

# A new polymeric phthalocyanine containing 16-membered tetrathia macrocyclic moieties by microwave irradiation: Synthesis and characterization

Halit Kantekin\*, Gülsev Dilber, Zekeriya Bıyıklıoğlu

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

Received 16 May 2007; received in revised form 11 December 2007; accepted 18 December 2007

Available online 28 December 2007

## Abstract

Tetranitrile monomer (**3**) was synthesized by nucleophilic aromatic substitution of 1,5,9,13-tetrathiacyclohexadecane-3,11-diol (**1**) onto 4-nitrophthalonitrile (**2**). The metal-free phthalocyanine polymer (**4**) was prepared by the reaction of a tetranitrile monomer with 4-({11-[3-cyano-4-(cyanomethyl)phenoxy]-1,5,9,13-tetrathiacyclohexadecan-3-yl}oxy)phthalonitrile in 2-(dimethylamino)ethanol. Ni(II), Co(II), Cu(I)-phthalocyanine polymers were prepared by the reaction of the tetranitrile compound with the chlorides of Ni(II), Co(II) and Cu(I) in DMAE. Zn(II)-phthalocyanine polymer was prepared by the reaction of the tetranitrile compound with the acetates of Zn(II) in DMAE. The new compounds were characterized by a combination of IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, UV–Vis, elemental analysis and MS spectral data.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Polymeric phthalocyanine; Bisphthalonitrile; Tetranitrile; Metal-free phthalocyanine

## 1. Introduction

In the recent years, a great deal of interest has been focused on the synthesis of phthalocyanine derivatives due to their applications in many field such as liquid crystals [1], chemical sensor [2], non-linear optics [3], gas sensor, electrochromic devices and photosensitizers. Substituted phthalocyanine derivatives can also be used for photodynamic cancer therapy and other processes driven by visible light [4,5]. The functions of metallophthalocyanine derivatives are almost based on their electron transfer properties and kinds and number of metal center and substituents because of their conjugated ring  $\pi$  electron system. Observation of electron transfer abilities of a compound is a principal activity for the estimation of functional materials [6].

A decisive disadvantage of phthalocyanine and metal phthalocyanines is their low solubility in organic solvents

or water. The solubility can be increased, however, by introducing alkyl or alkoxy group into the peripheral and non-peripheral positions of the phthalocyanine framework [7]. Also phthalocyanines containing thia macrocycles enhanced the solubility of the product with bulky macrocycles on the periphery.

Compared to the low molecular weight phthalocyanines, relatively few reports describe the synthesis and properties of polymeric phthalocyanines. Polymeric phthalocyanines were mainly prepared via cyclotetramerization reactions of bifunctional monomers, such as tetracarbonitriles [8,9], various oxy-, arylenedioxi-, alkylendioxy-, bridged diphtalonitriles [10,11] and other nitriles [12,13] or tetracarbonylic acid derivatives [14,15] in the presence of metal salts or metals.

Network phthalocyanine polymers usually possess high thermal stability [16] and conductivities of semiconducting polymeric phthalocyanines can be higher than those of the corresponding low molecular weight phthalocyanines [17,18]. However, polymeric phthalocyanines can only be

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

used in some fields because of their insolubility in water and common solvents [19].

The growing use of phthalocyanines as advanced materials during the last decade has encouraged the research on the synthesis of newly derivatized materials which differ from one another in the central metal ion and in the periphery substituents [20]. In addition to the synthetic advantage in using a linked diphthalonitrile as opposed to a rigid monomer, such as benzenetetracarboxitrile, in the synthesis of polymeric phthalocyanines is the higher flexibility of the linkage resulting in a higher group mobility [10,16,21].

We have previously synthesized phthalocyanines [22–26] by microwave irradiation. In this paper, we describe the synthesis and characterization of metal-free phthalocyanine polymer (**4**) and metallophthalocyanine polymers (**5–8**) by microwave irradiation containing 16-membered tetrathia macrocyclic moieties.

## 2. Experimental

1,5,9,13-tetrathiacyclohexadecane-3,11-diol (**1**) and 4-nitrophthalonitrile [27,28] (**2**) were prepared according to the literature. 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 and Armarego [29]. The IR spectra were recorded on a Perkin–Elmer 1600 FT-IR Spectrophotometer, using KBr pellets or NaCl disc.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in  $\text{CDCl}_3$ , DMSO, and chemical shifts were reported ( $\delta$ ) relative to  $\text{Me}_4\text{Si}$  as the internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC–MS/MS spectrometer. Elemental analyses were determined by a LECO Elemental Analyser (CHNS O932) and a Unicam 929 AA spectrophotometer, respectively. 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. Domestic oven was used for all the syntheses of phthalocyanines (see Fig. 1).

### 2.1. 4-({11-[3-cyano-4-(cyanomethyl)phenoxy]-1,5,9,13-tetrathiacyclohexadecan-3-yl}oxy)phthalonitrile (**3**)

1,5,9,13-tetrathiacyclohexadecane-3,11-diol (**1**) (2 g, 6.09 mmol) was dissolved in dry DMF (20 ml) under  $\text{N}_2$  atmosphere and 4-nitrophthalonitrile (**2**) (2.10 g, 12.19 mmol) was added to the solution. After stirring for 10 min, finely ground anhydrous  $\text{K}_2\text{CO}_3$  (2.52 g, 18.27 mmol) was added portionwise within 2 h with efficient stirring. The reaction mixture was stirred under  $\text{N}_2$  at 50 °C for 4 days. Then the solution was poured into ice-water (200 ml). The precipitate formed was filtered off, washed first with water until the filtrate was neutral and then with diethyl ether and dried in vacuo over  $\text{P}_2\text{O}_5$ . The crude product was crystallized from ethanol. Yield: 1.97 g (56%), m.p.: 186–188 °C. Anal. Calc. for  $\text{C}_{28}\text{H}_{28}\text{N}_4\text{O}_2\text{S}_4$ : C, 57.90; H, 4.85; N, 9.65. Found: C, 57.14; H, 4.66; N, 9.69%. IR (KBr tablet)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3071 (Ar–H), 2924–2851 (Aliph. C–H), 2230 ( $\text{C}\equiv\text{N}$ ), 1591, 1561, 1498, 1319, 1256, 1085, 989, 845, 525.  $^1\text{H}$  NMR. (DMSO- $d_6$ ), ( $\delta$ : ppm): 8.06 (d, 2H, Ar–H), 7.81 (s, 2H, Ar–H), 7.49 (d, 2H, Ar–H), 4.89 (m, 2H, CH–O), 2.99 (d, 8H,  $\text{CH}_2$ –S), 2.67 (t, 8H,  $\text{CH}_2$ –S), 1.86 (m, 4H,  $\text{CH}_2$ – $\text{CH}_2$ – $\text{CH}_2$ ).  $^{13}\text{C}$  NMR. (DMSO- $d_6$ ), ( $\delta$ : ppm): 160.73, 135.79, 120.95, 120.62, 116.34, 116.02, 115.55, 106.21, 77.79, 33.52, 30.39, 28.95. MS (EI), ( $m/z$ ): 581  $[\text{M}+1]^+$ .

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

A mixture of 4-({11-[3-cyano-4-(cyanomethyl)phenoxy]-1,5,9,13-tetrathiacyclohexadecan-3-yl}oxy)phthalonitrile (**3**) (0.3 g, 0.52 mmol) and 2-(dimethylamino)ethanol (DMAE) (3 ml) was irradiated in a microwave oven at

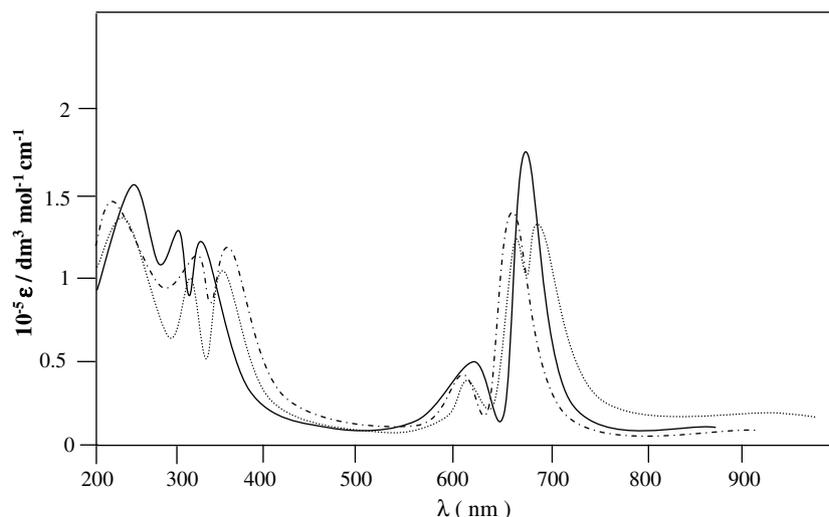


Fig. 1. UV–Vis spectra of compounds **4** (···), **5** (----) and **7** (—) in pyridine.

175 °C, 350 W for 8 min. After cooling to room temperature, the reaction mixture was refluxed with ethanol (45 ml) to precipitate the product which was filtered off. The green solid product was washed with hot ethanol, diethyl ether and dried in vacuo. This product is soluble in pyridine. Yield: 110 mg, m.p. > 300 °C. Elemental analyses (for CN end groups) (C<sub>112</sub>H<sub>114</sub>N<sub>16</sub>O<sub>8</sub>S<sub>16</sub>)<sub>n</sub>(2325.19)<sub>n</sub>. Calc.: C, 57.85; H, 4.94; N, 9.64. Found: C, 57.66; H, 4.02; N, 10.16%. IR (KBr tablet)  $\nu_{\max}/\text{cm}^{-1}$ : 3281 (N–H), 3071 (Ar–H), 2924–2846 (Aliph. C–H), 2229 (C≡N), 1591, 1558, 1488, 1319, 1255 (Ar–O–C), 1084, 845, 527. UV–Vis (pyridine):  $\lambda_{\max}/\text{nm}$ : [(10<sup>-5</sup> ε dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 248 (5.13), 332 (4.99), 354 (5.02), 617 (4.57), 683 (5.09), 703 (5.11). MS (FAB), (*m/z*): 2325 [M]<sup>+</sup>.

### 2.3. Ni(II)-containing polymer (5)

A mixture of 4-({11-[3-cyano-4-(cyanomethyl)phenoxy]-1,5,9,13-tetrathiacyclohexadecan-3-yl}oxy)phthalonitrile (3) (0.3 g, 0.52 mmol), anhydrous NiCl<sub>2</sub> (16.8 mg, 0.13 mmol) and 2-(dimethylamino)ethanol (DMAE) (3 ml) was irradiated in a microwave oven at 175 °C, 350 W for 8 min. After cooling to room temperature, the reaction mixture was refluxed with ethanol (40 ml) to precipitate the product which was filtered off. The green solid product was washed with hot ethanol, diethyl ether and dried in vacuo. This product is soluble in pyridine. Yield: 204 mg, m.p. > 300 °C. Elemental analyses (for imide end groups) (C<sub>112</sub>H<sub>116</sub>N<sub>12</sub>O<sub>16</sub>S<sub>16</sub>Ni)<sub>n</sub> (2457.87)<sub>n</sub>. Calc.: C, 54.73; H, 4.76; N, 6.84; Ni, 2.39. Found: C, 55.11; H, 5.21; N, 6.02; Ni, 2.56%. IR (KBr tablet)  $\nu_{\max}/\text{cm}^{-1}$ : 3436 (imide N–H), 3065 (Ar–H), 2917–2851 (Aliph. C–H), 1775 (sym. C=O), 1714 (asym. C=O), 1610 (C=N), 1595, 1471, 1314, 1226 (Ar–O–C), 1086, 1055, 946, 837, 524. UV–Vis (pyridine):  $\lambda_{\max}/\text{nm}$ : [(10<sup>-5</sup> ε dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 240 (5.17), 340 (5.07), 362 (5.08), 611 (4.60), 680 (5.16). MS (FAB), (*m/z*): 2458 [M+1]<sup>+</sup>.

### 2.4. Zn(II)-containing polymer (6)

A mixture of 4-({11-[3-cyano-4-(cyanomethyl)phenoxy]-1,5,9,13-tetrathiacyclohexadecan-3-yl}oxy)phthalonitrile (3) (0.3 g, 0.52 mmol), anhydrous Zn(CH<sub>3</sub>COO)<sub>2</sub> (23.8 mg, 0.13 mmol) and 2-(dimethylamino)ethanol (DMAE) (3 ml) was irradiated in a microwave oven at 175 °C, 350 W for 8 min. After cooling to room temperature, the reaction mixture was refluxed with ethanol (40 ml) to precipitate the product which was filtered off. The green solid product was washed with hot ethanol, diethyl ether and dried in vacuo. This product is soluble in pyridine. Yield: 220 mg, m.p. > 300 °C. Elemental analyses (for imide end groups) (C<sub>112</sub>H<sub>116</sub>N<sub>12</sub>O<sub>16</sub>S<sub>16</sub>Zn)<sub>n</sub> (2464.56)<sub>n</sub>. Calc.: C, 54.58; H, 4.74; N, 6.82; Zn, 2.65. Found: C, 54.71; H, 5.15; N, 6.35; Zn, 2.89%. IR (KBr tablet)  $\nu_{\max}/\text{cm}^{-1}$ : 3434 (imide N–H), 3060 (Ar–H), 2920–2851 (Aliph. C–H), 1778 (sym. C=O), 1711 (asym. C=O), 1614 (C=N), 1595, 1479, 1308, 1251 (Ar–O–C), 1090, 1017, 954, 836, 761, 523.

UV–Vis (pyridine):  $\lambda_{\max}/\text{nm}$ : [(10<sup>-5</sup> ε dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 254 (5.18), 321 (5.11), 344 (5.10), 620 (4.65), 692 (5.24). MS (FAB), (*m/z*): 2465 [M+1]<sup>+</sup>.

### 2.5. Co(II)-containing polymer (7)

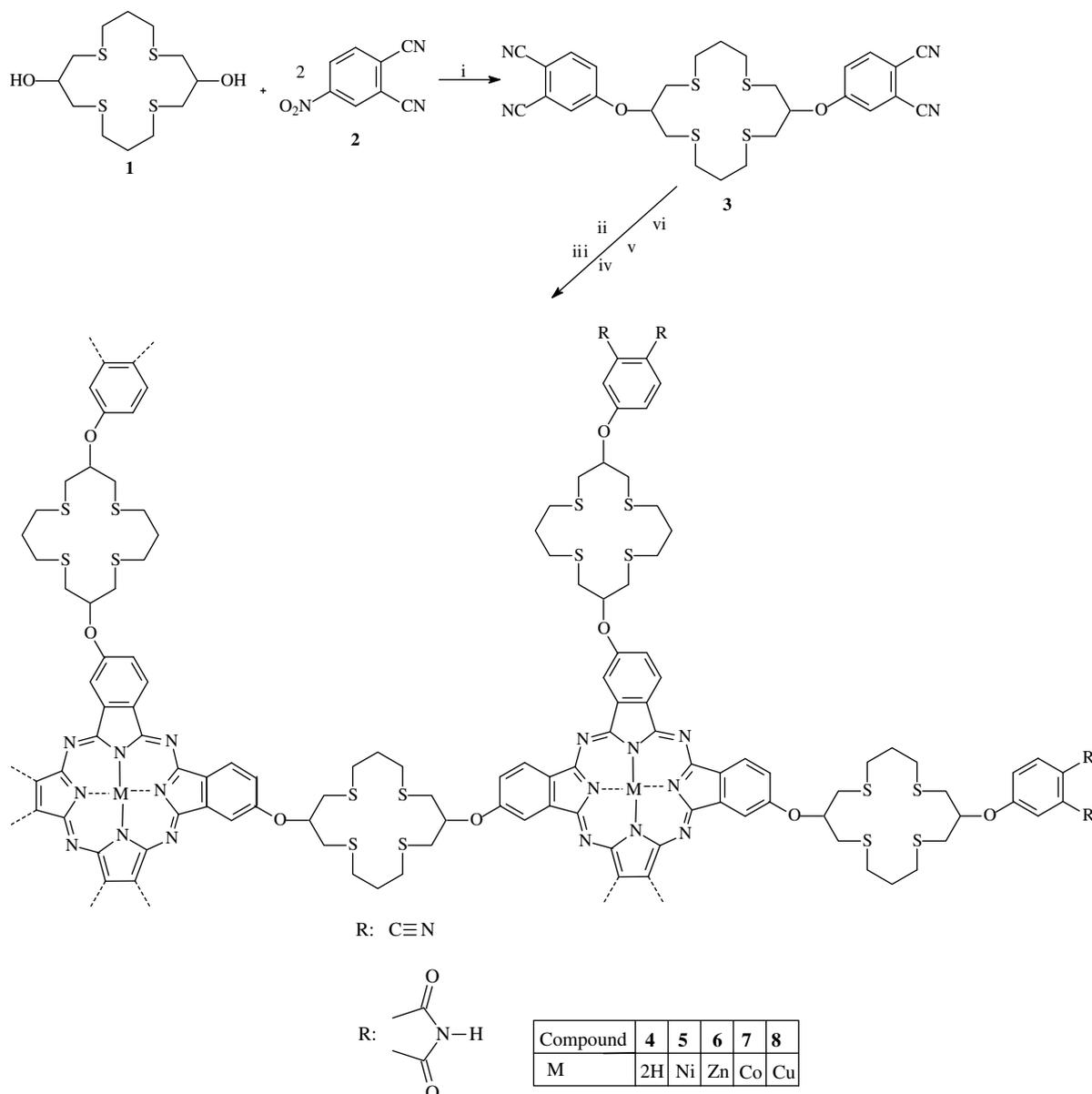
A mixture of 4-({11-[3-cyano-4-(cyanomethyl)phenoxy]-1,5,9,13-tetrathiacyclohexadecan-3-yl}oxy)phthalonitrile (3) (0.3 g, 0.52 mmol), anhydrous CoCl<sub>2</sub> (16.8 mg, 0.63 mmol) and 2-(dimethylamino)ethanol (DMAE) (3 ml) was irradiated in a microwave oven at 175 °C, 350 W for 8 min. After cooling to room temperature, the reaction mixture was refluxed with ethanol (45 ml) to precipitate the product which was filtered off. The green solid product was washed with hot ethanol, diethyl ether and dried in vacuo. This product is soluble in pyridine. Yield: 218 mg, m.p. > 300 °C. Elemental analyses (for imide end groups) (C<sub>112</sub>H<sub>116</sub>N<sub>12</sub>O<sub>16</sub>S<sub>16</sub>Co)<sub>n</sub> (2458.12)<sub>n</sub>. Calc.: C, 54.72; H, 4.76; N, 6.84; Co, 2.40. Found: C, 54.11; H, 5.06; N, 6.41; Co, 2.58%. IR (KBr tablet)  $\nu_{\max}/\text{cm}^{-1}$ : 3423 (imide N–H), 3082 (Ar–H), 2916–2851 (Aliph. C–H), 1774 (sym. C=O), 1718 (asym. C=O), 1596, 1472, 1314, 1225 (Ar–O–C), 1092, 1019, 836, 773. UV–Vis (pyridine):  $\lambda_{\max}/\text{nm}$ : [(10<sup>-5</sup> ε dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 261 (5.16), 318 (5.14), 373 (5.11), 614 (4.62), 681 (5.17). MS (FAB), (*m/z*): 2458 [M]<sup>+</sup>.

### 2.6. Cu(I)-containing polymer (8)

A mixture of 4-({11-[3-cyano-4-(cyanomethyl)phenoxy]-1,5,9,13-tetrathiacyclohexadecan-3-yl}oxy)phthalonitrile (3) (0.3 g, 0.52 mmol), anhydrous CuCl (12.8 mg, 0.13 mmol) and 2-(dimethylamino)ethanol (DMAE) (3 ml) was irradiated in a microwave oven at 175 °C, 350 W for 8 min. After cooling to room temperature, the reaction mixture was refluxed with ethanol (45 ml) to precipitate the product which was filtered off. The green solid product was washed with hot ethanol, diethyl ether and dried in vacuo. This product is soluble in pyridine. Yield: 229 mg, m.p. > 300 °C. Elemental analyses (for imide end groups) (C<sub>112</sub>H<sub>116</sub>N<sub>12</sub>O<sub>16</sub>S<sub>16</sub>Cu)<sub>n</sub>(2462.73)<sub>n</sub>. Calc.: C, 54.62; H, 4.75; N, 6.82; Cu, 2.58. Found: C, 54.22; H, 5.02; N, 6.19; Cu, 2.68%. IR (KBr tablet)  $\nu_{\max}/\text{cm}^{-1}$ : 3433 (imide N–H), 3071 (Ar–H), 2917–2846 (Aliph. C–H), 1770 (sym. C=O), 1712 (asym. C=O), 1594, 1485, 1316, 1251 (Ar–O–C), 1088, 999, 837, 718, 523. UV–Vis (pyridine):  $\lambda_{\max}/\text{nm}$ : [(10<sup>-5</sup> ε dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 249 (5.14), 320 (5.12), 361 (5.10), 617 (4.57), 689(5.17). MS (FAB), (*m/z*): 2463 [M+1]<sup>+</sup>.

## 3. Results and discussion

Metal-free phthalocyanine polymer (4) and metallophthalocyanine polymers (5–8) were synthesized in two steps (Scheme 1). In the first step, the base-catalyzed nucleophilic aromatic nitro displacement [30,31] of 4-nitrophthalonitrile (2) with 1,5,9,13-tetrathiacyclohexadecane-3,11-diol (1) afforded tetranitrile monomer (3). In the second step,



- i: dry DMF, dry  $K_2CO_3$ ,  $N_2$ , 50 °C  
 ii: Microwave, 350 W, 4 min, DMAE, 175 °C  
 iii: Microwave, 350 W, 4 min, DMAE, 175 °C, anhydrous  $NiCl_2$   
 iv: Microwave, 350 W, 4 min, DMAE, 175 °C, anhydrous  $Zn(CH_3COO)_2$   
 v: Microwave, 350 W, 4 min, DMAE, 175 °C, anhydrous  $CoCl_2$   
 vi: Microwave, 350 W, 4 min, DMAE, 175 °C, anhydrous  $CuCl$

Scheme 1.

metal-free and metallophthalocyanine polymers were synthesized. The metal-free phthalocyanine (**4**) was synthesized by microwave irradiation of the corresponding dicyano compound **3** in 2-(dimethylamino)ethanol for 8 min. Metallophthalocyanines (**5–8**) were obtained from tetracyano derivative **3** and corresponding anhydrous metal salts  $NiCl_2$ ,  $Zn(CH_3COO)_2$ ,  $CoCl_2$  and  $CuCl$ , respectively, by microwave irradiation in 2-(dimethylamino)ethanol for 8 min.

The molecular weights of the polymers could not be determined using traditional methods owing to their poor solubility in organic solvents, but also by comparison of

the IR absorption bands of the end groups with those of the bridging groups [10,32–36].

In the IR spectrum of **3**, the disappearance of  $NO_2$  and OH stretches, along with the appearance of new bands at 2230 and  $1256\text{ cm}^{-1}$  arising from  $C\equiv N$  and  $Ar-O-C$  groups, respectively, are in agreement with the proposed structure. In the  $^1H$  NMR spectrum of **3**, OH group of compound **1** disappeared as expected.  $^1H$  NMR spectrum of **3** showed new signals at  $\delta = 8.06$  (d, 2H, Ar-H), 7.81 (s, 2H, Ar-H), 7.49 (d, 2H, Ar-H), 4.89 (m, 2H, CH-O). In the  $^{13}C$  NMR spectrum of **3**, the presence of nitrile car-

bon atoms in **3** at  $\delta$ 116.02 and 115.55 ppm was indicated. Elemental analysis and EI mass spectral data were satisfactory: 581  $[M+1]^+$ .

In the IR spectrum of **4**, characteristic peaks for phthalocyanines were observed. The peak at  $3281\text{ cm}^{-1}$  is the characteristic metal-free phthalocyanine N–H stretching bands. Also,  $2229\text{ cm}^{-1}$  (C $\equiv$ N),  $1255\text{ cm}^{-1}$  (Ar–O–C) bands were present in the spectrum. The MS spectrum of compound **4** displayed the  $[M]^+$  parent ion peak at  $m/z = 2325$ , which confirms the same structure. Elemental analysis was satisfactory.

The IR spectra of the metallophthalocyanine polymers (**5–8**) were very similar, except for the metal-free phthalocyanine polymer (**4**) which showed an N–H stretching band at  $3281$  and  $1084\text{ cm}^{-1}$  due to the inner core [37,38]. These bands disappear in the spectra of the metallophthalocyanine polymers. These bands are especially beneficial for the characterization of metal-free phthalocyanine polymers, as there is little frequency dependence on ring substitution and they are not overlapped by strong bisphthalonitrile monomer absorptions [16]. The end groups of the metal-free phthalocyanine polymer were cyano groups ( $2229\text{ cm}^{-1}$ ) while the end groups of the metallophthalocyanine polymers were imido groups ( $\sim 1778$ – $1711\text{ cm}^{-1}$ ). In the mass spectrum of Ni, Zn, Co, and Cu phthalocyanines, the presence of molecular ion peaks at  $m/z = 2458$   $[M+1]^+$ ,  $2465$   $[M+1]^+$ ,  $2458$   $[M]^+$  and  $2463$   $[M+1]^+$ , respectively, confirmed the proposed structures.

The lower solubility of the polymers meant that their spectra could be obtained in pyridine. The UV–Vis absorption spectra of these polymers exhibit Q and B bands, which are the characteristic bands for phthalocyanine polymers.

There were the split Q-band as expected and there were two strong bands in the visible region [39]. The split Q-band, which is characteristic for metal-free phthalocyanines observed at  $\lambda_{\text{max}} = 703$  and  $683\text{ nm}$  with a shoulder at  $617\text{ nm}$ , indicates the monomeric species with  $D_{2h}$  symmetry, and shows two intense absorptions at around  $700\text{ nm}$  [40,41]. On the other hand, such split Q-band absorptions in pyridine are due to  $\pi$ – $\pi^*$  transition of this fully conjugated  $18\pi$  electron systems [42].

## Acknowledgement

This study was supported by the Research Fund of Karadeniz Technical University, Trabzon, Turkey.

## References

- [1] (a) C. Piechocki, J. Simon, A. Skoulioussi, D. Gullioni, P.J. Weberi, *J. Am. Chem. Soc.* 104 (1982) 5245;  
(b) C. Piechocki, J. Simon, *Nouv. J. Chim.* 9 (1985) 154.
- [2] (a) A.W. Snow, W.R. Barger, M. Klusty, H. Wohltjen, N.L. Jarvis, *Langmuir* 2 (1986) 513;

- (b) D. Wöhrle, M. Kaneko, *Yuki Gosei Kagaku Kyokai Shi* 45 (1987) 837.
- [3] A. Grund, A. Kaltbeitzel, A. Mathy, R. Schwarz, C. Bubeck, P. Vernmehren, M. Hanack, *J. Phys. Chem.* 96 (1992) 7450.
- [4] C.C. Leznoff, A.B.P. Lever (Eds.), *Phthalocyanines, Properties, and Applications*, vols. 1–4, VCH, New York, 1989, 1993.
- [5] M. Hanack, M. Lang, *Adv. Mater.* 6 (1994) 819.
- [6] A. Koca, H.A. Dinçer, H. Çerlek, A. Gül, M.B. Koçak, *Electrochim. Acta* 52 (2006) 1199.
- [7] A. Beck, K.M. Mangold, M. Hanack, *Chem. Ber.* 124 (1991) 2315.
- [8] A.A. Berlin, A.I. Sherle, *Inorg. Macromol. Rev.* 1 (1971) 235.
- [9] H. Inoue, Y. Kida, E. Imato, *Bull. Chem. Soc. Jpn.* 40 (1967) 184.
- [10] D. Wöhrle, B. Schulte, *Makromol. Chem.* 189 (1988) 1167.
- [11] J.A. Hinkley, *J. Appl. Polym. Sci.* 29 (1984) 3339.
- [12] G. Manecke, D. Wöhrle, *Makromol. Chem.* 102 (1967) 1.
- [13] A.G. Gürek, Ö. Bekaroğlu, *J. Porphyr. Phthalocya.* 1 (1997) 67.
- [14] M. Koß, M. Rohde, *Makromol. Chem.* 178 (1977) 715.
- [15] B.D. Berezin, L.P. Shormanova, *Vysokomol. Soedin Ser. A* 10 (1968) 338.
- [16] D. Wöhrle, U. Marose, R. Knoop, *Makromol. Chem.* 186 (1985) 2209.
- [17] D. Wöhrle, R. Benters, O. Suvorova, G. Schnurpfeil, N. Trombach, T. Bogdahn-Rai, *J. Porphyr. Phthalocya.* 4 (2000) 491.
- [18] R.P. Kingsborough, T.M. Swager, *Angew. Chem., Int. Ed.* 39 (2000) 2897.
- [19] F. Cataldo, *Dyes Pigments* 34 (1997) 75.
- [20] C.C. Leznoff, A.B.P. Lever (Eds.), *Phthalocyanines, Properties, and Applications*, vol. 4, VCH, New York, 1996.
- [21] D. Wöhrle, E. Preubner, *Makromol. Chem.* 186 (1985) 2189.
- [22] Z. Bıyıklıoğlu, H. Kantekin, M. Özil, *J. Organomet. Chem.* 692 (2007) 2436.
- [23] H. Kantekin, Z. Bıyıklıoğlu, *Dyes Pigments* 77 (2008) 98.
- [24] Z. Bıyıklıoğlu, H. Kantekin, *Transition Met. Chem.* 32 (2007) 851.
- [25] H. Kantekin, Z. Bıyıklıoğlu, *Dyes Pigments* 77 (2008) 432.
- [26] Z. Bıyıklıoğlu, H. Kantekin, *J. Organomet. Chem.* 693 (2008) 505.
- [27] V.B. Pett, G.H. Leggett, T.H. Cooper, P.R. Reed, D. Situmeang, L.A. Ochrymowycz, D.B. Rorabacher, *Inorg. Chem.* 27 (1988) 2164.
- [28] G.J. Young, W. Onyebugu, *J. Org. Chem.* 55 (1990) 2155.
- [29] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, *Purification of Laboratory Chemicals*, second ed., Pergamon Press, New York, 1985.
- [30] M. Brewis, G.J. Clarkson, M. Helliwell, A.M. Holder, N.B. McKeown, *Chem. Eur. J.* 6 (2000) 4630.
- [31] T.M. Keller, T.R. Price, J.R. Griffith, *Synthesis* 54 (1980) 2990.
- [32] F. Chavez, A.D. Sherry, *J. Org. Chem.* 54 (1989) 2990.
- [33] E. Agar, S. Sasmaz, I. Keskin, N. Akdemir, *Dyes Pigments* 36 (1998) 249.
- [34] A. Bilgin, Ç. Yağcı, U. Yıldız, *Macromol. Chem. Phys.* 206 (2005) 2257.
- [35] A. Bilgin, Ç. Yağcı, A. Mendi, U. Yıldız, *Polyhedron* 26 (2007) 617.
- [36] A. Bilgin, A. Mendi, U. Yıldız, *Polymer* 47 (2006) 8462.
- [37] M. Avram, G. Mateescu, *Infrared Spectroscopy*, Wiley-Interscience, New York, 1966, p. 298.
- [38] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, second ed., Wiley, New York, 1970, p. 325.
- [39] I. Yılmaz, Ö. Bekaroğlu, *Chem. Ber.* 129 (1996) 967.
- [40] O.E. Sielcken, M.M. van Tilborg, R. Hendricks, W. Drenth, R.J.M. Nolte, *J. Am. Chem. Soc.* 109 (1987) 4261.
- [41] E.A. Cuellar, T.J. Marks, *Inorg. Chem.* 20 (1981) 3766.
- [42] Y. Gök, H. Kantekin, A. Bilgin, D. Mendi, İ. Değirmencioglu, *J. Chem. Soc., Chem. Commun.* 3 (2001) 285.