Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 2436–2440
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Microwave-assisted synthesis and characterization of novel metal-free and metallophthalocyanines containing four 14-membered tetraaza macrocycles

Zekeriya Bıyıklıoğlu [a], Halit Kantekin [a,*], Musa Özil [b]

[a] Department of Chemistry, Faculty of Arts and Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey
[b] Department of Chemistry, Rize Faculty of Arts and Sciences, Rize University, 53050 Rize, Turkey

Received 16 November 2006; received in revised form 13 February 2007; accepted 15 February 2007
Available online 20 February 2007

Abstract

The novel tetrasubstituted metal-free phthalocyanine (**6**) and metallophthalocyanines (**7**, **8**) bearing four 14-membered tetraaza macrocycles moieties on peripheral positions have been synthesized by cyclotetramerization reaction of phthalonitrile derivative (**5**) in a multi-step reaction sequence. The new compounds were characterized by a combination of IR, ^{1}H NMR, ^{13}C NMR, UV–vis, elemental analysis and MS spectral data.

Keywords: Phthalocyanine; Tetraazamacrocycle; Template effect; Macrocyclization; Tosylation

1. Introduction

Phthalocyanines and their metal complexes have attracted considerable attention as a result of their diverse optical, electronic, and coordination properties which have led to wide-ranging research for over 60 years [1–3]. In the last 20 years, phthalocyanine chemistry is undergoing a renaissance because these compounds and their derivatives exhibit singular and unconventional properties interesting for applications in the areas of non-linear optics, liquid crystals, electrochromic processes involving thin films, gas or chemical sensors photosensitizers, catalysts and for mercaptan oxidations and as therapeutic agents in pharmacology [4–9]. A disadvantage of phthalocyanines is their limited solubility in common organic solvents. For most of these applications, phthalocyanines with long chains or macrocyclic moieties [10,11] had to be synthesized in order to facilitate the above mentioned purposes and to enhance solubility.

The growing use of phthalocyanines as advanced materials during the last decade has encouraged research on the synthesis of new derivatized materials which differ in the central metal ion or in the peripheral substituents. Despite this extensive interest, there are relatively few synthetic routes to phthalocyanine derivatives, covering mainly phthalonitrile derivatives compounds [2].

Microwave-promoted organic reactions as well known as environmentally benign methods that can accelerate a great number of chemical processes. In particular, the reaction time and energy input are supposed to be mostly reduced in the reactions that are run for a long time at high temperatures under conventional conditions [12]. Microwave-assisted synthesis of phthalocyanines is novel [13–22].

We have previously synthesized phyhalocyanines containing tetrathiadiaza [23] and diazatetrathia [24] macrobicyclic moieties. In this paper, we have rapidly prepared metal-free and metallophthalocyanines by microwave irradiation and we describe characterization of the new metal-free and metallophthalocyanines, bearing tetraaza macrocyclic moieties.

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

0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.02.013

2. Experimental

3,3′-Piperazine-1,4-diyldipropan-1-amine **1** [25], 1,2-dichloro-4,5-dicyanobenzene **4** [26] were prepared according to the literatures. 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 [27]. 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 $CDCl_3$, DMSO-d_6, 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. Elemental analyses were determined by a LECO Elemental Analyser (CHNS O932) and 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 microwave oven were used all synthesis of phthalocyanines.

2.1. 1,12-Bis[(4-methyl)sulfonyl]-1,2,3,4,6,7,9,10,11,12-decahydro-5,8-ethanododecine (3)

3,3′-Piperazine-1,4-diyldipropan-1-amine **1** (3 g, 14.97 mmol) was dissolved in pyridine (30 ml) under nitrogen and powdered toluene-*p*-sulfonylchloride **2** (7.13 g, 37.42 mmol) was added portionwise over 0.5 h to the stirred and cooled in ice-salt bath at −10 °C. Stirring and cooling of the reaction mixture was continued for 1.5 h at −10 °C, then the mixture was stirred at room temperature overnight. The solution was poured slowly on ice (100 g) and diluted with water (100 ml). The precipitated ditosylate was filtered off and washed with cold water and diethyl ether . The product was dried in vacuo and obtained as a yellow solid. Yield: 4.95 g (65%), mp: 181–183 °C. Anal. Calc. for $C_{24}H_{36}N_4O_4S_2$: C, 56.66; H, 7.13; N, 11.01. Found: C, 56.38; H, 7.28; N, 11.28%. IR (KBr tablet) ν_{max}/cm^{-1}: 3250 (N–H), 3027 (Ar–H), 2956–2848 (Aliph. C–H), 1596 (N–H bending), 1478, 1321–1157 (SO_2), 1096, 990, 810, 658, 572. ^{1}H NMR. ($CDCl_3$), (δ: ppm): 7.63 (d, 4H, Ar–H), 7.25 (d, 4H, Ar–H), 6.12 (s, 2H, NH), 3.45 (t, 4H, CH_2–N), 2.43 (t, 8H, CH_2–N), 2.40 (s, 6H, CH_3), 2.31 (t, 4H, CH_2–N), 1.81 (m, 4H, CH_2–CH_2). ^{13}C NMR. ($CDCl_3$), (δ: ppm): 143.11, 137.01, 129.60, 126.95, 57.85, 53.02, 44.21, 23.85, 21.51. MS (EI), (*m*/*z*): 509 $[M+1]^+$.

2.2. 1,12-Bis[(4-methyl)sulfonyl]-1,2,3,4,6,7,9,10,11,12-decahydro-5,8-ethano- 1,5,8,12-benzo tetraazacyclotetradecine-14,15-dicarbonitrile (5)

1,12-Bis[(4-methyl)sulfonyl]-1,2,3,4,6,7,9,10,11,12-decahydro-5,8-ethanododecine **3** (4 g, 7.86 mmol) was dissolved in dry acetonitrile (200 ml),finely ground anhydrous K_2CO_3 (3.25 g, 23.58 mmol) was added and the mixture stirred for 2 h at 50 °C. A solution of 1,2-dichloro-4,5-dicyanobenzene **4** (1.54 g, 7.86 mmol) in dry acetonitrile (60 ml) was added dropwise over 4 h. After stirring for 4 days at 85 °C, the reaction mixture was poured into ice-water and stirred for 2 h. The mixture was evaporated until 20 ml under reduced pressure. The residue was extracted with (2 × 100) ml of chloroform. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure to give a orange crude product. The crude product was chromatographed on silica gel with chloroform as eluents. Yield: 3.03 g (61%), mp: 155–157 °C. Anal. Calc. for $C_{32}H_{36}N_6O_4S_2$: C, 60.74; H, 5.73; N, 13.28. Found: C, 60.39; H, 5.93; N, 13.56%. IR (KBr tablet) ν_{max}/cm^{-1}: 3082 (Ar–H), 2924–2853 (Aliph. C–H), 2237 (C≡N), 1591 (N–H bending), 1467, 1320–1142 (SO_2), 1092, 916, 810, 733, 659, 550. ^{1}H NMR. ($CDCl_3$), (δ: ppm): 7.98 (s, 2H, Ar–H), 7.57 (d, 4H, Ar–H), 7.33 (d, 4H, Ar–H), 4.57 (t, 4H, CH_2–N), 2.60 (t, 4H, CH_2–N), 2.41 (s, 6H, CH_3), 2.39 (t, 8H, CH_2–N), 1.71 (m, 4H, CH_2–CH_2). ^{13}C NMR. ($CDCl_3$), (δ: ppm): 144.72, 135.18, 129.86, 128.56, 127.21, 119.43, 115.31, 112,72, 59.41, 58.41, 52.97, 29.92, 21.74 . MS (FAB), (*m*/*z*): 635 $[M+3]^+$, 671 $[M+K]^+$.

2.3. Metal-free phthalocyanine (6)

A mixture of 1,12-bis[(4-methyl)sulfonyl]-1,2,3,4,6,7,9,10,11,12-decahydro-5,8-ehano-1,5,8,12-benzotetraazacyclotetradecine-14,15-dicarbonitrile **5** (0.7 g, 1.10 mmol) and 2-(dimethylamino)ethanol (2 ml) was irradiated in a microwave oven at 175 °C, 350 W for 8 min. After cooling to room temperature the reaction mixture refluxed with ethanol to precipitate the product which was filtered off. The dark green product was washed with hot ethanol (40 ml) and dried in vacuo. The solid product was chromatographed on silica gel with chloroform/methanol (9:1) as eluents. This product is soluble in DMF, DMSO and pyridine. Yield: 215 mg (31%), mp > 300 °C. Anal. Calc. for $C_{128}H_{146}N_{24}O_{16}S_8$: C, 60.68; H, 5.80; N, 13.26. Found: C, 60.39; H, 6.28; N, 13.03%. IR (KBr tablet) ν_{max}/cm^{-1}: 3325 (N–H), 3075 (Ar–H), 2923–2846 (Aliph. C–H), 1621, 1596, 1443, 1399–1155 (SO_2), 1079, 1015, 932, 886, 749. ^{1}H NMR. (DMSO-d_6), (δ: ppm) 8.23–7.70 (m, 8H, Ar–H), 7.57–7.31 (d, 32H, tosyl Ar–H), 4.53 (t, 16H, CH_2–N), 2.67 (t, 32H, CH_2–N), 2.59 (t, 16H, CH_2–N), 2.40 (s, 24H, CH_3), 1.67 (m, 16H, CH_2–CH_2), −4.98 (br, 2H, D_2O exchangeable NH) : UV–vis (pyridine): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 288 (4.96), 321 (4.88), 344 (4.75), 431 (4.56), 620 (4.61), 686 (4.72). MS (FAB), (*m*/*z*): 2533 $[M]^+$.

2.4. Nickel(II) phthalocyanine (7)

A mixture of 1,12-bis[(4-methyl)sulfonyl]-1,2,3,4,6,7,9,10,11,12-decahydro-5,8-ehano-1,5,8,12-benzotetra-

azacyclotetradecine-14,15-dicarbonitrile **5** (0.7 g, 1.10 mmol), anhydrous $NiCl_2$ (35.66 mg, 0.27 mmol) and 2-(dimethylamino)ethanol (2 ml) was irradiated in a microwave oven at 175 °C, 350 W for 8 min. After cooling to room temperature the reaction mixture refluxed with ethanol to precipitate the product which was filtered off. The green product was washed with hot ethanol (30 ml) and dried in vacuo. The solid product was chromatographed on silica gel with chloroform/methanol (3:1) as eluents. This product is soluble in DMF, DMSO and pyridine. Yield: 195 mg (28%), mp > 300 °C. Anal. Calc. for $C_{128}H_{144}N_{24}O_{16}S_8Ni$: C, 59.36; H, 5.60; N, 12.97; Ni, 2.26. Found: C, 58.97; H, 5.82; N, 12.43; Ni, 2.58%. IR (KBr tablet) ν_{max}/cm^{-1}: 3076 (Ar–H), 2924–2840 (Aliph. C–H), 1618, 1597, 1418, 1391–1153 (SO_2), 1075, 966, 888, 785. ^1H NMR. (DMSO-d_6), (δ: ppm): 8.25–7.72 (m, 8H, Ar–H), 7.60–7.33 (d, 32H, tosyl Ar–H), 4.68 (t, 16H, CH_2–N), 2.74 (t, 32H, CH_2–N), 2.65 (t, 16H, CH_2–N), 2.49 (s, 24H, CH_3), 1.81 (m, 16H, CH_2–CH_2) UV–vis (pyridine): λ_{max}/nm: [(10^{-5} ε $dm^3\,mol^{-1}\,cm^{-1}$)]: 278 (4.87), 305 (4.74), 395 (4.68), 611 (4.45), 687 (4.68). MS (FAB), (m/z): 2589 $[M]^+$.

2.5. Zinc(II) phthalocyanine (8)

A mixture of 1,12-bis[(4-methyl)sulfonyl]-1,2,3,4,6,7,9,10,11,12-decahydro-5,8-ehano-1,5,8,12-benzotetraazacyclotetradecine-14,15-dicarbonitrile **5** (0.7 g, 1.10 mmol), anhydrous zinc acetate (50.42 mg, 0.27 mmol) and 2-(dimethylamino)ethanol (2 ml) was irradiated in a microwave oven at 175 °C, 350 W for 8 min. After cooling to room temperature the reaction mixture refluxed with ethanol to precipitate the product which was filtered off. The blue product was washed with hot ethanol (35 ml) and dried in vacuo. The solid product was chromatographed on silica gel with chloroform/ethanol (3:2) as eluents. This product is soluble in DMF, DMSO and pyridine. Yield: 229 mg (32%), mp > 300 °C. Anal. Calc. for $C_{128}H_{146}N_{24}O_{16}S_8Zn$: C, 59.20; H, 5.58; N, 12.94; Zn, 2.51. Found: C, 58.78; H, 6.04; N, 12.61; Zn, 2.88%. IR (KBr tablet) ν_{max}/cm^{-1}: 3082 (Ar–H), 2923–2851 (Aliph. C–H), 1624, 1598, 1410, 1371–1182 (SO_2), 1087, 938, 891, 742. ^1H NMR. (DMSO-d_6), (δ: ppm): 8.27–7.74 (m, 8H, Ar–H), 7.59–7.32 (d, 32H, tosyl Ar–H), 4.55 (t, 16H, CH_2–N), 2.70 (t, 32H, CH_2–N), 2.60 (t, 16H, CH_2–N), 2.42 (s, 24H, CH_3), 1.71 (m, 16H, CH_2–CH_2). UV–vis (pyridine): λ_{max}/nm: [(10^{-5} ε $dm^3\,mol^{-1}\,cm^{-1}$)]: 268 (5.15), 310 (5.01), 350 (4.84), 620 (4.53), 686 (4.94). MS (FAB), (m/z): 2597 $[M+1]^+$.

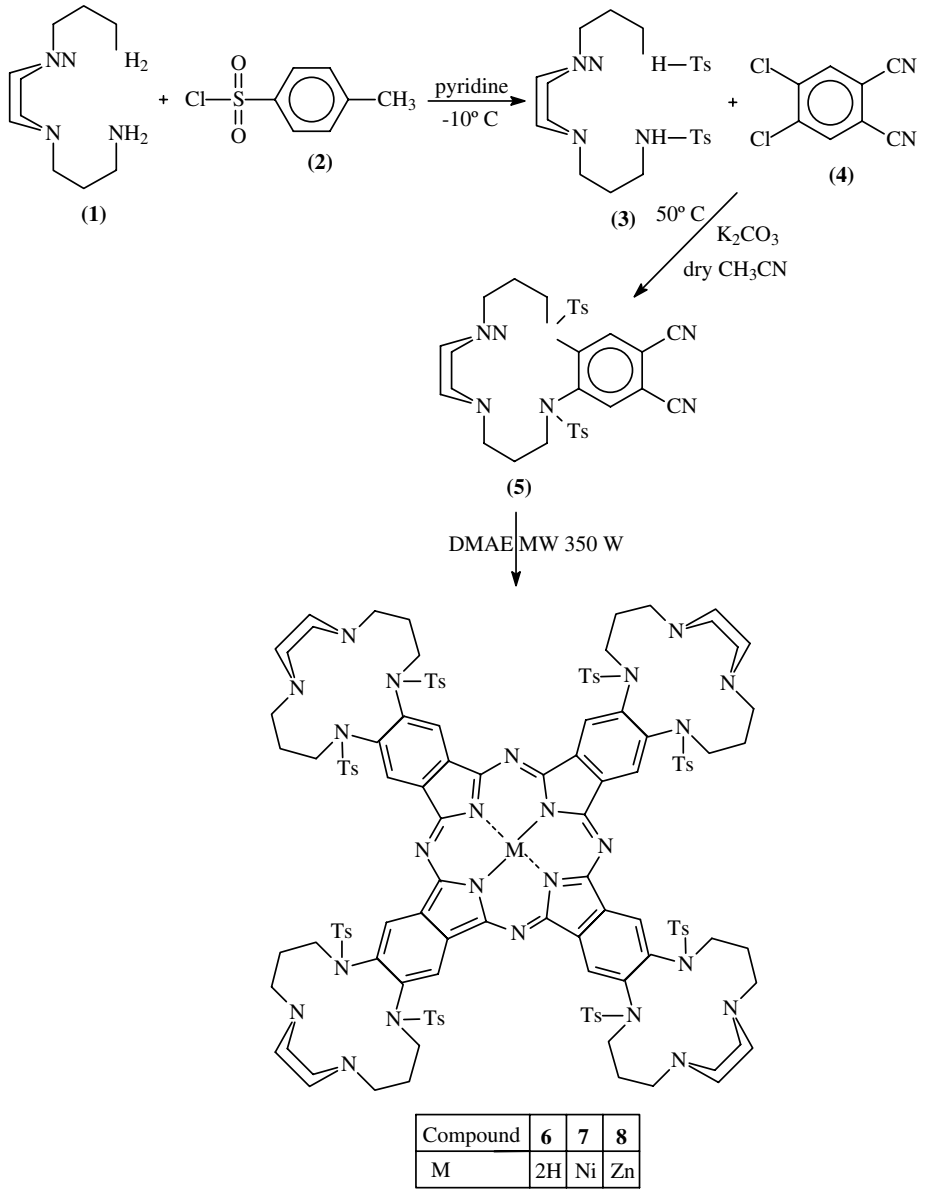
3. Results and discussion

The preparation of the target metal-free **6** and metallophthalocyanines **7**, **8** is shown in Scheme 1. The structures of novel compounds were characterized by a combination of ^1H NMR, ^{13}C NMR, IR, UV–vis, elemental analysis and MS spectral data. 3,3′-Piperazine-1,4-diyldipropan-1-amine **1** [25], 1,2-dichloro-4,5-dicyanobenzene **4** [26] were prepared according to the literatures (Fig. 1).

The aliphatic amine groups of **1** was tosylated in pyridine at −10 °C with *p*-toluenesulfonylchloride **2** to protect amino groups and to make use of the high reactivity of tosylamides in further cyclization reactions. ^1H NMR, ^{13}C NMR, IR, and MS spectra verified the structure of **3**. In the IR spectrum of **1**, the intense absorption bands at 3351–3292 cm^{-1} for **1**, corresponding to the $–NH_2$ groups, disappear after the conversion to the tosylamino compounds. The rest of the spectra of **1** resembles closely that of **3** including the characteristic vibration of aliphatic and other groups. The IR spectrum of **3** clearly indicates the presence of N–H group by the intense stretching bands at 3250 cm^{-1}. ^1H NMR spectra of 3 are almost identical, with only small changes in shifts. The difference between the two spectra of tosylated amino and free amino groups **1** and **3** is clear from the presence of sulfonamide bands in **3** at 6.12 ppm. ^{13}C NMR spectrum of **3** clearly indicates the presence of tosyl Ar–H group by the intense bands in **3** at 143.11, 137.01, 129.60 and 126.95 ppm. The MS mass spectrum of **3**, which shows a peak at $m/z = 509$ $[M+1]^+$ support the proposed formula for this compound.

Compound **5** was prepared from 1,12-bis[(4-methyl)sulfonyl]-1,2,3,4,6,7,9,10,11,12-decahydro-5,8- ethanododecine **3** with 1,2-dichloro-4,5-dicyanobanzene **4** in dry acetonitrile containing potassium carbonate as the base [28,29]. The reaction was carried out in dry acetonitrile at 85 °C and gave moderate yields (61%). Comparison of the IR spectral data clearly indicated the formation of compound **5** by the disappearance of the C–Cl band of 1,2-dichloro-4,5-dicyanobanzene at 684 cm^{-1} and of NH band of compound **3** at 3250 cm^{-1}, and the appearance of a new absorption at 2237 cm^{-1} (C≡N). The spectrum of **5** also indicates the presence of alkyl, CN, and SO_2 groups by the intense stretching bands at 2924–2853 (C–H), 2237 (C≡N) and 1320–1142 cm^{-1} ($–SO_2$). ^1H NMR spectra of **5** showed a new signal due to aromatic proton at $\delta = 7.98$ ppm, as expected. While the ^1H NMR spectra of **3** and **5** are similar, the proton-decoupled ^{13}C NMR spectrum indicated the presence of the nitrile carbon atoms in 5 at $\delta = 112.72$ ppm. The MS mass spectrum of compound **5**, which shows a peak at $m/z = 635$ $[M+3]^+$, 671 $[M+K]^+$ support the proposed formula for this compound.

Metal-free phthalocyanine **6** was synthesized by microwave irradiation of the corresponding dicyano compound **5** in 2-(dimethylamino)ethanol for 8 min. The IR spectrum of metal-free phthalocyanine **6** shows the 3325 (NH), 3075 (Ar–H) vibrations. The inner core N–H protons of metal-free phthalocyanine **6** were also identified in the ^1H NMR spectrum. At high concentration strong shielding of the cavity protons in the phthalocyanine core of this compound was indicated by a broad resonance at $\delta = -4.98$ ppm [23,30] which could be attributed to the NH resonance. The signals related to aromatic protons and aliphatic protons in the macrocyclic moieties and phthalocyanine skeleton gave significant absorbance char-



Compound	6	7	8
M	2H	Ni	Zn

Scheme 1. The synthesis of the metal-free phthalocyanine and metallophthalocyanines (Ts = *p*-toluenesulphonyl).

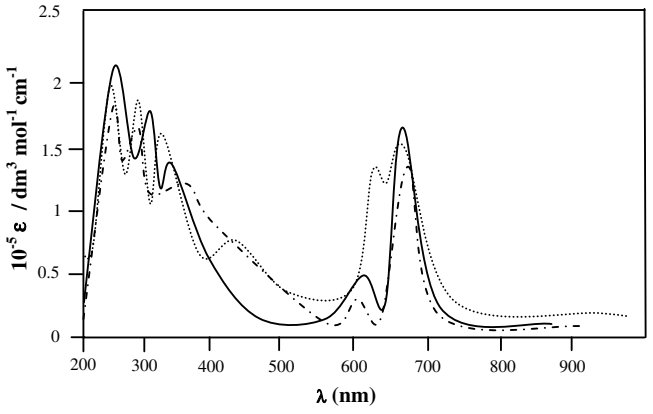


Fig. 1. UV–vis spectra of compounds **6** (...), **7** (–·–·) and **8** (—) in pyridine.

acteristic of the proposed structure. The disappearance of the C≡N stretching vibration on the IR spectra of **5** suggested the formation of compound **6**. The MS mass spectrum of compound **6**, which shows a peak at $m/z = 2533$ $[M]^+$ support the proposed formula for this compound.

The metallophthalocyanines **7**, **8** were synthesized in moderate yield 28%, 32%, respectively. The metallophthalocyanines **7** and **8** were obtained from dicyano derivative **5** and corresponding anhydrous metal salts $NiCl_2$ and $Zn(CH_3COO)_2$ respectively, by microwave irradiation in 2-(dimethylamino)ethanol for 8 min. The IR spectra of metallophthalocyanines **7** and **8** the disappearance of strong C≡N stretching vibration of **5** is an evidence for the formation of metallophthalocyanines **7** and **8**. The rest of the IR spectra of metallophthalocyanines are very similar to those of the metal-free phthalocyanine **6**. In the ^1H

NMR spectra of these compounds are almost identical to those of metal-free phthalocyanine **6**. 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 **7** and **8**, 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 compounds **7** and **8**, the presence of molecular ion peaks at $m/z = 2589$ $[M]^+$, 2597 $[M+1]^+$respectively, confirmed the proposed structures. We used a domestic oven synthesis of compounds **6**–**9** including 300 W, 175 °C as conditions.

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 **6**, which are characteristic for metal-free phthalocyanines were observed at $\lambda_{max} = 686$ and 620 nm. These Q band absorptions broad and non-symmetric because of aggregation [32,33]. Also an increase in the concentration leads to aggregation which is easily monitored by the position of the Q-band which is shifted to shorter wavelengths, and to a decrease in molar absorption coefficient [34–36]. The presence of strong absorption bands in **6** in the near UV region at $\lambda_{max} = 431$, 344, 321 and 288 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 **7** and **8** in pyridine show intense Q absorption at $\lambda_{max} = 687$ and 686 nm, with a weaker absorptions at 611 and 620 nm, respectively. The single Q bands in metallo derivatives **7** and **8** are characteristic. This result is typical of metal complexes of substituted and unsubstituted metallophthalocyanines with D_{4h} symmetry [37]. Soret region B band absorptions of nickel(II) phthalocyanine **7** and zinc(II) phthalocyanine **8** were observed at $\lambda_{max} = 395$, 305, 278 and 350, 310, 268 nm as expected, respectively.

Acknowledgement

This study was supported by the Research Fund of Karadeniz Technical University, Project No: 2002.111.002.6 (Trabzon–Turkey).

References

[1] F.H. Moser, A.L. Thomas, The Phthalocyanines, CRC Press, Boca Raton, 1983.
[2] C.C. Leznoff, A.B.P. Lever, Phthalocyanines: Properties and Applications, VCH, New York, 1989.
[3] H. Schultz, H. Lehman, M. Rein, M. Hanack, Struc. Bond (Berlin) 74 (1990) 41.
[4] C.G. Claessens, W.J. Blau, M. Cook, M. Hanack, R.J.M. Nolte, T. Torres, D. Wöhrle, Monatsh. Chem. 132 (2001) 3.
[5] Ö. Bekaroğlu, Appl. Organomet. Chem. 10 (1996) 605.
[6] Ö. Bekaroğlu, J. Porphyrin. Phthalocyan. 4 (2000) 65.
[7] M.J. Cook, J. Mater. Chem. 6 (1996) 677.
[8] R. Zhou, F. Jore, W. Gopel, Z.Z. Oztürk, Ö. Bekaroglu, Appl. Organomet. Chem. 10 (1996) 557.
[9] J.J. Simon, J. Andre, Molecular Semiconductors, Springer, Berlin, 1985.
[10] A.R. Koray, V. Ahsen, Ö. Bekaroğlu, J. Chem. Soc., Chem. Commun. (1986) 932.
[11] A. Beck, K.M. Mangold, M. Hanack, Chem. Ber. 124 (1991) 2315.
[12] A. Loupy, Microwave in Organic Synthesis, Wiley-VCH, Weinheim, 2002.
[13] M. Özil, E. Ağar, S. Şaşmaz, B. Kahveci, N. Akdemir, İ.E. Gümrükçüoğlu, Dyes Pigments, in press.
[14] M.O. Liu, A.T. Hu, J. Organomet. Chem. 689 (2004) 2450.
[15] A. Shaabani, R.M. Maleki, A. Maleki, A.H. Rezayan, Dyes Pigments, in press.
[16] M.O. Liu, C.H. Tai, W.Y. Wang, J.R. Chen, A.T. Hu, T.H. Wei, J. Organomet. Chem. 689 (2004) 1078.
[17] C. Kantar, N. Akdemir, E. Ağar, N. Ocak, S. Şaşmaz. Dyes Pigments, in press.
[18] V. Csokai, G. Parlagh, A. Grofcsik, M. Kubinyi, I. Bitter, ChemInform 34 (2003) 37.
[19] N. Jain, A. Kumar, S.M.S. Chauhan, Synth. Commun. 35 (2005) 1223.
[20] B. Kahveci, S. Şaşmaz, M. Özil, C. Kantar, B. Koşar, O. Büyükgüngör, Turk. J. Chem. 30 (2006) 681.
[21] R.S. Varma, K.P. Naicker, D. Kumar, R. Dahiya, P.J.J. Liesen, Microwave Power Electromag. Energy 34 (1999) 113.
[22] S.K. Junk, H.J. Kwon, M.S. Shon, P.J. Ko, S.K. Shin, S.S. Park, J. Mater. Sci. 39 (2004) 723.
[23] Y. Gök, H. Kantekin, İ. Değirmencioglu, Supramol. Chem. 15 (2003) 335.
[24] Y. Gök, H. Kantekin, A. Bilgin, D. Mendil, İ. Değirmencioglu, Chem. Commun. (2001) 285.
[25] F. Chuburu, R. Tripier, M. Le Baccon, H. Handel, Eur. J. Org. Chem. (2003) 1050.
[26] D. Wöhrle, M. Eskes, K. Shigehura, A. Yamada, Syntheses (1993) 194.
[27] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, second ed., Pergamon, Oxford, 1989.
[28] E. Ağar, S. Şaşmaz, N. Akdemir, İ. Keskin, J. Chem. Soc., Dalton Trans. (1997) 2087.
[29] B.K. Vriesema, J. Buter, R.M. Kellogg, J. Org. Chem. 49 (1984) 110.
[30] A. Bilgin, B. Ertem, Y. Gök, Tetrahedron Lett. 44 (2003) 3829;
I. Gürol, V. Ahsen, J. Porphyrin. Phthalocyan. 4 (2000) 621.
[31] R.J. Motekaitis, A.E. Martell, B. Dietrich, J.M. Lehn, Inorg. Chem. 23 (1984) 1588.
[32] C.F. van Nostrum, S.J. Picken, R.J.M. Nolte, Angew. Chem., Int. Ed. Engl. 33 (1994) 2173.
[33] C.F. van Nostrum, S.J. Picken, A.J. Schouten, R.J.M. Nolte, J. Am. Chem. Soc. 117 (1995) 9957.
[34] M. Kandaz, J. Porphrin. Phthalocyan. 3 (1999) 339.
[35] A.I. Okur, A. Gül, A. Cihan, N. Tan, Ö. Bekaroğlu, Synth. React. Inorg. Met. Org. Chem. 20 (1990) 139.
[36] I. Yılmaz, Ö. Bekaroğlu, J. Chem. Soc., Dalton Trans. (1992) 2485.
[37] A. Reisen, M. Zehnder, T.A. Kaden, Helv. Chim. Acta 69 (1986) 2074.