Polyhedron 51 (2013) 142-155

Contents lists available at SciVerse ScienceDirect

Polyhedron



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

Synthesis, characterization, aggregation, fluorescence, electrical and thermal properties of novel octasubstituted metal-free and metallophthalocyanines

Çiğdem Yağcı, Ahmet Bilgin*

Department of Science Education, Kocaeli University, 41380 Kocaeli, Turkey

ARTICLE INFO

Article history: Received 2 November 2012 Accepted 11 December 2012 Available online 8 January 2013

Keywords: Phthalocyanine Metallophthalocyanines Aggregation AC Electrical conductivity DSC Fluorescence

ABSTRACT

A dinitrile precursor, 1,2-bis(3-hydroxypropylmercapto)-4,5-dicyanobenzene (**3**), was synthesized via base-catalyzed nucleophilic aromatic chlorine displacement of 4,5-dichlorophthalonitrile with 3-mercapto-1-propanol. A novel metal-free phthalocyanine (**4**) (M = 2H) and its metal complexes (**5**)-(**8**) (M = Zn, Ni, Cu and Co) were prepared by the cyclotetramerization reaction of (**3**) with the appropriate materials. The aggregation property of the zinc(II) phthalocyanine (**5**) was investigated in terms of concentration, Ag⁺, Hg²⁺, Pb²⁺ and Cd²⁺ cations and also different solvents, such as dimethylformamide and pyridine. Complexation of the peripheral dithia groups of (**5**) with Ag⁺ or Pd²⁺ yields the pentanuclear complex (**9**) or (**10**), respectively. The fluorescence spectrum of compound (**5**) was also studied. The electrical conductivities of (**5**)–(**10**) in air and under vacuum were found to be $\sim 10^{-9}-10^{-5}$ S m⁻¹. All the novel compounds were characterized by elemental analysis, UV–Vis, FT-IR, NMR and MS spectral data and DSC techniques.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Phthalocyanines (Pcs) and their metal complexes (MPcs) have attracted considerable attention due to their impressive and useful chemical and physical properties. The diverse functionality of the phthalocyanine macrocycle originates from its $18-\pi$ electron aromatic system [1]. Functional phthalocyanines are of interest for making Pcs available for further chemical reactions and new applications. In addition to their use as highly stable blue and green colorants, Pcs have found applications in an ever increasing number of diverse fields, including high technology fields such as non-linear optics [2,3], photosensitizers [4], gas sensors [5], catalysts [6], liquid crystals [7], optical data storage [8], sensitizers for photodynamic therapy of cancer [9] and Langmuir–Blodgett films [10] amongst others.

The substituents on the phthalocyanine ligand influence the solution and solid-state properties to a large degree and the photophysical properties of the Pc dyes are strongly influenced by the presence and nature of the central metal ion. Metallophthalocyanine complexes substituted with peripheral alkylsulfanyl derivates show especially excellent spectroscopic and photochemical properties, such as wavelength absorption over 700 nm. A systematic comparison of oxygen and sulfur as covalent linkers on octasubstituted zinc(II) phthalocyaninates shows a bathochromic shift of \sim 30 nm in the absorption and emission maxima, and of \sim 60 nm

in the triplet-triplet absorption spectra when alkylsulfanyl instead of alkyloxy moieties were present. The excited states of phthalocyanines are expected to play an important role in phthalocyanine applications. However, relatively little work has been done on phthalocyanines in solutions [11].

Phthalocyanines are the most extensively studied materials among organic semiconductors [12,13]. The electrical conductivities of phthalocyanines are influenced by the nature of the central metal or metalloid, substituents at the peripheral benzene rings and the surrounding atmosphere [14], and change by many (multi) orders of magnitude under the influence of gases [15] and in the presence of dopants [16].

The central metal ion and peripheral functional groups having rich electron-donor units strongly affect the optical and electrochemical properties of the phthalocyanine compounds [17]. The introduction of electron donating sulfur groups at the peripheral position will result in the shift of the Q band to even longer wavelengths [18,19]. Our primary aim has been the synthesis of new phthalocyanines with various functional groups and macrocycles. We have previously synthesized novel polymeric phthalocyanines having O-, S- and N- containing functionalities, such as peripherally long triazadioxa derivatives and very flexible 1,3,6,9,11-pentathiaundecane moieties [20], macrocyclic groups [21], and monomeric phthalocyanine with ethylmercapto-tetrathiamonoaza macrocycles and an α -methylferrocenylmethoxy unit [22]. These compounds have shown a high tendency to bind alkali- or transition-metal ions and also to form molecular assemblies through intermolecular interactions. Although phthalocyanines



^{*} Corresponding author. Fax: +90 262 303 2403. E-mail address: abilgin@kocaeli.edu.tr (A. Bilgin).

^{0277-5387/\$ -} see front matter © 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.poly.2012.12.023

with N- and O-donor substituents have been frequently encountered, those with thioether moieties are relatively few [18]. Also a small number of recent patents and proceedings describe the use of these types of compounds as IR absorbers [23].

In this present work, we described the synthesis and characterization of hydroxyl-functionalized metal-free and metallophthalocyanines (**5–8**) with eight comparatively long-chain peripheral alkyl thioether groups which can not only enable the potential use as surface anchors [24] but also can be adapted to preparation of new compounds. The complexation of the thio-donor groups of (**5**) with Ag⁺ or Pd²⁺ has been investigated. The AC electrical conductivities of the metal free and metallophthalocyanines were measured in air atmosphere and under vacuum in the sandwich form covered with silver paste. The aggregation and the fluorescence properties of compound (**5**) were examined. The thermal properties of the compounds were investigated by DSC with a scanning rate of 10 °C/min between -4 and 440 °C. The new compounds were characterized using elemental analysis, UV–Vis, FT-IR, NMR and MS spectral data.

2. Experimental

2.1. Materials

Reactions were performed under an atmosphere of argon using standard Schlenk techniques unless otherwise specified. 4,5-Dichlorophthalonitrile was synthesized according to the literature method [25]. 3-Mercapto-1-propanol, 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU), hydrochloric acid (HCl), dichloromethane (CH₂₋ Cl₂), methanol (MeOH), phosphorus pentoxide (P₂O₅), 1-pentanol, dimethylsulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF), chloroform (CHCl₃), pyridine, 2-dimethylaminoethanol (DMAE), petroleum ether, toluene, ethylene glycol, ethanol, acetone and diethyl ether were received from commercial suppliers. Anhydrous metal salts were prepared using Zn(CH₃₋ COO)₂·2H₂O, NiCl₂·6H₂O, CuCl₂·2H₂O and CoCl₂·6H₂O after drying in a vacuum oven for 4 h at 150, 290, 120 and 150 °C, respectively [26–29]. Na₂CO₃ was used after drying in a vacuum oven at 180 °C for 36 h [30]. All organic solvents were dried and purified as described by Perrin and Armarego [31].

2.2. Equipment

¹H NMR spectra were recorded on a BRUKER DRX-500 AVANCE spectrometer at 500 MHz and a Varian Mercury Plus 300 MHz spectrometer with d_6 -DMSO as the solvent and tetramethylsilane as the internal standard. ¹³C NMR spectra were recorded on a Varian Mercury Plus 75 MHz spectrometer with d_6 -DMSO as the solvent and tetramethylsilane as the internal standard. Transmission IR spectra of the samples were recorded on a FTIR spectrophotometer (Schimadzu FTIR-8201 PC) in the spectral range 4000-400 cm⁻¹ with samples in KBr pellets. UV–Vis spectra were recorded on a model T80+ UV/Vis spectrometer using a 1 cm pathlength quartz UV cell. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluoremeter in 1 cm pathlength cuvettes at room temperature. Mass spectra were acquired in linear modes with average of 50 shots on a Bruker Daltonics Microflex Maldi-TOF mass spectrometer (Bremen, Germany) equipped with a nitrogen UV-Laser operating at 337 nm and a Bruker Daltonics Micro-TOF mass spectrometer with an orthogonal electrospray ionization (ESI) source. The melting points of the compounds were determined using an electrothermal melting point apparatus (Barnstead Electrothermal IA9100) and were uncorrected. The elemental analysis of the compounds was determined on a CHNS-932 LECO and Elementar Vario MICRO Cube instrument. The metal contents of the metallophthalocyanines were determined on a Unicam 929 AA spectrophotometer. For the electrical measurements, the surfaces of the samples were covered with silver paste to form electrodes. An LCR meter (AGILENT 4284A) equipped with an OXFORD-ITC-502 temperature controller was used for dielectric measurements in the range 1 kHz to 1 MHz frequency and 300–400 K temperature under vacuum ($\sim 10^{-3}$ Torr). Thermal properties were determined by DSC (Perkin Elmer DSC 4000) measurements with a 10 °C min⁻¹ heating rate between -4 and 440 °C.

2.3. Synthesis

2.3.1. 1,2-Bis(3-hydroxypropylmercapto)-4,5-dicyanobenzene (3)

3-Mercapto-1-propanol (0.7 mL, 7.68 mmol) was added to a solution of 4.5-dichlorophthalonitrile (5.25 g, 30 mmol) in dry DMF (10 mL) at room temperature and the reaction mixture was degassed twice. Thereafter the temperature was increased to 55 °C. Finely ground dry Na₂CO₃ (2.04 g, 19.2 mmol) was added to the reaction medium in six equal portions at 30 min intervals with efficient stirring. After degassing one more time, the reaction mixture was stirred at the same temperature for 5 days. At the end of this period, the reaction mixture was cooled to room temperature, filtered off and then evaporated to dryness under reduced pressure. A minimum amount of dichloromethane was added to the semi-solid part. After filtering off, the obtained part was washed with cold dichloromethane. The crude product was dissolved in a minimum amount of MeOH at 55 °C. After filtering the hot solution, the solution was kept in a refrigerator overnight and the precipitated yellow colored microcrystals that subsequently formed were filtered. The pure product (3) was dried over P₂O₅ at 50 °C in a vacuum atmosphere. R_f 0.72 (7:2:1 Chloroform:petroleum ether:MeOH).Yield: 0.42 g (54%); m.p.: 162 °C. C₁₄₋ H₁₆N₂O₂S₂ (308.06): Calc. C 54.52, H 5.23, N 9.08, S 20.79; found C 53.49, H 5.08, N 8.91, S 20.87%. IR (KBr) v_{max} (cm⁻¹): 3454 (-OH), 3078 (=CH aromatic), 2939, 2893 (-CH₂ aliphatic), 2227 (-C≡N), 1564 (aromatic -C=C), 686 (C-S). ¹H NMR (ppm, d_6 -DMSO) δ : 7.87 (s. 2H, ArH), 4.68 (t, 2H, OH), 3.49 (q, 4H, OCH₂), 3.19 (t, 4H, SCH₂), 1.75 (p, 4H, -CH₂). ¹³C NMR (ppm, d₆-DMSO): 143.67 (ArCS), 128.83 (ArCH), 116.90 (C=N), 110.78 (ArC), 59.69 (CH₂OH), 31.67 (SCH₂), 28.77 (SCH₂CH₂). MS (ESI-MS) *m*/*z*: 367.11 [M+2H₂O+Na]⁺.

2.3.2. 2,3,9,10,16,17,23,24-Octakis(3-hydroxypropylmercapto) phthalocyanine (**4**)

A standard Schlenk tube was charged with (0.150 g, 0.48 mmol) (3), 4.0 mL dry 1-pentanol and 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.15 mL, 0.16 g, 1.0 mmol) and degassed several times. The temperature was gradually increased up to 90 °C and the flask was degassed again with argon. Then the reaction mixture was stirred at 145 °C for 3 days. After cooling to room temperature, the reaction mixture was poured into 120 mL of ice-water mixture and stirred until the ice melted. The obtained dark green product was filtered off and washed with chloroform, petroleum ether and then acetone. The crude residue was purified by silica gel column chromatography (eluant: THF/MeOH, 10:1, v/v). The final petroleum greenish product was dried under vacuum over P2O5 at 55 °C until dryness. Yield: 53 mg (71%); m.p. >340 °C. C₅₆H₆₆N₈O₈S₈ (1233.27): Calc. C 54.43, H 5.38, N 9.07, S 20.76; found: C 54.01, H 5.17, N 9.51, S 20.98%. IR (KBr) v_{max} (cm $^{-1}$): 3371 (–OH), 3290 (-N-H), 3073 (=CH aromatic), 2923-2854 (-CH₂ aliphatic), 1618, 1560 (aromatic -C=C-), 1058 (-N-H), 666 (-C-S). ¹H NMR (ppm, d₆-DMSO) δ: 8.022 (s, br, 8H, ArH), 4.92 (t, br, 8H, OH), 3.83 (q, br, 16H, OCH₂), 3.54 (t, 16H, SCH₂), 2.12 (p, br, 16H, -CH₂), -3.97 (br, 2H, N–H). λ_{max} , nm (log ε): 733 (4.77), 706 (4.76), 671 (4.40), 638 (4.28), 362 (4.66), 331 (4.72). MS (MALDI-TOF) m/z: 1234.80 [M+1]⁺.

2.3.3. 2,3,9,10,16,17,23,24-Octakis(3-hydroxypropylmercapto) phthalocyaninatozinc(II) (**5**) and 2,3,9,10,16,17,23,24-octakis (3-hydroxypropylmercapto)phthalocyaninatocopper(II) (**7**)

Compound (**3**) (0.200 g, 0.64 mmol), anhydrous $Zn(CH_3COO)_2$ (0.119 g, 0.64 mmol) or anhydrous $CuCl_2$ (0.064 g, 0.48 mmol) and 4.0 mL of dry 1-pentanol were placed in a standard Schlenk tube under an argon atmosphere and degassed several times. The temperature was gradually increased up to 90 °C and DBU (0.15 mL, 0.16 g, 1.0 mmol) was added to the reaction medium. After degassing with argon, the temperature was increased up to 160 °C and held at reflux temperature for 3 days in an argon atmosphere. Thereafter the reaction mixture was cooled to room temperature and poured into 50 mL ice–water mixture and stirred until all the ice melted. The resultant greenish precipitate was filtered off and washed with water, diethyl ether and acetone to remove organic and inorganic residues. The final green product (**5**) was then isolated by silica gel column chromatography with THF/MeOH (10:1, v/v) and dried under vacuum over P_2O_5 at 55 $^\circ\text{C}$ until dry.

Compound (**5**): Yield: 93 mg (88%); m.p.: 335 °C. $C_{56}H_{64}N_8O_8S_8$. Zn (1296.19): Calc. C 51.78, H 4.97, N 8.63, S 19.74, Zn 5.03; found: C 51.57, H 4.79, N 8.57, S 19.49, Zn 5.25%. IR (KBr) v_{max} (cm⁻¹): 3315 (-OH), 3066 (=CH aromatic), 2925–2867 (-CH₂ aliphatic), 1647–1591, (aromatic -C=C-), 698 (-C-S). ¹H NMR (ppm, *d*₆-DMSO) δ : 8.29 (s,br, 8H, ArH), 4.96 (t, br, 8H, OH), 3.82 (q, br, 16H, OCH₂), 3.53 (t, br, 16H, SCH₂), 2.16 (p, br, 16H, -CH₂). UV/ Vis (DMF) λ_{max} , nm (log ε): 705 (4.82), 669 (4.16), 633 (4.16), 372 (4.51), 283 (4.51). MS (MALDI-TOF) *m/z*: 1299.84 [M+3]⁺.

Compound (7): Yield: 58 mg (76%); m.p.: >335 °C. $C_{56}H_{64}N_8O_8S_8$. Cu (1295.19): Calc. C 51.85, H 4.97, S 19.77, N 8.64, Cu 4.90; found: C 51.56, H 4.73, S 19.98, N 8.85, Cu 4.68%. IR (KBr) v_{max} (cm⁻¹): 3326 (-OH), 3064 (=CH aromatic), 2972–2854 (-CH₂ aliphatic), 1620–1595 (aromatic -C=C-), 696 (C–S). UV/Vis (DMF) λ_{max} , nm (log ε): 707 (4.58), 634 (4.18), 362 (4.73), 285 (4.99). MS (MALDI-TOF) m/z: 1297.75 [M+2]⁺.



Scheme 1. Synthesis of the phthalonitrile (3) and compounds (4), (5), (6), (7) and (8).

2.3.4. 2,3,9,10,16,17,23,24-Octakis(3-hydroxypropylmercapto) phthalocyaninatonickel(II) (6)

A mixture of (3) (0.200 g, 0.64 mmol), anhydrous NiCl₂ (0.130 g, 1.00 mmol) and 3 mL 2-dimethylaminoethanol (DMAE) was placed in a Schlenk tube under an argon atmosphere. Then the temperature was gradually increased up to 90 °C and DBU (0.15 mL, 0.16 g, 1.0 mmol) was added to the reaction mixture. The reaction system was stirred at 170 °C for 3 days under an argon atmosphere. The resulting green reaction mixture was cooled to room temperature and the solvent was evaporated at reduced pressure until dry. Twenty milliliters of ethanol/water (2:1) mixture was added to the reaction medium and stirred for 30 min. The obtained crude product was washed with water, ethanol and then acetone. The final petroleum greenish product (6) was isolated by silica gel column chromatography (eluant: THF/MeOH, 10:1, v/v) and then dried under vacuum over P₂O₅ at 55 °C until dry. Yield: 84 mg (80%); m.p. 305 °C. C₅₆H₆₄N₈O₈S₈Ni (1290.19) Calc.: C 52.05, H 4.99, N 8.67, S 19.85, Ni 4.54%; found: C 51.95, H 4.78, N 8.58, S 19.56, Ni 4.76%. IR (KBr) v_{max} (cm⁻¹): 3382 (-OH), 3064 (=CH aromatic), 2925-2854 (-CH₂ aliphatic), 1618 (aromatic -C=C-), 662 (-C-S). ¹H NMR (ppm, d_6 -DMSO) δ : 8.07 (s,br, 8H, ArH), 4.72 (t, br, 8H, OH), 3.85 (q, br, 16H, OCH₂), 3.53 (t, br, 16H, SCH₂), 1.80 (p, br, 16H, $-CH_2$). UV/Vis (DMF) λ_{max} , nm (log ε): 705 (4.98), 670 (4.30), 633 (4.31), 383 (4.66), 311 (4.54). MS (MALDI-TOF) m/z: 1292.6 [M+2]⁺.

2.3.5. 2,3,9,10,16,17,23,24-Octakis(3-hydroxypropylmercapto) phthalocyaninatocobalt(II) (**8**)

A mixture of compound (3) (0.150 g, 0.48 mmol), ethylene glycol (4.0 mL) and CoCl₂ (0.062 g, 0.48 mmol) was kept in a Schlenk tube and degassed several times with argon. The reaction was treated at 195 °C for 3 days in an inert argon atmosphere. The reaction mixture was cooled to room temperature and then poured into an ice–water mixture and stirred until the ice melted. The solid part was filtered off and washed with acetone and diethyl ether. The crude residue was purified by silica gel column chromatography (eluant: THF/MeOH, 10:1, v/v). The final dark green product (**8**) was dried under vacuum over P₂O₅ at 55 °C. Yield: 60 mg (76%); m.p.: > 378 °C. C₅₆H₆₄N₈O₈S₈Co (1291.19) Calc.: C 52.04, H 4.99, N 8.67, S 19.84, Co 4.56; found: C 52.25, H 4.63, N 8.24, S 19.59, Co 4.85%. IR (KBr) v_{max} (cm⁻¹): 3353 (–OH), 3073 (=CH aromatic), 2925–2856 (–CH₂ aliphatic), 1620 (aromatic –C=C–), 672 (C–S). UV/Vis (DMF) λ_{max} , nm (log ε): 698 (4.43), 628 (4.13), 313 (4.90), 286 (5.09). MS (MALDI-TOF) m/z: 1292.67 [M+1]⁺.

2.3.6. The silver(I) complex of zinc(II) phthalocyanine 5 (9)

Compound (**5**) (45 mg, 0.035 mmol) was dissolved in DMFwater (3 + 0.2 mL) and silver nitrate (0.0473 g, 0.277 mmol) in DMF-water (3 + 0.2 mL) was added. The mixture was refluxed for 18 h. The reaction mixture was filtered to separate any silver oxide formed. The product was obtained by evaporation of the solvent. It was dissolved in CHCl₃, filtered and reprecipitated by addition of ethanol. Yield: 24 mg (40%). $C_{56}H_{64}Ag_4N_{12}O_{20}S_8Zn$ (1971.76) Calc.: C 34.00, H 3.26, Ag 21.81, N 8.50, S 12.96, Zn 3.30%; found: C 34.52, H 2.97, Ag 21.32, N 8.78, S 13.17, Zn 3.02%. IR (KBr) v_{max} (cm⁻¹): 3413 (-OH), 3170 (=CH aromatic), 2918–2848 (-CH₂ aliphatic), 1637 (aromatic -C=C-), 1384 (-NO₃-), 669 (-C-S). ¹H NMR (ppm, d_6 -DMSO) δ : 8.61 (s, br, 8H, ArH), 5.14 (t, br, 8H, OH), 4.01 (q, br, 16H, OCH₂), 3.81 (t, br, 16H, SCH₂), 2.24 (p, br, 16H, -CH₂). UV/Vis (DMF) λ_{max} , nm (log ε): 705 (4.78), 672 (4.49), 632 (4.27), 367 (5.12), 288 (5.53). MS (MALDI-TOF) *m*/*z*: 1973.65 [M+2]⁺



Fig. 1. The ¹H NMR spectrum of the compound (**3**) in d_6 -DMSO.

2.3.7. The palladium(II) complex of zinc(II) phthalocyanine 5 (10)

 $Na_2[PdC1_4]$ was prepared by refluxing $PdCl_2$ (0.061 g, 0.344 mmol) and NaCl (0.042 g, 0.688 mmol) in 30 mL ethanol overnight. The reaction mixture was filtered to remove any unreacted species and the solvent was evaporated under reduced pressure. Compound (5) (45 mg, 0.035 mmol) was dissolved in DMF-water (3 + 0.2 mL) and Na₂[PdC1₄] (0.081 g, 0.277 mmol) in DMF-water (3+0.2 mL) was added. The mixture was refluxed for 18 h. The resulting green reaction was filtered off and then solvent was evaporated. The product was washed several times with water and diethyl ether. Yield: 40 mg (67%); C₅₆H₆₄Cl₈N₈O₈Pd₄S₈Zn (1999.55) Calc.: C 33.49, H 3.21, Cl 14.12, N 5.58, Pd 21.20, S 12.77, Zn 3.26%; found: C 33.24, H 3.56, Cl 14.75, N 5.71, S 12.64, Zn 3.56, Pd 21.65%. IR (KBr) υ_{max} (cm^{-1}): 3425 (–OH), 3129 (=CH aromatic), 2921–2858 (-CH₂ aliphatic), 1639 (aromatic -C=C-), 742–719 (–C–S). ¹H NMR (ppm, d_6 -DMSO) δ : 8.44 (s, br, 8H, ArH), 5.04 (t, br, 8H, OH), 3.96 (q, br, 16H, OCH₂), 3.65 (t, br, 16H, SCH₂), 2.21 (p, br, 16H, $-CH_2$). UV/Vis (DMF) λ_{max} , nm (log ε): 706 (4.85), 632 (4.21), 368 (4.87), 286 (5.15). MS (MALDI-TOF) m/z: 2000.67 [M+1]⁺.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of 1,2-bis(3-hydroxypropylmercapto)-4,5-dicyanobenzene (**3**) was performed via based-catalyzed nucleophilic aromatic chlorine displacement [25,32] of 4,5-dichlorophthalonitrile with 3-mercapto-1-propanol in dry DMF using finely ground anhydrous Na₂CO₃ as described in the Experimental section (Scheme 1), with a yield of 54% after recrystallization from methanol. Elemental analysis and mass spectral data were satisfactory: m/z = 367.11 [M+2H₂O+Na]⁺. Compound (**3**) was also characterized by NMR and IR spectroscopy techniques. The ¹H NMR spectrum of compound (**3**) (in *d*₆-DMSO) shows signals at $\delta = 7.87$ (s, 2H, ArH), 4.68 (t, 2H, OH), 3.49 (q, 4H, OCH₂), 3.19 (t, 4H, SCH₂) and 1.75 (p, 4H, – *CH*₂), ppm, Fig. 1. Furthermore, when treated with D₂O, the peak at 4.69 ppm, corresponding to the protons of O–H groups, was displaced with deuterium. The ¹³C NMR spectrum of (**3**) indicates the primary alcohol atoms at $\delta = 59.69$ ppm (CH₂OH) and other carbon atoms at $\delta = 143.67$ (ArCS), 128.83 (ArCH), 116.90 (C=N), 110.78 (ArC), 31.67 (SCH₂) and 28.77 (SCH₂CH₂) ppm, Fig. 2. In the IR spectrum of (**3**), the disappearance of the S–H stretching vibration at 2560 cm⁻¹, along with the appearance of new bands at 2227 and 686 cm⁻¹, arising from C=N and Ar–S–C groups, respectively, are in agreement with the proposed structure.

The metal free compound (**4**) was synthesized by refluxing a mixture of (**3**), DBU and dry 1-pentanol in a Schlenk tube under a dry argon atmosphere. After purification with silica gel column chromatography using THF/methanol (10:1, v/v) as the eluent, the pure product (**4**) was obtained in a yield of 53%. In the IR spectrum of compound (**4**), the peaks at 3290 and 1058 cm⁻¹ are characteristic peaks for the metal free phthalocyanine N–H stretching and pyrrole ring vibration bands respectively [33]. A weak absorption for C=N at 1618 cm⁻¹ was also detected. The ¹H NMR spectrum of (**4**) exhibits the typical shielding of inner core protons as a broad signal at around $\delta = -3.94$ ppm which could be attributed to the N–H resonances, as confirmed by deuterium exchange [34]. The elemental analysis was satisfactory. The molecular ion peak at m/z = 1236.85 [M+1]⁺ also supports the proposed structure.

The zinc(II) phthalocyanine (**5**) was prepared from the phthalonitrile compound (**3**) and anhydrous $Zn(CH_3COO)_2$ in the presence



Fig. 2. The ¹³C NMR spectrum of the compound (**3**) in d_6 -DMSO.



Fig. 3. The ¹H NMR spectra of the compounds (9) and (10) in d_6 -DMSO.

of DBU as a base catalyst in dry 1-pentanol. The Ni(II) phthalocyanine (**6**) was synthesized by the reaction of compound (**3**) with anhydrous NiCl₂ in dry DMAE in the presence of DBU. Compound (**7**) was synthesized by the reaction of anhydrous CuCl₂ and compound (**3**) in dry 1-pentanol with DBU as a base catalyst. The Co(II) phthalocyanine (**8**) was prepared from compound (**3**) and anhydrous CoCl₂ in ethylene glycol. The metallophthalocyanines were purified by column chromatography on silica gel using THF/MeOH (10:1, v/v) eluent as the mobile phase in 76–88% yields. The Ag⁺ or Pd^{2+} complexes of compound (**5**) was prepared by using AgNO₃ or Na₂[PdCl₄] in a DMF-water mixture with yields of 40 and 67% respectively. The IR spectra of the compounds (**5**)–(**10**) were very similar with the exception of the N–H stretching bands at 3290 and 1058 cm⁻¹ due to the inner core of the metal free phthalocyanine. In the IR spectrum of (**9**) there was a new band at 1384 cm⁻¹ corresponding to NO₃⁻¹ groups. Metal-N vibrations were expected to appear at 400–100 cm⁻¹, but they were not detected for the spectra recorded in KBr pellets [35]. The ¹H NMR spectra of (**5**),





(6), (9) and (10) were similar to those of the precursor phthalonitrile (3), but the peaks were broadened due to the phthalocyanine aggregation at the concentrations used for the NMR measurements and shifted to the higher resonances than those of the precursor [36]. The ¹H NMR spectra of (9) and (10) are given in Fig. 3. ¹H NMR measurements were precluded for (7) and (8) because of the paramagnetic nature of the compounds. The mass spectra of the compounds exhibited peaks at m/z = 1299.84 [M+2]⁺, 1292.6 [M+2]⁺, 1297.75 [M+2]⁺, 1292.67 [M+1]⁺, 1973.65 [M+2]⁺ and 2000.67 [M+1]⁺ for (5)–(10) respectively, and are given in Fig. 4 for compounds (7), (9) and (10). The elemental analyses of the compounds were satisfactory.

3.2. Ground-state electronic absorption spectra

The phthalocyanine system is characterized by strong absorption bands in the UV region (the Soret band) and in the visible region (the Q-band); low intensity bands in the visible region to shorter wavelength of the Q-band are vibronic in origin [37]. The UV–Vis spectra of (4)–(10) were recorded in solutions of DMF or pyridine. As seen in Fig. 5, there is a shoulder at the slightly higher energy side for the metal-free phthalocyanine and its metal complexes. The presence of shoulders in the UV-Vis spectra of compounds corresponds to aggregated or non-aggregated species in pyridine or DMF. There was a single Q-band for (5)-(8), whereas there was a split Q-band, as expected, and two strong bands were in the visible region for (4). The split Q-band, which is characteristic for metal-free phthalocyanines, was observed at λ_{max} values of 733 and 706 with shoulders at 670 and 636 nm, for (4), indicating the monomeric species; monomeric species with D_{2h} symmetry show two intense absorptions around 700 nm [38,39]. On the other hand, such split O-band absorptions are due to the $\pi \Rightarrow \pi^*$ transition of this fully conjugated 18- π electron system [40]. The Bbands of compound (4) were observed at 364 and 332 nm. The



Fig. 5. Absorption spectra of (4) (a) in pyridine and (5) (b), (6) (c), (7) (d), (8) (e) in DMF at different concentrations. (Inset: Plot of absorbance versus concentration at 670, 705, 633, 635 and 626 nm for compounds (4), (5), (6), (7) and (8) respectively).

Q-band absorption of the metallophthalocyanines (5)–(8) is observed as a single band of high intensity in the visible region at 705, 706, 707 and 698 nm, respectively, with shoulders at the slightly higher energy side of the Q-band for each complex, as expected. All the phthalocyanine compounds exhibit intense Q-bands at long wavelengths. It is known that the shift to the lower energy



Fig. 6. Changes in the visible spectra of (a) (5) in DMF (C = 1.2×10^{-5} mol/L) after the addition of (b) 0.2 mL, (c) 0.4 mL, (d) 0.6 mL, (e) 0.8 mL, (f) 1.0 mL methanol.



Fig. 7. Changes in the visible spectra of (a) (5) in DMF (C = 1.0×10^{-5} mol/L) after addition of (b) 0.2 mL, (c) 0.4 mL, (d) 0.6 mL, (e) 0.8 mL, (f) 1.0 mL 0.001 M AgNO₃ in methanol.



Fig. 8. Changes in the visible spectra of (a) (5) in DMF (C = 1.0×10^{-5} mol/L) after addition of (b) 0.2 mL, (c) 0.4 mL, (d) 0.6 mL, (e) 0.8 mL, (f) 1.0 mL 0.1 M Hg(NO₃)₂ in methanol.

side is a result of electron-donating -S substituents [20b,41]. The electronic spectra of the metal free phthalocyanine in pyridine and metallophthalocyanine compounds in DMF were investigated at different concentrations. As the concentration of the phthalocyanines was increased, the intensity of the Q-band absorption also increased. There were no shifts or new bands that can be attributed to aggregation. In order to investigate whether or not the complexes obey the Lambert–Beer law, absorbance versus concentration graphs were plotted and gave nearly straight lines. This indicates that the prepared phthalocyanine compounds (**4**)–(**8**) nearly comply with the Lambert–Beer law in the concentration range given, Fig. 5. This observation indicates that the compounds mainly exist in the monomeric form under the conditions employed.

Aggregation is usually depicted as a coplanar association of rings, processing from monomer to dimer and higher order complexes and driven by non-bonded attractive interactions. It is dependent on the concentration, nature of solvent, nature of substituents, complexed metal ions and temperature [42]. In this work we studied the aggregation behavior of compound (**5**) using UV–Vis spectroscopy. Thus different concentrations of metal salts, such as AgNO₃, Hg(NO₃)₂, Pb(NO₃)₂ and Cd(NO₃)₂ in methanol, were added to the solution of compound (**5**) in DMF (1×10^{-5} M). First, in order to clarify whether methanol has any effect on UV–Vis spectra of (**5**), different amounts of metanol were added to the solution of compound (**5**) in DMF. As can be seen from Fig. 6, there



Fig. 9. Changes in the visible spectra of (a) (5) in DMF (C = 1.0×10^{-5} mol/L) after addition of (b) 0.2 mL, (c) 0.4 mL, (d) 0.6 mL, (e) 0.8 mL, (f) 1.0 mL 0.1 M Pb(NO₃)₂ in methanol.



Fig. 10. Changes in the visible spectra of (a) (5) in DMF (C = 1.0×10^{-5} mol/L) after addition of (b) 0.2 mL, (c) 0.4 mL, (d) 0.6 mL, (e) 0.8 mL, (f) 1.0 mL (g) 1.2 mL 0.1 M Cd(NO₃)₂ in methanol.



Fig. 11. Changes in the visible spectra of (5) (C = $1\times 10^{-5}\,mol/L)$ in different solvents.



Fig. 12. Changes in the absorption, excitation and emission spectra of compound (5) in THF (C = 1×10^{-5} M). Excitation wavelength = 671 nm.

was a decrease in the intensities of the Q bands without any shifts in wavelength in the visible absorption spectra of (**5**) with an increase of the methanol amount. This decrease could be the result of the dilution effect. When Ag⁺ solutions in methanol were added to a solution of compound (5) in DMF, with the increase in the amount of Ag⁺, the intensity of the main Q band of (5) decreased with a slight shift of 2 nm (705-703 nm). On the other hand, the shoulder at 669 nm and the Q band at 634 nm were displaced with a new broadened band at 657 nm, Fig. 7. In the case of Hg²⁺ solutions in methanol, the Q band of (5) was broadened and blue shifted by \sim 5 nm as a result of aggregation, Fig. 8. This behavior can be attributed to the aggregation phenomena. Dimerization of the phthalocyanine units by intermolecular complexation through peripheral dithia groups with Ag⁺ and Hg²⁺ ions forms sandwich type complexes arising from π -stacking interactions, which causes the new absorption band. The new bands can be ascribed to the presence of dimeric and oligomeric phthalocyanine species [20b,43]. Further addition of AgNO₃ or Hg(NO₃)₂ did not change the spectrum.

On the other hand, when Pb^{2+} , Fig. 9, and Cd^{2+} , Fig. 10, solutions in methanol were added, the intensity of the Q absorption bands at 705 and 634 nm decreased gradually without any shift. There was no change in the visible spectrum of (**5**) with the addition of Pb^{2+} and Cd^{2+} ions. In addition to the dilution effect, this behaviour in the visible spectrum may be attributed to very weak or no coordination of the peripheral S atoms to the Pb^{2+} and Cd^{2+} ions [44]. The aggregation behavior of the zinc(II) phthalocyanine compound (**5**) was also investigated in different solvents, such as DMF and pyridine. There is a blue shift in the case of DMF due to the polar character of the solvent, Fig. 11 [45].

The absorption, excitation and emission spectra of compound (**5**) were studied and are given in Fig. 12. The excitation spectrum was similar to the absorption spectrum and both were mirror images of the fluorescent spectrum in THF. The proximity of the wavelength of the Q-band absorption to the Q-band maxima of the excitation spectrum for compound (**5**) suggests that the nuclear configurations of the ground and excited states are similar and are not affected by excitation in THF [46]. Fluorescence emission peak was observed at $\lambda = 710$ nm.

In order to investigate the interaction of (**5**) with Ag^+ and Pd^{2+} ions, complexes (**9**) and (**10**) were prepared (Scheme 2). As can be seen in Figs. 13 and 14, the UV–Vis spectra of complexes (**9**)



Scheme 2. Synthesis of compounds (9) and (10).



Fig. 13. UV-Vis spectra of compounds (5) and (9) in DMF (C = 6×10^{-6} M).



Fig. 14. UV–Vis spectra of compounds (**5**) and (**10**) in DMF ($C = 1 \times 10^{-5}$ M).



Fig. 15. The frequency versus AC conductivity of compounds (4)–(8) at 300 K (Inset: Plot of frequency versus concentration).

and (**10**) are similar to those of compound (**5**), except for broadening. These broadened bands can be attributed to the interaction of the thio groups with the different sized cations [18,44,47]. Figs. 13 and 14 show the UV–Vis spectra of compounds (**9**) and (**10**), as Ag^+ and Pd^{2+} complexes of compound (**5**) respectively, whereas Fig. 7 indicates the interaction of (**5**) with Ag^+ ions as a solution in DMF. The visible spectra of the titration of (**5**) with an AgNO₃ solution and the isolated complex (**9**) are expected to be similar, but as can be seen in Fig. 13 they are not very similar. This can be attributed to the difference of the working conditions whilst recording the spectra.

3.3. Conductivity measurements

The AC electrical conductivities of the metal free and metallophthalocyanines were measured in air atmosphere and under vacuum in the sandwich form covered with silver paste to form electrodes. The capacitance and the dielectric loss factor of each sample were measured between 1 kHz and 1 MHz frequency and 300–400 K using an LCR meter. The AC conductivity values at different frequencies were calculated using the dielectric permittivity and the dielectric loss factor according to the given equations, and the results are given in Table 1.

$$C=\frac{\varepsilon_0\varepsilon_r A}{d}$$

$\sigma_{\rm AC}=2\pi f\varepsilon_{\rm o}\varepsilon_{\rm r}\tan\delta$

where *C* is the capacitance of the sample, ε_0 is the permittivity of air, *A* is the surface area of the sample, d is the thickness of the sample, ε_r is the dielectric permittivity of the sample, *f* is the frequency and tan δ is the dielectric loss [48]. According to Table 1, the AC electrical conductivity values correspond to those of semi-conductive materials, encountered in most of the substituted phthalocyanines [49]. The AC conductivity values obtained under air conditions were higher than those of under vacuum, probably due to absorbed oxy-

Table 1	
The AC conductivity values of (4)-(10) at different frequencies.	

Compound	Pellet thickness (mm)	Conductivity (S m ⁻¹)					
		1 kHz		10 kHz		1 MHz	
		In air	In vacuum	In air	In vacuum	In air	In vacuum
4	0.457	3.62×10^{-6}	$\textbf{2.13}\times \textbf{10}^{-6}$	$\textbf{6.46}\times 10^{-6}$	$\textbf{4.84}\times 10^{-6}$	8.71×10^{-5}	$\textbf{5.87}\times \textbf{10}^{-5}$
5	0.600	$3.72 imes 10^{-8}$	$1.20 imes 10^{-8}$	$1.79 imes 10^{-7}$	$1.12 imes 10^{-7}$	$2.72 imes 10^{-5}$	$1.47 imes 10^{-5}$
6	0.677	$9.24 imes10^{-8}$	$1.57 imes10^{-7}$	$4.49 imes 10^{-7}$	$5.53 imes10^{-7}$	$4.44 imes 10^{-5}$	$3.03 imes 10^{-5}$
7	0.600	$2.44 imes 10^{-8}$	$5.67 imes10^{-9}$	$1.81 imes 10^{-7}$	$6.93 imes10^{-8}$	$1.34 imes10^{-5}$	8.04×10^{-6}
8	0.617	$5.97 imes10^{-6}$	$7.23 imes 10^{-7}$	$1.08 imes 10^{-5}$	$2.07 imes10^{-6}$	$1.31 imes 10^{-4}$	4.23×10^{-5}
9	0.524	$8.98 imes 10^{-9}$	$7.65 imes 10^{-9}$	$8.81 imes 10^{-8}$	$8.16 imes 10^{-8}$	$7.19 imes10^{-6}$	$6.91 imes 10^{-6}$
10	0.571	$\textbf{7.14}\times 10^{-9}$	$\textbf{1.86}\times\textbf{10}^{-9}$	$\textbf{3.6}\times \textbf{10}^{-8}$	$\textbf{2.40}\times \textbf{10}^{-8}$	5.67×10^{-6}	$\textbf{2.38}\times 10^{-6}$



Fig. 16. Temperature versus AC conductivity values of compounds (4)-(8) at 1 and 10 kHz.

gen from the air atmosphere. There is not a significant change in the conductivity values after complexation of the S-donors with the Ag(I) and Pd(II) ions in case of the compounds (9) and (10) [50]. The frequency versus AC conductivity graph was plotted at 300 K and is given in Fig. 15. The AC conductivity values of the complexes are not strongly frequency dependent at lower frequencies and do not show a clear variation. On the other hand, at higher frequencies, above about 10⁵ Hz, the AC conductivity shows a strong frequency dependence and there is a significant increase with frequency [20c,51]. The AC conductivity values of the phthalocyanine compounds versus temperature at 1 and 10 kHz are given in Fig. 16. The temperature dependent increase in the AC conductivity can be attributed to the increase in free volume and thermal mobility of the charge carriers. It is shown in Fig. 16 that only the conductivity of compound 5 reduces with increasing temperature at higher frequency. This phenomenon is inconsistent with the classical theory of conductivity. It may be related to its polarization under a mutative electric field [52].



Fig. 17. The DSC Thermograms of (4)-(8).

Table 2

Thermal	properties	of phthalocyanin	es (4)–(10).
---------	------------	------------------	--------------------------------

Compound	Dissociation of $NO_3^- T_{max}$ (°C)	Initial decomposition temperature (°C)	Main decomposition temperature (°C)
4	-	346	378
5	-	390	426
6	-	351	374
7	-	333	368
8	-	348	379
9	227	325	359
10	-	338	371

3.4. DSC measurements

Thermal properties of the metal free (4) and metallophthalocyanines (5)-(8) were investigated by DSC (Fig. 17). DSC measurements were performed on raw materials with a scanning rate of 10 °C/min between -4 and 440 °C. DSC curves exhibit both endothermic and exothermic changes for all the phthalocyanines in the region investigated [53]. All the metal free and metallophthalocyanines show a broad endothermic peak between 50 and 125 °C attributed to the desorption of alcohol and water during the preparation or the desorption of adsorbed humidity or air gases during the storage of the phthalocyanine complexes [20c,54]. Compound (5) exhibits a broad melting point at 337 °C, whereas compound (6) exhibits a sharp melting point at 305 °C. The DSC curves of the compounds (4) and (7)–(10) do not show melting points. There is a significant exothermic peak indicating oxidation right before the decomposition effect for compounds (5) and (7), but this exothermic peak is not very significant in the other compounds. The DSC thermogram of (9) showed an endothermic peak at 227 °C which may be due to the dissociation of nitrate groups. The thermal stabilities of (9) and (10) were lower than that of compound (5). The thermal history study did not show any heat flow effects during the second heating to 440 °C. The initial decomposition effect decreased in the order (5) > (6) > (8) > (4) > (10) > (7) > (9)(Table 2). The thermal stabilities of (9) and (10) indicate that the Ag⁺ and Pd²⁺ ions are rather weakly bound to the peripheral dithia atoms [55]. The Cu-containing metallophthalocyanine (7) was the most rapidly degraded metallophthalocyanine, while Zn-, Ni- and Co-containing metallophthalocyanines showed good thermal stability under the working conditions. These results are in good agreement with the literature data [20a,56].

4. Conclusion

We have presented the synthesis and characterization of 1,2bis(3-hydroxypropylmercapto)-4,5-dicyanobenzene (3) and the metal-free phthalocyanine and its metal complexes. The precursor phthalonitrile derivative was prepared by a based catalyzed nucleophilic aromatic chlorine displacement reaction of 4,5-dichlorophthalonitrile with 3-mercapto-1-propanol in dry DMF. The metal-free phthalocyanine (4) was prepared from precursor compound (3) and DBU in dry 1-pentanol. The metallophthalocyanines (M = Zn, Ni, Cu and Co) were prepared by the reaction of compound (3) with the appropriate materials. The compounds were characterized by elemental analysis, UV-Vis, IR, ¹H NMR, ¹³C NMR, MS spectral data and DSC techniques. The zinc complex (5) had a clear aggregation tendency on addition of Ag^+ and Hg^{2+} . On the other hand, there was no shift or optical change on addition of Pb²⁺ and Cd²⁺. The aggregation behavior of the zinc(II) phthalocyanine compound (5) was also investigated in different solvents, such as DMF and pyridine. The thio groups of the phthalocyanine peripheral positions provided good interactions with Ag⁺ and Pd²⁺ ions, resulting in a clear broadening of the UV–Vis spectra. The excitation and emission spectra of compound (**5**) were also studied in THF and were found to be similar to the absorption spectrum of (**5**). The electrical conductivities of the compounds were measured in air and vacuum atmosphere at room temperature and were found to be $\sim 10^{-9} - 10^{-5}$ S m⁻¹. The dependence of the AC conductivity on the frequency and temperature were also evaluated. The metal free and the Zn(II), Ni(II) and Co(II) metallophthalocyanines showed good thermal stability under the working conditions, whilst the Cu(II) phthalocyanine (**7**) was the most rapidly degraded metallophthalocyanine. Polymerization of the appropriate monomers with the terminal hydroxyl functionalized groups of phthalocyanine as an initiator, prepared in this work, will be discussed in future studies.

Acknowledgements

This work has been supported by Kocaeli University, Scientific Research Projects Unit, Project number : BAP-2010 / 38 (Kocaeli, Turkey). We are also indebted to Asisst. Prof. Dr. Ersel Özkazanç (Kocaeli University) for assistance with the DSC and conductivity measurements.

References

- (a) C.C. Leznoff, A.B.P. Lever, Phthalocyanines: Properties and Applications, vol. 1, VCH, New York, 1989;
 - (b) C.C. Leznoff, A.B.P. Lever, Phthalocyanines: Properties and Applications, vol. 2, VCH, New York, 1993;
 - (c) C.C. Leznoff, A.B.P. Lever, Phthalocyanines: Properties and Applications, vol. 3, VCH, New York, 1993;
 - (d) C.C. Leznoff, A.B.P. Lever, Phthalocyanines: Properties and Applications, vol. 4, VCH, New York, 1996.
- [2] G. Rojo, G. Martín, F. Agulló-López, T. Torres, H. Heckmann, M. Hanack, J. Phys. Chem. B 104 (2000) 7066.
- [3] G. Torre, T. Torres, A.F. Lopez, Adv. Mater. 9 (1997) 265.
- [4] H. Ali, J.E. Lier, Chem. Rev. 99 (1999) 2379.
- [5] G. Guillaud, J. Simon, J.P. Germain, Coord. Chem. Rev. 178-180 (1998) 1433.
- [6] N. Nombona, P. Tau, N. Sehlotho, T. Nyokong, Electrochim. Acta 53 (2008) 3139.
- [7] C. Piechocki, J. Simon, A. Skoulios, D. Guillon, P. Weber, J. Am. Chem. Soc. 104 (1982) 5245.
- [8] M. Moussavi, A. Cian, J. Fischer, R. Weiss, Inorg. Chem. 27 (1988) 1287.
- [9] (a) T.J. Farrell, B.J. Wilson, M.S. Patterson, M. Olivo, Photochem. Photobiol. 68 (1998) 394;
- (b) N. Nombona, E. Antunes, C. Litwinski, T. Nyokong, Dalton Trans. 40 (2011) 11876.
- [10] M.J. Cook, N.B. McKeown, J.M. Simmons, A.J. Thomson, M.F. Daniel, K.J. Harrison, R.M. Richardson, S.J. Roser, J. Mater. Chem. 1 (1991) 121.
- [11] (a) L. Howe, J.Z. Zhang, J. Phys. Chem. A 101 (1997) 3207;
- (b) M. Durmuş, H. Yaman, C. Göl, V. Ahsen, T. Nyokong, Dyes Pigm. 91 (2011) 153;
 - (c) E. Hamuryudan, S. Merey, Z.A. Bayir, Dyes Pigm. 59 (2003) 263;
 - (d) G.M.C. Vior, L.E. Dicelio, J. Awruch, Dyes Pigm. 83 (2009) 375;
 - (e) C.A. Strassert, G.M. Bilmes, J. Awruch, L.E. Dicelio, Photochem. Photobiol. 7 (2008) 738.
- [12] (a) D.D. Eley, Nature 162 (1948) 819;
- (b) A.T. Vartanyan, Zh. Fiz. Khim. 22 (1948) 769;
 (c) N.B. McKeown, J. Mater. Chem. 10 (2000) 1979.
- [13] J.L. Petersen, C.S. Schramm, D.R. Stojakovic, B.M. Hofmann, T.J. Marks, J. Am. Chem. Soc 99 (1977) 286.
- [14] T.M.M. Kumar, B.N. Achar, J. Organomet. Chem. 691 (2006) 331.
- [15] J.D. Wright, Prog. Surf. Sci. 31 (1989) l.
- [16] J.J. Andre, J. Simon, R. Even, B. Boudjema, G. Guillaud, M. Maitrot, Synth. Met. 18 (1987) 683.
- [17] D. Wöhrle, V. Schmidt, J. Chem. Soc. Dalton Trans. (1988) 549.
- [18] A.G. Gürek, Ö. Bekaroğlu, J. Chem. Soc. Dalton Trans. (1994) 1419.
- [19] N. Sehlotho, M. Durmuş, V. Ahsen, T. Nyokong, Chem. Comm. 11 (2008) 479.
- [20] (a) A. Bilgin, Ç. Yağcı, U. Yıldız, Macromol. Chem. Phys. 206 (2005) 2257;
 (b) A. Bilgin, A. Mendi, U. Yıldız, Polymer 47 (2006) 8462;
 (c) A. Bilgin, Ç. Yağcı, U. Yıldız, E. Özkazanç, E. Tarcan, Polyhedron 28 (2009)
 - (c) A. Bilgin, Ç. Tagel, U. Thuiz, E. Ozkazanç, E. Tarcan, Polyheuron 28 (2009) 2268.
- [21] (a) A. Bilgin, Ç. Yağcı, A. Mendi, U. Yıldız, Polyhedron 26 (2007) 617;
- (b) A. Bilgin, Ç. Yağcı, A. Mendi, U. Yıldız, J. Appl. Polym. Sci. 110 (2008) 2115. [22] (a) B. Ertem, A. Bilgin, Y. Gök, H. Kantekin, Dyes Pigm. 77 (2008) 537;
- (b) A. Bilgin, C. Yağcı, A. Mendi, U. Yıldız, J. Inclusion. Phenom. Macrocyclclic Chem. 67 (2010) 377.

- [23] (a) H. Matsuda, S. Okada, A. Masaki, H. Nakanishi, Y. Suda, K. Shigehara, A. Yamada, Proc. SPIE-Int. SOC. Opt. Eng. 1337 (1990) 105; (b) Y. Suda, K. Shigehara, A. Yamada, H. Matsuda, S. Okada, A. Masaki, H. Nakanishi, Proc. SPIE-Int. SOC. Opt. Eng. 1560 (1991) 75;

 - (c) P.J. Duggan, P.F. Gordon., Eur. Pat. Appl. EP 0155780 A2, 1985, p. 1.; (d) H. Matsuda, S. Okada, A. Masaki, H. Nakanishi, Y. Suda, S. Ehashi, J. Shigehara, A. Yamada, Jpn. Kokai Tokkyo Koha JP 03-249742, 1991, p. 1.
- [24] K. Chen, B.R. Herr, T.E. Singewald, C.A. Mirkin, Langmuir 8 (1992) 2585.
- [25] D. Wöhrle, M. Eskes, K. Shigehera, A. Yamada, Synthesis (1993) 194.
- [26] D.A. Deshpande, K.R. Ghormare, V.L. Jawadekar, N.D. Desphande, Thermochim. Acta 60 (1983) 295.
- T. Arii, A. Kishi, Thermochim. Acta 400 (2003) 175.
- [28] J.N. Charles, N.D. Desphande, D.A. Desphande, Thermochim. Acta 375 (2001) 169
- [29] M. Schmitt, O. Janson, M. Schmidt, S. Hoffmann, W. Schnelle, S.L. Drechsler, H. Rosner, Phys. Rev. B 79 (245119) (2009) 1.
- [30] J. Ribas, A. Escuer, M. Serra, R. Vicente, Thermochim. Acta 102 (1986) 125.
- [31] D.D. Perin, W.L.F. Armarego, Purification of Laboratory Chemicals, 2nd ed., Pergamon Press, Oxford, 1989.
- (a) Z.A. Bayır, Dyes Pigm. 65 (2005) 235; [32]
- (b) A.I. Adebayo, T. Nyokong, Polyhedron 28 (2009) 2831.
- [33] A.W. Snow, J.R. Griffith, N.P. Marullo, Macromolecules 17 (1984) 1614.
- [34] B. Ertem, A. Bilgin, H. Kantekin, Y. Gök, Polyhedron 27 (2008) 2186. [35] M. Avram, G. Mateescu, Infrared Spectroscopy, Wiley Interscience, NewYork, 1966. p. 298;
 - (b) K. Nakomato, Infrared Spectra of Inorganic and Coordination Compounds, 2nd ed., Wiley, New York, 1970.
- [36] M. Durmuş, T. Nyokong, Polyhedron 26 (2007) 2767.
- [37] M.J. Cook, A.J. Dunn, S.D. Howe, A.J. Thomson, K.J. Harrison, J. Chem. Soc., Perkin Trans. 1 (1988) 2453.
- [38] İ. Özçeşmeci, A.İ.A. Gül, Dyes Pigm. 75 (2007) 761.
- [39] E.A. Cuellar, T.J. Marks, Inorg. Chem. 20 (1981) 3766.

- [40] Y. Gök, H. Kantekin, A. Bilgin, D. Mendil, İ. Değirmencioğlu, Chem. Commun. 3 (2001) 285.
- [41] (a) P. Gregory, J. Porphyrins Phthalocyanines 4 (2000) 432; (b) M. Kandaz, M.N. Yaraşır, A. Koca, Polyhedron 28 (2000) 257;
- (c) M.N. Yaraşır, M. Kandaz, A. Koca, B. Salih, Polyhedron 26 (2007) 1139. [42] A.W. Snow, Phthalocyanine aggregation, in: K.M. Kadish, K.M. Simith, R.
- Guilgard (Eds.), Porphyrin Handbook, vol. 17, Academic Press, 2003, p. 132. [43] (a) O.E. Sielcken, M.M. van Tilborg, M.F.M. Roks, R. Hendriks, W. Drenth, R.M.J.
- Nolte, J. Am. Chem. Soc. 109 (1987) 4261; (b) M. Kandaz, A.T. Bilgiçli, A. Altındal, Synth. Met. 160 (2010) 52.
- [44] S.J. Lange, J.W. Sibert, A.G.M. Barrett, B.M. Hoffman, Tetrahedron 56 (2000)
- 7371.
- [45] M. Durmuş, T. Nyokong, Polyhedron 26 (2007) 2767.
- [46] A. Erdoğmuş, T. Nyokong, Dyes Pigm. 86 (2010) 174.
- [47] İ. Gürol, V. Ahsen, Ö. Bekâroğlu, J. Chem. Soc. Dalton Trans. (1994) 497.
- [48] S. Saravanan, J.S. Mathai, M.R. Anantharaman, S. Venkatachalam, P.V. Prabhakaran, J. Appl. Polym. Sci. 91 (2004) 2529.
- [49] G. Gümüş, R.Z. Öztürk, V. Ahsen, A. Gül, Ö. Bekâroğlu, J. Chem. Soc. Dalton Trans. (1992) 2485.
- [50] (a) V. Ahsen, M. Özdemir, Z.Z. Öztürk, A. Gül, Ö. Bekaroğlu, J. Chem. Res. (1995) 348:
- (b) Z.A. Bayır, E. Hamuryudan, A.G. Gürek, Ö. Bekaroğlu, J. Porphyrins Phthalocyanines. (1997) 349.
- [51] Z. Odabaş, E.B. Orman, M. Durmuş, F. Dumludağ, A.R. Özkaya, M. Bulut, Dyes Pigm, 95 (2012) 540.
- [52] A. Kang, L. Li, X. Deng, X. Wang, Mater. Sci. Eng. B 132 (2006) 288.
- [53] A.S. Milev, N. Tran, G.S.K. Kannangara, M.A. Wilson, I. Avramov, J. Phys. Chem. C 112 (2008) 5339.
- [54] T. Lopez, E. Ortiz, M. Alvarez, J. Navarrete, J.A. Odriozola, F.M. Ortega, E.A. Páez-Mozo, P.E. Escobar, K.A. Espinoza, I.A. Rivero, Biol. Med. 6 (2010) 777.
- [55] A. Bilgin, B. Ertem, Y. Gök, Eur. J. Inorg. Chem. (2007) 1703.
- [56] T.R. Walton, J.R. Griffith, J. Appl. Polym. Sci. Appl. Polym. Symp. 26 (1975) 429.