Dyes and Pigments 80 (2009) 17–21

Contents lists available at ScienceDirect

Dyes and Pigments

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

The synthesis, using microwave irradiation and characterization of novel, organosoluble metal-free and metallophthalocyanines substituted with flexible crown ether moieties

Zekeriya Biyiklioğlu, Halit Kantekin*

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

ARTICLE INFO

Article history:
Received 15 January 2008
Received in revised form 29 March 2008
Accepted 14 April 2008
Available online 7 May 2008

Keywords:
Crown ether
Metallophthalocyanine
Synthesis
Microwave
Phthalonitrile
Nickel

ABSTRACT

Cyclotetramerization of a phthalonitrile derivative to the metal-free phthalocyanine was accomplished in *n*-pentanol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene at reflux under an argon atmosphere. Ni(II), Zn(II), Co(II), Cu(II) phthalocyanines with four, peripheral 4-[methyleneoxy(12-crown-4)] groups were synthesized from 4-[{(12-crown-4)-yl}methyleneoxy]phthalonitrile in the presence of the anhydrous, divalent metal salts ($NiCl_2$, $Zn(CH_3COO)_2$, $CoCl_2$ and $CuCl_2$). The green phthalocyanines were soluble in common organic solvents such as $CHCl_3$, CH_2Cl_2, CH_3COCH_3, THF, DMF and DMSO. The structures of the target compounds were confirmed using elemental analysis, IR, ^{1}H NMR, ^{13}C NMR, UV–vis and MS spectral data.

1. Introduction

Metal-free and metallophthalocyanines have been known to have very interesting properties coupled with excellent stability to heat, light and harsh chemical environments. Their optical and electronic properties have been exploited in various applications for example pigments in paints and printing inks, infrared security devices, information storage and computer disk writing, in photodynamic therapy of cancer [1–3]. Phthalocyanines have been applied as photoconducting agents in photocopiers and laser printers. They are expected to show a more versatile role in material chemistry because of their potential applications in molecular electronics [4], nonlinear optics [5] and electrocatalytic reagents [6]. All of them are connected by their high thermal stabilities, which in turn are closely related to the electrochemical properties of phthalocyanine macromolecules [7].

Applications of phthalocyanines are restricted owing to their insolubility in common solvents and water [8]. The solubility of phthalocyanines can be improved by introducing different kinds of substituents, such as crown ethers, alkyl, alkoxy and alkylthio, at the periphery of the phthalocyanines [9].

Phthalocyanines substituted by crown ether rings, which show a high tendency towards aggregation by solvents and cations, have been described [10]. They can be used for the colorimetric determination of alkali cations [11] and as selective extracting reagents [12,13]. It has been proved that they are capable of forming ion channels and transport ions by arranging the pendant crown ether rings in stacks [14].

Microwaves have been previously used for the synthesis of phthalocyanines and include a wider range of references on the topic [15–20]. In recent years, a growing interest has focused on the application of microwave irradiation in organic synthesis. Microwave-assisted synthesis reduces chemical reaction times from hours to minutes, and also, reduces side reactions, increases the yield, and improves reproducibility. So, many academic and industrial research groups are already using microwave-assisted synthesis for the efficient synthesis of new chemical reactivity [21]. In this paper, we describe the synthesis and characterization of metal-free **4** and metallophthalocyanines **5**–**8** containing four flexible 12-crown-4(1,4,7,10-tetraoxacyclododecane) moieties on the periphery through methyleneoxy bridges by microwave irradiation.

2. Experimental

2-Hydroxymethyl(12-crown-4) **1** and 4-nitrophthalonitrile **2** were prepared by reported procedures [22,23]. All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin

---

* Corresponding author. Tel.: +90 462 377 2589; fax: +90 462 325 3196.
E-mail address: halit@ktu.edu.tr (H. Kantekin).

0143-7208/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2008.04.006

and Armarego [24]. The IR spectra were recorded on a Perkin Elmer 1600 FT-IR Spectrophotometer, using KBr pellets or NaCl disc. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$ and chemical shifts were reported (δ) relative to Me_4Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. The elemental analyses were performed on a Costech ECS 4010 instrument. Melting points were measured on an electrothermal apparatus and are uncorrected. Optical spectra in the UV–vis region were recorded with a Unicam UV2-100 spectrophotometer, using 1 cm pathlength cuvettes at room temperature.

*2.1. Synthesis of 4-[{(12-crown-4)-yl}methyleneoxy] phthalonitrile (**3**)*

2-Hydroxymethyl-12-crown-4 (**1**) (2.31 g, 11.20 mmol) was dissolved in anhydrous DMF (40 ml) under N_2 atmosphere and 4-nitrophthalonitrile (**2**) (1.94 g, 11.20 mmol) was added to the solution. After stirring 10 min, finely ground anhydrous K_2CO_3 (4.64 g, 33.60 mmol) was added portionwise within 2 h with efficient stirring. The reaction mixture was stirred under N_2 at 50 °C for 3 days. Then the solution was poured into ice-water (100 ml) and the aqueous phase was extracted with chloroform (3×50 ml). The combined extracts were dried over anhydrous sodium sulfate. The crude product was crystallized from ethanol. Yield: 2.34 g (63%), mp: 107–108 °C. Anal. Calcd for $C_{17}H_{20}N_2O_5$: C, 61.44; H, 6.07; N, 8.43%. Found: C, 61.46; H, 6.12; N, 8.03. IR (KBr tablet), ν_{max}/cm^{-1}: 3076 (Ar–H), 2915–2863 (Aliph. C–H), 2230 (C≡N), 1597, 1562, 1491, 1460, 1319, 1254, 1134, 1098, 1024, 915, 840, 524. ^{1}H NMR ($CDCl_3$), (δ:ppm): 7.71 (d, 1H, Ar–H), 7.29 (s, 1H, Ar–H), 7.23 (d, 1H, Ar–H), 4.11–3.65 (m, 17H, CH_2–O). ^{13}C NMR ($CDCl_3$), (δ:ppm): 161.93, 135.14, 119.81, 119.41, 117.24, 115.62, 115.18, 107.25, 76.40, 71.28, 70.54, 70.40, 70.30, 70.06, 69.53. MS (ES$^+$), (*m*/*z*): 355 $[M+Na]^+$.

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

A standard Schlenk tube was charged with 0.4 g, 1.20 mmol of compound **3**, 6 ml of dry *n*-pentanol and 0.186 g (1.8 ml, 1.2 mmol) of 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) under argon atmosphere and degassed several times. The temperature was gradually increased up to 90 °C and degassed again by argon atmosphere. Then the reaction mixture was stirred at 160 °C for 12 h. After the reaction mixture was cooled and decanted, the remaining dark green solid was stirred with 30 ml of ethanol:diethyl ether mixture (1/1; v/v). The dark green product **4** was filtered off and then dried in vacuo. The solid product was purified by preparative thin layer chromatography (TLC) using chloroform/petroleum ether/methanol (7:2:1) solvent system. This product is soluble in $CHCl_3$, CH_2Cl_2, CH_3COCH_3 (acetone), THF, DMF, and DMSO. Yield: 176 mg (44%), mp 137–139 °C. Anal. Calcd for $C_{68}H_{82}N_8O_{20}$: C, 61.34; H, 6.21; N, 8.42%. Found: C, 61.37; H, 6.27; N, 8.49. IR (KBr tablet) ν_{max}/cm^{-1}: 3289 (N–H), 3065 (Ar–H), 2909–2860 (Aliph. C–H), 1611, 1481, 1396, 1342, 1239, 1130, 1095, 1016, 914, 824, 746. ^{1}H NMR ($CDCl_3$), (δ:ppm): 8.16 (d, 4H, Ar–H), 7.75 (d, 4H, Ar–H), 6.96 (s, 4H, Ar–H), 4.06–3.41 (m, 68H, CH_2–O). ^{13}C NMR ($CDCl_3$), (δ:ppm): 167.80, 132.98, 132.44, 130.90, 128.81, 120.32, 120.14, 107.80, 72.65–68.15. UV–vis (chloroform): λ_{max}/nm: [($10^{-5}\,\epsilon$ dm^3 mol^{-1} cm^{-1})]: 290 (4.92), 341 (5.17), 389 (4.47), 614 (4.34), 647 (4.86), 671 (5.25), 707 (5.29). MS (ES$^+$), (*m*/*z*): 1332 $[M+H]^+$.

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

4-[{(12-crown-4)-yl}Methyleneoxy]phthalonitrile **3** (0.4 g, 1.2 mmol) and anhydrous $NiCl_2$ (39 mg, 0.3 mmol) were ground together in a microwave oven and 2-(dimethylamino)ethanol (2.5 ml) was added. The reaction mixture was irradiated in microwave reaction oven at 175 °C, 350 W for 7 min. After cooling to room temperature, diethyl ether (6 ml) was added. The precipitated green solid product was filtered off and then dried. The obtained green product was purified by preparative thin layer chromatography (TLC) using chloroform/petroleum ether/methanol (4:4:2) solvent system. This product is soluble in $CHCl_3$, CH_2Cl_2, CH_3COCH_3 (acetone), THF, DMF, and DMSO. Yield: 229 mg (55%), mp 258–260 °C. Anal. Calcd for $C_{68}H_{80}N_8O_{20}Ni$: C, 58.84; H, 5.81; N, 8.07%. Found: C, 58.94; H, 5.87; N, 8.02. IR (KBr tablet) ν_{max}/cm^{-1}: 3054 (Ar–H), 2917–2858 (Aliph. C–H), 1608, 1531, 1463, 1411, 1349, 1279, 1237, 1127, 1092, 1020, 912, 848, 749. ^{1}H NMR ($CDCl_3$), (δ:ppm): 7.70 (d, 4H, Ar–H), 7.25 (br s, 4H, Ar–H), 7.16 (m, 4H, Ar–H), 4.09–3.69 (m, 68H, CH_2–O). ^{13}C NMR ($CDCl_3$), (δ:ppm): 161.68, 135.01, 121.90, 119.63, 119.23, 117.04, 115.89, 107.10, 71.10–69.33. UV–vis (chloroform): λ_{max}/nm: [($10^{-5}\,\epsilon$ dm^3 mol^{-1} cm^{-1})]: 275 (4.87), 328 (4.96), 382 (4.79), 616 (4.39), 678 (5.22). MS (ES$^+$), (*m*/*z*): 1388 $[M]^+$.

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

4-[{(12-crown-4)-yl}Methyleneoxy]phthalonitrile **3** (0.4 g, 1.2 mmol) and anhydrous $Zn(CH_3COO)_2$ (55 mg, 0.3 mmol) were ground together in a microwave oven and 2-(dimethylamino)ethanol (2.5 ml) was added. The reaction mixture was irradiated in microwave reaction oven at 175 °C, 350 W for 7 min. After cooling to room temperature, diethyl ether (6 ml) was added. The precipitated green solid product was filtered off and then dried. The obtained green product was purified by preparative thin layer chromatography (TLC) using chloroform/petroleum ether/methanol (7:2:1) solvent system. This product is soluble in $CHCl_3$, CH_2Cl_2, CH_3COCH_3 (acetone), THF, DMF, and DMSO. Yield: 263 mg (63%), mp 243–245 °C. Anal. Calcd for $C_{68}H_{80}N_8O_{20}Zn$: C, 58.56; H, 5.78; N, 8.03%. Found: C, 58.71; H, 5.85; N, 8.00. IR (KBr tablet) ν_{max}/cm^{-1}: 3043 (Ar–H), 2917–2860 (Aliph. C–H), 1606, 1487, 1451, 1393, 1335, 1226, 1130, 1093, 1051, 914, 850, 745. ^{1}H NMR ($CDCl_3$), (δ:ppm): 7.72 (d, 4H, Ar–H), 7.36 (s, 4H, Ar–H), 7.17 (d, 4H, Ar–H), 4.10–3.69 (m, 68H, CH_2–O). UV–vis (chloroform): λ_{max}/nm: [($10^{-5}\,\epsilon$ dm^3 mol^{-1} cm^{-1})]: 281 (4.74), 353 (4.91), 617 (4.54), 686 (5.29). MS (ES$^+$), (*m*/*z*): 1394 $[M]^+$.

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

4-[{(12-crown-4)-yl}methyleneoxy]Phthalonitrile **3** (0.4 g, 1.2 mmol) and anhydrous $CoCl_2$ (39 mg, 0.3 mmol) were ground together in a microwave oven and 2-(dimethylamino)ethanol (2.5 ml) was added. The reaction mixture was irradiated in microwave reaction oven at 175 °C, 350 W for 7 min. After cooling to room temperature, diethyl ether (6 ml) was added. The precipitated green solid product was filtered off and then dried. The obtained green product was purified by preparative thin layer chromatography (TLC) using chloroform/petroleum ether/methanol (5:3:2) solvent system. This product is soluble in $CHCl_3$, CH_2Cl_2, CH_3COCH_3 (acetone), THF, DMF, and DMSO. Yield: 241 mg (58%), mp 198–200 °C. Anal. Calcd for $C_{68}H_{80}N_8O_{20}Co$: C, 58.83; H, 5.81; N, 8.07%. Found: C, 58.81; H, 5.86; N, 8.12. IR (KBr tablet) ν_{max}/cm^{-1}: 3065 (Ar–H), 2923–2856 (Aliph. C–H), 1609, 1524, 1484, 1456, 1416, 1346, 1284, 1242, 1129, 1097, 1023, 916, 850, 751. ^{1}H NMR ($CDCl_3$), (δ:ppm): 7.62 (d, 4H, Ar–H), 7.55 (s, 4H, Ar–H), 7.20 (m, 4H, Ar–H), 4.06–3.62 (m, 68H, CH_2–O). ^{13}C NMR ($CDCl_3$), (δ:ppm): 165.89, 138.42, 120.78, 120.56, 119.71, 119.68, 118.49, 104.22, 70.30–66.75. UV–vis (chloroform): λ_{max}/nm: [($10^{-5}\,\epsilon$ dm^3 mol^{-1} cm^{-1})]: 280 (4.62), 328 (4.85), 618 (4.47), 678 (5.23). MS (ES$^+$), (*m*/*z*): 1388 $[M]^+$.

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

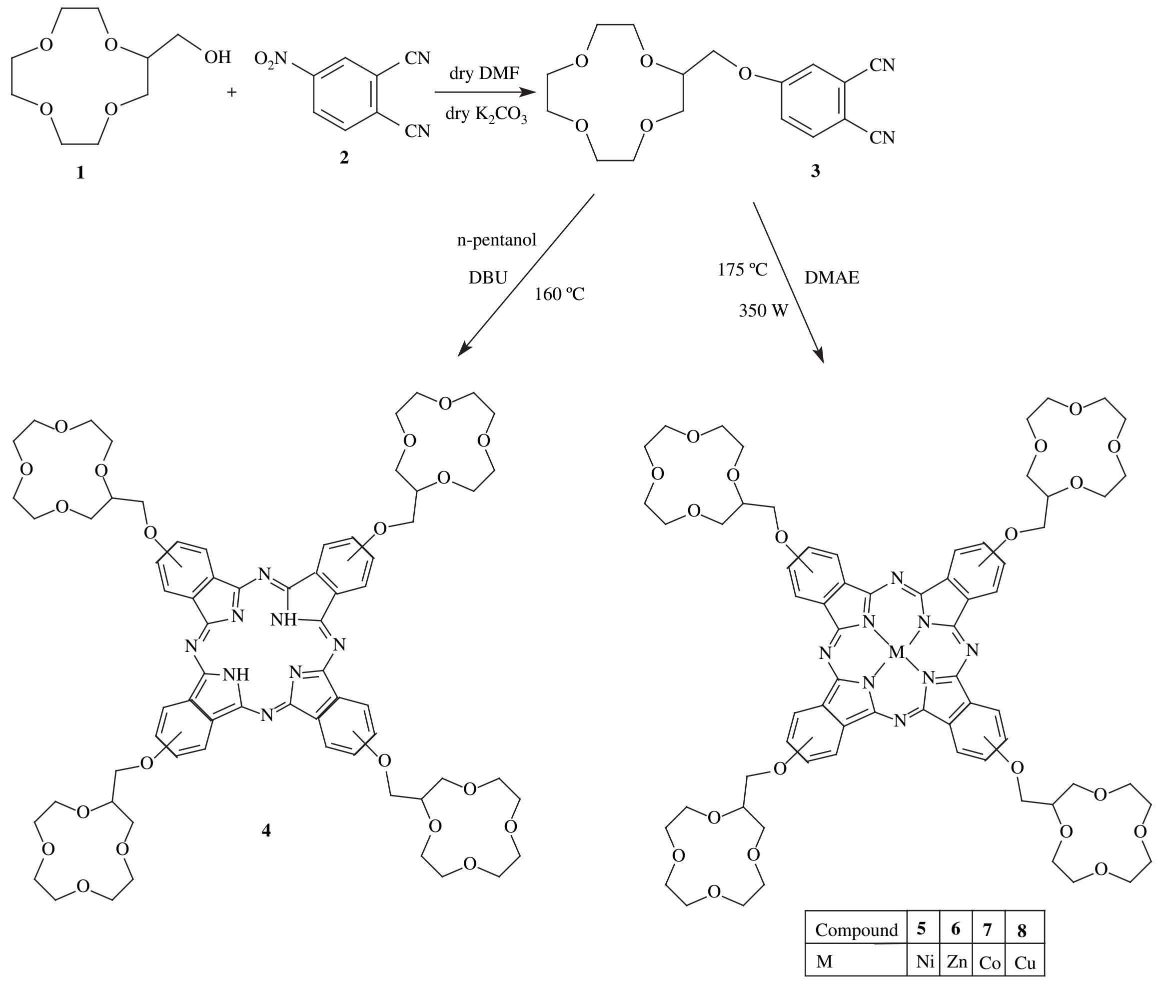
4-[{(12-crown-4)-yl}Methyleneoxy]phthalonitrile **3** (0.4 g, 1.2 mmol) and anhydrous $CuCl_2$ (40 mg, 0.3 mmol) were ground together in a microwave oven and 2-(dimethylamino)ethanol (2.5 ml) was added. The reaction mixture was irradiated in microwave reaction oven at 175 °C, 350 W for 7 min. After cooling to room temperature, diethyl ether (6 ml) was added. The precipitated green solid product was filtered off and then dried. The obtained green product was purified by preparative thin layer chromatography (TLC) using chloroform solvent system. This product is soluble in $CHCl_3$, CH_2Cl_2, CH_3COCH_3 (acetone), THF, DMF, and DMSO. Yield: 250 mg (60%), mp 265–267 °C. Anal. Calcd for $C_{68}H_{80}N_8O_{20}Cu$: C, 58.63; H, 5.79; N, 8.04%. Found: C, 58.65; H, 5.75; N, 8.08. IR (KBr tablet) ν_{max}/cm^{-1}: 3054 (Ar–H), 2919–2862 (Aliph. C–H), 1595, 1486, 1287, 1245, 1189, 1133, 1095, 1020, 913. UV–vis (chloroform): λ_{max}/nm: [$(10^{-5}\,\epsilon\,dm^3\,mol^{-1}\,cm^{-1})$]: 288 (4.67), 338 (4.90), 620 (4.51), 689 (5.25). MS (ES^+), (*m*/*z*): 1415 $[M+Na]^+$.

3. Results and discussion

The synthetic routes to **3**–**8** are summarized in Scheme 1. The first step in the synthetic procedure was to obtain 4-[{(12-crown-4)yl}methyleneoxy]phthalonitrile **3**. This reaction was accomplished by a base-catalysed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile with 2-hydroxymethyl(12-crown-4) **1** [10]. The reaction was carried out at 50 °C in dimethylformamide with K_2CO_3 as the base, and the yield was reasonably (*ca.* 63%). Cyclotetramerization of the phthalonitrile derivative **3** to the metal-free phthalocyanine **4** was accomplished in *n*-pentanol in the presence of a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base at reflux temperature under argon atmosphere. The metallophthalocyanines **5**–**8** were obtained by the anhydrous metal salts [$NiCl_2$, $Zn(CH_3COO)_2$, $CoCl_2$ and $CuCl_2$] in 2-(dimethylamino)ethanol by microwave irradiation. We used a domestic oven synthesis of compounds **4**–**8** including 350 W, 175 °C as conditions. The solubility of phthalocyanines is summarized in Table 1.

In the IR spectra, the formation of compound **3** was clearly confirmed by the disappearance of the OH and NO_2 bands at 3338 and 1538–1355 cm^{-1} and appearance of the C≡N band at 2230 cm^{-1}. In the ^1H NMR spectrum of **3**, OH group of compound **1** disappeared as expected. ^1H NMR spectrum of **3** showed new signals at $\delta = 7.71$ (d, 1H, Ar–H), 7.29 (s, 1H, Ar–H), 7.23 (d, 1H, Ar–H) belonging to aromatic protons. The ^{13}C NMR spectrum of **3** indicated the presence of nitrile carbon atoms in **3** at $\delta = 115.62$ and 115.18 ppm. The MS mass spectrum of compound **3**, which shows a peak at $m/z = 355$ $[M+Na]^+$ supports the proposed formula for this compound. The results of the elemental analysis confirmed the proposed structure of compound **3**.

The synthesis of metal-free phthalocyanine **4** was accomplished by reacting **3** in *n*-pentanol in the presence of a few drops of DBU as a strong base at reflux temperature under argon atmosphere. The IR spectra of metal-free **4** and metallophthalocyanines **5**–**8** are very similar. The significant difference is the presence of N–H vibrations of the inner phthalocyanine core which are assigned to a weak vibration at 3289 cm^{-1} in the metal-free molecule. The ^1H NMR



Compound	5	6	7	8
M	Ni	Zn	Co	Cu

Scheme 1. The synthesis of the metal-free phthalocyanine and metallophthalocyanines.

Table 1
The solubility of phthalocyanines in different solvents

Compound	Solubility in mg/ml					
	CH_2Cl_2	$CHCl_3$	Acetone	THF	DMF	DMSO
H_2-Pc **4**	10.3	9.8	2.5	4.4	11.7	12.4
Ni-Pc **5**	10.4	9.6	2.4	4.3	11.6	12.4
Zn-Pc **6**	10.4	9.7	2.5	4.3	11.6	12.3
Co-Pc **7**	10.6	9.9	2.6	4.5	11.8	12.5
Cu-Pc **8**	10.3	9.6	2.3	4.4	11.6	12.3

spectrum of compound **4** indicates the aromatic protons at δ 8.16, 7.75, 6.96 and the aliphatic ether protons at δ 4.06–3.41. The NH protons of compound **4** could not be observed owing to the probable strong aggregation of the molecules [25]. The MS mass spectrum of compound **4** displayed the $[M+H]^+$ parent ion peak at $m/z=1332$, which confirms the same structure. The results of the elemental analysis confirmed the proposed structure of compound **4**.

In the IR spectra of metallophthalocyanines **5**–**8**, cyclotetramerization of dinitriles **3** to Pcs **5**–**8** was confirmed by the disappearance of the sharp $-C{\equiv}N$ vibration at 2230 cm^{-1}. The ^1H NMR spectra of these compounds are almost identical to those of metal-free phthalocyanine **4**. The ^1H NMR spectra of complexes **5**–**7** showed almost identical chemical shifts. ^1H NMR measurement of the copper(II) phthalocyanine **8** was precluded owing to its paramagnetic nature. In the mass spectrum of Ni, Zn, Co, and Cu phthalocyanines, the presence of molecular ion peaks at $m/z=1388$ $[M]^+$, 1394 $[M]^+$, 1388 $[M]^+$ and 1415 $[M+Na]^+$, respectively, confirmed the proposed structures. Elemental analysis data were satisfactory.

The best indications for phthalocyanine systems are given by their UV–vis spectra in solution (Fig. 1). Metal-free phthalocyanine **4** and metallophthalocyanines **5**–**8** showed typical UV–vis electronic spectra with two significant absorption bands, one of them in the visible region at about 614–707 nm corresponding to the Q band, and the other in the UV, approximately at 300 nm. The Q band was attributed to $\pi \rightarrow \pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring. The other bands (B) in the UV region at 275–389 nm are observed due to the transitions from the deeper π levels to the LUMO [3,26]. The Q band absorptions of **4** in chloroform at $\lambda_{max}=707$, 671, 647, 614 nm and the other absorption at 290, 341 and 389 nm are consistent with the results for similar phthalocyanines [17].

Metallophthalocyanines **5**–**8** showed the expected absorptions at the main peaks of the Q and B bands appearing at $\lambda_{max}=678$, 686, 678, 689 nm and 328, 353, 328, 338 nm, respectively. This result is typical of metal complexes of substituted and unsubstituted Pc with D_{4h} symmetry [27].

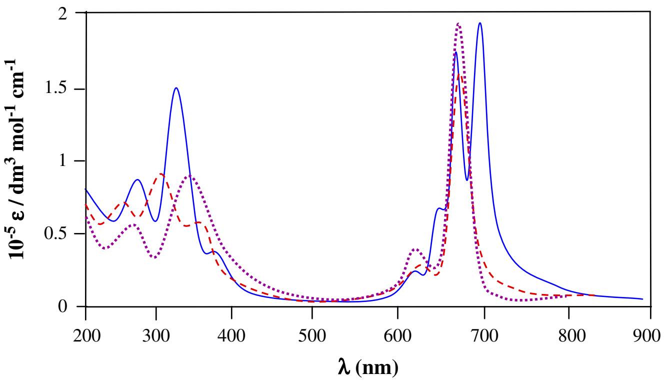


Fig. 1. UV–vis spectra of compounds **4** (—), **5** (---) and **6** (…) in chloroform.

Acknowledgement

This study was supported by the Research Fund of Karadeniz Technical University, (project no: 2006.111.002.1) and The Scientific and Technological Research Council of Turkey (TÜBİTAK, project no: 107T429).

References

[1] Bouvet M. The porphyrin handbook, vol. 19. New York: Academic Press; 2003. p. 1–36.
[2] Leznoff CC, Lever ABP. Phthalocyanines: properties and applications, vols. 1–4. Weinheim: VCH; 1989–1996.
[3] Bilgin A, Ertem B, Gök Y. Highly organosoluble metal-free and metallophthalocyanines: synthesis and characterization. European Journal of Inorganic Chemistry 2007;12:1703–12.
[4] Turek P, Petit JJ, Andre JJ, Simon J, Even R, Boudjema B, et al. A new series of molecular semiconductors: phthalocyanine radicals. Journal of American Chemical Society 1987;109:5119–22.
[5] De la Torre G, Torres T, Agullo-Lopez F. The phthalocyanine approach to second harmonic generation. Advanced Materials 1997;9:265–9.
[6] Lever ABP, Hempstead MR, Leznoff CC, Liu W, Menlik M, Nevin WA, et al. Recent studies in phthalocyanine chemistry. Pure and Applied Chemistry 1986;58:1467–76.
[7] Ertem B, Bilgin A, Gök Y, Kantekin H. The synthesis and characterization of novel metal-free and metallophthalocyanines bearing eight 16-membered macrocycles. Dyes and Pigments 2008;77:537–44.
[8] Bhardwaj N, Andraos J, Leznoff CC. The syntheses and NMR studies of hexadeca- and octaneopentoxyphthalocyanines. Canadian Journal of Chemistry 2002;80:141–7.
[9] Wie S, Huang D, Li L, Meng Q. Synthesis and properties of some novel soluble metallophthalocyanines containing the 3-trifluromethylphenyoxy moiety. Dyes and Pigments 2003;56:1–6.
[10] Gürol I, Ahsen V. Synthesis and aggregation behaviour of phthalocyanines substituted with flexible crown ether. Journal of Porphyrins and Phthalocyanines 2000;4:621–6.
[11] Kobayashi N, Nishiyama Y. A copper phthalocyanine with 4 crown-ether voids. Journal of the Chemical Society. Chemical Communications 1986;19:1462–3.
[12] Koray AR, Ahsen V, Bekaroğlu Ö. Preparation of a novel, soluble copper phthalocyanine with crown-ether moieties. Journal of the Chemical Society. Chemical Communications 1986;12:932–3.
[13] Ahsen V, Yilmazer E, Ertaş M, Bekaroğlu Ö. Synthesis and characterization of metal-free and metal derivatives of a novel soluble crown-ether-containing phthalocyanine. Journal of the Chemical Society-Dalton Transactions 1988;2: 401–6.
[14] Sirlin C, Bosio L, Simon J, Ahsen V, Yilmazer E, Bekaroğlu Ö. Annelide 25 ion channel containing mesophases – structural characteristics of condensed phases of crown-ether-substituted phthalocyanines. Chemical Physics Letters 1987;139:362–4.
[15] Biyiklioğlu Z, Kantekin H, Özil M. Microwave-assisted synthesis and characterization of novel metal-free and metallophthalocyanines containing four 14-membered tetraaza macrocycles. Journal of Organometallic Chemistry 2007; 692:2436–40.
[16] Biyiklioğlu Z, Kantekin H. Microwave assisted synthesis and characterization of novel metal-free and metallophthalocyanines containing four pyridyl groups. Transition Metal Chemistry 2007;32:851–6.
[17] Kantekin H, Biyiklioğlu Z. Microwave-assisted synthesis and characterization of novel metal-free and metallophthalocyanines containing four 13-membered dithiadiaza macrocycles. Dyes and Pigments 2008;77: 98–102.
[18] Kantekin H, Biyiklioğlu Z. Synthesis and characterization of new polymeric phthalocyanines substituted with pyridine through methyleneoxy bridges by microwave irradiation. Dyes and Pigments 2008;77:432–6.
[19] Biyiklioğlu Z, Kantekin H. A novel metal-free and metallophthalocyanines containing four 19-membered dithiadiazadioxa macrocycles by microwave irradiation: synthesis and characterization. Journal of Organometallic Chemistry 2008;693:505–9.
[20] Kantekin H, Dilber G, Biyiklioğlu Z. A new polymeric phthalocyanines containing 16-membered tetrathia macrocyclic moieties by microwave irradiation: synthesis and characterization. Journal of Organometallic Chemistry 2008;693:1038–42.
[21] Kahveci B, Özil M, Kantar C, Şaşmaz S, Işik Ş, Köysal Y. Microwave assisted and conventional synthesis of new phthalocyanines containing 4-(*p*-fluorophenyl)-3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one moieties. Journal of Organometallic Chemistry 2007;692:4835–42.
[22] Ikeda I, Yamamura S, Nakatsuji Y, Okahara M. Synthesis of substituted crown ethers from oligoethylene glycols. Journal of Organic Chemistry 1980;45: 5355–8.

[23] Young GJ, Onyebuagu W. Synthesis and characterization of di-disubstituted phthalocyanines. Journal of Organic Chemistry 1990;55:2155–9.

[24] Perin DD, Armarego WLF, Perin DR. Purification of laboratory chemicals. 2nd ed. New York: Pergamon Press; 1985.

[25] van Nostrum CF, Picken SJ, Schouten AJ, Nolte RJM. Synthesis and supramolecular chemistry of novel liquid crystalline crown ether-substituted phthalocyanines: toward molecular wires and molecular ionoelectronics. Journal of American Chemical Society 1995;117:9957–65.

[26] Özer M, Altindal A, Özkaya AR, Salih B, Bulut M, Bekaroğlu Ö. Synthesis, characterization, and electrochemical and electrical properties of novel pentaerythritol-bridged cofacial bismetallophthalocyanines and their water-soluble derivatives. European Journal of Inorganic Chemistry 2007;22: 3519–26.

[27] Takahashi K, Kawashima M, Tomita Y, Itoh M. Synthesis and spectral and electrochemical properties of 2,3,9,10,16,17,23,24-octabutylthiophthalocyaninatozinc(II). Inorganica Chimica Acta 1995;232:69–73.