

Conducting Polymer as Potential fluorescent sensor for the detection of Cu(II) ions

Elsayed Elbayoumy*, Nasser A. El-Ghamaz, Farid Sh. Mohamed, Mostafa A. Diab

Abstract— Conducting polymer (CP) based on Michal's addition of aromatic sulphanyl compound to phenylenediamine was synthesized as a selective and stable fluorescent sensor for the detection of Cu²⁺ ions. In the absence of Cu²⁺ ions, CP shows a strong fluorescence emission spectrum at $\lambda_{em} = 490$ nm while addition of Cu²⁺ ions cause a quenching for its fluorescence emission due to the coordination bond between Cu²⁺ ions and CP functional groups. Selectivity of fluorescent sensor for the detection of Cu²⁺ was investigated by using various numbers of different metal ions. Also, the stability test of fluorescent sensor in different pH media appears the sensor is stable in pH range 1-9. In addition, the sensor exhibits stability toward a strong ionic strength medium as well as in exposure to visible light for about 48 h.

Index Terms— Fluorescent sensor, Metal ion detection, Conjugated polymers, Chemosensor.

1 INTRODUCTION

Although metals are the essential backbone of the modern technological applications and industries, their accumulation in the environment cause a bad effect on the human health [1, 2]. When the living organisms expose to the wastewater, these metals deposit on it which destroy the metabolism cycle of the living organisms. These metals cannot be destroyed or degraded as well as they accumulated in the living organisms with levels higher than the acceptable and acting a harmful effect for human beings [3–5]. Among metal ions, copper plays an important part in many physiological processes not only in a large number of organisms but also in human life [6–8]. When the amount of Cu²⁺ increases from the normal level, the excess amount of Cu²⁺ ions react with oxygen molecules and form reactive oxygen species which has the ability to destroy proteins, nucleic acids and lipids [9, 10] as well as the toxicity of Cu²⁺ ions can cause a serious of neurodegenerative diseases [11–13]. Also, copper is used in many industrial applications which pollutes the environment through the disposal of industrial waste water containing Cu²⁺ ion [14]. Furthermore, the amount of Cu²⁺ must not increase from the fixed limit of 2 mg L⁻¹ in drinking water [15]. Therefore, investigating fast, sensitive and selective method to detect the low concentration of metals especially copper have been attractive a lot of interest to maintain the human health and the environment.

In the recent years, the standard methods for detection of Cu²⁺ ions are either atomic absorption spectroscopy (AAS) [16] or inductively coupled plasma mass spectroscopy

(ICPMS) [17]. Although these methods are highly sensitive, they suffer from the selectivity since most of their copper recognition elements are sensitive for other heavy metals and need very expensive instruments [14, 18]. That is why founding a novel selective, sensitive and economic method for the detection of Cu²⁺ is a necessary requirement.

Conjugated polymers (CPs) are easily prepared, low-cost, low cytotoxicity, high stability and excellent optical properties [19–21]. CPs are characterized by the presence of large number of absorbing units with high stocks shift as well as they can modified by introducing donating atoms or functional groups and used as fluorescent probe chemosensors [22]. According to Gou et al, [23] fluorescent sensors consist of two main parts. The first one is a metal-discerning unit to selectivity recognize the ion and the second is the fluorophore which translate the metal binding event into a useful signal response. The binding interaction between conjugated polymer and metal ion may be electrostatic, coordination or conformational charges caused by the aggregations.

According to Song et al, [24], conjugated polymers which containing active donating atoms such as oxygen and sulfur have the ability to coordinate with the metal ions and forming stable complexes and resulting fluorescence quenching of the polymer.

In our previous work [19] we prepared poly(bis-m-phenylenediaminosulphoxide) (PPDS) as a conjugated polymer by Michal addition of m-phenylenediamine and N,N'-bissulphanyl-m-phenylenediamin. PPDS is characterized by strong photoluminescence (PL) at wavelength 490 nm with high stocks shift equal to 150, so in this work we aims to apply PPDS as a novel selective and sensitive fluorescent sensor for the detection of Cu²⁺ ions.

- Elsayed Elbayoumy*: Chemistry Department, Faculty of Science, Damietta University, New Damietta 34517, Egypt.
E-mail: sayedelbayoumy@du.edu.eg
- Nasser A. El-Ghamaz: Physics Department, Faculty of Science, Damietta University, New Damietta 34517, Egypt.
E-mail: Elghamaz@du.edu.eg
- Farid Sh. Mohamed: Chemistry Department, Faculty of Science, Damietta University, New Damietta 34517, Egypt.
E-mail: faridsh@mans.edu.eg
- Mostafa A. Diab: Chemistry Department, Faculty of Science, Damietta University, New Damietta 34517, Egypt.
E-mail: m_adiab@du.edu.eg

2 EXPERIMENTAL

2.1 Materials

m-Phenylenediamine (Research-Lab Fine Chem. Industries, Mumbai, India) was purified by dissolving in hot water. Then the solutions are left to cool, the pure material then being collected by filtration forming light brown crystals with melting point 64 °C. Thionyl chloride (Research-Lab Fine Chem. Industries, Mumbai, India) was freshly distilled before use. All metal salts were of analytical reagent grade and highest purity available. They included BaCl₂·2H₂O, CaCl₂·2H₂O, CdCl₂, CrCl₃·6H₂O, CuCl₂·2H₂O, KCl, MnSO₄, MgSO₄·7H₂O, NaCl, NiCl₂ and Pb(CH₃COO)₂ (Alpha Chemika, Mumbai, India).

All other reagent and organic solvent including pyridine, DMF, benzene and ethanol were used as received without any purification. The water used in all experiment was deionized water.

2.2 Measurements

Elemental microanalyses of the polymer complex for C and H and N were performed in the Microanalytical Center, Cairo University, Egypt. The Fourier transform infrared analyses, FTIR, spectra were recorded by using KBr plates on a JASCO FT/IR-4100 Fourier transform infrared spectrometer. The ¹H-NMR spectrum was obtained with a JEOL FX90 Fourier transform spectrometer with (DMSO-d₆) as a solvent and TMS as an internal reference. Thermogravimetric analysis (TGA) was performed using a TGA- 50H detector under flowing N₂ gas (20 ml/min) on platinum crucible with a heating rate 10 °C/min from ambient temperature to 1000 °C. Fluorescence measurements were carried out at room temperature by using fluorescence spectrophotometer model 6285. The excitation wavelength λ_{ex} was 405 nm and the emission spectrum was in the range 200 – 600 nm.

2.3 Synthesis of Poly(bis-m-phenylenediaminosulphoxide)

PPDS was prepared according to our previous method from the Michael addition of N,N'-bis-sulphinyl-m-phenylenediamine (Scheme 1.) [19]. Thionyl chloride was added drop by drop to m-phenylenediamine (3:1) at 0 °C, and then the reaction mixture was refluxed for about 5-6 hr. The excess of thionyl chloride was removed by distillation followed by extraction in dry benzene and producing yellowish orange crystals of N,N'-bis-sulphinyl-m-phenylenediamine (BSPD). The formed crystals of BSPD were refluxed with m-phenylenediamine (1:1) in DMF as solvent and drop of pyridine for about 10 hr. The reaction mixture was transferred into ice-water to produce PPDS. The brown precipitate of PPDS was collected, filtered off, washed by distilled water, dried in a vacuum oven, and was kept for further usage.

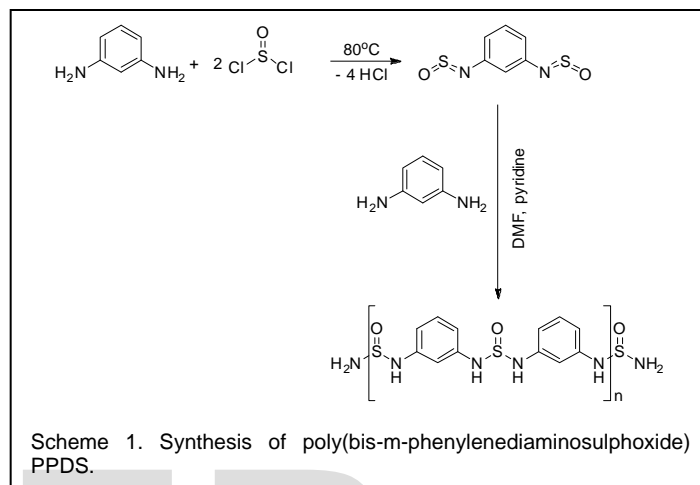
2.4 Synthesis of PPDS-CuCl₂ polymer complex

To investigate the mode of interaction between PPDS and Cu²⁺ ion, PPDS-CuCl₂ polymer complex was prepared by the reaction of PPDS and CuCl₂·2H₂O [25]. A solution of CuCl₂·2H₂O (1 mmol) in ethanol was added dropwise to a solution of PPDS (1 mmol) in DMF. The reaction mixture was refluxed for

2 h. The solution was settled overnight and then was poured into distilled water forming dark brown precipitate. The product of Cu-PPDS was collected, filtered off, washed by distilled water, ethanol and dried in a vacuum oven.

2.5 Sample preparation

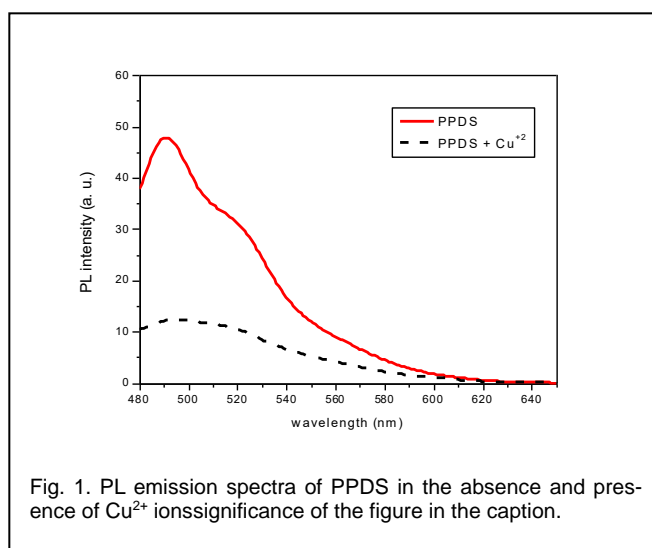
Stock solutions (1×10⁻³ M) of PPDS and each metal salt were prepared in DMF and deionized water, respectively. The stock solutions were then used to prepare all the test samples in the present study.



3 RESULTS AND DISCUSSION

3.1 Detection of Cu²⁺ ions

It is observed from Fig. 1 that, PPDS shows strong PL peak in the absence of Cu²⁺ ions at λ_{em} = 490 nm, while in the presence of Cu²⁺ ions, the PL intensity of PPDS shows obviously depression in its value which indicating the strong coordination between Cu²⁺ ions and SO group along PPDS and resulting the quenching of PPDS fluorescence.



To confirm the feasibility of PPDS for the detection of Cu²⁺ ions, we study the change of PL peak intensity of PPDS in the presence of different concentrations of Cu²⁺ ions. Fig. 2 shows

the PL intensity of PPDS in the presence of Cu^{2+} ions at the concentration range $0 - 2 \times 10^{-4}$ M. It is observed from this figure that, the PL peak intensity of PPDS was inversely proportional to the concentration of Cu^{2+} ions. The obtained data follows the well known stern-volmer equation (1) [16, 17, 26].

$$F_0 / F - 1 = K_{sv}C \quad (1)$$

where F_0 and F are the PL intensity of PPDS at $\lambda_{em} = 490$ nm in the absence and presence of Cu^{2+} ions, respectively. K_{sv} is the stern-volmer quenching constant and C is the analyte (Cu^{2+}) concentration.

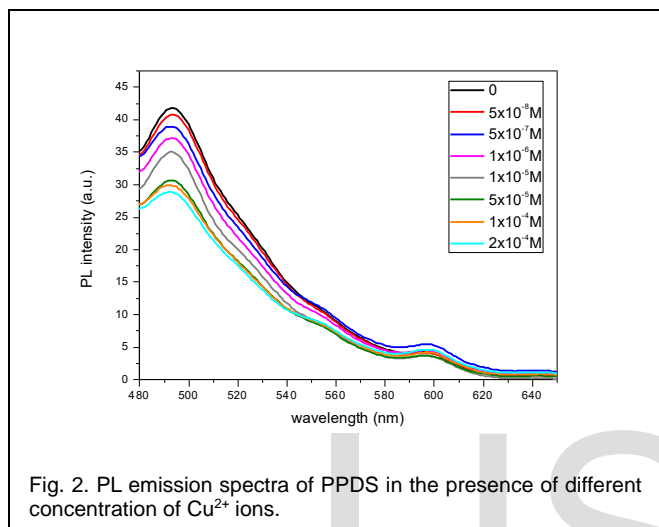


Fig. 2. PL emission spectra of PPDS in the presence of different concentration of Cu^{2+} ions.

The stern-volmer plot is shown in Fig. 3. A straight line is observed in the concentration range $0 - 16 \times 10^{-6}$ M with a correlation coefficient $R = 0.99496$ which confirm the good correlation between the PL intensity of PPDS and the Cu^{2+} ions concentration. The value of K_{sv} is calculated from the slope of Fig. 3 and is found to be 0.02812. The same behavior is observed in many papers [16, 17, 23, 26-29] which indicate that, the system follows stern-volmer equation.

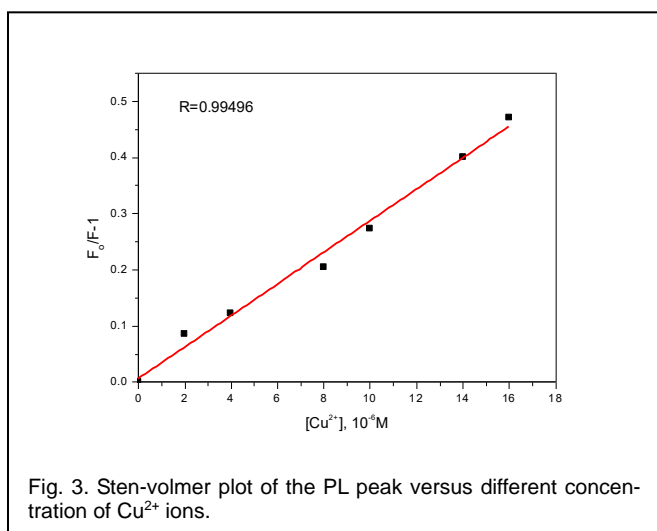


Fig. 3. Stern-volmer plot of the PL peak versus different concentration of Cu^{2+} ions.

3.2 Selectivity of poly(bis-m-phenylenediaminosulphoxide) for Cu^{2+} ions

To confirm the selectivity of PPDS for Cu^{2+} ions, we chose a large various number of metal ions such as Ba^{2+} , Ca^{2+} , Cd^{2+} , Cr^{3+} , K^+ , Mg^{2+} , Mn^{2+} , Na^+ , Ni^{2+} and Pb^{2+} . All the metal ions are in the same concentration (2×10^{-4} M) and in the same environmental conditions. From the experimental results, we observed that, when Cu^{2+} ions are added to PPDS, the PL peak intensity at $\lambda = 490$ nm obviously decrease to about 15 % of its original value. While with the other metal ions do not show this behavior as in Fig. 4. This behavior confirms the high selectivity of PPDS to coordinate with Cu^{2+} ions and form stable complex rather than any metal ions.

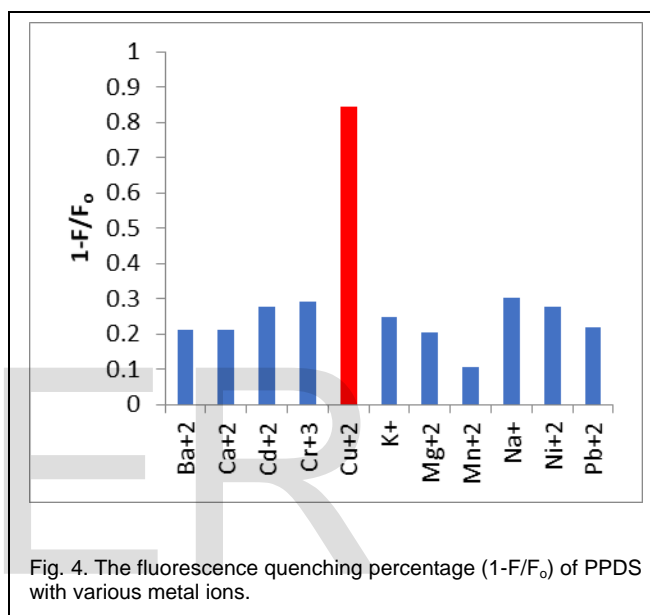


Fig. 4. The fluorescence quenching percentage ($1-F/F_0$) of PPDS with various metal ions.

3.3 Stability of poly(bis-m-phenylenediaminosulphoxide)

It is very important for any fluorescence sensor to be stable in the variable factors which can effect on the result accuracy of the test experiment. Three different influencing factors such as different values of pH, ionic strength and visible light irradiate are taken in our consideration to confirm the good ability of the use of PPDS as fluorescence sensor for Cu^{2+} ions. Fig. 5 shows the effect of pH values of the PL intensity of PPDS. It is clear that, the PL intensity of PPDS is approximately stable in the pH range 1 - 9 and the more increase in pH value lead to obviously decrease its value. So that PPDS can be used as fluorescence sensor for Cu^{2+} ions in both acidic and slightly basic environment.

Fig. 6 shows the effect of ionic strength (different NaCl concentrations) on the PL intensity of PPDS. It is observed that the PL intensity of PPDS is approximately unchanged by increasing the concentration of NaCl from 0.1 M to 1 M which indicate the high stability of PPDS in a higher ionic strength environment. Fig. 7 shows the stability of PL intensity of PPDS in the visible light. It is found that, PL intensity is approximately stable for 48 hrs and its value show a slightly decrease by increasing the times more than 48 hrs.

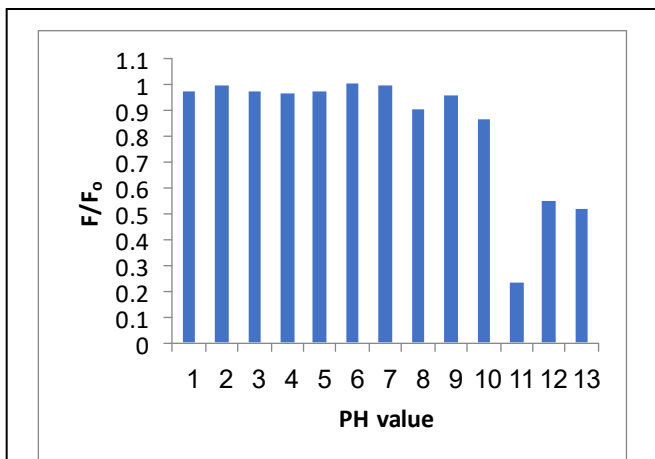


Fig. 5. Stability of PPDS at different pH. F_0 and F are PL intensities of PPDS solution and specify pH, respectively.

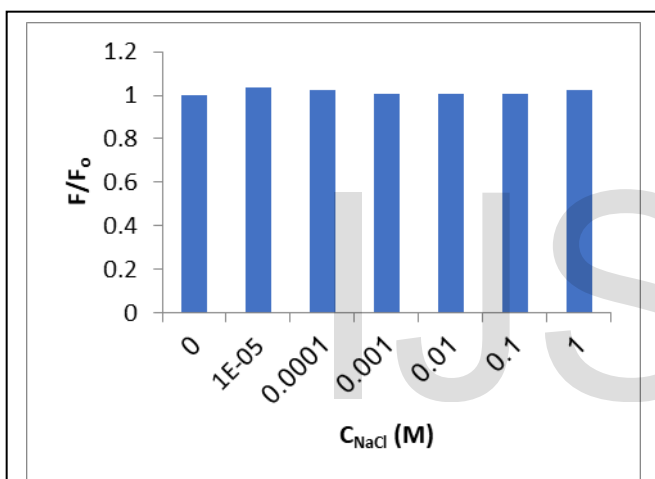


Fig. 6. Stability of the PPDS in the different concentration of NaCl.

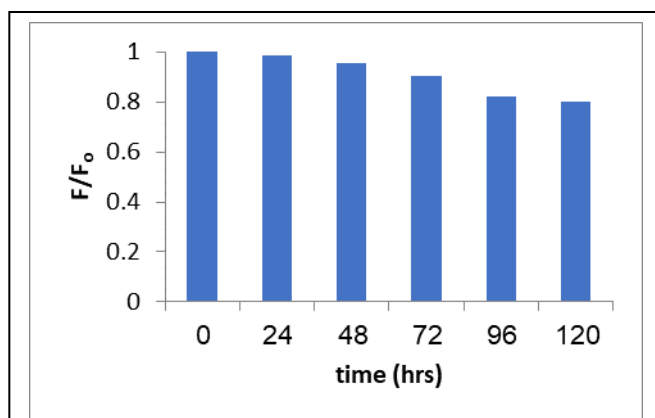


Fig. 7. Stability of PPDS in the different time under visible light. F_0 and F are PL intensities at 0 hr and specify time, respectively.

3.4 Binding mode for the interaction between PPDS and Cu^{2+} ion

The IR spectra of PPDS- $CuCl_2$ polymer complex is shown in Fig. 8 The bands at 1460, 1625, 2928 and 3360 cm^{-1} are related to $\nu(S=O)$, $\nu(C=C, Ar)$, $\nu(H-C, Ar)$ and $\nu(NH)$, respectively. By comparing the IR data of PPDS- $CuCl_2$ polymer complex and the IR data of PPDS Fig. 8 [19], we found that, the band of sulphanyl group ($S=O$) is shifted to higher frequency from 1360 to 1460 cm^{-1} indicating the probable participation of the oxygen atom of sulphanyl group in complex formation, while the frequency band of $-NH$ group is not shifted which suggesting the non involvement in coordination.

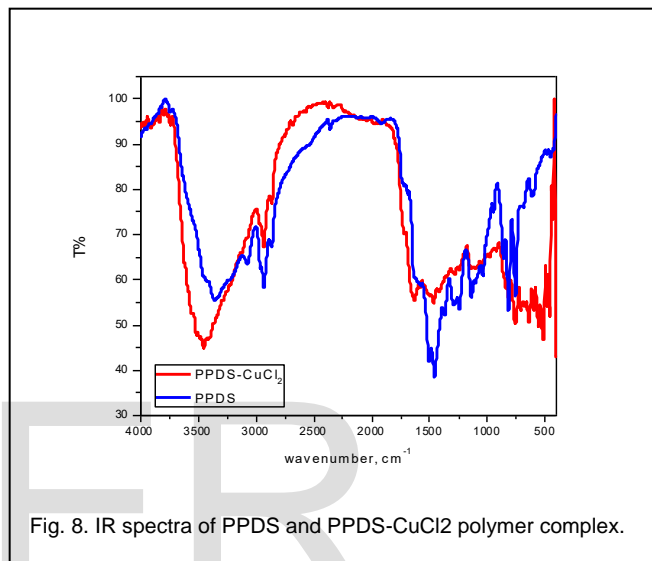


Fig. 8. IR spectra of PPDS and PPDS- $CuCl_2$ polymer complex.

The calculated analysis for $C_{12}H_{12}S_2O_2N_4CuCl_2$ (%): C = 32.54, H = 2.71, O = 7.23, N = 12.65, S = 14.46, Cu = 14.35, Cl = 16.04 and found C = 32.46, H = 2.81, N = 12.54 %. Thermogravimetric analysis (TGA) of PPDS- $CuCl_2$ polymer complex shows one decomposition stage starts at ~ 110 $^{\circ}C$ with a mass loss 82 % (Fig. 9). Molar conductivity (10^{-3} M, DMSO) $< 8 \Omega cm^2 mol^{-1}$, $\mu_{eff} = 1.82$ B. M. (paramagnetic). From the above results it is clear that PPDS react with $CuCl_2$ forming polymer complex with a tetrahedral geometrical structure as in Scheme 2.

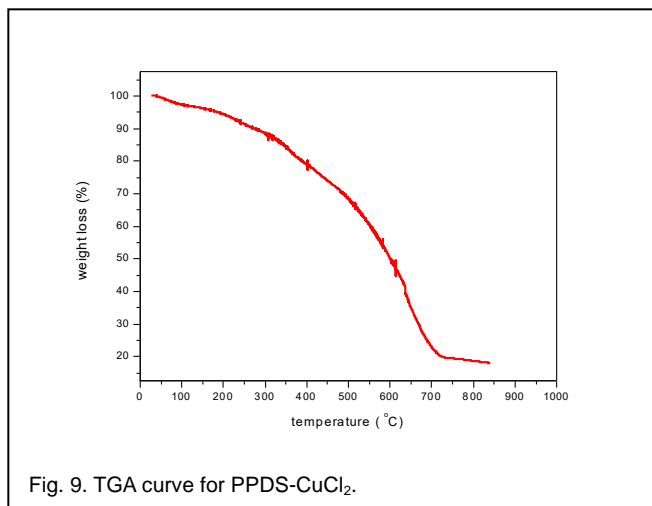
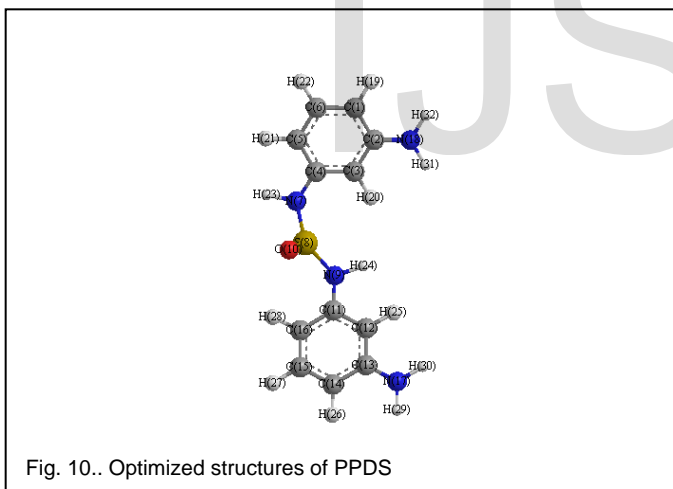
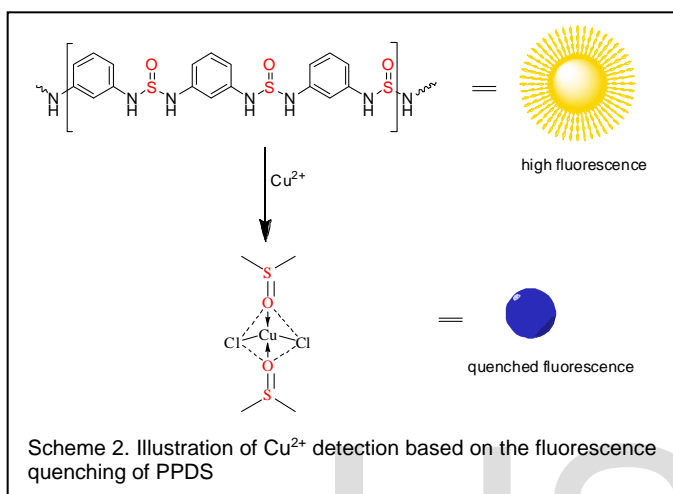


Fig. 9. TGA curve for PPDS- $CuCl_2$.

The HOMO-LUMO energy gap, ΔE , which is an important stability index, is applied to develop theoretical models for explaining the structure and confirmation barriers in many molecular systems [30, 31]. The bond lengths and bond angles for PPDS are listed in Table 1. The geometrical structures, HOMO and LUMO of PPDS are shown in Figure 10 and 11. The computed net charge on active centers for PPDS, it is found that the most negative charges in PPDS are N(7), N(9) and O(10) in which their values are -0.50, -0.50 and -0.52, respectively that make them to react stronger with the metal ion.



Both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbital takes part in chemical stability. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. From the theoretical results, the probability of binding between O atom of PPDS and Cu^{2+} is high which leading to form a tetrahedral geometrical structure as in scheme 2. The calculated quantum chemical parameters of PPDS are given in Table 2. Additional parameters such as HOMO-LUMO energy gap, ΔE , absolute electronegativities, χ , chemical potentials, μ , absolute hardness, η , absolute softness, σ , global electrophilicity, ω , global softness, S , and additional electronic charge, ΔN_{max} were calculated according to the following equations [30, 31]:

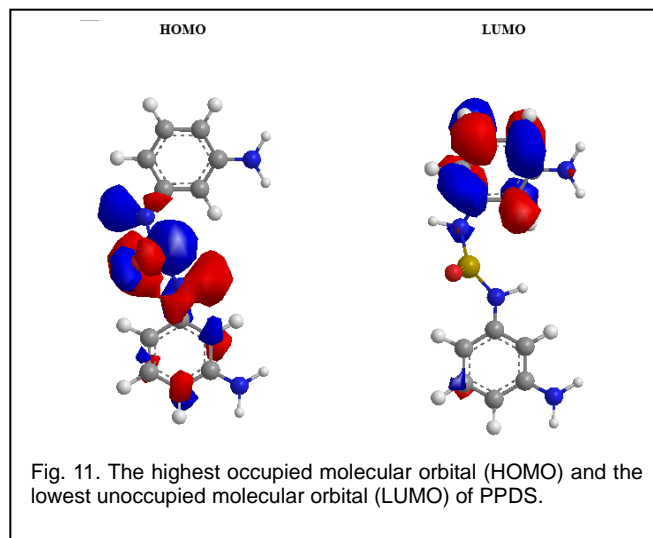


TABLE 1
THE SELECTED GEOMETRIC PARAMETERS FOR PPDS

Bond lengths (Å)		Bond angles (°)	
N(18)-H(32)	1.049	H(27)-C(15)-C(16)	119.958
N(18)-H(31)	1.049	H(27)-C(15)-C(14)	119.847
N(17)-H(30)	1.049	C(16)-C(15)-C(14)	120.194
N(17)-H(29)	1.049	H(30)-N(17)-H(29)	119.577
C(16)-H(28)	1.103	H(30)-N(17)-C(13)	120.311
C(15)-H(27)	1.103	H(29)-N(17)-C(13)	120.112
C(14)-H(26)	1.103	H(26)-C(14)-C(15)	119.499
C(12)-H(25)	1.104	H(26)-C(14)-C(13)	120.841
N(9)-H(24)	1.053	C(15)-C(14)-C(13)	119.658
N(7)-H(23)	1.053	C(14)-C(13)-C(12)	119.971
C(6)-H(22)	1.103	C(14)-C(13)-N(17)	119.891
C(5)-H(21)	1.104	C(12)-C(13)-N(17)	120.138
C(3)-H(20)	1.104	H(28)-C(16)-C(11)	121.047
C(1)-H(19)	1.103	H(28)-C(16)-C(15)	118.287
C(11)-C(16)	1.346	C(11)-C(16)-C(15)	120.665
C(15)-C(16)	1.342	H(25)-C(12)-C(13)	119.084
C(14)-C(15)	1.341	H(25)-C(12)-C(11)	120.104
C(13)-C(14)	1.342	C(13)-C(12)-C(11)	120.812
C(12)-C(13)	1.343	C(16)-C(11)-C(12)	118.691
C(11)-C(12)	1.346	C(16)-C(11)-N(9)	122.775
C(1)-C(6)	1.341	C(12)-C(11)-N(9)	118.522
C(5)-C(6)	1.342	H(24)-N(9)-C(11)	110.794
C(4)-C(5)	1.346	H(24)-N(9)-S(8)	112.363
C(3)-C(4)	1.347	C(11)-N(9)-S(8)	119.905
C(2)-C(3)	1.343	O(10)-S(8)-N(9)	120.494
C(1)-C(2)	1.342	O(10)-S(8)-N(7)	119.595
C(2)-N(18)	1.268	N(9)-S(8)-N(7)	119.849
C(13)-N(17)	1.268	H(22)-C(6)-C(1)	119.859
N(9)-C(11)	1.274	H(22)-C(6)-C(5)	119.966
S(8)-O(10)	1.46	C(1)-C(6)-C(5)	120.175
S(8)-N(9)	1.691	H(23)-N(7)-S(8)	111.765
N(7)-S(8)	1.691	H(23)-N(7)-C(4)	110.065
C(4)-N(7)	1.274	S(8)-N(7)-C(4)	118.867
		H(21)-C(5)-C(6)	118.466
		H(21)-C(5)-C(4)	120.862
		C(6)-C(5)-C(4)	120.671
		C(5)-C(4)-N(7)	118.64
		C(3)-C(4)-N(7)	122.615
		H(32)-N(18)-H(31)	119.532
		H(32)-N(18)-C(2)	120.132
		H(31)-N(18)-C(2)	120.336
		H(20)-C(3)-C(4)	120.324
		C(4)-C(3)-C(2)	120.75
		C(3)-C(2)-C(1)	119.994
		C(3)-C(2)-N(18)	120.096
		C(1)-C(2)-N(18)	119.91

$$\Delta E = E_{LUMO} - E_{HOMO} \quad (2)$$

$$X = -(E_{HOMO} + E_{LUMO})/2 \quad (3)$$

$$\eta = (E_{LUMO} - E_{HOMO})/2 \quad (4)$$

$$\sigma = 1/\eta \quad (5)$$

$$P_i = -\chi \quad (6)$$

$$S = 1/2\eta \quad (7)$$

$$\omega = (P_i^2)/2\eta \quad (8)$$

$$\Delta N_{max} = -P_i/\eta \quad (9)$$

TABLE 2

THE CALCULATED QUANTUM CHEMICAL PARAMETERS FOR PPDS

E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	χ (eV)	η (eV)	σ (eV) ⁻¹	P_i (eV)	S (eV) ⁻¹	ω (eV)	ΔN_s
-2.000	1.943	3.943	0.029	1.972	0.507	-0.029	0.254	0.00021	0.01

4 CONCLUSION

A novel conjugated polymer poly(bis-m-phenylenediaminosulphoxide) (PPDS) is designed to be easily prepared, low-cost and low cytotoxicity fluorescent sensor for the detection of Cu²⁺ ions. The fluorescent sensor shows high selectivity and sensitivity for Cu²⁺ ions. PPDS as fluorescent sensor for Cu²⁺ can be used in both acidic or slightly basic environment with higher ionic strength. The interaction between PPDS and Cu²⁺ is due to the coordination bonds between Cu²⁺ and SO groups along the polymeric chain forming polymer complex with a tetrahedral geometrical structure.

REFERENCES

[1] Y. Wu et al., "Environmental remediation of heavy metal ions by novel-nanomaterials: a review," *Environ. Pollut.*, vol. 246, pp. 608–620, 2019.

[2] J. Li et al., "Metal-organic framework-based materials: superior adsorbents for the capture of toxic and radioactive metal ions," *Chem. Soc. Rev.*, vol. 47, no. 7, pp. 2322–2356, 2018.

[3] Q. Y. Chen, T. DesMarais, and M. Costa, "Metals and mechanisms of carcinogenesis," *Annu. Rev. Pharmacol. Toxicol.*, vol. 59, pp. 537–554, 2019.

[4] S. S. Leonard, J. J. Bower, and X. Shi, "Metal-induced toxicity, carcinogenesis, mechanisms and cellular responses," *Mol. Cell. Biochem.*, vol. 255, no. 1, pp. 3–10, 2004.

[5] S. Wang and X. Shi, "Molecular mechanisms of metal toxicity and carcinogenesis," *Mol. Cell. Biochem.*, vol. 222, no. 1, pp. 3–9, 2001.

[6] R. Uauy, M. Olivares, and M. Gonzalez, "Essentiality of copper in humans 1–3," vol. 3970009, pp. 952–959, 1998.

[7] S. Okamoto and L. D. Eltis, "The biological occurrence and trafficking of cobalt," *Metallomics*, vol. 3, no. 10, pp. 963–970, 2011.

[8] H. Tapiero, D. M. Townsend, and K. D. Tew, "Trace elements in human physiology and pathology . Copper," vol. 57, pp. 386–398, 2003, doi: 10.1016/S0753-3322(03)00012-X.

[9] M. Valko, C. J. Rhodes, J. Moncol, M. M. Izakovic, and M. Mazur, "Free radicals, metals and antioxidants in oxidative stress-induced cancer," *Chem. Biol. Interact.*, vol. 160, no. 1, pp. 1–40, 2006.

[10] M. DiDonato and B. Sarkar, "Copper transport and its alterations in Menkes and Wilson diseases," *Biochim. Biophys. Acta (BBA)-Molecular Basis Dis.*, vol. 1360, no. 1, pp. 3–16, 1997.

[11] E. Gaggelli, H. Kozlowski, D. Valensin, and G. Valensin, "Copper Homeostasis and Neurodegenerative Disorders (Alzheimer ' s , Prion , and Parkinson ' s Diseases and Amyotrophic Lateral Sclerosis)," 2006.

[12] C. Vulpe, B. Levinson, S. Whitney, S. Packman, and J. Gitschier, "Isolation of a candidate gene for Menkes disease and evidence that it encodes a copper-transporting ATPase," *Nat. Genet.*, vol. 3, no. 1, pp. 7–13, 1993.

[13] D. R. Brown et al., "The cellular prion protein binds copper in vivo," *Nature*, vol. 390, no. 6661, pp. 684–687, 1997.

[14] Q. Wu and E. V. Anslyn, "Catalytic signal amplification using a heck reaction. An example in the fluorescence sensing of Cu (II)," *J. Am. Chem. Soc.*, vol. 126, no. 45, pp. 14682–14683, 2004.

[15] Q. Shen, X. Zhao, S. Zhou, W. Hou, and J.-J. Zhu, "ZnO/CdS hierarchical nanospheres for photoelectrochemical sensing of Cu²⁺," *J. Phys. Chem. C*, vol. 115, no. 36, pp. 17958–17964, 2011.

[16] S. G. Liu, N. Li, Y. Z. Fan, N. B. Li, and H. Q. Luo, "Intrinsically fluorescent polymer nanoparticles for sensing Cu²⁺ in aqueous media and constructing an IMPLICATION logic gate," *Sensors Actuators B Chem.*, vol. 243, pp. 634–641, 2017.

[17] X. Wang, J. Zhao, C. Guo, M. Pei, and G. Zhang, "Simple hydrazide-based fluorescent sensors for highly sensitive and selective optical signaling of Cu²⁺ and Hg²⁺ in aqueous solution," *Sensors Actuators B Chem.*, vol. 193, pp. 157–165, 2014.

[18] G.-Y. Lan, C.-C. Huang, and H.-T. Chang, "Silver nanoclusters as fluorescent probes for selective and sensitive detection of copper ions," *Chem. Commun.*, vol. 46, no. 8, pp. 1257–1259, 2010.

[19] M. A. Diab, N. A. El-Ghamaz, F. S. Mohamed, and E. M. El-Bayoumy, "Conducting polymers VIII: Optical and electrical conductivity of poly (bis-m-phenylenediaminosulphoxide)," *Polym. Test.*, vol. 63, pp. 440–447, 2017.

[20] E. Elbayoumy et al., "Pd Nanoparticles-Loaded Vinyl Polymer Gels: Preparation, Structure and Catalysis," *Catalysts*, vol. 11, no. 1, p. 137, 2021.

[21] E. Elbayoumy, N. A. El-Ghamaz, F. S. Mohamed, M. A. Diab, and T. Nakano, "Dielectric Permittivity, AC Electrical Conductivity and Conduction Mechanism of High Crosslinked-Vinyl Polymers and Their Pd (OAc)₂ Composites," *Polymers (Basel)*, vol. 13, no. 17, p. 3005, 2021.

[22] Y. L. Pak, Y. Wang, and Q. Xu, "Conjugated polymer based fluorescent probes for metal ions," *Coord. Chem. Rev.*, vol. 433, p. 213745, 2021.

[23] R. C. Smith, A. G. Tennyson, M. H. Lim, and S. J. Lippard, "Conjugated polymer-based fluorescence turn-on sensor for nitric oxide," *Org. Lett.*, vol. 7, no. 16, p. 3573, 2005.

[24] X. Song, H. Sun, S. Yang, S. Zhao, and F. Liao, "Synthesis of photoluminescent o-phenylenediamine-m-phenylenediamine copolymer nanospheres: An effective fluorescent sensing platform for selective and sensitive detection of chromium (VI) ion," *J. Lumin.*, vol. 169, pp. 186–190, 2016.

[25] M. A. Diab, A. Z. El-Sonbati, and M. M. Ghoniem, "Polymer complexes. IX. Thermal stability of poly [bis (2, 6-diaminopyridine sulphoxide)] and polymer complexes of bis (2, 6-diaminopyridine sulphoxide) with copper halides," *Acta Polym.*, vol. 40, no. 8, pp. 545–547, 1989.

[26] A. Alvarez, J. M. Costa-Fernández, R. Pereiro, A. Sanz-Medel, and A. Salinas-Castillo, "Fluorescent conjugated polymers for chemical and biochemical sensing," *TrAC Trends Anal. Chem.*, vol. 30, no. 9, pp. 1513–1525, 2011.

[27] C. Xing, Z. Shi, M. Yu, and S. Wang, "Cationic conjugated polyelectrolyte-based fluorometric detection of copper (II) ions in aqueous solution," *Polymer (Guildf)*, vol. 49, no. 11, pp. 2698–2703, 2008.

[28] S. W. Thomas, G. D. Joly, and T. M. Swager, "Chemical sensors based on amplifying fluorescent conjugated polymers," *Chem. Rev.*, vol. 107, no. 4, pp. 1339–1386, 2007.

[29] C. Guo, X. Yang, X. Yang, W. Zhu, M. Pei, and G. Zhang, "Fluorescent probes for Cu²⁺, Hg²⁺ and amino acids in aqueous solutions based on two mechanisms," *Sensors Actuators B Chem.*, vol. 205, pp. 345–351, 2014.

[30] M. A. Diab, A. Z. El-Sonbati, A. F. Shoair, A. M. Eldesoky, and N. M. El-Far, "Synthesis, structural, spectroscopic and biological studies of Schiff base complexes," *J. Mol. Struct.*, vol. 1141, pp. 710–739, 2017.

[31] A. Z. El-Sonbati, M. A. Diab, and S. M. Morgan, "Thermal properties, antimicrobial activity and DNA binding of Ni (II) complexes of azo dye compounds," *J. Mol. Liq.*, vol. 225, pp. 195–206, 2017.