MW Journal of Science

e-ISSN: 3023-770X

https://doi.org/10.5281/zenodo.14786670 MW Journal of Science, 2024, 1, 3, 25-41

Synthesis, Thermal and Electrochemical Properties of Dipeptide Substituted Metallo-Phthalocyanine Complexes

Sunusi IDRIS[1]*, Eray ÇALIŞKAN[2], Sinan SAYDAM[3]

[1] Department of Chemistry, Aliko Dangote, University of Science and Technology, Wudil, NIGERIA
[2] Bingöl University, Faculty of Science, Department of Chemistry, Bingöl / TÜRKİYE
[3] Fırat University, Faculty of Science, Department of Chemistry, 23200 Elazığ / TÜRKİYE

*Corresponding author: sunusiidris73@gmail.com

Abstract

A novel Tyrosine-Phenylalanine dipeptide substituted metallo phthalocyanine complexes was Synthesis, characterized, their thermal and electrochemical properties was established as the main purpose for this work. The dipeptide methyl (tert-butoxycarbonyl) tyrosyl-D-phenylalaninate (3) was synthesis through peptide coupling reaction of (tert-butoxycarbonyl) tyrosine (1), and phenylalanine (2) and it was reacted with 4-nitrophthalonitrile (4) to form dipeptide substituted phthalonitrile (5).

The dipeptide substituted phthalonitrile ligand undergo cyclotetramerization in the presence of metals salt of Co(II), Cr(III) and Ni(II) acetate in Dimethylformamide (DMF) at 150 °C to form Tyrosine-Phenylalanine dipeptide substituted phthalocyanine complexes of respective metals. The formation of these synthesized compounds was verified by melting point, FT-IR, UV-visible, 1H NMR and 13C NMR and mass spectroscopy techniques. Thermal properties were investigated by TGA and DTA analysis. Electrochemical measurements of phthalocyanine complexes were performed by Cyclic or Square wave voltammetry in DMF

Keywords: Phenylalanine, Phthalocyanine, Thermal analysis, Electrochemistry, Dipeptide, Metallo-phthalocyanine

1. Introduction

Phthalocyanines (Pcs) has been a subject of a great deal of a wide range of research for over 100 years. These has led to the synthesis of both metallo and non-metallo varieties of substituted Pcs [1]. In view of that, the main purpose for these substitutions was to enhance the properties and diversified the applications of Pcs into broader scientific and technological aspects. Pcs with an 18-π electron configuration from 8 carbons and 8 nitrogen-containing atoms in the innermost ring, are stable and useful chemical substances [2, 3] . Pcs have several uses in materials science, including gas, biosensors and chemical sensors, molecular solar cells, industrial catalytic systems, photodynamic cancer therapy, optical data storage, printer inks, nonlinear optic, nanotechnology, electrochromic displays, electrochemical and electrical applications [1, 4-6].

The spectroscopic characteristics of phthalocyanines can vary significantly on account of the difference of substituents attachment[3, 7, 8]. Therefore, Pc possess properties of being easily modified with same or various substituents and forming or generating diverse properties depending on the substituent connected[9, 10]. Because the bulk properties of a Pcs macromolecule are substantially tied on the characteristics of distinct molecules, different alterations to these individual compounds have been attempted to increase their efficiency as advanced materials[6, 11].

Recent research has focused on developing novel functional structures employing peptides and its derivatives, taking into account the function of both amino acids and peptides. The goal of assembling peptides into Pc is to enhance the effectiveness of the desired molecules. The usage of peptide conjugates in macro molecule design has increased in recent years, making the synthesis of these families of molecules crucial [9, 12, 13].

The objective of this study is to synthesize a new tetra dipeptide substituted metallo phthalocyanines using cyclotetramerization approach [12-15], characterize and evaluate their thermal and electrochemistry properties. The characterization of complex can be successfully achieving through FT-IR and UV-vis spectroscopies. Generally, two characteristic peaks are usually seen in UV-visible spectrum of phthalocyanine compounds with or without metals. The presence of these peaks can be used to estimate whether phthalocyanine complex is formed and whether the complex is metallo or non-metal form. The first UV-vis absorption of phthalocyanine known as **B**-band or Soret occurs around 320-370 nm due to transitions from the deeper **n** level to the lowest unoccupied molecular orbital (LUMO) **($n \rightarrow \pi^*$)**. While the second absorption peak **Q**-band occur around 650-700 nm as a result of transition **($\pi \rightarrow \pi^*$)** from highest occupied molecular orbital (HOMO) to (LUMO) [16, 17]. Further more, there is a shoulder-shape peak seen around 600-650 nm due to the peaks aggregation.

In view of this, 3 first row transition metals Cr, Co and Ni was selected to coordinate with 4 Tyrosine-Phenylalanine dipeptides substituted phthalonitrile compounds. The dipeptide was obtained from the coupling reaction [18, 19] of tyrosine amino acid (Boc-Tyr-OH) with methyl esters of *L*-phenylalanine in presence of coupling reagent 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) and N-Methyl Morpholine (NMM) base as catalyst as shown in **Scheme 1.** The dipeptide was later treated with 4-nitrophthalonitrile in Argon atmosphere with action of K_2CO_3 to formed the dipeptide substituted phthalonitrile. Although there are few numbers of report where peptides link as substituent on phthalocyanine but there was none of such record was published in the literature for dipeptide derivatives.

2. Experimental

2.1 Materials and equipment

FT-IR spectra of the intermediate step products and complexes were formed into discs with KBr, and their spectra were obtained in the range of 4000-400 cm^{-1} with the Perkin Elmer Spectrum 1000 Series FT-IR spectrometer. ^{13}C and ^{1}H NMR spectra were taken with the Bruker ultra-shield DPX-400 MHz NMR spectrometer with DMSO-d_6 as solvent and Tetra methyl silane as an internal standard. The Mass measurement of both dipeptide, intermediate steps products and complexes were performed on a Bruker Microflex LT MALDI-TOF MS Spectrometer. UV spectra of samples were analysing with UV-1900i SHIMADZU UV-VIS Spectrophotometer Instruments with wavelength range between 200 -800 nm, using 1 cm quartz cell with light path in DMF solvent containing sample. While the Thermal analysis was taken with Shimadzu TA-60WS (TGA/DTA). All of the solvents and reagents were purchased from commercial sellers and were of reagent grade purity. Anhydrous metal salts were dried at 100°C after being finely crushed. Thin-layer chromatography (TLC) was used in each step to assess the products' purity.

2.2 Synthesis of Methyl (tert-butoxycarbonyl) tyrosyl-*L*-phenylalaninate (Boc-Tyr-Phe-OCH_3) **(3)**

The reaction as shown in **Scheme 1** was conducted by addition of 2g of Tyrosine amino acid (Boc-Tyr-OH) (1.0 equivalent) **(1)** with the amine group protected, 1.53g of Phenylalanine methyl ester (NH_2-Phe-OCH_3.HCl) (1.0 equivalent) **(2)** and 1.37g of coupling reagent 2-Chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) (1.10 equivalent) as coupling agent in 250 ml plate bottom flask. An appropriate amount 25 ml of Acetonitrile solvent were added in to the reaction flask at room temperature with constants stirring. On continuous stirring, 1.95 ml of N-Methyl Morpholine (NMM) Base were added to the reaction mixture dropwise. The reaction was allowed to continuous stirring for 16 to 24 hours with sequences of Thin Layer Chromatography (TLC) tests to monitor the completion of reaction using free coated Aluminum TLC Paper as stationary phase and mixture of Ethyl acetate and n-Hexane solvent system in a ratio of 3:4 as mobile phase [9, 20, 21].

On completion of the reaction, then the solution of the mixture was filtered to remove any unreacted residue and the solvent in the filtrate was evaporated under a reduced pressure using vacuum rotary evaporator. The residue was dissolved in 10 ml Acetone and precipitated in 200 ml of water in a Baker. The precipitate was filtered and dried at room temperature. The product is white powder weight 2.84g with percentage yield of 90.16%, molecular weight 442.51 and molecular formula $C_{24}H_{30}N_2O_6$. FT-IR (ATR, cm^{-1}) $\boldsymbol{\nu}_{\mathbf{N\text{-}H}}$**,** $\boldsymbol{\nu}_{\mathbf{OH}}$ 3214, 3304, 3339, $\boldsymbol{\nu}_{\mathbf{C\text{-}H(Aliphatic)}}$ 2855, 2932, 2963, $\boldsymbol{\nu}_{\mathbf{C\text{-}H(Aromatic)}}$ 3030, 3064, 3087, $\boldsymbol{\nu}_{\mathbf{C=O}}$ 1660 (Amid C=O), 1686 (Boc group C=O), 1706 (Ester C=O), $\boldsymbol{\nu}_{\mathbf{C=C}}$ 1518, 1536, 1597, 1615, **(Figure 1)**. ^{13}C –APT NMR, DMSO-d_6, 298 K: δ ppm, 155.57 C^1, 115.24 C^2, 128.74 C^3, 128.50 C^4, 037.09 C^6, 056.35 C^7, 156.18 C^9, 074.44 C^{10}, 028.61 C^{11}, 172.48 C^{12}, 053.97 C^{14}, 172.31 C^{15}, 052.32 C^{16}, 037.18 C^{17}, 137.49 C^{18}, 129.61 C^{19}, 130.54 C^{20}, 127.05 C^{21}, **(Figure 2)**. ^1H NMR, DMSO-d6, 298 K: δ ppm, 9.19 (1H, s, H^5 (–OH)), 8.32–8.34 (1H, d, H^{13} (–NH)), 7.23–7.30 (5H, m, H^{19}, H^{20} and H^{21}), 7.0–7.02 (2H, d, J = 8.8 Hz, H^3), 6.81–6.83 (1H, d, H^8 (–NH)), 6.63–6.65 (2H, d, J = 8.4 Hz, H^2), 4.49–4.53 (1H, q, H^7), 4.08–4.09 (1H, q, H^{14}), 2.96–3.07 (2H, m, H^{17}), 2.56–2.59 and 2.74–2.79 (2H, H^5), 1.31 (9H, s, H^{11}) **(Figure 3).** MS (MALDI − TOF) m/*z* (%): calculated for ($C_{24}H_{20}N_2O_6$), 442.51; found, 442.548 $[M]^+$, 386.609 [M− C(CH3)3], 342.542 [M− Boc] **(Figure 4)**.

2.3. Synthesis of Methyl ((S)-2-((tert-butoxycarbonyl) amino)-3-(4-(3,4-dicyanophenoxy) phenyl) propanoyl)-*D*-phenylalaninate (Boc-Tyr-Phe-OCH_3-O-PN) (5)

In a 250 ml three neck bottom flask placed on hot plate fitted with magnetic stirrer, thermometer and rubber tube suppling Argon gas, 1.98g (11.41 mmol) of dried 4-Nitrophthalonitrile (**4**) and 5.0g (11.30 mmol) of dried Methyl (tert-butoxycarbonyl) tyrosyl-*L*-phenylalaninate (**3**) was place in the flask. The temperature was rise between 80 – 95 ^{0}C with addition of K_2CO_3 as catalyst in portion over 1.5 hours while maintaining the temperature at 90 ^{0}C. On the addition of K_2CO_3 the colour of the reaction medium gradually changed to dark brown. The reaction as shown in **Scheme 2** was proceeded for 48 hours on constants stirring and supplied of Argon gas at 90 ^{0}C with regular checking of FT-IR spectral of the reaction mixture at certain intervals for monitoring a completely disappearance of $–NO_2$ peak at 1538 cm^{-1} and 1356 cm^{-1} and appearance of -C≡N band at 2230 cm^{-1}[22] as shown in (**Figure 5**) . The mixture was cooled to room temperature, precipitated in 600 ml of distilled water with addition of few drops of 1M HCl (to bring down pH of the medium from basic to pH 6) and salt solution all to facilitation a good precipitation of the product. The precipitated product was filtered, washed with plenty of water and air dried at room temperature. The colour of the resulting product Methyl (2-((tert-butoxycarbonyl) amino)-3-(4-(3,4-dicyanophenoxy) phenyl) propanoyl)-*L*-phenylalaninate **(5)** is light brown, the yield is 4.35g (67.64%). The FT-IR (ATR, cm^{-1}) $\boldsymbol{\nu}_{\mathbf{C\equiv N\ (Nitrile)}}$ 2230, $\boldsymbol{\nu}_{\mathbf{N\text{-}H(Amide)}}$ 3300, $\boldsymbol{\nu}_{\mathbf{C\text{-}H(Aliphatic)}}$ 2928, 2934, 2977, $\boldsymbol{\nu}_{\mathbf{C\text{-}H(Aromatic)}}$ 3032, 3039, 3065, $\boldsymbol{\nu}_{\mathbf{C=O}}$ 1660 (Amide C=O), 1717 (Boc group C=O), 1743 (Ester C=O), $\boldsymbol{\nu}_{\mathbf{C=C(Aromatic)}}$ 1564, 1591**(Figure 5)**.

2.3 Synthesis of Phthalocyanine complexes of Methyl ((S)-2-((tert-butoxycarbonyl) amino)-3-(4-(3,4-dicyanophenoxy) phenyl) propanoyl)-*D*-phenylalaninate compounds (6a,6b and 6c)

An Argon gas was passed for 2 minutes through 3 ml of DMF at 130 ^{0}C in a Borosilicate Glass Vacuum Cold Trap Glass Bubbler with 10 mm serrated Hose, 225 mm length below the 29/42 joint reaction tube. 0.204g (0.359 mmol) of **(5)** was added in to each of the reaction tubes follow by addition of 0.0270g (0.0897mmol) of $Cr(Ac)_3 4H_2O$, 0.0223g (0.0897 mmol) of $Co(Ac)_2 4H_2O$ and 0.0191g (0.0897 mmol) of $Ni(Ac)_2 4H_2O$ respectively as shown in **Scheme 2**. After 1 hour, if there is no colour change, 3 drops of Triethanolamine (TEA) was added to the reaction medium and the temperature was increased to 150 ^{0}C. The product **6a-**CrPc was refluxed for 48 hours, **6b-**CoPc for 2 hours and **6c-**NiPc was reflux for 2 hours. The green colour products formed and the disappearance of -C≡N band at 2230 cm^{-1} in the FT-IR and appearance Q band between 660 and 700 nm in UV-visible spectral confirmed the formation of complexes[22]. The products were precipitated in 200 ml of water and filtered to dried at 60 ^{0}C in oven. These was later purified by stirring in hot ethanol for 1hour, filtered and dried in a vacuum oven at 60 ^{0}C.

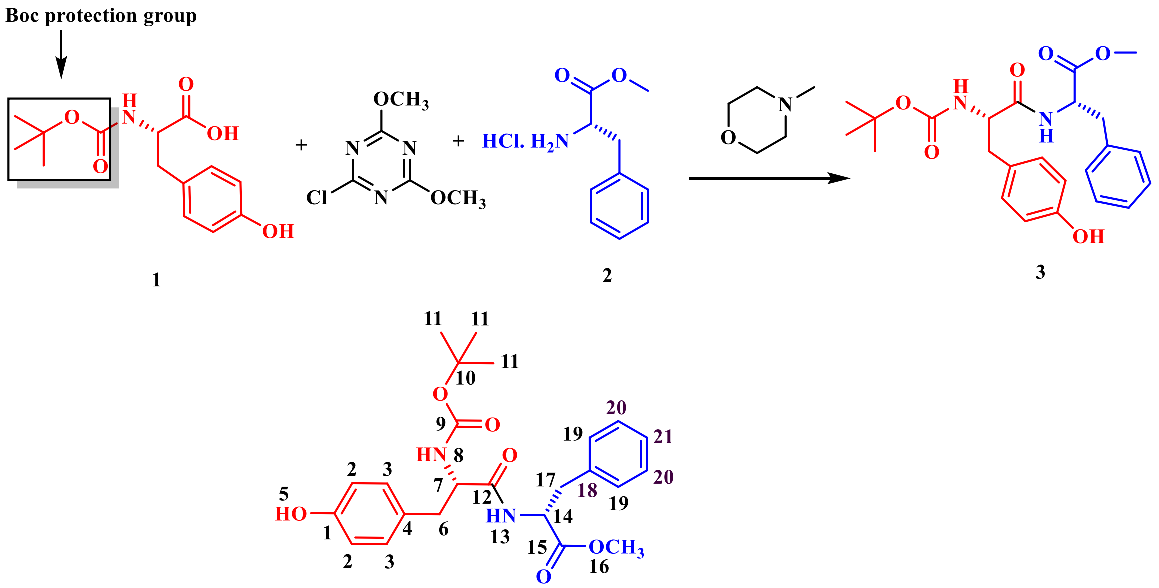
2.4. Electrochemistry Experimental

A reagent grade chemical was used throughout the experiment. The solvents were purified following standard technique reported in [23, 24] and stored over molecular sieves. Cyclic voltammetry (CV) experiments were conducted in non-aqueous reagent employed tetra butyl ammonium tetra fluoro borate (TBAFB) (Fluka) as the supporting electrolyte and a Gamry 600 Potentiostat/Galvanostat/ZRA as reference. For CV measurements in dimethylformamide (DMF), a three-electrode setup was employed, consisting of a glassy carbon working electrode, a platinum wire counter, and a platinum wire quasi-reference electrode. The ferrocene/ferrocenium pair (Fc/Fc+) was employed as an internal standard, and potentials were reported in relation to Fc/Fc+ in non-aqueous solutions. Square wave voltammetry analysis was performed at a frequency of 5 or 10 Hz, amplitude of 40 mV, and step potential of 4 mV. High purity Argon is used to de-oxygenate the cell at least 10 minutes before conducting electrochemical tests, and the solution is shielded from air by an argon cover throughout the entire process[5].

3. Results and discussion

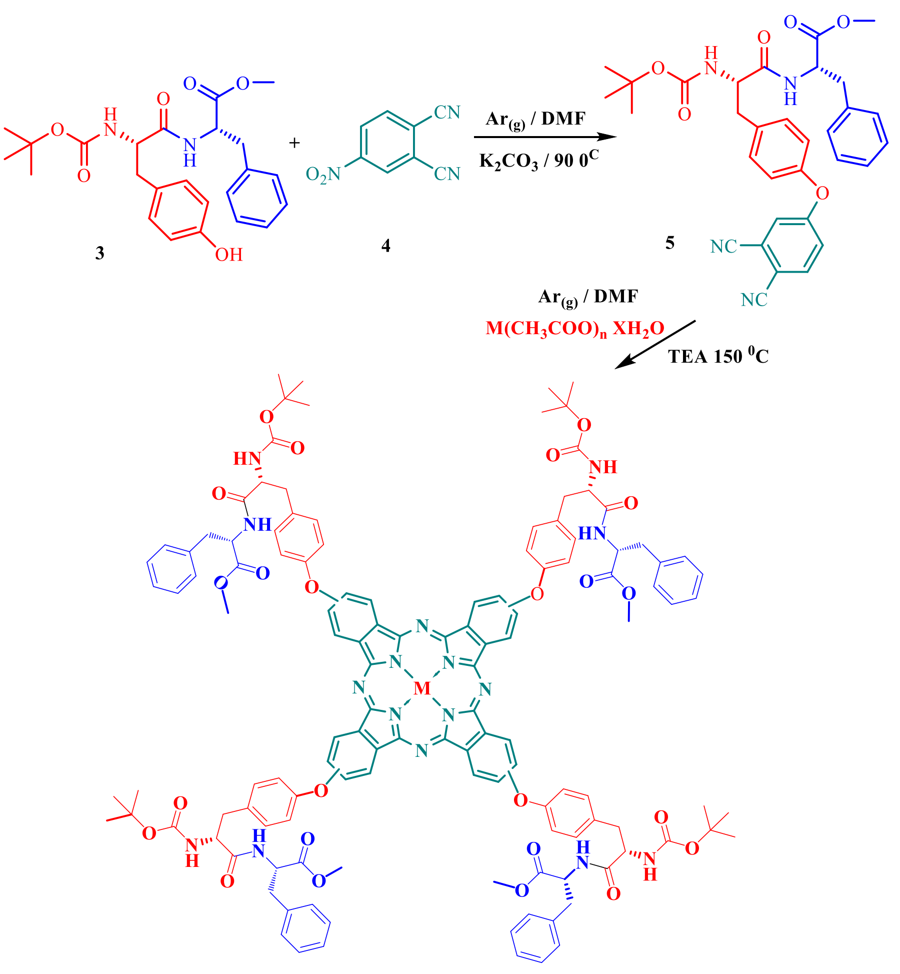
3.1 Synthesis and Characterization of Dipeptide and Dipeptide Substituted Phthalocyanine complexes.

The synthesis, characterization and evaluation of Dipeptide and Dipeptide substituted phthalocyanine was started with amino group protected, carboxyl group active Tyrosine amino acid (Boc-*L*-Tyrosine) **(1)** that is Tyr-OH as starting compound coupled with Phenylalanine amino acid methyl ester **(2)** in the presence of (CDMT) coupling reagent and (NMM) base as catalyst to formed Tyr-Phe dipeptide[21] **(Scheme 1)**.



methyl (*tert*-butoxycarbonyl)-*L*-tyrosyl-*D*-phenylalaninate

Scheme 1. Synthesis of Tyr-Phe Dipeptide Substituent



Where M= Cr, Co or Ni
X= 4
n = 2 or 3

6a=CrPc
6b=CoPc
6c =NiPc

Scheme 2. Synthesis Tyr-Phe Dipeptide Substituted Metallo Phthalocyanine complexes

Table 1. Summary Spectroscopies and Elemental Analyses values interpretations of Methyl (tert-butoxycarbonyl) tyrosyl-*L*-phenylalaninate (Boc-Tyr-Phe-OCH_3) (3).

<table>
<tr><th>FT-IR (cm^{-1})</th><th>^{1}H-NMR (ppm)</th><th>^{13}C –APT NMR (ppm)</th></tr>
<tr><td rowspan="2">ν_{N-H}, ν_{OH}
3214, 3304, 3339
$\nu_{C-H(Aromatic)}$,
3030, 3064, 3087
$\nu_{C-H(Aliphatic)}$
2855, 2932, 2963
$\nu_{C=C}$
1518, 1536, 1597, 1615
$\nu_{C=O}$
1660 (Amide C=O)
1686 (Boc Protection Group C=O),
1706 (Ester C=O),</td><td rowspan="2">1.31 (9H, s, H^{11}),
2.56-2.59 and 2.74-2.79 (2H, H^5),
2.96-3.07 (2H, m, H^{17}),
3.06 (3H, s, H^{16}),
4.08-4.09 (1H, q, H^{14}),
4.49-4.53 (1H, q, H^7),
6.63-6.65 (2H, d, J=8.4 Hz, H^2),
6.81-6.83 (1H, d, H^8 (-NH)),
7.0-7.02 (2H, d, J=8.8 Hz, H^3),
7.23-7.30 (5H, m, H^{19}, H^{20} and H^{21}),
8.32-8.34 (1H, d, H^{13} (-NH)),
9.19 (1H, s, H^5 (-OH))</td><td>155.57 C^1 , 172.48 C^{12},
115.24 C^2 , 053.97 C^{14},
128.74 C^3 , 172.31 C^{15},
128.50 C^4 , 052.32 C^{16},
037.09 C^6 , 037.18 C^{17},
056.35 C^7 , 137.49 C^{18},
156.18 C^9 , 129.61 C^{19}
074.44 C^{10} , 130.54 C^{20}
028.61 C^{11}, 127.05 C^{21}</td></tr>
<tr><td>**DMSO-d$_6$**
^{13}C –APT : 39
^{1}H-NMR : 2.51 and 3.36</td></tr>
<tr><th>MALDI-TOF MSc</th><th colspan="2">Elemental analyses (%)</th></tr>
<tr><td>**Theoretical**
Mw : 442.51 g/mol
Experimental
[M] : 442.548 m/z
[M-C(CH_3)$_3$] : 386.609 m/z
[M-Boc] : 342.542 m/z</td><td colspan="2">**$C_{24}H_{20}N_2O_6$ (Mw: 442.51 g/mol)**
Theoretical: C, 65.14; H, 6.83; N, 6.33
Experimental: C, 65.20; H, 6.88; N, 6.30</td></tr>
</table>

The structure of the **(3)** were characterized and verified using FT-IR, MALDI-TOF mass spectrometry, ^{1}H and ^{13}C-APT NMR spectroscopy and elemental analysis. The summary of major and most important Spectroscopies peaks and Elemental analysis values interpreted for Methyl (tert-butoxycarbonyl) tyrosyl-*L*-phenylalaninate dipeptide compound is given in Table 1. The FT-IR spectra of the dipeptide were interpreted and evaluated by comparing with the major peaks of the (Boc-*L*-Tyrosine) amino acid FT-IR (cm^{-1}) spectra. There are some slightly shifts in the stretching vibration of carbonyl peaks of Tyrosine $\nu_{C=O(Amide)}$ 1674**,** $\nu_{C=O(Ester)}$ 1726**,** and $\nu_{C=O(Boc\ Protection\ group)}$ 1699 compare with that of the dipeptide with $\nu_{C=O(Amide)}$ 1660, $\nu_{C=O(Ester)}$ 1706, $\nu_{C=O(Boc\ Protection\ group)}$1686 as observed in **Figure 1a** . The disappearance of asymmetric stretching and symmetric stretching peaks at 1538 and1356 cm^{-1} and appearance of sharp single stretching peak at 2230 cm^{-1} in **Figure 1b** which is associated with - NO_2 and –CN groups respectively of 4-nitrophthalonitrile **(4)** confirmed the formation of Boc-Tyr-Phe-OCH_3-O-PN **(5)** (**Scheme 2)**.

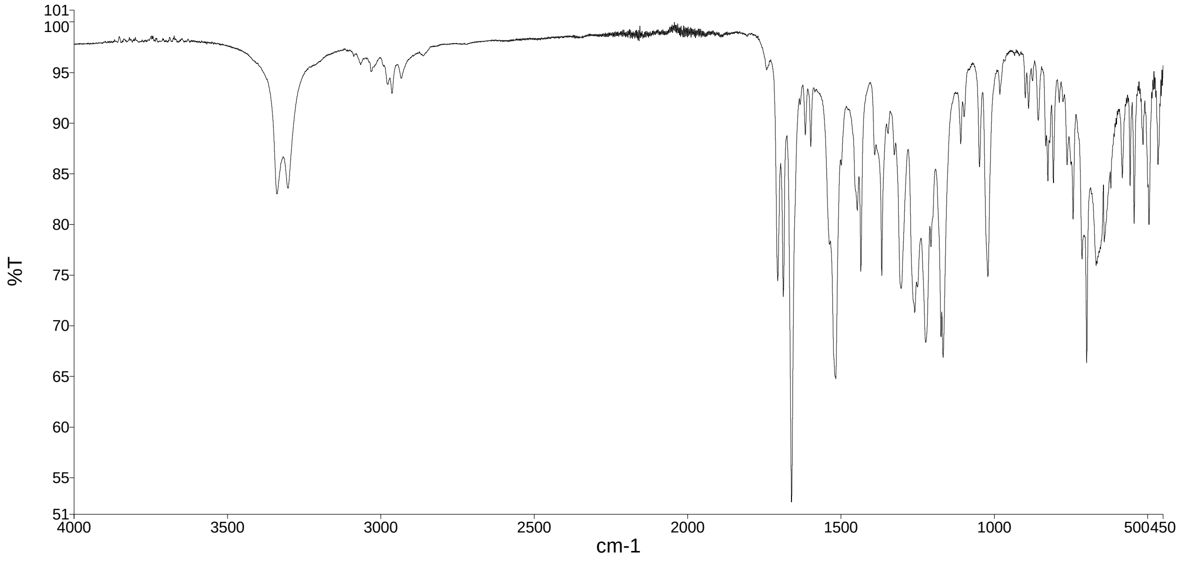


Figure 1a. FT-IR Spectrum (ATR) of Boc-Tyr-Phe-OCH_3 Compound (3)

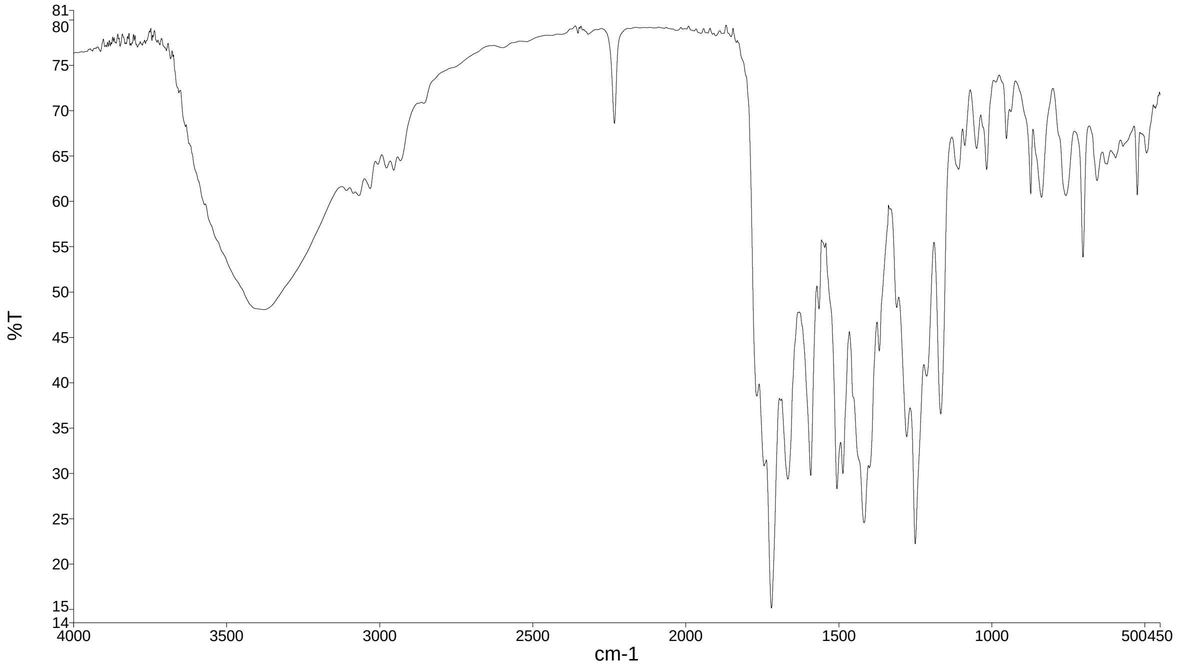


Figure 1b. FT-IR Spectrum (ATR) of Boc-Tyr-Phe-OCH_3-O-PN Compound (5)

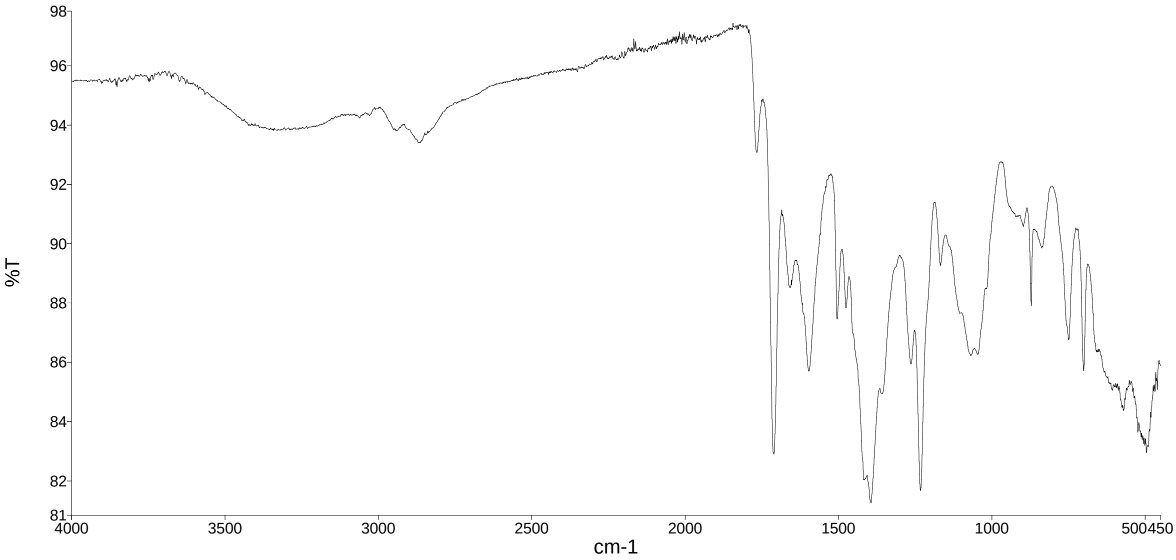


Figure 1c: FT-IR Spectrum (ATR) of CrPc Complex (6a)

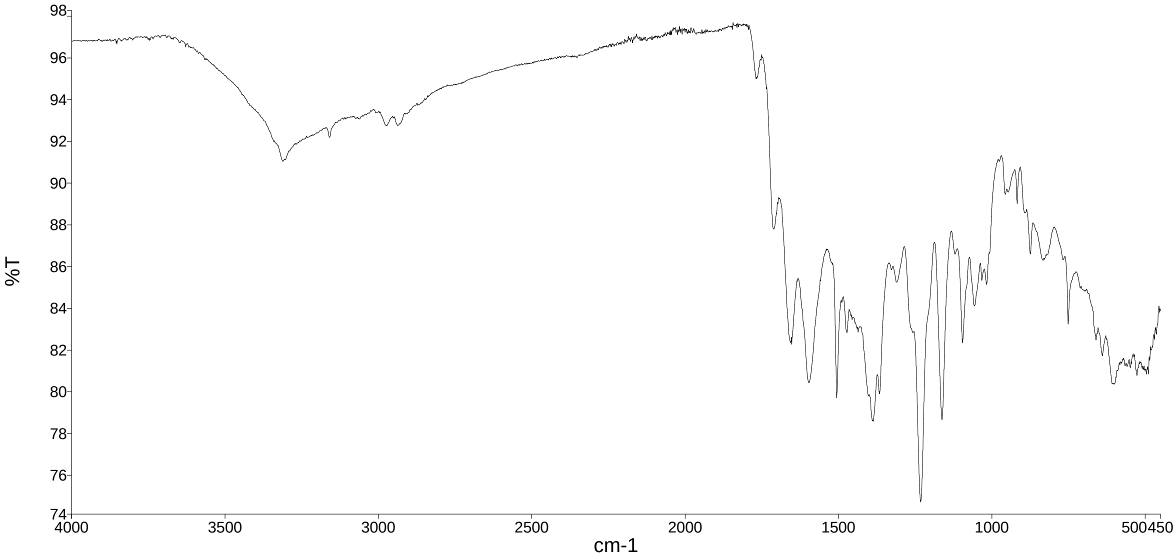


Figure 1d. FT-IR Spectrum (ATR) of CoPc Complex (6b)

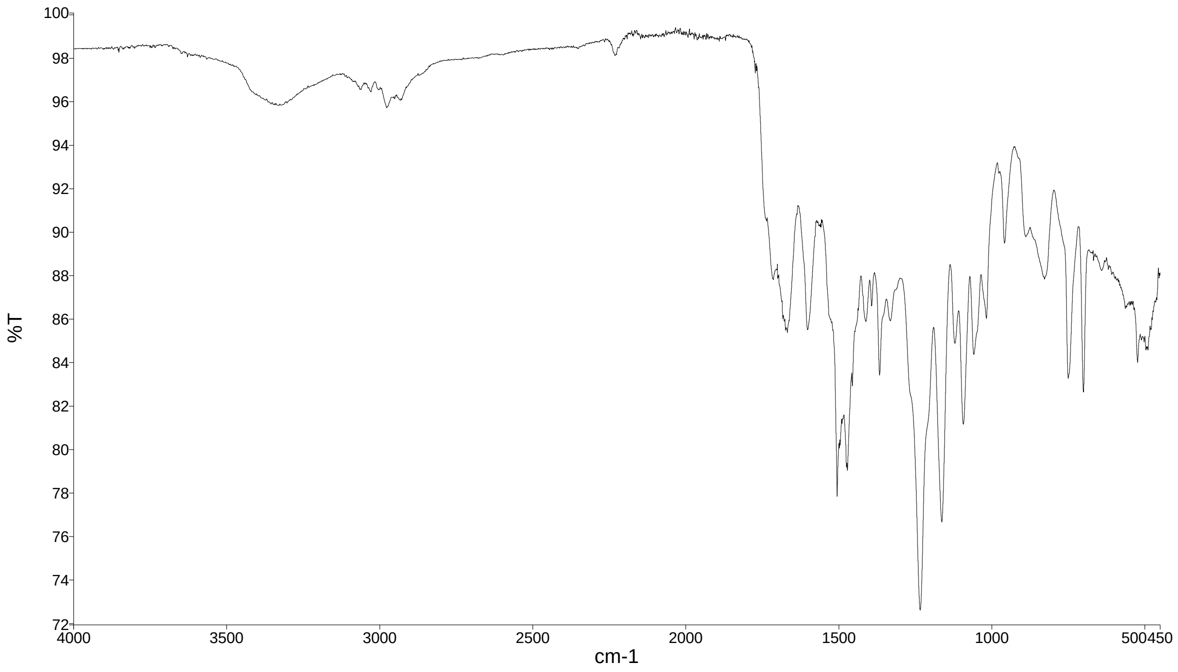


Figure 1e. FT-IR Spectrum (ATR) of NiPc Complex (6c)

The synthesized complexes compounds have been characterized by UV–vis and FT- IR. However, the absence of $\nu_{C\equiv N}$ 2230 cm^{-1} bond absorption in FT-IR spectra of CrPc, CoPc and NiPc in **Figure 1c,1d and 1e** indicate the cyclotetramerization of **(5)** for the formation of **(6a), (6b)** and **(6c)** dipeptide substituted metallo phthalocyanine respectively in **Scheme 2.**

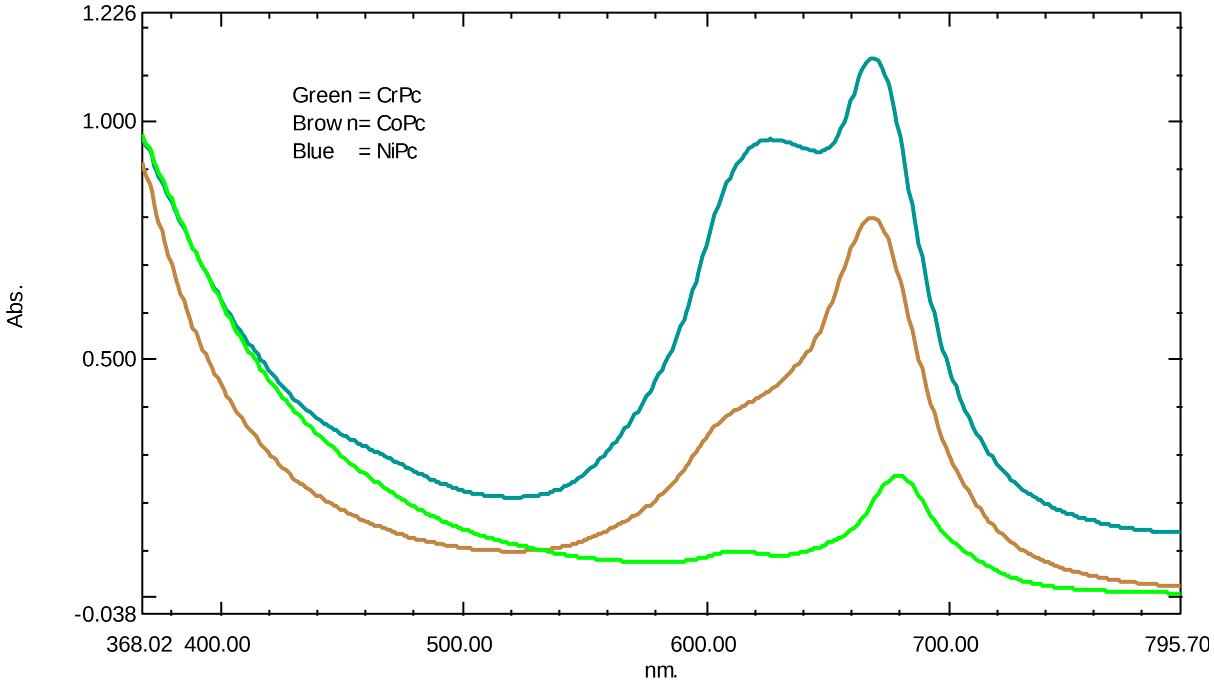


Figure 2. Absorption spectra of 6a (DMF 1x10^{-5}) (Green), 6b (DMF 1x10^{-5}) (Brown), and 6c (DMF 1x10^{-5}) (Blue)

The UV-vis spectra of dipeptide substituted metallo phthalocyanines complexes of **(6a), (6b)** and **(6c)** in DMF solvent showed characteristic absorptions between 660-700 nm in Q-band region[17, 25] as shown in **Figure 2** above. The Q-band of each compound is caused by the **(π→π*)** transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring. The comparison of absorption spectra of the three complexes **(6a), (6b)** and **(6c)** in DMF solvent indicated that the Q-bands of **(6c)** complex are broader than those of **(6b)** and **(6a).**

In the ^{1}H NMR spectrum of **(3)** singlet -OH proton of 9.19 ppm was observed in the spectrum of the dipeptide. The presence of peaks of –NH protons at 6.81-6.83ppm (1H, d, H^8 (-NH)) and 8,32-8.34ppm (1H, d, H^{13} (-NH)), aromatic protons at 6.63-6.65ppm (2H, d, J=8.4 Hz, H^2) and 7.0-7.02 (2H, d, J=8.8 Hz, H^3), methoxy protons at 3.06 (3H, s, H^{16}) and other aliphatic protons peaks at 2.56-2.59 and 2.74-2.79 (2H, H^5), 4.49-4.53 (1H, q, H^7), 1.31 (9H, s, H^{11}), 4.08-4.09 (1H, q, H^{14}), 3.06 (3H, s, H^{16}) and 2.96-3.07 (2H, m, H^{17}) as clearly shown in **Figure 2a.**

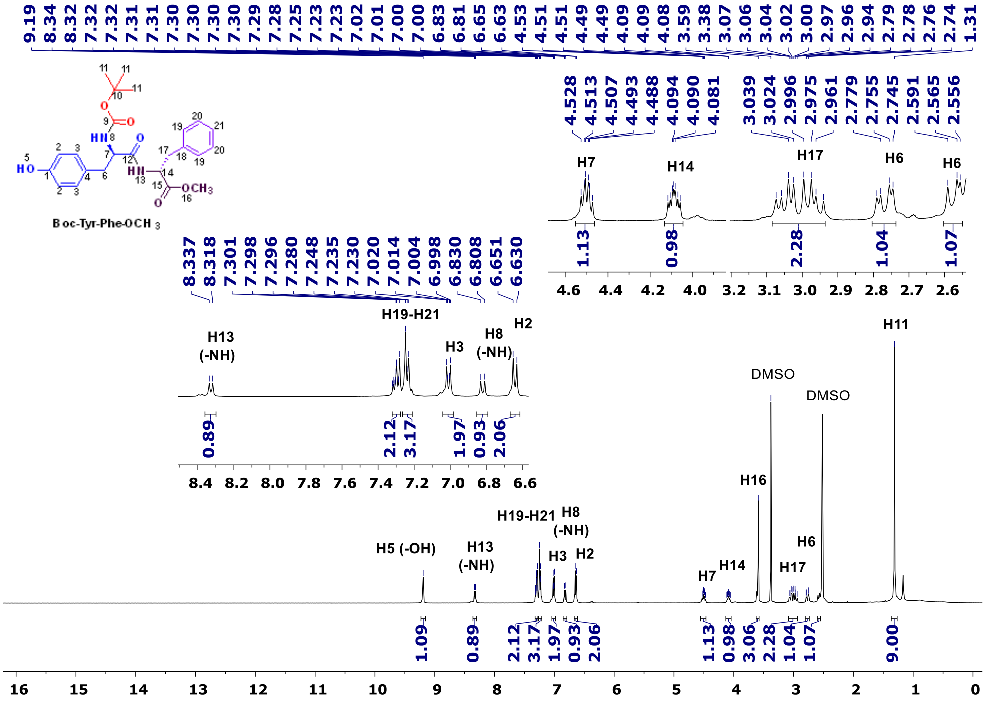


Figure 3a. ^{1}H-NMR Spectrum of Boc-Tyr-Phe-OCH$_3$ Compound (DMSO-d6)

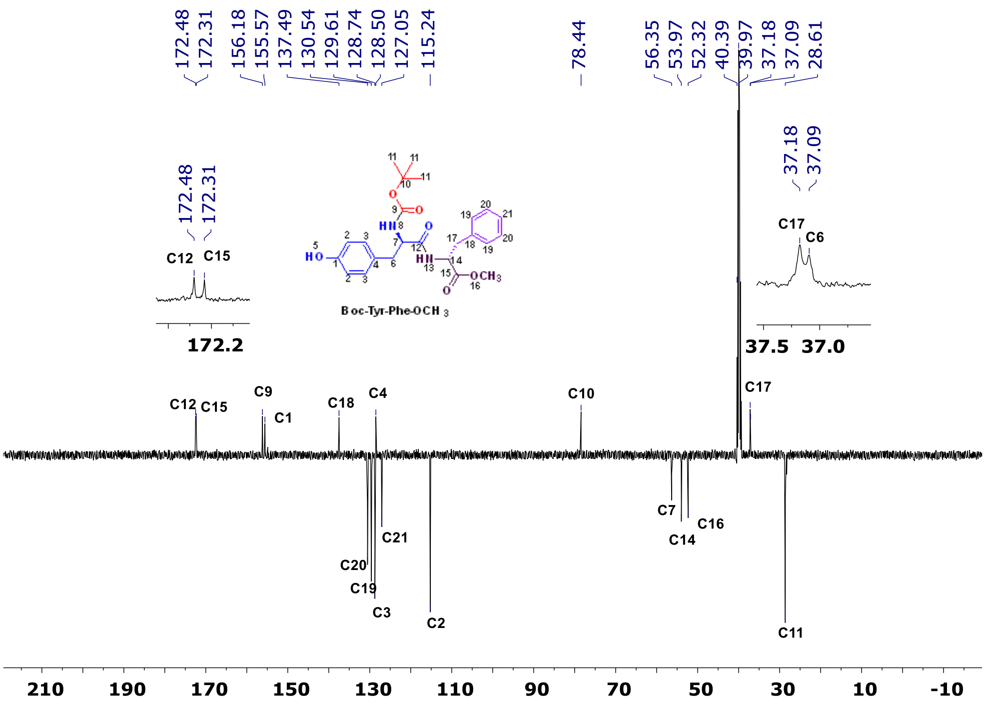


Figure 3b. ^{13}C-APT NMR Spectrum of Boc-Tyr-Phe-OCH$_3$ Compound (DMSO-d6)

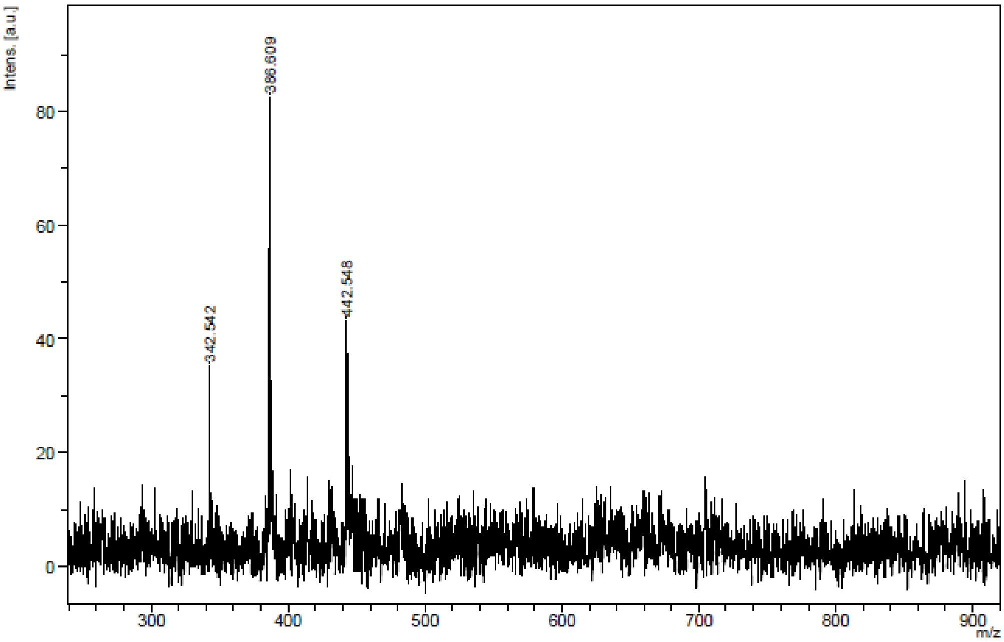


Figure 3c. MALDI-TOF MS Spectrum of Boc-Tyr-Phe-OCH$_3$ Compound (3)

The theoretically calculated molecular weight of the Boc-Tyr-Phe-OCH$_3$ compound is 442.51 g/mol. In the MALDI-TOF MS Spectrum, the 442.548 [M] peak belongs to the compound. The peaks observed under this peak indicate the compound resulting from the groups leaving the structure. According to calculations, the peak at 386.609 corresponds to the rupture of the -C(CH$_3$)$_3$ group in the Boc protecting group, 386.609 [M-C(CH$_3$)$_3$]. The peak at 342.542 corresponds to the complete separation of the Boc group from the structure. 342.542 [M-Boc].

3.2 Electrochemical Properties

Electrochemical activities of macro molecule materials are utilized in numerous technological uses. Investigation of the complexes electrochemical behaviors will allow us to determine their potential applications in various electrochemical disciplines such as electro catalysis and electro-sensing[26-28].

Metal Complexes **6a, 6b** and **6c** Cyclic and Square Wave Voltammetry in DMF, tetrabutylammonium tetra fluoroborate as electrolyte, Pt, counter electrode and Glassy carbon electrode as working electrode, Ferrocene / Ferrocenium (Fc/Fc+) pseudo-reference electrode. A broader potential range (-2.5 to +1.0 V versus Fc/Fc+) was employed to explore electrochemical characteristics of all the phthalocyanine complexes. **Table 2** gives the redox potential (volt) of both the reduction and oxidation processes. The phthalocyanines compounds can undergo numerous one electron oxidation and reduction of the conjugated macrocycle to formed cation and anion radicals respectively[29, 30]. For the major group of phthalocyanines, the redox activity is directly connected with the oxidation by removing electrons from the highest occupied molecular orbital (HOMO) and adding electrons to the lowest unoccupied molecular orbital (LUMO) of phthalocyanines[31, 32].

Table 2. Redox potential from SW voltammograms at 5 Hz, 50 mV amplitude and 4 mV step potential of 6a, 6b and 6c phthalocyanine complexes.

Complex code	Solvent/ Supporting electrolyte	RE	Redox Potentials (Volt)						
			R4	R3	R2	Metal	R1	O1	O2
6a	DMF/ TBAFB	Fc/Fc$^+$	-2.17	-1.88	-1.62		-0.98	0.37	0.58
6b	DMF/ TBAFB	Fc/Fc$^+$	-2.22	-1.93	-1.69	Co -1.05	-0.74	0.54	0.79
6c	DMF/ TBAFB	Fc/Fc$^+$	-2.36	-2.07	-1.8	Ni -1.58	-1.15	0.09	0.4

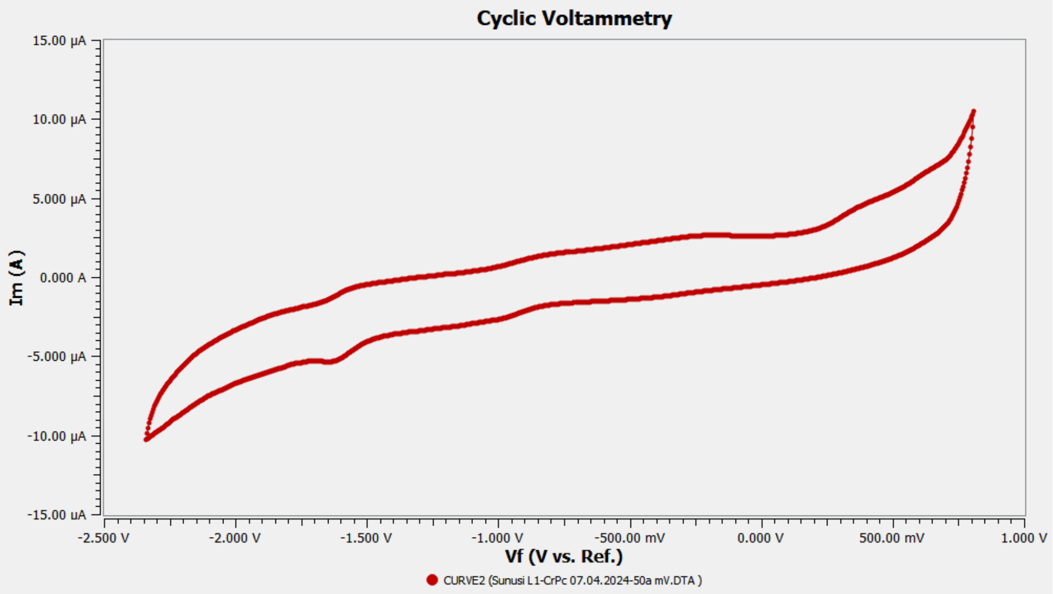


Figure 4a. Cyclic voltammograms of 6a in DMF containing 0.1 M TBAFB, scan rate 50 mV s^{-1}.

The complex **6b** (Figure 4b) demonstrated both oxidation and reduction waves of the metal centre and phthalocyanine ring, labelled O1 and O2 and R1, R2, R3 and R4, in the electrochemical window of DMF containing 0.1 M TBAFB. The initial oxidation (O1) and initial reduction (R1) processes of complex **6b** occurred at 0.54 V and -0.74 V might be ascribed to CoII(Pc-2)/CoIII(Pc-2) and CoII(Pc-2)/CoI(Pc-2) [33-36] respectively, and The remaining oxidation and reduction waves may be traced to the phthalocyanine ring in DMF.

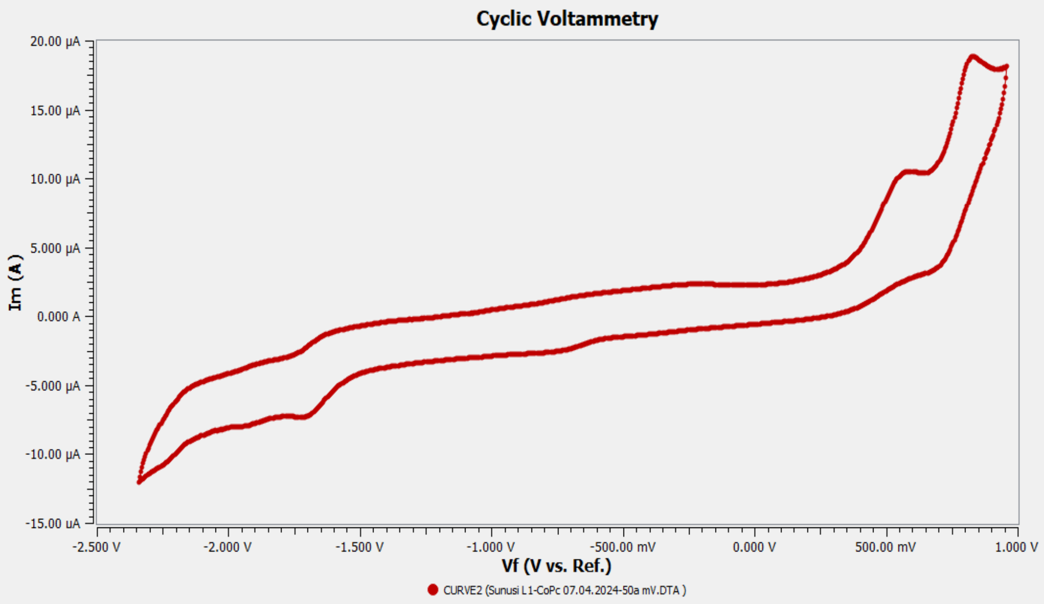


Figure 4b. Cyclic voltammograms of 6b in DMF containing 0.1 M TBAFB, scan rate 50 mV s^{-1}.

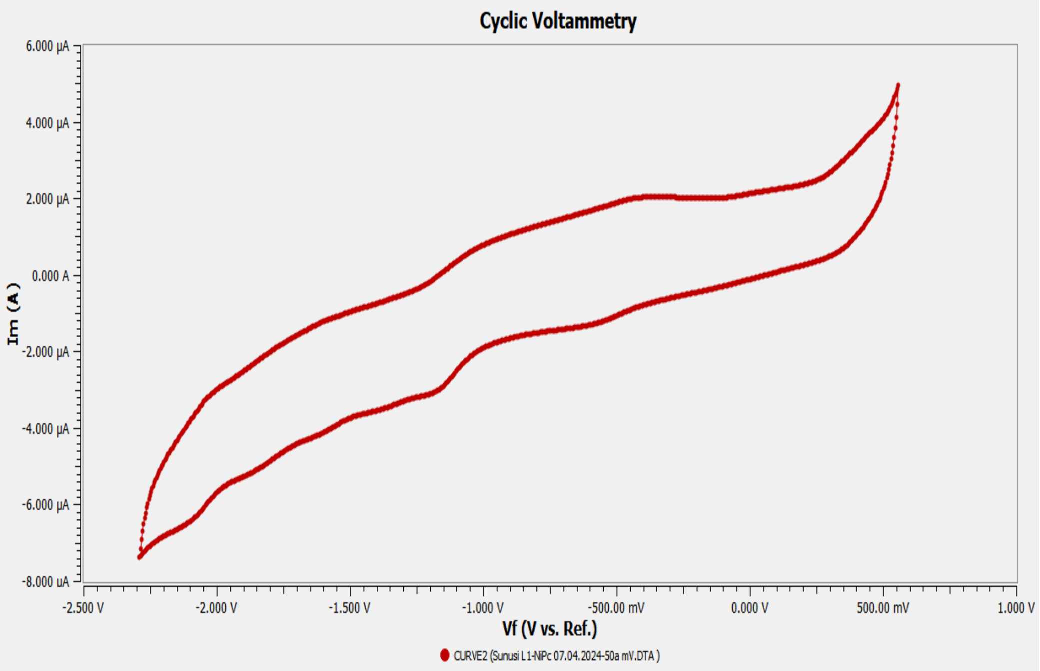


Figure 4c: Cyclic voltammograms of 6c in DMF containing 0.1 M TBAFB, scan rate 50 mV s^{-1}.

3.3 Thermal properties

As it was observed from the TGA curves of the Pc complexes **6a**, **6b** and **6c** are thermally stable up to 180, 200 and 100 °C respectively. After, each complex undergoes two stages of degradation [37, 38]. A weight loss of 50% was recorded between 180 - 420 °C for **6a** in the first stage of degradation followed by weight loss of 28% in-between 420 - 460 °C in the second stage of degradation with leftover of 22% not to decompose as residue as shown in **Figure 5a**. The weight loss of 50% was accounted between 200 - 450 °C for **6c** complex and 38% was observed between 450 - 475 °C for both first and second stage of degradation respectively with 12% remaining as residue which could be provably it metal oxide as in observed in **Figure 5c**.

However, complex **6b** being the less stable in comparison with the rest two complexes, started weight loss of 50% between 100 - 450 °C followed by 43% weight loss in the second stage of degradation with only 7% remain as provably it metal oxide. It is indicated from the DTA curves of all the three Pc complexes that they all decomposes without melting. Therefore, under normal condition complexes **6a**, **6b** and **6c** does not have a melting point and all their stages of degradation follows exothermic decomposition.

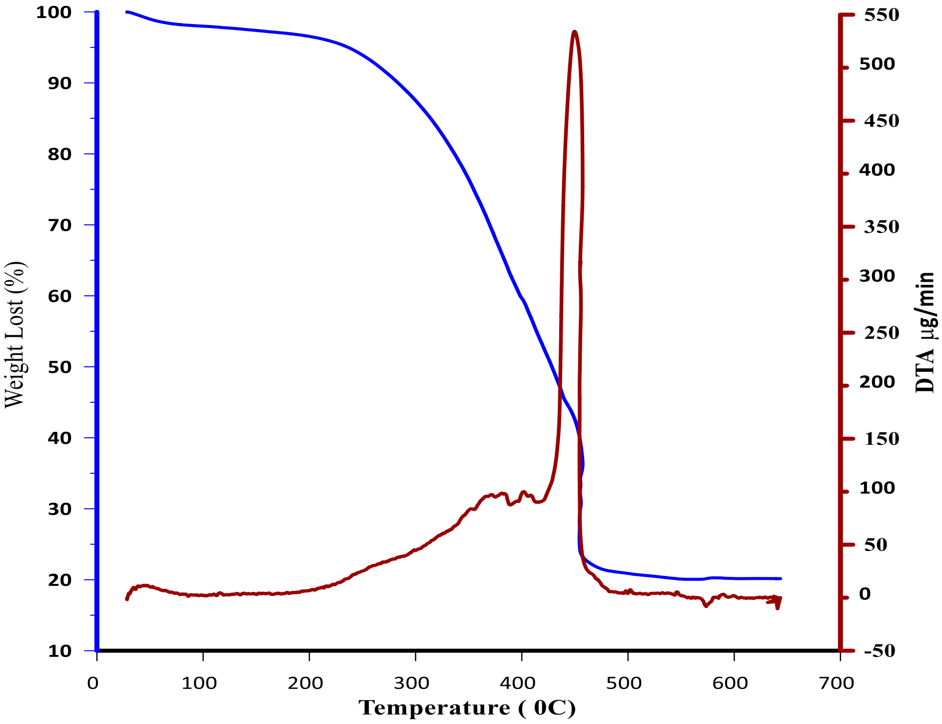


Figure 5a. TGA (blue) and DTA (red) Thermograms of complex (6a)

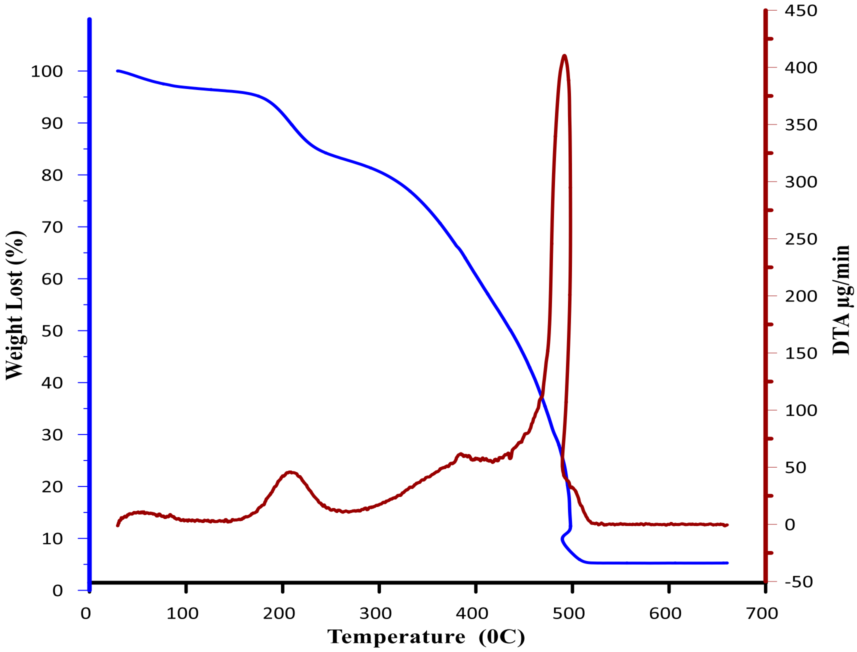


Figure 5b. TGA (blue) and DTA (red) Thermograms of complex (6b)

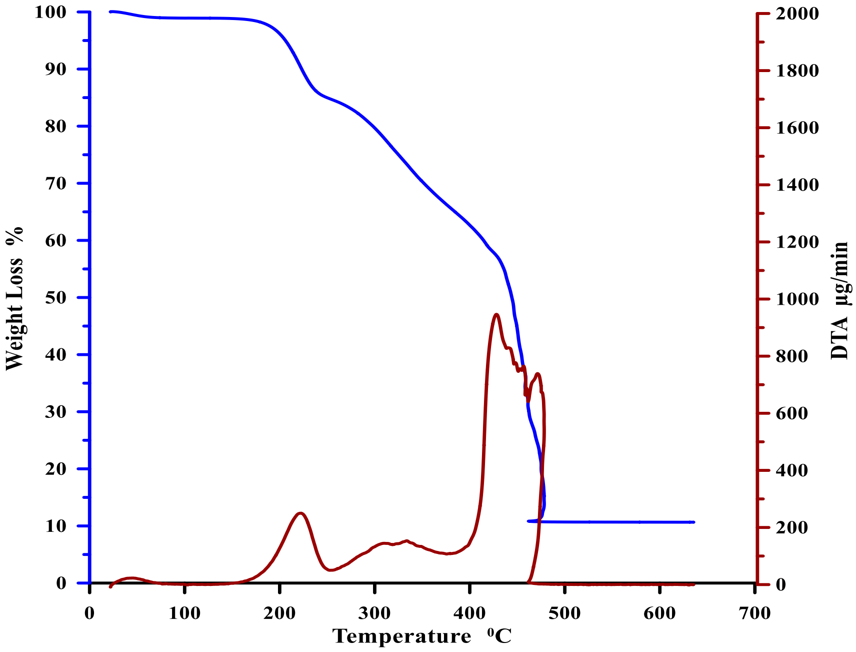


Figure 5c. TGA (blue) and DTA (red) Thermograms of complex (6c)

4. Conclusion

The synthesis of dipeptide compound (Boc-Tyr-Phe-OMe) was successfully obtained from the reactions of phenylalanine (NH$_2$-Phe-OCH$_3$.HCl) methyl ester hydrochloride with tyrosine amino acid (Tyr-OH) in acetonitrile solvent in the presence of (CDMT) coupling reagent and (NMM) base as catalyst. The dipeptide reacted with 4-nitrophthalonitrile to formed the ligand which was used to undergo cyclotetramerization in the presence of metals salt of Co(II), Cr(III) and Ni(II) acetate in (DMF) solvent at 150 °C to form Tyrosine- Phenylalanine dipeptide substituted phthalocyanine complexes of respective metals. The simplest and most basic method of showing the formation of phthalocyanine complex is to observed the formation of green or blue colour as characteristic of phthalocyanine compounds[39]. The fact that all of the obtained compounds are green indicates that phthalocyanine compounds are formed. In addition, the disappearance of the C≡N peaks at 2230 cm^{-1} absorption bond in the FT-IR spectra of the complexes indicates the formation of phthalocyanine compounds. The complexes were characterized and evaluated result as a good material for both scientific and technological application. Thermograph of the complexes translate that the compounds have a thermal stability between 100-200 °C as the case may be, beyond that, they begin to decompose without undergoing melting, that means under normal conditions the complexes do not have a melting point. And DTA graph shows their degradation is exothermic in nature.

Contributions

All the authors have contributed equally.

Conflict of Interest Statement

Authors declare that they have no known conflict of interest.

References

1. Das, P., et al., Reduced Graphene Oxide-Zinc Phthalocyanine Composites as Fascinating Material for Optoelectronic and Photocatalytic Applications. ChemistrySelect, 2017. **2**(11): p. 3297-3305.
2. Ertem, B., et al., The synthesis and electrochemical characterization of new metallophthalocyanines containing 4-aminoantipyrine moieties on peripherally positions. Inorganica Chimica Acta, 2017. **462**: p. 123-129.
3. Demirol, M., et al., Synthesis and photodiode properties of chalcone substituted metallo-phthalocyanine. Journal of Molecular Structure, 2020. **1219**: p. 128571.
4. Kurt, Ö., et al., Synthesis, photophysical and electrochemical properties of novel hexadeca-substituted phthalocyanines bearing naphthoxy groups. Dyes and Pigments, 2017. **137**: p. 236-243.
5. Ağırtaş, M.S., et al., Synthesis, characterization, and electrochemical and electrical properties of novel mono and ball-type metallophthalocyanines with four 9, 9-bis (4-hydroxyphenyl) fluorene. Dalton Transactions, 2011. **40**(13): p. 3315-3324.
6. Ceyhan, T., et al., Synthesis, Characterization, Nonlinear Absorption and Electrochromic Properties of Double-Decker Octakis (mercaptopropylisobutyl-POSS) phthalocyaninatolanthanide (III) Complexes. 2008, Wiley Online Library.
7. Liu, W., et al., Synthesis and cellular studies of nonaggregated water-soluble phthalocyanines. Journal of medicinal chemistry, 2005. **48**(4): p. 1033-1041.
8. Wang, J., A.K. Khanamiryan, and C.C. Leznoff, Multisubstituted phthalonitriles for phthalocyanine synthesis. Journal of Porphyrins and Phthalocyanines, 2004. **8**(11): p. 1293-1299.
9. Koran, K., et al., The first peptide derivatives of dioxybiphenyl-bridged spiro cyclotriphosphazenes: In vitro cytotoxicity activities and DNA damage studies. Bioorganic Chemistry, 2023. **132**: p. 106338.
10. Tataroglu, A., et al., Metallo-Phthalocyanines Based Photocapacitors. Silicon, 2019. **11**: p. 1275-1286.
11. Jia, N., et al., Effect of central metals and peripheral substituents on the third-order nonlinear optical properties of tetra-benzimidazole and benzothiazole substituted phthalocyanines. Optical Materials, 2018. **76**: p. 81-89.
12. Mudyiwa, M., et al., Microwave assisted solid-phase synthesis of substituted tetraazaporphyrins and a phthalocyanine-peptide conjugate. Journal of Porphyrins and Phthalocyanines, 2010. **14**(10): p. 891-903.
13. Erdem, S.S., et al., Mono-amine functionalized phthalocyanines: microwave-assisted solid-phase synthesis and bioconjugation strategies. The Journal of organic chemistry, 2009. **74**(24): p. 9280-9286.
14. Erdem, S.S., et al., Solid-phase synthesis of asymmetrically substituted “AB3-type” phthalocyanines. The Journal of organic chemistry, 2008. **73**(13): p. 5003-5007.
15. Nemykin, V.N. and E.A. Lukyanets, Synthesis of substituted phthalocyanines. ARKIVOC: Online Journal of Organic Chemistry, 2010.
16. Hamam, K.J. and M.I. Alomari, A study of the optical band gap of zinc phthalocyanine nanoparticles using UV–Vis spectroscopy and DFT function. Applied Nanoscience, 2017. **7**(5): p. 261-268.
17. El-Nahass, M., K. Abd-El-Rahman, and A. Darwish, Fourier-transform infrared and UV–vis spectroscopes of nickel phthalocyanine thin films. Materials Chemistry and Physics, 2005. **92**(1): p. 185-189.
18. Albeiicio, F., et al., New trends in peptide coupling reagents. Organic Preparations and Procedures International, 2001. **33**(3): p. 203-303.
19. Montalbetti, C.A. and V. Falque, Amide bond formation and peptide coupling. Tetrahedron, 2005. **61**(46): p. 10827-10852.
20. Sheehan, J.C. and G.P. Hess, A new method of forming peptide bonds. Journal of the American Chemical Society, 1955. **77**(4): p. 1067-1068.
21. Garrett, C.E., et al., New observations on peptide bond formation using CDMT. Tetrahedron letters, 2002. **43**(23): p. 4161-4165.

22. Abubakar, A.M., et al., Characterization and preparation of green colored intramolecular novel ball type cobalt phthalocyanine complexes with single-chain polymer structure. Journal of Molecular Structure, 2021. **1227**: p. 129389.
23. Özdemir, Ü.Ö., et al., Characterization, antibacterial, anticarbonic anhydrase II isoenzyme, anticancer, electrochemical and computational studies of sulfonic acid hydrazide derivative and its Cu (II) complex. Inorganica Chimica Acta, 2014. **423**: p. 194-203.
24. Armarego, W.L., Purification of laboratory chemicals: Part 2 inorganic chemicals, catalysts, biochemicals, physiologically active chemicals, nanomaterials. 2022: Butterworth-Heinemann.
25. Önal, E., F. Dumoulin, and C. Hirel, Tetraimidazophthalocyanines: influence of protonation and aggregation on spectroscopic observations. Journal of Porphyrins and Phthalocyanines, 2009. **13**(06): p. 702-711.
26. Pekbelgin Karaoğlu, H. and A. Kalkan Burat, α-and β-substituted metal-free phthalocyanines: synthesis, photophysical and electrochemical properties. Molecules, 2020. **25**(2): p. 363.
27. Aytan Kiliçarslan, F., et al., Synthesis, characterization and electrochemical properties of new phthalocyanines. Journal of Coordination Chemistry, 2017. **70**(15): p. 2671-2683.
28. Chen, J., et al., Advances in phthalocyanine compounds and their photochemical and electro-chemical properties. Current Organic Chemistry, 2018. **22**(5): p. 485-504.
29. De La Torre, G., et al., Role of structural factors in the nonlinear optical properties of phthalocyanines and related compounds. Chemical Reviews, 2004. **104**(9): p. 3723-3750.
30. Koifman, O.I., et al., Macroheterocyclic compounds a key building block in new functional materials and molecular devices. Макрогетероциклы, 2020. **13**(4): p. 311-467.
31. Kadish, K.M., et al., Electrochemistry of a double-decker lutetium (III) phthalocyanine in aqueous media. The first evidence for five reductions. The Journal of Physical Chemistry B, 2001. **105**(40): p. 9817-9821.
32. Nakanishi, T., et al., Thermodynamic study of ion-pairing effects between reduced double-decker lutetium (III) phthalocyanines and a cationic matrix. The Journal of Physical Chemistry B, 2003. **107**(46): p. 12789-12796.
33. Brown, R.J. and A.R. Kucernak, The electrochemistry of platinum phthalocyanine microcrystals: III. Electrochemical behaviour in aqueous electrolytes. Electrochimica acta, 2001. **46**(16): p. 2573-2582.
34. Boutin, E., et al., Aqueous electrochemical reduction of carbon dioxide and carbon monoxide into methanol with cobalt phthalocyanine. Angewandte Chemie International Edition, 2019. **58**(45): p. 16172-16176.
35. Li, R., et al., Electrochemistry of homoleptic bis [3 (4), 12 (13), 21 (22), 30 (31)-tetra (tert-butyl)-naphthalocyaninato] rare earth (III) complexes. Journal of Porphyrins and Phthalocyanines, 2005. **9**(01): p. 40-46.
36. Sekhosana, K.E., et al., Synthesis, photophysical and nonlinear optical behavior of neodymium based trisphthalocyanine. Inorganica Chimica Acta, 2015. **426**: p. 221-226.
37. Hacıvelioğlu, F., et al., The synthesis, spectroscopic and thermal properties of phenoxycyclotriphosphazenyl-substituted phthalocyanines. Dyes and Pigments, 2008. **79**(1): p. 14-23.
38. Şahin, S. and E. Ağar, Synthesis, spectroscopic properties, thermal properties and aggregation behaviors of macrogol-substituted phthalocyanines. Journal of Molecular Structure, 2019. **1187**: p. 121-131.
39. Dahlen, M.A., The phthalocyanines a new class of synthetic pigments and dyes. Industrial & Engineering Chemistry, 1939. **31**(7): p. 839-847.