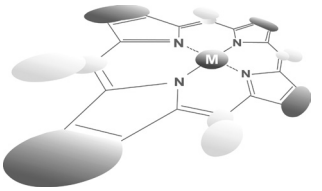
Journal of Porphyrins and Phthalocyanines
J. Porphyrins Phthalocyanines 2010; **14**: 1034–1039
DOI: 10.1142/S1088424610002884

Published at http://www.worldscinet.com/jpp/



Synthesis and fluorescence studies of porphyrin appended 1,3,4-oxadiazoles

K.P. Chandra Shekar[a], Bhupendra Mishra[a], Anil Kumar[a], S. Phukan[b], S. Mitra[b] and Dalip Kumar*[a]

[a] *Department of Chemistry, Birla Institute of Technology & Science, Pilani 333 031, India*
[b] *Department of Chemistry, North-Eastern Hill University, Permanent Campus, Umshing, Shillong 793 022, India*

Received 29 April 2010
Accepted 10 December 2010

ABSTRACT: A modular synthetic approach for preparing a family of porphyrin appended 1,3,4-oxadiazoles **9** is described. The porphyrin hydrazides are reacted with aryl aldehydes in presence of $Yb(OTf)_3$ as catalyst to give porphyrin hydrazones **8** which are then cyclized to porphyrin appended 1,3,4-oxadiazoles **9** using iodobenzene diacetate. Photophysical studies in $CHCl_3$ solvent shows that the electronic structure of the porphyrin chromophore is not greatly perturbed by the incorporation of the oxadiazole group onto the *meso*-phenyl ring. Efficient quenching of porphyrin fluorescence was observed in **9g** with a pyridinium moiety.

KEYWORDS: porphyrin, 1,3,4-oxadiazoles, porphyrin hydrazide, porphyrin oxadiazoles, iodobenzene diacetate.

INTRODUCTION

Porphyrin and its derivatives have received a significant attention in the last two decades due to their applications in electrooptical and nonlinear optics [1], two-photon absorption [2], field-effect transistors [3], organic synthesis, phosphorescent oxygen sensors [4] and photodynamic therapy [5]. Porphyrin appended heterocycles have also widely utilized for their potential applications in medicine, switches, photochemical energy conservation and molecular electronics [6]. Variation of peripheral and *meso*-substituents, and the central metal ion of porphyrins have shown to modulate their physical and biological properties [5]. On the other hand, five-membered 1,3,4-oxadiazoles are an important class of heterocyclic compounds with broad range of biological activities including antibacterial, antimycobacterial, antiinflammatory, anticonvulsant, tyrosinase inhibitory and anticancer activities [7, 8]. Some of the 1,3,4-oxadiazoles have also been investigated as electron-transporting materials within multilayered devices and color tunable luminescence [9]. Due to interesting physical and biological properties of porphyrin heterocycles, we have synthesized novel porphyrins containing 1,3,4-oxadiazole moiety and studied their physical properties.

Organoiodine(III) reagents are very important for the oxidation of various functional groups in organic chemistry due to their low toxicity, ready availability, ease of manipulation and high stability [10]. Iodobenzene diacetate (IBD) mediated oxidation of *N*-acylhydrazones has been reported to yield 1,3,4-oxadiazoles [11]. Subsequently this protocol has been utilized for the synthesis of naphthyridine analogs by grinding a mixture of appropriate hydrazones and IBD in solid state. Recently, we have synthesized a series of biologically interesting indolyl 1,3,4-oxadiazoles from indolyl acylhydrazones [8]. In this paper, we report preparation of various porphyrin oxadiazoles using IBD mediated oxidation of porphyrin *N*-acylhydrazones in very good yield.

EXPERIMENTAL

General

The synthesized porphyrin derivatives (**1**–**7**) and the free base (**8**) were characterized by UV-vis and

*Correspondence to: Dalip Kumar, email: dalipk@bits-pilani.ac.in, tel: +91 1596-245073-279, fax: +91 (1596)-244183

fluorescence spectroscopy. Steady-state absorption spectra were recorded on a Perkin-Elmer model Lambda25 absorption spectrophotometer. Fluorescence spectra were taken in a Hitachi model 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 unless otherwise mentioned, whereas, excitation spectra were obtained by monitoring at the respective emission maximum. In both cases, 5 nm bandpass was used in the excitation and emission side. Fluorescence quantum yields (ϕ_f) were calculated by using compound **8** as reference. The relative experimental error of the measured quantum yield was estimated within ±5%. ^{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. The 5-(4′-methylcarboxylate)-10,15,20-triphenylporphyrin **4** and 5-[(4′-methylcarboxylate)-10,15,20-triphenylporphyrinato]zinc(II) **5** were prepared according to literature procedure [12].

Synthesis

Preparation of (5-(4′-phenylhydrazide)-10,15,20-triphenylporphyrinato)zinc(II) 6. A solution of compound **5** (0.6 g, 0.81 mmol) in 15 mL of dimethylformamide was treated with 98% hydrazine hydrate (20 mL) and heated to 80 °C for 4 h. After the completion of the reaction, the reaction mixture was cooled 10–15 °C and filtered to afford **6** in 96% (0.58 g) yield. ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si): ™$_H$, ppm 8.97–8.74 (m, 8H), 8.29–8.03 (m, 6H), 7.92 (s, 1H), 7.81–7.63 (m, 9H), 7.34 (d, 2H, *J* = 8.2 Hz), 7.06 (d, 2H, *J* = 8.2 Hz). MS: *m/z* 735.3, calcd. for $[M + H]^+$ 735.5.

Preparation of 5-(4′-phenylhydrazide)-10,15,20-triphenylporphyrin 7. To a solution of porphyrin hydrazide **6** (0.73 g, 0.99 mmol) in dichloromethane was added 10 mL of dilute HCl (6N) and the reaction mixture was stirred for half an hour at room temperature. The reaction contents were basified to pH ~ 8 with sodium carbonate and the organic layer was separated. Remaining aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic phase was dried over sodium sulphate and distilled off at reduced pressure to obtain pure hydrazide **7** in 91% (0.51 g) yield. ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si): ™$_H$, ppm 8.98–8.67 (m, 8H), 8.29–8.07 (m, 6H), 7.82–7.60 (m, 9H), 7.33 (d, 2H, *J* = 8.2 Hz), 7.06 (d, 2H, *J* = 8.3 Hz). MS: *m/z* 672.5, calcd. for $[M+H]^+$ 672.3.

Preparation of 5-(4′-benzoylhydrazono-phenyl)-10,15,20-triphenylporphyrin 8. To a solution of porphyrin hydrazide **7** (0.1 g, 0.148 mmol) and aldehyde (15.8 mmol) in tetrahydrofuran (5 mL) was added ytterbium triflate (18 mg, 0.029 mmol) and the reaction mixture was stirred for 4 h at room temperature. After completion of the reaction, the solvent was distilled off and the residual mass was taken into water (5 mL) and basified to pH ~ 8 with sodium carbonate. The aqueous solution was extracted with dichloromethane (3 × 20 mL), and combined organic phase was dried over sodium sulphate and distilled off the excess solvent to afford porphyrin hydrazone **8** in 69–83% yields. **5-(*N*-4-methylbenzylidene-4-phenylhydrazino)-10,15,20-triphenylporphyrin (8a).** Yield 78%. ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si): ™$_H$, ppm 9.79 (s, 1H), 8.99–8.71 (m, 8H), 8.52 (s, 1H), 8.33–8.35 (m, 4H), 8.21–8.19 (m, 6H), 7.89 (d, 2H, *J* = 8.2 Hz), 7.80–7.71 (m, 9H), 7.69 (d, 2H, *J* = 8.4 Hz), 2.41 (s, 3H). MS: *m/z* 774.5, calcd. for $[M + H]^+$ 773.9. **5-(*N*-4-pyridylidene-4-phenylhydrazino)-10,15,20-triphenylporphyrin (8b).** Yield 70%. ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si): ™$_H$, ppm 10.48 (s, 1H), 8.99–8.71 (m, 8H), 8.58 (s, 1H), 8.52 (d, 2H, *J* = 7.9 Hz), 8.36–8.33 (m, 4H), 8.21–8.19 (m, 6H), 7.84–7.65 (m, 9H), 7.57 (d, 2H, *J* = 8.3 Hz). MS: *m/z* 761.8, calcd. for $[M + H]^+$ 761.9. **5-(*N*-4-methoxy-benzylidene-4-phenylhydrazino)-10,15,20-triphenyl-porphyrin (8c).** Yield 74%. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): ™$_H$, ppm 10.05 (s, 1H), 8.99–8.74 (m, 8H), 8.45 (s, 1H), 8.31–8.29 (m, 4H), 8.23-8.20 (m, 6H), 7.82–7.79 (m, 9H), 7.65 (d, 2H, *J* = 8.2 Hz), 7.35 (d, 2H, *J* = 8.3 Hz), 3.85 (s, 3H). MS: *m/z* 790.8, calcd. for $[M + H]^+$ 790.9. **5-(*N*-4-chlorobenzylidene-4-phenylhydrazino)-10,15,20-triphenylporphyrin (8d).** Yield 76%. ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si): ™$_H$, ppm 9.66 (s, 1H), 8.99–8.65 (m, 8H), 8.38 (d, 2H, *J* = 7.5 Hz), 8.31–8.29 (m, 4H), 8.26–8.17 (m, 6H), 8.03 (d, 2H, *J* = 7.8 Hz), 7.84–7.66 (m, 9H), -2.78 (s, 2H). MS: *m/z* 795.3, calcd. for $[M + H]^+$ 795.3. **5-(*N*-benzylidene-4-phenylhydrazino)-10,15,20-triphenylporphyrin (8e).** Yield 83%. ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si): ™$_H$, ppm 9.93 (s, 1H), 8.97–8.76 (m, 8H), 8.62 (d, *J* = 8.4 Hz, 2H), 8.34 (d, 2H, *J* = 7.8 Hz), 8.23–8.20 (m, 6H), 7.88 (d, 3H, *J* = 8.2 Hz), 7.78–7.73 (m, 9H), 7.45 (d, 2H, *J* = 8.4 Hz), -2.79 (s, 2H). MS: *m/z* 760.7, calcd. for $[M + H]^+$ 760.9. **5-(*N*-4-nitrobenzylidene-4-phenylhydrazino)-10,15,20-triphenylporphyrin (8f).** Yield 69%. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): ™$_H$, ppm 9.66 (s, 1H), 8.99–8.65 (m, 8H), 8.38 (d, 2H, *J* = 7.5 Hz), 8.31–8.28 (m, 4H), 8.26–8.17 (m, 6H), 8.03 (d, 2H, *J* = 7.8 Hz), 7.84–7.66 (m, 9H), -2.78 (s, 2H). MS: *m/z* 805.9, calcd. for $[M + H]^+$ 805.9.

Preparation of 5-(4-phenyl-(2-aryl-1,3,4-oxadiazol-5-yl)-10,15,20-triphenylporphyrin 9a–f. Iodobenzene diacetate (0.039 g, 0.114 mmol) was added to a solution of porphyrin hydrazones **8** (0.118 mmol) in dichloromethane (5 mL) and the reaction mixture was stirred at room temperature for 8 h. After completion of reaction as indicated by TLC, the contents were poured into water (5 mL). The product was extracted with dichloromethane (3 × 15 mL). Combined organic phase was dried over sodium sulphate and distilled off the excess solvent to afford **9** which was purified by column chromatography

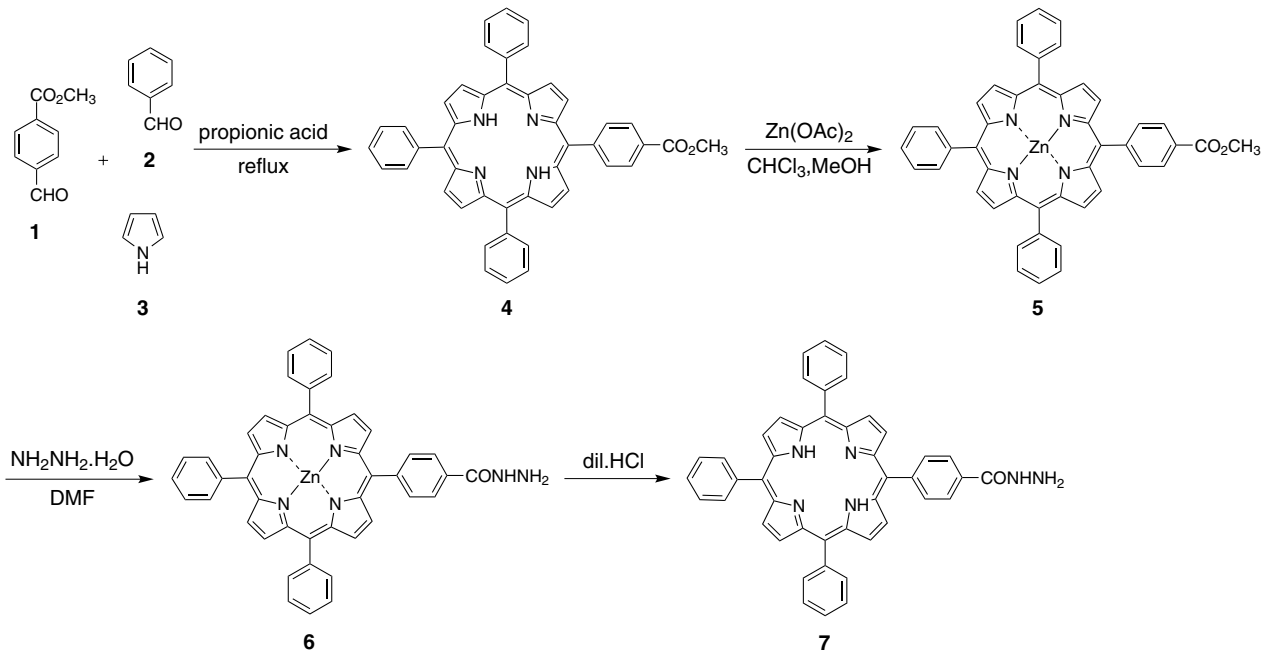
using chloroform-hexane (3:2, v/v) as a solvent system. **5-(4-phenyl-(2-tolyl-1,3,4-oxadiazol-5-yl)-10,15,20-triphenylporphyrin (9a).** Yield 71%. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.89 (d, 2H, J = 4 Hz), 8.85 (s, 8H), 8.56 (d, 2H, J = 12 Hz), 8.41 (d, 2H, J = 8 Hz), 8.23 (d, 6H, J = 8 Hz), 8.17 (d, 2H, J = 8 Hz), 7.77 (d, 9H, J = 8 Hz), 3.71 (s, 3H), -2.75 (s, 2H). MS: 773.1698, calcd. for $[M + H]^+$ 773.3029. **5-(4-phenyl-(4-pyridyl-1,3,4-oxadiazol-5-yl)-10,15,20-triphenylporphyrin (9b).** Yield 75%. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.94 (d, 2H, J = 8 Hz), 8.84 (s, 8H), 8.63 (d, 2H, J = 8 Hz), 8.52 (d, 2H, J = 8 Hz), 8.24 (d, 6H, J = 8 Hz), 8.21 (d, 2H, J = 8 Hz), 7.85 (m, 9H), -2.86 (s, 2H). MS: *m/z* 760.1547, calcd. for $[M + H]^+$ 760.2825. **5-(4-phenyl-(2-(4-methoxyphenyl)-1,3,4-oxadiazol-5-yl)-10,15,20-triphenylporphyrin (9c).** Yield 64%. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.89 (d, 2H, J = 4 Hz), 8.85 (s, 8H), 8.54 (d, 2H, J = 8 Hz), 8.41 (d, 2H, J = 8 Hz), 8.23 (d, 6H, J = 8 Hz), 7.78 (d, 9H, J = 8 Hz), 7.12 (d, 2H, J = 8 Hz), 3.93 (s, 3H), -2.75 (s, 2H). MS: *m/z* 789.1601, calcd. for $[M + H]^+$ 789.2978. **5-(4-phenyl-(2-(4-chlorophenyl)-1,3,4-oxadiazol-5-yl)-10,15,20-triphenyl-porphyrin (9d).** Yield 74%. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.89 (d, 2H, J = 4 Hz), 8.85 (s, 8H), 8.55 (d, 2H, J = 8 Hz), 8.42 (d, 2H, J = 8 Hz), 8.23 (d, 6H, J = 8 Hz), 7.79 (d, 9H, J = 8 Hz), 7.61 (d, 2H, J = 8 Hz), -2.75 (s, 2H). MS: *m/z* 793.1147, calcd. for $[M + H]^+$ 793.2483. **5-(4-phenyl-(2-phenyl-1,3,4-oxadiazol-5-yl)-10,15,20-triphenylporphyrin (9e).** Yield 66%. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.89 (d, 2H, J = 4 Hz), 8.86 (s, 8H), 8.57 (d, 2H, J = 12 Hz), 8.42 (d, 2H, J = 8 Hz), 8.23 (d, 6H, J = 8Hz), 7.77 (d, 9H, J = 8 Hz), 7.61 (t, 3H, J = 8 Hz), -2.75 (s, 2H). MS: *m/z* 759.1574, calcd. for $[M + H]^+$ 759.2872. **5-(4-phenyl-(2-(4-nitrophenyl)-1,3,4-oxadiazol-5-yl)-10,15,20-triphenylporphyrin (9f).** Yield 80%. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.89 (d, 2H, J = 4 Hz), 8.85 (s, 8H), 8.55 (d, 2H, J = 8 Hz), 8.42 (d, 2H, J = 8 Hz), 8.23 (d, 6H, J = 8 Hz), 7.79 (d, 9H, J = 8 Hz), 7.61 (d, 2H, J = 8 Hz), -2.75 (s, 2H). MS: *m/z* 803.1592, calcd. for $[M + H]^+$ 803.2654. **5-(4-phenyl-(4-methylpyridinium-1,3,4-oxadiazol-5-yl)-10,15,20-triphenylporphyrin (9g).** Yield 95%. ^{1}H NMR (400 MHz, $CDCl_3$) $^{TM}\delta_H$, ppm 9.08 (d, J = 7.6 Hz, 2H), 8.97–8.77 (m, 8H), 8.59 (d, 2H, J = 7.9 Hz), 8.49 (d, 4H, J = 7.9 Hz), 8.30–8.11 (m, 6H), 7.88–7.66 (m, 9H), 4.53 (s, 3H), -2.85 (s, 1H). MS: *m/z* 774.5, calcd. for $[M + H]^+$ 774.7.

RESULTS AND DISCUSSION

Synthesis and characterization

The synthesis of porphyrin **4** was carried out from the reaction of 4-formyl methylbenzoate **1** (1 equiv.), benzaldehyde **2** (3 equiv.) and pyrrole **3** (4 equiv.) in refluxing propionic acid (Scheme 1) followed by oxidation with DDQ in dry chloroform [13]. The desired porphyrin **4** was separated from the crude mixture by column chromatography in 7% yield. The metallation of the porphyrin **4** was carried out with zinc acetate in a mixture of chloroform-methanol (1:1, v/v) to give porphyrin **5** in 95% yield. The reaction of porphyrin **5** with hydrazine hydrate in *N,N′*-dimethylformamide resulted in the formation of hydrazide **6** in 96% yield.

However, direct attempt to prepare porphyrin hydrazide failed to yield desired porphyrin hydrazide. Demetalation of **6** was effected with dilute hydrochloric acid



Scheme 1. Synthesis of porphyrin hydrazide **7**

Table 1. Synthesis of porphyrin oxadiazoles (**9a–g**)[a]

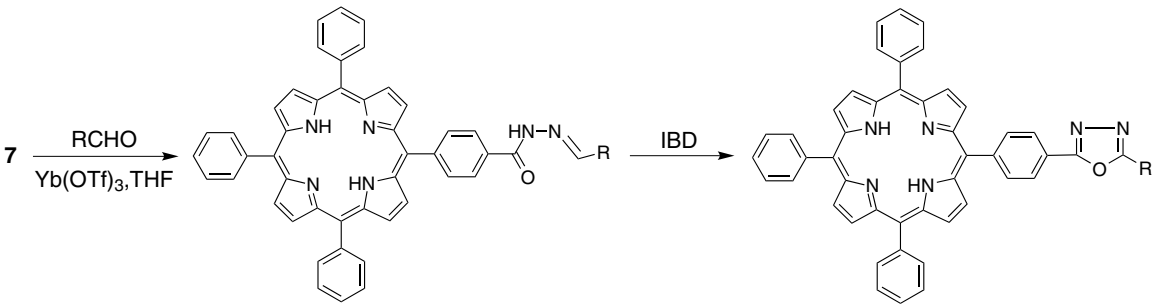
Entry	R	Product	Yield, %[b]
1	4-$CH_3C_6H_4$	**9a**	71
2	4-pyridyl	**9b**	75
3	4-$OCH_3C_6H_4$	**9c**	64
4	4-ClC_6H_4	**9d**	74
5	C_6H_5	**9e**	66
6	4-$NO_2C_6H_4$	**9f**	80
7	4-methylpyridinium	**9g**	94[c]

Reaction conditions: [a] **8** $PhI(OAc)_2$, DCM; [b] isolated yield; [c] **9b** $CHCl_3$, CH_3I, reflux, 36 h.

in dichloromethane to obtain pure porphyrin hydrazide **7**. The porphyrin hydrazone **8** was synthesized from the reaction of **7** with aldehydes in presence of ytterbium triflate (0.2 equiv.) in tetrahydrofuran at room temperature (Scheme 2). This reaction was found to be sluggish in ethanol and catalytic amount of conc. HCl due to insolubility of porphyrin **7** even at higher temperature. The formation of hydrazone with compound **6** was also attempted but it took 48 h for the completion of the reaction whereas with metallated porphyrin **7**, the reaction completed within 3–5 h. Further, the oxidative cyclization of compound **8** was carried out in presence of hypervalent iodine reagent, iodobenzene diacetate (1 equiv.) in dichloromethane to give desired porphyrin **9** in good yields (Scheme 2).

Photophysical properties

The most acceptable interpretation of electronic absorption spectra of porphyrin derivatives is based on theoretical analysis of the experimental data and quantum chemical calculations. According to this model, the porphyrins do not exhibit $n\rightarrow\pi^*$ transition due to the symmetry of the n orbitals and asymmetry of the π orbitals. 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 [14]. The characteristic peak positions for absorption spectra are given in Table 2 along with the molar absorption coefficient of each of them. In general, all the compounds exhibited characteristically one intense Soret band and four weak Q-bands. The peak position of the Soret band is around 420 nm; whereas the Y-polarized bands IV [$Q_{Y(0,1)}$] and III [$Q_{Y(0,0)}$] around 515 and 551 nm, respectively, and the X-polarized bands II [$Q_{X(0,1)}$] and I [$Q_{X(0,0)}$] around 590 and 648 nm, respectively. Compared to the H_2TPP (418 nm), the Soret band of all the prophyrin derivatives appear slightly red-shifted at 420 nm except in case porphyrin **9g**, where it appears at *ca*. 416 nm. Similar observation is made for



8a-f **9a-f**

a) R = 4-$CH_3C_6H_4$; **b**) 4-pyridyl; **c**) 4-$OCH_3C_6H_4$; **d**) 4-ClC_6H_4; **e**) C_6H_5; **f**) 4-$NO_2C_6H_4$

Scheme 2. Synthesis of porphyrin oxadiazoles **9**

Table 2. Absorption and emission data of porphyrin 1,3,4-oxadiazoles **9a–g** in chloroform

Compound	(Absorption) λ_{max} nm (ε/10^4 $M^{-1}.cm^{-1}$)					(Emission) λ_{max} nm		Quantum yield, Φ_f
	(Soret)	[$Q_Y(0,1)$]	[$Q_{Y(0,0)}$]	[$Q_{X(0,1)}$]	[$Q_{X(0,0)}$]			
9a	420 (14.00)	516 (2.30)	552 (2.00)	592 (1.90)	647 (1.80)	647	707	0.063
9b	420 (7.10)	515 (1.30)	551 (1.10)	591 (1.09)	649 (1.08)	648	707	0.102
9c	420 (36.80)	516 (4.50)	550 (3.70)	590 (3.50)	646 (3.30)	648	708	0.160
9d	420 (21.30)	515 (3.00)	551 (2.60)	590 (2.40)	647 (2.30)	647	707	0.073
9e	420 (34.60)	516 (4.20)	551 (3.70)	590 (3.30)	646 (3.10)	647	708	0.085
9f	420 (11.80)	517 (2.60)	550 (2.30)	590 (2.20)	648 (2.10)	648	708	0.062
9g	416 (4.20)	540 (0.79)	614 (0.65)	653 (0.64)	682 (0.61)	no characteristic emission		
H_2TPP	418 (42.00)	516 (4.60)	552 (3.70)	592 (3.40)	647 (3.20)	647	707	0.110

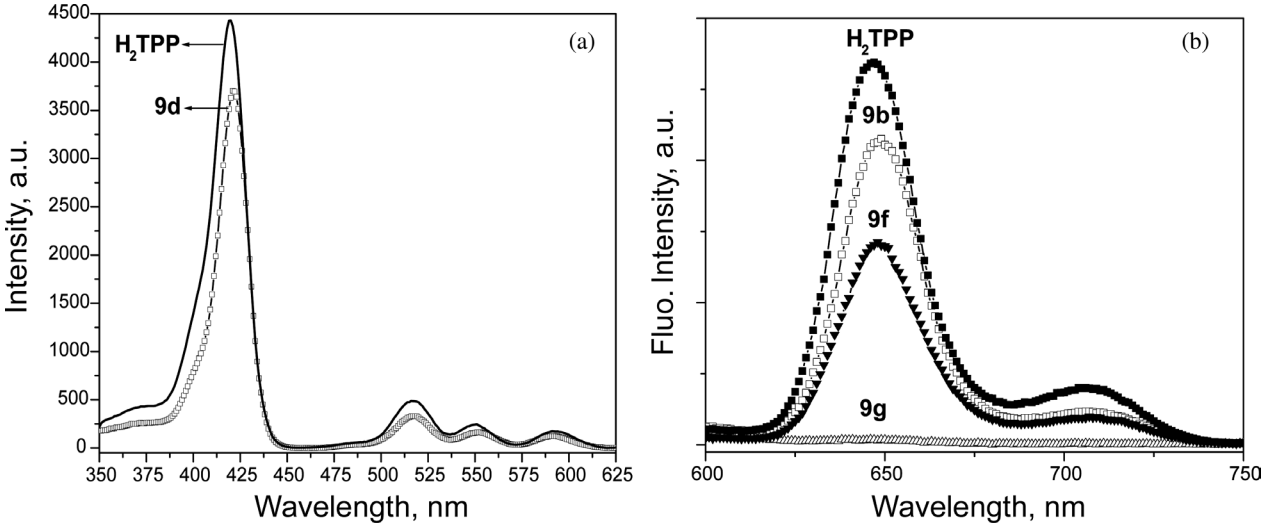


Fig. 1. (a) Fluorescence excitation spectra of different porphyrin derivatives in chloroform obtained by monitoring the fluorescence emission at 648 nm. (b) Fluorescence emission spectra of porphyrin derivatives in chloroform (λ_{exc} = 515 nm)

the Q-bands also; where all the porphyrin derivatives are observed to behave similarly except **9g**.

The small shift in both the Soret and Q-bands from the model compound indicates that introduction of new groups in *meso*-phenyl of the porphyrin moiety did not affect the energy levels substantially. The electronic structure of the porphyrin chromophore is not greatly perturbed by the incorporation of the oxadiazole group onto the *meso*-phenyl ring. Some of the representative fluorescence spectra are shown in Fig. 1. The fluorescence peak position of all the compounds in chloroform are given in Table 2 along with the relative yield of fluorescence. The fluorescence spectra of all the compounds except **9g** are characterized by two emission bands at around 647 and 707 nm, when excited at 515 nm. Excitation at Soret band also gives similar emission spectra (not shown). Interestingly, the fluorescence emission peak position is remarkably insensitive to the nature of substitution. However, porphyrin **9g** that contains a positively charged pyridinium moiety does not show any fluorescence emission behavior in the whole spectral range. This is also in accordance with the observation that compound **9f** containing a neutral electron withdrawing nitro group show comparable fluorescence property (although having relatively lesser magnitude of fluorescence quantum yield) when compared with other fluorescing porphyrin derivatives however, the fluorescence quantum yield is significantly quenched. Complete quenching of fluorescence in case of **9g** may be due to some specific interaction of the porphyrin ring with pyridinium moiety. Table 2 also shows substantial difference in Q-band positions for **9g** with other synthesized porphyrin derivatives as well as the model compound H_2TPP. This further indicates that the energy levels are perturbed in **9g** and the nature of interaction is different in this case from the rest of the group. In porphyrin **9g**, pyridyl ring is connected with porphyrin through a linking bridge; it would make up a "donor-space-acceptor" intramolecular PET transfer system. The fluorescence of porphyrin is quenched by way of transfer of the excited state electron from porphyrin to pyridinium ring through the oxadiazole spacer. The fluorescence quantum yields of **9b** and **9c** was higher than that of H_2TPP, indicating the substantial electronic interaction between porphyrin ring and aryl ring through oxadiazole spacer whereas fluorescence quantum yields decreased in other porphyrin derivatives (**9a**, **9d–e** and **9f**). Also, it has been observed that fluorescence excitation spectra (Fig. 2) for all the porphyrins are in very good agreement with the absorption data, given in Table 2.

Acknowledgements

The authors thank the Department of Science and Technology, New Delhi for the financial support and SAIF, Panjab University for providing analytical support.

REFERENCES

1. a) Guldi DM. *Chem. Soc. Rev.* 2002; **31**: 22. b) Drain CM, Russell KC and Lehn J-M. *Chem. Commun.* 1996; 337. c) Lin VS-Y, DiMagno SG and Therien MJ. *Science* 1994; **264**: 1105. d) Shediac R, Gray MHB, Uyeda HT, Johnson RC, Hupp JT, Angiolillo PJ and Therien MJ. *J. Am. Chem. Soc*. 2000; **122**: 7017. e) Rubtsov IV, Susumu K, Rubtsov GI and Therien MJ. *J. Am. Chem. Soc.* 2003; **125**: 2687.
2. a) Ahn TK, Kim KS, Kim DY, Noh SB, Aratani N, Ikeda C, Osuka A and Kim D. *J. Am. Chem. Soc.* 2006; **128**: 1700. b) Inokuma Y, Ono N, Uno H, Kim DY, Noh SB, Kim D and Osuka A. *Chem. Commun.* 2005; **30**: 3782. c) Drobizhev M, Stepanenko Y, Dzenis Y, Karotki A, Rebane A, Taylor PN and Anderson HL. *J. Phys. Chem. B* 2005; **109**: 7223. d) Luo Y, Rubio-Pons O, Guo JD and Agren H.

J. Chem. Phys. 2005; **122**: 096101. e) Collini E, Ferrante C and Bozio R. *J. Phys. Chem. B* 2005; **109**: 2.

3. a) Katz HE. *J. Mater. Chem*. 1997; **7**: 369. b) Katz HE, Bao Z and Gilat SL. *Acc. Chem. Res*. 2001; **34**: 359.
4. Brinas RP, Troxler T, Hochstrasser RM and Vinogradov SA. *J. Am. Chem. Soc*. 2005; **127**: 11851.
5. a) Drobizhev M, Karotki A, Kruk M, Mamardashvili NZ and Rebane A. *Chem. Phys. Lett*. 2002; **361**: 504. b) Karotki A, Drobizhev M, Kruk M, Spangler C, Nickel E, Mamardashvili N and Rebane A. *J. Opt. Soc. Am. B* 2003; **20**: 321. c) Dichtel WR, Serin JM, Edder C, Frechet JMJ, Matuszewski M, Tan L-S, Ohulchanskyy TY and Prasad PN. *J. Am. Chem. Soc*. 2004; **126**: 5380. d) Bonnett R. *Chemical Aspects of Photodynamic Therapy*, Gordon and Breach Science: Amsterdam, 2000.
6. Guo CC, Li HP and Zhao XB. *Bioorg. Med. Chem.* 2003; **11**: 1745.
7. Gaonkar SL, Rai KML and Prabhuswamy B. *Eur. J. Med. Chem.* 2006; **41**: 841.
8. Kumar D, Sundaree S, Johnson EO and Shah K. *Bioorg. Med. Chem. Lett*. 2009; **19**: 4492.
9. Meng H and Huang W. *J. Org. Chem.* 2000; **65**: 3894.
10. Koser GF. *Adv. Heterocyclic Chem*. 2004; **86**: 225.
11. Yang R-Y and Dai L-X. *J. Org. Chem.* 1993; **58**: 3301.
12. a) Stefanelli M, Monti D, Van Axel Castelli V, Ercolani G, Venanzi M, Pomarico G and Paolesse R. *J. Porphyrins Phthalocyanines* 2008; **12**: 1279. b) Swamy N, James DA, Mohr SC, Hanson RN and Ray R. *Bioorg. Med. Chem.* 2002*;* **10**: 3237.
13. Adler AD, Longo FR, Finarelli JD, Goldmacher J, Assour J and Korsakoff L. *J. Org. Chem*. 1967; **32**: 476.
14. Gouterman M. In *The Porphyrins*, Vol. 3, Dolphin D. (Ed.) Academic Press: NY, 1978; p 1.