Facile Synthesis, Characterization, and Fluorescence Studies of Novel Porphyrin Appended Thiazoles

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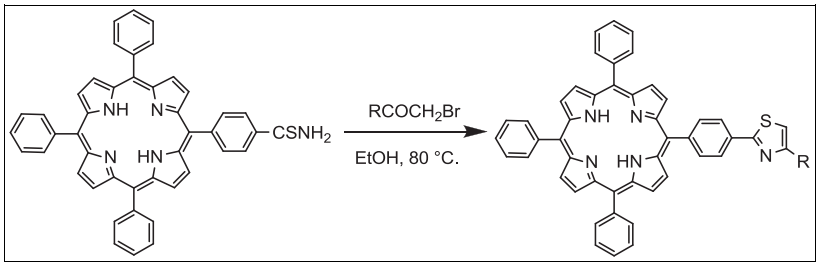

A facile and high yielding synthesis of porphyrin appended thiazoles **5** from the reaction of 5-(4-thiocarboxamidophenyl)-10,15,20-triphenylporphyrin with α-bromo ketones has been described. The fluorescence studies of synthesized porphyrin appended thiazoles **5** in chloroform indicate that porphyrin π system is not greatly perturbed by substitution of a thiazole moiety at *meso*-phenyl ring even in the excited state.

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INTRODUCTION

Porphyrins are tetrapyrrolic heterocyclic molecules that play important role in many biological processes such as light harvesting [1], oxygen transport [2], metabolism, and catalysis [3]. In recent years, there has been a growing interest in the use of porphyrins and related compounds as therapeutic drugs, especially as photosensitizers in photodynamic therapy of cancer [4]. The presence of a conjugated double-bond system in the tetrapyrrole nucleus is the structural feature responsible for the strong and characteristic absorption and fluorescence [5]. Biological effects of porphyrins largely depend on their physicochemical properties, which in turn lead to important changes in their photophysical behavior [6]. The photochemical properties of porphyrins are largely dependent on the nature of substituents and the type of metal in the porphyrin cavity and can be tuned appropriately by modification at β-pyrrolic and peripheral positions [7]. As a result, functional group interconversion and synthetic transformations related to porphyrin chemistry are continuously being explored and improved. In literature, there are various methods available for the synthesis of porphyrins molecules [8]; however, methods for structural modification of porphyrin molecules are rare. Thus, development of facile, efficient, and versatile synthetic strategy to functionalize porphyrin molecules with appended heterocycles is of high interest to broaden their scope of utilizations. In continuation of our efforts toward the development of novel porphyrin molecules for anticancer agents, herein we report the synthesis, characterization, and preliminary results on fluorescence properties of novel porphyrin appended thiazoles (Scheme 1).

RESULTS AND DISCUSSION

5-(4-Carbomethoxyphenyl)-10,15,20-triphenyporphyrin **1** was prepared by condensation of benzaldehyde, 4-carboxymethylbenzaldehyde, and pyrrole under Adler–Longo [9] conditions followed by the hydrolysis and reaction with thionyl chloride and ammonia as shown in Scheme 1. Porphyrin thiamide **3** was obtained from the reaction of 5-(4-carboxamido-phenyl)-10,15,20-triphenylporphyrin **2** with Lawesson's reagent at 100 °C in toluene. Presence of a characteristic peak at 1618 cm^{-1} in IR and a peak at *m/z* 674 in ESI–MS confirmed the structure of **3**. Porphyrin thiazoles (**5a–g**) were prepared by the reaction of **3** with appropriate α-bromoketones (**4a–g**) in ethanol under refluxing conditions in high yields (75–85%) (Table 1, Scheme 2).

The porphyrin thiazoles (**5a–g**) showed $[M + H]^+$ ion peak in the mass spectra. Along with other peripheral aryl and β-pyrrolic protons, a singlet peak appeared in ^1H NMR spectra at around δ_H 7.50–7.58 corresponding to thiazole H-5″ for **5a–d** and **5g**, whereas this singlet was shifted downfield at δ_H 8.24 and 8.64, respectively for **5e** and **5f**.

All the synthesized prophyrins are readily soluble in $CHCl_3$ displaying a very sharp and intense B (Soret) band centered at 420 nm, accompanied by four weaker Q bands (515, 550, 590, and 645 nm) and a shoulder at around

Scheme 1. Reagents and conditions: (i) KOH, MeOH: H_2O, 90 °C, 30 h, 82%; (ii) $SOCl_2$, toluene, 110 °C, 1 h; (iii) NH_3 (g), CH_2Cl_2, 0–25 °C, 45 min, 85%; and (iv) Lawesson's reagent, toluene, 100 °C, 1 h, 85%.

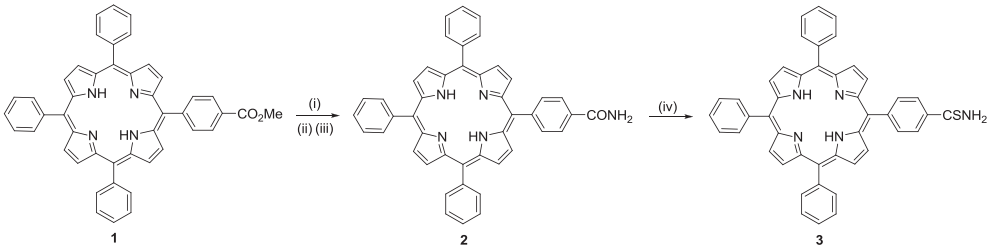
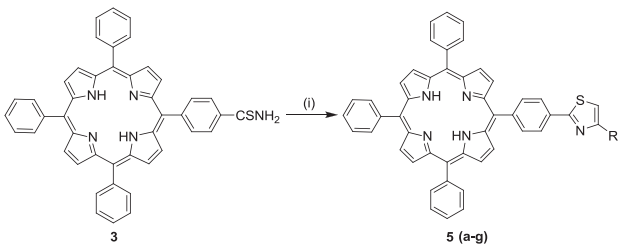


Table 1

Synthesis of porphyrin thiazoles **5a–f**.

Sr. No.	R	Time (h)	Yield (%)
5a	C_6H_5	2	82
5b	4-$CH_3OC_6H_4$	3	80
5c	4-BrC_6H_4	2	85
5d	2-Thienyl	4	80
5e	2-Pyridyl	4	79
5f	3-Coumarinyl	8	77
5g	3-Indolyl	8	75

Scheme 2. Reagents and conditions: (i) $RCOCH_2Br$ (**4a–g**), EtOH, 80 °C.



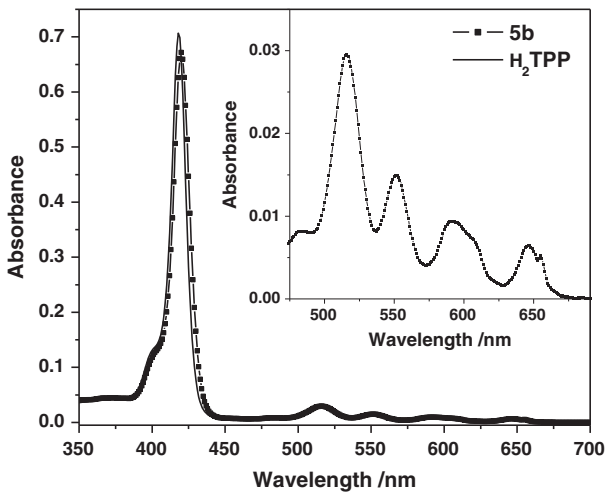


Figure 1. Absorption spectrum of **5b** (line and symbol) along with the model compound 5,10,15,20-tetraphenylporphyrin (**H_2TPP**) (solid line) in chloroform. Inset shows the zoomed spectrum in the region of Q-bands for **5b**.

400 nm in the absorption spectra (Fig. 1). Excitation of the samples at 515 nm gives two fluorescence peaks in all cases, namely at 648 and 710 nm (Fig. 2). All bands are of $\pi \rightarrow \pi^*$ type. The Soret band is due to an allowed $^1A_{1g} \rightarrow {}^1E_u'$ transition; and consequently, the intensity of this band is very high [10]. The characteristic peak positions of absorption spectrum for individual porphyrin derivatives are given in Table 2 along with the molar absorption coefficient of each of them. Very small shift in both the Soret band and Q band position for the synthesized derivatives from the model compound 5,10,15,20-tetraphenylporphyrin (H_2TPP) indicates little ground state interaction between the porphyrin moiety and the thiazole ring. Although the main fluorescence peak position (ca. 648 nm) is also insensitive to the substitution, the other fluorescence band shows a blue-shift of ca. 2–6 nm from the model compound H_2TPP (712 nm). This shift is more prominent in **5e**, where a strong electron deficient pyridyl ring is involved. Table 2 also includes the relative fluorescence yield of all the synthesized prophyrin derivatives along with that of the model compound H_2TPP. It is seen that the fluorescence quantum yield (ϕ_f) is reduced to almost half by the substitution.

The most pronounced reduction in ϕ_f is again observed for **5e**, which may be because of facile electron transfer from the excited state of porphyrin moiety to the strong acceptor pyridyl ring. In porphyrin **5e**, pyridyl ring is

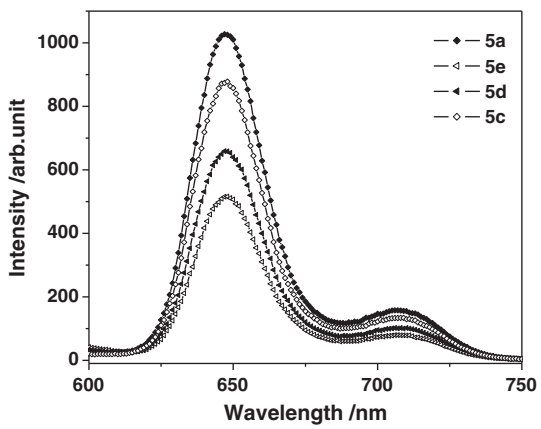


Figure 2. Representative fluorescence emission spectra of some of the synthesized porphyrin thiazoles **5** in chloroform ($\lambda_{exc.} = 515$ nm).

Table 2

Absorption and emission data of porphyrins **5a–g** in chloroform.

	(absorption) λ_{max} nm ($\varepsilon/10^4\,M^{-1}\,cm^{-1}$)					(Emission) λ_{max} nm		Quantum yield (Φ_f)
Compound	(Soret)	[$Q_{Y(0,1)}$]	[$Q_{Y(0,0)}$]	[$Q_{X(0,1)}$]	[$Q_{X(0,0)}$]			
5a	420 (66.00)	516 (5.80)	552 (4.40)	590 (3.90)	646 (3.70)	648	706	0.048
5b	420 (72.00)	516 (6.30)	552 (4.80)	592 (4.20)	646 (4.00)	648	710	0.053
5c	420 (65.00)	516 (5.90)	552 (4.50)	591 (4.00)	647 (3.80)	648	710	0.040
5d	420 (88.00)	516 (10.0)	552 (8.40)	591 (7.70)	643 (7.40)	648	710	0.039
5e	420 (55.00)	516 (7.50)	551 (6.30)	590 (5.90)	647 (5.70)	648	712	0.040
5f	420 (32.00)	516 (4.50)	551 (3.90)	594 (3.60)	644 (3.60)	649	706	0.025
5g	420 (220.0)	516 (19.0)	552 (14.0)	591 (12.0)	647 (12.0)	648	707	0.047
H_2TPP	418 (250.0)	515 (19.0)	550 (15.0)	592 (13.0)	647 (13.0)	648	712	0.110

H_2TPP: 5,10,15,20-tetraphenylporphyrin.

connected with porphyrin through a linking bridge; it would make up a "donor-space-acceptor" intramolecular photoinduced electron transfer system. The fluorescence of porphyrin is quenched by way of transfer of the excited state electron from porphyrin to pyridyl ring through the thiazole spacer. The reduced fluorescence quantum yields compared with H_2TPP indicate that there is distortion in the electronic structure of porphyrin ring because of appended heterocyclic thiazole ring on aryl group.

EXPERIMENTAL

The aldehydes, pyrrole, and $Yb(OTf)_3$ were purchased from Sigma-Aldrich (India). All other reagents and solvents were purchased from Merck (India) and Spectrochem, India Ltd. The synthesized porphyrin derivatives (**5a–g**), H_2TPP were characterized by UV–vis and fluorescence spectroscopy. ^{1}H NMR spectra were recorded on Brucker Heaven 11400 (400 MHz), and mass spectra were recorded on QSTAR Elite LX/MS/MS from applied biosystems. Steady-state absorption spectra were recorded on a Perkin Elmer Lambda25 absorption spectrophotometer. Fluorescence spectra were taken in a Hitachi FL4500 spectrofluorimeter, and all the spectra were corrected for the instrument response function. Quartz cuvettes of 10 mm optical path length received from PerkinElmer, USA (part no. B0831009) and Hellma, Germany (type 111-QS) were used for measuring absorption and fluorescence spectra, respectively. For fluorescence emission, the sample was excited at 515 nm, whereas excitation spectra were obtained by monitoring at the respective emission maximum. In both the cases, 5 nm bandpass was used in the excitation and emission side. Fluorescence quantum yields (ϕ_f) were calculated by comparing the total fluorescence intensity under the whole fluorescence spectral range by taking H_2TPP as standard. The relative experimental error of the measured quantum yield was estimated within ±5%.

5-(4-Carbomethoxyphenyl)-10,15,20-triphenylporphyrin 1. To a refluxing solution of methyl 4-formylbenzoate (10 g, 61 mmol) in propionic acid (280 mL) were added freshly distilled benzaldehyde (17.8 g, 167 mmol) and pyrrole (22.25 g, 333 mmol) simultaneously at the same rates. The reaction mixture was heated under reflux for 1 h. After completion of the reaction, the propionic acid was distilled off under vacuum, the residue was cooled to room temperature and basified to pH (~8) with saturated sodium carbonate solution and extracted with chloroform (3 × 50 mL). The organic layers were collected, dried over anhydrous Na_2SO_4 and then evaporated. The residue was purified by column chromatography on silica gel using $CHCl_3$-hexane (7:3 v/v) as eluent to afford **1** (second fraction in column) in 10% yield (4.09 g). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.19–8.49 (m, 8H), 8.37–8.34 (m, 2H), 8.24–8.09 (m, 6H), 7.93–7.60 (m, 9H), 7.20–7.14 (m, 2H), 4.02 (s, 3H), −2.88 (s, 2H).

Preparation of 5-(4-carboxamidophenyl)-10,15,20-triphenylporphyrin 2. To a stirred suspension of 5-(4-carbomethoxyphenyl)-10,15,20-triphenyl-porphyrin (**1**) (200 mg, 0.297 mmol) in methanol (15 mL) was added KOH (30 mL, 1N aqueous solution) and heated under reflux for 30 h. After completion of the reaction as indicated by TLC, the mixture was cooled to room temperature; solid was filtered, washed with water and 1N HCl solution. The residue so obtained was dissolved in $CHCl_3$: MeOH, dried over anhydrous Na_2SO_4 and evaporated to dryness to afford 5-(4-carboxyphenyl)-10,15,20-triphenylporphyrin as a purple solid in 82% yield. 5-(4-Carboxyphenyl)-10,15,20-triphenylporphyrin (150 mg, 0.228 mmol) was dissolved in dry toluene (15 mL) and added thionyl chloride (200 µL, 0.273 mmol) and heated under reflux for 1 h. After removal of solvent under vacuum, the greenish residue obtained was dissolved in dry CH_2Cl_2 (10 mL) and cooled in an ice bath. In the cooled reaction mixture, ammonia gas was purged until all acid chloride was consumed (10 min). The mixture was stirred at room temperature for 30 min and diluted with water (20 mL). The organic phase was separated, dried over anhydrous Na_2SO_4, and distilled off to afford **2** as a purple solid (125 mg, 85%).

5-(4-Thiocarboxamidophenyl)-10,15,20-triphenylporphyrin 3. Lawesson's reagent (70 mg, 0.175 mmol) was added to stirred suspension of **2** (110 mg, 0.167 mmol) in dry toluene (25 mL) and heated the reaction mixture at 100 °C for 1 h. After completion of reaction, the solvent was evaporated under vacuum and the residue so obtained was purified by column chromatography on silica gel using $CHCl_3$: MeOH (99:1 v/v) as eluent to obtain **3** as purple solid (95 mg, 85%).

5-{4′-(4″-Phenyl)-2″-thiazolyl}-10,15,20-triphenylporphyrin 5a. To a solution of **3** (50 mg, 0.074 mmol) in ethanol (5 mL) was added phenacyl bromide **4a** (14 mg, 0.074 mmol) and the reaction mixture was heated under reflux for 4 h. After completion of the reaction, solvent was evaporated and the resulting mixture was extracted with $CHCl_3$, washed with water (2 × 20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure on a rotary evaporator to give crude **5a**, which was

purified by column chromatography on silica gel using chloroform as eluent. **5a**: yield 82% (47 mg); UV–vis [λ_{max}, nm] in $CHCl_3$: 420, 516, 552, 590, 646: ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = -2.77$ (s, 2H, NH), 7.41–7.45 (m, 1H), 7.54 (t, $J = 7.6$ Hz, 2H), 7.64 (s, 1H, 5″-H thiazole), 7.73–7.79 (m, 9H), 8.12–8.14 (m, 2H), 8.21–8.24 (m, 6H), 8.34 (d, $J = 8.2$ Hz, 2H), 8.45 (d, $J = 7.3$ Hz, 2H), 8.87–8.92 (m, 8H, β-pyrrole); MS *m/z* calcd for $C_{53}H_{35}N_5S$ 773.2613, found 774.2920 $(M + H)^+$.

5b was obtained in 80% yield (48 mg) starting from 3 and 2-bromo-1-(4-methoxyphenyl)ethanone 4b as described for 5a:. UV–vis [λ_{max}, nm] in $CHCl_3$: 420, 516, 552, 592, 646; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = -2.77$ (s, 2H, NH), 3.90 (s, 3H,–OCH_3), 7.05 (d, $J = 8.8$ Hz, 2H), 7.50 (s, 1H, 5″-H thiazole), 7.74–7.79 (m, 9H), 8.07 (d, $J = 8.9$ Hz, 2H), 8.21–8.24 (m, 6H), 8.33 (d, $J = 8.2$ Hz, 2H), 8.44 (d, $J = 7.4$ Hz, 2H), 8.87–8.92, (m, 8H, β-pyrrole); MS *m/z* calcd for $C_{54}H_{37}N_5OS$ 803.2719, found 804.3091 $(M + H)^+$.

5c was obtained in 85% yield (48 mg) starting from 3 and 2-bromo-1-(4-bromophenyl)ethanone 4c as described for 5a;. UV–vis [λ_{max}, nm] in $CHCl_3$: 420, 516, 552, 591, 647; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = -2.77$ (s, 2H, NH), 7.63–7.67 (m, 2H), 7.72–7.81 (m, 9H), 8.21–8.24 (m, 6H), 8.32–8.36 (m, 3H), 8.44 (d, $J = 8.2$ Hz, 2H), 8.72–8.74 (m, 2H), 8.86–8.91 (m, 8H, β-pyrrole); MS *m/z* calcd for $C_{53}H_{34}BrN_5S$ 851.1718, found 852.4110 $(M + H)^+$.

5d was obtained in 80% yield (46 mg) starting from 3 and 2-bromo-1-(thiophen-2-yl)ethanone 4d as described for 5a;. UV–vis [λ_{max}, nm] in $CHCl_3$: 420, 516, 552, 591, 643; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = -2.76$ (s, 2H, NH), 7.16 (dd, $J = 3.9$ Hz, $J = 5.0$ Hz, 1H), 7.38 (dd, $J = 5.2$ Hz, $J = 1.0$ Hz, 1H), 7.49 (s, 1H, 5″-H thiazole), 7.64 (dd, $J = 3.5$ Hz, $J = 1.0$ Hz, 1H), 7.73–7.81 (m, 9H), 8.21–8.23 (m, 6H), 8.33 (d, $J = 8.0$ Hz, 2H), 8.42 (d, $J = 7.0$ Hz, 2H), 8.85–8.90 (m, 8H, β-pyrrole); MS *m/z* calcd for $C_{51}H_{33}N_5S_2$ 779.2177, found 780.2522 $(M + H)^+$.

5e was obtained in 79% yield (45 mg) starting from 3 and 2-bromo-1-(pyridin-2-yl)ethanone hydrobromide 4e as described for 5a;. UV–vis [λ_{max}, nm] in $CHCl_3$: 420, 516, 551, 590, 647; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = -2.76$ (s, 2H, NH), 7.29–7.32 (m, 1H), 7.73–7.81 (m, 9H), 7.89 (t, $J = 7.7$ Hz, 1H), 8.21–8.25 (m, 7H), 8.34 (dd, $J = 1.7$ Hz, $J = 6.4$ Hz, 2H), 8.45–8.41 (m, 3H), 8.69–8.71 (m, 1H), 8.86–8.91 (m, 8H, β-pyrrole): MS *m/z* calcd for $C_{52}H_{34}N_6S$, 774.2566, found 775.2920 $(M + H)^+$.

5f was obtained in 77% yield (48 mg) starting from 3 and 3-(2-bromoacetyl)-2H-chromen-2-one 4f as described for 5a;. UV–vis [λ_{max}, nm] in $CHCl_3$: 420, 516, 551, 594, 644; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = -2.76$ (s, 2H, NH), 7.35–7.38 (m, 1H), 7.45 (d, $J = 8.4$ Hz, 1H), 7.57–7.58 (m, 1H), 7.74–7.81 (m, 10H), 8.22–8.24 (m, 6H), 8.37 (dd, $J = 1.7$ Hz, $J = 6.4$ Hz, 2H), 8.47 (dd, $J = 1.8$ Hz, $J = 6.4$ Hz, 2H), 8.64 (s, 1H), 8.86–8.92 (m, 8H, β-pyrrole), 9.05 (s, 1H); MS *m/z* calcd for $C_{56}H_{35}N_5O_2S$ 841.2511, found 842.2730 $(M + H)^+$.

5g was obtained in 75% yield (45 mg) starting from 3 and 2-bromo-1-(1H-indol-3-yl)ethanone 4g as described for 5a;. UV–vis [λ_{max}, nm] in $CHCl_3$: 420, 516, 552, 591, 647; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = -2.76$ (s, 2H, NH), 7.30–7.32 (m, 2H), 7.45–7.47 (m, 1H), 7.55 (s, 1H), 7.73–7.81 (m, 9H), 7.95 (d, $J = 2.6$ Hz, 1H), 8.22–8.25 (m, 7H), 8.32–8.34 (m, 3H), 8.48 (dd, $J = 1.8$ Hz, $J = 6.4$ Hz, 2H), 8.86–8.93 (m, 8H, β-pyrrole); MS *m/z* calcd for $C_{55}H_{36}N_6S$ 812.2722, found 813.3018 $(M + H)^+$.

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