meso-Tetrathienylporphyrins: Steady-state emission and structural properties

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Abstract. *meso*-Tetra (2′- and 3′-thienyl)porphyrins and their Zn(II)-complexes were examined by steady-state fluorescence measurements. These molecules exhibit significant bathochromic shift in their emission bands with decreased quantum yields relative to their corresponding *meso*-tetraphenylporphyrin derivatives. The crystal structure of 5,10,15,20-*tetrakis*(3′-thienyl)porphinato zinc(II) shows planar and nonplanar stereochemical features of the macrocycle. One of the macrocycle shows nearly planar while the other exhibited predominantly saddle-shaped geometry. The extent of displacement of the ***b***-pyrrole carbons in the nonplanar (saddle) conformation is as high as ± 0·422 Å.

Keywords. Metalloporphyrins; thienylporphyrins; steady-state emission; crystal structure.

1. Introduction

Porphyrins and metalloporphyrins are of considerable importance for their use as biomimetic model compounds.[1–3] In recent years, they have been receiving increasing attention due to their interesting physico-chemical properties and material applications.[4–6] *Meso*-tetraphenylporphyrins are the most widely employed compounds for their synthetic utility and facile functionalisation.[1,2] The introduction of substituents at the ***b***-pyrrole and *meso*-positions induces a dramatic influence over the optical spectral, electro-chemical redox and stereochemical features.[7] Unusual properties of such sterically crowded porphyrins have been attributed partly to the nonplanar conformation of the porphyrin macrocycle arising from steric repulsion among the peripheral substituents. Such systems have been employed as models for nonplanar conformations of various tetrapyrrole pigments in nature.

A wide variety of substituted metallotetraphenylporphyrins (MTPPs) have been structurally characterized.[8,9] The stereochemistry of the porphyrin core of MTPPs is found to vary with the shape, size and number of substituents at the periphery.[7,9] It has been shown that the shape and size of the susbtituents

may vary the non-planarity of the porphyrin macrocycle. Of particular interest are the *meso*-tetrathienylporphyrins and their oligomeric derivatives that show interesting physico-chemical properties.[10–15] However, the steady-state emission and structural features of these *meso*-tetrathienylporphyrins (figure 1) have been largely unexamined.[16,17] In an effort to delineate the role of thienyl substitution on the photophysical properties of thienylporphyrins, we have examined their steady-state fluorescence properties. In addition, the crystal structure of ZnT(3′-Thia)P complex has also been determined and shows unusual stereochemical features.
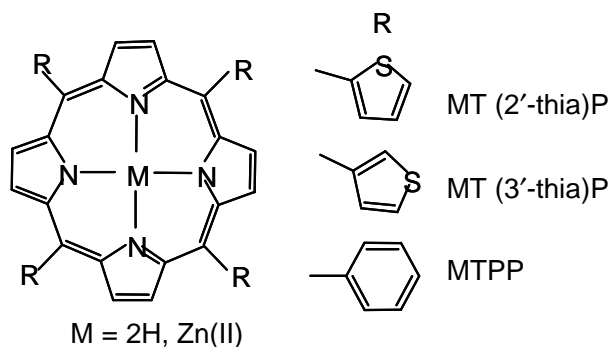

Figure 1. Chemical structures of *meso*-tetraarylporphyrins.

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2. Experimental

meso-Tetra(2′- and 3′-thienylporphyrins and their Zn(II)-complexes were prepared using reported literature methods.[13] *meso*-Tetraphenylporphyrin, H$_2$TPP, and its Zn(II)-complex were synthesised using conventional procedures.[18,19] All the solvents employed in the present study were of analytical grade and were distilled prior to use. Toluene was refluxed and distilled from sodium before use. Dichloromethane and chloroform were distilled from CaH$_2$ twice and stored over 4A molecular sieves.

3. Methods

Optical absorption spectra of the porphyrins were recorded on a Jasco V550 model UV-visible absorption spectrophotometer using a pair of matched 1 cm path length cells in CH$_2$Cl$_2$ at 298 K. Fluorescence spectra of the porphyrins were obtained on a Fluorolog-3 Jobin Yvon Horiba model spectrofluorimeter in CH$_2$Cl$_2$ solvent using a quartz cell of 10 mm path length at ambient temperature. Right angled detection was employed for the fluorescence measurements. Reference porphyrin standards, MTPPs (M = 2H, Zn(II)), were also measured under similar conditions. The excitation wavelengths employed were in the '*Q*' band energy region and the absorbance value was maintained in the range 0·03–0·10. The singlet emission quantum yields of the thienylporphyrins were calculated using the literature method.[20] The quantum yields obtained from Soret excitation are found to be similar to that of *Q*-band excitations.

3.1 *Crystal structure of ZnT(3-Thia)P complex*

ZnC$_{36}$H$_{20}$N$_4$S$_4$, Mr = 702·20. Crystal dimensions: 0·3 × 0·3 × 0·2 mm, dark pink, triclinic, *P*-1, *a* = 13·203 (2) Å, *b* = 13·460 (2) Å, *c* = 14·976 (3) Å, *a* = 64·16 (3)°, *b* = 70·646 (15)°, *g* = 89·25 (3)°, *V* = 2232·9 (7) A^3, *Z* = 3, *r*$_{calcd}$ = 1·567 mg m^{-3}. Diffractometer: Enraf–Nonius CAD-4 with a MoK*a* radiation (0·71073 Å), *T* = 298 K. *q* = 10–15°. Number of reflections collected, 8585, 7847 independent reflections. Refinement on *F*^{2} with the results *R*1 = 0·0595, *Rw* = 0·1737. The crystal structures were solved by the direct method using Shelxs97 and refined using Shelxl97.[21] In the ZnT(3′-thia)P structures, the thienyl groups exhibit two-fold rotational disorder. For ZnT(3′-thia)P structure, two-fold rotational disorder was found about C2–C21, C7–C25, C12–C29

and C17–C33 bonds in the nonplanar molecule and about C4–C51 and C46–C47 bonds in the planar molecule, which was also noticed at the structure solution stage itself. The occupancies of the two components refined to unequal values for S1/S1′ (0·388 and 0·611), S4/S4′ (0·659 and 0·340), S5/S5′ (0·592 and 0·407) and S6/S6′ (0·718 and 0·282) and equal values for S2/S2′ (0·492 and 0·508) and S3/S3′ (0·501 and 0·498). Except for the disordered thienyl groups, H atoms are fixed geometrically and were treated as riding on their parent atoms. The occupancies of the two components refined to unequal values for S1/S1′ (0·388 and 0·611), S4/S4′ (0·659 and 0·340), S5/S5′ (0·592 and 0·407) and S6/S6′ (0·718 and 0·282) and equal values for S2/S2′ (0·492 and 0·508) and S3/S3′ (0·501 and 0·498). Except for the disordered thienyl groups, H atoms are fixed geometrically and were treated as riding on their parent atoms.

4. Results and discussion

Free base tetrathienylporphyrins and their Zn(II) complexes exhibit characteristic singlet emission properties. Typical fluorescence spectra of the free base thienylporphyrins are shown in figure 2. The thienylporphyrins exhibit two bands in the 550–800 nm region. A comparison of the emission spectral data of the complexes was made with the corresponding MTPP derivatives to delineate the influence of thienyl groups on the singlet emission properties of porphyrin *p*-system. The emission data of thethienylporphyrins is listed in table 1. The thienyl-
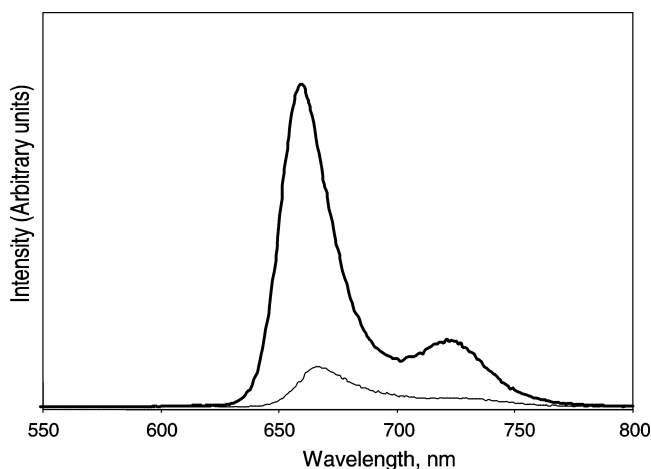

Figure 2. Steady-state emission spectrum of H$_2$T(2′-thia)P (thin line) and H$_2$T(3′-thia)P (thick line) in CH$_2$Cl$_2$ at 298 K.

porphyrins show significant red-shift in the emission bands relative to their corresponding MTPPs (table 1). Further, the singlet quantum yields of the thienyl-porphyrins are decreased relative to unsubstituted MTPPs. Earlier reports on the *meso*-tetraarylpor-phyrins have shown that the decrease in quantum yield is anticipated for the presence of heavy atom effect of the substituents on the position of the *meso*-aryl groups and the extent of decrease in the quantum yield follows in the order: para > meta > ortho positions.[22,23] The decreased quantum yield of the 2-thienylporphyrins is possibly due to the close proximity of the thienyl group to the porphyrin *p*-system relative to that in *meso*-tetra(3′-thienyl) porphyrin and also the 2-thienyl group show lower dihedral angles relative to the porphyrin core.[16] The observed quantum yield of the $H_2T(2′$-thia)P is comparable to that reported in the literature.[24]

In an effort to examine the role of 3-thienyl group on the stereochemistry of the complex, the crystal structure of the Zn(II)-complex was examined. *The Zn(II)-centre shows essentially four-coordinate geometry.* The unit cell has three porphyrin molecules with one nearly planar and two nonplanar units and is free of any solvate molecules in the lattice. ORTEP of the ZnT(3-thia)P complex for the planar macrocycle is shown in figure 3. Figure 4a shows the side-on view of the structure of planar and non-planar porphyrin units. The mean plane deviation of the 24-atom core is shown in figure 4b. The core atoms show displacement from the mean plane formed by 24-atom core and the geometry is fairly close to saddle-like conformation (figure 4). In case of the planar core, *b*-pyrrole carbons show marginal deviation (± 0.034 Å) from the mean plane while in case of the nonplanar ring there has been significant deviation (± 0.422 Å). The deviation of the *meso*-car-bons from the mean plane seems to suggest that the

conformation of the porphyrin core is a combination of saddle and marginal ruffled conformations.[25] In case of the nearly planar conformation, the porphy-rin unit is located at the corner of the unit cell with Zn(II) as the centre of inversion. Figure 4a(i) shows very minimal deviation from planarity of the por-phyrin core.

The two non-planar porphyrin entities are located at the centre of the unit cell in an offset fashion with the closest inter-porphyrin separation of 3.15 Å bet-ween them. This indicates the existence of minimal *p–p* interactions between the two entities. The closest interporphyrin distance of 3.22 Å is found between the Zn(II) ion of the planar molecule and the S-group of the nonplanar molecule. Interestingly, the Zn(II)-to-Zn(II) distance between the two close-lying non-planar entities is 4.702 Å, whereas the closest sepa-ration between the two planar entities is the fairly larger distance of 14.976 Å.

The selected bond lengths and bond angles of ZnT(3′-thio)P are given in table 2. A comparison of the data of the planar and nonplanar porphyrin enti-ties were made with the reported ZnT(2′-thia)P to elucidate the differences in the conformation fea-tures. The average bond distance, Zn–N (2.041 (4) Å) in planar unit is marginally high relative to that observed for nonplanar porphyrin (2.027 (4) Å). In case of the planar molecule, the Zn(II) atom is almost in the plane of the four pyrrolic nitrogens

Table 1. The singlet fluorescence emission data of *meso*-tetrathienylporphyrins in CH_2Cl_2 at 298 K.

Porphyrin	l_{em} (nm)	l_{ex} (nm)	f^a	Shift[b] (cm^{-1})
$H_2T(2′$-thia)P	666, 722 (*sh*)	426	0·006	322
$H_2T(3′$-thia)P	658, 723	421	0·010	140
H_2TPP	652, 716	417	0·120	–
ZnT(2′-thia)P	618, 658	427	0·0013	569
ZnT(3′-thia)P	605, 653	422	0·004	221
ZnTPP	597, 645	422	0·0330	–

[a]Uncertainty in values: $\pm 8\%$; [b]shift of emission band (0, 0) relative to corresponding MTPP bands
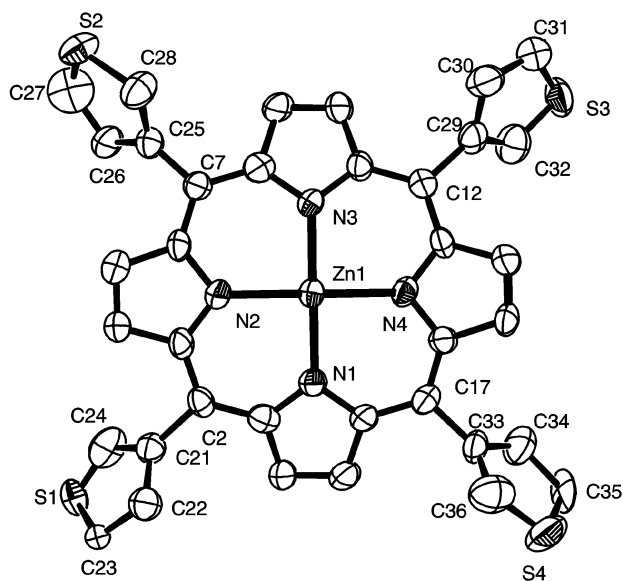

Figure 3. ORTEP of planar unit of the ZnT(3-thia)P complex. Only selected atoms are labeled for clarity. The thermal ellipsoids are shown at 40% probability level.
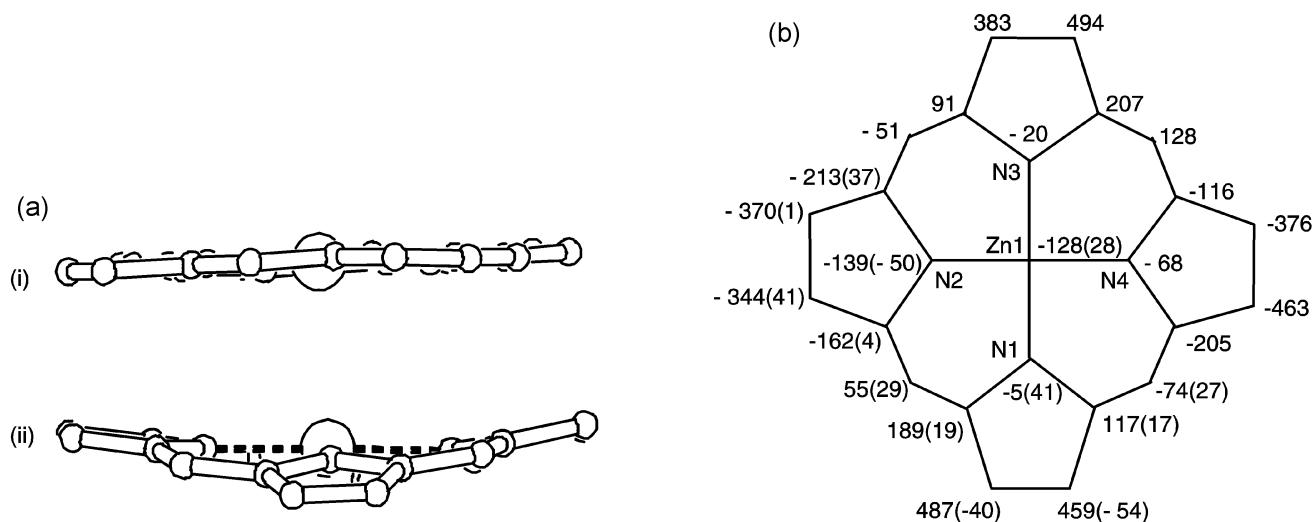
Figure 4. (**a**) (i) and (ii) indicate the side and top views of the planar and nonplanar porphyrin units respectively. (**b**) The mean plane deviation of atoms is shown in 0·001 Å units from the 24-atom core. Values in parentheses are displacements of the core atoms of the planar macrocycle.

Table 2. Selected bond lengths and geometric parameters of ZnT(3′-thia)P structure

	Nonplanar unit	Planar unit	ZnT(2′-thia)P[b]
Distance (Å)			
$(Zn-N)_{av}$	2·027 (4)	2·041 (4)	2·020 (5)
$(Zn-C_{meso})_{av}$	3·452 (5)	3·445 (5)	3·411 (5)
Dihedral angle (°)[a]			
(Core-thienyl ring)$_{av}$	53·7 (5)	85·7 (5)	68·5 (2)

[a]Core refers to nonplanar or planar porphyrin rings; [b]data from [ref. 16]

whereas it lies about 0·129 Å above in the nonplanar porphyrin unit. This is further reflected in the decrease in the Zn(II)-*meso*-carbon distance of about 0·0065 Å. Similar behaviour was reported for ZnT(2′-thia)P structure.[16] The closest distances between the Zn(II) centres of the planar and nonplanar units are 8·236 Å. The observed bond lengths and angles of planar porphyrin unit are not significantly different from those observed for the solvate free ZnT(2′-thia)P[16] and CuT(3′-thia)P[17] structures.

The thienyl rings are almost perpendicular (85·70°) to the porphyrin ring in the planar molecule, whereas there is a reduction in the dihedral angles formed by the thienyl rings with the porphyrin core in the nonplanar molecule (53·77°). *The dihedral angle observed for the planar ZnT(3¢thia)P structure is higher than that reported for ZnT(2¢thia)P structure.*[16] The closest distance between the Zn(II) centre of the planar entity to the thienyl-S group in the nonplanar entity shows weak intramolecular interactions between them. This affinity of the Zn(II) centre to interact with the thienyl S-group and the *p–p* interaction between the two nonplanar porphyrins favours the tight packing of the molecules. The intermolecular interactions are responsible for the existence of such conformations in the solid state. It was reported earlier that the Ni(II)-porphyrins tend to show such features in their structures.[7,26,27]

5. Conclusions

A series of tetrathienylporphyrins and their Zn(II)-complexes were examined by steady-state fluorescence to elucidate the role of position of the thienyl group on the singlet emission properties of the porphyrin *p*-system. These porphyrins show red-shifted emission bands with decreased quantum yields relative to their corresponding MTPPs. The decreased quantum yield of the thienylporphyrins is possibly due to the presence of thienyl groups. Further, the ZnT(3′-thia)P complex exhibits an unusual planar and non-planar conformational features in the solid state. One of the planar macrocycles is nearly planar, while the non-planar porphyrin unit has saddle-like

conformational features. This arises possibly due to the presence of weak intermolecular interactions in the lattice.

The crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 178679. Copies of the data can be obtained, free of charge, on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgement

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