



Synthesis and Characterization of Metal Phthalocyanine Complex Using Substituted 4-Nitrophthalonitrile Ligand

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Abstract:

In this research work, four compounds: 4-nitrophthalamide, 4-nitrophthalonitrile and 4-(ciproxy) phthalonitrile and phthalocyanine complex were synthesized. The synthesis began with the nitration in the position 4 of phthalamide which led to the formation of 4-nitrophthalamide. Dehydration by the thionyl chloride in N,N-dimethylformamide (DMF) led to the formation of 4-nitrophthalonitrile and further reaction of ciprofloxacin with 4-nitrophthalonitrile in DMF forms the phthalonitrile derivative, cyclotetramerization of 4-(ciproxy) phthalonitrile in the presence of nickel salt gave substituted metal phthalocyanine complex. The

structures of the synthesized compounds were characterized by NMR, FT-IR spectrophotometry and UV-VIS. Melting point of the compounds were checked by Griffin MFB-590. The melting points of 4-nitrophthalamide and 4-nitrophthalonitrile were found to be 223 °C and 175 °C respectively. Solubility of the compounds was confirmed in some common laboratory solvent (acetone, methanol and DMF). The electronic spectra of nickel phthalocyanine compound in DMF showed intense Q absorption at 690 nm. The thermal stability of the phthalocyanine derivatives was checked by TGA; the phthalocyanine was heated up to 700 °C to determine the degradation temperature. The temperatures at which the phthalocyanine began to exhibit weight loss was 309 °C. It could, therefore, be concluded that the metal phthalocyanines prepared in this study showed suitably high thermal stability and can be used for further analysis.

Keywords: *Phthalocyanine, Ciprofloxacin, Phthalamide.*

Introduction

The word phthalocyanine (Pc) was derived from the Greek word naphtha, meaning rock oil and cyanine, meaning blue (Chohan, 2015). Phthalocyanines (Pcs) are symmetrical 18 π -

electron aromatic macrocycles, closely related to the naturally occurring porphyrins (Chen et al., 2021). They are chemically and thermally stable compounds which can host more than seventy different metal ions in the central cavity



(Zawadzka et al., 2014). They are an important industrial commodity that can be prepared from aromatic ortho-disubstituted derivatives including o-cyanobenzamides, phthalic acids, phthalic anhydrides, phthalimides, phthalamides, 1,3-diiminoisoindolines, and phthalonitriles (Yamada et al., 2018). The most useful of all the phthalocyanine precursors are phthalonitriles (Yamada et al., 2018). Heating of phthalonitriles in high boiling solvents in the presence of metal salts results in templated cyclotetramerization and formation of a phthalocyanine dye. Non-substituted and some simple substituted phthalonitriles are available from commercial sources, but the vast majority needs to be synthesized, often via multi-step, challenging routes (Liu et al., 2014).

Phthalocyanines have a wide range of applications, such as a catalysis, chemical sensors, dyes, pigments and colours, gas sensors, electrochromism, batteries, semiconductive materials, liquid crystals, nonlinear optics and photodynamic therapy (Eriyilmaz et al., 2017). 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 properties and applications of phthalocyanine complexes can be tuned by modifying the structure of the ligand and the choice of the metal ion (Yang et al., 2021). Researchers continue to explore and develop new phthalocyanine complexes with improved properties for various technological applications.

Most Phthalocyanines lack affinity to water, and are prone to add up in aqueous medium, or they do not have a very reactive group purposely for bio conjugation. The first commercially available phthalocyanine dye is La jolla Blue, with two free carboxylic acids for bio conjugation and two axial polyethylene glycol moieties (Alharbi, 2014). Axial glycol moieties make the dye non hydrophobic and soluble and therefore, appealing as a biomarker. Various biomolecules like proteins and peptides can link to

phthalocyanine dyes which are therefore, used in bioanalytical and bioimaging fields (Yang et al., 2020). Natarajan et al. (2017) synthesized a form of phthalocyanines which are hydrophobic axial groups, but contains both hydrophilic groups and a reactive group that is attached to the benzo-ring. Another metalloid like silicon can replace copper in this structure which will allow it to have two axial ligands (Natarajan et al. 2017).

Metal phthalocyanine complexes have also attracted attention in various engineering and technological fields such as electronic devices due to their structure rich in π -conjugation system owing to potential applications (Ghosh et al., 1974). However, the poor solubility of metal phthalocyanine limits their applications in some biological fields. To solve this problem, introducing certain substituent at their peripheral ring (Seelan et al., 2001) will be a promising way.

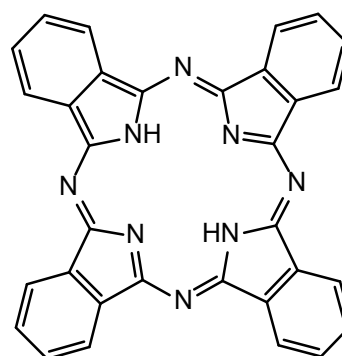


Figure 1. Structure of Phthalocyanine

Materials and Methods

Materials

Phthalamide was obtained from Merck, Nitric acid, thionyl chloride and Sulphuric acid were procured from Qualikems, Ciprofloxacin was obtained from Fidson, 1,8-diazabicyclo [5.4.0] -undec7-ene (DBU), nickel and Potassium carbonate (K_2CO_3) were purchased from Merck and used after drying. Anhydrous N,N-dimethyl formamide (DMF), glycerol solution, were obtained from Sigma-Aldrich and used as received without further purification.. Melting

points of the compounds were determined with Griffin MFB-590.

Methods

FT-IR spectrum of the samples were recorded on an FT-IR spectrophotometer (Perkin Elmer). UV-Vis spectra were recorded on a T80+UV/VIS spectrophotometer. At a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$, TGA was conducted under Argon using a SHIMADZU Thermogravimetric Analyzer TGA-50 Instruments. ^1H spectra were taken using Bruker Ultra-shield 400 MHz with DMSO-d_6 as solvents and tetramethylsilane as an internal standard. Synthesis of the metal phthalocyanines began with the nitration in the position 4 of the phthalamide which led to the formation of the 4-nitrophthalamide; then dehydration by the thionyl chloride in N,N-dimethylformamide led to the formation of 4-nitrophthalonitrile. Phthalonitrile derivative containing a ciprofloxacin as substituent was prepared by nucleophilic substitution reaction of 4-nitrophthalonitrile in the presence of K_2CO_3 as a base in non-aqueous organic solvent.

The cyclotetramerization of dinitrile with metal salt in the presence of DBU was performed with glycerol and DMF solutions.

For the purpose of this research, phthalamide was used as a precursor and the proposed stepwise procedure which is a modification of a reported synthesis and characterization of New Zn-phthalocyanine compound (Touaiti *et al.*, 2017) and the chain for the alternative method of this synthesis were shown.

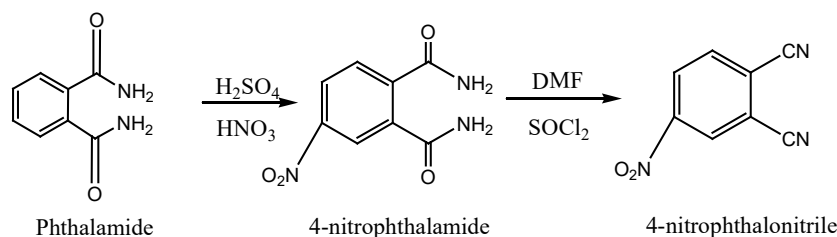


Figure 2. Synthesis of 4-Nitrophthalonitrile

Synthesis of 4-(Ciproxy)phthalonitrile

0.866g (5.0mmol) of 4-nitrophthalonitrile was dissolved in 10 ml of dried N,N-

Synthesis of 4-Nitrophthalamide

30 ml of nitric acid was measured into 500 ml round bottom flask and cooled to $0\text{ }^{\circ}\text{C}$. 30 ml sulphuric acid was slowly added at a temperature of $0\text{--}5\text{ }^{\circ}\text{C}$ after it had properly mixed. The temperature was then increased to a room temperature. 15g (91.4mmol) phthalamide was added and the temperature was increased to $110\text{ }^{\circ}\text{C}$ 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 57.12% and $223\text{ }^{\circ}\text{C}$ respectively.

Synthesis of 4-Nitrophthalonitrile

25 ml of thionyl chloride was added drop wise (keeping the temperature between 5 and $7\text{ }^{\circ}\text{C}$) to 38 ml of dry N,N-dimethylformamide (DMF) in a round bottom flask which was already cooled to $0\text{ }^{\circ}\text{C}$, and was stirred for 3 hours at this temperature ($5\text{--}7\text{ }^{\circ}\text{C}$) in an ice bath. 7.0 g (33.5 mmol) of 4-Nitrophthalamide was slowly added to this reagent mixture at such a rate keeping the temperature below $10\text{ }^{\circ}\text{C}$. The mixture was stirred for 6 hours at $0\text{--}5\text{ }^{\circ}\text{C}$ and then 72 hours at room temperature, the reaction mixture was slowly poured into an ice, precipitated and vacuum filtered, rinsed with cold water three times. It was air dried to constant weight. Melting point and percentage yield were found to be $175\text{ }^{\circ}\text{C}$ and 56% respectively.

dimethylformamide (DMF) under argon and 0.623 g (1.88mmol) of 1-cyclopropyl-6-fluoro-4-oxo-7-piperazin-1-ylquinoline-3-carboxylic acid

(Ciprofloxacin) was added and stirred for 15 minutes at room temperature. The temperature was increased to 80 °C. 0.691 g (5.0mmol) of finely ground anhydrous potassium carbonate was added in portions for 1hour with efficient stirring for 3 hours. It was occasionally checked

for the disappearance of NO₂ peak at 1535 cm⁻¹ and 1353 cm⁻¹ by F-TIR. The ensuing mixture was then poured into 100 ml distilled water and the precipitate was filtered, washed and dried to constant weight with melting point of 250 °C and percentage yield of 41% (Touaiti et al., 2017).

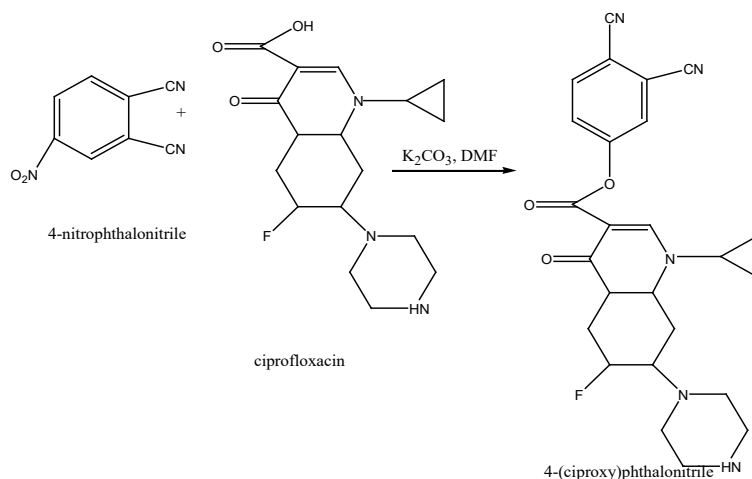


Figure 3. Synthesis of 4-(ciproxy)phthalonitrile

Synthesis of Nickel phthalocyanine

0.40 g (0.9 mmol) of Phthalonitrile was added to 10ml of glycerol and stirred, 0.100g (0.057mmol) of nickel acetate and 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (4 drops) was added, stirred and heated at a reflux temperature under an argon atmosphere for 24 hours. After cooling to room temperature, the reaction mixture was precipitated by dropwise addition to distilled

water (200 ml). The product was collected by filtration, washed with distilled water, dried. (Touaiti *et al.*, 2017). The compound was purified by dissolving in 3.0 ml of sulphuric acid, stirred and precipitated in distilled water, vacuum filtered and washed several times with distilled water until the pH of the water was neutral. The green product was dried and weight yield of 0.375 g, 57.8 % was obtained.

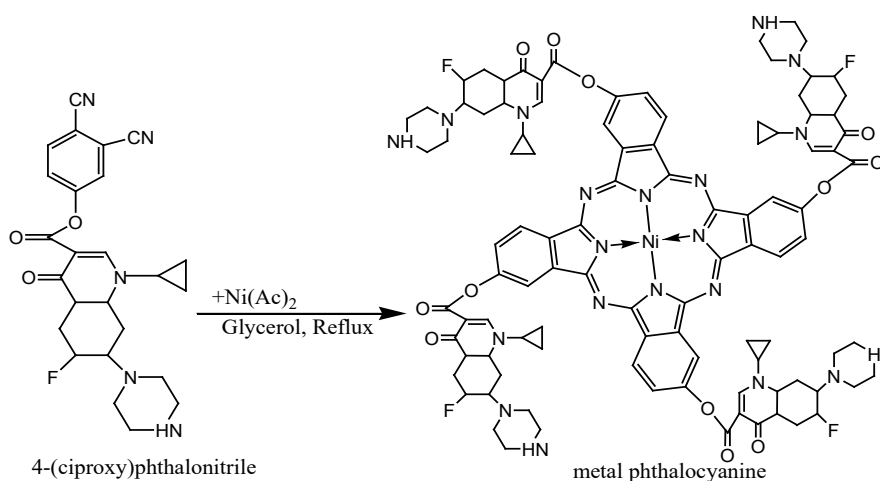


Figure 5. Synthesis of Nickel Phthalocyanine Complex

All reactions were performed under argon atmosphere.

Results and Discussion

The synthesized 4-nitrophthalonitrile is presented in Figure 11. It was obtained through nitration in position 4 of phthalamide leading to the formation of the 4-nitrophthalamide; then dehydration by the thionyl chloride in N,N-dimethylformamide led to the production of 4-nitrophthalonitrile. Phthalonitrile derivative was obtained through the nucleophilic substitution reaction between 4-nitrophthalonitrile and ciprofloxacin at 80 °C under argon atmosphere in dry DMF in the presence of K_2CO_3 as a base with 40.9 % yield. Cyclotetramerization of the phthalonitrile derivative in a high-boiling glycerol in the presence of a few drops 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) as a strong base and metal salt at reflux temperature under an argon atmosphere afforded the synthesized phthalocyanine. Characterization of the compounds were carried out by NMR, FT-IR, UV-vis spectra and TGA. FT-IR spectrum of 4-nitrophthalamide and 4-nitrophthalonitrile

compound were observed as expected, at 1540 cm^{-1} and 2243 cm^{-1} respectively which confirmed the formation of NO_2 and $C\equiv N$ peaks. The most important proof of the cyclotetramerization of nitrile groups is the absence of the $-C\equiv N$ vibrations at 2230 cm^{-1} for Phthalocyanine compound in IR spectra of the substituted metal phthalocyanine compounds. The melting points of the synthesized 4-nitrophthalamide and 4-nitrophthalonitrile was $223\text{ }^\circ\text{C}$ and $175\text{ }^\circ\text{C}$ respectively.

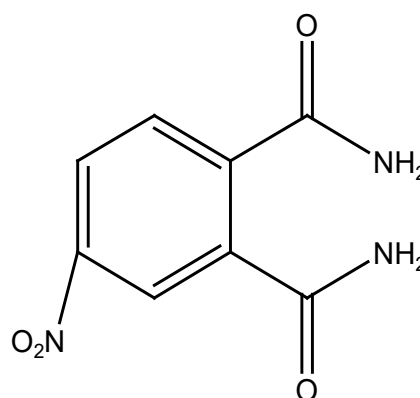


Figure 6. 4-Nitrophthalamide

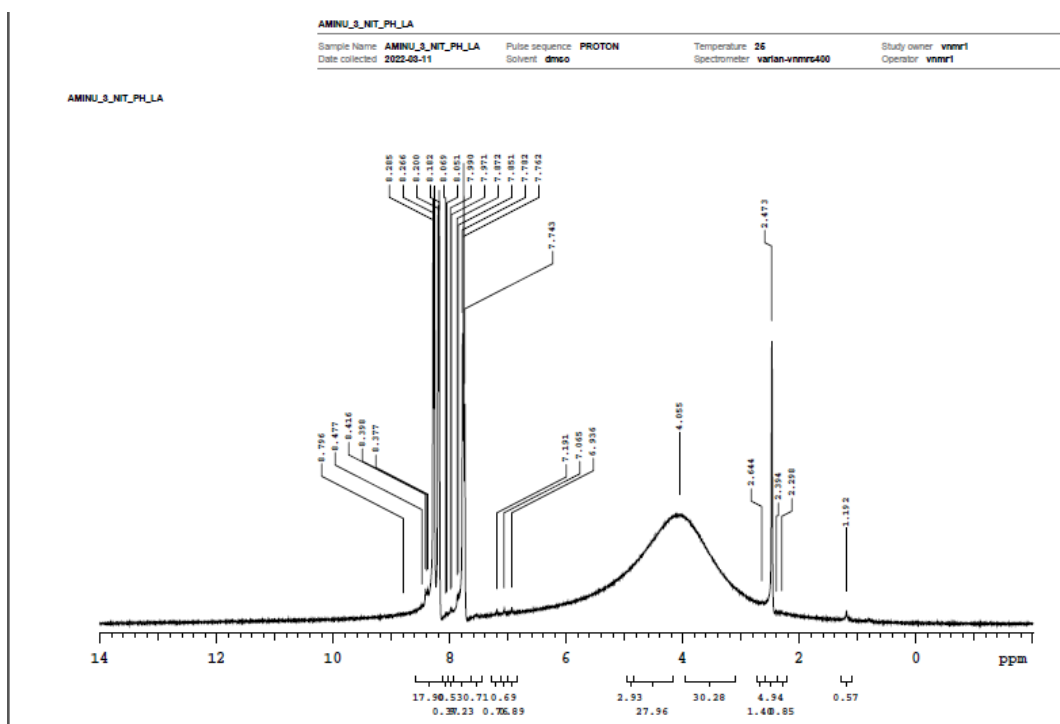


Figure 7. NMR of 4-Nitrophthalamide

¹H NMR (DMSO-d₆, 500 MHz, TMS, δppm)

Data:

7.74 (s, 4H), 8.06 (d, 1H), 8.18 (s, 1H), 8.28 (d, 1H).

Sharp and intense singlet peak at 7.74 ppm is due to four amide protons which are at the same chemical environment. The doublet peaks at 8.06 ppm is assignable to auto C-H proton, similarly the singlet peak at 8.18 ppm is attributed to meta C-H proton, whereas the

doublet peaks at 8.28 ppm which goes to downfield is assigned to C-H proton which is para to amide group.

Table 1. FT-IR Results of 4-Nitrophthalamide

Frequency (Cm ⁻¹)	Bond Vibration
3115	Ar-CH
877	C-N
1681	C=C
1540	Ar-NO ₂

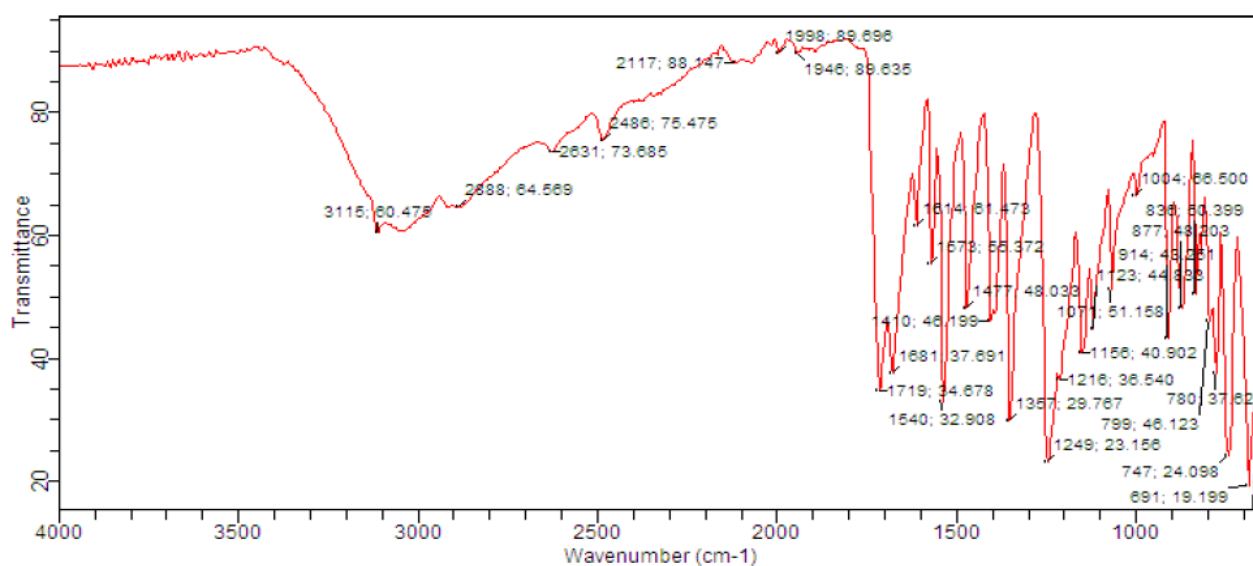


Figure 8. FT-IR of 4-Nitrophthalamide

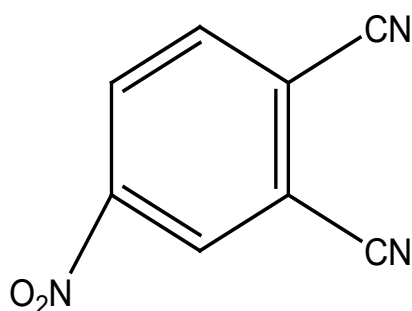


Figure 9. 4-Nitrophthalonitrile

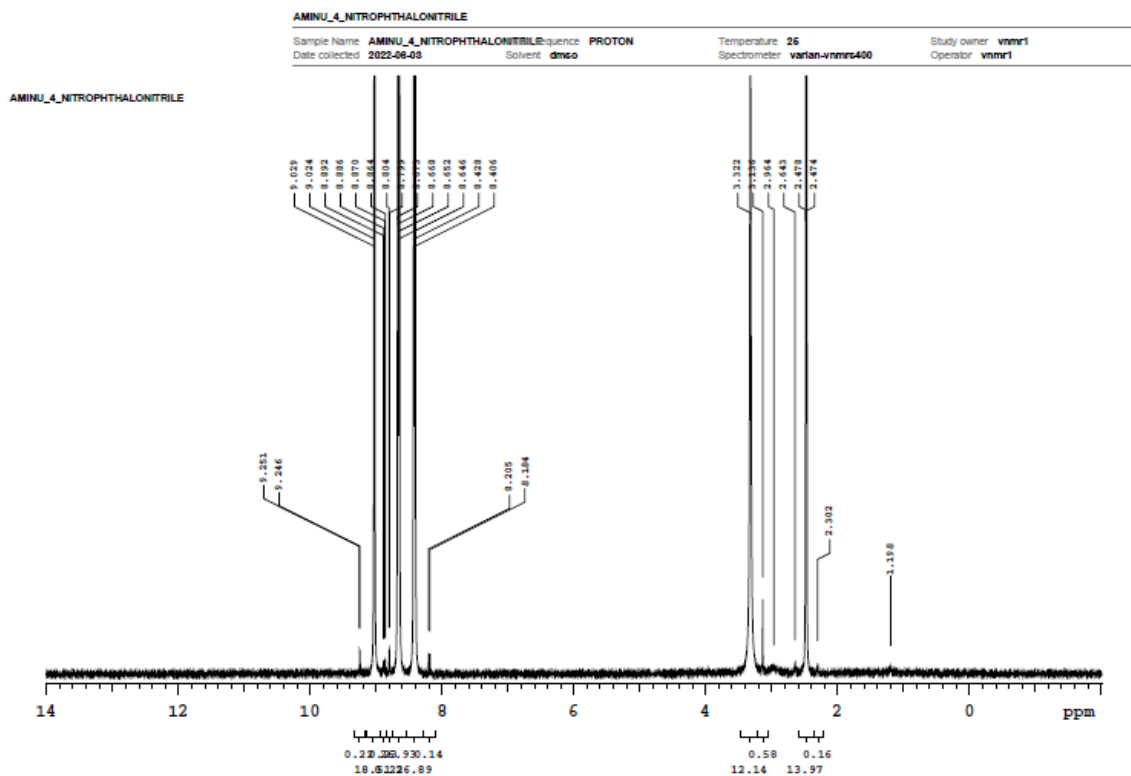


Figure 10. NMR of 4-Nitrophthalonitrile

4-nitrophthalonitrile ^1H NMR (DMSO- d_6 , 500 MHz, TMS, δ ppm) Data:

8.19 (d, 1H), 8.804 (s, 1H), 9.25 (d, 1H).

The doublet peak at 8.79 ppm is due to one proton at auto-position, whereas, the singlet peak at exactly 8.804 ppm is attributed to one proton at meta-position. It is single since it has no neighboring proton and the doublet at 9.25 ppm is assigned to one proton at position 5. It is para to strong electron withdrawing group (nitrile) and as well neighboring another strong electron withdrawing group (nitro) as such it goes to downfield (higher chemical shift value).

Table 2. FT-IR Results of 4-Nitrophthalonitrile

Vibration (Cm^{-1})	Vibration
3086	Ar-CH
2243	$\text{C}\equiv\text{N}$
1610	$\text{C}=\text{C}$
1535	Ar- NO_2

Table 3. FT-IR Results of 4-(Ciproxy)phthalonitrile

Frequency (Cm^{-1})	Bond Vibration
3078	Ar-CH
2236	$\text{C}\equiv\text{N}$
1629	$\text{C}=\text{C}$

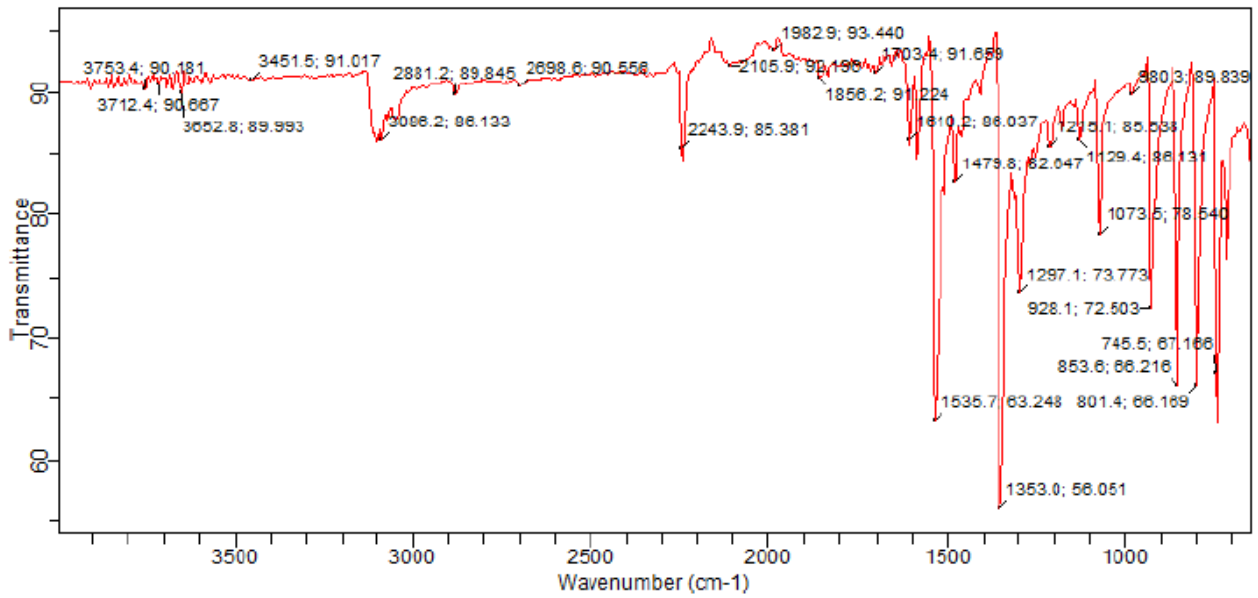


Figure 11. FT-IR of 4-Nitrophthalonitrile

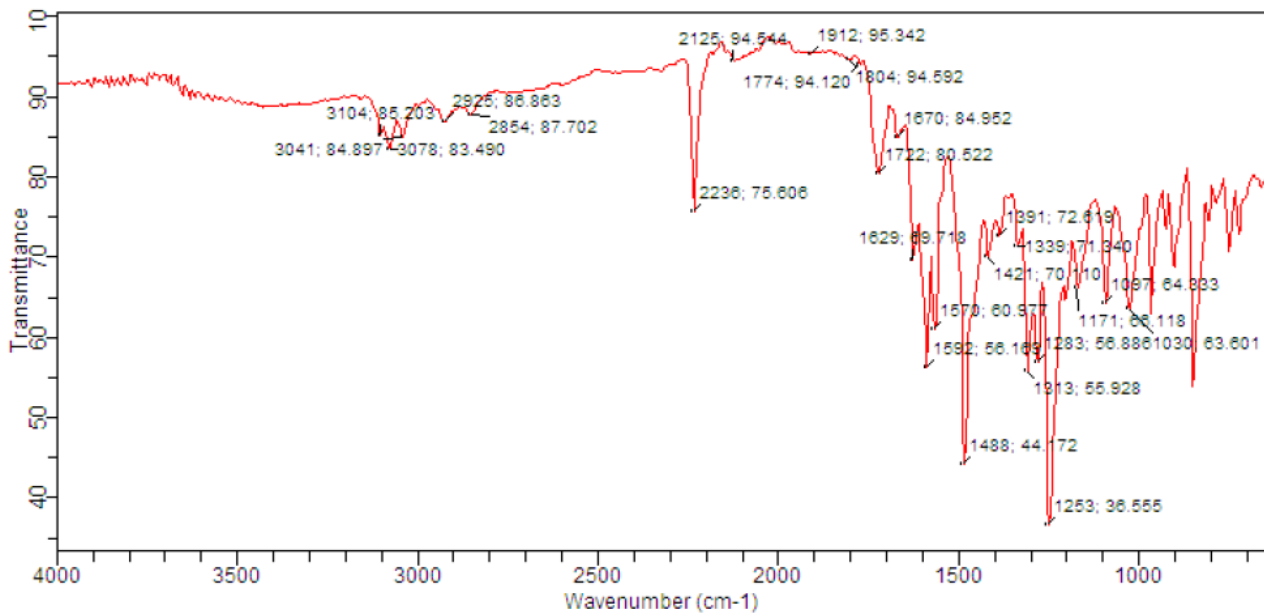


Figure 12. FT-IR of 4-(Ciproxy)phthalonitrile

This compound was synthesized using 4-Phthalonitrile and Nickel acetate in DMF and Glycerol solutions (1:3).

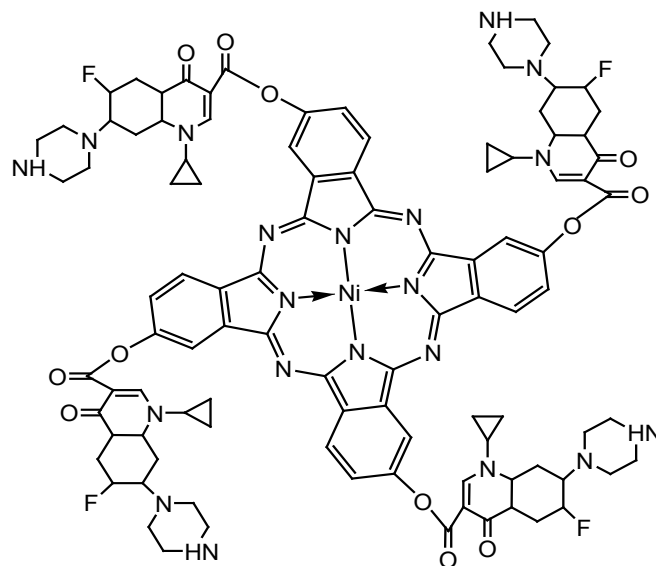


Figure 13. Nickel Phthalocyanine

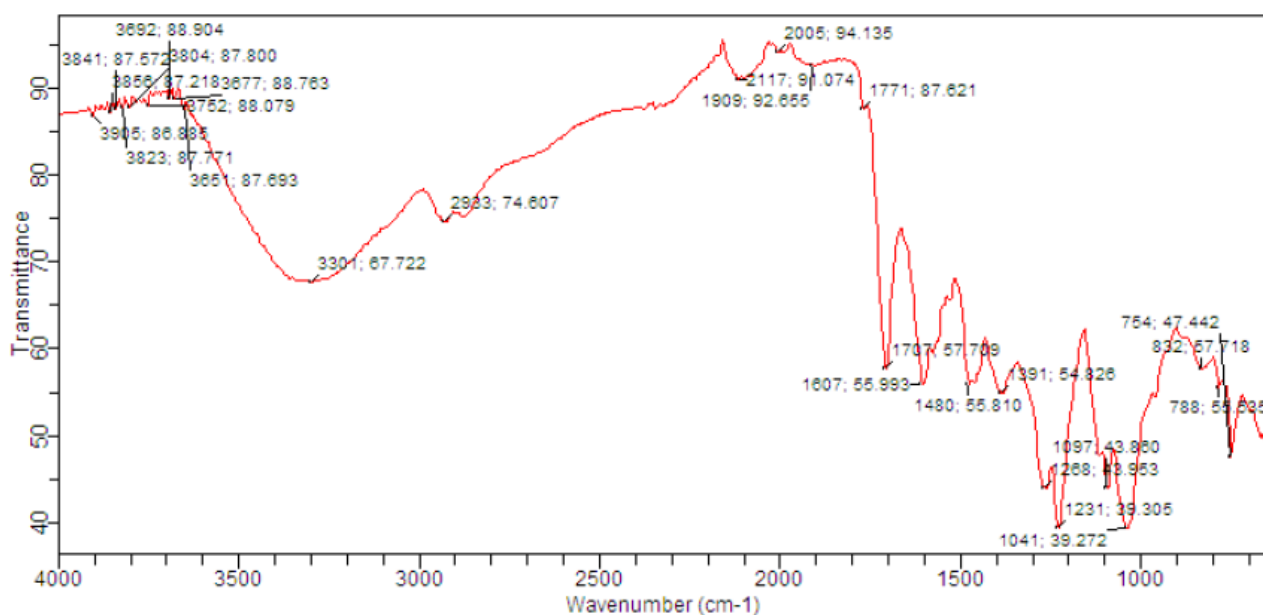


Figure 14. FT-IR of Nickel phthalocyanine

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

Table 5. FT-IR results of Nickel(II) phthalocyanine

Vibration (Cm ⁻¹)	Vibration
2925	Ar-CH
1732	C=O
1615	C=C
1276	C-O

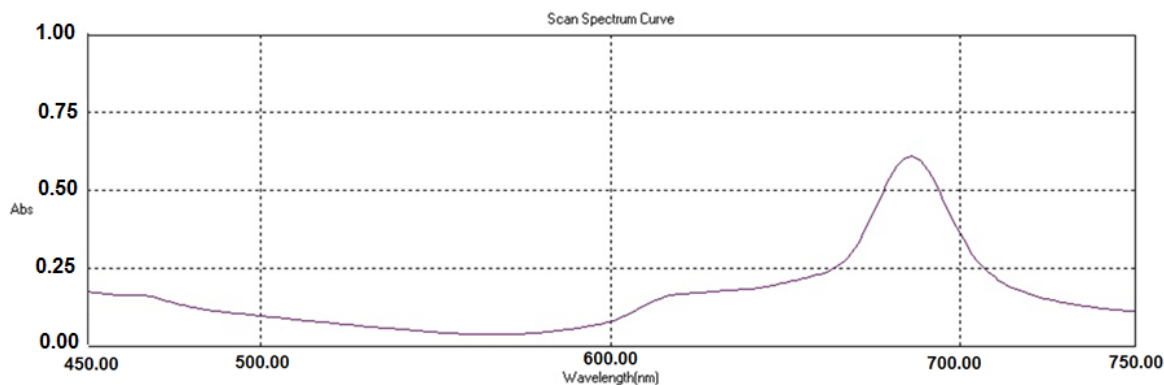


Figure 15. UV spectrum of Nickel phthalocyanine

The synthesized NiPc compound showed 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 (HOMO) to lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring. Aggregation was also observed at 615 nm.

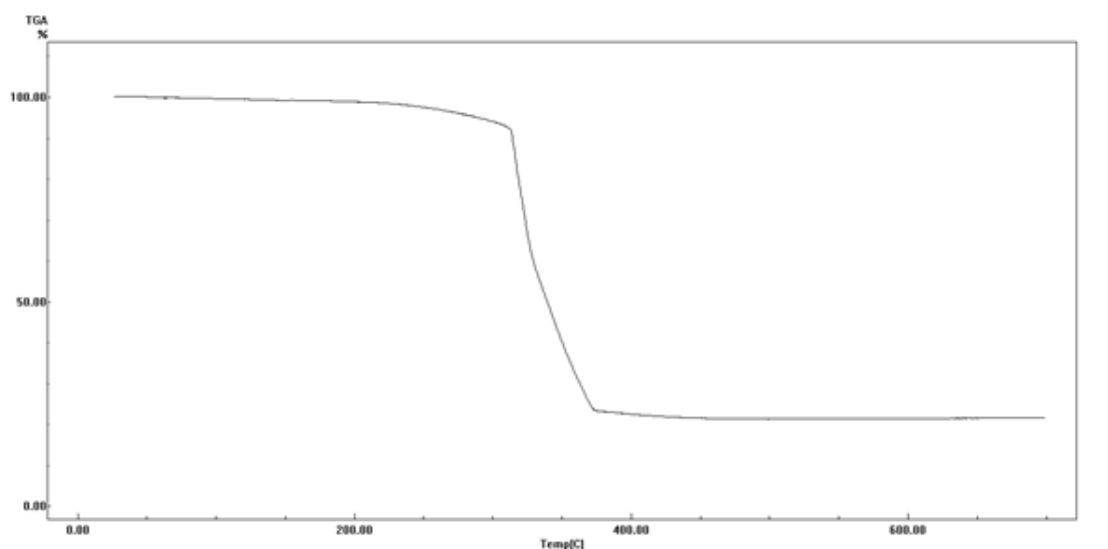


Figure 16. TGA of Nickel Phthalocyanine

The thermographic analysis result of the synthesized nickel phthalocyanine compound it showed that the compound began to exhibit weight loss at a temperature of 309 °C which indicates a suitably high thermal stability for the newly synthesized compound.

Conclusion

The synthesis and characterization of 4-nitrophthalamide, 4-nitrophthalonitrile and metal phthalocyanine complex bearing ciprofloxacin as substituents was achieved. These compounds were characterized by NMR and FT-IR. The study shows that 4-nitrophthalamide and 4-nitrophthalonitrile compounds are partially soluble in some organic

solvents such as acetone, methanol, and DMF. The complex could also be considered to exhibit high thermal stability. The result of this study shows that the synthesized metal phthalocyanine complex could be useful in various industrial processes such as oxidation, catalysis and solar screens.

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