used as the standard for free base porphyrins and their dications, and zinc (II) tetraphenylporphyrin (ZnTPP) was used as standard ($\phi_f S_1 = 0.033$ and $\phi_f S_2 = 0.00039$) for the Zn^{2+} derivative of *meso*-tetrathienylporphyrin (Zn5) [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

$$I(t) = A\exp\left(\frac{-t}{\tau_f}\right) \tag{2}$$

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 [11] by following equations

$$\sum K = \frac{1}{\tau_f} \tag{3}$$

$$k_r = \phi_f k \tag{4}$$

$$k_{nr} = k - k_r \tag{5}$$

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

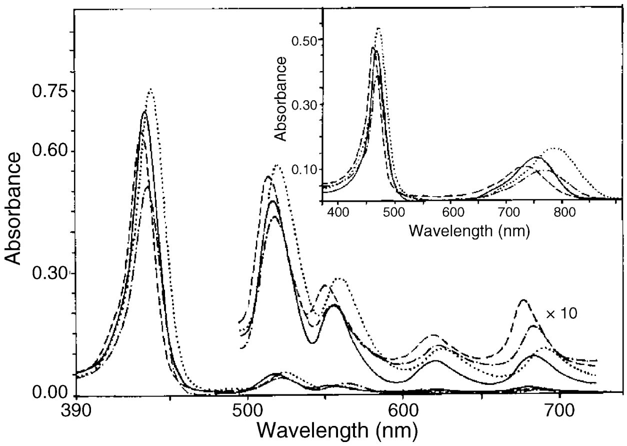

Fig. 2. Comparison of Soret- and Q-band absorption spectra of *meso*-thienyl-21-thiaporphyrins **1** (- - -), **2** (—), **3** (-·-·-) and **4** (. . .) in toluene. The inset shows the absorption spectra of **1**H_3^{2+} (- - -), **2**H_3^{2+} (—), **3**H_3^{2+} (-·-·-) and **4**H_3^{2+} (. . .) in toluene. The concentrations used were 3×10^{-6} M.

[12] (STPPH) are listed in Table 1. The *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*-tetrathienyl-2l-thiaporphyrin **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 N_3S 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-2l-thiaporphyrins **1**H_3^{2+}, **2**H_3^{2}, **3**H_3^{2+}, and **4**H_3^{2+}, recorded in toluene are shown in Fig. 2 (inset) and data are tabulated in Table 2 along with dication of *meso*-tetraphenyl-2l-thiaporphyrin $STPPH_3^{2+}$ [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 $STPPH_3^{2+}$, the dication derivative of STPPH. It was explained [14] that, on protonation, 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 $STPPH_3^{2+}$ 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*-tetrathienylporphyrins having different porphyrin cores such as N_4 **5**, N_3S **4**, N_3O **6** and N_2S_2 **7** cores and compared the properties with those of corresponding *meso*-tetraphenyl analogues H_2TPP, STPPH, OTPPH and S_2TPP respectively [12]. The absorption spectra of

Table 2
Absorption data of dications of *meso*-thienyl and *meso*-arylporphyrins in toluene

Porphyrin	Soret-band λ (nm) ($\varepsilon \times 10^{-4}$)		Q-bands λ (nm) ($\varepsilon \times 10^{-3}$)
$STPPH_3^{2+}$	456 (19.0)		699 (24.0)
1H_3^{2+}	467 (16.3)		738 (27.5)
2H_3^{2+}	472 (19.5)		756 (51.4)
3H_3^{2+}	473 (12.8)		766 (26.1)
4H_3^{2+}	478 (21.8)		790 (57.6)
$TPPH_4^{2+}$	448 (43.6)	608 (9.0)	659 (50.9)
5H_4^{2+}	461 (26.5)		730 (45.3)
$OTPPH_3^{2+}$	434 (26.8)	621 (12.0)	656 (14.0)
6H_3^{2+}	482 (16.8)		705 (13.1)
$S_2TPPH_2^{2+}$	463 (28.0)	697 (31.5)	735 (29.7)
7H_2^{2+}	482 (16.8)		817 (57.8)
8H_2^{2+}	471 (9.9)		757 (17.5)

Table 1
Absorption data of *meso*-thienyl-21-thiaporphyrins along with STPPH in toluene

Porphyrin	Soret-band λ (nm) ($\varepsilon \times 10^{-4)}$	Q-bands λ (nm) ($\varepsilon \times 10^{-3}$)			
		IV	III	II	I
STPPH	429 (18.7)	513 (17.1)	547 (4.4)	618 (1.9)	675 (3.0)
1	433 (34.4)	517 (24.1)	553 (9.6)	620 (3.3)	679 (4.5)
2	436 (29.3)	520 (20.6)	557 (9.4)	622 (3.1)	684 (3.4)
3	437 (23.9)	521 (17.5)	557 (9.4)	624 (2.6)	687 (3.2)
4	440 (33.7)	523 (22.7)	562 (11.3)	627 (3.8)	692 (3.6)

Table 3
Absorption data of *meso*-thienyl and *meso*-arylporphyrins in toluene

Porphyrin	Soret-band λ (nm) ($\varepsilon \times 10^{-4}$)	Q-bands λ (nm) ($\varepsilon \times 10^{-3}$)			
		IV	III	II	I
H_2TPP	419 (46.4)	515 (18.7)	548 (8.6)	592 (5.5)	647 (3.9)
5	426 (38.9)	523 (19.9)	560 (10.5)	597 (7.6)	661 (7.2)
ZnTPP	422 (61.7)	553 (25.7)		595 (10.0)	
Zn5	427 (46.8)	555 (25.1)		595 (6.2)	
STPPH	429 (18.7)	513 (17.1)	547 (4.4)	618 (1.9)	675 (3.0)
4	440 (33.7)	523 (22.7)	562 (11.3)	627 (3.8)	692 (3.6)
OTPPH	419 (21.9)	507 (15.9)	539 (3.0)	569 (2.6)	671 (2.8)
6	430 (10.1)	516 (5.5)	553 (3.0)	598 (2.1)	682 (0.98)
S_2TPP	435 (25.0)	514 (26.0)	547 (7.0)	633 (2.2)	696 (4.5)
7	447 (17.0)	525 (19.2)	563 (11.9)	642 (1.8)	713 (3.3)
8	440 (15.4)	519 (13.5)	554 (6.6)	638 (1.2)	704 (2.9)

meso-tetrathienyl-21-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*-tetrathienylporphyrins **4**–**7** experienced red shifts and peak broadening as porphyrin core changes from N_4 to N_3S to N_2S_2 and maximum effects were observed for *meso*-tetrathienylporphyrin having N_2S_2 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) ca1culations [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 oxygens in place of nitrogens 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 H_2TPP [16]. Furthermore, the tetrathienylporphyrins **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 thienyl 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 S_2TPP supporting the maximum shifts in the absorption bands observed for **7**.

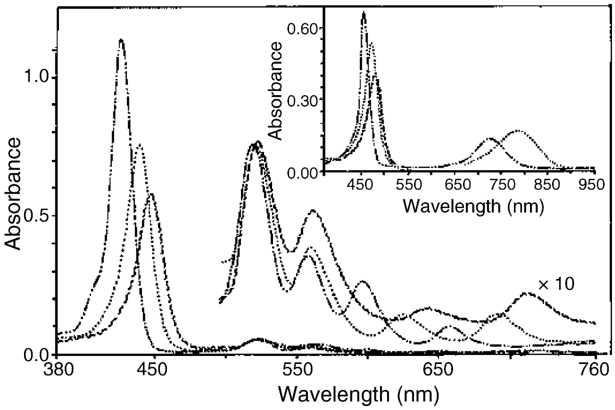

Fig. 3. Comparison of Soret- and Q-band absorption spectra of *meso*-thienylporphyrins **4** (. . .), **5** (-·-·-) and **7** (~ ~ ~) in toluene. The inset shows the absorption spectra of **4**H_3^{2+} (. . .), **5**H_4^{2+} (-·-·-·-) and **7**H_2^{2+} (~ ~ ~) in toluene. The concentrations used were 3×10^{-6} M.

The absorption spectral properties were studied for *meso*-tetrathienylporphyrins with N_2S_2 core by varying the S-group from 2- to 3-position on the thienyl groups as well as for Zn^{2+} derivative of **5**. The N_2S_2 porphyrin with 3-thienyl groups at *meso*-position **8** showed less shifts in the Soret- and Q-bands compared to N_2S_2 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 **4**H_3^{2+}, **5**H_4^{2+}, **6**H_3^{2+}, **7**H_2^{2+} and **8**H_2^{2+} 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 thienyl group attached to porphyrin. As evident from the Table 3, the maximum shifts were noted for **7**H_2^{2+} which has N_2S_2 core having 2-thienyl groups at *meso*-position.

3.2. Fluorescence properties

In order to understand the effect of *meso*-thienyl 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 21-thiaporphyrins containing one, two, three and four thienyl groups at *meso*-positions **1**–**4** and the fluorescence data are listed in Table 4. In particular, the

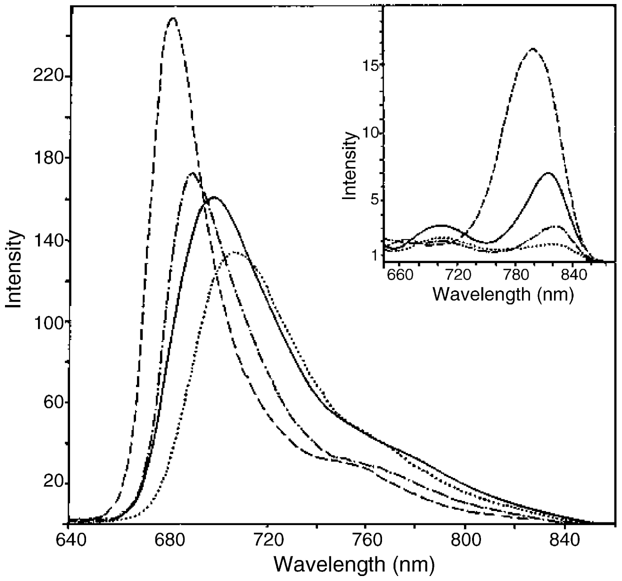

Fig. 4. Comparison of emission spectra of *meso*-thienyl-21-thiaporphyrins **1** (- - -), **2** (—), **3** (-·-·-) and **4** (. . .) recorded at excitation wavelength 440 nm in toluene. The inset shows the emission spectra of **1**H_3^{2+} (- - -), **2**H_3^{2+} (—), **3**H_3^{2+} (-·-·-) and 4H_3^{2+} (. . .) recorded at excitation wavelength 450 nm in toluene. The concentrations used were 3×10^{-6} M.

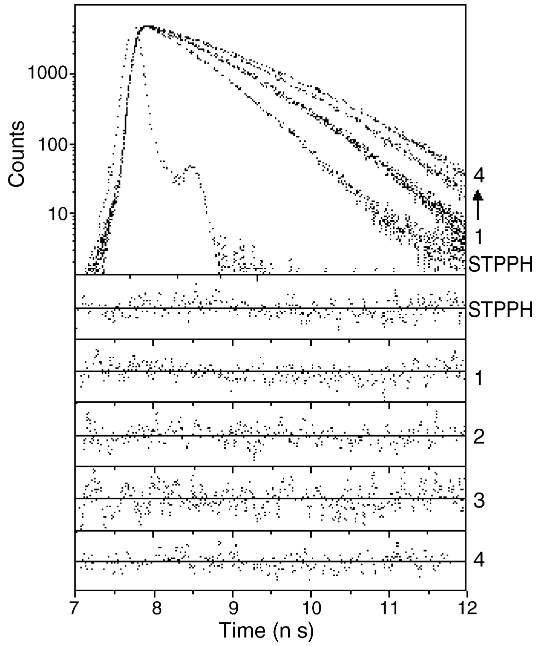

Fig. 5. Fluorescence decay profiles of *meso*-thienyl-21-thiaporphyrins **1**, **2**, **3** and **4** along with STPPH and the weighted residual distribution fits of fluorescence decays of **1**–**4** along with STPPH in toluene. The excitation wavelength is 406 nm and emissions were detected at different wavelengths depending on the emission peak positions of the porphyrins.

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 [17]; (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].

Table 4
Emission data of *meso*-thieny1porphyrins and *meso*-ary1porphyrins in toluene

Porphyrin	Q (0.0) λ_{em} (nm)	Q (0.1) λ_{em} (nm)	ϕ_f	Absorption/emission shift (cm^{-1})
STPPH	678	750 (sh)	0.0168	66
1	683	761 (sh)	0.0061	85
2	699	761 (sh)	0.0024	314
3	691	765 (sh)	0.0026	85
4	709	–	0.0012	346
H_2TPP	652	718 (sh)	0.110	118
5	670	727 (sh)	0.0046	203
OTPPH	676	–	0.0860	110
6	690	–	0.0046	170
S_2TPP	706	781 (sh)	0.0076	243
7	738	–	0.0022	475
8	717	–	0.0039	257

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 τ, 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 τ 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 π-system of porphyrin

Table 5
Photophysical data of *meso*-thienylporphyrins and *meso*-arylporphyrins in toluene

Porphyrin	τ_f (ns)	K_r (10^8 s^{-1})	K_{nr} (10^8 s^{-1})
STPPH	1.77 ± 0.005	0.0949	5.555
1	1.95 ± 0.005	0.0312	5.097
2	1.45 ± 0.005	0.0165	6.880
3	1.35 ± 0.004	0.0192	7.385
4	0.97 ± 0.003	0.0123	10.255
H_2TPP	9.32 ± 0.032	0.1180	0.955
5	0.927 ± 0.004	0.0500	10.737
OTPPH	8.18 ± 0.0133	0.1051	1.117
6	5.84 ± 0.005	0.0078	1.707
S_2TPP	1.34 ± 0.008	0.0567	7.406
7	1.12 ± 0.004	0.0196	8.909
8	1.20 ± 0.000	0.0325	10.033

resulting in the decrease of S_1 state lifetimes. The S_1 state lifetimes mainly depends 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 **1**H_3^{2+}, **2**H_3^{2+}, **3**H_3^{2+} and **4**H_3^{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*-tetrathienyl-21-thiaporphyrin, **4**H_3^{2+} relative to STPPH_3^{2+} suggest a greater resonance interaction between porphyrin and *meso*-thienyl groups. A similar conclusion was drawn from the ground state absorption studies. However, the dications were less fluorescent than the neutral porphyrins as evident in their very low quantum yields (Table 6).

The comparison of emission spectra of *meso*-tetrathienylporphyrins with N_4 core **5**, N_3S 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.

Table 6
Emission data of dications of *meso*-thienylporphyrins and *meso*-arylporphyrins in toluene

Porphyrin	Q (0.0) λ_{em} (nm)	Q (0.1) λ_{em} (nm)	ϕ_f
STPPH_3^{2+}	748	–	0.00440
1H_3^{2+}	799	–	0.00051
2H_3^{2+}	704	816	0.00031
3H_3^{2+}	705	823	0.00028
4H_3^{2+}	705	825	0.00013
TPPH_4^{2+}	700	–	0.01664
5H_4^{2+}	807	–	1.1×10^{-5}
OTPPH_3^{2+}	699	–	0.03426
6H_3^{2+}	797	–	9.5×10^{-4}
S_2TPPH_2^{2+}	771	–	0.00665
7H_2^{2+}	700	833	2.9×10^{-5}
8H_2^{2+}	690	817	2.3×10^{-3}

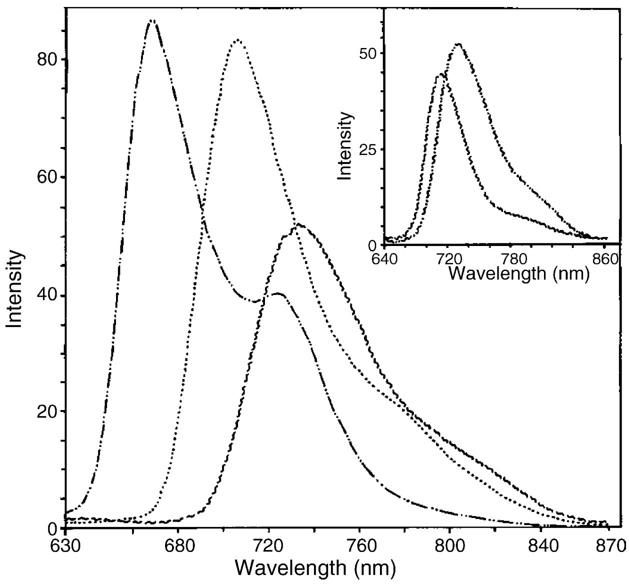

Fig. 6. Comparison of emission spectra of *meso*-thienylporphyrins **4** (. . .), **5** (-·-·-) and **7** (~ ~ ~) recorded at excitation wavelength 440 nm in toluene. The inset shows the emission spectra of **7** (~ ~ ~) and **8** (~·~·~) recorded at excitation wavelength 450 nm in toluene. The concentrations used were 3×10^{-6} M.

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 noted for *meso*-tetrathienylporphyrins compared to corresponding *meso*-tetraphenylporphyrins; (3) the quantum yields of *meso*-tetrathienylporphyrins were very low compared to corresponding *meso*-tetraphenylporphyrins [16]; (4) the maximum red shifts of fluorescence bands and reduction in quantum yields were observed for *meso*-tetrathienylporphyrin with N_2S_2 porphyrin core **7**. 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*-tetrathienylporphyrins with different cores **4**–**7** were low compared to their corresponding *meso*-tetraphenylporphyrins. The decreased lifetimes τ_f for **4**–**7** was supported by the increased k_{nr} and decreased of k_r for all *meso*-tetrathienylporphyrins compared to the corresponding *meso*-tetraphenylporphyrins.

The comparison of *meso*-tetrathienyl-21,23-dithiaporphyrins 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 τ_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*-tetrathienylporphyrins with different porphyrin cores **4**H_3^{2+}, **5**H_4^{2+}, **6**H_3^{2+}, **7**H_2^{2+},

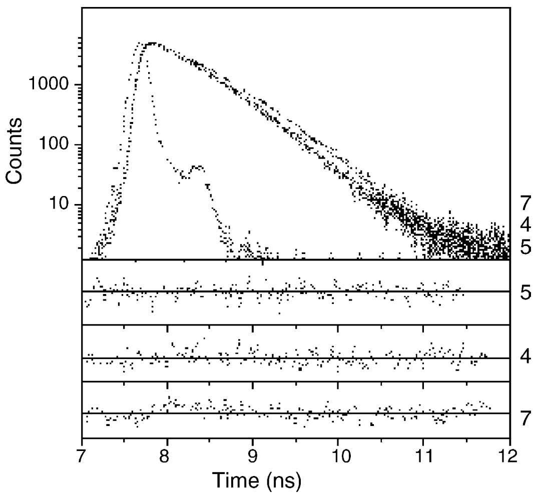

Fig. 7. Fluorescence decay profiles of *meso*-thienyl-21-thiaporphyrins **4**, **5**, **7** and the weighted residual distribution fits of fluorescence decays of **4**, **5** and **7** in toluene. The excitation wavelength was 406 nm and emissions were detected at different wavelengths depending on the emission peak positions of the porphyrins.

8H_2^{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 S_1 and S_2 excited states [20]. The comparison of S_1 and S_2 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 S_1 {$\lambda_{em} = 620$, 656 (sh)} and S_2 ($\lambda_{em} = 445$) emission maxima of Zn5 relative to ZnTPP S_1 {$\lambda_{em} = 598$, 645 (sh)} and S_2 ($\lambda_{em} = 435$); (2) a reduction in the S_1 ($\phi_f = 0.0054$) and S_2 ($\phi_f = 3.8 \times 10^{-5}$) fluorescence yields of Zn5 relative to ZnTPP S_1 ($\phi_f = 0.033$) and S_2 ($\phi_f = 0.00039$); (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*-thienylporphyrins indicating that the replacement of phenyl groups by thienyl groups at *meso*-positions alter the electronic properties significantly.

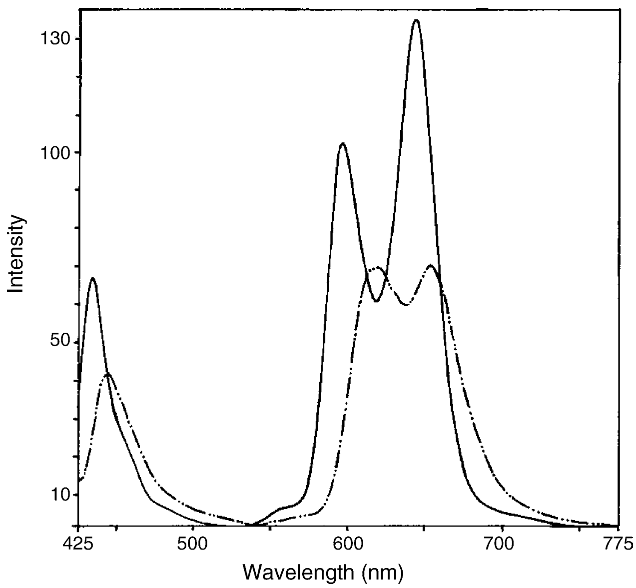

Fig. 8. S_1 and S_2 fluorescence spectra of Zn5 (-·-·-) and ZnTPP (—) in toluene using concentration 5×10^{-6} M. The excitation wavelengths used for S_1 emission was 450 nm and for S_2 emission was 405 nm.

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*-thienylporphyrins due to the stronger resonance interaction between porphyrin and *meso*-thienyl groups.

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