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Synthesis and characterization of novel soluble octa-cationic phthalocyanines

Zehra Altuntaş Bayır*

Department of Chemistry, Technical University of Istanbul, 34469 Maslak, Istanbul, Turkey

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Abstract

Metal-free **3** and metallophthalocyanines **4**, **5** (M = Zn, Co) having diethylaminoethylsulfanyl substituents on peripheral positions were prepared. Quaternization of **4**, **5** produced cationic metallophthalocyanines soluble in water and slightly soluble in ethanol. Zinc(II) and Co(II) phthalocyanines reacted with palladium(II) salt to form complexes with a phthalocyanine/metal ratio of 1:4. The new compounds have been characterized by elemental analyses, IR, UV–Vis, mass, ^{1}H NMR and ^{13}C NMR spectroscopies.

Keywords: Phthalocyanines; Water-soluble; Cationic photosensitizers; Pentanuclear complexes

1. Introduction

Phthalocyanines constitute one of the most extensively studied class of functional organic materials owing to their catalytic, structural, electronic and optical properties in addition to their wide spread use as dyes and pigments. These compounds have found wide applications in diverse areas such as liquid crystals, electronic devices, gas sensors, photosensitizers, nonlinear optics, electrochromic devices and Langmuir–Blodgett films [1,2].

One of the most prominent new applications of phthalocyanine derivatives is their application as photosensitizers for the photodynamic therapy of cancer. Photodynamic therapy is a binary therapy that involves the combination of visible light and a photosensitizer. Phthalocyanines display cytotoxic effects when activated by light. Upon irradiation, these photosensitizers are promoted to their excited states and generate singlet oxygen. Surrounding biomolecules are damaged and this starts a cascade of biological response leading to the tumour death. It has been reported that water-soluble phthalocyanine derivatives, especially aluminium and zinc complexes, are the most studied as photosensitizers for PDT [3–5].

A disadvantage of metal-free and metallophthalocyanines is their limited solubility in common organic solvents. It is possible to attach a wide variety of substituents at the periphery of the phthalocyanine, but most of the time they can alter the electronic structure of the system. Substituents are introduced either by substitution reactions on the preformed macrocycle or, more commonly, through the use of appropriately substituted precursors, especially phthalonitrile derivatives. Substituents provide the prime means of solubilizing the ring system in either aqueous media or organic solvents and offer a useful way of tuning the wavelength of the visible region absorption band [6–8].

Soluble phthalocyanines are essentially obtained by peripheral substitution with long alkyl or alkoxy units,

* Fax: +90 212 2856386.
E-mail address: bayir@itu.edu.tr

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which are mostly bulky groups; when electron donating moieties (e.g. oxa-, thia- etc.) are present between the phthalocyanine core and the substituents, a bathochromic shift of the Q-band occurs simultaneously [9–16]. The introduction of carboxy or amino groups gives water-soluble products [17,18].

The aim of the present paper has been to introduce bulky diethylaminoethylsulfanyl substituents on the periphery of metal-free and metallophthalocyanines, while quaternization with methyliodide is expected to yield products soluble in water and also other less polar solvents such as alcohols. Complexation of peripheral donor groups of Zn(II) and Co(II) phthalocyanines with Pd(II) ions to obtain multinuclear products has also been investigated.

2. Experimental

IR spectra were recorded on an ATI Unicam-Mattison 1000 spectrophotometer using KBr pellets, electronic spectra on a Unicam UV2 spectrophotometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of TUBITAK Marmara Research Center. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 250 MHz spectrometer. Mass spectra were recorded on a VG Zab-Spec spectrometer. All reagents and solvents were of reagent grade quality obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [19]. The solvents were stored over molecular sieves. The homogeneity of the products was tested in each step using TLC. 1,2-Dichloro-4,5-dicyanobenzene (**1**) was synthesized according to the reported procedure [20].

Cyclic voltammetry (CV) was carried out with a Princeton Applied Research Model 273 potentiostat/galvanostat controlled by an external PC using the computer program HEADSTRT and utilizing a three electrode configuration at 25 °C. An Origin 6.0 graph program was used to evaluate HEADSTRT data, to draw voltammograms, and to analyze them. A Pt wire served as the counter electrode. A saturated calomel electrode (SCE) was employed as the reference electrode. The working electrode was a Pt plate with an area of 1.0 cm^2. The surface of the working electrode was polished with a H_2O suspension of Al_2O_3 before each run. The last polishing was done with a particle size of 50 nm. Electrochemical grade tetrabutyl ammonium perchlorate (TBAP) in extra pure DMSO was employed as the supporting electrolyte at a concentration of 0.1 mol dm^{-3}. High purity N_2 was used for deaeration and to maintain a nitrogen blanket for at least 15 min prior to each run. For the Controlled Potential Coulometry (CPC) studies, a Pt gauze working electrode (10.5 cm^2 surface area), a Pt wire counter electrode separated with a double bridge, an SCE as reference electrode, and a model 377/12 synchronous stirrer were used.

2.1. 1,2-Bis-(diethylaminoethylsufanyl)-4,5-dicyanobenzene (2)

1,2-Dichloro-4,5-dicyanobenzene (1.16 g, 5.88 mmol) was dissolved in anhydrous dimethyl formamide (50 mL) under N_2 and 2-diethylaminoethanethiolhydrochloride (3 g, 17.67 mmol) was added. After stirring for 10 min, finely ground anhydrous K_2CO_3 (9.75 g, 70.68 mmol) was added in portions over 2 h with efficient stirring. The reaction mixture was stirred at 32 °C for 48 h under nitrogen. Then the solution was poured into ice water (300 g). The precipitate was filtered off, washed with water until the filtrate was neutral and dried in vacuo. Purification of the product was accomplished by column chromatography with neutral alumina (eluent: $CHCl_3$:MeOH, 7:1). Yield: 1.65 g (72%), m.p.: 59 °C (Found: C, 61.36%; H, 7.65%; N, 14.31%. Calc. for $C_{20}H_{30}N_4S_2$: C, 61.54%; H, 7.69%; N, 14.36%); IR (KBr) ν_{max}/cm^{-1}: 3080, 2978–2828, 2238, 1574, 1472, 1395, 1344, 1293, 1217, 1140, 1089, 910, 740, 659. ^{1}H NMR ($CDCl_3$) $\delta = 7.52$ (s, 2H, Ar–H), 3.10 (t, 4H, SCH_2), 2.78 (t, 4H, NCH_2), 2.60 (qnt, 8H, CH_2C), 1.03 (t, 12H, CH_3) ppm. ^{13}C NMR (APT) ($CDCl_3$) $\delta = 144.51$ (aromatic C–S), 128.98 (aromatic CH), 115.49 (C ≡ N), 111.27 (aromatic C), 51.37 (CH_2N), 47.11 (NCH_2), 31.61 (SCH_2), 11.89 (CH_3) ppm.

2.2. Octakis-(2-diethylaminoethylsulfanyl)-phthalocyanine (3)

A solution of **2** (0.250 g, 0.64 mmol) in 2-(dimethylaminoethanol) (1 ml) was refluxed under N_2 for 15 h. After cooling to room temperature the green mixture was treated with MeOH:H_2O (1:1, 10 ml) to precipitate the product completely. The green precipitate was filtered off and chromatographed on a neutral alumina with THF:MeOH (30:1) as eluent. Yield: 0.028 g (11%) (Found: C, 61.06%; H, 7.24%; N, 14.11%. Calc. for $C_{80}H_{122}N_{16}S_8$: C, 61.46%; H, 7.81%; N, 14.34%); IR (KBr) ν_{max}/cm^{-1}: 3320 (NH), 2978–2880 (CH_2), 1610, 1574, 1421, 1350, 1320, 1063, 961, 757, 680. ^{1}H NMR ($CDCl_3$): $\delta = 8.35$ (s, 8H, Ar–H), 3.45 (t, 16H, SCH_2), 2.96 (t, 16H, NCH_2), 2.83 (qnt, 32H, CH_2C), 1.12 (t, 48H, CH_3), −4.79(s, NH, 2H) ppm.

2.3. Octakis-(2-diethylaminoethylsulfanyl)-phthalocyaninatozinc (II) (4)

A mixture of **2** (0.500 g, 1.28 mmol), 2-(dimethylaminoethanol) (1.8 ml) and anhydrous $Zn(CH_3COO)_2$ (0.059 g, 0.32 mmol) was refluxed under N_2 for 18 h. After cooling to room temperature, MeOH:H_2O (1:1,

20 ml) was added in order to precipitate the product. The dark green product was filtered off and washed with water. It was isolated on a neutral alumina column with THF:MeOH (30:1) as eluent. Yield: 0.098 g (19%) (Found: C, 58.95%; H, 7.13%, N, 13.29%. Calc. for $C_{80}H_{120}N_{16}S_8Zn$: C, 59.06%; H, 7.38%; N, 13.78%); IR (KBr) ν_{max}/cm^{-1}: 2953–2876 (CH_2), 1676, 1472, 1395, 1268, 1089, 961, 740, 644. ^1H NMR ($CDCl_3$): $\delta = 8.28$ (s, 8H, Ar–H), 3.11 (t, 16H, SCH_2), 2.77 (t, 16H, NCH_2), 2.56 (qnt, 32H, CH_2C), 1.05 (t, 48H, CH_3) ppm.

2.4. Octakis-(2-diethylaminoethylsulfanyl)-phthalocyaninatocobalt (II) (**5**)

A mixture of compound **2** (0.300 g, 0.77 mmol), anhydrous $CoCl_2$ (0.025 g, 0.19 mmol) and 2-(dimethylaminoethanol) (1.1 ml) was refluxed for 12 h under N_2. After cooling to room temperature, it was treated with MeOH:H_2O (1:1, 10 ml) and the green product filtered off. The dark green metallophthalocyanine was isolated on a neutral alumina column with THF/MeOH (20:1) as eluent. Yield: 0.043 g (14%) (Found: C, 59.07%; H, 7.25%, N, 13.14%. Calc. for $C_{80}H_{120}N_{16}S_8Co$: C, 59.30%; H, 7.41%; N, 13.84%); IR (KBr) ν_{max}/cm^{-1}: 2978–2825 (CH_2), 1600, 1523, 1421, 1319, 1140, 1089, 987, 755, 700, 658. MS (FAB) *m/z*: 1619.5.

2.5. Octakis-((2-diethylmethylaminoethylsulfanyl)-pthalocyaninatozinc(II))octaiodide (**4a**)

Compound **4** (0.120 g, 0.074 mmol) was dissolved in $CHCl_3$ (4.5 ml) and methyl iodide (0.094 g, 0.664 mmol) was added to this solution. The mixture was refluxed for 3 h. After cooling to room temperature, the green precipitate was filtered off, washed with $CHCl_3$ and dried. Yield: 0.112 g (55%) (Found: C, 38.13%; H, 5.12%; N, 8.01%. Calc. for $C_{88}H_{144}N_{16}S_8I_8Zn$: C, 38.24%; H, 5.21%; N, 8.11%); IR (KBr) ν_{max}/cm^{-1}: 2976–2952 (CH_2), 1621, 1548, 1420, 1396, 1277, 1140, 1088, 987, 737, 701, 670. ^1H NMR (DMSO): $\delta = 9.26$ (s, 8H, Ar–H), 4.05 (t, 16H, SCH_2), 3.78 (t, 16H, NCH_2), 3.60 (qnt, 32H, CH_2C), 3.21(s, 24H, CH_3), 1.35 (t, 48H, CCH_3) ppm.

2.6. Octakis-((2-diethylmethylaminoethylsulfanyl)-phthalocyaninatocobalt(II))octaiodide (**5a**)

Prepared as described for **4a**, starting from **5** (0.100 g, 0.062 mmol) in $CHCl_3$ (4 ml) and CH_3I (0.079 g, 0.555 mmol). Yield: 0.076 g (45%) (Found: C, 38.15%; H, 5.09%; N, 8.10%. Calc. for $C_{88}H_{144}N_{16}S_8I_8Co$: C, 38.33%; H, 5.23%; N, 8.13%) IR (KBr) ν_{max}/cm^{-1}: 2978–2953 (CH_2), 1625, 1548, 1421, 1395, 1278, 1140, 1089, 987, 738, 701, 672.

2.7. Octakis-(2-diethylaminoethylsulfanyl)-phthalocyaninato-zinc(II)tetrapalladium(II)) octa chloride (**4b**)

Complex **4** (0.110 g, 0.068 mmol) was dissolved in tetrahydrofuran–water (7 + 0.2 ml) and a solution of $Na_2[PdCl_4]$ $3H_2O$ (0.188 g, 0.54 mmol) in the same solvent mixture was added. The reaction mixture became dark green while refluxing for 2 h and precipitation occurred. The product was separated by centrifuging and washed several times successively with hot water, hot ethanol. The blue-green product was filtered off. Yield: 0.127 g (80%) (Found: C, 40.95%; H, 5.10%; N, 9.52%. Calc. for $C_{80}H_{120}Cl_8N_{16}Pd_4S_8Zn$: C, 41.11%; H, 5.14%; N, 9.60%). IR (KBr) ν_{max}/cm^{-1}: 2976–2859 (CH_2), 1625, 1547, 1472, 1420, 1319, 1143, 1083, 961, 810, 759, 708.

2.8. Octakis-(2-diethylaminoethylsulfanyl)-phthalocyaninato-cobalt(II)tetrapalladium (II) octachloride (**5b**)

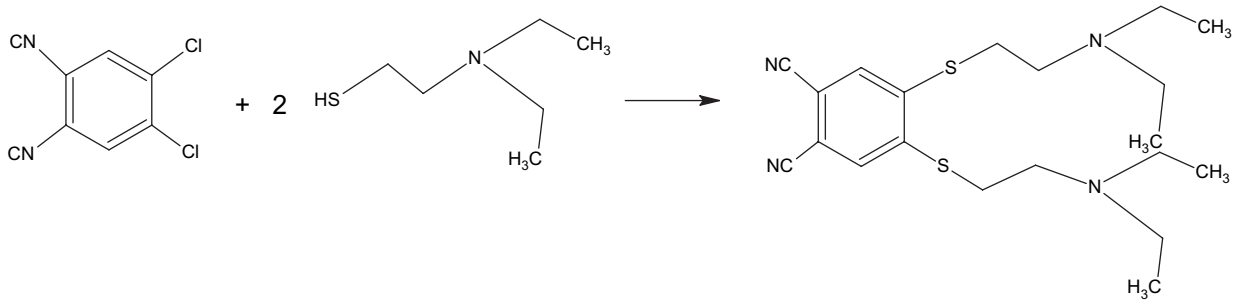
Prepared as described for **4b**, starting from **5** (0.100 g, 0.062 mmol) in tetrahydrofuran–water (7.2 ml) and $Na_2[PdCl_4]$ $3H_2O$ (0.172 g, 0.49 mmol) in the same solvent. Yield: 0.117 g (81%) (Found: C, 41.15%; H, 5.06%; N, 9.28%. Calc. for $C_{80}H_{120}Cl_8N_{16}Pd_4S_8Co$: C, 41.22%; H, 5.15%; N, 9.62%). IR (KBr) ν_{max}/cm^{-1}: 2978–2860 (CH_2), 1625, 1548, 1472, 1421, 1319, 1140, 1089, 961, 808, 757, 706.

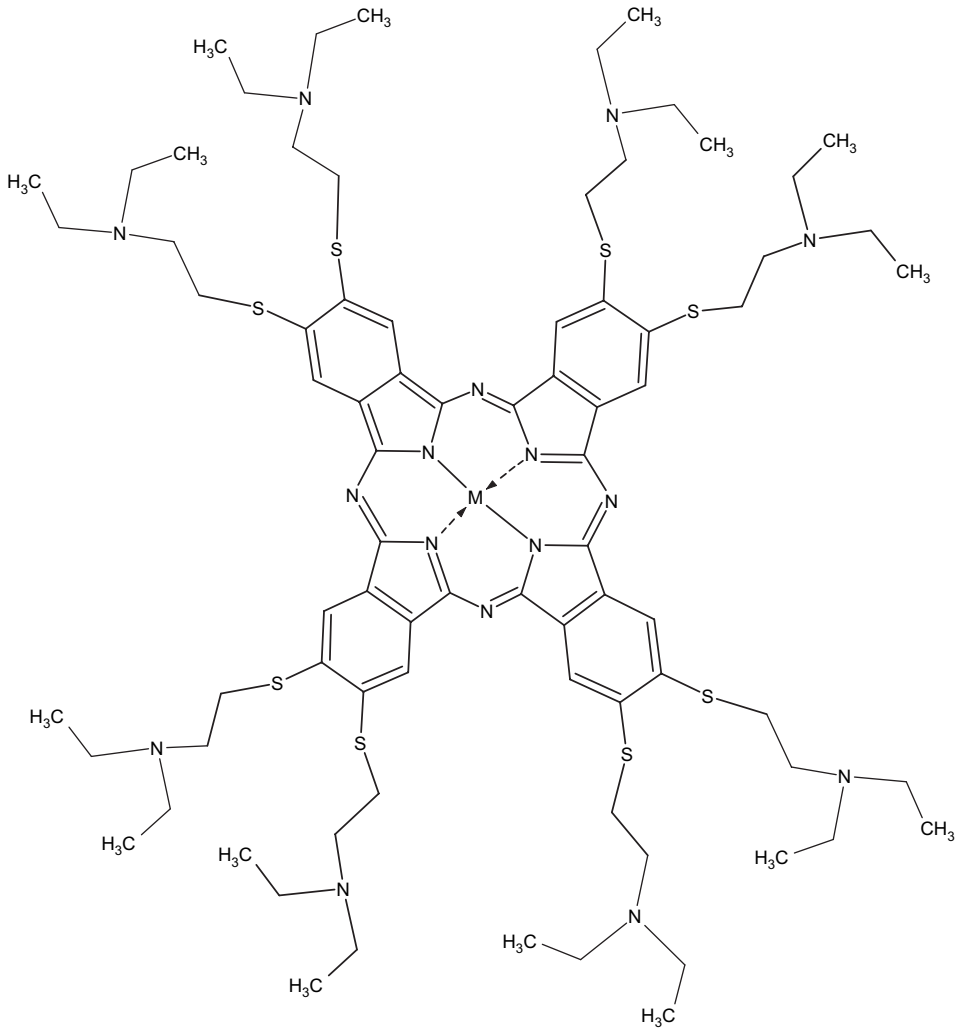
3. Results and discussion

3.1. Synthesis

The synthetic route followed in this work is shown in Scheme 1. 1,2-Bis-(2-diethylaminoethylsulfanlyl)-4,5-dicyanobenzene (**2**) was prepared by a base-catalyzed nucleophilic aromatic displacement of 1,2-dichloro-4,5-dicyanobenzene with 2-diethylaminoethanthiol. The reaction was carried out at 32 °C in dry DMF with K_2CO_3 as the base. This reaction has been used in the preparation of a variety of ether or thioether-substituted phthalonitriles [21,22].

Cyclotetramerization of the dinitrile compound **2** in the presence of anhydrous metal salts [$Zn(CH_3COO)_2$] or $CoCl_2$ gave the desired metallophthalocyanines **4**, **5**. Metal-free phthalocyanine **3** was obtained directly by refluxing phthalonitrile derivative **2** in 2-dimethylaminoethanol. Column chromatographic purification, with experimental conditions that may slightly vary from one complex to another, was efficient. The green products were isolated by column chromatography on alumina. The most obvious feature of these phthalocyanines is





3 M = 2H

4 M = Zn

5 M = Co

Scheme 1.

their solubility in various solvents such as chloroform, THF, DMSO.

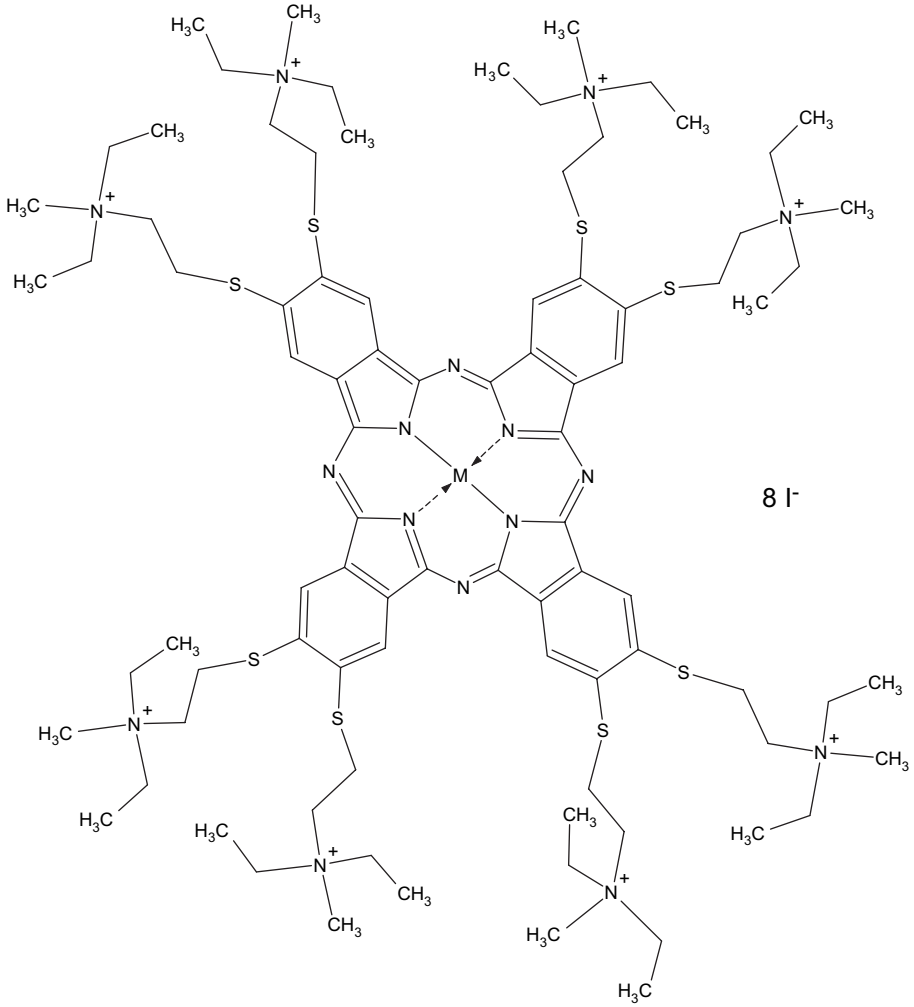
When water-soluble phthalocyanine derivatives are required, sulfonium or quaternary ammonium groups are introduced on the periphery. Peripheral diethylaminoethyl substituents of metallophthalocyanines **4**, **5** are extremely suitable for conversion into quaternary ammonium groups by alkylation with methyl iodide. Metallophthalocyanines **4a**, **5a** with eight quaternary ammonium groups were obtained from the reaction of corresponding phthalocyanines **4**, **5** with methyliodide in chloroform. Solubility of these quaternized

phthalocyanines in water are at 6.3×10^{-3} M range for **4a** and 9×10^{-3} M for **5a**. As expected, the solubility values in ethanol are not at such high level, but it is still meaningful (ca. 10^{-5} M).

The sulfanyl groups of the phthalocyanines **4**, **5** represent suitable donor sites for binding various transition metal ions [23]. Pd(II) complexes were obtained upon treatment with $PdCl_2$ in tetrahydrofuran–water. According to elemental analytical results, Pd^{+2}/Pc ratio is 4:1 and it indicates that a palladium ion is interacting with each dialkylthiobenzo moiety of phthalocyanines **4** or **5**. The solubility of these multinuclear complexes is lower than corresponding Zn(II) and Co(II) phthalocyanines.

Characterization of the products involved a combination of methods including elemental analysis, ^{1}H and ^{13}C NMR, UV/Vis and IR spectroscopy. Spectral investigations on the newly synthesized compounds are in accordance with the proposed structures (Figs. 1 and 2). IR spectrum of **2** indicated the presence of alkyl and C ≡ N groups by the intense stretching bands at 2978–2828 (C–H) and 2238 (C ≡ N) cm^{-1}. ^{1}H NMR spectrum of **2** exhibited aromatic protons at 7.52 ppm as a singlet and the SCH_2, NCH_2 and CH_2C protons at 3.10, 2.78 and 2.60 ppm, respectively. Also CH_3 protons of **2** were observed as a triplet at 1.03 ppm. In the attached proton test (APT) ^{13}C NMR spectrum of the phthalonitrile derivative **2**, four different signals for aliphatic carbon atoms between 51.37 and 11.89 ppm and also four for the unsaturated carbon atoms between 144.51 and 111.27 ppm, one of them arising from C ≡ N (115.49 ppm), comply with the proposed structure.

Cyclotetramerization of dinitriles was confirmed by the disappearance of the sharp C ≡ N vibration at 2238 cm^{-1} of **2**. The IR spectra of metal-free and



4a M = Zn

5a M = Co

Fig. 1. Quaternized metallophthalocyanines.

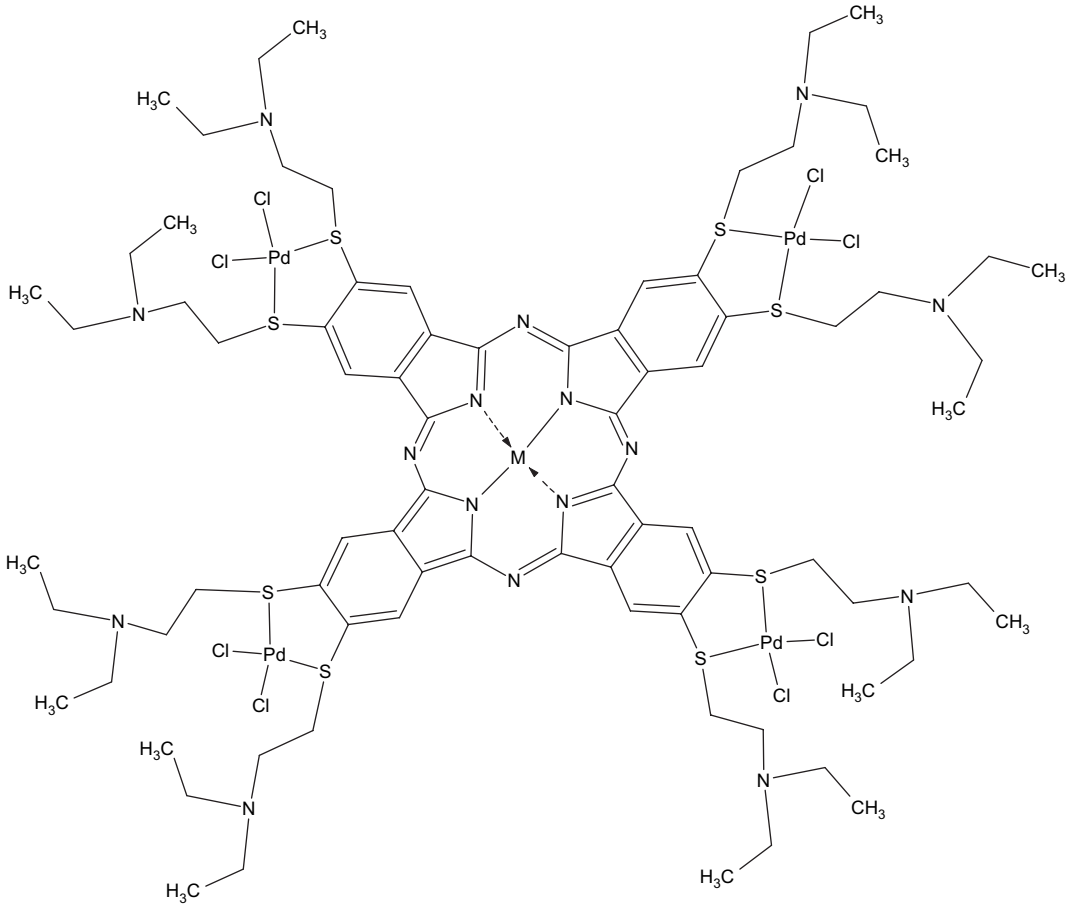


Fig. 2. Pentanuclear complexes (**4b**, **5b**) derived from metallophthalocyanines.

metallophthalocyanines are very similar. NH groups in the inner core of the metal-free phthalocyanine **3** gave an absorption at 3320 cm^{-1}. The ^1H NMR of **3** exhibited the typical chemical shifts of 2-diethylaminoethylsulfanyl substituents together with a single peak for aromatic protons. SCH_2 and NCH_2 protons appeared as triplets at 3.45 and 2.96 ppm, respectively. Strong shielding of the protons in the phthalocyanine core of **3** was manifested by weak broad absorption at δ − 4.79 ppm. The rest of the ^1H NMR spectra of metal-free and zinc(II) phthalocyanine were almost identical. A distinct difference encountered in the ^1H NMR spectra of the phthalocyanines **3** and **4** when compared with previously obtained macrocycle substituted ones is the sharp peaks which indicate a lower tendency to aggregation even at concentrations used for NMR measurements [24]. The ^1H NMR data of **4a** showed signals due to the appearance of aromatic, SCH_2 and NCH_2 protons at 9.26 ppm, 4.05 and 3.78 ppm, respectively. The CH_3 group of **4a** was indicated as an additional singlet at 3.21 ppm.

The typical UV–Vis spectra of the phthalocyanines **3**–**5** exhibited characteristic Q- and B-bands, one in the visible region at approximately 600–750 nm (Q-band) attributed to the π–π^* transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc^{2-} ring, and the other in the UV region at 300–400 nm (B-band) arising from the deeper π-levels → LUMO transition [1]. The characteristic Q-band transitions of zinc and cobalt phthalocyanines (**4**, **5**) with D_{4h} symmetry were observed as a single band of high intensity at 701 and 690 nm, respectively. The D_{2h} symmetry of the metal-free phthalocyanine **3** was verified by two absorption in the visible region at 731 and 701 nm. In the spectra of **4a**, **5a** in water, Q-bands were shifted to 666 and 651 nm as a result of solvent effect (Table 1).

3.2. Electrochemical measurement

The electrochemical properties of ZnPc were studied by cyclic voltammetry (CV) and controlled potential coulometry (CPC). The voltammograms of ZnPc were

Table 1
Electronic spectra of the phthalocyanines

Compound	λ_{max}/nm (10^{-4} ε/dm^3 mol^{-1} cm^{-1})
3[a]	731 (0.480), 701 (0.450), 668 (0.147), 636 (0.105), 337 (0.250)
4[a]	701 (0.464), 632 (0.148), 342 (0.249)
5[a]	690 (0.357), 635 (0.136), 331 (0.287)
4a[b]	666 (0.523), 420 (0.155), 322 (0.387)
5a[b]	651 (0.313), 319 (0.466)
4b[c]	706 (0.424), 329 (0.681)
5b[c]	701 (0.228), 336 (0.376)

[a] In THF.
[b] In water.
[c] In DMSO.

recorded at different scan rates and presented in Fig. 3. Within the available scale of the DMSO/TBAP solvent system, ZnPc shows three cathodic peaks at −0.730, −1.060, and −1.360 V and one anodic peak at 0.800 V vs SCE at 0.1 V s^{-1} scan rate. ZnPc displays a reversible reduction couple (Ic/Ia) at −0.730 V with a peak separation (ΔE) of 69 mV at 0.1 V s^{-1} scan rate and $\delta E_{pc}/\delta \log \nu$ value of 33 mV, a *quasi*-reversible reduction (IIc) ($\delta E_{pc}/\delta \log \nu = 67$ mV) having a reverse anodic couple just after the scan rate faster than 0.250 V s^{-1} and a totally irreversible reduction wave (IIIc) ($\delta E_{pc}/\delta \log \nu = 117$ mV) at −1.360 V without anodic peak during the reverse scan. On scanning the potential to the positive side, an irreversible oxidation process (IVa) with $\delta E_{pc}/\delta \log \nu$ values of 132 mV at 0.960 V vs SCE at 0.1 V s^{-1} scan rate is also recorded. If the transition metal ion concerned has no accessible d orbital levels lying within the $1a_{1u}$(HOMO)−$1e_g$(LUMO) gap of a phthalocyanine species, then its redox chemistry will appear like that of free phthalocyanine compounds. Many transition metals such as nickel and palladium behave in this fashion with the M(II) central ion being unchanged as the MPc unit is either oxidized or reduced. Zinc(II) also appears invariant in the MPc framework, with reduction and oxidation occurring at the ring rather than at the zinc ion [25–27]. According to these records, all redox processes recorded with ZnPc are easily assigned to successive ring reductions and oxidation of the bulk species.

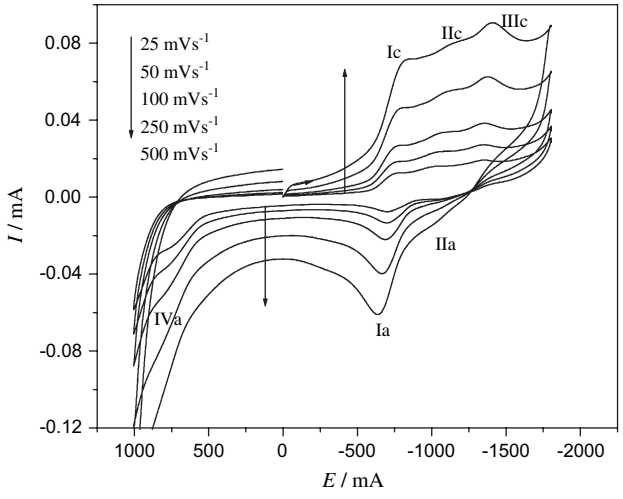


Fig. 3. Cyclic voltammogram of 5.0×10^{-4} mol dm^{-3} **4** in DMSO/TBAP vs SCE.

The linear dependance of the I_{pc} of Ic to the $\nu^{1/2}$ suggest diffusion-controlled processes of the couple recorded with ZnPc. However, I_{pc} of IIc and IIIc are not linearly changing with the $\nu^{1/2}$. This indicates that IIc and IIIc processes are not just diffusion-controlled. The relationship between the I_{pa}/I_{pc} of a reversible couple with scan rate serves as a quick test for an electrochemical mechanism associated with a preceding or succeeding chemical reaction [26]. It is shown that I_{pa}/I_{pc} ratio is 0.6 at 0.025 V s^{-1} scan rate and increase almost to unity with increasing scan rates for Ic/Ia redox couple of ZnPc. This is an indication of a reversible chemical reaction succeeding the electron transfer reaction. The CPC studies indicated that the number of electrons transferred for all these electron transfer reactions is one.

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