SYNTHESIS, CHARACTERIZATION AND APPLICATION OF A FERROCENYL AZO-BASED LIGAND AS AG+- DETECTOR IN AN AQUEOUS SYSTEM

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ABSTRACT

Over the years, humans and the environment have been exposed to various toxic ionic species that emanated, majorly, from anthropogenic sources. In this study, a new ferrocenyl-azo based chemosensor, ferrocenyl 1-(2-phenylazo)-2-naphtholate (FPN) for the determination of silver ions was developed via catalytic reduction and diazotization routes. The structural features were confirmed by spectroscopic methods involving proton NMR, GC/MS and FTIR. Having exposed the product to different metal solutions, Ag^+ was distinctively recognized, revealing FPN as an effective and sensitive chemosensor. The binding behavior of FPN towards the sensitive silver ion was investigated using Job's plot, and a metal:ligand ratio of 1:1 was revealed. The study showed a bathochromic shift and a new peak band was observed at 275 nm in the absorption spectra of FPN. The absorption experiments demonstrate that FPN as a rapid and reliable sensor capable of determining silver and ferric ions. Therefore, ferrocenyl 1-(2-phenylazo)-2-naphtholate ligand is highly recommended as an alternative route in detecting silver ions in both organic and aqueous media.

Keywords: ferrocene, chemosensor, absorption, silver ion, aqueous

INTRODUCTION

Anthropogenic activities in industries, mining sites, refineries, refuse dumping and burning sites as well as farming, release innumerable contaminants into the atmosphere, ground and aquatic environment, threatening both biotic and abiotic ecosystems (Huang *et al.,* 2016). Most contaminants are not biodegradable, reaching water sources, and causing ecological and human health threats (Dada and Kutu, 2022). Human and environmental contaminants are composed of all forms of ionic species, which have agglomerated into cationic and anionic contaminants, some of which are highly essential such as; Ca^{2+}, K^+, Ag^+, Na^+, Co^{2+}, Fe^{2+}, Fe^{3+} and Mg^{2+} but harmful at excessive exposure or ingestion to humans. However, some ions are very toxic, even at low concentrations, like Pb^{2+}, Hg^{2+}, Cd^{2+} if ingested beyond permissible limits (Ullah *et al.,* 2022). Untamed exposure to these ions, especially Ag^+, could lead to debilitating diseases such as agyria on the skin, due to long use of Ag protein (Pradipta and Irunsah, 2022), agyrosis in the eye and colour change in nails (Krassnig *et. al.,* 2021; Thangam and Kowsalya, 2020). Generally, unguided exposure of silver to human bodies has proven to be cosmetically undesirable (David and Moldovan, 2020).

It has been discovered that these billions of pollutants introduced into the ecosystem can be determined and controlled (Aguilar and Borrell, 2020; Othmani *et al.,* 2022; Wang *et al.,* 2020). Moreover, in this study, silver was detected in aqueous solution by the synthesized ligand. The permissible limit of Ag^+ in drinking water and industrial discharge waste water is 0.1 mg/L and 2 mg/L respectively (WHO, 2021).

Instrumentations had been used to monitor these toxic cations but had proven to be very expensive and tedious to use, requiring skilled operators. Over the years, several studies have been established by researchers in developing and improving receptors for cations (Devaraj *et al.,* 2011), in which this field of study has witnessed an upsurge in recent years (Kaur *et al.,* 2015). The development of receptors has brought a huge interest, in recent times, for the detection and recognition of highly harmful cations, mainly due to their pernicious effects on man and other living organisms (Adewuyi *et. al.,* 2016; Malik *et al*., 2019; Ngororabanga *et al.,* 2019). Ionic species, in the form of cations and anions, make up most of the human and environmental contaminants. Due to the negative effect of cation usage on the environment and nature, much effort had been made by researchers in the provision of selective and sensitive compounds to sense these toxic ions (Alfonso *et al.,* 2010). Moreover, in this study, ferrocene was used as a pre-cursor due to its potent stability (Webb *et al.,* 2022), non-toxicity and effective tool in sensing (Kaur *et al.,* 2015, Palomera *et al.,* 2011), which had been applied in pharmaceutical industries and nanomedicine (Ornelas, 2011), as established by several researchers.

To curtail these contaminants, chemosensors have been widely used due to their ability to easily detect analytes in solutions and environment. Chemical species which undergo a reversible change, binding to an analyte, such that the signal is measured are referred to as "chemosensors". The research strategy used in this study deals with the signaling unit binding with the receptor, such that the analyte is sensed with the aid of the chromophore, to obtain a sensor-analyte complex. A chemosensor usually consists a receptor and a photoactive unit (Kaur *et al*., 2015). Organic heterocyclic molecules giving visible responses in the presence of an analyte are referred to as chemosensors (Huang *et al*., 2019); which could be obtained from small organic molecules various functionalized to detect chemical species through non-covalent interactions (Nolan and Lippard, 2008).

It had been established that techniques like inductively coupled plasma mass spectroscopy (ICP-MS), atomic absorption spectroscopy (AAS), liquid chromatography (LC) anodic stripping voltammetry, potentiometric, titrimetric, electrochemical can be used in achieving quantitative analyses of several ionic species (Badakhshan et al., 2019; Huang *et al*., 2019; Mansor *et. al,* 2021, Park *et. al.,* 2020), however, they require extensive sample preparation, complex instrumentations, and skilled operators making the process very expensive and time-consuming. Hence, there is a dire

need for approaches that can effectively detect and quantify heavy metal ions and anions, especially, highly toxic species to monitor biological, industrial and environmental, biological and industrial samples with minimum simplicity and cost, for maximum reliability. Recently, attention has been given to techniques based on optical properties changes having contacted the target analytes (Qazi, 2012), had been developed to provide better routes to analyte detection because of being technically simple, cheap, sensitive with fast detection and (Kang *et al,* 2010, HeeáLee and SeungáKim, 2015).

In order to combat these challenges of toxicity exposure and environmental pollution, this study aimed at the use of multichannel signaling receptors via multiple signaling patterns for selective detection and adsorption of some of these toxic ions in both aqueous and organic media. Therefore, there is a huge necessity for the use of simple, reversible and highly sensitive optical chemosensors. Hence, the need for this study for the synthesis of simple, specific, sensitive and cheap silver detectors, applied in both aqueous and organic media.

MATERIALS AND METHODS

Ferrocenyl 1-(2-phenylazo)-2-naphtholate (FPN) was synthesized and the product was characterized using both analytical and spectroscopic techniques, such as Ultraviolet visible spectroscopy (UV-Vis), Fourier transform infrared (FTIR), Nuclear magnetic resonance spectroscopy and Gas-chromatography mass spectroscopy (GC-MS). The chemosensing abilities of ferrocenyl 1-(2-phenylazo)-2-naphtholate towards some transition metal ions were investigated and it was discovered that silver ions were selectively sensitive.

All starting materials used were obtained from commercial sources (Sigma-Aldrich) at their analytical grades and were used without further purification. Solvents were dried by storing them over $4A^o$ molecular sieves. The FTIR spectra were recorded using a ThermoScientific Nicolet 6700 Spectrometer in the frequency range of 4000-400 cm^{-1} in ATR mode. ^{1}H NMR spectra were recorded on a Bruker Avance III, 300MHz NMR Spectrometer for liquid state samples manufactured by BRUKER BioSpin GMBH, Rheinstetten, Germany. The studies were performed in appropriate solvents ($CDCl_3$ and DMSO-d_6) using tetramethylsilane (δ 0.00) as the internal reference. GC-MS studies were achieved using a model of 7890A GC systems of 5975C VL MSD, manufactured by Agilent Technologies, Santa Clara, California, United States of America. This instrumentation is made with a triple axis detector in the presence of helium gas. The capillary column has a thickness of 30 m x 0.25 mm x 0.25 µm with CN10481136 serial number. The particle size of the silica gel used, as the stationary phase, is in the range of 0.040 mm to 0.063 mm while an appropriate combination of organic solvents was used as the mobile phase. The eluent was constantly monitored via thin-layer chromatography (TLC). All these were carried out using 60 F254 a pre-coated silica gel and 0.063-0.2 mm / 70-230 mesh aluminum sheets under Ultra-violet lamp. The same sample constituents were added together and concentrated in the fume cupboard, after which were further analyzed.

Spectrophotometric studies were performed using Ultra-violet visible and flame emission instrumentations for absorption. Studies involving solvent screening, the determination of organic-aqueous media ratio, complexation, competition of analyte with other metal ions, ligand-metal complexation, titration, pH, reversibility and time dependence were carried out.

The UV-Vis absorption spectra measurement of the photophysical studies were carried out at room temperature, and recorded on a Shimadzu MPC-3100 (12520) spectrophotometer, made in Kyoto, Japan. Spectra recordings were observed between 200 and 800 nm. Quartz cuvettes were used while the experiments were carried out with a 3 mL sample solution using Millipore water and a suitable organic stock solution of the ligand to give a concentration of 1×10^{-4} M for the synthesized ligands and metal ions respectively. To determine the limit of quantification and detection, a concentration of 1×10^{-5} M was used for the ligands and metal ions solutions respectively. All spectra were recorded after each addition of an aliquot of various metal ion solutions.

Synthesis of *para*-nitrophenylferrocene

Under phase transfer conditions, a modified synthesis of *para*-nitrophenylferrocene was performed via ferrocene arylation, using a diazonium salt solution of sodium nitrite in *para*-nitroaniline, under ice (Hu *et al.,* 2001). The cold diazonium salt was added dropwisely into a pre-cleaned volumetric flask of a solution of ferrocene in hexadecyltrimethylammonium bromide with continuous stirring at 0-5°C after which the temperature was increased to 25°C. 4-nitrophenylferrocene was obtained as violet plates after concentration and steam distillation was done to obtain a pure product. The melting point was obtained at 59°C with a yield of 82.9 %.

Ferrocenyl aniline was synthesized by the reduction of *para*-nitrophenylferrocene with palladium on charcoal (Pd/C) in dichloromethane and ethanol. The reaction was completed under hydrogen, and monitored on a Thin Layer Chromatography plate. On completion, after rotary evaporation, an orange-yellow crude solid was obtained. With the aid of the column chromatography for the purification of the crude product, eluent of ethylacetate:hexane (20:80) from silica gel-packed column, afforded golden yellow crystals in 75% yield. The melting point of the product was in the range of 157-159 ºC.
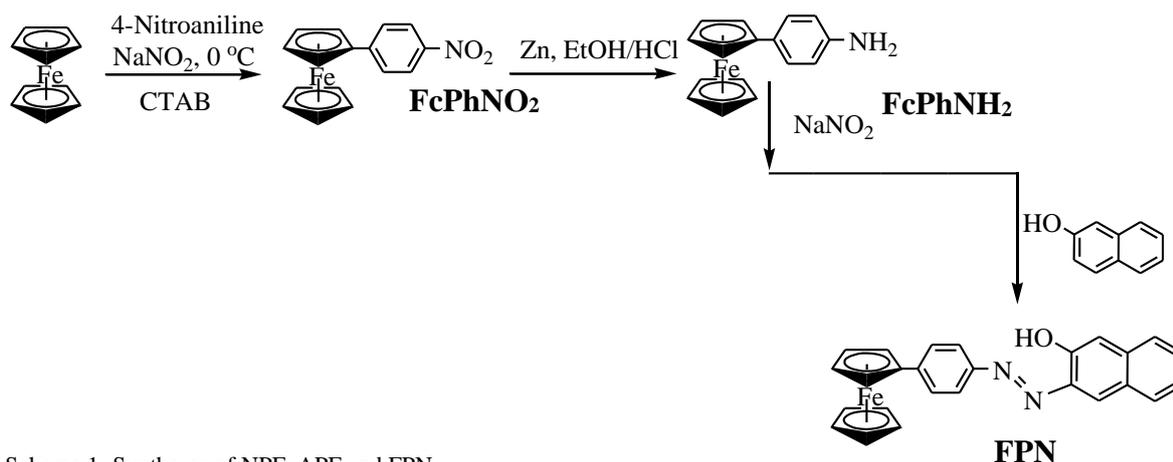
Scheme 1: Syntheses of NPF, APF and FPN

RESULT AND DISCUSSION

Figure 1 showed the FTIR (cm^{-1}) spectrum of FcPhNO$_2$ as: υ (N-O stretch) 1335.72, υ (N-O stretch) 1504.15, υ (aromatic C-H stretch) 3081.15, 3083.01, while the FTIR (cm^{-1}) bands of FcPhNH$_2$ as: υ (N-H stretches, primary amine) 3469.47, 3371.30, υ (aromatic C-H stretch) 3110.62, υ (N-H bend, primary amine) 1614.66, υ (C-N stretch) 1183.72, π (Fc C=C,

C-H stretches) 1526.79, 1455.20, 1013.42, (N-H wag) 813.43. The FTIR bands of FPN depicted the expected product with the broad –OH band observed at 3400 cm^{-1}. The UV/visible spectrum of FPN showed transitions at the absorption maxima; $n \rightarrow \pi^*$ (245 nm, 282 nm); such that the n-electron, π electron and π^* antibonding were obtained from nitrogen lone pair, π of C=O and N=N respectively (Figure 2).
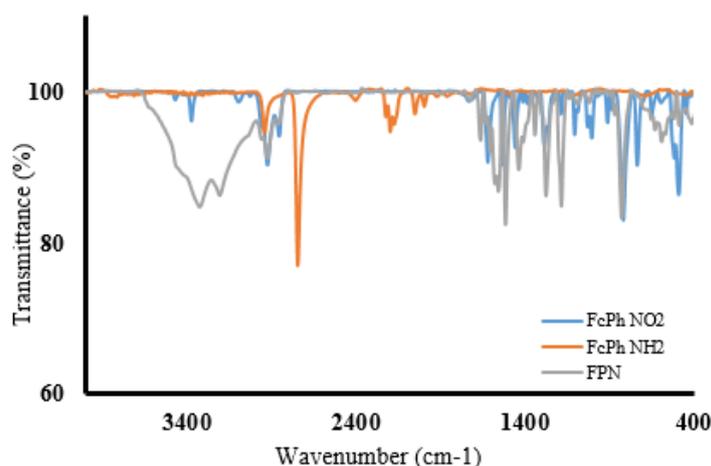
Figure 1: FT-IR Spectra of FcPhNO$_2$, FcPhNH$_2$ & FPN
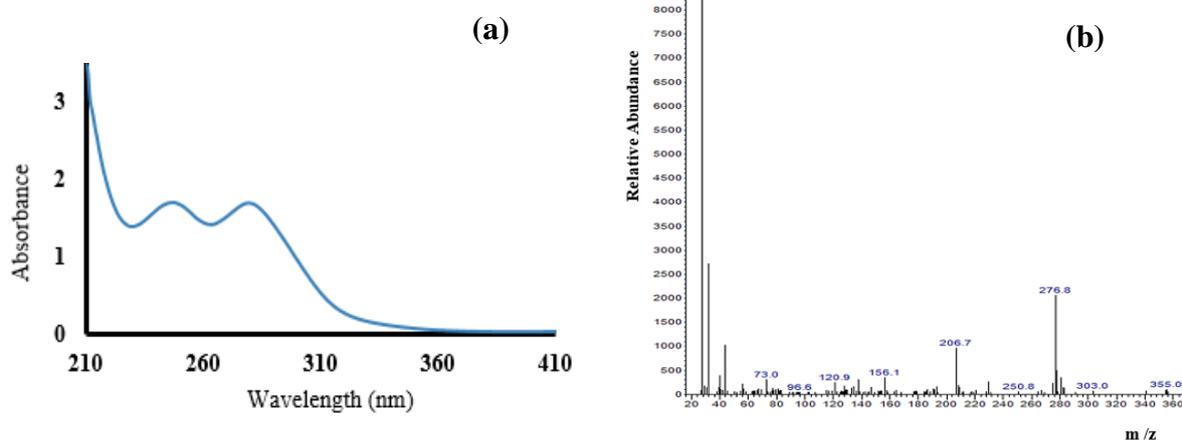
Figure 2: (a) UV/ Visible and (b) GC Mass Spectra of FPN
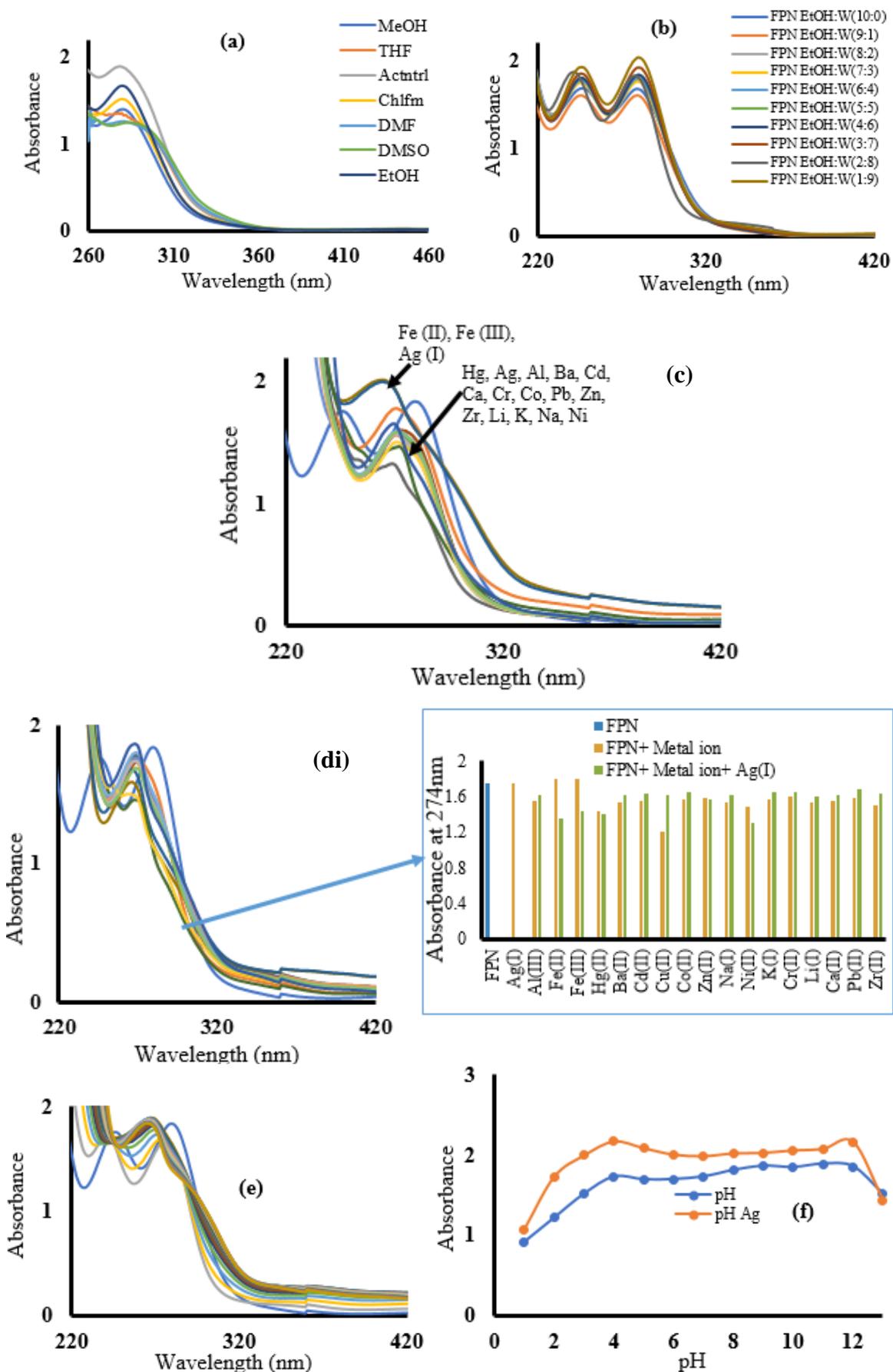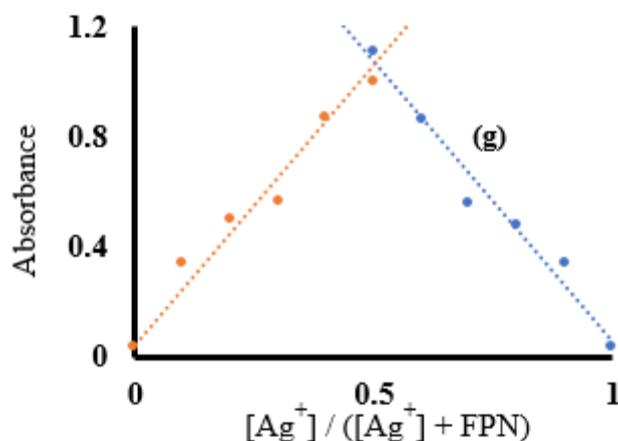
Figure 3: Absorbance responses showing the (a). Solvent Screening for FPN (b). Water-Ethanol Screening for FPN (c). Complexation of FPN with metals (di). Competition of Ag^+ with other metals in FPN (dii) Bar chart of FPN in the presence of Ag^+ with an equimolar amount of other metal ions (e). Titration of Ag (I) ion in FPN (f).pH studies of FPN with Ag^+ (g). Job's Plot of FPN in the presence of Ag^+

In order to discover the most suitable solvent for the absorption studies, solvent screening was done using different organic solvents: Tetrahydrofuran (THF), methanol (MeOH), ethanol (EtOH), dimethylsulphoxide (DMSO), dimethylformamide (DMF), acetonitrile (Actntrl) and chloroform (Chlfm) were used in this experiment. 15 mg of FPN was quantitatively weighed into a 50 mL volumetric flask and made up to mark with each of the solvents used. The order of solubility is as follows: DMSO, DMF, THF > acetonitrile, chloroform > ethanol, methanol. Complete solubility of QND was ensured in all prepared solutions (Fig. 3a). Maximum absorption band at 285 nm was displayed with increasing order of DMF=DMSO < THF< MeOH< Chlfm< EtOH) < Actntrl. Ethanol was chosen as the suitable solvent system due to its eco-friendliness as compared with acetonitrile. Using a different ratio of organic and aqueous media, the least volume of ethanol:water was used for this study due to effective absorbing region like other ratios (Fig. 3b).

It is evident from the absorption studies (Fig. 3c), that amongst all metal ions that were complexed with the ligand, FPN, three cations distinctively displayed spectral changes. Significant shifts were observed with Ag^+, Fe^{2+} and Fe^{3+}. As presented in Figure 3d, the selectivity of FPN for Ag^+ competition experiments involving Ag^+ mixed with a molar equivalent of other competing metal ions was performed, in absorption studies. There was no considerable effect in absorbance responses of FPN-Ag^+ solution in the presence of other metal ions. This experiment signifies that FPN and Ag^+ interactions result in a stable complex, which cannot be affected by the presence of other competing metal ions. The inset of Fig. 3d shows the bar chart showing the responses of FPN (0.1 mM) upon addition of various metal ions (0.1 mM) (orange bars) and in the presence of Ag^+ (0.1 mM) with an equimolar amount of other metal ions (0.1 mM) (grey bars) in ethanol:water (50:50) at 274 nm. To further investigate the chemosensing properties of FPN towards Ag^+ in solution, titration was performed using 1-15 equivalents of the metal ion (Fig. 3e). This suggested the limit of detection and quantification of the probe in metal ions. With a gradual addition of Ag^+ aliquots to the ethanolic solution of FPN, a hyperchromic shift was observed. The saturation level was achieved after the addition of 15 equivalents. The limit of detection (LOD) and quantification (LOQ) of Ag^+ in FPN was found to be 27.5 µM and 459.7 µM respectively. The LOD is within range with some reported values such as 0.5 µM

(Arumugam and Kim, 2018) and 9 ppb (Liu *et al.,* 2021), 59 nM (Tang *et al*., 2022), 1.125 µM (Chen *et al.,* 2021). However, the permissible limit of silver ions in drinking water and effluents are 100 µg/L and 0.05 mg/L (WHO, 2021), and the ligand can still be used for the determination of silver ions in wastewater bodies.

The effect of pH on the absorption response of FPN in the presence of Ag^+ in a series of pH values was revealed as shown in Figure 3f. A series of solutions (using Millipore water) with pH values ranging from 1 to 13 was prepared using sodium hydroxide solution and hydrochloric acid solutions. Having obtained the desired pH, the aliquot was added to an equal amount of ethanol in 0.01 mmol FPN, the absorbance was taken. Good stability with a little and gradual hyperchromic shift was observed from the acidic region through the basic region between pH 4 and 12, with absorption maxima at those acidic and alkalinity points.

In order to determine the stochiometry ratio of the metal ion to the ligand, FPN, Job's plot of the continuous variation method was used for this study. A plot of absorbance at 274 nm versus the molar fraction at a constant concentration of 1 x 10^{-5} M was constructed (Fig. 3g). In ethanol/water (50:50) solution, equimolar concentrations of both FPN and Ag^+ solutions (1 x 10^{-5} M) were initially prepared, such that a constant volume of 3 mL was maintained for 11 measurements (solutions) and each measurement was prepared and recorded in duplicate. Remarkably, the ratio of ligand to metal; FPN: Ag^+ complex was established as 1:1 from the Job's plot. This ratio of ligand: Ag^+ complex is in agreement with the outcomes of some researchers (Sen *et al*., 2021; Zhao *et al.*, 2022).

CONCLUSION

An azo-based ferrocenyl chemosensor had been successfully synthesized and characterized. The proposed chemosensor showed sensitivity towards Ag^+ in aqueous medium over other competing cations in optical sensing. The results obtained from Job's continuous method of variation displayed a possible stoichiometry ratio of the ligand and Ag^+ of 1:1. A fast, sensitive and reliable response time was observed for FPN, thereby suggesting a useful chemosensor in real-time analysis, which can be employed in both aqueous and organic media.

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