



Arid Zone Journal of Basic and Applied Research

Faculty of Science, Borno State University
Maiduguri, Nigeria

Journal homepage: <https://www.azjournalbar.com>



Research Article

Synthesis, Characterization, and Evaluation of Electrochemical and Thermal Properties of New Cobalt Phthalocyanine (Copc) using Phthalamide as Precursor

Aminu Dauda^{1*}, Abdul Ademola Olaleye¹, Sinan Saydam² and M.N.Yaro¹

¹Department of Chemistry, Faculty of Science, Federal University Dutse, P.M.B. 7156, Jigawa State, Nigeria

²Department of Chemistry, Faculty of Science, Firat University Elazig, Turkey

*Corresponding author: tasekkur@gmail.com

ARTICLE INFO:

Keyword:

Phthalamide,
cobalt phthalocyanine,
electrochemistry,
3-nitrophthalonitrile

ABSTRACT

Cobalt phthalocyanine was synthesized from 3-nitrophthalonitrile using phthalamide as a precursor. Nitration in position 3 of the phthalamide led to the formation of 3-nitrophthalamide; then dehydration by thionyl chloride in N, N-dimethylformamide led to the formation of 3-nitrophthalonitrile. Phthalonitrile derivative was prepared by a nucleophilic substitution reaction of 3-nitrophthalonitrile in the presence of K_2CO_3 as a base in a non-aqueous organic solvent. Cyclotetramerization of phthalonitrile in the presence of metal acetate,

$(Co(Ac)_2 \cdot 4H_2O)$ gave peripherally substituted metal phthalocyanine complexes. The structure of the synthesized compounds was characterized by different analytical tools such as UV-Vis, FT-IR spectrophotometry and cyclic voltammetry. The disappearance of the $C \equiv N$ stretching vibration from the IR spectra of phthalonitrile was observed at 2230 cm^{-1} . The FT-IR vibration results for cobalt phthalocyanine were found to be 1709 cm^{-1} , 1611 cm^{-1} and 1275 cm^{-1} for C=O, C=C and C-O respectively. Solubility of metal phthalocyanine complexes was found to be very low in common laboratory solvents such as tetrahydrofuran (THF) and dimethylformamide (DMF). The electronic spectrum of CoPc in dimethylformamide (DMF) showed intense Q absorption at 677 nm. UV-Vis spectra of phthalocyanines showed electronic spectra with two strong absorption bands, Q and B bands. The Q band was found in 600–750 nm and B at 300–400 nm for both. The thermal stability of the phthalocyanine derivative was checked by T.G.A and the degradation was observed to start at 300°C , which showed that the complex could withstand fairly high temperature. It could therefore be concluded that the metal phthalocyanine prepared in this study showed fairly high thermal stability and can be used for various applications such as dye.

Corresponding author: Aminu DAUDA, Email: tasekkur@gmail.com, Department of Chemistry, Federal University Dutse.

INTRODUCTION

Phthalocyanines are chemically and thermally stable compounds that can host more than seventy different metal ions in the central cavity (Zawadzka *et al.*, 2014). Since their discovery, phthalocyanines have been extensively used as colourants, but they also have been employed in different technological areas, such as photoconductive materials, light-absorbing layers in recordable CDs, photosensitizers in cancer therapy, and industrial catalysts (Gounden *et al.*, 2020). The word phthalocyanine was derived from the Greek word naphtha, meaning rock oil and cyanine, meaning blue (Chohan, 2015). Phthalocyanines are believed to have been discovered in 1907 as an accidental by-product of the synthesis of O-cyanobenzamide. The development of phthalocyanine started in the year 1928 (Alharbi, 2014). Phthalimide was found to be contaminated with a dark coloured impurity and the product was isolated to determine its nature. Samples of the impurity were collected but it was still mixed with the phthalimide. The two compounds were separated after treating the impure substance with boiling water. Phthalimide dissolved in the water but the impurity remained in its solid form, simple filtration separated the two. Further investigation found that the impurity was extremely resistant to both heat and most reagents (Alharbi, 2014). Phthalimide was made from phthalic anhydride and ammonia in a large enamel-coated iron drum (Cragg, 2010). Some small chips were found in the enamel of the drum leading them to believe that some iron had gotten into the phthalimide and created the impurity. It was determined that iron was the source of the dark colour and they set out to remove the iron. It was boiled in hydrochloric acid and the filtered liquid was tested with ammonium thiocyanate. Iron was not removable by these means. Attempts were made to dissolve iron compounds in

concentrated sulphuric acid. Concentrated nitric acid removed the colour and turned the substance into white precipitate when poured into ice-cold water. Isolation and examination revealed that it consisted of phthalimide (Armour, 2016).

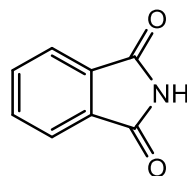


Figure 1: Phthalimide

There was a vigorous reaction with the formulation of a coloured product when cuprous chloride was added to molten phthalimide (Nuttet *et al.*, 2021). It was determined that the metals had to be a key part of the structure of this new compound. With this new element in the mix, the structure of the molecule was discovered. First, the empirical formula was determined using micro-combustion techniques. Once the empirical formula was obtained, the molecular weight was also determined, using the molecular weight and knowing that the product must have an isoindole skeleton similar to phthalimide, the structure was deduced. This structure was later confirmed by x-ray contour diagrams (Ding *et al.*, 2011). Phthalocyanine can be synthesized by many processes, such as heating derivatives of phthalic acid containing nitrogen as a functional group (Ding *et al.*, 2011). Conventional precursors are diiminoisoindoline and phthalonitrile. The heating of phthal anhydride is a useful route to metal-free phthalocyanine in the presence of Urea. The addition of metal salts helps this reaction to be more efficient. Other precursors include phthalimide and O-cyanobenzamide. Heating phthalonitrile in a sealed tube at a temperature of 350-360 °C for 7 hours, or by

heating the phthalonitrile to a temperature of 170-180 °C in triethanolamine for 4 hours will leads to the formation of phthalocyanine compound (Moser, 1963). Also adding 4 moles of phthalonitrile to 1 mole of metal salt at 220-250 °C for 2-6 hours would result in a 70-77 per cent

MATERIALS AND METHODS

7-Hydroxy coumarin and 1,8-diazabicyclo [5.4.0] - undec7-ene (DBU) were obtained from Merck. Phthalamide from AFG scientific, Potassium carbonate (K_2CO_3) was also obtained from Merck and used after drying. $Co(Ac)_2 \cdot 4H_2O$, anhydrous dimethylformamide (DMF), glycerol solution, nitric acid, sulphuric acid, tetrahydrofuran (THF), thionyl chloride, ammonium hydroxide were obtained from Sigma-Aldrich and used as received without further purification. Other chemicals used were of reagent grade and high purity and all reactions were performed under an argon atmosphere.

Melting points of the compounds were determined with Griffin MFB-590. 1H spectra

yield of Phthalocyanine on a plant scale (Moser, 1963). This study, therefore, shows how new Cobalt Phthalocyanine(Copc) could be synthesized and characterized using phthalamide as a precursor.

were recorded using Bruker Ultra-shield 400 MHz with dimethylsulphoxide, DMSO- d_6 as solvent and tetramethylsilane (TMS) as an internal standard. Transmissions FT- IR spectra of the samples were recorded on an FT-IR spectrophotometer (Perkin Elmer); solid substances were ground with KBr and pressed to pellets. UV-Vis spectra were recorded on a T80+UV/VIS spectrophotometer. The transition temperatures and enthalpies were measured by differential scanning calorimeter, SHIMADZU DSC-50 instrument operated at a scanning rate of 10 °C/ min on heating. At a heating rate of 10 °Cmin⁻¹, TGA was conducted under Argon using a SHIMADZU Thermogravimetric Analyzer TGA-50 Instruments.

Synthesis of 3-Nitrophthalamide

30 ml of Nitric acid was measured into a 500 ml round bottom flask and cooled to 0 °C. 30 ml sulphuric acid was slowly added at a temperature of 0-5 °C after which it was properly mixed using a magnetic stirrer. The temperature was increased to room temperature. 15 g phthalamide was added and the temperature was increased to 110 °C and stirred for 4 hours. When the reaction was completed, the content was poured into iced water, filtered and washed with distilled water and dried. The yield and the melting point were determined to be 56.89% and 223 °C respectively.

SYNTHESIS OF 3-NITROPHthalONITRILE

25 ml of thionyl chloride was added dropwise (keeping the temperature between 5 and 7 °C) to 38 ml of dry DMF in a round bottom flask which was already cooled to 0 °C and was stirred for 3 hours at this temperature (5-7 °C) in an ice bath. 7.0 g of 3-Nitrophthalamide was slowly added to

this reagent mixture at such a rate keeping the temperature below 10 °C. The mixture was stirred for 6 hours at 0-5 °C and then 72 hours at room temperature, the reaction mixture was slowly poured into ice, precipitated and vacuum filtered, rinsed with cold distilled water three times. It was air-dried to a constant weight melting point (175 °C) and the yield (93.15%) was obtained.

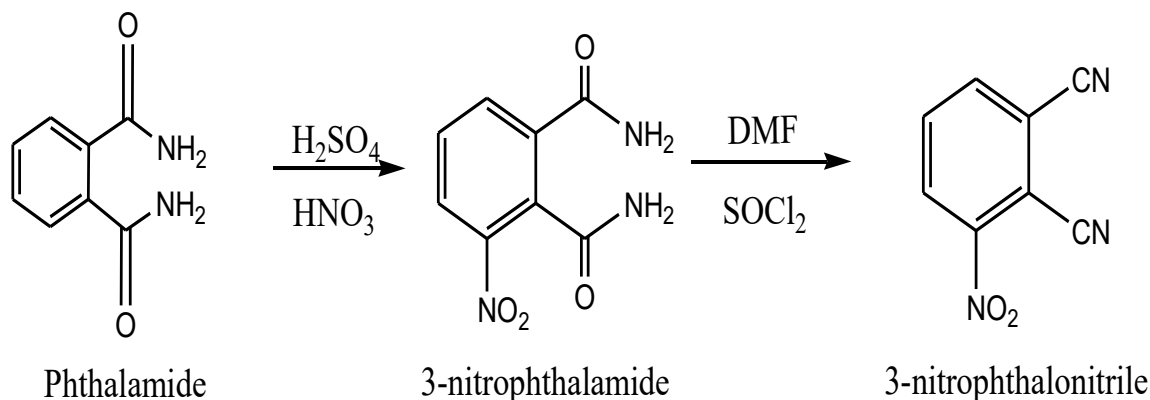


Figure 2: Preparation of 3-Nitrophthalonitrile

SYNTHESIS OF 3-(2-OXO-2H-CHROMEN-7-YL) OXYPHTHALONITRILE

3-Nitrophthalonitrile (0.866 g) was dissolved in dry DMF (10 mL) under argon and 7-hydroxycoumarin (0.623 g) was added. After stirring for 15 minutes at room temperature, the temperature was increased to

80 °C. Finely ground anhydrous potassium carbonate (0.691 g) was added in portions for 1h with efficient stirring. The disappearance of NO₂ peak at 153 cm⁻¹ and 1355 cm⁻¹ was occasionally checked by FTIR, the ensuing mixture was poured into 100 mL distilled water, and the precipitate filtered off, washed and dried. Yield: 0.908 g, 62 %. M.P: 253-255°C.

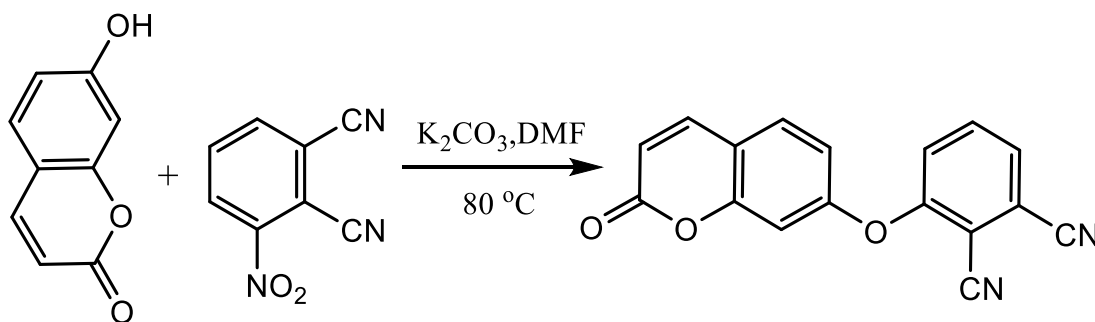


Figure 3: Synthesis Reaction of 3-((2-oxo-2H-chromen-7-yl)oxy)phthalonitrile

Synthesis of 1,8,15,22-Tetrakis [3-(oxo-2H-chromen-7-yloxy) coumarin]Cobalt Phthalocyanine

Phthalonitrile (0.20 g), Cobalt acetate Co(OAc)₂·4 H₂O (0.05 g) and 1,8-diazabicyclo [5.4.0] under-7-ene (DBU) (2 drops) in Glycerol (10 mL) was stirred and heated at reflux temperature under argon atmosphere for 24 hours. After cooling to

room temperature, the reaction mixture was precipitated by adding it dropwise to distilled water and the precipitate collected by filtration, washed with distilled water.

The compound was purified by dissolving it in 3.0 ml of sulphuric acid and stirred, it was precipitated in distilled water, vacuum filtered and washed several times with distilled water until the pH of

the water is neutral, the green product was dried and weighted yield: 0.359 g, 43 %

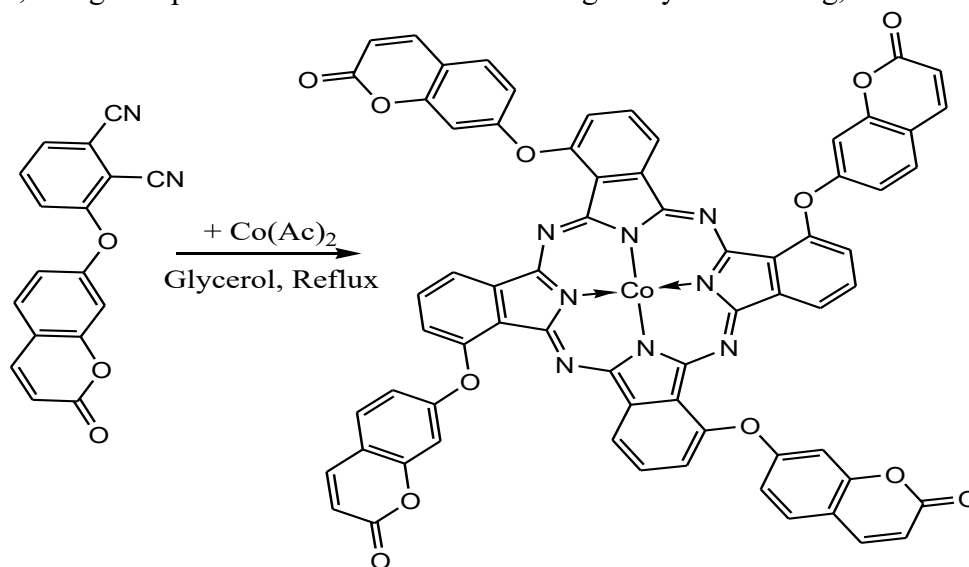


Figure 4: Synthesis of Cobalt phthalocyanine

RESULTS AND DISCUSSION

The synthesis of the metal phthalocyanine started with the nitration of phthalamide in position 3 followed by the formation of 3-nitrophthalamide; then dehydration by the thionyl chloride in N,N-dimethylformamide led to 3-nitrophthalonitrile. Phthalonitrile derivative containing 7-hydroxycoumarin as substituent was prepared by nucleophilic substitution reaction of 3-nitrophthalonitrile in the presence of K_2CO_3 as a base in non-aqueous organic solvent. The cyclotetramerization of dinitrile with metal salts in the presence of DBU was performed with glycerol and DMF solutions (Dauda *et al.*, 2020).

Phthalonitrile derivative was obtained through the nucleophilic substitution reaction between 3-nitrophthalonitrile and 7-Hydroxycoumarin at 80 °C under argon atmosphere in dry DMF in the presence of K_2CO_3 as a base with 62 % yield. This reaction has been used in the preparation of a variety of ether or thioether substituted phthalonitriles (Chohan, 2015).

Cyclotetramerization of the phthalonitrile derivative in a high-boiling solvent Glycerol in the presence of a few drops 1,8-diazabicyclo [5.4.0] undec-7-ene DBU as a strong base and Metals acetate at reflux temperature under an Argon atmosphere afforded the synthesized phthalocyanines. The route for the synthesis of Phthalonitrile, and Phthalocyanine compounds were shown in Figures 2 and 4 respectively. The characterization of the compounds was carried out by the combination of several methods, including, Elemental analysis, FT-IR, UV-vis spectra and TGA and the results showed that the $-C\equiv N$ band in the IR spectrum of Phthalonitrile compound was observed, as expected, at 2230 cm^{-1} . The most important proof of the cyclotetramerization of nitrile groups in the absence of the $-C\equiv N$ vibrations at 2230 cm^{-1} for Phthalocyanines compounds in IR spectra of the substituted phthalocyanine compounds.

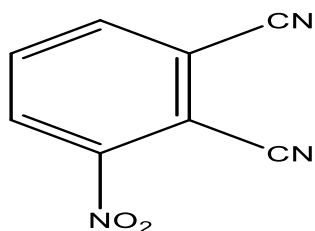


Figure 5: 3-Nitrophthalonitrile

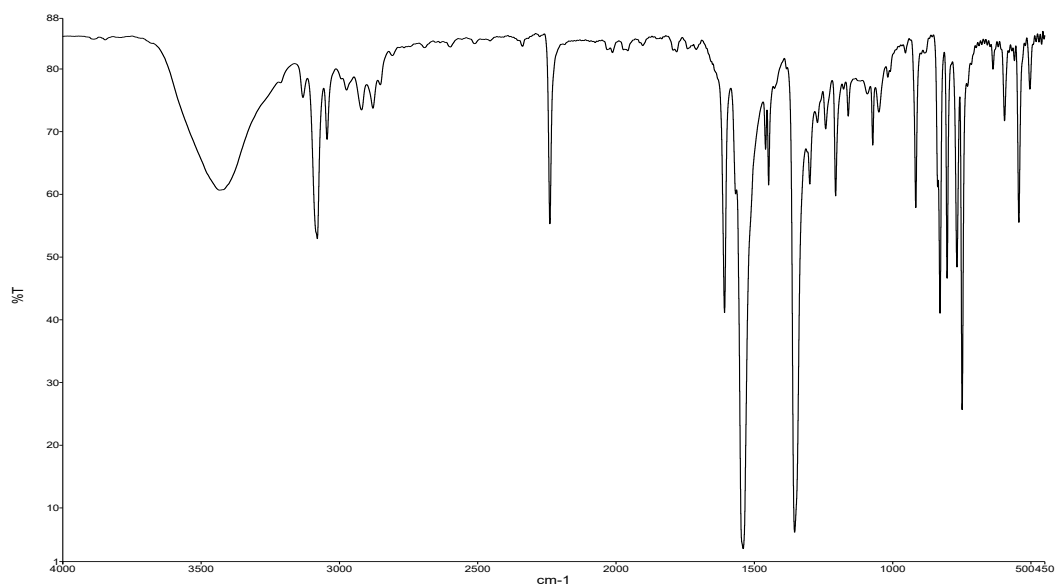


Figure 6: FT-IR of 3-Nitrophthalonitrile

Table 1: FT-IR results of 3-Nitrophthalonitrile

Wavelength (Cm ⁻¹)	Vibration
3080	Ar-CH
2230	C≡N
1607	C=C
1540	Aromatic NO ₂

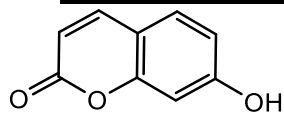


Figure7: 7-Hydroxy coumarin

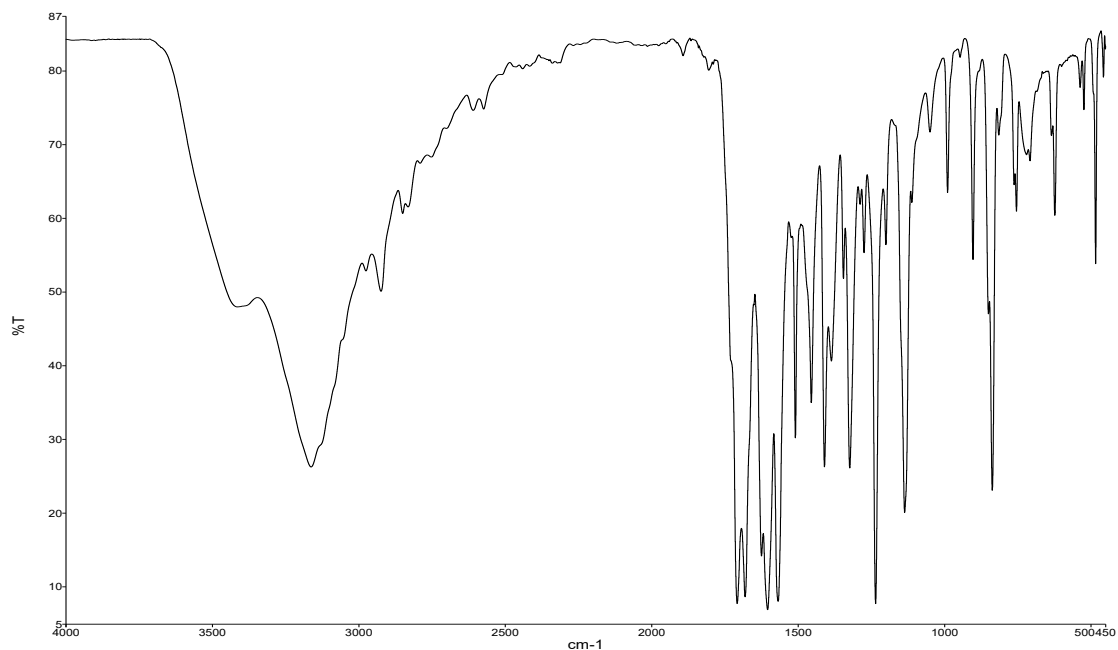


Figure 8: FT-IR of 7-Hydroxy coumarin

Table 2: FT-IR results of 7-Hydroxy coumarin

Wavelength (Cm ⁻¹)	Vibration
3158	Ar-CH
1603	C=C
1707	C=O
1274	C-O-C

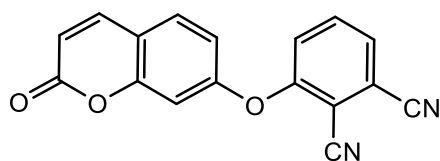


Figure 9: Structure of 3-(oxo-2H-chromen-7-yloxy coumarin)phthalonitrile

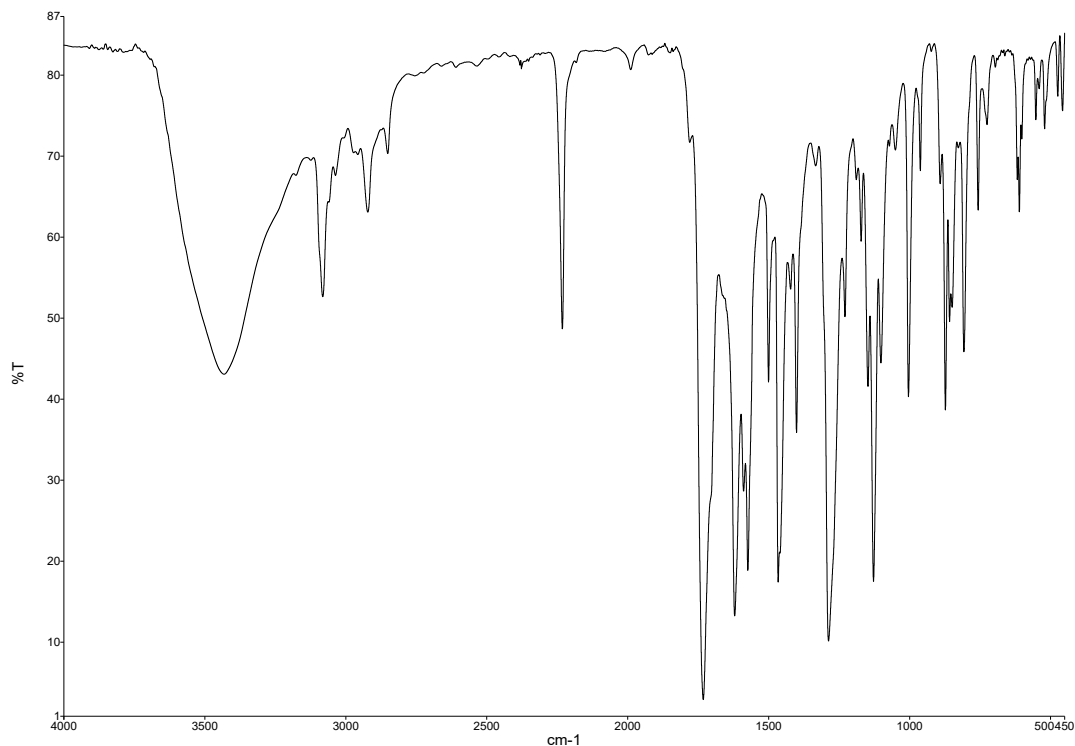


Figure 10: FT-IR of 3-(oxo-2H-chromen-7-yloxy coumarin)phthalonitrile

The IR spectrum of the compound was investigated using a KBr tablet, the disappearance of NO_2 peak at 1540 cm^{-1} and 1355 cm^{-1} on the IR spectra of 3-Nitrophthalonitrile compound suggested the formation of the compound.

Table 3: FT-IR results of 3-(oxo-2H-chromen-7-yloxy coumarin)phthalonitrile

Wavelength (Cm^{-1})	Vibration
2921	Ar-CH
2230	$\text{C}\equiv\text{N}$
1620	$\text{C}=\text{C}$
1731	$\text{C}=\text{O}$
1288	$\text{C}-\text{O}-\text{C}$

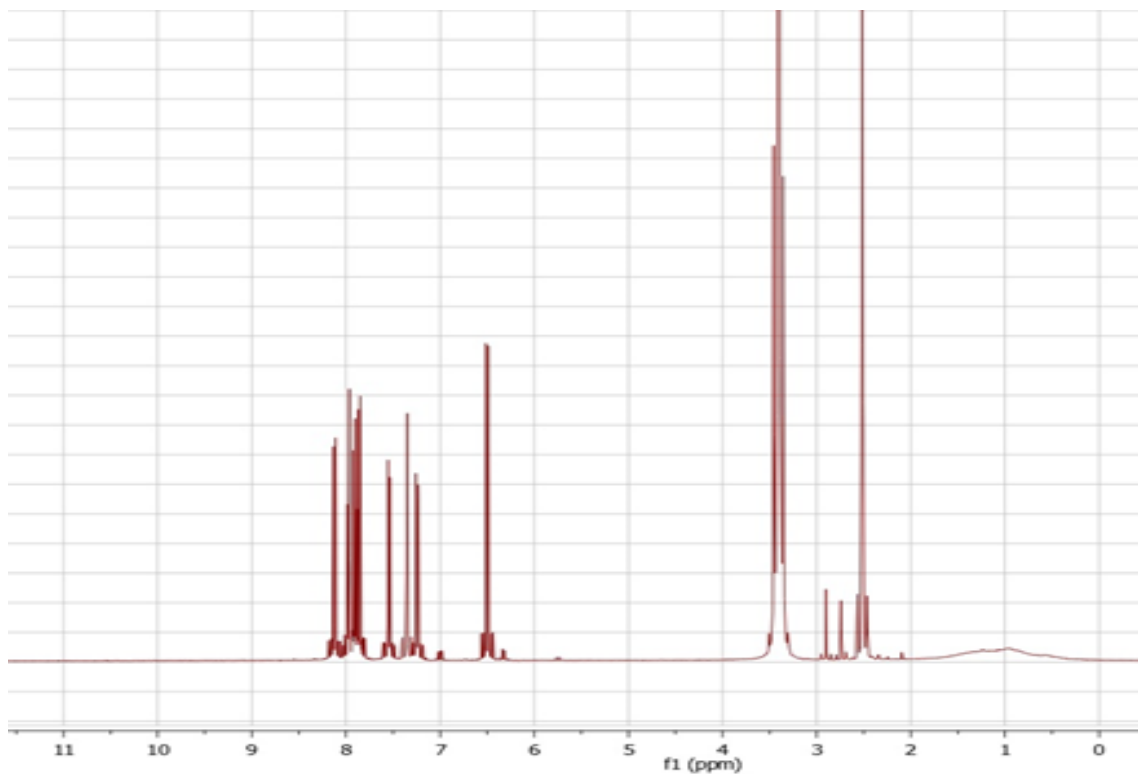


Figure 11: ^1H NMR spectrum of 3-(oxo-2H-chromen-7-yloxy coumarin)phthalonitrile
 ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ , ppm): 6.50-8.13.

When the ^1H NMR spectrum is examined, DMSO peak was observed at about 3.4 ppm and the residual DMSO- d_6 peak at about 2.5 ppm, and the multiplet peaks at about 6.50-8.13 ppm belong to protons in the aromatic ring.

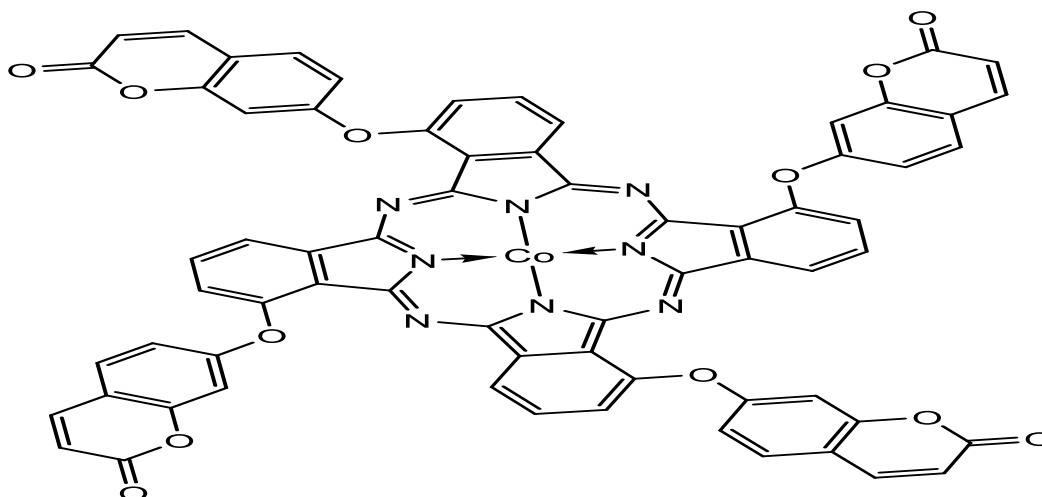
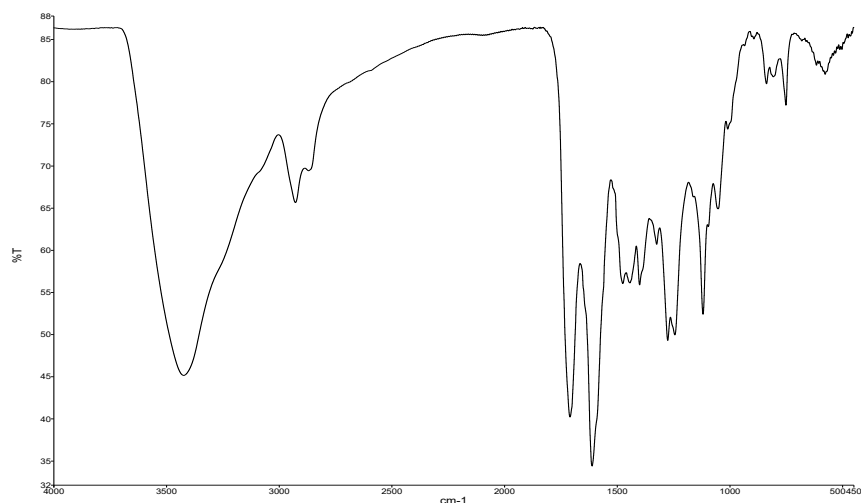


Figure 12: Cobalt Phthalocyanine



Figur 13: FT-IR of Cobalt phthalocyanine

The IR spectrum of the compound was investigated using a KBr tablet, the disappearance of the $\text{C}\equiv\text{N}$ stretching vibration at 2230 cm^{-1} on the IR spectra of phthalonitrile compound suggested the formation of compound phthalocyanine derivative.

Table 4: FT-IR results of Cobalt phthalocyanine

Wavelength (Cm^{-1})	Vibration
2928	Ar-CH
1709	C=O
1611	C=C
1275	C-O

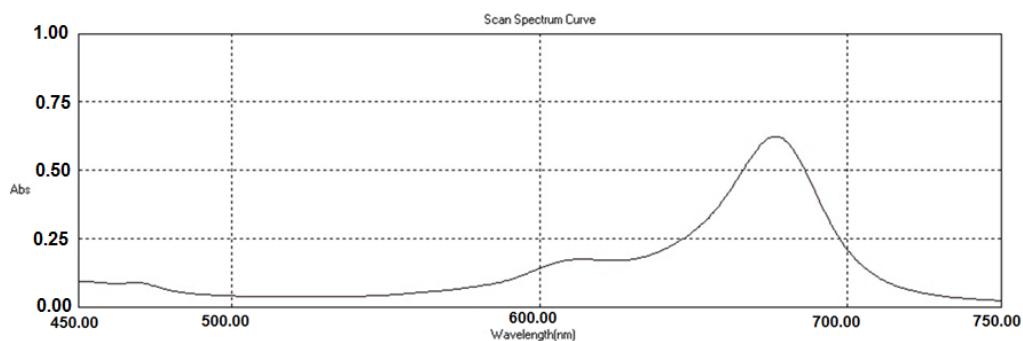


Figure 14: UV spectrum of Cobalt phthalocyanine

The ground state electronic spectra are especially important to understand the structure of phthalocyanines, generally, UV-Vis spectra of phthalocyanines showed electronic spectra with two strong absorption bands popularly known as Q and B bands. The Q band was found in the visible region, 600–750 nm and is attributed to the π - π^* transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring and the B band in the UV region at 300–400 nm. The ground state electronic absorption spectra of the synthesized non-peripherally tetra-substituted phthalocyanine complex showed monomeric behaviour evidenced by a single (narrow) Q band.

The electronic spectrum of the Cobalt phthalocyanine compound (CoPc) in DMF is given in figure 7. The synthesized CoPc compound showed an intense Q band at 677 nm, in the UV-VIS spectrum obtained in DMF solvent, this is attributed to π - π^* transition from the highest occupied molecular orbital (HUMO) to lowest occupied molecular orbital (LUMO) of the phthalocyanine ring. Aggregation was also observed at 610 nm. The electronic absorption transitions of these compounds strongly rely on the nature of the substituent (withdrawing or donating groups) as well as the type of the metal ion and its position (the center or non-peripheral position).

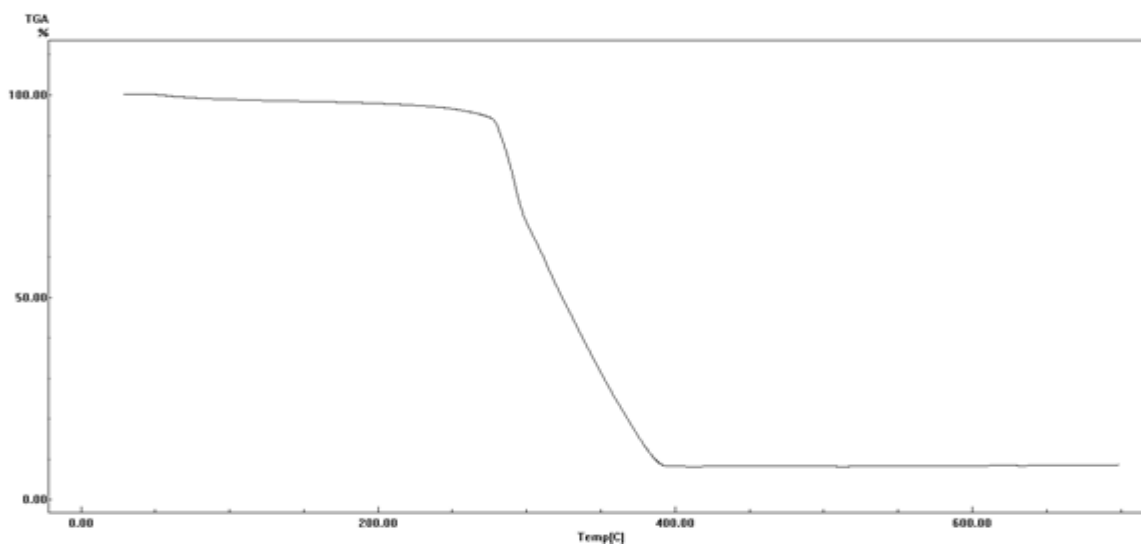


Figure 15: TGA of Cobalt Phthalocyanine

The thermal stability of the compound derivative was checked by TGA, the phthalocyanine was heated to 700 °C to determine their degradation temperature. From the thermographic analysis

result of the synthesized Cobalt phthalocyanine compound showed that the compound began to exhibit weight loss at a temperature of 300 °C which indicate a suitably high thermal stability for the newly synthesized compound.

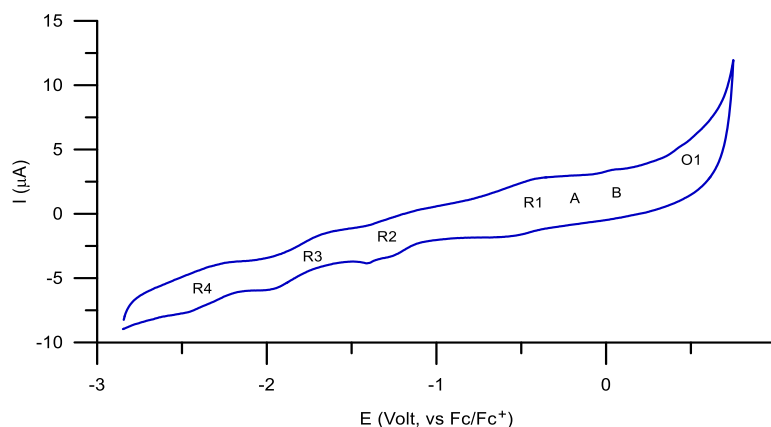


Figure 16: Cyclic Voltammogram of CoPc

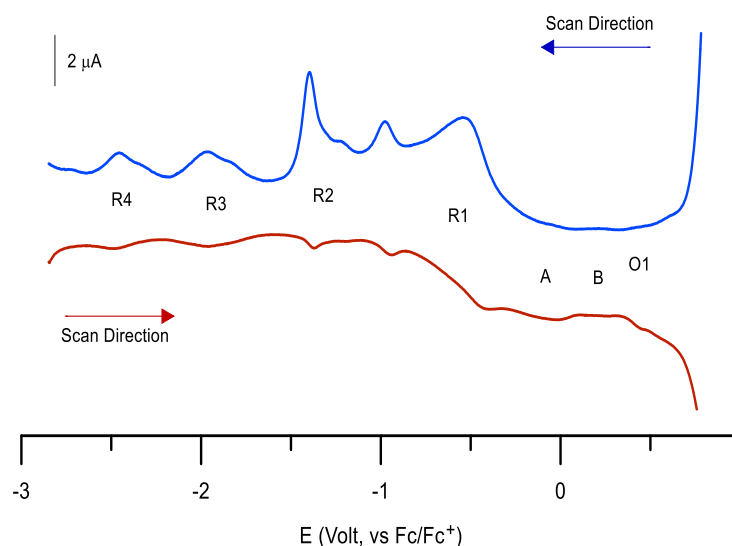


Figure 17: Square Wave voltammogram of CoPc

The cyclic and square wave voltammograms of CoPc shown in Figure 9 and Figure 10 respectively, display four reduction processes at A at -0.93 , R1 at -1.37 , R2 at -1.92 , and R3 at -2.46 V together with two oxidation processes at B at 0.26 and O1 at 0.60 V during the cathodic and anodic scan vs. Fc^+/Fc at 0.100 V/s scan rate within the available potential range of TBAFB/DMF solvent system. The potential difference between the first reduction A (-0.93 V)

and first oxidation B (0.27 V) due to reduction and oxidation of Co(II) and these can therefore be assigned to the $[\text{Pc}^{2-}\text{Co(II)}]/[\text{Pc}^{2-}\text{Co(I)}]$ and $[\text{Pc}^{2-}\text{Co(II)}]/[\text{Pc}^{2-}\text{Co(III)}]$ couples in DMF respectively. Phthalocyanine centered first reduction and first oxidation took place at R1 (-1.37 V) and O1 (0.60 V) respectively.

CONCLUSION

This research work shows the synthesis, characterization and investigation of thermal and electrical properties of cobalt phthalocyanine bearing 7-Hydroxy coumarin substituents on the peripheral position. The synthesized phthalocyanine complex showed partial

solubility in some organic solvents such as tetrahydrofuran, dimethylsulphoxide, and dimethylformamide. The complex also exhibited high thermal stability. The results of this study showed that the synthesized cobalt phthalocyanine complex could be useful in various industrial processes such as in oxidation, catalysis, solar screens and dye.

ACKNOWLEDGEMENT

I sincerely acknowledge the immense contribution of the Chemistry Department, Firat University, Elazig, Turkey. The department

provided all the reagents and apparatus/equipment used for this research. Sincere appreciation goes to Prof. SINAN Saydam whose scientific contributions will never be forgotten.

References

- Alharbi, N. (2014). *Synthesis and functionalization of novel meso-substituted tetrabenzotriazaporphyrins* (Doctoral dissertation, University of East Anglia).
- Armour, M. A. (2016). *Hazardous laboratory chemicals disposal guide*. CRC press.
- Ding, Z., Chen, X., Antonietti, M., & Wang, X. (2011). Synthesis of transition metal-modified carbon nitride polymers for selective hydrocarbon oxidation. *ChemSusChem*, 4(2), 274-281.
- Chohan, S. (2015). *The synthesis, characterization and electrocatalytic behaviour of novel cobalt (II) and iron (II) phthalocyanines bearing benzopyrone, benzoxazole, tetrahydropyran and furan moieties* (Doctoral dissertation).
- Cragg, P. J. (2010). Supramolecular Therapeutics. In *Supramolecular Chemistry* (pp. 207-229). Springer, Dordrecht.
- Dauda, A., Olaleye, A. A., & Abdullahi, H. I. (2020). The Synthesis and Characterization of Iron Phthalocyanine (Fe₂PC) Compound Containing 7-Hydroxycoumarin and Investigation of Its Thermal and Electrochemical Properties. *SLU Journal of Science and Technology*, 1(2), 61-67.
- Gounden, D., Nombona, N., & Van Zyl, W. E. (2020). Recent advances in phthalocyanines for chemical sensor, non-linear optics (NLO) and energy storage applications. *Coordination Chemistry Reviews*, 420, 213359.
- Moser, T. (1963). Towards "The Good Soldier": Discovery of a Sexual Theme. *Daedalus*, 312-325.
- Nutt, M. J., Yee, Y. S., Buyan, A., Andrewartha, N., Corry, B., Yeoh, G. C., & Stewart, S. G. (2021). In pursuit of a selective hepatocellular carcinoma therapeutic agent: Novel thalidomide derivatives with antiproliferative, antimigratory and STAT3 inhibitory properties. *European Journal of Medicinal Chemistry*, 217, 113353.

Zawadzka, A., Płóciennik, P., Strzelecki, J., Korcala, A., Arof, A. K., & Sahraoui, B. (2014). Impact of annealing process on stacking orientations and second order

nonlinear optical properties of metallophthalocyanine thin films and nanostructures. *Dyes and Pigments*, 101, 212-220.