

ONE POT SYNTHESSES AND CHARACTERIZATION OF MESO-5, 10, 15, 20-COPPER TETRAPHENYLPORPHYRIN

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ABSTRACT

A one pot synthesis route was used to produce meso substituted copper based metalloporphyrin [copper-tetraphenyl porphyrin (CuTPP)] using N, N-Di Methyl Formamide (DMF) as the solvent with 258 mg yield on the actual precursor using nitrogen as inert gas. 11.4% yield was obtained with the current strategy. The synthesized CuTPP was characterized using Carbon-Hydrogen-Nitrogen (CHN) analysis, Ultraviolet-Visible (UV-Vis) spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy, X-Ray Diffraction (XRD) and Microwave Plasma - Atomic Emission Spectroscopy (MP-AES). The metal loading was found to be about 20.375 % on the porphyrinic ligands.

Keywords: Copper Tetraphenylporphyrin(CuTPP);CO₂; Methanol.

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INTRODUCTION

Metalloporphyrins (MTPP) being remarkable precursors in the supra-molecular chemistry have established their importance for photodynamic, photochemical and photo-physical research and a green alternative. Porphyrins (P) with a general arrangement of delocalized π electrons are a kind of macro-cyclic organic molecules. They may easily be modified by linking different peripheral surrogates, exchanging the central metal or expanding the size of the macrocycle^{1,2}. MTPP have shown enhanced photocatalytic properties over bare metal oxide catalysts when used as a catalyst³⁻⁶ and copper (Cu) as a metal has shown to be very effective as a catalytic support in the carbon dioxide hydrogenation⁷.

The metalloporphyrins can be made through various different methods but the most dominant of them is the condensation of an aldehyde with a pyrrole counterpart in a solvent because of higher yields⁸. The current work aimed to synthesize metallized tetraphenyl porphyrin (TPP) in a one-step conversion of the TPP precursors to MTPP (M=Copper, Cu), that, has been used with a modification of the previously published procedure⁸, but the yield was calculated based on the original precursor and not on the porphyrin. Nitrogen was used instead of argon in order to study the effect on the catalyst yield but no possible conclusion could be reached so far as the free base porphyrin removal could not be achieved completely.

EXPERIMENTAL

Pyrrole (>97%), benzaldehyde (>99%) copper chloride dihydrate (99%) and N, N-di-methyl formamide (>99.8%), methanol (>99.9%), hydrochloric acid (37%) were received from Merck. Dichloromethane (CH₂Cl₂) (99.5) and chloroform (CHCl₃) (>99.4) were purchased from R&M Chemicals locally. Nitrogen gas with a purity of 99.995% was supplied by MOX.

Synthesis of CuTPP

Equimolar ratios of freshly distilled pyrrole and benzaldehyde were mixed with HCl as the catalyst in N, N-dimethylformamide using a one pot synthesis route⁸ under nitrogen atmosphere for one hour. The

mixture was refluxed over an oil bath at 145°C and 160°C for 3, 4 and 8 hours respectively but the yield of the resulting metalloporphyrin remained same which infers that there is no effect of temperature and time on the product quantity. After cooling, the purple catalyst crystals were removed via vacuum filtration and then washed with DMF (50 ml) 3 times, methanol (50 ml) 3 times and then with hot DI water. The crystals were subsequently dried in an oven for 12 hours at 110°C and finally dried under vacuum for 4 hrs.

The product was then dissolved in dichloromethane and passed over alumina column for purification and analyzed via TLC for purity. The dichloromethane was then dried using rotary evaporator under vacuum. The product was then stored in a desiccator prior to characterization. The yield of the CuTPP was calculated using Equation-1. Yield of 258 mg CuTPP was obtained through this procedure which is an acceptable yield based on the initial porphyrin⁸.

$$\text{Yield} = \frac{\text{Actual yield}}{\text{Theoretical Yield}} \times 100 \quad (1)$$

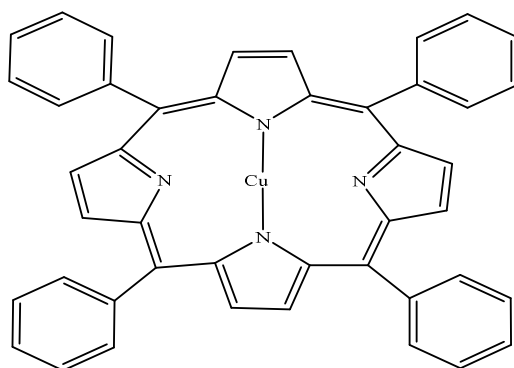


Fig.-1: CuTPP molecular structure

RESULTS AND DISCUSSION

CHN Analysis

The CHN analysis was performed using the elementary vario micro cube which gives; (anal.) C-86.16%, H-4.565%, N-9.266%, (calc) C-86.27%, H-4.57%, N-9.15%, which is in a good agreement with ⁹ with the product $\text{CuC}_{44}\text{H}_{28}\text{N}_4$.

XRD Analysis

The XRD analysis was done using Bruker D8 Advance instrument with Cu K alpha radiation from 10-30 (2θ range) with step size of 0.020 and at 25°C. The XRD pattern clearly depicts the metalloporphyrin.¹⁰⁻¹² and the following peaks could be identified based on the published results with the indication in the Figure-2, wherein it can be seen that the most prominent growth was along the (2 2 1) plane along the phenyl rings conjugation with the pyrrole ring structure.

FTIR Analysis

FTIR spectra in Figure 3, was obtained using Shimadzu FTIR-8400S from 400 cm^{-1} till 4000 cm^{-1} to study the functional groups of the synthesized CuTPP. The results are in good agreement with the literature for the metallation of porphyrin ligands.¹⁰⁻¹⁴ Table-1 contains the specific information on the identified peaks. In FT-IR spectra, the peak at 999.06 cm^{-1} is due to the pyrrole ring breathing mode, which also confirms the formation CuTPP. The vibrational stretching of the half and quarter-ring is in the range of $1342\text{--}1398\text{ cm}^{-1}$ as depicted by the peak at 1340.43 cm^{-1} . The 833.19 cm^{-1} peak correspond to the in-plane distortion of the pyrrole ring. The peak at 1593.09 cm^{-1} credited to the asymmetric vibrational stretching of the C--bond.

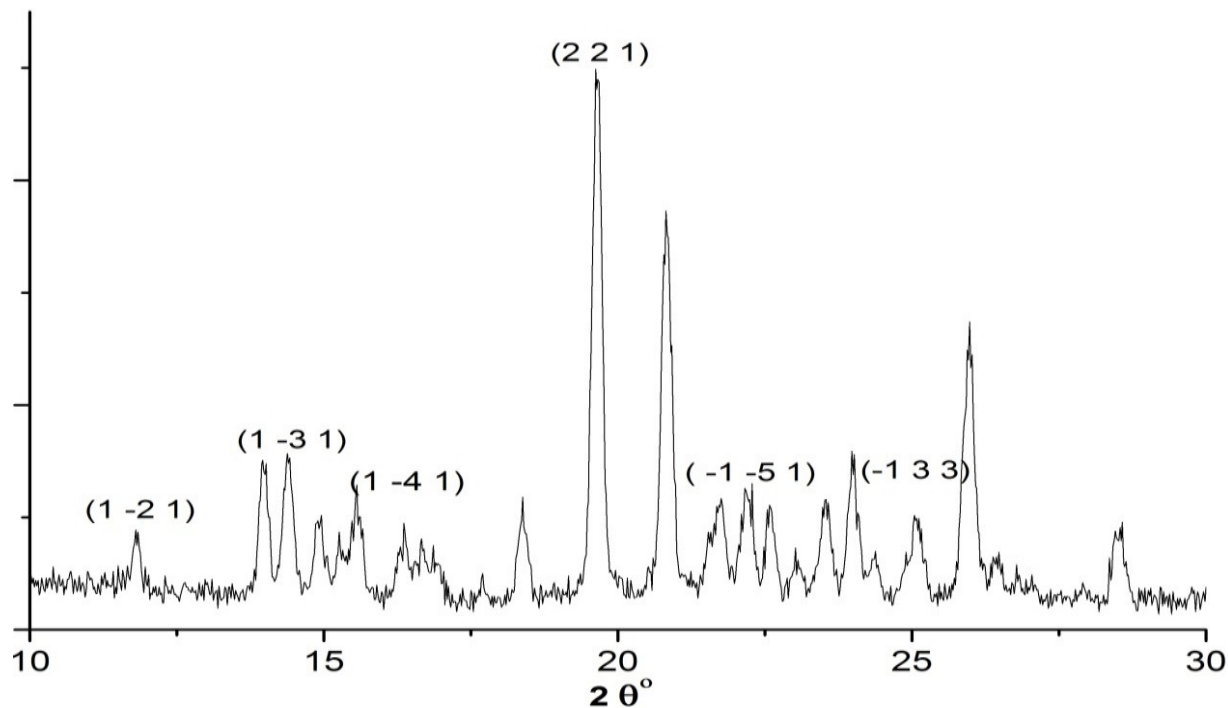


Fig.-2: XRD pattern of the CuTPP

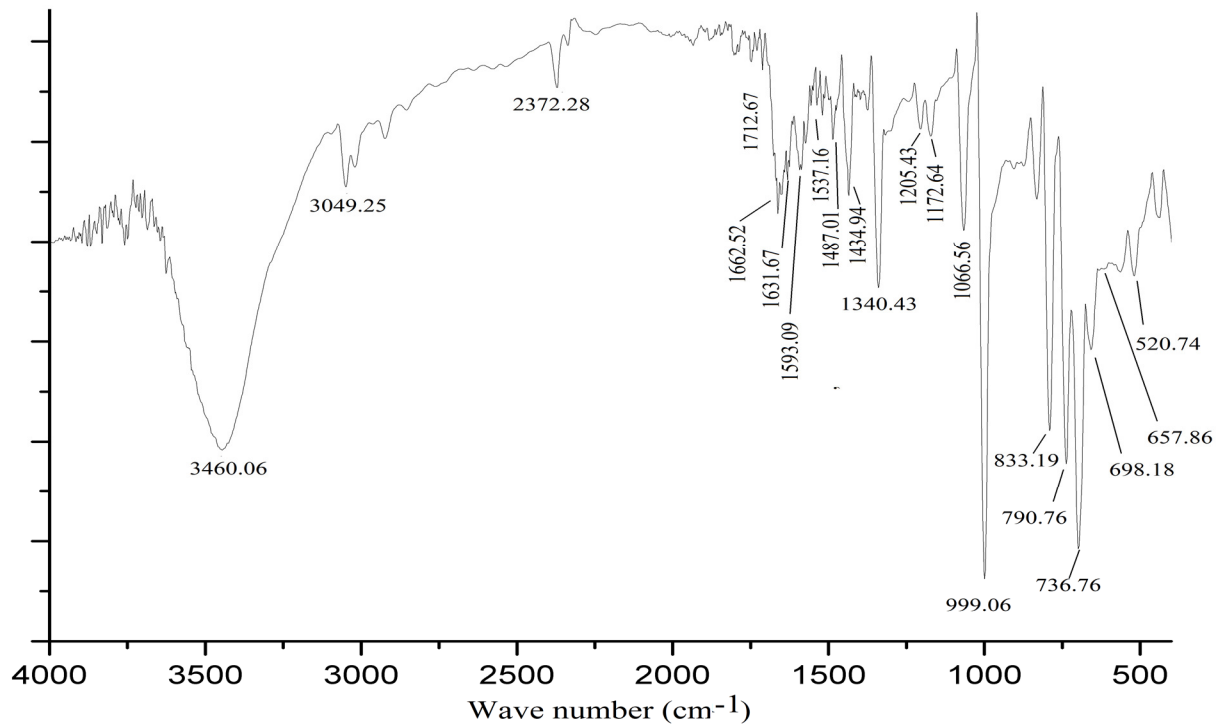


Fig.-3: FTIR spectrum of CuTPP

The peaks, at the 1631.67 cm^{-1} and 1662.52 cm^{-1} , are due to the asymmetric stretching of C=C vibrational mode. The 1432–1536 cm^{-1} spectral region in the IR spectra contains several closely spaced bands. The 1572–1576, 1484–1507 and 1432–1441 cm^{-1} peaks are identified as the stretching vibration of the C-C bond. The signal at 1066.56 cm^{-1} gives the stretching vibrations of the C-C and C-N bonds. The peak at 3460.06 cm^{-1} can be ascribed to the O-H stretching.

Table-1: FTIR spectra in Tabular form

Peak(s) cm^{-1}	Mode	Description
657.86	--	Phenyl ring bendings
736.76	C-C-H	Out of plane bending vibrations
790.76	C-C-N	Out of plane bending vibrations
833.19	--	in-plane distortion of the pyrrole ring
999.06	C-C,C-N	pyrrole ring breathing mode
1066.56	C-C-H,C-C-N	stretching vibrations
1172.64, 1205.43	C-H	Bending vibrations
1340.43	N-C-C, C-N-C	pyrrole half ring modes
1432–1441	C-C	stretching vibration of the C-C bond
1484–1507	C-C	stretching vibration of the C-C bond
1572–1576	C-C	Symmetric stretching vibration of the C-C bond
1593.09	C-C	Asymmetric stretching vibrations
1631.67, 1662.52	C=C	asymmetric stretching of C=C vibrational mode
3049.25	C-H	Stretching vibrations
3460.06	O-H	Broad O-H stretching for water molecules

UV-Vis Analysis

UV-Vis spectrum of CuTPP was obtained in chloroform using Agilent Cary 100 UV-Vis Spectrophotometer and diffuse reflectance spectroscopy is used to determine the optical absorption in the visible light region. The UV-Vis spectrum shows transition of electrons as a result of UV-Vis light interactions with chemical bonds. The wavelength absorbed by a bond is shown in the form of peaks. It produces information of the type of bonds present in the sample. The peaks in the range of 380-800 nm conclude that CuTPP is visible light active. In this region, peaks are given either by coloured compounds or aromatic compounds with longer conjugation e.g. natural products.⁶ The metalloporphyrins typically show smaller number of Q bands as compared to the free base porphyrin because the metallation increases the symmetry that results in less Q bands.¹

As shown in Figure-4, three peaks in the range of 250-600 nm represent the presence of conjugated compounds. The higher absorbance means that the sample is concentrated and that the data could be interpreted at even lower concentrations with ease. The 427 nm peak is the solet (S) band which indicates the presence of the porphyrin moiety in the catalyst sample and two Q bands 538 nm and 620 nm with large absorbance shows transition from free base porphyrin to confirm metallation.⁶

MP-AES Analysis

The mixed plasma atomic emission spectroscopy (MP-AES) model MY15100003 Agilent technologies was used in order to determine the copper loading into the porphyrin cages. The metalloporphyrin had to be dissolved in a concentrated acid for the organic ligands to be completely digested. For this procedure 50 mg of metalloporphyrin was dissolved in 24 ml nitric acid 65% and 4 ml HF for 10 hrs at 95°C over a hotplate until clear solution was obtained in a water bath and then the solution was filtered and deionized water was added till the solution was 250 ml and was calculated to be 40.75 ppm which is equivalent to 20.375 % copper loading on to the porphyrin. This is in good agreement with the values provided in literature.¹⁵

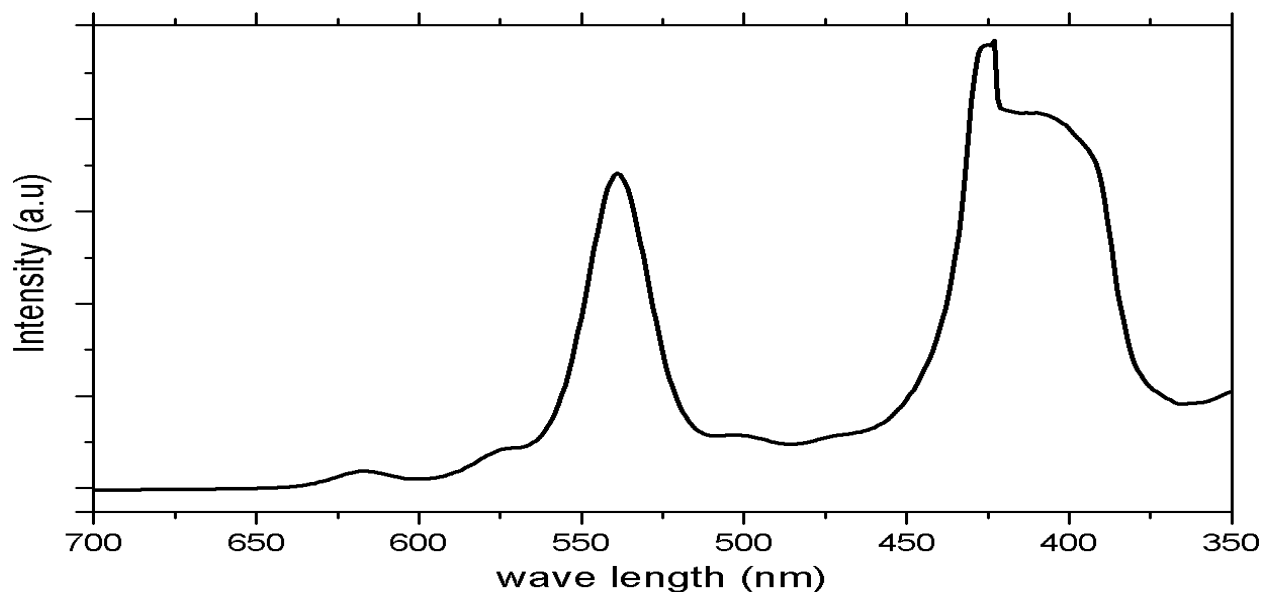


Fig.-4: UV-Vis spectra of CuTPP

CONCLUSION

Dark purple crystals of copper based tetraphenyl porphyrin (CuTPP) were successfully synthesized using pyrrole condensation under reflux (258 mg yield) and characterized for its photocatalytic behavioral studies which will be discussed in other publication. The UV-Vis spectra showed distinctive Soret (427 nm) and Q bands (538 and 620 nm) characteristic of the metalloporphyrin, FTIR spectra and XRD results have confirmed the synthesis of the target molecule and its UV and Visible light absorbance makes it a valid material for photocatalytic application. The metal loading was found to be in 11.35 % with the target porphyrin moieties. The initial mixture was kept in nitrogen atmosphere for better mixing without any oxidation of the pyrrole precursor, hence it can be said that, the prepared catalyst has a great potential to be used as photo catalyst under ultraviolet as well as visible light region for the reduction of CO₂.

ACKNOWLEDGEMENTS

Financial assistant from Universiti Teknologi PETRONAS (UTP) and Ministry of Higher Education Malaysia, FRGS No: FRGS/2/2013/SG01/UTP/02/2 is gratefully acknowledged.

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[RJC-1393/2016]