TÜRKİYE
FIRAT UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

SYNTHESIS OF 4-(2,6-DI-TERT-BUTYL-4-METHYL PHENOXY) SUBSTITUTED PHTHALOCYANINE COMPLEXES AND INVESTIGATION OF ELECTROCHEMICAL AND THERMAL PROPERTIES

Peshang Khdir Omer MANGURI

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I hereby declare that I wrote this Master's Thesis titled “Synthesis of 4-(2,6-di-tert-butyl-4-methyl phenoxy) Substituted Phthalocyanine Complexes and Investigation of Electrochemical and Thermal Properties ” in consistent with the thesis writing guide of the Graduate School of Natural and Applied Sciences, Firat University. I also declare that all information in it is correct, that I acted according to scientific ethics in producing and presenting the findings, cited all the references I used, express all institutions or organizations or persons who supported the thesis financially. I have never used the data and information I provide here in order to get a degree in any way.

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Peshang Khdir Omer MANGURI

PREFACE

Phthalocyanines are macrocycle compounds with an electron delocalization of 18- π consisting of four iminoisoindoline groups. These compounds have potential applications in several technical areas owing to their fascinating electronic structures, stability, physical, and chemical properties. The structures of the synthetic compounds were analyzed by a variation of ^{1}H-NMR, ^{13}C-NMR, UV-Vis, and FT-IR spectroscopy.

First of all, I would like to express my gratitude to almighty Allah to enable me to complete this thesis on phthalocyanines. We have to make an effort into this assignment. However, it would not have been possible without the kind support and help of many individuals, we would like to extend our sincere thanks to all of them.

Preparing a thesis on any sector or subject is really challenging work for anyone. being the student of management and to prepare a report on the specific topic, I accept it with challenges, opportunity and also became successful to present the thesis with our full endeavor

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ABSTRACT

Synthesis of 4-(2,6-di-tert-butyl-4-methyl phenoxy) Substituted Phthalocyanine Complexes and Investigation of Electrochemical and Thermal Properties

Peshang Khdir Omer MANGURI

Master's Thesis

FIRAT UNIVERSITY
Graduate School of Natural and Applied Sciences
Department of Chemistry

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Phthalocyanines are macrocycle compounds with delocalized 18-π electron, consisting of four iminoisoindoline groups. These compounds have potential, applications in several technical areas owing to their electronic structures, stability, physical, and chemical properties. Butylated hydroxy toluene is one of the cresol derivatives substituted with tertiary butyl group which have wider range of applications.

In this work, 4-(2,6-di-tert-butyl-4-methylphenoxy)phthalonitrile synthesised from butylated hydroxy tolune (2,6-di-tert-butyl-4-methylphenol) and 4-nitrophthalonitrile. Then phthalocyanine complexes substituted with butylated hydroxy toluene (Li_2Pc CoPc, NiPc, CuPc, and ZnPc,) were synthesised. The structures of the synthetic compounds were analysed by various spectroscopic techniques, ^{1}H NMR, ^{13}C NMR, UV-Vis, FT-IR spectroscopy and elemental analysis. The UV-Visible absorption spectra of the metal phthalocyanine complexes showed an intense Q band which started from 669 nm for CoPc, 675 nm Li_2Pc, 677 nm NiPc, 679 nm ZnPc, and last one 723 nm of CuPc. Thermal analysis was performed by thermogravimetric (TGA) and differential thermal analysis (DTA) method showed phthalocyanine complexes stable in wide range of temperature (weight lost start from 200, 230, 230, 250, and 250 °C) for (Li_2Pc, ZnPc, CuPc, CoPc, and NiPc) respectively. Electrochemical properties were investigated in DMSO by cyclic voltammetry (CV) and square wave voltammetry (SWV). All the metal phthalocyanine complexes showed redox waves both in oxidation and reduction potentials belong to phthalocyanine ring. CoPc complexes have extra redox potential belong to central metal atom cobalt.

Keywords: Phthalocyanine, Butylated hydroxytoluene, 2,6-di-tert-butyl-4-methylphenol, Phthalonitrile, Macrocyclic compound, Thermal analysis, Electrochemistry

ÖZET

4- (2,6-di-tert-butil-4-metil fenoksi) Sübstitüe Ftalosiyanin kompkslerinin Sentezi ile Elektrokimyasal ve Termal Özelliklerinin Araştırılması

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Ftalosiyaninler, dört iminoisoindolin grubundan oluşan, delokalize olmuş 18-π elektrona sahip makrosiklik bileşiklerdir. Ftalosiyanin bileşikleri, elektronik yapıları, kararlılıkları, fiziksel ve kimyasal özellikleri sebebi ile birçok teknik alanda potansiyel uygulama alanlarına sahiptir. Butillenmiş hidroksi toluen, geniş uygulama alanına sahip olan tersiyer butil grubu taşıyan kresol türevleridir.

Bu çalışmada, bütillenmiş hidroksi tolune (2,6-di-tert-butil-4-metilfenol) ve 4-nitroftalonitril bileşiklerinden 4-(2,6-di-tert-butil-4-metilfenoksi) ftalonitril bileşiği sentezlenmiştir. Daha sonra bütillenmiş hidroksi toluen grubu taşıyan ftalosiyanin kompleksleri (Li_2Pc CoPc, NiPc, CuPc ve ZnPc) sentezlenmiştir. Sentezlenen bileşiklerin yapıları çeşitli spektroskopik teknikler, ^{1}H NMR, ^{13}C NMR, UV-Vis, FT-IR spektroskopisi ve element analizi metotları kullanılarak karakterize edilmiştir. Metalli ftalosiyanin komplekslerinin UV-Görünür bölge spektrumlarında, şiddetli absorpsiyona sahip Q bandı göstermiştir (CoPc 675, Li2Pc, 677, NiPc, 679, ZnPc ve son 723, CuPc). Ftalosiyanin komplekslerinin termal özellikleri, termogravimetrik (TGA) ve diferansiyel termal analiz (DTA) yöntemleri kullanılarak araştırılmıştır. Kompekslerin geniş bir sıcaklık aralığında kararlı olduğu, bozunmaya başlama sıcaklığının Li_2Pc, ZnPc, CuPc, CoPc ve NiPc bileşikleri için sırasıyla 200, 230, 230, 250, ve 250 °C olduğu görülmüştür. Sentezlenmiş olan ftalosiyanin bileşiklerinin elektrokimyasal özellikler DMSO'da dönüşümlü voltametri (CV) ve kare dalga voltametri (SWV) yöntemleri ile kullanılarak yapılmıştır. Bütün metal ftalosiyanin komplekslerinin, ftalosiyanin halkasına ait yükseltgenme ve indirgeme potansiyellerine sahip olduğu görülmüştür. CoPc kompleksinde ise, ftalosiyanin halkası yükseltgenme ve indirgenme potansiyeli arasında merkez metal atomu kobalt'a ait ekstra yükseltgenme ve indirgenme potansiyelinin varlığı da tespit edilmiştir.

Anahtar Kelimeler: Ftalosiyanin, Butillenmiş hidroksitoluen, 2,6-di-tert-butil-4-metilfenol, Ftalonitril, Termal analiz, elektrokimya

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SYMBOLS AND ABBREVIATIONS

Abbreviations

Pc : Phthalocyanine
Pcs : Phthalocyanines
DBPC : 2,6-di-tert-butyl-p-cresol
DMSO : Dimethyl sulfoxide
CuPc : Cupper phthalocyanine
ZnPc : Zinc phthalocyanine
CoPc : Cobalt phthalocyanine
NiPc : Nickel phthalocyanine
H_2Pc : Metal free phthalocyanine
Li_2Pc : dilithium phthalocyanine
MPc : Metal phthalocyanine
NPN : Nitro phthalonitrile
np : Non-peripheral
PDT : Photodynamic therapy
DMF : Dimethylformamide
THF : Tetrahydrofuran
DBN : 1,8-diazabicyclo-5-ene
DBU : 1,8-diazabicyclo(5,4,0)undec-7-ene
FT-IR : Fourier-transform infrared spectroscopy
UV-vis : Ultraviolet visible spectroscopy
NMR : Nuclear magnetic resonance
HOMO : Highest occupied molecular orbital
LUMO : Lowest unoccupied molecular orbital
CV : Cyclic voltammetry
SWV : Square wave voltammetry
DTA : Differential thermal analysis
TGA : Thermogravimetric analysis
TBAFB : Tetra butyl ammonium tetrafluoroborate
L : Litter
mL : Millilitre
g : Gram

1. INTRODUCTION

Coordination chemistry is the chemistry of compounds that has a central metal surrounded by one or more anions and molecules and bonded directly with the metal called coordination compounds (complex), that may be neutral or charged. If the complex charged; it is stabilized by neighbouring counter-ions. The centre of complexes are metal ions, which are surrounded by the number of neutral molecules and/or ions. These may be assumed to be bound to the central ion by coordinating covalent bonds and in some situations, bonding is often more complicated than that. Molecules or ions that surrounded the central metal ion are called ligands [1].

The first coordination compound was synthesized in nearly the 18th century by the famous painter “Diesbach”. He found Prussian blue (KFe [Fe (CN)$_6$]). The central metal can be in any oxidation state that makes a different geometrical shape like a tetrahedral, square planner and octahedral, etc. According to the number of ligands around it is called coordination geometry [2].

Phthalocyanine compounds are compounds that do not exist in nature and are synthetically synthesized, they are a class of compounds that draw interest for their resemblance to chlorophyll found in plants and haemoglobin found in other living organisms. The phthalocyanine ring can form coordination compounds with almost all metal ions and typically form four-coordinated square-plane complexes [3].

Phthalocyanine compounds have many technical uses and new ones are introduced every day. The effect of phthalocyanine compounds on iron corrosion in the acidic environment has been studied, and its anti-corrosion properties have been shown electrochemically [4]. It has been shown that the copper phthalocyanine has very strong photodetector properties in the near-infrared region [5].

Phthalocyanines have been commonly used as pigments in the textile, polymer, and paint industries for many years since their accidental synthesis as a by-product of Braun and Tcherniac. Phthalocyanines have unique properties such as brightness, colour tolerance and resistance to environmental conditions such as heat and light. These properties of the phthalocyanine placed the focus of many studies in material science its discovery and now being used in many different fields. Phthalocyanine compounds are biologically and chemically important compounds due to their unique structure, chemical, and optical properties [6].

Phthalocyanine compounds, in general, are used; as Langmuir-Blodgett films [7], photoconductive agent in photocopiers [8], laser printers [9], gas sensors, electrochromic imaging equipment, and photodynamic cancer treatment [10] in various health applications, electronic optical recording information storage systems, liquid crystal colour monitor applications [11], catalyst in fuel cells, increasing the octane levels of gasoline [12], gas diffusion electrodes [13], reaction catalysis for the reduction of CO_2 to formic acid is used in conductive and semiconductor polymers, non-linear optics, and biosensors.[14].

Most phthalocyanines have poor solubility in organic solvents and water. This is because the phthalocyanine molecules are conveniently stacked due to their bulky and planar shape. The solubility of phthalocyanines can be improved by applying different replacements to the peripheral and axial positions of the ring to reduce this propensity to stack. For example, the addition of groups such as lipophilic alkyl, alkoxy, phenoxy prevents the development of dimeric structures due to structural barriers that increase solubility in organic solvents [15, 16]. Similarly, water-soluble phthalocyanine can be obtained by adding carboxyl [17] or sulfonyl groups to peripheral positions [18].

The derivatives of phthalocyanine are commonly used in many different fields. The replacements that are added to the phthalocyanine group affects their properties significantly. Pcs are usually prepared using high heat cyclotetrizer methods from either phthalonitriles, phthalic anhydrides, and diiminoisoindoles. Where the template provided by the suitable metal cation is needed, reactions can be made in various solvents, besides, under solvent-free conditions, which takes a long time and a temperature of almost 200 °C [19].

Butylated Hydroxytoluene (BHT), also called 2,6-Di-tert-butyl-4-methyl phenol or 2,6-di-tert-butyl-p-cresol (DBPC) is a lipophilic phenolic antioxidant [20, 21]. BHT can be part of the primary substructure for chemical, medicinal and pharmaceutical feed and food products. It is commonly used in the plastics, fermentation and bio-industrial chemicals sectors. Researchers found that BHT has been applied to extend cryopreservation, minimizes cold sperm disruption from multiple animal species [22, 23]. BHT occurs naturally in litchi and is produced by certain types of freshwater planktons [24].

BHT is also commonly used for the stabilization of oils and high-fat foods in association with other antioxidants, propyl gallate, and citric acid. Furthermore, the regeneration of Alpha-Tocopherol α-TOH uses butylated hydroxytoluene as an antioxidant. BHT and its derivatives have become a desirable antioxidant community due to these broad applications [25, 26].

In this work, 4-(2,6-di-tert-butyl-4-methylphenoxy)phthalonitrile synthesized precursor of phthalocyanines compounds. Then Co, Cu, Ni, Zn and Li, complexes of phthalocyanine were synthesized. After purification of the phthalocyanine compounds, spectroscopic, electrochemical and thermal properties were investigated by UV-Visible spectroscopy, cyclic and square wave voltammetry and thermogravimetric and differential scanning calorimetry. Which is 2,10,16,24-Tetrakis (2,6-di-tert-butyl-4-methyl phenoxy) cobalt, copper, zinc, nickel, and di-lithium Pcs from phthalonitrile in dimethyl sulfoxide (DMSO), and described its electrochemical conductivity and the ability for thermal decomposition. Due to its higher stability, researching the applications of these types of Pcs especially CuPc for painting and ZnPc for photodynamic therapy is possible.

2. LITERATURE REVIEW

This section defines the general information about phthalocyanines. Which is includes history, discovering and nomenclature of phthalocyanines with general properties of Pcs. Also, synthesis of some type of phthalocyanines and using deferent starting materials with the most important application was describes in this chapter. At the end of this part, Butylated hydroxy toluene and the way for synthesize of this compound was illustrated.

2.1. History of Phthalocyanines

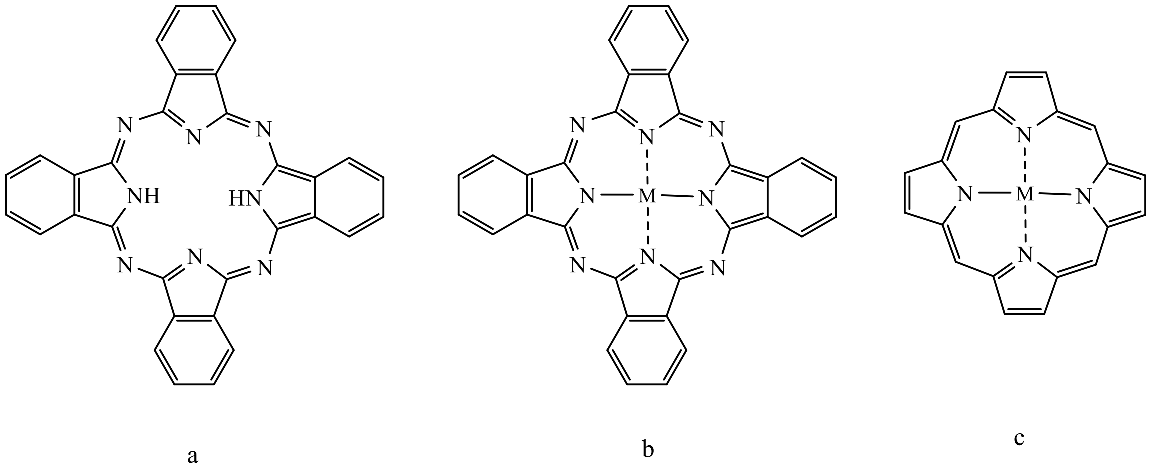
The original name of phthalocyanines (Pcs) is a combination of the Greek word for mineral oil (naphtha) and dark blue (cyanine). Their color may vary from blue to yellowish-green. Phthalocyanine (pc) was first produced in 1907 by two researchers, Braun and Tcherniac, in London from phthalimide and acetic anhydride as an undesirable by-product during o-cyanobenzamide synthesis [27].

In 1927 De Diesbach and Von Der Wied prepared copper-phthalocyanine from the reaction between copper (I) cyanine and 1,2-di bromobenzene in pyridine. After that, at 1928 Iron phthalocyanine was made and characterized by Scottish dye LTD from phthalic anhydride and ammonia phthalimide by chance and it became a powerful pigment [28].

After 1928, phthalocyanine was the most important industrial product used in printing colours and dyes and also in dyeing plastics, aluminium surfaces and textiles [29]. The term phthalocyanines was first used by Linstead in 1933. Between 1929 and 1939, Linstead clarified Pc structures and developed synthetic methods for various metallic Pcs [30].

2.2. Structure and Nomenclature of Phthalocyanines

Pcs are known as metal-free phthalocyanines (H_2Pc) and metal phthalocyanines (MPc). They are a class of bivalent compounds. Like porphyrins, phthalocyanines are tetradentate, planar, and consisting 18-π electron system which makes an aromatic electron ring system of the macrocyclic compounds. Phthalocyanines consisting of four pyrrole units which are joined by four aza (—N=C—) groups in the α-carbon, and pyrrole unit have four phenylene rings, showed at Figure 2.1.



a b c

Figure 2.1. Metal-free phthalocyanine (H_2Pc) (a), metal phthalocyanine(M-Pc) (b), porphyrins (c)

The cation (s) in the central cavity is simply indicated by the normal notation. Additionally, many of the Pcs have organic skeleton substitution. Therefore, the abbreviation is necessary to avoid the long and complicated nature of Pc nomenclature using the IUPAC system. There are sixteen potential sites connected with four benzo sub-units for macrocycle substitution. Eight carbon atoms of 2,3,9,10,16,17,23, and 24 is labelled peripheral (p) sites and eight non-peripherals (np) are indicated by 1,4,8,11,15,18,22, and 25 carbon atoms [12], showed at Figure 2.2.

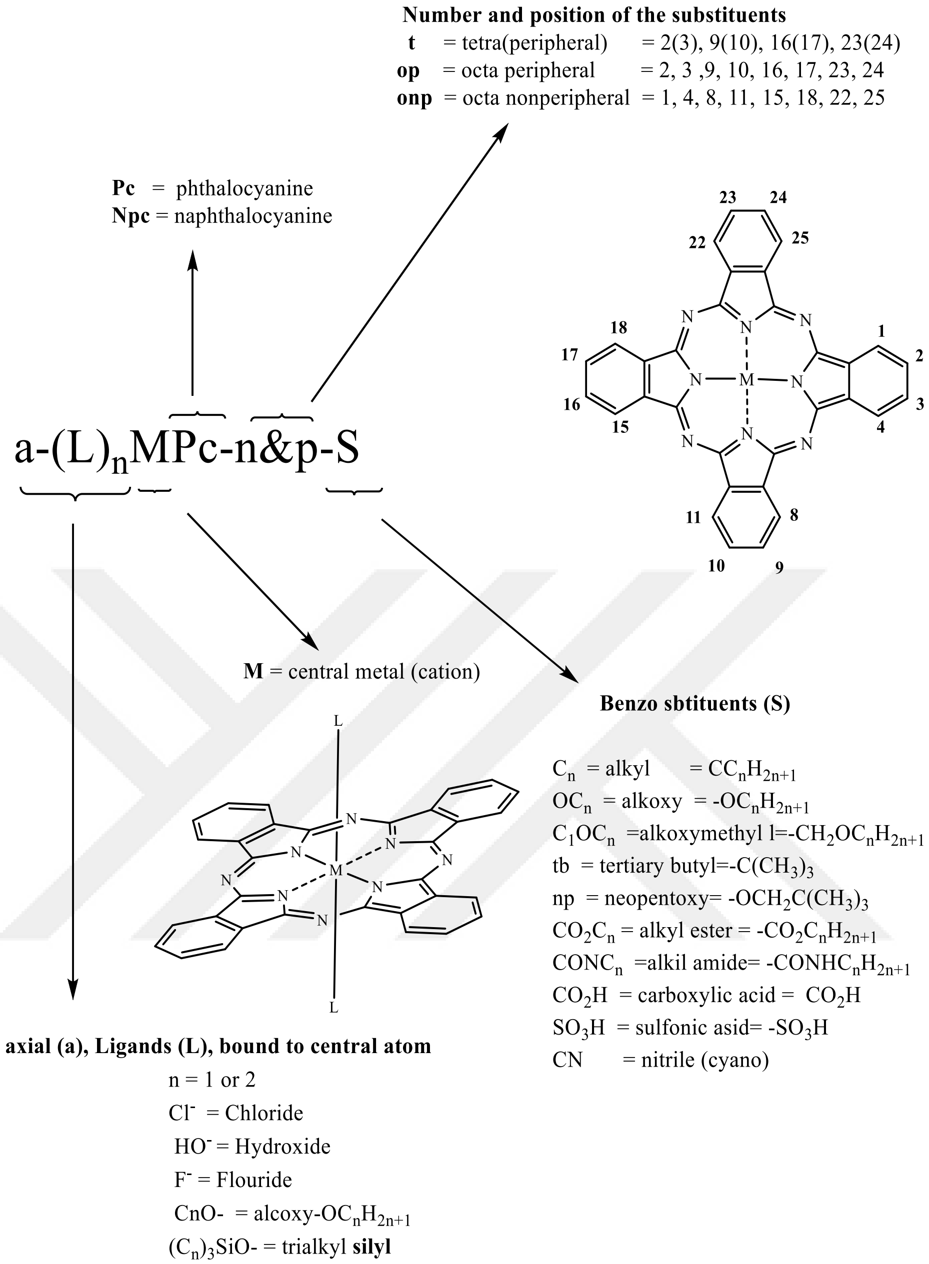


Figure 2.2. Schematic notation of phthalocyanine nomenclature [12]

2.3. General Properties of Phthalocyanines

Phthalocyanines are planer aromatic compounds that have 18-π electron system, they are very stable compounds due to presence of resonance stability inside the macrocyclic ring. Most of the phthalocyanine compounds have bluish and green colours [31]. Generally, phthalocyanine compounds don't have melting point, and most of them are not undergoing notable break down in the air under 200 °C. The macrocycle ring of phthalocyanine degrades only by the influence of heavy oxidants (dichromate or cerium salts) by breaking down into phthalic acid or phthalamide [32].

Phthalocyanines stability depends on the association between central cavity diameter and the metal atomic diameter. The Pcs have a central cavity diameter of 1.35 Å. When the atomic diameters of metals are slightly greater or smaller than this value, the metal atoms look inwards or outwards of the phthalocyanine ring. Oxidation and reduction of Pcs can happen reversibly or irreversibly easily on the metal atom and also on the phthalocyanine ring. Strong oxidizing agents such as nitric acid and potassium permanganate can oxidize all Pcs to phthalimide.[33].

Unsubstituted phthalocyanines have three types of crystalline structures; α-form, β-form, and γ-form. α-form can be produced from the spontaneous recrystallization of crystalline phthalocyanine [34]. β -form can be produced from heating α-form to higher than 300 °C and γ-form can be obtained by grinding α-form [35].

These crystal structures differ in colour, solubility, shape, and stability, γ-form differs from α-form in the size of particles, and β-form is the most common structure more stable form than other forms. Synthesis of α-form occurs in the polar solvents but the preparation of β-form occurs in organic solvents [36].

Unsubstituted phthalocyanines sublimes over 500 °C under high vacuum, most of them do not have a melting point. Phthalocyanines have conductive properties ranging from 10^{-15} to 10^{-4} Scm^{-1} depending on the central metal atom [37]. The phthalocyanine crystal structure suggests the presence of roughly circular and central symmetry plane molecules. The centre of Pcs either have two hydrogens or metal atom[38].

There are a wide range of applications of phthalocyanines are based on their remarkable properties. Pcs strongly absorb light in the low-energy region of the visible spectrum to give bright blue or green colors [39, 40]. The two main peaks are seen in the UV-Visible spectrum of phthalocyanine compounds. These peaks can be used for the phthalocyanine compound formation, and it also indicate that the formed phthalocyanine is either metallated or metal free. The first peak occurs due to the transition ($n \rightarrow \pi^*$) around 320-370 nm called the B or soret band. The second peak is formed due to the transition around 650-700 nm ($\pi \rightarrow \pi^*$) and is called the Q band. In addition, a shoulder-shaped peak is seen around 600-650 nm. This peak is due to aggregation. The property of the Q band is showing the shape of molecule according to its symmetry. For example; While a single peak is seen in the metallic phthalocyanine molecule (MPc) which is in D_4h symmetry as showed at Figure 2.3, a double peak is seen in the metal-free phthalocyanine molecule (H_2Pc) in D_2h symmetry, as showed at Figure 2.4 [41].

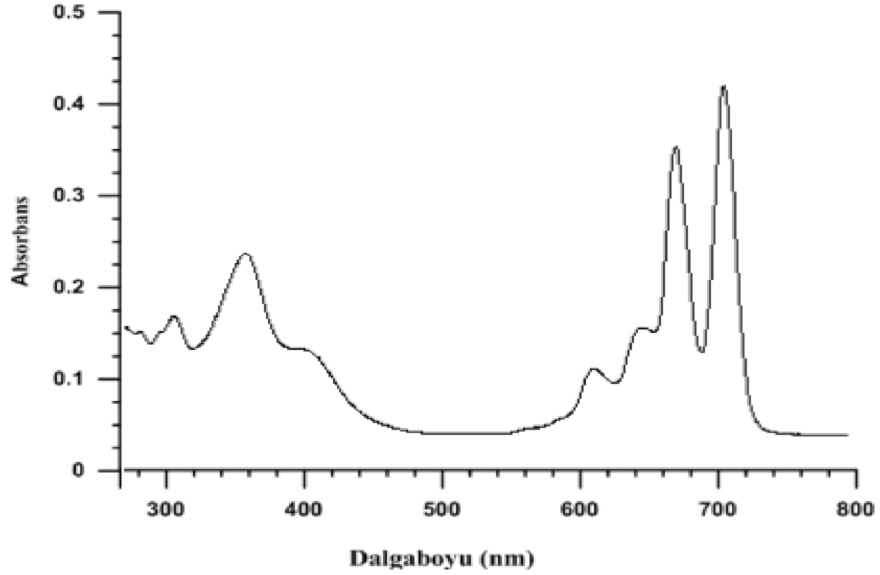


Figure 2.3. Overall UV / visible spectrum expected for metal-free phthalocyanine [41]

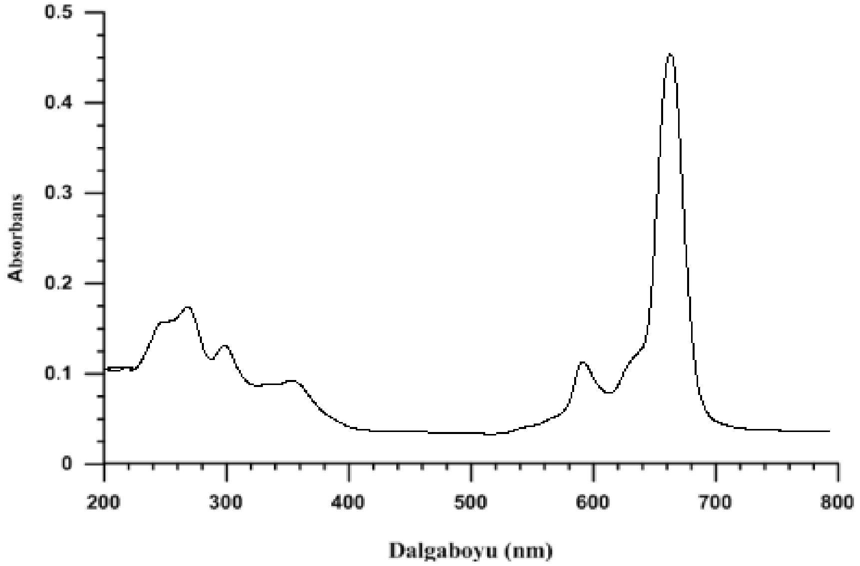


Figure 2.4. General expected UV / visible spectrum for metal phthalocyanine [41]

Q-band absorption occurs by the transition from the highest occupied molecular orbital (HOMO) in a_{1u} symmetry to the lowest unoccupied molecular orbital (LUMO) in e_g symmetry ($\pi \rightarrow \pi^*$). B-band or soret band absorption occurs with the transition of $n \rightarrow \pi^*$. Electronic transitions in the UV / visible region [41], are shown in Figure 2.5.

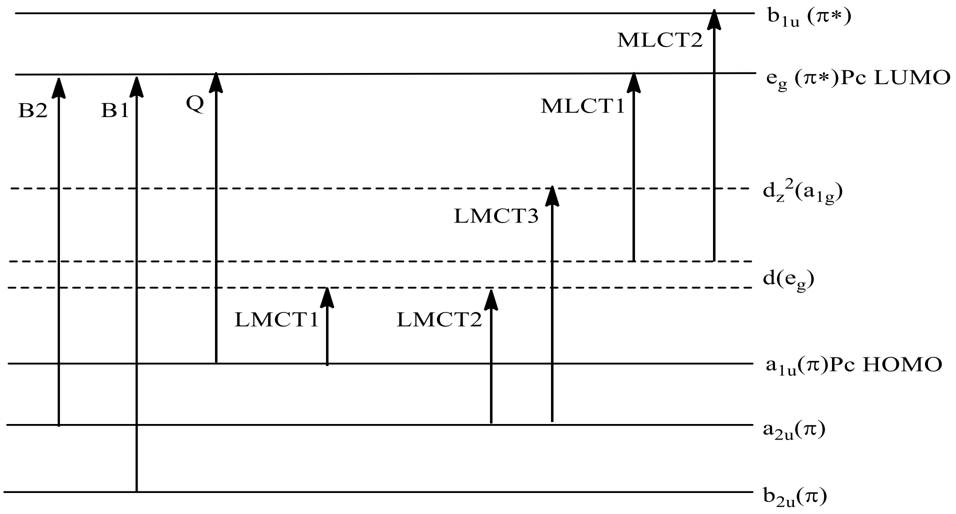


Figure 2.5. Electronic transitions of energy levels in the UV / visible region (Q and B bands and Ligand-to-Metal (LMCT) and Metal-to-Ligand (MLCT) load transfer transition bands) [42].

2.4. Application of Phthalocyanines

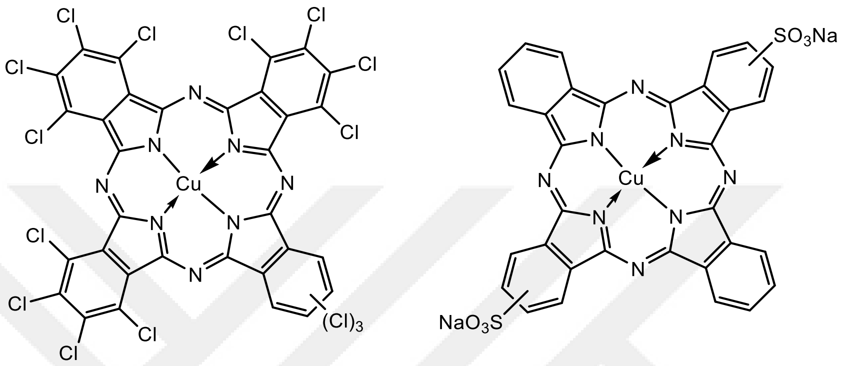
The phthalocyanines trade influence depends on three major factors; the first is its shining blue to green colours. The second factor is its extraordinary chemical stability, for example, copper-phthalocyanine sublimes over 580 °C, and it can be purified by dissolving in concentrated sulfuric acid without decomposition. And finally, the excellent color fastness to light is the third important factor. The combination of these properties makes it highly usable in too many applications e.g. pigments, dyes, electrophotography, optical data storage, non-linear optical devices and photodynamic therapy of cancerous tissue etc. [43, 44].

2.4.1. Pigments and Dyes

Phthalocyanines, especially copper phthalocyanines have a very important applications as a pigment. Copper Pc crystal structure exists in two forms, which are α-form and β-form. As a pigment, α-form is more suitable. The stability of β-form is higher and the colour is greener than α-form, but it is unsuitable for using as a pigment. The usable β-polymorphic copper Pc pigments can be obtain in a good crystalline form, from milling and adding fatty amines as an additive, and any other additives to prevent formation of α-form [45].

Besides being used as pigments, phthalocyanines are also used in many types of dyestuffs. Copper phthalocyanine (Figure 2.6) was started to be produced industrially for the first time in 1953 with the trade name Monastral blue. The brightness of the copper phthalocyanine pigment was further increased by producing α-form particles with the technique of dissolving and reprecipitating in sulfuric acid. It increases the solubility of copper phthalocyanine derivatives contain more than one sulfo group were synthesized [12]. Which are the best and first industrial dyes of Pc. They are applicable for strong and big size materials. They are used for making polyesters fiber, polyacrylonitrile, and especially for nylon. However, they are also used for dyeing paper and cotton substrates of cellulose [46, 47].

In addition, copper phthalocyanine pigments are used in the colouring of detergents, soaps and other cleaners, and in the colouring of polymers coated on woven or non-woven glass fiber. Today, thousands of tons of phthalocyanine are produced as blue and green dyestuffs per year to meet the increasing demand of the industry [48].



Copper phthalocyanine pigments

Copper phthalocyanine dyes

Figure 2.6. Copper phthalocyanines pigment and dyes

Phthalocyanines with excellent blue-green colors are used in inkjet, fountain pen inks, paper industry, plastic and metal surfaces as well as textile industry [49]. Inkjet printers of the early or first-generation which emerged in the late 1980s would have to use nonstandard dyes but refined to a much different level for inkjet use. The picked cyan dye at the time was copper phthalocyanine (Figure 2.7) which is now commonly used by today's inkjet printers. This dye has excellent properties, but being a water-soluble coloring, it shows poor water speed on simple paper in most conditions [50, 51].

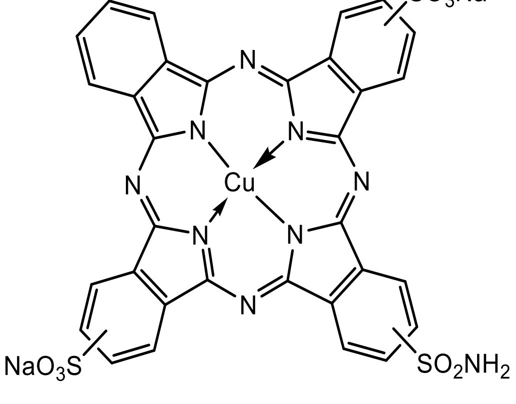


Figure 2.7. Copper phthalocyanine for Inkjets printers

2.4.2. Electrophotography

Electrophotography is an important technology that uses light and electricity to produce a photocopy. The first photocopy made in 1938, when Chester F. Carslon created the first xerographic image, and after developing his project called electrophotography in 1944. It continued with a license agreement with a US company for the development and marketing of copying machines using its own technology. The term electrophotography was adopted in the definition of the process (Xerography) and the description of the product (Xerox) in 1948 [52].

Electrophotography is another important technology of Phthalocyanines, it is perhaps best known as laser printing and photocopying. Phthalocyanines are key chemicals in both the photoconductor, photo forming process and the production of visible images on the substrate surface. Titanyloxy phthalocyanine type IV polymorph (Figure 2.8) is the best material to produce the latent image in modern laser printers [53]. It is very compatible with the infrared lasers in semiconductor and a photo-induced discharge rate extremely fast. In the colour photocopiers and laser printers, the toner created the image using pigments, the copper-phthalocyanine pigment is based on the cyan toner [50].

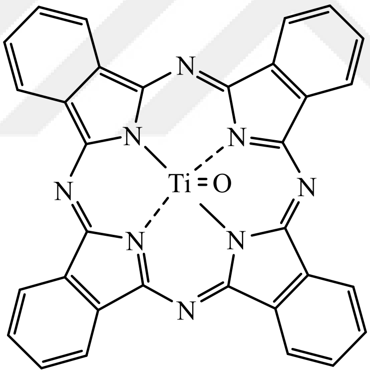


Figure 2.8. Titanyloxy phthalocyanine

2.4.3. Optical Data Storage

Electronic storage media uses laser beams for optical (binary) data collecting and recovery. In optical computing technology, a laser beam transmits digital data in the shape of holes on an optical disk or laser in a circular track on the surface of the disk. The low-power laser detector "reads" these holes and transforms them into electrical signals through changes in the strength of the reflected light from the pits. The CD-ROM (compact disk read-only memory), which stores text, sound, as well as images; in WORM (writing-once read-many), a form of a disk that can once be stored and read every time; and in new disks which are rewritable entirely. This is the newest compact record technology [54].

Recordable CDs (CD-R) disks have a polycarbonate sheet with a spiral groove that directs the laser beam as it writes and reads data. The spiral groove is covered with a thin layer of paint and then with a thin layer of gold (Au) or silver (Ag). Finally, on the metal reflector, protection against abrasion and corrosion is added with the protective acrylic coat. Cyanine, azo dyes, or phthalocyanines are usually used to form the data sheet as organic dyes. Radiation at 780 nm of phthalocyanines made it very stable for a hundred years and is produced by the infrared laser used to write CD-R [55].

Compounds of phthalocyanine have been studied in early-stages as optical data storage colorants. The maximum absorption of Pc is free-base at 686 nm. However, the actual absorbance of lead, titanyl, or vanadyl Pc is around 800 nm and can be exquisite [56].

2.4.4. Non-linear Optical Devices

Non-linear optical device is a branch of optics, that investigates the behaviour of light in a nonlinear medium. The invention of high intense light sources with laser mechanisms after the 1960s made it necessary to do research for the protection of optical sensors and the human eye from laser. Today, some materials and devices related to this subject have been developed. Among these materials, some of them are highly suitable for reducing the intensity of laser light which are organic and organometallic compounds with nonlinear optical properties. Examples of such materials are porphyrins, phthalocyanines, fullerenes and organometallic compounds. Especially porphyrins and phthalocyanines are much more useful because their nonlinear optical properties can be changed with some structural modifications, their fast response times, their low absorption losses, low dielectric constants, and resistance to heat and environmental conditions [57, 58].

2.4.5. Photodynamic Therapy

Photodynamic therapy (PDT) is a medical procedure currently used for conditions including malignancies or mild disorders. The techniques used in PDT uses a light absorbing compound called photosensitizer [59-62]. Photosensitizers are important for PDT in surgery, chemotherapy and radiation therapy [63, 64].

PDT involves two ways, the first way is to administer a light-sensitive photosensitizer selectively in the target tissue and/or cells, either topically or systemically. The second way is performed to provide the specific wavelength lights to the lesion and to activate the accumulation of photosensitizer, if the concentration of photosensitizer on the lesion is sufficiently high and has an acceptable ratio to the neighbouring normal tissue cells, then the photosensitizer transfers the energy of cytotoxic reactive oxygen species (ROS) to the surrounding oxygen. In response to a series of cells and molecules activities, targeted degradation of lesions occurs [65, 66].

In 1993 in Canada, for clinical use in bladder cancer, the first commercial photosensitizer was authorized. After that, PDT was used to indicate oesophagus, skin, neck head, and lung tumours, in countries like Japan, Netherlands, and the United States [67-69].

Reactive oxygen species (ROS), causes permanent cancer tissue damage. For the PDT photosensitizers, there has been significant interest in porphyrin derivatives and organic dyes in the Pcs family [70].

The ROS is primarily singlet molecular oxygen (${}^1O_2$) [71]. The singlet oxygen electronic state, corresponding to the lowest excited state, is defined as O_2 (${}^1\Delta_g$) as showed at Figure 2.9. Due to the prohibition of direct excitation from triplet molecular oxygen (O_2 (${}^3\sum_g$)) to O_2 (${}^1\Delta_g$), singlet oxygen is usually produced by the transfer of energy from a photosensitizer to O_2 (${}^3\sum_g$) [40].

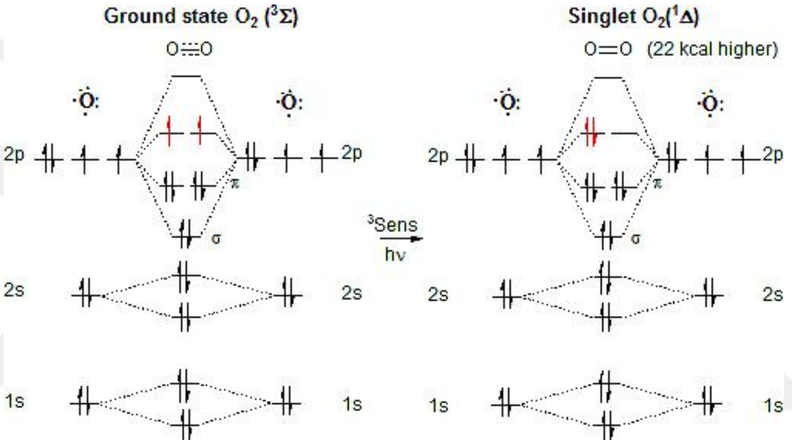


Figure 2.9. Singlet oxegen O_2 (${}^1\Delta g$) and triplet oxegen O_2 (${}^3\sum_g$) electronic configurations

The photosensitizer formed by light absorption in the lowest excited singlet (S_1) state is transferred into the lowest excited triplet (T_1) state, and then O_2 (${}^1\Delta_g$) is created by the transfer of energy from the T_1 photosensitizer to O_2 (${}^3\sum_g$) as described at Figure 2.10. Because of its strong oxidation capability, singlet oxygen (${}^1\Delta_g$) is useful for applications in photodynamic cancer therapy (PDT), photooxidation of toxic molecules, and photoproduction of essential intermediates for different chemicals. A significant number of photosensitizers were studied as singlet oxygen generators [72].

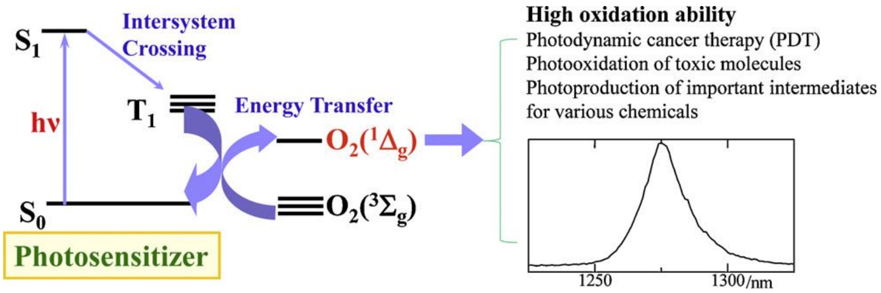


Figure 2.10. Mechanism of generation singlet oxygen and it is luminescence

In addition to the first-generation photosensitizer, photofrin, the second and third generation photosensitizers, such as phthalocyanines, naphthalocyanines (Ncs), have been studied for the treatment of a variety of cancers in order to achieve high tumour to normal tissue aggregation ratios and high extinction coefficients in visible red to near-IR regions where light can penetrate [73].

Zinc phthalocyanine is a promising class of PDT photo-sensitizers with relatively high photodynamic efficiencies and with high molar absorption coefficients ($\varepsilon \sim 10^5$ $M^{-1}cm^{-1}$) in the red spectrum of the visible light. Interestingly, these macrocycles can interact with each other by attractive π-π stacking interactions due to their extended flat, hydrophobic aromatic surface, leading to solution aggregation [74]. Zninc phthalocyanine produces ROS within the range of 650-900 nm upon irradiation, leading to penetration into the target tissue. In order to improve effectiveness and also to reduce cytotoxicity against non-target tissue, various ligands, antibodies and drug carrier structures are used to provide selectivity for these molecules [75, 76].

The high singlet oxygen quantum rates in Pcs coordinated with the shell of the zinc Pc were found in the diamagnetic ions (such as Zn^{2+}, Al^{3+}, Si^{4+}, etc.). [77, 78]. Many of these compounds exhibit higher aggregation levels in ordinary organic and aqueous solutions. Silicon Pcs has a high solubility and fluorescence lifetimes because of less aggregation compared with others. Although there are a significant number of derivatives of non-aggregated, silicon and zinc in recent years, these systems exhibit similar broad emission qualities [79, 80].

2.5. General Synthesis of Phthalocyanines

Phthalocyanines are synthesized as metal free phthalocyanine and metalliated phthalocyanine Complexes. The central metal atom in phthalocyanine can be axially coordinated by a ligand forming square pyramidal or octahedral complex. Their good thermal conductivity and chemical stability of non-substituted Pcs make them used as a stable colour agent and used for organic light-emitting device applications [81]. Pcs that are substituted are more soluble than non-substituted forms. Besides, the introduction of phthalocyanines into macromolecules increases their properties and produces new material. A polymer containing Pc are named according to their side group, main chain, or polymeric cycle formation. Their usefulness and functionality are difficult for Pcs that are polymeric or macrocyclic because of non-solubility in organic solvents [82].

Metal Pc complexes of almost all metals in the periodic table can be synthesized from phthalonitrile, phthalic anhydride, diiminoisoindoline, and phthalimide reactions in the high boiling point of the solvents (DMF, DMSO, and pentanol etc.) as showed at Figure 2.11 [40, 83].

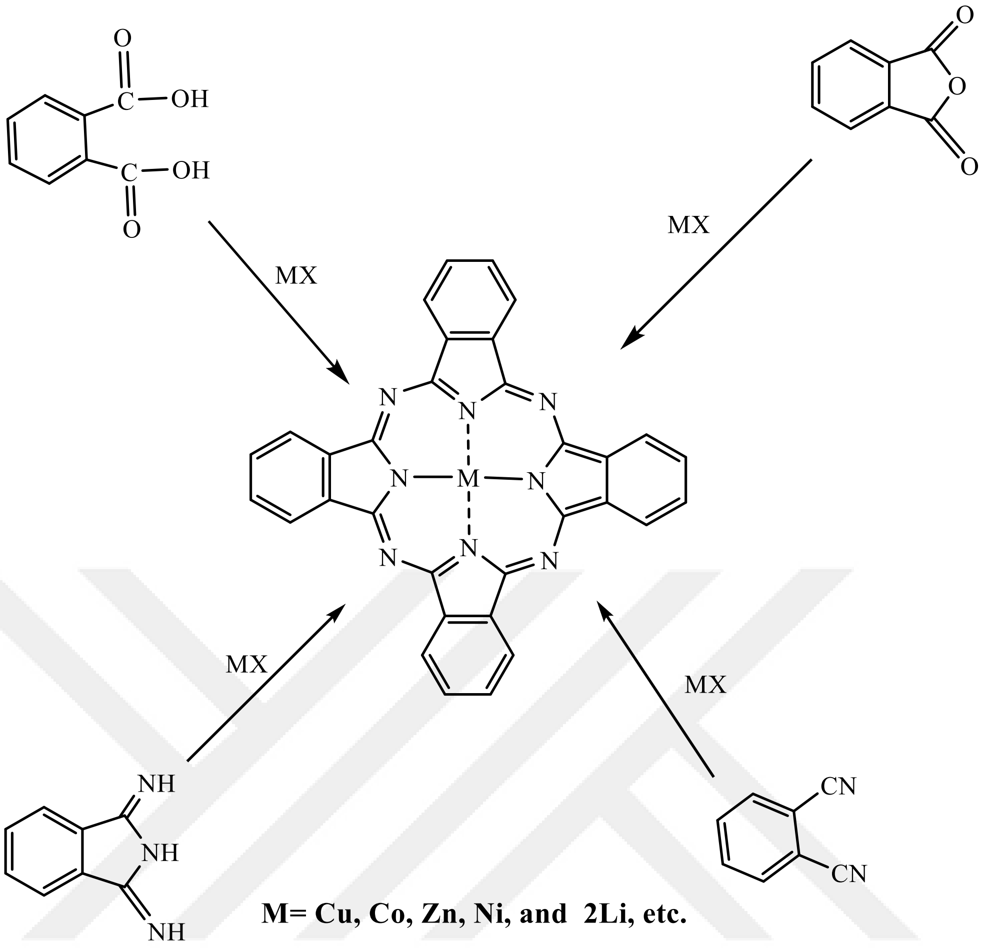


Figure 2.11. General synthesis methods for preparing phthalocyanines [84]

2.5.1. Synthesis of Phthalocyanines Using Phthalic Anhydride

Pc can be synthesized from phthalic anhydride from the reaction which take place between Phthalic anhydride, urea, metal chloride salts, and ammonium molybdate as a catalyst. The reaction was carried out microwave under continuously stirring and at temperature of 120 °C. Then the reaction temperature was gradually increased to 230 °C in microwave by heating rate of 5 °C /min, for 4 hours [85], shown in Figure 2.12.

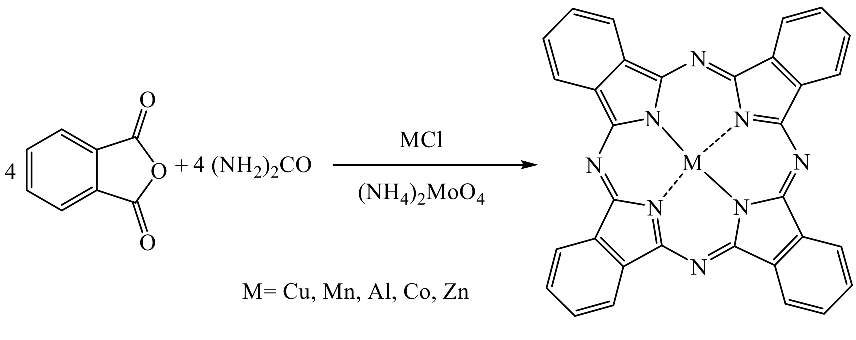


Figure 2.12. Phthalocyanines synthesis using phthalic anhydride as starting material

2.5.2. Synthesis of Phthalocyanines Using Phthalonitrile

Metal free phthalocyanine (H_2Pc) can be obtained 60 % from dilithium phthalocyanines Li_2Pc by treating in dilute acid that can be synthesized from phthalonitriles by refluxing it with lithium metal in boiling phenol as described at Figure 2.13 [86].

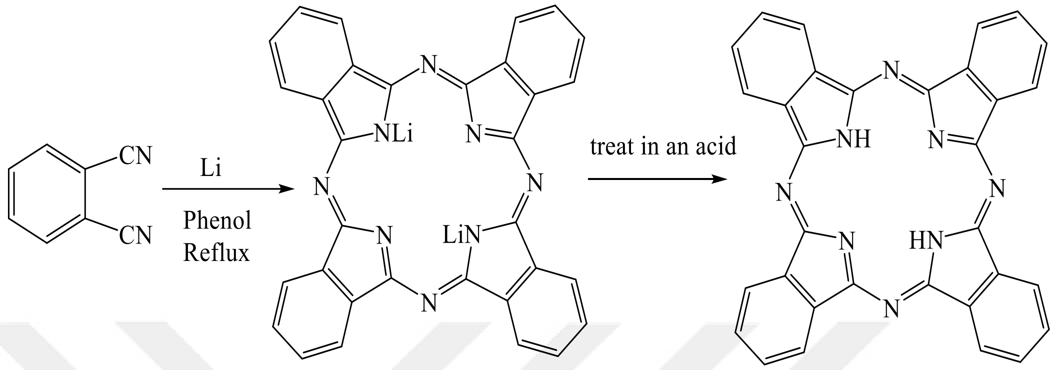


Figure 2.13. Synthesis of metal free phthalocyanine from phthalonitrile

Also, metal Pcs can be prepared from phthalonitriles reaction with metal salt in pentanol using 1,8-diazabicyclonon- 5-ene (DBN) and 1,8- diazabicyclo [5.4.0] undec-7-ene (DBU) as basic catalyst [87]. As shown in Figure 2.14.

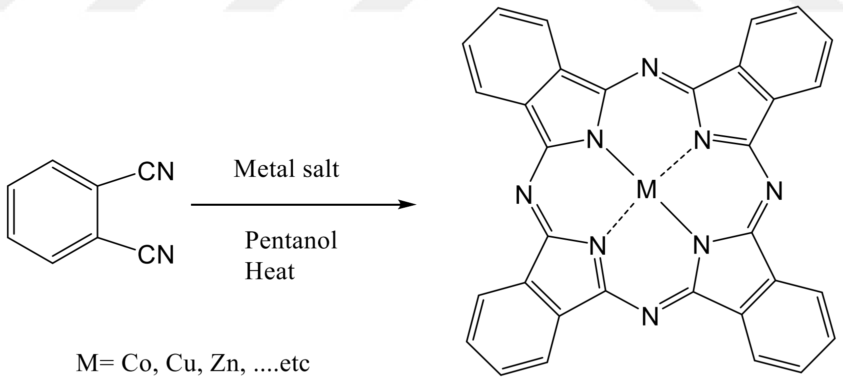


Figure 2.14. Metal phthalocyanines prepared from phthalonitrile

2.5.3. Synthesis of Phthalocyanines Using Diiminoisoindoline

Pcs was synthesized from diiminoisoindoline, the reaction carried out in a simple reflux at 135 °C in 2-N,N-dimethylaminoethanol (DMAE) the yield is about 85 % [88] as shown in Figure 2.15.

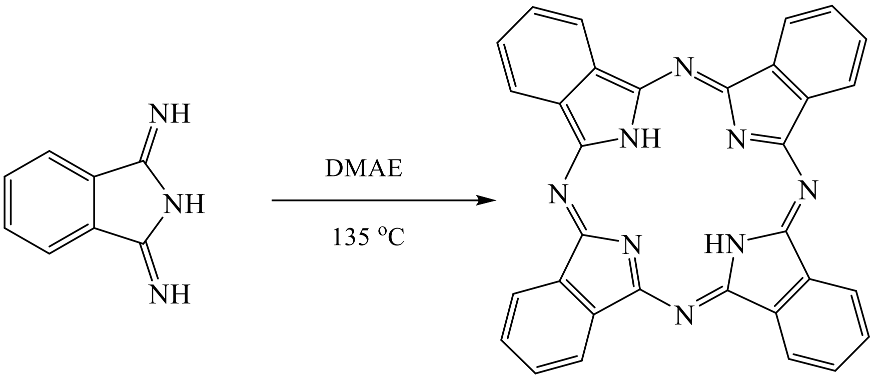


Figure 2.15. Phthalocyanine synthesized from diiminoisoindoline in reflux for 135 °C in DMAE

2.5.4. Synthesis of Phthalocyanines Using Phthalimide

The palladium phthalocyanine (PdPc) can obtain from phthalimides, that used as a precursor for synthesize phthalocyanines. The reaction was taking place under high temperature as showed at Figure 2.16. Phthalimides doesn't have a significant role in phthalocyanines formation [89, 90].

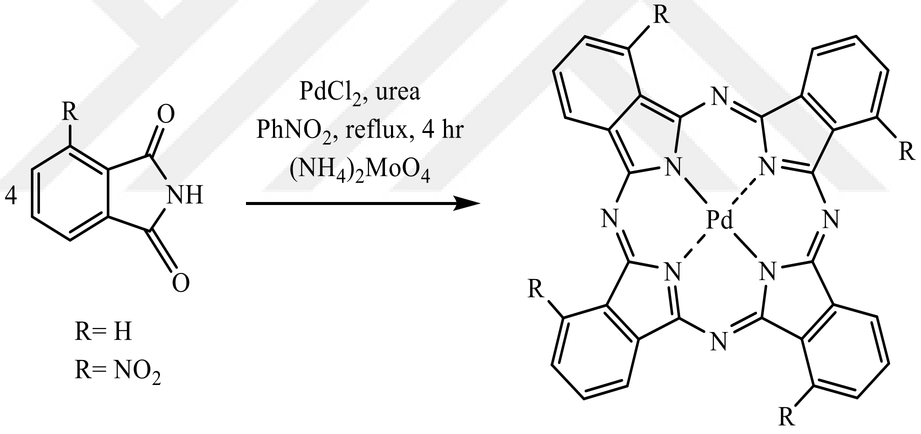


Figure 2.16. Phthalocyanines prepared from phthalimides

2.5.5. Synthesis of Double-deckers Phthalocyanines

The reaction was performed by using K_2CO_3 as the base for the nitro displacement in dry DMF under an argon atmosphere at 70-90 °C in a single step and 4-(2-(2H-1,2,3-Benzotriazole-2-yl)-4,6-bis(2-phenyl propane-2-yl)phenoxy) phthalonitrile formed. Then by the reaction catalysed by ammonia in sodium methoxide in methanol and refluxing temperature giving 90% of 5-(2 -(2H-1,2,3-Benzotriazole-2-yl)-4,6-bis(2-phenyl propane-2-yl)phenoxy) 1,3-diiminoisoindoline. The complex of lutetium Pc synthesized in the reaction of diiminoisoindoline compound and lutetium acetate in octanol solution. The reaction was done under argon atmosphere for 12 hours catalysed by DBU, at elevated temperature. The product was purified and 25% yield obtained by using column chromatography on silica gel (THF/methanol, 10:1), showed at Figure 2.17 [91].

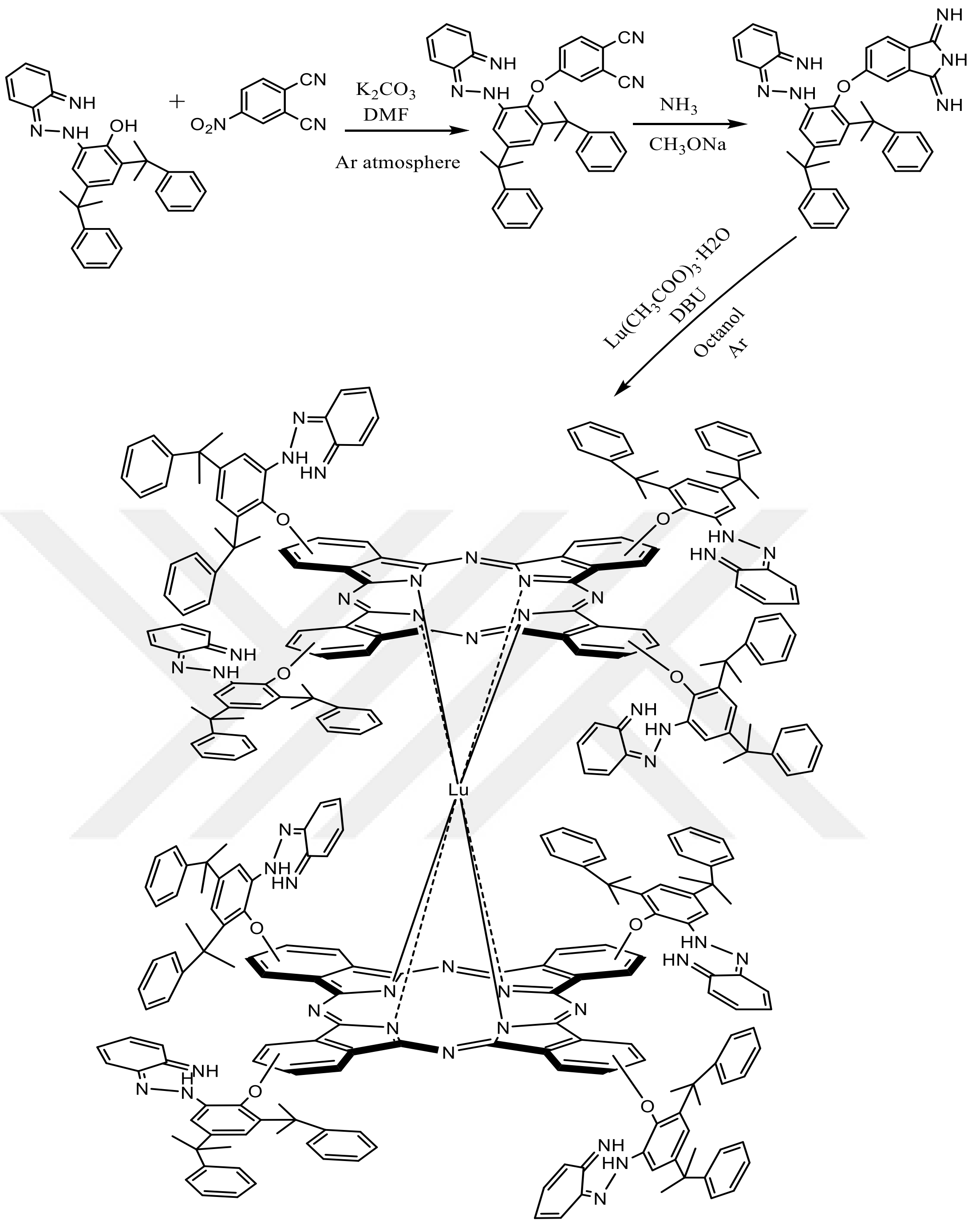


Figure 2.17. Synthesis double decker Lutetium phthalocyanine form diiminoisoindoline

2.5.6. Synthesis of Triple Decker Phthalocyanines

Dieuropium(III)tris2,3,9,10,16,17,23,24octa(cyclohexylmethoxy)Phthalocyanine (Figure 2.18) synthesized from di-lithium 2,3,9,10,16,17,23,24 octa(cyclohexyl methoxy)phthalocyanine using 1-chloronaphthalene as a solvent and the reaction was done in argon atmosphere [92].

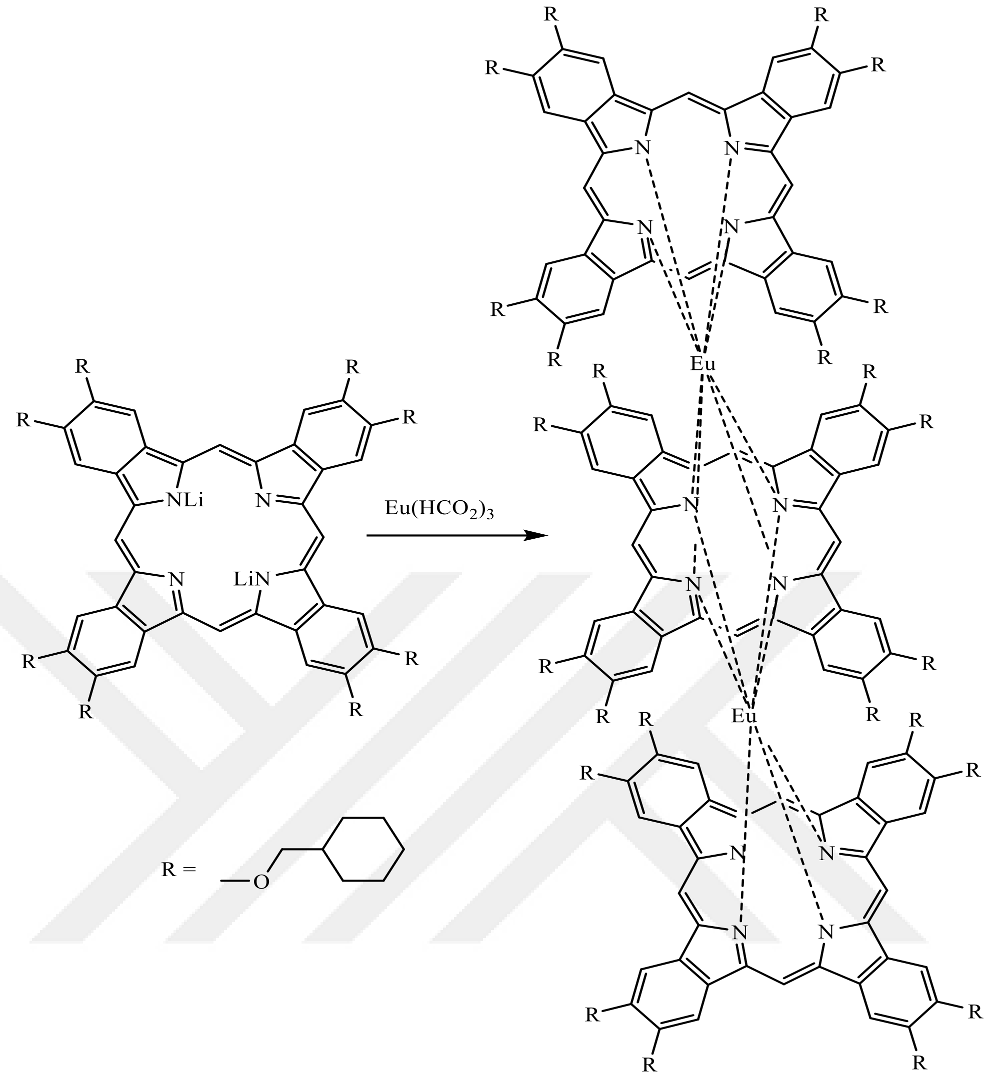


Figure 2.18. Synthesis of triple deaker phthalocyanine, using 1-chloronaphthaleneas solvent at 260 °C for 15 h

2.5.7. Synthesis of Ball-type Metal Phthalocyanines

Ball type 9,9-tetrakis-bis(2′,10′,16′,24′)-phthalocyaninato-copper (II)4-oxyphenyl fluorene obtained in the presence of nitrogen atmosphere and $CuCl_2$ addition, from 4,4-(9,9-bis(4-oxyphenyl)fluorene)diphthalonitrile at 360 °C for 5 minutes that was prepared from 4-nitrophthalonitrile with 9,9-bis(4-hydroxyphenyl) fluorene and K_2CO_3 in dry DMF at room temperature for 24 hours as showed at Figure 2.19 [93].

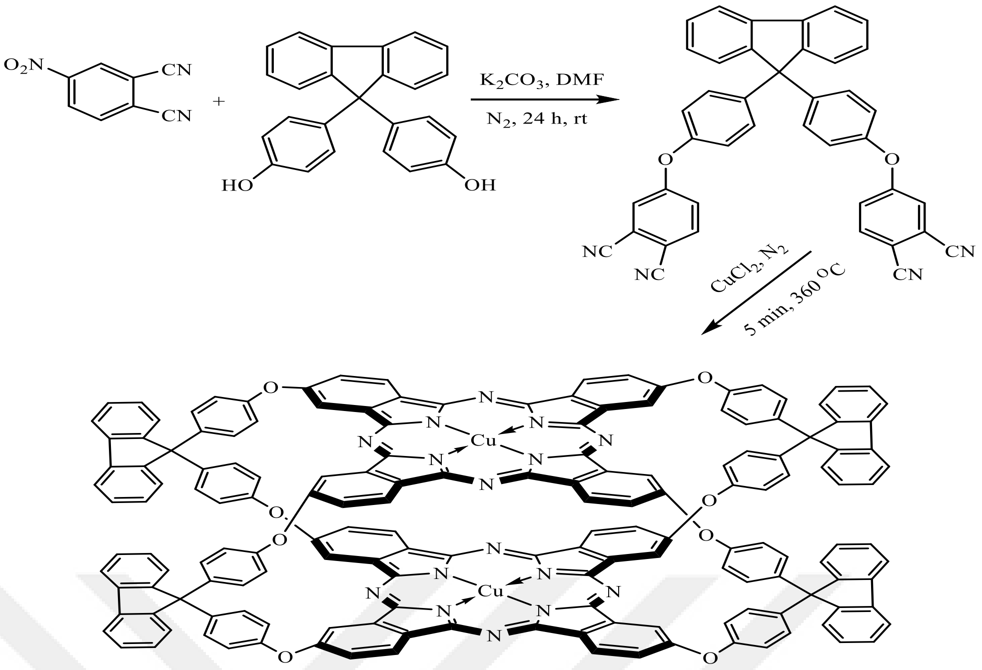


Figure 2.19. Ball type phthalocyanine synthesized from phthalonitrile

2.5.8. Synthesis of Triad Phthalocyanines

Suzuki coupling also was extended to the preparation, directly by means of C-C connectivity, of covalently-assembled Pc-Pc hetero-dyads, Pc–(Pc)$_2$ homo-triad and Pc-porphyrin hetero-dyads. Those compounds were formed using a one-step method which depend on a Suzuki cross-coupling palladium mediated reaction of a Pc boronated precursor coupled with either a Pc or the porphyrin of the aryl halide function as showed at Figure 2.20 [94].

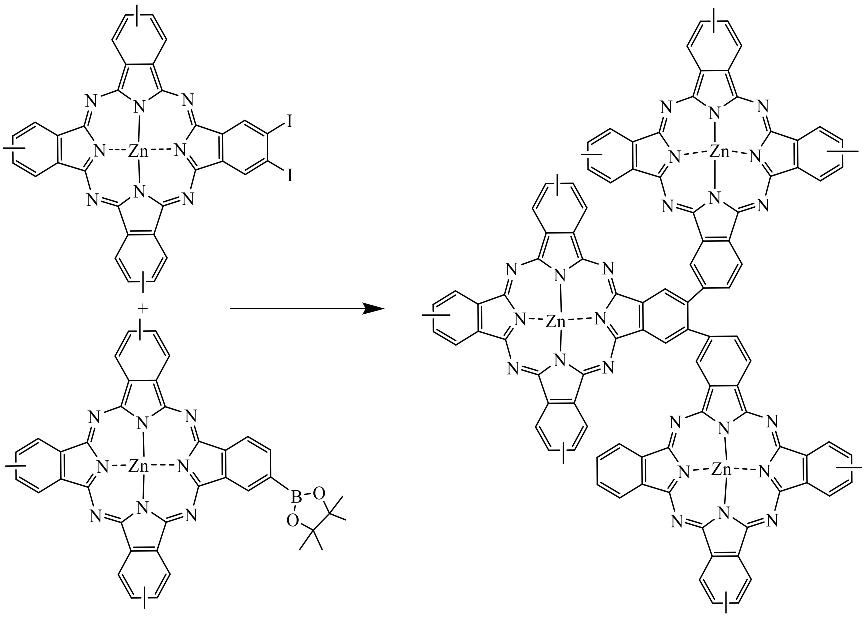


Figure 2.20. Suzuki coupling reaction for synthesize homo triad phthalocyanines

2.5.9. Synthesis of Polymer Phthalocyanines

“Hanack” and co-workers have developed main-chain polymers based on Pcs that use appropriate bivalent bridges to bind metal ions inside the centre [95].

This form is also known as 'shish-kebab' polymer, an example of this type of polymers is phthalocyaninato-polysiloxane, which includes a crown connected to the chiral alkylic side chains in its Pc-units Figure 2.21.

The backbone of polysiloxane moves through the core of the Pc rings and causes the Pc molecules to stack tightly. This method gives macromolecules electrical conductivity due to orbital overlap. These polysiloxane Pc bundles head to tail configurations in a dry film and solid-fluid interface that make the polymer appropriate to the molecular electronic scale. “Kobayashi” and colleagues who have published on organic and inorganic composite preparedness with a sol-gel technique have identified another structured polysiloxane Pc system, in which the polymers of a rod-like Pc are inserts into the ordered hexagon channels [96].

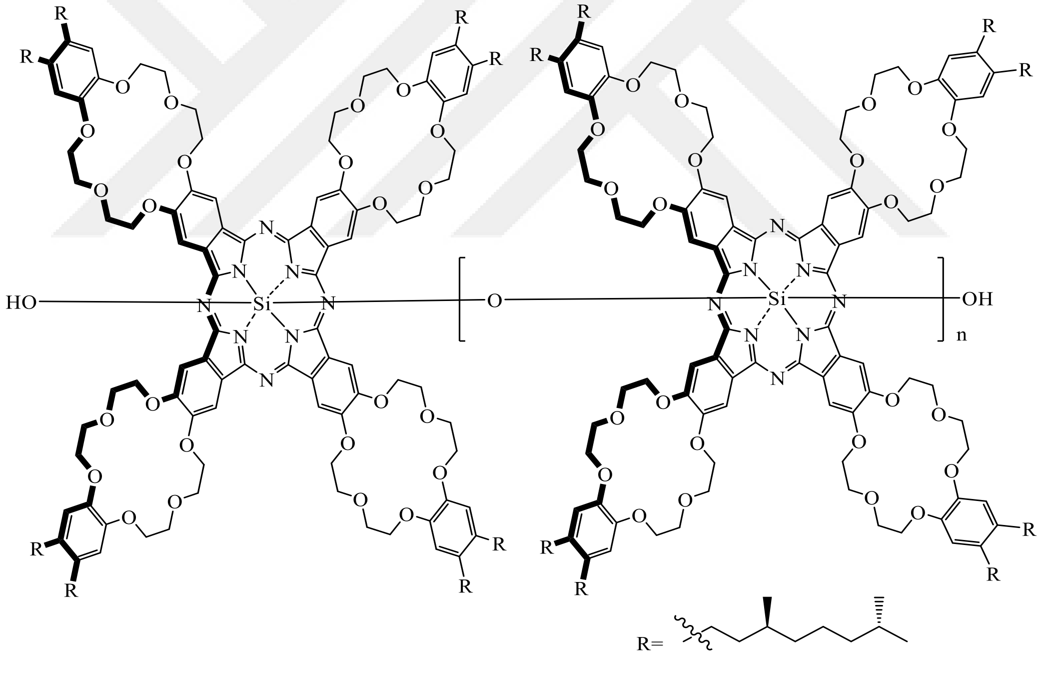


Figure 2.21. Main chain polysiloxane polymer Pcs

2.6. Di-tert-butyl-4-methylphenol

2,6-Di-tert-butyl-4-methylphenol is one of the cresol derivatives. It is an organic product which is an aromatic compound like benzenes only substituted by tertiary butyls in two additional hydrogens. In its pure state, BHT is a white crystalline substance with a melting point of 70 °C and boiling point 265 °C. It is typically insoluble in water [97], but it dissolved in some organic solvents like, alcohol, DMF, DMSO, petroleum ether, benzene and toluene, etc. [98].

In 1947, BHT was used as phenolic antioxidant for the first time [99]. Up to now, BHT and its implementations include more than fifteen thousand articles, thousands of studies reviewed, patents, and conferences have reported the role of BHT as a crucial suspension for feed and food medicinal, and pharmaceuticals. It has been extensively used in the plastics, fermentation, and bio-industrial chemistry sectors. Besides its role as an additive in natural products and makeup, BHT is also ideal as an additive for use in oils [100].

BHT is considered healthy antioxidant, which is one of its best use in foods. The biochemical properties of BHT have been researched thoroughly because of their broad use as a dietary supplement [101]. On the other hand, high concentrations of BHT produce centrilobular tissue damage, serum transaminase activity, and liver internal bleeding [102].

For industrial uses, BHT remains the most common antioxidant, mainly, for cosmetic formulations. In 1998, the food and drug administration FDA announced that BHT was used in 1709 formulations on the basis of the industrial sources. [103].

2.6.1. Synthesis of Butylated Hydroxy Toluene

2,6-di-tert-butylcresol can be synthesized from the reaction of anhydrous para cresol with 2 moles isobutene, and concentrated H_2SO_4 under 0.1 Mpa pressure at 70 °C as showed Figure 2.22 [104].

The typical work method involves extracting acid with water at 70 °C by multiple washing sessions, crystallizing the crude product, and recrystallizing in ethanol-water. [105, 106].

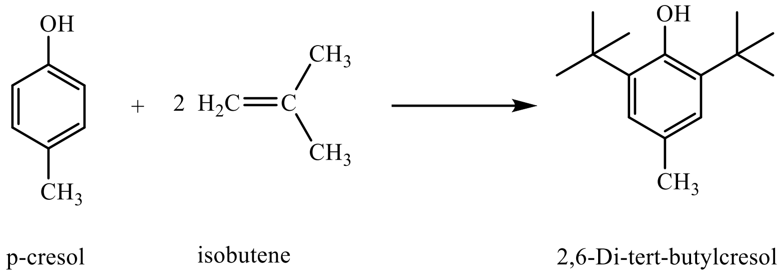


Figure 2.22. Synthesis of 2,6-Di-tert-butylcresol

3. MATERIAL AND METHOD

Common glassware and other general laboratory equipments that are used during the synthesis, purification and identification of the synthesized compounds in the laboratory.

3.1. Instruments

Infrared Spectrophotometer: Perkin Elmer, Spectrum one 1600 FT-IR Spectrophotometer (Chemistry Department-Fırat University).

NMR Spectrophotometer: Bruker Advance III 400 MHz Spectrophotometer with DMSO-d_6 as solvents and tetramethyl silane as an internal standard (Chemistry Department-Firat university).

UV-Vis Spectrophotometer: PG Instrument Ltd, T80+UV/VIS spectrophotometer (Chemistry Department-Fırat University).

Thermal analysis: Perkin Elmer, Pyris Diamond TG/DTA Thermogravimetric/Differential Thermal Analyzer (Physics Department-Fırat University).

Voltammetric Analyzer: Gamry Instrument, Interface 1000-B Potentiostat/Galvanostat (Chemistry Department-Firat university).

Microanalysis: Leco, CNSO,

3.2. Materials

Argon (HABAŞ), Ammonia gas (NH_3) (HABAŞ), 65% nitric acid (Merck), 98% sulfuric acid (Sigma Aldrich), NH_3 (25%) (Merck), anhydrous potassium carbonate (Merck), thionyl chloride (Merck), Copper(II) acetate (Merck), Nickel(II) acetate (Merck), Cobalt(II) acetate (Merck), Zinc(II) acetate (Merck), 99% 2,6-Di-tert-butyl-4-methylphenol (Acros Organics), (DMF) (CHEM SOLUTE), dimethyl sulfoxide (DMSO) (Carlo Erba), tetrahydrofuran (THF) acetonitrile (Merck), acetone (Carlo Erba), chloroform (Merck), and Ethanol (Sigma Aldrich).

3.3. Methods

The preparation of phthalocyanine compounds, metalated and metal free phthalocyanines, made from the synthesis of 4-nitrophthalonitrile. For this reason, phthalimide nitrated to form 4-nitrophthalimide, then 4-nitrophthalimide transformed to 4-nitrophthalamide in ammonia solution, after that, it was converted to 4-nitrophthalonitrile by thionyl chloride in DMF. 4-nitrophthalonitrile substituted by nucleophilic substitution reaction with 2,6-di-tert-butyl-4-methylphenol to form 4(2,6-Di-tert-butyl-4-methylphenoxy)phthalonitrile. Then metalated phthalocyanine complexes were synthesized by cyclotetramerization of the 4(2,6-Di-tert-butyl-4-methylphenoxy)phthalonitrile in the presence of DBU. After that, the thermal analysis and electrochemical studies were performed for the synthesized phthalocyanine compounds.

3.3.1. Synthesis of 4-Nitratophthalimide

A one litter of three-neck round bottom flask was placed in to the ice bath on the magnetic stirrer. Then 280 mL of sulfuric acid (H_2SO_4) transferred to the flask, and 48 mL of nitric acid (HNO_3) was added in small portion sulfuric acid under 10 °C temperature while continuously stirring the solution mixture. After that 40 grams (0.27 mole) phthalimide was added in small portions in 90 minutes under 10 °C. When all phthalimide has dissolved the solution allowed to warm to room temperature and left overnight.

The solution was precipitated in about 500 grams of ice and stirred until all ice melted then filtered, the precipitate was washed by mixing with 250 ml of ice water three times, at the third time left again overnight, filtered, dried. Yield 30 gram (0.16 mole) 57.4% white 4-nitrophthalimide was synthesized as showed at Figure 3.1 [91].

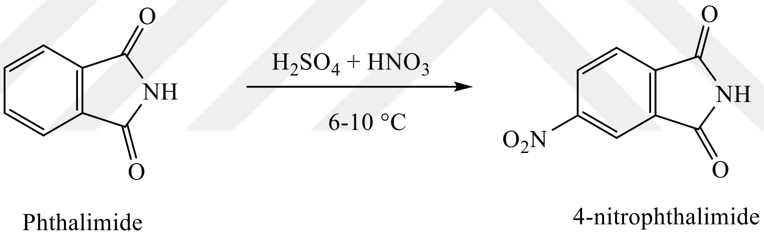


Figure 3.1. Synthesis of 4-nitro phthalimide

3.3.2. Synthesis of 4-Nitropthalamide

In a 500 mL of three-neck round bottom flask, 200 mL methanol and 25 mL of tetrahydrofuran (THF) was added and then 30 grams (0.16 mole) of 4-nitrophthalimide was transferred under continuously stirring at 40 °C, after that ammonia gas was bubbled through the reaction mixture and reaction was monitored by FTIR in 10 minutes interval until the reaction was taken place. The reaction was completed in about 90 minutes. Then the solution was filtered and washed several times with water and then dried at room temperature. Yield 31 gram (0.15 mole) 94.9% white of 4-nitrophthalamide was obtained as showed at Figure 3.2.

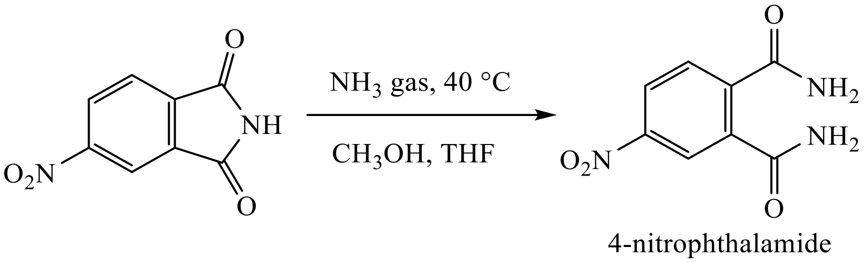


Figure 3.2. Synthesize of 4-nitrophthalamide

3.3.3. Synthesis of 4-Nitro Phthalonitrile

In 250 mL of three-neck round bottom flask, 120 mL DMF was cooled down to 0 °C in an ice bath under Argon atmosphere while stirring continuously. 21 mL thionyl chloride ($SoCl_2$) was added drop by drop and temperature was stabilized under 5 °C, after that 20 grams (0.095 mol), of 4-nitrophthalamide added slowly to the reaction vessel, the solution was left for one hour in an ice bath, then 6 hours at room temperature. Then the reaction was stopped and poured to 500 gram of ice water, and filtered, washed with 200-gram ice water at first and then 250 ml of 5% Na_2CO_3, at the final washed with cold water several times, and dried, 12.5 gram, (0.07 mole), 75.9% of 4-nitro phthalonitrile was synthesized as showed at Figure 3.3.

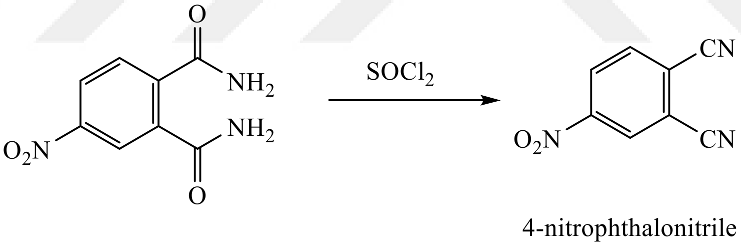


Figure 3.3. Synthesis of 4-nitrophthalonitrile

3.3.4. Synthesis of 4(2,6-Di-tert-butyl-4-methylphenoxy)phthalonitrile

In 100 ml of three-neck round bottom flask, 15 mL DMSO was added then the reaction vessel flashed with argon gas for 10 minutes. 1.10 gram (0.50 mol) 2,6-Di-tert-butyl-4-methylphenol (99 %) was added, then 0.860 gram (0.50 mol) of 4-nitrophthalonitrile was added, the colour of the solution was changed to yellow, after 15 minutes, 0.100 gram potassium carbonate (K_2CO_3) was added to the solution, the colour of solution changed step by step to brown, green, dark green, violet after one hour of the reaction the colour was settled down at purple colour, the overall reaction was done under argon atmosphere and 60 °C, the reaction was finished after 24 hours. And cheeked by IR spectrum, after that the reaction was stopped, mixed with 15 ml ethyl alcohol (CH_3CH_2OH) and precipitated in 400 ml of water and 10 mL saturated sodium chloride stirred overnight at room temperature, after settling down of precipitate, filtered and collected on filter paper, then dried at first at room temperature and then on the oven at 70 °C, 1.50 gram (4.33 mmol), 83.3% of the ligand was synthesized as showed at Figure 3.4 and Table 3.1.

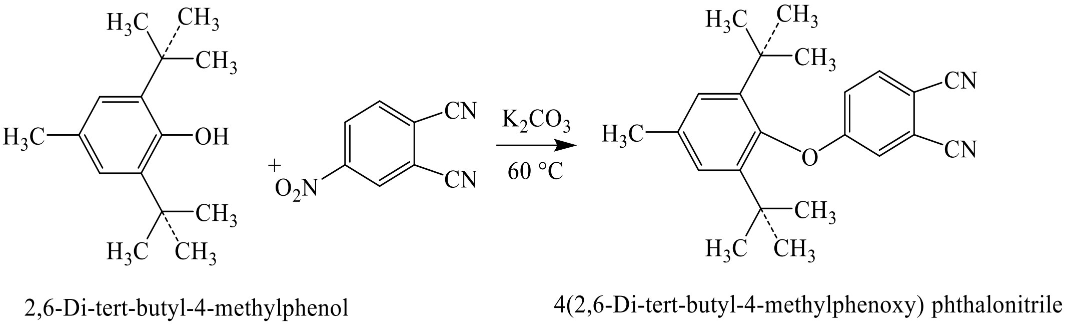


Figure 3.4. Synthesis of 4(2,6-Di-tert-butyl-4-methyl phenoxy) phthalonitrile

3.3.5. Synthesis of 2,10,16,24-Tetrakis (2,6-di-tert-butyl-4-methylphenoxy)zinc phthalocyanine

In a 20 mL test tube, 0.250 gram (0.72 mmol) of 4(2,6-Di-tert-butyl-4-methylphenoxy) phthalonitrile, and 0.100 gram (0.46 mmol) Zinc(II) acetate dihydrate, and 4.0 mL DMSO was added under argon atmosphere. Then reaction mixture heated to reflux temperature of solvent (154 °C). and the reaction was carried out for 12 hours, then the reaction was cool down and diluted into 15 mL of ethyl alcohol and precipitated in 100 mL of water with stirring. The precipitate washed several times with water, then with alcohol until the dark colour of eluent was disappeared, and become clear. Green product dried at room temperature followed by at 75 °C in drying oven, yield was 0.122 gram (0.08 mmol), 46.5%, showed at Figure 3.5 and Table 3.1.

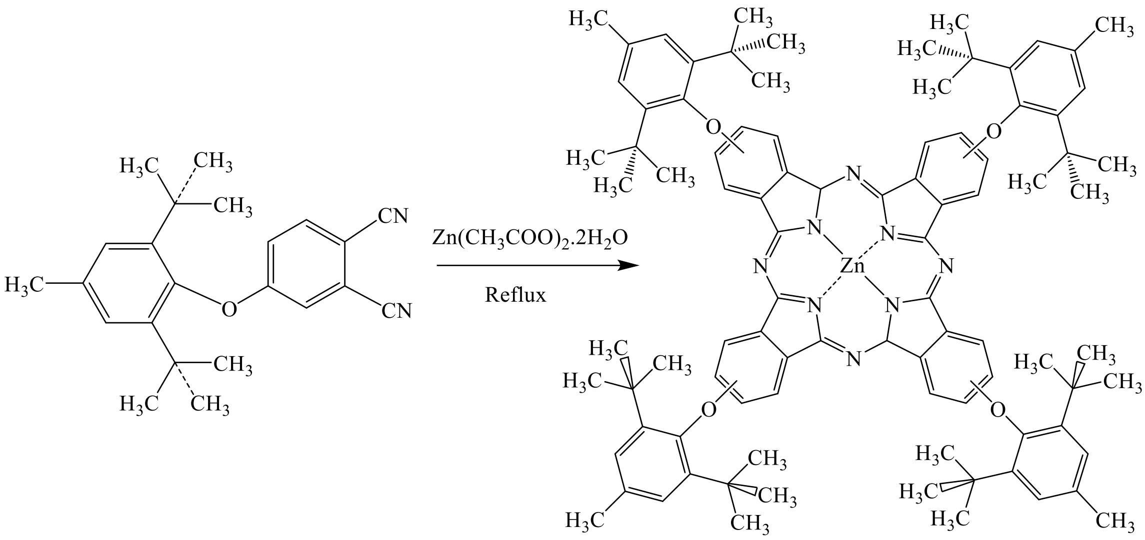


Figure 3.5. synthesis of 2,10,16,24-Tetrakis (2,6-di-tert-butyl-4-methyl phenoxy)zinc phthalocyanine

3.3.6. Synthesis of 2,10,16,24-Tetrakis (2,6-di-tert-butyl-4-methylphenoxy)cupper phthalocyanine

In a long and large test tube, 0.250 gram (0.72 mmol) of 4(2,6-Di-tert-butyl-4-methylphenoxy) phthalonitrile, and 0.100 g (0.50 mmol) copper acetate monohydrate, 4.0 mL of DMSO was added, under argon atmosphere, and heated to boiling (160 °C) for about 12 hour. Then the reaction was cool down to room temperature and diluted with 15 ml of ethyl alcohol. Diluted solution of reaction mixture precipitated in 200 mL of water while it is stirring. The precipitate was filtered washed several times by distilled water and ethyl alcohol until the dark colour of eluent was become colourless. Dark green product was dried first at room temperature then at 75 °C in drying oven. Yield 0.110 gram (0.08 mmol), 42% Copper(II)phthalocyanine, as showed at Figure 3.6 and Table 3.1.

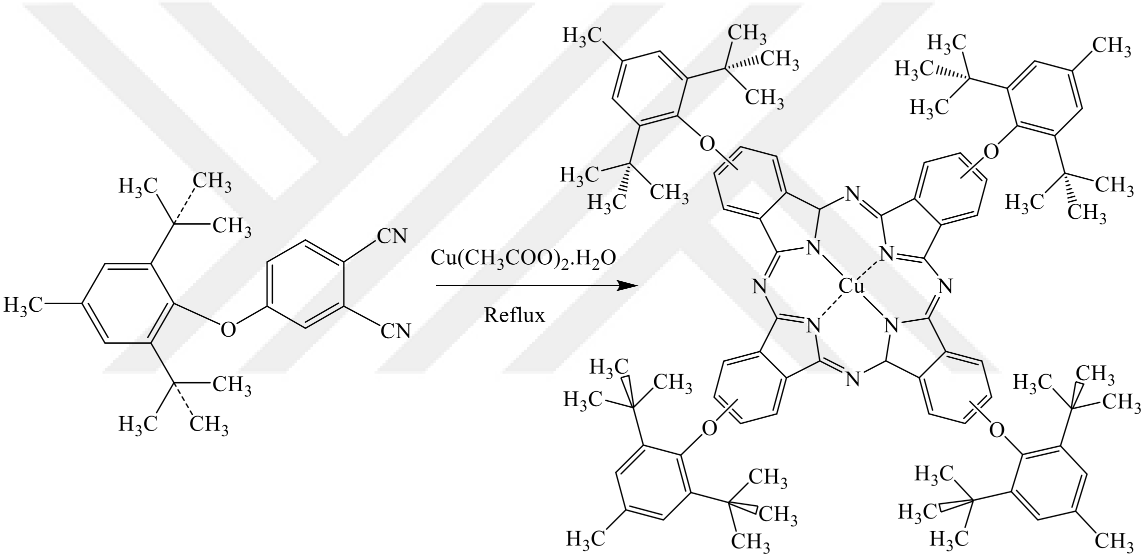


Figure 3.6. Synthesis of 2,10,16,24-Tetrakis (2,6-di-tert-butyl-4-methyl phenoxy)cupper phthalocyanine

3.3.7. Synthesis 2,10,16,24-Tetrakis (2,6-di-tert-butyl-4-methylphenoxy)cobalt phthalocyanine

In a long and large test tube, (0.250 gram, 0.72 mmol) of 4(2,6-Di-tert-butyl-4-methylphenoxy) phthalonitrile, and (0.100 gram, 0.40 mmol) cobalt acetate tetrahydrate, 4.0 ml of DMSO was added, under argon atmosphere then heated to boiling temperature of solvent 164 °C for about 40 hours. The reaction was monitored CN peak of ligand at 2230 cm^{-1} by FTIR. After completion of reaction observed, it was cool down and diluted with 15 ml of ethyl alcohol and precipitated in 200 ml of water while stirring. The precipitate filtered of washed several times by distilled water first then ethyl alcohol until the dark colour of eluent become colourless. Solid green product dried at room temperature first then at 75 °C in drying oven. Yield 0.134 gram (0.09 mmol), 51.3% Cobalt(II)phthalocyanine was obtained, as showed at Figure 3.7 and Table 3.1.

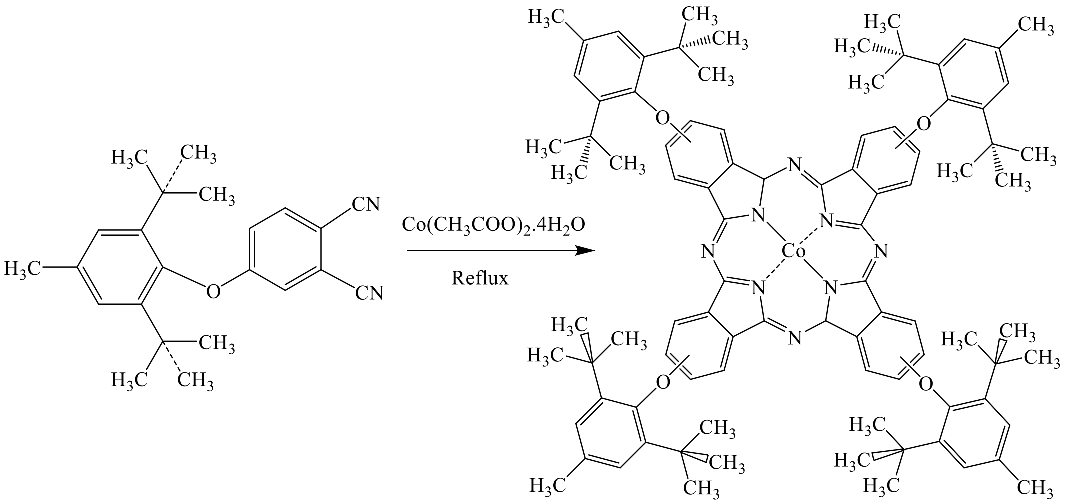


Figure 3.7. Synthesis of 2,10,16,24-Tetrakis(2,6-di-tert-butyl-4-methyl phenoxy)cobalt phthalocyanine

3.3.8. Synthesis 2,10,16,24-Tetrakis (2,6-di-tert-butyl-4-methylphenoxy)nickel(II) phthalocyanine

In a long and large test tube, (0.250 gram, 0.72 mmol) of 4(2,6-Di-tert-butyl-4-methylphenoxy) phthalonitrile, and (0.100 gram, 0.40 mmol) Nickel(II) acetate tetrahydrate, 4.0 mL of DMSO was added, under argon atmosphere heating it to boiling temperature of solvent 154 °C for 16 hours. The reaction was monitored CN peak of ligand at 2230 cm^{-1} by FTIR. After completion of reaction observed, it was cool down and diluted with 15 mL of ethyl alcohol and precipitated in 200 mL of water while stirring. The precipitate filtered of washed several times by distilled water first then ethyl alcohol until the dark colour of eluent become colourless. Solid blue-green product dried at room temperature first then at 75 °C in drying oven. Yield 0.062 gram (0.04 mmol), 23.8% of Nickel(II)phthalocyanine was obtained, as showed at Figure 3.8 and Table 3.1.

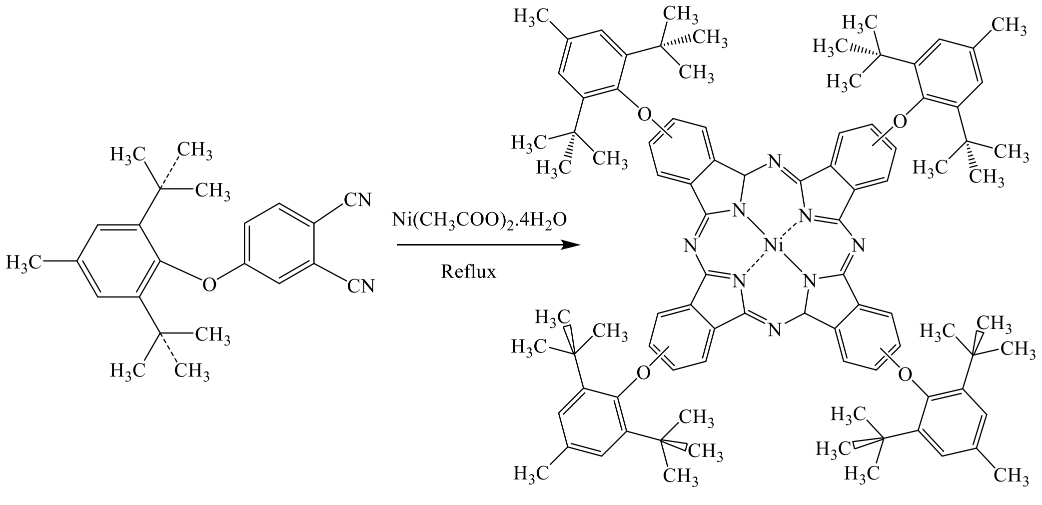


Figure 3.8. Synthesis of 2,10,16,24-Tetrakis(2,6-di-tert-butyl-4-methyl phenoxy)nickel phthalocyanine

3.3.9. Synthesis 2,10,16,24-Tetrakis (2,6-di-tert-butyl-4-methylphenoxy) di-lithium phthalocyanine

In a long and large test tube, (0.200 gram, 0.58 mmol) of 4(2,6-Di-tert-butyl-4-methylphenoxy) phthalonitrile, and (0.020 gram, 0.67 mmol) lithium oxide, 4.0 mL of DMSO and 4 drop of DBU as catalyst was added, under argon atmosphere and heated to reflux (154 °C). The reaction was monitored CN peak of ligand at 2230 cm^{-1} by FTIR. After completion of reaction observed in 24 hours, it was cool down and diluted with 15 mL of ethyl alcohol and precipitated in 200 ml of water while stirring. The precipitate filtered of washed several times by distilled water first then ethyl alcohol until the dark colour of eluent become colourless. Solid bright-green product dried at room temperature first then at 75 °C in drying oven. Yield 0.102 gram (0.07 mmol), 40.4% of di-lithium phthalocyanine was obtained, as showed at Figure 3.9 and Table 3.1.

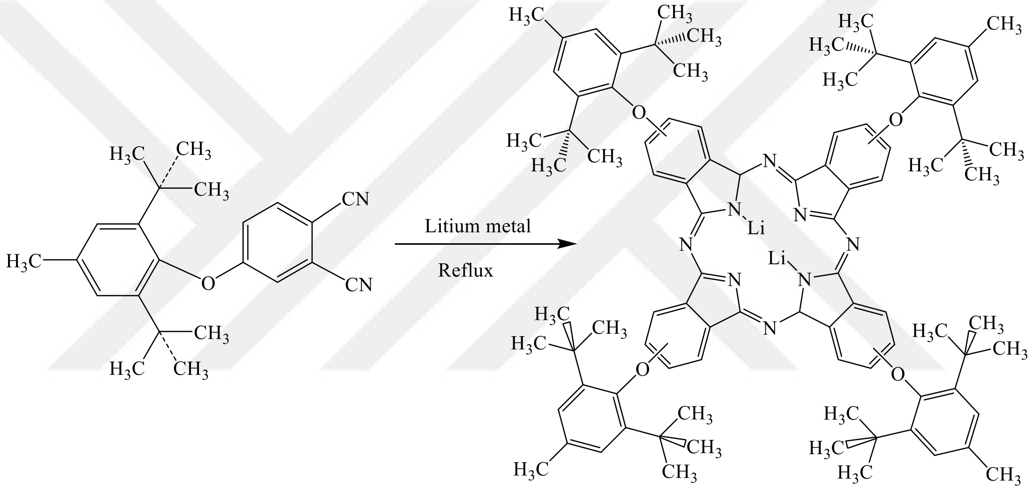


Figure 3.9. Synthesis of 2,10,16,24-Tetrakis(2,6-di-tert-butyl-4-methyl phenoxy)di-lithium phthalocyanine

3.3.10. Synthesis 2,10,16,24-Tetrakis (2,6-di-tert-butyl-4-methylphenoxy) di-hydrogen phthalocyanine

Three different reaction pathways followed to synthesise the metal free phthalocyanine, but in unfortunately we have not got the expected results.

In first attempt, 4(2,6-Di-tert-butyl-4-methylphenoxy) phthalonitrile and DBU refluxed in DMSO under argon atmosphere for about 48 hours. The colour of reaction turn to brown-black, when it was precipitated in water, brown solid was obtained. When it was investigated by UV-visible spectra, Q-band of phthalocyanine which is characteristic to metal free phthalocyanine was not observed.

In second attempt; di-lithium phthalocyanine was boiled in acetic acid, to exchange lithium metal with hydrogen, UV-Visible spectra showed no difference between di-lithium phthalocyanine UV-Visible spectra.

In third attempt; di-lithium phthalocyanine was dissolved in concentrated H_2SO_4 and heated to 50 °C, for 2 hours and precipitated in water, filtered of dried at room temperature and UV-Visible spectra of product showed no metal free phthalocyanine, instead we obtained di-lithium phthalocyanine with single sharp one Q band the same as di-lithium phthalocyanine, the all reactions described at Figure 3.10.

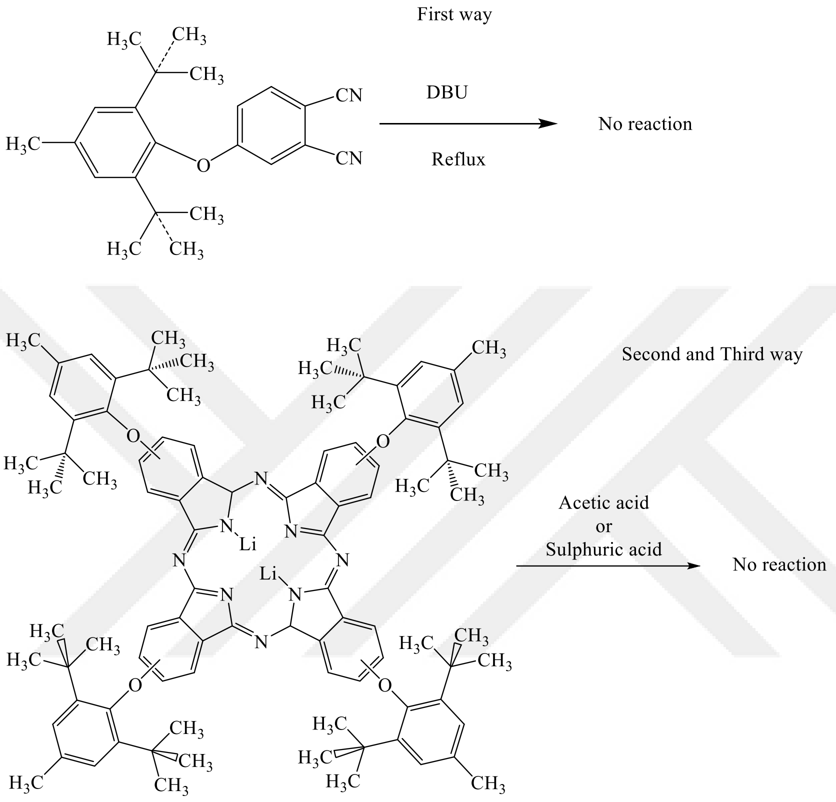


Figure 3.10. Three different ways to synthesize metal free phthalocyanine

Table 3.1. Molecular formula, molecular weight, experimental yield and elemental analysis results of ligand and phthalocyanine complexes.

Name	Molecular Formula	Molecular Weight (g/mol)	Yield %	Elemental Analysis (Teo.) Exp.		
				%C	%H	%N
Ligand	$C_{23}H_{26}N_2O$	346.47	%83.3	(58.20) 58.47	(3.01) 2.86	(20.96) 20.39
Li_2Pc	$Li_2[C_{92}H_{106}N_8O_4]$	1401.79	%43.0	(78.83) 78.12	(7.62) 7.43	(7.99) 7.31
CoPc	$Co[C_{92}H_{106}N_8O_4]$	1446.85	%51.3	(76.37) 76.92	(7.38) 6.92	(7.74) 7.53
NiPc	$Ni[C_{92}H_{106}N_8O_4]$	1446.61	%23.8	(76.39) 75.87	(7.39) 7.06	(7.75) 7.38
CuPc	$Cu[C_{92}H_{106}N_8O_4]$	1451.46	%42.0	(76.13) 76.35	(7.36) 7.23	(7.72) 7.21
ZnPc	$Zn[C_{92}H_{106}N_8O_4]$	1453.29	%46.5	(76.04) 75.65	(7.35) 7.87	(7.71) 7.16

4. RESULTS AND DISCUSSION

In this study, 4-Nitrophthalonitrile which is available commercially, synthesized from phthalimide and then the ligand 4(2,6-Di-tert-butyl-4-methylphenoxy)phthalonitrile was synthesized from the reaction between 2,6-Di-tert-butyl-4-methyl phenol, and 4-Nitrophthalonitrile in one stage reaction. By cyclotetramerization of the ligand compound with dry Zinc acetate $Zn(CH_3COO)_2{\cdot}4H_2O$, Copper acetate $Cu(CH_3COO)_2{\cdot}2H_2O$, Nickle acetate $Ni(CH_3COO)_2{\cdot}4H_2O$, Cobalt acetate $Co(CH_3COO)_2{\cdot}4H_2O$ and Lithium oxide Li_2O in the noble gas atmosphere 2,10,16,24-Tetrakis(2,6-di-tert-butyl-4-methylphenoxy) cobalt, copper, zinc, nickel, and di-lithium phthalocyanine were obtained.

The characterization of synthesized compounds was performed by elemental analysis, FT-IR, UV-visible, ^{1}H-and ^{13}C NMR spectroscopy. FT-IR spectrum there are two regions which is important for the identification of structure of the compounds. The first region is functional group region, 4000-1400 cm^{-1}, showed important peaks which are -C=C aromatic, C-H aromatic and -NH, the second region was fingerprint region 1400- 900 cm^{-1}. Phthalocyanine compounds have a characteristic UV-Visible spectrum with a strong band at about 650 nm for metalated phthalocyanine, and a double band for metal free phthalocyanine which gives them their characteristic green to blue colours called Q band. A second band appear at about 400 nm which is generally overlapped by other bands called B or Soret band.

Also, the thermal characterization of synthesized phthalocyanine compounds performed by differential thermal analysis DTA, and thermogravimetric analysis TGA. Electrochemical analysis studied by cyclic, square wave or differential pulse voltammetry.

4.1. 4-Nitrophthalonitrile

4-Nitrophthalonitrile was synthesized from phthalimide according to well-known procedure given below at Figure 4.1. In the first step, phthalimide nitrated to form 4-Nitrophthalimide (Figure 4.2).

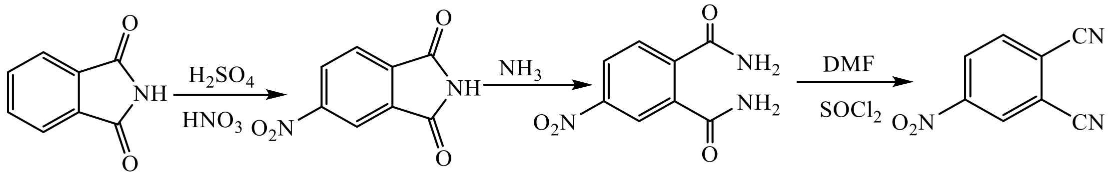


Figure 4.1. General synthesis of 4-Nitrophthalonitrile from phthalimide

In the second step, 4-nitrophthalimide converted to 4-nitrophthalamide (Figure 4.4) by NH_3. The last step was the conversion of 4-nitrphthalamide to 4-nitrphtalonitrile (Figure 4.6) by $SOCl_2$ in DMF.

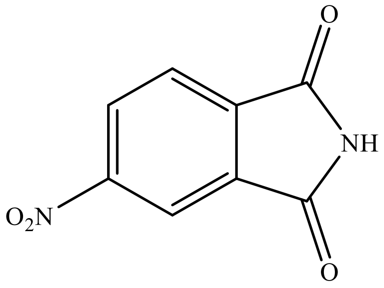


Figure 4.2. 4-Nitrophthalimide structure

The yield obtained: 30.00 gram (0.16 mole) 57.4 %

Formula product: $C_8H_4N_2O_4$

Mw: 192.13 gram/mol

Colour of product: white

- **IR Spectrum:**

The compound's IR spectrum was examined prepared in KBr tablet. The formation of two sharp peaks of nitro NO_2 group 1350 cm^{-1} and 1546 cm^{-1} showed that the phthalimide was nitrated at position number 4 as given at Figure 4.3.

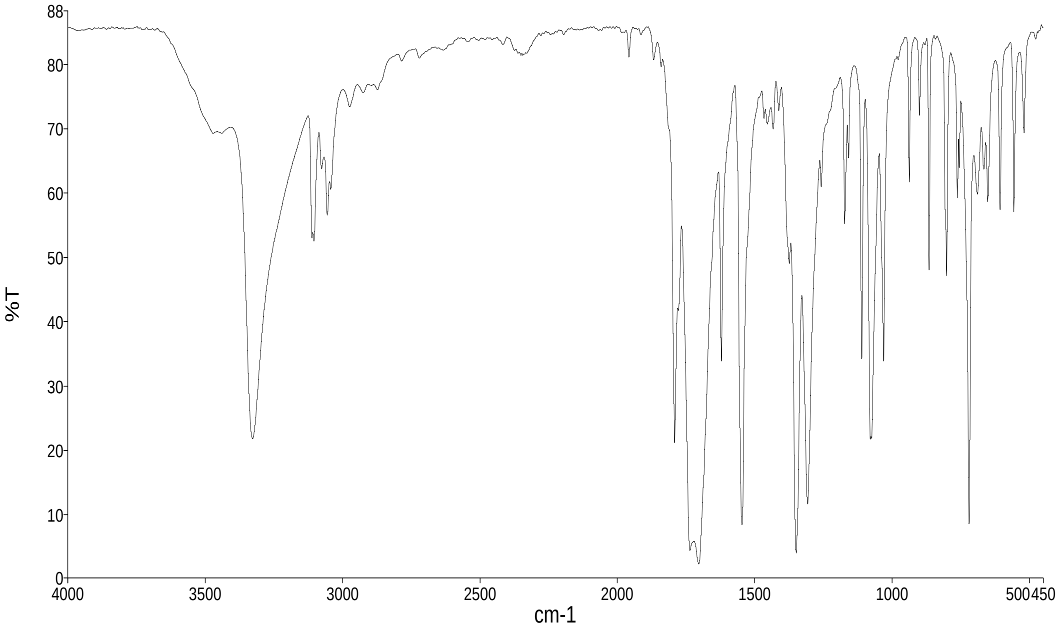


Figure 4.3. FT-IR spectrum of 4-Nitrophthalimide

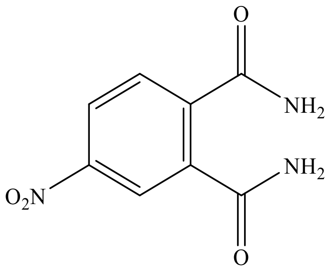


Figure 4.4. 4-Nitrophthalamide structure

The yield obtained: 31.00 gm, (0.15 mole), 94.9 %

Formula product: $C_8H_7N_3O_4$

Mw: 209.16 gram/mol

Colour of product: white

- **IR spectrum**

The compound's IR spectrum was examined prepared in KBr tablet. The FTIR spectrum corrected synthesized 4-nitrophthalamide by showing NH stress peak at 3437 cm^{-1} referring to amides, and an amide carbonyl (C=O) peaks were formed at 1662 cm^{-1} as showed at Figure 4.5.

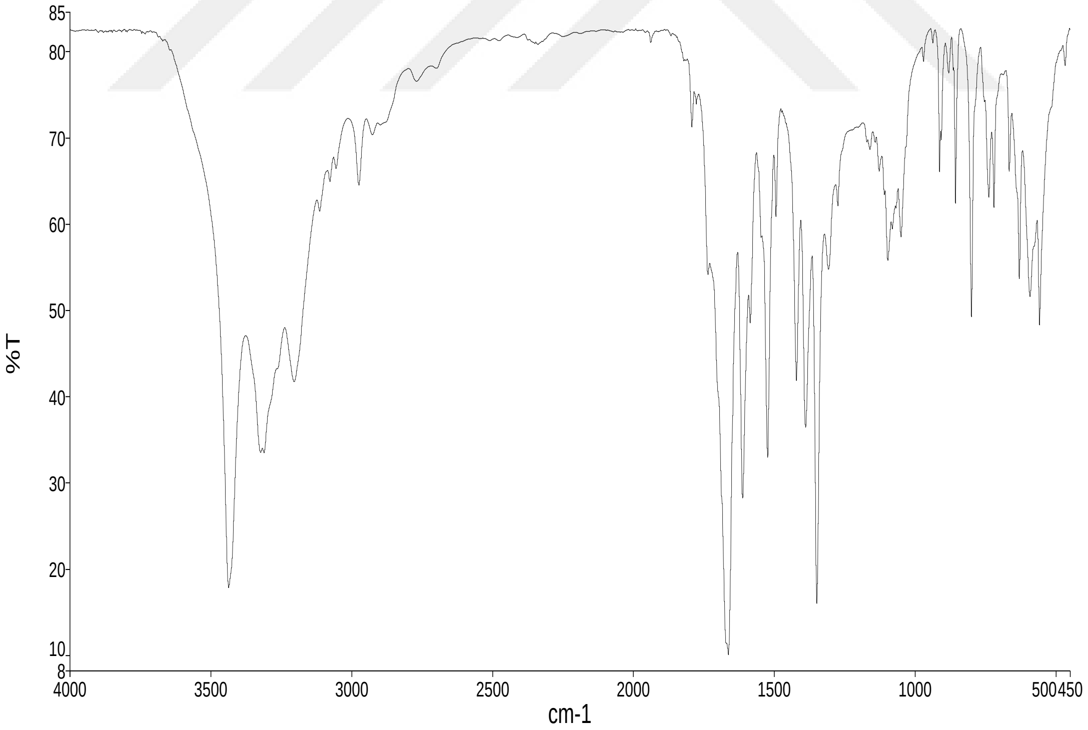


Figure 4.5. FT-IR spectrum of 4-Nitrophthalamide

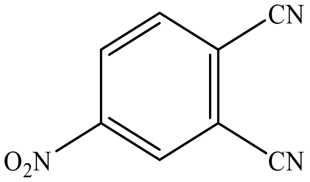


Figure 4.6. 4-Nitrophthalonitrile structure

The yield obtained: 12.50 gm (0.072 mole), 75.9 %

Formula product: $C_8H_3N_3O_2$

Mw: 173.13 gram/mol

Colour of product: white micro crystals

- **IR spectrum**

The compound's IR spectrum was examined prepared in KBr tablet. The observation of the very important nitrile -C≡N peak at 2240 shows the synthesize of 4-nitrophthalonitrile as given at Figure 4.7 and Table 4.1.

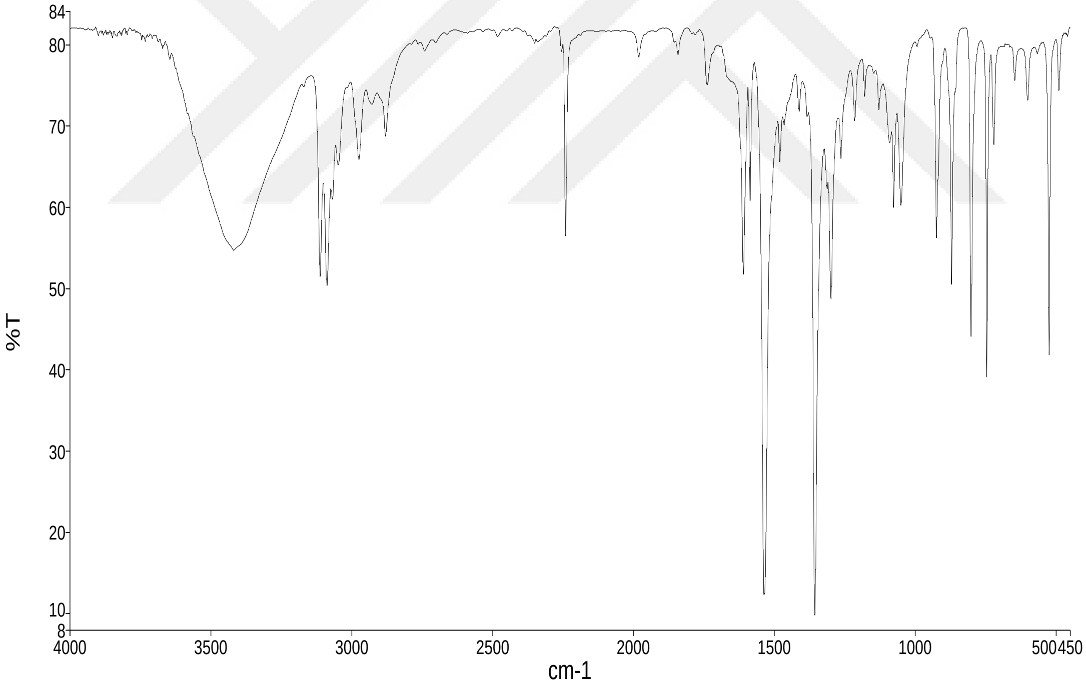


Figure 4.7. FT-IR spectrum of 4-Nitrophthalonitrile

Table 4.1. Important FT-IR spectrum of 4-Nitrophthalonitrile

Vibrations (cm^{-1})	**Assignment**
3088	Ar-CH
2240	C≡N
1610	C=C
1356, 1536	Aromatic NO_2

4.2. 2,6-Di-tert-butyl-4-methylphenol (BHT)

2,6-Di-tert-butyl-4-methylphenol (BHT) obtained from Acros and used as it is. The structure and some of the properties is given below in Figure 4.8.

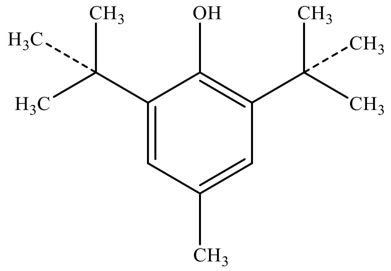


Figure 4.8. 2,6-Di-tert-butyl-4-methylphenol structure

Formula product: $C_{15}H_{24}O$

Mw: 220.36 gram/mol

Colour of product: white shiny crystalline

- IR **spectrum**

2,6-Di-tert-butyl-4-methylphenol was mixed with potassium bromide to form a plate and IR spectrum was read and the result was showed at Figure 4.9 and Table 4.2.

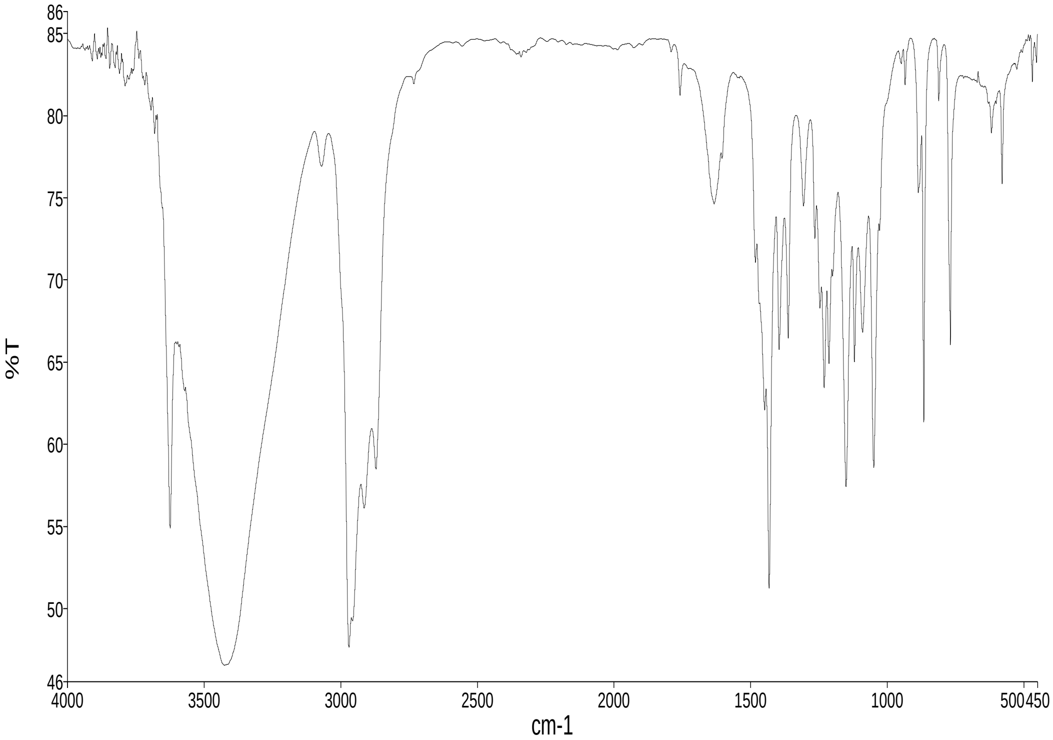


Figure 4.9. FT-IR spectrum of 2,6-Di-tert-butyl-4-methylphenol

Table 4.2. Important FT-IR spectrum of 2,6-Di-tert-butyl-4-methylphenol (BHT)

Vibration (cm^{-1})	Assignment
3626	O-H
3071	Ar-C-H
2970	(CH_3), tb
1634	C=C
1306	C=C (HOC)
1230	HCC ring

4.3. 4(2,6-Di-tert-butyl-4-methylphenoxy)phthalonitrile

4(2,6-Di-tert-butyl-4-methylphenoxy)phthalonitrile, the ligand, compound was prepared by the reaction between BHT and 4-Nitrophthalonitrile in DMSO under argon atmosphere at 70 °C as given at Figure 4.10.

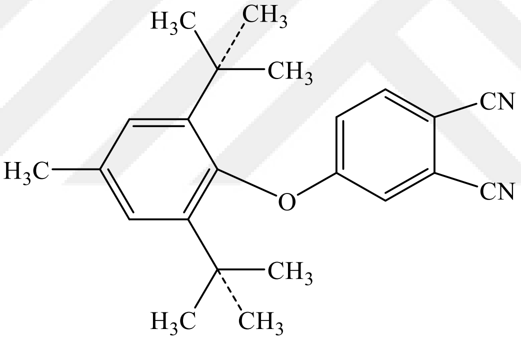


Figure 4.10. 4(2,6-Di-tert-butyl-4-methylphenoxy)phthalonitrile structure

The yield obtained: 1.50 gram, (4.33 mmol), 83.3 %

Formula product: $C_{23}H_{26}N_2O$

Mw: 346.47 gram/mol

Color of product: white crystals

- **IR spectrum**

The compound's IR spectrum was examined prepared in KBr tablet, the formation of the expected compound confirmed by the absence of its two sharp NO_2 peaks at 1546 cm^{-1} and 1350 cm^{-1} on the 4-Nitrophthalonitrile IR spectrum as given at Figure 4.11 and Table 4.3.

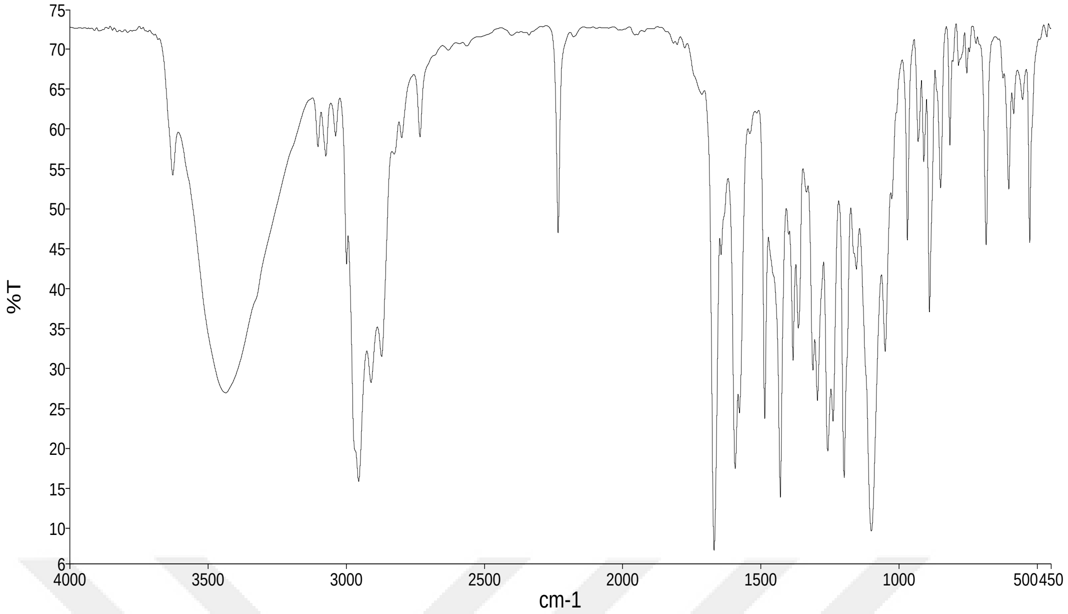


Figure 4.11. FT-IR spectrum of 4(2,6-Di-tert-butyl-4-methylphenoxy)phthalonitrile

Table 4.3. Important FT-IR peaks of 4(2,6-Di-tert-butyl-4-methylphenoxy)phthalonitrile

Vibration (cm^{-1})	Assignment
3102-3038	C-H Aromatic
2955-2872	C-H (CH3) tb
2233	C≡N
1643	C=C
1594, 1295	C-O-C

- **^{1}HNMR spectrums**

^{1}HNMR was taken in DMSO-d$_6$. Tertiary butyl hydrogen peak (H8), (H9), (H10), (H12), (H13), and (H14) was observed at 1.34 ppm as a doublet in Figure 4.12. Methyl hydrogen peak was seen at 2.18 ppm as singlet (H22). Solvent peak (DMSO-d$_6$) and water as impurity were observed at 2.49 and 3.29 ppm respectively. Aromatic hydrogen the peak were identified as a doublet at 6.87 ppm (H4), (H5), and at 7.75 ppm (H17), (H21), singlet at 9.82 ppm (H20) as showed at Figure 4.12.

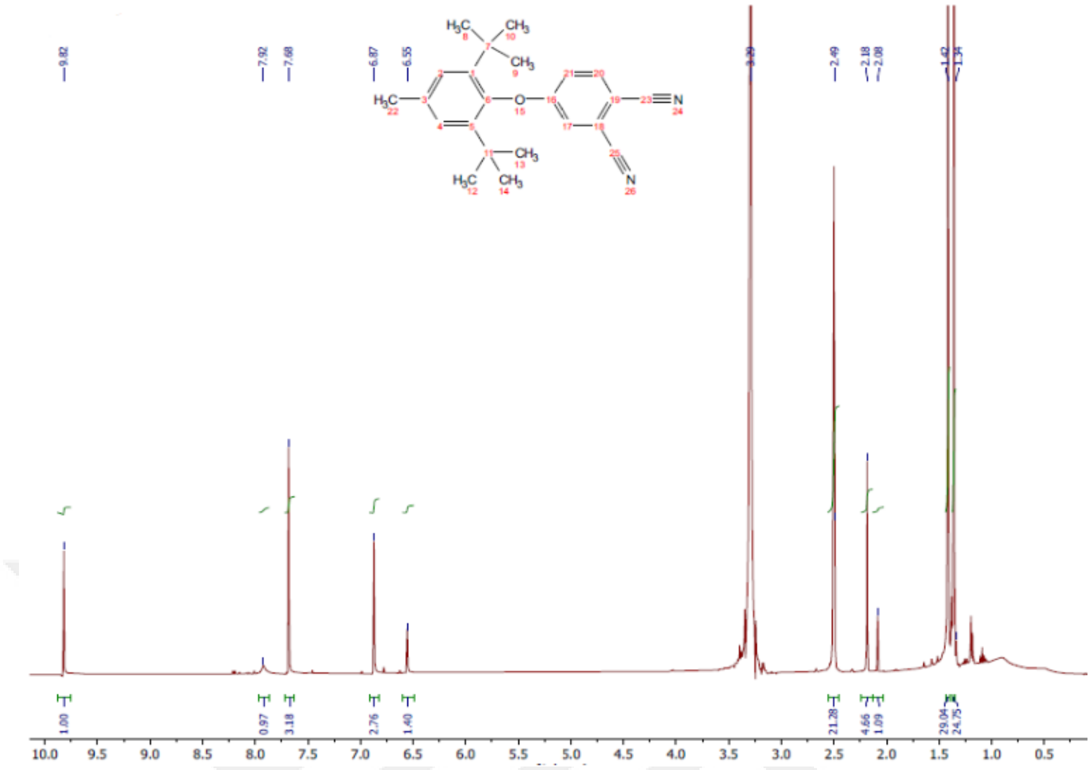


Figure 4.12. The ^{1}H-NMR spectrum of 4(2,6-Di-tert-butyl-4-methylphenoxy)phthalonitrile

- **^{13}CNMR spectrums**

^{13}CNMR was taken in DMSO-d$_6$, two different spectra were formed according to the attached proton test (APT), the upper side was positive spectra which belonged to tertiary carbons and CH$_2$-carbons atoms, and the lower side was negative spectra shows CH and CH$_3$ carbons atoms [107].

The peaks were seen at 21.45 ppm identified as methyl group of (C7) carbon atom. Tertiary butyl side carbons (C13), (C14), and (C15) peaked at 30.41 ppm and (C10), (C11), and (C12), was observed at 30.92 ppm. Aromatic peaks were started from 124.35 ppm belongs to (C18) and (C22), and peaked at 127.30 ppm belongs to (C2) and (C4), and peak that formed at 192.49 ppm belonged to (C21), of the negative side spectra.

Tertiary carbons (C8) and (C9) peaked at 34.83 ppm and 34.92 ppm respectively, and peaks at 128.49 ppm that belongs (C19), (C20) and 128.84 ppm belongs to, (C23), (C25), and another tertiary carbons peaks at 139.25 ppm belongs to (C1) and (C5) and 139.62 ppm was belonged to (C3), two spectra connected directly to the electronegative oxygen that was (C6) peaked at 151.92 ppm and (C17) peaked at 160.44 ppm, of the positive side spectra.

There was a very intense peak at 39.65 ppm was belongs to a solvent which was DMSO-d$_6$, as given in Figure 4.13.

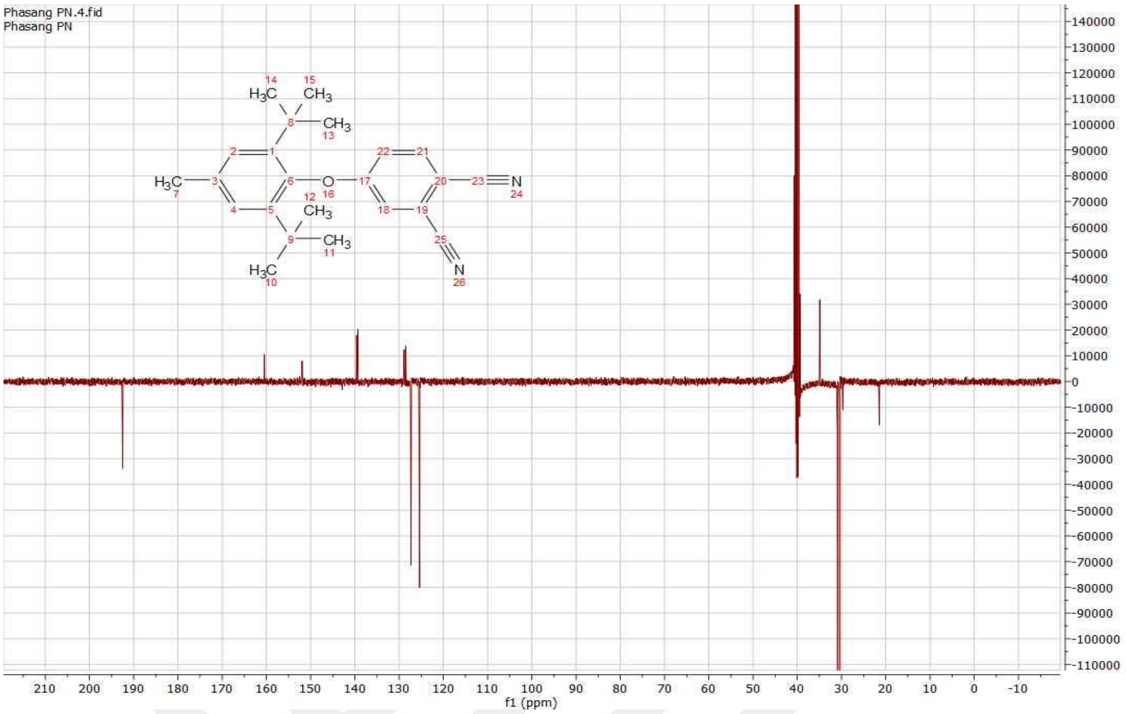


Figure 4.13. The ^{13}C-NMR spectrum of 4(2,6-Di-tert-butyl-4-methylphenoxy)phthalonitrile

4.4. 2,10,16,24-Tetrakis(2,6-di-tert-butyl-4-methylphenoxy)zinc phthalocyanine

Zinc phthalocyanine compound was prepared from 4(2,6-Di-tert-butyl-4-methylphenoxy) phthalonitrile with zinc(II) acetate under argon atmosphere in DMSO at elevated temperature shown in Figure 4.14.

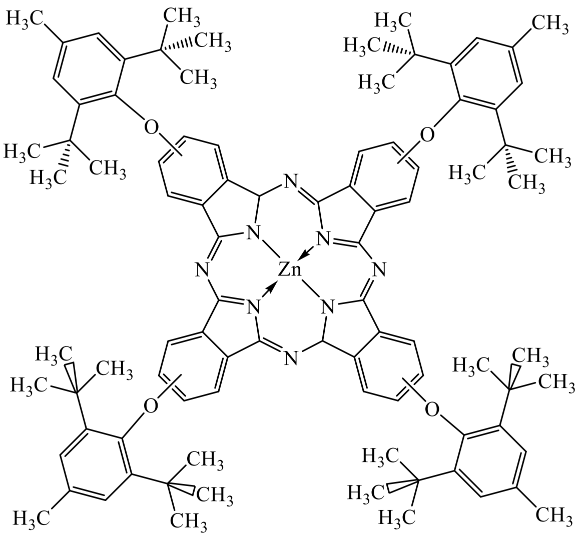


Figure 4.14. 2,10,16,24-Tetrakis (2,6-di-tert-butyl-4-methyl-phenoxy)zinc phthalocyanine structure

The yield obtained: 0.122 gram (0.08 mmol)), 46.5 %

Formula product: $C_{92}H_{106}N_8O_4Zn$

M_W: 1453.29 gram/mol

Colour of product: green

- **FT-IR spectrum**

FT-IR spectrum of the zinc(II)phthalocyanine complex in KBr was confirmsed, the absence of nitrile C≡N stretching peak at 2233 cm^{-1} of phthalonitrile formation of zinc phthalocyanine complexed with the formation of green colour, and also absence of unreacted starting material in the complex as described at Figure 4.15 and Table 4.4.

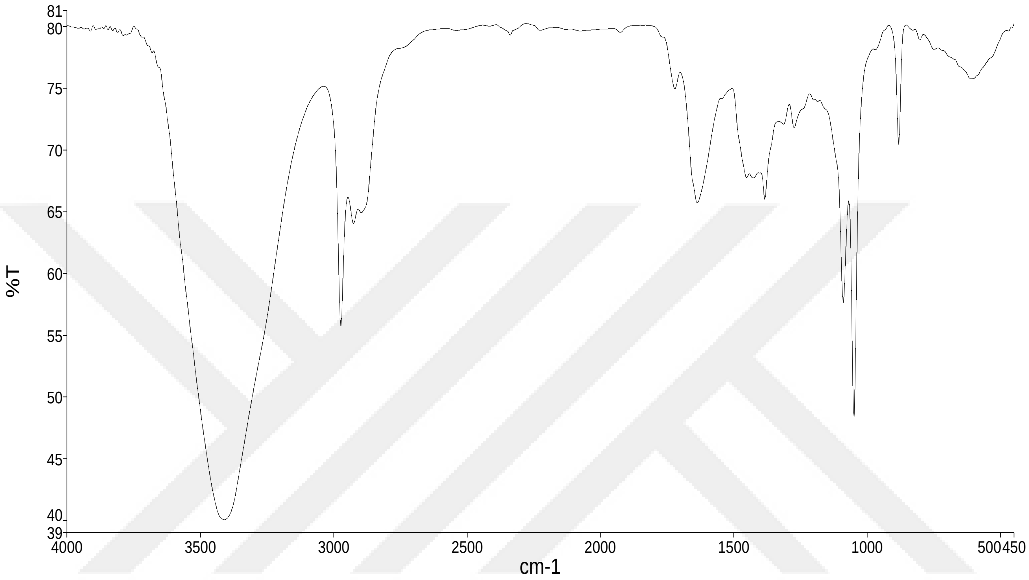


Figure 4.15. FT-IR spectrum of zinc(II)phthalocyanine

Table 4.4. An important FT-IR spectrum of zinc(II)phthalocyanine

Vibration (cm^{-1})	**Assignment**
2972	C-H Ar
2926	C-H (CH_3) tb
1641	C=C Ar
1273	C-O-C

- **UV spectrum**

The UV-visible spectrum of ZnPc was taken in DMSO shown in Figure 4.16. The intense Q band was seen at 679 nm due to transition of the Pc ring in π-π^* from HOMO to LUMO, the Soret band (B) band was observed as a shoulder at about 460 nm. Also the less intense peak at 620 nm characteristic of phthalocyanine is also observed. The sharp Q band with shape and less intense shoulder at 620 nm of the peak suggest that less aggregation of phthalocyanine is occurs in DMSO solvent.

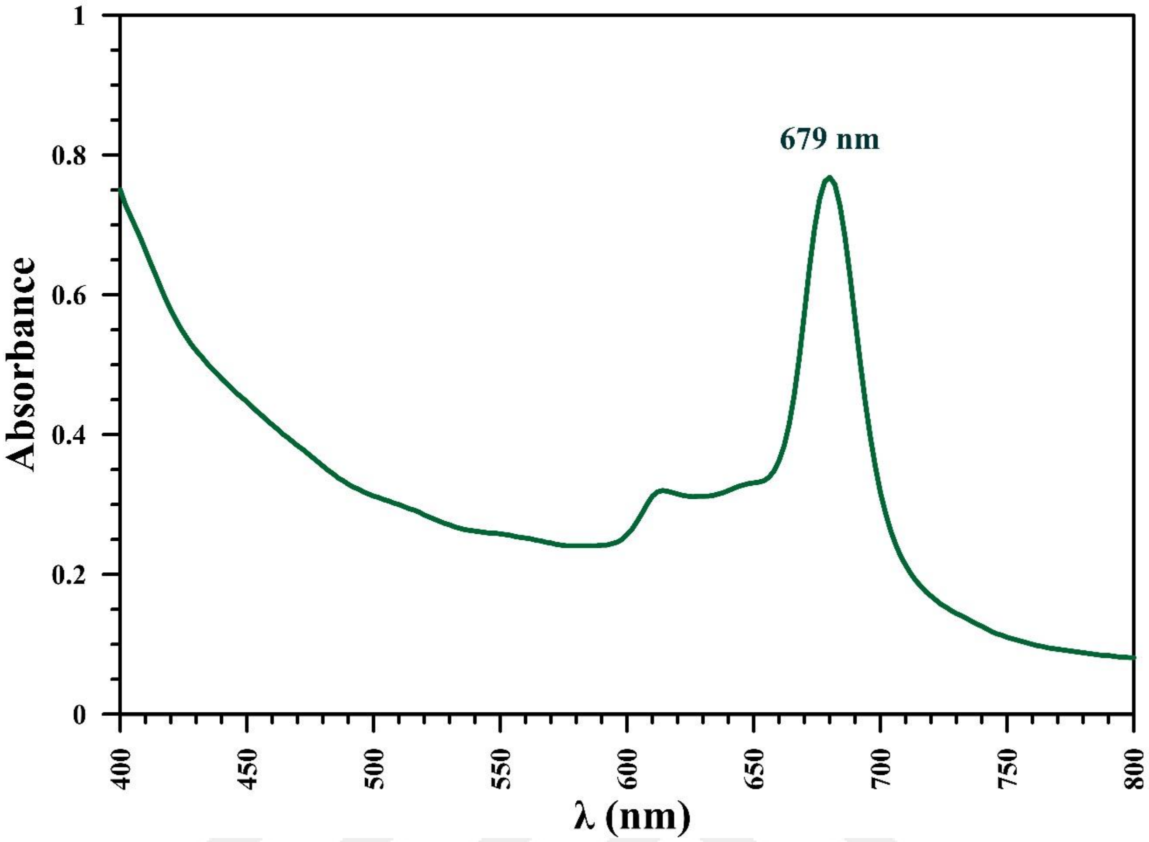


Figure 4.16. UV-visible spectrum of zinc(II)phthalocyanine

- **Thermal analysis**

The thermogravimetric analysis TGA of ZnPc complex showed that it has thermal stable up to 230 °C, then it decomposes in four steps to lose nearly 70% of its weight. Exothermic decomposition of complex starts from 230 °C to 400 °C with the loses 20% of weight. Then second exothermic decomposition in between 400 to 500 °C with the weight loss of 25% observed. Third decomposition seen in between 500 °C to 600 °C with the total weight loss of 18%. The last decomposition steps starts from 600 °C and with the weight loss of 10% as showed at Figure 4.17. DTA thermograms suggest that, ZnPc decompose without showing melting point, with the total weight loss of 75% up to 900 °C [91].

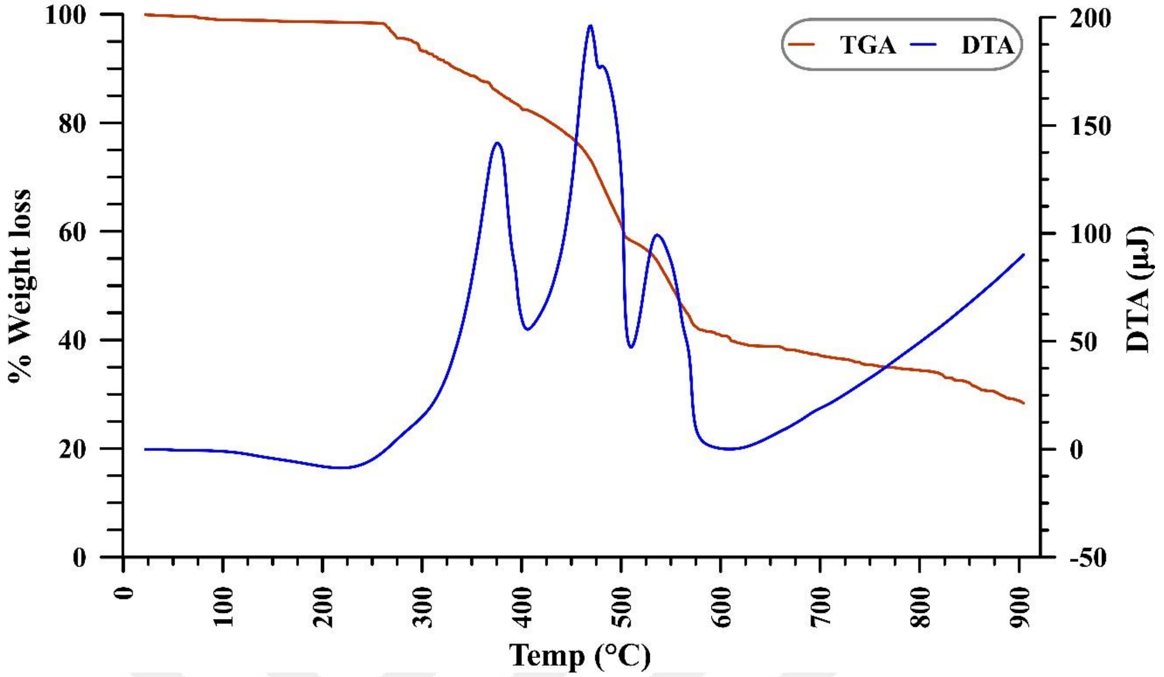


Figure 4.17. TGA and DTA of zinc(II)phthalocyanine

- **Electrochemical Properties**

Electrochemical study of the ZnPc were performed by cyclic (CV Figure 4.18) and square wave voltammogram (SWV Figure 4.19) in DMSO, tetra butyl ammonium tetrafluoroborate (TBAFB) as supporting electrolyte. The ferrocene/ferrocenium couple (Fc/Fc^+) was used as a pseudo reference electrode and potentials reported versus Fc/Fc^+ in non-aqueous solutions. Because of low solubility of ZnPc, CV voltammogram (Figure 4.18) did not come out well to show redox processes. For that reason, experiment repeated with SW voltammogram (Figure 4.19) which has better representation of individual redox processes.

ZnPc can be oxidized and reduced several times over macrocycles moiety Figure 4.18 and Figure 4.19. From electrochemical voltammogram of ZnPc shows four reduction, R_1, R_2, R_3, and R_4 at -0.87, -1.5, -1.82, and -2.67 with one oxidation wave O_1 at 0.67 respectively. All these redox processes are macrocycle ring origin, because redox inactive Zn(II) metal, in phthalocyanine complexes. The redox behaviour is specifically related to the elimination of electrons from HOMO of phthalocyanine ring, while up to four more electrons can be attached to LUMO of phthalocyanine ring. Generally, potential difference between first reduction and oxidation is about 1.50 V for metalliated phthalocyanine, and for ZnPc this value is 1.54 Volt and in good agreement with the literature [40, 108].

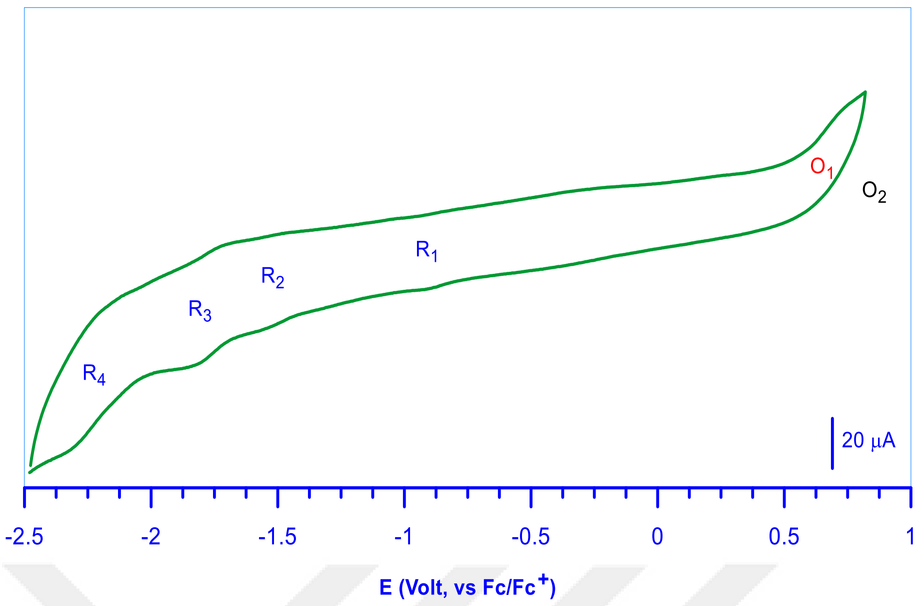


Figure 4.18. Cyclic voltammogram of zinc(II)phthalocyanine

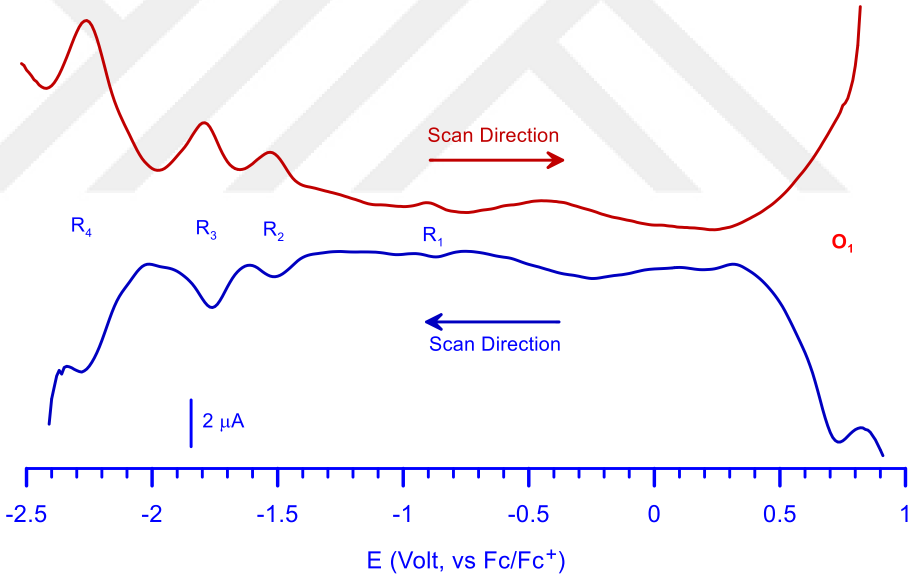


Figure 4.19. Square wave voltammogram of zinc(II)phthalocyanine

4.5. 2,10,16,24-Tetrakis(2,6-di-tert-butyl-4-methylphenoxy)copper phthalocyanine

The copper phthalocyanine (CuPc) was prepared from 4(2,6-Di-tert-butyl-4-methylphenoxy)phthalonitrile with copper(II)acetate under argon atmosphere in DMSO, Figure 4.20.

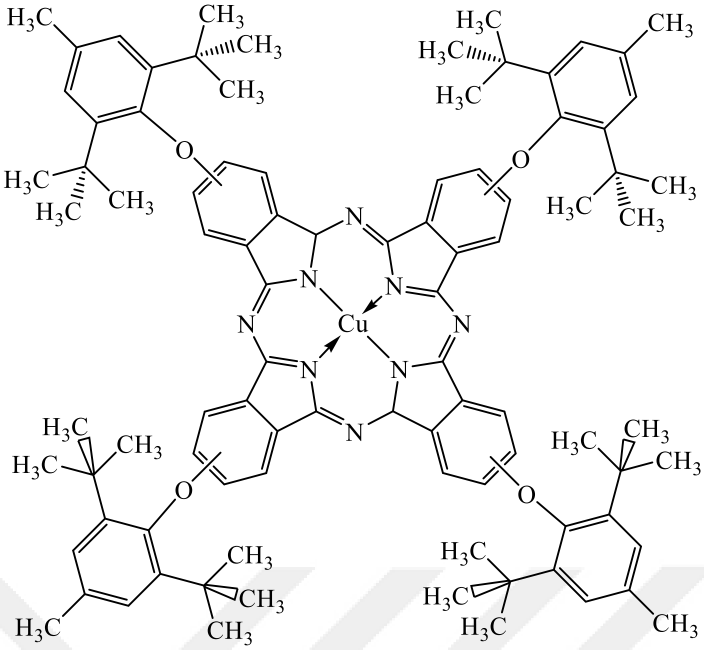


Figure 4.20. 2,10,16,24-Tetrakis (2,6-di-tert-butyl-4-methylphenoxy)cupper phthalocyanine structure

The yield obtained: 0.11 gram (0.0758 mmol), 42 %

Formula product: $C_{92}H_{106}CuN_8O_4$

M_W: 1451.46 gram/mol

Colour of product: dark brown

- **FT-IR spectrum**

IR spectrum was obtained as KBr tablet, showed that the absence of nitrile $C\equiv N$ stretching peak at 2233 cm^{-1} of phthalonitrile group indicate that CuPc complex free from starting material and cyclotetramerization of 4 phthalonitriles ligand in the presence of Cu(II) salt formed green coloured CuPc which is a characteristic to phthalocyanines (Figure 4.21) and (Table 4.5).

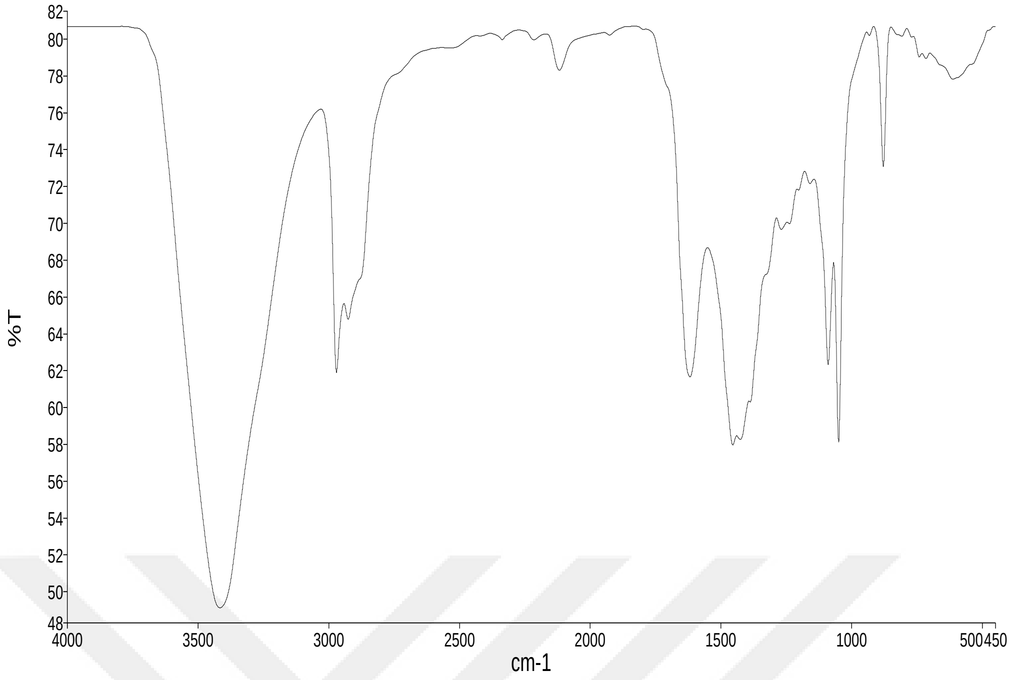


Figure 4.21. FT-IR spectrum of Cu(II)phthalocyanine

Table 4.5. An important FT-IR spectrum of Cu(II)phthalocyanine

Vibration (cm^{-1})	Assignment
2970	C-H Ar
2926	C-H (CH_3) tb
1618	C=C Ar
1261	C-O-C

- **UV spectrum**

The UV-Visible spectra of Cu(II)phthalocyanine were taken in DMSO, shown in Figure 4.22. The intense Q band was observed at 723 nm which is due to transition of π-π^* from HOMO to LUMO of phthalocyanine ring. The Soret band (B band) was seen as shoulder at about 425 nm. Because of high aggregation of phthalocyanine ring, intensity of peak at 600 nm increased a new peak appeared as shoulder at about 675 nm. Q band of CuPc is observed quite shifted to red side of the spectrum, therefore the colour of the CuPc brown or dark red instead of usual green or blue colour of CuPc which is quite interesting as showed at Table 4.9.

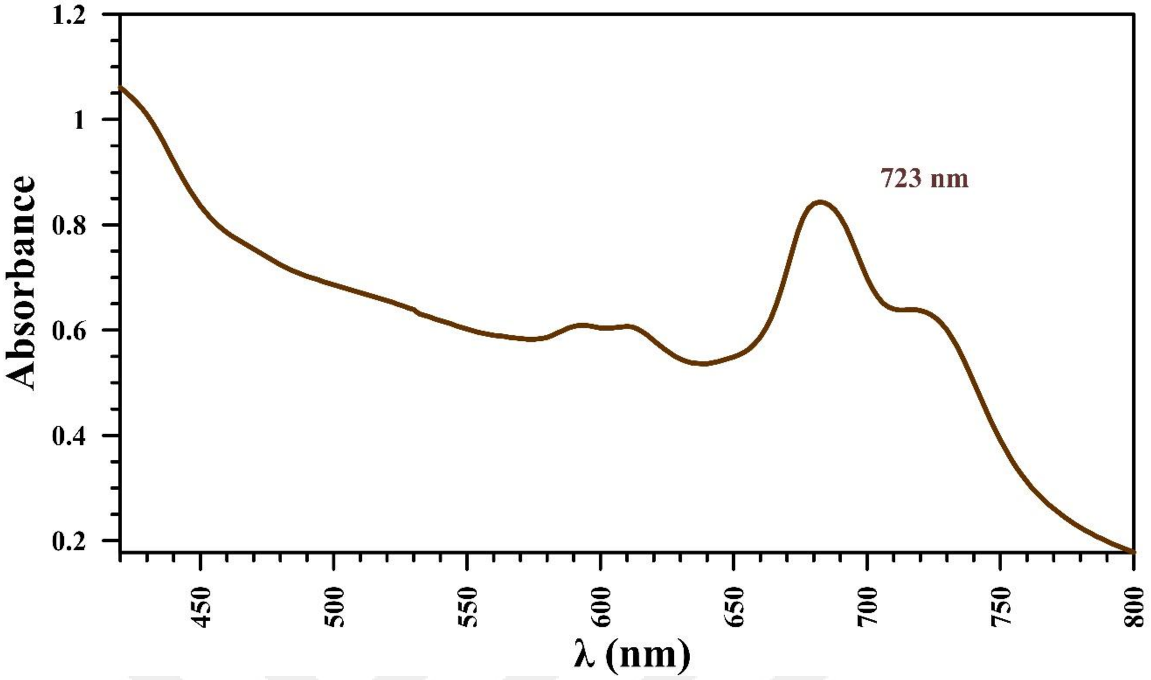


Figure 4.22. UV-visible spectra of Cu(II)phthalocyanine

- **Thermal analysis**

There is a small weight loss observed up to 230 °C, most probably from the loss of absorbed water from the surface of complex. Cu(II)phthalocyanine complex showed no decomposition up to nearly 400 °C, whit about 10% weight loss might be from absorbed moisture on the surface of the CuPc. Degradation takes place in two steps, as seen in the TGA thermogram in Figure 4.23. The exothermic decomposition of 60% of weight loss occurred between 410-520 °C as the first degradation. The second degradation was seen with 28% weight loss within the range of 520-750 °C in the second degradation region, in both degradation processes 81% of the complex were decomposed which can be seen at Figure 4.23. TGA thermogram of the CuPc indicate that about 7% of residue left which is comparable to decomposition of CuPc to form CuO.

DTA curve showed that CuPc has one exothermic degradation process forming CuO and it decomposes completely at 750 °C [91].

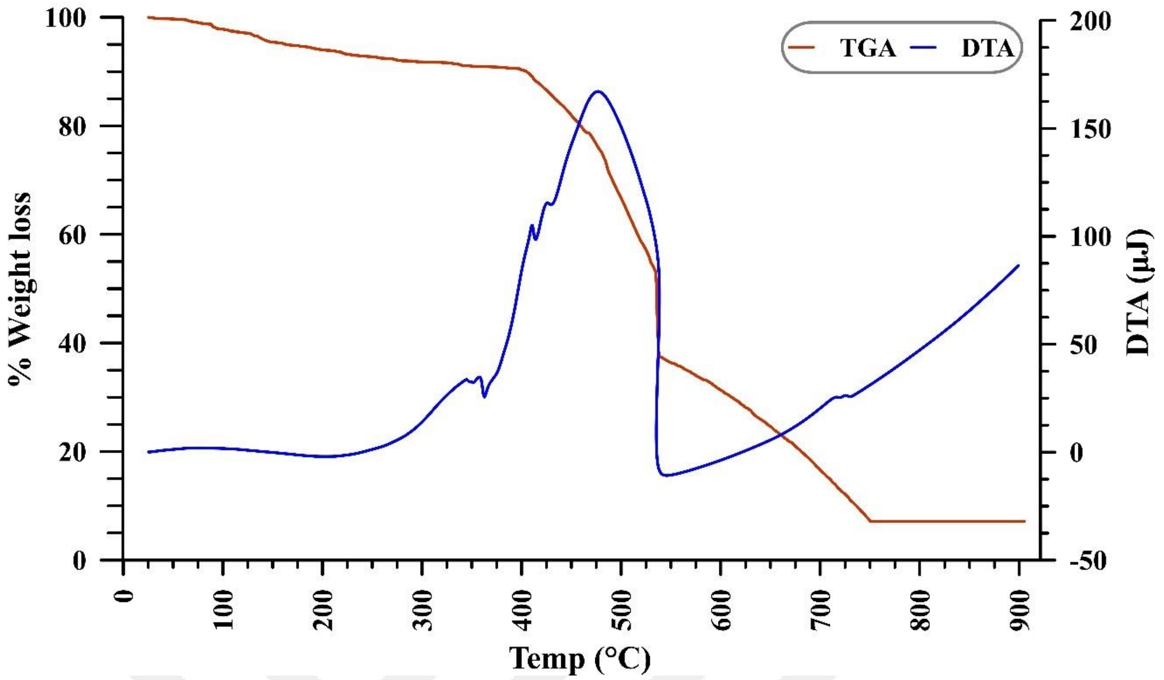
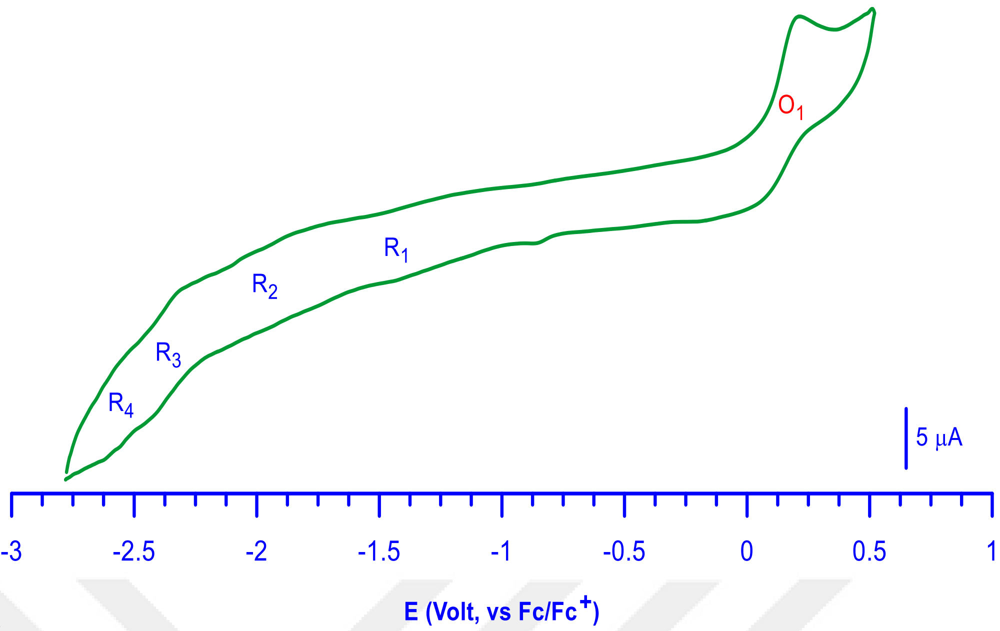


Figure 4.23. TGA and DTA of Cu(II)phthalocyanine

- **Electrochemical Properties**

Electrochemical study of the CuPc were performed by CV Figure 4.24 and SWV Figure 4.25 in DMSO, (TBAFB) as supporting electrolyte. The ferrocene/ferrocenium couple (Fc/Fc^+) was used as a pseudo reference electrode and potentials reported versus Fc/Fc^+ in non-aqueous solutions. Because of low solubility of CuPc, CV voltammogram (Figure 4.24) did not come out well to show redox processes. For that reason, experiment repeated with SW voltammogram (Figure 4.25) which has better representation of individual redox processes.

CuPc can be oxidized and reduced several times over macrocycles moiety Figure 4.24 and Figure 4.25. From electrochemical voltammogram of CuPc shows four reduction, R_1, R_2, R_3, and R_4 at -1.39, -1.90, -2.40, and -2.62 with one oxidation wave O_1 at 0.22 respectively. All these redox processes are macrocycle ring origin, because redox inactive Cu(II) metal, in phthalocyanine complexes. The redox behaviour is specifically related to the elimination of electrons from HOMO of phthalocyanine ring, while up to four more electrons can be attached to LUMO of phthalocyanine ring. Generally, potential difference between first reduction and oxidation is about 1.50 V for metalliated phthalocyanine, and for CuPc this value is 1.61 Volt and in good agreement with the literature. Also before the first oxidation wave there are three absorbed waves which were labelled as A_1, A_2 And A_3 at (-0,19, -0.81 and -1.08) respectively, showed at SWV at Figure 4.25, which disappearing at increasing scan speed and which can be allocated an additional ligand from the DMF donor solvent molecule to five or six coordinated Pc complexes [108].



m

Figure 4.24. Cyclic voltammogram of Cu(II)phthalocyanine

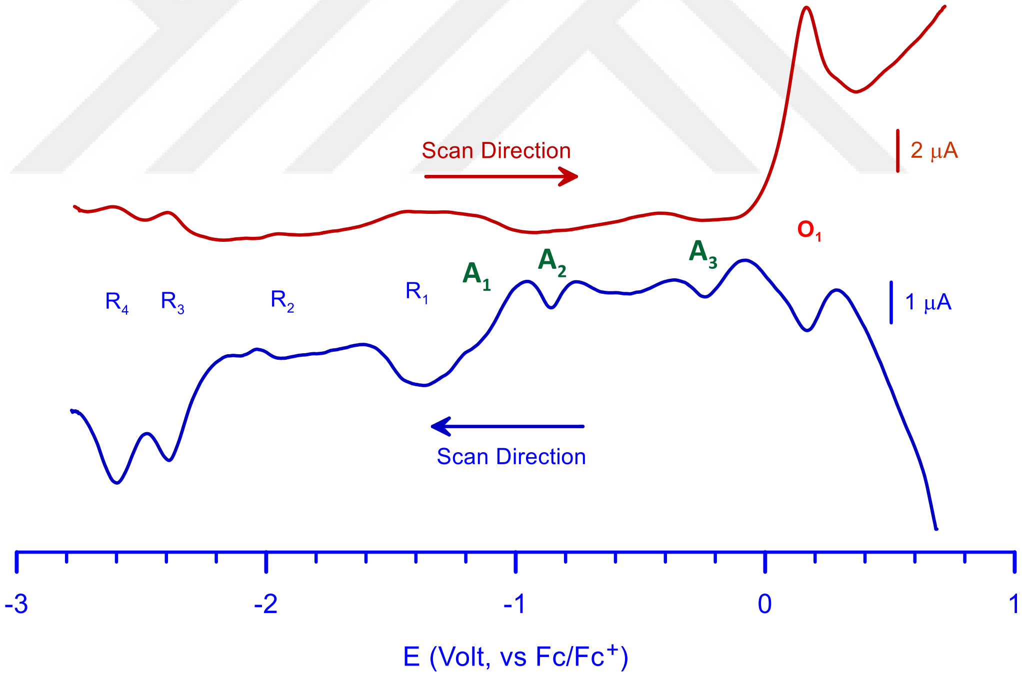


Figure 4.25. Square wave voltammogram of Cu(II)phthalocyanine

4.6. 2,10,16,24-Tetrakis(2,6-di-tert-butyl-4-methylphenoxy)cobalt phthalocyanine

The cobalt phthalocyanine (CoPc) was prepared from 4(2,6-Di-tert-butyl-4-methylphenoxy)phthalonitrile with cobalt(II)acetate under argon atmosphere in DMSO, showed at Figure 4.26.

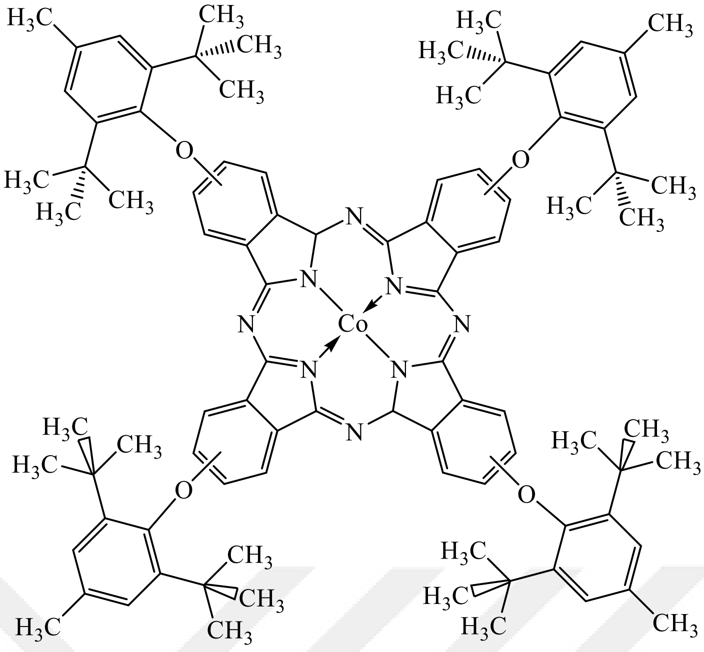


Figure 4.26. 2,10,16,24-Tetrakis (2,6-di-tert-butyl-4-methylphenoxy)cobalt phthalocyanine structure

The yield obtained: 0.134 gram (0.09 mmol), 51.3 %

Formula product: $C_{92}H_{106}CoN_8O_4$

Mw: 1446.85 gram/mol

Color of product: greenish precipitate

FT-IR spectrums

IR spectrum was obtained as KBr tablet, showed that the absence of Nitrile C≡N stretching peak at 2233 cm^{-1} of phthalonitrile group indicate that Co(II)phthalocyanine complex free from starting material and cyclotetramerization of 4 phthalonitriles ligand in the presence of Co(II) salt formed green coloured CoPc which is a characteristic to phthalocyanines (Figure 4.27) and (Table 4.6).

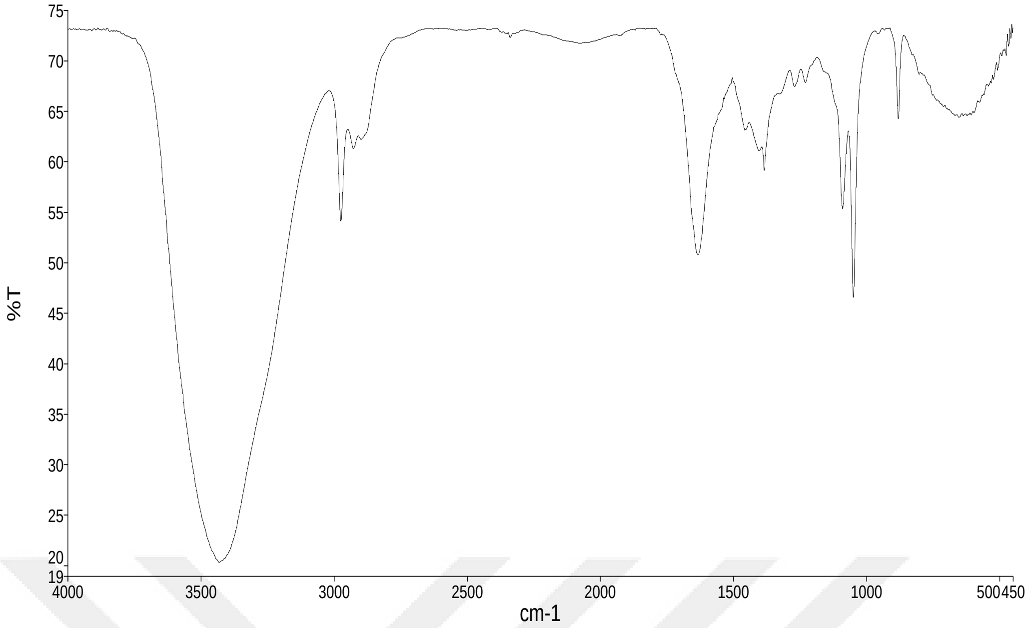


Figure 4.27. FT-IR spectrum of Co(II)phthalocyanine

Table 4.6. An important FT-IR spectrum of Co(II)phthalocyanine

Vibration (cm^{-1})	Assignment
2974	C-H Ar
2928	C-H (CH_3) tb
1633	C=C Ar
1276	C-O-C

- **UV spectrum**

The UV-visible spectrum of Co(II)phthalocyanine was taken in DMSO shown in Figure 4.28. The intense Q band was seen at 669 nm due to transition of the Pc ring in π-π* from HOMO to LUMO, the Soret band (B) band was observed as a shoulder at about 440 nm. Also, the less intense peak at 615 nm characteristic of phthalocyanine is also observed. The sharp Q band with shape and less intense shoulder at 615 nm of the peak suggest that less aggregation of cobalt phthalocyanine occurs in DMSO solvent.

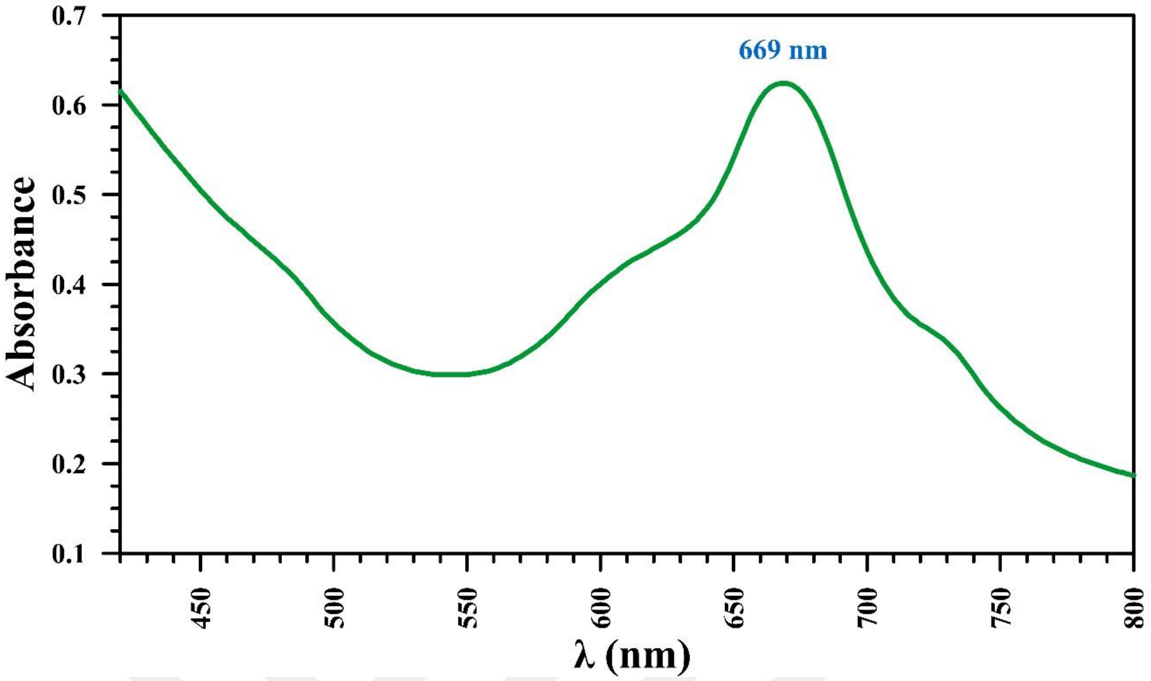


Figure 4.28. UV-visible spectrum of Co(II)phthalocyanine

- **Thermal analysis**

There is a small weight loss observed up to 250 °C, most probably from the loss of absorbed water from the surface of complex. Co(II)phthalocyanine complex showed no decomposition up to nearly 400 °C, whit about 11% weight loss might be from absorbed moisture on the surface of the CoPc. Degradation takes place in three steps, as seen in the TGA thermogram in Figure 4.29. The exothermic decomposition of 12% of weight loss occurred between 400-500 °C as the first degradation. The second degradation was seen with 32% weight loss within the range of 500 to 580 °C. The last decomposition steps start from 580 °C and with the weight loss of 22%. In all degradation processes 77% of the complex were decomposed which can be seen in Figure 4.29. TGA thermogram of the CoPc indicate that 23% of residue left which is comparable to decomposition of CoPc to form CoO.

DTA curve showed that CoPc has one exothermic degradation process forming CoO and it decomposes completely at 850 °C [109].

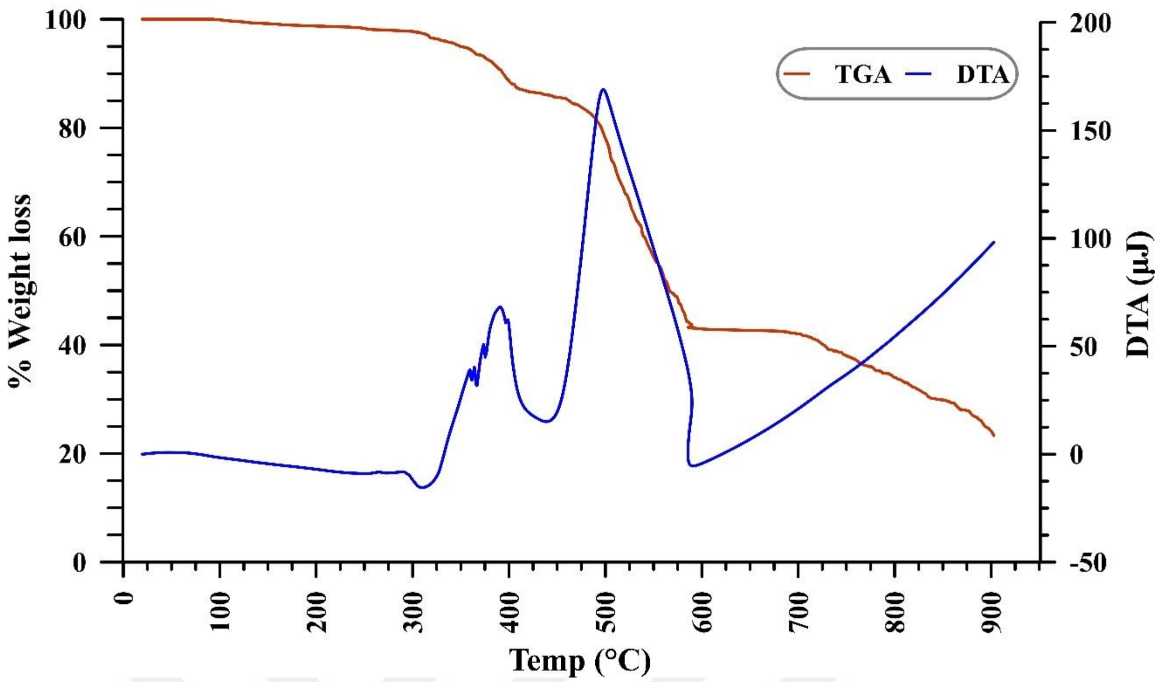


Figure 4.29. TGA and DTA of Co(II)phthalocyanine

- **Electrochemical analysis**

Electrochemical study of the CoPc were performed by CV Figure 4.30 and SWV Figure 4.31 in DMSO, (TBAFB) as supporting electrolyte. The (Fc/Fc$^+$) couple was used as a pseudo reference electrode and potentials reported versus Fc/Fc$^+$ in non-aqueous solutions. Because of low solubility of CoPc, CV voltammogram (Figure 4.30) did not come out well to show redox processes. For that reason, experiment repeated with SW voltammogram (Figure 4.31) which has better representation of individual redox processes.

CoPc can be oxidized and reduced several times over macrocycles moiety Figure 4.30 and Figure 4.31. From electrochemical voltammogram of CoPc shows four reduction, R_1, R_2, R_3, and R_4 at -0.90, -1.72, -2.02, and -2.44 with two oxidation waves O_1 at 0.18 and O_2 at 0.6 respectively. All these redox processes are macrocycle ring origin, because redox inactive Co(II) metal, in phthalocyanine complexes. The redox behaviour is specifically related to the elimination of electrons from HOMO of phthalocyanine ring, while up to four more electrons can be attached to LUMO of phthalocyanine ring. Generally, potential difference between first reduction and oxidation is about 1.50 V for metalated phthalocyanine, and for CoPc this value is 1.08 Volt.

The redox-active metals labelled as M_X which appeared at -0.62 at both CV and SWV diagrams showed at Figure 4.30 and Figure 4.31, it was the oxidation and the reduction of the metal that occurred between the oxidation and reduction of the phthalocyanine ring [108].

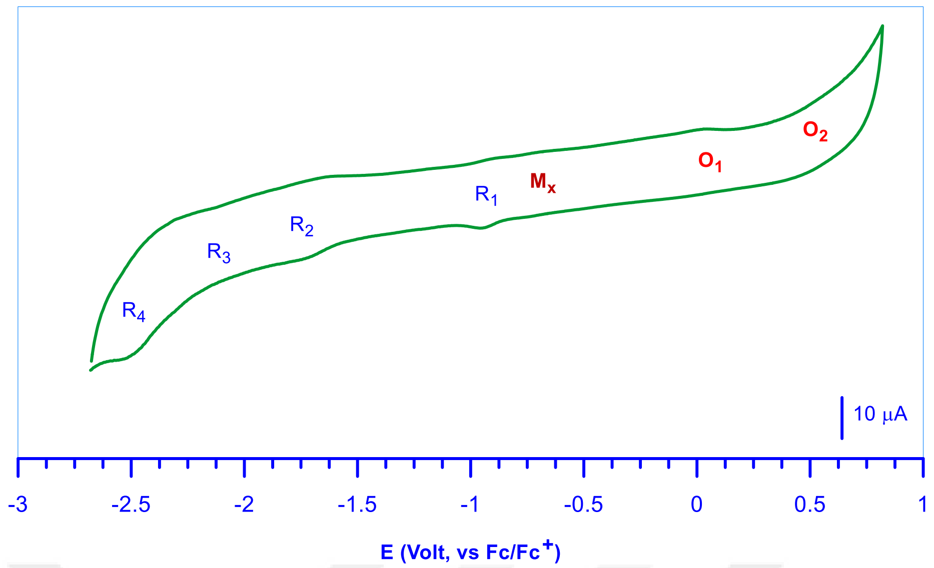


Figure 4.30. Cyclic voltammogram of Co(II)phthalocyanine

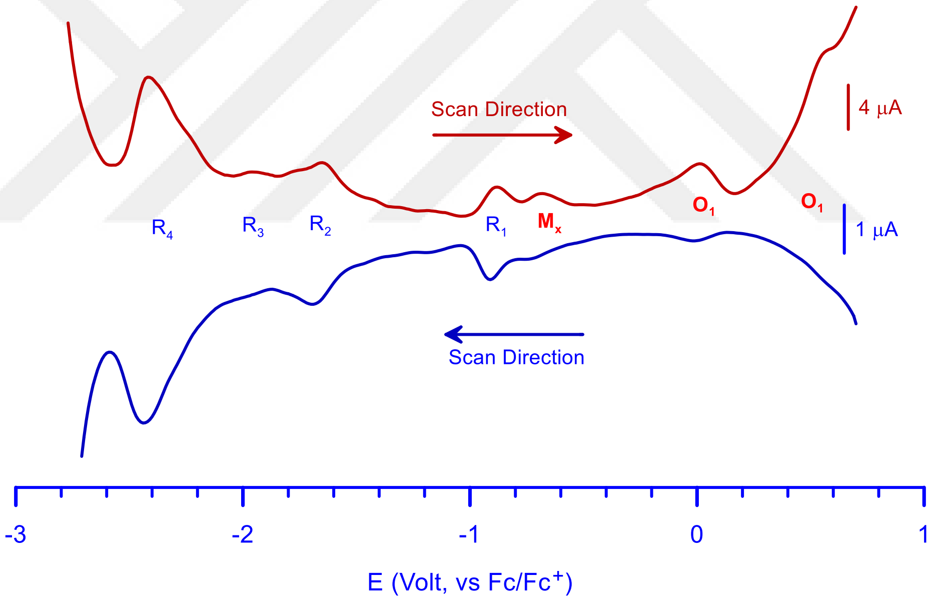


Figure 4.31. Square wave voltammogram of Co(II)phthalocyanine

4.7. 2,10,16,24-Tetrakis(2,6-di-tert-butyl-4-methylphenoxy)nickel phthalocyanine

The Nickel phthalocyanine (NiPc) was prepared from 4(2,6-Di-tert-butyl-4-methylphenoxy)phthalonitrile with nickel(II)acetate under argon atmosphere in DMSO, Figure 4.32.

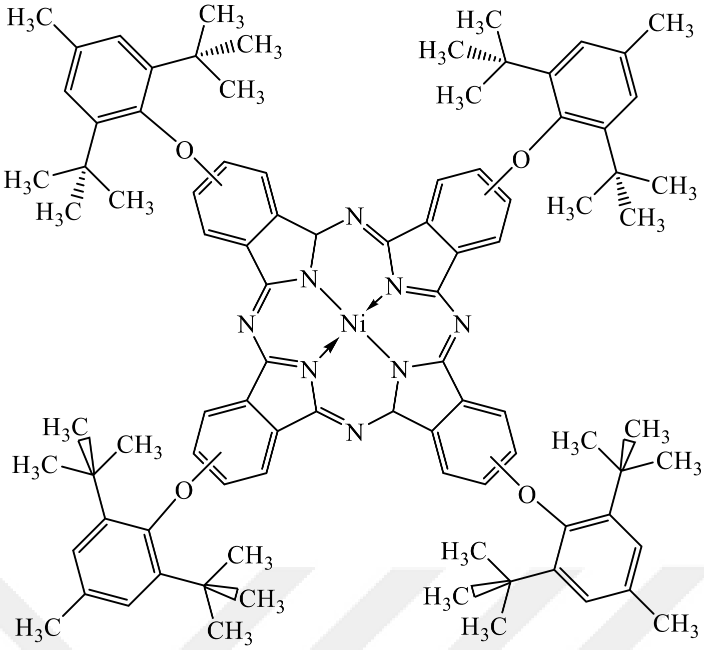


Figure 4.32. 2,10,16,24-Tetrakis (2,6-di-tert-butyl-4-methylphenoxy)nickel phthalocyanine structure

The yield obtained: 0.062 gram (0.04 mmol), 23.8 %

Formula product: $C_{92}H_{106}N_8NiO_4$

Mw: 1446.61 g/mol

Color of product: greenish precipitate

- **FT-IR spectrums**

FT-IR spectrum of the nickel(II)phthalocyanine complex KBr was confirms the absence of Nitrile C≡N stretching peak at 2233 cm^{-1} of phthalonitrile formation of nickel phthalocyanine complexed with the formation of green colour, and also absence of unreacted starting material in the complex (Figure 4.33) and (Table 4.7).

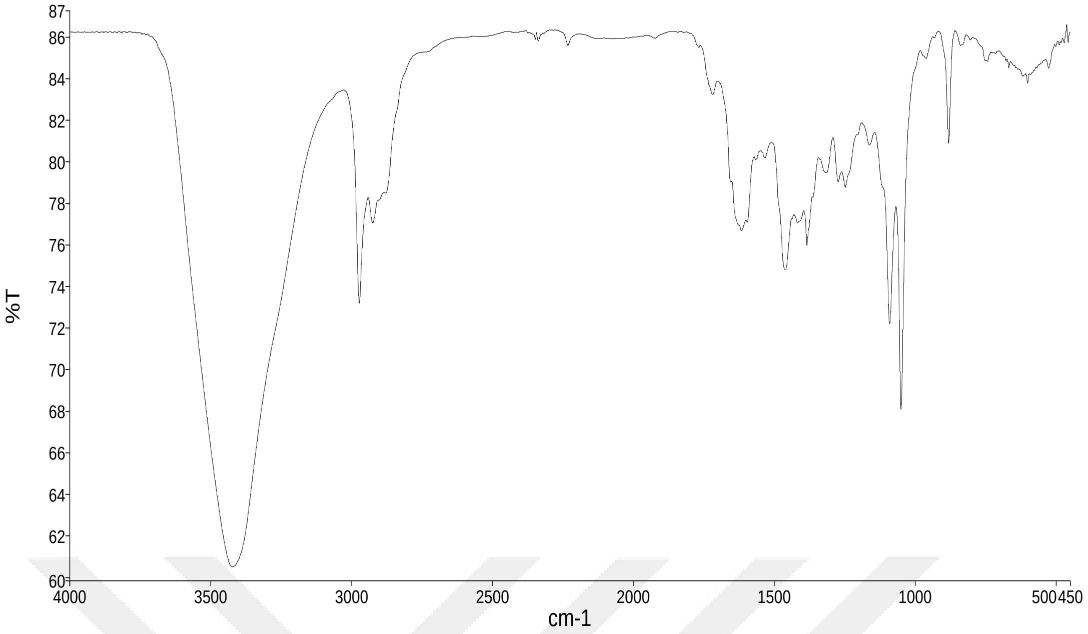


Figure 4.33. FT-IR spectrum of Ni(II)phthalocyanine

Table 4.7. An important FT-IR spectrum of Ni(II)phthalocyanine

Vibration (cm^{-1})	Assignment
2973	C-H Ar
2924	C-H (CH_3) tb
1616	C=C Ar
1240	C-O-C

- **UV spectrum**

The UV-Visible spectra of NiPc was taken in DMSO, shown in Figure 4.34. The intense Q band was observed at 677 nm which is due to transition of π-π* from HOMO to LUMO of phthalocyanine ring. The Soret band (B band) was seen as shoulder at about 460 nm. Because of high aggregation of phthalocyanine ring, intensity of peak at 580 nm increased a new peak appeared as shoulder at about 621 nm. Q band of NiPc is observed.

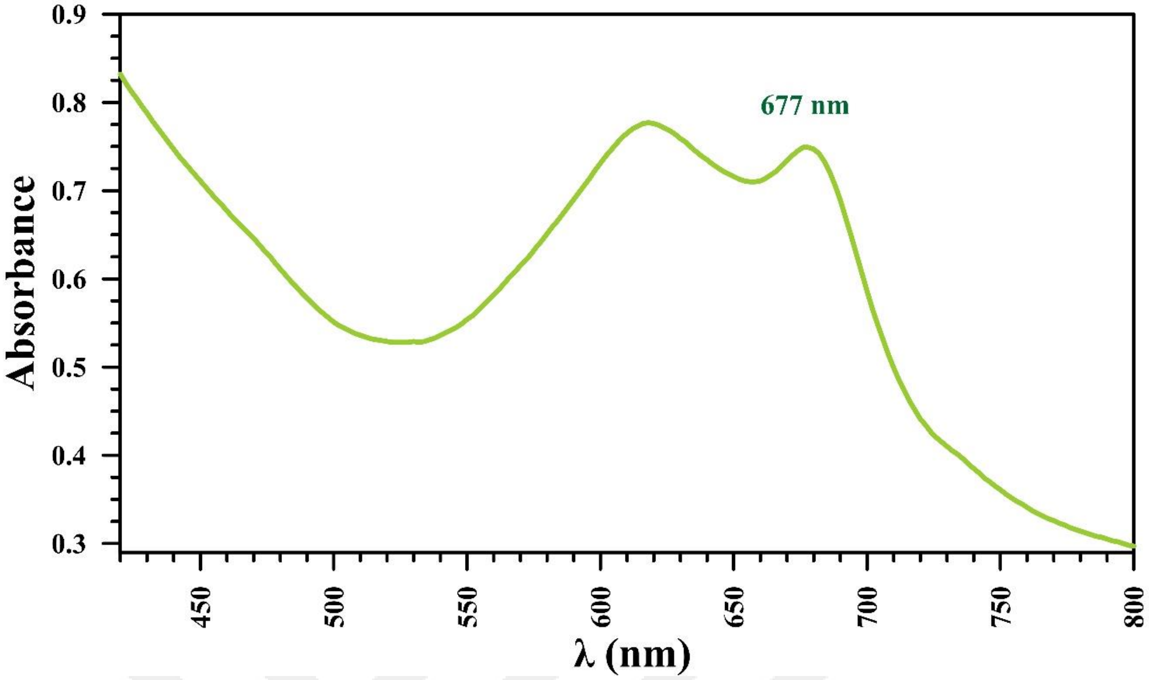


Figure 4.34. UV-visible spectrum of Ni(II)phthalocyanine

- **Thermal analysis**

There is a small weight loss observed up to 250 °C, most probably from the loss of absorbed water from the surface of complex. NiPc complex showed no decomposition up to nearly 380 °C, whit about 12% weight loss might be from absorbed moisture on the surface of the NiPc. Degradation takes place in three steps, as seen in the TGA thermogram in Figure 4.35. The exothermic decomposition of 32% of weight loss occurred between 380-450 °C as the first degradation. The second degradation was seen with 37% weight loss within the range of 450-550 °C in the second degradation region. The third degradation starts at 550 °C and with the weight loss of 8%. in all degradation processes 77% of the complex were decomposed which can be seen in Figure 4.35. TGA thermogram of the NiPc indicate that 11% of residue left which is comparable to decomposition of NiPc to form NiO.

DTA curve showed that NiPc has one exothermic degradation process forming NiO and it decomposes completely at 850 °C [110].

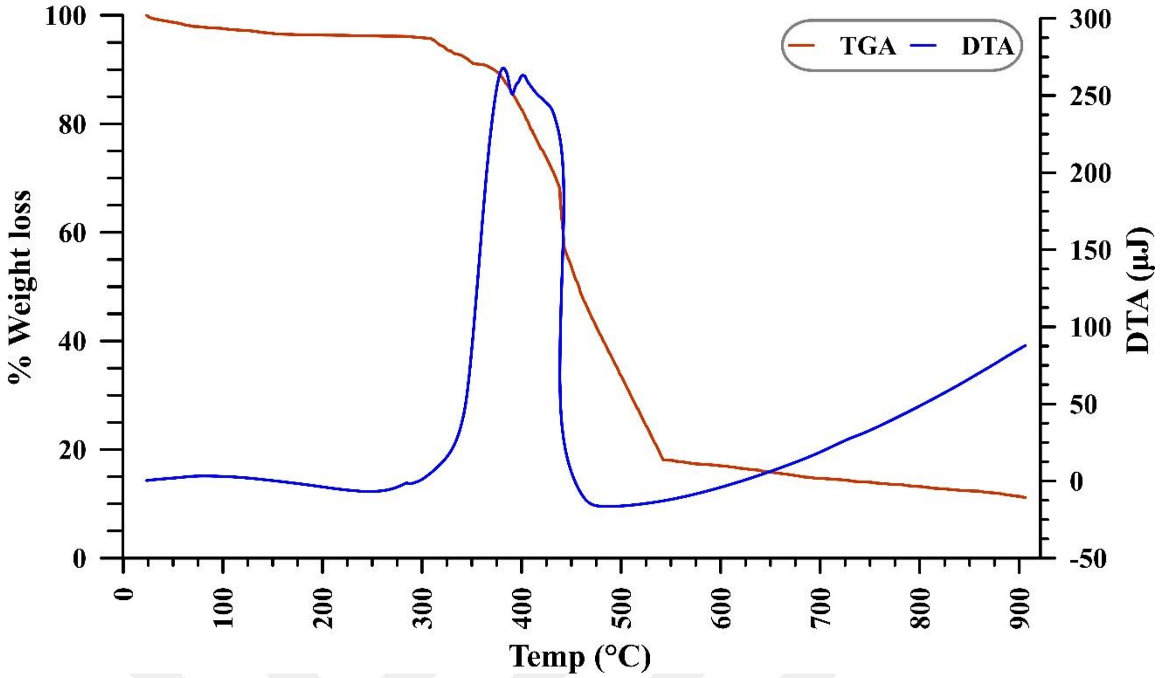


Figure 4.35. TGA and DTA of Ni(II)phthalocyanine

- **Electrochemical analysis**

Electrochemical study of the NiPc were performed by CV Figure 4.36 and SWV Figure 4.37 in DMSO, (TBAFB) as supporting electrolyte. The (Fc/Fc$^+$) couple was used as a pseudo reference electrode and potentials reported versus Fc/Fc$^+$ in non-aqueous solutions. Because of low solubility of NiPc, CV voltammogram (Figure 4.36) did not come out well to show redox processes. For that reason, experiment repeated with SW voltammogram (Figure 4.37) which has better representation of individual redox processes.

NiPc can be oxidized and reduced several times over macrocycles moiety Figure 4.36 and Figure 4.37. From electrochemical voltammogram of NiPc shows four reduction, R_1, R_2, R_3, and R_4 at -1.39, -1.95, -2.16, and -2.49 with two oxidation waves O_1 at 0.19 and O_2 at 0.52 respectively. All these redox processes are macrocycle ring origin, because redox inactive Ni(II) metal, in phthalocyanine complexes. The redox behaviour is specifically related to the elimination of electrons from HOMO of phthalocyanine ring, while up to four more electrons can be attached to LUMO of phthalocyanine ring. Generally, potential difference between first reduction and oxidation is about 1.50 volt for metalliated phthalocyanine, and for NiPc this value is 1.58 volt and in good agreement with the literature [93].

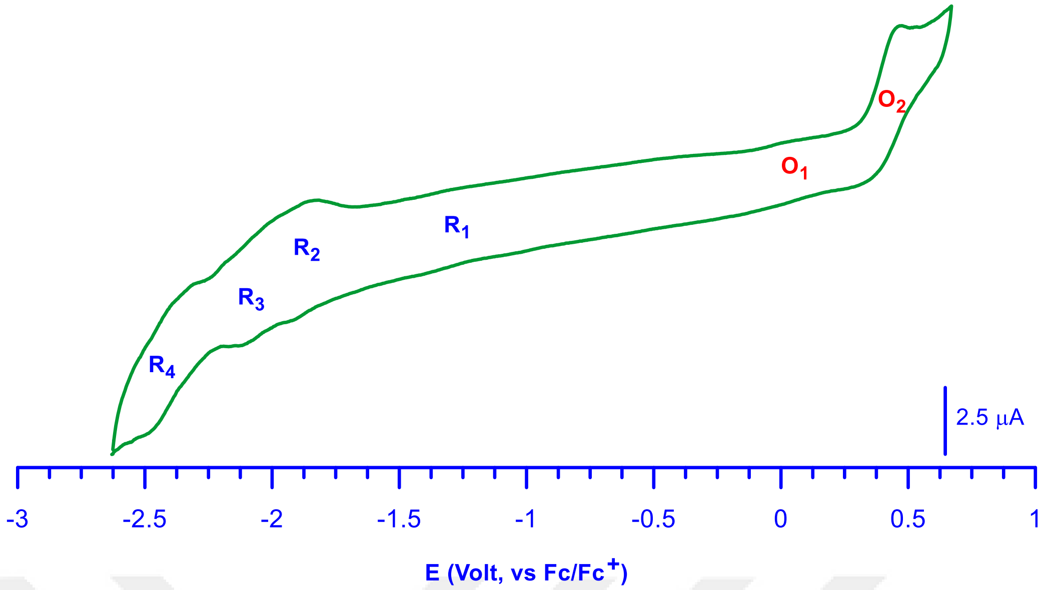


Figure 4.36. Cyclic voltammogram of Ni(II)phthalocyanine

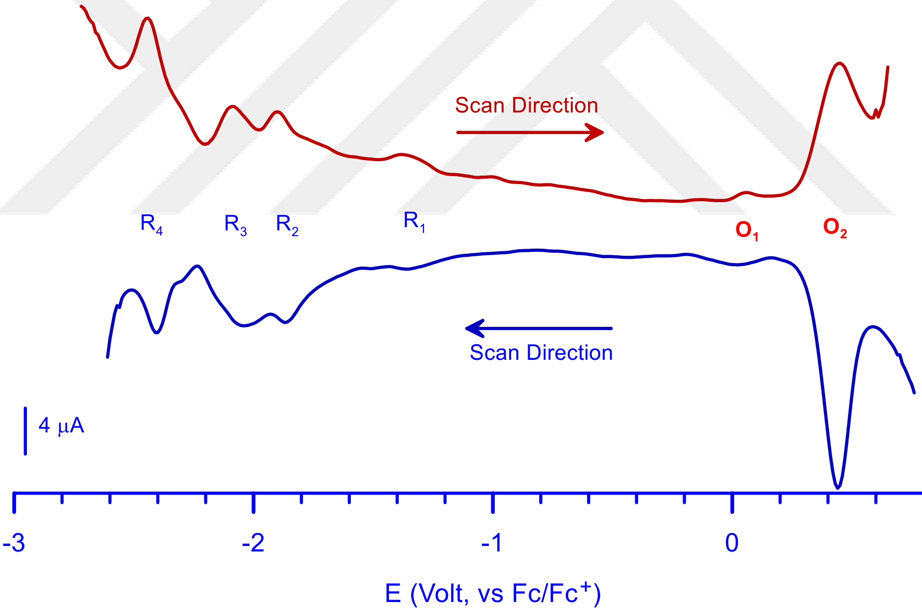


Figure 4.37. Square wave voltammogram of Ni(II)phthalocyanine

4.8. 2,10,16,24-Tetrakis(2,6-di-tert-butyl-4-methylphenoxy)di-lithium phthalocyanine

The di lithium phthalocyanine (Li_2Pc) was prepared from 4(2,6-Di-tert-butyl-4-methylphenoxy)phthalonitrile with lithium(I)oxide under argon atmosphere in DMSO, Figure 4.38.

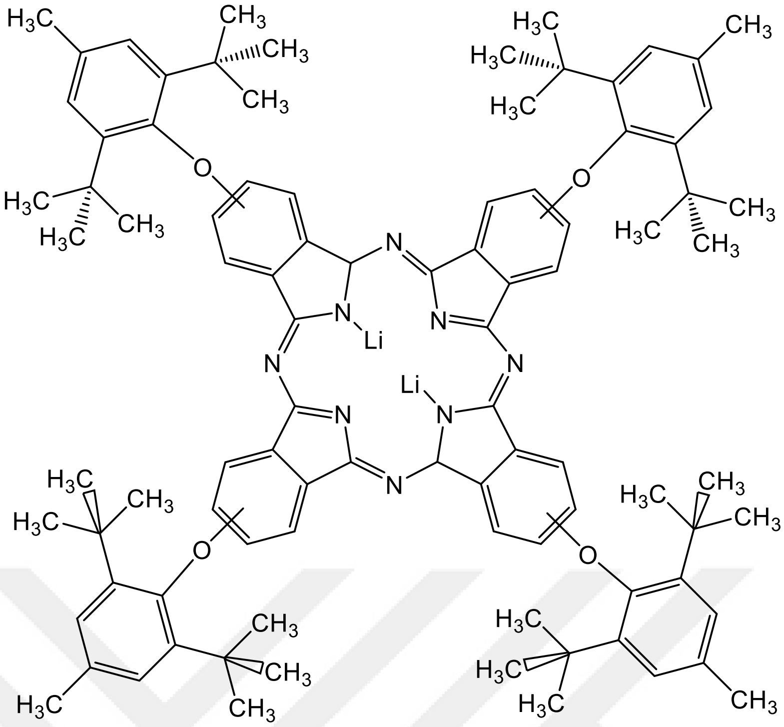


Figure 4.38. 2,10,16,24-Tetrakis (2,6-di-tert-butyl-4-methyl phenoxy)di-lithium phthalocyanine structure

The yield obtained: 0.102 gram (0.07 mmol), 40.4 %

Formula product: $C_{92}H_{106}Li_2N_8O_4$

Mw: 1401.79 gram/mol

Colour of product: green

- **FT-IR spectrums**

FT-IR spectrum of the di lithium(I)phthalocyanine complex KBr was confirms the absence of nitrile C≡N stretching peak at 2233 cm^{-1} of phthalonitrile formation of di lithium phthalocyanine complexed with the formation of green colour, and also absence of unreacted starting material in the complex (Figure 4.39) and (Table 4.8).

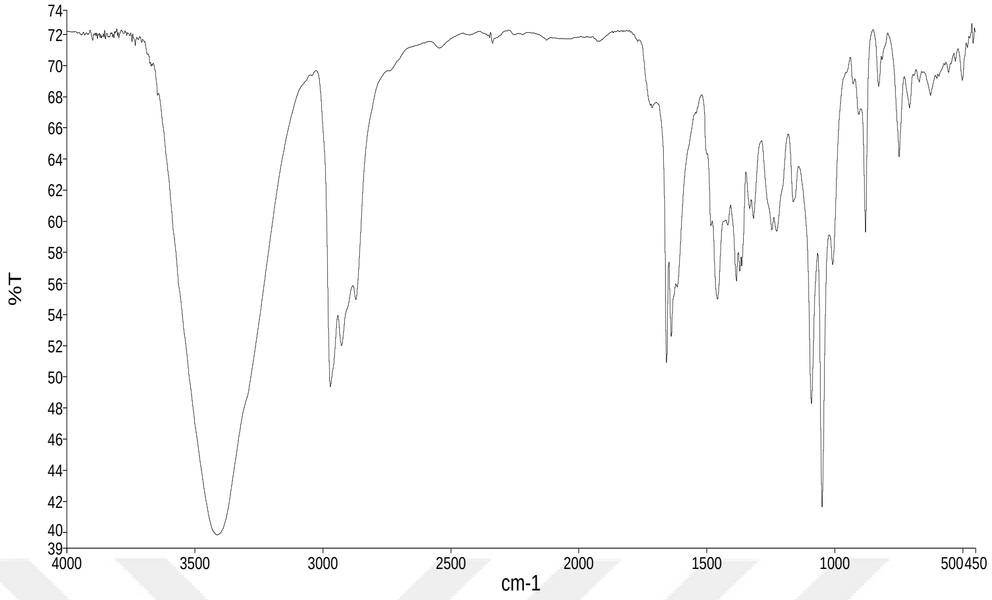


Figure 4.39. FT-IR spectrum of Li_2Pc

Table 4.8. An important FT-IR spectrum of Li_2Pc

Vibration (cm^{-1})	**Assignment**
2970	C-H Ar
2927	C-H (CH_3) tb
1657	C=C Ar
1242	C-O-C

- **UV spectrum**

The UV-visible spectrum of Li_2Pc was taken in DMSO shown in Figure 4.40. The intense Q band was seen at 675 nm due to transition of the phthalocyanine ring in π-π^* from HOMO to LUMO, the Soret band (B) band was observed as a shoulder at about 440 nm. Relatively less intense peak at 620 nm characteristic of phthalocyanine is also observed. The sharp Q band with shape and less intense shoulder at 615 nm of the peak suggest that less aggregation of phthalocyanine occurs in DMSO solvent.

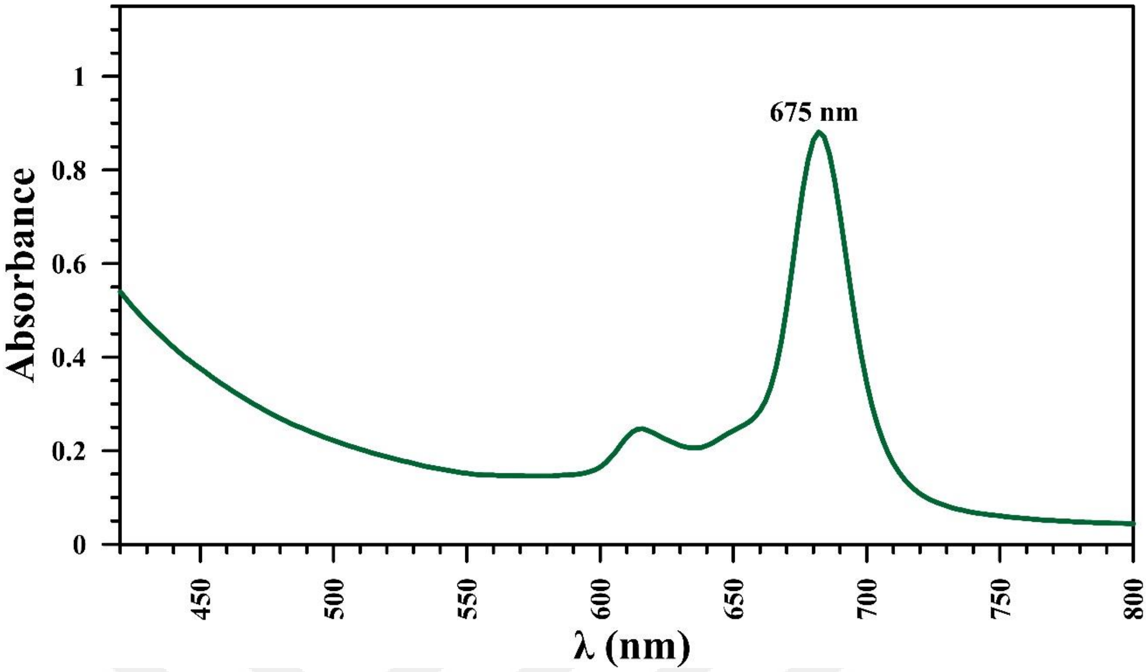


Figure 4.40. UV-visible spectrum for Li_2Pc

- **Thermal analysis**

There is a small weight loss observed up to 200 °C, most probably from the loss of absorbed water from the surface of complex. Li_2Pc complex showed no decomposition up to nearly 240 °C, whit about 12% weight loss might be from absorbed moisture on the surface of the Li_2Pc complex. Degradation takes place in one step, as seen in the TGA thermogram in Figure 4.41. The exothermic decomposition of 74% of weight loss occurred between 240-600 °C. TGA thermogram of the Li_2Pc indicate that about 14% of residue left.

DTA curve showed that Li_2Pc has one endothermic degradation process forming a residue inside Li_2O and it decomposes completely at 750 °C [109].

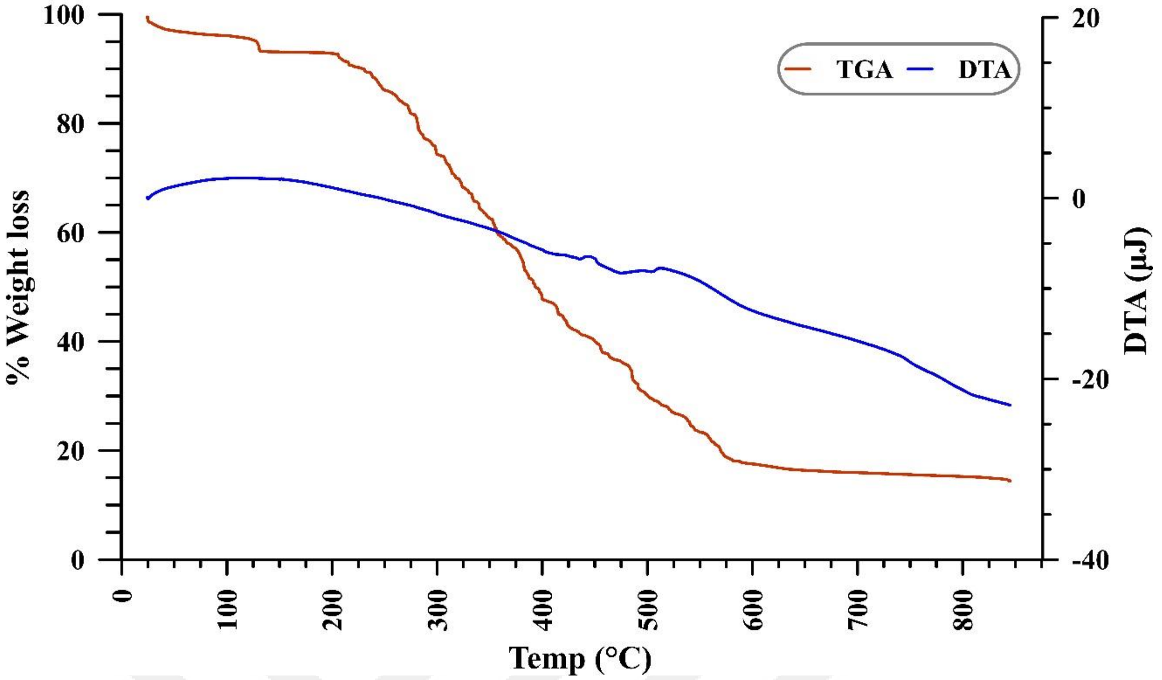


Figure 4.41. TGA and DTA of Li_2Pc

- **Electrochemical analysis**

Electrochemical study of the Li_2Pc were performed by CV Figure 4.42 and SWV Figure 4.43 in DMSO, (TBAFB) as supporting electrolyte. The (Fc/Fc^+) couple was used as a pseudo reference electrode and potentials reported versus Fc/Fc^+ in non-aqueous solutions. Because of low solubility of Li_2Pc, CV voltammogram (Figure 4.42) did not come out well to show redox processes. For that reason, experiment repeated with SW voltammogram (Figure 4.43) which has better representation of individual redox processes.

Li_2Pc can be oxidized and reduced several times over macrocycles moiety Figure 4.42 and Figure 4.43. From electrochemical voltammogram of Li_2Pc shows four reduction, R_1, R_2, R_3, and R_4 at -1.19, -1.72, -2.28, and -2.56 with one oxidation wave O_1 at 0.45 respectively. All these redox processes are macrocycle ring origin, because redox inactive Li(I) metal, in phthalocyanine complexes. The redox behaviour is specifically related to the elimination of electrons from HOMO of phthalocyanine ring, while up to four more electrons can be attached to LUMO of phthalocyanine ring. Generally, potential difference between first reduction and oxidation is about 1.50 volt for metalliated phthalocyanine, and for Li_2Pc this value is 1.64 Volt and in good agreement with the literature [111, 112].

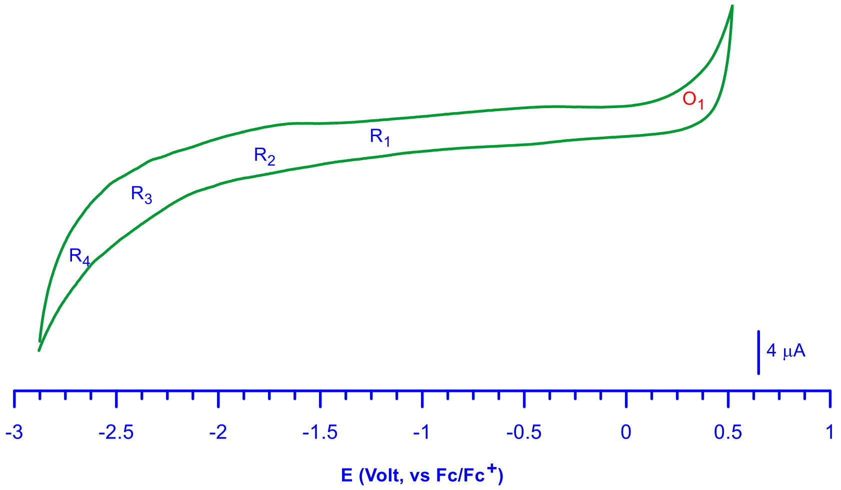


Figure 4.42. Cyclic voltammogram of Li_2Pc

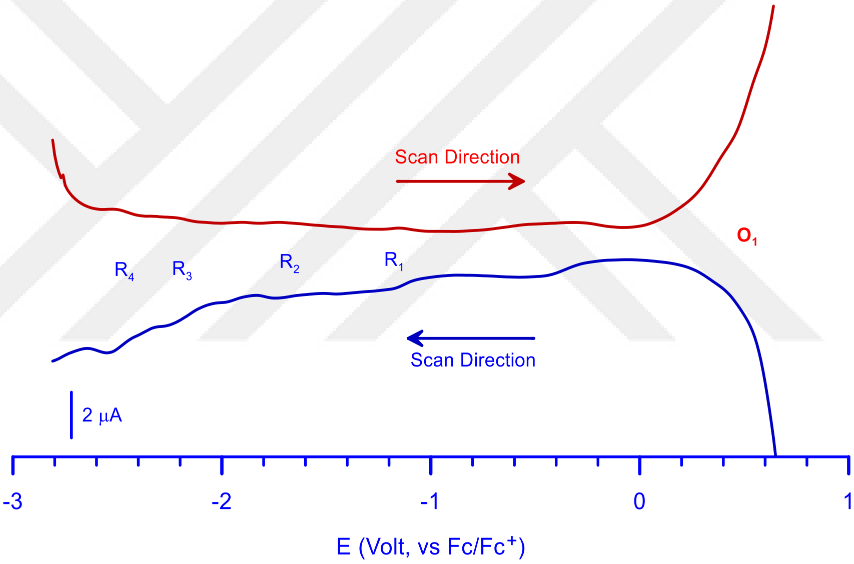


Figure 4.43. Square wave voltammogram of Li_2Pc

Table 4.9. Colour and UV-Visible spectra of Q band of metal Phthalocyanines

MPc	Li_2Pc	NiPc	CoPc	ZnPc	CuPc
Colour					
Q-band	675 nm	677 nm	669	679 nm	723 nm

5. CONCLUSIONS

The current study explains the synthesis and characterization of tetra peripheral positions of five different metal phthalocyanines (Zinc, Copper, Cobalt, Nickel, and Lithium) containing butylated hydroxytoluene as substituents from 4-Nitrophthalonitrile, characterized by electronic absorption spectra, FT-IR, Uv-Vis spectroscopy, thermal stability, and electrochemical analysis.

The result of metal phthalocyanines elemental analysis described as below,

✓ The FT-IR spectrum of the complete formation MPc complexes was correctified by disappearing nitrile C≡N stretching peak at 2233 cm^{-1}, and formation the cycle pyrrole group inside the Pc ring.

✓ The UV-visible absorption spectra showed an intense Q band which started from 669 nm for CoPc, 675 nm Li_2Pc, 677 nm NiPc, 679 nm ZnPc, and last one 723 nm of CuPc, with the high aggregation of NiPc of CuPc at 621 and 683 nm and small aggregation at 615, 615, 620 nm for Li_2Pc, CoPc, and ZnPc respectively.

✓ Thermal analysis was performed both TGA and DTA method showed starting weight loss at (200, 230, 230, 250, and 250 °C) for (Li_2Pc, ZnPc, CuPc, CoPc, and NiPc) respectively, and complexes are did not decayed until more than 900 °C.

✓ The electrical analysis was performed both CV and SWV showed four reduction states of each complex with one oxidation state for (Li, Cu, and Zn) Pcs, and two oxidation states for both NiPc and CoPc, and the redox behaviour for eliminating electron from HOMO to LUMO was (1.08, 1.54, 1.58, 1.61, 1.64) volt for (CoPc, ZnPc, NiPc, CuPc, and Li_2Pc) respectively.

In conclusion, these newly synthesized peripheral metal phthalocyanine complexes from 4-nitrophthalonitrile and 2,6-di-tert-butyl-methylphenol showed very good thermal stability and high redox behaviour, with dissolving easily in some organic solvents like THF, DMF, and DMSO.

The synthesis of unmetalled phthalocyanine was failed and did not form.

RECOMMENDATIONS

For the further investigation to whom who would concern to work and synthesis this type of phthalocyanine, starting to synthesis Iron and Chromium phthalocyanines also unmetalled phthalocyanine but try to another way from these two ways we are failed in synthesize of it, and compare electrical properties results oxidation and reduction of them to our metal phthalocyanines.

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APPENDICES

APPENDIX- 1:

Figure A. 1. The reaction of 4-nitrophthalimide synthesis

Figure A. 2. Reaction of 4-nitrophthalamide synthesis

Figure A. 3. 4-Nitrophthalonitrile reaction synthesis

Figure A. 4. Synthesis of 4(2,6-Di-tert-butyl-4-methylphenoxy)phthalonitrile ligand

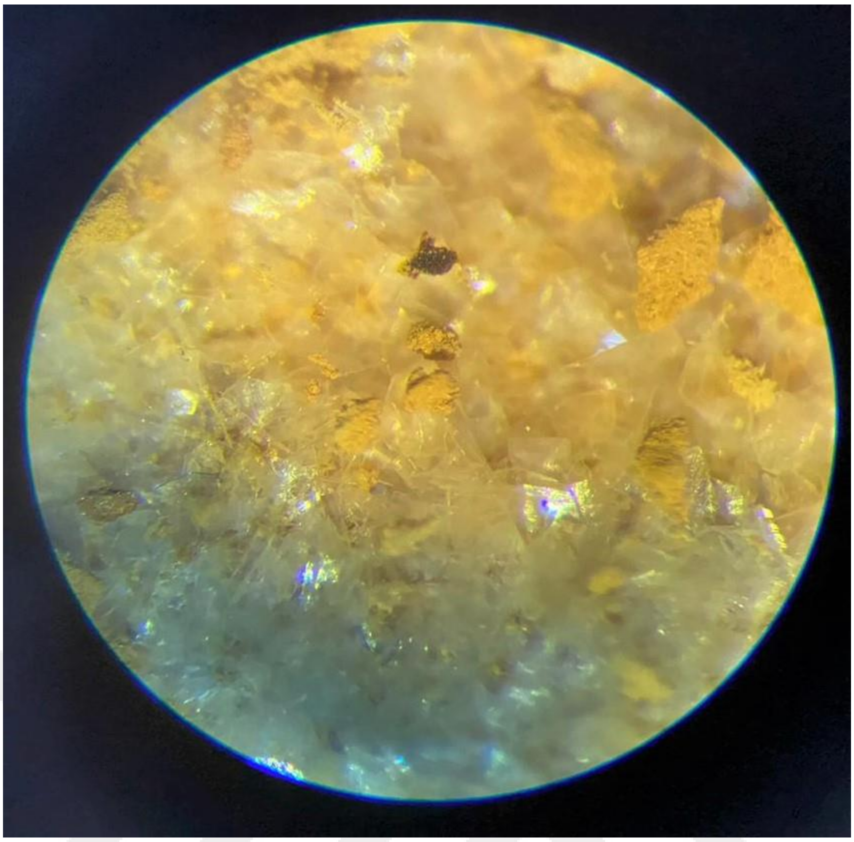

Figure A. 5. Crystalline of 4(2,6-Di-tert-butyl-4-methylphenoxy) phthalonitrile ligand under microscope

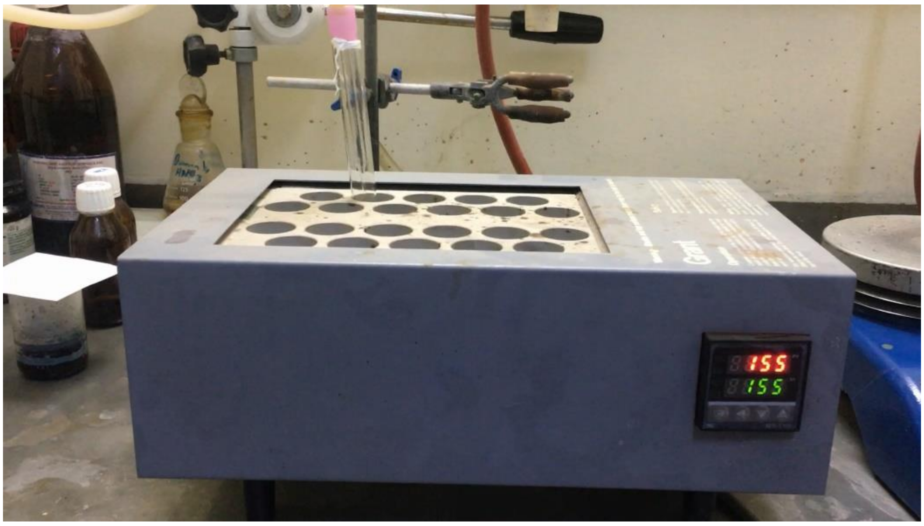

Figure A. 6. Synthesis of metal phthalocyanines under argon atmosphere

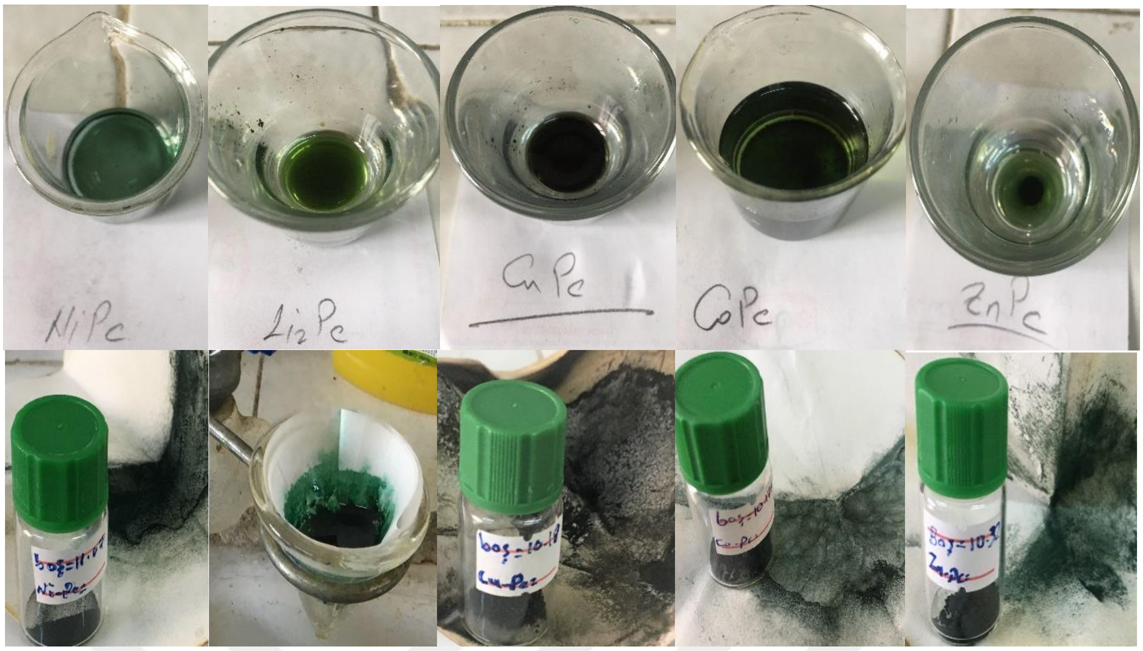

Figure A. 7. Phthalocyanines at both solid and liquid phase

Figure A. 8. Perkin Elmer 1600 FT-IR spectrophotometer

Figure A. 9. Bruker advance III 400 MHz NMR spectrophotometer

Figure A. 10. PG instrument Ltd T80+UV/VIS spectrophotometer

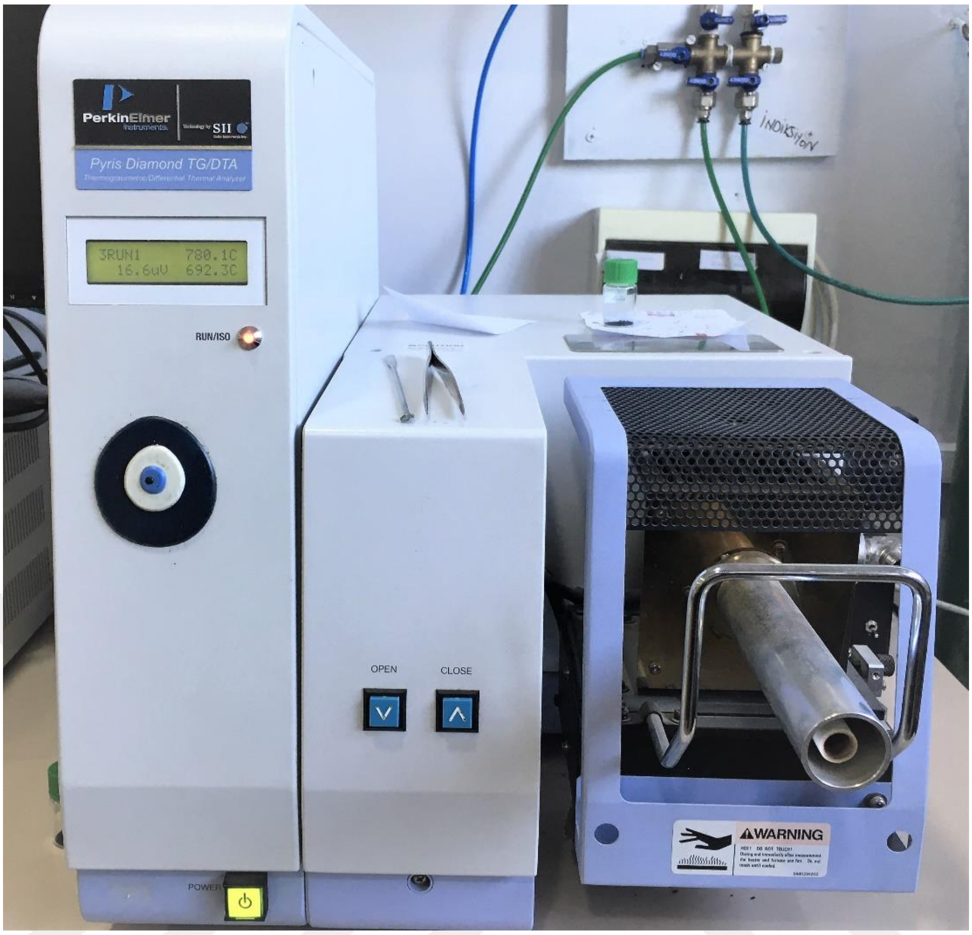

Figure A. 11. Pyris Diamond TG/DTA thermogravimetric/differential thermal analyser

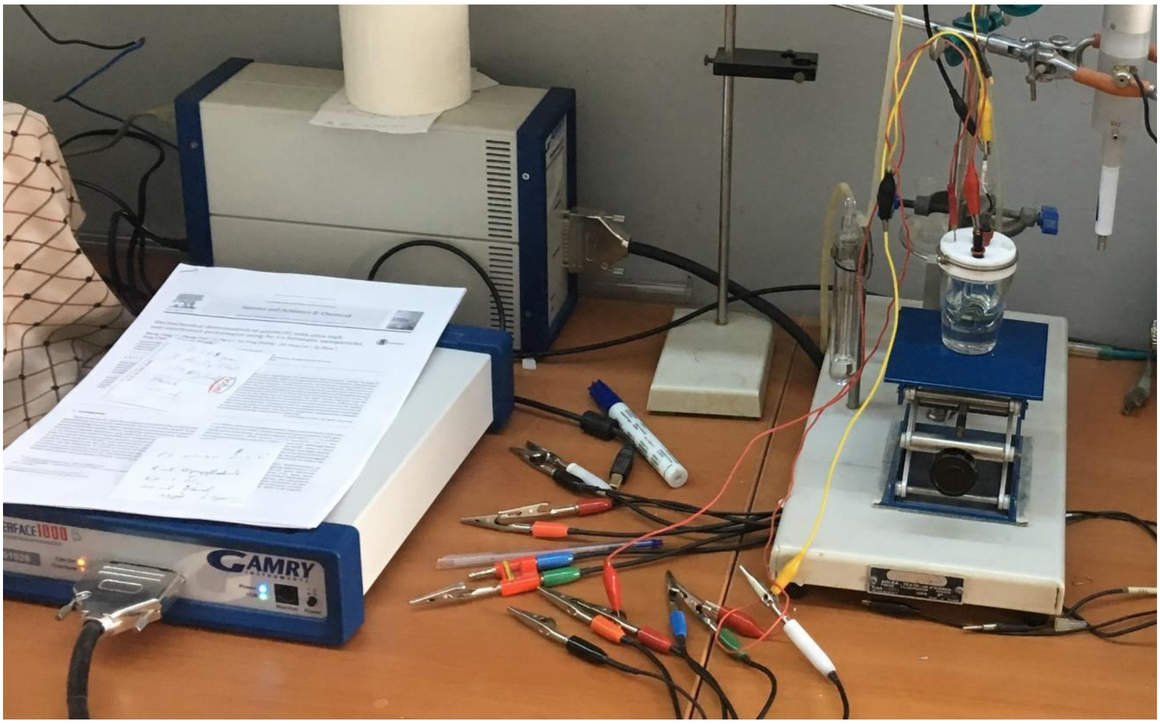

Figure A. 12. Voltametric analyser: Gamry interface 1000 potentiostat/galvanostat

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[redacted]

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