REPUBLIC OF TURKEY
FIRAT UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES

SYNTHESIS AND CHARACTERIZATION OF 7-HYDROXYCOUMARIN CONTAINING NEW TYPE OF PHTHALOCYANINE COMPOUNDS AND INVESTIGATION OF THERMAL AND ELECTROCHEMICAL PROPERTIES

Master Thesis

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Department: Chemistry

Supervisor: Prof. Dr. Sinan SAYDAM

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June-2017

DEDICATION

This work is dedicated to my dear parents, son and wife. This is a sign of my gratitude because, i can never thank you as much as necessary for your guidance, love, patient, encouragement, and prayers.

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All praises and thanks are due to almighty Allah by whose grace all good deeds are accomplished. Peace and blessing be upon our noble Prophet Muhammad (Sallallahu alaihi wasallam) his household and companions.

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7-HİDROKSİKUMARİN GRUBU BULUNDURAN YENİ TİP FTALOSİYANİN BİLEŞİKLERİNİN SENTEZİ, TERMAL VE ELEKTROKİMYASAL ÖZELLİKLERİNİN ARAŞTIRILMASI

Bu çalışmada, 3-((2-okso-2H-kromen-7-yil)oksi)ftalonitril, bileşiği DMF ortamında, 7-hidroksikumarin ve 3-nitroftalonitrilden sentezlendi. Daha sonra, 3-((2-okso-2H-kromen-7-yil)oksi)ftalonitril'in metal tuzları (Ni(II), Co(II), Zn(II), Cu(II), Fe(II)) yanında tetrameşleştirilmesi ile, metalli periferal ftalosiyanin kompleksleri sentezlendi. Metalsiz ftalosiyanin bileşiğini sentezleme girişimleri başarısızlıkla sonuçlanmıştır. Sentezlenmiş olan bileşiklerin karekterizasyonu, mikroanaliz, NMR, UV-Görünür bölge ve FT-IR spektroskopik teknikleri ile karekterize edildi.

Sentezlenmiş olon ftalosiyanin komplekslerinin genel labaratuvar çözücülerindeki çözünürlüklerinin çok az olduğu gözelndi. Kompleklerden nikel, bakır ve çinkonun Q bandının DMF içinde alınan UV-Görünür bölge spektrumlarında 690 nm de gözlenirken, kobalt ve demir ftalosiyanin komplekslerinin 670 nm de olduğu görüldü.

Komplekslerin oda sıcaklığından 700 ^{o}C ye kadar, terma özellikleri TGA ile yapıldı. NiPc, CoPc, ZnPc, CuPc, and FePc ftalosiyanin komplekslerinin ağırlık kaybının sırası ile 309, 300, 306, 354 ve 380 ^{o}C den itibaren başladığı görüldü.

Sentezlenmiş olan ftalosiyanin komplekslerinin elektrokimyasal ölçümleri, DMF ortamında dönüşümlü voltametri ve kare dalga voltametri yöntemleri ile yapıldı. Bütün komplekslerde ftalosiyanin komplekslerine ait karekteristik yükseltgenme ve indirgenme potansiyelleri gözlenirken, kobalt ve demir ftalosiyanin komplekslerinde bunlara ilaveten, metal atomlarının elektroaktif olmaları sebebi ile, metal atomlarına ait yükseltgenme ve indirgenme potansiyelleri de gözlendi.

Metal ftalosiyanin komplekslerinin düşük çözünürlükleri deney kapsamını sınırlamasına rağmen, fakat hazırlanan metal ftalosiyanin bileşiklerinin yüksek termal kararlılık göstermelerinden dolayı çeşitli uygulamalar için kullanılabilirler.

Anahtar Kelimeler : Ftalosiyanin, 3-nitroftalonitrile, 3-((2-okso-2H-kromen-7-yil)oksi)ftalonitril, kumarin, 7-hidroksikumarin, elektrokimya, dönüşümlü voltametri, karedalga voltametri, termal analiz.

ABSTRACT

In this work, 3-((2-oxo-2H-chromen-7-yl)oxy)phthalonitrile has been synthesized from the reaction of 7-hydroxycoumarin with 3-nitrophthalonitrile in DMF. Then cyclotetramerization of 3-((2-oxo-2H-chromen-7-yl)oxy)phthalonitrile in the presence of metal salts, (Ni(II), Co(II), Zn(II), Cu(II), Fe(II)) gave peripherally substituted metallated phthalocyanine complexes. We failed to synthesize the metal-free phthalocyanine compound. The structures of the synthesized compounds were characterized by a combination of microanalysis, NMR, UV-Vis, and FT-IR spectrophotometry.

Solubility of metallated phthalocyanine complexes found to be very low in common laboratory solvent. The electronic spectra of iron, cobalt, nickel, copper, zinc phthalocyanine compounds (NiPc, CuPc, ZnPc) in DMF in DMF, showed intense Q absorption at 690 nm. The Q band absorptions were observed at 670 nm, for CoPc, and FePc.

The thermal stability of the phthalocyanine derivatives were checked by TGA and then the phthalocyanines were heated up to 700 ^oC to determine their degradation temperature. The temperatures at which the phthalocyanine began to exhibit weight loss were 309, 300, 306, 354 and 380 ^oC for NiPc, CoPc, ZnPc, CuPc, and FePc respectively.

Electrochemical measurements of the phthalocyanine complexes synthesized were carried out by means of cyclic voltammetry and square wave voltammetry in DMF. Characteristic oxidation and reduction potentials of phthalocyanine complexes were observed in all the compounds. In addition to these, in the complexes of cobalt and iron phthalocyanine, the oxidation and reduction potentials of metal atoms were observed due to the electroactive nature of metal atoms.

Although the low solubility of the metal phthalocyanines complexes limited the scope of experiments, but the metal phthalocyanines prepared in this study showed suitably high thermal stability and can be used for various applications.

Keywords: Phthalocyanine, 3-Phthalonitrile, 3-((2-oxo-2H-chromen-7-yl)oxy) phthalonitrile, Coumarine, 7-hydroxycoumarine, electrochemistry, cyclic voltammetry, square wave voltammetry, thermal analysis.

TABLE LIST

FIGURE LIST

ABBREVIATION

CoPc	Cobalt Phthalocyanine
CuPc	Copper phthalocyanine
NiPc	Nickel Phthalocyanine
ZnPc	Zinc Phthalocyanine
FePc	Iron Phthalocyanine
DBU	1,8-diazabicyclo[5.4.0]-undec7-ene
DMF	N, N-dimethylformamide
DMSO	Dimethyl solfoxide
THF	Tetrahydrofuran
FT-IR	Fourier Transform Infrared
MPc	Metal Phthalocyanine
NMR	Nuclear Magnetic Resonance
Pc	Phthalocyanine
UV-VIS	Ultraviolet Visible Spectrum
^{1}H-NMR	Proton nuclear magnetic resonance

1. INTRODUCTION

Phthalocyanines (Pcs) are symmetrical 18 π-electron aromatic macrocycles, closely related to the naturally occuring porphyrins [1]. Phthalocyanines are chemically and thermally stable compounds which can host more than seventy different metal ions in the central cavity [2]. 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 [3]. Despite the number of actual applications, further research is still in dispensable since many other future applications are envisaged. The physical properties and the processability required for technological applications can be chemically tuned by changing the peripheral substituents and/or the central metal [4]. 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, for example as molecular switches and solar cells, among others [5].

Coumarins are a group of polyphenolic compounds first isolated from plant product Tonka bean, coumarou in 1820. Coumarins are colorless and crystalline phytochemical substances [6]. 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 Figure 3.3 [7,8]. Benzopyrones are subdivided into benzo-α-pyrones and benzo-γ-pyrones of which coumarins and flavonoids are prime members of benzo-α-pyrones and benzo- γ –pyrones class respectively. The biochemical, pharmacological and therapeutic applications of simple coumarins could be influenced by the substitution pattern. Studies have proven that coumarins act as competitive inhibitors of vitamin K. Other intricate compounds are based on the coumarin nucleus which comprises of the anticoagulants like warfarin, aflatoxins and the psoralens [9]. Studies have also shown that they function as blood diluting agent and also exhibits anti-fungicidal property. Researches have also proved the selective cytotoxicity of coumarins for tumor cells and also the effect of coumarins in the regulation of immune response, cell growth and differentiation [10]. Nowadays, coumarins are also used as additives in food and cosmetic industry, as laser dyes, agrochemical industries and also as optical brightening agents. Coumarin covers a very wide range of compounds throughout the plant kingdom and are found rich in fruits, roots, stems and leaves. They are rich in cassia leaf oil, lavender oil and cinnamon bark oil. Richest sources are found in Rutaceae and Umbelliferone. Coumarins are also found in selective microorganisms. Members of coumarins isolated from microbial sources are novobiocin from Streptomycin and aflatoxin from Aspergillus species. They are also used as enhancing agent in cosmetic products like perfumes, soap, detergents, toothpaste and alcoholic beverages [11]. It is also used as a neutralizer in rubber and plastic materials and also in paints and sprays to dilute the unpleasant odors [12].

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 [13].

1.1. History of phthalocyanine

The word phthalocyanine is derived from the Greek words for naphtha, meaning rock oil and cyanine, meaning blue [14]. Sir Patrick Linstead in 1933 was the first to use this term to describe a new class of organic compounds [15].

Phthalocyanine itself, however, is believed to have been discovered in 1907 as an accidental by-product of the synthesis of o-cyanobenzamide. The development of phthalocyanine started in 1928 at Scotland Dyes Works [16]. The workers using phthalimide found it to be contaminated with a dark colored impurity. They called in their scientists to isolate the product and determine its nature. They collected samples of the impurity 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, with further investigation it was found that the impurity was extremely resistant to both heat and most reagents [17].

Phthalimide was made from phthalic anhydride and ammonia in a large enamel coated iron drum [18]. They found some small chips in the enamel of the drum leading them to believe that some iron had gotten into the phthalimide and created the impurity. They determined that Iron was the source of the dark color and they set out to remove the iron. They boiled it in hydrochloric acid and the filtered liquid was tested with ammonium thiocyanate. Iron was not removable by these means.

The problem was sent to Royal College of Science where attempts were made to dissolve iron compound in concentrated sulphuric acid. Concentrated nitric acid removed color and turned substance into white precipitate when poured into ice-coldwater. Isolation and examination revealed that it consisted of pthalimide [19].

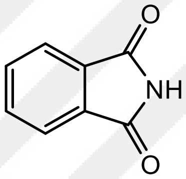

Figure 1.1. Phthalimide

There was a vigorous reaction with the formulation of a colored product when cuprous chloride was added to molten phthalimide [20]. They determined that the metals had to be a key part of the structure of this new compound. With this new element in the mix, J. Monteath Robertson at the Royal College of Science set out to discover the structure of the molecule. First he determined the empirical formula using micro-combustion techniques. Once he had the empirical formula the molecular weight was also determined, using the molecular weight and knowing that the product must have an isoindole skeleton similar to phthalimide, he deduced the structure. This structure was later confirmed by x-ray contour diagrams [21].

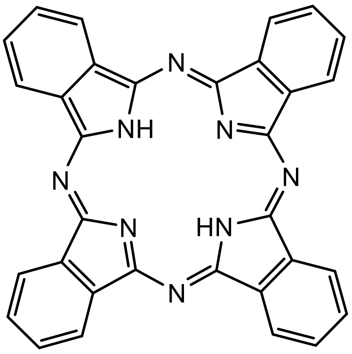

Figure 1.2. Phthalocyanine

1.2 Synthesis of Phthalocyanine

Phthalocyanine can be synthesized by many processes, such as heating derivatives of phthalic acid containing nitrogen as a functional group. Conventional precursors are diiminoisoindoline and phthalonitrile. The heating of phthal anhydride is a useful route to metal free phthalocyanine in the presence of Urea. Addition of metal salts helps this reaction to be more efficient. Other precursors include phthalimide and o-cyanobenzamide. In the figure below are some of the presursors.

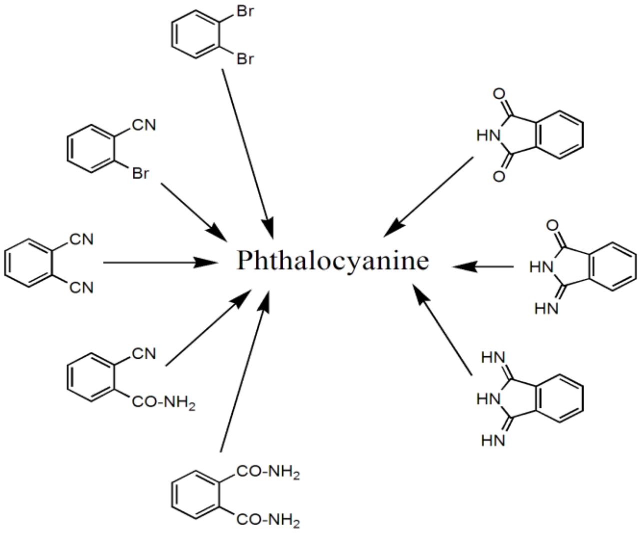

Figure 1.3. Precursors

Industrially, phthalocyanines are synthesized by one of two routes: (i) phthalic anhydride/urea or (ii) phthalonitrile [22].

In the first route, phthalic anhydride, urea (which functions as a non-volatile nitrogen source), a copper salt and a catalyst, ammonium molybdate, are heated together to form copper phthalocyanine [23]. This methoduses inexpensive materials and is therefore used to produce phthalocyanines for high-volume, lower-cost applications, such as blue and green pigments for cars and blue/cyan dyesfor textiles and paper [24].

In the second, more expensive route, phthalonitrile is treated with base to form the phthalocyanine. This route is used where high-quality, high-purity phthalocyanines are required, such as charge generation materials for electrophotography [25].

The first phthalocyanine to be manufactured commercially was copper phthalocyanine. It was made in 1934, in England. A similar product was synthesized in the United States in 1937 by Du Pont [26].

For efficient synthesis, the central metal must be a particular size, if too large metal is introduced, the synthesis may not take place, the ideal size for the central metal of the Pc is in the low 70 pm ionic radius range [27].

Heating the solution for a greater amount of time may have significantly increased the yields of the products, running the reaction under an inert gas such as Argon or under vacuum may have helped the reaction [28].

1.3. Application And Properties of Phthalocyanine

The major commercial impact of phthalocyanines is based on three factors; the first is their beautiful bright blue to green colours and high tinctorial strength; the second is their remarkable chemical stability, e.g. copper phthalocyanine sublimes unchanged at 580 °C and dissolves in concentrated sulfuric acid without decomposition [29]. Indeed, it is purified by this technique. The third factor is their excellent fastness to light. This combination of properties is extremely difficult, if not impossible, to achieve in other colorants. By comparison, the natural dyes chlorophyll and haemin are highly sensitive compounds easily decomposed by light, heat and mild chemical reagents [30].

1.3.1 Dyes

Bluephthalocyanine are commonly use in paints, inks, coatings and many plastics [31], it has to be used with great care, as it is a very powerful tinter and tends to overwhelm other pigments. When used alone, it should be mixed with some white, as it is transparent and almost black on its own. In application it is transparent. The pigment is insoluble and has no tendency to migrate in the material. The pigment is used in packaging industry and also in printing inks [32]. Phthalocyanine Green G is simple chlorinated CuPc, it is also used in tattoos and cosmetics [33].

1.3.2 Fuel cells

Its very apparant electrocatalysts in fuel cells should have a catalytic activities toward electrochemical reactions and good electric conductivity [34]. Knowing that some macrocyclic compounds with p-electrons have electric conductivities which are comparable to metals because p-electrons can move through overlaps of p-electron cloud, electrochemists have tried to apply these compounds to act as the eletrocatalysts in fuel cells [35]. Phthalocyanines normally have structures with alternating nitrogen–carbon atom ring. With four isoindole nitrogen atoms, phthalocyanines can also coordinate metal cations or hydrogen [36]. MN4 center is generated when a phthalocyanine molecule is encapsulated with a metal cation to form metallophthalocyanine. Metallophthalocyanines are normally studied and developed as colorant or dyes, it has been investigated that many metallated phthalocyanines have appreciable electric conductivities. It shows that macrocyclic compounds or their catalysts that are modified can be substitute Platinum as the electrocatalysts that can be use for fuel cells [37].

Many important reactions are catalyse by phthalocyanine with redox-active metals like iron and cobalt [38]. Oxygen reduction reaction has recently received significant attention, which include the reduction of molecular oxygen to water. This can be accomplished in a two steps electron each or single four-electron reduction step, yielding peroxide as an intermediate. Water is the final product since there is availability of oxygen in air, oxygen reduction reaction has been applied in clean energy production, especially in fuel cells and air-lithium batteries. The activity of these systems solely depend on the catalytic effectiveness of the cathode toward oxygen reduction reaction, iron and cobalt complexes have been investigated recently as a partial replacement for expensive materials such as Au and Pt [39]. CoPc was reported as the first substitute of cathode to noble metals, and its activity on liquid− liquid interfaces and electrode surfaces has been investigated [40]. Iron phthalocyanine has also been studied, showing effectiveness as a material for both O_2 and H_2O_2 fuel cells that are operated [41]. Corroles and porphyrins, have also displayed catalytic activity toward oxygen reduction reaction. for the same amount of metal, the pyrolized tetraphenylporphyrin of iron(II) accumulated on carbon black, was reported to target almost half the performance of Pt [33]. At very anodic potentials, with increased maximum power density of the cell Cobalt(III) corroles were proved to catalyze the oxygen reduction reaction [42]. Apart from operation in fuel cells, oxygen reduction reaction is also paramount for the control of the growth of microorganism and the oxidation of molecules like thiols, which are good for deodorant [43] and antibacterial purposes. In these cases, Phthalocyanines solubility in polar solvents can be increased by introducing a substituents group and also bind to fibers and other substrates is usually needed. For the oxidation of 2-mercaptoethanol in aqueous solution, Shirai and co-workers demonstrated the catalytic effectiveness of di-tetra- and octacarboxy phthalocyanines with various metal in the centers. They found that the octa-substituted complexes of Fe(III) and Co(II) had the most appreciable catalytic effect [42]. Though there are a many number of reports on Phthalocyanines with negatively charged groups, the properties of the cationic species was only reported in few articles. furthermore, positively charged phthalocyanines displayed good cell uptake from both gram positive and gram negative bacteria, [42-48] and also increases inactivation efficiency

The uses for phthalocyanines are expanding from their roles primarily as pigments and dyes, they are becoming important aspects of research in the areas of Organic Light Emitting Diodes (OLEDs), HIV Treatment and Photodynamic Therapy [49].

1.3.3 Photodynamic Therapy

Photodynamic therapy is receiving much attention in the treatment of cancer [47]. It involves a photosensitizer and a visible light both combined together. Death and oxidative cell damage may eventually ocur if its combine with molecular oxygen [48-49]. İt has higher selectivity in destroying diseased tissue because of it binary treatment and also only exposed cells to the photosentisizer, and oxygen are subjected to the cytotoxic agent that are produced in the process of photodynamic therapy [50]. This brings a two fold selectivity, as the photosensitizer selectively uptake the diseased tissue as well as to compliment activation of the photosensitizer to the tumor by blocking the light towards that particular space [51]. As such, Photodynamic therapy permit the complete removal of the tumor tissue while protecting available cells that are healthy cells from damage. This processs can be dated from primitive when man uses sunlight and the extract of plant to cure many skin problems. In countries like India, psoralens was obtained from the seeds of Psoralea corylifolia as early as 1400 B.C, which were used to treat infections like vitiligo [52]. There was no comprehensive report on photodynamic action, until around twentieth century when a medical student, Oscar Raab, working under the direction of Dr. H. VonTappeiner in Munich, observed the deathly effects of orange solution on Paramecia, which rely on the intensity of light in the laboratory [53]. Von Tappeiner and Jodlbauer extensively studied this process [54] who give the term “photodynamic action”. It was observed that other compounds like eosin were able to kill the cells rapidly in the presence of light. For reaction to ocur it was found that dissolved molecular oxygen is needed. Photohemolysis of rabbit erythrocytes by applying hematoporphyrin (Hp) was reported by Hausmann in 1908 [55-59]. Photosensitization of man, guinea pigs and mice respectively was shown by many scholars, by using hematoporphyrin (Hp) [54-56]. A comprehensive historical approches has been published [57].

1.3.4 Bioconjugation

Phthalocyanines has been used as dyes and colorants [58-59]. However, little phthalocyanine has been reported as reported as agent of fluorescent, that are good for applications in bioconjugation [60]. Most Phthalocyanines lack affinity to water, and are prone to add up in aqueous medium, or they dont 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 [61]. 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 [62-63]. Renzoni, et al, synthesized a form of phthalocyanines which are hydrophobic axial groups mentioned by La jolla blue [64], but contains both hydrophilic groups and a reactive group that is attached to the benzo-ring. Another metal, like silicon can replaced copper in this structure which will allow it to have two axial ligands [65].

The conjugated phthalocyanines with antibodies or peptide ligands directed at particular receptors over-expressed in cancer cells, like human epidermal growth factor receptor, is an excellent strategy for accelerating their biological effectiveness [66-70]. Epidermal growth factor receptor over expressed many cancers, such as, dysplastic and aberrant crypt foci, small cancers and the flat which are known for the development of cancer [71-73]. For the choosen delivery of cytotoxic drugs to the tumor sites [74-80], two small peptides with sequences LARLLT [81] and YHWYGYTPQNVI [82] which are very fascinating because of their, low immunogenicity, availability, ease of conjugation to other molecules, and an excellent higher epidermal growth factor receptor targeting ability. Phthalocyanines conjugated to peptides through many linkers for colorectal cancer (CRC) diagnostic applications have been investigated both in vivo and also in vitro [83].

Polyethylene glycols may be covalently-bound to phthalocyanies for inproved delivery to target tissues [84-87]. To increase their, serum life, tumor build up, solubility in water, and also minimizes their uptake by the reticuloendothelial system pegylation of photosensitizers is important [88,89].

2. MATERIAL AND METHODS

2.1.Materials

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-Phthlonitrile from AFG scientific, Potassium carbonate (K_2CO_3) was received from Merck and used after drying, Phthalimide, $Zn(ac)_2$.2H2O, $Cu(Ac)_2.H_2O$, $Ni(Ac)_2.4H_2O$, $Co(Ac)_2.4H_2O$, $FeCl_2$, $Cr(NO_3).H_2O$, 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 reagent grade.

2.2.Apparatus

Melting points of the compounds were determined with Griffin MFB-590. ^1H spectra were taken using 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 ^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. Electrochemistry experiments performed by Gamry Reference 600 or Interface 1000, in DMF under argon atmosphere.

2.3. Methodology

The synthesis of the metallated phthalocyanines begins with the nitration in position 3 of phthalimide followed by the formation of the 3-nitrophthalamide; then dehydration by the thionyl chloride in N,N-dimethylformamide [14] leads to 3-nitrophthalonitrile. Pthalonitrile derivative containing a 7-hydroxycoumarine as substituent was prepared by nucleophillic substitution reaction of 3-nitrophthalonitrile in the pressence 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 perform with Glycerol and DMF solutions.

2.4. Synthesis of 3-Nitrophthalimide

30 ml of Nitric acid was added into 500 ml round botton flask and stirred, 30 ml sulphuric acid was slowly added at a temperature of less than 0-5 ^{o}C after it has properly mix, the temperature was allowed to rised to room temperature, 15 g Phthalimide was added and increased the temperature to 110 ^{o}C and stirred for 7 hours. When the reaction was completed the content was poured into an iced water filtered and washed with distiled water, dried. Yield: 4.88 g, 36,9 %, M.P: 214 ^{o}C,

2.5. Synthesis of 3-Nitrophthalamide

4.0 g (20.8 mmol) of 3-Nitrophthalimide was Pulverized and added to 40 ml of Ethanol, the temperature was slightly rised to 35 ^{o}C and 5.6 ml of 32 % ammonia was added and stirred to form off white uspension. The reaction mixture was slightly heated to 45^{o}C and stirred for 5 hours, the resulting solid from the reaction mixture was filtered and rinsed with cold water, air dried to a constant weight. Yield: 4.21 g, 97 % M.P: 223 ^{o}C.

2.6. Synthesis of 3-Nitrophthalonitrile

3.5 ml of thionyl chloride was added dropwise in an ice bath (keeping the temperature between 5 and 7 ^{o}C to 5 ml of DMF which was already cooled to 0 ^{o}C and stirred for 3 hours at this temperature, 1.0 g (4.78 mmol) 3-Nitrophthalamide was slowly added to this reagent mixture at such rate keeping the temperature below 10 ^{o}C. The mixture was Stirred for 6 hours at 0-5 ^{o}C and then 24 hours at room temperature, the reaction mixture was slowly poured into an ice, precipitated then vaccum filtered, rinsed with cold water 3 times. Air dried to constant weight. Yield: 0.1 g 12 % M.P: 174-176 ^{o}C

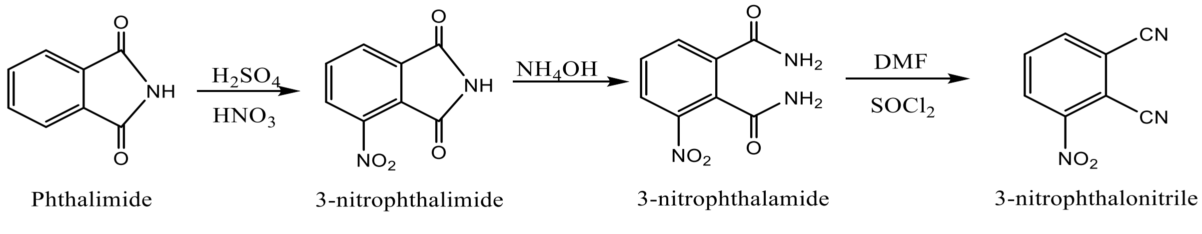

Figure 2.1. Synthesis of 3-Nitrophthalonitrile

2.7. 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 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.

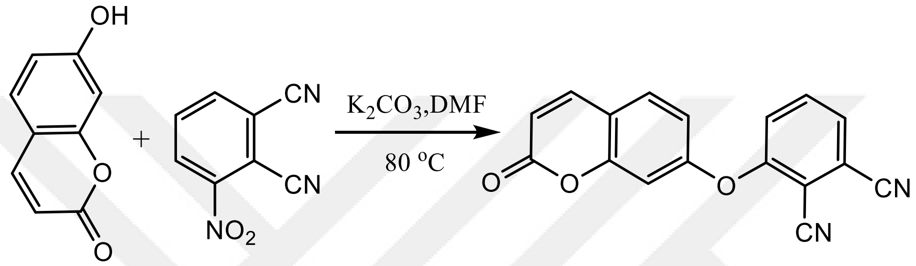

Figure 2.2. Synthesis Reaction of 3-((2-oxo-2H-chromen-7-yl)oxy)phthalonitrile

2.8. 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

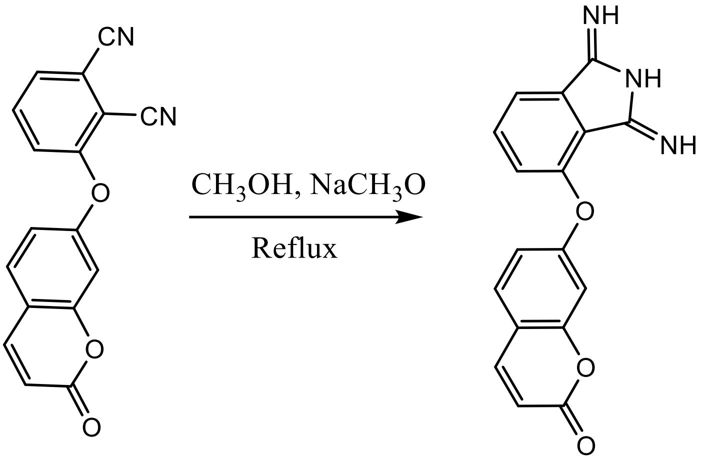

Figure 2.3. Synthesis of 7-((1,3-diiminoisoindolin-4-yl)oxy)-2H-chromen-2-one

2.9. Synthesis of 1,8,15,22-Tetrakis [3-(oxo-2H-chromen-7-yl)oxy) coumarin] Nickel 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 compund 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 untill the pH of the water is neutral, the green product was dried and weighted yield: 0.262 g, 16 %.

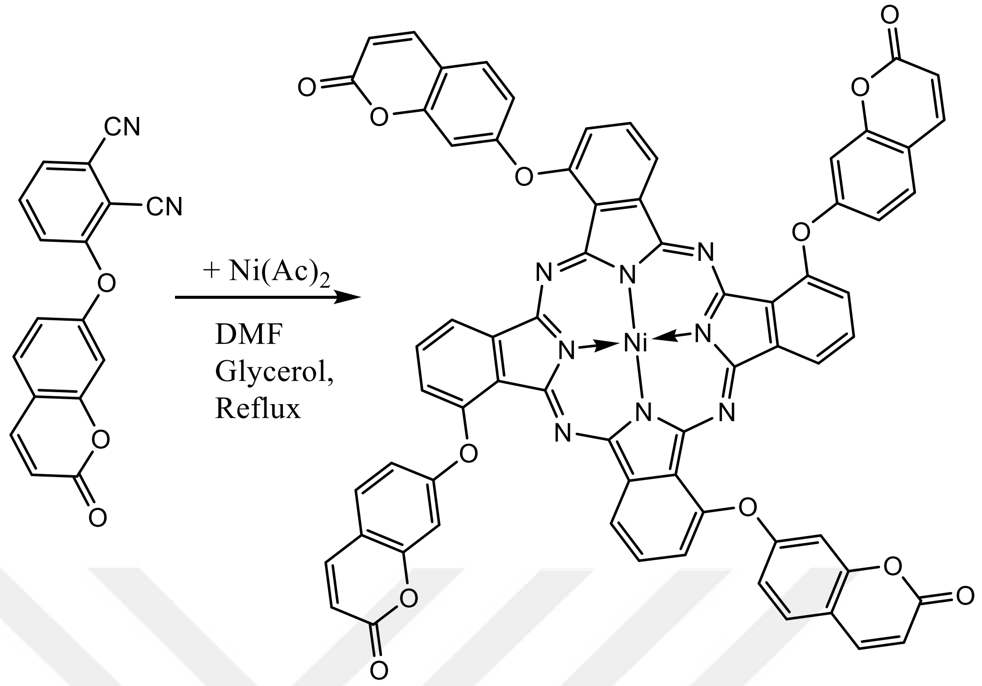

Figure 2.4. Synthesis of Nickel phthalocyanine

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

Phthalonitrile (0,20 g, 0.694 mmol), Cobalt acetate $Co(OAc)_2\cdot 4\ H_2O$ (0.05 g, 0.201 mmol) and1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (2 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. The product was precipitated, collected by filtration, washed with distilled water.

The compund 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 untill the pH of the water is neutral, the green product was dried and weighted yield: 0.359 g, 43 %

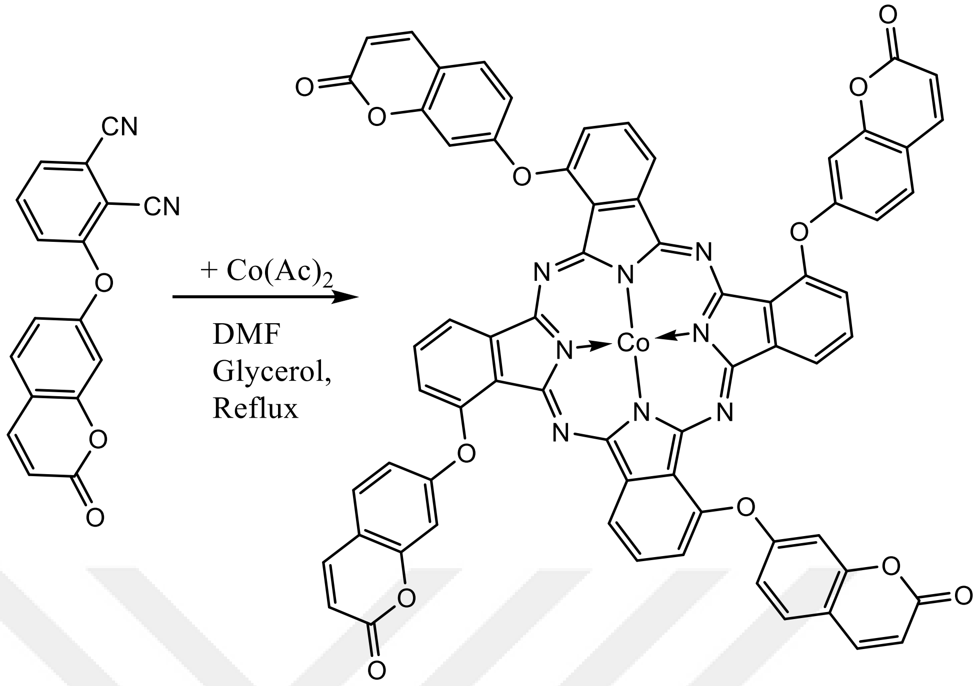

Figure 2.5. Synthesis of Cobalt phathalocyanine

2.11. Synthesis of 1,8,15,22-Tetrakis [3-(oxo-2H-chromen-7-yloxy) coumarin]Zinc Pththalocyanine

1,3-diiminoisoindoline (0.200 g, 0.655 mmol), zinc acetate $Zn(OAc)_2$. $2H_2O$ (0.065 g, 0.296 mmol) and1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (2 drops) in dry DMF/Glycerol 10 ml (1:3) 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 (100 ml). The product was precipitated, collected by filtration, washed with distilled water.

The compund 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 untill the pH of the water is neutral, the green product was dried and weighted yield: 0.237 g, 30 %,

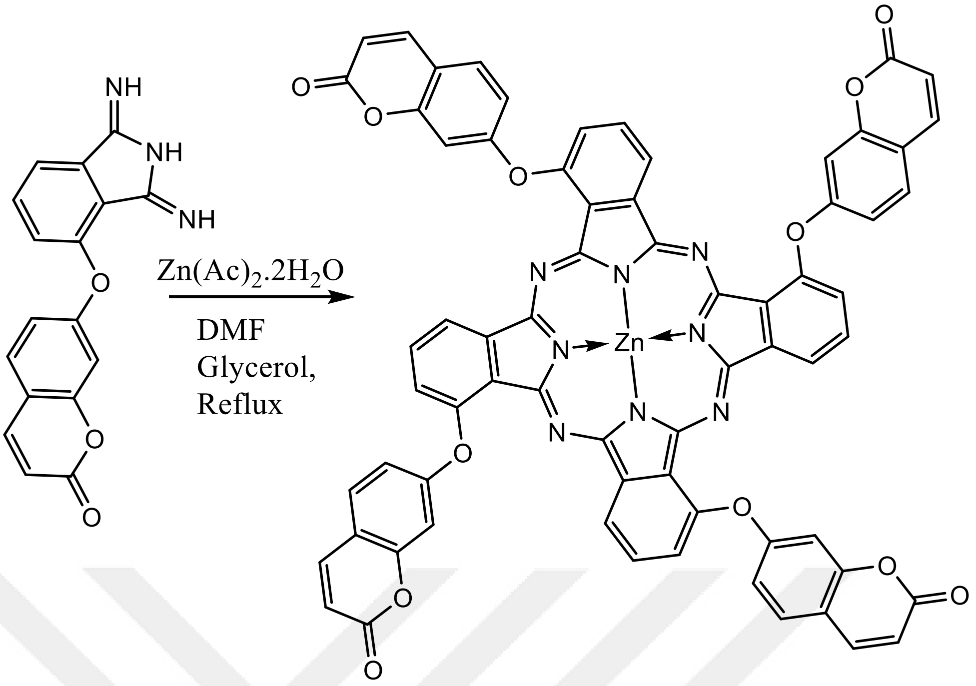

Figure 2.6. Synthesis of Zinc Phthalocyanine

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

1,3-diiminoisoindoline (0.200 g, 0.655 mmol), copper(II) acetate Cu(OAc)2. H_2O (0.060g, 0.300 mmol) and1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (3 drops) in THF (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 (150 ml). The product was precipitated, collected by filtration, washed with distilled water.

The compund 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 untill the pH of the water is neutral, the green product was dried and weighted yield: 0.22 g, 28 %,

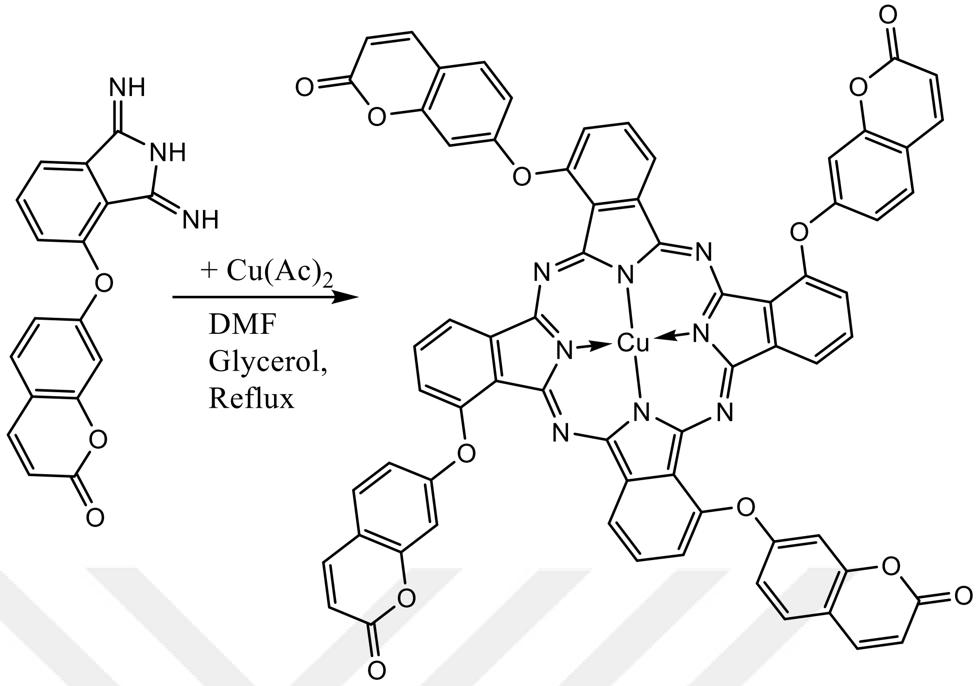

Figure 2.7. Synthesis of copper phthalocyanine

2.13. 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 $FeCl_2$ (0.059 g, 0.299 mmol) and1,8-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 precipitated by adding it dropwise to distilled water (100 ml). The product was precipitated, collected by filtration, washed with distilled water.

The compund 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 untill the pH of the water is neutral, the green product was dried and weighted yield: 0.202 g, 26 %.

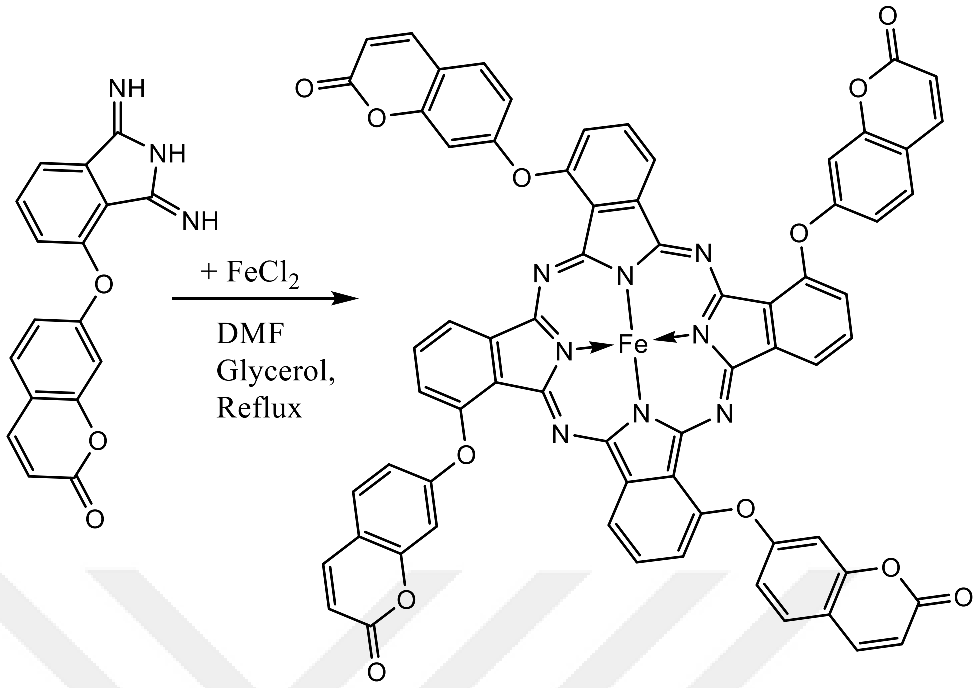

Figure 2.8. Synthesis of Iron phthalocyanine

3. RESULTS AND DISCUSSION

The synthetic route followed for the synthesis of phthalonitrile derivative and phthalocyanine complexes are given above.

Phthalonitrile derivative was obtained through the nucleophilic substitution reaction between 3- nitro phthalonitrile and 7-Hydroxycourmarin at 80 ^{o}C under Argon atmosphere in dry DMF in the presence of K_2CO_3 as a base with 62 % yield (Figure 2.2). This reaction has been used in the preparation of a variety of ether or thioether substituted phthalonitriles [32,33]. The 1,3-diiminoisoindoline derivative was also obtained as stated in the procedure above (Figure 2.3).

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 salt at reflux temperature under an Argon atmosphere afforded the synthesized phthalocyanines**.** The route for the synthesis of Phthalonitrile, 1,3-diiminoisoindoline and Phthalocyanine compounds were shown. The characterization of the compounds was carried out by the combination of several methods, including, Elemental analysis, FT-IR, ^{1}H NMR, UV–vis spectra and TGA. The compounds structures were confirmed by the results of these analyses.

The -C≡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 is the absence of the -C≡N vibrations at 2230 cm^{-1} for Phthalocyanines compounds in FT-IR spectra of the substituted phthalocyanine compounds.

Cyclic voltammograms (CV) and Square Wave voltammograms (SWV) were carried out using a Gamry Reference 600 Potentiostat/ Galvanostat/ZRA. A three electrode system was used for CV and SWV measurements in dimethylformamide (DMF) consist of glassy carbon working electrode, and a platinum wire counter and a platinum wire quasi reference electrode. Electrochemical grade tetra butyl ammonium tetra fluoro borate (TBAFB) (Fluka) was used as the supporting electrolyte in voltammetric measurements in non-aqueous solvents. The ferrocene/ferrocenium couple (Fc/Fc$^+$) was used as an internal standard and potentials reported with respect to Fc/Fc$^+$ in non-aqueous solutions. Square wave voltammetric analysis was carried out at frequency of 25 or 40 Hz, amplitude of 25 to 40 mV and step potential of 4 mV. High purity argon is used for the deoxygenation of the cell at least 10 minutes prior to electrochemical measurements and the solution was protected from air by a blanket of argon during the experiments.

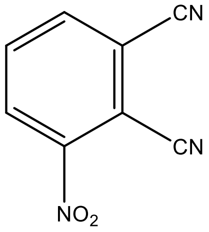

Figure 3.1. 3-Nitrophthalonitrile

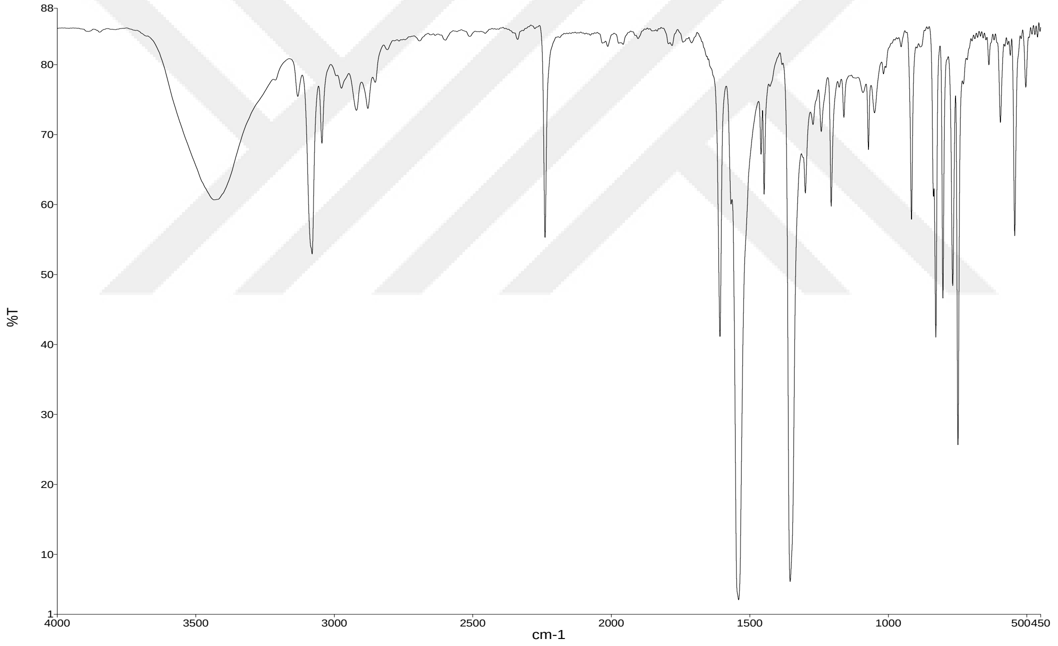

Figure 3.2. FT-IR of 3-Nitrophthalonitrile

Table 3.1. FT-IR results of 3-Nitrophthalonitrile

Vibration (cm^{-1})	**Vibration**
3080	Ar-CH
2230	C≡N
1607	C=C
1540	Aromatic NO_2

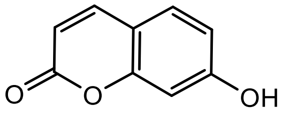

Figure 3.3. 7-Hydroxy coumarin

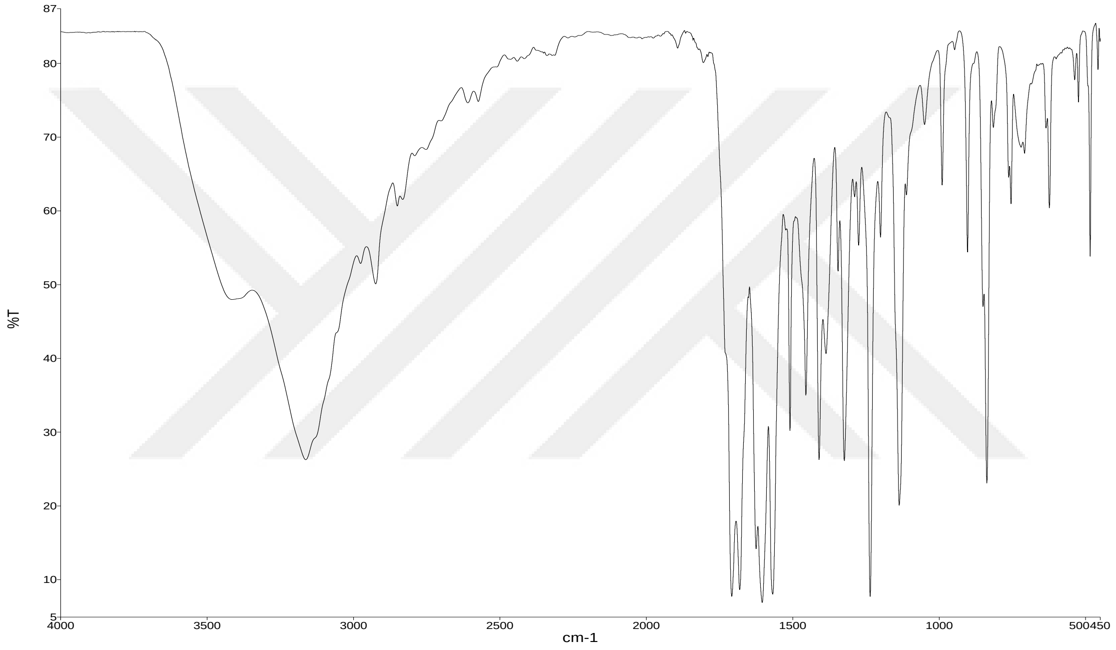

Figure 3.4. FT-IR of 7-Hydroxy coumarin

Table 3.2. FT-IR results of 7-Hydroxy coumarin

Vibration (cm^{-1})	**Vibration**
3158	Ar-CH
1603	C=C
1707	C=O
1274	C-O-C

3.1. 3-(2-oxo-2H-chromen-7-yl)oxy) phthalonitrile

3.1.1. Experimental results

This compoud was synthesized using **7**-Hydroxy coumarin and **3**-Nitrophthalonirile

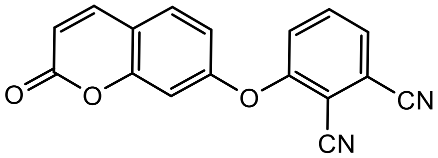

Figure 3.5. Structure of 3-(oxo-2H-chromen-7-yloxy coumarin)phthalonitrile

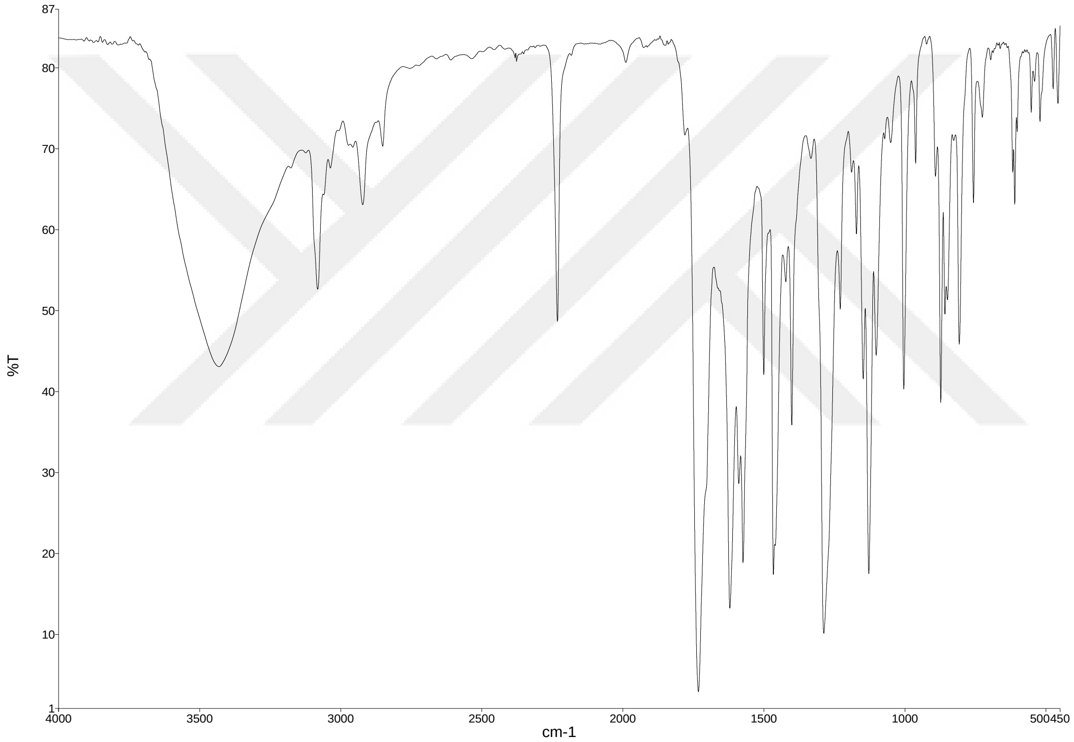

Figure 3.6. FT-IR of 3-(oxo-2H-chromen-7-yl)oxy coumarin)phthalonitrile

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 3.3. FT-IR results of 3-(oxo-2H-chromen-7-yl)oxy coumarin)phthalonitrile

Vibration (cm^{-1})	**Vibration**
2921	Ar-CH
2230	C≡N
1620	C=C
1731	C=O
1288	C-O-C

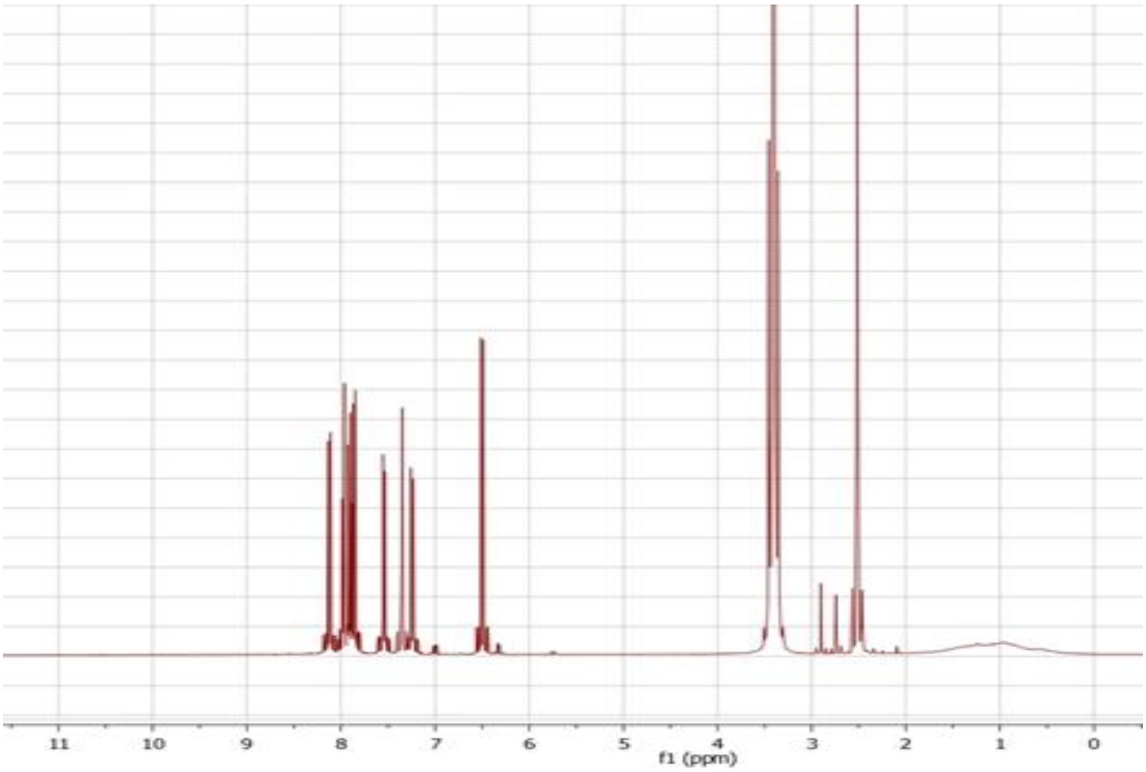

Figure 3.7. ^{1}HNMR spectrum of 3-(oxo-2H-chromen-7-yl)oxy coumarin).

When the ^{1}HNMR spectrum is examined, DMSO peak was observed at about 3.4 ppm and the residual DMSO-d6 peak at about 2.5 ppm, and the multiplet peaks at about 6.50-8.13 ppm belong to protons in the aromatic ring.

3.2. 4-(2-oxo-2H-chromen-7-yl)oxy) 1,3-Diiminoisoindoline

3.2.1. Experimental results

This compoudwas synthesized using 3-(oxo-2H-chromen-7-yl)oxy coumarin) phthalonitrile and sodium methoxide in methanol

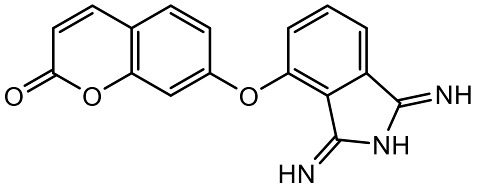

Figure 3.8. Structure of 3-(oxo-2H-chromen-7-yl)oxy coumarin)1,3-diiminoisoindoline

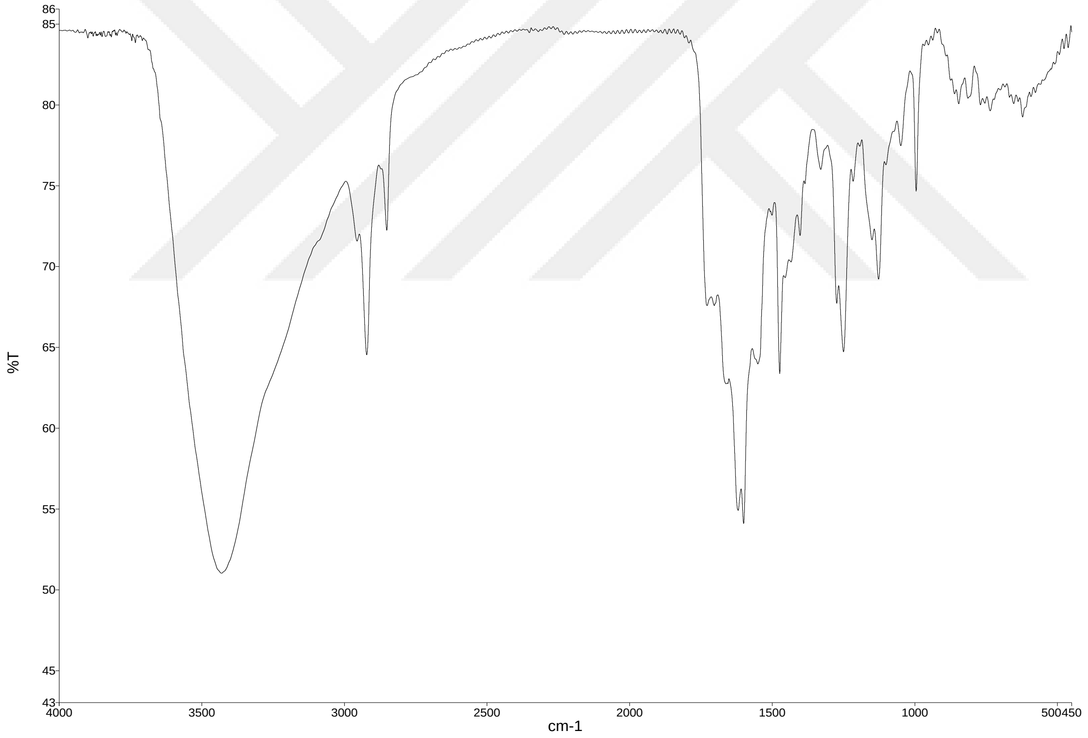

Figure 3.9. FT-IR of 4-(oxo-2H-chromen-7-yl)oxy coumarin)1,3-diiminoisoindolin

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 the compound.

Table 3.4. FT-IR results of 4-(oxo-2H-chromen-7-yl)oxy coumarin)1,3-diiminoisoindoline

Vibration (cm^{-1})	**Vibration**
2921	Ar-CH
1473	C=C
1619	C=O
1249	C-O-C

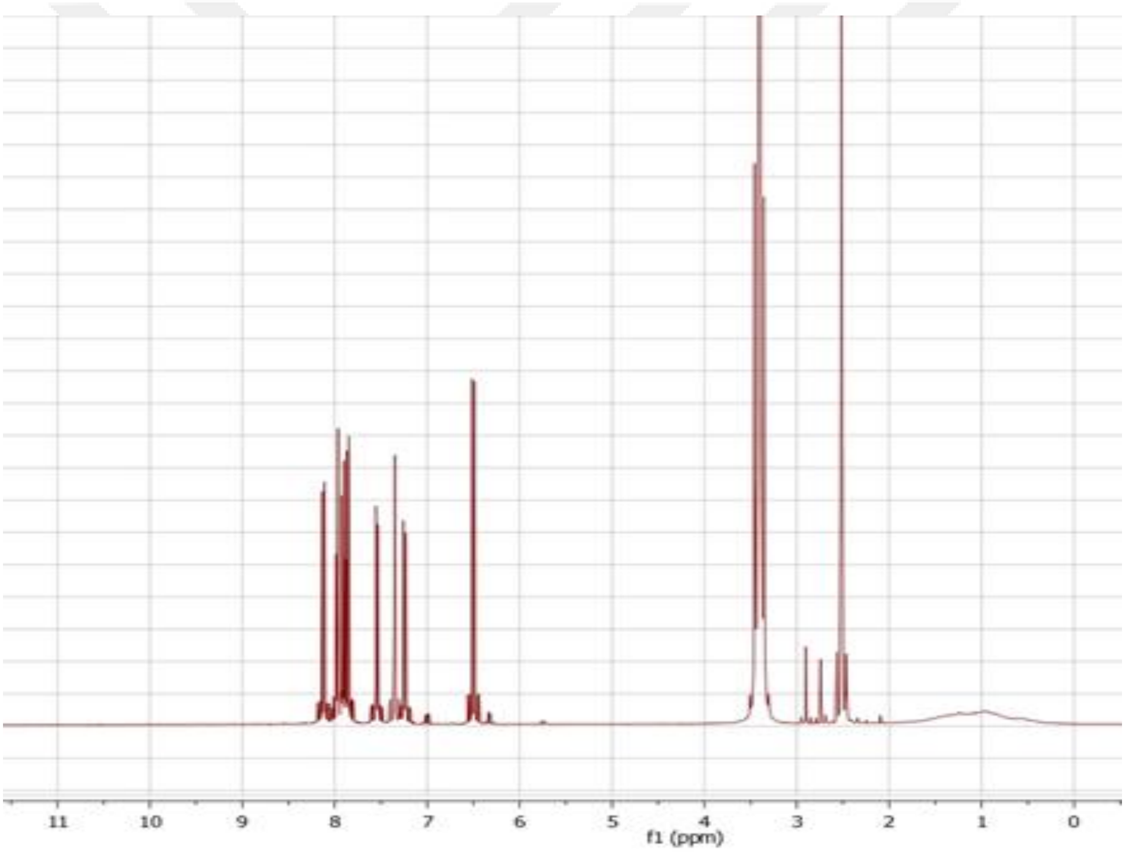

Figure 3.10. ^{1}H-NMR spectrum of 4-(oxo-2H-chromen-7-yl)oxy coumarin)1,3-diiminoisoindoline.

3.3. 1,8,15,22-Tetrakis [3-(oxo-2H-chromen-7-yl)oxy) coumarin]nickel pththalocyanine

3.3.1. Experimental results

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

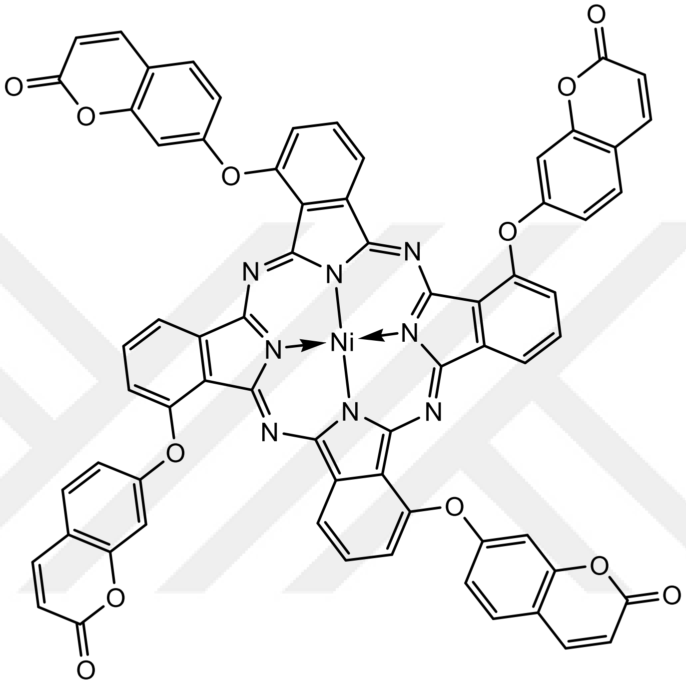

Figure 3.11. Nickel Phthalocyanine

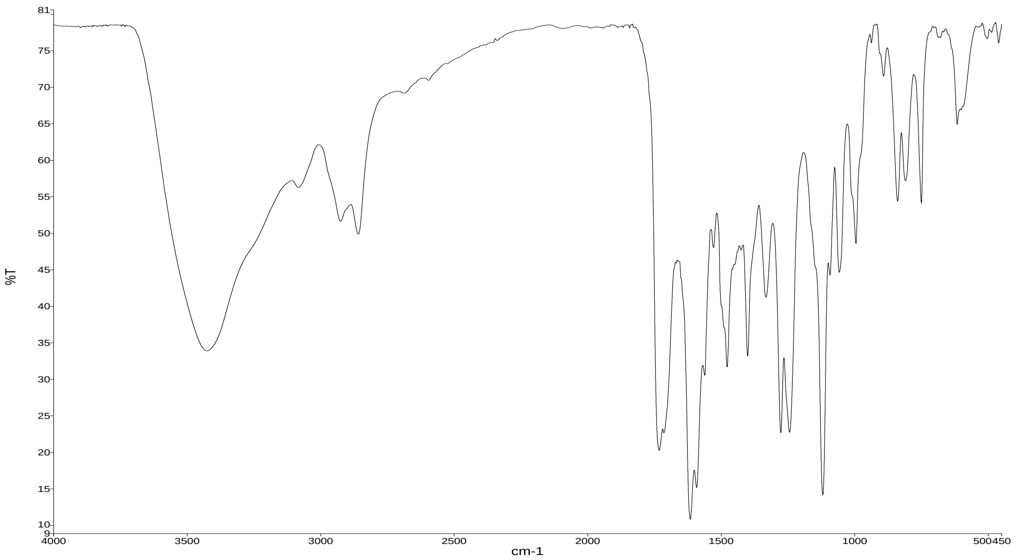

Figure 3.12. FT-IR of Nickel(II) phthalocyanine

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 3.5. FT-IR results of Nickel(II) phthalocyanine

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

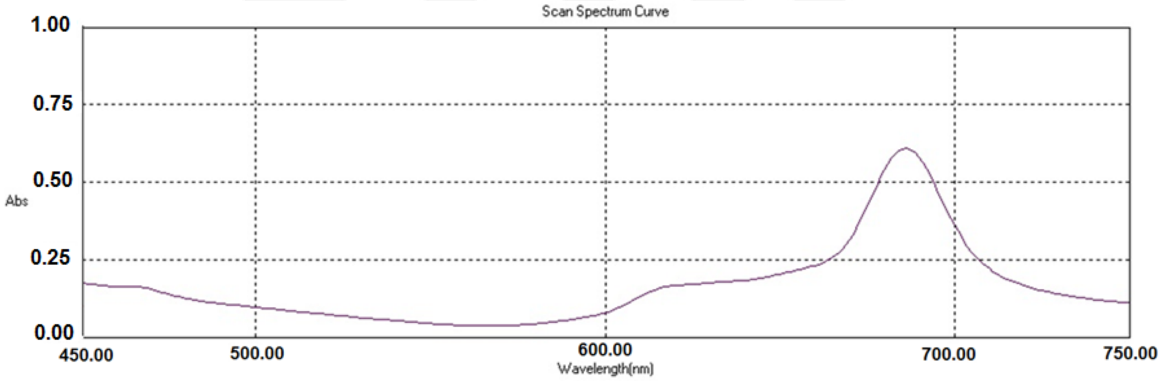

Figure 3.13. UV spectrum of Nickel phthalocyanine

The synthesized NiPc compound shows 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 lowest occupied molecular orbital (LUMO) of the phthalocyanine ring. Aggregation was also observed at 615 nm.

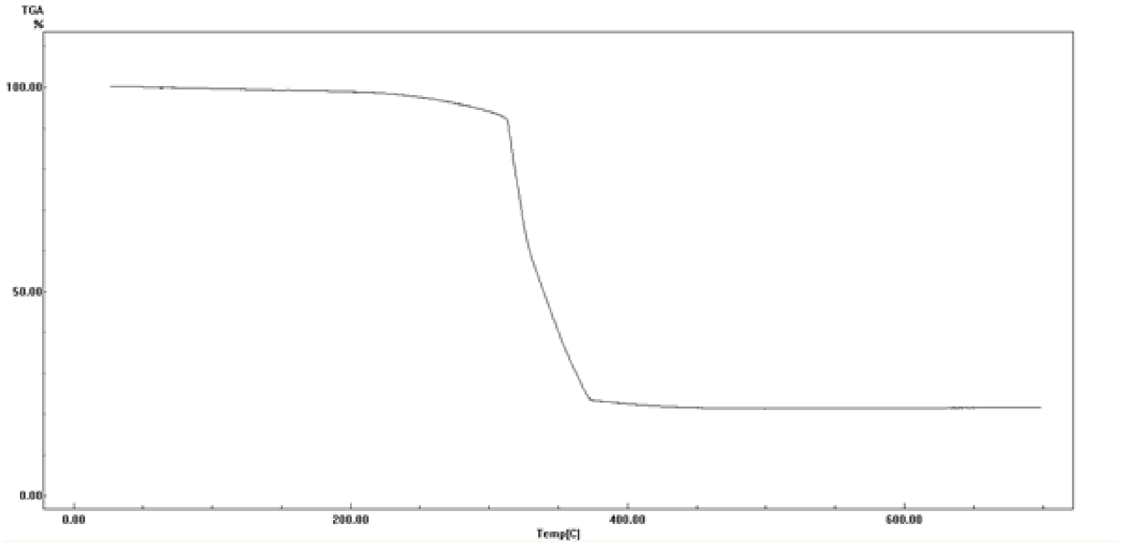

Figure 3.14. TGA of Nickel Phthalocyaninne

From the thermographic analysis result of the synthesized Nickel phthalocyanine compound it shows that the synthesized compound begin to exhibit weight loss at a temperature of 309 ºC which indicate a suitabley high thermal stability for the newly synthesized compound.

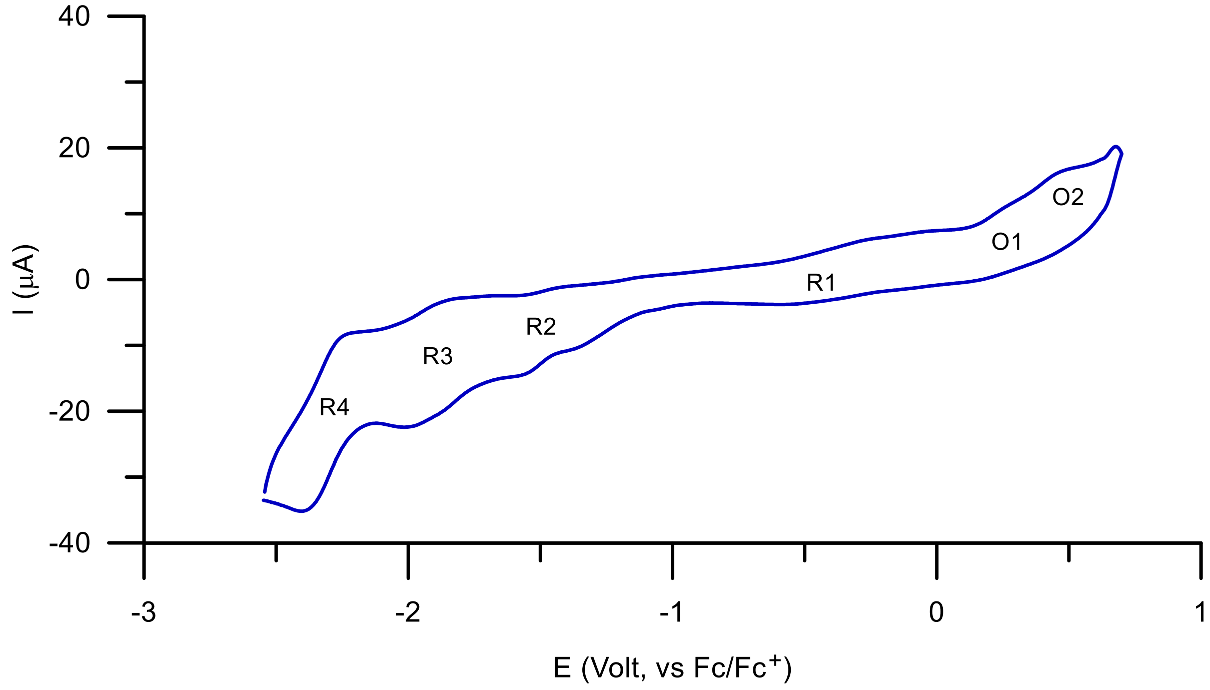

Figure 3.15. Cyclic Voltamogram of NiPc

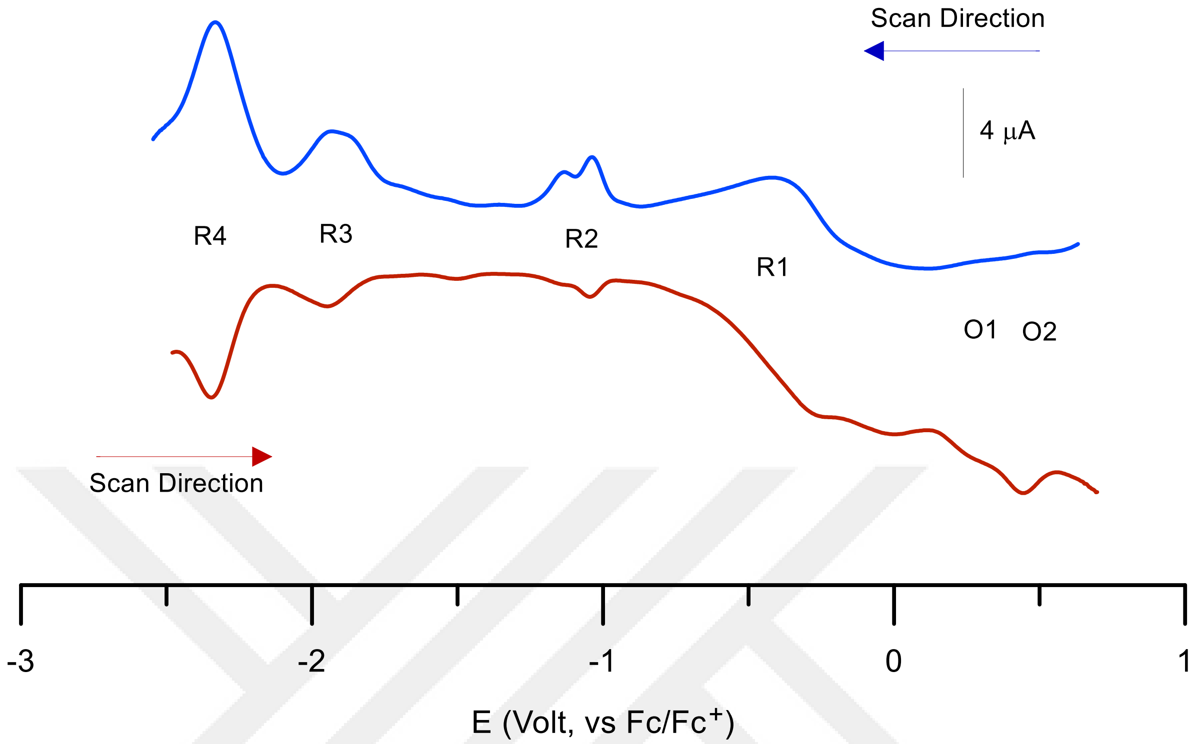

Figure 3.16. Square Wave voltamogram of NiPc

Fig. 3.15 and 3.16 represents CV and SWV responses of NiPc in DMF/TBAFB electrolyte on a glassy carbon working electrode. NiPc gives two reversible reduction reactions, R1 at -1.04 V, R2 at -1.94 V, R3 at -2.33 V and two irreversible oxidation reaction 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 [96,97] SWV of the NiPc support these quasi reversible characters of the processes (Fig. 3.16).

3.4. 1,8,15,22-Tetrakis [3-(oxo-2H-chromen-7-yl)oxy) coumarin]Cobalt Pththalocyanine

3.4.1. Experimental results

This compound was synthesized using 3-Phathalonitrile and Cobalt acetate in DMF and Glycerol solutions (1:3)

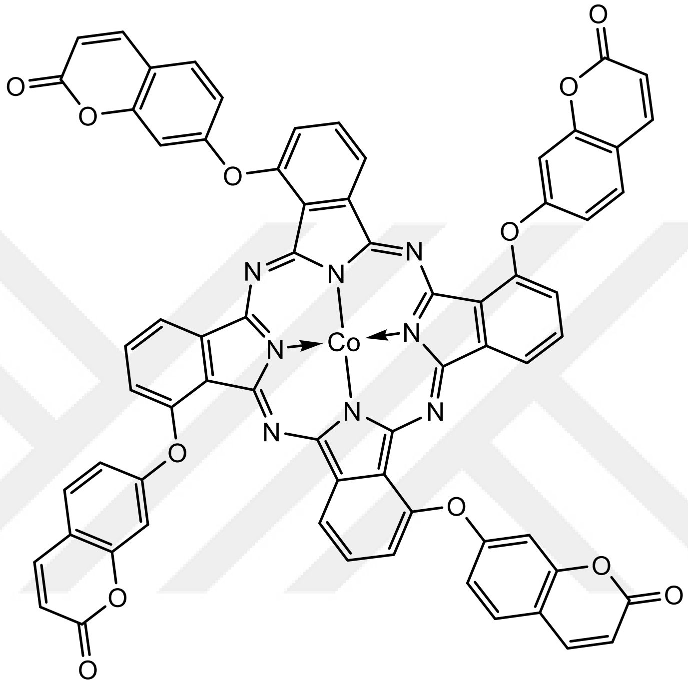

Figure 3.17. Cobalt Phthalocyanine

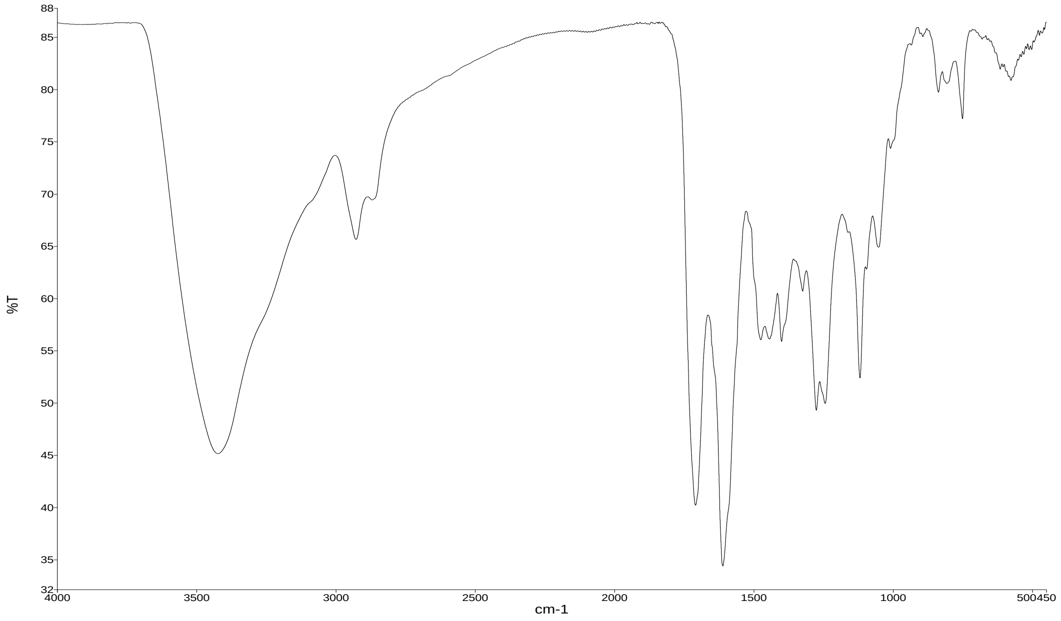

Figure 3.18. FT-IR of Cobalt phthalocyanine

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 3.6. FT-IR results of Cobalt phthalocyanine

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

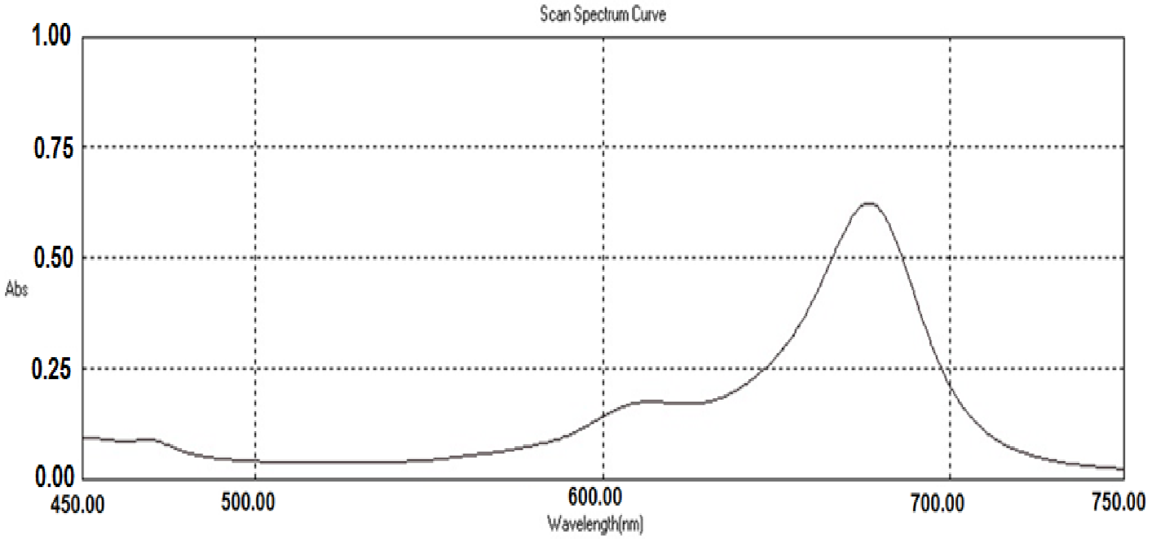

Figure 3.19. UV spectrum of Cobalt phthalocyanine

The synthesized CoPc compound shows 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.

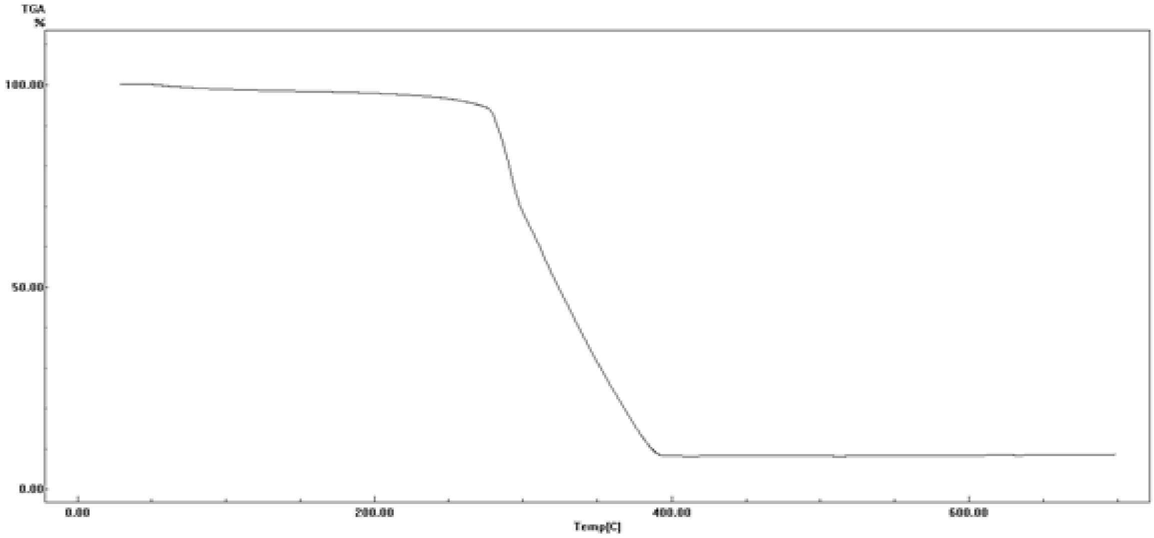

Figure 3.20. TGA of Cobalt Phthalocyaninne

From the thermographic analysis result of the synthesized Cobalt phthalocyanine compound it shows that the synthesized compound begin to exhibit weight loss at a temperature of 300 °C which indicate a suitably high thermal stability for the newly synthesized compound.

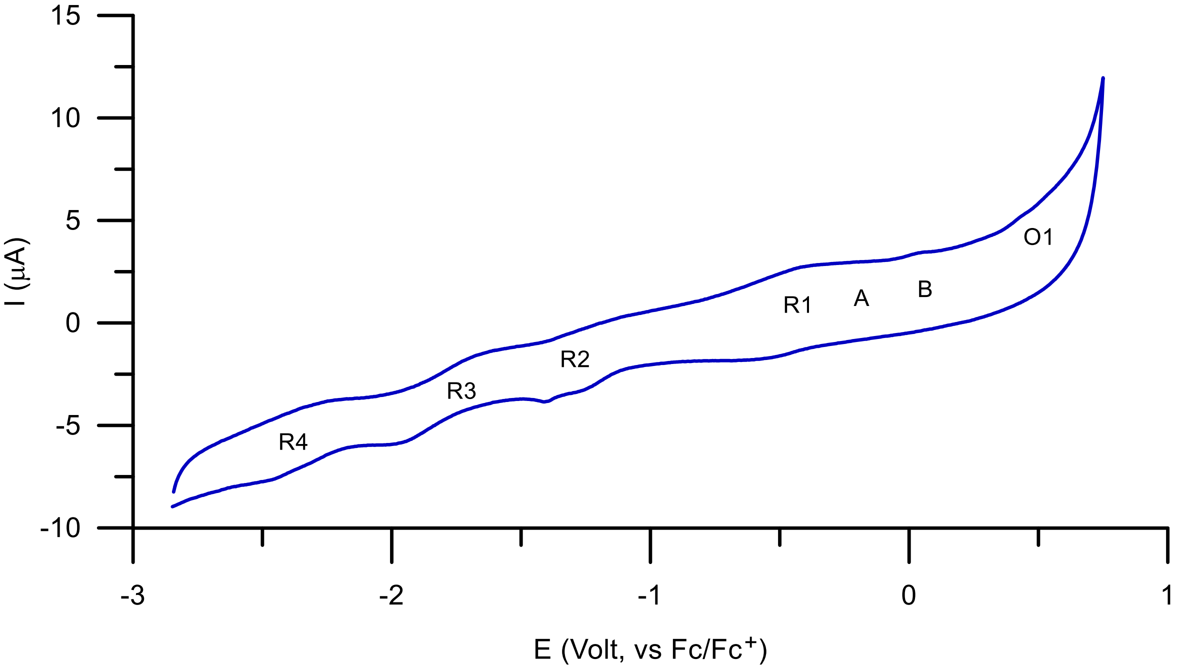

Figure 3.21. Cyclic Voltamogram of CoPc

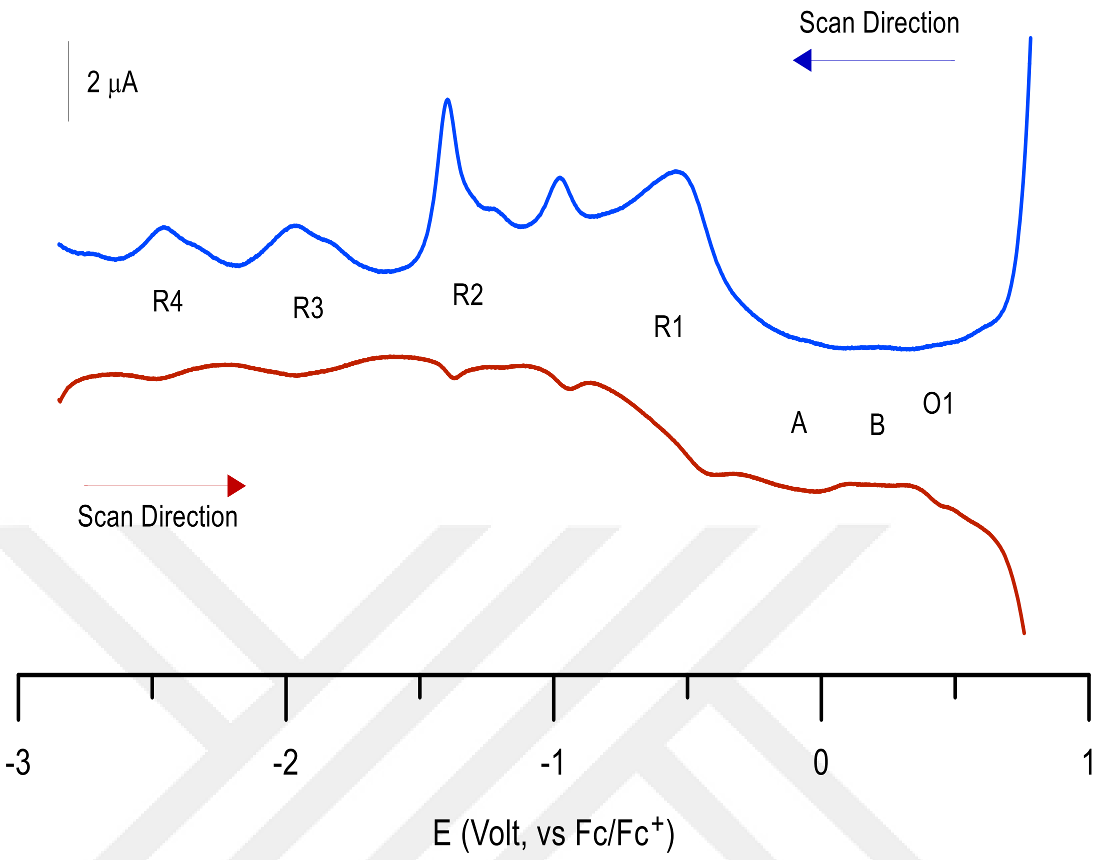

Figure 3.22. Square Wave voltamogram of CoPc

The cyclic and square wave voltammograms of CoPc shown in Fig. 3.21 and Fig. 3.22 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 $[Pc^{2-}Co(II)]/[Pc^{2-}$ Co(I)] and $[Pc^{-2}$ Co(II)]/$[Pc^{2-}$ Co(III)] couples, in DMF respectively. Phthalocyanine centered first reduction and first oxidation takes place at R1 (-1.37 V) and O1 (0.60 V) respectively.

3.5. 1,8,15,22-Tetrakis [3-(oxo-2H-chromen-7-yloxy) coumarin]Zinc Pththalocyanine

3.5.1. Experimental results

This compound was synthesized using 1,3-diiminoisoindoline and Zinc acetate in DMF and Glycerol solutions (1:3)

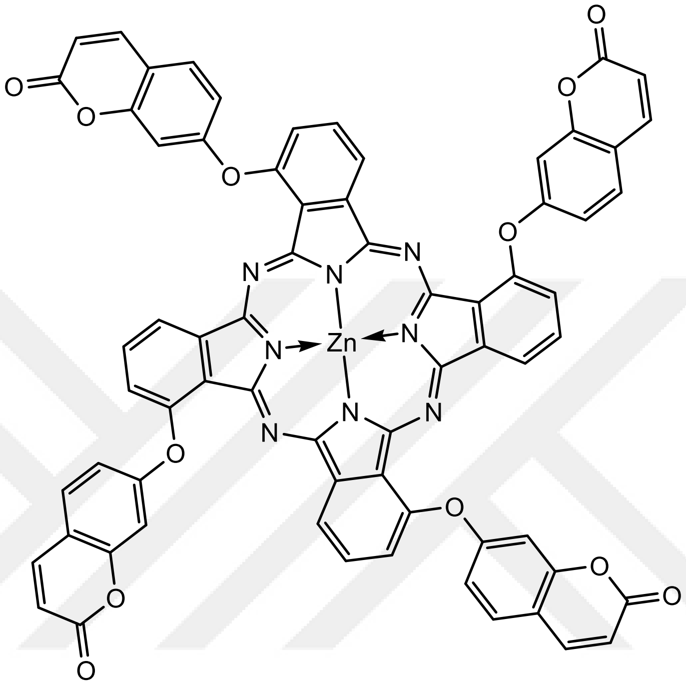

Figure 3.23. Zinc Phthlocyanine

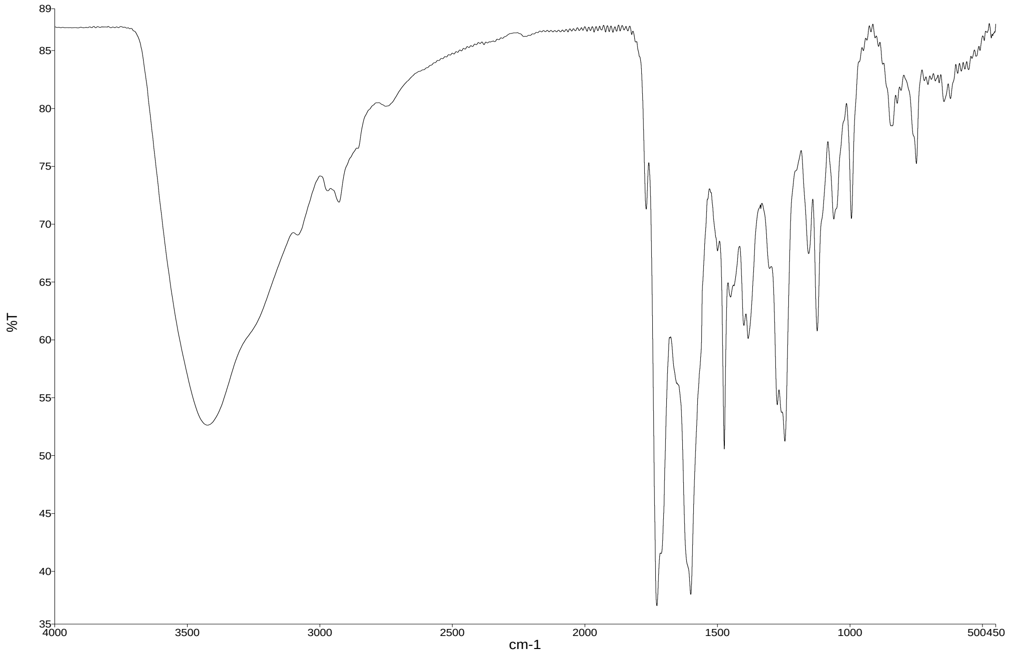

Figure 3.24. FT-IR of zinc(II) Phthalocyanine

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 3.7. FT-IR results of zinc(II) Phthalocyanine

Vibration (cm^{-1})	**Vibration**
2928	Ar-CH
1728	C=O
1600	C=C
1274	C-O

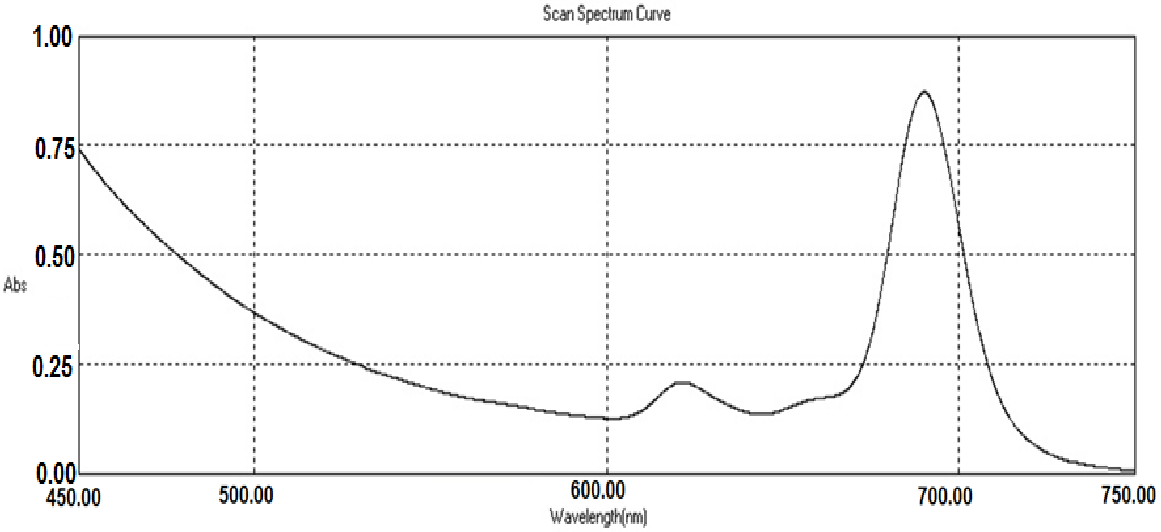

Figure 3.25. UV spectrum of zinc(II) Phthalocyanine

The synthesized ZnPc compound shows 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 lowest occupied molecular orbital (LUMO) of the phthalocyanine ring. Aggregation was also observed at 615 nm.

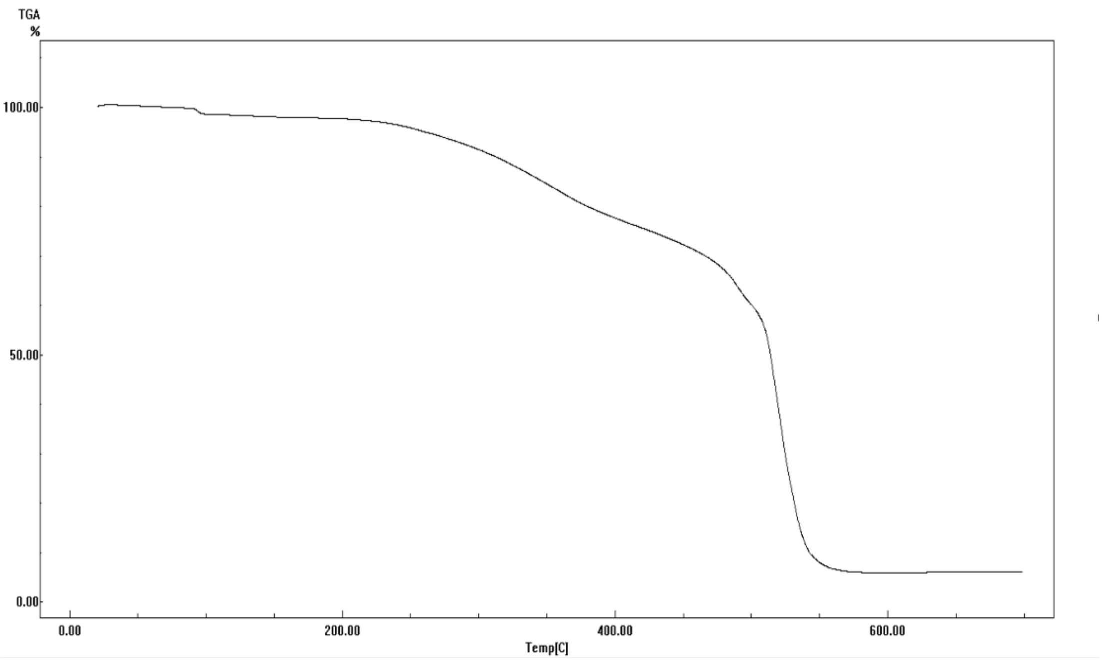

Figure 3.26. TGA of Zinc Phthalocyaninne

From the thermographic analysis result of the synthesized Zinc phthalocyanine compound it shows that the synthesized compound begin to exhibit weight loss at a temperature of 306 °C which indicate a suitably high thermal stability for the newly synthesized compound.

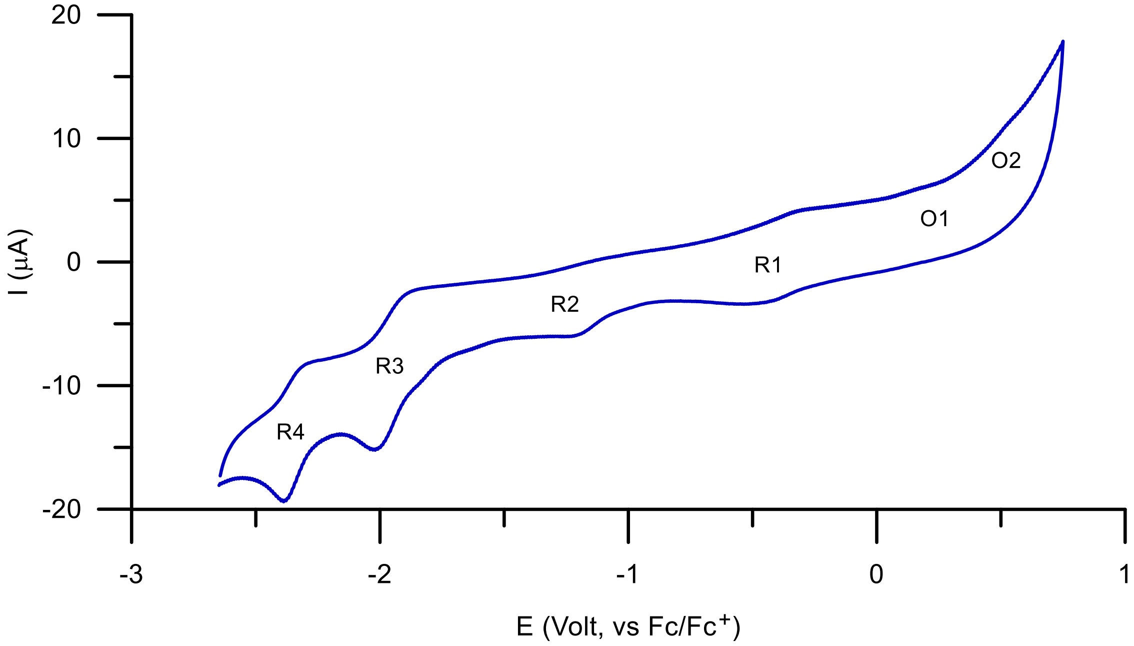

Figure 3.27. Cyclic Voltamogram of ZnPc

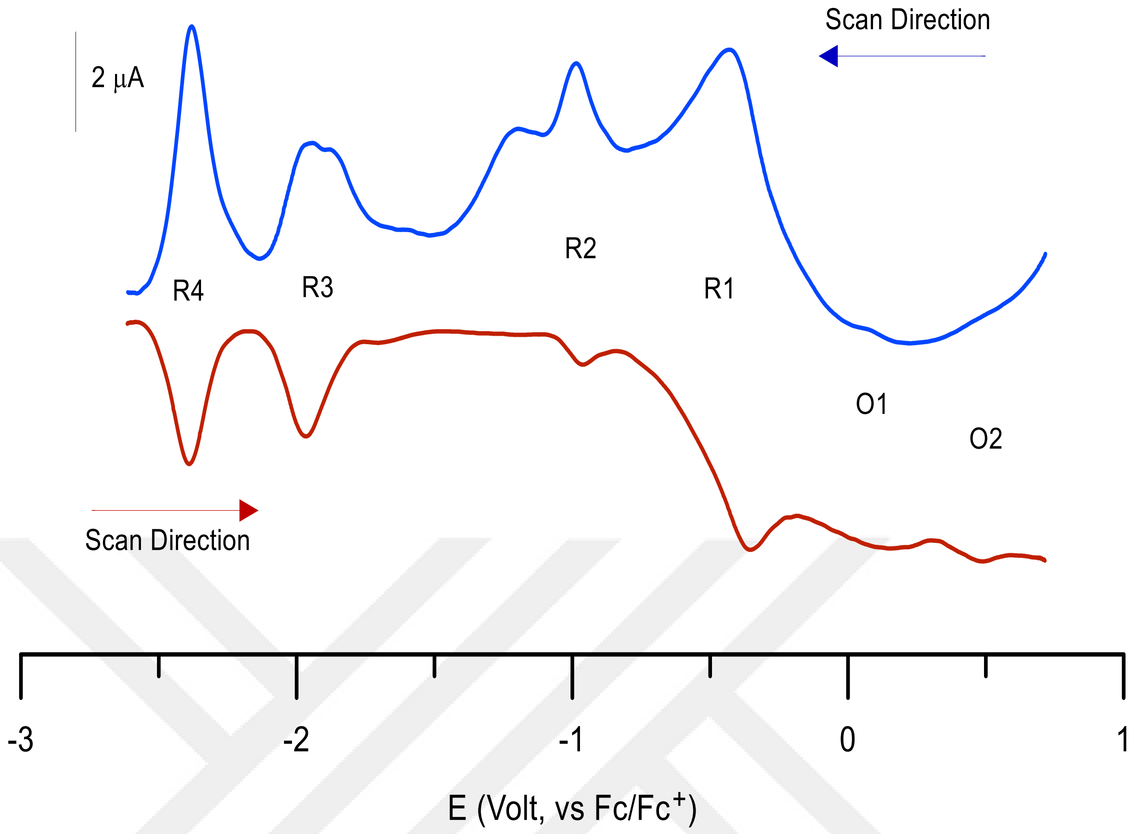

Figure 3.28. Square Wave voltamogram of ZnPc

Fig. 3.31 and 3.32 represents CV and SWV responses of ZnPc in DMF/TBAFB. ZnPc gives three quasi reversible reduction reactions, R1 at -0.98 V, R2 at -1.96 V, R3 at -2.38 V and two quasi reversible oxidation reaction O1 at 0.09 V and O2 at 0.49 V. The potential difference between the first reduction step and the first oxidation step of redox inactive metallophthalocyanine complex is about 1.18 V which is lower than the expected value of 1.5 V and corresponds to the energy difference between the first reduction and the first oxidation potential [97,98] SWV of the ZnPc support these quasi reversible characters of the processes (Fig. 3.32).

3.6. 1,8,15,22,-Tetrakis [3-(oxo-2H-chromen-7-yloxy) coumarin]Copper Pththalocyanıne

3.6.1. Experimental results

This compound was synthesized using 3-Phathalonitrile and Copper(II) acetate in THF and DMF (2:1)

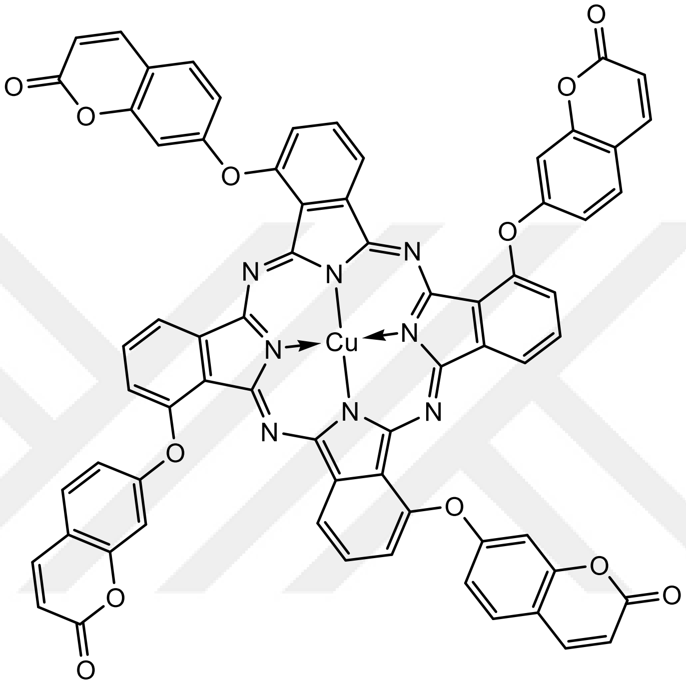

Figure 3.29. Copper Phthalocyanine

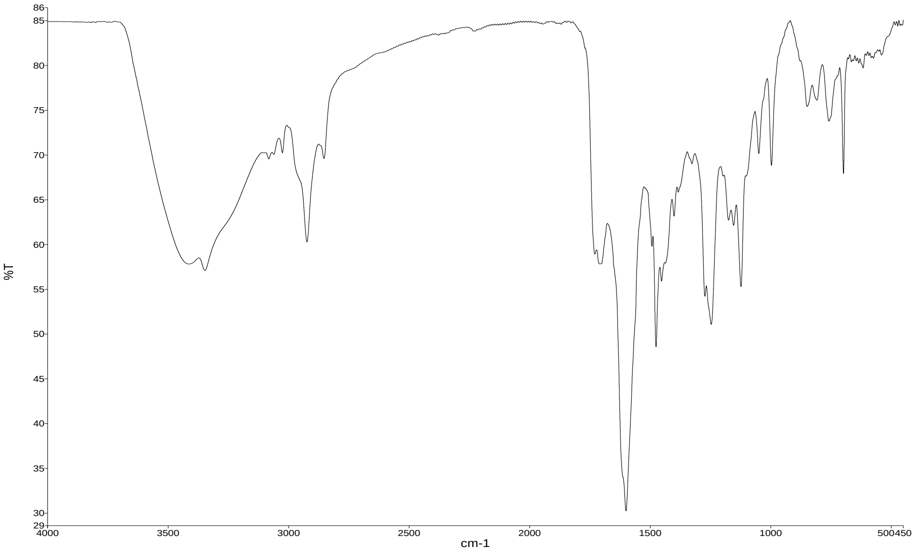

Figure 3.30. FT-IR of Copper(II) Phthalocyanine

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 3.8. FT-IR results of copper(II) Phthalocyanine

Vibration (cm^{-1})	**Vibration**
2924	Ar-CH
1708	C=O
1600	C=C
1273	C-O

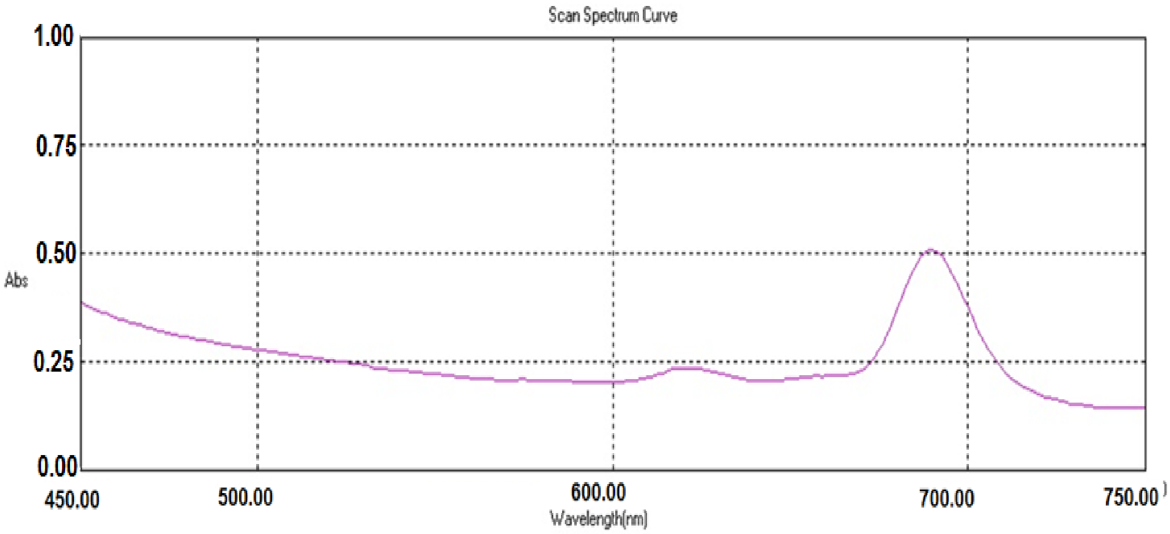

Figure 3.31. UV-spectrum of Copper(II) Phthalocyanine

The synthesized CuPc compound shows intense Q band at 690nm, 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.

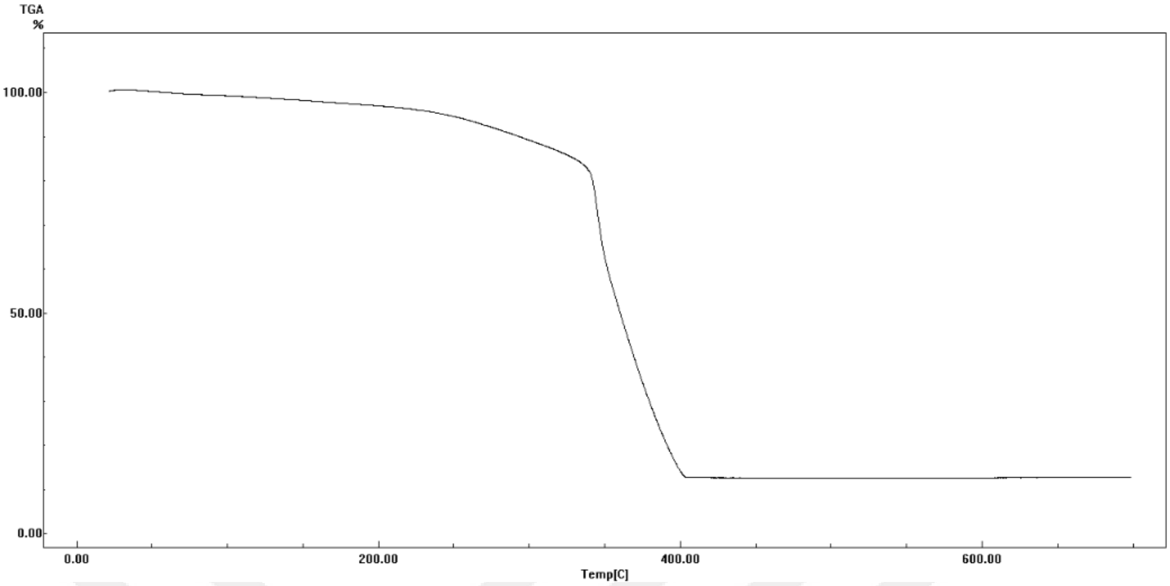

Figure 3.32. TGA of Cu Phthalocyaninne

From the thermographic analysis result of the synthesized Copper phthalocyanine compound it shows that the synthesized compound begin to exhibit weight loss at a temperature of 354 °C which indicate a suitably high thermal stability for the newly synthesized compound.

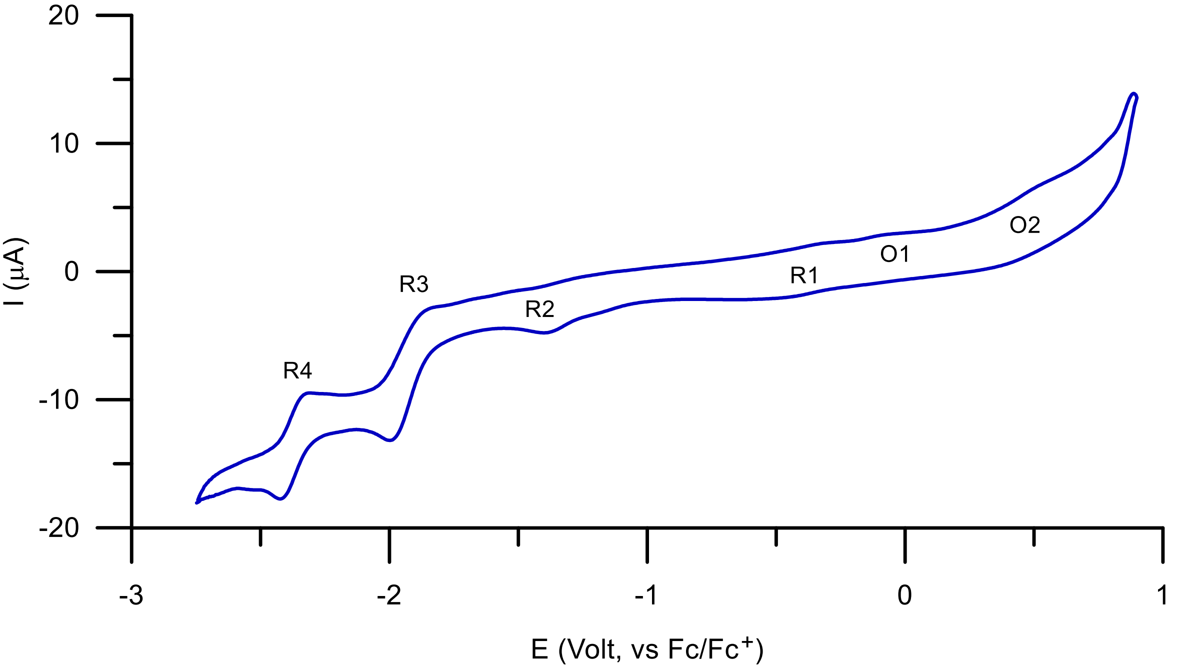

Figure 3.33. Cyclic Voltamogram of CuPc

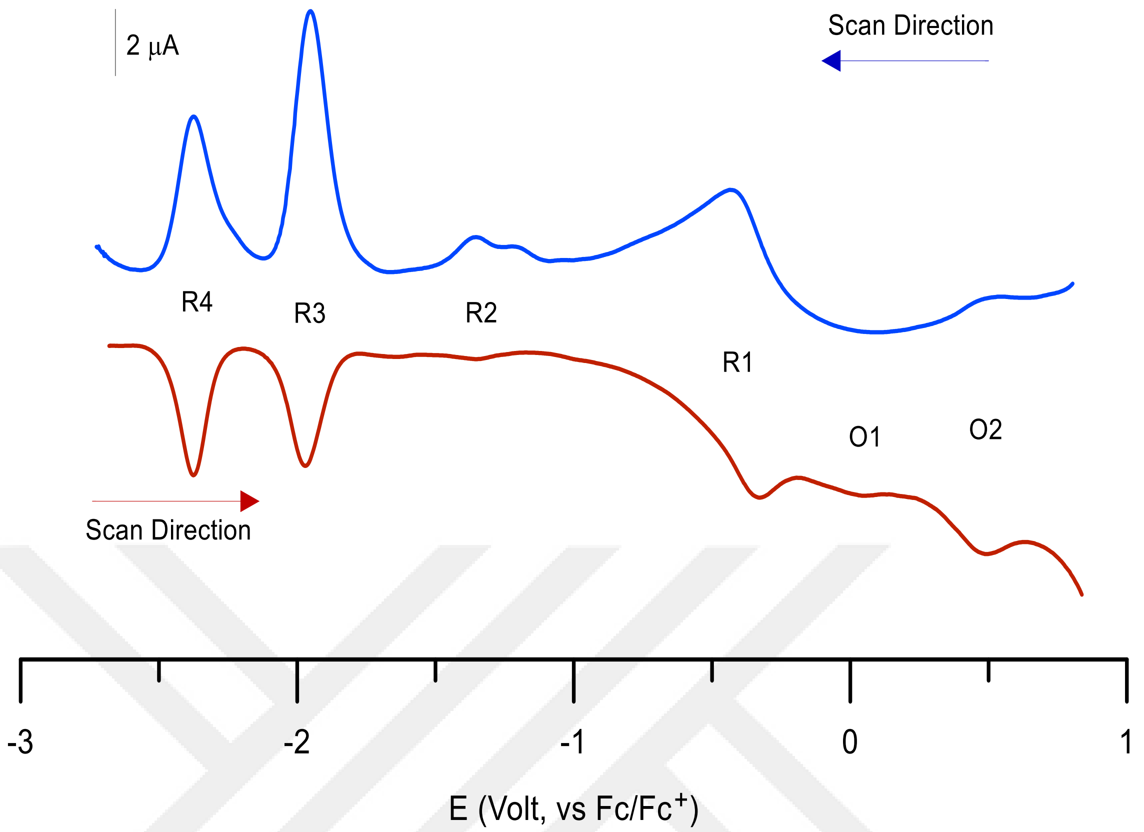

Figure 3.34. Square Wave voltamogram of CuPc

Fig. 3.37 and 3.38 represents the CV and SWV of CuPc recorded in the TBAFB/DMF electrolyte system Fc^+/Fc as quasi reference electrode. CuPc gives a ligand based three quasi reversible reduction couple R1 at -1.34V, R2 at -1.94 V and R3 at -2.37 V, together two quasi reversible oxidation reaction O1 at 0.07 V and O2 at 0.47 V. Because Cu(II) is not redox active metal for the phthalocyanine compounds, these reduction and oxidations are belong to phthalocyanine ring system. The potential difference (1.41 V) between the first reduction R1 (-1.34 V) and first oxidation O1 (0.07 V) due to reduction and oxidation of phthalocyanine rings.

3.7. 1,8,15,22-Tetrakis [3-(oxo-2H-chromen-7-yloxy) coumarin]Iron Pththalocyanine

3.7.1. Experimental results

This compound was synthesized using 3-Phathalonitrile and Iron (II) Chloride in DMF and Glycerol (1:3)

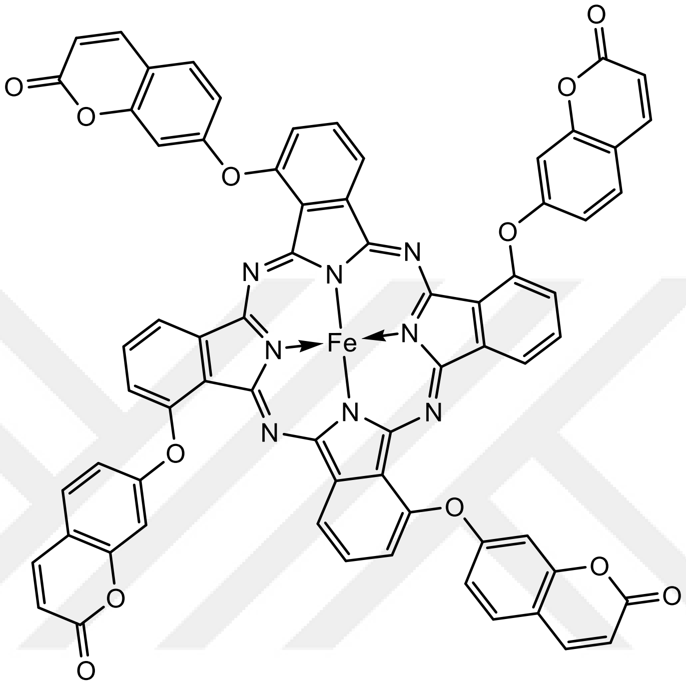

Figure 3.35. Iron Phthalocyanine

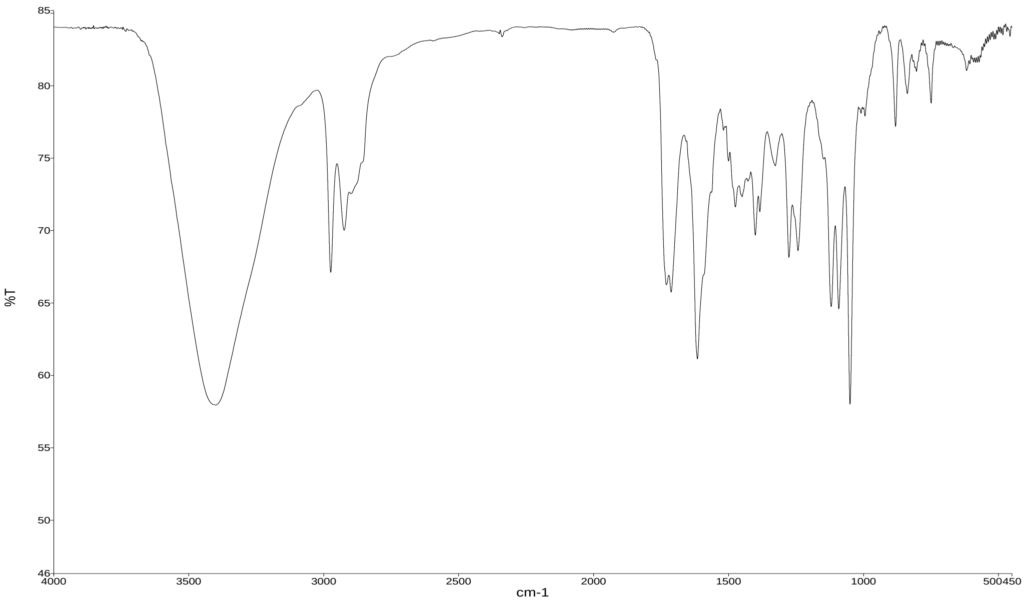

Figure 3.36. FT-IR of Iron(II) Phthalocyanine

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 3.9. FT-IR results of Iron(II) Phthalocyanine

Vibration (Cm^{-1})	**Vibration**
2974	Ar-CH
1712	C=O
1615	C=C
1276	C-O

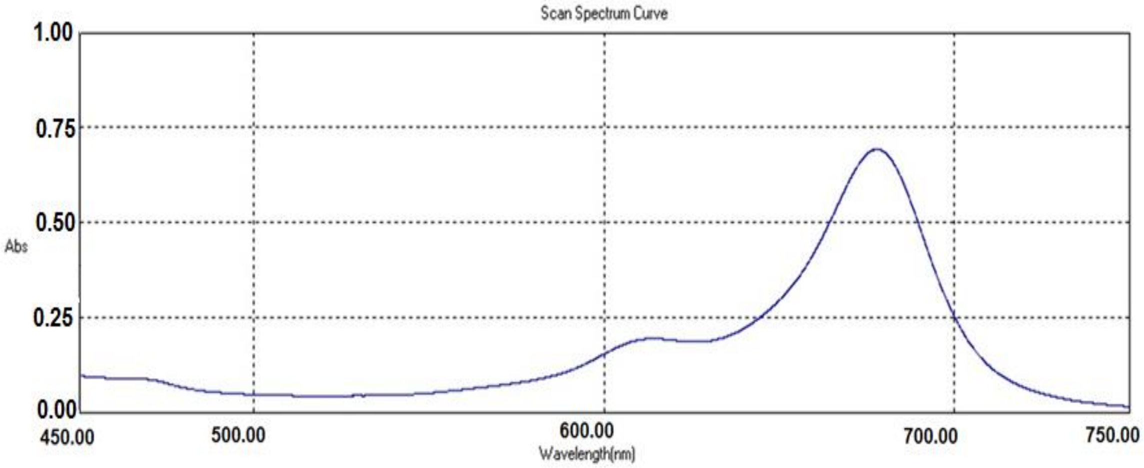

Figure 3.37. UV spectrum of Iron(II) Phthalocyanine

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

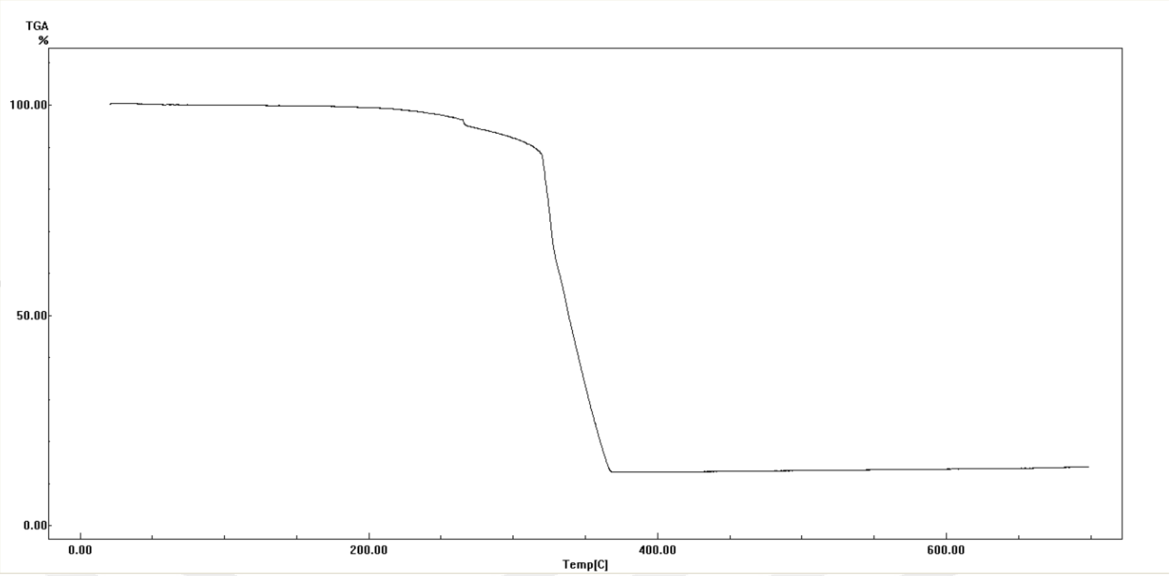

Figure 3.38. TGA of Iron Phthalocyaninne

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 °C which indicate a suitably high thermal stability for the newly synthesized compound.

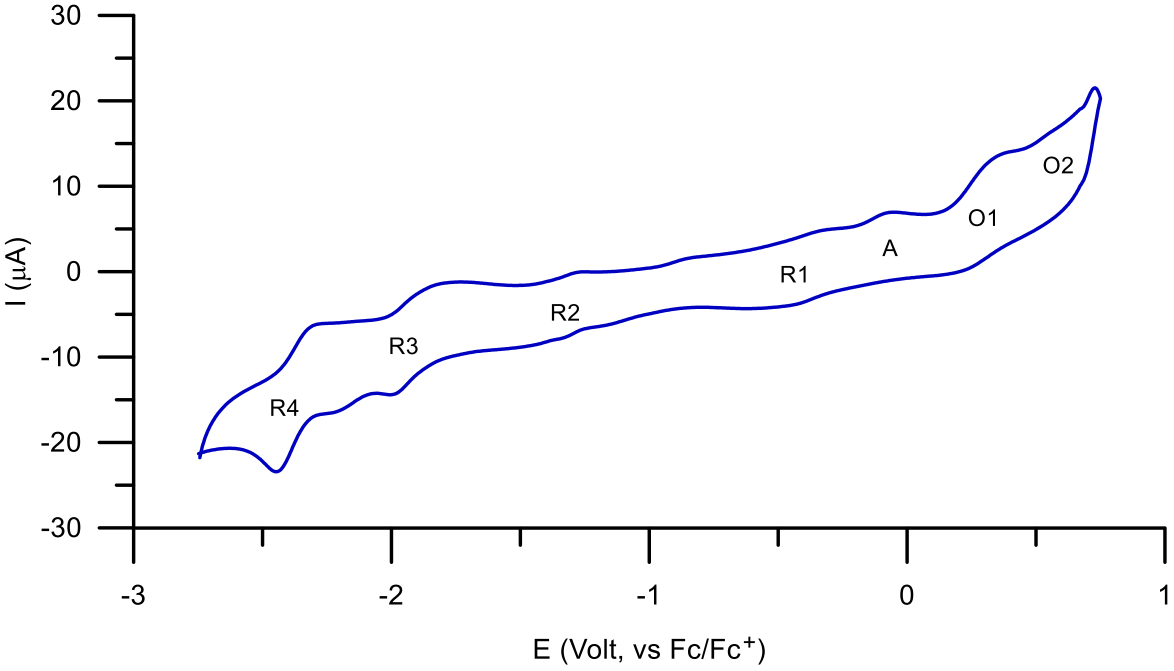

Figure 3.39. Cyclic Voltamogram of FePc

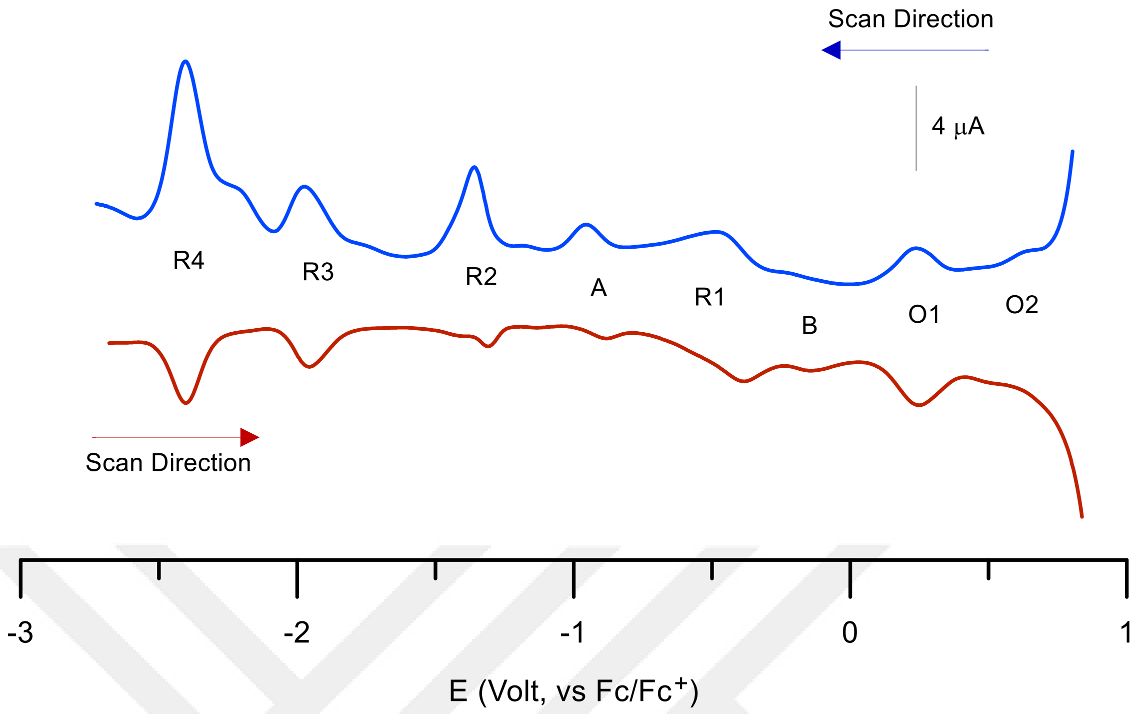

Figure 3.40. Square Wave voltamogram of FePc

FePc has redox active metal centre, therefore it can give metal based redox processes in the electrochemical potential window of DMF. Figure 3.43 and 3.44 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. Electrochemical properties of FePc is closely resembles the electrochemical properties of CoPc, because both have redox active metal centre.

3.8. Electronics Absorption Spectra

The ground state electronic spectra are especially important to understand the structure of the phthalocyanines. Generally, UV-Vis spectra of phthalocyanines show electronic spectra with two strong absorption bands popularly known as Q and B bands. The Q band is 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

[32, 33]. The ground state electronic absorption spectra of the synthesized non-peripherally tetra-substituted phthalocyanine complexes showed monomeric behavior evidenced by a single (narrow) Q band.

The electronic spectra of Nickel, Cobalt, Zinc, Copper, and Iron phthalocyanine compounds (NiPc, CoPc, ZnPc, CuPc, FePc,) in DMF are given in figure above. The UV-Vis absorption spectra of ZnPc, CuPc, and NiPc, in DMF showed intense Q absorption at 690nm (Figure: 3.25, 3.31, 3.13.). The Q band absorptions were also observed at 677 nm and 678 nm, respectively, for CoPc, and FePc (Figure: 3.19, 3.37).

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).

3.9. Thermal Stability Of The Synthesized Phthalocyanines

The thermal stability of the compound derivative was checked by TGA**.** The Phthalocyanine were heated to 700 ^{o}C to determine their degradation temperature. The temperatures at which the phthalocyanine began to exhibit weight loss were 309 ^{o}C, 300 ^{o}C, 306 ^{o}C, 354 ^{o}C and 380 ^{o}C for NiPc, CoPc, ZnPc, CuPc, and FePc respectively (Figure: 3.14, 3.20, 3.26, 3.32, 3.38).

3.10. Electrochemistry

Cyclic voltammograms (CV) and Square Wave voltammograms (SWV) were carried out using a Gamry Reference 600 Potentiostat/ Galvanostat/ZRA. A three electrode system was used for CV and SWV measurements in dimethylformamide (DMF) consist of glassy carbon working electrode, and a platinum wire counter and a platinum wire quasi reference electrode. Electrochemical grade tetra butyl ammonium tetra fluoro borate (TBAFB) (Fluka) was used as the supporting electrolyte in voltammetric measurements in non-aqueous solvents. The ferrocene/ferrocenium couple (Fc/Fc^{+}) was used as an internal standard and potentials reported with respect to Fc/Fc^{+} in non-aqueous solutions. Square wave voltammetric analysis was carried out at frequency of 25 or 40 Hz, amplitude of 25 to 40 mV and step potential of 4 mV. High purity argon is used for the deoxygenation of the cell at least 10 minutes prior to electrochemical measurements and the solution was protected from air by a blanket of argon during the experiments. The low solubility of the metal phthalocyanines limited the scope of experiments of the non-peripherally substituted phthalocyanines.

In Table 3.10, the SW voltammogram of all the complexes studied data are listed. Generaly the reduction and oxidation behaviour of metallophthalocyanine derivatives is due to the interaction of phthalocyanine ring and the central metal ions. Because of low solubility of phthalocyanine complexes in DMF, we could not get satisfactorily good cyclic voltammogram from electrochemical work. This is coupled with aggregation of phthalocyanines in DMF/TBAFB solvent system, and it caused the appearance of aggregation wave of phthalocyanine at about -0.4 V in the voltammogram of all the Metallophthalocyanines complexes studied. In all the metal phthalocyanine complexes have broad adsorption or aggregation oxidation-reduction wave at -0.4 V. Therefore the first reduction process marked (Ad) has an adsorption or aggregation character [90-91].

Table 3.10 Electrochemical properties of metal phthalocyanines in DMF/TBAFB versus Fc^+/Fc

	CoPc	CuPc	FePc	NiPc	ZnPc
R4	-2.46		-2.401		
R3	-1.92	-2.37	-1.95	-2.336	-2.384
R2	-1.37	-1.936	-1.336	-1.936	-1.961
R1	-0.93	-1.341	-0.915	-1.04	-0.978
Ad	-0.46	-0.37	-0.415	-0.328	-0.38
B	0.012	0.07	-0.125	0.27	0.093
O1	0.595	0.47	0.25	0.465	0.493
O2			0.67		

Electrochemical properties of Co(II) and Fe(II) Pc’s complexes differ from those of the redox inactive metallophthalocyanines. It is due to the fact that metal *d* orbitals positioned between HOMO and LUMO of the phthalocyanine ligand. For example, Ni, Cu, Zn, Pd, and similar metallophthalocyanines, redox processes take place on the phthalocyanine’s ring. For those metallophthalocyanine derivatives, such as Mn(II), Fe(II), and Co(II) derivatives having accessible *d* orbital levels lying within the HOMO–LUMO gap of a phthalocyanine species; the first oxidation and first reduction processes occur on the metal centre, depend on whether there are any available suitable coordinating species that would stabilize the M(II) centre. However, these tendencies of the metallophthalocyanines containing an electroactive metal centre differ in different solvents. Generally oxidation of phthlalocyanine with redox active metal in donor solvent system, the metal centre oxidation takes place before the ring oxidation process, because donor solvents strongly favour M(III) species. In non donor solvents, the ring oxidation process takes place before the metal centre oxidation.

4. CONCLUSION

The present work describes the synthesis and characterization of five metals phthalocyanines bearing 7-Hydroxy coumarin substituents on the α non-peripheral positions, these new complexes were characterized by Electronic absorption spectra, FT-IR, Uv-Vis spectroscopy, Thermal stability and Electrochemical analysis.

Coumarin are of interest because of their physiological, photodynamic, anticoagulant, spasmolytic, bacteriostatic and anti tumor activity. Coumarin and their derivatives have been studied extensively for their complexation with metal ions. They are also extensively used as analytical reagents.

3-nitrophthalonitrile was used as precusor because phthalocyanine with non-phripheral substituents located on the inner sterically crowded α-position of the benzo rings of the macrocyle exhibit more interesting electronic properties than phthalocyanines with substituents attached at the outer carbon of the benzo ring [92]. A significant bathochromic shift of the Q-band (π-π* transition) compared to pheripherally subtituted Phthalocyanine has been observed in the studies of the few known non-pheripherally substituted phthalocyanine [93]. However, the synthesis of precursors to α-substituted phthalocyanine is generally very difficult and the corresponding phthalocyanine yields are lower than phthalocyanines substituted at the outer less crowded positions of the benzo ring (4-nitrophthalonitrile) [94].

In conclusion this research work shows the synthesis of 3-nitrophthalonitrile and its versatility as a synthestic precursor to new class of phthalocyanine. The availability of this compound as a general synthetic reagent to polymeric and phthalocyanine based materils much like the studied 4-nitrophthalonitrile [95] provide opportuninity for alteration of physical properties through steric hinderance effects, and for perturbation of phthalocyanine electronic structure by the introduction of substituents at electronically influential non-pheripheral sites. The synthesized phthalocyanine complexes Shows partial solubility in some organic solvents. such as, THF, DMF and DMSO, it also exhibit a suitably high thermal stability.

Synthesis of unmetallated Phthlocyanine was aborted as the compound did not formed.

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RESUME

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