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Synthesis, Characterization and Photocatalytic Evaluation of Metal (II) Chelates Based on Schiff Base Ligand

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Abstract: *In the present investigation, we report the synthesis of transition metal(II) complexes based on Schiff base ligand derived from the condensation of acenaphthoquinone and L-methionine. The formation of Schiff base by condensation and complexation of the ligand with Cu(II) and Zn(II) is analysed by FTIR spectroscopy.The geometry of the ligand is optimised by energy minimization using molecular mechanics (MM2) force field method. The frontier molecular orbitals (FMO), HOMO and LUMO, of the optimized structure is calculated using semi empirical extended Hückel molecular orbital method. The photocatalytic activity of the Cu(II) chelates were investigated for degradation of thiazine dye, methylene blue, following the absorbance of dye with time.The binding affinity of Schiff base complexes ZnL and CuL with the recombinant protein human phospholysinephosphohistidine inorganic pyrophosphate phosphatase has been investigated by docking studies, whose binding score is estimated to be -7.1 and -7.2 kcal/mol respectively.*

Keywords: Schiff base, transition metal complexes, photocatalytic degradation, docking studies.

I. INTRODUCTION

The chemistry of coordination compounds is at present undergoing rapid development primarily driven by scientific curiosity and the ensuing technological applications. There has been a significant rising interest in the design of metal complexes as drugs and diagnostic agents is currently observed in the area of scientific inquiry, appropriately termed medicinal chemistry[1]. Investigations in the medicinal area focus mostly on the specialization of metal species in biological media based on the investigations of metal ions with diverse biomolecules [2-4]. Recent investigations in the area of co-ordination chemistry have led to developments in cancer care, infection control, diabetes, ulcers and anti-inflammatory drugs.

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II. SYNTHESIS

All the reagents and solvents used in the present study were of analytical grade and were used as received without further purification. Copper(II) chloride dihydrate ($CuCl_2.2H_2O$, 99%, Merck), Zinc(II) chloride ($ZnCl_2$, 98%, Merck), Acenapthenequinone($C_{12}H_6O_2$, 99%, Sigma-Aldrich), and L-Methionine ($C_5H_{11}NO_2S$, 99%,*LobaChemie)*. All other reagents and solvents were purchased from commercial sources and were of analytical grade.

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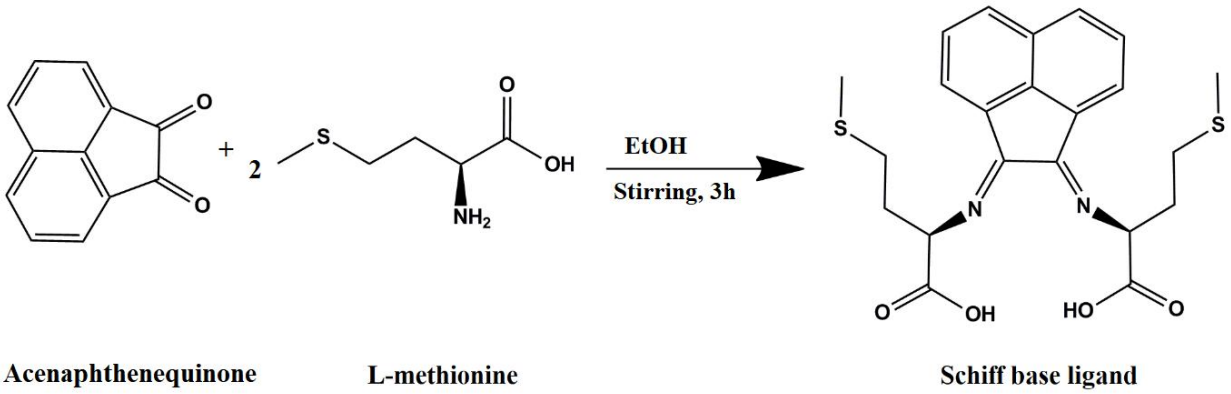
2.1 Synthesis of ligand (H_2L)

About 10 mmol of acenapthoquinone (1.82 g) was taken in a two-neck round bottomed flask along with 40 mL of ethanol. To this, 20 mmol of L-Methionine (2.98 g) dissolved in 20 mmol of sodium hydroxide was added. The reaction mixture was stirred for 3 hours to obtain a bright yellow colored precipitate. The precipitate was repeatedly washed with water and diethyl ether and it was then dried *in vacuo* over anhydrous calcium chloride.



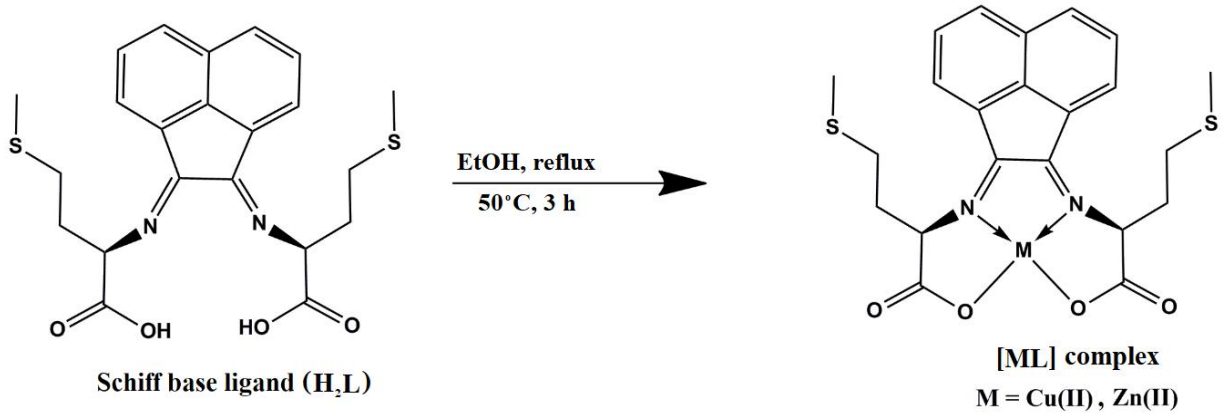
Acenaphthenequinone **L-methionine** **Schiff base ligand**

Scheme 1: Schiff base formed by the condensation of Acenapthenoquinone with L-methionine.

2.2 Synthesis of Metal Complexes

2.2.1 [ZnL] Complexes

In a typical reaction, finely powdered ligand (1 mmol; 0.45 g) is dissolved in 20 mL ethanol. To this solution, 20 mL ethanolic solution containing 1 mmol metal salt were added dropwise. Then, the mixture was stirred and refluxed at 50 °C for 3 hours. The resulting solution was then slowly evaporated to dryness at room temperature and the product obtained was washed several times with ethanol and dried *in vacuo* over anhydrous calcium chloride.



Schiff base ligand (H_2L) **[ML] complex**
M = Cu(II), Zn(II)

Scheme 2. Complexation of the Schiff with Cu(II) and Z(II) metalions.

2.2.2 [CuL] Complexes:

In a typical reaction, finely powdered ligand (1 mmol; 0.45 g) is dissolved in 20 mL ethanol. To this, 20 mL ethanolic solution of 1 mmol metal salt (Copper(II) chloride- 0.17 g) were added dropwise. Then the mixture was stirred and refluxed at 50 °C for 3 hours. The resulting solution was then slowly evaporated to dryness at room temperature and the product obtained was washed several times with ethanol and dried *in vacuo* over anhydrous calcium chloride.

2.3 Photocatalysis Experiment

In a typical photocatalytic experiment, 0.1 g photocatalyst was added to 20 mL Methylene Blue (MB) aqueous solution (10 mg/L) in a beaker to prepare the suspension for experiment. Before irradiation, the suspension was vigorously stirred in dark for 30 minutes to attain the adsorption/desorption equilibrium. The suspension was then exposed to

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daylight under constant stirring at ambient temperature. From the reaction mixture, aliquots of 2 mL were withdrawn at definite time intervals and centrifuged at 3000 rpm for 2 minutes to obtain a clear supernatant for measuring absorbance. The transient response of absorbance for the resulting supernatant, at 660 nm was followed to monitor the progress of the photocatalytic degradation. The photodegradation efficiency (%) was calculated according to the following equation:

$$\text{Degradation Efficiency (\%)} = \frac{A_0 - A_t}{A_0} \times 100\ \%$$

where A_0 represents the absorbance of dye solution before visible light irradiation and A_t is the absorbance of dye at a certain time period 't' after illumination.

III. RESULT AND DISCUSSION

3.1 Vibrational Spectroscopy

FTIR spectroscopy is a powerful tool to characterize the synthesized Schiff base ligand and the metal complexes based on molecular vibrational frequencies. The FTIR spectra of the free ligand, shown in fig. 1, exhibits a strong band at 1588.27 cm^{-1} caused by the υ(C=N) stretching from azomethine linkage in the Schiff base [29].

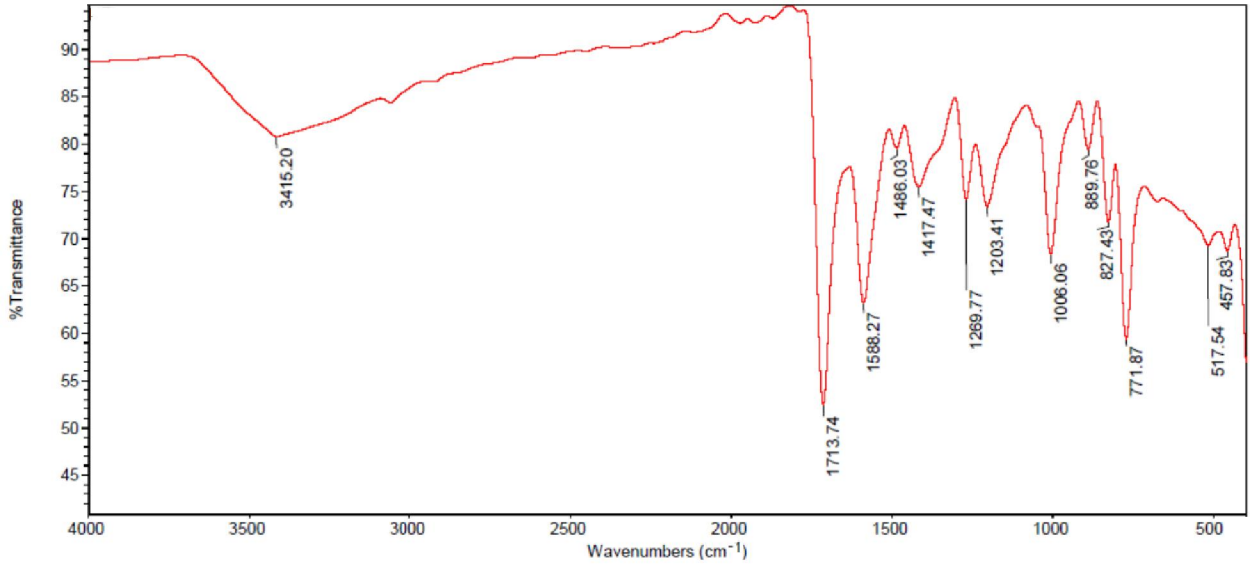

Fig. 1 Fourier transform - Infrared (FT-IR) spectra of the synthesized Schiff base ligand

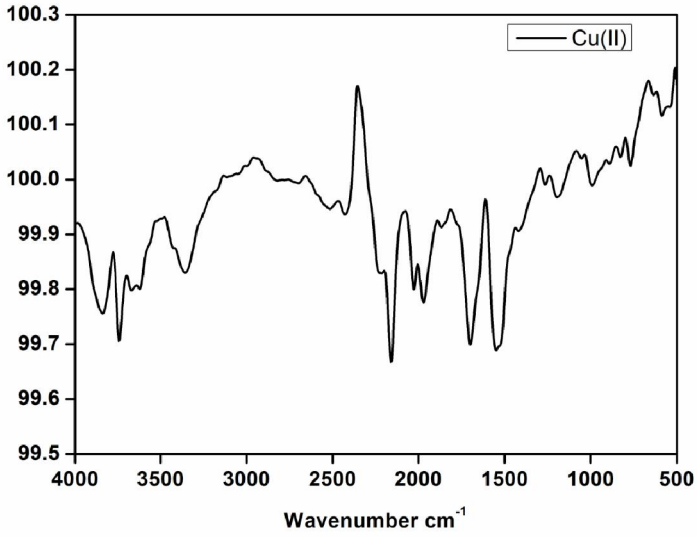

Fig 2: FTIR spectra of the synthesized Cu(II) complex with Schiff base ligand

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The broad band centred around 3415.20 cm^{-1} could be assigned to the hydroxyl υ(O-H) stretching from caboxylic acid functional group along with finite contribution from aromatic υ(C-H) Stretching as well. The sharp band observed at 1713.74 cm^{-1} could be ascribed to carbonyl υ(C=O) stretching from -COOH group. The narrow bands seen at 1269.77 and 1203.41 cm^{-1} could be attributed to υ(C-O) stretching. The weak intense bands appear at 1489.03 and 1417.47 cm^{-1} are due to υ(C-H) bending vibrations. All the IR absorption bands observed of the free ligand agree well with the proposed structure. The IR spectra of Cu(II) and Zn(II) metal complexes of the Schiff base ligand is presented in fig. 2 & 3.

In the metal complexes, the characteristic υ (C=N) stretching from azomethine observed at 1549.19 cm^{-1} is found to have shifted by 40 cm^{-1} with respect to the free ligand. The reduction in vibrational frequency confirms the complexation of the Schiff base with the metal ion where the ligand co-ordinates through the N-atom, which eventually reduces the double bond character of the C=N bond. Thus, the reduction in double bond character causes the observed shift in the spectra. The carbonyl vibrational frequency of the carboxylic group seen at 1699.24 cm^{-1} in the spectrum is appeared to have shifted due to co-ordination through carboxyl oxygen atom. Moreover, the aromatic moiety also exhibts the characteristic υ(C-H) vibrations at 3355.73cm^{-1}.

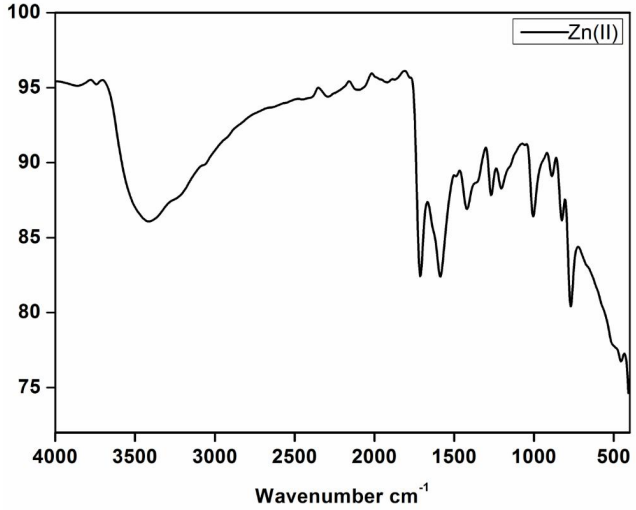

Fig.3 FTIR spectra of the synthesized Zn(II) complex with Schiff base ligand

3.2 NMR Spectroscopy

Proton NMR spectroscopy is a unique tool to characterize the molecular structure of synthesized Schiff base ligand and the metal complexes. The NMR spectrum of the Schiff base ligand is predicted by PerkinElmer ChemDraw 2018 v18.0.0.231 and is shown in figure 4.

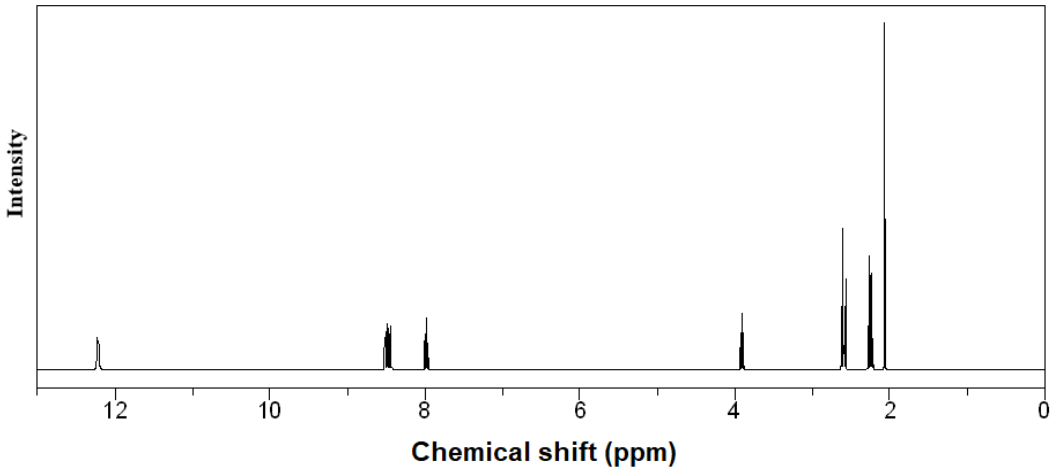

Fig.4 Predicted NMR spectra of the ligand derived from acenaphthoquinone and L-methionine

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The NMR spectra confirms the presence of eight unique protons in the ligand which is to be confirmed with the experimental data.

3.3 Electronic Structure Calculations

The structure optimization of the Schiff base ligand is carried out by performing molecular mechanics (MM2) force field calculations by minimizing the energy of the ligand. using the software suite PerkinElmer ChemOffice Suite 2018 v18.0.0.231. The energy minimized structure of the ligand is shown in fig. 5.

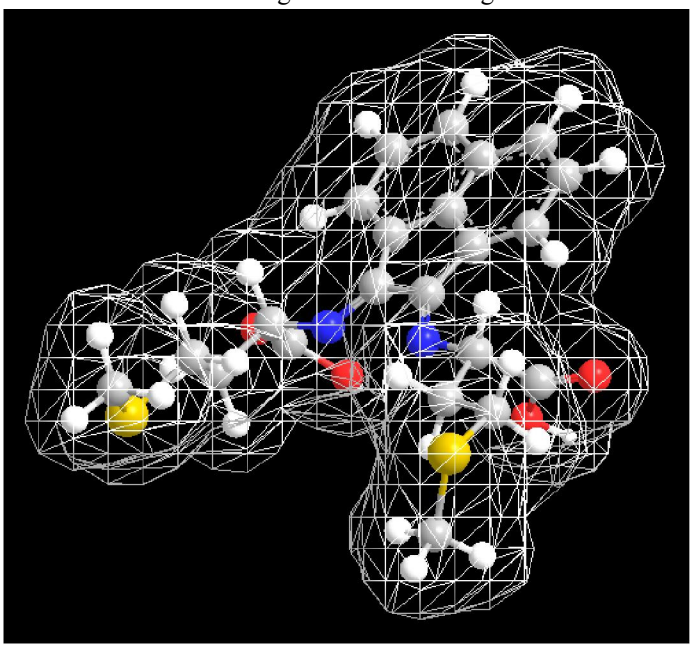

Fig. 5 Wire mesh model of the energy minimized Schiff base ligand.

The frontier molecular orbitals (FMO) in any given molecule, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), are crucial in determining the reactivity of the chemical species as they involve in chemical reaction either by gaining or losing electrons. The HOMO and LUMO of the optimized structure of ligand was calculated by extended Hückel method in ChemOffice Suite 2018 v18.0.0.231 and is shown in fig. 6.

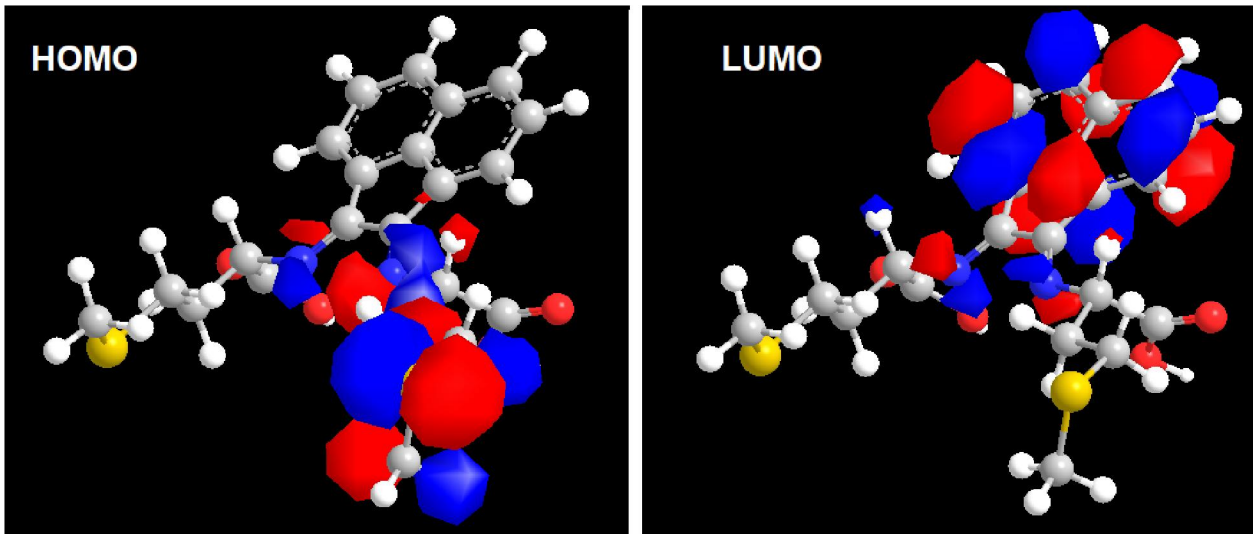

Fig.6 HOMO and LUMO of the structure optimized Schiff base ligand.

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3.4 Photocatalytic Characterization

The photocatalytic degradation efficiency of the synthesized Cu(II) Schiff base complex under sunlight were assessed by employing the thiazine dye, methylene blue, as the model in our experiments.

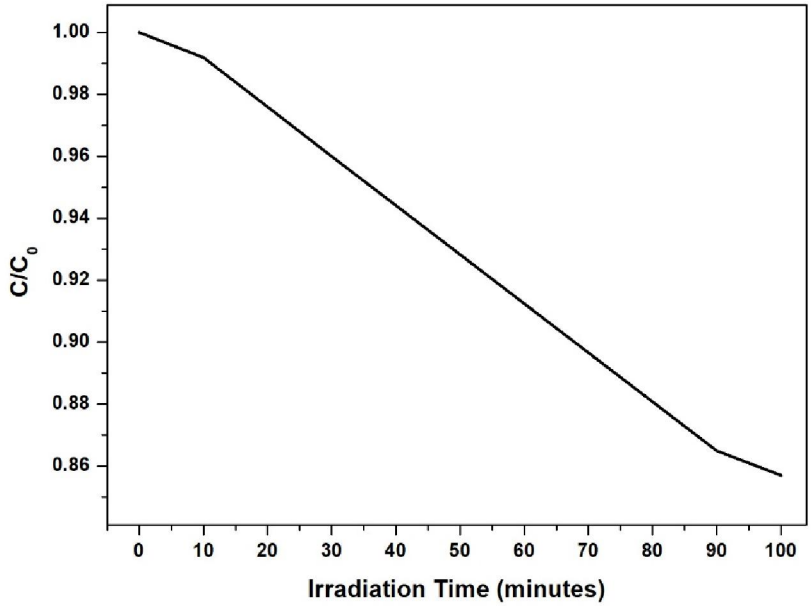

Fig.7 Sunlight-driven photocatalytic degradation of methylene blue as a function of time with Cu(II) Schiff base complex as the photocatalyst.

The change in absorbance of the dye with and without Cu(II) Schiff base complex (0.1 g of photocatalyst) was monitored as a function of time by withdrawing aliquots of 2 mL at regular time intervals. The relative change in the concentration of methylene blue dye as a function of time upon illumination with sunlight is shown in fig.7. It is obvious from the above plot that Cu(II) Schiff base complex demonstrates excellent photocatalytic activity.

The photocatalytic degradation of methylene blue dye with Cu(II) Schiff base complex appears to follow pseudo-first order kinetics as shown in fig. 8. However, a systematic analysis is necessary to understand the effect of dosage, dye concentration, pH and temperature.

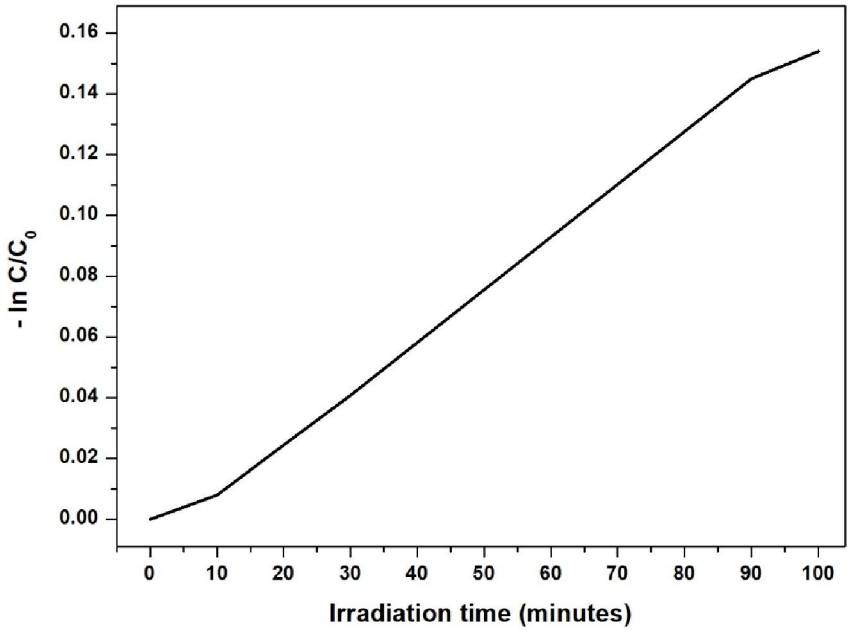

Fig. 8 Pseudo-first order kinetic plot showing the photodegradation of methylene blue.

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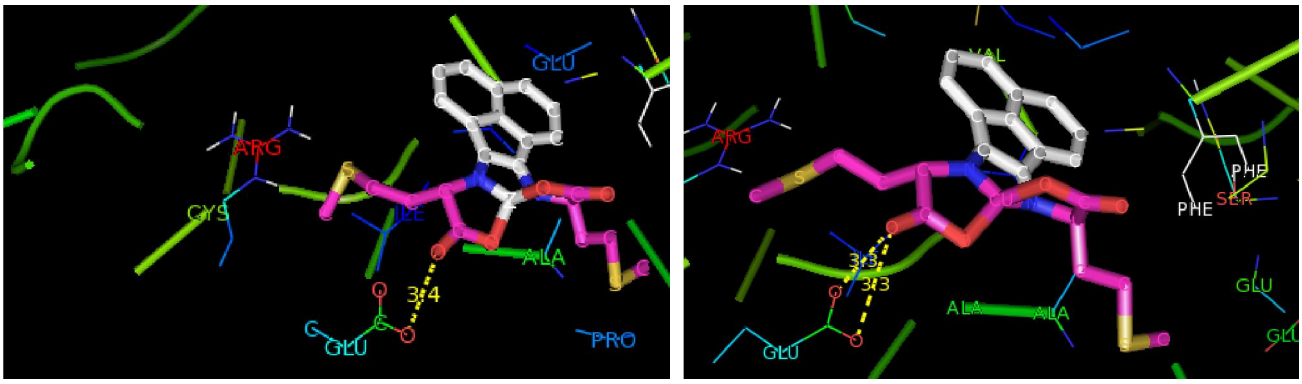
The preliminary results obtained in the present investigation suggests that Cu(II) Schiff base complex is a better photocatalyst in photodegradation of methylene blue dye under solar light illumination. The kinetics of photodegradation can be further established by acquiring more data to confirm the validity of the obtained results as well as to extract other kinetic parameters.

Molecular Docking Studies

The crystal structure of Crystal of human phospholysinephosphohistidine inorganic pyrophosphate phosphatase LHPP (PDB CODE: 2X4D) was retrieved from RCSB protein data bank and then minimized by Discovery studio (Accelyrisis). The synthesized Schiff base complex were drawn in the ACD Chemsketch tool and minimized by Avogadro. Molecular docking studies have been performed by PyRx software [30]. The Schiff base complex ZnL and CuL are having better binding against 2X4D protein with -7.1 and -7.2 kcal/mol respectively.

Table 1: The docking scores and hydrogen bond interaction of ZnL and CuL complexes with 2X4D

Protein	PDB	Schiff base complex	Binding score (kcal/mol)	No. of Hydrogen bonds	Complex atoms	Residues	Distance (Å)
Human phospholysinephosphohistidine inorganic pyrophosphate phosphatase LHPP	2X4D	ZnL complex	-7.2	1	O	GLU	3.4
		CuL complex	-7.1	2	O	GLU	3.3
					O	GLU	3.3



(a) ZnL with 2X4D **(b) CuL with 2X4D**

Fig. 9 The hydrogen bond interaction between ZnL and CuL complex with the protein 2X4D

The binding pose of metal complexes with 2X4D is obtained by PyMOL graphical system. The docking scores and hydrogen bond interactions are shown in Table 1. Only one hydrogen bond is formed between the protein-ZnL complex with distance 3.4Å and two hydrogen bonds are formed between the protein-CuL complex with 3.3 Å and 3.3 Å respectively. The hydrogen bond interaction, bonded residues and bond distances of metal complexes ZnL and CuL with 2X4D protein is shown in fig. 9. The molecular docking studies clearly explain the synthesized Schiff base complexes are having good biological activity.

IV. CONCLUSION

The present investigation deals with the synthesis of transition metal(II) complexes based on Schiff base ligand derived from the condensation of acenaphthoquinone and L-methionine. The formation of Schiff base by condensation and complexation of the ligand with Cu(II) and Zn(II) is analysed by FTIR spectroscopy.The geometry of the ligand is optimised by energy minimization using molecular mechanics (MM2) force field method. The frontier molecular orbitals (FMO), HOMO and LUMO, of the optimized structure is calculated using semi empirical extended Hückel molecular orbital method. The photocatalytic activity of the Cu(II) chelates were investigated for degradation of thiazine dye, methylene blue, following the absorbance of dye with time.The results of the present study indicate that Cu(II) chelates are good candidate for process involving light harvest applications, photocatalysis, artificial photosynthesis and water splitting. The binding affinity of Schiff base complexes ZnL and CuL with the recombinant

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protein human phospholysinephosphohistidine inorganic pyrophosphate phosphatase has been investigated by docking studies, whose binding score is estimated to be -7.1 and -7.2 kcal/mol respectively.

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