Polyhedron 30 (2011) 1085–1090

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and characterization of a new organo-soluble metal-free and metallophthalocyanines bearing flexible moieties

Asiye Nas, Halit Kantekin *

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

ARTICLE INFO

Article history:
Received 30 September 2010
Accepted 9 January 2011
Available online 19 January 2011

Keywords:
1,2-Dihydroacenaphthylen-1-ol
Metallophthalocyanine
Microwave-assisted
4-Nitrophthalonitrile
Thermal stability

ABSTRACT

This paper describes a new symmetric metal-free phthalocyanine and its transition metal complexes which were prepared by a condensation of 1,2-dihydroacenaphthylen-1-ol **1** and 4-nitro phthalonitrile **2** with Co(II), Ni(II), Cu(II), and Zn(II) salts in 2-(dimethylamino)ethanol, respectively. The novel phthalocyanines bearing oxygen donor atoms on peripheral position have been characterized by IR, UV–Vis, ^{1}H NMR, ^{13}C NMR, Mass spectra and elemental analysis. The thermal behaviours of **4–8** were investigated by TG/DTA.

1. Introduction

Since their first synthesis early in the last century, phthalocyanines, which are also called as blue-green products, are produced with increasing amount and diversity in many countries per year. The syntheses of metal-free and metallophthalocyanines play an extremely important role not only in the development of chemistry and its related branches but also in the development of current economy.

Phthalocyanines (pcs) and their derivatives have attracted a good deal of interest due to their fascinating features such as high thermal stability [1], semi-conductivity [2], and besides in several application areas such as laser dyes, new red-sensitive photocopying applications [3,4], and optical computer read/write discs. [5]. Pcs are an important industrial commodity which was firstly used in productions of inks, and also colouring for plastics, metal surfaces, dye stuffs for jeans and other clothing [3]. Phthalocyanines' electronic and optical properties for use in many applications, such as chemical sensors [6–9], liquid crystals [10–12], catalysis, considerably depend upon the peripheral and axial substitution patterns [13,14]. Besides, pcs can also be subsequently used in various implementation areas, for instance, production of solar energy conversions [15,16], antimycotic materials [17], corrosion inhibitors [18,19], for the prevention and treatment of infectious diseases [20], eye [21] and neurodegenerative diseases [22]. In the last few years, substituted phthalocyanine derivatives have also been used in photodynamic cancer therapy (PDT) and other processes by visible light [23–27].

Pcs can be obtained by the classical template reactions of phthalonitrile, cyano-benzamide, phthalic acid and phthalamide with metal salts in high-boiling nonaqueous solvents at required temperatures [28,29]. On the other hand, microwave processing techniques have attracted a great deal of potential interest as alternatives to classical thermal processing techniques because of the diverse and convenient advantages of microwave heating, which is selective, direct, rapid, internal, and controllable [30,31]. It is well known that microwave (MW) irradiation can accelerate a great number of chemical processes; in particular, the reaction time and energy input are supposed to be mostly reduced in the chemical processes that are run for a long time at high temperatures under conventional conditions [32].

The present work contains the preparation and the characterization of metal-free (**4**) and metallophthalocyanines (**5–8**) containing 1,2-dihydroacenaphthylen-1-ol moieties by the microwave irradiation. Additionally, we have carried out the thermogravimetric study of tetrasubstituted metal-free phthalocyanine (**4**) and metallophthalocyanines (**5–8**) to compare their thermal stabilities.

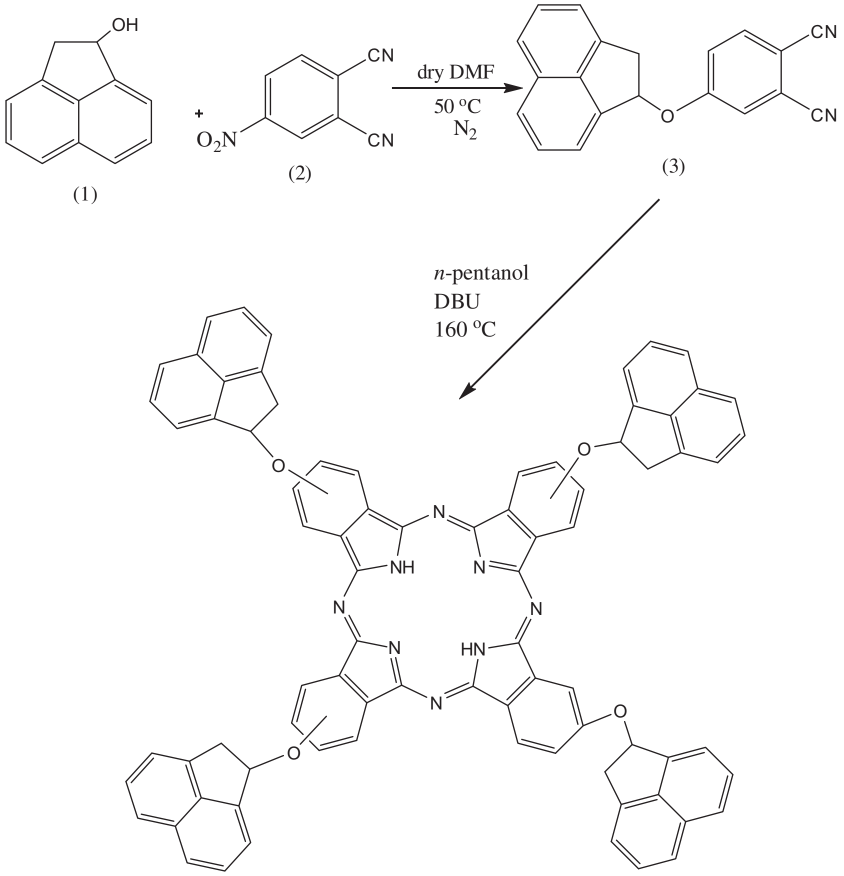
2. Experimental

All reactions were carried out under a dry nitrogen atmosphere using Standard Schlenk techniques. All chemicals, solvents, and reagents were of reagent grade quality and were obtained from commercial suppliers. All reagents and solvents were dried and

---

* Corresponding author. Tel.: +90 462 377 25 89; fax: +90 462 325 31 96.
E-mail address: halit@ktu.edu.tr (H. Kantekin).

0277-5387/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2011.01.005



Scheme 1. The synthesis of the metal-free phthalocyanine (**4**) by using classical method.

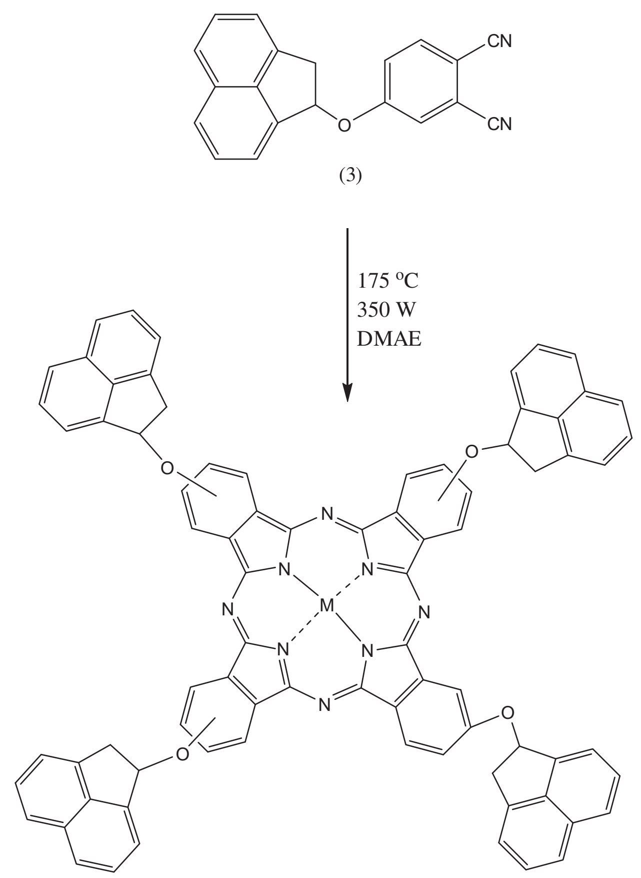
purified before use as described by Perrin and Armarego [33]. FT-IR spectra were obtained using a Perkin–Elmer 1600 FTIR spectrophotometer with the samples prepared as KBr pellets. Elemental analyses and metal contents of novel compounds were performed on a Vario MICRO Elemental Analyser at Anadolu University in Turkey. A Seiko II Exstar 6000 thermal analyzer was used to record the DTA curves under a nitrogen atmosphere with a heating rate of 20 °C min^{-1} in the temperature range of 30–900 °C using platinum crucibles. UV–Vis spectra were recorded using a Unicam UV–Vis spectrometer operating in the wavelength range of 200–850 nm with quartz cells. All ^{1}H and ^{13}C NMR spectra were recorded in CDCl3 on a Varian Mercury NMR spectrometer operating at 200 MHz. Chemical shifts are expressed in ppm relative to TMS as an internal standard. Mass spectra were recorded using a Micromass Quatro LC/ULTIMA LC–MS/MS spectrometer. Melting points were measured on an electrothermal apparatus. Domestic microwave oven was used for carrying out all synthesis of phthalocyanines.

2.1. 4-(1,2-Dihydroacenaphthylen-1-yloxy)phthalonitrile (**3**)

1,2-Dihydroacenaphthylen-1-ol **1** (1 g, 5.88 mmol) was dissolved in anhydrous DMF (8 ml) under a nitrogen atmosphere at 50 °C and 4-nitrophthalonitrile **2** [34] (1.02 g, 5.88 mmol) was added to the solution. After stirring for 15 min, finely ground dry K_2CO_3 (2.84 g, 20.58 mmol) was added portionwise within 2 h with efficient stirring. The reaction mixture was stirred under a nitrogen atmosphere at 50 °C for 3 days. The reaction mixture was monitored by thin layer chromatography (TLC) using chloroform solvent system. At the end of the elapsed period, the obtained mixture was poured into ice (100 g) and it was shown that the light-green product precipitated. This product was filtered off, washed with distilled water and diethylether. Finally, obtained crude product was crystallized from ethanol. Yield: 1.2 g (69%), m.p.: 176–177 °C. *Anal.* Calc. for $C_{20}H_{12}N_2O$: C, 81.07; H, 4.08; N, 9.45. Found: C, 81.03; H, 4.05; N, 9.48%. IR (KBr tablet) ν_{max}/cm^{-1}: 3081 (Ar-H), 2920–2850 (Aliph. C–H), 2227 ($C{\equiv}N$), 1594, 1497, 1325, 1253, 1165, 1019, 838, 780. ^{1}H NMR ($CDCl_3$) (δ: ppm): 7.85–7.81 (d, 3H, Ar-H), 7.64 (s, 1H, Ar-H), 7.59–7.56 (t, 2H, Ar-H), 7.43–7.34 (m, 3H, Ar-H), 6.31 (t, 1H, CH), 3.70 (d, 2H, CH_2). ^{13}C NMR ($CDCl_3$) (δ: ppm): 161.32, 140.58, 140.18, 137.90, 135.62, 131.52, 128.73, 128.29, 126.48, 123.59, 121.85, 120.72, 120.55, 120.49, 117.85, 115.90, 115.51, 107.78, 80.41, 38.87. MS (FAB), (m/z): 296[M]$^{+}$.

2.2. Metal-free phthalocyanine (**4**)

A standard Schlenk tube was charged with 4-(1,2-dihydroacenaphthylen-1-yloxy)phthalonitrile **3** (0.2 g, 0.675 mmol), 3 ml of anhydrous *n*-pentanol and 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU, 2 drops) under a nitrogen atmosphere and degassed several times. Then the reaction mixture was stirred at 160 °C for 12 h. After cooling to room temperature, the reaction mixture was stirred with ethanol (30 ml) to precipitate the product. The precipitated dark green product **4** was filtered off, washed with hot ethanol (3 × 50 ml) and dried *in vacuo* over P_2O_5. Finally, it was purified by preparative thin layer chromatography (TLC) using solely chloroform solvent system. This product is soluble in $CHCl_3$, CH_2Cl_2, THF, DMF, DMSO and pyridine. Yield: 40 mg (20%), m.p.: 269–292 °C. *Anal.* Calc. for $C_{80}H_{50}N_8O_4$: C, 80.93; H, 4.24; N, 9.44. Found: C, 80.90; H, 4.26; N, 9.49%. IR (KBr tablet) ν_{max}/cm^{-1}: 3285 (N–H), 3039 (Ar-H), 2916–2847 (Aliph. C–H), 1602, 1520, 1477, 1418, 1344, 1236, 1096, 1015, 936, 776, 746. ^{1}H NMR ($CDCl_3$)



Compound	5	6	7	8
M	Zn^{+2}	Cu^{+2}	Ni^{+2}	Co^{+2}

Scheme 2. The synthesis of the metallophthalocyanines (**5–8**) by using microwave process.

(δ: ppm): 7.86–7.74 (d, 4H, Ar-H), 7.62–7.53 (d, 20H, Ar-H), 7.39–7.36 (m, 12H, Ar-H), 6.32 (t, 4H, CH), 3.65 (d, 8H, CH_2). ^{13}C NMR ($CDCl_3$) (δ: ppm): 174.20, 166.71, 163.54, 163.27, 141.24, 140.62, 134.73, 130.72, 126.57, 126.29, 125.15, 124.11, 123.04, 122.44, 121.27, 120.97, 109.33, 80.78, 40.01, 35.52. UV–Vis ($CHCl_3$): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 712 (5.15), 679 (5.12), 650 (4.93), 618 (4.88), 305 (5.15). MS (FAB), (*m*/*z*): 1185 $[M-2]^+$.

2.3. Zinc(II) phthalocyanine (*5*)

4-(1,2-Dihydroacenaphthylen-1-yloxy)phthalonitrile **3** (0.2 g, 0.675 mmol) was dissolved in 2-(dimethylamino)ethanol (2 ml) and dry $Zn(CH_3COO)_2$ (30.74 mg, 0.168 mmol) was added to this solution. The reaction mixture was irradiated in a microwave oven at 175 °C, 350 W, for 7 min. After the reaction mixture was cooled to room temperature, 30 ml of ethanol was added to the mixture and stirred overnight. At the end of this period, this mixture was filtered off. The green crude product was refluxed with ethanol for 5 h. Then it was filtered off again. Obtained dark green product was dried *in vacuo* over P_2O_5. Finally it was purified by preparative thin layer chromatography (TLC) using solely chloroform solvent system. This product is soluble in $CHCl_3$, CH_2Cl_2, THF, DMF, DMSO and pyridine. Yield: 67 mg (32%), m.p.: 269–297 °C. *Anal.* Calc. for $C_{80}H_{48}N_8O_4Zn$: C, 76.83; H, 3.87; N, 8.96. Found: C, 76.86; H, 3.82; N, 8.94%. IR (KBr tablet) ν_{max}/cm^{-1}: 3038 (Ar-H), 2917–2857 (Aliph. C–H), 1606, 1483, 1396, 1339, 1275, 1224, 1097, 1049, 943, 779, 745. ^1H NMR ($CDCl_3$) (δ: ppm): 7.84–7.70 (d, 4H, Ar-H), 7.58–7.53 (d, 20H, Ar-H), 7.36–7.33 (m, 12H, Ar-H), 6.38 (t, 4H, CH), 3.75 (d, 8H, CH_2). ^{13}C NMR ($CDCl_3$) (δ: ppm): 173.30, 167.81, 163.57, 163.32, 141.35, 140.71, 135.51, 131.50, 128.60, 128.29, 126.17, 125.82, 123.42, 122.17, 121.83, 120.34, 109.59, 80.32, 39.09, 29.35. UV–Vis ($CHCl_3$): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 691 (5.27), 620 (4.60), 360 (4.98). MS (FAB), (*m*/*z*): 1251$[M+1]^+$.

2.4. Copper(II) phthalocyanine (*6*)

4-(1,2-Dihydroacenaphthylen-1-yloxy)phthalonitrile **3** (0.2 g, 0.675 mmol) was dissolved in 2-(dimethylamino)ethanol (2 ml) and dry $CuCl_2$ (22.69 mg, 0.168 mmol) was added to this solution. The reaction mixture was irradiated in a microwave oven at 175 °C, 350 W, for 9 min. After the reaction mixture was cooled to room temperature, 30 ml of ethanol was added to the mixture and stirred overnight. At the end of this period, this mixture was filtered off. The green crude product was refluxed with ethanol for 5 h. Then it was filtered off again. Obtained dark green product was dried *in vacuo* over P_2O_5. Finally, it was purified by preparative thin layer chromatography (TLC) using solely chloroform solvent system. This product is soluble in $CHCl_3$, CH_2Cl_2, THF, DMF, DMSO and pyridine. Yield: 60 mg (28%), m.p.: 364–414 °C. *Anal.* Calc. for $C_{80}H_{48}N_8O_4Cu$: C, 76.94; H, 3.87; N, 8.97. Found: C, 76.90; H, 3.85; N, 8.96%. IR (KBr tablet) ν_{max}/cm^{-1}: 3032 (Ar-H), 2923–2846 (Aliph. C–H), 1596, 1477, 1341, 1270, 1226, 1174, 1096, 1053, 869, 779. UV–Vis ($CHCl_3$): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 690 (5.27), 618 (4.69), 291 (4.98), 264 (5.09). MS (FAB), (*m*/*z*): 1287$[M+K]^+$.

2.5. Nickel(II) phthalocyanine (*7*)

4-(1,2-Dihydroacenaphthylen-1-yloxy)phthalonitrile **3** (0.2 g, 0.675 mmol) was dissolved in 2-(dimethylamino)ethanol (2 ml) and dry $NiCl_2$ (21.84 mg, 0.168 mmol) was added to this solution. The reaction mixture was irradiated in a microwave oven at 175 °C, 350 W, for 7 min. After the reaction mixture was cooled to room temperature, 30 ml of ethanol was added to the mixture and stirred overnight. At the end of this period, this mixture was filtered off. The green crude product was refluxed with ethanol for 5 h. Then it was filtered off again. Obtained dark green product was dried *in vacuo* over P_2O_5. Finally, it was purified by preparative thin layer chromatography (TLC) using solely chloroform solvent system. This product is soluble in $CHCl_3$, CH_2Cl_2, THF, DMF, DMSO and pyridine. Yield: 88 mg (42%), m.p.: 260–296 °C. *Anal.* Calc. for $C_{80}H_{48}N_8O_4Ni$: C, 77.24; H, 3.89; N, 9.01. Found: C, 77.22; H, 3.86; N, 9.04%. IR (KBr tablet) ν_{max}/cm^{-1}: 3038 (Ar-H), 2925–2854 (Aliph. C–H), 1732, 1601, 1465, 1377, 1274, 1122, 1067, 778. ^1H NMR ($CDCl_3$) (δ: ppm): 7.80–7.71 (d, 4H, Ar-H), 7.57–7.53 (d, 20H, Ar-H), 7.37–7.34 (m, 12H, Ar-H), 6.34 (t, 4H, CH), 3.55 (d, 8H, CH_2). ^{13}C NMR ($CDCl_3$) (δ: ppm): 170.96, 148.24, 142.69, 141.43, 138.26, 137.48, 131.28, 130.43, 128.37, 127.63, 126.38, 123.14, 122.13, 121.54, 120.30, 119.84, 105.00, 92.14, 55.42, 29.95. UV–Vis ($CHCl_3$): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 681 (5.23), 622 (5.11), 290 (5.04). MS (FAB), (*m*/*z*): 1243$[M]^+$.

2.6. Cobalt(II) phthalocyanine (*8*)

4-(1,2-Dihydroacenaphthylen-1-yloxy)phthalonitrile **3** (0.2 g, 0.675 mmol) was dissolved in 2-(dimethylamino)ethanol (2 ml) and dry $CoCl_2$ (21.84 mg, 0.168 mmol) was added to this solution. The reaction mixture was irradiated in a microwave oven at 175 °C, 350 W, for 10 min. After the reaction mixture was cooled to room temperature, 30 ml of ethanol was added to the mixture and stirred overnight. At the end of this period, this mixture was filtered off. The green crude product was refluxed with ethanol for 5 h. Then it was filtered off again. Obtained dark green product was

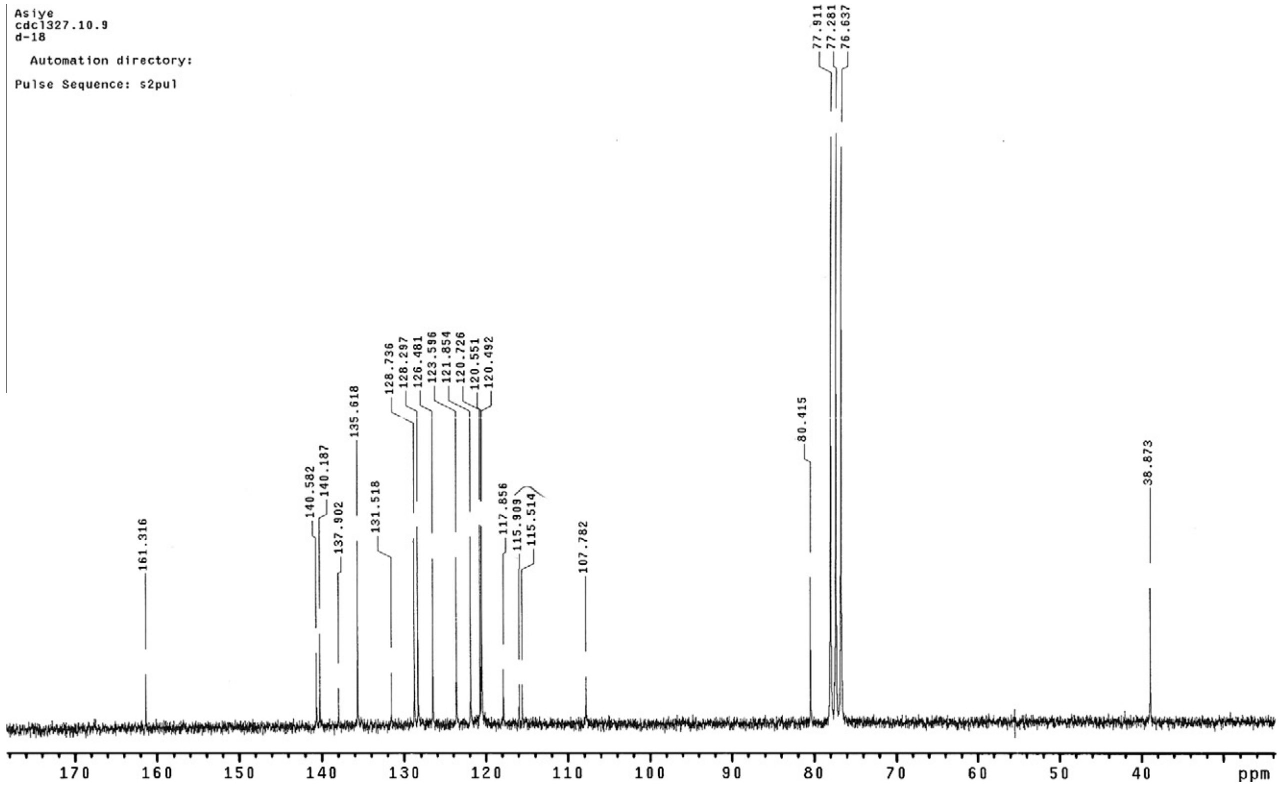


Fig. 1. ^{13}C NMR spectrum of 4-(1,2-dihydroacenaphthylen-1-yloxy)phthalonitrile (**3**) in $CDCl_3$.

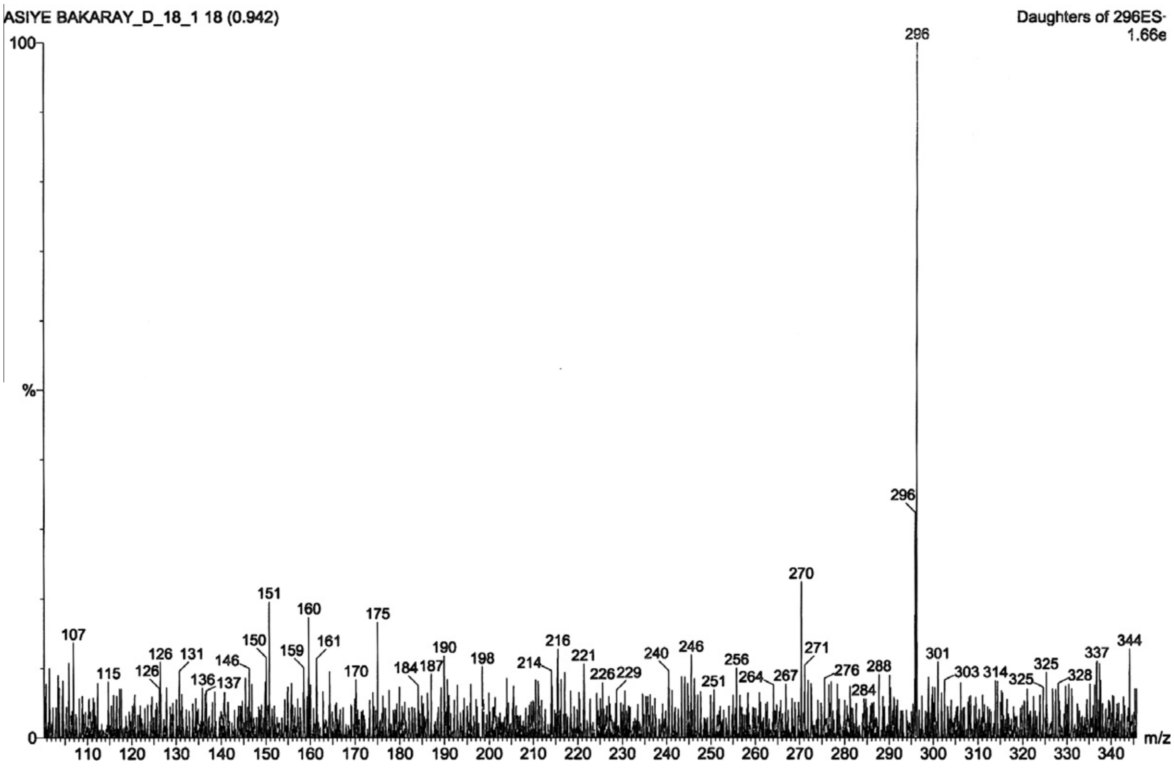


Fig. 2. Mass spectrum of 4-(1,2-dihydroacenaphthylen-1-yloxy)phthalonitrile (**3**).

dried *in vacuo* over P_2O_5. Finally, it was purified by preparative thin layer chromatography (TLC) using solely chloroform solvent system. This product is soluble in $CHCl_3$, CH_2Cl_2, THF, DMF, DMSO and pyridine. Yield: 76 mg (36%), m.p.: 264–291 °C. *Anal.* Calc. for $C_{80}H_{48}N_8O_4Co$: C, 77.23; H, 3.89; N, 9.01; Co, 4.74. Found: C, 77.27; H, 3.91; N, 9.05, Co, 4.76%. IR (KBr tablet) ν_{max}/cm^{-1}: 3032

(Ar-H), 2923–2853 (Aliph. C–H), 1606, 1517, 1475, 1413, 1342, 1227, 1123, 1095, 778, 752. UV–Vis ($CHCl_3$): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 684 (5.18), 621 (4.81), 366 (4.80). MS (FAB), (*m/z*): 1244[M+1]$^+$.

3. Results and discussion

The synthesis of substituted target metal-free phthalocyanine (**4**) and metallophthalocyanines (**5–8**) were outlined in Schemes 1 and 2. Initially, the synthesis of 4-(1,2-dihydroacenaphthylen-1-yloxy)phthalonitrile (**3**) was obtained by base-catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile (**2**) with the –OH function of 1,2-dihydroacenaphthylen-1-ol (**1**). This reaction was carried out in anhydrous DMF containing finely ground dry K_2CO_3 as a base in a Schlenk system under a nitrogen atmosphere at 50 °C for 3 days. Compound (**3**) was obtained in 69% yield. A new metal-free phthalocyanine (**4**) was accomplished by cyclotetramerization reaction of dicyano compound (**3**) in *n*-pentanol with the presence of a few drops of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) as a strong base at 160 °C under a nitrogen atmosphere. The conversion of this new dicyano compound (**3**) into the metallophthalocyanines (**5–8**) was accomplished by cyclotetramerization in 2-(dimethylamino)ethanol (DMAE) in the presence of metal salts ($Zn(CH_3COO)_2$, $CuCl_2$, $NiCl_2$, $CoCl_2$) at 175 °C, 350 W by microwave irradiation in the range of 7–10 min. In contrast to the analogous compounds with bulky moieties, phthalocyanines generally have low solubility. However, the novel phthalocyanines (**4–8**) that synthesized are soluble in $CHCl_3$, CH_2Cl_2, THF, DMF, DMSO and pyridine.

The characterization of all new products were performed by a combination of methods involving elemental analysis, IR, ^{1}H NMR, ^{13}C NMR, UV–Vis spectroscopy, mass spectrometry. Elemental analysis results of the dicyano compound and phthalocyanines demonstrated a good agreement with the calculated values.

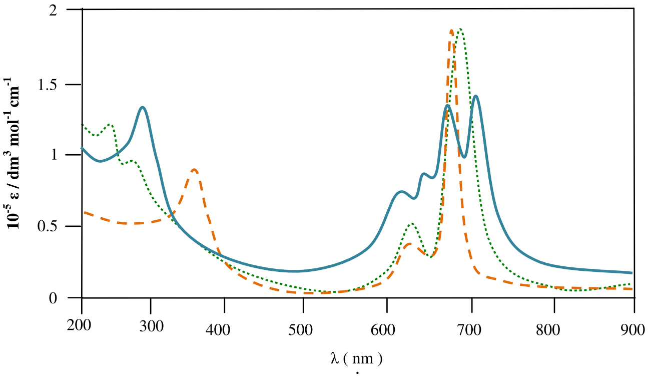


Fig. 3. UV–Vis spectra of compounds **4** (—), **5** (- - -) and **6** (. . .) in chloroform.

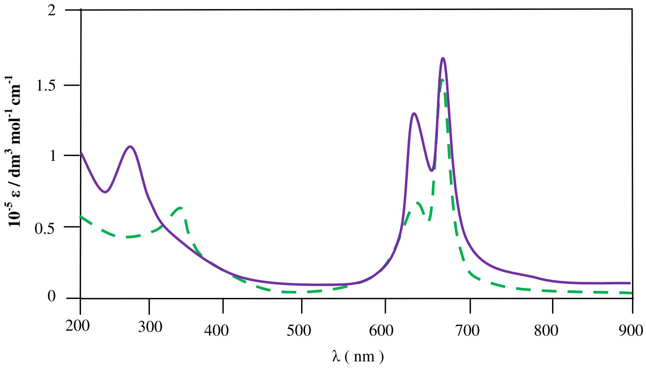


Fig. 4. UV–Vis spectra of compounds **7** (—) and **8** (- - -) in chloroform.

In the IR spectrum of **3**, the disappearance of broad –OH peaks and the presence of Ar–O–C at 1253 cm^{-1} and the presence of sharp C≡N functional group at 2227 cm^{-1} supported the formation of desired compound **3**. The ^{1}H NMR spectrum of **3** indicated that the proton of –OH group of compound **1** disappeared, as expected. In addition, new signals belonging to aromatic protons appeared in the range of δ = 7.85–7.34 ppm, and aliphatic protons at 6.31 and 3.70 ppm. The ^{13}C NMR spectrum of **3** in deuterated $CDCl_3$ gave new signals at δ = 115.9 and 115.51 ppm belonging to dicyano carbon atoms (Fig. 1). In the MS (FAB) spectrum of **3**, we also observed the molecular ion peak at (*m/z*): 296[M]$^+$, which confirmed the proposed structure (Fig. 2).

When the IR spectra of compound **3** compared with compound **4**, the stretching vibrations at 2227 cm^{-1} belonging to C≡N functional group of **3** disappeared after formation of metal-free phthalocyanine (**4**). The weak vibration at 3285 cm^{-1} indicated the presence of N–H stretching vibrations of the inner phthalocyanine core in metal-free phthalocyanine (**4**). On the other hand, this vibration band disappeared in the IR spectra of metallophthalocyanines. In the ^{1}H NMR spectrum of **4**, the NH protons could not be observed because of the strong aggregation of the molecules [35]. In the MS (FAB) spectrum of **4**, we observed the molecular ion peak at (*m/z*): 1185 [M−2]$^+$, which confirmed the proposed structure.

The IR spectra of metallophthalocyanines, which were very similar to metal-free phthalocyanine **(4)**, clearly indicated the formation of compounds **5–8** with the disappearance of the C≡N functional group of **3**. Because of their paramagnetic nature, ^{1}H NMR and ^{13}C NMR of the copper(II) phthalocyanine **6** and cobalt (II) phthalocyanine **8** were precluded. In the MS (FAB) spectra of **5–8**, we observed the molecular ion peaks at (*m/z*): 1251[M+1]$^+$, (*m/z*): 1287[M+K]$^+$, (*m/z*): 1243[M]$^+$, (*m/z*): 1244[M+1]$^+$, respectively, which confirmed the proposed structure.

It is known that the best confirming indicator for the phthalocyanines is their UV–Vis spectra. The spectra of metallophthalocyanine complexes consist of an intense absorption band in the visible region traditionally near 670 nm called the Q band and a generally weaker band near 340 nm called the Soret or B band both being π–π^* transitions [36]. The Q band of all the compounds was attributed to the π–π^* transition from the highest occupied molecular orbital to the lowest unoccupied molecular orbital of the phthalocyanine (−2) ring [37,38].

In the electronic spectrum of the metal-free phthalocyanine **(4)** (Fig. 3) in chloroform at the room temperature, the characteristic split Q absorption band was observed with absorptions at λ_{max}: 679 and 712 nm with shoulders at 650 and 618 nm as expected. In the UV–Vis absorption spectra of zinc(II) **5**, copper(II) **6**, nickel(II) **7**, cobalt(II) **8** phthalocyanines (Figs. 3 and 4) in chloroform at the room temperature, the absorptions were observed as expected. It was observed that the intense Q absorption at λ_{max}: 691, 690, 681 and 684 nm with weaker absorptions at 620, 618, 622 and 621 nm, respectively (Figs. 3 and 4). Besides, the UV–Vis spectra of **5**, **6**, **7** and **8** in chloroform were observed the intense B absorption at λ_{max}: 360, (264 and 291), 290 and 366 nm as expected.

Table 1
Thermal properties of the novel phthalocyanines.

Compound	M	Initial decomposition temperature in °C	Main decomposition temperature in °C
4	2H	269.9	292.2
5	Zn	269.6	297.7
6	Cu	364.4	414.3
7	Ni	260.5	296.9
8	Co	264.9	291.9

In addition to these supportive spectral data confirming the desired structure of novel molecules of **3–8**, the thermal behaviours of the metal-free (**4**) and metallophthalocyanines (**5–8**) were investigated by TG/DTA. Though the potential thermal stabilities of phthalocyanines are well known, the obtained novel phthalocyanines (**4–8**) were observed not to be stable above 260 °C. The initial and main decomposition temperatures were given in Table 1. The initial decomposition temperatures decreased in the order of **6** > **4** > **5** > **8** > **7**.

4. Conclusion

We have synthesized and characterized a new symmetrically substituted metal-free phthalocyanine and its transition metal complexes (**5–8**) which were prepared by a condensation of 1,2-dihydroacenaphthylen-1-ol **1** and 4-nitro phthalonitrile 2 with Co(II), Ni(II), Cu(II), or Zn(II) salts in DMAE, respectively. Phthalonitrile compound **3** was synthesized by reaction of 1,2-dihydroacenaphthylen-1-ol (**1**) with 4-nitro phthalonitrile (**2**). The structures of the new compounds were both characterized and illuminated by several spectral methods.

Acknowledgement

This study was supported by the Research Fund of Karadeniz Technical University, Project no: 2006.111.02.1 (Trabzon-Turkey).

References

[1] F.H. Moser, A.L. Thomas, The Phthalocyanines, Manufacture and Applications, vols. 1 and 2, CRC Press, Boca Raton, Florida, 1983.
[2] T.M.M. Kumar, B.N. Ahcar, J. Organomet. Chem. 691 (2006) 331.
[3] C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines, Properties and Applications, vol. 4, VCH, New York, 1996.
[4] C.S. Frampton, J.M. O'Connor, J. Peterson, J. Silver, Enhanced Colours and Properties in the Electrochromic Behaviour of Mixed Rare-earth Bisphthalocyanines, Displays October, 1988, pp. 174–178.
[5] M. Emmelius, G. Pawlowski, H.W. Vollmann, Angew. Chem., Int. Ed. 28 (1989) 1445.
[6] A.W. Snow, W.R. Barger, M. Klusty, H. Wohltjen, N.L. Jarvis, Langmuir 2 (1986) 513.
[7] Y.J. Zhang, W.P. Hu, Sci. China Ser. B 52 (2009) 751.
[8] L. Alagna, A. Capobianchi, A.M. Paoletti, G. Pennesi, G. Rossi, M.P. Casaletto, A. Generosi, B. Paci, V.R. Albertini, Thin Solid Films 515 (2006) 2748.
[9] M. Kimura, T. Muto, H. Takimoto, K. Wada, K. Ohta, K. Hanabusa, H. Shirai, N. Kobayashi, Langmuir 16 (2000) 2078.
[10] J.A. Duro, G. de la Torre, J. Barbera, J.L. Serrano, T. Torres, Chem. Mater. 8 (1996) 1061.
[11] A.G. Gürek, M. Durmuş, V. Ahsen, SPIE- Int. Soc. Opt. Eng. 4759 (2002) 1.
[12] P. Humberstone, G.J. Clarkson, N.B. McKeown, K.E. Treacher, J. Mater. Chem. 6 (1996) 315.
[13] K.M. Kadish, M.S. Kevin, R. Guilard. The Porphyrin Handbook, Phthalocyanines: Synthesis, vol. 15, Academic Press, 2003.
[14] N.B. McKeown. Phthalocyanine Materials: Synthesis, Structure and Function, Cambridge University Press, Cambridge, 1998.
[15] Y. Rio, P. Vazquez, E. Palomares, J. Porphyr. Phthalocya 13 (2009) 645.
[16] A.L. Thomas, Phthalocyanine Research and Applications, CRC Press, Boca Raton, Florida, 1990.
[17] B. Cosomelli, G. Roncucci, D. Dei, L. Fantetti, F. Ferroni, M. Ricci, D. Spinelli, Tetrahedron 59 (2003) 10025.
[18] H.I. Beltrán, R. Esquivel, A. Sosa-Sánchez, J.L. Sosa-Sánchez, H. Höpfl, V. Barba, N. Farfán, M.G. García, O. Olivares-Xometl, L.S. Zamudio-Rivera, Inorg. Chem. 43 (2004) 3555.
[19] I.V. Aoki, I.C. Guedes, S.L.A. Maranhao, J. Appl. Electrochem. 32 (2002) 915.
[20] M.R. Hamblin, T. Hasan, Photochem. Photobiol. Sci. 3 (2004) 436.
[21] M.J. Rivellese, C.R. Baumal, Ophthal. Surg. Lasers 30 (1999) 653.
[22] S.A. Priola, A. Raines, W. Caughey, J. Infect. Dis. 188 (2003) 699.
[23] M. Ochsner, J. Photochem. Photobiol. B. 39 (1997) 1.
[24] J. Huang, N. Chen, J. Huang, E. Liu, J. Xue, S. Yang, Z. Huang, J. Sun Sci. China Ser. B 44 (2001) 113.
[25] N. Brasseur, R. Ouellet, C. La Madeleine, J.E. van Lier, Br. J. Cancer 80 (1999) 1533.
[26] L.M. Moreira, F.V. dos Santos, J.P. Lyon, M. Maftoum-Costa, C. Pacheco-Soares, N.S. da Silva, Aust. J. Chem. 61 (2008) 741.
[27] E.A. Lukyanets, Porphyr. Phthalocyan. 3 (1999) 424.
[28] W. Herbst, K. Hunger, Industrial Organic Pigments, VCH, New York, 1993.
[29] B.I. Kharisov, L.M. Blanco, L.M. Torres-Martinez, A. Garcia-Luna, Ind. Eng. Chem. Res. 38 (1999) 2880.
[30] N. Safari, P.R. Jamaat, M. Pirouzmand, A. Shaabani, J. Porphyr. Phthalocya. 8 (2004) 1209.
[31] F. Bahadoran, S. Dialameh, J. Porphyr. Phthalocya. 9 (2005) 163.
[32] A. Loupy, Microwave in Organic Synthesis, Wiley VCH, Weinheim, 2002.
[33] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, second ed., Pergamon, Oxford, 1989.
[34] G.J. Young, W. Onyebuagu, J. Org. Chem. 55 (1990) 2155.
[35] C.F. von Nostrum, S.J. Picken, A.J. Schouten, R.J.M. Nolte, J. Am. Chem. Soc. 117 (1995) 9957.
[36] T. Nyokong, Struct. Bond. 135 (2010) 45.
[37] S. Dabak, G. Gümüş, A. Gül, Ö. Bekaroğlu, J. Coord. Chem. 8 (1996) 287.
[38] J. Simon, P. Bassoul, Design of Molecular Materials, Wiley, New York, 2000, pp. 196–296 (Chapter 6).