

SYNTHESIS AND CHARACTERIZATION OF POTENTIAL ANTIOXIDANT AGENT OF NOVEL PYRIDYLAZO LIGAND AND ITS PALLADIUM COMPLEX

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ABSTRACT. A new azo dye ligand namely ((E)-1-(4-hydroxy-3-(pyridin-3-yl diazenyl)phenyl)ethan-1-one) (HPPE) was synthesized by the coupling reaction of diazoinium salt of 3-aminopyridine and 4-hydroxyacetophenone. The palladium complex was prepared by reacting palladium chloride with the HPPE ligand. These compounds were characterized by different techniques such as mass, ¹H-NMR, infrared, UV-Vis spectroscopies. The infrared data reveal that azo ligand reacting as bidentate via oxygen and nitrogen atom of azo group and it reveals the important functions as carbonyl group, methyl group, and azo group in the ligand and the complex such. The palladium complex is square planer. The ligand showed a visible colorimetric pH sensitive chemosensor, fast response time and is fully reversible and exhibited a large wavelength shift more than 170 nm accompanied by excellent sensitivity of pH in the range of 3-9. The HPPE ligand and palladium complex showed potential antioxidant activity especially the ligand showed activity so close to the ascorbic acid.

KEY WORDS: Antioxidant, Palladium complex, Pyridyl, Azo dye, Acidity

INTRODUCTION

Azo dyes, azo-Schiff base ligand and their complexes showed important antioxidant activity that was more potent than that of the standard antioxidant BHT (Butylated hydroxytoluene) which was determined via DPPH (2,2-Diphenyl-1-picrylhydrazyl) free radical scavenging assay and nitric oxide radical scavenging assay [1-3].

Azo compounds are considered one of the most important chemical compounds with a wide range of uses such as dyeing textile fibres, organic synthesis, liquid crystalline displays, and electro-optical devices. Azo compounds exhibit potential biological activity including antibacterial activity, pesticidal activities, antiseptic and antiprotozoal properties [1].

Recently, the spectroscopic characteristics such as color sensor, pH sensor [4, 5] and metastable states [6-8] of the azo dyes and their complexes received great interest. The existence of a pyridine nucleus in the azo dye ligand performs a decisive role in the chemistry of azo dye systems, and these properties are present originate in a number of physiologically active compounds [9]. Therefore we are focused on the synthesis azo dye of 3-aminopyridine and its palladium complex and their identification confirmations which were carried out by using numerous analytical and spectroscopic methods. Additionally, antioxidant studies were investigated for the synthesized compounds.

EXPERIMENTAL

Materials

The used materials were supplied commercially and used without further purification, 3-aminopyridine (Sigma Aldrich), hydrochloric acid, sodium hydroxide and palladium chloride(II) were supplied from Merck. Solvents were purchased from Scharlau Company.

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Instrumentations

The infrared and the electronic spectra were measured using Fourier transform infrared spectrophotometer (FT-IR-8400S) (4000-400 cm^{-1}) from Shimadzu and spectrophotometer CECIT CE 7200, 7000 series) from Aquaris respectively. The $^1\text{H-NMR}$ spectra were done by Bruker spectrometer instrument operating at (400 MHz) and the conductivity was measured using WTW SERIES, cond 722. The melting points were measured by SMP30 Stuart apparatus.

Synthesis of HPPE ligand

An ethanolic solution of 3-aminopyridine (5 mmol, 0.47 g) was mixed with 3 mL of concentrated hydrochloric acid. The acidic solution was put under cooling. Sodium nitrite (5 mmol, 0.35 g) was dissolved in distillate water (5 mL) and it was added to acidic solution of 3-aminopyridine to form diazonium salt. The 4-hydroxyacetophenone (5 mmol, 0.68 g) was dissolved in 25 mL of ethanol and it was mixed with 10 mL of (10% sodium hydroxide). The cold solution of diazonium solution was added to cold basic solution of 4-hydroxyacetophenone. The mixture was cooled for one hour. The brown solid was filtered off, washed with distillate water and dried at room temperature with 80% yield, m.p. 86 $^{\circ}\text{C}$. Chemical shifts (ppm) of H-NMR for the HPPE ligand are OH 9.23 (H, s), 8.73 (H, s), 8.36 (H, d, $J = 8.31$), 8.23 (H,s), 8.05 (H, dd, $J = 8.65, 2.26$), 7.63 (H, dd, $J = 8.23, 4.68$), 7.19 (H, d, $J = 8.68$), 6.84 (H.d, $J = 8.68$), 2.6 (CH_3 , s). FT-IR (cm^{-1}): 3368 (OH), 3064 (CH aromatic), 2940 (CH aliphatic), 1666 (C=O), 1596 (C=N), 1500 (C=C), 1491 (-N=N-).

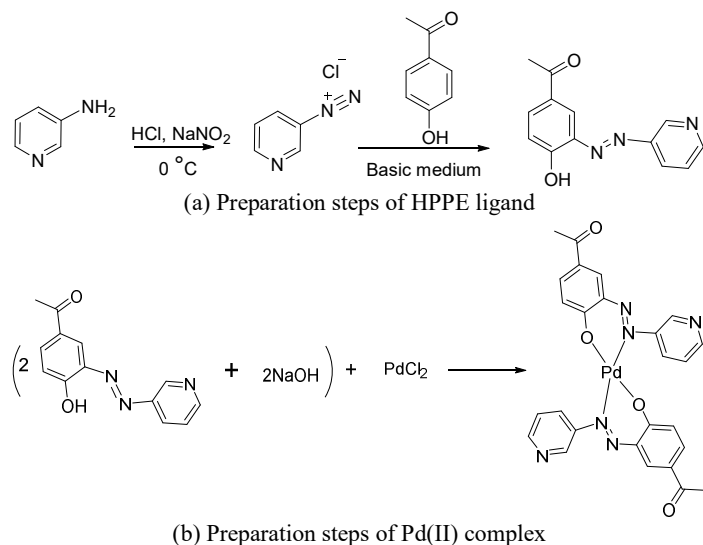
Synthesis of Pd(II) complex

The HPPE ligand (2 mmol, 0.48 g) was dissolved in hot ethanol (20 mL) in a round-bottomed flask with equivalent sodium hydroxide. Palladium(II) chloride (1 mmol, 0.18 g) was dissolved separately in hot water (20 mL) with little bit of hydrochloric acid to complete the solubility and added into the flask containing the ligand solution. The pH of mixture was justified at 8 and it stirred and refluxed for 2 hours. The precipitate was isolated by filtration after overnight, washed with ice-cold ethanol and air dried at room temperature. The solid product was recrystallized from ethanol yielding dark brown crystals with 75% yield, m.p 328 $^{\circ}\text{C}$. Chemical shifts (ppm) of $^1\text{H-NMR}$ for the palladium(II) complex for HPPE ligand are 8.81 (H, s), 8.62 (H, d, $J = 6.10$), 8.25 (H,s), 8.22 (H,d, $J = 6.5$), 7.78 (m), 7.24 (H, d, $J = 8.68$), 2.6 (CH_3 , s). FT-IR (cm^{-1}): 3450 (OH hydrate), 3070 (CH aromatic), 2960 (CH aliphatic), 1676 (C=O), 1606 (C=N), 1480 (C=C), 1434 (-N=N-), 568 (Pd-N), 469 (Pd-O).

RESULTS AND DISCUSSION

Synthesis and characterization

The 3-(3-pyridylazo)-4-hydroxyacetophenone ligand was formed by reacting diazonium salt of 3-aminopyridine with 4-hydroxyacetophenone in basic medium as shown in Scheme 1(a). The palladium complex was formed by reacting two equivalents of azo ligand with one equivalent of palladium chloride as shown in Scheme 1(b), which is in agreement with elemental analyses that showed metal-to-ligand ratio equivalent to 1:2.



Scheme 1. Preparation steps of the ligand and its palladium complex.

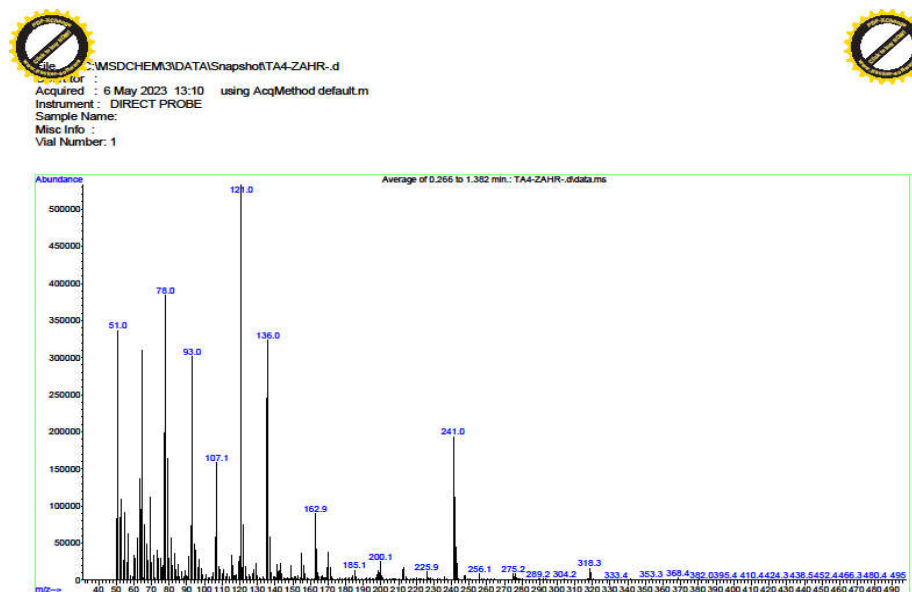
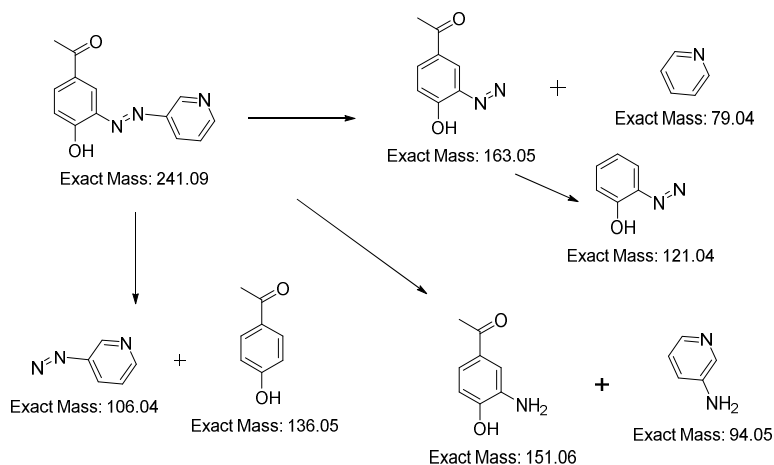


Figure 1. Mass spectrum of HPPE ligand.

The Pd(II) complex and azo dye ligand were formed in high yields. The mass spectrum of the HPPE ligand is depicted in Figure 1. Mass spectrometry can be used in the investigation the fragmentation patterns of the azo ligand and the relative abundance. The spectrum of dye revealed peaks at m/z value of 237.03 corresponding to C₁₃H₁₁N₃O₂ which represent molecular weight of

the dye. The spectrum of dye revealed peaks at m/z values of 163.9 and 79.0 corresponding to $C_8H_7N_2O_2$ and C_5H_5N fragments respectively that resulted from the cleavage one side of the azo group. The spectrum of dye revealed also signals at m/z values of 136 and 106 corresponding to $C_8H_8O_2$ and $C_5H_4N_3$ fragments respectively that resulted from the cleavage the other side of the azo group. The mass spectrum of ligand also revealed other the signals as shown in Scheme 2, which represents the fragments of the synthesized ligand. The palladium complex is 586.2 in agreement with the chemical formula $C_{26}H_{20}N_6O_4Pd$.



Scheme 2. The important fragments of HPPE ligand.

Measurements of FTIR spectroscopy

The FTIR method is quick and very useful even for tiny quantities of the compounds. It uses to determine the functional groups which may lead to monitor the dyes in environment and in consumer products. The chromophors of the HPPE ligand are $C=O$, $C=N$, $-C=C-$, $-N=N-$, which showed 1666 , 1596 , 1500 and 1491cm^{-1} at respectively [10,11]. The OH, CH aromatic and CH aliphatic groups of HPPE dye represent auxochromes showing at 3368 , 3064 and 2940cm^{-1} , respectively [12, 13]. The Infrared spectrum of ligand is presented in Figure 2. The Pd-O and Pd-N bonds in Pd(II) complex showed at 500cm^{-1} and 440cm^{-1} , respectively [14]. The OH peak of ligand disappeared upon complexation with Pd that means that the phenolic oxygen participates under bonding with the metal centre. The frequencies of the $N=N$ and $C-O$ values in the palladium complex showed a redshift which shifted to a lower frequency upon complexation to Pd(II) compared to the ligand [15]. The shifting indicated that both the N and O donor atoms in the ligand were involved in the chelation to the metal centre.

The $^1\text{H-NMR}$ spectra of HPPE ligand and its palladium complex were recorded in $\text{DMSO-}d_6$ solution. The signal of amino group in 3-aminopyridine disappeared in the spectrum of the HPPE ligand as shown in Figure 3, that means that the start material reacted and converted to the azo dye. The protons aromatic on the carbon atoms besides the nitrogen atom in the pyridine ring appeared at high chemical shift. These signals appeared as singlet signal at 8.73ppm and doublet signal at 8.36ppm . The protons of Methyl group appeared at 2.6ppm as singlet signal. The OH group appeared at 9.23ppm as a singlet signal while it disappears in the palladium complex which refers to deprotonate the OH group in the complex. The aromatic protons of ligand and complex appeared in the range of $6.90\text{-}7.80\text{ppm}$. On complexation, the protons on the appeared chemical shifts more or less values in the complex as shown in the Figure 4 comparing to the ligand.

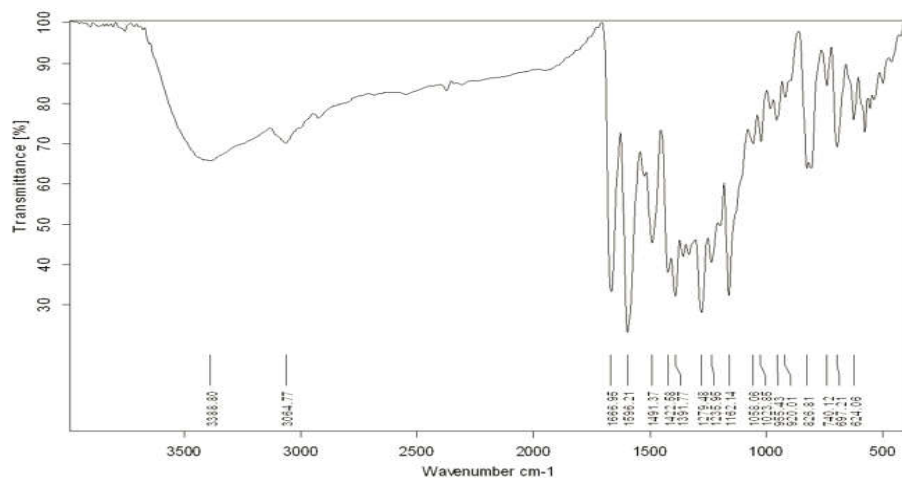
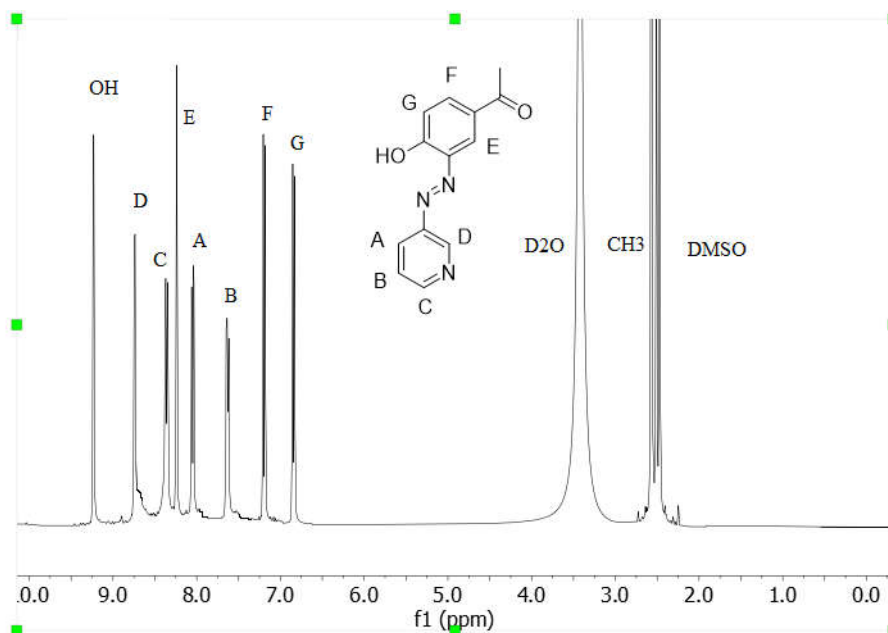


Figure 2. Infrared spectrum of HPPE ligand.


 Figure 3. $^1\text{H-NMR}$ spectrum of HPPE ligand in DMSO_d_6 .

Electronic spectra of HPPE ligand and palladium complex

The electronic spectra of the HPPE dye and its palladium complex in DMSO solution (10^{-5} M) are depicted in Figure 5. The electronic spectrum of HPPE ligand showed two types of transitions. The first electronic transition at 272 and 320 nm can be assigned to $\pi \rightarrow \pi^*$ transition centered on the phenolic ring [16]. The second electronic transition at 370 nm is assigned to $n \rightarrow \pi^*$ based on the azo group and benzene ring [17, 18]. The third electronic transition was at 483 to 600 nm

which is due to intramolecular electron transition. The palladium complex showed band at 484 nm due to charge transfer and other bands at 625, and 714 nm are assigned to the d–d transitions which are represented $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1A_{2g}$ respectively [19-22]. The Pd(II) complex showed bands at 282 and 327 nm of $\pi \rightarrow \pi^*$ with higher intensity than that of the azo dye ligand.

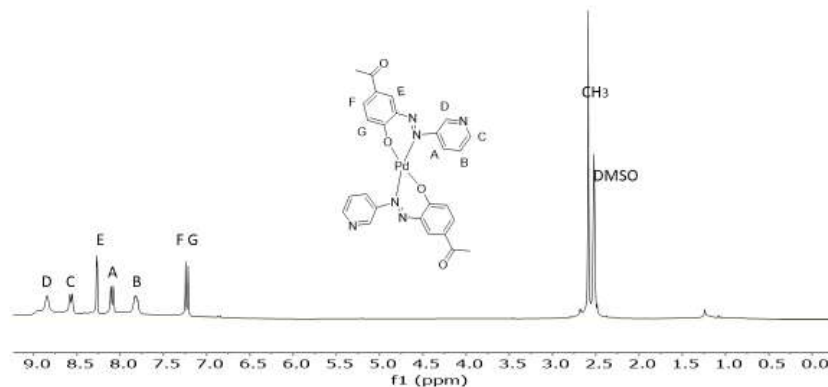


Figure 4. $^1\text{H-NMR}$ spectrum of Pd(II) complex for HPPE ligand in $\text{DMSO}d_6$.

Molar conductance and magnetic moment

The molar conductance value of the palladium complex was determined using 1×10^{-3} M DMF solution. Molar conductivity measurements of the palladium (II) complex revealed the nonconductivity nature of the solution at room temperature where the standard values were done at this temperature indicating the absence of any electrolytes. That means that there are no ions existing in the outer sphere coordination of the complex. The magnetic susceptibility measurements showed diamagnetic behaviour which is consistent with the zero unpaired electrons of Pd(II) d^8 species having square planar geometry.

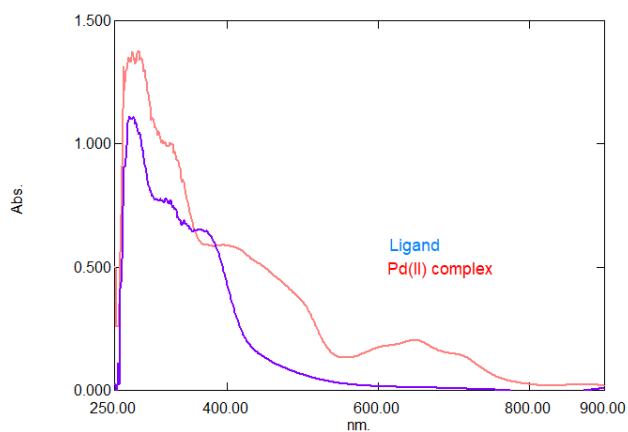


Figure 5. UV-VIS spectra of HPPE ligand and palladium complex in DMSO at room temperature.

pH effect on HPPE dye

At different pH values, the azo dye of HPPE dye displays bright yellow (pH = 3), red (pH = 7) and dark red color (pH = 9). The UV–Vis absorption spectra of azo dye were represented in Figure 6. The azo dye exists in the azoic form (I) while in neutral condition exists in the azoic form and little bit hydrazone form (II) possible exhibiting. In acidic solvent because of protonated nitrogen atoms, the hydrazone form will be controlled by hydrazone form. It sounds that under basic condition, there are intraligand charge transfer and resonance. Under acidic condition, the protonation process finished the intraligand charge transfer and reduced the resonance therefore the color converted from dark to yellow [4, 23, 24].

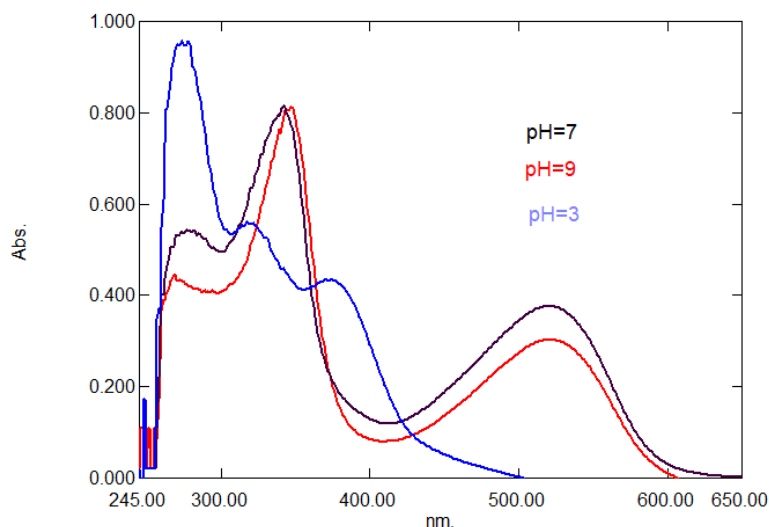


Figure 6. pH effect on the HPPE dye in aqueous solution.

The HPPE ligand and palladium complex were tested their antioxidant activity by using the DPPH. Both compounds are efficient scavengers for free radical species. The synthesized compounds showed potential scavenging for target oxidative damage which are listed in Table 1 [25, 26]. The antioxidant activity of the HPPE ligand and palladium complex was determined by using the 1,1-diphenyl-2-picrylhydrazyl (DPPH) free radical scavenging activity. The HPPE ligand as shown in Figure 7, showed a higher DPPH radical-scavenging activity comparing to the ascorbic acid and the palladium complex. We conclude that the azo ligand is useful source as antioxidants, which confer significant protection against free radical damage.

Table 1. The data of antioxidant activity of HPPE ligand and its palladium(II) complex.

Concentration	Ascorbic acid		HPPE ligand		Pd(II) complex	
	Mean	SD	Mean	SD	Mean	SD
200	79.7	2.095233	81.09533	1.621776	32.099	2.012252
100	74.06667	1.006645	69.483	3.707903	27.04467	1.187479
50	64.26667	4.14769	55.247	2.960621	17.207	2.245389
25	54.66667	5.773503	44.29033	1.801796	13.92767	0.770639
12.5	36.23333	4.868607	29.12833	2.52614	13.38733	1.237732

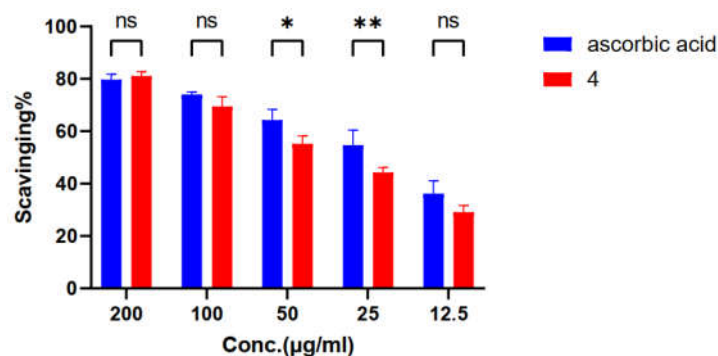


Figure 7. Antioxidant activity of HPPE ligand.

CONCLUSION

To sum up, we have described the design, synthesis and characterized of a visible colorimetric sensitive chemosensor namely ((E)-1-(4-hydroxy-3-(pyridin-3-yl-diazenyl)phenyl)ethan-1-one) (HPPE) which was prepared by coupling diazonium salt of 3-aminopyridine and 4-hydroxyacetophenone. The HPPE ligand is bidentate and it coordinates via N and O atoms to the palladium ion. Compound of Pd(III) with HPPE ligand were synthesized. The palladium complex was formulated as [Pd(HPPE)₂] and its shape is square planar. The palladium complex is a neutral species and it is square planar. We conclude that the azo ligand is useful source as antioxidants, which confer significant protection against free radical damage.

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