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Soluble Anionic Porphyrin for Detecting Hg(II), Cd(II), Pb(II), Cu(II), Fe(III), and Zn(II) Ions by Fluorescence and UV-Visible Spectral Studies

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ABSTRACT

Optical sensors for detecting metal ion contaminants in the environment are being developed because of a growing need for timely, simple, and reliable techniques required for monitoring or controlling the presence of some toxic cations released. A water-soluble anionic porphyrin was synthesized by a simple and affordable procedure that entails sulfonation of *meso*-tetraphenylporphyrin and purification, using modified standard methods. The effect of the presence of 0.33 mM Ca^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, Cu^{2+}, Zn^{2+}, and Fe^{3+} ions on absorption and fluorescence spectra of *meso*-tetrakis(4-sulfonatophenyl)porphyrin ($TPPS_4$) was investigated at 25 °C within 25 minutes of interaction. Shifts in wavelength of fluorescence peaks (Hg^{2+} and Cd^{2+}) and Soret absorption band (Cd^{2+} and Zn^{2+}); emergence of new fluorescence peaks (Pb^{2+}, Fe^{3+}, and Zn^{2+}); splitting of B band (Fe^{3+}); and the reduction in the number of Q bands ($Zn^{2+}$and Hg^{2+}) as well as outright fluorescence quenching or near quenching (in the case of Cu^{2+} and Hg^{2+} ions respectively) have been used to describe the characteristic behaviour of the porphyrin in the presence of these metal ions. The technique used were easy, sensitive, fast, and inexpensive, and the organic molecule was chemically stable. These selective and reversible interactions of the ligand with heavy metal ions in aqueous solution could be used to detect and monitor the presence of some toxic cations released into water bodies and the environment.

1. INTRODUCTION

Naturally, metals are present in biological systems and in earth crusts as minerals. However, they are also found as environmental pollutants mostly through several human activities. This wonderful environment and ecosystem of ours are constantly being affected by harmful chemicals and toxic metal ions, leading to various avoidable or unintended health issues. Cadmium, mercury, and lead get into the environment through their usage in mines and as components in batteries, pigments,

gasoline and several devices. These non-biodegradable metals can be absorbed through the skin or inhaled as vapour which accumulates in the body. They easily find their way into water bodies, soil, food items, aqueous mixtures, and the atmosphere [1]. Most heavy metals and some light ones (such as aluminium and selenium) are potentially harmful to humans and the environment [2]. Effects of such metals (Hg, Cd, Pb, and Cr) have caused damage to the body organs, hampering their normal functioning, and often result in breakdown of the immune system. Mercury has been reported to have adverse effects on the kidney, lung, and the central nervous system, resulting in cognitive and motor Neurons disorders [3]. On the other hand, biologically important metals such as potassium, sodium, calcium, copper, iron, and zinc are only useful at certain concentrations beyond which they become injurious [4,5]. For example, overload of copper (II) ion in the body may lead to Alzheimer, Wilson or Menke's diseases [6]. Similarly, high soil content of zinc may hinder microbial activity, causing harmful effects on plants, and it may also be a contaminant in food wastes [7]. Detection or sensing of these ions is therefore essential in toxicology and for establishing trace evidence of social vices such as suicide, homicide, illegal drugs, explosion, robbery, and terrorism [8].

Techniques used for sensing metal ions, such as chromatography, mass spectrometry, and room temperature phosphorimetry, are often costly, tedious, and sophisticated. To circumvent this, affordable chemical sensors (chemosensors) are being developed and reported [9,10]. A chemical sensor is defined as "a miniaturized device that can deliver real-time and online information on the presence of specific compounds or ions even in complex samples" [11]. Optical sensors use colorimetric, electronic absorption, or fluorescence to detect chemical substances. Optical fluorescent sensors for the detection of ions and molecules (often developed from fluorophores) are getting increased attention, giving rise to improved selectivity, sensitivity, and reduced time required for sensing [8].

Substances that have been proven useful as chemosensors include Schiff bases, metal-organic frameworks (MOFs), quantum dots, and functionalised dyes such as porphyrins [12-15]. Porphyrins are tetrapyrrolic macromolecules [16], readily available, cheap, highly selective, and sensitive to metal ions and biocompatible. Porphyrins and metalloporphyrins have a high absorption coefficient in the visible region and are stable in the presence of light. They also exhibit strong fluorescence in the visible region due to the conjugated π-system of highly mobile delocalized electrons [10]. Hence, they have been studied for the detection or sensing of toxic or biologically important metal ions and other chemicals [17-19]. Certain metalloporphyrins lend themselves to chemical modification at the periphery of their structure, making their emission properties suitable as tunable chemosensors [6]. Solubility properties usually limit the applications of the macromolecule as a sensor for water soluble contaminants because most porphyrin molecules are insoluble [10]. Certain soluble porphyrins, such as *meso*-tetrakis(4-sulfonatophenyl)porphyrin ($TPPS_4$) and their derivatives (e.g., 5-(4-aminophenyl)-10,15,20-tris(4-sulfonatophenyl)porphyrin) have been found suitable for the detection of Cu^{2+}, $Sn^{2+,}$ and Zn^{2+} ions by electronic absorption and fluorescence measurements [17,20]. Some ions and organic molecules that have been investigated using $TPPS_4$ also include Al^{3+}, Fe^{3+} [21]; Hg^{2+}, Cd^{2+} [22,23], and trinitrotoluene (TNT) [24]. Techniques used for the few ions are mostly colorimetric (on papers or mesoporous silica) and absorption spectral. But there is a need to study the detection ability of the porphyrin on a broader number of metal ions at a particular concentration using both absorption and fluorescence spectral techniques simultaneously,

and investigate their time-dependent responses. In this work, a simpler and cheaper procedure was utilized for synthesizing the anionic soluble dye. The porphyrin, $TPPS_4$, produced different diagnostic optical absorptions and fluorescence emissions for Hg^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, and Fe^{3+} ions, confirming its ability to act as a fast potential multi-signal optical sensor.

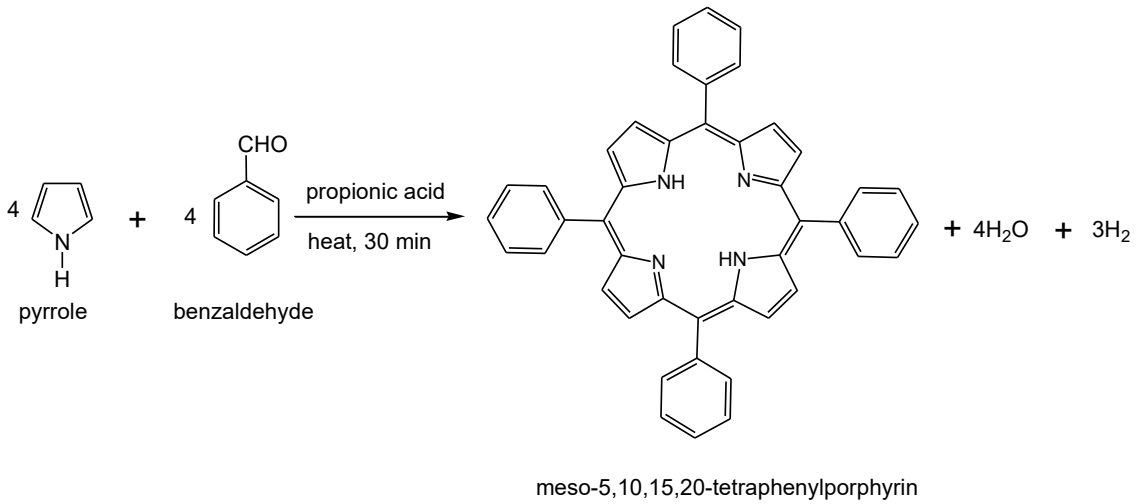
2. MATERIALS AND METHOD

2.1. *Materials and sample preparation*

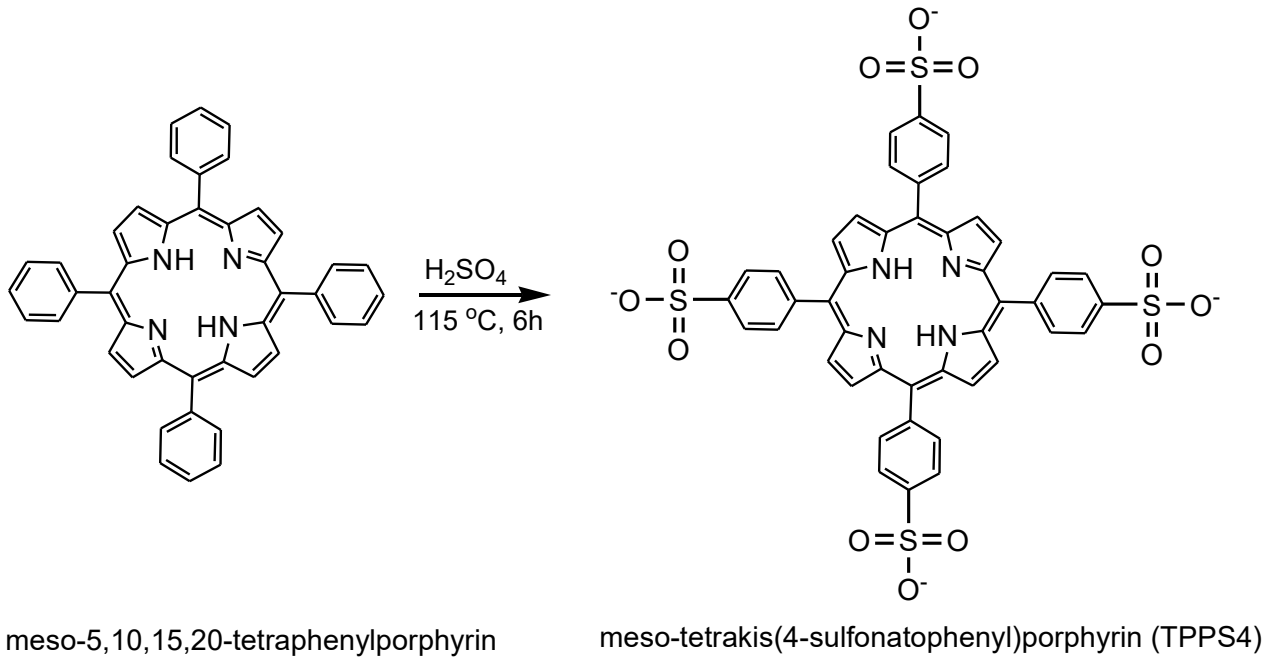
All reagents and chemicals used were of analytical grade and used without further purification. Deionized water was obtained from Glassworld& Chemical Suppliers Randburg, South Africa. Lead (II) nitrate, anhydrous calcium chloride, iron (III) chloride hexahydrate, zinc chloride, cadmium chloride, anhydrous copper (II) chloride, and mercury (II) chloride were obtained from Sigma Aldrich, USA. Synthesis of the soluble porphyrin was carried out as discussed below using modified literature procedures [25,26]. UV-Vis spectra were recorded on a Perkin Elmer Lambda 25 Spectrophotometer, UK, while fluorescence was measured on RF-6000 Spectrofluorophotometer, Shimadzu, Japan. All measurements were performed at ambient temperature and under atmospheric pressure. Metal salt solution of 1×10^{-3} M and solution of $TPPS_4$ (1.0×10^{-5} M) were prepared. Quartz cuvettes of 1.00 cm path length and 4.375 mL capacity were used for all measurements. Each sample mixture contained 2 mL of the $TPPS_4$ solution and 1 mL of deionized water or metal ion solution, thoroughly mixed in the cuvette at an ambient temperature of 25 °C. The same process was used in taking both fluorescence and absorption spectra.

2.2. *Synthesis of $TPPS_4$*

Sulphonation of *meso*-tetraphenylporphyrin ($TPPH_2$) was carried out based on our previously reported procedure [27]. Briefly, purified crystalline powder of $TPPH_2$ (0.8998 g, 1.46 mmol), prepared by Adler-Longo method [28], was suspended in 25 mL concentrated sulphuric acid inside a 250 mL round bottom flask equipped with fused $CaCl_2$-packed drying tube. This mixture was heated on a heating mantle at 115℃ for 6 h with occasional swirling in the first two hours. The resulting green solution was allowed to stand overnight with some ice-cold distilled water added to obtain a dark green precipitate. After filtration residue was washed with acetone and dried. It was then suspended in 75 mL of distilled water and 2.5 g of Celite was added with stirring. Saturated $NaHCO_3$ solution (100 mL) was added to the mixture until the solution turned purple (pH 8-9) while cooling in an ice bath. The concentrated filtrate was cooled in an ice bath overnight. Reddish residue obtained was washed with methanol and the evaporated filtrate was re-dissolved in water. The process of concentration, cooling, filtration, and washing was repeated until a light-yellow residue was obtained having no precipitate on cooling. The porphyrin-containing purple filtrate was evaporated to dryness and dried overnight at 70℃.



Scheme 1: Synthesis of *meso*-tetraphenylporphyrin ($TPPH_2$)



Scheme 2: *Synthesis of meso-tetrakis(4-sulfonatophenyl)porphyrin ($TPPS_4$)*

This crude product was recrystallised from ethanol/methanol (1:5 v/v), dried in the oven for 1 h 10 min at 125°C and, then under vacuum at ambient temperature to obtain the hydrated sodium salt of the porphyrin. This was finally converted to the anhydrous form by further drying at 150°C under vacuum for 24 h. Final yield = 1.2932 g (86.39 %).

3. RESULTS AND DISCUSSION

3.1. *Photochemical properties of $TPPS_4$*

Melting point of the anhydrous $TPPS_4$ is above 400°C. The compound is soluble in water, DMF and DMSO.Selected FTIR bands (cm^{-1}) for $TPPS_4$: 3433 m,br (O-Hstr of H_2O and N-Hstr); 1595w, 1426s (C=Cstr Ph); 1178s, 1124s, 1039s (S-Ostr). δ(ppm): ^1H NMR (60 MHz, D_2O, δ(ppm)): -

2.39 (NH, 2H, s); 7.58, 7.72 (*o,m*-PhH, 16H, d); 8.09, 8.22 (8H β-pyrrole), d); UV-Vis /nm (A, ε/$M^{-1}cm^{-1}$ in H_2O, 9.78 x 10^{-6} $molL^{-1}$ at 24°C) of anhydrous $TPPS_4$: 413 (2.626, 2.69 x 10^5), 515 (0.150, 1.53 x 10^4), 552 (0.066, 6.74 x 10^3), 579 (0.063, 6.45 x 10^3), 633 (0.037, 3.76 x 10^3). Fluorescence emission peaks (nm): 639, 703.

Analytical and spectral results are comparable with those earlier reported, exhibiting a peak as the Soret or B band ($S_0 \rightarrow S_2$) and four peaks as the Q band ($S_0 \rightarrow S_1$), a strong fluorescence emission peak and another weak one [17,26]. The yield obtained in this work is very high compared to the previously reported synthesis. The volume of acetone used was drastically reduced to only 20 mL and the usage of cellulose dialysis tubing for filtration or reverse column chromatography was also bypassed [28-30].

3.2. *Detection of metal ions by the porphyrin ligand*

The metal-free porphyrin fluorescent emission spectra were recorded immediately after mixing and until when no further changes occur. This took a maximum of 25 minutes after mixing 1 mL (1000 µM, 330 mM overall, or 50 equivalent) of the aqueous metal ion (Ca^{2+}, Zn^{2+}, Fe^{3+}, Cu^{2+}, Cd^{2+}, Pb^{2+} or Hg^{2+}) with 2 mL (10 µM, 6.67 µM overall) of aqueous solution of $TPPS_4$. It was immediately followed by measurements of electronic absorption spectrum of the same sample (between 5 and 25 minutes after mixing) to investigate the porphyrin sensing capacity. Two characteristic and important absorption bands in the visible region are known to be exhibited by porphyrins – B band or the Soret band (400-500 nm) and Q bands (500-700 nm). According to the literature, Soret band of the porphyrin was at 413 nm while the Q bands were found at 515, 552, 580, and 634 nm [26]. $TPPS_4$ has also been reported to have strong emission peak at 641.8 nm [17,25,31,32]. Changes in the intensity and position of the peaks of absorption and emission spectra of the anionic porphyrin in the absence of the cation and in the presence of the cations were compared. Intensities of the fluorescence emission peaks and Soret band of the metal-free porphyrin decreased in all cases when the metal ions were added [10] which may be attributed to changes in molecular concentration. Appearance of new peaks upon addition of the metal ion solution and the pattern of such a change were observed as parameters for sensing the metal ions. These new absorption peaks suggest the formation of porphyrin-metal ion complex. Only the UV-Vis spectra of $TPPS_4$ in the presence of copper (II) and mercury (II) ions were found similar as neither of them produce any significant shift in its Soret band in agreement with previous workers [17,21]. However, Balaji et al. [23] reported a red shift from 410 to 448 nm in the presence of Hg(II) ion when monolayer mesoporous silica was functionalized with TPPS acid anchored by N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride. The new chemical environment of the porphyrin might be responsible for the spectral change compared with an aqueous medium. New emission peaks appearing in the spectra of the porphyrin when the cations are present confirm the possibility of using the organic macromolecule to detect the metal ion [31].

3.2.1. *Interaction with Ca^{2+}; electronic absorption and fluorescent emission*

When aqueous solutions of calcium ion and the porphyrin were mixed the intensity of the Soret and Q bands in the UV-Vis spectrum and those of the fluorescence peaks reduced but no shift of the bands or additional peak was observed (Figures 1a and 1b). This decrease in intensity or absorbance may be attributed to a reduction in concentration of the chromophore in the porphyrin since no calcium-porphyrin complex was formed that could have resulted in spectral change after more than five minutes interaction period.

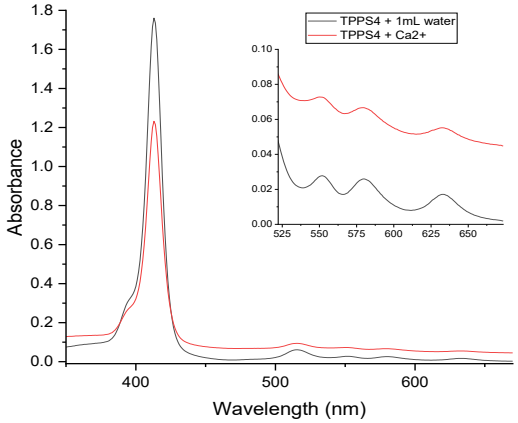


Fig 1a: *UV-Visible spectra of $TPPS_4$ in aqueous solution and the porphyrin with Ca^{2+} ion at 25℃ after 5 min.* ***Inset:*** *Q band in the spectra of aqueous $TPPS_4$ and the porphyrin with Ca^{2+} ion*

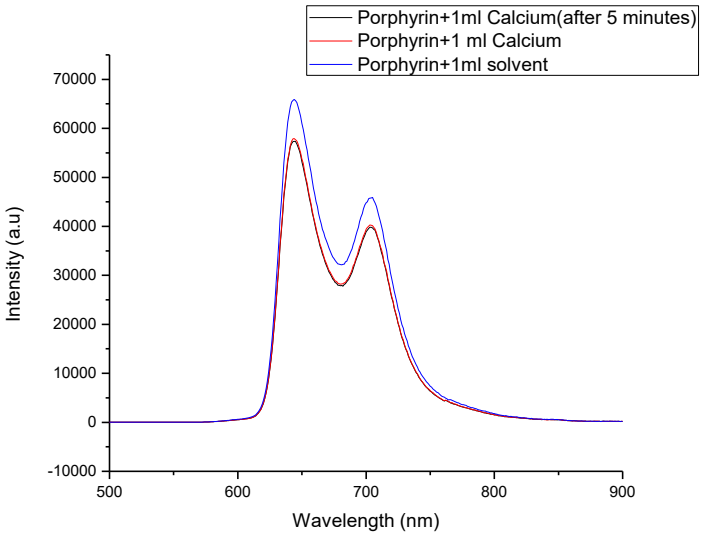


Figure 1b: *Fluorescence emission spectra of $TPPS_4$(aq) and with Ca^{2+} ion at 25℃ taken at time intervals of < 1 min and at 5 min.*

Metal ions from *s* and *p*-blocks form metal complexes less readily compared to their *d*-block counterpart [13] due to the absence of low-lying empty orbital of suitable symmetry that can effectively interact with the ligand orbital. Beyene et al. (2020) similarly reported that when Ca^{2+} ion was added to $TPPS_4$ insignificant changes occurred in their fluorescent emission and electronic absorption spectra. This confirms the unsuitability of the organic molecule for detecting the alkaline earth metal ion.

3.2.2. *Detection of Zn^{2+}; electronic absorption and fluorescent emission*

In the presence of Zn (II) ions the UV-Vis peaks clearly underwent red shift of Soret band to 421 nm with slightly reduced absorbance while the four Q bands reduced to two at 558 nm and 598 nm (Figure 2a). The same number of peaks in the Q band on coordination with the metal had been observed for ZnTPP when the Soret band shifted to longer wavelength [32]. The electronic spectrum was taken after the 25 minutes of reaction. Earlier workers [17] reported three absorption maxima in the Q band (517, 558, and 598 nm) possibly because the measurement was taken while reaction was yet to complete suggesting that the number and position of the bands are time dependent. The change in the UV-Vis bands of $TPPS_4$ particularly those at 421 nm and 598 nm (peak at 558 nm is also observed in the presence of Cd(II) ions) could therefore be unambiguously used to sense Zn^{2+} ions after allowing for some minutes of reaction.

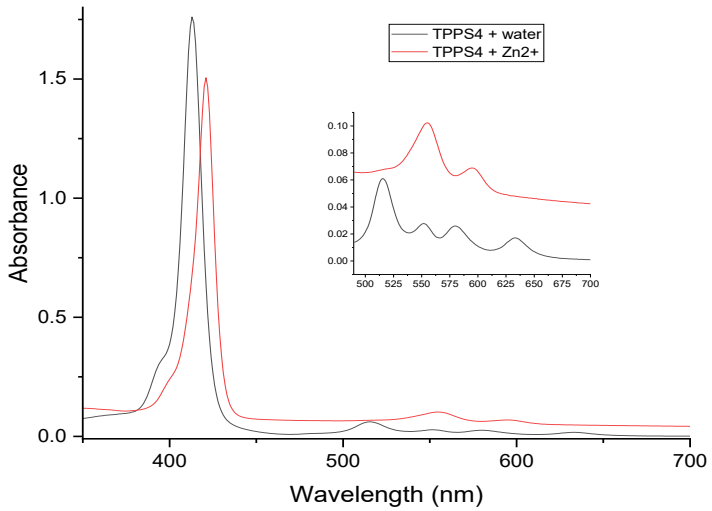


Figure 2a: *UV-Visible spectra of $TPPS_4$ in aqueous solution and the porphyrin with Zn^{2+} ion at 25℃ after 25 min of interaction.* ***Inset:*** *Q band (enlarged) in the spectra of aqueous $TPPS_4$ and the porphyrin with Zn^{2+} ion*

Emission spectra (Figure 2b) that were taken immediately after mixing the solutions suggested an ongoing complex formation between porphyrin and zinc (II) ions. This is because of gradual and time-dependent reduction in intensity of the original two peaks (at 639 and 703 nm) which progressively collapsed into new one at 655 nm after 25 min. Fluorescence decay observed was attributed to ligand-centered excited state quenching pathways by the ions in complexes or inhibition of photoinduced electron transfer (PET) [33,34]. Another new peak gradually emerged at 605 nm at the same time. The peak at 655 nm possibly indicates the presence of zinc (II) ion when the soluble porphyrin interacted. Enhancement of emission intensity was not observed in the presence of 50 equivalent Zn (II) ions as against what was reported earlier [17] that used up to 10 equivalent Zn (II) ions. It could be that a maximum ratio for fluorescence enhancement lies somewhere between 10 and 50 equivalents of the metal ion. It could be concluded that even when up to 20 equivalent

aqueous solutions of Ca^{2+}, Na^{+}, Ag^{+}, Mn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, and Co^{2+} metal ions were added to $TPPS_4$ insignificant changes occurred in their fluorescent emission and electronic absorption spectra.

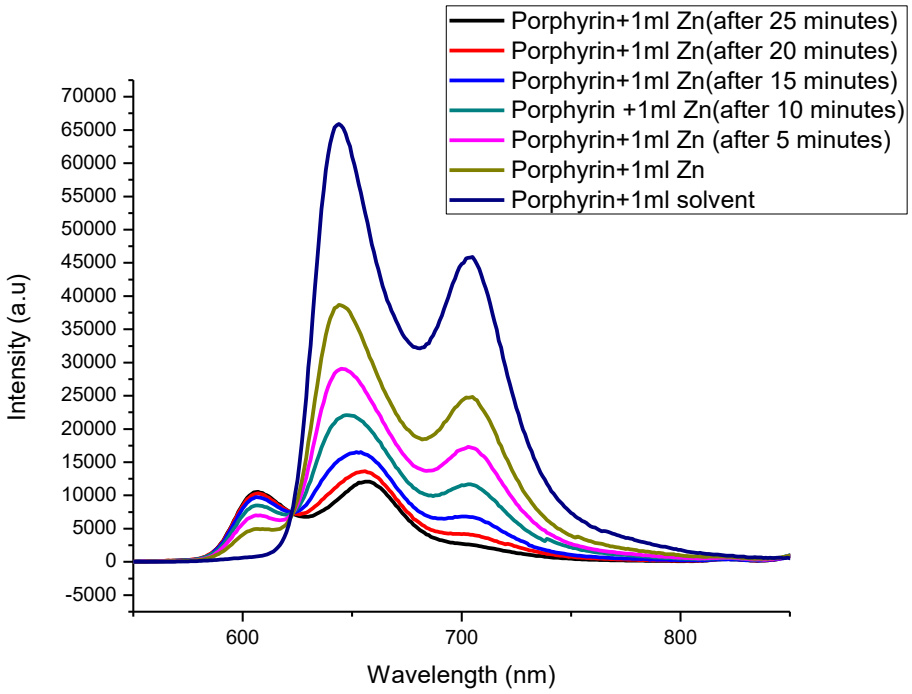


Figure 2b: *Fluorescence emission spectra of $TPPS_4$(aq) and the porphyrin with Zn^{2+} ion at 25℃ (< 1 min, at 5 min, 10 min, 15 min, 20 min and, at 25 min)*

3.2.3. *Detection of Pb^{2+}: electronic absorption and fluorescent emission*

Addition of Pb (II) ions significantly decreased the intensity of B band with a slight red shift (from 413 to 419 nm) and a very weak peak appearing at 466 nm while Q bands reduced to a broad peak around 548 and a weak one around 598 nm (Figure 3a). This dramatic difference in the electronic absorption pattern particularly the Soret band and the Q band at 548 nm could be used to sense the presence of the metal ion by the porphyrin in aqueous medium. However, the porphyrin in lower concentration environment of lead (II) ion was previously reported to give insignificant emission and absorption spectra [17]. This might mean that the detection concentration is above 20 equivalents but may be less than 50 equivalents used in this work.

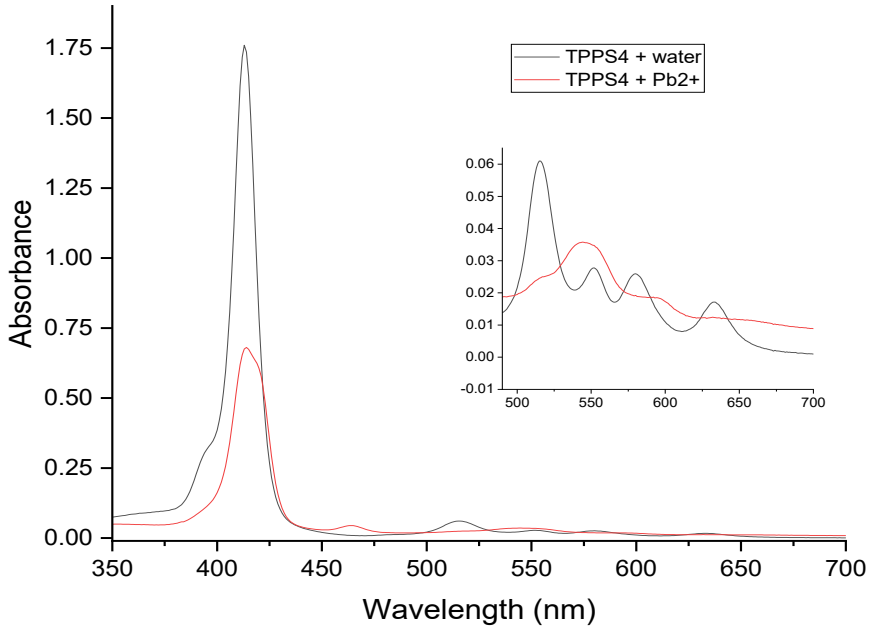


Figure 3a: *UV-Visible spectra of $TPPS_4$ in aqueous solution and the porphyrin with Pb^{2+} ion at 25℃ after 10 min of interaction.* ***Inset:*** *Q band (enlarged) in the spectra of aqueous $TPPS_4$ and the porphyrin with Pb^{2+} ion*

In the emission spectrum (Figure 3b), the position of the two peaks appeared unchanged though their intensities reduced significantly, and a peak of very weak intensity emerged around 605 nm. It is interesting to note that with time the emission spectrum appeared unchanged (time-independent). Absorption spectral changes may be used to sense the lead (II) ions in aqueous media while fluorescence appeared unsuitable.

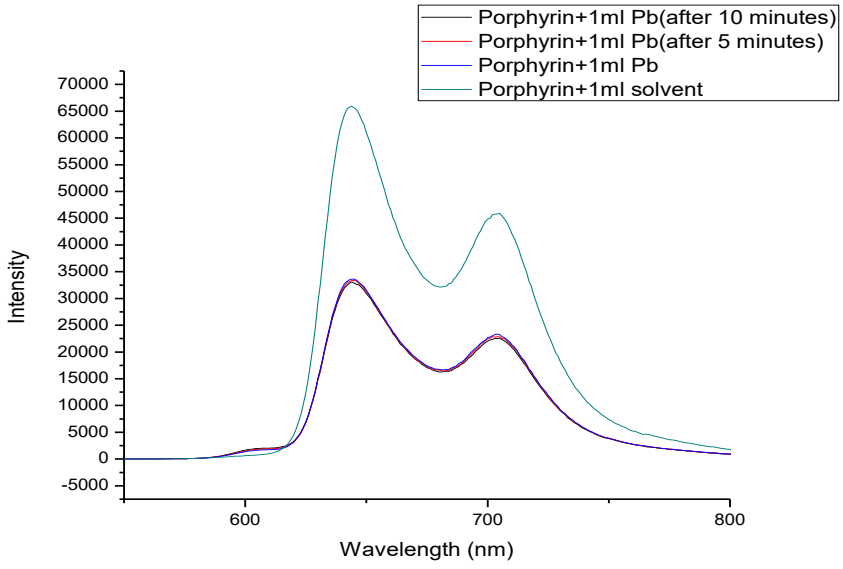


Figure 3b: *Fluorescence emission spectra of $TPPS_4$(aq) and the porphyrin with Pb^{2+} ion at 25℃ (< 1 min, at 5 min and, after 10 min of interaction)*

3.2.4. *Detection of Cd^{2+}; electronic absorption and fluorescent emission*

UV-Vis spectral changes revealed a red shift of Soret band to 435 nm and a shoulder at 426 nm while the four porphyrin Q bands were replaced by three peaks all appearing at longer wavelength in the presence of cadmium (II) ions after 5 min of interaction (Figure 4a). These Soret and Q bands (particularly those at 600 and 646 nm) could be diagnostic in detecting Cd^{2+} ions in aqueous solution. The band at 558 nm is similar to the one observed when Zn(II) ions were present.

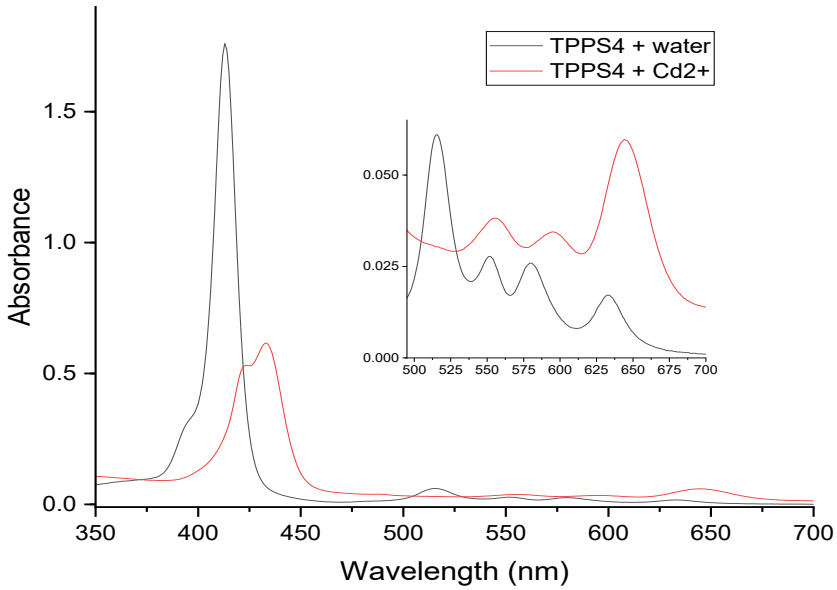


Figure 4a: *UV-Visible spectra of $TPPS_4$ in aqueous solution and the porphyrin with Cd^{2+} ion at 25℃ after 5 min of interaction.* ***Inset:*** *Q band (enlarged) in the spectra of aqueous $TPPS_4$ and the porphyrin with Cd^{2+} ion*

The two photoluminescence (PL) porphyrin peaks (Figure 4b) collapsed into one of reduced intensity at 665 nm while the usual new weak band was also observed at 605 nm. The change is instantaneous and remains the same after 5 min. The emission peak at 665 nm could be useful for detecting the heavy metal ion. The peak at 605 nm may not be useful for sensing cations since it appeared in most of the emission spectra.

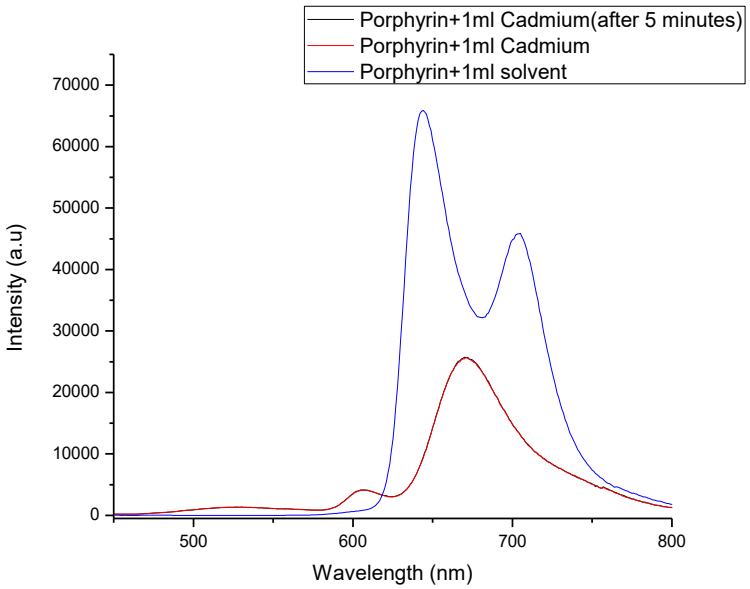


Figure 4b: *Fluorescence emission spectra of $TPPS_4$(aq) and the porphyrin with Cd^{2+} ion at 25℃ (< 1 min and after 5 min of interaction)*

3.2.5. *Detection of Hg^{2+}; electronic absorption and fluorescent emission*

A strong, greenish yellow colour was observed after adding the mercury (II) ion to the organic molecule [22]. The position of the metal ion-free porphyrin Soret band did not shift but showed drastically reduced intensity while the four Q bands were replaced by a peak at 542 nm and another weak, broad band around 600 nm (Figure 5a) accounting for the colorimetric change. In a different chemical environment and pH the Soret band could also experience a red shift [23]. The observed new bands could be useful for sensing the heavy metal ion.

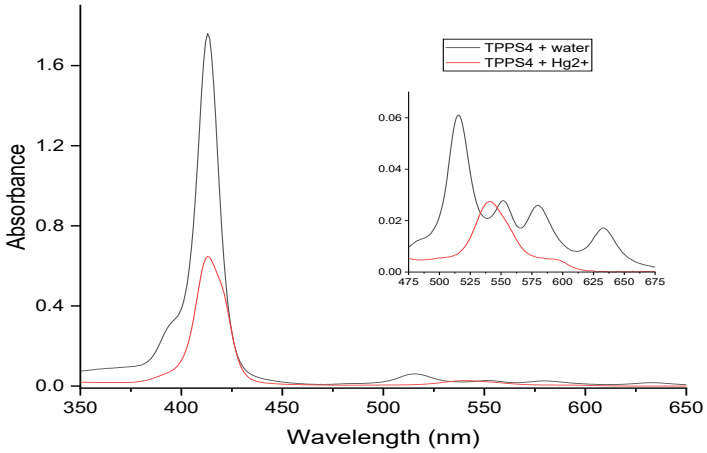


Figure 5a: *UV-Visible spectra of $TPPS_4$ in aqueous solution and the porphyrin with Hg^{2+} ion at 25℃ after 20 min of interaction.* ***Inset:*** *Q band (enlarged) in the spectra of aqueous $TPPS_4$ and the porphyrin with Hg^{2+} ion*

In the emission spectrum (Figure 5b), the two peaks of the metal ion-free porphyrin were replaced by peaks of greatly reduced intensity (but not totally quenched) at 610 and 660 nm (blue shift) in the environment of Hg (II) ions within five minutes of reaction. These changes were unaffected by time during the reaction and the pattern could be instrumental in detecting the mercury (II) ion in aqueous medium. This porphyrin sensing of mercury (II) ion by emission spectroscopy has not been found reported before to the best of our knowledge unlike UV-Vis spectral and colorimetric studies [23]. Tetra(*p*-dimethylaminophenyl)porphyrin (TDMAPP) also displays much decreased fluorescence (quenching) in the presence of Hg(II) ions [10].

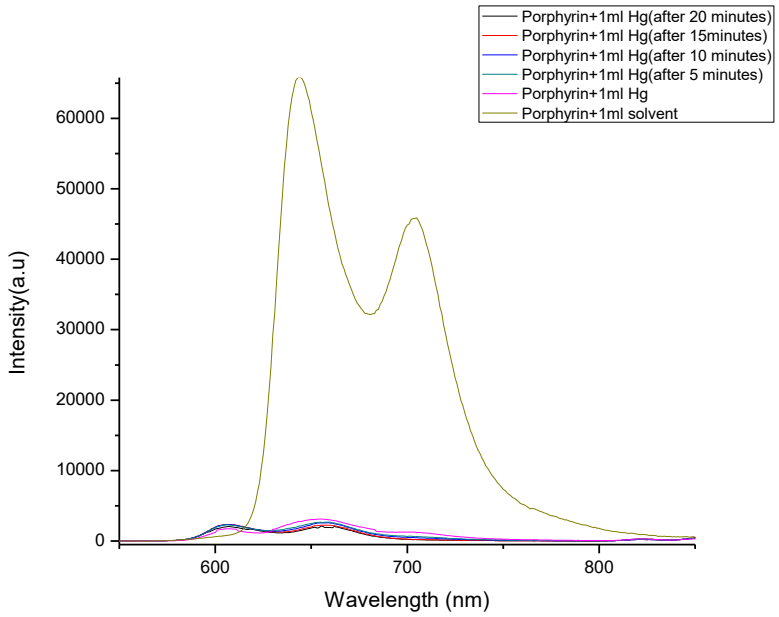


Figure 5b: *Fluorescence emission spectra of $TPPS_4$(aq) and the porphyrin with Hg^{2+} ion at 25℃ (< 1 min, 5 min, 10 min, 15 min and after 20 min of interaction)*

3.2.6. *Detection of Fe^{3+}; electronic absorption and fluorescent emission*

There was a visible colour change to dull yellow when the metal ion interacted with the porphyrin. According to the absorption spectrum shown in Figure 6a, the Soret B band at 413 nm of porphyrin was replaced by two peaks (blue and red shifts) of reduced intensity at 405 nm and 437 nm while only one Q band was observed at 650 nm in the presence of Fe(III) ions. The new Soret B bands (particularly that at 405 nm which is characteristic) and the Q band are peculiar to the iron (III)-porphyrin complex and could lead to recognising the presence of the metal ion in water and aqueous solutions. Li et al. (2012) [21] reported a similar shift in the Soret band from 414 nm to 434 nm and Q bands at 495 and 648 nm with a colour change from pink to golden rod at much higher metal ion concentration.

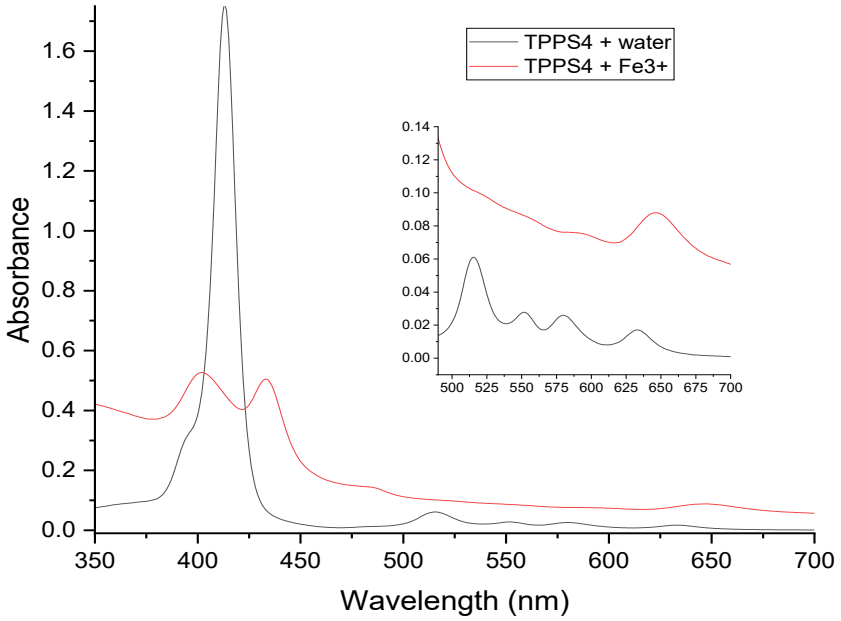


Figure 6a: *UV-Visible spectra of $TPPS_4$ in aqueous solution and the porphyrin with Fe^{3+} ion at 25℃ after 15 min of interaction.* ***Inset:*** *Q band (enlarged) in the spectra of aqueous $TPPS_4$ and the porphyrin with Fe^{3+} ion*

Two porphyrin peaks in the fluorescence emission collapsed into one characteristic peak around 670 nm of greatly reduced intensity (Figure 6b) and an entirely new peak at 825 nm in the presence of Fe (III) ions. These new emission peaks may equally be diagnostic for the presence of the metal ion.

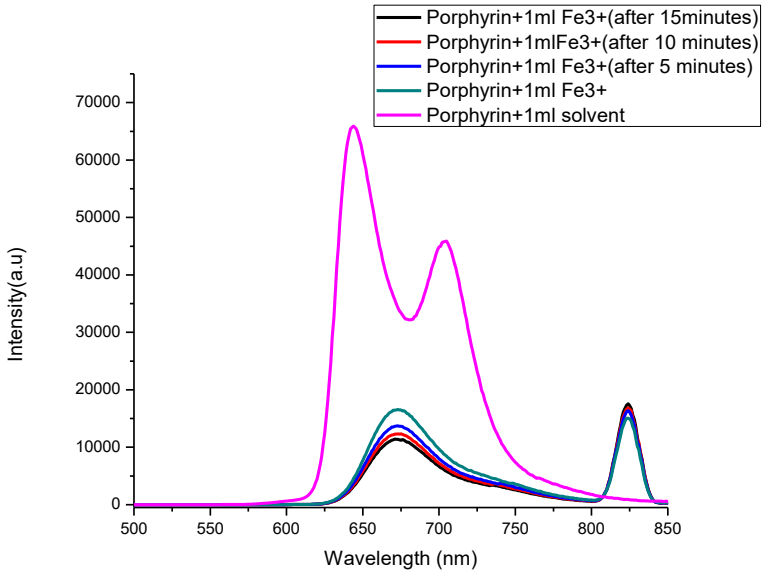


Figure 6b*: Fluorescence emission spectra of $TPPS_4$(aq) and the porphyrin with Fe^{3+} ion at 25℃ (< 1 min, 5 min, 10 min and after 15 min of interaction)*

3.2.7. *Detection of Cu^{2+}; electronic absorption and fluorescent emission*

There was no shift in the peak position, but a reduced intensity observed for the B band of the porphyrin at 413 nm. Meanwhile, the four Q bands in the visible spectrum metal ion-free porphyrin were replaced by a new peak at 542 nm (Figures 7(a)). This band is similar to the result obtained earlier by Bayene et al. (2020) [17] and could be a means of detecting copper (II) ion by the porphyrin in an aqueous medium.

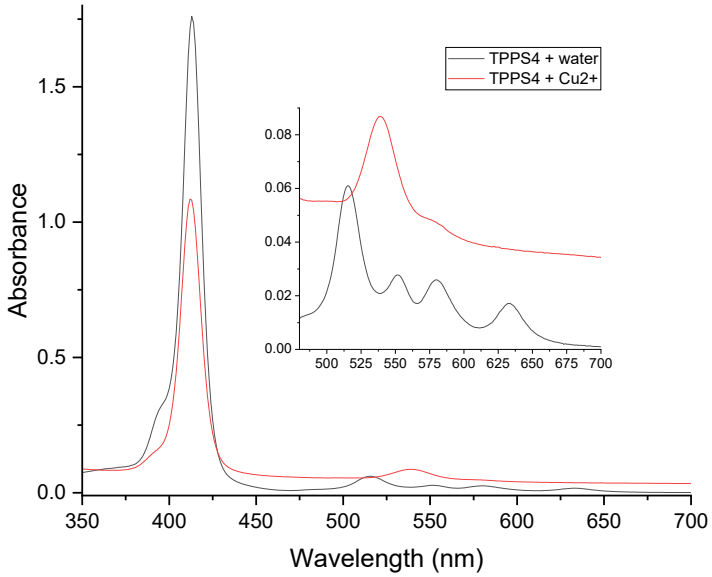


Figure 7a: *UV-Visible spectra of $TPPS_4$ in aqueous solution and the porphyrin with Cu^{2+} ion at 25℃ after 5 min of interaction.* ***Inset:*** *Q band (enlarged) in the spectra of aqueous $TPPS_4$ and the porphyrin with Cu^{2+} ion*

The UV-Vis spectral response of the porphyrin in the presence of copper (II) and mercury (II) ions appeared to be similar with regard to the position of the peaks. The slight difference observed was the enhanced Q band of Cu(II) ions and the reduced band of Hg(II) ions present when compared with the spectrum of the porphyrin as shown in Figures 7b and 7c. This may imply that Cu(II) ions cannot be unambiguously sensed in the presence of Hg(II) ions by $TPPS_4$ using the technique. However, their emission spectra are distinctively different. This again suggests that emission is more powerful but more expensive as a sensing tool than absorption spectroscopy [8].

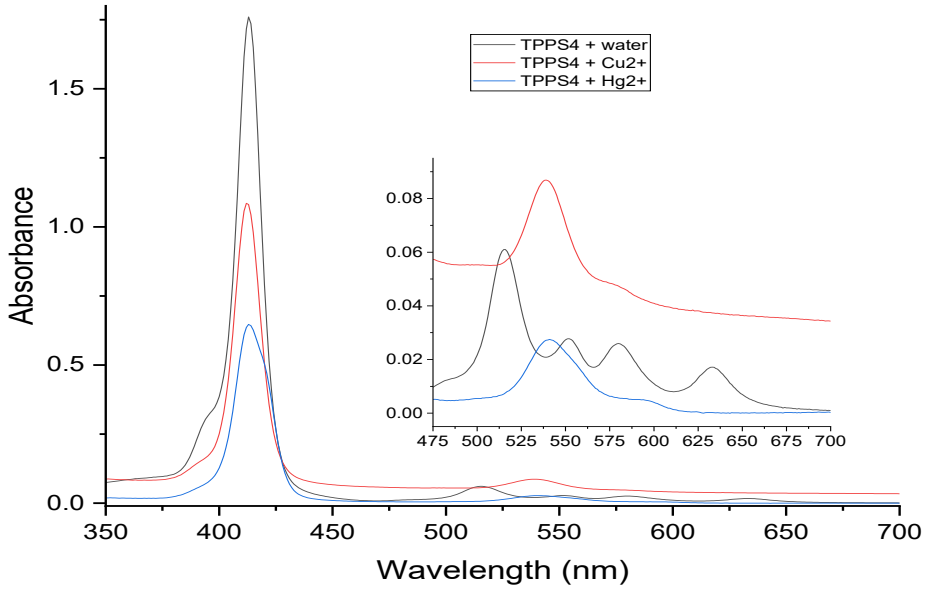


Figure 7b: *UV-Visible spectra of TPPS4(aq), $TPPS_4$ (aq) with Cu^{2+} ions and the porphyrin with Hg^{2+} ions at 25℃.* ***Inset:*** *Q bands of $TPPS_4$ (aq) with Cu^{2+} ions and the porphyrin with Hg^{2+} ions*

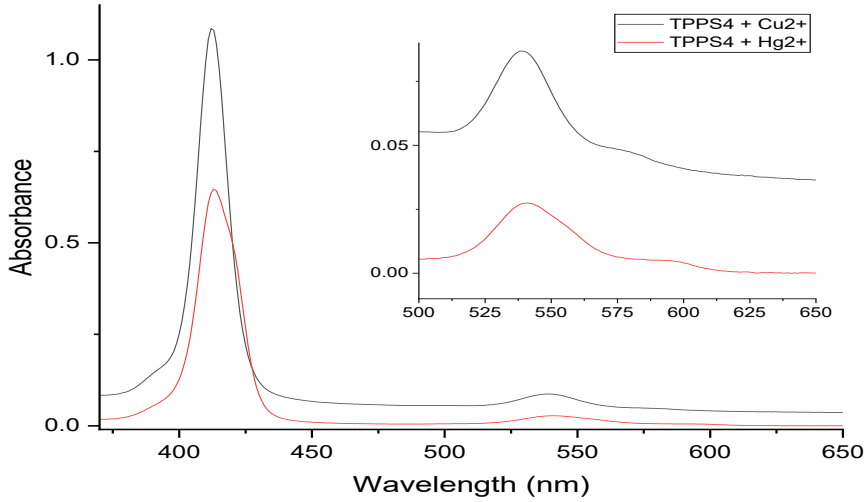


Figure 7c: *UV-Visible spectra of $TPPS_4$ (aq) with Cu^{2+} ions and the porphyrin with Hg^{2+} ions at 25℃*
Inset: *Q bands of $TPPS_4$ (aq) with Cu^{2+} ions and the porphyrin with Hg^{2+} ions*

In the fluorescent emission spectra porphyrin peaks were instantly quenched when Cu (II) ions were added (Figure 7d). This has been described as a "turn off" of fluorescence and has been suggested as a means of sensing the transition metal ion [17,22] at a lower metal ion concentration relative to the porphyrin. Trinitrotoluene (TNT) was also found to produce similar effect on $TPPS_4$ in a 1:1

interaction at pH 7 [24]. Loss of fluorescence on coordination with the metal containing unpaired electrons (paramagnetism) might have affected the double bond electron mobility and conjugation [10].

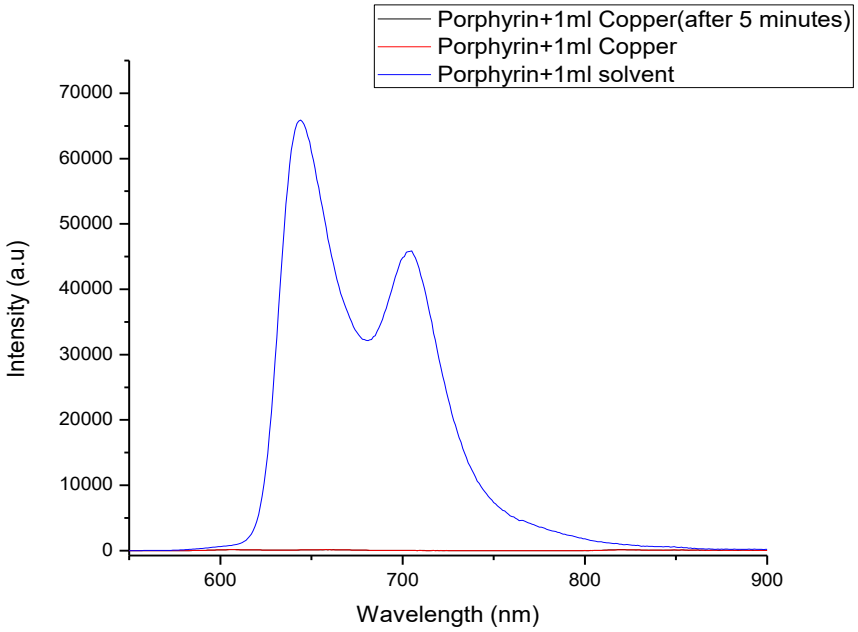


Figure 7d: *Fluorescence emission spectra of $TPPS_4$(aq) and the porphyrin with Cu^{2+} ion at 25℃ (< 1 min and after 5 min of interaction)*

Tables 1 and 2 below summarise absorption and emission spectral responses of the anionic soluble porphyrin to the presence of selected heavy and essential metal ions in aqueous medium.

Table 1*: Visible absorption bands for Hg^{2+}, Cd^{2+}, Pb^{2+}, Fe^{3+}, Cu^{2+}, and Zn^{2+} in aqueous $TPPS_4$*

Compound	**Time of interaction (min)**	**Soret (B) bands (nm)**	**Q bands (nm)**	**Characteristic sensing bands (nm)**
$TPPS_4$	-	413	518, 552, 583, 634	-
Hg^{2+} + $TPPS_4$	20	413	542	similar to Cu^{2+}
Cu^{2+} + $TPPS_4$	5	413	542	similar to Hg^{2+}
Zn^{2+} + $TPPS_4$	25	421	558, 594	421, 594
Cd^{2+} + $TPPS_4$	5	435	558, 600, 646	435, 646
Pb^{2+} + $TPPS_4$	10	419, 466	548, 598	419, 466, 548
Fe^{3+} + $TPPS_4$	15	405, 437	650	405, 437, 650

***Table 2**: Fluorescence emission bands for Hg^{2+}, Cd^{2+}, Pb^{2+}, Fe^{3+}, Cu^{2+}, and Zn^{2+} in aqueous $TPPS_4$ (Excitation wavelength = 413 nm)*

Compound	Shift in spectra position with time	Total time of interaction (min)	Emission bands (nm)	Characteristic sensing bands (nm)
$TPPS_4$	-	-	640, 690	-
Hg^{2+}-$TPPS_4$	Constant	20	610, 660	610, 660
Cu^{2+}-$TPPS_4$	Constant	5	Quenched	Quenching
Zn^{2+}-$TPPS_4$	Time-dependent	25	605, 655	655
Cd^{2+}-$TPPS_4$	Constant	5	605, 665	665
Pb^{2+}-$TPPS_4$	Constant	10	605, 640, 690	-
Fe^{3+}-$TPPS_4$	Almost constant	15	670, 825	670, 825

4. CONCLUSION

The anionic porphyrin was prepared by a convenient and fast method using easily affordable reagents. $TPPS_4$ solution was capable of sensing the presence of six out of the seven cations investigated based on the changes in spectral position, new peak formation or fast fluorescence quenching at 25℃. Absorption spectra revealed that aqueous solution of porphyrin could be used to unambiguously detect Cd^{2+}, Pb^{2+}, Fe^{3+}, and Zn^{2+} ions as observed from either or both of their characteristic Soret and Q bands at 25°C. Electronic absorption was unable to distinguish between the presence of Hg^{2+} and Cu^{2+} while that of Ca^{2+} ions was not detected. In the emission spectra, Hg^{2+}, Cd^{2+} and Fe^{3+} ions were distinctly sensed for the first time. The presence of Pb^{2+} ions only resulted in reduced fluorescence intensity whereas absorption spectroscopy gave characteristic detection peaks. Only in the presence of zinc (II) ions was the position of emission peaks varied with time. It can be concluded that both techniques were efficient in detecting Zn^{2+}, Cd^{2+} and Fe^{3+} ions. Spectral behaviour in the presence of two or more of these cations will be interesting and give more information on the capacity of this anionic porphyrin for sensing the metal ions.

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Conflict of Interest Declaration
The author(s) declare none

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