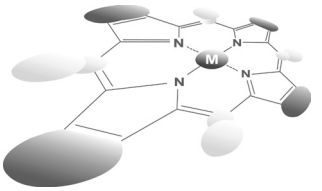
Journal of Porphyrins and Phthalocyanines
J. Porphyrins Phthalocyanines 2013; **17**: 480–488
DOI: 10.1142/S1088424613500600

Published at http://www.worldscinet.com/jpp/



Synthesis of metal-free and zinc phthalocyanines containing 2-pyridyl-methyl pendant arm linked with NS_4-donor macrocyclic moiety and their selectivity towards Cu(II) cations

Nilgün Kabay[a], Ümmühan Ocak[b], Serhat Gün[b] and Yaşar Gök*[a]

[a] *Department of Chemistry, Pamukkale University, 20017, Denizli, Turkey*
[b] *Department of Chemistry, Karadeniz Technical University, Trabzon, Turkey*

Dedicated to Professor Özer Bekaroğlu on the occasion of his 80th birthday

Received 24 January 2013
Accepted 17 April 2013

ABSTRACT: New phthalonitrile **(L1)**, metal-free phthalocyanine **(H_2Pc)** and zinc-phthalocyanine **(ZnPc)** substituted in peripheral positions with 2-pyridyl methyl pendant arm linked mixed donor macrocyclic ligands have been prepared in a multi-step reaction sequence. The novel compounds were characterized by a combination of elemental anlaysis, ^{1}H NMR, ^{13}C NMR, IR, UV-vis and MS spectral data. The influence of metal cations such as Cd^{2+}, Zn^{2+}, Hg^{2+}, Al^{3+}, Fe^{3+} and Cu^{2+} on the spectroscopic properties of dinitrile compound **L1** and free phthalocyanine **H_2Pc** was investigated by means of absorption spectrophotometry. Spectrophotometric titrations were carried out with these ligands for Cu^{2+} ion. The complex composition of Cu-L1 was found 1:1 by means of spectrophotometric titration data. The spectrophotometric method showed good sensitivity for Cu^{2+} with linear range of 2.6×10^{-6} to 1.3×10^{-4} M with dinitrile compound.

KEYWORDS: metal-free phthalocyanines, zinc-phthalocyanines, mixed donor macrocycle, pendant arm, transition metals, spectrophotometric titration.

J. Porphyrins Phthalocyanines 2013.17:480-488. Downloaded from www.worldscientific.com
by UNIVERSIDADE FEDERAL DO PARANA on 08/30/13. For personal use only.

INTRODUCTION

Synthetic macrocycles have been known for over 75 years, although a real spate of publications in this area was observed in the late 1960s [1]. In that period, more than 5000 macrocyclic compounds were reported and since then their number has increased markedly from year to year.

Phthalocyanines and their metal complexes have been studied for many years, and they are still the subject of intense investigation. They exhibit a number of extraordinary properties leading to their potential applications in various scientific and technological areas such as pigments in paints and printing inks, infrared security devices, information storage, computer disk writing, conducting polymers and photoconductors, catalysts for oxidation of thiols, disulfides, chemical sensors and photodynamic theraphy of cancer [2]. A disadvantage of metal-free and metallophthalocyanines is their low solubility in common organic solvents. For most of these applications, metal-free or metallophthalocyanines with long alkyl or alkoxy chains or macrocyclic polyether moieties had to be synthesized in order to facilitate the above-mentioned purposes and also to enhance solubility [3].

The physical and chemical properties of a phthalocyanine containing macrocyclic moieties could also be modified by the substitution and arrangement of N, O, S atoms in the ring system. The "hard" ether-oxygen-containing macrocycles show a binding preference toward "hard" alkali and alkaline earth metal cation, but the incorporation of "soft" sulfide

*Correspondence to: Yaşar Gök, email: gyasar@pau.edu.tr
tel.: +90 258-296-3567, fax: +90 258-296-3535

Copyright © 2013 World Scientific Publishing Company

J. Porphyrins Phthalocyanines 2013.17:480-488. Downloaded from www.worldscientific.com
by UNIVERSIDADE FEDERAL DO PARANA on 08/30/13. For personal use only.

or amine linkages shifts its preference toward "soft" heavy metal cations [4]. It has been demonstrated that macrocyclic ligands containing nitrogen-sulfur donor atoms can behave as highly selective complexing agents for transition metal cations [5]. The aza-ligands are more selective against hard ions whereas the thia-ligands preferentially bind soft ions. Selectivity can be enhanced by combining different donor atoms in one ring system. Therefore, nitrogen-sulfur macrocycles having different cycle size or arrangement have been prepared and their complexation properties have been investigated with various metal cations [6].

Pendant arm substitution also affects the complexation properties of a macrocycle. Such a substitution can increase the coordination capability of the unsubstituted macrocycles as they can encapsulate the metal into the macrocyclic cavity [7]. The cation-binding ability of these kind of macrocycles is essentially controlled by the nature of the macrocyclic cavity and pendant arms [8].

Transition metal ions represent a typical class of heavy metal ions that are generally considered to have deleterious effect on human beings and biological systems [9]. The dedection and measurement of copper(II) ions have been actively investigated due to its important role in various biological processes within the human body as an essential trace element [10]. The higher concentration of this cation causes liver and kidney failure as in the case of Wilson disease [11].

In this work, we have been synthesized novel phthalonitrile (L1), metal-free phthalocyanine (H_2Pc) and zinc-phthalocyanine (ZnPc) substituted in peripheral positions with four 2-pyridyl methyl pendant arm linked macrocyclic ligand with nitrogen-sulfur donor atoms and also spectrophotometric titrations with L1 and H_2Pc for Cu(II) cation were investigated.

EXPERIMENTAL

General methods and materials

Unless otherwise stated, all operations were carried out under argon atmosphere in a vacuum line or using standard Schlenk techniques. All solvents were freshly purified by standard procedures before use [12]. The metal perchlorates purchased from Acros were of the highest quality available and vacuum dried over silicagel blue before use. 2,2′-(pyridin-2-ylmethylazanediyl) diethanethiol (5) was synthesized according to the known procedure [13]. 4,5-dichlorophthalonitrile (1) and other chemicals were purchased from Merck and Aldrich as analytical grade and used without purification. ^{1}H and ^{13}C NMR spectra were measured on Varian Mercury 200-NMR and Varian Mercury Plus 300-MHz instruments. Infrared spectra were recorded on a Perkin Elmer Spectrum BX FT-IR spectrometre as KBr pellets. Mass spectra measured on micrOTOF and Micromass Quattro Ultima LC-MS/MS instruments. Electronic spectra were determined on a Perkin Elmer Lambda 25 spectrophotometer which is double-beamed with thermostatically controlled cell block. The elemental analysis were performed on a Costech ECS 4010 insrument. Melting points were determined on an electrothermal apparatus and are uncorrected.

Synthesis

4,5-Bis-(3-chloro-propylsulfanyl)-phthalonitrile (3). 3-chloro 1-propanthiol 2 (3.32 g, 30 mmol) was added to a solution of 4,5-dichlorophthalonitrile 1 (2.95 g, 15 mmol) in dry dimethyl formamide (20 mL) under argon atmosphere. After stirring for 15 min at 50 °C, dry fine-powdered sodium carbonate (1.85 g, 17.45 mmol) was added portion wise over 2 h with efficient stirring to this solution. The reaction mixture was stirred under argon at 50 °C for 7 days and monitored by thin layer chromatography [silica gel (chloroform:hexane) (95:5)]. After cooling to room temperature, the orange mixture was filtered off and the solvent was evaporated under reduced pressure and dried *in vacuo* and then diethyl ether (25 mL) was added to the residue and stirred overnight. The mixture was filtered and washed with diethyl ether and then dried *in vacuo*. The solid product was purified by crystallized from the acetone:diethyl ether mixture. Yield 3.36 g (65%), mp 106–107 °C. Anal. calcd. for $C_{14}H_{14}N_2S_2Cl_2$: C, 48.70; H, 4.09; N, 8.11%. Found C, 48.43; H, 3.97; N, 7.84. IR: δ, cm^{-1} 3083 (ArCH), 2957–2862 (CH_2), 2231 (C≡N), 1566, 1463, 1435, 1351, 1244, 1227, 1114, 957, 648. ^{1}H NMR (200 MHz, $CDCl_3$): δ_H, ppm 7.53 (s, 2H, ArH), 3.72 (t, 4H, $ClCH_2$), 3.22 (t, 4H, SCH_2), 2.19 (m, 4H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ_C, ppm 143.55, 133.27, 128.97, 114.52, 42.95, 30.40, 28.63. MS (LC-MS/MS): *m/z* 345.19 $[M]^+$.

4,5-Bis-(3-iodo-propylsulfanyl)-phthalonitrile (4). A solution of 3 (0.92 g, 2.67 mmol) in dry acetone (15 mL) was added into a solution of dry NaI (1.60 g, 10.68 mmol) in dry acetone (30 mL) in a round-bottom two-necked flask under argon atmosphere. The reaction mixture was refluxed and stirred for 3 h. The reaction was monitored by a thin layer chromatography [silica gel (chloroform)]. At the end of this period, the reaction mixture was cooled to room temperature and the precipitate was filtered off, washed with dry acetone and then the solution was evaporated to dryness under reduced pressure. The pale yellow crude product was crystallized from methanol. Yield 1.02 g (72%), mp 156 °C. Anal. calcd. for $C_{14}H_{14}N_2S_2I_2$: C, 31.83; H, 2.67; N, 5.30%. Found C, 31.65; H, 2.60; N, 5.18. IR: ν, cm^{-1} 3081 (ArH), 2958–2918 (CH_2), 2229 (C≡N), 1569, 1458, 1435, 1350, 1283, 1204, 1170, 1154, 1118, 959, 584. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H, ppm 7.65 (s, 2H, ArCH), 3.32 (t, 4H, ICH_2), 2.47 (t, 4H, SCH_2), 2.13 (m, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C, ppm 141.73, 135.67, 124.52, 111.43, 41.49, 32.63, 26.44. MS (LC-MS/MS): *m/z* 550.7 $[M + Na]^+$, 582.7 $[M + 3H_2O]^+$.

Copyright © 2013 World Scientific Publishing Company

J. Porphyrins Phthalocyanines 2013.17:480-488. Downloaded from www.worldscientific.com by UNIVERSIDADE FEDERAL DO PARANA on 08/30/13. For personal use only.

12-Pyridin-2-ylmethyl-7,8,11,12,13,14,17,18-octahydro-6H,10H,16H-5,9,15,19-tetrathia-12-azabenzocyclo-heptadecene-2,3-dicarbonitrile (L1). A solution of 4 (0.528 g, 1.0 mmol) in dry DMF (50 mL) and 5 (0.228 g, 1.0 mmol) in dry DMF (50 mL) was added *via* syringe pump under argon atmosphere over a period of 20 h to a stirred suspension of pre-dried Cs_2CO_3 (2.96 g, 9.1 mmol) in dry DMF (250 mL) at 35 °C. The reaction mixture was stirred at this temperature for a further 7 days. The reaction was monitored by thin layer chromatography (silica gel (ethyl acetate)). After cooling to room temperature the reaction mixture was evaporated under reduced pressure and the residue was dissolved with chloroform (150 mL). The organic phase was washed with water (30 mL × 3) and dried over $MgSO_4$ and then evaporated under reduced pressure to give brown oil product. The crude product was purified by column chromatography technique (silica gel (ethyl acetate)). Yield 0.29 g (58%). Anal. calcd. for $C_{24}H_{28}N_4S_4$: C, 57.56; H, 5.64; N, 11.19%. Found C, 57.26; H, 5.46; N, 11.08. IR: ν, cm^{-1} 3082 (ArH), 3059 (PyH), 2923–2852 (CH_2), 2227 (C≡N), 1648, 1588, 1560, 1457, 1431, 1346, 1257, 1224, 1112, 1044, 993. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H, ppm 8.55 (d, 1H, py-H), 7.75 (t, 1H, py-H), 7.69 (s, 2H, Ar-H), 7.58 (d, 1H, Py-H), 7.28 (t, 1H, Py-H), 3.77 (s, 2H, Py-CH_2), 2.73 (m, 4H, NCH_2), 2.63 (m, 4H, Ar-SCH_2), 2.55 (m, 8H, SCH_2), 2.01 (m, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C, ppm 159.49, 149.32, 144.78, 136.83, 135.51, 131.23, 123.40, 128.62, 123.40, 122.91, 115.60, 112.34, 60.34, 55.71, 40.18, 32.31, 27.82. MS (LC-MS/MS): *m/z* 501.13 $[M + 1]^+$.

Synthesis of metal-free phthalocyanine (H_2Pc). Dicarbonitrile compound (L1) (0.1352 g, 0.2704 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 0.3 mL) and dry pentanol (2.5 mL) were added into a Schlenk tube and then heated and stirred at 155 °C for 6 h under argon. After the reaction mixture cooled, the product was precipitated by adding methanol. Solid product was filtered and washed with methanol and diethyl ether. The purification of the dark green precipitate was carried out in a soxhlet extractor with chloroform. The solvent was then evaporated to give a deep green metal-free phthalocyanine. The product was dried *in vacuo*. Yield 0.035 g (26%). Anal. calcd. for $C_{96}H_{114}N_{16}S_{16}$: C, 57.51; H, 5.73; N 11.18%. Found C, 57.27; H, 5.58; N, 10.95. IR: ν, cm^{-1} 3221 (NH), 3090, 3062 (ArH), 2927–2858 (CH_2), 1645 (C=N), 1541, 1424, 1261, 1196, 1022, 856. UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 731 (4.50), 699 (4.53), 670 (4.37), 447 (4.20), 296 (4.74), 352 (4.65). ^{1}H NMR (200 MHz, $CDCl_3$): δ_H, ppm 8.65 (m, 4H, Py-H), 7.78 (m, 4H, Py-H), 7.65 (s, 8H, Ar-H), 7.55–7.14 (m, 4H, Py-H), 7.39 (m, 4H, Py-H), 3.97 (m, 8H, Py-CH_2), 2.89 (m, 16, NCH_2), 2.58 (m, 16H, Ar-S-CH_2), 2.48 (m, 32H, SCH_2), 1.93 (m, 16H, CH_2), -2.29 (s, 2H, N-H).

Synthesis of zinc phthalocyanine (ZnPc). A mixture of compound (H_2Pc) (0.037 g, 0.0185 mmol), anhydrous $Zn(OAc)_2$ (0.0034 g, 0.0185 mmol) and quinoline (1 mL) were added into a Schlenk tube and then heated and stirred at 180 °C for 6 h under argon. After having cooled to room temperature, the product was precipitated by adding methanol. Solid product was filtered and washed with methanol and diethyl ether. The purification of the green precipitate was carried out in a soxhlet extractor with chloroform. The solvent was then evaporated to give a green zinc phthalocyanine. The product was dried *in vacuo*. Yield 0.020 g (53%). Anal. calcd. for $C_{96}H_{112}N_{16}S_{16}Zn$: C, 55.74; H, 5.46; N, 10.83%. Found C, 55.49; H, 5.38; N, 10.75. IR: ν, cm^{-1} 3096 (CH_{Ar}), 2846–2921 (CH_3), 1645 (C=N), 1551, 1412, 1399, 1373, 1114, 1087, 1067, 943, 745, 699. UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 709 (4.84), 660 (4.56), 365 (4.79), 301 (4.80). ^{1}H NMR (200 MHz, $CDCl_3$): δ_H, ppm 8.72 (m, 4H, Py-H), 8.01 (m, 4H, Py-H), 7.74 (m, 8H, Ar-H), 7.49 (m, 4H, Py-H), 7.35 (m, 4H, Py-H), 4.09 (m, 8H, Py-CH_2), 2.83 (m, 16H NCH_2), 2.51 (m, 16H, Ar-S-CH_2), 2.39 (m, 32H, SCH_2), 1.89 (m, 16H, CH_2).

RESULTS AND DISCUSSION

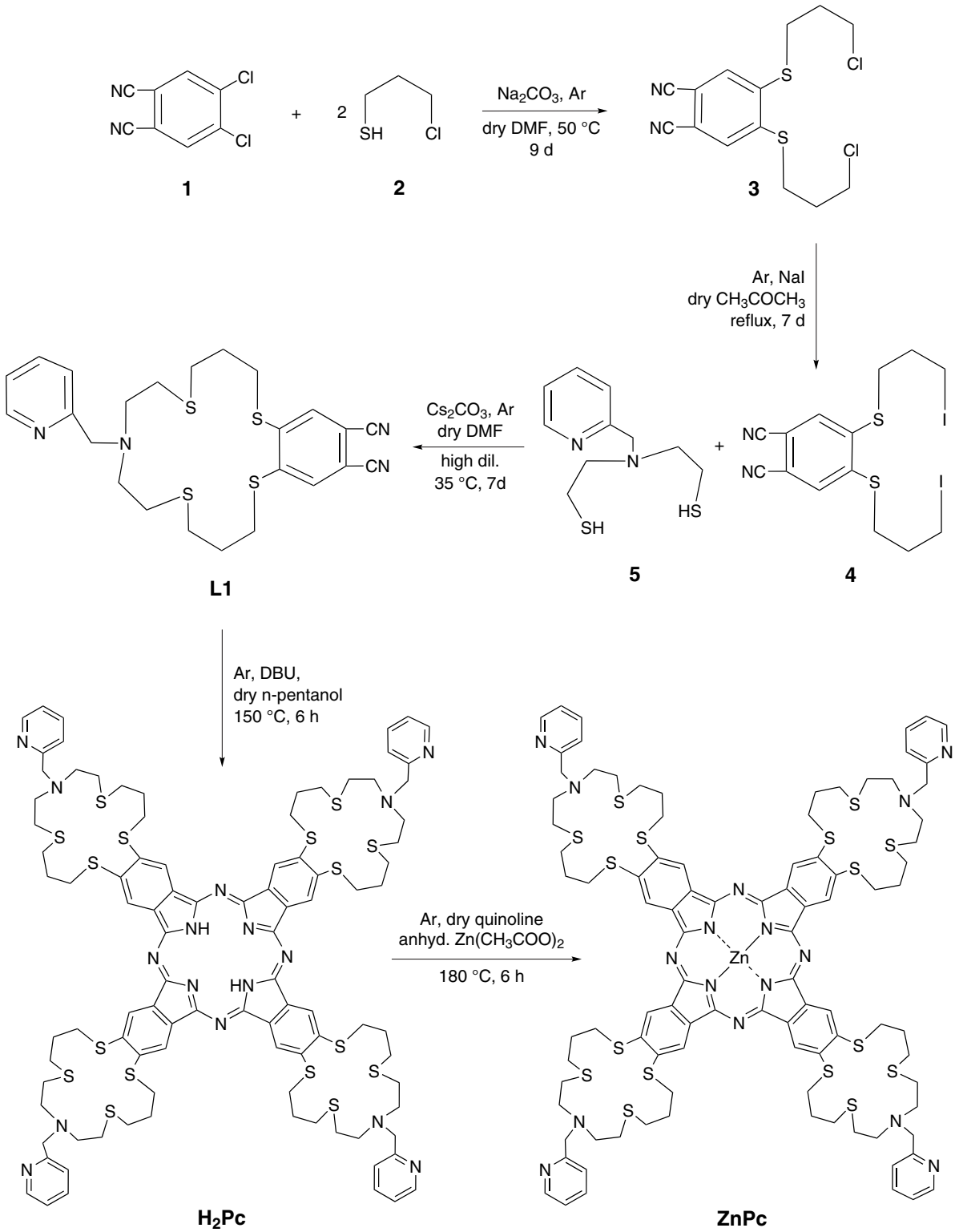
The preparation of the target metal-free (H_2Pc) and zinc(II) phthalocyanines (ZnPc) is shown in Scheme 1. To prepare the compound 3, 1,2-dichloro-4,5-dicyanobenzene (1) was reacted with 3-chloro-1-propanthiol (2) in dry DMF and Na_2CO_3. This displacement reaction was recognized in the ^{1}H NMR spectrum from the proton resonance of the CH_2Cl, CH_2S and CH_2 groups. By proton-decoupled ^{13}C NMR spectral data of the same compound, the presence of new signals due to the same groups also supported the formation of the proposed compound (3). The mass spectrum of 3, which showed a peak at *m/z* = 345 $[M]^+$ supported the proposed formula of this compound.

Conversion of 3 to 4 in 72% yield was carried out in dry acetone in the presence of dry NaI. The resonances of the aromatic protons and aromatic carbons in the proton or carbon-13 NMR spectra of 4 were very similar to those of the precursor compound 3 except for the chemical shifts of carbons and protons connected to CH_2-I groups. The elemental analysis and mass spectrum of 4 also supported the replacement of chlorine by iodine with the peaks at *m/z* = 550 and 582 indicating $[M + Na]^+$ and $[M + 3H_2O]^+$ formation, respectively.

17-membered monoaza-tetrathiamacrocycle (L1) was obtained in 58% yield from compound 4 with 2,2′-(pyridine-2-ylmethylazadiyl)-diethanethiol (5) at 35 °C. It was found that ^{1}H NMR spectrum of L1 clearly indicated the characteristic emerged resonances for the 17-membered macrocycles. This compound contained a pyridyl moieties and was substantiated by two characteristic resonances as expected. ^{13}C NMR spectrum of this compound showed individual resonances for the novel methylene connected to N, S atoms clearly suggesting the desired macrocyclization had accurred. Compound L1 displayed the expected molecular ion

Copyright © 2013 World Scientific Publishing Company

J. Porphyrins Phthalocyanines 2013.17:480-488. Downloaded from www.worldscientific.com
by UNIVERSIDADE FEDERAL DO PARANA on 08/30/13. For personal use only.



Scheme 1. Synthesis of metal-free (**H_2Pc**) and zinc phthalocyanine (**ZnPc**)

peak at *m/z* = 501 $[M + 1]^+$ in its mass spectrum, which supported the structure. The result of the mass spectrum of L1 is shown in Fig. S1 (Supplementary information).

Cyclotetramerization of four dicyano compound (L1) into the metal-free phthalocyanine was carried out in dry *n*-pentanol in 26% yield as deep green solid after purification. The ^{1}H NMR spectrum of H_2Pc in $CDCl_3$ exhibited the characteristic resonances of the macrocycle and phtahaolcyanine moieties. Strong shielding of the cavity protons in the phthalocyanine core of this compound

Copyright © 2013 World Scientific Publishing Company

J. Porphyrins Phthalocyanines 2013.17:480-488. Downloaded from www.worldscientific.com
by UNIVERSIDADE FEDERAL DO PARANA on 08/30/13. For personal use only.

was manifested by a broad signal at δ = -2.29 ppm at the high concentration which is attributed to the N–H resonance and easily confirmed with deuterium exchange [14]. In the IR spectrum of this compound, a diagnostic feature of the formation of L1 was the disappearance of the sharp C≡N resonances and the presence of C=N and N–H vibrations at 1645 and 3221 cm^{-1}, respectivley, confirmed the formation of metal-free phthalocyanine.

The synthesis of zinc(II) phthalocyanine (ZnPc) was accomplished with metal-free phthalocyanine (H_2Pc) and anhydrous $Zn(CH_3COO)_2$ in dry quinoline. The ^1H NMR spectrum of ZnPc was identical with those of the precursor metal-free phthalocyanine (H_2Pc), a significant difference being the disappearance of the broad inner core NH protons. However, aromatic protons which are neighbourhood to phthalocyanine core were shifted to lower field because of the π-electron ring current effect of the phthalocyanine core even after complexation with zinc(II) [15]. The characteristic proton resonances of the proposed structure of ZnPc exhibited the pyridyl and aliphatic resonances of monoazatetrathia macrocycle moieties at the expected region.

The UV-vis spectra of H_2Pc and ZnPc in chloroform showed characteristic absorption in the Q-band region at 731–670 and 709–660 nm, respectively (Fig. 1). The split Q-band for metal-free phthalocyanine which is the characteristics of this class of compounds showed the Q-band absorptions of D_{2h} symmetry [16]. This two absorptions around 731(Q_x) and 699 (Q_y) nm were due to the π→π* trasition of the fully conjugated 18 π electron system [17]. For H_2Pc, the effect of macrocyclic thia substitution caused a shift of intense Q-band to higher wavelengths compared to substituted alkyl or alkoxy derivatives [18]. The bands of H_2Pc were broadened due to the superimposition of the B_1 and B_2 bands in the 350 nm region [19]. The electronic spectrum of ZnPc showed characteristic Q-band absorption as a singlet peak at 709 nm and a shoulder at 660 nm. The formation of ZnPc caused significant change in the Q-band with incresing of the intensity of the peak at 731 nm which observed for H_2Pc. The absorption spectrum of ZnPc also showed monomeric behavior evidenced by a single and narrow Q-band typical for tetrasubstituted derivatives of metallophthalocyanines [18a].

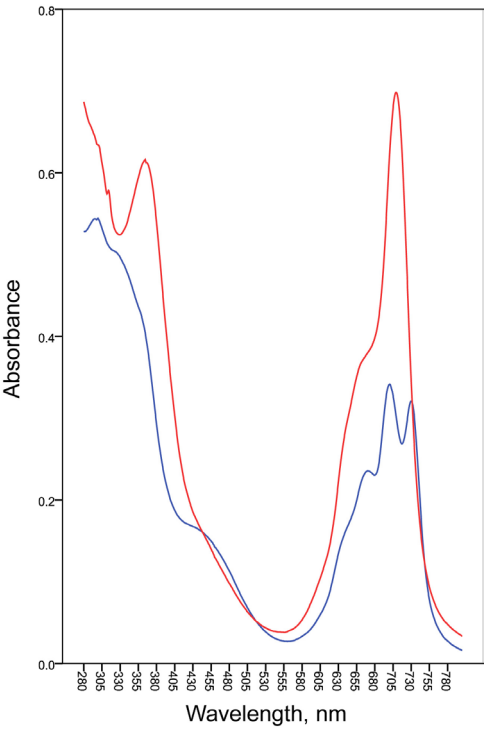


Fig. 1. UV-vis spectra of H_2Pc (–) and ZnPc (–) (1×10^{-5} M in chloroform)

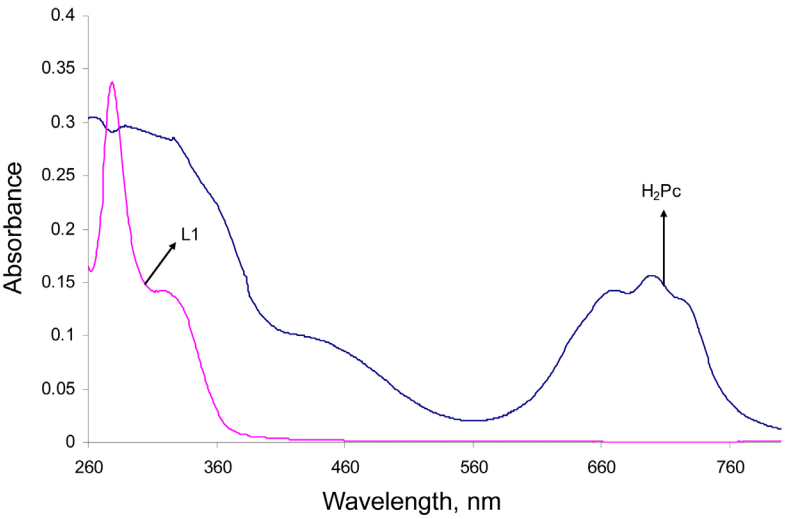


Fig. 2. The absorption spectra of the ligands (**L1**) and **H_2Pc**. Concentration: 1.3×10^{-5} M. Solvent:chloroform-acetonitrile (1/1)

The UV-vis spectra of L1 and H_2Pc in acetonitrile-chloroform solution (1/1) are given Fig. 2. Absorption spectra of L1 with a concentration of 1.29×10^{-5} M in acetonitrile-chloroform solution (1/1) containing 10 molar equivalents of appropriate metal perchlorate salt were measured using 1 cm long absorption cell. Figure 3 shows the effect of Al^{3+}, Fe^{3+}, Cd^{2+}, Zn^{2+}, Hg^{2+} and Cu^{2+} cations on the absorptions of the nitrile compound, L1. As seen from Fig. 3, all metal cations caused moderate change in absorbance at 278 nm except for Cu^{2+}. Cu^{2+} caused a significant enhancement in absorption at 278 nm. This finding suggested that the nitrile compound L1 interacted strongly with Cu^{2+} compared to other metal cations.

Copyright © 2013 World Scientific Publishing Company

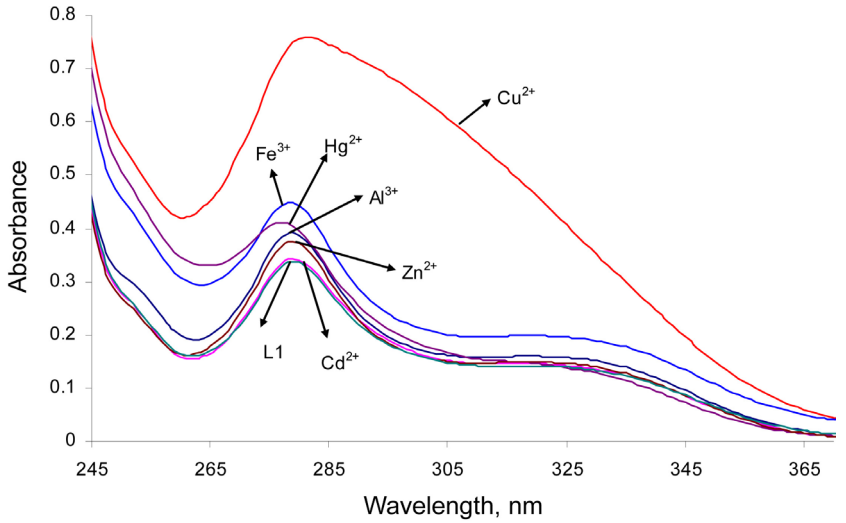


Fig. 3. The effects of metal cations on the absorption spectra of **L1**. Solvent: acetonitrile-chloroform (1/1), Ligand concentration: 1.3×10^{-5} M. Metal perchlorate concentration: 1.3×10^{-4} M

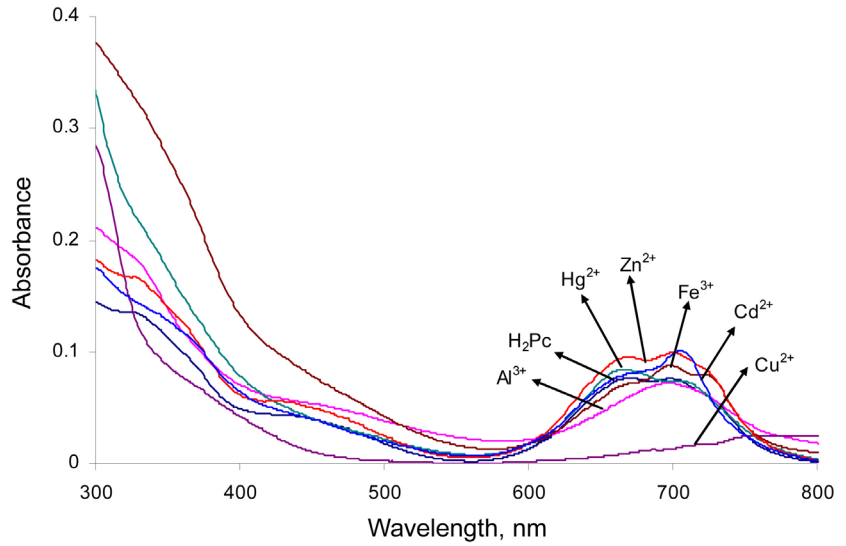


Fig. 4. The effects of metal cations on the absorption spectra of **H_2Pc**. Solvent: acetonitrile-chloroform (1/1), Ligand concentration: 1.3×10^{-5} M. Metal perchlorate concentration: 1.3×10^{-3} M

J. Porphyrins Phthalocyanines 2013.17:480-488. Downloaded from www.worldscientific.com by UNIVERSIDADE FEDERAL DO PARANA on 08/30/13. For personal use only.

The effect of Al^{3+}, Fe^{3+}, Cd^{2+}, Zn^{2+}, Hg^{2+} and Cu^{2+} cations in the absorption of the free phthalocyanine H_2Pc with a concentration of 1.29×10^{-5} M in acetonitrile-chloroform solution (1/1) were shown in Fig. 4. 100-fold metal concentrations were used in measurements. As seen from Fig. 4, all metal cations caused moderate changes in absorbance within the Q-band region (699 nm) except for Cu^{2+}. This result was similar to that of L1. However, a significant decrease in absorbance was observed for Cu^{2+} in the case of H_2Pc. This finding suggested that the free phthalocyanine compound H_2Pc also interacted strongly with Cu^{2+} compared to other metal cations.

The interaction of Cu^{2+} ion with both ligands can be explained with the crown ether ring having soft donor atoms. Soft donor atoms, especially sulfur, prefer interaction with soft metal ion such as Cu^{2+} [20]. This is well-known as HSAB concept [21]. In this content, crown ether rings on the peripheral positions of the phthalocyanine compound H_2Pc may be effective with the interaction with Cu^{2+}.

Spectrophotometric titrations

According to the results of Figs 3 and 4, we decided to carry out spectrophotometric titrations with L1 and H_2Pc for Cu^{2+} ion. Spectrophotometric titration was not carried out with ZnPc because it does not have good solubility in acetonitrile-chloroform solution (1/1). Figure 5 shows the

Copyright © 2013 World Scientific Publishing Company

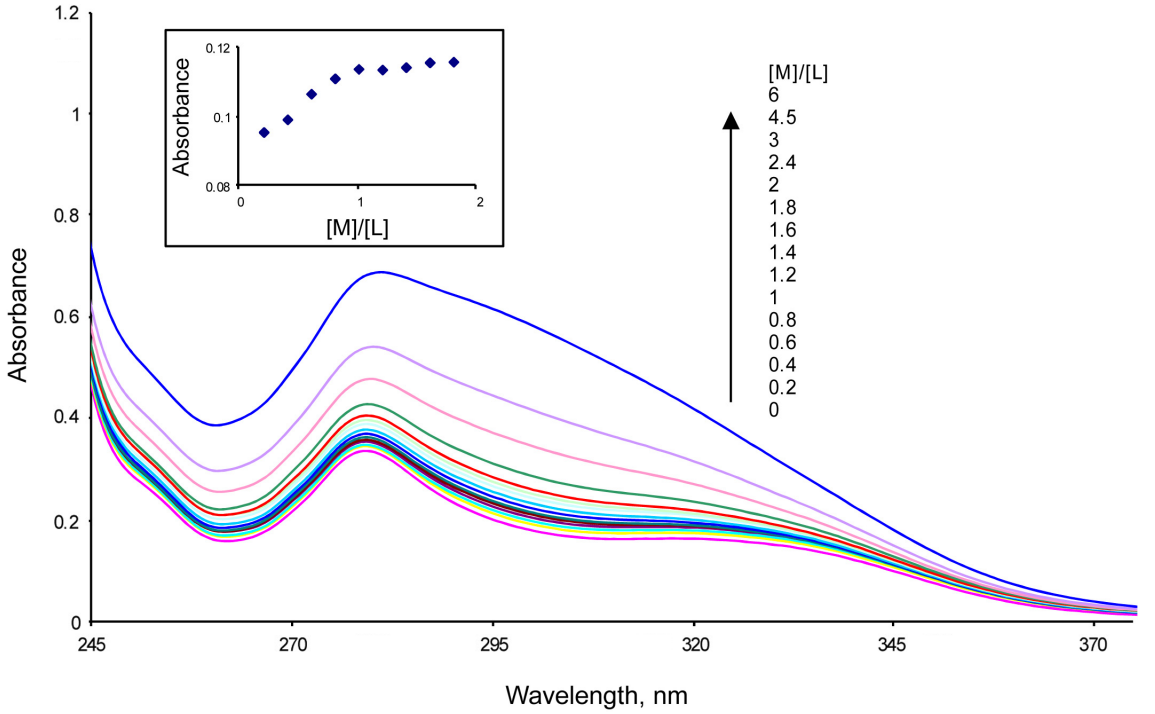


Fig. 5. Absorption spectra of **(L1)** complexed with Cu^{2+}. The spectral changes during the addition of 0–6 equivalents of $Cu(ClO_4)_2$. Ligand concentration: 1.3×10^{-5} M. Inset: Molar ratio plot for the Cu-L1 complex. Wavelength: 345 nm

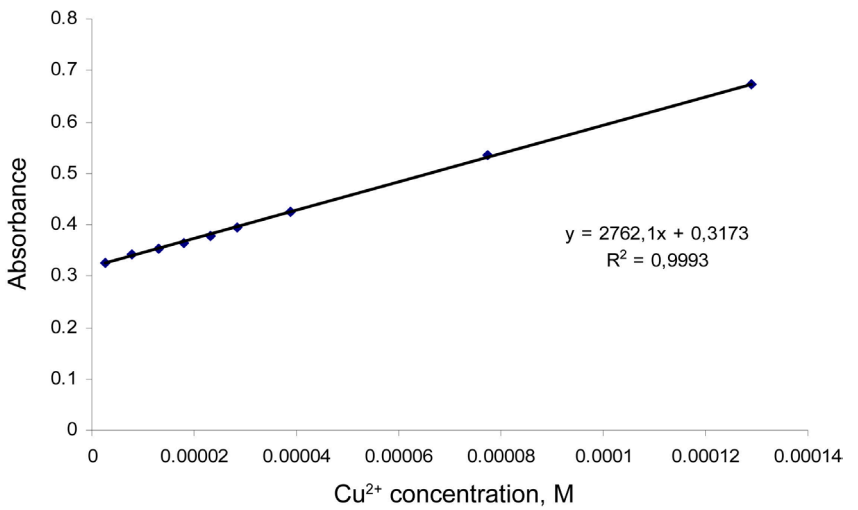


Fig. 6. Absorbance of the **L1** *vs.* the Cu^{2+} concentration for the spectrophotometric titration. Wavelength: 278 nm, ligand concentration = 1.3×10^{-5} M

change of absorption spectra of L1 with increasing Cu^{2+} concentration. The spectral changes were recorded during the addition of 0–6 equivalents of $Cu(ClO_4)_2$. Inset shows molar ratio plot for the Cu-L1 complex. The inflection point was 1.0 ([M]/[L]). It can thus be concluded that L1 formed a stable 1:1 (M:L) complex with Cu^{2+}. Figure 6 shows the regular absorbance enhancement depending on increasing Cu^{2+} concentrations with L1. A linear response of the absorbance at 278 nm as a function of Cu^{2+} concentration was observed from 2.6×10^{-6} to 1.3×10^{-4} M with linearly dependent coefficient R^2 = 0.9993 (Fig. 6).

The change in the absorption spectra of the ligand H_2Pc with increasing concentrations of Cu^{2+} is shown in Fig. 7. There are three isosbestic points at 486, 596, and 758 nm. This result indicates that there were three equilibriums during the complexation. Isosbestic points were not clear when it was observed in detail. This seems to be due to the presence of small amounts of free ligand. The presence of many isosbestic points may

J. Porphyrins Phthalocyanines 2013.17:480-488. Downloaded from www.worldscientific.com
by UNIVERSIDADE FEDERAL DO PARANA on 08/30/13. For personal use only.

Copyright © 2013 World Scientific Publishing Company

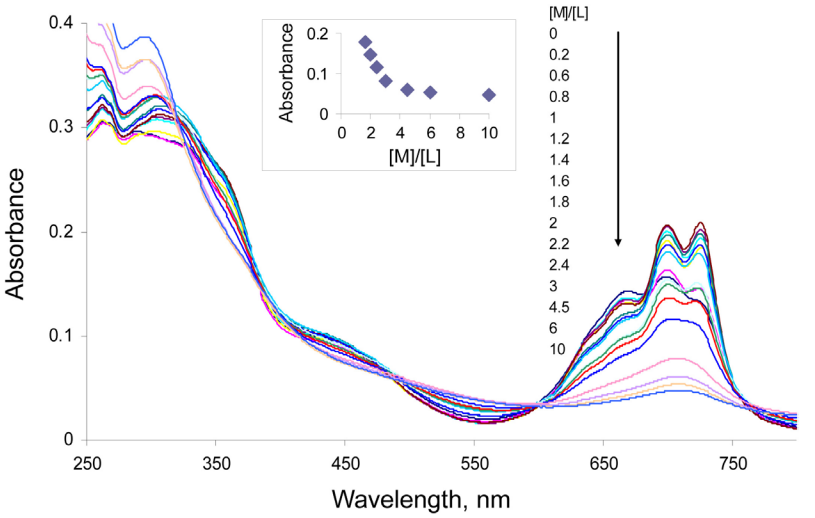


Fig. 7. The change in absorption spectra of **H_2Pc** increasing Cu^{2+} concentration. 0–10 equivalents of $Cu(ClO_4)_2$. Ligand concentration: 1.3×10^{-5} M. Inset: Molar ratio plot, 698 nm

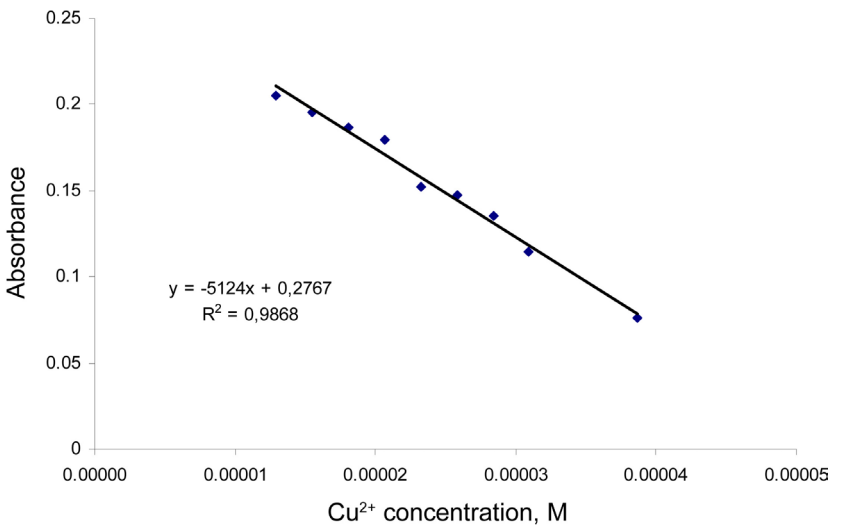


Fig. 8. Absorbance of the **H_2Pc** *vs.* the Cu^{2+} concentration for the spectrophotometric titration. Wavelength: 698 nm, ligand concentration = 1.3×10^{-5} M

result from different complex compositions. Figure 7 inset shows the molar ratio plot for Cu-Pc complex. As seen from the inset, the break point is [M]/[L] = 4. This result shows that the complex stoichiometry for Cu-Pc is 4:1 (M:L). In this case, one can be say that Cu^{2+} ions insert monoazatetrathia crown ether cavities in peripheral positions of the free phthalocyanine compound H_2Pc. Reason of this is affinity of soft sulfur donor atoms to soft metal ion such as Cu^{2+} as expected from HSAB concept. We also found a regular change in the absorption spectra of H_2Pc with increasing concentrations of Cu^{2+}. A linear decrease of the absorbance at 698 nm as a function of Cu^{2+} concentration were observed from 1.3×10^{-5} to 3.4×10^{-5} M with linearly dependent coefficient $R^2 = 0.9868$ (Fig. 8).

CONCLUSION

A peripherally substituted phthalocyanine derivative containing pendant armed linked 17-membered monoaza-tetrathia macrocycle was synthesized in good yield by the cycloteramerization reaction of 12-pyridine-2-ylmethyl-7,8,11,12,13,14,17,18-octahydro-6H,10H,16H-5,9,15,19-tetrathia-12-azabenzocycloheptadecene-2,3-dicarbonitrile in the presence of DBU in dry n-pentanol. With the desired anhydrous zinc(II) acetate, it became possible to convert the metal-free phthalocyanine into metallo derivative (ZnPc). This acetate of Zn(II) has been used in dry quinoline to prepare metallphthalocyanine. All structures of the novel compounds have been unequivocally identified by using elemental analaysis, IR, NMR, UV-vis and MS techniques.

J. Porphyrins Phthalocyanines 2013.17:480-488. Downloaded from www.worldscientific.com by UNIVERSIDADE FEDERAL DO PARANA on 08/30/13. For personal use only.

Copyright © 2013 World Scientific Publishing Company

On the other hand, both L1 and H_2Pc can be used as selective ligands to determinate Cu^{2+} ion in various real samples by spectrophotometric method. This result has an important role in a possible selective system. We observed that L1 showed a selectivity for Cu(II) cation as seen in Fig. 6, that may lead to practical applications in the field of environmental sciences. It is obvious that, L1 is better than H_2Pc because of it's larger linear range for Cu^{2+} concentration (2.6×10^{-6} to 1.3×10^{-4} M), the higher linear dependent coefficient ($R^2 = 0.9993$) and the simpler chemical structure.

Supporting information

Mass spectrum of L1 is given in the supplementary material (Fig. S1). This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

Acknowledgements

The authors thank to the Research Fund of Pamukkale University, Project number: 2008 FBE 002 (Denizli/Turkey) for financial support.

J. Porphyrins Phthalocyanines 2013.17:480-488. Downloaded from www.worldscientific.com by UNIVERSIDADE FEDERAL DO PARANA on 08/30/13. For personal use only.

REFERENCES

1. a) Melson GA. *Coordination Chemistry of Macrocyclic Compounds*, Plenum: New York, 1979. b) Formanowskii AA and Mikhura IV. In *Synthesis of Macrocyclic Compounds*, *Macrocyclic Compounds in Analytical Chemistry*, Zolotov YA. (Ed.) Wiley-Interscience: New York, 1997; pp 5–39.
2. *Phthalocyanines: Properties and Applications*, Vol. 1–4, Leznoff CC and Lever ABP. (Eds.) VCH: Weinheim 1989–1996.
3. a) Beck A, Mangold KM and Hanack M. *Chem. Ber*. 1991; **124**: 2315–2321. b) Ahsen V, Gül A and Bekaroğlu Ö. *ibid*. 1991; **124**: 2531–2536.
4. a) Chartres JD, Davies MS, Lindoy LF, Meehan GV and Wei G. *Inorg. Chem. Commun.* 2006; **9**: 751–754. b) Kabay N and Gök Y. *ibid*. 2011; **14**: 1880–1883.
5. a) Fujiwara M, Matsushita T and Shono T. *Polyhedron* 1984; **3**: 1357–1363. b) Beklemishev MK, Dmitrenko SG and Isakova NV. In *Macrocyclic Compounds in Analytical Chemistry*, Zolotov YA. (Ed.) Wiley-Interscience: New York, 1997; pp 63–208. c) Gök Y, Kantekin H, Bilgin A, Mendil D and Değirmencioğlu İ. *Chem. Commun.* 2001; 285–286.
6. a) Lindoy LF and Baldwin DS. *Pure Appl. Chem*. 1989; **61**: 909–914. b) Groth AM, Lindoy LF and Meehan GV. *J. Chem. Soc. Perkin Trans*. 1996; **1**: 1553–1558. c) Alp H, Gök HZ, Kantekin H and Ocak Ü. *J. Hazard. Mater*. 2008; **159**: 519–522. d) Tanaka M, Nakamura M, Ikeda T, Ando H, Shibutani Y, Yaji-ma S and Kimura K. *J. Org. Chem*. 2001; **66**: 7008–7012.
7. Tsukube H. *J. Coord. Chem*. 1987; **16**: 101–129.
8. Botana L, Bastida R, Macias A, Perez-Lourido P and Valencia L. *Inorg. Chem. Commun*. 2009; **12**: 249–251.
9. Förstner U and William GTW. *Metal Pollution in the Aquatic Environment*, Springer-Verlag: Berlin, 1983.
10. Kim HY, Kim SH, Kim JH, Anh LN, Lee JH, Lee CH and Kim JS. *Tetrahedron Letters* 2009; **50**: 2782–2786.
11. a) Linder MC and Hazegh-Azam M. *Am. J. Clin. Nutr.* 1996; **63**: 797S–811S. b) Uauy R, Oliveras M and Gonzales M. *ibid.* 1998; **67**: 952S–959S.
12. Perrin DD, Armarego WLF and Perin DR. *Purification of Laboratory Chemicals*, 2nd Ed. Pergamon Press: Oxford, 1980.
13. Peng Y, Li Z, Niu Z, Liu Y, Zeng X, Luo Q, Hughes DL and Liu X. *Inorg Chim Acta* 2009; **362**: 3975–3981.
14. Kaboyashi T, Kurukawa F, Uyeda N and Satio E. *Spectrochim Acta Part A: Mol. Spect.* 1970; **26**: 1305.
15. Ahsen V, Yılmazer E, Erbaş M and Bekaroğlu Ö. *J. Chem. Soc., Dalton Trans.* 1988; 401–406.
16. Dabak S, Gümüş G, Gül A and Bekaroğlu Ö. *J. Coor. Chem.* 1996; **38**: 287–293.
17. a) Hanack M, Heckman H and Polley R. *Methods of Organic Chemistry*, Additional Suıpplementary Volume, George Thieme: Stutgard, 1998; pp 776. b) Bilgin A and Gök Y. *Supramol. Chem.* 2006; **18**: 491–499.
18. a) Stillman MJ and Nyokong T. *Absorption and Magnetic Circular Dichroism Spectral Properties of Phthalocyanines Part 1: Complexes of Dianion, Pc (-2), in Phthalocyanines: Properties and Applications*, Leznoff CC and Lever ABP. (Eds.) VCH: New York, 1989; pp 133–289. b) Atilla D, Saydan N, Durmuş M, Gürek AG, Khanc T, Ruck A, Walt H, Nyokong T and Ahsen V. *J. Photochem. Photobiol. A: Chemistry* 2007; **186**: 298–307. c) Gürek AG and Bekaroğlu Ö. *Helv. Chim. Acta* 1994; **77**: 1616–1622.
19. Atilla D, Durmuş M, Yılmaz Ö, Gürek AG, Ahsen V and Nyokong T. *Eur. J. Inorg. Chem.* 2007; 3573–3581.
20. a) Saito K, Taninaka I, Yamamato Y, Murakami S and Muromatsu A. *Talanta* 2000; **51**: 913–919. b) Ohki A, Takagi M and Ueno K. *Anal. Chim. Acta* 1984; **159**: 245–253. c) Ikeda K and Abe S. *Anal. Chim. Acta* 1998; **363**: 165–170.
21. Beer PD, Gale PA and Smith DK. In *Supramolecular Chemistry*, Evans J. (Ed.) Oxford Universty Press Inc.: New York, 1999; pp 15–30.

Copyright © 2013 World Scientific Publishing Company