Anadolu Üniversitesi Bilim ve Teknoloji Dergisi A- Uygulamalı Bilimler ve Mühendislik
Anadolu University Journal of Science and Technology A- Applied Sciences and Engineering

2016 - Volume: 17 Number: 2
Page: 327 - 336
DOI: 10.18038/btda.54345
Received: 04 February 2016 Revised: 06 April 2016 Accepted: 30 May 2016

MICROWAVE-ASSISTED SYNTHESIS AND CHARACTERIZATION OF A NEW METAL-FREE PHTHALOCYANINE AND FOUR METALLOPHTHALOCYANINES BEARING 9-FLOURENE METHANOL MOITIES

Meltem Betül SAĞLAM

Department of Chemistry, Faculty of Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey

ABSTRACT

The new metal-free phthalocyanine 2 and metallophtalocyanines 3, 4, 5, 6 containing 9-flourene methanol units on peripheral positions have been synthesized by cyclotetramerization reaction of a corresponding nitrile compound. The metal-free phthalocyanine 2 was synthesized in dry n-pentanol by a classical method. Hovewer, metal phthalocyanines complexes 3, 4, 5, 6, were synthesized by the reaction of dinitrile derivative 2 in DMAE, by microwave irradiation. The structure of the new compounds were characterized by using spectroscopic data and elemental analysis.

Keywords: Nitrile, Metallophthalocyanine, Cyclotetramerization, Macrocyclic

1. INTRODUCTION

Phthalocyanines (Pcs) are not flexible group of compounds for industrial manufacture of most important characteristics and properties. Especially, their intense blue and green colors and stability towards heat, acids and bases allow them to be extensively used as pigments and dyes. In recent years, Pcs attracted much attention because of their active properties and potential application to fuel cells, gas sensors, electro photography, solar energy conversion, non-linear optics, optical data storage, etc [1-3, 4-10].

In recent years, microwave (MW) irradiation are preferred because of the accelerated procedure compared to the classic reaction speed, reduced reaction times from hours to minutes at high temperatures and high yields of compounds [11]. In other words, the most successful examples of microwave applications are necessarily found to be related to the use of non-solvent systems, in which reagents and microwaves interact directly, therefore, chemical reactions can be driven more efficiently [12-15].

In this study, we have obtained a new metal-free phthalocyanine and four metallophthalocyanines containing 9-fluorene methanol groups. The metal-free phthalocyanine **2** was synthesized in dry n-pentanol by a classical method. Hovewer, metal phthalocyanines complexes **3, 4, 5, 6**, were synthesized by the reaction of dinitrile derivative **2** in DMAE, by microwave irradiation. The structure of the new compounds were characterized by using spectroscopic data and elemental analysis.[16, 17].

2. MATERIAL AND METHOD

All reactions were realized under nitrogen atmosphere. 9-fluorene methanol was acquired from Aldrich. 4-nitrophtalonitrile according to literature procedures was ready-made [18, 19].

Corresponding Author: meltemkilicaslan@hotmail.com

2.1. Synthesis of 4-(9H-flouren-9-ylmethoxy) phthalonitrile (1)

9-fluorenemethanol (2.00 g, 10.20 mmol) was dissolved in dry DMF (37.6 mL) and then 4-nitrophthalonitrile (1.765 g, 10.20 mmol) was added to the solution under nitrogen atmosphere. After stirring about for 15 min, at 25 ºC, dry K_2CO_3 (4.22 g, 30.60 mmol) was extended portion wise within 2 hrs. The reaction mixture was refluxed under nitrogen atmosphere at 50 ºC about for 4 days. Then, it was poured into ice-water (416 mL) and organic phase was extracted with chloroform (3x60 mL). The mixed extracts were drained dry over Na_2SO_4. The raw product was refined by column chromatography with silica gel, using chloroform: methanol (97:3) solvent system and 2.24 g (68 %) yield was obtained. Melting point was measured 136-137 °C. Analytical calculation for, $C_{22}H_{14}N_2O$: C, 81.98; H, 4.34; N, 8.69 %. Found: C, 82.08; H, 4.41; N, 8.65. IR, υ_{max}/cm^{-1}: 3062 (Ar-H), 2921-2857 (Aliph.C-H), 2228 (C≡N), 1713, 1660, 1599, 1449, 1251, 1099, 734. ^1H NMR (200MHz, chloroform), δ, 7.86 (d, J=8.29 Hz, 1H, Ar-H), 7.80 (d, J=7.69 Hz, 2H, Ar-H), 7.60 (s, 1H, Ar-H), 7.44 (d, J=8.32Hz, 1H, Ar-H), 7.34 (d, J=7.33 Hz, 2H, Ar-H), 7.15 (t, J=7.28 Hz, 2H, Ar-H), 7.13 (t, J=7.37 Hz, 2H, Ar-H), 4.90 (d, J=6.35 Hz, 2H, CH_2-O), 4.26 (s, 1H, C-H). ^{13}C NMR (200MHz, chloroform), δ, 160.24, 142.46, 139.70, 132.79, 126.75, 126.32, 123.51, 119.81, 119.06, 118.66, 115.87, 113.74, 110.76, 104.89, 71.01, 48.12. MS (FAB) (m/z): 322 $[M]^+$.

2.2. Metal-free Phthalocyanine (2), H_2Pc

2 was prepared with the compound **1** (0.3 g, 0.932 mmol) in n-pentanol (4.30 mL) and 3-5 drops of 1, 8-diazabicyclo[5.4.0]undec-7-ene in a Schlenk tube under nitrogen atmosphere. The temperature was slowly increased up to 90 ºC and saturated with nitrogen gas. Then the reaction mixture was stirred at 160 °C for about 24 hrs. After this period, it was cooled at room temperature, refluxed with ethanol (30 mL) to precipitate. The green powder was washed with hot ethanol and diethyl ether. Then it was purified with preparative thin layer chromatography by using chloroform: methanol (9:1) solvent system and 0.104 g (34.7 %) yield was obtained. Melting point was measured >300 ºC. Analytical calculation for $C_{88}H_{58}N_8O_4$: C, 81.86; H, 4.49; N, 8.68 %. Found: C, 81.93; H, 4.43; N, 8.73. IR, υ_{max}/cm^{-1}: 3258 (N-H), 3060 (Ar-H), 2926-2846 (Aliph.C-H), 1712, 1600, 1448, 1347, 1212, 1100, 734. ^1H NMR (200MHz, chloroform), δ, 8.08 (d, J=8.89 Hz, 8H, Ar-H), 7.72 (d, J=7.63 Hz, 4H, Ar-H), 7.54 (s, 4H, Ar-H), 7.37 (d, J=7.38 Hz, 8H, Ar-H), 7.15 (t, J=7.37 Hz, 8H, Ar-H), 7.11 (t, J=7.35 Hz, 8H, Ar-H), 6.74 (d, J=8.62 Hz, 4H, Ar-H), 4.98 (d, J=6.45 Hz, 8H, -CH_2-O), 4.18 (t, J=6.42 Hz, 4H, C-H). ^{13}C NMR (200MHz, chloroform), δ, 164.26, 160.87, 159.24, 146.54, 140.35, 131.87, 128.75, 126.76, 126.32, 124.04, 121.36, 119.72, 119.12, 105.12, 70.97, 50.09. UV-vis: [λ_{max} (nm): (10^{-5} ε dm^3/mol cm) (chloroform)]: 245 (4.10), 260 (4.15), 272 (4.17), 650 (4.02), 707 (4.12) MS (FAB) (m/z): 1292 $[M+2]^+$.

2.3. General Procedure for Metallophthalocyanine Derivatives (3, 4, 5, 6)

The compounds **3, 4, 5** and **6** were prepared with **1** (0.2 g, 0.621 mmol) and dry metal salts $CoCl_2$ (0.04037 g, 0.310 mmol), $CuCl_2$ (0.04169 g, 0.310 mmol), $NiCl_2$ (0.03999 g, 0.310 mmol), $Zn(CH_3COOH)_2$ (0.04216 g, 0.310 mmol), respectively, and DMAE (3 mL) was added. The reaction mixture was irradiated by microwave at 175 °C, 350 W, for 7-8 min. After this period, it was cooled to room temperature and refluxed with ethanol (30 mL). The green raw powder was separated by filtration and then washed with hot diethyl ether and ethanol. The product was refined by preparative thin layer chromatography using chloroform: methanol (8.5:1.5) solvent system.

2.3.1. Co (II) phthalocyanine (3), CoPc

According to general procedure, compound **3** metallophthalocyanine derivatives was prepared as a dark green solid and 0.078 g (37.3 %) yield was obtained. Melting point was measured >300 °C. Analytical calculation for $C_{88}H_{56}N_8O_4Co$: C, 78.39; H, 4.15; N, 8.31. Found: C, 78.44, H, 4.20; N, 8.38 %. IR (KBr tablet) ʋ$_{max}$/cm^{-1}: 3059 (Ar-H), 2925-2853 (Aliph.C-H), 1616, 1476, 1226, 1095, 735. UV-vis: [λ_{max} (nm): (10^{-5} ε dm^3/mol cm) (chloroform)]: 305 (4.18), 338 (4.00), 614 (3.72), 677 (4.10). MS (FAB) (m/z): 1349 [M+2]$^+$.

2.3.2. Cu (II) phthalocyanine (4), CuPc

According to general procedure, compound **4** metallophthalocyanine derivatives was prepared as a green solid and 0.089 g (42 %) yield was obtained. Melting point was measured >300 ºC. Analytical calculation for $C_{88}H_{56}N_8O_4Cu$: C, 78.16; H, 4.14; N, 8.29. Found: C, 78.20, H, 4.17; N, 8.32%. IR (KBr tablet) ʋ$_{max}$/cm^{-1}: 3054 (Ar-H), 2917 (Aliph.C-H), 1651, 1598, 1447, 1251, 1185, 735. UV-vis: [λ_{max} (nm): (10^{-5} ε dm^3/ mol cm) (chloroform)]: 305 (4.05), 308 (4.02), 632 (3.09), 701 (4.11). MS (FAB) (m/z): 1351 [M]$^+$.

2.3.3. Ni (II) phthalocyanine (5), NiPc.

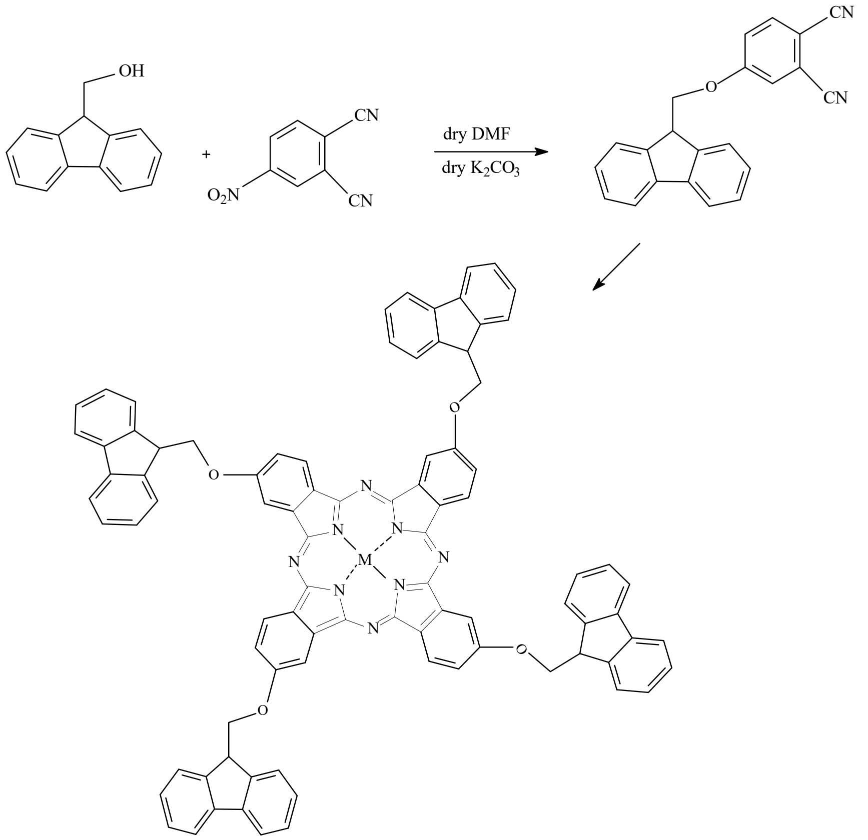
According to general procedure, compound **5** metallophthalocyanine derivatives was prepared as a light green solid and 0.096 g (46 %) yield was obtained. Melting point was measured >300 ºC. Analytical calculation for $C_{88}H_{56}N_8O_4Ni$: C, 78.45; H, 4.16; N, 8.32. Found: C, 78.49, H, 4.21; N, 8.38 %. IR (KBr tablet) ʋ$_{max}$/cm^{-1}: 3050 (Ar-H), 2924-2856 (Aliph.C-H), 1651, 1469, 1221, 1093, 730. ^{1}H NMR (200MHz, chloroform), δ, 7.83 (d, J=7.73 Hz, 8H, Ar-H), 7.72 (d, J=9.06 Hz, 4H, Ar-H), 7.61 (s, 4H, Ar-H), 7.35 (d, J=7.36 Hz, 8H, Ar-H), 7.17 (t, J=7.38 Hz, 8H, Ar-H), 7.15 (t, J=7.35 Hz, 8H, Ar-H), 6.86 (d, J=2.50 Hz, 4H, Ar-H), 4.87 (d, J=6.34 Hz, 8H, -CH_2-O), 4.24 (t, J=6.40 Hz, 4H, C-H). ^{13}C NMR (200MHz, chloroform), δ, 164.46, 161.36, 160.65, 145.64, 143.87, 132.52, 130.65, 126.76, 126.23, 124.18, 122.56, 119.94, 119.18, 107.11, 70.34, 49.03. UV-vis: [λ_{max} (nm): (10^{-5} ε dm^3/mol cm) (chloroform)]: 353 (3.75), 374 (3.86), 608 (3.69), 671 (4.18). MS (FAB) (m/z): 1348 [M+1]$^+$.

2.3.4. Zn (II) phthalocyanine (6), ZnPc.

According to general procedure, compound **6** metallophthalocyanine derivatives was prepared as a dark green solid and 0.089 g (42.4 %) yield was obtained. Melting point was measured >300 °C. Analytical calculation for, $C_{88}H_{56}N_8O_4Zn$: C, 78.04; H, 4.13; N, 8.27. Found: C, 78.10, H, 4.19; N, 8.21 %. IR (KBr tablet) ʋ$_{max}$/cm^{-1}: 3063 (Ar-H), 2917 (Aliph.C-H), 1600, 1449, 1226, 1093, 735. ^{1}H NMR (200MHz, chloroform), δ, 7.81 (d, J=7.73 Hz, 8H, Ar-H), 7.73 (d, J=9.00 Hz, 4H, Ar-H), 7.62 (s, 4H, Ar-H), 7.35 (d, J=7.36 Hz, 8H, Ar-H), 7.18 (t, J=7.39 Hz, 8H, Ar-H), 7.13 (t, J=8.50 Hz, 8H, Ar-H), 6.82 (d, J=2.52 Hz, 4H, Ar-H), 4.87 (d, J=6.36 Hz, 8H, -CH_2-O), 4.22 (t, J=6.38 Hz, 4H, C-H). ^{13}C NMR (200MHz, chloroform), δ, 162.78, 161.98, 160.11, 143.54, 142.32, 134.67, 130.31, 124.54, 124.09, 123.49, 122.45, 119.77, 119.06, 107.21, 70.22, 49.24. UV-vis: [λ_{max} (nm): (10^{-5} ε dm^3/mol cm) (chloroform)]: 305 (4.15), 356 (3.86), 632 (3.66), 701 (4.30). MS (FAB) (m/z): 1354 [M+1]$^+$.

3. RESULTS AND DISCUSSIONS

The preparation of H_2Pc **2** and CoPc **3**, CuPc **4**, NiPc **5** and ZnPc **6** are shown in Figure 1. The structures of new compounds were characterized by using spectroscopic data and elemental analysis.



Compound	2	3	4	5	6
M	2H	Co	Cu	Ni	Zn

Figure 1. The synthesis of the metal-free phthalocyanine and metallophthalocyanines derivatives. Reagents and conditions (i) n-pentanol, DBU, 165°C, (ii) dry $CoCl_2$, dry $CuCl_2$, dry $NiCl_2$, dry $Zn(CH_3COOH)_2$, in DMAE by microwave at 175 °C, 350 W, for 7-8 min.

Initially, 4-(9H-flouren-9-ylmethoxy) phthalonitrile **1** was prepared by aromatic nucleophilic substitution reaction between 4-nitrophthalonitrile and 9-flourenemethanol [20]. The reaction was achieved at reflux temperature in dry DMF with dry K_2CO_3 as the base under nitrogen atmosphere. IR spectrum of compound **1**, shows characteristic frequencies at 3062 (Ar-H), 2921-2857 (C-H) and the intense stretching absorption band at 2228 cm^{-1} points out to the C≡N groups . The ^{13}C NMR spectrum of compound **1**, indicated the presence of nitrile carbon atoms at $\delta = 115.87$ ppm. The FAB mass spectrum of **1**, which shows a peak at m/z = 322 $[M]^+$, and elemental analysis also confirm the formation of the suggested formula for this compound.

H_2Pc **2** was synthesized using n-penthanol and a few drops of 1,8-diaza bicyclo[5.4.0]undec-7-ene at reflux temperature under nitrogen atmosphere. IR spectrum of **2** shows 3258 cm^{-1} (N-H) vibrations. The disappearance of the C≡N stretching vibration on the IR spectra of **2** suggested formation of **2**. In the ^{1}H NMR spectra of this compound, the inner core of Pc-2H protons could not be observed due to strong aggregation of molecules [21]. The mass spectrum of **2** (is shown in **Figure 3**), which exhibits a peak at m/z = 1292 $[M+2]^+$, supports the sectional formula for this compound. The elemental analysis confirms the expected **2.**

CoPc **3**, CuPc **4**, NiPc **5** and ZnPc **6** were synthesized with yields of 37.3, 42, 46, 42.4 %, respectively. The metallophthalocyanines **3, 4, 5** and **6** were gained from the reaction of dicyano derivative **3** with dry metal salts $CoCl_2$, $CuCl_2$, $NiCl_2$, $Zn(CH_3COOH)_2$ by microwave irradiation in DMAE, approximately for 8, 8, 7, 7 minutes, respectively. IR spectra of **3, 4, 5** and **6** show the disappearance of strong C≡N stretching vibration of **1** for the formation of **3, 4, 5** and **6**. The IR spectra of metallophthalocyanines are very similar to those of the metal-free phthalocyanine **2**. The ^1H NMR spectra of these compounds are almost the same as that of H_2Pc **2**. In the mass spectrum of compounds **3, 4, 5** and **6**, molecular ion peaks at m/z = 1349 $[M+2]^+$, 1351 $[M]^+$, 1348 $[M+1]^+$ and 1354 $[M+1]^+$ (are shown in **Figures 4, 5, 6,7**), are accepted by the suggested structures. The elemental analysis of the expected affirms compounds **3, 4, 5, 6**.

Usually, phthalocyanines show typical electronic spectra with two strong absorption regions, one in the UV region concerned with the B band at about 300-500 nm in the visible region and the other concerned with the Q band at 600-700 nm [22]. The UV-vis absorption spectra of **2, 3, 5** and **6** are shown in **Figure 2**. The split Q bands in **2**, which are characteristic for metal-free phthalocyanines were watched over at λ_{max}= 707 and 650 nm. These Q band absorptions show the monomeric species with D_{2h} symmetry and due to the phthalocyanine ring concerned with the fully conjugated 18 π electron system [23-25]. The existence of strong absorption bands in **2** in the near UV region at λ_{max} = 272, 260 and 245 nm also shows Soret B bands which have also been attributed to the deeper π-π* levels of LUMO transitions.

The UV-vis absorption spectra of **3, 4, 5** and **6** show intense Q absorption in chloroform at λ_{max} = 677, 701, 671 and 701 nm, with weaker absorptions at 614, 632, 608, and 632 nm, respectively. The single Q bands in metallo derivatives **3, 4, 5** and **6** are characteristic. This result is typical for metal complexes of substituted and unsubstituted metallophthalocyanines with D_{4h} symmetry [26]. Soret region B band absorptions of compounds **3, 4, 5** and **6** were watched over λ_{max} = (338 and 305), (308 and 305), (374 and 353), (356 and 305) nm as expected, respectively [27].

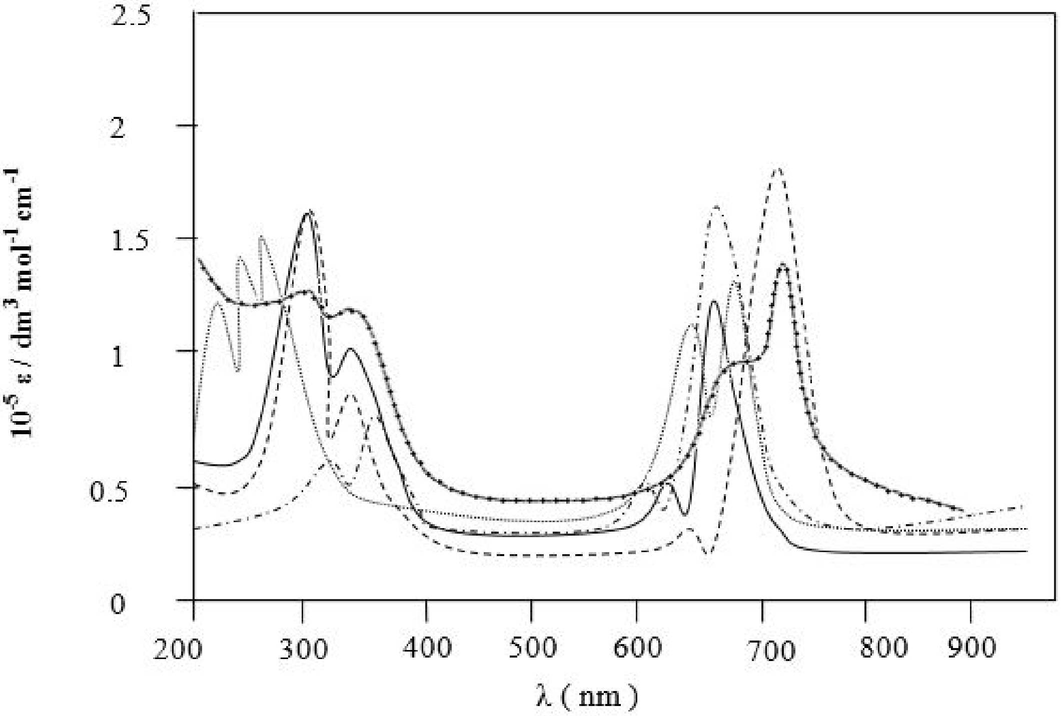


Figure 2. UV-vis spectra of compounds H_2Pc **2** (····), CoPc **3** (—), CuPc **4** (-+-), NiPc **5** (–·–·) and ZnPc **6** (_ _ _) in chloroform

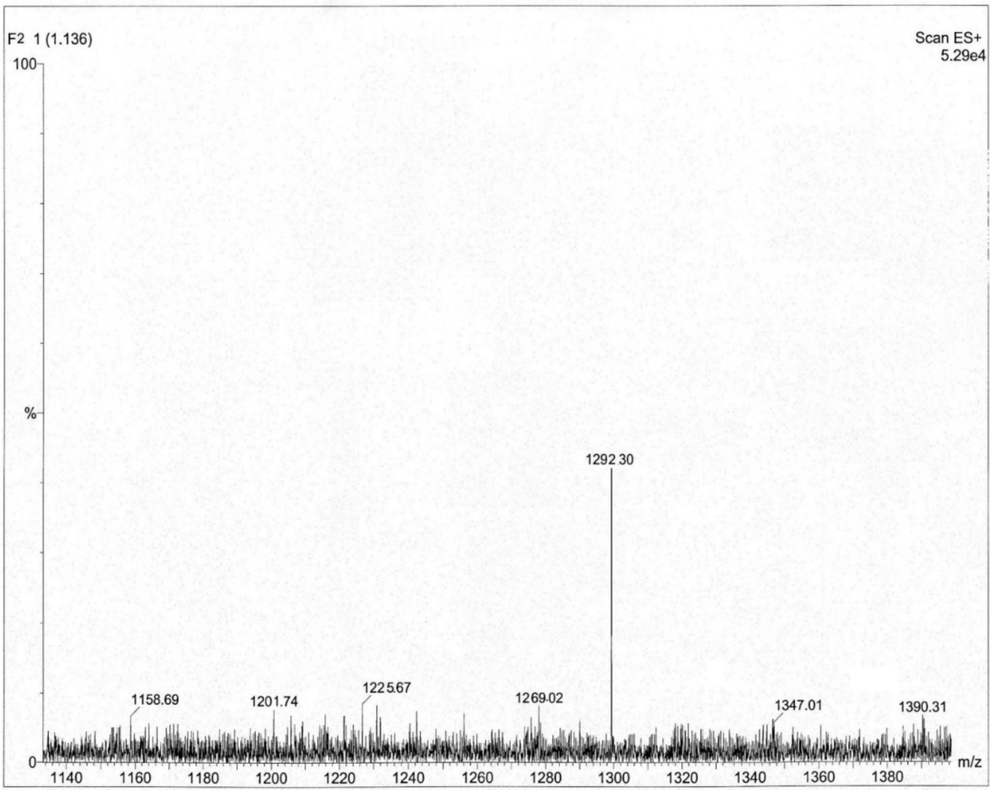


Figure 3. Mass spectrum of metal free phthalocyanine **(2)**

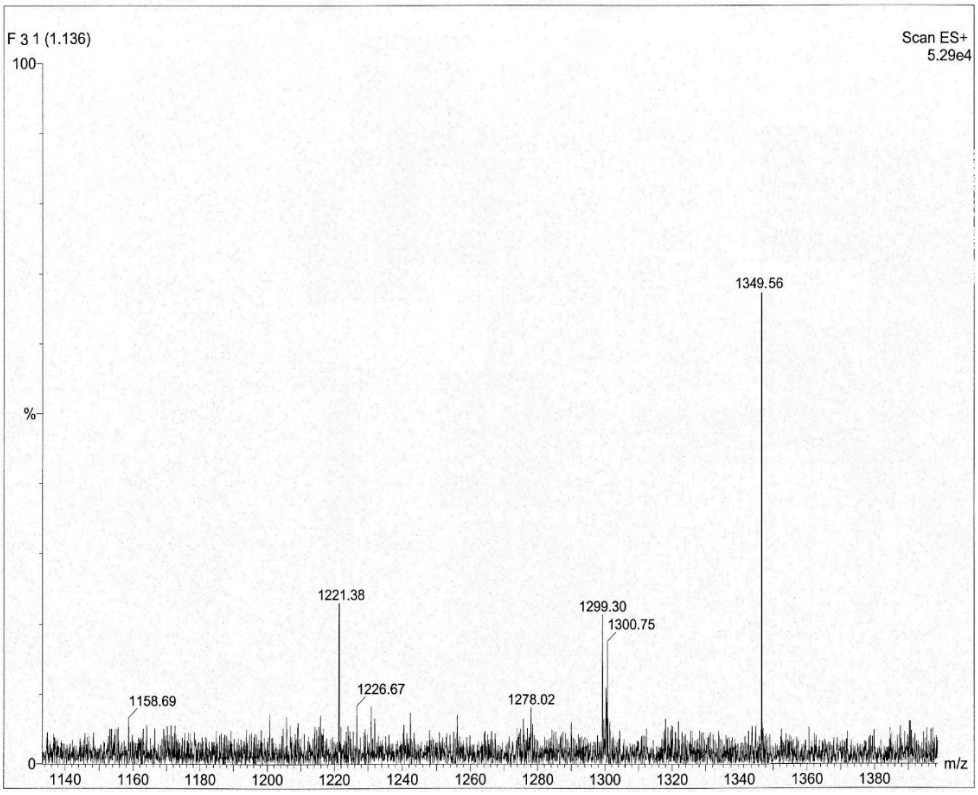


Figure 4. Mass spectrum of Co(II) phthalocyanine **(3)**

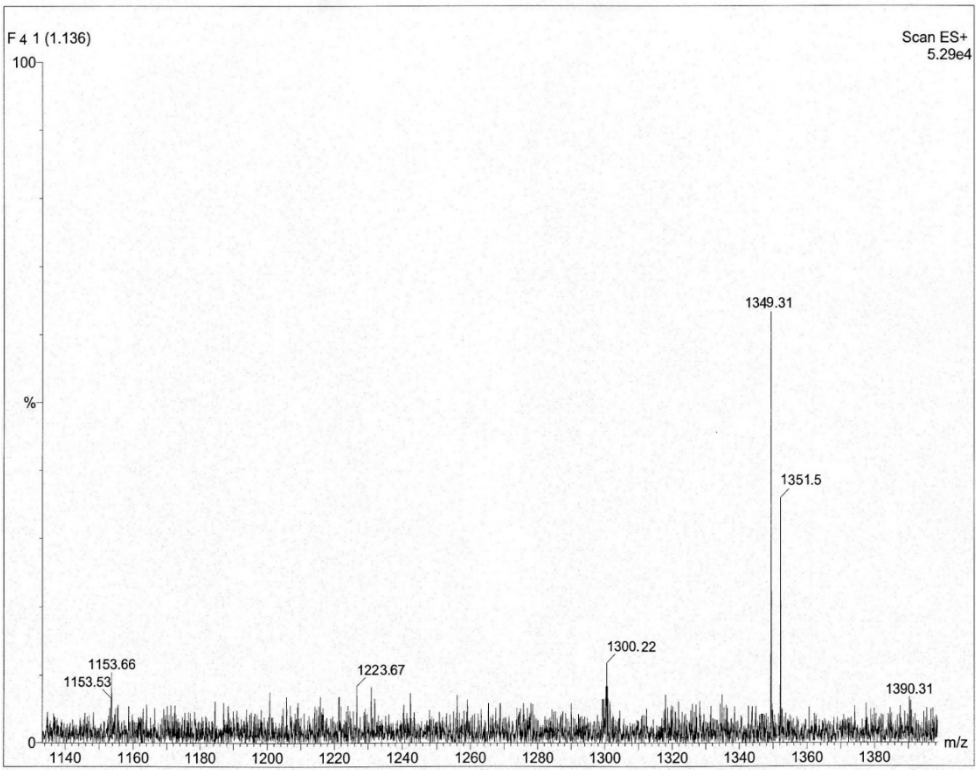


Figure 5. Mass spectrum of Cu(II) phthalocyanine **(4)**

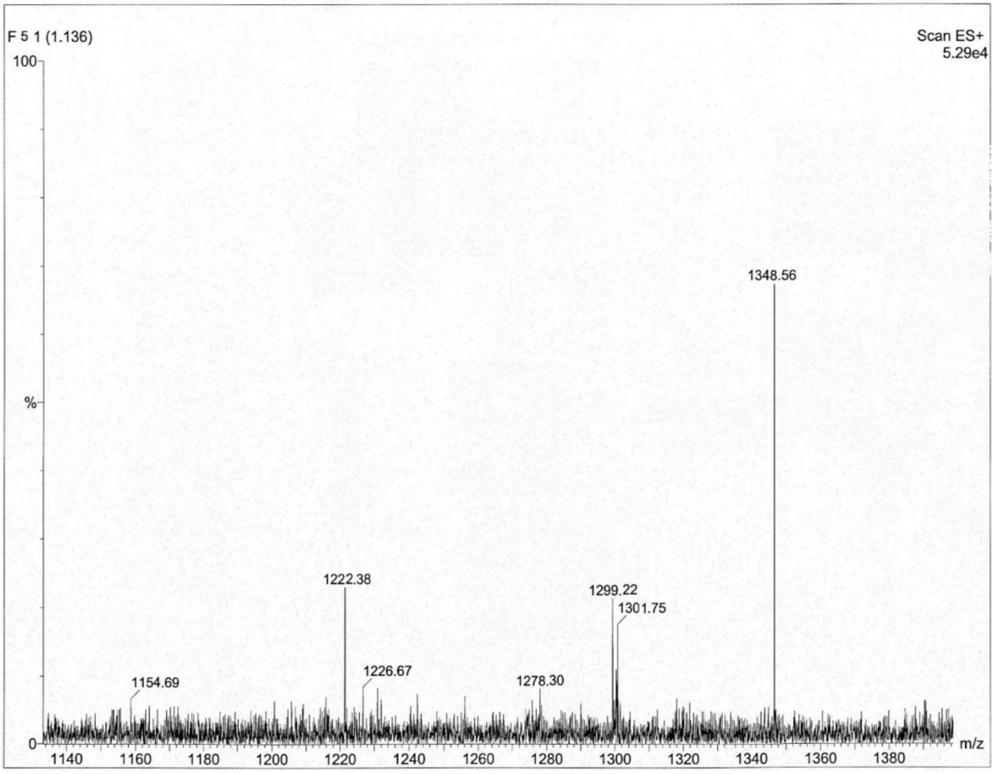


Figure 6. Mass spectrum of Ni(II) phthalocyanine **(5)**

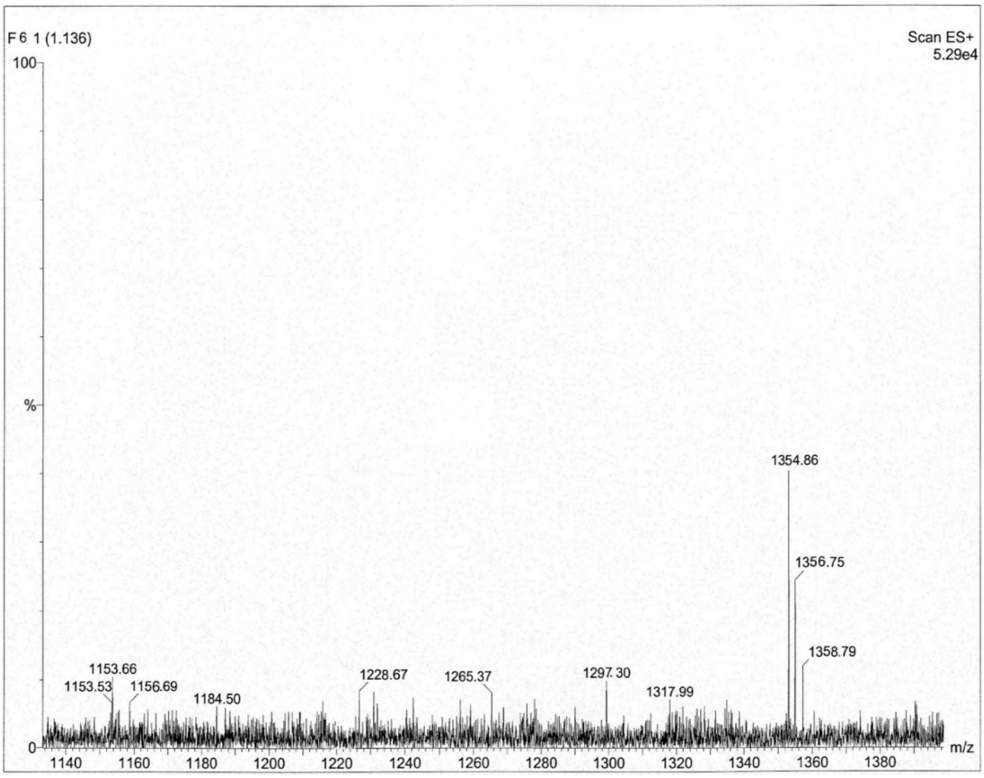


Figure 7. Mass spectrum of Zn(II) phthalocyanine **(6)**

4. CONCLUSIONS

We have investigated a new metal-free phthalocyanine **2** and four metallophthalocyanines **3, 4, 5** and **6**. The new dinitrile compound **1** was gained from the reaction of 9-fluorenemethanol with 4-nitrophtlonitrile in dry DMF under nitrogen atmosphere. The metal-free phtalocyanine **2** was gained from the reaction of **1** with n-penthanol and 1,8-diazabicyclo[5.4.0]undec-7-ene. The new metallophthalocyanines were CoPc, CuPc, NiPc, ZnPc which were gained by the reaction of the dinitrile compound **1** with $CoCl_2$, $CuCl_2$, $NiCl_2$, $Zn(CH_3COOH)_2$ in DMAE, respectively. The structures of new compounds were demonstrated by using spectroscopic data and elemental analysis.

REFERENCES

[1] Gregory P. High Technology Applications of Organic Colorants, Plenum Press: New York, 1991.

[2] Lezznoff CC, Lever ABP. Phthalocyanines properties and applications, Springer, Berlin, vol. 2, 1993.

[3] Rosenthal I. Phthalocyanines as photodynamic sensitizers. Photochem Photobiol 1991; 53(6): 859-870.

[4] Keown NB. Mc Editor, Phthalocyanine Materials. Cambridge: Cambridge University Press,1998.

[5] Scalise A, Durantimi EN. Synthesis, properties, and photodynamic inactivation of Escherichia coli using a cationic and a noncharged Zn(II) pyridyloxyphthalocyanine derivatives. Bioorg Med Chem 2005; 13(8): 3037-3045.

[6] Sakamoto K, Kato T, Ohno-Okumura E, Watanabe M, Cook MJ. Synthesis of novel cationic amphiphilic phthalocyanine derivatives for next generation photosensitizer using photodynamic therapy of cancer. Dyes and Pigments 2005; 64: 63-71.

[7] Newton MI, Starke TKH, Willis MR, McHale G. NO_2 detection at room temperature with copper phthalocyanine thin film devices. Sens Actuators B 2000; 67(3), 307-311.

[8] Kobayashi N, Nevin WA Electrocatalytic Reduction of Oxygen Using Water-Soluble Iron and Cobalt Phthalocyanines and Porphyrins. Appl Organom Chem 1996; 10(8): 579-590.

[9] Wöhrle D, Gitzel J, Krawezyk G, Tsuchida E, Ohno H, Nishisaka TJ. Synthesis, Redox Behavior, Sensitizer Activity, and Oxygen Transfer of Covalently Bound Polymeric. Porphyrins Macromol Sci Chem A. 1988; 25(10-11): 1227-1254.

[10] Hanack M, Lang M. Conducting Stacked Metallophthalocyanines and Related Compounds Adv Mater 1994; 6(11): 819-833.

[11] Loupy A, editor. Microwaves in Organic Synthesis, Weinheim: Wiley VCH, 2002.

[12] Deshayes S, Liagre M, LoupyA, Luche JL, Petit A. Microwave activation in phase transfer catalysis. Tetrahedron 1999; 55(36): 10851-10870.

[13] Loupy A, Petit A, Hamelin J, Texier-Boullet F, Jacquault P, Mathe D. New Solvent-Free Organic Synthesis Using Focused Microwaves. Synthesis (Stuttgart) 1998; 9: 1213-14.

[14] Bogdal D, Pielichowski J, Penczek P, Prociak A, Microwave Assisted Synthesis, Crosslinking, and Processing of Polymeric Materials. Advances in Polymer Science 2003; 163: 193-263.

[15] Aijian W, Lingliang L, Chi Z. Synthesis of unsymmetrical phthalocyanines: a brief overview. Tetrahedron 2012; 68(11): 2433-2451.

[16] Bıyıklıoğlu Z, Kantekin H, Özil M. Microwave-assisted synthesis and characterization of novel metal-free and metallophthalocyanines containing four14-membered tetraaza macrocycles. J Organomet Chem 2007 ; 692 : 2436-2440.

[17] Bıyıklıoğlu Z, Kantekin H. Microwave assisted synthesis and characterization of novel metal-free and metallophthalocyanines containing four pyridyl groups. TransMet Chem 2007; 32(7):851-859.

[18] Young G. J, Onyebuagu W. Synthesis and characterization of di-disubstituted phthalocyanines. J Org Chem 1990; 55: 2155-2159.

[19] Perrin DD, Armarego WLF, Perrin DR. Purification of Laboratory Chemicals, 2nd ed., Pergamon Press: New York, 1989.

[20] Snow AW, Griffith JR. Syntheses and Characterization of Heteroatom-Bridged Metal free Phthalocyanine Network Polymers and Model Compounds. Macromolecules 1984; 17**:** 1614-1624.

[21] Von Nostrum CF, Picken SJ, Schouten AJ, Nolte RJM. Synthesis and supramolecular chemistry of novel liquid crystalline crown ether substituted phthalocyanines: towards molecular wires and molecular ionoelectronics. Journal of the American Chemical Society 1995; 117: 9957-9960.

[22] Motekaitis RJ, Martell AE, Dietrich B, Lehn JM. Anion binding in macrobicyclic metal cryptate complexes: copper(II)-BISTREN. Inorg Chem 1984; 23(11): 1588-1591.

[23] Agnus Y, Louis R, Gisselbrecht JP, Weiss R. Dicopper(II) chloro and azido inclusion complexes of the [24-ane-N2S4] binucleating macrocycle. Synthesis, crystal and molecular structures, and spectral, magnetic, and electrochemical properties. J Am Chem Soc 1984; 106(1): 93-102**.**

[24] Martin AE, Bulkowski JE. General synthetic route to hexaamine macrocycles. J. Org Chem 1982; 47(3): 415-418.

[25] Lehn JM. Dinuclear cryptates: dimetallic macropolycyclic inclusion complexes: concepts-design-prospects. Pure Appl Chem 1980; 52(1): 2441-2459.

[26] Reisen A, Zehnder M, Kaden TA. Metal complexes of macrocyclic ligands. Part XXIV. Binuclear complexes with tetraazamacrocycle-N,N′,N″,N‴-tetraacetic acids Helvetica Chimica Acta 1986; 69(8): 2074-2080.

[27] Jiang JZ. Advances in functional phthalocyanine materials, Structure and Bonding, Heidlberg: Springer –Verlag, 2010, 135.