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Synthesis and aggregation properties of 2, 9, 16, 23 - tetrakis(chloro) - 3, 10, 17, 24-tetrakis [2 - (4 - allyl - 2- methoxyphenoxy)ethoxy]phthalocyaninato cobalt(II), manganese(III), zinc(II)

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Abstract

The synthesis of original cobalt, manganese, and zinc phthalocyanines including four chlorine and four 2-(4-allyl-2-methoxyphenoxy)ethoxy moieties were realized by cyclotetramerization of 4-(2-(4-allyl-2-methoxyphenoxy)ethoxy)-5-chlorophthalonitrile with suitable metal salts. New compounds were characterized by spectroscopic techniques such as FT-IR, UV-vis, ^{1}H NMR, ^{13}C NMR, and mass spectra. Then, the aggregation properties of the synthesized phthalocyanines were investigated in polar and apolar solvents.

Keywords: Phthalocyanines, eugenol, aggregation

1. Introduction

The word phthalocyanine, known as tetrabenzotetraazaporphyrin, is consist of a combination of the words naphtha (mineral oil) and cyanine (dark blue). The phthalocyanine molecule has a very tense structure and is formed as a result of the condensation of four isoindoline units. Phthalocyanines and their derivatives are synthetic compounds not found naturally in nature [1,2].

Because phthalocyanines have a wide variety of uses, they are among the most studied compounds recently. These macrocyclic compounds are tetra pyrrole derivatives that have outstanding features such as high symmetry, conjugated π-electron system, planarity, and electron delocalization. They have utilized in very different areas of technology and medical applications such as photodynamic therapy [3-5], chemical sensors [6], photoconductors [7], electrochromic display [8], catalysis [9-14], liquid crystal [15], and anti-cancer researches [16,17]. Besides, phthalocyanines are used for the energy conversion thanks to features of the planar macro ring having a powerful delocalization system with 18 π-electron [18]. Also, the color of phthalocyanines change from blue to green and they are used as dyestuffs in industry. In addition, due to their photochromic nature, phthalocyanines are used in data reading, writing, and deletion processes in field CD-ROM and DVD-ROM technologies.

4-allyl-2-methoxyhenol (eugenol) is a member of the phenylpropanoids [19]. Eugenol is a significant compound used in many different areas as a local antiseptic and anesthetic in perfumeries, flavorings, essential oils, and in medicine.

The most important disadvantage of phthalocyanines, which have a planar and voluminous structure is their low solubility in organic solvents [20]. The most important factor reducing solubility is the strong π electron interaction between phthalocyanine molecules, and this interaction is called stacking [21]. Aggregation significantly affects the spectral, photophysical, photochemical, redox processes, and solubilities of phthalocyanine compounds, so aggregation determines usage in different technological applications [22,23]. The aggregation of phthalocyanine molecules in the solution is closely related to the polarity of the solvent, the concentration, temperature of the solution, and the type and position of ligands linked to the phthalocyanine ring [24].

In this study, new cobalt, manganese, and zinc phthalocyanines including four chlorine and four 2-(4-allyl-2-methoxyphenoxy)ethoxy moieties (3-5) are

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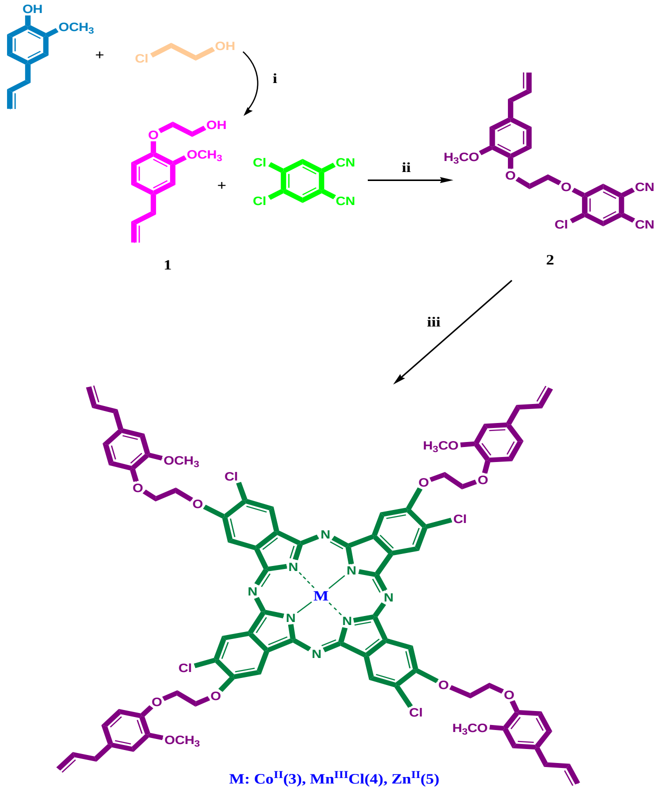
designed, synthesized, and characterized (Scheme 1). Then, the effect of the phthalocyanine derivatives and type of the central metal atoms (cobalt, manganese, and zinc) on the aggregation properties are investigated.



Scheme 1. The synthesis route of compounds 2-(4-allyl-2-methoxy-phenoxy) ethanol (1), 4-(2-(4-allyl-2-methoxyphenoxy)ethoxy)-5-chlorophthalonitrile (2) and phthalocyanines (3-5) (M= Co^{II}, Mn^{III}Cl, Zn^{II}. Reaction conditions; i: N_2, dry ethanol, NaOH, reflux temperature. ii: N_2, K_2CO_3, dry acetonitrile, reflux temperature. iii: DMAE, anhydrous $CoCl_2$, $MnCl_2$, $Zn(OAc)_2$, DBU, reflux temperature.

2. Experimental

2.1. Materials

4 - Allyl - 2 - methoxyphenol, 4,5 - dichlorophthalonitrile, other reagents, and solvents were of reagent grade quality and were obtained from commercial suppliers.

2.2. Equipments

Perkin Elmer 1600 FT-IR spectrophotometer was used to record the infrared spectra. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrophotometer with $CDCl_3$ chemical shifts were reported (d) relative to Me_4Si (tetramethylsilane) as the internal standard. An electrothermal apparatus was used to determine the melting points and were uncorrected. Mass spectra were measured with Bruker Microflex LT MALDI-TOF mass spectrometer and Micromass Quattro LC-MS / MS was recorded. The absorption spectra were recorded with a Perkin Elmer Lambda 25 UV/vis spectrophotometer by using a 1 cm pathlength cuvette at room temperature.

2.3. Synthesis

2.3.1. *Synthesis of 2-(4-allyl-2-methoxyphenoxy)ethanol (1)*

4-Allyl-2-methoxyphenol (5.0 g, 30 mmol) and 50 mL ethanol was stirred for 30 min at 50 °C, afterward, NaOH (1.8 g 45 mmol) was added to the mixture. After stirring about 90 min at 90 °C, 2-chloroethanol (3.05 mL 45 mmol) in ethanol (6 mL) was added dropwise for 2 h at the same temperature. The reaction mixture was stirred under N_2 at reflux temperature for 24 h. At the end of one day, the reaction mixture cooled at room temperature was filtered then ethanol was concentrated thanks to the evaporator. Afterward, water (20 mL) and NaOH (10 mL, 10%) were added and the aqueous phase extracted with chloroform (3×30 mL). Before being filtered, the combined extracts were treated with water and dried over anhydrous magnesium sulfate. The solvent was evaporated. Purification of the dark red product was accomplished by column chromatography which is placed silica gel using $CHCl_3$:CH_3CH_2OH (5:1) as a solvent system. The product was dark red colored liquid. Yield: 3.57 g (56%). Anal.calc. for $C_{12}H_{16}O_3$ IR (ATR), ν_{max}/cm^{-1}: 3449 (O-H), 3078, 3004, (Ar-H), 2936, 2841 (Aliph. C-H), 1638-1511, 1463, 1431, 1263, 1231, 1122, 1148, 1079, 994, 911, 850, 815, 795, 598. ^{1}H-NMR ($CDCl_3$), (δ: ppm): 6.78 (d, 1H, Ar-H), 6.68 (s, 1H, Ar-H), 6.65 (m, 1H, Ar-H), 5.92 (m, 1H, -CH=), 5.04 (m, 2H, =CH_2), 4.08 (t, 2H, O-CH_2), 3.88 (t, 2H, CH_2-O), 3.78 (s, 3H, OCH_3), 3.29 (d, 2H, CH_2), 1.56 (s, 1H, OH). ^{13}C-NMR ($CDCl_3$), (δ:ppm): 149.31, 146.48, 137.60, 133.33, 120.72, 115.63, 112.27, 77.74, 70.98, 60.99, 55.70, 39.76. MS (ES$^+$), (m/z): Calculated: 208.25; Found: 210.00 [M+2H]$^+$.

2.3.2. *Synthesis of 4-(2-(4-allyl-2-methoxyphenoxy)ethoxy)-5-chlorophthalonitrile (2)*

2-(4-ally-2-methoxyhenoxy)ethanol 1 (3 g, 14.4 mmol) was dissolved in 50 mL dry CH_3CN under N_2 atmosphere after 50 °C heated, anhydrous K_2CO_3 (5.96 g, 43.20 mmol) was added to the mixture. 4,5-Dichlorophthalonitrile (1.42 g, 7.2 mmol) in CH_3CN (30 mL) was added to drop by drop during 1 h at reflux temperature. The reaction mixture was stirred under N_2 at reflux temperature for 7 days. The reaction mixture was controlled with TLC. At the end of seven days, the reaction mixture was cooled at room temperature and filtered, then CH_3CN has concentrated thanks to the evaporator. Afterwards, the mixture extracted with chloroform (3×30 mL) and water (30 mL). The combined organic phases were dried over anhydrous magnesium sulfate and then filtered. The solvent was evaporated. The product was green colored solid. The product was dried in a vacuum desiccator and purification of the green solid product was accomplished by column chromatography which is placed silica gel using $CHCl_3$: CH_3CH_2OH (5:1) as solvent system. Yield: 1.32 g (25%). m.p.: 129-133 °C. Anal.calc. for $C_{20}H_{17}ClN_2O_3$. IR (ATR),

ν/cm^{-1}: 3078, 3009, (Ar-H), 2939, 2843, (Aliph. C-H), 2233 (C≡N), 1638-1502, 1486, 1466, 1464, 1384, 1186, 1120, 1031, 995, 820. ^{1}H-NMR ($CDCl_3$), (δ:ppm) : 7.85 (s, 1H, Ar-H), 7.28 (s, 1H, Ar-H), 7.11-7.06 (m, 2H, Ar-H), 6.94-6.87 (m, 1H, Ar-H), 6.06-5,98 (m, 1H, -CH=), 5.19-5.15 (t, 2H, =CH_2), 3.83 (s, 4H, CH_2-O), 3.79 (s, 3H, -OCH_3), 3,45 (d, 2H, -CH_2). ^{13}C-NMR ($CDCl_3$), (δ:ppm): 158.09, 151.51, 150.71, 136.55, 135.21, 128.37, 122.28, 121.64, 119.63, 119.25, 116.72, 115.57, 115.21, 114.54, 113.56, 108.96, 77.38, 66.96, 55.91, 40.08. MS (ES$^+$), (m/z): Calculated: 368.81; Found: 453.81 [M+2Na+K]$^+$.

2.3.3. General synthetic procedures for metallophthalocyanine derivatives (3-5)

A mixture of 2 (0.1 g, 0.271 mmol), DMAE (3 mL), anhydrous metal salts (0.0176 g, 0.135 mmol) $CoCl_2$ or (0.0170 g, 0.135 mmol) $MnCl_2$ or $Zn(OAc)_2$ (0.025 g, 0.135 mmol) and 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) (10 drops) was refluxed under N_2 for 24 h. After cooling to room temperature, the product was precipitated by adding ethanol. The green-colored product was filtered off and washed ethanol and water. Finally, metallophthalocyanines were purified by column chromatography which is placed silica gel using $CHCl_3$:C_2H_5OH (5:2) as a solvent system.

2.3.3.1. 2,9,16,23-Tetrakis(chloro)-3,10,17,24-tetrakis[2-(4-allyl-2-methoxyphenoxy)ethoxy] phthalocyaninato cobalt(II) (3)

Yield: 0.090 g (88%), m.p.>300 °C. Anal.calc. for $C_{80}H_{68}Cl_4N_8O_{12}Co$. IR (ATR), ν/cm^{-1}: 3063, 3019 (Ar-H), 2918, 2851 (Aliph. C-H), 1730, 1614, 1505, 1406, 1352, 1153, 1097, 1031, 962, 857, 751. UV-vis (THF): λ_{max}, nm (log ε): 384 (4.67), 604 (4.53), 666 (5.07). MALDI-TOF-MS m/z: Calculated: 1534.203; Found: 1612.99 [M+2K]$^+$.

2.3.3.2. 2,9,16,23-Tetrakis(chloro)-3,10,17,24-tetrakis [2-(4-allyl-2-methoxyphenoxy)ethoxy] phthalocyaninato manganese(III)chloride (4)

Yield: 0.052 g (50%), m.p.>300 °C. Anal.calc. for $C_{80}H_{68}Cl_5N_8O_{12}Mn$. IR (ATR), ν/cm^{-1}: 3074, 3005 (Ar-H), 2919, 2850 (Aliph. C-H), 1716, 1596, 1505, 1448, 1285, 1151, 1120, 1032, 895, 818, 744. UV-vis (THF): λ_{max}, nm (log ε): 415 (4.72), 502 (4.42), 659 (4.38), 722 (5.03). MALDI-TOF-MS m/z: Calculated: 1565.661; Found: 1560.83 [M-5H]$^+$.

2.3.3.3. 2,9,16,23-Tetrakis(chloro)-3,10,17,24-tetrakis[2-(4-allyl-2-methoxyphenoxy)ethoxy] phthalocyaninato zinc(II) (5)

Yield: 0.062 g (60%), m.p.>300 °C. Anal.calc. for $C_{80}H_{68}Cl_4N_8O_{12}Zn$. IR (ATR), ν/cm^{-1}: 3067, 3009 (Ar-H), 2920, 2850 (Aliph. C-H), 1603, 1508, 1438, 1256, 1138, 1098, 961, 780, 742. ^{1}H-NMR ($CDCl_3$), (δ:ppm): 7.88 (m, 4H, Ar-H), 7.49 (m, 4H, Ar-H), 7.01-6.72 (m, 8H, Ar-H), 6.39-6.27 (m, 4H, Ar-H), 6.12-5.99 (m, 4H, -CH=), 4.28 (t, 8H, =CH_2), 4.26 (s, 16H, CH_2-O), 3.82 (s, 12H, -OCH_3), 3.29 (d, 8H, -CH_2). UV-vis (THF): λ_{max}, nm (log ε): 352 (4.85), 611 (4.49), 675 (5.02). MALDI-TOF-MS m/z: Calculated: 1540.679; Found: 1571.71 [M+Na+Li+H]$^+$.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routes for new compounds (1-5) are shown in Scheme 1. In the first step, 2-(4-allyl-2-methoxyphenoxy)ethanol (1) was synthesized by the reaction of 4-Allyl-2-methoxyphenol and 2-chloroethanol in dry ethanol, with NaOH at reflux temperature under a nitrogen atmosphere for 24 hours. In the second step, phthalonitrile derivative was obtained by the reaction of compound (1) with 4,5-Dichlorophthalonitrile in dry acetonitrile at reflux temperature under a nitrogen atmosphere. Anhydrous potassium carbonate was used as a base. The synthesis of peripheral octa substituted phthalocyanines (3-5) were carried out using phthalonitrile compounds 2. 1,8-Diazabicyclo [5.4.0]undec-7-ene (DBU) was used as a strong base and the corresponding metal salts (anhydrous $CoCl_2$, $MnCl_2$ and $Zn(OAc)_2$) were used as a metal source in the DMAE at reflux temperature under a nitrogen atmosphere for 24 hours. The structures of the newly synthesized compounds (1-5) were elucidated by IR, ^{1}H-NMR, ^{13}C NMR, UV-vis, and MS spectral data.

In the IR spectrum of 1, the appearance of the new absorptions at 3449 cm^{-1} (O-H stretching) confirmed the proposed structure of the compound 1. In addition, aromatic groups and aliphatic groups gave characteristic peaks at 3004 cm^{-1}, 2936-2841 cm^{-1} respectively. ^{1}H NMR spectrum of 1 was taken in $CDCl_3$, aliphatic protons were observed 5.92 (m, 1H, -CH=), 5.04 (m, 2H, =CH_2), 4.08 (t, 2H, O-CH_2), 3.88 (t, 2H, CH_2-O), 3.78 (s, 3H, OCH_3), 3.29 (d, 2H, CH_2), 1.56 (s, 1H, OH). Aromatic protons were observed 6.78 (d, 1H, Ar-H), 6.68 (s, 1H, Ar-H), 6.65 (m, 1H, Ar-H). ^{13}C NMR spectrum of 1 as showed in Fig. 7, O-CH_2 groups were observed δ= 70.98 and 60.99 ppm, and the O-CH_3 group was observed δ= 149.31 ppm. In the mass spectrum taken by LC-MS / MS technique, the molecular ion peak was determined as m/z= 210.00 [M+2H]$^+$.

In the IR spectrum of 2, the disappearance of the stretching vibrations of OH group at 3449 cm^{-1} and the appearance of the sharp -C≡N vibration at 2233 cm^{-1} confirmed the proposed structure of the compound 2. ^{1}H NMR spectrum of 2 as showed in Fig. 9 was taken in $CDCl_3$, aromatic and aliphatic protons were observed at 7.85 (s, 1H, Ar-H), 7.28 (s, 1H, Ar-H), 7.11-7.06 (m, 2H, Ar-H), 6.94-6.87 (m, 1H, Ar-H), 6.06-5,98 (m, 1H, -CH=), 5.19-5.15 (t, 2H, =CH_2), 3.83 (s, 4H, CH_2-O), 3.79 (s, 3H, -OCH_3), 3,45 (d, 2H, -CH_2).

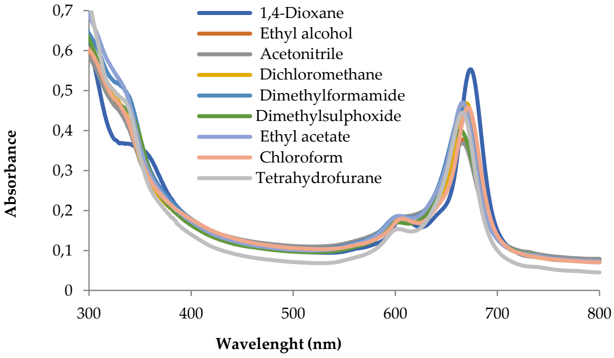


Figure 1. UV-vis spectrum of cobalt phthalocyanine 3 in different solvents.

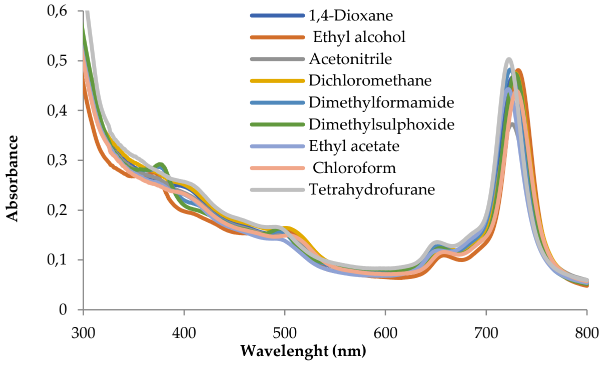


Figure 2. UV-vis spectrum of manganese phthalocyanine 4 in different solvents.

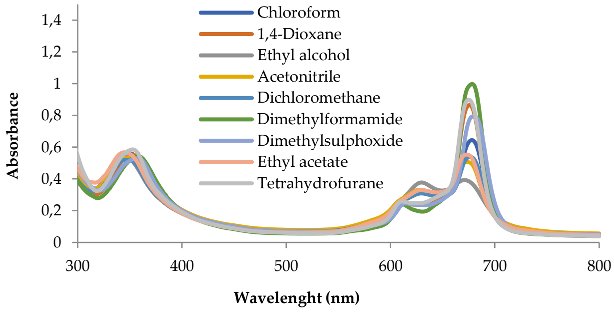


Figure 3. UV-vis spectrum of zinc phthalocyanine 5 in different solvents.

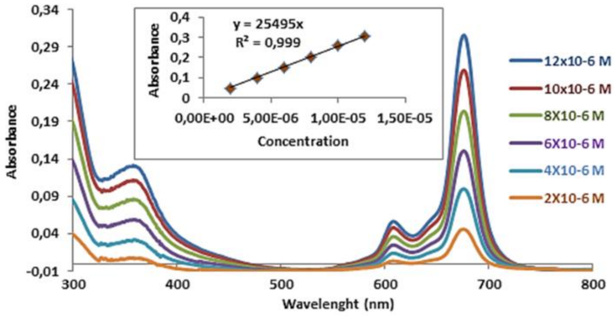


Figure 4. UV-vis spectrum of cobalt phthalocyanine 3 in 1,4-dioxane at different concentration.

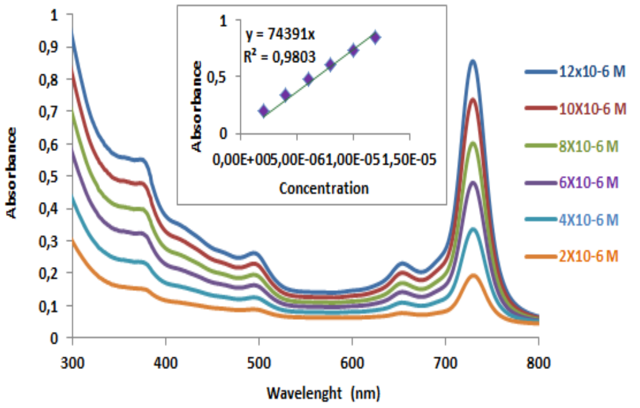


Figure 5. UV-vis spectrum of manganese phthalocyanine 4 in 1,4-dioxane at different concentration.

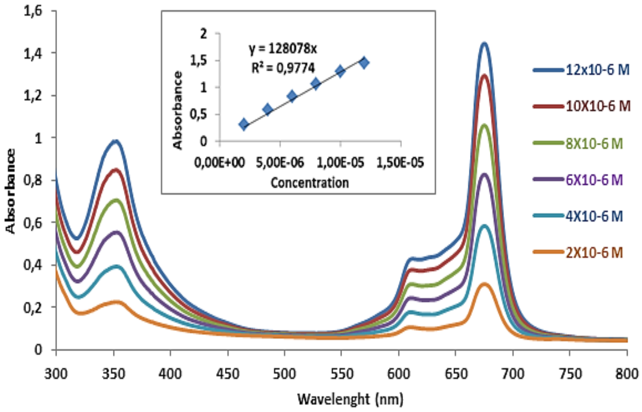


Figure 6. UV-vis spectrum of manganese phthalocyanine 4 in 1,4-dioxane at different concentration.

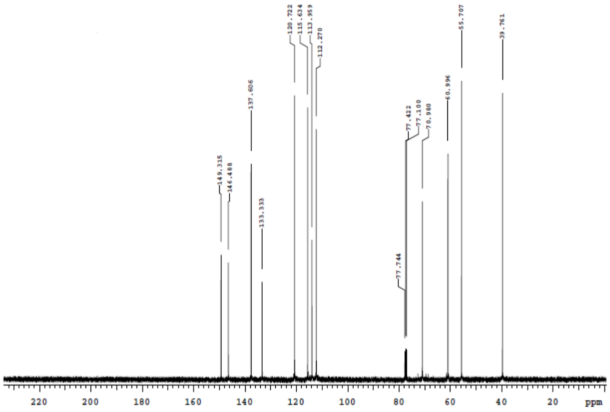


Figure 7. ^{13}C NMR spectrum of compound 1.

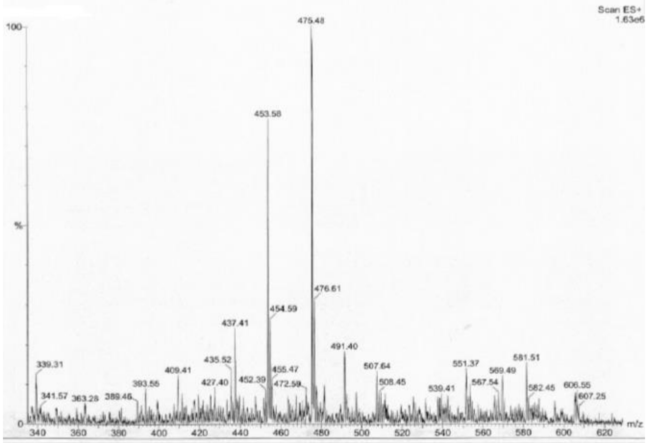


Figure 8. LC-MS/MS spectrum of compound 2.

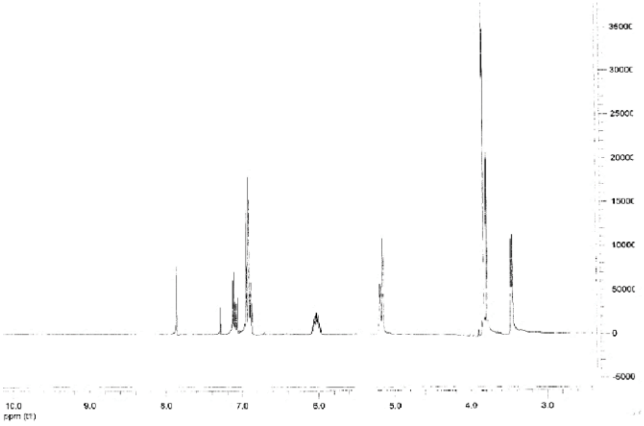


Figure 9. ^{1}H NMR spectrum of compound **2**.

^{13}C NMR spectrum of 2 showed the -C≡N group at δ= 115.57 and 115.21 ppm. As shown in Fig. 8, in the mass spectrum taken by LC-MS/MS technique the molecular ion peak was observed at m/z= 453.81 $[M+2Na+K]^+$.

In the IR spectrums of 3, 4, and 5 disappearances of the the sharp -C≡N stretching vibration at 2233 cm^{-1} confirmed the proposed structure of the compounds. In the mass spectrum taken by MALDI-TOF-MS technique the molecular ion peaks of newly synthesized phthalocyanine compounds (3-5) were observed at m/z= 1612.99 for 3 as $[M+2K]^+$, 1560.83 for 4 as $[M-5H]^+$, 1571.71 for 5 as $[M+Na+Li+H]^+$. The UV-vis spectra of the acquired phthalocyanine complexes (3-5) were recorded in THF. The Q bands of the synthesized phthalocyanines (3-5) were exhibited single narrow bands which is an indication of the monomeric behavior of these phthalocyanines in THF. The Q bands of these phthalocyanines were observed at λ_{max} nm (logε): 666 (5.07) for 3, 722 (5.03) for 4, and 675 (5.02) for 5 in THF. The B bands of these complexes (3-5) were obtained at λ_{max} nm (logε): 384 (4.67) for 3, 425 (4.72) for 4 and 352 (4.85) for 5 in THF. ^{1}H NMR spectra of compounds 3 and 4 could not be determined because of its paramagnetic nature [25]. ^{1}H NMR signal values of the eugenol substituted zinc phthalocyanine (5) was given in the experimental part, aliphatic and aromatic protons were observed at 7.88 (m, 4H, Ar-H), 7.49 (m, 4H, Ar-H), 7.01-6.72 (m, 8H, Ar-H), 6.39-6.27 (m, 4H, Ar-H), 6.12-5.99 (m, 4H, -CH=), 4.28 (t, 8H, $=CH_2$), 4.26 (s, 16H, CH_2-O), 3.82 (s, 12H, $-OCH_3$), 3.29 (d, 8H, $-CH_2$).

3.2. Aggregation studies

Aggregation is the clustering of two or more phthalocyanine rings that come together in a liquid due to intermolecular attraction forces. These clusters are called aggregates. J-type aggregates are formed by aligning molecules side by side and H-type aggregates are formed by aligning face to face. Aggregation significantly influence some properties of the phthalocyanine compounds such as the spectral, photophysical, and photochemical. The essential factors causing aggregation are concentration of the solution, temperature, metal ions placed in the central space, kind of the substituents, and the solvents used. In this work, the effect of solvent and concentration on aggregation was investigated for phthalocyanine complexes (3, 4, and 5). The effect of the solvent on the aggregation behavior of the 2-(4-allyl-2-methoxyphenoxy)ethoxy substituted phthalocyanines (3, 4 and 5) were examined in different organic solvents such as in chloroform, 1,4-dioxane, acetonitrile, tetrahydrofuran, dimethylformamide, ethyl acetate, dimethyl sulfoxide, dichloromethane, and ethyl alcohol as showed in Fig. 1 for the compound 3, Fig. 2 for the compound 4 and Fig. 3 for compound 5 respectively. The effect of the concentration on the aggregation behavior of these phthalocyanines was examined at different concentrations range changed from 2×10^{-6} to 12×10^{-6} M in 1,4-dioxane for compounds 3, 4, and 5 (Fig. 4 for the compound 3, Fig. 5 for the compound 4 and Fig. 6 for compound 5). When these UV-vis spectra were examined, it was seen that the ratio between absorption and concentration at maximum wavelength was changed harmoniously according to Lambert-Beer law. Therefore, it was concluded that all phthalocyanine (3, 4, and 5) compounds did not exhibit aggregated species in this concentration range in using a solvent. UV-vis spectra are examined to observe the effect of the solvents on the aggregation behavior of these phthalocyanines. The compound (3) has aggregated in other solvents (H type), excluding 1,4-dioxane while the compound (4) has aggregated in a small amount (H type) in other solvents, excluding in ethyl alcohol, dimethylformamide, and dimethyl sulfoxide. Compound (5) has aggregated in other solvents (H type), excluding dimethyl sulfoxide, 1,4-dioxane, dimethylformamide, and tetrahydrofuran.

4. Conclusions

Consequently, cobalt, manganese, and zinc phthalocyanines (3-5) including four chlorine and four 2-(4-allyl-2-methoxyphenoxy)ethoxy moieties were synthesized and characterized by different spectroscopic methods and confirmed the suggested structures. Compounds 3, 4, and 5 did not exhibit aggregated species in the concentration range of 2×10^{-6}-12×10^{-6} M in 1,4-dioxane. Phthalocyanines are one of the most researched substance groups. Makes such a compound important is that there is no solubility problem. Therefore, non-aggregated compounds will have used in various fields. Because the aggregation and solubility of phthalocyanines are important for their applications, we used eugenol derivative containing long-chain in this paper. It is known that the cobalt phthalocyanine compound containing eugenol has good electrochemical and catalytic properties [26]. In this paper, it is thought that the synthesized phthalocyanine compounds can be used in these and different areas.

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