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Research Article

Synthesis and Characterization of Zinc Phthalocyanines Containing 2-Hydroxy-6-methoxyisonicotinic Acid Moieties

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Abstract : Novel zinc phthalocyanines were synthesized by the reaction of phthalonitriles containing methyl 2-hydroxy-6-methoxyisonicotinate. These compounds were obtained via aromatic nucleophilic substitution reactions. All compounds have been determined by elemental analysis, FT-IR, NMR, MS and electronic absorption. The solubility of phthalocyanines is very low in DMSO and DMF but high in alkaline aqueous solution. The UV-Vis spectra of the Zn(II) phthalocyanines were recorded in different concentration in DMF, DMSO and also in different solvents as DMF, DMSO, and water. Peripheral substitute zincphthalocyanines (5 and 7) showed aggregation in water. Nonperipheral substitute zincphthalocyanine (7) showed monomeric behavior in DMSO, DMF, and water. Beer's law was obeyed for zinc phthalocyanines.

Keywords : Methyl 2-Hydroxy 6-methoxyisonicotinate, Phthalonitrile, Water Soluble Phthalocyanines.

1 Introduction

Phthalocyanines are aromatic chemical compounds that have many applications [1], [2]. These are dyes and pigments [3], liquid crystal [4], [5], optical applications [6], [7], HIV inactivation [8], [9], electrochromism [10], [11], molecular solar cells [12], [13], chemical sensors [13]–[15], semiconductors for organic field-effect transistors [16], [17], and photodynamic therapy [18]–[20]. Phthalocyanines, whose central atom can contain 70 different metals, have high thermal and chemical stability. While unsubstituted phthalocyanines are insoluble in common organic solvents and water, substituted ones are soluble. Phthalocyanines must contain some groups such as carboxyl in order to be soluble in water [21]. Various substituents can be added to the periphery, nonperiphery or axial positions of phthalocyanines. These substituents are macrocyclic moieties [22]–[24], thiol [25], naphthalene-amide groups [26], phenol groups [27]–[29], pyridine derivatives [30], [31], alcohols [32], [33]. In this study, the synthesis and characterization of water soluble zinc phthalocyanines containing 2-Hydroxy-6-methoxyisonicotinic Acid, a pyridine derivative, in peripheral and nonperipheral positions, and their UV-Vis spectra in different solvents and concentrations are reported.

2 Experimental Methods

2.1 Materials

IR spectra was recorded on a Perkin Elmer Frontier FT-IR Spectrometer as KBR pellets. UV-VIS spectra were recorded on a Perkin Elmer Lambda 35 UV/VIS Spectrometer. 1H-NMR and 13C-NMR studies were done on an Agilent 600 MHz spectrometer (Giresun University NMR Laboratory). Mass spectra were measured on an Agilent GC-MSD - 7890B GC-5977MSD (Amasya University-AUMAULAB). Elemental analyses were performed on a Leco Truspect Micro Analyzer. Methyl 2-hydroxy-6-methoxyisonicotinate, 4,5-dichlorophthalonitrile, 3- or 4-Nitrophthalonitrile were synthesized by following the procedure reported in [34]–[37].

2.2 Synthesis

Synthesis of Methyl 2-(2-Chloro-4,5-dicyanophenoxy)-6-methoxyisonicotinate (2): Methyl 2-hydroxy-6-methoxyisonicotinate 6,24g (34,10 mmol) was dissolved in dry DMF (50 mL) under nitrogen atmosphere at 70°C and K_2CO_3 7,03g (50,94 mmol) was added. After stirring for 2h, a solution of 4,5-dichlorophthalonitrile 6,68g (33,91 mmol) in dry DMF (70 mL) was added dropwise over 5h. The reaction mixture was stirred at 70°C under nitrogen atmosphere for 72 h. The mixture was then poured in to ice-water (400 g). The precipitate was filtered off washed with (10% w/w) NaOH solution and water until the filtrate was neutral. Recrystallization from ethanol gave a compound 2. The product is soluble in methanol, Ethyl alcohol, Ethyl acetate, aceton, THF, 1,4-dioxane, acetonitrile, Toluene, benzene, chlorobenzene, DMF, DMSO, DCM, $CHCl_3$ and insoluble in hexane.

Yield: 6.91 g (59%); mp: 155°C; anal. calcd. for $C_{16}H_{10}ClN_3O_4$: C, 55.91; H, 2.93; N, 12.23%. Found: C, 55.71; H, 2.83; N, 12.34%. FT-IR :ν_{max}, cm^{-1} 3102 (Aromatic CH), 3036, 2962 (aliphatic CH), 2901, 2743, 2581, 2237 (CN), 2023, 1730 (Ester C=O), 1623, 1592, 1575, 1564, 1490, 1447,1399, 1376,1251, 1157, 1029, 772, 536. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 7,94-7,17 (m, Aromatic and Pyridine CH, 5H), 3,99 (s, OCH_3, 3H), 3,74 (s, OCH_3, 3H). ^{13}C NMR ($CDCl_3$):δ, ppm 164.53 (C=O), 163.72, 160.26, 153.84, 144.26, 135.53, 127.57, 115.02, 114.29 (CN), 114.13 (CN), 112.44, 106.79, 102.63, 54.31 (OCH_3), 53.00 (OCH_3). GC MS; 343

Synthesis of Methyl 2-(3,4-dicyanophenoxy)-6-Methoxyisonicotinate (3): Compounds 3 and 4 were synthesized as discussed above. Yield: 2.55 g (61%); mp: 153°C; anal. calcd. for $C_{16}H_{11}N_3O_4$: C, 62.14; H, 3.58; N, 13.59%. Found: C, 62.34; H, 3.48; N, 13.49%. FT-IR :ν_{max}, cm^{-1} 3104 (Aromatic CH), 3078, 3047, 2965 (aliphatic CH), 2233 (CN), 1733 (Ester C=O), 1620, 1601, 1563, 1490, 1447, 1394, 1362, 10131, 770, 525. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 7,84-7,13 (m, Aromatic ve Pyridine CH, 5H), 3,97 (s, OCH_3, 3H), 3,78 (s, OCH_3, 3H). ^{13}C NMR ($CDCl_3$):δ, ppm 164.57 (C=O), 163.83, 159.93, 157.56, 144.14, 135.01, 125. 41, 125.22, 117.26, 115.22 (CN), 114.86 (CN), 110.94, 107.11, 103.33, 54.35 (OCH_3), 52.97 (OCH_3). GC MS; 309

Synthesis of Methyl 2-(2,3-dicyanophenoxy)-6-Methoxyisonicotinate (4): Yield: 5.38 g (64%); mp: 155°C; anal. calcd. for $C_{16}H_{11}N_3O_4$: C, 62.14; H, 3.58; N, 13.59%. Found: C, 62.24; H, 3.52; N, 13.66%. FT-IR :ν_{max}, cm^{-1} 3104 (Aromatic CH), 3123 (Aromatic CH), 3104, 3000, 2960 (aliphatic CH.), 2235 (CN), 1741 (Ester C=O), 1709, 1627, 1589, 1567, 1395, 1238, 1031, 872, 769, 552, 454.. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 7,77-7,16 (m, Aromatic ve Pyridine CH, 5H), 3,98 (s, OCH_3, 3H), 3,74 (s, OCH_3, 3H). ^{13}C NMR ($CDCl_3$):δ, ppm 164.56 (C=O), 163.66, 160.26, 156.68, 144.22, 133.92, 129.29, 126.66, 117.03, 114.93 (CN), 112.34 (CN), 109.81, 106.70, 102.93, 54.16 (OCH_3), 52.86 (OCH_3). GC MS; 309

Synthesis of zinc phthalocyanines (5): The mixture of Methyl 2-(2-Chloro-4,5-dicyanophenoxy)-6-methoxyisonicotinate (2) 2.50 g (7,28 mmol) , $Zn(CH_3COO)_2 \cdot 2\,H_2O$ 0.52 g (2,37 mmol) and dry quinoline (12 mL) was heated and stirred at 185-190°C for 24 h in a nitrogen atmosphere. Then, the mixture was cooled to room temperature; it was precipitated by adding methanol and filtered off. The green precipitate were washed with hot methanol, hot ethanol, diethyl ether, hexane and hot water. They were washed with methanol for 24 h in the soxhlet apparatus and dried in vacuo. The green products were stirred in LiOH solution at room temperature for 3 days and filtered. HCl solution was added to the filtrate and filtered off. Compound was washed with hot water and dried in vacuo. Yield: 1.81 g (72%); mp > 250°C; anal. calcd. for $C_{60}H_{32}Cl_4N_{12}O_{16}Zn$: C, 52.06; H, 2.33; N, 12.14%. Found: C, 52.12; H, 2.25; N, 12.24%. FT-IR :ν_{max}, cm^{-1} 3818-2500 (Carboxylic acid OH), 2978 (aliphatic CH), 1730 (Carboxylic acid C=O), 1617, 1575, 1492, 1455, 1395, 1368, 1241, 1185, 1105, 1085, 876, 749.

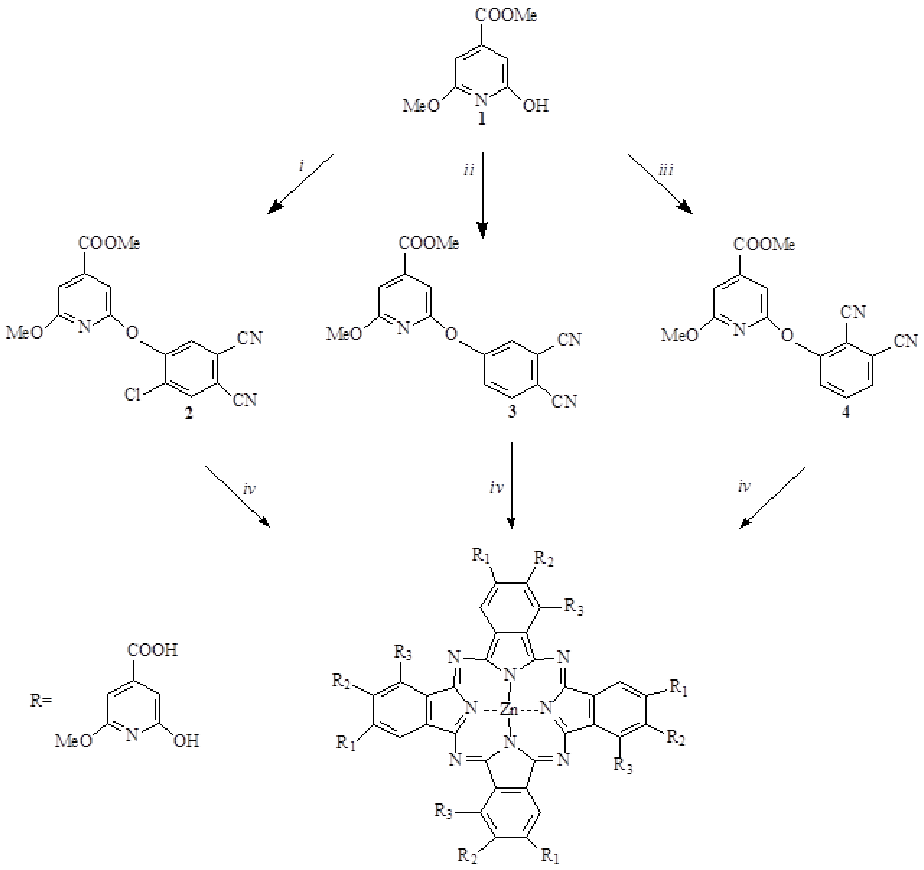
Synthesis of zinc phthalocyanines (6): Zinc phthalocyanines 6 and 7 were synthesized as discussed above. Yield: 1.14 g (56%); mp > 250°C; anal. calcd. for $C_{60}H_{36}N_{12}O_{16}Zn$: C, 57.82; H, 2.91; N, 13.49%. Found: C, 57.78; H, 2.86; N, 13.54%. FT-IR :ν_{max}, cm^{-1} 3500-2500 (Carboxylic acid OH), 2957 (aliphatic CH), 1727 (Carboxylic acid C=O), 1615, 1573, 1474, 1472, 1394, 1347, 1220, 1211, 1098, 1052, 999, 974, 874, 776, 775.

Synthesis of zinc phthalocyanines (7): Yield: 1.03 g (51%); mp > 250°C; anal. calcd. for $C_{60}H_{36}N_{12}O_{16}Zn$: C, 57.82; H, 2.91; N, 13.49%. Found: C, 57.90; H, 2.96; N, 13.44%. FT-IR :ν_{max}, cm^{-1} 3306-2500 (Carboxylic acid OH), 2957 (aliphatic CH), 1728 (Carboxylic acid C=O), 1616, 1570, 1486, 1465, 1392, 1344, 1238, 1185, 1129, 1096, 1042, 879, 752.

3 Results and Discussion

3.1 Synthesis and Characterization

Scheme 1 presents the synthetic route to Zinc Phthalocyanines Containing 2-Hydroxy-6-methoxyisonicotinic Acid. The phthalonitriles containing methyl 2-hydroxy-6-methoxyisonicotinate (2, 3, 4) were firstly prepared by treating 4,5-dichlorophthalonitrile, 3 or 4-nitrophthalonitrile with 2-Hydroxy-6-methoxyisonicotinic Acid in DMF using K_2CO_3 as the base for nucleophilic displacement reaction and gave moderate yield (59-64 %). The zinc phthalocyanines (5-7) containing 2-Hydroxy-6-methoxyisonicotinic Acid are obtained directly by cyclotetramerization of the corresponding phthalonitriles in the presence of the $Zn(CH_3COO)_2 \cdot 2\,H_2O$ in quinoline. In these reactions, it was observed that some of the ester groups transformed into carboxylic acid. It was observed that the resulting product dissolved in aqueous sodium hydroxide and there were peaks belonging to carboxylic acid groups in the FT-IR spectra. Considering that not all ester groups were converted to carboxylic acid, the products were hydrolyzed in aqueous LiOH. The yields of phthalocyanines 5, 6 and 7 were 72%, 56% and 51%, respectively. The phthalocyanines showed solubility in DMF, DMSO and water, but insolubility in common organic solvents. The new phthalocyanines and phthalonitriles were characterized by UV-Vis, FT-IR, ^{1}H NMR, ^{13}C NMR, MS spectra and elemental analysis. All the spectroscopic results of compounds show good agreement with target structures. The FT-IR spectra of synthesized phthalocyanines and phthalonitriles are very similar with the exception of small stretching shifts. In the FT-IR spectrum of phthalonitriles (2, 3, 4), aromatic CH, aliphatic CH, nitrile CN, carbonyl C=O, aromatic C=C, ether Ar-O-Ar stretching vibrations appeared at ca. 3100, 2964, 2231, 1597 and 1278 cm^{-1}, respectively. The new phthalocyanines (5-7) have carboxylic acid, aromatic CH, aliphatic CH, nitrile CN, carbonyl, aromatic C=C, ether Ar-O-Ar stretching vibrations appeared at ca. 3091, 2964, 2237, 1733, 1592 and 1251 cm^{-1}, respectively. While the strong -CN band of phthalonitriles (2-4) appeared at ca 2231 cm^{-1}, this band completely disappeared after cyclotetramerization to compounds (5-7) and strong carboxylic acid and



	R_1	R_2	R_3
5	Cl	R	H
6	H	R	H
7	H	H	R

Scheme: Synthetic route for Zn(II) Phthalocyanines (5, 6 and 7) i: 4,5-dichloroftalonitrile, DMF, K_2CO_3, N_2, 70°C, 72h ii: 4-nitroftalonitrile, DMF, K_2CO_3, N_2, 70°C, 72h iii: 3-nitroftalonitrile, DMF, K_2CO_3 , N_2, 70oC, 72h iv: quinoline, $Zn(CH_3COO)_2 \cdot 2\,H_2O$, N_2, 24h, 190°C

carbonyl band appeared at ca 3500-2500, 1730 respectively (Figure 1 and 2). In contrast to the phenoxy groups, the solubility of these phthalocyanines is very low in DMSO and DMF. ^{1}H NMR and ^{13}C NMR spectra of phthalocyanines (5-7) could not be measured due to the low solubility [23].

3.2 UV-Vis Spectra

UV-Vis spectrum of phthalocyanine is characteristic. The spectrum observed two strong absorption regions. These regions are B band Q band [1], [2]. The UV-Vis spectra of Zinc(II)phthalocyanines (5-7) were archived in DMSO, DMF and water (Figure 3, 6, 9). The results were shown in Table 1. Nonperipheral substitute zincphthalocyanine (7) showed monomeric behavior in DMSO, DMF and Water, evidenced by a single (narrow) Q-band at 688-696. However peripheral substitute zincphthalocyanines (5 and 6) showed aggregation in water (Figures 3 and 6). Also, compound 5 aggregated in DMSO (Figure 3, 4). B-Band absorbtions of zinc phthalosyanines in different solvents were observed at 342-346 nm for 5, 338-352 for 6 and 306-330 nm for 7. Figure 4, 5, 7, 8, 10 and 11 show UV-Vis spectra of phthalocyanines (5, 6 and 7) in the concentration range $1 \times 10^{-6} - 1.50 \times 10^{-5}$ M in DMSO and DMF. As shown in the 4, 5 7, 8, 10 and 11, the Q band decreases in intensity with decreasing concentration of phthalocyanines (5, 6 and 7). Beer's law was obeyed for 5, 6 and 7 in the concentration range $1 \times 10^{-6} - 1.50 \times 10^{-5}$ M.

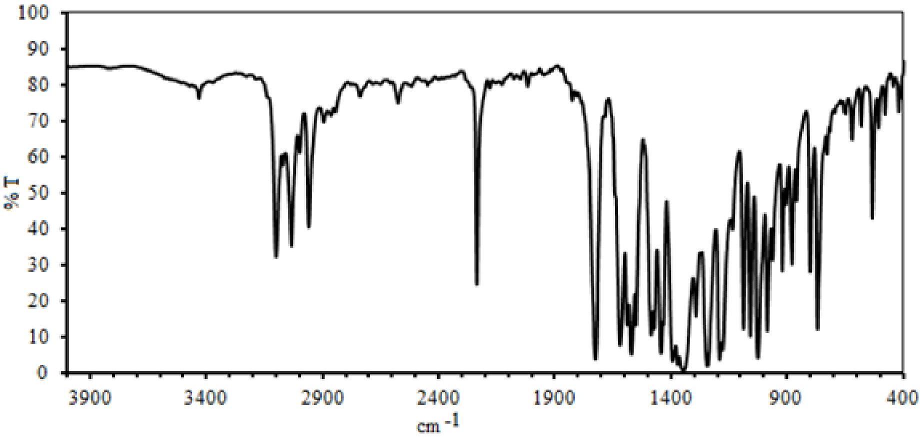


Figure 1: FT-IR Spectrum of Methyl 2-(2-Chloro-4,5-dicyanophenoxy)-6-methoxyisonicotinate (2)

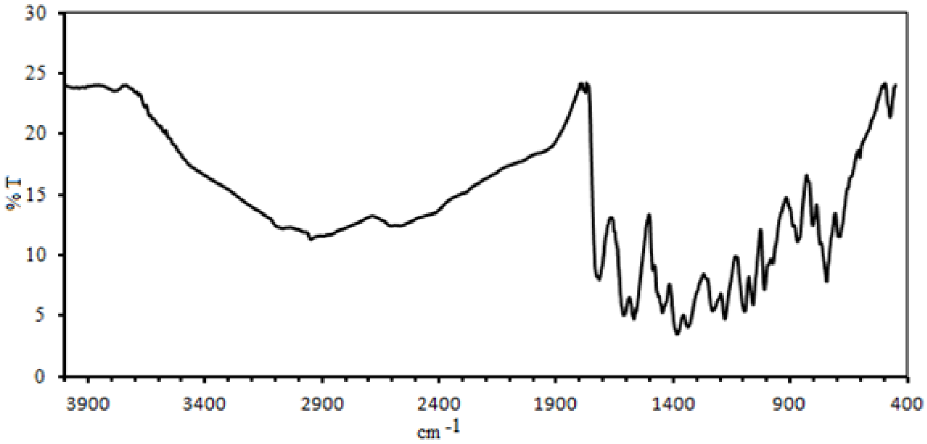


Figure 2: FT-IR Spectrum of the Zn(II)phthalocyanine (5) containing chlorine and methyl 2-hydroxy-6-methoxyisonicotinate in the peripheral position

Table 1: UV-vis spectral results for zinc(II)phthalocyanines (5-7) in various solvents at a concentration of $0,8 \times 10^{-5}$ M

Compound	Solvent	Q-Band		B-Band	
		λ_{max} (nm)	log ϵ	λ_{max} (nm)	log ϵ
5	DMSO	676, 635, 607	4.624; 4.921; 4.235	346, 381	4.851; 4.542
5	DMF	676, 642, 611	5.083; 4.388; 4.379	353	4.768
5	Water	671, 639	4.284; 4.769	342	4.732
6	DMSO	677, 640, 611	5.199; 4.555; 4.513	352	4.858
6	DMF	675, 645, 609	5.153; 4.434; 4.457	353	4.765
6	Water	671, 639, 585	4.433; 4.892; 4.095	286, 338	4.579; 4.770
7	DMSO	690, 660, 622	5.123; 4.363; 4.375	317	4.742
7	DMF	688, 657, 621	5.190; 4.436; 4.454	330	4.693
7	Water	696, 627	4.752; 4.224	306	4.574

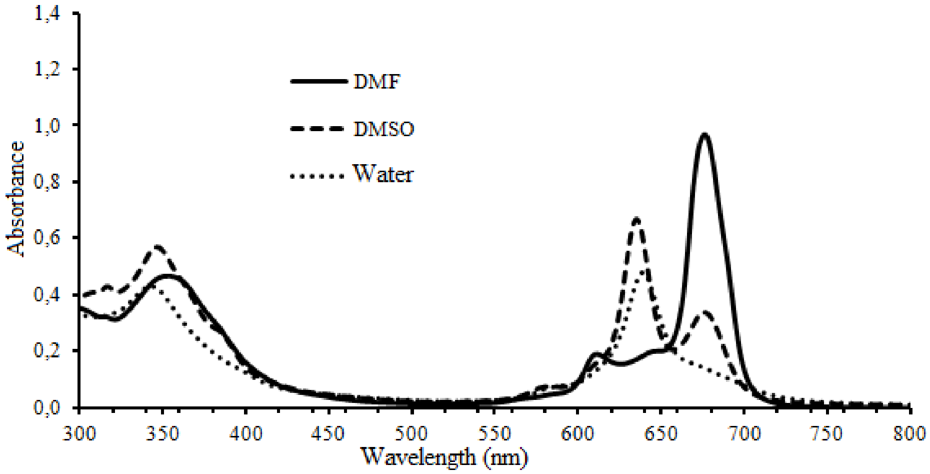


Figure 3: Uv-Vis Spectra of the Zn(II)phthalocyanine (5) containing chlorine and methyl 2-hydroxy-6-methoxyisonicotinate in the peripheral position in different solvents (Pc/NaOH mol ratio in aqueous solution: 1/4) (Concentration: $0,8 \times 10^{-5}$ M

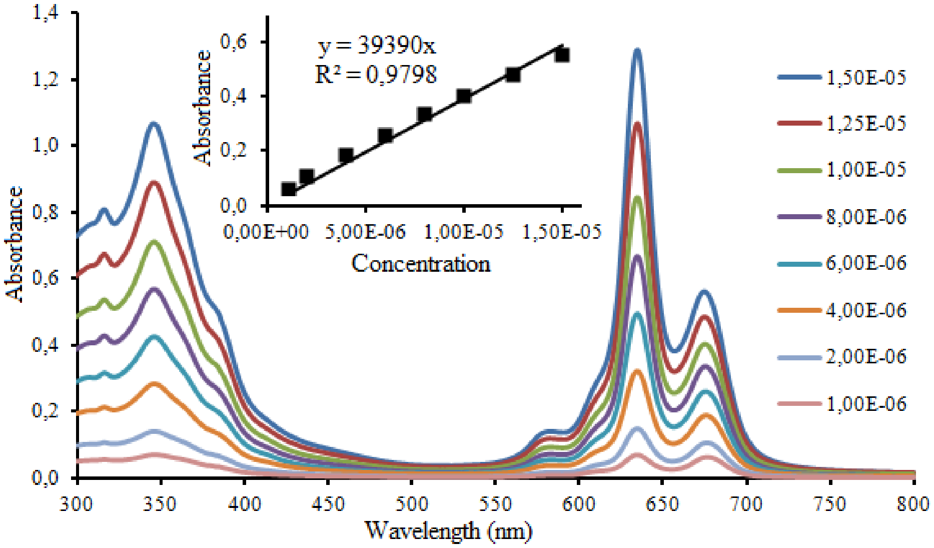


Figure 4: Uv-Vis Spectra of the Zn(II)phthalocyanine (5) containing chlorine and methyl 2-hydroxy-6-methoxyisonicotinate in the peripheral position in DMSO

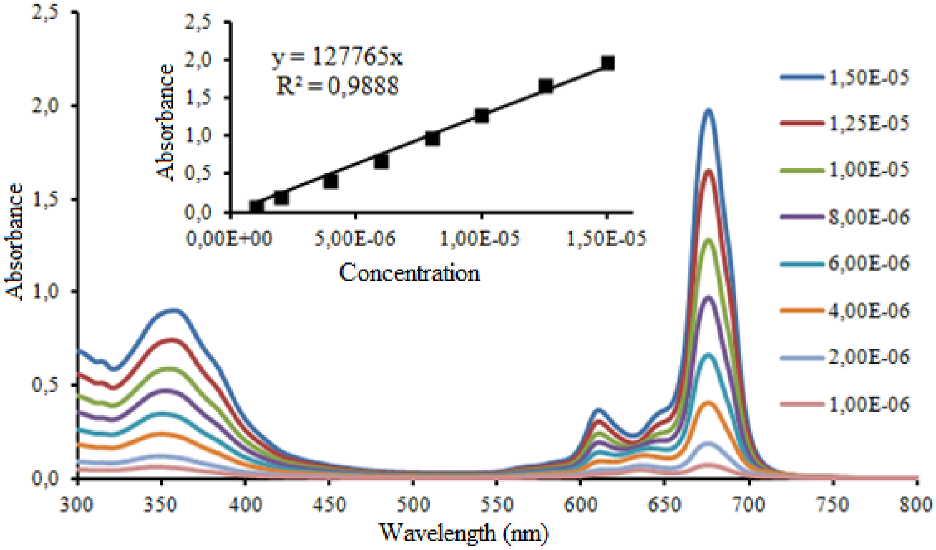


Figure 5: Uv-Vis Spectra of the Zn(II)phthalocyanine (5) containing chlorine and methyl 2-hydroxy-6-methoxyisonicotinate in the peripheral position in DMF

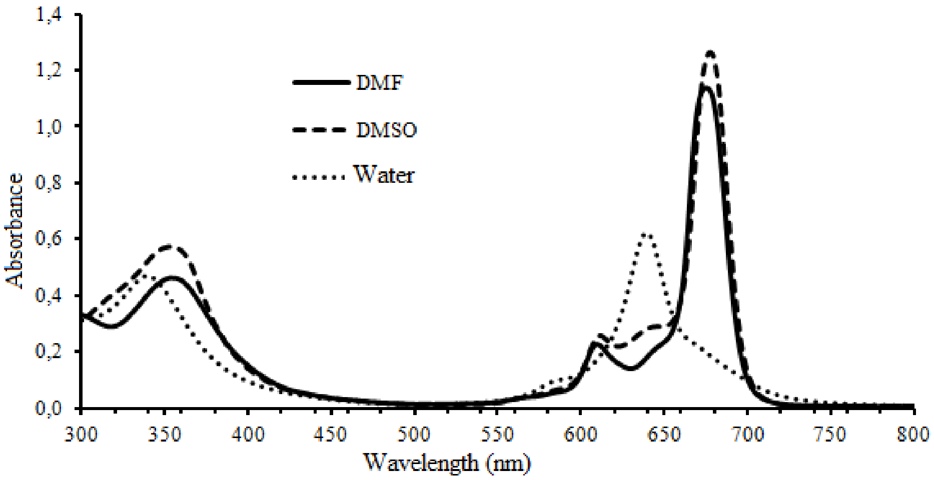


Figure 6: Uv-Vis Spectra of the Zn(II)phthalocyanine (6) containing methyl 2-hydroxy-6-methoxyisonicotinate in the peripheral position in different solvents (Pc/NaOH mol ratio in aqueous solution: 1/4) (Concentration: $0,8 \times 10^{-5}$ M)

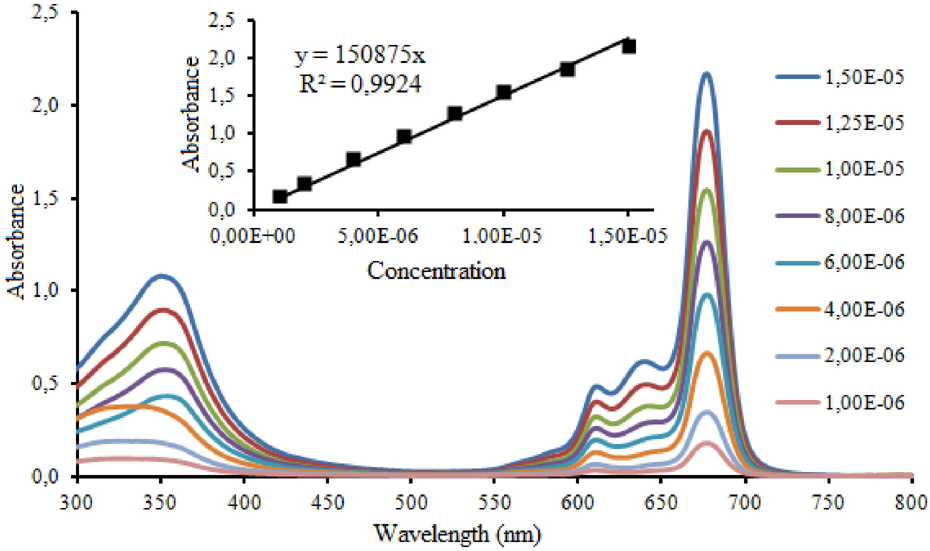


Figure 7: Uv-Vis Spectra of the Zn(II)phthalocyanine (6) containing methyl 2-hydroxy-6-methoxyisonicotinate in the peripheral position in DMSO

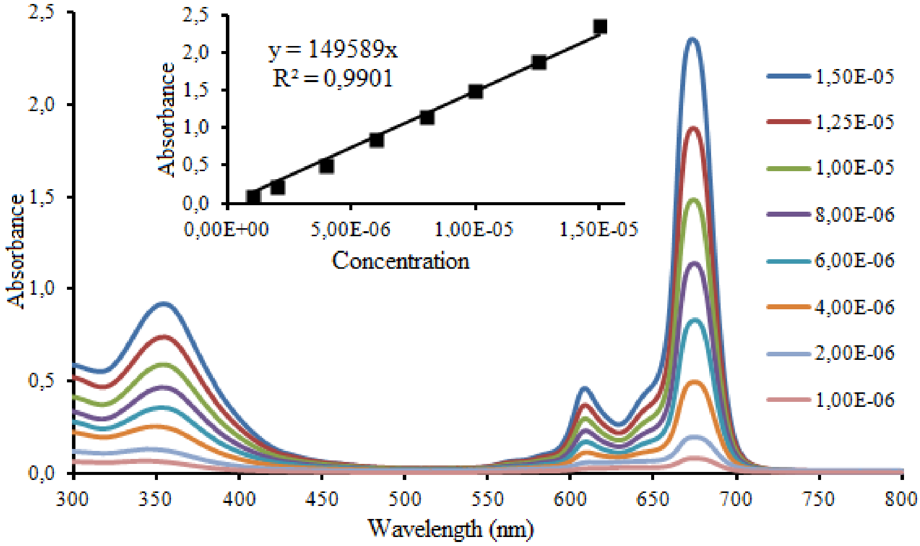


Figure 8: Uv-Vis Spectra of the Zn(II)phthalocyanine (6) containing methyl 2-hydroxy-6-methoxyisonicotinate in the peripheral position in DMF

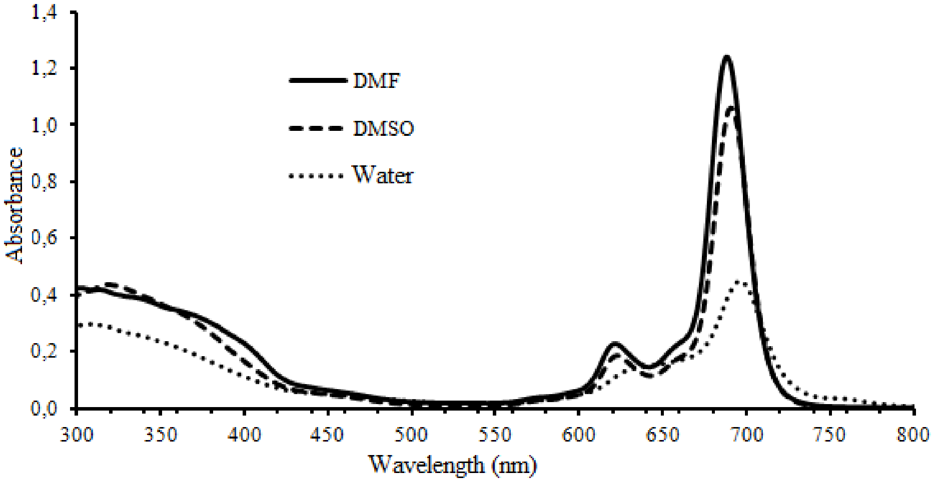


Figure 9: Uv-Vis Spectra of the Zn(II)phthalocyanine (7) containing methyl 2-hydroxy-6-methoxyisonicotinate in the nonperipheral position in different solvents (Pc/NaOH mol ratio in aqueous solution: 1/4) (Concentration: $0,8 \times 10^{-5}$ M)

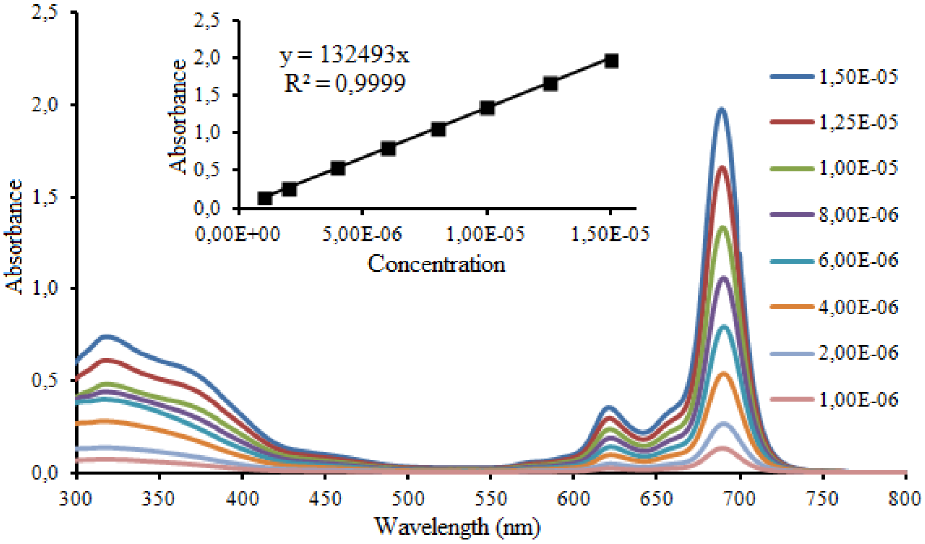


Figure 10: Uv-Vis Spectra of the Zn(II)phthalocyanine (7) containing methyl 2-hydroxy-6-methoxyisonicotinate in the peripheral position in DMSO

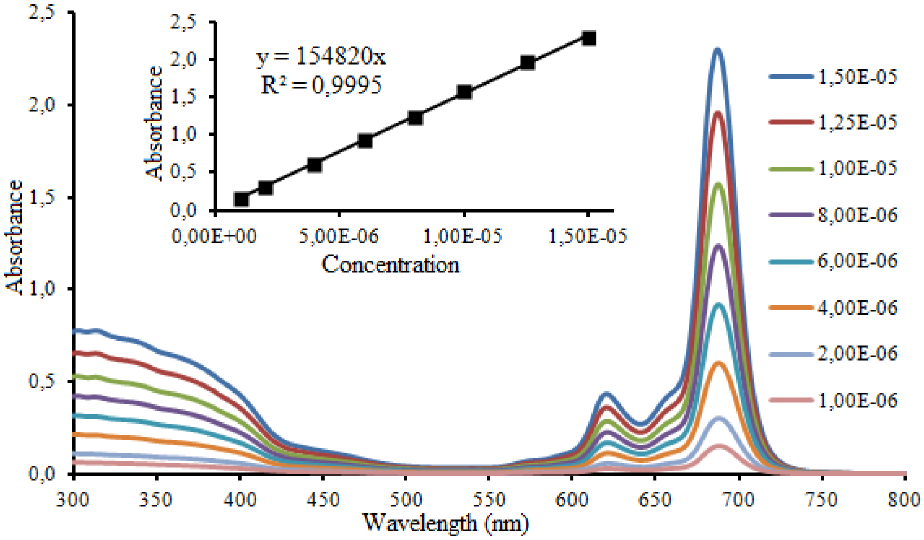


Figure 11: Uv-Vis Spectra of the Zn(II)phthalocyanine (7) containing methyl 2-hydroxy-6-methoxyisonicotinate in the nonperipheral position in DMF

4 Conclusions

Zn(II) phthalocyanines containing 2-Hydroxy-6-methoxyisonicotinic Acid on the periphery or nonperiphery were successfully synthesized. Characterization of all synthesized phthalonitriles and phthalocyanines were determined by elemental analyses, UV-Vis, ^{1}H NMR, ^{13}C NMR, Mass spectra and FT-IR spectroscopy. The solubility of phthalocyanines is very low in DMSO and DMF but high in alkaline aqueous solution. The UV-vis spectra of the zinc phthalocyanines were recorded in different solvents. Peripheral substitue zincphthalocyanines (5 and 7) showed aggregation in water. Beer's law was obeyed for zinc phthalocyanines (5-7).

Acknowledgments

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Authors' Contributions

NA and AY designed the structure, carried out the experiments work and wrote up the article. Both authors read and approved the final manuscript.

Competing Interests

The authors declare that they have no competing interests.

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