

Synthesis of 4-Aminophenoxy Substituted Nickel Phthalocyanine Complex and Investigation of Electrochemical and Thermal Properties

Othman Abdulrahman Hamad Juki^{1*} and Fatih Biryan²

¹ Chemistry Department, College of Science, University of Raparin, Al Sulaymaniah, 46012 Ranya, IRAQ

² Firat University, Science Faculty, Department of Chemistry, 23200 Elazığ / TÜRKİYE

*Corresponding author: othman.hamad@uor.edu.krd

Abstract

Phthalocyanines, also known as Pc's, are a versatile class of organic compounds that have gained significant attention in various fields including chemistry, materials science, and biology. These macrocyclic compounds are derived from the parent structure of phthalocyanine, which consists of four isoindole units linked by nitrogen atoms to form a ring structure. Phthalocyanines possess unique properties such as high thermal and chemical stability, strong absorption in the visible and near-infrared regions, and good electron-accepting capabilities, making them attractive candidates for a wide range of applications.

In this thesis work, new phthalocyanines metal complexes with p-aminophenol substituted to peripheral position of phthalocyanine ring synthesized. In the first step, reaction of 4-nitrophthalonitrile and p-aminophenol to form 4-(4-aminophenoxy) compound performed. Then the reaction of Nickel(II)acetate salts with 4-(4-aminophenoxy)phthalonitrile in DMF afforded the 4-(4-aminophenoxy)phthalonitrile substituted new nickel phthalocyanine complex. The structures of the synthesized compounds elucidated by melting point, FT-IR, proton and carbon 13 NMR and UV-Visible spectroscopic methods. Additionally, the electrochemical properties investigated by Cyclic and Differential Pulse voltammetry and thermal properties studied by Thermogravimetric Analysis and Differential Thermal Analysis.

Keywords: p-hydroxyphenol, 4-(4-aminophenoxy)phthalonitrile, Nickel Phthalocyanine, Electrochemistry, Thermal analysis.

1. Introduction

Phthalocyanine (H₂Pc) is a organic compound formed by four interconnected isoindole building blocks, creating a large, cyclic aromatic structure. The term phthalocyanine was first used by Linstead in 1933 and developed the first synthetic methods for phthalocyanines [1]. Phthalocyanines and their metal complexes (MPc) tend to aggregate, resulting in low solubility in common solvents. Solubility of phthalocyanines can be increased by adding various substituents to the peripheral and non-peripheral positions of the phthalocyanine [2]. For example, by adding lipophilic groups such as alkyl, alkoxy, and phenoxy groups, which increases the solubility in organic solvents [3, 4]. Similarly, water-soluble phthalocyanine can be obtained by adding carboxyl [5] or sulfonyl [6] groups to peripheral positions of phthalocyanine compounds.

Phthalocyanine has 18 π -electrons, which means it's highly delocalized. This extensive electron cloud gives it wide range of properties and applications in different fields. Phthalocyanines compounds intensely absorb light in the range of 600 to 700 nm, making them appear blue or green. Substituting atoms or functional groups can shift this absorption, altering this absorption range making them to shift colour of phthalocyanine compounds [7].

Phthalocyanines represent an important class of compounds with a broad range of applications. Their unique molecular structures and properties such as thermal and chemical stability, strong absorption in the visible and near-infrared regions, and good charge transport capabilities make them a subject of intensive research. While unsubstituted phthalocyanine most metal complexes are thermally stable up to 500 °C on the other hand, substituted phthalocyanine tend to start decompose over 200 °C. Rich physicochemical properties of phthalocyanine compounds make them attractive candidates for used to be investigated in different field of science and technologies. Some of the most studied field of applications can be given as catalysis [8], electrochemical sensor [9], oxidation reduction catalyst [10], semiconducting research [11], photodynamic therapy of cancers [12] are some of them can be listed. Synthesis of new functionalized of phthalocyanines is expected to further expand their potential applications and impact in the future research.

4-Aminophenol (or para-aminophenol or p-aminophenol) is commonly used use as a developer for black-and-white film, marketed under the name Rodinal.2 [13] 4-Aminophenol is also used as the intermediate of pharmaceutical intermediates, dyes and other fine chemicals and is mainly for the synthesis of paracetamol, clofibrate ketone, vitamin B1 and compound nicotinamide. It can also be used for gold assay as well as determination of copper, iron, magnesium, vanadium, nitrite and cyanate, antioxidants.

2. Experimental

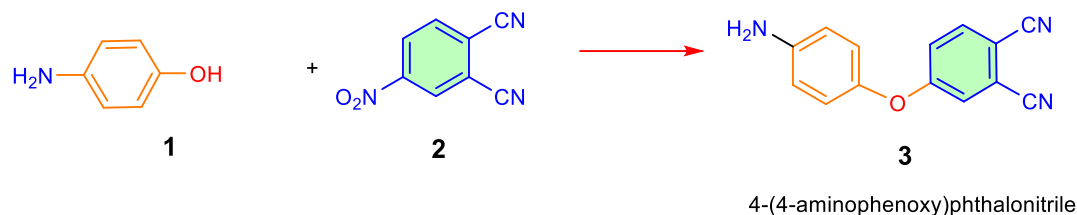
Electronic spectra obtain by Shimadzu 1900 UV–Visible spectrophotometers. IR spectra were recorded on a Perkin Elmer Spectrum one FTIR spectrometer in KBr pellets. ^1H NMR spectra were recorded on a Bruker 400 MHz Avance spectrometer with tetramethyl silane as internal standard. Elemental analyses were performed by Leco CHNS 932. Electrochemical works done by Gamry Interface 1010 B, in DMF, with glassy carbon electrode as working electrode, H_2SO_4 as supporting electrolyte using ferrocene/ferrocenium as sudo reference electrode. Thermal characterizations were determined by SHIMADZU TGA 50 series thermal analysis instrument with 20 °C/min scan rate. All other reagents and solvents were of reagent-grade quality and were obtained from commercial suppliers. DMF used for electrochemical works was purified as described by Perrin and Armarego [14]

3. Result and Discussions

3.1. Synthesis of 4-(4-aminophenoxy)phthalonitrile

In 100 ml of three-neck round bottom flask, 25 mL DMF was added then the reaction vessel flashed with Argon gas for 10 minutes. 1.09 gram (10 mmol) 4-aminophenoyl was added, then (1.73 gram, 10 mmol) of 4-Nitrophthalonitrile was added at room temperature and after 15 minutes, the reaction temperature increased 90 °C under argon atmosphere. 2.50 Gram potassium carbonate was added the reaction mixture, portion wise during in an hour. the colour of mixture changed to dark brown. The reaction was monitored by by FTIR spectroscopy following the intense $-\text{NO}_2$ peak at 1531 and 1354 cm^{-1} . The reaction was completed after 24 hours after cooling down to room temperature, it was precipitated in water and washed with distilled water, then dried at room temperature yield was 1.65 g, (70.2 %). $\text{C}_{14}\text{H}_9\text{N}_3\text{O}$,

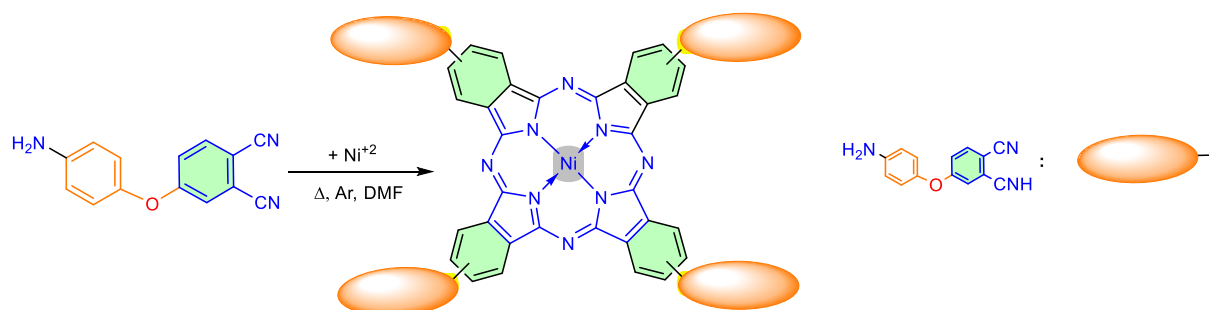
Elemental Analysis (%): C, 71.37; H, 3.69; N, 17.62. IR spectrum (cm^{-1}): 3349, 3212, 3053, 2228, 2208, 1568, 1504, 1481, 1362, 1246, 1226, 1200, 1081, 1008, 949, 831, 729, 662, 524, 497. ^1H NMR: (DMSO d_6): δ = 8.16 (H, d, Ar-H), 7.94 (1H, s, Ar-H), 7.58-7.46 (1H, m, Ar-H), 6.72-7.86 (4H, m, Ar-H), 5.36 (2H, s NH_2)



Scheme 1. Synthesis of 4-(4-aminophenoxy)phthalonitrile

3.2. Synthesis of 4-aminophenoxy substituted nickel phthalocyanine

0.250 gram (1.06 mmol) of 4-(4-aminophenoxy)phthalonitrile, and 0.100 gram (0.56 mmol) Ni(II) acetate, 3.0 mL DMF and 3 drop of DBU was added in to a 20 cm long test tube under Argon atmosphere. Then reaction mixture heated to reflux temperature (153 °C) on the temperature-controlled heating block under argon atmosphere, the colour of the reaction mixture turned to dark green in about 12 hours, then the reaction was cool down to room temperature and diluted with 5 ml of ethanol to slow down the precipitation. The reaction mixture added drop by drop to 100 ml of water while stirring to precipitate. The precipitate filtered washed several times with water, then with ethanol. Green product dried at room temperature first then at 80 °C in drying oven, yield was 0.105 g (39.5 %). $\text{C}_{56}\text{H}_{36}\text{N}_{12}\text{NiO}_4$ Elemental Analysis (%): C, 66.88; H, 3.41; N, 16.45. IR spectrum (cm^{-1}): 2978, 2922, 2852, 1632, 1506, 1472, 1383, 1269, 1229, 1162, 1092, 1048, 879.



Scheme 2. Synthesis of NiPc

3.3. UV Spectroscopy of NiPc

In UV/Vis measurements of phthalocyanines at about 10^{-5} M concentrations in known organic solvents, gives an intense π - π^* transitions, called **Q** bands, are observed in the range of 600-700 nm. This region is also a characteristic to distinguish metal-free and metal-containing phthalocyanines. Metal-free phthalocyanines give two equal bands in this region on the other hand metallic phthalocyanines give a single intense band and a shoulder in the same region. In general, a strong band at 675 nm, a shoulder at 630 nm is observed in the UV/Vis spectra of metallo-phthalocyanines in organic solvents. These bands arise from monomeric phthalocyanine. It is seen that the intensity of the **Q** band at 675 nm decreases considerably while increasing the band at 630 nm in the spectrum which shows us the formation of aggregation. Likewise, when the concentration is low enough, only the monomer structure is present and

the band seen around 700 nm from the two absorption bands becomes stronger. Since the increase in concentration creates aggregation; dimer, trimer etc [6]. The characteristic bands seen around 300 nm in the UV/Vis spectra of phthalocyanines correspond to $\pi\text{-}\pi^*$ transitions called Soret or **B** band.

UV-visible Spectra of NiPc complex (Figure 1) obtained in DMF, to increase the solubility of NiPc two drops of concentrated H_2SO_4 added to the DMF. The spectra have three bands in the 300-800 nm range, a shoulder at 390 nm (Soret band), 620 and 670 nm **Q** bands [15]. As it can be seen from the UV-visible spectra of NiPc, there is a strong aggregation of the complex can be seen as the intensity of bands at 620 nm is higher than 670 nm. This shows the strong aggregation of NiPc even with the addition of H_2SO_4 .

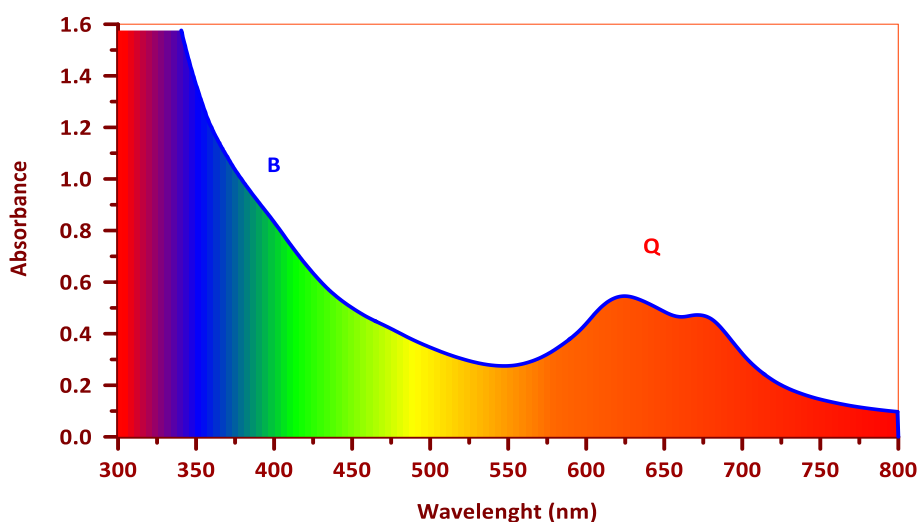


Figure 1 UV Spectra of NiPc in DMF

3.4. Thermal Analysis of NiPc

Thermogram of NiPc shows the degradation of complex starting at about 240 °C with two step decompositions with a total of 62% weight loss (Figure 2). In the first step starting from 240 to 410 °C, with 37% weight loss followed by the second step to 480 °C with 25% weight loss. Both decompositions are exothermic and the complex started to decompose before melting. The first decomposition is about the loss of four 4-aminophenyl groups from the phthalocyanine ring (calculated 36.8%). Because the thermogram went up to 700 °C, we could not get complete decomposition of the compound.

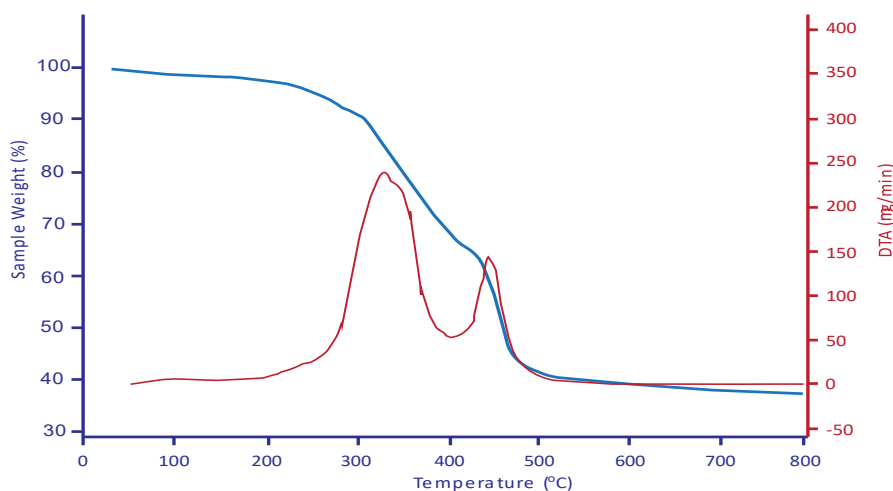


Figure 2. Thermogram of NiPc, 20 °C/min scan rate under N_2 atmosphere, (Blue line TGA, Red line DTA)

3.5. Electrochemistry of NiPc

The voltammogram of NiPc (Figure 3) shows four redox processes (R1, R2, X and O1). Because of poor solubility of NiPc complex in DMF, the ratio of peak currents is vague, therefore nature of the reversibility of redox can not be judged from CV voltammogram. On the other hand, DPV voltammogram gives clearer results compared to CV, these four redox potentials can be seen more clearly. Three of the four redox potentials R1 (-1.21 V), R2 (-1.45 V) and O1 (0.15 V) are NiPc based redox potentials indicated by X (-0.45 V) comes from the solvent containing H₂SO₄ as supporting electrolyte as well as contributing to increase the solubility of NiPc. The same redox wave appeared when DMF and H₂SO₄ (as supporting electrolyte) used for background check for the CV and DPV. The R1 and R2 redox processes are due to Ni(II)Pc-2/Ni(II)Pc-3 and Ni(II)Pc-3/Ni(II)Pc-4 respectively. On the other hand O1 is belong to first oxidation process of NiPc (Ni(II)Pc-2/Ni(II)Pc-1). In addition, no metal-based redox process since the Ni²⁺ ion is not redox active in phthalocyanine complexes [16].

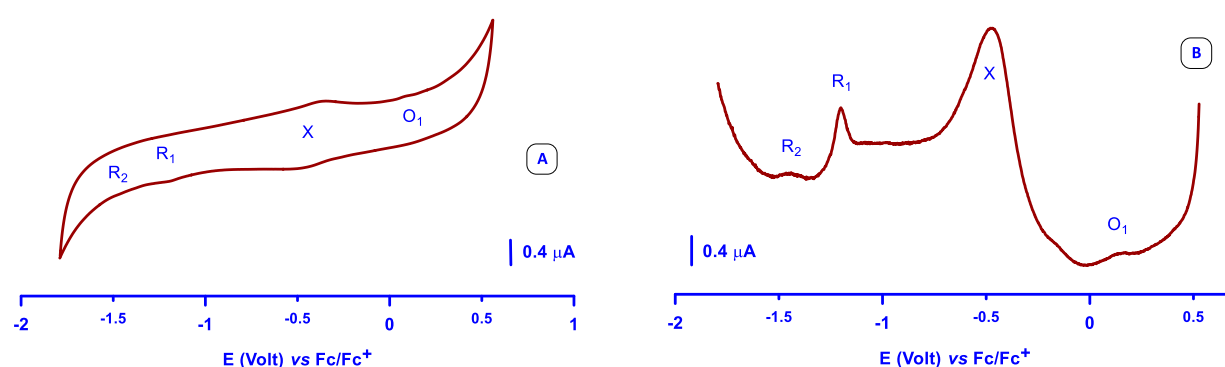


Figure 2 Cyclic voltammogram (A) of NiPc in DMF as H₂SO₄ supporting electrolyte, 100 mV/s, glassy carbon working electrode and Differential Pulse (B) voltammogram, in DMF, glassy carbon working electrode against ferrocene/ferrocenium sudo reference electrode.

4. Conclusions

A new NiPc peripherally substituted with 4-aminophenol moieties was synthesised and characterised utilising numerous physicochemical techniques. UV-visible spectra show strong aggregation of NiPc in DMF and exhibiting electronic properties typical of symmetrical NiPcs. Its absorption spectral data agreed well with the phthalocyanine complexes. Thermal analysis and electrochemical results supporting the structure of the NiPc.

Conflict of Interests

The authors declare no conflict of interest.

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