

Synthesis and Characterization of Nitrotetrasubstituted Metallophthalocyanine (Zn, Co, Ni, Cu) Derivatives

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Abstract

4-(2,4-dinitrophenoxy)phthalonitrile, **1**, was prepared by the reaction of 4-hydroxyphthalonitrile and 1-chloro-2,4-dinitrobenzene in the presence of K_2CO_3 . Zn(II), **2**, metallophthalocyanine was synthesized by the reaction of phthalonitrile derivative with $Zn(OAc)_2 \cdot 2H_2O$ in quinoline. Co(II), **3**, Ni(II), **4**, and Cu(II), **5**, metallophthalocyanine derivatives were synthesized by the reaction of phthalonitrile derivative **1** with $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $CuCl_2$ salts in ethylene glycol, respectively. Compound **1** has been characterized by FT-IR and 1H -NMR spectroscopies. Metallophthalocyanin compounds **2-5** have been characterized by the UV/Vis, and FT-IR spectroscopies.

Keywords: Phthalocyanine, Nitrophthalocyanine, Zinc, Cobalt, Nickel, Copper

1. Introduction

Phthalocyanines are used in many application areas such as catalysts, gas sensors [1-3], solar cells [4,5], liquid crystals [6-8], nonlinear optical materials [9-11], photodynamic cancer therapy [12-16] due to their catalytic, electronic and optical properties [17].

By using very different groups at the peripheral [18, 19] and non-peripheral [20] positions of phthalocyanines, a large number of mononuclear, polynuclear [21-24], basket type [25-28] derivatives have been synthesized and characterized.

Many nitro-substituted phthalocyanines have been synthesized and are used in different applications such as optical limiters, gas sensors, organic thin film transistors, memory elements, single molecular magnets, in medicinal chemistry and in the preparation of hybrid nanoparticles [29]. Some of them have high electro-catalytic activity [30], high photovoltaic properties [31] and have been shown to have high capacity and good cycling performance in rechargeable lithium batteries [32].

In this study, tetrasubstituted zinc, cobalt, nickel and copper phthalocyanines containing electron-withdrawing nitro groups were synthesized and characterized by 1H -NMR, FT-IR and UV-vis spectroscopy. Many new phthalocyanine derivatives can be prepared by preparing aromatic amino phthalocyanine derivatives obtained by reducing the aromatic nitro groups, for example, water solubility can be gained by quaternization of amino groups.

In this study, tetrasubstituted zinc, cobalt, nickel and copper phthalocyanines containing electron-withdrawing nitro groups were synthesized and characterized by 1H -NMR, FT-IR and UV-vis spectroscopy.

Water-soluble phthalocyanine derivatives can be prepared by quaternization of amino-substituted phthalocyanines obtained by reduction of aromatic nitro groups. Studies clearly show that water-soluble phthalocyanines are important in biological applications.

2. Experimental

All the reactions were carried out under argon atmosphere and the solvents were dried using molecular sieves or appropriate methods [33]. 4-Nitrophthalonitrile was prepared according to the literature [34]. $^1\text{H-NMR}$ spectra was taken at room temperature on a Bruker 300 MHz spectrometer and chemical shifts are given in ppm. FT-IR spectra were measured by preparing a KBr pellet on a Shimadzu Mattson 1000 spectrophotometer, and UV-vis spectra were measured on an ATI Unicam spectrophotometer.

2.1. Synthesis of 4-(2,4-dinitrophenoxy)phthalonitrile, 1,

To a solution of 4-hydroxyphthalonitrile (500 mg, 3.47 mmol) and 1-chloro-2,4-dinitrobenzene (1.1 g, 5.20 mmol) in 20 mL of DMSO, anhydrous K_2CO_3 (1.4 g, 10.41 mmol) was added over 30 min and the mixture was stirred at room temperature for 72 h. At the end of the reaction, the dark red mixture was poured into 150 mL of ice water, the solid formed was filtered, washed with 3x50 mL of water, and dried in vacuo. Yield: 0.76 g (% 70.6) $\text{C}_{14}\text{H}_6\text{N}_4\text{O}_5$ (310.23 $\text{g}\cdot\text{mol}^{-1}$). IR spectrum, ν , cm^{-1} : Ft: 3500, 3150, 2233, 1611, 1572, 1541, 1492, 1477, 1347, 1306, 1276, 1255, 1243, 1151, 1070, 951, 847, 835, 726, 527.

$^1\text{H NMR}$ spectrum, δ , ppm (CDCl_3): 8.99 d (1H), 8.59 dxd (1H), 7.88 d (1H), 7.45 d (1H), 7.40 d (1H), 7.37 d (1H).

2.2. Synthesis of 4-(2,4-dinitrophenoxy) Substituted Zinc Phthalocyanine, 2,

A mixture of 1 (200 mg, 0.65 mmol) and $\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ (36 mg, 0.16 mmol) in quinoline (1.0 mL) was heated at 185 °C for 60 min. The completion of the reaction was monitored by UV-Vis spectrometry by taking samples at certain intervals. The product was precipitated by adding diethylether to the dark green mixture formed, the solid was filtered, washed with alcohol, water, alcohol and diethylether respectively, and dried in air. The dark green solid was soluble in DMF and DMSO. Yield: 79 mg (% 37.8). $\text{C}_{56}\text{H}_{24}\text{N}_{16}\text{O}_{20}\text{Zn}$ (1306.29 $\text{g}\cdot\text{mol}^{-1}$), IR: (ATR) 3510, 2950, 1646, 1597, 1523, 1463, 1331, 1299, 1171, 1055, 936, 823, 733 cm^{-1} , UV-VIS: (DMF, λ_{Max} , nm ($\log \epsilon$, $\text{M}^{-1}\text{cm}^{-1}$)) 671 (2.38) 605 (2.15) 307(2.74).

2.3. Synthesis of 4-(2,4-dinitrophenoxy) Substituted Cobalt Phthalocyanine, 3,

A mixture of 1 (200 mg, 0.65 mmol) and $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (38.2 mg, 0.16 mmol) in ethylene glycol (10 mL) was heated at 200 °C for 90 minutes. The completion of the reaction was monitored by UV-Vis spectrometry by taking samples at regular intervals. The product was precipitated by adding diethylether to the dark green mixture formed, the solid was filtered, washed with alcohol, water, alcohol and diethylether respectively, and dried in air. The dark green solid is soluble in DMF and DMSO. Yield: 65 mg (% 31.2). $\text{C}_{56}\text{H}_{24}\text{N}_{16}\text{O}_{20}\text{Co}$ (1299.83 $\text{g}\cdot\text{mol}^{-1}$), IR: (ATR) 3485, 3100, 2955, 1599, 1532, 1464, 1408, 1342, 1263, 1118, 1089, 1061, 951, 830, 744, 635 cm^{-1} , UV-VIS: (DMF, λ_{Max} , nm ($\log \epsilon$, $\text{M}^{-1}\text{cm}^{-1}$)) 661 (2.78) 595 (2.31) 324 (2.92).

2.4. Synthesis of 4-(2,4-dinitrophenoxy) Substituted Nickel Phthalocyanine, 4,

A mixture of 1 (200 mg, 0.65 mmol) and $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (38.1 mg, 0.16 mmol) in ethylene glycol (10 mL) was heated at 200 °C for 120 minutes. The completion of the reaction was monitored by UV-Vis spectrometry by taking samples at regular intervals. The product was precipitated by adding diethylether to the dark

green mixture formed, the solid was filtered, washed with alcohol, water, alcohol and diethylether respectively, and dried in air. The dark green solid is soluble in DMF and DMSO. Yield: 58mg (%27.9). $C_{56}H_{24}N_{16}O_{20}Ni$ (1299.59 g.mol⁻¹), IR: (ATR) 3495, 3145, 3015, 1602, 1535, 1469, 1346, 1267, 1120, 1092, 1066, 954, 833, 743. cm⁻¹, UV-VIS: (DMF, λ_{Max} , nm (log ϵ , M⁻¹cm⁻¹)) 672 (3.00) 607 (2.42) 345 (2.78).

2.5. Synthesis of 4-(2,4-dinitrophenoxy) Substituted Copper Phthalocyanine, 5,

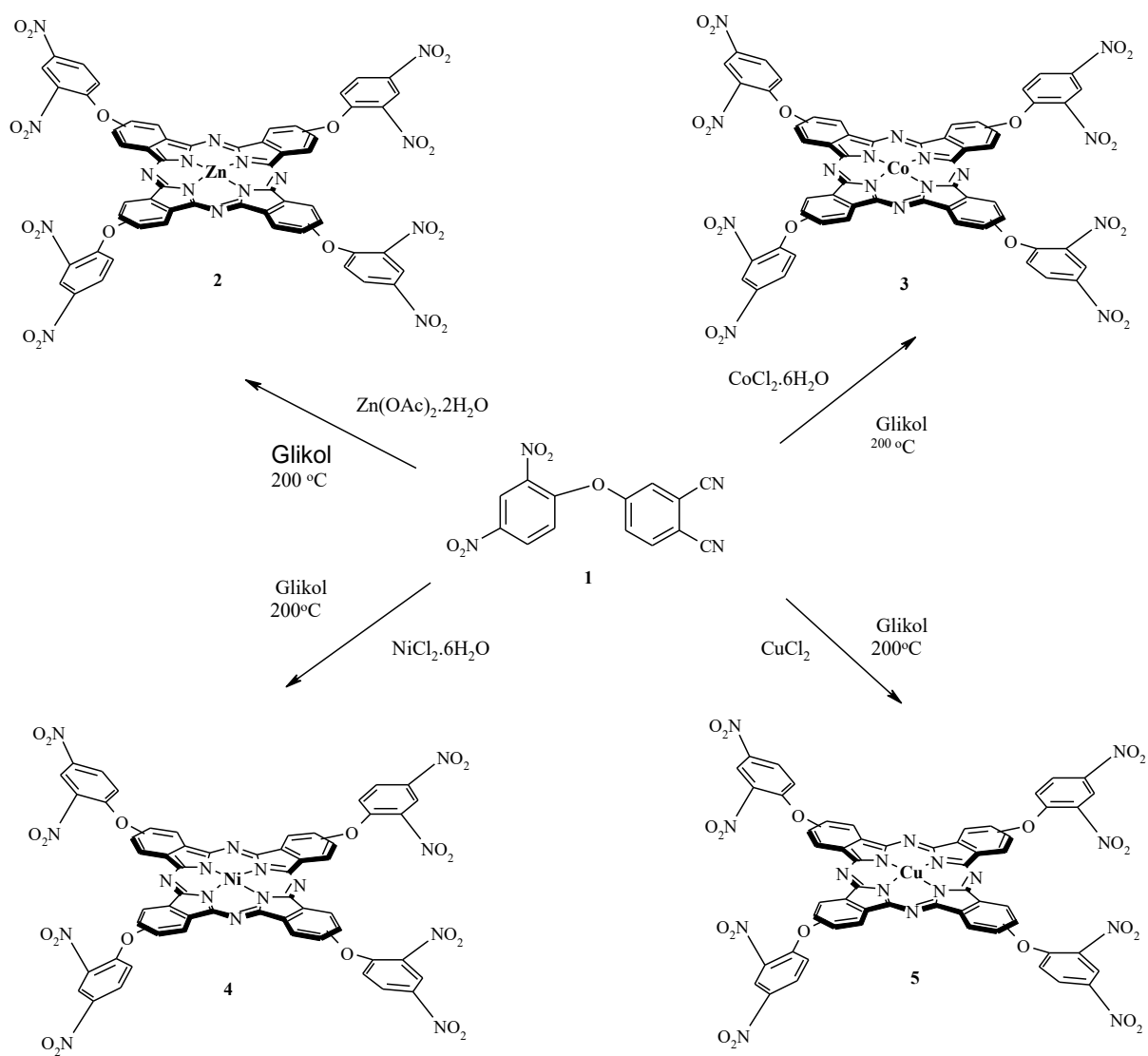
A mixture of 1 (200 mg, 0.65 mmol) and CuCl₂ (21.5 mg, 0.16 mmol) in ethylene glycol (10 mL) was heated at 200 °C for 210 minutes. The completion of the reaction was monitored by UV-Vis spectrometry by taking samples at regular intervals. The product was precipitated by adding diethylether to the dark green mixture formed, the solid was filtered, washed with alcohol, water, alcohol and diethylether repectively, and dried in air. The dark green solid is soluble in DMF and DMSO. Yield: 82mg (% 39.3). $C_{56}H_{24}N_{16}O_{20}Cu$ (1304.45 g.mol⁻¹), IR: (ATR) 3493, 3150, 3008, 1741, 1642, 1601,1535, 1469, 1343, 1267, 1089, 948, 832, 744, 662, 507. cm⁻¹, UV-VIS: (DMF, λ_{Max} , nm (log ϵ , M⁻¹cm⁻¹)) 672 (2.81) 606 (2.18) 346 (2.78).

3. Results and discussion

The synthesis of starting material 1 and phthalocyanine derivatives 2-5 is summarized in scheme 1. 4-(2,4-dinitrophenoxy)phthalonitrile, 1, was prepared by the reaction of 4-hydroxyphthalonitrile and 1-chloro-2,4-dinitrobenzene in the presence of K₂CO₃ at room temperature. By heating the mixture of 1 and Zn(OAc)₂·2H₂O in quinoline, zinc phthalocyanine derivative 2 was obtained.

By heating the mixture of compound 1 and CoCl₂·6H₂O, NiCl₂·6H₂O and CuCl₂ in ethyleneglycol at 200 °C, metal phthalocyanine derivatives 3, 4 and 5 were obtained, respectively. The characterization results of compounds 1-5 confirmed the proposed structure of the starting compound and phthalocyanines.

In the IR spectrum of compound 1 (Figure 1), the –CN vibration band of phthalonitrile is observed at 2233 cm⁻¹ [10, 45, 60] and this vibration band disappeared in the IR spectra of metallo phthalocyanine derivatives. In the IR spectra of all compounds 1-5, the vibration bands of aromatic nitro groups were observed at 1347 cm⁻¹, 1331 cm⁻¹, 1342 cm⁻¹, 1346 cm⁻¹ and 1343 cm⁻¹, respectively.



Scheme 1. The synthesis of starting material and phthalocyanine derivatives **1-5**

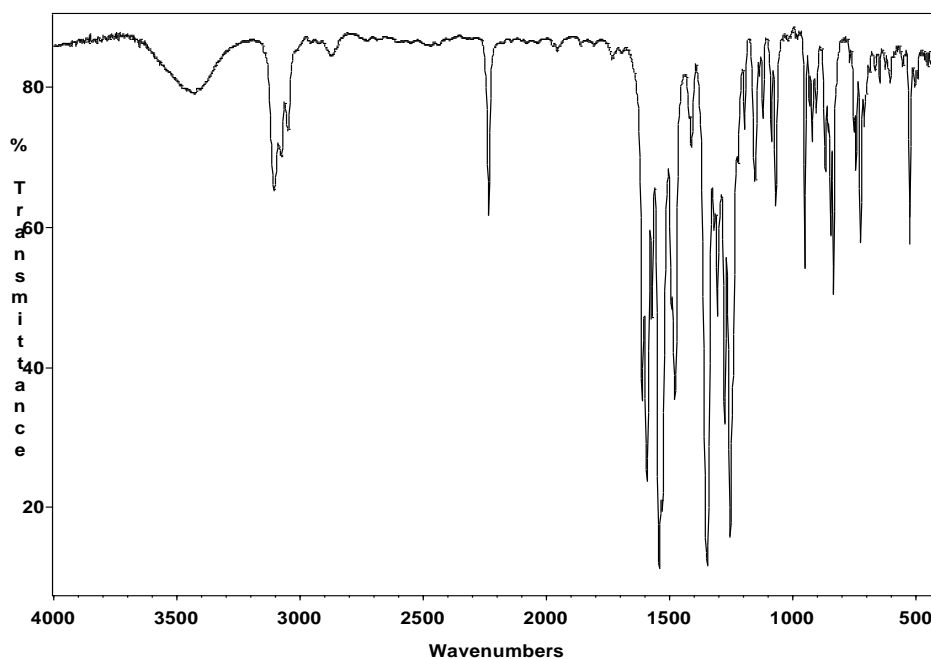


Figure 1. FT-IR spectrum of compound 1

In the ¹H-NMR spectrum of compound 1 measured in CDCl₃ (Figure 2), aromatic proton peaks are observed in the range of 8.99-7.37 ppm.

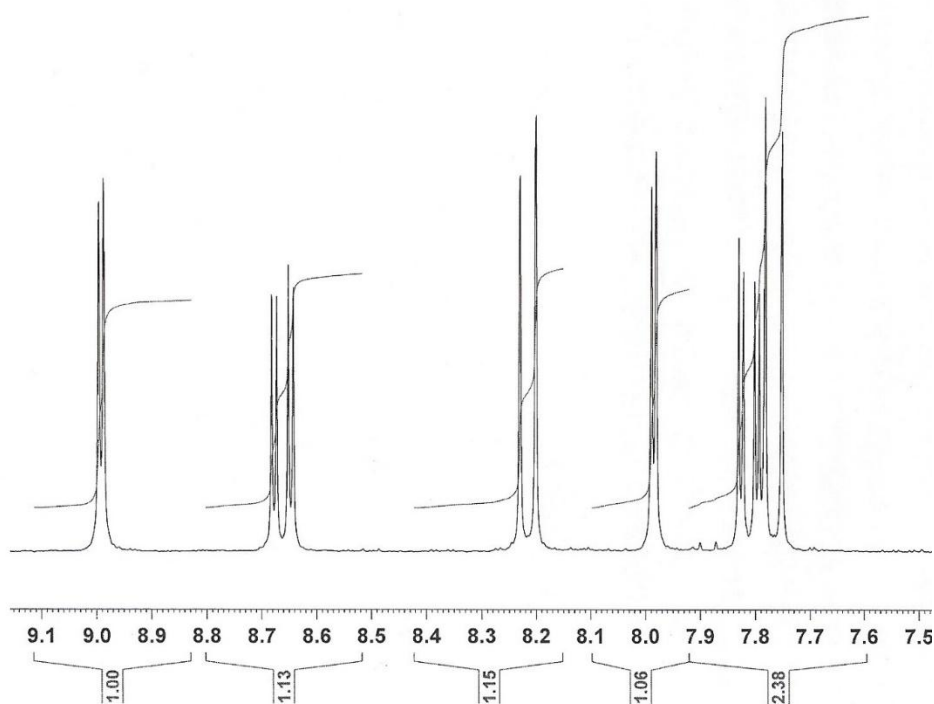


Figure 2. ¹H-NMR spectrum of compound 1 (CDCl₃)

The Q band of all compounds was attributed to the π - π^* transition from highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring. UV-vis

spectra of 2–5 phthalocyanine derivatives in DMF showed typical absorption in the Q band region between 600–700 nm (Figure 3).

The UV–vis spectra of compounds 2–5 in DMF give the characteristic Q-band absorption for metallophthalocyanines a peak at around 671 nm, 661 nm, 672 nm and 672 nm, respectively. In addition, a shoulder was observed at 605 nm, 595 nm, 607 nm and 606 nm in the UV-vis spectra of compounds 2–5, respectively.

In addition, the B-band of all phthalocyanines were seen from the deeper π Levels-LUMO transitions. The B-band of compounds 2–5 appeared at around 307 nm, 324 nm, 345 nm, and 346 nm, respectively (Figure 3).

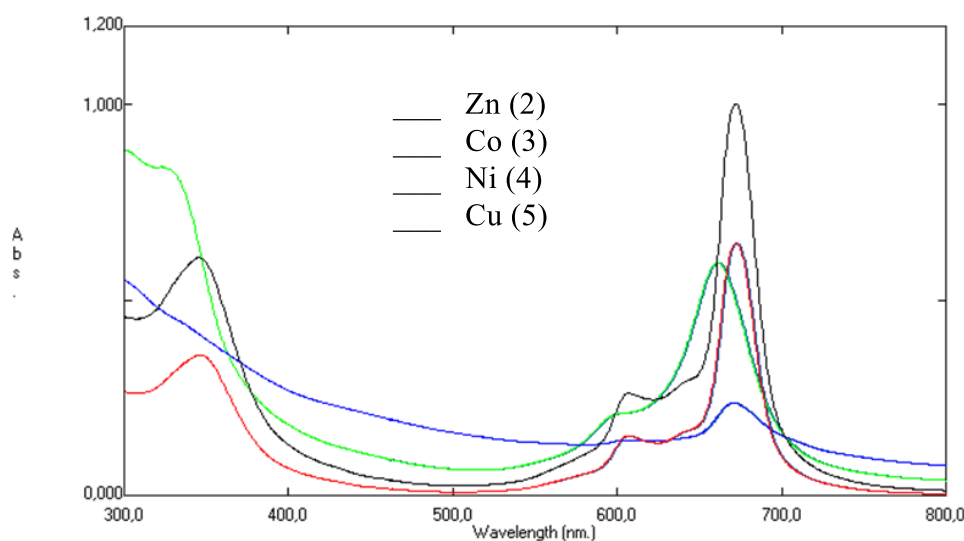


Figure 3. UV-vis spectra of compounds 2-5

4. Conclusions

Tetrasubstituted zinc, cobalt, nickel and copper phthalocyanines containing electron-withdrawing nitro groups were synthesized and characterized by $^1\text{H-NMR}$, FT-IR and UV-vis spectroscopy. Preparation of water-soluble phthalocyanine derivatives by reduction and quartinization of aromatic nitro groups in synthesized phthalocyanine derivatives will further increase the importance of phthalocyanines in many biological applications, such as photodynamic cancer therapy.

Conflict of Interests

The author declares that there is no conflict of interest.

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