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Synthesis and characterization of new metal-free and metal-substituted phthalocyanine compounds and study Molecular docking

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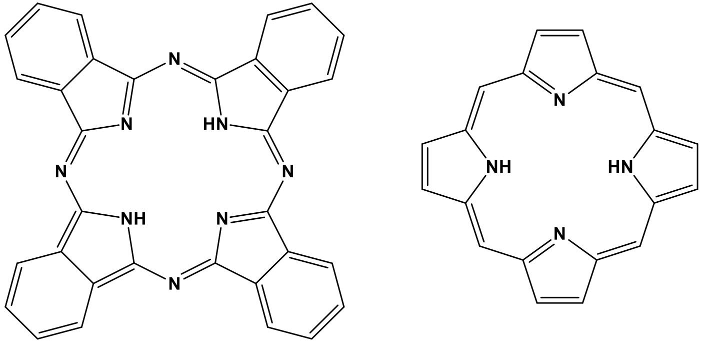
Abstract

A newly of cobalt and nickel derivative of phthlocyanine were synthesized. Tetra nitro cobalt phthalocyanine, tetra-(5-amino-2-hydroxybenzoic) cobalt phthalocyanine were synthesized and recrystalized. By adding 5-aminosalicylic acid, tetra-(5-amino salicylic acid) Cobalt phthalocyanine was synthesized. Nickel derivatives were synthesized via the same pattern. Phthalocyanine without metal is synthesized also. All the derivatives were separated, recrystallized and identified using elemental analysis, FTIR, 1H NMR, and UV spectroscopy, The band energy was calculated at electron V recorded via optical means and The molecular docking study was addressed in this work and reviled a promising biological activities especialy the compound with molecule not containing metal element.

Keywords: Nickel phthalocyanine, Cobalt phthalocyanine, metal-free phthalocyanine, 5-Amino-2-hydroxybenzoic acid, Molecular docking.

Introduction

Macrocyclic Phthalocyanine contains four isoindoles a dye compound, bonded with four nitrogen atoms forming a conjugated chain, forming a structure able to bond with several metal ions in the molecule centre. Its molecules are normally intensely coloured macrocyclic. structure like porphyrinsm (biopigments) is highly coloured Phthalocyanine derivatives derived from the basic compound of (C6H4C2N)4N4 and are used as light-fast blue or green pigments Figure 1 [1-2]. Since green and blue pigments is the main importance of organometallic dyes. Cyanines are characterized by homogeneity, stability, fastness when the cyanines bonded with svanine metals [3] Color fastness, homogeneity, intensity, stability combined with a simple synthetic rout [4,5]. Phthalocyaanine has wide application in the ink jet printing applications and several use in electrophotography as well as laser printing beside the colour toner [6]. Some application in longer wavelength beyond 700 nm up 1000nm, and also in infrared region [7]

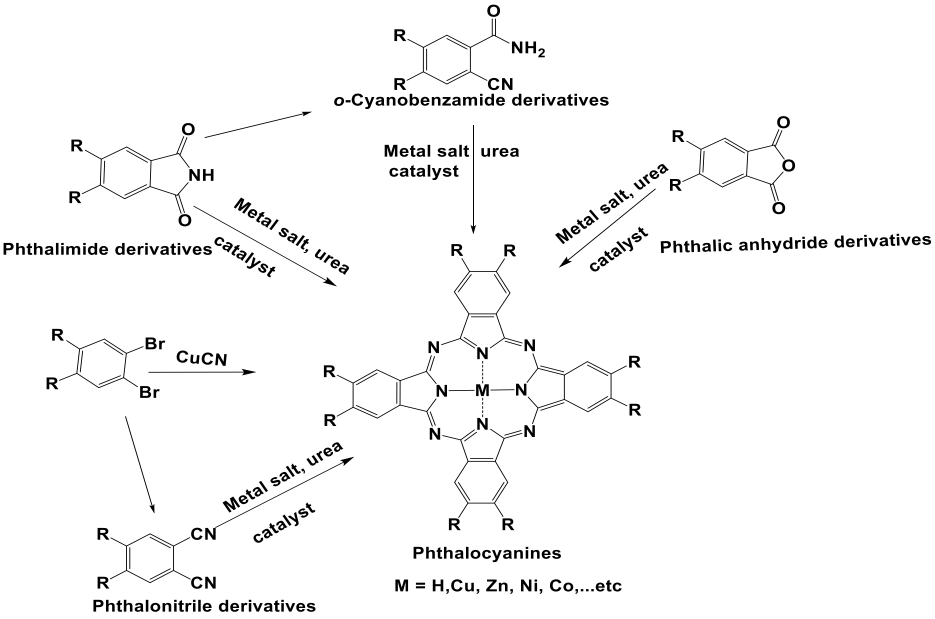


(1)

(2)

Figure 1. structures of phthalocyanines (1) and porphyrin (2)

Phthalocyanines can be synthesised using several methods, depending on the need for symmetrical, asymmetrical, or metal-free phthalocyanines. Factors such as the kind of The necessary conditions for preliminary metal salts (such as metal salts, oxides, halides, and sulfates) include the level of temperature required to promote precursor dissolving and fast cyclotetramerization. The catalyst and base influence the synthesis of synthetic phthalocyanine.. The synthesis of Pcs involves the cyclotetramerization of phthalimide, phthalic acids, phthalonitrile precursors, and phthalic anhydrides, either with or without a metal salt in the case of unmetallated Pcs, Scheme 1 [8-9].



Scheme 1. Depiction of the synthesis pathways for metallophthalocyanines derived from various precursors.

Owing to their exceptional electrical, optical, and thermal stability, PCs find extensive utility in the realm of material science. [10-14]. This chemical synthesis entailed the chemical reaction between metal salts, urea and either phthalonitrile, phthalimide, or phthalic anhydride. Usually, such processes need temperatures approaching 200 °C for 3 hours [15-19].

Experimental

Instruments

1- The infra-red spectra of the prepared compounds were recorded using FT-IR-8400s Shimadzu-EA 1108, I.R. spectrophotometer/ Babylon University (Iraq)
2- (1H-NMR) spectra were recorded on nuclear magnetic resonance Bruker spectrophotometer model Ultra sheild 400 MHz using DMSO-d6 as solvent (Isfahan University of Technology (IUT) and Sharif University of Technology)SUT) Iran).
3- UV/VIS Spectrophotometer PG Instruments Ltd CECIL- CE7200/ Babylon University (Iraq)
4- Melting point (M.P.) was determined by Gallenkamp melting point apparatus Babylon University (Iraq).
5- C.H.N- Elemental Analysis, Euro EA 1106/ Babylon University (Iraq)

Materials and method

All materials were obtained from Sigma Aldrich. All solvents and reagents were used without further purification. Every compound was isolated, recrystallized and identified. The synthesized derivatives were labelled as K1, K2, K3 and K4.

Synthesis of 4,4′,4′′,4′′′- tetranitro Cobalt phthalocyanine (K1) [20]

4-nitro phthalonitrile 5.78 mmol, $CoCl_2$ 7.31 mmol, and 3 ml of dimethylaminoethanol (DMAE) were combined and agitated for one hour at 185°C in a nitrogen environment. After bringing the dark green liquid to room temperature, it was purified using ethanol and water. An eluent consisting of a 50:10 ratio of DMF to n-hexane was employed in column chromatography over silica gel to facilitate the purification of the precipitate. A green precipitate containing 56.46% of compound (K1), weighing 2.47g. the material is observed to be stable even above 300˚C and has a TLC R*f* of 0.45 (DMF: DCM: n-hexane) (7:2:1).

Synthesis of tetra-(5-amino salicylic acid) Cobalt phthalocyanine (K2) [21]

DMF (15 mL) was mixed with Compound (K1) 1.32 mmol, 5-Amino-2-hydroxybenzoic Acid (1.60g, 10.44 mmol), and K_2CO_3 (0.72 g, 5.26 mmol) and then heated to 70°C and agitated for nine hours under a nitrogen environment. Following that, 0.36 grammes of K_2CO_3 (2.63 millimolar) were introduced, and the mixture was agitated for further nine hours. Upon cooling the liquid to ambient temperature, 1N hydrochloric acid was introduced. An eluent consisting of a 50:10 ratio of DMF to n-hexane was employed in column chromatography over silica gel to purify the filtered precipitate. The reaction yielded a green precipitate (0.46 g, 61.31%) of compound (K2) with a TLC R*f* of 0.8 (DMF:DCM: n-hexane)(6:3:1) and stable above 300°C.

Synthesis of 4,4′,4′′,4′′′- tetranitro phthalocyanine (K3) [22]

A mixture of 4-nitro phthalonitrile 11.54 mmol in 4 milliliters of dimethylaminoethanol was stirred under N_2 gas and held at a temperature of 185°C. Once the dark green solution had been cooled to 25^{o}C, it was then washed with water and ethanol. Through column chromatography using silica gel and a 100:20 eluent consisting of dimethylformamide (DMF) and n-hexane, the precipitate was purified. An aqueous precipitate weighing 3.59g, accounting for 68.46% of the chemical (K3), was obtained. The retention factor R*f* of thin-layer chromatography (TLC) was found to be 0.45 when using a mixture of dimethylformamide (DMF), dimethylformamide (DCM), and n-hexane in weight ratios of 7:2:1. The compound demonstrates a stability above 300^{o}C.

Synthesis of 4,4′,4′′,4′′′- tetranitro Nickel phthalocyanine (K4) [22]

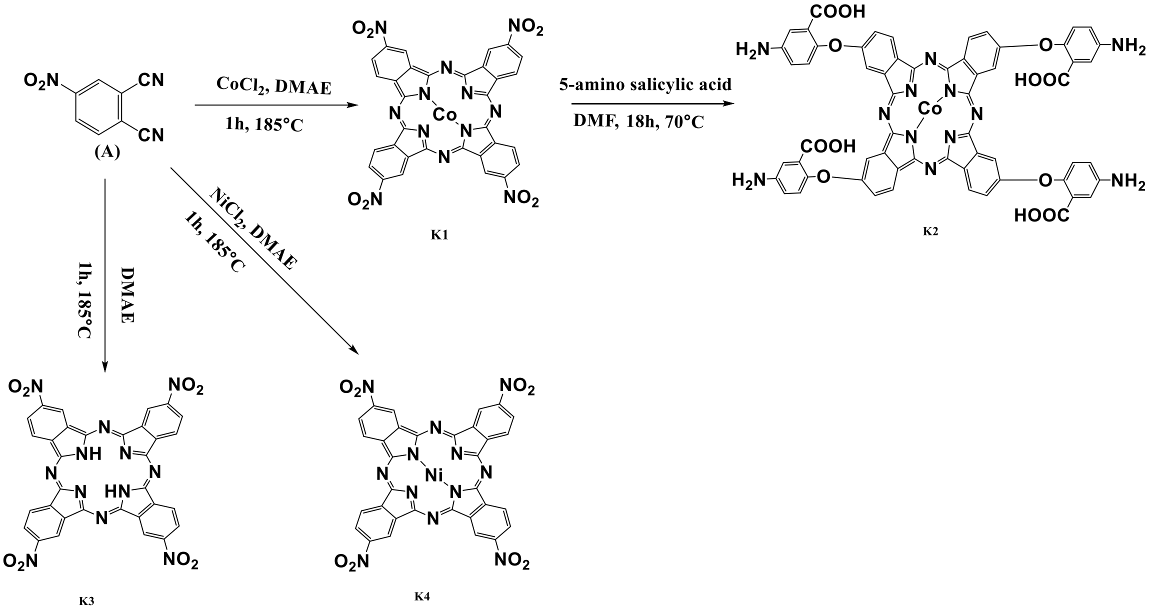
A solution containing 4-nitro phthalonitrile 5.78 mmol, $NiCl_2$ 7.21 mmol, and DMAE (dimethylaminoethanol) 2 milliliters was mixed and agitated under a nitrogen atmosphere at a temperature of 185°C for a duration of 1 hour. After cooling, the dark green solution was After that, it was cleaned with pure water and ethanol. To purify the powder, column chromatography was performed on silica gel and an eluent mixture of (DMF: n-hexane) in a 50:10 ratio. A green precipitate weighing 2.47g (56.46% yield) of compound (K4) was obtained. The compound had a TLC R*f* value of 0.45 when using a mixture of DMF, DCM, and n-hexane in a ratio of 7:2:1. The melting point of the compound was over 300˚C.

Docking study

Molecular docking data enhance comprehension of ligand-enzyme interactions, forecast probable binding conformations for each molecule at a protein's active site, and promote the creation of innovative and effective inhibitors. Molecular docking was conducted on the enzyme utilizing the Molecular Operation Environment tool (MOE version 2019.0102) to accomplish this objective. The protein structures were acquired from the Protein Data Bank in PDB file format. Water molecules associated with these enzymes were eliminated to prevent interference during the docking analysis. The structures of the compounds were delineated and refined using ChemDraw 22.2.0 software, followed by processing and minimization with Molecular Operating Environment (MOE) software. Subsequently, each ligand was individually docked into the binding site of the two pre-prepared proteins. The docking outcomes for all derivatives of both proteins were assessed based on the binding score (s) and (RMSD).

Results and discussion

Cobalt derivatives K1&K2, nickel derivative K4, as well as none metal tetranitro phthalocyanine K3 derivatives were synthesized and presented in Scheme 2. The structure of all these compounds were well define by normal analysis methods.



Scheme 2. Syntheses of compounds K1, K2, K3 and K4

The scheme is indicated the synthesis rout of the Co and Ni phthalocyanin. The metal with the nitrogen atom is coordinate bond, while the rest are π. All these compound are coloured. Compound K1 and K2 are blue in colour, K3 and K4 are dark green in colour. All of them are absorbing in the range of 700nm, with the thermal stability beyond 300oC. UV spectrum of these compounds exhibited two zone first band, known as the B or soret-band, occurs at a wavelength on the range of 400 to 200 nm with a peak of 258.25 nm. The second band, called the Q-band, occurs at a wavelength range of 750 to 600 nm with the maximum of 686.5 nm.

The Transform Infrared FT-IR of compound (A) When comparing Figure 2 with compound (K1) Figure 3 displays peaks FTIR cm^{-1}: ν: corresponding to the C-H bonds in the aromatic compound at 3090, the C=C bonds in the aromatic compound at 1466 and 1607, the NO_2 group at 1340 and 1527, and the aromatic group at 724. The absence of the CN group band at 2243 indicates that the conversion of 4-nitro phthalonitrile (A) into 4,4′,4″,4‴-tetranitro zinc Phthalocyanine has been successfully achieved.

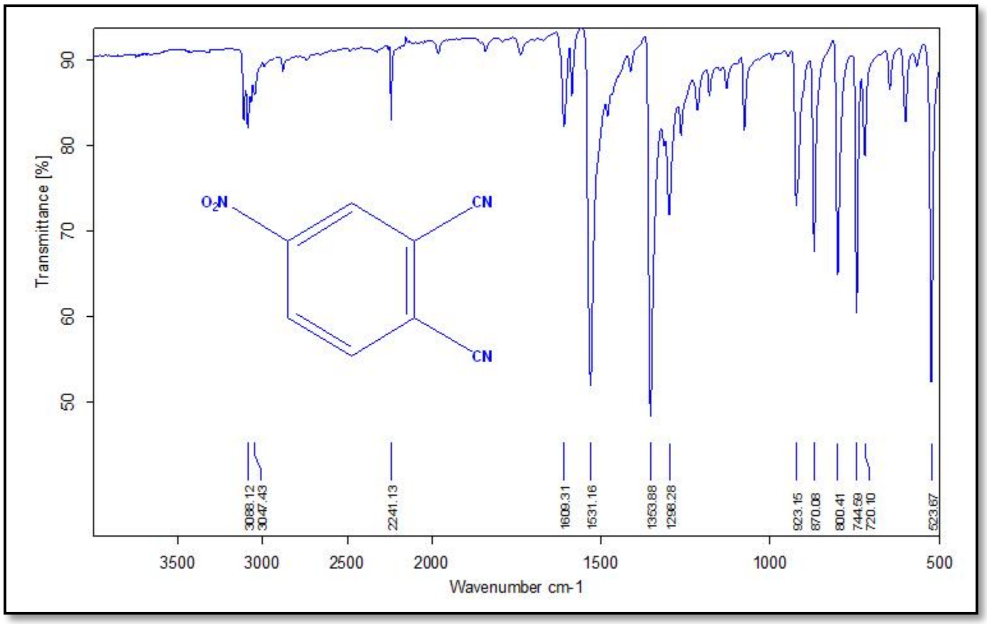


Figure 2. FT-IR of compound A.

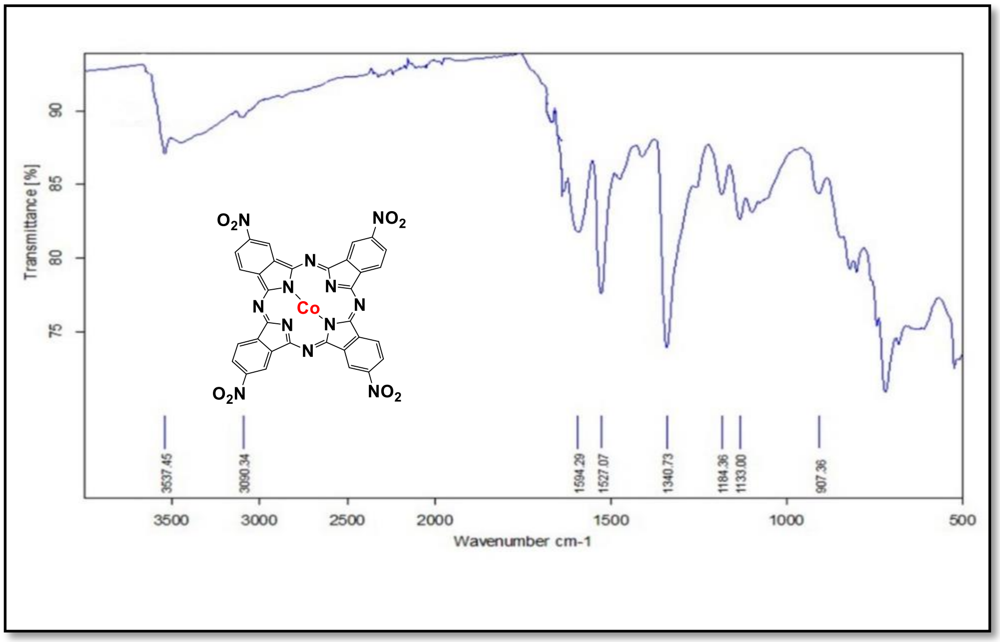
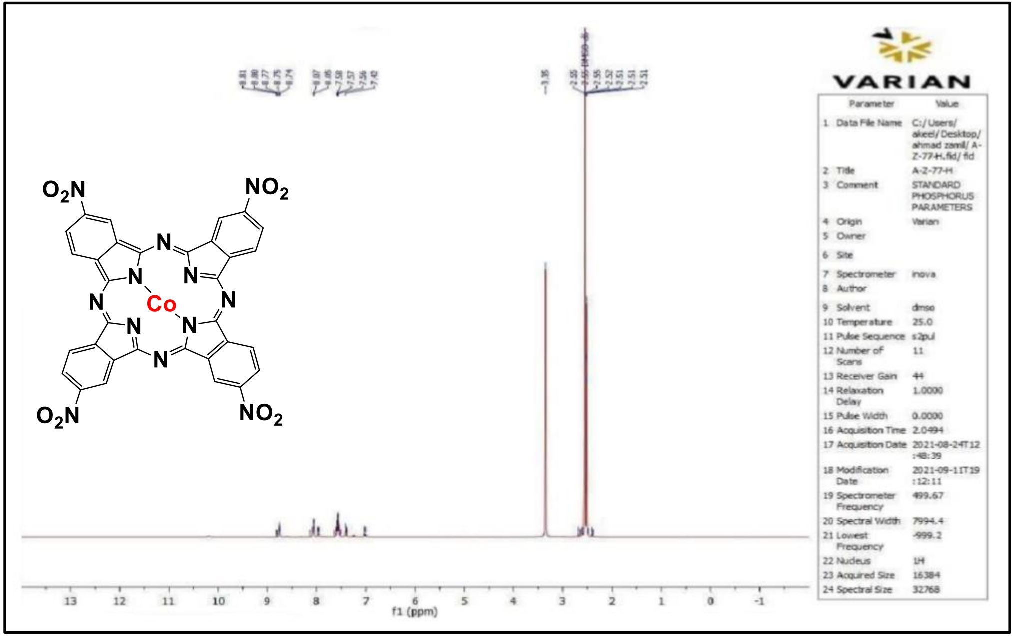


Figure 3. FT-IR of compound (**K1**)

^{1}H NMR of (**K1**) shows appearance peaks at (6.7- 7.7) ppm of (12H , Pc-CH) and (3.35)ppm of (H_2O), Figure 4.



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24 Spectral Size	32768

Figure 4. ^{1}H NMR of compound (**K1**)

The compound (K1) exhibits two absorption bands in its UV-Visible spectrum, as shown in figure 5. The first band, known as the B or soret-band, occurs at a wavelength of 258.25 nm. The second band, called the Q-band, occurs at a wavelength of 686.5 nm, which is close to the infrared (IR) region. In optical spectroscopy, the Q-band is associated with a band gap energy of 1.63 eV.

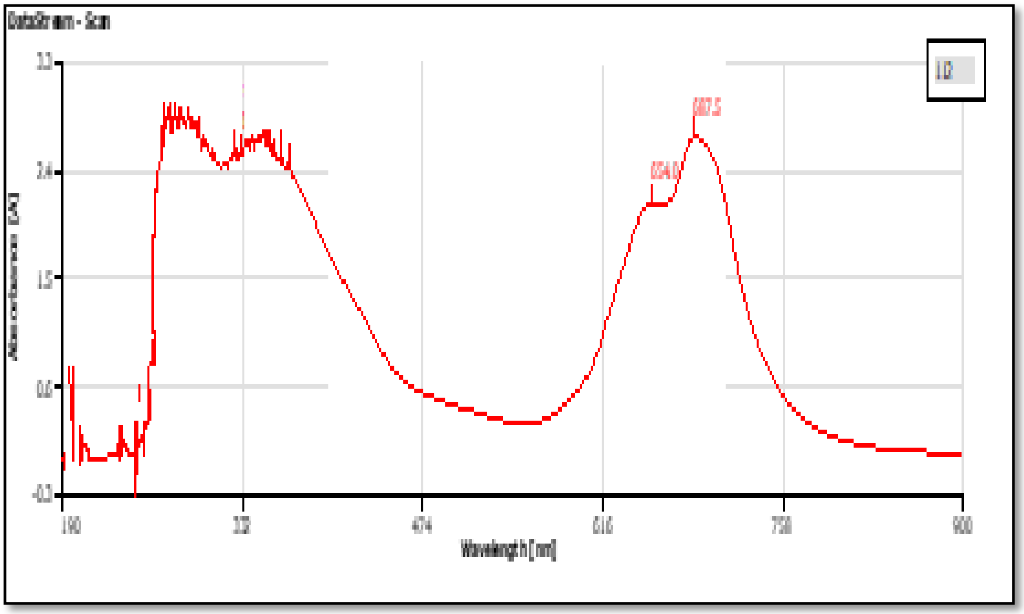

Figure (5) UV – Visible of compound **K1** (Blue line) in DMF ($1×10^{-5}$ M)

The FT-IR of compound (K2) in figure 6 exhibits peaks at specific wavenumbers indicating the presence of certain functional groups. FTIR cm-1: ν: NH_2 at 3217 and 3349, C–H of aromatic at 3100, O–H of carboxylic acids at 2500-3000, C=O of carboxylic acid at 1658, –C=C– stretch of aromatic at 1520, C–O ether at 1128, and aromatic group at 728. The absence of the NO_2 band at 1340 cm-1 and 1527 cm-1 confirms the connection between (A1) and 5-amino salicylic acid.

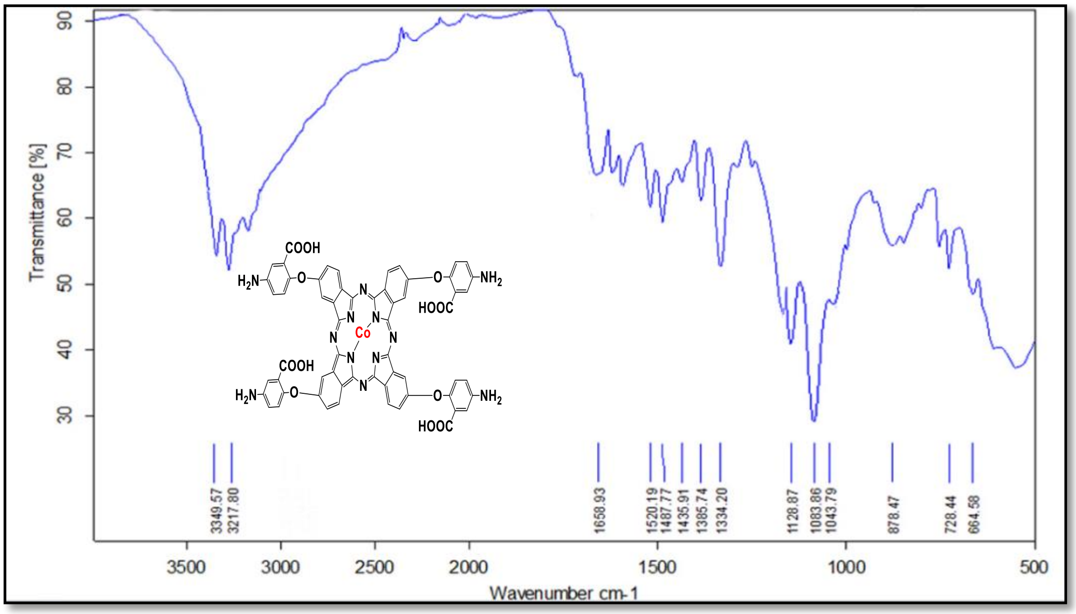

Figure 6. FT-IR of compound (K2)

The 1H NMR of (K2) figure (7) protons ppm, the (12H, Pc-CH) peaks appear at (7.56-8.60) ppm, the (12H, benzoic rings) peaks appear at (6.51-7.21) ppm, NH_2 proton appears at 5.41 ppm , OH protons of carboxylic acid at (10.30) ppm and (3.35)ppm of (H_2O).

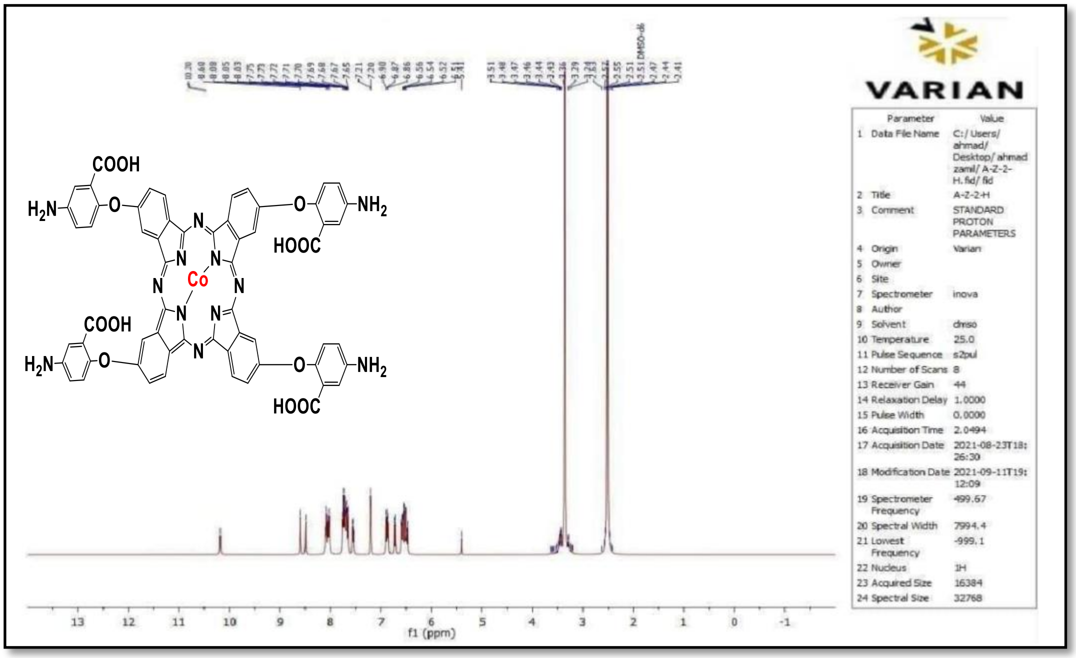

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Figure (7) ^1H NMR of compound (K2)

The UV-Visible spectrum of compound (K2), as depicted in figure 8, exhibits two absorption bands. The first band, known as the B or soret band, appears at a wavelength of 468 nm. The second band, referred to as the Q-band, occurs at a wavelength of 704.5 nm. Notably, the Q-band undergoes a shift of approximately 18 nm towards the infrared (IR) region. This shift corresponds to a band gap energy of 1.77 eV calculated via optical means.

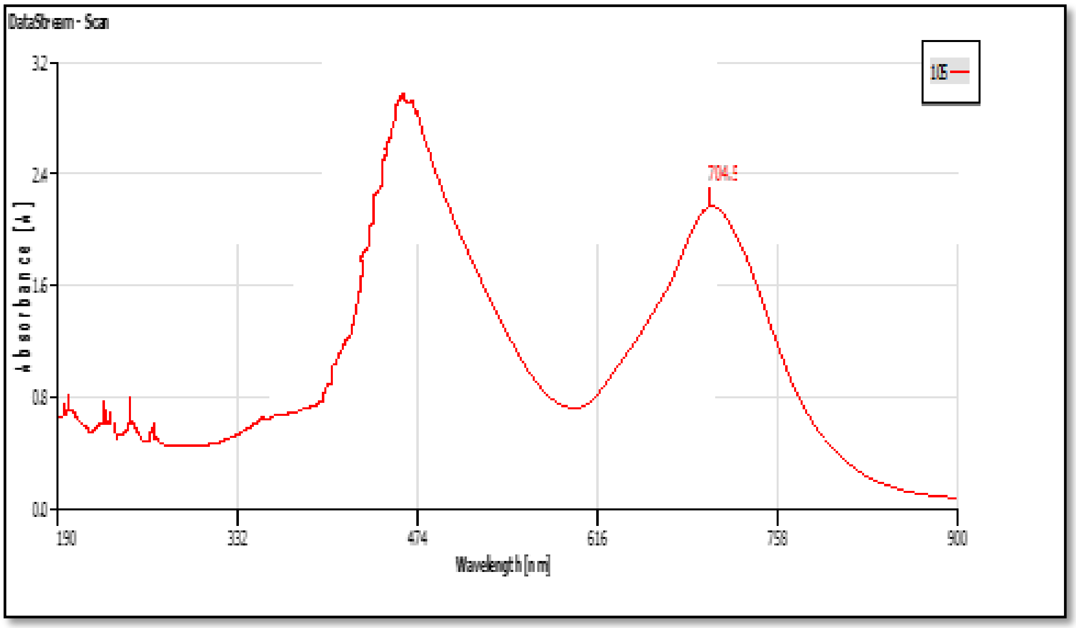

Figure (8) UV – Visible of compound K2 in DMF (1×10^{-5} M).

The FT-IR of compound (K3), shown in figure 9, is compared with that of 4-nitro phthalonitrile, shown in figure 2. The FTIR cm^{-1}: ν: presence of C–H bonds in the aromatic ring at a frequency of 3100, and the presence of –C=C– bonds in the aromatic ring at a frequency of 1561. Additionally, peaks are observed at frequencies of 1331 and 1561, which can be attributed to the presence of NO_2 groups, and a peak is observed at 719, which corresponds to the aromatic group. The absence of the nitrile group at 2241 in the FT-IR indicates the conversion of 4-nitro phthalonitrile into (K3).

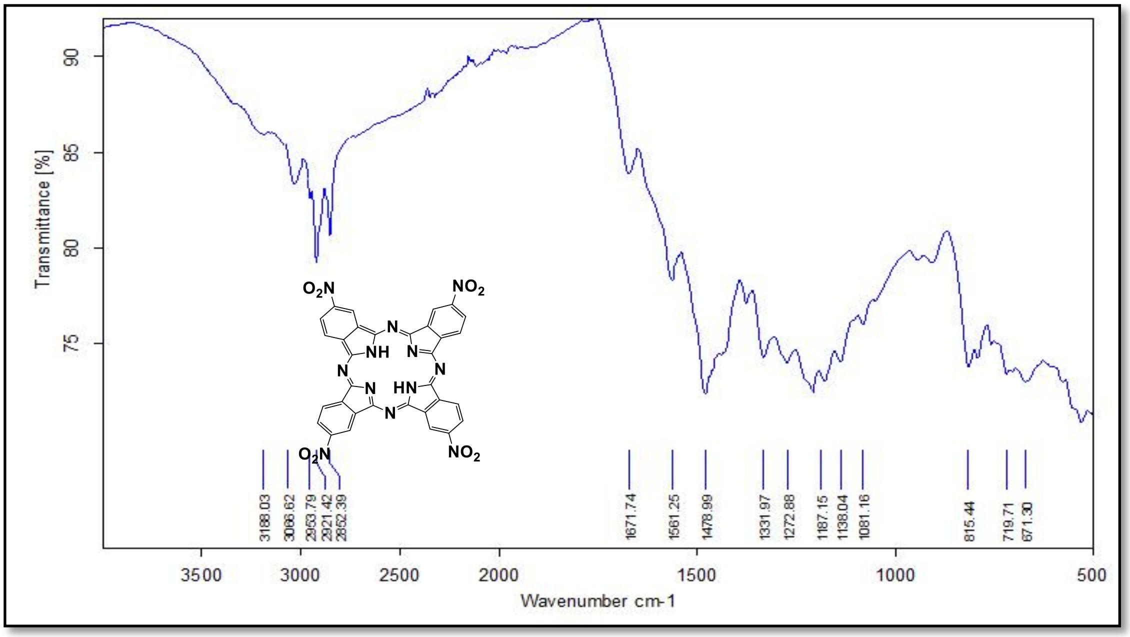

Figure 9. FT-IR of compound (K3)

The 1H NMR of (K3) figure (10) protons ppm, the (12H, Pc-CH) peaks appear at (6.82-8.26) ppm and NH proton appears at 9.71 ppm

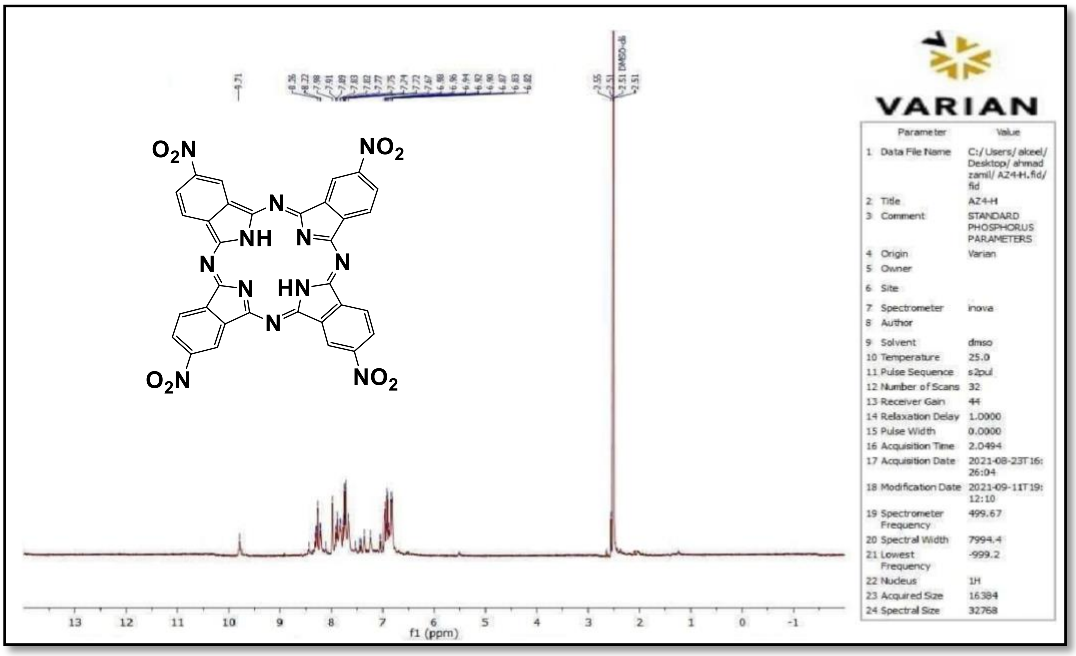

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Figure 10. ^{1}H NMR of compound (K3)

The compound (K3) exhibits two absorption bands in its UV-Visible spectrum. The first band, known as the B or soret band, appears at a wavelength of 252.2 nm. The second peak, called the Q-band, is observed at 689 nm, which is close to the infrared (IR) region. In optical spectroscopy, the Q-band is associated with a band gap energy of 1.68 eV, as shown in Figure 11.

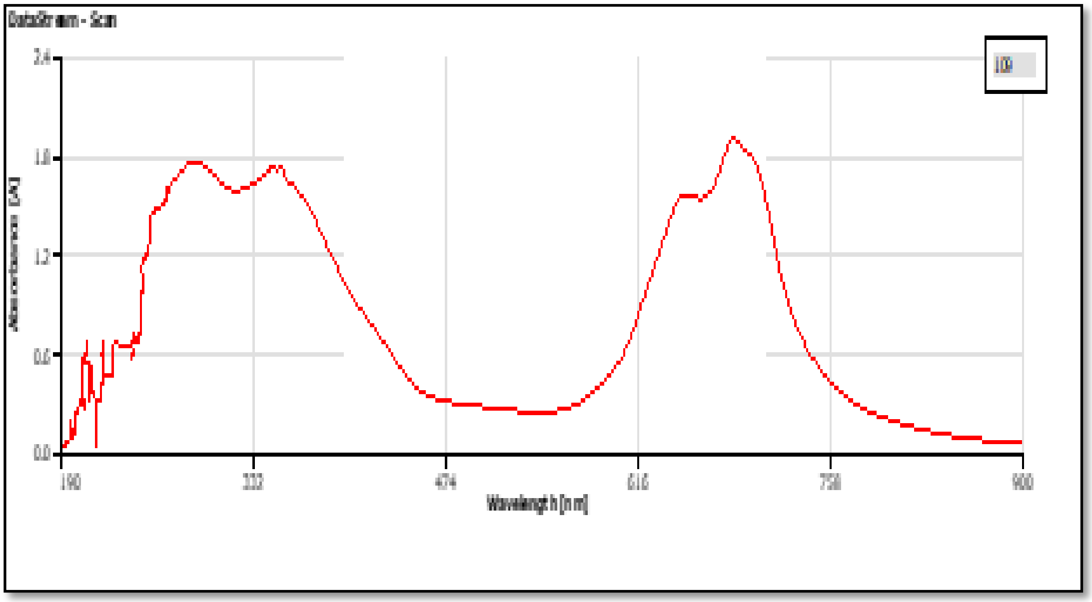

Figure 11. UV – Visible of compound K3 in DMF (1×10^{-5} M)

The compound (K3) was synthesized by the combination of 6.21 mmol of $ZnCl_2$ with 5.77 mmol of 4-nitrophthalonitrile. The Fourier Transform Infrared FT-IR of compound (K3) shown in Figure 12 are being compared to those of 4-nitrophthalonitrile. The spectrum cm^{-1} of Figure 2 exhibits peaks associated with the C–H bonds in the aromatic molecule at 3090, the –C=C– bonds at 1466 and 1607, the NO_2 group at 1326 and 1519, and the aromatic group at 724. The lack of the nitrile group peak at 2241 confirms the effective conversion of 4-nitro phthalonitrile(A) into compound (K3).

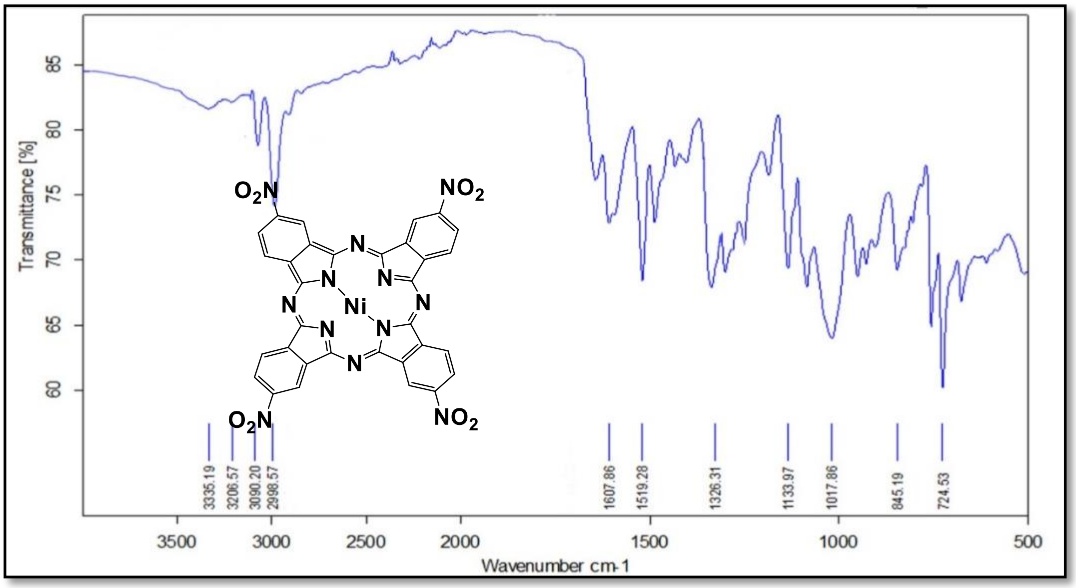

Figure 12. FT-IR of compound (K3)

The 1H NMR of (K3) figure (13) protons ppm, the (12H, Pc-CH) peaks appear at (6.15-8.46) ppm and H_2O at (3.35)

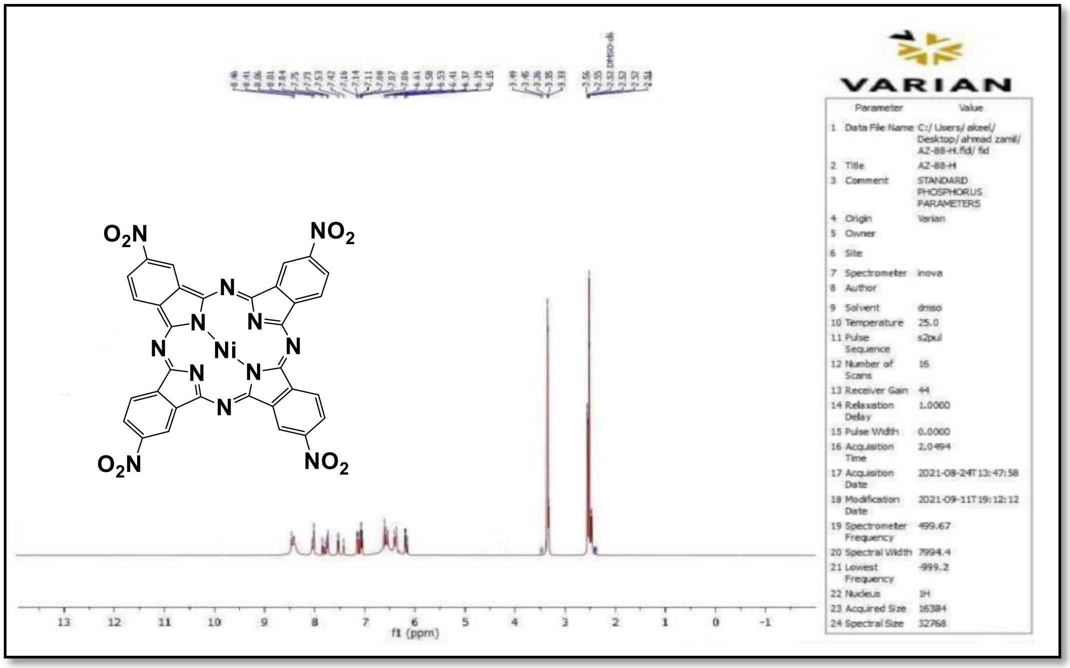

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Figure 13. ^{1}H NMR of compound (K4)

The compound (K3) exhibits two absorption bands in its UV-Visible spectrum, as shown in Figure 14. The first band, known as the B or soret-band, occurs at a wavelength of 359.25 nm. The second band, called the Q-band, occurs at a wavelength of 685.5 nm, which is close to the infrared (IR) region. In optical spectroscopy, the Q-band is associated with a band gap energy of 1.66 eV.

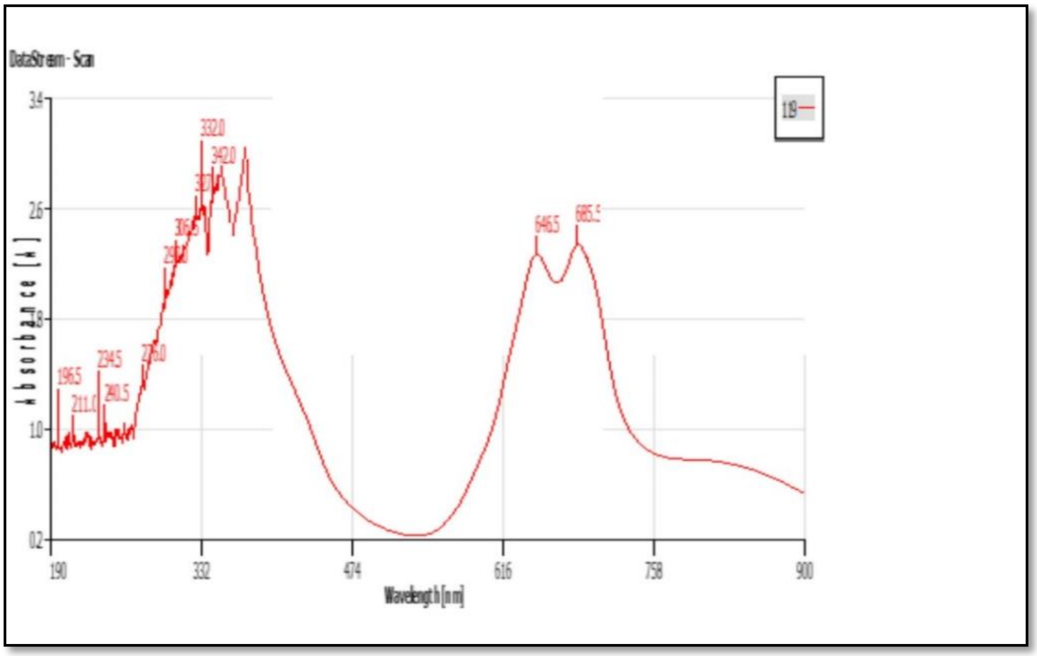

Figure 14. UV – Visible of compound K3 in DMF (1×10^{-5} M)

Table 1. UV – Visible data of compounds **K1, K2, K3 and K4** in dimethylformamide (1×10^{-5} M).

Compound	**λAbs(nm)**	**λAbs(nm)**	**λAbs(nm)**	**λMax(nm)**	**Band gap (eV)**
K1	258.2	-	-	686.5	1.63
K2	468	-	-	704.5	1.77
K3	252.2	-	-	689.0	1.68
K4	342.0	359.25	646.5	685.5	1.66

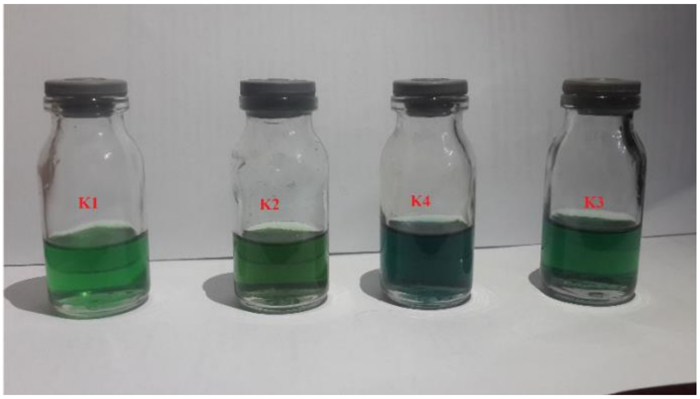

Figure 15. Photographs of solutions of compounds K1,K2,K3 and K4 in DMF (1×10^{-4}M)

Table 2. Elemental Analysis substituted metallophthalocyanine of compounds K1,K2,K3 and K4

			C%		***H%***		***N%***	
Comp.	**Chemical Formula**	**Mol Wt (g/mol)**	**Fou.**	**Calc.**	**Fou.**	**Calc.**	**Fou.**	***Calc.***
K1	$C_{32}H_{12}CoN_{12}O_8$	751.46	51.15	50.02	1.61	2.12	22.37	23.34
K2	$C_{60}H_{36}CoN_{12}O_{12}$	1175.95	61.28	60.11	3.09	4.22	14.29	15.33
K3	$C_{32}H_{14}N_{12}O_8$	694.54	55.34	56.05	2.03	3.34	24.20	25.76
K4	$C_{32}H_{12}N_{12}NiO_8$	751.22	51.16	52.22	1.61	2.34	22.37	23.81

The recently synthesized compounds (K1-k4) showed low rmsd values ranging from 1.1750 to 2.049 with the enzyme active site and enhanced binding energy (S.score) ranging from -9.8024 to -10.4765 Kcal/mol. The compounds exhibited strong conformity to the original ligand position, as illustrated in Figure 15. This indicates that the novel derivatives exhibit enhanced binding affinity to the target protein, which is advantageous for therapeutic efficacy and offers a more precise structural representation compared to the reference ligand, as demonstrated in Table 3.

Table 3. Molecular docking Etotal energy value for studies molecule

Compound	**S score (K cal/mol)**	**Rmsd**	**No. of binding sites**	**Binding amino acids**
K1, K3, K4	-10.4765	2.049	9	ASP 163, LYS 147, LYS 111, LYS 111, ASP 104, ASP 104, LYS 147, LYS 111, LYS 111, ILE 19, VAL 27, THR 107
K2	-9.8024	1.1750	5	ASP 163, LYS 147, ILE 19, ILE 19, VAL 27

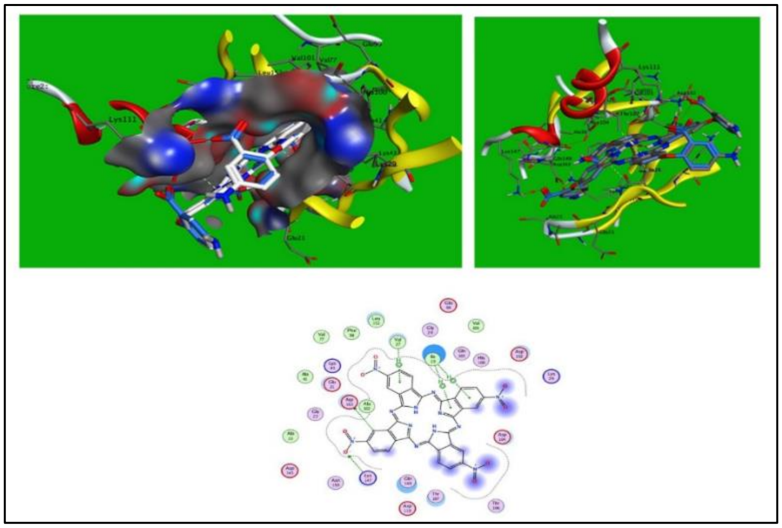

Figure 15. Docking representation of ligand (K1,K3,K4) against Enzyme 4AUA: Transferase

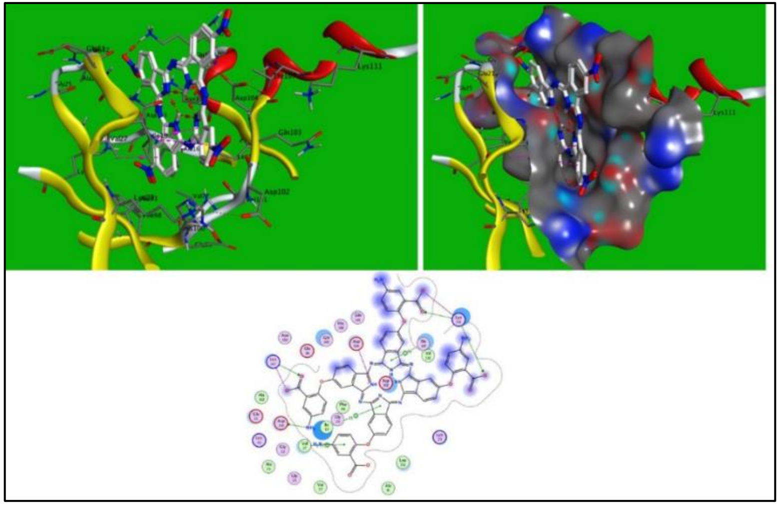

Figure 16. Docking representation of ligand K2 against Enzyme 4AUA: Transferase

Conclusion

1- A new nitro phthalonitrile precursor was used to successfully make cobalt and nickel phthalocyanines.
2- The molecules that were made in this work have been given their photophysical and photochemical features. All of the phthalocyanines can be mixed with standard organic solvents like DCM, THF, DMSO, and DMF.
3- The 1H NMR and FT-IR of all the synthesised phthalocyanines showed unique bands, showing that the starting material was used to make the desired Pc.
4- The UV-vis spectrum shows that these new chemicals strongly absorb light in the near-infrared range (646–720 nm).
5- The compounds exhibited strong conformity to the original ligand position

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