Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 75 (2007) 606–611

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

The synthesis and characterization of new metal-free and metallophthalocyanines containing four 27-membered diazaheptathia macrocycles

H. Zeki Gök [a], Halit Kantekin [a,*], Yaşar Gök [a], Gerrit Herman [b]

[a] *Department of Chemistry, Karadeniz Technical University, 61080 Trabzon, Turkey*
[b] *Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 (S.3), B-9000 Gent, Belgium*

Received 23 June 2006; received in revised form 29 June 2006; accepted 2 July 2006

Abstract

A new metal-free **5** and metallophthalocyanines **6** and **7** containing four 27-membered diazaheptathia macrocyclic moieties on peripheral positions have been synthesized. The metal-free phthalocyanine **5** was synthesized by the reaction 27,28-dicyano-9,10,12,13,23,24,31,32-octahydro-5*H*,15*H*-tribenzo[*b*,*h*,*w*][1,4,7,13,16,19,25,10,22]heptathia diazacycloheptacosine-6,16 (7*H*,17*H*)-dione **4** with anhydrous 2-(dimethylamino)ethanol under reflux for 28 h. Metallophthalocyanines **6** and **7** were synthesized by the reaction of **4** with anhydrous $NiCl_2$ and $Zn(CH_3CO)_2$ in dry quinoline, respectively. The new compounds were characterized by a combination of elemental analysis and ^1H NMR, ^{13}C NMR, IR, UV–vis and MS spectral data.

Keywords: 2-Aminothiophenol; Mixed-donor macrocycle; Phthalocyanines; Template effect; Transition metal

---

1. Introduction

Phthalocyanine, which was first developed as a pigment, has found widespread applications in materials science [1]. It has been employed as charge carriers in photocopiers and laser printers, as well as materials for optical storage in recent years [2,3]. Many potential applications are expected for these molecular materials which have a high thermal and chemical stability, for instance oxidation catalysis [4], solar cell functional materials [5], gas sensors [6], nonlinear optical limiting devices [7], photodynamic therapy agents [8], antimycotic material [9], and corrosion inhibitors [10], infectious diseases [11], and eye and neurodegenerative diseases [12]. The electrochemical and spectroscopic properties can be altered by changing the metal center. The other way to tune the properties of phthalocyanine compounds is to introduce different kinds of substituents onto the peripheral and nonperipheral positions of the phthalocyanine ring. Particularly, the optical and electrochemical properties of phthalocyanines can be significantly altered by incorporating substituents at the nonperipheral positions. Because of their potential applications, tens of thousands of tons of phthalocyanines (Pcs) are produced per year worldwide [13].

In the last few decades the synthesis of artificial receptors that are able to coordinate metal cations undergone a spectacular growth [14,15]. Most of the attention has been focused on macrocyclic receptors capable to bind more than one transition metal ion [16–22]. Depending on the nature of subunits used for their construction, a variety of macropolycyclic structures have been synthesized. Most of these ligands contain both nitrogen and oxygen donor atoms and have a great affinity for alkali-metal and alkaline-earth metal cations. To enhance the coordinating properties of these macrocycles, different modifications have been made such as the ring size, the nature of substituents, and the type of donor atoms [23]. There are only a few reports concerning the Ag^+ complexabilities and

---

* 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 © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.07.008

selectivities of thiazacrown ether derivatives containing sulfur and nitrogen atoms on the crown ring [24,25]. Macrocycles which contain some sulfur and nitrogen atoms as donor atoms have high complexabilities for some transition metal ions.

We have previously described the synthesis of metal-free and metal phthalocyanines which contain four 20-membered diazatetraoxa macrocycles each attached to a 15-crown-5 unit [26] and macrobicyclic moieties [27]. In this study, the synthesis and characterization and structural investigation of metal-free and Ni(II), Zn(II) phthalocyanines, which contain sulfur and nitrogen donor atoms macrocyclic moieties, are described, suggesting that the suitable combination of diazaheptathia macrocycles and phthalocyanine may allow new functionalized materials to be prepared, which are of importance for analytical chemistry as transition metal extraction agents.

2. Experimental

1,2-Bis(2-iodoethylmercapto)-4,5-dicyanobenzene **1** was prepared according to the literature [27]. All reagents and solvent were of reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [28]. Melting points were determined with an electrothermal apparatus and were uncorrected. FTIR spectra were measured on a Mattson 1001 Fourier-transform spectrometer using KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer using $CDCl_3$ and DMSO-d_6 (99.9%). Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC–MS/MS spectrometer. Optical spectra in the UV–vis region were recorded with a Varian Cary 50 Conc spectrophotometer using 1 cm pathlength cuvettes at room temperature. Elemental analyses were obtained from LECO Elemental Analyser (CHNS 0932) and Unicam 929 AA spectrophotometer. The homogeneity of the products was tested in each step using TLC.

2.1. *1,2-Bis(2′-aminophenylsulfanylethoxy)-4,5-dicyanobenzene (**2**)*

2-Aminothiophenol (6.75 g, 54 mmol) was dissolved in dry tetrahydrofuran (480 ml) under argon atmosphere. Finely ground anhydrous sodium carbonate (8.90 g, 84 mmol) was added to the solution. After stirring for 0.5 h efficiently at reflux temperature, a solution of 1,2-bis(2-iodoethylmercapto)-4,5-dicyanobenzene **1** [27] (12 g, 24 mmol) in dry tetrahydrofuran (240 ml) was added dropwise over 2 h under argon atmosphere at reflux temperature and the reaction mixture was heated and stirred at reflux temperature for 20 h. The reaction was monitored by thin layer chromatography [pentane–ethyl acetate (8.5:1.5)]. At the end of this period, the mixture was cooled to room temperature, evaporated to dryness under reduced pressure, water (200 ml) was added to residue and filtered off. The precipitate was washed with water, sodium carbonate (5%), then water and finally washed with ethanol and diethyl ether. The light yellow powdered mixture was purified by silica gel column chromatography using pentane–ethyl acetate (8.5:1.5) as eluents. The appropriate fraction was evaporated to give the desired product. The white crystalline solid was separated by filtration and dried in vacuum. Yield: 11.20 g (93%), mp 131–132 °C. Anal. Calcd for $C_{24}H_{22}N_4S_4$: C, 58.27; H, 4.48; N, 11.32%. Found: C, 58.20; H, 4.56; N, 11.18. IR (KBr disc) ν_{max}/cm^{-1}: 3449–3354 (NH_2), 3066 (CH_{Ar}), 2912 (CH_3), 2232 ($C{\equiv}N$), 1605 (NH_2), 1564, 1477, 1457, 1348, 1200, 879, 747. ^1H NMR ($CDCl_3$) δ: 7.41 (d, 2H, ArH), 7.22 (t, 2H, ArH), 7.16 (s, 2H, ArH), 6.87 (d, 2H, ArH), 6.71 (t, 2H, ArH), 4.35 (s, 4H, NH_2), 3.14–2.92 (m, 8H, SCH_2). ^{13}C NMR ($CDCl_3$) δ: 148.63, 143.15, 136.72, 131.07, 128.65, 118.95, 115.65 (ArC), 115.31 ($C{\equiv}N$), 114.98, 111.92 (ArC), 31.92, 31.84 (SCH_2). MS (LC–MS/MS) *m/z*: 495 $[M+1]^+$.

2.2. *2-Chloro-N-{2-[2-(4,5-dicyano-2-{2-[2-(2-chloro-acetylamino)-phenylsulfanyl]-ethoxy}-phenoxy)-ethylsulfanyl]-phenyl}-acetamide (**3**)*

Chloroacetic anhydride (3.40 g, 30.18 mmol) in CH_2Cl_2 (100 ml) was added dropwise through a dropping funnel to a stirred solution of 1,2-bis(2′-aminophenylsulfanylethoxy)-4,5-dicyanobenzene **2** (6 g, 12.07 mmol) in CH_2Cl_2 (300 ml) at 0–5 °C over a 1.5 h period. The mixture was stirred for additional overnight under argon atmosphere at room temperature. At the end of this period, the saturated aqueous $NaHCO_3$ was added to neutralize the reaction mixture. The organic layer was separated and washed twice with 50 ml portion of saturated aqueous $NaHCO_3$ and then twice with portions of water. The organic layer was dried over anhydrous Na_2SO_4, the solvent was evaporated under reduced pressure to give a crude product. This white solid was used to prepare the appropriate macrocyclic without further purification. The yield was 7.5 g (95%), mp 161–162 °C. Anal. Calcd for $C_{28}H_{24}Cl_2N_4O_2S_4$: C, 51.92; H, 3.74; N, 8.65%. Found: C, 51.30; H, 3.92; N, 8.38. IR (KBr disc) ν_{max}/cm^{-1}: 3271 (NH), 3072 (CH_{Ar}), 2966–2857 (CH_3), 2230 ($C{\equiv}N$), 1673 (C=O), 1581, 1528, 1438, 1305, 1203, 1113, 931, 763. ^1H NMR ($CDCl_3$) δ: 9.68 (s, 2H, NH), 8.44 (d, 2H, ArH), 7.60 (d, 2H, ArH), 7.45 (t, 2H, ArH), 7.20 (s, 2H, ArH), 7.16 (t, 2H, ArH), 4.26 (s, 4H, $O{=}CCH_2Cl$), 3.11–2.97 (m, 8H, SCH_2). ^{13}C NMR ($CDCl_3$) δ: 163.93 (C=O), 143.15, 139.05, 135.84, 131.03, 129.52, 125.42, 121.43, 120.46 (ArC), 115.00 ($C{\equiv}N$), 112.50 (ArC), 43.47 ($O{=}CCH_2Cl$), 34.41, 32.13 (SCH_2). MS (LC–MS/MS) *m/z*: 648 $[M+1]^+$.

2.3. *27,28-Dicyano-9,10,12,13,23,24,31,32-octahydro-5H,15H-tribenzo[b,h,w][1,4,7,13,16,19,25,10,22] heptathia diazacycloheptacosine-6,16(7H,17H)-dione (**4**)*

A solution of 2,2′-dithioethanolthiol (0.95 g, 6.17 mmol) in dry dimethylformamide (200 ml) in a dropping funnel and a solution of **3** (4 g, 6.17 mmol) in dry dimethylformamide (200 ml) in a dropping funnel were added simultaneously under stirring and dry inert gas to dry dimethylformamide (200 ml) containing anhydrous sodium carbonate (2.61 g, 24.69 mmol) over 8 h at room temperature. After addition, reaction mixture was stirred at room temperature for another 24 h, and then filtered off. The precipitate was washed with water, ethanol and ether. The crude product was recrystallized from dimethylformamide. The product was collected by filtration and washed with ethanol and diethyl ether and then dried in vacuum. The yield was 3.2 g (71%), mp 240–241 °C. Anal. Calcd for $C_{32}H_{32}N_4O_2S_7$: C, 52.72; H, 4.42; N, 7.68%. Found: C, 52.28; H, 4.65; N, 7.41. IR (KBr disc) ν_{max}/cm^{-1}: 3289 (NH), 3097–3063 (CH_{Ar}), 2954–2917 (CH_3), 2228 (C≡N), 1662 (C=O), 1578, 1514, 1433, 1295, 1257, 1153, 1112, 931, 872, 751. ^1H NMR (DMSO-d_6) δ: 9.66 (s, 2H, NH), 7.81 (d, 2H, ArH), 7.76 (s, 2H, ArH), 7.58 (d, 2H, ArH), 7.33 (t, 2H, ArH), 7.18 (t, 2H, ArH), 3.44 (s, 4H, $O{=}CCH_2S$), 3.35–3.16 (m, 8H, $ArSCH_2$), 2.79 (m, 8H, SCH_2). ^{13}C NMR (DMSO-d_6) δ: 167.94 (C=O), 142.45, 138.35, 133.34, 129.32, 128.59, 126.36, 125.48, 123.58 (ArC), 115.87 (C≡N), 110.95 (ArC), 35.43 ($O{=}CCH_2S$), 33.32, 32.32, 31.56, 30.88 (SCH_2). MS (LC–MS/MS) *m/z*: 729 $[M+1]^+$.

2.4. Metal-free phthalocyanine (**5**)

A mixture of **4** (0.3 g, 0.411 mmol) and dry 2-(dimethylamino)ethanol (1.5 ml) was placed under argon atmosphere in a standard Schlenk tube. The reaction mixture was refluxed and stirred under argon for 28 h. After cooling to the room temperature, the green mixture was diluted with ethanol (10 ml) until the product precipitated and then the product was filtered off, washed with ethanol, diethyl ether, CH_2Cl_2 and dried in vacuum. The yield was 0.046 g (15.39%), mp > 300 °C. Anal. Calcd. for $C_{128}H_{130}N_{16}O_8S_{28}$: C, 52.68; H, 4.49; N, 7.68%. Found: C, 52.24; H, 4.89; N, 7.32. IR (KBr disc) ν_{max}/cm^{-1}: 3285 (NH), 3053 (CH_{Ar}), 2960–2925 (CH_3), 1673 (C=O), 1579, 1513, 1492, 1411, 1299, 1200, 1158, 1125, 1074, 1018, 866, 751, 665. ^1H NMR (DMSO-d_6) δ: 9.67 (s, 8H, NH), 7.79 (d, 8H, ArH), 7.76 (s, 8H, ArH), 7.58 (d, 8H, ArH), 7.32 (t, 8H, ArH), 7.17 (t, 8H, ArH), 3.44 (s, 16H, $O{=}CCH_2S$), 3.31–3.16 (m, 32H, $ArSCH_2$), 2.80 (m, 32H, SCH_2). UV–vis (DMF): λ (nm): $[(10^{-5}\,\varepsilon\,dm^3\,mol^{-1}\,cm^{-1})]$: 296 (4.62), 326 (4.49), 368 (4.43), 449 (4.18), 656 (4.17), 707 (4.18). MS (LC–MS/MS) *m/z*: 2918 $[M]^+$.

2.5. Nickel(II) phthalocyanine (**6**)

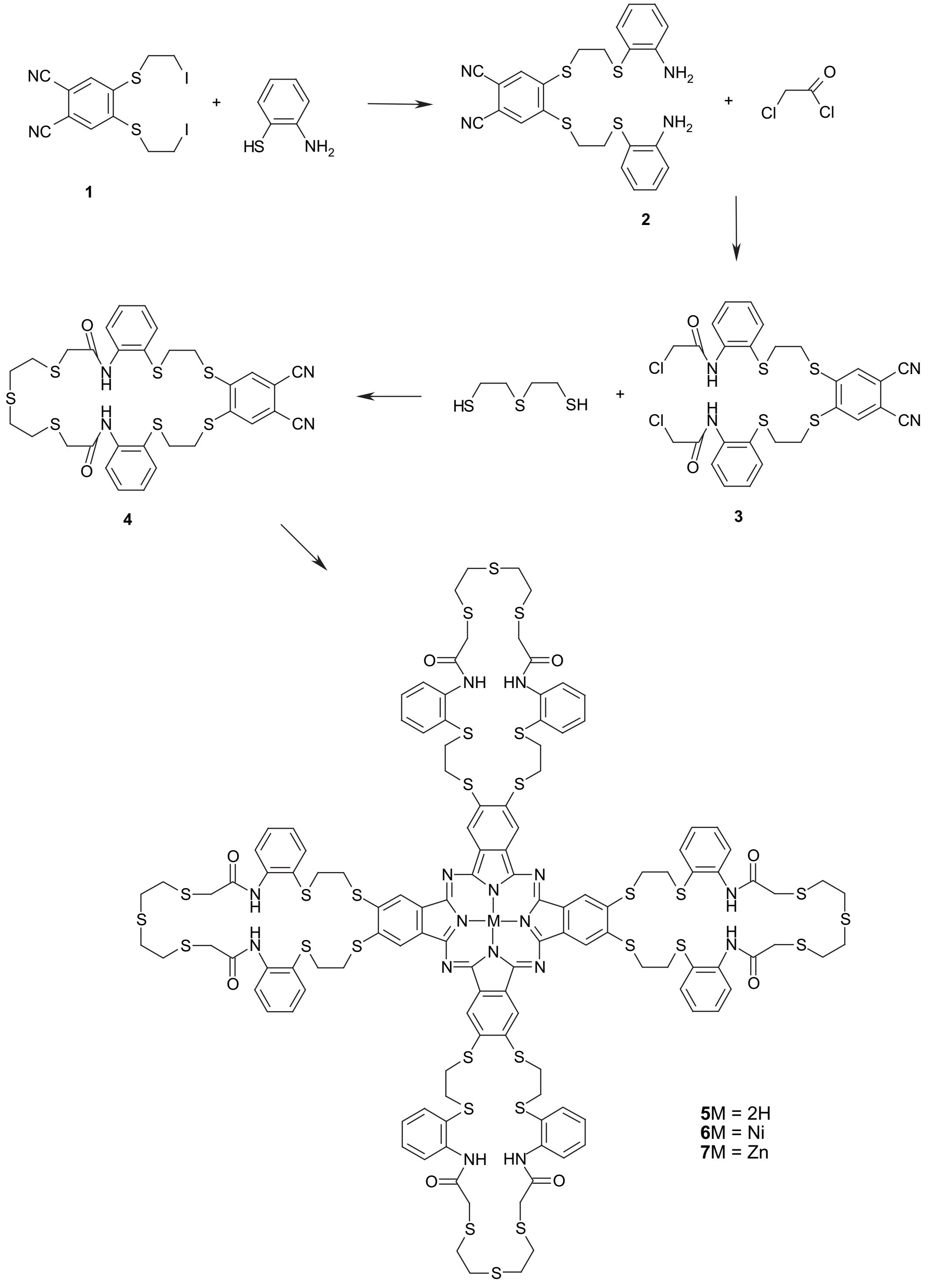
A mixture of **4** (0.3 g, 0.411 mmol), anhydrous $NiCl_2$ (0.013 g, 0.102 mmol) and quinoline (1.23 ml) was heated and stirred at 190 °C for 7 h in a Schlenk tube under argon. After cooling to room temperature, the dark green mixture was diluted with 10 ml of ethanol. The product was filtered off and washed with the same hot solvent to remove the unreacted metal salts, then with ethyl acetate, dichloromethane, acetone, diethyl ether and then dried in vacuum. This product is soluble in DMF, DMSO, pyridine and moderately in THF. The yield was 0.114 g (38%), mp > 300 °C. Anal. calcd. for $C_{128}H_{128}N_{16}NiO_8S_{28}$: C, 51.64; H, 4.40; N, 7.53%. Found: C, 51.18; H 4.57; N, 7.21. IR (KBr disc) ν_{max}/cm^{-1}: 3301 (NH), 3054 (CH_{Ar}), 2959–2913 (CH_3), 1666 (C=O), 1602, 1577, 1510, 1476, 1433, 1298, 1198, 1156, 1124, 1072, 750. ^1H NMR (DMSO-d_6) δ: 9.69 (s, 8H, NH), 7.95–6.50 (m, 40H, ArH), 3.44 (s, 16H, $O{=}CCH_2S$), 3.31–2.80 (m, 64H, $ArSCH_2$). UV–vis (DMF): λ (nm): $[(10^{-5}\,\varepsilon\,dm^3\,mol^{-1}\,cm^{-1})]$: 275 (5.05), 311 (4.93), 410 (4.58), 482 (4.41), 656 (4.20), 701 (4.35). MS (LC–MS/MS) *m/z*: 2977 $[M+2]^+$.

2.6. Zinc(II) phthalocyanine (**7**)

A mixture of **4** (0.3 g, 0.411 mmol), anhydrous $Zn(CH_3CO)_2$ (0.018 g, 0.102 mmol) and quinoline (1.23 ml) was heated and stirred at 195 °C for 8 h in a Schlenk tube under argon. After cooling to room temperature, the product was precipitated by adding ethanol (10 ml), filtered off and washed with the same hot solvent, then ethyl acetate, dichloromethane, acetone, diethyl ether and then dried in vacuum. This product is soluble in DMF, DMSO, pyridine and moderately in THF. The yield was 0.107 g (35.6%), mp > 300 °C. Anal. Calcd. for $C_{128}H_{128}N_{16}O_8S_{28}Zn$: C, 51.53; H, 4.39; N, 7.51%. Found: C, 50.87; H, 4.70; N, 7.11. IR (KBr disc) ν_{max}/cm^{-1}: 3306 (NH), 3058 (CH_{Ar}), 2964–2911 (CH_3), 1658 (C=O), 1600, 1578, 1512, 1477, 1433, 1401, 1334, 1298, 1198, 1157, 1113, 1985, 1066, 1035, 752. ^1H NMR (DMSO-d_6): δ 9.71 (s, 8H, NH), 7.79–6.48 (m, 40H, ArH), 3.44 (s, 16H, $O{=}CCH_2S$), 3.31–2.80 (m, 64H, $ArSCH_2$). UV–vis (DMF): λ (nm): $[(10^{-5}\,\varepsilon\,dm^3\,mol^{-1}\,cm^{-1})]$: 272 (5.03), 371 (4.73), 644 (4.21), 681 (4.30), 713 (4.65). MS (LC–MS/MS) *m/z*: 2981 $[M]^+$.

3. Results and discussion

The preparation of the target metal-free **5** and metallophthalocyanines **6**, **7** is shown in Scheme 1. The structures of novel compounds were characterized by a combination of elemental analysis and ^1H NMR, ^{13}C NMR, IR, UV–vis and MS spectral data. 1,2-Bis(2-iodoethylmercapto)-4,5-dicyanobenzene **1** was synthesized as described according to reported procedure [27]. 1,2-Bis(2-iodoethylmercapto)-4,5-dicyanobenzene **1** was converted to compound **2** in THF containing Na_2CO_3 as a base at reflux temperature for 20 h under an argon atmosphere, affording the 1,2-bis(2′-aminophenylsulfanylethoxy)-4,5-dicyanobenzene **2** in 93% yield. ^1H and ^{13}C NMR, IR, and MS spectra verified the structure of **2**. The IR spectrum of **2** clearly indicates the presence of NH_2, C≡N groups by the intense stretching bands at 3349–3354 (NH_2), 2232 (C≡N) cm^{-1}, respectively. In the ^1H NMR spectrum of **2** in $CDCl_3$, the aromatic protons belonging to 2-aminothiophenol appear as doublet at $\delta = 7.41$, 6.87 and as triplet at $\delta = 7.22$, 6.71 ppm. The singlet at $\delta = 7.16$ ppm belongs to aromatic protons of cyano-substituted benzene. Also the new signal for NH_2 protons was observed as singlet at $\delta = 4.35$ ppm. The multiplet at $\delta = 3.14$–2.92 ppm for SCH_2 protons confirms the proposed structure. ^{13}C NMR spectrum of this compound exhibits signals characteristic of aromatic carbons at 148.63, 143.15, 136.72, 131.07, 128.65, 118.94, 115.61, 114.98, 111.92 ppm



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

and the aliphatic carbon atoms also gave two signals at 31.92 and 31.84 ppm. The LC–MS mass spectrum of **2**, which shows a peak at $m/z = 495$ $[M + 1]^+$, and elemental analysis support the proposed formula for this compound.

Compound **3** was synthesized by acylating **2** with acetyl chloride. Thus, the precursor compound for synthesis of the macrocycle has the amide portions which increase the reactivity of chloro-substituted carbon toward the nucleophilic substitution [29]. In the IR spectrum of **3**, the presence of intense C≡N stretching band at 2230 cm^{-1}, the disappearance of the strong NH_2 stretching vibrations at 3449–3354 cm^{-1}, the appearance of NH stretching vibration at 3271 cm^{-1} and the sharp C=O vibration at 1673 cm^{-1} confirm the formation of this compound. The ^1H NMR spectrum of **3** indicates the presence of a new resonance for methylene protons of amide portion at 4.26 ppm as a singlet. The resonance of NH proton shifts downfield by as much as 5.33 ppm on going from compound **2** to compound **3** and it appears at 9.68 ppm as a singlet. In the ^{13}C NMR spectrum of **3**, the peak at 115.00 ppm arises from unsaturated carbon atoms of C≡N groups. The appearance of new peaks at $\delta = 163.93$ and 43.47 ppm, which were assigned to C═O and −CH$_2$Cl groups of amide portion, the other chemical shifts at 143.15, 139.05, 135.84, 131.03, 129.52, 125.42, 121.43, 120.46, 112.50 concerning aromatic carbons and at 34.41, 32.15 concerning aliphatic carbons such as C−S are in agreement with the proposed structure. The LC−MS mass spectra of **3**, the presence of the molecular ion peak at $m/z = 648$ $[M + 1]^+$, confirm the proposed structure.

The macrocyclization was performed by adding simultaneously a solution of 2,2′-dithioethanthiol in DMF and a solution of **3** in DMF through dropping funnels to stirring DMF containing anhydrous Na_2CO_3 as the base at room temperature for 8 h under an argon atmosphere, affording the macrocycle 27,28-dicyano-9,10,12,13,23,24,31,32-octahydro-5*H*,15*H*-tribenzo[*b*,*h*,*w*][1,4,7,13,16,19,25,10,22]heptathia diazacycloheptacosine-6,16(7*H*,17*H*)-dione **4** in 71% yield. The relatively high yield for macrocyclization reaction may be attributable to the hydrogen bonding between the amide oxygen atoms of the bis(α-chloroamide) and the amine hydrogen atoms of the bis-secondary amines which would keep the chloride units in the positions needed for the cyclization reaction [29]. The IR spectrum of **4** is very similar to that of **3** with small shifts in wavenumbers. The intense NH stretching vibration in **4** was observed at 3289 cm^{-1}. The ^{1}H NMR spectrum of **4** was collected in DMSO-d_6. There is a new signal at $\delta = 2.79$ ppm as multiplet, which supports the formation of macrocycle, due to SCH$_2$ protons of 2,2′-dithioethanthiol. The ^{13}C NMR spectrum of **4** also supports this situation with two new signals belonging to SCH$_2$ carbons and is consistent with the proposed formulation. The LC−MS mass spectra of **4**, the presence of the molecular ion peak at $m/z = 729$ $[M + 1]^+$, confirm the proposed structure.

The cyclotetramerization of phthalonitrile derivative **4** to the metal-free phthalocyanine **5** was accomplished in dry 2-(dimethylamino)ethanol at reflux temperature for 28 h under an argon atmosphere. In the ^{1}H NMR spectrum of **5**, the typical shielding of inner core protons could not be observed due to the probable strong aggregation of the molecules [30]. The signals related to aromatic protons and aliphatic protons in the macrocyclic moieties and phthalocyanine skeleton gave significant absorbance characteristic of the proposed structure. The disappearance of the C≡N stretching vibration on the IR spectra of **4** suggested the formation of compound **5**. In addition to the results of elemental analysis, the mass spectrum was determined. The mass spectrum of metal-free phthalocyanine **5** was obtained by the LC−MS/MS technique and the molecular ion peak at $m/z = 2918$ $[M]^+$ was observed.

The metallophthalocyanines **6** and **7** were synthesized in good yield. The metallophthalocyanines **6** and **7** were obtained from dicyano derivative **4** and corresponding anhydrous metal salts [NiCl$_2$ and Zn(CH$_3$CO$_2$)$_2$] in a Schlenk system in quinoline at 190 °C for 7 and 8 h, respectively. The IR spectra of metallophthalocyanines **6** and **7** indicate the presence of NH group in the macrocyclic ring by the intense vibration at 3301 and 3306 cm^{-1}, respectively. The disappearance of strong C≡N stretching vibration of **4** is an evidence for the formation of metallophthalocyanines **6** and **7**. The rest of the IR spectra of metallophthalocyanines are very similar to those of the metal-free phthalocyanine **5**. The ^{1}H NMR spectra of these compounds are almost identical to those of metal-free phthalocyanine **5**. Also, it should be mentioned that the other differences in the ^{1}H NMR spectra of metal-free phthalocyanine and metallophthalocyanines were the broad signals encountered in the case of compounds **6** and **7**, owing to the aggregation of planar phthalocyanine molecules at the considerably high concentration used for NMR measurements. They are in agreement with the structural information. In the mass spectrum of **6** and **7**, the presence of molecular ion peaks at $m/z = 2977$ $[M + 2]^+$ and 2981 $[M]^+$, respectively, confirmed the proposed structures.

In general, phthalocyanines show typical electronic spectra with two strong absorption regions, one in the UV region at about 300−500 nm related to the B band and the other in the visible region at 600−700 nm related to the Q band [31]. The split Q bands in **5**, which are characteristic for metal-free phthalocyanines, were observed at $\lambda_{max} = 707$ and 656 nm. These Q band absorptions show the monomeric species with D_{2h} symmetry and due to the phthalocyanine ring related to the fully conjugated 18π electron system [32−34]. The presence of strong absorption bands in **5** in the near UV region at $\lambda_{max} = 449$,368, 326 and 296 nm also shows Soret region B bands which have been ascribed to the deeper π−π* levels of LUMO transitions.

The UV−vis absorption spectra of metallophthalocyanines **6** and **7** in DMF show intense Q absorption at $\lambda_{max} = 701$ and 713 nm, with a weaker absorptions at 656 and 681, 644 nm, respectively (Fig. 1). The single Q bands in metallo derivatives **6** and **7** are characteristic. This result is typical of metal complexes of substituted and unsubstituted metallophthalocyanines with D_{4h} symmetry [35]. B band absorptions of nickel(II) phthalocyanine **6** and zinc(II) phthalocyanine **7** were observed at $\lambda_{max} = 482$, 410, 311, 275 and 371, 272 nm as expected, respectively.

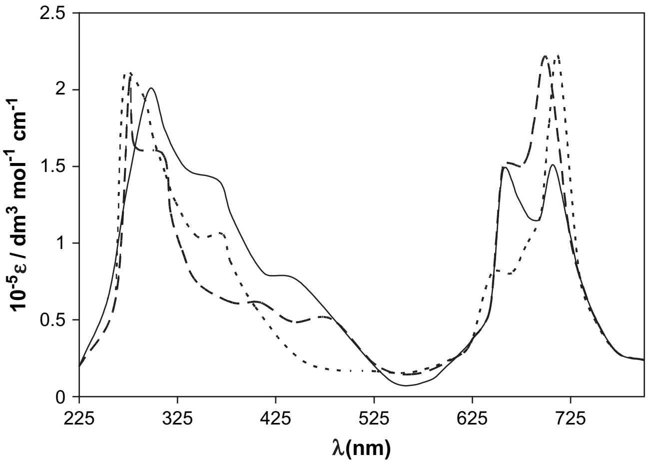


Fig. 1. UV−vis spectra of **5** (—), **6** (- - -) and **7** (· · ·) in dimethylformamide.

Acknowledgements

This study was supported by the Research Fund of Karadeniz Technical University, Project No. 2002.111.002.6 (Trabzon/Turkey). One of us, HZG, is grateful to Ghent University and The Scientific & Technological Research Council of Turkey (TÜBİTAK) for their supports. Technical assistance from Department of Organic Chemistry (S4) in Ghent University is gratefully acknowledged.

References

[1] Leznoff CC, Lever ABP. Phthalocyanines: properties and applications, vols. 1–4. Weinheim: VCH; 1989, 1993 and 1996.

[2] (a) Gregory P. High-technology applications of organic colorants. New York: Plenum Press; 1991;
(b) Gregory P. J Porphyrins Phthalocyanines 2000;4:432.

[3] (a) Kilmmert L, Haarer D. Adv Mater 1995;7:495;
(b) Birkett D. Chem Ind 2000;178.

[4] Moser FH, Thomas AL. The phthalocyanines. In: Manufacture and applications, vols. 1 and 2. Boca Raton, FL: CRC Press; 1983.

[5] (a) Wöhrle D, Meissner D. Adv Mater 1991;3:129;
(b) Eichhorn H. J Porphyrins Phthalocyanines 2000;4:88.

[6] Wright JD. Prog Surf Sci 1989;31:1.

[7] (a) Nalwa HS, Shirk JS. In: Leznoff CC, Lever ABP, editors. Phthalocyanines: properties and applications. New York: VCH; 1996. p. 79–118;
(b) Shirk JS, Pong RGS, Flom SR, Heckmann H, Hanack M. J Phys Chem 2000;104:1438;
(c) de la Torre G, Vazquez P, Agullo-Lopez F, Torres T. J Mater Chem 1998;8:1671.

[8] (a) Luk Centyanets EA. J Porphyrins Phthalocyanines 1999;3:424;
(b) Ali H, van Lier JE. Chem Rev 1999;99:2379.

[9] Cosomelli B, Roncuccin G, Dei D, Fantetti L, Ferroin F, Ricci M, et al. Tetrahedron 2003;59:10025.

[10] Beltrán HI, Esquivel R, Sosa-Sánchez A, Sosa-Sánchez JL, Höpfl H, Barba V, et al. Inorg Chem 2004;43:3555.

[11] (a) Rouhi AM. Chem Eng News November 1998;2:22;
(b) Ali H, van Lier JE. Chem Rev 1999;99:2379.

[12] (a) Rivellese MJ, Baumal CR. Ophthal Surg Lasers 1999;30:653;
(b) Priola SA, Raines A, Caughey WS. Science 2000;287:1503.

[13] Toyota K, Hasegava J, Nakatsuji H. J Phys Chem A 1997;101:446–51.

[14] Melson GA. Coordination chemistry of macrocyclic compounds. New York: Plenum; 1979.

[15] Lindoy LF. The chemistry of macrocyclic ligand complexes. UK: Press Syndicate of The University of Cambridge; 1989.

[16] Coughlin PK, Lippard SJ. Inorg Chem 1984;23:1446–51.

[17] Motekaitis RJ, Martell AE, Dietrich B, Lehn JM. Inorg Chem 1984;23:1588–91.

[18] Agnus Y, Louis R, Gisselbrecht JP, Weiss R. J Am Chem Soc 1984;106:93–102.

[19] Martin AE, Bulkowski JE. J Org Chem 1982;47:415–8.

[20] Lehn JM. Pure Appl Chem 1980;52:2441–59.

[21] Riesen A, Zehnder M, Kaden TA. Helv Chim Acta 1986;69:2074–9.

[22] Travis K, Busch DH. J Chem Soc Chem Commun 1970;1041–2.

[23] An H, Bradshaw JS, Izatt RM. Chem Rev 1992;92:543–72.

[24] Adam KR, Baldwin DS, Bashall A, Lindoy LF, McPartlin M, Powell HR. J Chem Soc Dalton Trans 1994;237.

[25] Craig AS, Kataky R, Parker D, Adams H, Bailey N, Schneider H. J Chem Soc Chem Commun 1989;1870.

[26] Kantekin H, Değirmencioğlu İ, Gök Y. Acta Chem Scand 1999;53:247.

[27] Gök Y, Kantekin H, Değirmencioğlu İ. Supramol Chem 2003;15:335.

[28] Perrin DD, Armarego WLF. Purification of laboratory chemicals. 2nd ed. Oxford: Pergamon; 1989.

[29] Yang Z, Bradshaw JS, Zhang XX, Savage PB, Krakowiak KE, Dalley NK, et al. J Org Chem 1999;64:3162–70.

[30] van Nostrum CF, Picken SJ, Schouten A-J, Nolte RJM. J Am Chem Soc 1995;117:9957–65.

[31] Yılmaz İ, Bekaroğlu Ö. Chem Ber 1996;129:967.

[32] Sielcken OE, Van Tilborg MM, Hendricks R, Drenth W, Nolte RJM. J Am Chem Soc 1987;109:4261.

[33] Cuellar EA, Marks T. Inorg Chem 1981;20:3766.

[34] Gök Y, Kantekin H, Bilgin A, Mendil D, Değirmencioğlu İ. J Chem Soc Chem Commun 2001;285–6.

[35] Takahashi K, Kawashima M, Tomita Y, Itoh M. Inorg Chim Acta 1995;232:69.