



Synthesis and Characterization of Iron Phthalocyanine (FePc) Compound Containing 7-Hydroxycoumarin and Investigation of Its Thermal and Electrochemical Properties

Aminu Dauda*, Abdul Ademola Olaleye and Hadiza Usman Abdullahi

Department of Chemistry, Faculty of Science, Federal University Dutse, P.M.B. 7156, Jigawa State, Nigeria.*
tasekkur@gmail.com

Abstract

In this research, phthalonitrile was synthesized from the reaction of 7-hydroxycoumarin with 3-nitrophthalonitrile in DMF. Cyclotetramerization of phthalonitrile in the presence of metal salt, Fe(II) gave peripherally substituted metal phthalocyanine complex. The structure of the synthesized compound was characterized by different analytical tools such as ¹H NMR, UV-Vis, and FT-IR spectrophotometry and cyclic voltammetry. Disappearance of the C≡N stretching vibration on the IR spectra of phthalonitrile was observed at 2230 cm⁻¹. The FTIR vibration results for C=O, C=C and C-O were 1712cm⁻¹, 1615 cm⁻¹ and 1276 cm⁻¹ respectively. Solubility of metal phthalocyanine complex was found to be very low in common laboratory solvents such as tetrahydrofuran (THF) and dimethylformamide (DMF). The electronic spectrum of FePc in DMF, shows intense Q absorption at 678 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. The thermal stability of the phthalocyanine derivative was checked by T.G.A and degradation was observed to start at 380oC which showed that the complex could withstand relatively high temperatures. It was, therefore, concluded that the metal phthalocyanine prepared in this study showed suitably high thermal stability and can be used for various applications.

Keywords: Phthalocyanine, 3-Phthalonitrile, electrochemistry, Thermal analysis

1. Introduction

Phthalocyanines (Pcs) are symmetrical 18 π -electron aromatic macrocycles, closely related to the naturally occurring porphyrins (Spiller, et al., 1996). Phthalocyanines are chemically and thermally stable compounds which can host more than seventy different metal ions in the central cavity (Calvete, et al., 2004). Since their discovery, phthalocyanines have been extensively used as colorants, but they also have been employed in different technological areas, i.e. photoconducting materials, light absorbing layers in recordable CDs, photosensitizers in cancer therapy, and industrial catalysts (Nakşi and Cihan, 2005). Despite the number of actual applications, further research is still in dispensable since many other future applications are envisaged. The physical properties and the processing ability required for technological applications can be chemically tuned by changing the peripheral substituent and/or the central metal (Liu and Zhang, 2014). The possibility of designing and synthesizing unsymmetrically substituted phthalocyanines, may enhance the technological applications of phthalocyanines, i.e. within the field of second-order nonlinear optics. Other feasible chemical manipulation is the alteration of the Pc skeleton that leads to various Pc analogues, such as subphthalocyanines, and expanded phthalocyanines. More recently, the construction of multinuclear and multicomponent Pc-based systems is attracting much attention owing to their potential capability of performing complex functions, as molecular switches and solar cells, among others (Asif, 2015).

Coumarins are a group of polyphenolic compounds first isolated from plant product Tonka bean in 1820. Coumarins are colorless and crystalline phytochemical substances (Zagal and Bedioui, 2016). It is an oxygen containing heterocycle, which occurs either in free or combined form with glucose. They belong to the family of benzopyrones, which consists of benzene ring joined by a pyrone ring (Chow, et al., 2016).

Metal phthalocyanine derivatives are known to exhibit high electron transfer abilities. The electron transfers properties of phthalocyanines depend on the kind and number of the substituents and are due to the interaction between the phthalocyanine ring and the metal center, which is influenced by the conjugated π electrons of the phthalocyanine ring. In spite of their high electron ability, electrochemical application of metal phthalocyanines is restricted in solution because of their lower solubilities in common organic solvents. Recently, many peripherally substituted phthalocyanine derivatives have been prepared and their increasing solubility has facilitated electrochemical and spectroscopic studies of them in solution (Zhang, et al., 2007). The objective of this research work is therefore to obtain a substituted metal phthalocyanine complex and check the solubility and thermal stability of the synthesized complex.

2. Materials and Methodologies

All reactions were performed under argon atmosphere. 7-Hydroxy coumarin and 1,8-diazabicyclo [5.4.0] -undec7-ene (DBU), were received from Merck. 3-Phthalonitrile from AFG scientific, Potassium carbonate (K_2CO_3) was received from Merck and used after drying, Phthalimide, $FeCl_2$, 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 reagent grade and of high purity.

2.1 Apparatus

Melting points of the compounds were determined with Griffin MFB-590. 1H spectra were taken using Bruker Ultra-shield 400 MHz with $DMSO-d_6$ as solvents and tetramethylsilane as an internal standard. Transmission FT-IR spectrum 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 calorimetry with a SHIMADZU DSC-50 instrument operated at a scanning rate of 10 $^{\circ}C/min$ on heating. At a heating rate of 10 $^{\circ}C/min$, TGA was conducted under Argon using a SHIMADZU Thermogravimetric Analyzer TGA-50 Instruments.

2.3 Methodology

The synthesis of the metal phthalocyanine started with the nitration in position 3 of phthalimide followed by the formation of the 3-nitrophthalimide; then dehydration by the thionyl chloride in N,N-dimethylformamide leads to 3-nitrophthalonitrile. Phthalonitrile derivative containing a 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 metals salts in the presence of DBU was performed with Glycerol and DMF solutions.

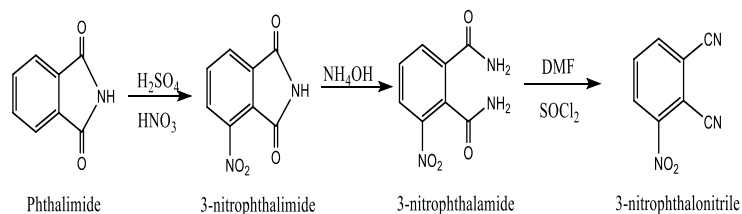


Figure: 1 Synthesis of 3-Nitrophthalonitrile

2.4 Synthesis of 3-(2-oxo-2H-chromen-7-yl)oxy)phthalonitrile

3-Nitrophthalonitrile (0.866 g, 5 mmol) was dissolved in dry DMF(10 mL) under argon and 7-hydroxycoumarin (0.623 g, 3.842 mmol) 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, 5.0 mmol) was added in portions during 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.

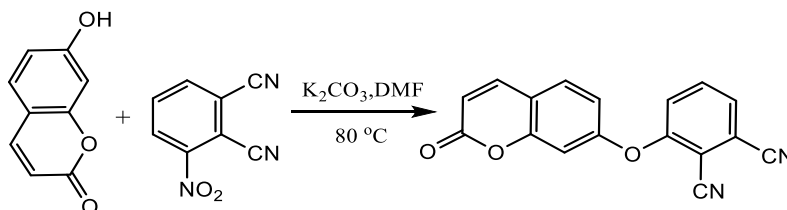


Figure 2 Synthesis Reaction of 3-((2-oxo-2H-chromen-7-yl)oxy)phthalonitrile

2.5 Synthesis of 7-((1,3-diiminoisoindolin-4-yl)oxy)-2H-chromen-2-one

To a solution of phthalonitrile 1.275g (4.423 mmol) in dry methanol (100 mL) was added sodium methoxide 0.139 g (2.576 mmol). Anhydrous ammonia was bubbled through the solution under reflux. The course of the reaction was followed by IR spectroscopy monitoring of the C≡N peak at 2230 cm⁻¹. After the completion of the reaction, the ammonia inlet was closed, and the volume of the reaction mixture was reduced to 10 mL under reduced pressure. The mixture was precipitated with distilled water (100 mL), and the solid was filtered off washed and dried yield: 1.108 g 74 % , M.P: 128 °C



Figure 3. Synthesis of 7-((1,3-diiminoisoindolin-4-yl)oxy)-2H-chromen-2-one

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

1,3-diiminoisoindoline (0.200 g, 0.6555 mmol), Iron (II) Chloride FeCl₂ (0.059 g, 0.299 mmol) and 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (3 drops) in ~DMF/Glycerol (10 mL) was stirred and heated at reflux temperature under an argon atmosphere for 24 hours. After cooling to room temperature, the reaction mixture was collected by adding it dropwise to distilled water (100 ml).

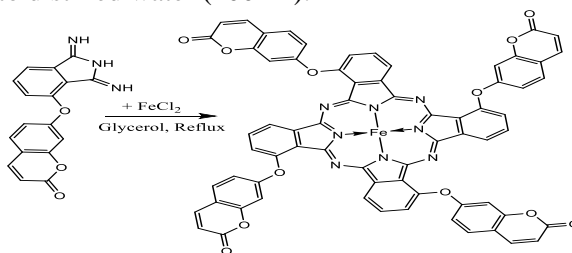


Figure 6. Synthesis of Iron phthalocyanine

The product was precipitated, 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 time with distilled water until the pH of the water is neutral, the green product was dried and weighted yield: 0.202 g, 26 %.

3. Results and Discussion

3.1 Results

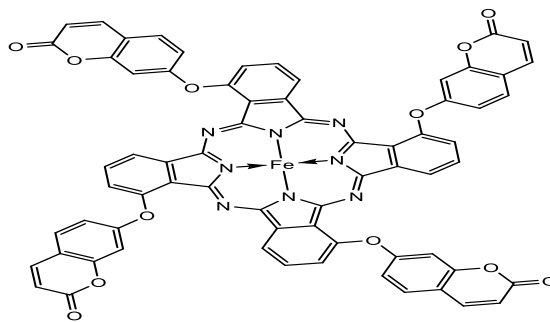


Figure 7. Iron Phthalocyanine

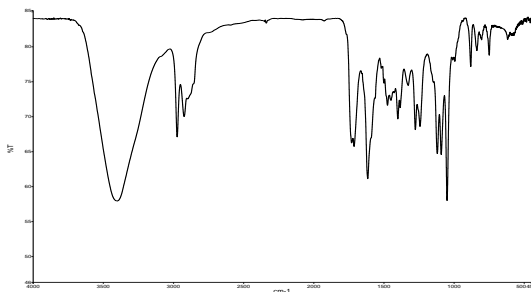


Figure 8. FT-IR of Iron (II) Phthalocyanine

The IR spectrum of the compound was investigated using a KBr tablet, the disappearance of the C≡N stretching vibration at 2230 cm⁻¹ on the IR spectra of phthalonitrile compound suggested the formation of compound phthalocyanine derivative.

Table 1. FT-IR results of Iron (II) Phthalocyanine

| Vibration (Cm-1) | Vibration |
|------------------|-----------|
| 2974 | Ar-CH |
| 1712 | C=O |
| 1615 | C=C |
| 1276 | C-O |

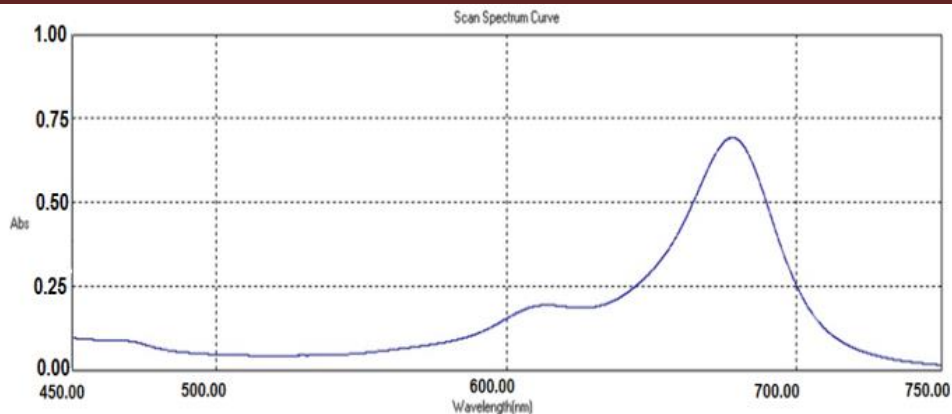


Figure 9. UV spectrum of Iron(II) Phthalocyanine

The synthesized FePc compound shows intense Q band at 678 nm, in the UV-VIS spectrum obtained in DMF solvent, this was 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.

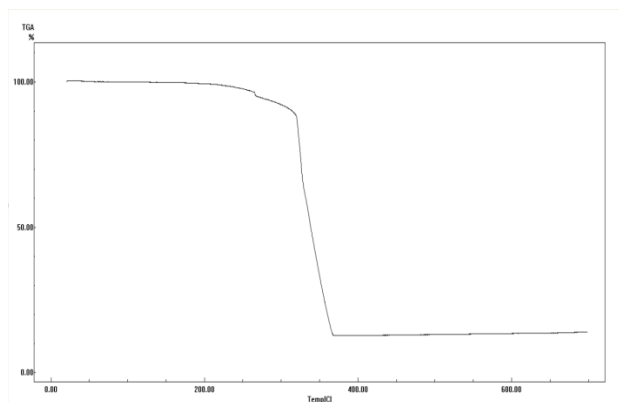


Figure 10. TGA of Iron Phthalocyanine

From the thermographic analysis result of the synthesized Iron phthalocyanine compound it shows that the synthesized compound begin to exhibit weight loss at a temperature of 380 oC which indicate a suitably high thermal stability for the newly synthesized compound.

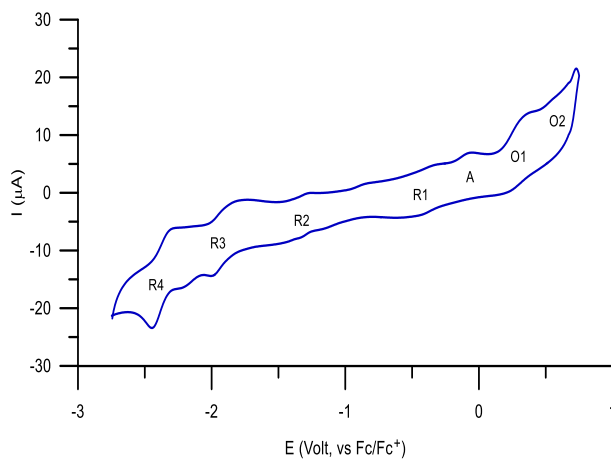


Figure 11. Cyclic Voltamogram of FePc

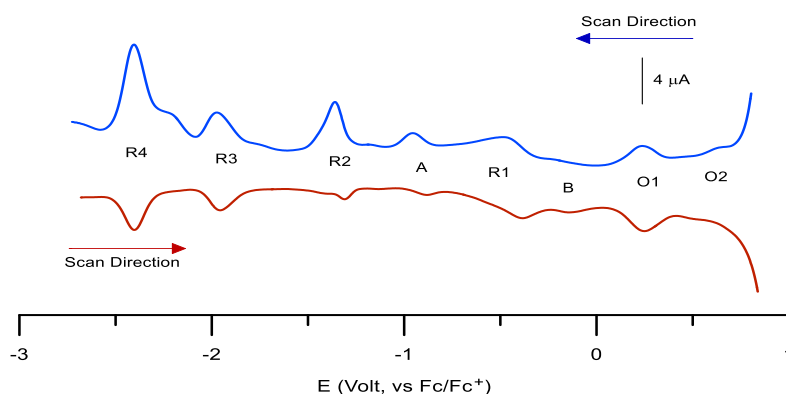
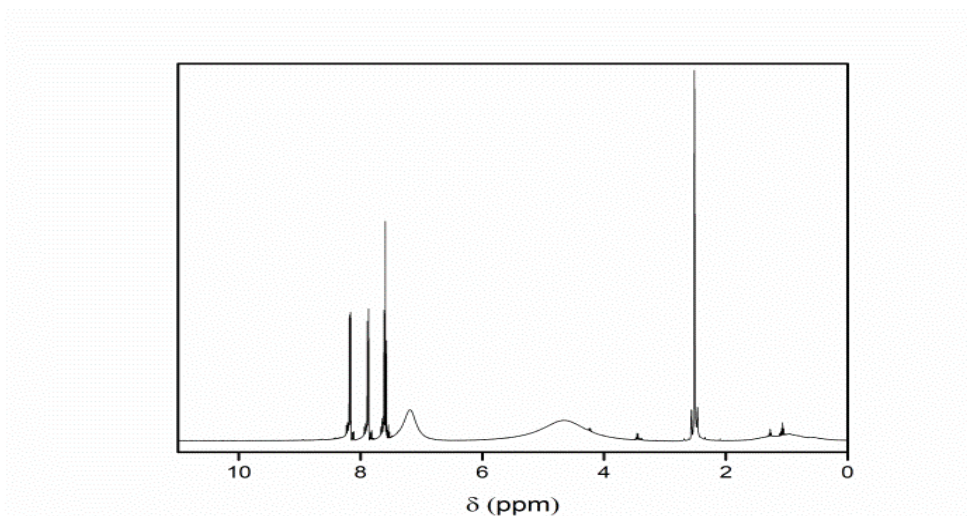


Figure 12. Square Wave voltammogram of FePc

FePc has redox active metal centre, therefore it can give metal based redox processes in the electrochemical potential window of DMF. Figure 18 and 19 shows CV and SWV of FePc in DMF/TBAFB solvent system. It can be seen from the voltammograms that FePc has four reduction processes, A at -0.92 , R1 at -1.34 , R2 at -1.95 , and R3 at -2.40 V together with three oxidation processes at B at -0.13 , O1 at 0.25 V and O2 at 0.67 V. Electrochemical properties of FePc is closely resembles the electrochemical properties of CoPc, because both have redox active metal centre.

Figure 13. 1H -NMR spectrum of 4-(oxo-2H-chromen-7-yl)oxy coumarin)1,3-diiminoisoindoline

3.2 Discussion

FePc has redox active metal centre, therefore it can give metal based redox processes in the electrochemical potential window of DMF. Figure 11 and 12 show CV and SWV of FePc in DMF/TBAFB solvent system. It can be seen from the voltammograms that FePc has four reduction processes, A at -0.92 , R1 at -1.34 , R2 at -1.95 , and R3 at -2.40 V together with three oxidation processes at B at -0.13 , O1 at 0.25 V and O2 at 0.67 V, generally the reduction and oxidation behaviour of metal phthalocyanine derivative is due to the interaction of phthalocyanine ring and the central metal ion. The thermal stability of the compound derivative was checked by TGA, the Phthalocyanine were heated to 700 oC to determine their degradation temperature, the temperatures at which the phthalocyanine begin to exhibit weight loss was 380 oC which indicate a suitably high thermal stability



for the compound. The ground state electronic spectra are especially important to understand the structure of the 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 spectra of iron phthalocyanine compound (FePc) in DMF is given in figure 9 above. The UV-Vis absorption spectra of FePc in DMF showed intense Q absorption at 678 nm, The electronic absorption transitions of these compounds are strongly rely on the nature of the substituent (withdrawing or donating groups) as well as the type of the metal ion and its position (in the center or on non-peripheral position).

4. Conclusions

This research work describes the synthesis and characterization of metal phthalocyanine bearing 7-Hydroxy coumarin substituents on the α non-peripheral positions, the synthesized phthalocyanine complex showed partial solubility in some organic solvents such as THF, DMSO and DMF, the complex also exhibited high thermal stability. The results of this study showed that the synthesized metal phthalocyanine complex will be suitable for application in oxidation catalysis and solar screens.

Acknowledgement

I sincerely acknowledge the immense contribution of Chemistry Department, Firat University, Elazig, Turkey for providing all the reagents and apparatus/equipment used for this research, most sincere appreciation to Prof. SINAN Saydam (Head of Department) whose scientific contributions will never be forgotten.

References

- Asif, M. (2015). Pharmacological activities and phytochemistry of various plant containing coumarin derivatives. *Current Science*, 1(13), pp. 77-90.
- Calvete, M., Yang, G. Y. and Hanack, M. (2004). Porphyrins and phthalocyanines as materials for optical limiting. *Synthetic Metals*, 141(3), pp. 231-243.
- Chow, S. Y. and Ng, D. K. (2016). Synthesis of an ABCD-Type Phthalocyanine by Intramolecular Cyclization Reaction. *Organic Letters*, 18(13), pp. 3234-3237.
- Liu, D., Zhang, X. and You, T. (2014). Electrochemical performance of electrospun free-standing nitrogen-doped carbon nanofibers and their application for glucose biosensing. *ACS applied materials & interfaces*, 6(9), pp. 6275-6280.
- Nakşi, M. and Cihan, A. (2005). Synthesis and electrochemical properties of phthalocyanines with four 8-quinolinoxy-substituents. *Transition metal chemistry*, 30(1), pp. 89-94.
- Spiller, W., Wöhrle, D., Schulz-Ekloff, G., Ford, W. T., Schneider, G. and Stark, J. (1996). Photo-oxidation of sodium sulfide by sulfonated phthalocyanines in oxygen-saturated aqueous solutions containing detergents or latexes. *Journal of Photochemistry and Photobiology A: Chemistry*, 95(2), pp. 161-173.
- Zagal, J. H. and Bedioui, F. (2016). *Electrochemistry of N4 Macrocyclic Metal Complexes: Volume 2: Biomimesis, Electroanalysis and Electrosynthesis of MN4 Metal Complexes* (No. 4). Springer.
- Zhang, P., Steelant, W., Kumar, M. and Scholfield, M. J. J. (2007). Versatile photosensitizers for photodynamic therapy at infrared excitation. *Journal of American Chemical Society*, 129(15), pp. 4526-4527.