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## Synthesis and Spectroscopic Properties of Axial Phenoxide and Para Amino Phenoxide Incorporated Indium (III) Porphyrins

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## Abstract

Tetrakis-4-methoxyphenyl indium(III) porphyrins containing phenolic and para amino phenolic moieties in the apical sites have been successfully prepared and characterized spectroscopically. The phases and structure evolutions of prepared porphyrins were deduced from powder X-ray diffraction (PXRD). The axial coordination of phenolic moieties induces slight shift of the <sup>1</sup>H NMR signals of indium porphyrin macrocycles. The measurements of UV-Visible absorptions of porphyrins in  $CH_2Cl_2$  and  $CH_3COOC_2H_5$  reflects that axially ligated metal chelates at neutral pH display hyperchromicity of absorption bands compared to unligated metal porphyrin. The most striking feature was the structural stability of indium porphyrins under basic (pH = 10) as well as acidic media (pH = 4). On the other hand, the metal free ligand 5, 10, 15, 20-Tetrakis-(4-methoxyphenyl) porphyrin,  $H_2TMP$  (I) undergoes J type aggregation in acidic media (pH = 4). The robustness of indium porphyrins especially in acidic media are in strong contrary to other sitting atop (SAT) or out of plane (OOP) complexes which are usually demetallized under acidic pH. All the prepared macro rings exhibit negative solvatochromism reflected by the blue shift of absorption bands in  $CH_3COOC_2H_5$  (more polar) than in  $CH_2Cl_2$  (less polar). The photoluminescence emissions in indium(III) species are significantly quenched relative to metal free ligand (I) due to internal heavy atom effect and distortion of ligand plane. The quenching of fluorescence bands are more pronounced in axially ligated metal porphyrins. The lesser excited state lifetimes of indium(III) porphyrins relative to free base analog (I) may be ascribed to spin orbit coupling induced by indium(III) ion in the respective metal chelates.

**Key words:** axial ligand; indium(III) porphyrins; solvatochromism; sitting atop (SAT); internal heavy atom effect

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## Introduction

Heavy metal porphyrins exhibit remarkable optical properties. For example, introducing Indium or Gallium metal into the central porphyrin ring has been reported to generate desirable photophysical properties such as long lifetime of the excited triplet state, low fluorescence lifetime, low fluorescence quantum yield ( $\Phi f$ ), deactivation directed by the singlet excited state, and a high quantum yield of singlet oxygen generation which are essential in an efficient sensitizer for use in photo responsive applications such as photodyanamic therapy [1-3]. Porphyrins and phthalocyanins offer versatile non linear optical (NLO) properties due to their extremely high chemical and thermal stability as well as rich photochemistry [4]. Moreover, the excited state properties of highly pi conjugated macrocycles can be easily tuned by metal complexation, axial ligation, functionalizations with various electron withdrawing and electro releasing substituents at the meso and beta positions of porphyrin ring [4]. In these lines, indium porphyrins (heavy metal porphyrins) are found to have enhanced optical limiting response [5]. For example, indium-Porphyrin functionalized with polymethylmethacrylate (InPor-MMA26) shows good reverse saturable absorption and reasonable positive refraction indicating their potential application in optical limiting both at picosecond and nanosecond timescale [6]. Similarly, indium porphyrinosmium cluster complexes are found to exhibit remarkable optical limiting performance for sensor protection in the visible region [7, 8]. Optical Limiting Properties of InTPP (indium tetraphenyl-porphyrin) and axially substituted InTTP (indium tetra-p-tolyl-porphyrin) with different axial ligands were further investigated and found that axial substitutions influence the nonlinear optical properties of the metalloporphyrins, mainly by chanting their excited state absorption cross-section [9]. Besides their enhanced NLO properties, indium porphyrins have other remarkable applications. For instance, a mesoporous indium-porphyrin framework, named JLU-Liu7 shows high adsorption performance for small gases and selectivity for CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> over CH<sub>4</sub> [10]. Another novel indium porphyrin framework named as NUPF-3 was found to possess a rarely seen 4-fold interpenetrated pts framework with segmented pores and dense metalloporphyrin central sites [11]. Due to this unique feature, NUPF-3 exhibits relative high CO<sub>2</sub> uptakes. Moreover, it has good heterogeneous catalytic property for cyclo addition of CO<sub>2</sub> and epoxides under relatively mild conditions with good recyclability [11]. Since the optical absorption behaviour of porphyrins are highly sensitive to change in pH of the media [12-14], the structural stability as well as optical behaviour of indium porphyrins in various media are needed to be investigated to further explore their potential applications especially in the field which demands their structural integrity under extreme conditions like presence of acid or base.

In our previous article, we had reported that the indium(III) derivative of Tetrakis-4methylphenyl porphyrin are easily demetallized under acidic media [14]. It was also reported that the indium(III) derivative of Tetrakis-4-methoxyphenyl porphyrin on the other hand was quite stable under such environmental conditions thereby reflecting a property unusual for a sitting atop (SAT) complex [15, 16]. Inspired by our previous work, we present the synthesis properties of Tetrakis-4-methoxyphenyl indium(III) porphyrin and spectroscopic [In(III)TMP]Cl, II coordinated with axial phenolic and para amino substituted phenolic groups generating the corresponding axially coordinated metal chelates with general formula [In(III)TMP]OPh, III and [In(III)TMP]OPh-pNH<sub>2</sub>, IV. The axial substituents with large pi planes are expected to influence the electronic absorption, emission as well as proton NMR spectra of unligated metal complex **II**. The study will clearly reveal particularly the optical absorption properties of synthesized porphyrins in three different media conditions which is the main aim of this work. The schematic diagram 1 shows the structures of synthesized metal chelates III and IV.



Scheme 1 Molecular structures of III and IV

#### 2. Experimental section

2.1 Materials and reagents

The analytical reagent (AR) grades chemicals were used for the synthesis of chelating ligand I and its corresponding metal chelates i.e. II–IV. The AR grade Chloroform, glacial acetic acid, pyrrole, 4-methoxybenzaldehyde, phenol, 4-amino phenol, propionic acid, concentrated HCl and KOH pellets were all purchased from Sigma-Aldrich and were used as received. The metal carrier, InCl<sub>3</sub> was also purchased from Sigma Aldrich.

#### 2.2 Measurements and Instrumentation

FT-IR was registered on Perkin Elmer Spectrum as KBr pellets. <sup>1</sup>H NMR spectra were recorded on Bruker spectrometer, model AV 400 N (400 MHZ), using CDCl<sub>3</sub> as solvent and TMS as internal reference. UV-Visible spectra were obtained on PG spectrophotometer; model T-90, using CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> as solvents. To introduce basic and acidic conditions in the organic solvents containing the porphyrin dyes, stock aqueous solutions of 0.1M KOH and 0.1M HCl were used. The pH values of the solutions were measured with a pH paper. Photoluminescence emission spectroscopic studies were recorded on Cary eclipse Agilent using CH<sub>2</sub>Cl<sub>2</sub> as solvent at room temperature. The phase purity and crystallite sizes of the as-prepared samples were determined from powder X-ray diffraction (PXRD) using D8 X-ray diffractometer (Bruker) at a scanning rate of 12° min<sup>-1</sup> in the 2*θ* range from 0° to 50°, with Cu Kα radiation ( $\lambda = 0.15405$  nm).

#### 2.3 Synthesis of starting material

The synthesis of the two starting materials **I** and **II** according to methods provided in the literature [18, 19] have been carried in similar manner as discussed previously [14].

2.4 Synthesis of axial phenolic and para amino phenolic coordinated In<sup>3+</sup> porphyrins

To a 250mL round bottomed flask containing 15mL methanolic solution of  $3.086 \times 10^{-2}$  mol of phenol (**III**) or  $3.086 \times 10^{-2}$  mol of 4-aminophenol (**IV**) was added  $6.602 \times 10^{-4}$  mol of **II** dissolved in 15mL chloroform. The reaction mixtures were then refluxed at 60°C with continuous stirring for 1 hour in dark in inert atmospheric conditions. At the end of the reactions, the mixtures were allowed to cool at room temperature and then filtered. The residues were washed repeatedly with pure methanol, dried and then finally re-crystallized using ethylacetate/petroleum ether (8:2) mixtures.

III was obtained as violet solid with 70% yield. FT-IR (KBr,  $v_{max}$ , cm<sup>-1</sup>): 717.38  $\gamma$ (C-H)ph, 800.31  $\gamma$ (C-H)pyrrole, 1338.35 v(C-N), 1571.70 v(C=N), 2834 v(C-H), 1062.58 v(C-O-C)<sub>sym</sub>,

1243.86 v(C-O-C)<sub>asym</sub>, 536.11 v(In-N), 690.39 v(In-O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz, δ, ppm): 4.15 (s., 12H, OCH<sub>3</sub>), 7.31-7.33 (d., 8H, ArH<sub>m</sub>), 7.36-7.38 (d., 8H, ArH<sub>m</sub>), 8.05-8.07 (d., 8H, ArH<sub>o</sub>), 8.30-8.32 (d., 8H, ArH<sub>o</sub>), 9.12 (s., 8H, βH), 6.85-6.87 (d., 2H, OPh<sub>o</sub>), 6.94-6.98 (t., 3H, OPh<sub>m,p</sub>). UV-Vis (λ<sub>max</sub>, nm, CH<sub>2</sub>Cl<sub>2</sub>): 430 (B band), 563, 606 (Q bands).

**IV** was obtained as violet solid with 75% yield. FT-IR (KBr,  $v_{max}$ , cm<sup>-1</sup>): 744.38 γ(C-H)ph, 813.81 γ(C-H)pyrrole, 1338.35 v(C-N), 1571.70 v(C=N), 2807.84 v(C-H), 1091.51 v(C-O-C)<sub>sym</sub>, 1234.21 v(C-O-C)<sub>asym</sub>, 520.68 v(In-N), 669.17 v(In-O), 3278.39 v(NH<sub>2</sub>)<sub>sym</sub>, 3338.17 v(NH<sub>2</sub>)<sub>asym</sub>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz, δ, ppm): 4.15 (s., 12H, OCH<sub>3</sub>), 7.31-7.33 (d., 8H, ArH<sub>m</sub>), 7.36-7.38 (d., 8H, ArH<sub>m</sub>), 8.05-8.07 (d., 8H, ArH<sub>o</sub>), 8.30-8.32 (d., 8H, ArH<sub>o</sub>), 9.12 (s., 8H, βH), 6.90 (s., 2H, NH<sub>2</sub>), 6.68-6.70 (d., 2H, OPh<sub>o</sub>), 6.61-6.63 (d., 2H, OPh<sub>m</sub>). UV-Vis (λ<sub>max</sub>, nm, CH<sub>2</sub>Cl<sub>2</sub>): 430 (B band), 563, 606 (Q bands).

#### 3. Results and Discussions

#### 3.1 Synthesis

The synthesis of porphyrins **I–IV** is shown in schematic diagram 2. Porphyrins being highly photosensitive in nature, the reactions were carried in the dark to avoid the effect of light on the highly conjugated macro rings. Inert conditions during the metal insertion and apical coordination of phenolic groups with indium–porphyrin unit were also maintained to ensure absence of any moisture or oxygen which may interfere with the metallation and apical ligation processes.



Scheme 2 synthetic route for I–IV

## 3.2 FT-IR Analysis

The axial coordination of phenolic and para amino phenolic moities with the indium(III) centre of macro ring **II** were characterized by FT-IR spectroscopy. Fig. 1 represents the FT-IR spectra of macro rings **I**–**IV**. The free base porphyrin **I** shows N–H stretching vibration at 3317 cm<sup>-1</sup>. When indium(III) ion is coordinated with the porphyrin ring of **I**, the characteristic band due to N–H stretching disappear and a new band due to In–N vibration appear at ~ 550–500 cm<sup>-1</sup>. This is attributed to the replacement of two acidic hydrogens by the metal ion. This also gives information about the presence or absence of **I** as an impurity in the metalloporphyrins. The FT-IR spectra of metal chelates **III** and **IV** consist of peaks due to In–O vibrations at 690.39 and 669.17 cm<sup>-1</sup> respectively. The FT-IR spectra further reveals no major changes in the vibration frequencies of aromatic skeleton of **I** after complexation and

axial ligation. A small peak ~ 2800–2900 cm<sup>-1</sup> corresponds to C–H stretching vibrations of macro rings **I–IV**. The metal complex **IV** display two characteristic peaks at 3278.39 and 3338.17 cm<sup>-1</sup> which are ascribed to  $NH_2$  symmetric and asymmetric stretching vibrations [20].



Fig. 1 FT-IR spectra of I–IV

## 3.3 <sup>1</sup>H NMR spectroscopy

Fig. 2 and Fig. 3 show the selected regions of the <sup>1</sup>H NMR spectra of **II**, **III** and **IV**. The complete spectra of free base ligand **I** and its corresponding indium(III) porphyrins are given in Fig S1-S4. The insertion of indium(III) ion within the porphyrinic core of **I** results in the disappearance of amino proton signal due to the replacement of NH protons by the metal ion. The coordinated metal ion exerts strong deshielding effect on the porphyrin ring protons resulting in the downfield shift of the resonance signals. The out of plane coordination of metal ion with the chelating ligand **I** results in the magnetic inequivalence of ortho as well as

meta phenyl protons. As a result the <sup>1</sup>H NMR spectra of metal chelates **II**, **III** and **IV** display two sets of doublets each ascribed for ortho and meta phenyl protons. The <sup>1</sup>H NMR spectra further reveals that the axial coordination of phenolic group with the indium- porphyrin unit causes slight downfield shift of the resonance signals relative to the metal chelate containing the chloro ligand **II** (Fig. 2). This is attributed to the deshielding effect induced by the axial phenoxide ion. The ortho (He) and meta/para (Hf) phenyl protons of axial phenolic group resonates in the upfield region as doublets ( $\delta$  6.85/6.87 ppm) and triplets ( $\delta$  6.94/6.96/6.98 ppm) respectively. The axial coordination of para amino phenolic group with indium porphyrin unit on the other hand induces slight upfield shift of resonance signals in comparison with resonance signals of macro ring **II** (Fig. 3). The upfield shift of proton signals in **IV** is expected to arise due to shielding effect exerted by the electron donating para amino group which resonates as singlet at  $\delta$  6.90 ppm. The other protons i.e. ortho and meta phenyl protons of para amino substituted phenoxide ion resonates as doublets at  $\delta$  6.68/6.70 and 6.61/6.63 ppm respectively.



**Fig. 2** The selected regions of the <sup>1</sup>H NMR spectra (400 MHz pulse FT) of **II** (purple) and **III** (olive green) at ~ 5 X  $10^{-3}$  M in CDCl<sub>3</sub>. Extra peaks at  $\delta$  7.2 ppm are due to presence of undeuterated chloroform



**Fig. 3** The selected regions of the <sup>1</sup>H NMR spectra (400 MHz pulse FT) of **II** (olive green) and **IV** (blue) at ~ 5 X 10<sup>-3</sup> M in CDCl<sub>3</sub>. Extra peaks at  $\delta$  7.2 ppm are due to presence of undeuterated chloroform

#### 3. 4 Powder XRD analysis

In order to determine the structure and phases of the resulting macro rings, powder X-ray diffraction (PXRD) measurement was performed. Fig. 4 shows the PXRD patterns of **I–IV**. All the significant diffraction peaks have been indexed. The XRD data indicates that the macrocyclic ligand **I** has face centered cubic geometry (JCPCDS card number 77-0437), while as its metal derivatives belongs to simple cubic (**II**, **III**) and body centered cubic (**IV**) symmetries (JCPCDS card number 45-0109). The average crystallite sizes of the samples were calculated according to Scherrer's formula (Eq. 1) using the three most intense diffraction peaks.

$$D = 0.9\lambda/\beta\cos\theta \tag{1}$$

Where D is the crystallite size,  $\lambda$  is the wavelength of the X- ray,  $\beta$  is the FWHM (full width at half maximum) of the diffraction peak,  $\theta$  is the diffraction angle and k is the Scherer's constant of the order of unity. The average crystalline sizes for **I**, **II**, **III** and **IV** were found to be 60.45, 80.56, 71.30 and 36.12 nm respectively. The high intensity of diffraction peaks particularly for NPs **I**, **II** and **III** reflects their high crystalline nature. In case of **IV**, the

diffraction peaks are comparatively broader which manifests that the NP has comparatively poor crystalline nature. The degrees of crystallinity of the NPs **I**–**IV** are also reflected from their average crystallite sizes. The crystallite size decreases as peak width increases. The XRD pattern of **I** confirms a uniform phase with no impurities. The XRD pattern of **II** is significantly different from that of **I** confirming the change in phase on metal coordination. The XRD pattern of **III** is very similar to that of **II** with diffraction peaks slightly shifted towards larger  $2\theta$  values in former. However, the XRD pattern of **IV** is completely different from that of NPs **II** and **III** indicating change in phase and formation of a new crystalline material, with no detectable amounts of starting materials present. The broad diffraction peaks in **IV** are further shifted to higher  $2\theta$  regions. The reduction in d spacing from **I** to **IV** is due to increase in thickness of porphyrin layers by functionalization with axial phenoxide and para amino phenoxide ions. The scattering angles and calculated *d*-spacings of the most intense scattering peaks are summarised in Table 1.

Samples	Position	FWHM	Crystallite	Lattice	d-spacing	Rel. Int.	Area
	[°20]	[°20]	size (nm)	strain	[Å]	[%]	$[cts^{*\circ}2\theta]$
	6.32	0.111	74.9	0.0088	13.97117	100.00	2557.46
Ι	18.85	0.135	62.15	0.0043	4.78753	10.32	1045.41
	25.18	0.192	44.3	0.0038	3.53359	16.74	841.47
	7.66	0.106	78.49	0.0069	11.52828	82.05	308.42
II	17.12	0.092	91.25	0.0027	5.17363	100.00	306.02
	19.03	0.117	71.94	0.0030	4.65917	80.31	292.28
	7.57	0.103	80.77	0.0068	11.66504	100.00	372.69
III	17.00	0.132	63.58	00.39	5.20936	75.85	274.79
	19.07	0.121	69.57	0.0031	4.64968	74.08	237.80
	19.94	0.377	22.36	0.0094	4.44739	32.41	167.25
IV	21.07	0.165	51.17	0.0039	4.21137	100.00	156.17
	22.60	0.243	34.83	0.0053	3.93028	30.82	73.88

Table 1 Scattering angles and *d*-spacings of the most intense scattering peaks



Fig. 4 The powder XRD patterns of I (green), II (blue), III (red) and IV (magenta)

3.5 Absorption spectroscopy

The electronic spectra of porphyrins manifest high sensitivity toward structural modifications as well as change in the polarity and pH of the surrounding environment.

Fig 5 and Fig. 6 show the UV-Visible absorption spectra of **I**–**IV** in pure organic solvents of CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>. The absorption spectra of **I** in both the organic solvents consists of one strong B band in the near UV region ~  $\lambda_{max}$  400 nm followed by four weaker Q bands in the visible region between  $\lambda_{max}$  500 to 700 nm. Similarly the metal chelates **II–IV** display one higher intensity B band ~  $\lambda_{max}$  400 nm followed by only two lower intensity Q bands between  $\lambda_{max}$  500 to 600 nm. The B and Q bands arise due to S<sub>0</sub> to S<sub>2</sub> and S<sub>0</sub> to S<sub>1</sub> ( $\pi$  to  $\pi^*$ ) transitions within the highly pi conjugated macro rings. The reduced number of Q bands in the metal porphyrins is due to increase in symmetry (from D<sub>2</sub>h to D<sub>4</sub>h). The lower symmetry (D<sub>2</sub>h) of free base porphyrin is ascribed to the presence of two diagonally positioned hydrogen atoms in its N4 core [21]. The coordination of indium(III) ion with the chelating ligand **I** induce bathochromic shift of B band and hypsochromic shift of Q bands as illustrated by Fig. 5 and Fig. 6. This phenomenon is attributed to ring distortion due to out of plane coordination of indium(III) ion. The distortion results in the extension of delocalization by the twisting of four aryl substituents from almost perpendicular orientation closer to the porphyrin plane [22].





**Fig. 5** (a) The UV/Vis absorption spectra of **I** (purple), **II** (magenta), **III** (red) and **IV** (blue) (b) magnified view of B bands (c) magnified view of Q bands at pH = 7 in  $CH_2Cl_2$  at ~ 5.0 x 10<sup>-5</sup>M (arrow signifies increase in intensity)





**Fig. 6** (a) The UV/Vis absorption spectra of **I** (blue), **II** (green), **III** (magenta) and **IV** (purple) (b) magnified view of B bands (c) magnified view of Q bands at pH = 7 in CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> at ~ 5.0 x 10<sup>-5</sup>M (arrow signifies increase in intensity)

Since the axial phenolic and para amino phenolic ligated metal chelates III and IV are now molecules. It was expected that the axially coordinated metal chelates will have their own electronic properties and may exhibit profound shifting of the absorption bands. However, from the experimental observation, it is found that the absorption spectra of uncomplexed metal porphyrin **II** and the monoligated complexes i.e. **III** and **IV** are very similar with negligible shift suggesting weak electronic coupling between the two constituent chromophores (phenolic/para amino phenolic group and indium-porphyrin) in the ground state [23]. The indium porphyrins however exhibits marked increase in the intensity of absorption bands relative to free ligand I. The intensity order of B bands of macro rings I-IV in both the non aqueous solvents follow the trend IV>III>II>I. The trend is almost similar for the Q bands as II > IV > III > I (CH<sub>2</sub>Cl<sub>2</sub>) and IV > III > II > I (CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>). The hyperchromicity of the absorption bands in the metal chelates relative to free base ligand is attributed to distortion of ligand plane by out of plane metal coordination [22]. The out of plane ring distortion is more pronounced when a fifth ligand bind the metal centre in the axial site. Porphyrins have strong tendency to undergo aggregation in solutions even at very low concentrations driven mainly by  $\pi$ - $\pi$  stacking interactions between the two neighbouring molecules [24, 25]. The magnitude of the  $\pi$ - $\pi$  interaction reduces in porphyrin coordinated with metal ions of large ionic radius. In addition when a ligand molecule coordinates with the metal centre on axial site, the metal is farther displaced away from the ligand plane which further results in diminished  $\pi$ - $\pi$  interaction and in fact generally leads to disaggregation [26].

This typical phenomenon of supramolecular aggregation and disaggregation is well manifested in the spectra of **I-IV** by closely observing the half widths of most intense B bands. The FWHM of B bands (Table 2) in  $CH_2Cl_2$  and  $CH_3COOC_2H_5$  follow the order **I>II>III>IV** and **I>II>IV>III**. The broadening of B band in **I** indicates favourable degree of aggregation relative to metal chelate **II**. The sharp and narrow bands in **III** and **IV** in turn reflect lesser degree of aggregation of the axially ligated species [27].

The metal chelates II (CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>), III (CH<sub>2</sub>Cl<sub>2</sub>) and IV (CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>) display hyper porphyrin spectra characterized by appearance of an additional band ~ 300nm. The extra band at ~ 300 (marked with star symbol) is attributed to charge transfer transition from allowed npz (filled metal orbital) to  $\pi^*$  (empty porphyrin orbital) in the near UV region [28]. The porphyrin rings I–IV also exhibit marked negative solvatochromism with absorption bands shifting towards higher energy in more polar solvent. It is known that solvatochromism arises due to different solvation of the ground and excited states of a molecule. The negative solvatochromism for I–IV is consistent with the ground state being more polar than the excited state. This result can be ascribed to a significant degree of charge transfer existing between the donor (peripheral para methoxy substituted phenyl rings) and acceptor (porphyrinic N4 core) species in the ground state with electron density pushing back to the donor from the acceptor moiety during excitation of the molecule resulting in a less-polar excited state [29].

#### Effect of pH

The absorption spectra of porphyrins **I–IV** were also measured under basic as well as acidic pH in both the organic solvents (Fig. 7 to Fig. 13). The optical behaviour of **I** in  $CH_2Cl_2$  under basic and acidic environment [Fig. S5] was already discussed previously [14]. The present study will therefore focus on the optical behaviour of **I** in  $CH_3COOC_2H_5$ .

The shape of the absorption spectra of porphyrins **I**–**IV** in basic media (pH = 10) are similar to that under neutral environment (pH = 7) in both the solvents indicating structural stability of the macro rings at higher pH. The hyperchromicity of the optical bands under basic conditions [Fig. 7 (left) to Fig. 13 (left)] may be attributed to association and finally precipitation of the porphyrins in aqueous alkali [30]. The half widths of B bands of metal porphyrins **II**–**IV** in CH<sub>2</sub>Cl<sub>2</sub> under basic media are greater than that in neutral media. On the other hand, the half widths of B bands of metal chelates **II**–**IV** in CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> at acidic pH is less than that at neutral pH.

In media of high ionic strength (pH = 4), the two inner nitrogen atoms of N4 core of I undergoes protonation followed by dramatic J type supramolecular aggregation of the resulting protonated species [31]. The J-aggregation of I results in the appearance of a higher intensity red shifted band at  $\lambda_{max}$  451 nm (J band) accompanied by one higher intensity QI band (which is otherwise forbidden) at  $\lambda_{max}$  683 nm as illustrated in Fig. 8 (right). The most striking feature was the optical behaviour of  $In^{3+}$  species under acidic media [Fig. 7 (right) to Fig. 13 (right)]. The metal ions in the two dyads III and IV remain intact with their macro rings in media of high ionic strength indicating their remarkable kinetic inertness and supreme robustness in highly acidic environment. This unique property (acid stability) of the indium(III) porphyrins is in strong contrary to other SAT complexes which are kinetically labile in nature. For e.g. the indium(III) derivative of Tetrakis-(4-methylphenyl) porphyrins are easily demetallized even in slight acidic environment [14]. All these observations clearly indicate that the judicious choice of chelating ligands may significantly enhance the lifetime and structural stability of even SAT metalloporphyrins under strongly acidic environment making them kinetically inert especially towards metal replacement reactions. It is also worth note that though the indium porphyrins in the present case are chemically stable under acidic media, the decreasing pH induces marked hypochromicity of the absorption bands of metalloporphyrins. The hypochromicity of optical bands of metal chelates at lower pH may be ascribed to peripheral protonation of the monomeric rings. The half widths of B bands of metal porphyrins in CH<sub>2</sub>Cl<sub>2</sub> under acidic media are greater than that in neutral media. On the other hand, the half widths of B bands of II-IV in CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> at acidic pH is less than that at neutral pH except for macro ring IV which exhibits narrow B band at neutral pH than at acidic pH. It can be also observed from Table 1 that the FWHM of B bands of macro rings nearly follow the trends as I>II>III>IV in both the organic solvents under alkaline as well as acidic environments. The change in neutral pH of the media also influences Hyperporphyrin behaviour exhibited by the metalloporphyrins. For example, the metal chelate II exhibits no hyper porphyrin effect in CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> under neutral pH. However as media becomes acidic, an additional band ~ 322nm appears in the spectra due to hyperporphyrin effect as illustrated in Fig. 9 (left). Hyper porphyrin effect is also displayed by III in CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> under basic [Fig. 10 (right)] as well as acidic media [Fig.11 (right)]. The absorption spectra of IV in acidic media display an additional band (marked with star symbol) at  $\lambda_{max}$  363 nm as illustrated in Fig. 13 (right). This band might be attributed to charge transfer electronic transitions from para methoxy substituted phenyl rings to the neutral porphyrinic N4 core.



**Fig. 7** The UV/Vis absorption spectra of **I** in  $CH_3COOC_2H_5$  under neutral (pH = 7) and basic (pH = 10) media [left] and under neutral and acidic (pH = 4) media [right] at ~ 5.0 x 10<sup>-5</sup>M



**Fig. 8** The UV/Vis absorption spectra of **II** in CH<sub>2</sub>Cl<sub>2</sub> [left] and CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> [right] under neutral (pH = 7) and basic (pH = 10) media conditions at ~  $5.0 \times 10^{-5}$ M



**Fig. 9** The UV/Vis absorption spectra of **II** in CH<sub>2</sub>Cl<sub>2</sub> [left] and CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> [right] under neutral (pH = 7) and acidic (pH = 4) media conditions at ~  $5.0 \times 10^{-5}$ M



**Fig. 10** The UV/Vis absorption spectra of **III** in  $CH_2Cl_2$  [left] and  $CH_3COOC_2H_5$  [right] under neutral (pH = 7) and basic (pH = 10) media conditions at ~ 5.0 x 10<sup>-5</sup>M



**Fig. 11** The UV/Vis absorption spectra of **III** in CH<sub>2</sub>Cl<sub>2</sub> [left] and CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> [right] under neutral (pH = 7) and acidic (pH = 4) media conditions at ~  $5.0 \times 10^{-5}$ M



**Fig. 12** The UV/Vis absorption spectra of **IV** in CH<sub>2</sub>Cl<sub>2</sub> [left] and CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> [right] under neutral (pH = 7) and basic (pH = 10) media conditions at ~  $5.0 \times 10^{-5}$ M



**Fig. 13** The UV/Vis absorption spectra of **IV** in CH<sub>2</sub>Cl<sub>2</sub> [left] and CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> [right] under neutral (pH = 7) and acidic (pH = 4) media conditions at ~  $5.0 \times 10^{-5}$ M

		pH = 7		pH = 10		<b>pH</b> = 4	
Solvent	codes	В	FWHM	<b>B</b> bands	FWHM	В	FWHM
		bands	(cm <sup>-1</sup> )	( <b>nm</b> )	( <b>cm</b> <sup>-1</sup> )	bands	( <b>cm</b> <sup>-1</sup> )
		(nm)				(nm)	
	Ι	421.22	11.99	421.18	11.47	448.7	11.36
CH.CL	II	430.11	10.35	430.09	10.51	430.00	12.36
	III	430.17	9.14	430.35	9.16	430.13	10.024
	IV	430.19	8.61	430.17	9.48	430.22	10.29
	Ι	418.30	9.70	417.56	12.56	451.70	13.55
	Π	427.83	9.10	428.07	8.71	428.09	9.06
CH3COOC2H5	ш	427.56	10.06	427.93	8.76	428.28	9.69
	IV	427.81	8.54	428.08	8.55	427.83	9.24

Table 2 FWHM of porphyrins (I-IV) at B band region in neutral, alkaline and acidic media

#### 3.5 Emission spectroscopy

The emission spectra of the synthesized macrocycles **I**–**IV** illustrated in Fig. 14 were recorded in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C. The macrocyclic ligand **I** and its three metal chelates **II**–**IV** at 390 nm excitation (~ soret band region) manifest both S<sub>1</sub> as well as S<sub>2</sub> (less common) fluorescence. The S<sub>1</sub> bands have been designated as Q(0,0) and Q(0,1) and that of S<sub>2</sub> emission (marked with star symbol) as B(0,0). The high energy S<sub>2</sub> emission in **I** appears at  $\lambda_{max}$  436 nm. In the metal chelates **II**–**IV**, the bathochromically shifted S<sub>2</sub> fluorescence

appears as weak band at  $\lambda_{max}$  458 nm. Similarly, the two S<sub>1</sub> bands in I are centered at  $\lambda_{max}$ 655 and 724 nm respectively. In the metal chelates II and III, the S<sub>1</sub> emission occurs at  $\lambda_{max}$ 659 and 721 nm. It can be observed from Fig. 14 that the emissions intensity of the Q(0,0)and Q(0,1) bands in IV decreases significantly and converges to the base line at ~ 750 nm unlike the other metal complexes. The presence of  $S_2$  as well as  $S_1$  emissions in these porphyrins signifies close mirror image relationship between their corresponding absorption and emission bands. The small stoke shift (Table 3) between the S<sub>2</sub> absorption and emission in macro rings I-IV further reflects that the structures of the near S2 excited porphyrins may be close to that already in the electronic ground state [32, 22]. Fig. 14 clearly depicts that the positions of  $S_1$  emission bands of the fluorophores II, III and IV are very similar with small shift suggesting weak excited state interactions between the two chromophoric units (phenolic/para amino phenolic group and indium-porphyrin). The quenching of emission bands in indium(III) porphyrins is attributed to combined internal heavy atom effect and distortion of ligand plane induced by complexation with metal cation of large ionic radius [33]. Indium(III) is, of course, lying above the N4 core plane ligand. However, it is also more heavy an atom to exert heavy-atom quenching. The emission intensities of metal chelates decreases in the order as II>III>IV. This kind of trend might be ascribed to greater degree of covalency of the empty porphyrin eg ( $\pi^*$ ) orbital with orbitals on the metal (heavy atom effect) on going from II to IV [34]. Fig. 15 represents the fluorescence decay profiles of I-IV. The excited state lifetime of I (7.56 ns) in  $CH_2Cl_2$  are greater than that of its metal chelates II-IV (Table 3). This behaviour may be attributed to the spin-orbit coupling induced by indium(III) ion (heavy metal effect) favouring the population of the triplet state [35].



**Fig. 14** The emission spectra of **I** (purple), **II** (blue), **III** (green) and **IV** (magenta) in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C,  $c = 10^{-5}$  M



Fig. 15 Fluorescence decays curves of I–IV

Samples	S <sub>2</sub> absorption (nm)	S <sub>2</sub> emission (nm)	Stoke shift (nm)	Average lifetime (ns)
Ι	421.22	436	14.78	7.56
II	430.11	458	27.89	0.312
III	430.17	458	27.83	0.108
IV	430.19	458	27.81	0.796

Table 3 S<sub>1</sub> absorption and emission data of porphyrins I--IV in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C.

Conclusion

In summary we have synthesized the axial phenolic and para amino phenolic incorporated indium(III) derivatives of **II**. The synthesized complexes were successfully characterised by FT-IR, <sup>1</sup>H NMR and UV-Visible spectroscopies. In the <sup>1</sup>H NMR spectra, the coordination of axial phenolic and para amino phenolic group on the metal centre of **II** causes slight shifting of the resonance signals. From the UV-Visible absorption data, it is found that the axially ligated metal chelates exhibits marked hyperchromicity of the optical bands relative to their free base analog **I**. A large spectroscopic change is also observed when the porphyrins are dissolved in organic solvent of different polarity under different pH conditions. The macro rings exhibits negative solvatochromic behaviour and may serve as potential optical probes. Upon exciting at 390 nm, the flourophores exhibits both S<sub>1</sub> as well as S<sub>2</sub> emissions. However, the emission bands in indium(III) species are significantly quenched due to internal heavy

atom effect and distortion of ligand plane. The quenching of emission bands are more pronounced in macro rings III and IV. The optical absorption and emission measurement data of axial coordinated macro rings III and IV further reveals weak ground state as well as excited state electronic interaction between the two chromophoric units (axial phenolic ligands and the indium–porphyrin). The desirable optical properties like high molar absorbance, remarkable acid stability and low fluorescence lifetime classifies the two synthesized dye molecules III and IV as optically efficient sensitizer for their potential use in many photo sensitive applications like photodyanamic therapy.

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- Axial coordination of phenolic and para amino phenolic with indium(III) porphyrin causes hyperchromicity of absorption bands.
- Axial phenolic group causes downfield shift of resonance signals whereas axial para amino phenolic group causes upfield shift of resonance signals of indium(III) porphyrin.
- In basic media, the absorption bands of porphyrins are of higher intensity.
- In acidic media, the absorption bands of porphyrins are of lower intensity.
- The indium(III) porphyrins exhibit remarkable stability under acidic media.
- Indium(III) ions induce quenching of fluorescence bands.

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