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SYNTHESIS AND CHARACTERIZATION OF NEW NICKEL PHTHALOCYANINE (NIPC) COMPLEX CONTAINING 7-HYDROXYCOUMARIN AND EVALUATION OF ITS ELECTROCHEMICAL AND THERMAL PROPERTIES

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ABSTRACT

In this study, 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 salt, Ni(II)) gave peripherally substituted metal phthalocyanine complexes. The structure of the synthesized compounds was characterized by different analytical tools such as ^1H NMR, UV-Vis, and FT-IR spectrophotometry and cyclic voltammetry. The disappearance of the C≡N stretching vibration from 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 complexes was found to be very low in common laboratory solvents such as tetrahydrofuran (THF) and dimethylformamide (DMF). The electronic spectrum of NiPc in dimethylformamide (DMF) showed intense Q absorption at 690 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 309 ^{oC,} which showed that the complex could withstand relatively high temperature. It could therefore be concluded that the metal phthalocyanine prepared in this study showed suitably high thermal stability and can be used for various applications.

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

INTRODUCTION

Phthalocyanines (Pcs) could be described as symmetrical 18 π-electron aromatic macrocycles, closely related to the naturally occuring porphyrins (Senge *et al*., 2021). Phthalocyanines are chemically and thermally stable compounds that can host more than seventy different metal ions in the central cavity (Yoshizawa and Catti, 2019). Since their discovery, phthalocyanines have been extensively used as colorants, but they also have been employed in different technological areas, i.e., photoconductive materials, light-absorbing layers in recordable CDs, photosensitizers in cancer therapy, and industrial catalysts (Gounden, *et al.,* 2020). Despite the number of actual applications, further research is still indispensable since many other future applications are envisaged. The physical properties and the processing capability 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. Another feasible chemical manipulation is the alteration of the phthalocyanine skeleton that leads to various phthalocyanine 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 such as molecular switches and solar cells, among others (Asif, 2015). Since their discovery, phthalocyanines have been extensively used as colourants, but they also have been employed in different technological areas, such as photoconducting 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 (Cohan, 2015). Sir Patrick Linstead in 1933 was the first to use this term to describe a new class of compound (Alharbi, 2014). Phthalocyanine itself, however, is believed to have been discovered in 1907 as an accidental by-product of the synthesis of o-cyanobenzamide (Alharbi, 2014).

Coumarins are a group of polyphenolic compounds first isolated from the plant product Tonka beans in 1820. Coumarins are colorless and crystalline phytochemical substances (Zagal and Bedioui, 2016). It is an oxygen-containing heterocycle, which occurs either in a free or combined form with glucose. They belong to the family of benzopyrones, which consists of benzene rings joined by a pyrone ring (Chow *et al*., 2016). Metal phthalocyanine derivatives are known to exhibit high electron transferability. The electron transfer properties of phthalocyanines depend on the kind and number of 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. Despite their high electron capability, the electrochemical application of metal phthalocyanines is restricted in solution because of their lower solubility in common organic solvents. Recently, many peripherally substituted phthalocyanine derivatives have been prepared and their increasing solubility has facilitated their electrochemical and spectroscopic studies in solution (Cjen *et al*., 2018). The objective of this research work is therefore to obtain a substituted metal phthalocyanine complex and evaluate the level of solubility and thermal stability of the synthesized complex.

MATERIALS AND METHODOLOGIES

All reactions were performed under an argon atmosphere. 7-Hydroxy coumarin and 1,8-diazabicyclo [5.4.0] - undec7-ene (DBU) were obtained from Merck. 3-Phthlonitrile from AFG scientific, Potassium carbonate (K_2CO_3) was also obtained from Merck and used after drying. Phthalimide, $Ni(Ac)_2.4H_2O$, 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.

Melting points of the compounds were determined with Griffin MFB-590. ^{1}H spectra were taken using Bruker Ultra-shield 400 MHz with dimethylsulphoxide, DMSO-d6 as solvent and tetramethylsilane (TMS) as an internal standard. Transmission 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 calorimetry with a SHIMADZU DSC-50 instrument operated at a scanning rate of 10 ^{oC}/ min on heating. At a heating rate of 10 ºC min-1, TGA was conducted under Argon using a SHIMADZU Thermogravimetric Analyzer TGA-50 Instruments.

The synthesis of the metal phthalocyanine started with the nitration in position 3 of phthalimide followed by the formation of 3-nitrophthalamide; then dehydration by the thionyl chloride in N, N-dimethylformamide leads to 3-nitrophthalonitrile. Pthalonitrile derivative containing 7-hydroxycoumarine as substituent was prepared by nucleophillic substitution reaction of 3-nitrophthalonitrile in the presence of K_2CO_3 as a base in a 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).

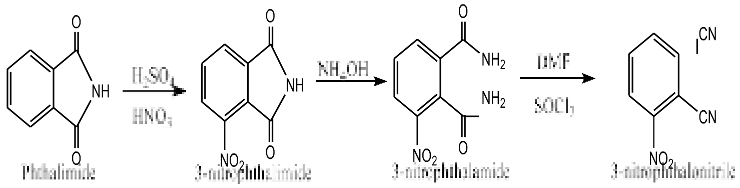
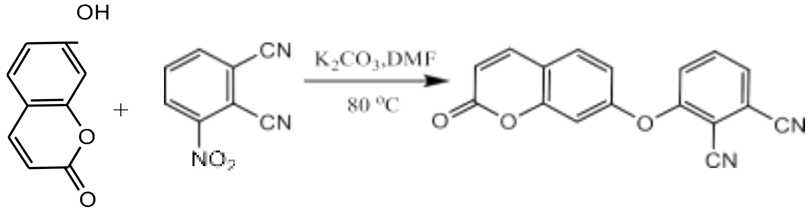


Fig. 1: Synthesis of 3-Nitrophthalonitrile

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 ºC, finely ground anhydrous potassium carbonate (0.691 g, 5.0 mmol) was added in portions for 1h with efficient stirring. The disappearance of NO_2 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.

Fig. 2: 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]Nickel (II) Phthalocyanine

Phthalonitrile (0.40 g, 1.388 mmol), Nickel (II) acetate, $Ni(OAc)_2$ $2H_2O$ (0.100 g, 0.402 mmol) and1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (4 drops) in 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 precipitated by adding it dropwise to distilled water (200 ml). The product was precipitated, collected by filtration, washed with distilled water, and dried.

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 the weight yield was 0.262 g, 16 %.

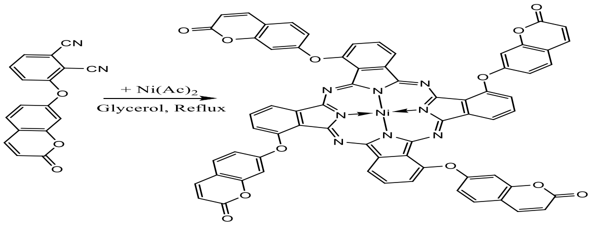


Fig. *3: Synthesis of Nickel phthalocyanine*

RESULTS AND DISCUSSION

Results

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 compounds suggested the formation of the compound phthalocyanine derivatives.

Table 1: FT-IR results of Nickel (II) phthalocyanine

Vibration (Cm^{-1})	Vibration
2925	Ar-CH
1732	C=O
1615	C=C
1276	C-O

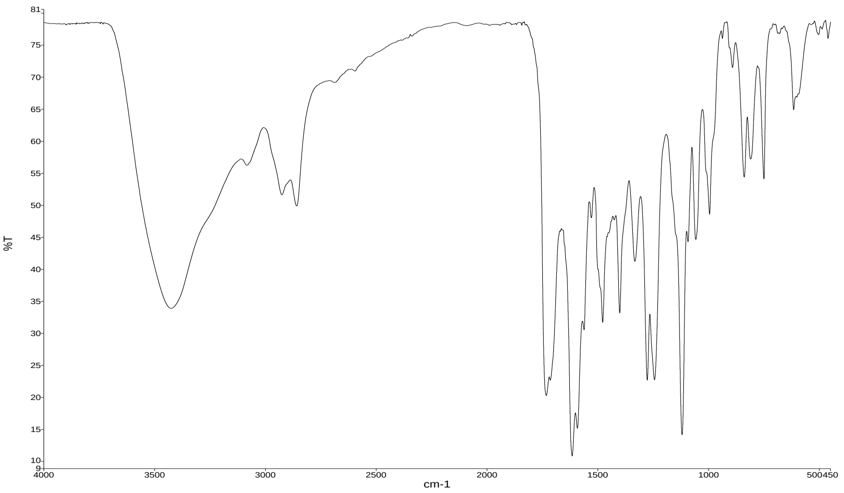


Fig. 4*: FT-IR of Nickel (II) phthalocyanine*

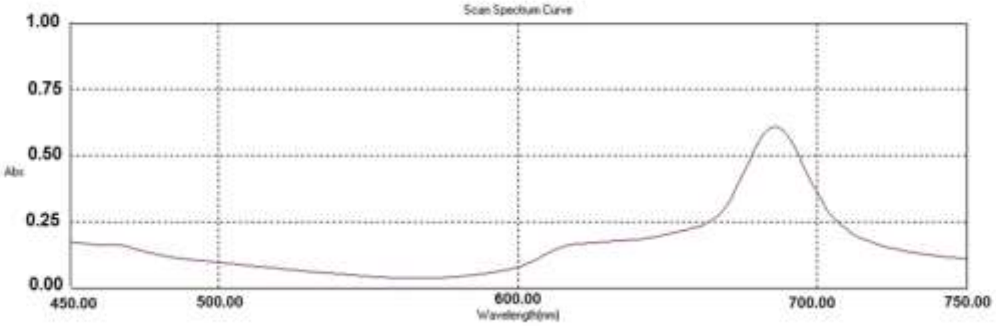


Fig. 5: *UV spectrum of Nickel phthalocyanine*

The synthesized NiPc compound showed an intense Q band at 690 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 the lowest occupied molecular orbital (LUMO) of the phthalocyanine ring. Aggregation was also observed at 615 nm.

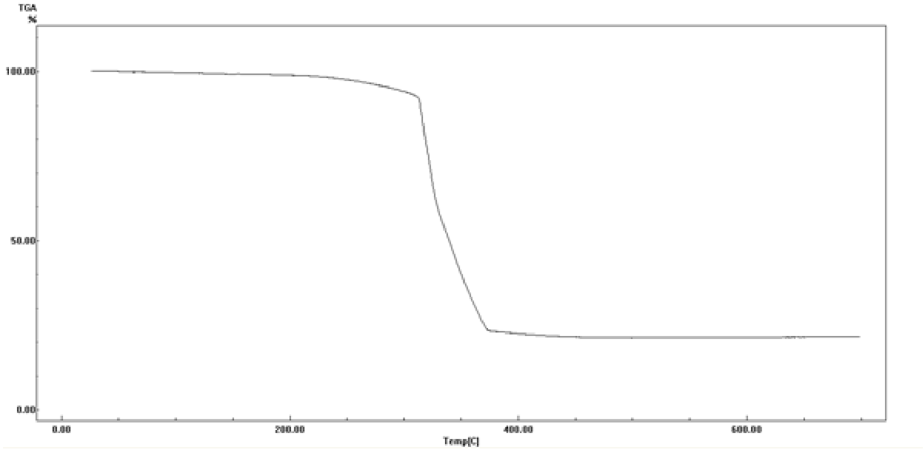


Fig. *6: TGA of Nickel Phthalocyaninne*

The thermographic analysis results of the synthesized nickel phthalocyanine compound showed that the synthesized compound began to exhibit weight loss at a temperature of 309 ºC, which indicated a suitably high thermal stability of the newly synthesized compound.

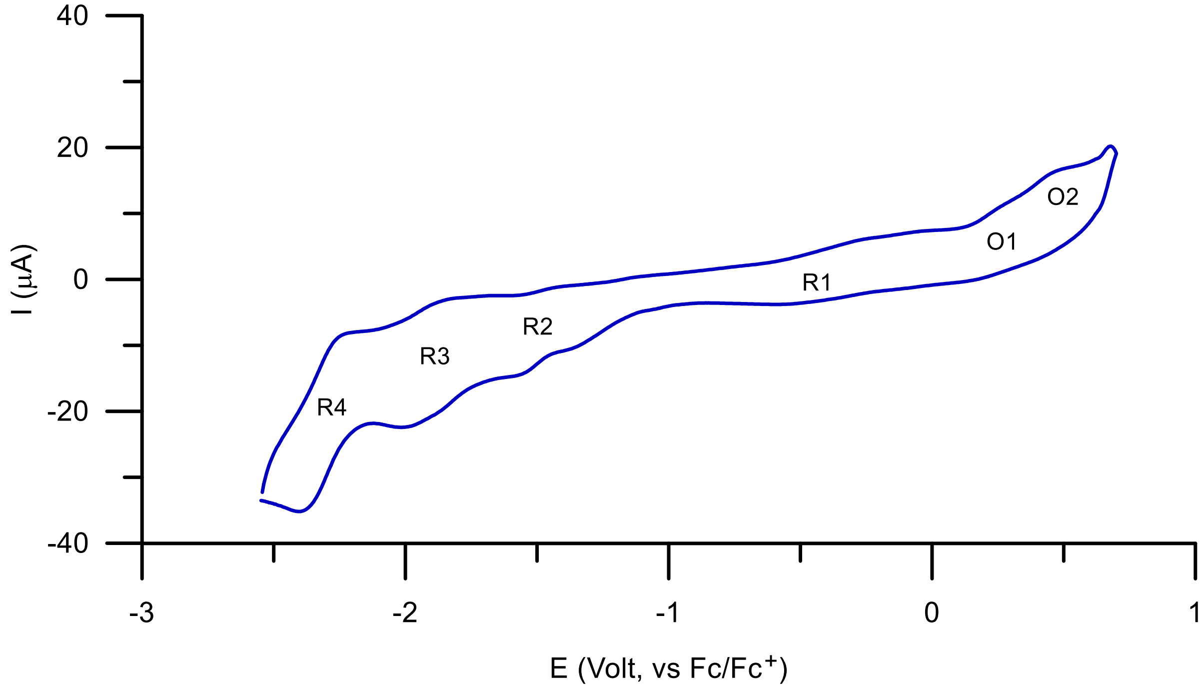


Fig. 7: *Cyclic Voltamogram of NiPc*

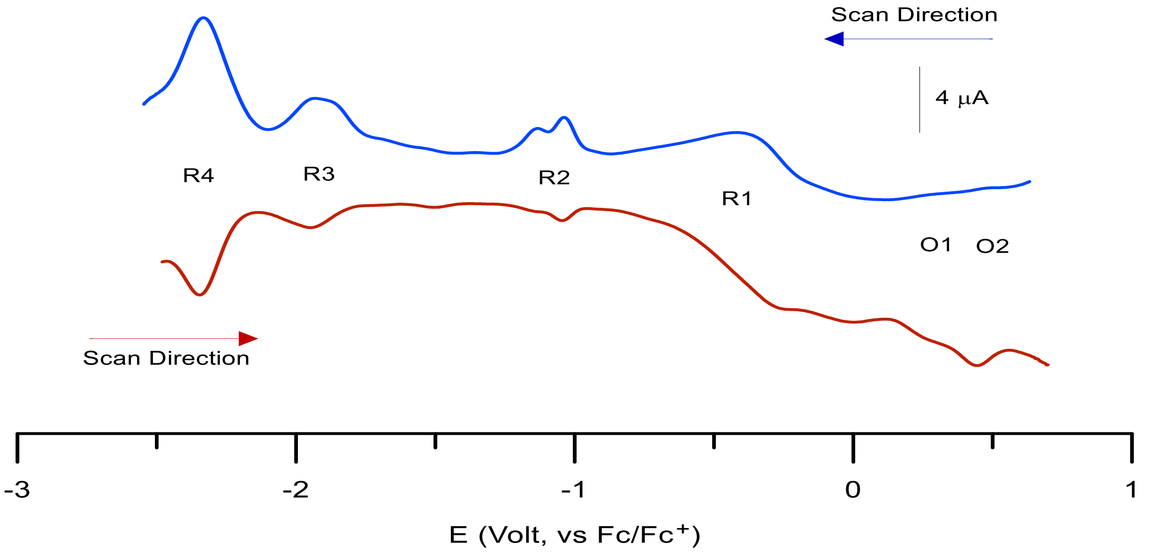


Fig. 8: *Square Wave voltamogram of NiPc*

Figs. 7 and 8 represent Cyclic Voltamogram (CV) and Square Wave voltamogram (SWV) responses of NiPc in DMF/TBAFB electrolyte on a glassy carbon working electrode. NiPc gave two reversible reduction reactions, R1 at -1.04 V, R2 at -1.94 V, R3 at -2.33 V and two irreversible oxidation reactions O1 at 0.27 V and O2 at 0.46 V. The potential difference between the first reduction step and the first oxidation step of redox inactive metallophthalocyanine complexes is about 1.31 V and corresponds to the energy difference between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) energy level of the phthalocyanine. SWV of the NiPc supports these quasi-reversible characters of the processes (Fig. 8). Generally, the reduction and oxidation behaviour of metal phthalocyanine derivatives 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 was heated to 700 °C to determine their degradation temperature, the temperature at which the phthalocyanines began to exhibit weight loss was 309 °C which indicates a suitably high thermal stability of the compound.

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 Nickel phthalocyanine compound (NiPc) in DMF is given in figure 5 above. The UV-Vis absorption spectra of NiPc in DMF showed intense Q absorption at 690 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 (in the center or non-peripheral position).

CONCLUSION

This research work shows the synthesis and characterization of metal phthalocyanine bearing 7-Hydroxy coumarin substituents on the α nonperipheral 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 metal phthalocyanine complex could be useful in various industrial processes such as oxidation, catalysis, and solar screens.

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