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Preparation of Symmetrical Tetraphenyl Porphyrin Metal Complexes and Their Spectroscopic Studies

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Abstract

Porphyrins molecules are gaining importance in the present era. Porphyrins are important part of biological molecules like hemoglobin and chlorophyll .Photo system 1 and photo system 2 is important sunlight trap in chloroplast. Electron transport chain is a series of chemical reaction in which energy is formed in the form of ATP (Adenosine triphosphate).The members of electron transport chains are cytochrome 450 which are Porphyrins like molecules. Porphyrins are important part of solar cells, apart from above mentioned application; Porphyrins have special importance in the photodynamic therapy. This therapy has special role in the treatment of acne; psoriasis .Photodynamic therapy has successfully treated various kinds of malignant cells and has special role to treat cancers. The present thesis addresses the formation of tetra phenyl porph1yrins through Adler and Ruthmend synthesis .This is the common chemical reaction which can be obtained in the university laboratories. The tetra phenylporphyrin, developed from above mentioned method were converted into metal complexes. Four metals iron, cobalt, copper and nickel have chosen in the form of their chlorides and acetates. Porphyrin synthesis is a challenging approach as it contains various forms of impurities and it is very difficult to analysis the complex formation. The present paper contains different Porphyrins metal complexes which have been developed and the formations of complexes were confirmed through IHNMR (nuclear magnetic resonance spectroscopy) analysis which is the strongest tool in the modern chemistry. The formation of complexes can be further confirmed by infra-red spectroscopy and ultraviolet spectroscopy. Atomic force microscopy was also conducted and all the analysis confirmed the formation of tetra phenylporphyrin and its metal complexes.

Keywords: Hematite; sol-gel method; photo-electrochemical cell; carbon nanotubes.

1. Introduction

Porphyrins are heterocyclic macromolecules composed of four modified pyrrole subunits connected through alpha carbon. This linkage is attached with methane bridges. [1]Porphyrin nucleus belongs to tetra dentate ligand. When two protons are removed from pyrrole nitrogen, leaving two negative charges, coordination occurs. Porphyrin nucleus contains 22 pi electrons. The extensive pi conjugation of the

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Porphyrin ring system originates the absorption of visible light. That is why most of the Porphyrins are colored compounds and they are derived from Greek word purple. Intetra phenylPorphyrin four pyrrole units are attached with four methanebridges. If the substituent is attached at meso position then these class of Porphyrins are called as mesotetra phenylPorphyrins. Porphyrinsmolecules are chiral in nature they are stereo selective molecules.

It is a pigment present in the plant cells. The basic role of chlorophyll molecule is the trap of sunlight through photo system 1 and photo system [2][3]. This energy is used in the process of photosynthesis during dark reaction. The light is absorbed during light reaction by Porphyrin like chlorophyll molecules.

The best example of energy trap can be explained in solar cell which contains Porphyrin as central role. In solar cells Porphyrins molecules can be used as sensitizer [4)][5].

Atoms are combined in molecules through covalent bonds. According to new horizons Porphyrins can attach other moieties through hydrogen bonding .This phenomenon can be seen in the DNA molecules. [6]

Porphyrins can be used to develop macro molecules .Dimerporphyrins can also be prepared and these macromolecules can be attached to any other molecules like dextrin's to enhance its capability of trapping the energy [7].

Porphyrins and its various metal complexes can be used as an excellent structure for the delivery of drug to the targeted sites. Cisplatin, an anticancer drug can be transported to malignant tissues through Porphyrin caged nanoparticles. Its photo sensitizer activity can be used to treat the cancer [8] and variety of infections and found effective against variety of viruses. Recently drugs are encapsulated in carbon nano tubes along with Porphyrins [9]. Various pharmaceutical companies have developed Porphyrins type ear drops [10]. Most of the drugs are not reached to the target tissues. Drug delivery can be enhanced with combining Porphyrins with other molecules. Shelf live and durability of drug can be enhanced by using Porphyrin molecules [12].

2. Materials and Methods

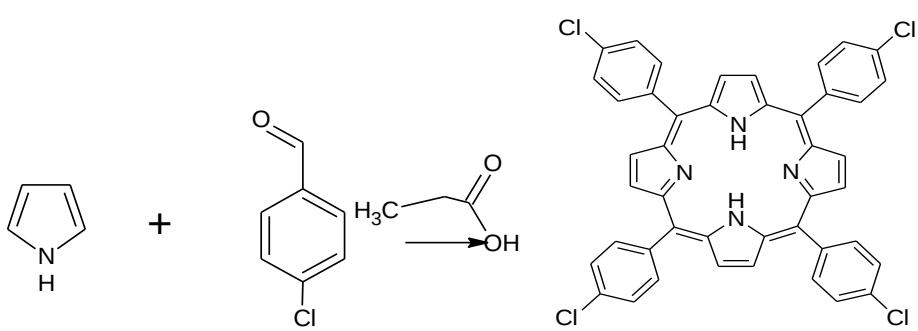
2.1 Chemicals and instrumentation

2.1.1 Materials

The chemicals used in the research were of analytical grades and were used in sigma and eldritch quality. The quality of Pyrrole and aldehydes were of Analytical grade. Solvents used in the research work were tetrahydrofuran, carbon tetrachloride, dichloromethane, n-hexane and Cyclohexane. Pyrrole taken was pure and was used as received without purification.

2.1.2 Instruments for Analysis

FT-IR model FTS 4800 MX spectrophotometer (USA) was employed in the frequency range of 4000-400 cm-1 using KBr pellets. 1H NMR and13CNMR spectra were obtained on a Bruker 300MHz NMR Spectrometer in deuterated chloroform using teteramethylsilane as internal reference. UV-Visible spectra of the Porphyrin and the complexes were recorded in chloroform by double beam UV-Visible Spectrophotometer 1601 in the range 200-800 nm, with a light source deuterium l. amp, 50 W halogen lamp and quartz cells with path length of 1 cm.



Scheme 1 Scheme of reaction

2.2 Formation of tetra phenylporphyrin and their metal complexes

2.2.1 Synthesis of tetra phenyl Porphyrins

The amount of 20.6 g of 4-chlorobenzaldehyde was taken in the round bottom flask and it was fitted with water condenser. Round bottom flask was placed on the heating mental. The amount of 350 ml of propionic acid was added in the round bottom flask and refluxes it 5 to 10 minutes. The temperature of heating mantle was set around 60 centigrade after 10 to 15 minute's pyrrole was added from the top of the condenser in 10 ml and the reflux time is 20 to 30 minutes. [23]Propionic acid is separated by vacuum distillation and the compound is washed with methanol and mixture was allowed to cool and the crystals of TPP were filtered through Buckner funnel. [24]The crystal was dried in vacuum desiccators. Purple color of compound was obtained and the yield is 13%. M.P is 350C0. The compound name is 5, 10, 15, 20-tetrakis (4'-chlorophynyl) Porphyrins (TCPP).

3.1 5,10,15,20-tetrakis (4-chlorophynyl) porphyrinatometal(II) synthesis

The amount of 0.5 g of TCPP was dissolved in 1.766g of metal chloride or cupric acetate with the presence of DMF (50 ml) and refluxed it for 5 to 6 hours. These chemicals were taken in the round bottom flasks and a condenser is set on a heating mental. The temperature was set at 60 to 70 °C. It is the continuation of two pot synthesis. The scheme of complex formation has been discussed in the scheme 118.The formation of the complex can be confirmed by TLC analysis after every half an hour. The solvent mixture is in the ratio of 1:3 of chloroform and normal hexane. TLC Analysis will show the two bands of which one will be of TCPPM and after the reflux the DMF will remove in half of quantity through vacuum distillation. In the final step the complex will be treated with 6M HCl solution. In this respect 20 ml of 6 M HCl solution will be taken. The complex formed will be filtered and TLC analysis will confirm the no color change in HCl solution. The melting point of the products are 350°C. Although one pot synthesis has advantage over two pot synthesis. In one pot synthesis yield of the complex is better but it is very difficult to handle the impurities. Secondly in one pot synthesis pure Porphyrins cannot be obtained. The remaining impurities in the complex can be removed by column chromatography.

4. Results and Discussion

4.1 Structural analysis of tetraphenyl porphyrin and its transition metal complexes

Structural analysis of tetraphenyl Porphyrin (TCPP) and its transition metal complexes was performed by NMR spectroscopy which is an important tool for the structural elucidation of the compounds. 1HNMR analysis of TCPP and its Fe, Co, Ni and Cu complexes TCPPFe, TCPPCo, TCPPNi and TCPPcu was carried out in CDCl3 solvent containing tetramethyl silane (TMS) as internal reference. The proton NMR data of the compounds analyzed is presented in table 1.

Table 1 Proton NMR data of tetraphenyl Porphyrins and its transition metal complex

	Chemical shift/ppm				
Porphyrin	**proton**				**Jo-m/HZ**
	B-pyrrolic H	**ortho**	**meta**	**N-H**	
TCPP	8.87	8.17	7.79	2.85	9
TCPPCo	9.08	8.04	7.78	Not obs	8.7
TCPPFe	8.59	8.56	8.05	Not obs	8.1
TCPPNi	8.7	7.9	7.7	Not obs	8.4
TCPPCu	8.87	8.17	7.79	Not obs	9

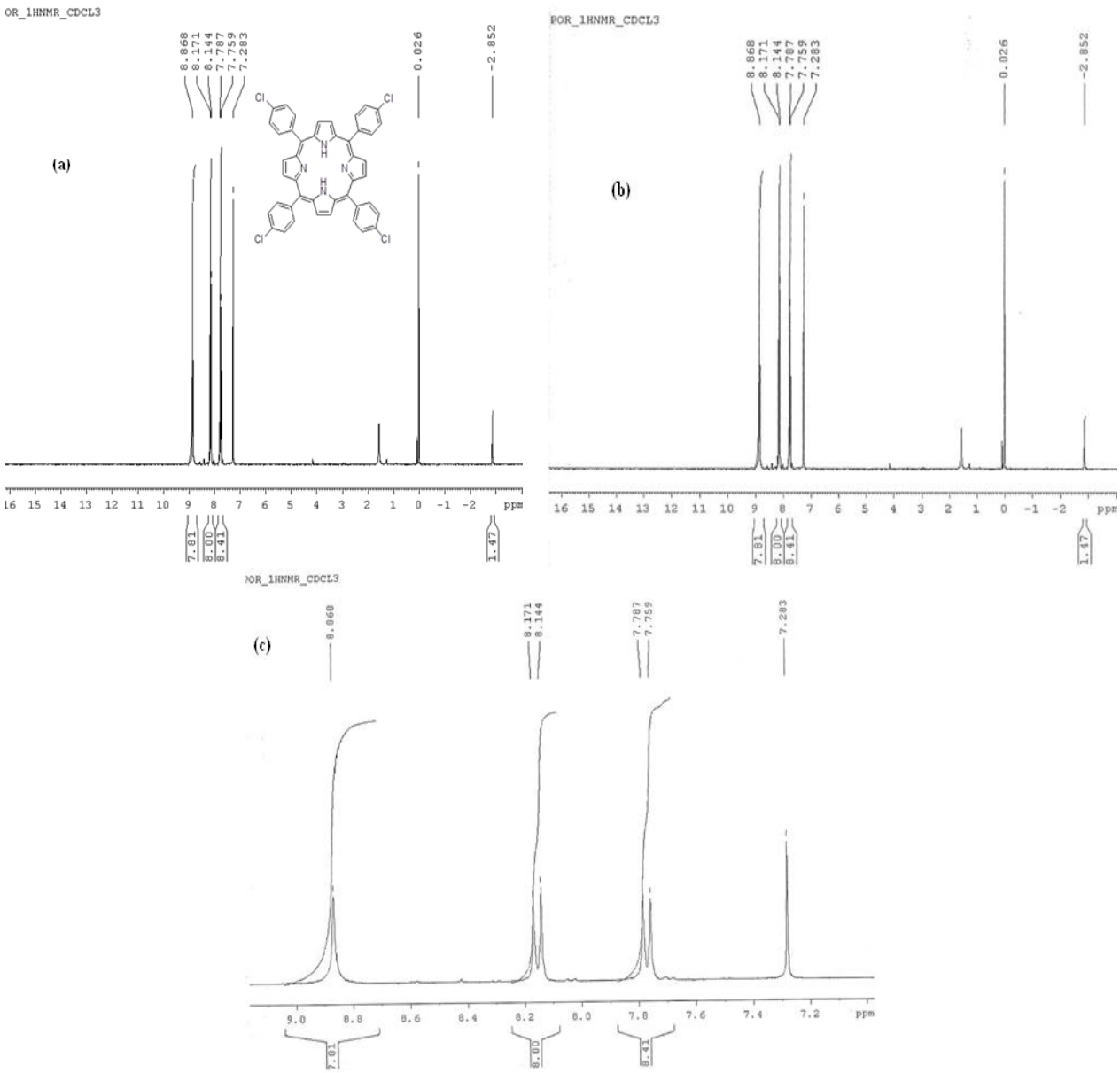


Figure 1(a). 1HNMR spectrum of tetraphenyl porphyrin recorded in CDCl3. **(b & c)**. 1HNMR spectra of tetraphenyl porphyrin recorded in CDCl3.

Table 2 Proton IR data of tetra phenyl Porphyrins and its transition metal complex

Compound	1νN-H cm	νC-H cm	NC=C cm	νC-N cm	νM-N cm	νM-Cl cm	2νN-H cm	ν(CH2)n cm
TCPP	3305.7	2926	1511	1177	---	---	981	730
TCPPFe	3522	3024	1395	1232	1012	416	997	723
TCPPCo	3361	2780	1634	1350	1014	434	965	715
TCPPNi	3365	2780	1626	1350	1014	440	1003	791
TCPPCu	2358	2170	1368	1218	980	411	986	702

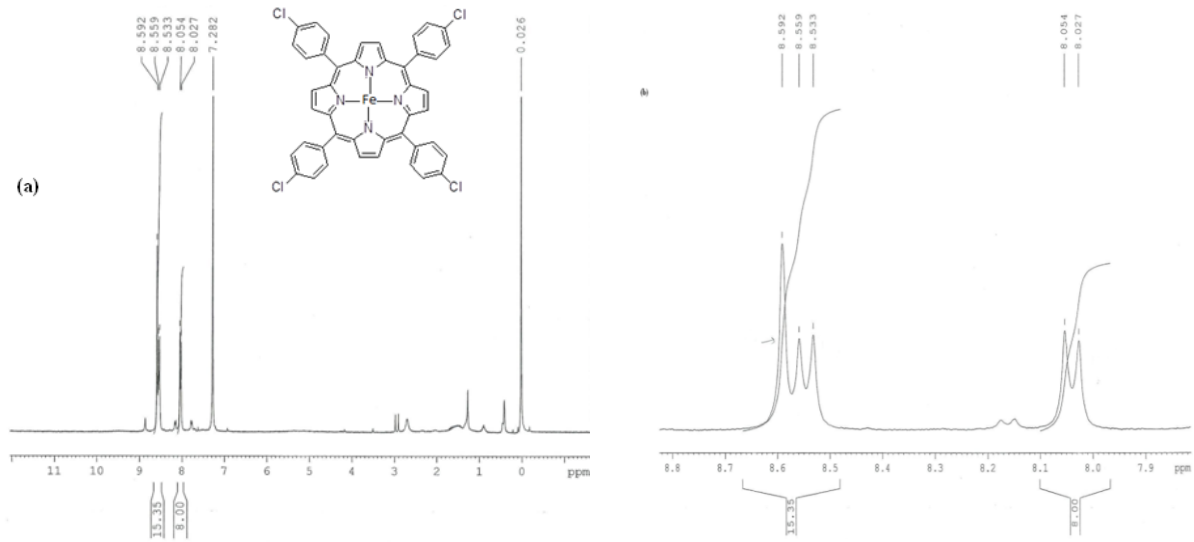


Figure 2. (a) 1HNMR spectrum of tetraphenyl porphyrin iron complex recorded in $CDCl_3$. (b) 1HNMR spectrum of tetraphenyl porphyrin iron complex recorded in $CDCl_3$.

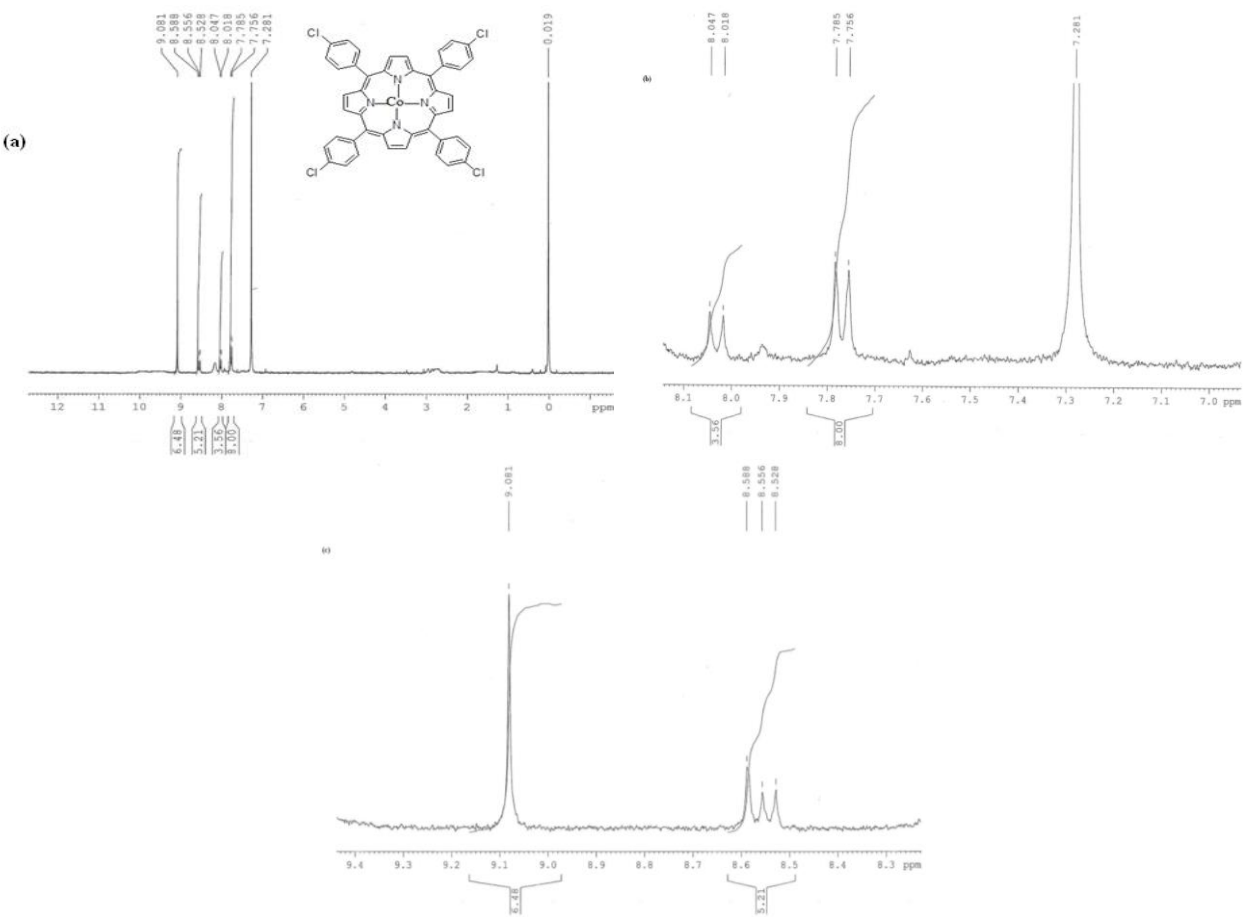


Figure 3. (a) 1HNMR spectrum of tetraphenyl porphyrin cobalt complex recorded in CDCl3. (b) 1HNMR spectrum of tetraphenyl porphyrin cobalt complex recorded in $CDCl_3$. (c) 1HNMR spectrum of tetraphenyl porphyrin cobalt complex recorded in $CDCl_3$

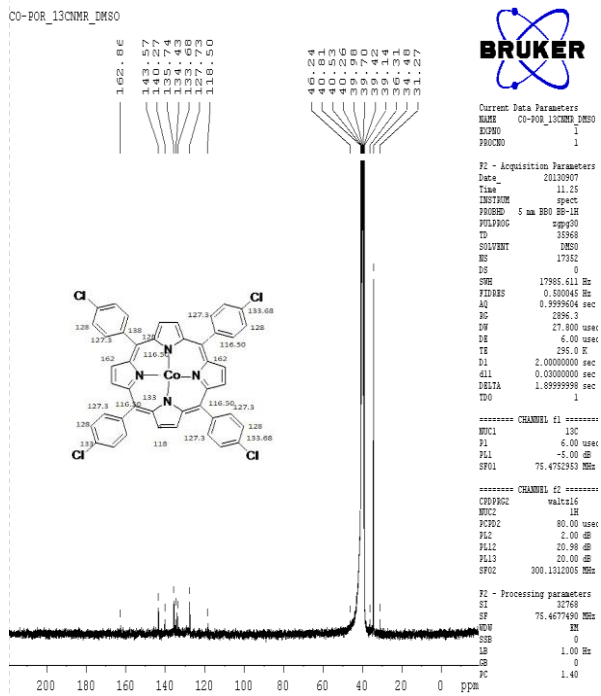


Figure 4. 13C NMR spectrum of tetraphenyl porphyrin cobalt complex recorded in DMSO.

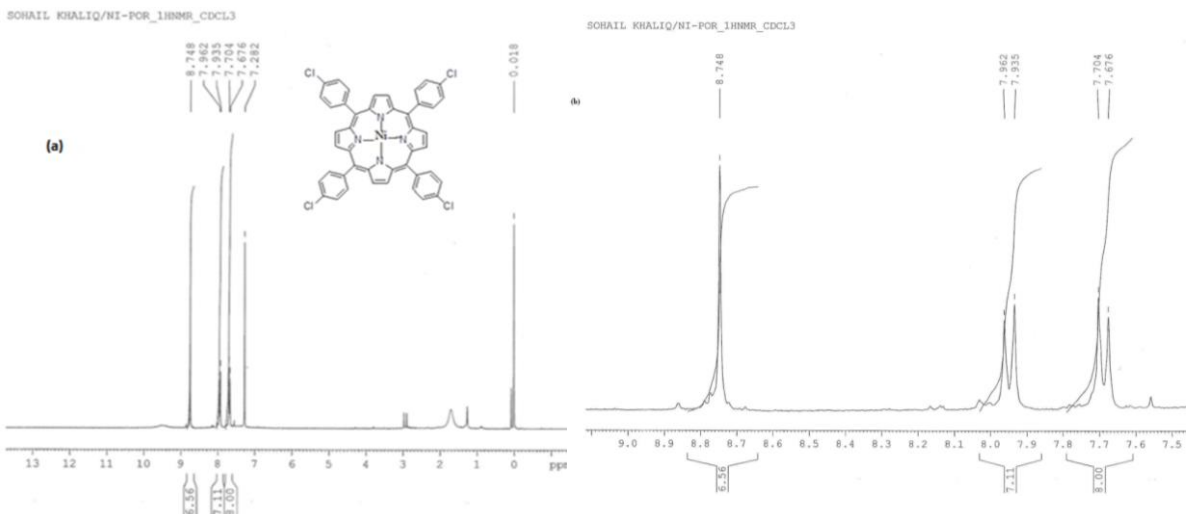


Figure 5. (a) 1HNMR spectrum of tetraphenyl porphyrin nickel complex recorded in $CDCl_3$. (b) 1HNMR spectrum of tetraphenyl porphyrin nickel complex recorded in $CDCl_3$.

Table 3 UV ANALYSIS RESULTS

Compounds	λmax/nm				
	Soret bands	**Q1 band**	**Q2 band**	**Q3 band**	**Q4 band**
TCPP	414, 424	516	550	590	648
TCPPFe	420, 449	514	550	610	665
TCPPCo	410, 430	527	587	615	648
TCPPNi	410.5, 440	527	547	588	663
TCPPCu	415, 448	516	550	590	648

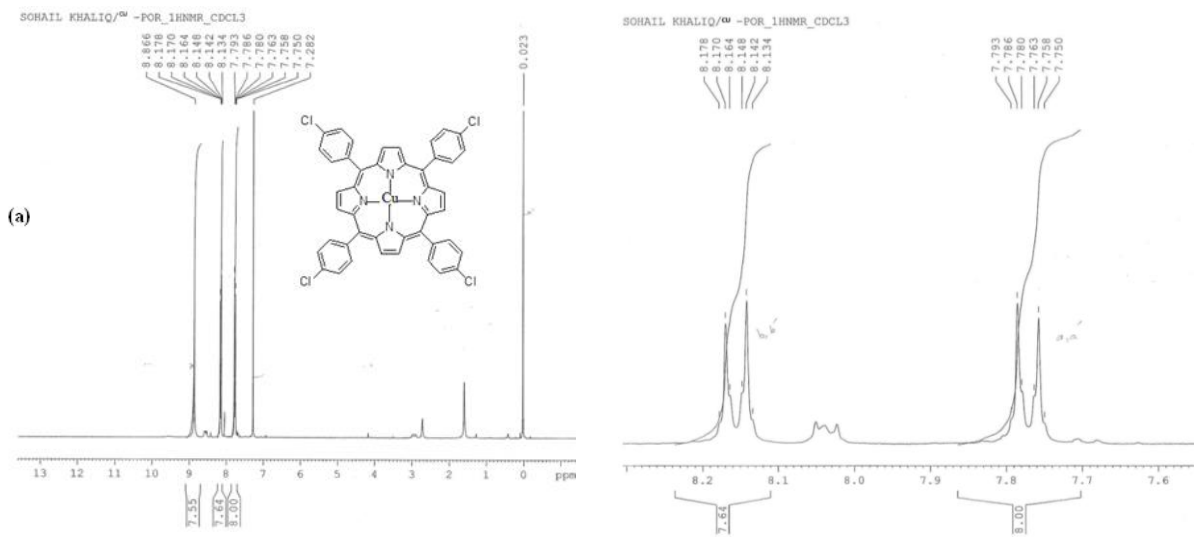


Figure 6. (a) 1HNMR spectrum of tetraphenyl porphyrin copper complex recorded in $CDCl_3$. (b) 1HNMR spectrum of tetraphenyl porphyrin copper complex recorded in $CDCl_3$.

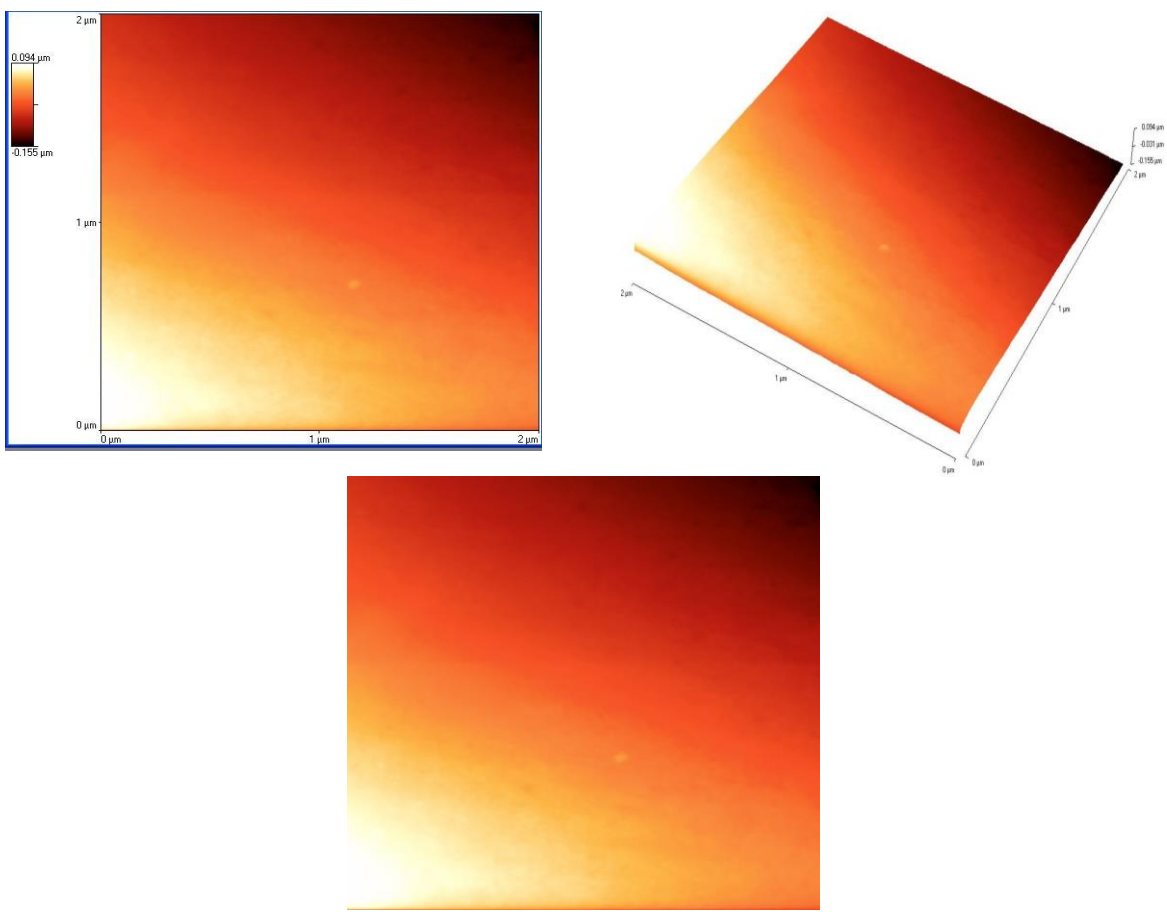


Figure 7. (a) Atomic force microscopic image of tetraphenyl porphyrin cobalt complex. (b) Atomic force microscopic image of tetraphenyl porphyrin cobalt complex. (c) Atomic force microscopic image of tetraphenyl porphyrin cobalt complex.

4.2 Infrared analysis of Porphyrin and its transition metal complexes

Infrared analysis of tetra phenyl Porphyrin and their metal complexes have been analyzed. It is an important tool to predict the presence of certain functional groups and also it predicts the formation of metal complexes of different ligands. The IR data of the Porphyrin and its metal complexes is given in tabulated form (Table 2).

The UV-Visible absorption spectra of TCPP and its complexes were recorded in chloroform as a solvent and corresponding spectroscopic data is given in table 3. UV-Visible analysis of TCPPFe was carried out in chloroform and its observed UV-Visible spectrum is presented in fig. 4.11. The observed Q bands are at 514, 550, 610 and 665 nm and the Soret bands are found at 420 and 449 nm. When the iron ion was inserted into the Porphyrin ring and then coordinated with four N atoms, the iron ion located in the center of Porphyrin ring to form the iron Porphyrin compound. Then the number and the intensity of the Q bands decreased and the Soret band occurred slightly red shift (from 414 to 420 nm), which was the characteristics of iron Porphyrin compound formed. The reason might be that the structure symmetry of iron Porphyrin compound with D4h point group was improved and the energy gap decreased comparing with free base Porphyrin with D2h point group. UV-Visible spectrum of the TCPPFe depicts that the intensity of Q1 band is greater than the Q2 band which is indication for the stability of Fe Porphyrin complex formed13.

Raman spectra agree the formation of metal complexes. Further atomic force microscopy was also conducted to evaluate the structural and morphological changes of Porphyrins and their metal complexes.

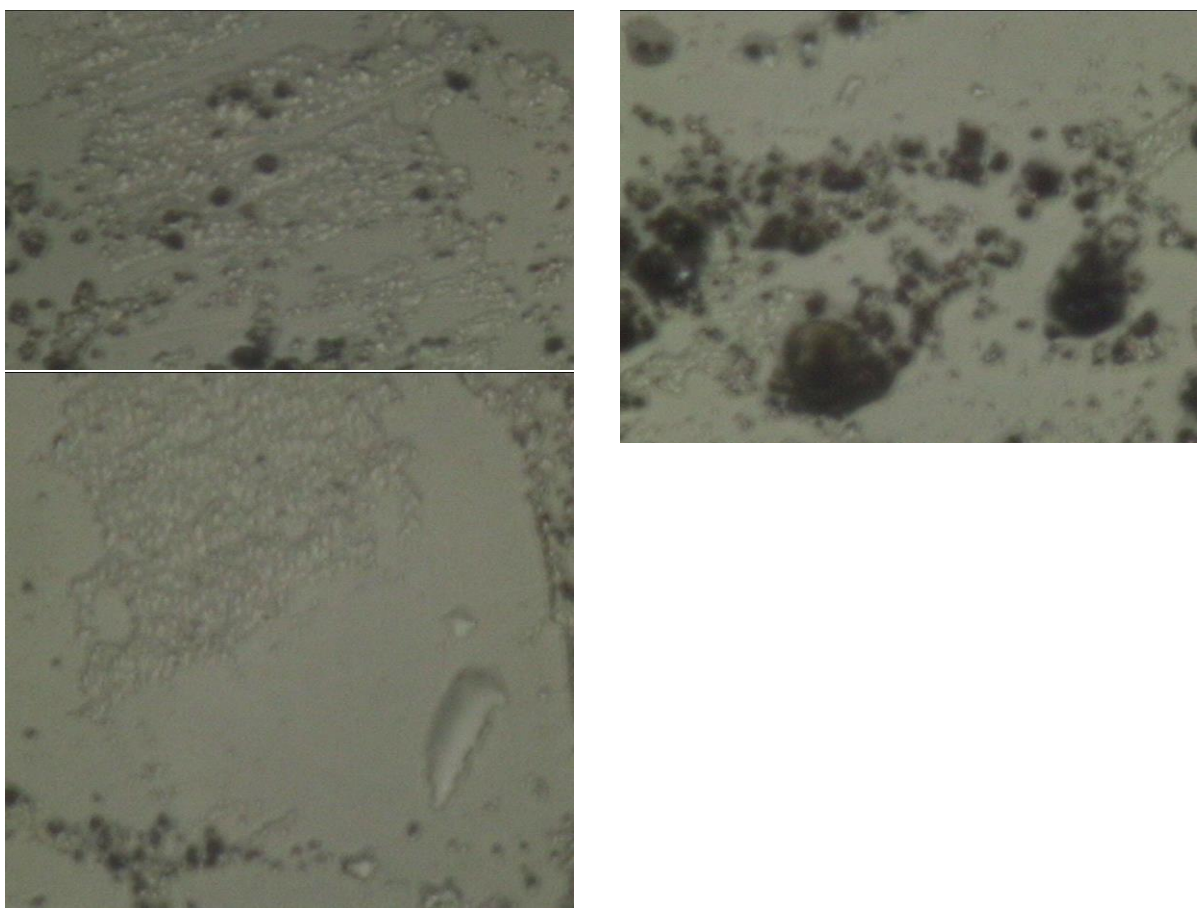


Figure 8. (a) AFM image showing aggregates of tetraphenyl porphyrin cobalt complex on glass surface. (b) AFM image of tetraphenyl porphyrin cobalt complex aggregates on glass surface

5. Conclusion

Different metal complexes of Porphyrins have been successfully prepared. These complexes can easily be used in the manufacturing of solar cells. Energy crisis can be solved by excellent energy trap of Porphyrins molecules. Tetra phenylporphyrin can be prepared in the laboratory and their synthesis at industrial level can be then turning point. Photodynamic therapy has revolutionized the world of medical science. Different diseases like cancer, infections and acne can easily be curbed by tetra phenylporphyrin used. Formation of tetra phenylporphyrin and their metal complexes can be confirmed by 1HNMR (Proton nuclear magnetic resonance spectroscopy), considering it the most powerful tool in the chemistry. The other tools were infrared spectroscopy along with ultraviolet spectroscopy. The synthesis of tetra phenylporphyrin addresses various kinds of impurities due to side reactions and their purification and spectroscopic studies are successfully conducted in the thesis. Raman spectra successfully explained the symmetry of tetra phenyl complexes and atomic force microscopy explained the behavior of complexes on various surfaces and proved the catalytic and sensing qualities of tetra phenyl Porphyrin complexes.

6. References

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