

R. Prasath and P. Bhavana*

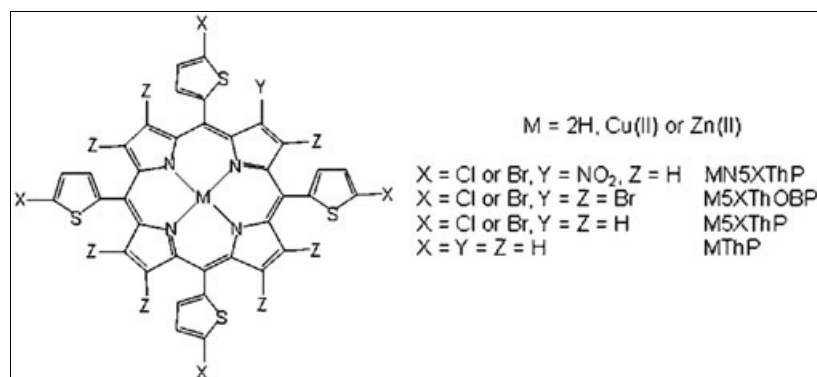
Department of Chemistry, Birla Institute of Technology and Science (BITS)
Pilani - K. K. Birla Goa Campus, Zuarinagar Goa 403726, India

*E-mail: juliebhavana@gmail.com

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Two types of β -functionalized (mono nitrated and perbrominated) *meso* tetrakis(5-halothien-2-yl)porphyrins, which can be used as precursors for the synthesis of other asymmetric and highly substituted porphyrins, have been synthesised and characterized. Introduction of a nitro group at the β -position shifted sorlet band 11–16 nm to the red region and redox potentials to > 170 mV for oxidation and > 250 mV for reduction anodically. Perbromination of halothienylporphyrins lead to enhanced bathochromically shifted uv-visible spectral bands, but had only marginal influence on oxidation potentials. Effect of mono nitro group and eight bromo groups on the electronic properties of the porphyrins is attributed, respectively to, the electron deficiency created in the porphyrin π -system and the nonplanar conformation induced by the bulky bromo groups.

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INTRODUCTION

The stable and highly tunable structure having delocalized π -system along with interesting physicochemical properties [1], catalytic [2], biomimetic [3], and medicinal applications [4], and the potential applications in the field of optoelectronics [5] make porphyrin an interesting class of compounds for research. Porphyrins with small heterocyclic groups like thienyl appended at the various peripheral positions or connected through the axial position are of growing interest owing to their efficiency in electron and energy transfer, and other physicochemical properties [6]. Thiophene appended porphyrins have also been studied for the ultrathin film formation [7] and for the nanofabrication of conducting materials [8]. *Meso* tetrathienylporphyrins show interesting electrochemical [9], structural [10], magnetic [11], and photophysical [9]a properties. Porphyrin with thienyl groups at the trans position form planar conformation in solid state, indicating that the heteroaromatic porphyrins can also be used as efficient building blocks for the porphyrin arrays [12]. Bromothienylporphyrins are good candidates for optoelectronics as they form ordered

films [13]. Sun *et al.* have studied absorption and fluorescence properties of a series of thienylporphyrins for elucidating the structural and electronic effect of the thienyl group at the *meso* position [14]. Research related to the β -substituted thienylporphyrins is less explored [15].

Nitroporphyrins are another interesting class of compounds because of their catalytic [16], photophysical [17], and nonlinear optical properties [18]. They are further attractive because of the role of nitro group in nucleophilic addition [19] and substitution [20] reactions for the preparation of a wide range of highly substituted systems. β -nitroporphyrins can be used for the synthesis of various asymmetric molecules which has potential application in the field of PDT [21]. In the report by Zhang *et al.*, linear and nonlinear optical properties of a series of zinc(II) porphyrin-based chromophores containing nitrothienyl group as the electron accepting moieties have been explained [22].

This work deals with the synthesis of two types of electron deficient thienylporphyrins achieved either by mononitration or by perbromination at the β -pyrrole position (s). The chemical structure of the porphyrins is shown in

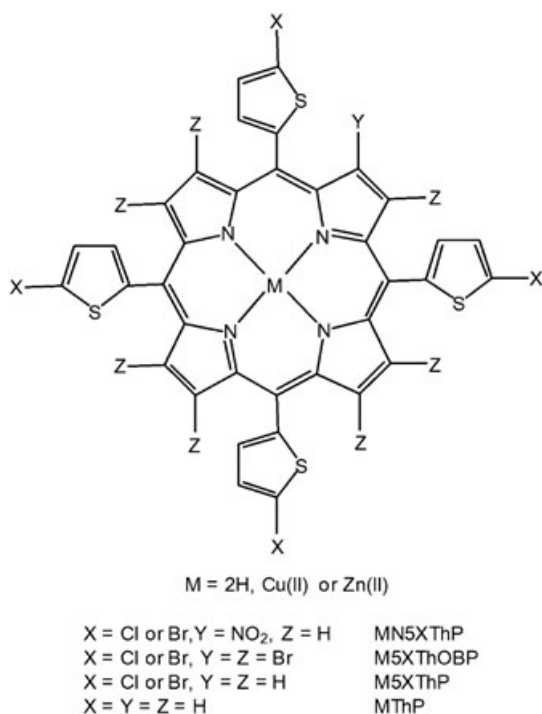


Figure 1. Chemical structure of *meso* tetrahalothien-2-ylporphyrins.

Figure 1. The synthesized compounds have been investigated for their spectral and electrochemical properties.

RESULTS AND DISCUSSION

Two series of β -functionalized halotetrathien-2-ylporphyrins, β -mono nitro halotetrathien-2-ylporphyrins, and β -perbrominated halotetrathien-2-ylporphyrins, have been synthesized and investigated for their electronic properties. The parent compound, i.e., chloro and bromo derivatives of *meso* tetrathien-2-ylporphyrin, was synthesized by condensing the relevant 5-halo-2-thiophenecarboxaldehyde with pyrrole in the presence of acid catalyst. The compounds were characterized by spectral techniques and the data confirmed the proposed structures.

Nitration of copper derivative of halothiénylporphyrins was carried out using cupric nitrate trihydrate as the nitrating agent under refluxing conditions. It is known that complexation with electronegative metals ions like Cu(II) and Ni(II) ensure β -nitration of tetraarylporphyrins in good yield [23]. Halothiényl groups can also direct the nitration towards β -position as strong electron withdrawing *meso* groups are known to stabilize preferentially the a_{2u} orbitals relative to the a_{1u} orbitals and favour β -nitration [24]. Because of asymmetry induced in the molecule by the introduction of the nitro group, the signals corresponding to the protons at the pyrrole β -positions and 3- and 4-positions of the thienyl groups were asymmetric in nature in the ¹HNMR of the synthesized nitroporphyrins [25]. Core NH resonances were downshielded by ~ 0.3 ppm on nitration of

halothiénylporphyrin which is ascribed to the electron deficiency created in the system. However, the chemical shift of thienyl proton resonances in 2-nitro-5,10,15,20-tetrakis(5-halothiényl)porphyrin (H₂N5XThP) is not significantly different from that of 5,10,15,20-tetrakis(5-halothiényl)porphyrin (H₂5XThP).

The UV-visible absorption maxima of all nitrated porphyrins are summarized in Table 1 along with that of non nitro analogues. Compared with *meso* tetraphenylporphyrins, *meso* tetrathien-2-ylporphyrins (MThP) show a bathochromic shift and this was assigned to the possible coplanarity of the relatively small thienyl groups with the porphyrin π -system [26]. Further red shift of the bands in *meso* tetrakis(5-halothiényl)porphyrins, M5XThP (X = Cl or Br) related to MThP indicates the effect of halo group at the fifth position on the thienyl ring. This was further red shifted by 11–16 nm on nitration at the β -position indicating the extension of conjugation of the π -system. As the halo groups are pointing away from the porphyrin π -system, it cannot impose restriction in bringing the thienyl ring coplanar with the central porphyrin ring. It is observed that the *Q*(0,0) transition has gained intensity compared with the *Q*(1,0) transition in CuN5XThP (X = Cl or Br). This can be due to the stabilization of the a_{1u} orbital which bear electron density at the pyrrole β -carbons, relative to a_{2u} orbitals, on nitration [27]. The number of *Q* bands in free base porphyrins was reduced to three on nitration. It is also noted from the full width at half maximum (FWHM, Table 1) that there is a significant band broadening for nitroporphyrins compared with its nonnitro analogues. This indicates the electronic communication between the nitro group and the porphyrin π -system [28].

Su *et al.* [15]b have synthesized and studied the photo-physical properties of perbrominated thienylporphyrins. They have reported yield of the reaction between substituted pyrrole and aldehyde which lead to the formation of perbrominated porphyrins as 15–30%. But this method requires the synthesis of 3,4-dibromopyrrole, synthesis of which involves reactions like bromination of *N*-(triisopropylsilyl)pyrrole under drastic reaction conditions. It is also known that 3,4-dibromopyrrole is highly unstable in nature [29]. In our synthesis, we have octabrominated the halothiénylporphyrins (halothiénylporphyrins were synthesised in 26–30% yield by following the reported procedure [7]b with modifications in it) in good yield using liquid bromine as the brominating agent under mild reaction conditions.

Octabromination of halothiénylporphyrins is ascertained from the absence of the signal corresponding to the pyrrole β -protons in the ¹HNMR of the porphyrins. In the mass spectrum, a clear isotopic pattern was observed around the intense molecular ion peak. Optical spectral data of all perbrominated compounds is given in Table 2. In the UV-visible spectrum, a shift of 44–52 nm towards higher

Table 1
UV-visible absorption spectral data^a of β - nitro tetrahalothien-2-ylporphyrins in CH₂Cl₂.

Porphyrin	Soret band (nm)	Q Bands (nm)	Q(0,0)/ Q(1,0) ^b	FWHM (nm)
H ₂ ThP	426 (5.59)	523 (4.30), 560 (4.02), 597 (3.88), 661 (3.86)		16.56
H ₂ 5ClThP	428 (5.44)	523 (4.13), 562 (3.80), 598 (3.69), 658 (3.06)		17.98
H ₂ 5BrThP	429 (5.55)	524 (4.22), 562 (3.92), 597 (3.75), 659 (3.22)		17.90
H ₂ N5ClThP	444 (5.36)	540 (4.12), 588 (3.74), 682 (3.84)		34.69
H ₂ N5BrThP	444 (5.52)	540 (4.28), 589 (3.86), 680 (4.00)		34.45
CuThP	421 (5.62)	546 (4.37), 582 (sh, 3.76)	0.86	14.83
Cu5ClThP	423 (5.59)	548 (4.37), 583 (sh, 3.57)	0.82	16.60
Cu5BrThP	424 (5.63)	548 (4.38), 583 (3.53)	0.81	16.49
CuN5ClThP	434 (5.32)	557 (4.22), 600 (4.00)	0.95	32.51
CuN5BrThP	436 (5.45)	558 (4.35), 602 (4.15)	0.95	32.27

^aThe values in parenthesis refer to log ϵ values, ϵ in dm³ mol⁻¹ cm⁻¹.

^bDenotes the ratio of log ϵ values.

wavelength region was observed for the Soret band of the tetraphenylporphyrin (MTPP, M = 2H, Zn, and Cu) on octabromination [30]. But in tetrahalothienylporphyrins, the extent of red shift of Soret band on similar bromination is 55–58 nm. This shows that on octabromination, the ruffling of the porphyrin ring (which is generally observed) give enough space for the *meso* substituted thienyl rings (which is relatively small compared to the phenyl ring in MTPP) to come more in plane with the porphyrin π -system. Similar to reported earlier [31] in the case of copper octabromotetraphenylporphyrin, synthesized Cu5XThOBP showed a broad Soret band. A shoulder was observed for the Soret band in the lower wavelength region. However, M5XThOBP (M = 2H or Zn, X = Cl or Br) showed very highly red shifted bands with a relatively less FWHM. The Q bands of copper derivatives showed similar shift as in zinc derivatives. Similar to nitroporphyrins, Q(0,0) transition has gained intensity in perbrominated porphyrins. It is very interesting to note that the number of Q bands in free base perbrominated porphyrins is only two.

To delineate the effect of the substituent(s) on the redox properties of thienylporphyrins, electrochemical studies were carried out. Representative cyclic voltammograms

of CuN5BrThP is shown in Figure 2 and the redox data of various nitrothienylporphyrins is compiled in Table 3. Generally porphyrins show two, one electron oxidations and two, one electron reductions which are ligand based. Compared to the respective *meso* tetrathien-2-ylporphyrins, bromo and chloro derivatives are found difficult to oxidize. Further anodic shift was observed on nitration. The shift is 195–270 mV for free base nitroporphyrins and ~170 mV for its copper derivatives. Reduction potentials shows the ease of reduction on functionalisation with a nitro group at the β -position of the porphyrin. Oxidation potentials are in the order MThP < M5XThP < MN5XThP and the magnitude of reduction potentials in the order MThP > M5XThP > MN5XThP. As expected, the introduction of the electronegative metal ion, Cu(II) brings an anodic shift in the oxidation potentials. MN5XThPs (M = 2H or Cu, X = Cl and Br) showed less difference in their redox potentials as in the case of M5XThPs (M = 2H or Cu, X = Cl and Br).

Oxidation potentials of β - perbrominated halothienylporphyrins on comparison with that of the β - nonbrominated analogues showed only marginal difference (Table 4). The shift is in the range -54 mV to +27 mV for all

Table 2
UV-visible absorption spectral data^a of perbrominated tetrahalothien-2-ylporphyrins in CH₂Cl₂.

Porphyrin	Soret bands (nm)	Q Bands (nm)	Q(0,0)/ Q(1,0) ^b	FWHM (nm)
H ₂ 5ClThOBP	366 (4.61), 484 (5.46)	654 (4.42), 760 (4.14)	0.93	44.79
H ₂ 5BrThOBP	365 (4.41), 484 (5.22)	654 (4.19), 761 (3.93)	0.93	45.02
Cu5ClThOBP	365 (4.33), 478 (5.07)	588 (4.16), 635 (3.79)	0.91	57.61
Cu5BrThOBP	366 (4.35), 479 (5.08)	591 (4.17), 640 (3.84)	0.92	56.33
Zn5ClThOBP	357 (4.54), 485 (5.41)	625 (4.06), 687 (4.20)	1.03	37.59
Zn5BrThOBP	361 (4.50), 488 (5.47)	625 (4.05), 687 (4.25)	1.05	24.74
ZnThP	427 (5.67)	555 (4.40), 595 (3.79)	0.86	13.92
Zn5ClThP	429 (5.31)	557 (4.02), 599 (2.93)	0.72	15.42
Zn5BrThP	430 (5.29)	557 (3.96), 599 (2.65)	0.67	15.46

^aThe values in parenthesis refer to log ϵ values, ϵ in dm³ mol⁻¹ cm⁻¹.

^bDenotes the ratio of log ϵ values.

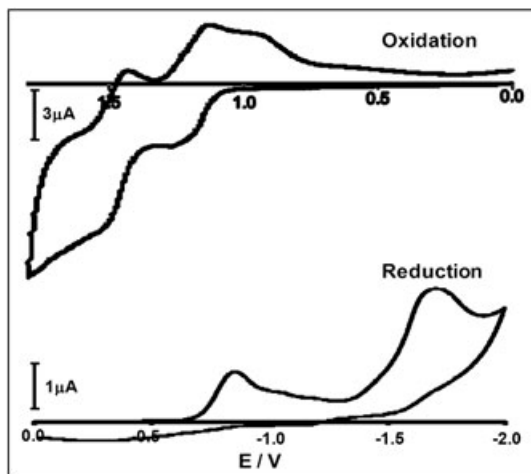


Figure 2. Cyclic voltammograms of CuN5BrThP in CH₂Cl₂ with 0.1M TBAHFP as the supporting electrolyte at a scan rate of 100 mVs⁻¹.

the M5XThOBP related to M5XThP (M = 2H, Cu or Zn). It is known that, generally on octabromination at β- positions, porphyrin attains nonplanar conformation which results in the unique physicochemical and stereochemical properties [32]. However, the reduction potentials are shifted anodically to 270–330 mV in all the Cu and Zn derivatives related to MThP (M = Cu or Zn). The reduction potentials were not clear for Zn5XThPs (X = Cl and Br) from the cyclic voltammogram. For free base porphyrins, three reduction potentials were observed. Perbromination has found to have less influence on the oxidation potentials, but affect significantly the reduction potentials.

Electrochemical results show that 2- nitro halothierylporphyrins are more electron deficient than the synthesized perbrominated porphyrins. Oxidation potentials of

Table 4
Half-wave redox potentials^a (mV) of perbrominated tetrahalothien-2-ylporphyrins in CH₂Cl₂ using 0.1 M TBAHFP at 25°C.

Porphyrin	Oxidation		Reduction		
	II	I	I	II	III
H ₂ 5ClThOBP	1179	887	-517 ^c	-923 ^c	-1205
H ₂ 5BrThOBP	1479	864	-529 ^c	-910	-1302
Cu5ClThOBP	1561	1081	-870 ^c	-	-
Cu5BrThOBP	1575	1009	-916 ^c	-	-
Zn5ClThOBP	1153	933	-892	-1315 ^c	-
Zn5BrThOBP	1213	980	-905	-1408 ^c	-
ZnThP	1085	885	-1225	-1425	-
Zn5ClThP	1116	925	-896 ^b	-	-
Zn5BrThP	1150	953	-580 ^b	-	-

^aVs Ag/AgCl electrode.

^bValues from differential pulse voltammetry.

^cIrreversible.

nitrothienylporphyrins are shifted > 190 mV anodically for free base (170 mV for copper derivative) compared to the non nitro analogue where in perbrominated porphyrins, there is no considerable shift. β- Nitro group is known for its high electron withdrawing effect and for its major role in the influencing the binding constants of nitrated porphyrins [25]. Redox potentials and the electrochemical gap ($E_1^{Ox} - E_1^{Redn}$) of nitro- and perbrominated- halothierylporphyrins in this study indicate that on mononitration, LUMO is getting stabilized more than the HOMO whereas on perbromination, LUMO is getting stabilized but energy of HOMO is not affected significantly. So the HOMO–LUMO gap is relatively less in perbrominated porphyrins, which is clear from the highly red shifted *Q*(0,0) band (optical gap) in the UV-visible spectrum.

CONCLUSIONS

Asymmetric and highly functionalized *meso* 5-halothierylporphyrins have been synthesized in good yield by appending, respectively, nitro group or bromo groups at the pyrrole β- positions and studied for their physicochemical properties. Upon introduction of a nitro group, halothierylporphyrins showed a significant anodic shift in redox potentials. Perbromination of M5XThP induced only less influence on the oxidation potentials, but reduction potentials are in the expected order. This unusual behavior can be due to the nonplanar conformation that porphyrins generally attain on perbromination. Electrochemical study shows that the nitro group has a very high influence in dictating the electronic properties of the porphyrin. The synthesized porphyrins can be used for the preparation of other unsymmetric and highly substituted porphyrins by taking advantage of the rich synthetic chemistry of the nitro group and the coupling properties

Table 3

Half-wave redox potentials^a (mV) of β- nitro tetrahalothien-2-ylporphyrins in CH₂Cl₂ using 0.1M TBAHFP at 25°C.

Porphyrin	Oxidation		Reduction	
	II	I	I	II
H ₂ ThP	1130	890	-1090	-1420
H ₂ 5ClThP	1450	918	-1039	-1347
H ₂ 5BrThP	1449	918	-1049	-1399 ^j
H ₂ 5N5ClThP	1368 ^b	1115	-714 ⁱ	-1010 ⁱ
H ₂ 5N5BrThP	-	1191	-707 ⁱ	-903
CuThP	1350	990	-1190	-1575
Cu5ClThP	1351	1063	-1145	-1684
Cu5BrThP	1412	1021	-1104	-1604
Cu5N5ClThP	1458	1232	-866	-1795
Cu5N5BrThP	1497 ^b	1196	-855 ⁱ	-1707 ⁱ

^aVs Ag/AgCl electrode.

^bValues from differential pulse voltammetry.

ⁱIrreversible.

of the bromo groups. Study on further functionalized thienylporphyrins is in progress in our laboratory.

EXPERIMENTAL

Materials. CH_2Cl_2 (SD Fine Chemicals, India) was refluxed and distilled over CaH_2 and stored over 4 Å molecular sieves. Pyrrole, dichlorodicyanobenzoquinone (DDQ), tetrabutylammonium hexafluorophosphate (TBAHFP) and various thiophenecarboxaldehydes were procured from Sigma - Aldrich and were used as received. Other required chemicals were purchased from SD Fine Chemicals, India.

Instrumentation and methods. Optical absorption spectra were recorded on a JASCO V-570 model UV/VIS/NIR spectrophotometer using quartz cells of 10 mm path length. ^1H NMR spectra were recorded on a Bruker Avance 300 spectrometer in deuteriochloroform using tetramethylsilane as the internal reference. BAS EPSILON model electrochemical system was employed for the cyclic voltammetric measurements. The electrochemical cell consists of three electrode cell assembly; a platinum working electrode, Ag/AgCl reference electrode and platinum wire counter electrode. The concentrations of all the porphyrins employed were ~ 1 mM. All the measurements were performed in CH_2Cl_2 solution which was purged with nitrogen, using 0.1 M TBAHFP as the supporting electrolyte. MALDI-TOF mass spectra were recorded on a Voyager-DE PRO Biospectrometry instrument and elemental analysis were carried out on Heraeus Vario EL III instrument.

Synthesis of meso tetrathienylporphyrins (MThP). Preparation of H_2ThP [15]a and its copper and zinc derivatives [25] were carried out as reported before. The products were characterized by spectral methods and spectral details are similar to those reported in literature.

Synthesis of 5,10,15,20-tetrakis(5-halothien-2-yl)porphyrin, $\text{H}_2\text{5XThP}$ ($X = \text{Cl}$ or Br). In a typical procedure, to the corresponding 5-halothiophene-2-carboxaldehyde (26.4 mmol) dissolved in CHCl_3 (100 mL), pyrrole (1.8 mL, 26.4 mmol) and $\text{BF}_3 \cdot \text{etherate}$ (1.1 mL, 8.8 mmol) were added and stirred for one hour at room temperature under nitrogen atmosphere. At the end of the period, DDQ (6.0 g, 26.4 mmol) was added and the stirring was continued for another 30 minutes. The reaction mixture was then treated with triethylamine (1.2 mL, 8.8 mmol) and the crude product was dried onto the silica gel. The product was purified by column chromatography using CHCl_3 . The yield of $\text{H}_2\text{5ClThP}$ and $\text{H}_2\text{5BrThP}$ is, respectively, 26 and 30% and both the compounds were purple in colour. ^1H HNMR of $\text{H}_2\text{5ClThP}$ (deuteriochloroform): δ 9.17 (s, 8H, pyrrole β -H), 7.64 (d, 4H, thienyl 3-H), 7.43 (d, 4H, thienyl 4-H), -2.70 (s, 2H, imino NH). ^1H HNMR of $\text{H}_2\text{5BrThP}$ (deuteriochloroform): δ 9.15 (s, 8H, pyrrole β -H), 7.63 (d, 4H, thienyl 3-H), 7.50 (d, 4H, thienyl 4-H), -2.72 (s, 2H, imino NH).

Copper derivative of both the porphyrins (Cu5XThP) were synthesised from $\text{H}_2\text{5XThP}$ using cupric acetate as the metal ion carrier in $\text{CHCl}_3/\text{CH}_3\text{OH}$ solvent system [25]

Synthesis of 2-nitro-5,10,15,20-tetrakis(5-halothien-2-yl)porphyrin, $\text{H}_2\text{N5XThP}$ ($X = \text{Cl}$ or Br). β -Mononitration of both porphyrins were carried out by following variant of the procedure reported for copper tetraphenylporphyrin [23]a. In a typical procedure, to a solution of Cu5XThP (0.25 mmol) in 70 mL of CHCl_3 and 3 mL of acetic acid, a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.06 g, 0.25 mmol) in 16 mL of acetic anhydride was added dropwise over a period of half an hour. The reaction mixture

was stirred under refluxing conditions. At the end of this period, the reaction mixture was washed with water (three times) followed by 20% aqueous NaHCO_3 (two times) and the non aqueous layer was dried over anhydrous Na_2SO_4 . The solvent was distilled off completely and the product was purified by column chromatography using 1 : 1 CHCl_3 and hexanes as the eluent. Trace amount of unreacted Cu5XThP , which was eluted first on the column was collected separately. $\text{H}_2\text{N5XThP}$ was synthesized by demetallating CuN5XThP using conc. H_2SO_4 at low temperature. The reaction flask containing the CuN5XThP (0.17 mmol) dissolved in 20 mL of CHCl_3 was kept in freezing mixture for 30 min. To this conc. H_2SO_4 (1 mL) was added carefully under stirring condition and the stirring was continued for half an hour. The reaction mixture was treated with water, and then the organic layer was treated with 20% aqueous NaHCO_3 solution (three times) and dried. The crude product was purified by column chromatography using CHCl_3 as the eluent.

Synthesis of CuN5ClThP required refluxing for 50 min. The yield of CuN5ClThP and $\text{H}_2\text{N5ClThP}$ is, respectively, 72 and 82% from the steps mentioned above and both the compounds were purple in color. ms of CuN5ClThP : m/z 882.24 (M^+). ^1H HNMR of $\text{H}_2\text{N5ClThP}$ (deuteriochloroform): δ 8.95–9.43 (m, 7H, pyrrole β -H), 7.63–7.75 (m, 4H, thienyl 3-H), 7.31–7.39 (m, 4H, thienyl 4-H), -2.45 (s, 2H, imino NH). *Anal. Calcd.* For $\text{C}_{36}\text{H}_{17}\text{N}_5\text{S}_4\text{O}_2\text{Cl}_4$: C, 52.63; H, 2.09; N, 8.52; S, 15.61. Found: C, 52.85; H, 2.24; N, 8.71; S, 15.78.

Synthesis of CuN5BrThP required refluxing for 30 min. The yield of CuN5BrThP and $\text{H}_2\text{N5BrThP}$ is, respectively, 66 and 84% from the steps mentioned above and both the compounds were purple in color. ms of CuN5BrThP : m/z 1060.35 (M^+). ^1H HNMR of $\text{H}_2\text{N5BrThP}$ (deuteriochloroform): δ 8.93–9.40 (m, 7H, pyrrole β -H), 7.61–7.72 (m, 4H, thienyl 3-H), 7.46–7.52 (m, 4H, thienyl 4-H), -2.45 (s, 2H, imino NH). *Anal. Calcd.* For $\text{C}_{36}\text{H}_{17}\text{N}_5\text{S}_4\text{O}_2\text{Br}_4$: C, 43.26; H, 1.71; N, 7.01; S, 12.83. Found: C, 43.38; H, 1.51; N, 7.17; S, 12.73.

Synthesis of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(5-halothien-2-yl)porphyrinato copper (II), Cu5XThOBP ($X = \text{Cl}$ or Br). To Cu5XThP (0.25 mmol) dissolved in CHCl_3 (30 mL), liquid bromine (0.4 mL, 7.80 mmol) in CHCl_3 (10 mL) was added dropwise over a period of 45 min under stirring conditions. Stirring was continued for 3 h. At the end of the period, pyridine (0.7 mL, 8.65 mmol) in CHCl_3 was added to the reaction mixture and the stirring was continued for another 4 h. The reaction mixture was then treated with 20% aqueous $\text{Na}_2\text{S}_2\text{O}_5$ solution (100 mL) followed by dil. HCl (2 times) and the organic layer was passed over anhydrous sodium sulphate. The crude product was chromatographed on a silica gel column using CHCl_3 as the eluent.

$\text{H}_2\text{5XThOBP}$ ($X = \text{Cl}$ or Br) were synthesized by demetallating Cu5XThOBP ($X = \text{Cl}$ or Br) using conc. H_2SO_4 at low temperature as described for nitroporphyrins. Zn5XThOBP were synthesized from $\text{H}_2\text{5XThOBP}$ using zinc acetate as the metal ion carrier in $\text{CHCl}_3/\text{CH}_3\text{OH}$ solvent system [25].

The yield of Cu5ClThOBP , $\text{H}_2\text{5ClThOBP}$, and Zn5ClThOBP are, respectively, 73, 78, and 90% from the steps mentioned above and all the three compounds were dark green in color. ^1H HNMR of Zn5ClThOBP (deuteriochloroform): δ 7.62 (d, 4 H, thienyl 3-H), 7.36 (d, 4 H, thienyl 4-H), ms for Zn5ClThOBP : m/z 1470.6 (M^+). *Anal. Calcd.* For $\text{C}_{36}\text{H}_8\text{N}_4\text{S}_4\text{Br}_8\text{Cl}_4\text{Zn}$: C, 29.39; H, 0.55; N, 3.80; S, 8.72. Found: C, 29.14; H, 0.61; N, 3.73; S, 8.93.

The yield of Cu5BrThOBP, H₂5BrThOBP, and Zn5BrThOBP are, respectively, 70, 82, and 92% from the steps mentioned above and all the three compounds were dark green in color. ¹HNMR of Zn5BrThOBP (deuteriochloroform): δ 7.60 (d, 4 H, thienyl 3- H), 7.48 (d, 4 H, thienyl 4- H), ms for Zn5BrThOBP: m/z 1648.48 (M⁺). *Anal.* Calcd. For C₃₆H₈N₄S₄Br₁₂Zn: C, 26.22; H, 0.48; N, 3.39; S, 7.79. Found: C, 26.07; H, 0.41; N, 3.28; S, 7.88.

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