

A simple alternative method for preparing Sn(IV) porphyrins

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ABSTRACT: Sn(IV) porphyrins are highly desirable for various applications because of their stability, their preference for oxygen-donor ligands and because they possess properties which can be easily characterized using various spectroscopic techniques. The most established method for the preparation of the Sn(IV) porphyrins is refluxing the porphyrin with SnCl₂·2H₂O in pyridine as solvent. Although this method works efficiently, we found that the work-up results in a lot of unwanted materials and using large quantities of pyridine as solvent is not good under laboratory conditions. In this paper, we show that the Sn(IV) porphyrins can be prepared easily by treating porphyrin with SnCl₂·2H₂O in chloroform, dichloromethane and toluene as solvent containing 25–50% ethanol as co-solvent. The reaction works smoothly and involves simple work-up and straightforward chromatographic purification. The method works efficiently for *meso* and β -substituted porphyrins. The spectral and electrochemical properties of various Sn(IV) were studied and our studies showed that the properties are sensitive to the nature of substituent present at the *meso*-position.

KEYWORDS: tin porphyrin, alternative method, chloroform, ethanol, *meso*-substituents, spectral properties.

INTRODUCTION

Tin(IV) porphyrins are widely used for various applications [1]. The preferential coordination of the Sn(IV) porphyrins to oxy anionic ligands has been used by Sanders et al. [2] and others [3] for the construction of novel elaborate multi-porphyrin arrays. Langford et al. [4] and others [5] used the six-coordinate tin(IV) porphyrins as building blocks in the design of functional materials with uniform channels. These compounds have also been investigated for applications such as catalysis [6], biomedicine [7] and synthesis of nanomaterials [8]. Tin(IV) porphyrins offer the chemist many advantages due to the particular properties conferred by the highly charged main group metal center. The Sn(IV) complexes are diamagnetic and usually six-coordinate with trans-diaxial anionic or occasionally neutral ligands which can be manipulated in most cases [1]. Sn(IV) porphyrins can be characterized easily by NMR, absorption, fluorescence, electrochemical and other techniques. We are interested in the synthesis of covalent and non-covalent unsymmetrical porphyrin arrays containing two or more different porphyrin subunits to study singlet-singlet energy transfer from one porphyrin subunit to another [9]. In continuation of our ongoing search for building new porphyrin arrays, we are interested in using dihydroxotin(IV) porphyrin building blocks to construct multiporphyrin arrays containing heteroatom-substituted porphyrin subunits as axial ligands. Unlike Zn(II) porphyrin building blocks, the Sn(IV) porphyrin building blocks are more stable and possess photophysical properties similar to those of Zn(II) porphyrins, hence dihydroxotin(IV) porphyrins are better building blocks for the construction of multiporphyrin arrays. Towards achieving the goal of the synthesis of Sn(IV) porphyrin-based multiporphyrin arrays containing heteroporphyrins as axial ligands, we first attempted the synthesis of dihydroxo(5,10,15,20tetratolylporphyrinato)tin(IV) [SnTTP(OH)₂] by following standard literature methods [10].

The Sn(IV) porphyrins were first synthesized in 1948 by Rothemund and co-workers by refluxing the porphyrin with SnCl₂·2H₂O in pyridine, followed by work-up and

[◊]SPP full member in good standing

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Scheme 1. Literature methods for the preparation of dihydroxoSn(IV) porphyrin

column chromatographic purification (Scheme 1) [10a]. Later, Adler et al. (1970) and Gouterman et al. (1973) synthesized Sn(IV) porphyrins by refluxing porphyrin with SnCl₂·2H₂O in high-boiling solvents like dimethylformamide [10b] and glacial acetic acid [10c] (Scheme 1). Among these methods, the pyridine method is most widely used to synthesize Sn(IV) porphyrins. The Sn(IV) porphyrins prepared by pyridine method have two chloride groups as axial ligands before passing through the column and changed to two hydroxo groups after the crude compound was subjected to basic alumina column chromatographic purification. However, in a recent report by Crossley and co-workers, it was noted that the pyridine method gave Sn(IV) porphyrins containing mixture of axial ligands such as chloro and hydroxo groups after column chromatographic purification instead of Sn(IV) porphyrins containing two axial hydroxyl groups. Hence, Crossley and co-workers [10d] developed an alternative method to synthesize Sn(IV)porphyrins containing two axial hydroxo groups. In Crossley's method, the dichlorotin(IV) porphyrin was obtained first by refluxing porphyrin with SnCl₂·2H₂O in pyridine for 3 h followed by precipitation with excess water. The dichlorotin(IV)porphyrin complex was then treated with K₂CO₃ in THF-H₂O (4:1) at refluxing temperature for 3 h and the compound was purified on neutral alumina column to afford dihydroxotin(IV)porphyrin 1 in 90% yield (Scheme 1). We initially attempted to prepare Sn(IV) derivative of 5,10,15,20-tetratolylporphyrin 1 by pyridine method. Although the reaction worked smoothly, we found that the work-up was tedious and laborious. Furthermore, the pyridine is not an environmentally friendly solvent to handle in large quantities [11]. Thus, we explored various alternative simple reaction conditions to prepare dihydroxotin(IV)tetratolylporphyrin 1.

Our studies indicate that the dihydroxotin(IV)tetratolylporphyrin 1 can be prepared by treating 5,10,15,20-tetratolylporphyrin (H_2TTP) with SnCl₂·2H₂O in chloroformethanol (1:1) under mild refluxing conditions followed by one column chromatographic purification (Scheme 2). Our modified method is beneficial over pyridine method because the following reasons: of (1) the work-up is simple, (2) low-boiling solvents such as CHCl₃ can be used which can be removed easily, and (3) it requires just one straightforward column chromatographic purification. The method works very efficiently and was demonstrated by synthesizing

dihydroxotin(IV) derivatives of various porphyrin macrocycles **2–6**. The effects of various *meso* substituents on spectral, electrochemical and photophysical properties of Sn(IV) porphyrins are also described.

EXPERIMENTAL

Chemicals

The free-base porphyrins were synthesized by following literature procedures [18]. All general chemicals and solvents were procured from S.D. Fine Chemicals, India. Column chromatography was performed using basic alumina obtained from Sisco Research Laboratories, India. Tetrabutylammonium perchlorate was purchased from Fluka and used without further purifications.

Instrumentation

¹H NMR spectra were recorded with a Varian 400 MHz instrument using tetramethylsilane as an internal standard. ¹³C NMR spectra were recorded on a Varian spectrometer operating at 100.6 MHz. ¹¹⁹Sn NMR was recorded with a Varian spectrometer operating at 111.8 MHz using tetraphenyltin as an internal standard (Ph₄Sn = 0 ppm). All NMR measurements were carried out at room temperature in deuterochloroform. Absorption and steady-state fluorescence spectra were obtained with Perkin-Elmer Lambda 35 and Lambda 55 instruments, respectively. The fluorescence quantum yields (Φ_r) of Sn(IV) porphyrins were estimated from the emission and absorption spectra by comparative method [15b]. The time-resolved fluorescence decay measurements [17] were carried out at magic angle using a picosecond



Dichloro[5,10,15,20-tetrakis(p-tolyl)porphyrinato]tin(IV)



Dihydroxo[5,10,15,20-tetrakis(p-tolyl)porphyrinato]tin(IV)

Scheme 2. Synthesis of dihydroxoSn(IV) porphyrin 1 by alternative method

diode laser-based time correlated single photon counting (TCSPC) fluorescence spectrometer from IBH, UK. All the decay curves were fitted to single exponential functions using IBH software. The radiative and non-radiative rate constants, k_r and k_{nr} , were calculated by the following equations:

$$\Sigma K = 1/\tau_f \tag{1}$$

$$k_r = \Phi_f k \tag{2}$$

$$k_{nr} = k - k_r \tag{3}$$

MALDI-TOF spectra were obtained from Axima-CFR manufactured by Kratos Analyticals. Cyclic Voltammetric (CV) and Differential Pulse Voltammetric (DPV) studies were carried out with BAS electrochemical system utilizing the three-electrode configuration consisting of a glassy carbon (working electrode), platinum wire (auxiliary electrode) and saturated calomel (reference electrode) electrodes in dry dichloromethane using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte.

General synthesis of dihydroxoporphyrinatotin(IV) 1-6

A sample of porphyrin (59 µmol) was dissolved in 10 mL of chloroform in a one-neck round-bottom flask. The solution of SnCl₂·2H₂O (0.59 mmol) in 10 mL of ethanol was added to it and the reaction mixture was stirred at refluxing temperature. The porphyrin solution turned green on addition of SnCl₂·2H₂O. The progress of the reaction was monitored by TLC analysis and absorption spectroscopy. The metalation was completed in four hours as judged by absorption spectroscopy. Triethylamine (0.5 mL) was added to the reaction mixture and the reaction mixture was stirred for an additional five minutes. The solvent was removed on rotary evaporator and crude compound was subjected to alumina column chromatographic purification. The residual unreacted free-base porphyrin was collected first with CH_2Cl_2 and the desired dihydroxoporphyrinatotin(IV) was eluted with CH2Cl2/1-2% CH3OH. The solvent was removed on rotary evaporator and afforded the pure Sn(IV) porphyrin 1–6 as purple solid.

Dihydroxo[**5**,10,15,20-tetrakis(*p*-tolyl)porphyrinato]tin(IV) [SnTTP(OH)₂] 1. Yield 90%, mp > 300 °C. Anal. calcd. for C₄₈H₃₈N₄O₂Sn: C, 70.17; H, 4.66; N, 8.17%. Found: C, 70.13; H, 4.70; N, 8.20. ¹H NMR (400 MHz; CDCl₃; Me₄Si): $\delta_{\rm H}$, ppm -7.43 (2H, br s, axial OH), 2.7 (s, 12H, tolyl), 7.61 (d, *J* = 7.8 Hz, 8H, Ar), 8.20 (d, *J* = 7.8 Hz, 8H, Ar) 9.13 (s, satellite, *J* = 10.7 Hz, 8H, β-pyrrole). ¹³C NMR (100 MHz; CDCl₃; Me₄Si): $\delta_{\rm C}$, ppm 21.4, 121.2, 127.6, 132.4, 135.0, 137.8, 138.4, 147.0. MS (MALDI-TOF): *m*/z 807 (calcd. for [M - OH]⁺ 807); 1609 (calcd. for [M₂ - 2OH]⁺ 1609).

Dihydroxo[octaethylporphyrinato]tin(IV) [**SnOEP(OH)**₂] **2.** Yield 80%, mp > 300 °C. Anal. calcd. for C₃₆H₄₆N₄O₂Sn: C, 63.08; H, 6.76; N, 8.17%. Found: C, 63.12; H, 6.71; N, 8.19. ¹H NMR (400 MHz; CDCl₃; Me₄Si): $\delta_{\rm H}$, ppm -8.06 (2H, br s, axial OH), 2.03 (t, J =7.6 Hz, 24H, CH₃), 4.20 (q, J = 7.6 Hz, 16H, CH₂), 10.47 (s, satellite, J = 2.8 Hz, 4H, *meso*-H). ¹³C NMR (100 MHz; CDCl₃; Me₄Si): $\delta_{\rm C}$, ppm 18.7, 20.1, 97.5, 143.7, 144.5. MS (MALDI-TOF): *m/z* 671 (calcd. for [M - OH]⁺ 671); 1337 (calcd. for [M₂ - 2OH]⁺ 1337).

Dihydroxo[**5**,10,15,20-tetrakis(2-thienyl)porphyrinato]tin(IV) [SnTThP(OH)₂] 3. Yield 65%, mp > 300 °C. Anal. calcd. for C₃₆H₂₂N₄O₂S₄Sn: C, 54.76; H, 2.81; N, 7.10%. Found: C, 54.78; H, 2.78; N, 7.08. ¹H NMR (400 MHz; CDCl₃; Me₄Si): $\delta_{\rm H}$, ppm -7.3 (2H, br s, axial OH), 7.54 (m, 4H, thienyl), 7.93 (d, *J* = 5.0 Hz, 4H, thienyl), 8.02 (m, 4H, thienyl), 9.32 (s, satellite, *J* = 10.1 Hz, 8H, β-pyrrole). ¹³C NMR (100 MHz; CDCl₃; Me₄Si): $\delta_{\rm C}$, ppm 114.0, 119.3, 126.4, 128.8, 131.0, 133.0, 135.0, 141.6, 147.9, 148.3. MS (MALDI-TOF): *m/z* 791 (calcd. for [M]⁺ 791); 775 (calcd. for [M - OH]⁺ 775); 1544 (calcd. for [M₂ - 2OH]⁺ 1544).

Dihydroxo[**5**,10,15,20-tetrakis(2-furyl)porphyrinato]tin(IV) [SnTFP(OH)₂] **4.** Yield 65%, mp > 300 °C. Anal. calcd. for C₃₆H₂₂N₄O₆Sn: C, 59.62; H, 3.06; N, 7.72%. Found: C, 59.64; H, 3.03; N, 7.73. ¹H NMR (400 MHz; CDCl₃; Me₄Si): $\delta_{\rm H}$, ppm -7.33 (2H, br s, axial OH), 7.09 (m, 4H, furyl), 7.45 (m, 4H, furyl), 8.19 (s, 4H, furyl), 9.52 (s, satellite, *J* = 13.6 Hz, 8H, β-pyrrole). MS (MALDI-TOF): *m/z* 729 (calcd. for [M]⁺ 729).

Dihydroxo[**5**,**10**,**15**,**20**-tetrakis(pentafluorophenyl) porphyrinato]tin(IV) [SnTPFPP(OH)₂] **5**. Yield 86%, mp > 300 °C. Anal. calcd. for C₄₄H₁₀F₂₀N₄O₂Sn: C, 46.96; H, 0.90; N, 4.98% Found: C, 46.92; H, 0.95; N 4.96. ¹H NMR (400 MHz; CDCl₃; Me₄Si): $\delta_{\rm H}$, ppm -7.31 (2H, br s, axial OH), 9.23 (s, satellite, *J* = 9.1 Hz, 8H, β-pyrrole). ¹³C NMR (100 MHz; CDCl₃; Me₄Si): $\delta_{\rm C}$, ppm 105.2, 132.9, 136.7, 139.2, 145.5, 147.1, 148.0. MS (MALDI-TOF): *m/z* 1109 (calcd. for [M - OH]⁺ 1109).

Dihydroxo[**5**,10,15,20-tetrakis(4-pyridyl)porphyrinato]tin(IV) [SnTPyP(OH)₂] **6.** Yield 60%, mp > 300 °C. Anal. calcd. for C₄₀H₂₆N₈O₂Sn: C, 62.44; H, 3.41; N, 14.56% Found: C, 62.46; H, 3.38; N 14.57. ¹H NMR (400 MHz; CDCl₃; Me₄Si): $\delta_{\rm H}$, ppm -7.36 (2H, br s, axial OH), 8.29 (d, *J* = 5.9 Hz, 8H, m-Py), 9.14 (d, *J* = 5.9 Hz, 8H, o-Py), 9.18 (s, satellite, *J* = 12.8 Hz, 8H, β-pyrrole). ¹³C NMR (100 MHz; CDCl₃; Me₄Si): δ_{c} , ppm 119.0, 129.8, 133.1, 146.2, 148.9. MS (MALDI-TOF): *m/z* 769 (calcd. for [M]⁺ 769); 755 (calcd. for [M - OH]⁺ 755); 1505 (calcd. for [M₂ - 2OH]⁺ 1505).

RESULTS AND DISCUSSION

In search of an alternative method to the existing, widely used pyridine method [10a] for preparing Sn(IV) porphyrins, we have chosen three solvents - CHCl₃, CH_2Cl_2 and toluene – in which porphyrins are readily soluble. The Sn(IV) insertion studies were carried out by taking H₂TTP as a model compound in CHCl₃ as solvent and ethanol as co-solvent. Although we discussed our results from the use of CHCl₃ as solvent, the results were similar when we used toluene and CH₂Cl₂ as solvents along with ethanol as co-solvent. The attempts to prepare Sn(IV) $TTP(OH)_2$ 1 were initiated by treating 3 mM of H₂TTP in $CHCl_3$ with 10 equivalents of $SnCl_2 \cdot 2H_2O$ in ethanol (1:1) v/v) at refluxing temperature. The progress of the reaction was monitored by TLC analysis and absorption spectroscopy by taking aliquots of the reaction mixture at regular intervals and checking the absorption spectra after addition of triethylamine. It was noted that the color of the porphyrin solution turned to green soon after the addition of alcoholic SnCl₂·2H₂O. The absorption spectroscopy of the green solution showed the formation of dication of H₂TTP. The absorption spectral analysis at frequent intervals indicated that the absorption bands corresponding to Sn(IV) derivative started to appear only after two hours; the reaction was completed in 4 h. After the completion of the reaction, triethylamine was added to the compound and the greenish color of the reaction mixture was changed to dark pink with green tinge. The solvent was removed on rotary evaporator and the crude compound was subjected to basic alumina column. The unreacted small amount of H₂TTP was removed initially and the required compound 1 was then collected in 90% yield as purple solid. For comparison purpose, compound 1 was also synthesized by pyridine method [10a]. A comparison of various spectroscopic data of 1 prepared by both methods showed the data to be exactly identical. To confirm that the two hydroxyl groups are the axial ligands in 1 prepared by CHCl₃/ethanol method, we used ¹H & ¹¹⁹Sn NMR and MALDI-TOF mass techniques (Fig. 1). In ¹H NMR, we observed a broad signal in the upfield region at -7.4 ppm (Fig. 1ai), corresponding to the axial OH protons, as noted previously for Sn(IV)porphyrin prepared by pyridine method. Similarly, in ¹H NMR, we also noted one singlet for eight β -pyrrole protons along with satellite peaks (Fig. 1aii), as noted earlier. In ¹¹⁹Sn NMR, only one signal at -570 ppm (Fig. 1b) was observed which is the characteristic feature of Sn(IV)porphyrin having two axial hydroxy groups [1]. If the axial ligands are two chloro groups, the signal was anticipated at -580 ppm in ¹¹⁹Sn NMR. If the mixture of axial ligands are present, it is expected to show more than one signal in ¹¹⁹Sn NMR. Furthermore, recently



Fig. 1. Spectroscopic evidences for the formation of 1: (a) partial ¹H NMR spectrum of 1 recorded in CDCl₃ showing (i) axial OH proton (ii) β -pyrrole protons with satellites, (b) ¹¹⁹Sn NMR spectrum of 1 recorded in CDCl₃, (c) MALDI-TOF mass spectrum of 1

Crossley and co-workers used MALDI-TOF mass spectral analysis to differentiate dichlorotin(IV)porphyrins and dihydroxotin(IV)porphyrins [10d]. They showed that under the conditions of MALDI-TOF mass spectral analysis, the dichlorotin(IV)porphyrins show parent ion resulting from the loss of one chloro ligand whereas the dihydroxotin(IV)porphyrins show (M - OH)⁺ peak and associated dimer peak with the loss of two hydroxo groups corresponding to $(M_2 - 2 \times OH)^+$. The Sn(IV)porphyrin 1 prepared by CHCl₃/ethanol method showed similar MALDI-TOF mass spectral features (Fig. 1c), supporting the argument that the two hydroxyl groups were present as axial ligands. However, the spectral analysis of crude compound before subjecting to column chromatography

indicated that the two chloride groups were present as axial ligands, as noted earlier in pyridine method.

The insertion of Sn(IV) ion into H_2TTP was then tested under various other experimental conditions. When the Sn(IV) insertion was carried out by treating the H₂TTP in CHCl₃ with ten equivalents of alcoholic SnCl₂·2H₂O solution at room temperature instead of refluxing conditions, no metalation was observed until 36 h, suggesting that the mild refluxing conditions are necessary for Sn(IV) insertion into the porphyrin macrocycle. The reaction was also carried out by changing the number of equivalents of SnCl₂·2H₂O. When we used five equivalents instead of ten equivalents of SnCl₂·2H₂O, no metalation was observed for 24 h. However, when we carried out the reaction with 20 and 40 equivalents of SnCl₂·2H₂O, the reaction was completed in 2 h with no further improvement in the yields. Thus, the optimized reaction conditions for the preparation of 1 are: treating the porphyrin with ten equivalents of SnCl₂·2H₂O in CHCl₃/ ethanol (1:1) at refluxing temperature for 4 h, followed by simple work-up and column chromatographic purification.

To understand the necesssity of alcohol in the synthesis of **1**, the following experiments were carried out: (1) The reaction was performed by addition of ten equivalents of solid $SnCl_2 \cdot 2H_2O$ to H_2TTP dissolved in reagent grade CHCl₃ which contains 0.6-1% ethanol as stabilizer at refluxing temperature conditions. The Sn(IV) insertion was noticed with reagent grade CHCl₃. However, the rate of Sn(IV) insertion was very slow and yielded **1** only in 30% after 30 h; (2) The Sn(IV) insertion into porphyrin was also carried out with ethanol free

CHCl₃ [12]. We observed that no Sn(IV) insertion into porphyrin macrocycle even after 48 h under refluxing conditions; (3) The reaction was carried out by changing the ratio of CHCl₃ to ethanol; we used 1:1 v/v for optimized reaction conditions. When metalation was carried out in 1:0.5 v/v of CHCl₃/ethanol, the reaction worked efficiently in the same duration of time. However, when we used 1:0.25 v/v of CHCl₃/ethanol, the required time for complete metalation was almost double and the yield also dropped to 50%. Thus, 1:0.5 v/v of CHCl₃/ethanol is compulsory for efficient metalation under these conditions; (4) To understand the effect of different alcohols, we carried out the reaction with various other alcohols under the same reaction conditions, *i.e.* ten equivalents of SnCl₂·2H₂O, CHCl₃/alcohol in 1:1 v/v and 4 h of reflux conditions. The reaction worked equally efficiently when we used methanol (90% yield) instead of ethanol. However, alcohols such as 2-methoxyethanol (12 h, 85%), butan-1-ol (8 h, 80%), dodecyl alcohol (12 h, 80%) and cyclohexanol (15 h, 80%) assisted in Sn(IV) metalation, but these require longer reaction periods and yields were relatively low compared to ethanol and methanol (see Supporting Information). No metalation was observed when isopropyl and *tert*-butyl alcohols were used which may be due to the poor solubility of $SnCl_2 \cdot 2H_2O$ in these two solvents. Thus, it is important to choose the alcohol which solubilizes the $SnCl_2 \cdot 2H_2O$ for rapid metalation.

We carried out the experiments to know the role of triethylamine. Since some amount of H_2TTP was converting to dicationic form on addition of $SnCl_2 \cdot 2H_2O$ and the reaction mixture was always green in color, we performed the reaction by adding triethylamine soon after the addition of $SnCl_2 \cdot 2H_2O$. The reaction mixture color was changed from green to purple but the metalation did not occur even after 24 hours. Similarly, when we treated the porphyrin in CHCl₃ containing 0.1% v/v triethylamine with alcoholic solution of $SnCl_2 \cdot 2H_2O$, the Sn(IV) insertion was not noticed. The addition of triethylamine to alcoholic solution of $SnCl_2 \cdot 2H_2O$ gave unknown white

precipitate which was not soluble even after heating. Thus, the presence of triethylamine during the reaction prevents metalation. Furthermore, when the triethylamine was not added to the reaction mixture at the end of the reaction, the metalation yields were not affected. These studies indicate that the addition of triethylamine was not needed in the reaction although we added small amount of triethylamine to the reaction mixture at the end to neutralize the acid generated in the reaction.

We also tested different Sn(II) salts for metal insertion reaction. Addition of Sn(CH₃)₂Cl₂, Sn(C₆H₅)₂Cl₂ and Sn(*n*-Bu)₂Cl₂ in ethanol to H₂TTP in CHCl₃ gave green coloration due to formation of dication but no metalation occurred under refluxing conditions even after one week. Also, no metalation was noticed with SnCl₄ under any reaction conditions which we explored. Thus, SnCl₂·2H₂O is the only salt which is cheap and readily available and can be used for preparation of Sn(IV) porphyrins.

Applications

To show the applicability of the method, we prepared Sn(IV) derivatives of five other porphyrin monomers 2–6 shown in Chart 1. The Sn(IV) insertion into



Chart 1. Various dihydroxotin(IV) porphyrin derivatives

the octaethylporphyrin (OEP) worked smoothly and SnOEP(OH)₂ 2 was isolated in decent yield (12 h, 80%) with one straightforward column chromatographic purification, However, the rate of Sn(IV) insertion into OEP was three times slower compared to Sn(IV) insertion into the TTP. Similarly, the Sn(IV) derivatives of 5,10,15,20meso-tetrathienylporphyrin (SnTThP(OH)₂) 3 (12 h, 65%), 5,10,15,20-*meso*-tetrafurylporphyrin (SnTFP(OH)₂) (20 h, 65%), 5,10,15,20-meso-tetrapentafluorophenylporphyrin (SnTPFPP(OH)₂) 5 (15 h, 86%) were prepared in decent yields under similar reaction conditions. The Sn(IV) derivative of 5,10,15,20-meso-tetra(4-pyridyl)porphyrin (SnTPyP(OH)₂) 6 required 40 h duration and yielded the pure compound in 60% yield after one column chromatographic purification. Thus, the method works efficiently with various types of porphyrins and requires simple column chromatographic purification to obtain the Sn(IV) derivatives in pure form in decent yields.

Spectral and electrochemical properties of Sn(IV) porphyrins 1–6

Interestingly, although the Sn(IV) derivatives of porphyrins with axial hydroxo ligands are very attractive components for various applications because of their favorable optical and coordination properties, the systematic investigation of their spectral and electrochemical [13] properties are scarce in literature. Hence, we investigated systematically the NMR, optical, electrochemical and photophysical studies of six Sn(IV) derivatives of different macrocycles.

NMR studies

NMR is very informative about the structure of Sn(IV) porphyrins. The six Sn(IV) porphyrin complexes were characterized by ¹H and ¹¹⁹Sn NMR spectroscopy; the selected data are presented in Table 1. In general, the signals corresponding to β -pyrrole and axial OH protons of Sn(IV) porphyrins in ¹H NMR spectra are quite informative. The eight β -pyrrole protons which appear

as singlet in metal-free porphyrins appeared as one strong central signal surrounded by small satellite peaks in Sn(IV) derivatives [14]. The satellite peaks appeared due to coupling of ¹¹⁹Sn and ¹¹⁷Sn with β-pyrrole protons and the coupling constant ${}^{4}J_{Sn-H}$ is normally in the range of 10–13 Hz [14]. In the case of Sn(IV)OEP(OH)₂, the coupling was observed between 119Sn and meso-H protons [1]. Furthermore, the β -pyrrole protons were downfield-shifted in $Sn(IV)TTP(OH)_2$ compared to H_2TTP . The axial OH protons in Sn(IV) derivatives experienced porphyrin ring current effect and appeared as broad signal at -7.3 ppm in tetraarylporphyrins and at -8.0 ppm in octaethylporphyrin (Table 1). The presence of mesosubstituents such as pyridyl, pentafluorophenyl, thienyl and furyl groups in place of tolyl groups alters the electronic properties and effects were clearly seen in β-pyrrole protons in ¹H NMR spectra. On replacement of meso-tolyl groups with six-membered meso-aryl groups such as pyridyl and pentafluorophenyl groups or five-membered meso-thienyl and meso-furyl groups, the β -pyrrole protons experienced downfield shifts and maximum shifts were noted for SnTFP(OH)₂ 4 (Table 1). However, the changes in δ_{Sn} in ^{119}Sn NMR are very minimal, indicating that the metal ion is not very sensitive to meso-substituents (Table 1).

Absorption properties

The Sn(IV) porphyrins exhibit normal spectra with one strong Soret band and two Q bands [1]. The comparison of normalized Soret band spectra of **1**, **2**, and **4** are shown in Fig. 2 and the data are presented in Table 2. The position and the intensity of the absorption bands depend on the kind of substituent present at the *meso*position. In **1**, the three absorption bands appeared at 429, 563 and 603 nm which were blue-shifted and appeared at 407, 537 and 574 nm in **2** with no *meso*-substituents. The absorption bands of **5** and **6** were blue-shifted compared to SnTTP(OH)₂ **1** but the absorption bands of **3** and **4** were red-shifted. Thus, the replacement of six-membered

Table 1. ¹H NMR and ¹¹⁹Sn NMR chemical shifts of various Sn(IV) porphyrins recorded in CDCl₃

Porphyrin	¹ H NMR	(δ in ppm)	¹¹⁹ Sn NMR
	OH resonance	β-pyrrole resonance	(δ in ppm)
1	-7.43	9.13	-570.20
2ª	-8.06	10.47	-569.24
3	-7.24	9.31	-568.97
4 ^b	-7.33	9.52	
5	-7.31	9.23	-567.15
6	-7.36	9.18	-569.39

^a The chemical shift of *meso*-H. ^b ¹¹⁹Sn resonance was not obtained due to poor solubility.



Fig. 2. Comparison of normalized Soret band absorption spectra of (a) 2 (b) 1 (c) 4 recorded in dichloromethane

Compound	Soret band, nm (log ε)	Q bands, nm (log ε)		Reduction potentials, V vs. SCE	
		Ι	II	Ι	II
1	429 (5.93)	563 (4.30)	603 (4.24)	-0.96	-1.36
2	407 (5.44)	537 (4.04)	574 (3.99)	-1.18	-1.59
3	437 (5.51)	569 (4.12)	614 (3.94)	-0.56	-0.96
4	448 (4.43)	578 (3.29)	635 (3.46)	-0.45	-0.86
5	422 (5.61)	553 (4.33)	588 (sh)	-0.46	-0.96
6	424 (5.55)	558 (4.20)	596 (3.70)	-0.52	-0.92

Table 2. Absorption and electrochemical data for various Sn(IV) porphyrins 1-6 recorded in dichloromethane



Fig. 3. Comparison of the normalized emission spectra of (a) 2 (b) 1 (c) 4 recorded at $\lambda_{ex} = 430$ nm in dichloromethane

aryl groups with five-membered thienyl and furyl groups resulted in red shifts in absorption bands and maximum shifts were noted for *meso*-furyl substituted Sn(IV) porphyrin **4** [15].

Fluorescence properties

The Sn(IV) porphyrins were shown as good energy donors and the photophysical properties are comparable to those of Zn(II) porphyrins. The comparision of fluorescence spectra of 1, 2 and 4 is shown in Fig. 3 and the photophysical data of Sn(IV) porphyrins 1-6 are presented in Table 3. The photophysical parameters of Sn(IV) porphyrins are sensitive to the nature of *meso*-substituent. The compound 1 showed two bands at 609 and 662 nm

Table 3. Photophysical data for various Sn(IV) porphyrins 1–6 recorded in dichloromethane

Compound	λ_{em}	, nm	$\Phi_{\!f}^{a}$	τ _f , 10 ⁻⁹ s	k_r , 10 ⁶ s ⁻¹	k_{nr} , 10 ⁸ s ⁻¹
1	609	662	0.025	1.21	20.66	8.05
2	576	630	0.024	0.55	43.63	17.74
3	637	_	0.031	0.73	42.46	13.27
4	656	_	0.014	1.14	12.28	8.64
5	593	647	0.0041	0.89	4.60	11.18
6	598	652	0.017	1.06	16.03	9.27

^a Quantum yields were calculated by taking ZnTPP ($\Phi_f = 0.036$) as reference at $\lambda_{ex} = 560$ nm.



Fig. 4. Fluorescence decay profiles and weighted residual fits of (a) 4 (b) 1

(Fig. 3) which were blue-shifted in the case of 2, 5 and 6. The quantum yields calculated by comparative method [16] and singlet excited state lifetime (Fig. 4) measured by single photon counting method [17] were decreased in the case of 2 and 6 compared to 1.

 k_{rad} and k_{nr} , the radiative and non-radiative rate constants, respectively, were also decreased and increased, respectively, for **5** and **6** compared to **1**. However, compounds **3** and **4** showed only one fluorescence band which was bathochromically shifted compared to **1**. These observations suggest that the five membered *meso*-furyl and *meso*-thienyl groups alter the electronic properties of the porphyrin more effectively compared to six-membered aryl groups.

Electrochemical properties

The redox properties of Sn(IV) porphyrins were probed through cyclic voltammetric studies with tetrabutylammonium perchlorate as supporting electrolyte (0.1 M) in dichloromethane as solvent. A comparison of reduction waves of Sn(IV) porphyrins 1, 3–6 is shown in Fig. 5 and the data are presented in Table 2. The compound 1 showed one irreversible oxidation and two reversible or quasireversible reductions (Fig. 5). These redox processes are due to oxidation and reduction



Fig. 5. Comparison of reduction waves of cyclic voltammograms of (a) 4 (b) 5 (c) 6 (d) 3 (e) 1 in dichloromethane containing 0.1 M TBAP as supporting electrolyte recorded at 50 mV/s scan speed

at porphyrin macrocycle. The other Sn(IV) porphyrins **3–6** did not show any oxidation but showed two reductions. The data shown in Table 2 clearly indicate that the two reductions become easier on replacement of *meso*-tolyl groups with other *meso*-substituents; maximum effects were observed with *meso*-furyl groups, followed by *meso*-pentafluorophenyl groups. Thus, the presence of different kinds of *meso*-substituents also influences the redox properties of the Sn(IV) porphyrins.

CONCLUSION

In this paper, we developed an easier method to synthesize Sn(IV) porphyrins by using SnCl₂·2H₂O in CHCl₃/ethanol mixture instead of pyridine, which is not an environmentally friendly solvent. The reaction works smoothly and requires simple column chromatographic purification to obtain dihydroxoSn(IV) porphyrins in 85–90% yields. The methodology was extended to synthesize dihydroxoSn(IV) derivatives of various porphyrins to study and compare their spectroscopic properties. It was shown that the electronic properties of dihydroxoSn(IV) porphyrins can be tuned upon introduction of suitable substituents at *meso*-positions.

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Supporting information

A full list of ¹H NMR, ¹¹⁹Sn NMR and MALDI-TOF spectra of selected compounds are given in the supplementary material. This material is available free-of-charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

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