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ScienceDirect
Dyes and Pigments 76 (2008) 825−831
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Novel phthalocyanines bearing both quaternizable and bulky substituents

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Received 29 June 2006; accepted 6 July 2006
Available online 25 February 2007

Abstract

A new phthalonitrile derivative bearing dimethylaminoethylsulfanyl- and diethoxymalonyl-substituents at peripheral positions has been synthesized. Cyclotetramerization of this dinitrile in hexanol gave the desired cobalt(II) and zinc(II) phthalocyanines (**4** and **5**) with dimethylaminoethylsulfanyl and dihexoxymalonyl groups on periphery. Four dimethylaminoethyl groups of the former were quaternized to yield a water-soluble cobalt(II) phthalocyanine. Electrochemical redox properties of these phthalocyanines were investigated by cyclic voltammetry and applied chronocoulometry techniques.

Keywords: Phthalocyanine; Phthalonitrile; Water-soluble; Zinc; Cobalt; Cyclic voltammetry

1. Introduction

Phthalocyanines with many remarkable features have become commercially and technologically important dyes and pigments for many decades [1,2]. These properties enable us to use them for several applications in contemporary technologies such as charge carriers in photocopiers, dyes in laser printers, laser light absorbers in optical data storage systems, solar cells, gas sensors, and nonlinear optical and optical limiting devices [3−7]. Moreover, phthalocyanines are efficient photosensitizers in the photodynamic therapy of cancer (PDT) [8]; this property results from their intense absorption in the red region between 600 and 800 nm with a greater penetration of tissue [9], and photo-sensitization of singlet oxygen [10].

Insolubility or lower solubility of unsubstituted derivatives has hindered the utilization of phthalocyanines (pcs) in many fields including PDT. Substituted phthalocyanines have become more soluble in common solvents [11−19]. Depending on the polarity of the substituents, pcs become more soluble in apolar or polar solvents [20,24,25,32]. Whereas lipophilic phthalocyanines are reported to have a higher tumor affinity, introduction of hydrophilic groups as substituents on phthalocyanines bring solubility in aqueous media which has a strong influence on the bioavailability and *in vivo* distribution [21]. Water-soluble phthalocyanines are among the most promising photosensitizers [22,23]. To date, a number of phthalocyanines bearing hydrophilic moieties, such as carboxylates, sulfonates, glucose, phosphonates, amino, and carboranyl groups have been reported [24−32].

Furthermore, owing to their extensively planar aromatic π system, phthalocyanines exhibit a high aggregation tendency which leads to insolubility in the case of unsubstituted parent derivatives or hinders purification and characterization of compounds in many respects together with a lower efficiency in their use in PDT [33,34]. The introduction of either long chains or bulky substituents onto the periphery of the macrocycle hinders the aggregation in organic solvents, but has almost no contribution to enhance solubility in aqueous medium; similarly, an ionic substituent such as sulfonate,

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doi:10.1016/j.dyepig.2006.07.035

carboxylate or ammonium leads to products extensively soluble in aqueous medium, but the molecules are still aggregated to a great extent due to the high polarity of solvent molecules [35,36].

We describe herein the synthesis and characterization of new phthalocyanines carrying four bulky dihexylmalonyl and four dimethylaminoethylsulfanyl groups at the peripheral positions, simultaneously. By bringing together a quaternizable substituent and a bulky one, we are trying to reach phthalocyanines soluble in aqueous solutions in unaggregated form.

2. Experimental

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer, electronic spectra on a Unicam UV2 spectrophotometer. ^{1}H NMR spectra were recorded on Bruker 250 MHz using TMS as internal standard. Mass spectra were performed on Ultima Fourier Transform and Varian 711 mass spectrometers. All reagents and solvents were of reagent grade quality obtained from commercial suppliers. The homogeneity of the products was tested in each step by TLC. The solvents were stored over molecular sieves. 1-Chloro-3,4-dicyano-6-(1,1-dicarbethoxy-methyl)benzene (**2**) was prepared from 1,2-dichloro-4,5-dicyanobenzene (**1**) according to reported procedures [24,37].

The CV and CPC measurements were 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* software data, to draw voltammograms and to analyze them. The working electrode was a Pt plate with an area of 1.0 cm^2. The surface of the working electrode was polished with an H_2O suspension of Al_2O_3 before each run. The last polishing was done with a particle size of 50 nm. A Pt wire served as the counter electrode. A saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge containing saturated KCl adjacent to SCE and solvent and carrier adjacent to the solution. Electrochemical grade tetrabutylammoniumperchlorate (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. During voltammetric measurements, the reference electrode tip was moved as close as possible to the working electrode so that uncompensated resistance of the solution was a smaller fraction of the total resistance, and therefore the potential control error was low. However, IR compensation was applied to the CV scans to further minimize the potential control error. For CPC studies, a Pt gauze working electrode (10.5 cm^2 surface area), a Pt wire counter electrode separated with a double bridge, a saturated calomel reference electrode (SCE), and a model 377/12 synchronous stirrer were used. The potential of the working electrode was set to E_p obtained in CV experiments. Then the solution was electrolyzed with efficient stirring.

*2.1. 1-(2-Dimethylaminoethylsulfanyl)-3,4-dicyano-6-(1,1-dicarbethoxy-methyl)benzene (**3**)*

Compound **2** (1 g, 3.12 mmol) was dissolved in 15 ml of dry DMF at 45 °C, and 2-dimethylaminoethanthiol hydrochloride (0.44 g, 3.12 mmol) was added. After stirring for 15 min, 1.3 g finely ground anhydrous K_2CO_3 (9.35 mmol) was added portion wise during 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at 45 °C for 48 h. Then the mixture was poured into 200 ml water and the product was extracted with chloroform and washed with water repeatedly. After drying over anhydrous sodium sulfate, chloroform was evaporated and the oily residue was recrystallized from hexane. The compound was soluble in $CHCl_3$, CH_2Cl_2, THF, methanol, ethanol, and acetone.

Yield: 0.972 g (80.0%); m.p.: 67 °C; ^{1}H NMR ($CDCl_3$, δ, 250 MHz): 8.15–7.78 (m, 2H, aromatic H), 5.24 (s, H, CH–COO), 4.38–4.15 (m, 4H, COO–CH_2), 3.36–3.30 (t, 2H, S–CH_2), 2.97–2.83 (t, 2H, S–C–CH_2), 2.50 (s, 6H, S–C–C–$N(CH_3)_2$, 1.37–1.17 (m, 6H, COO–C–CH_3); IR, γ_{max} (cm^{-1}): 3080 (CH, aromatic), 2981–2778 (CH, aliphatic), 2232 (C≡N), 1728 (C=O), 1285 (C–O ester), 1207–1151 (C–O–C), $C_{19}H_{23}N_3O_4S$. FAB-MS calc. (found) *m*/*e*: 390.2 (389.5) [M$^+$]. Found %: C, 58.26; H, 5.85; N, 10.87; calculated %: C, 58.59; H, 5.95; N, 10.79.

*2.2. 2,9,16,23-Tetra(dihexoxymalonyl)-3,10,17,24-tetra(2-dimethylaminoethylsulfanyl) phthalocyaninatocobalt(II) (**4**)*

A mixture of dinitrile **3** (100 mg, 0.256 mmol), $CoCl_2$ (8.33 mg, 0.064 mmol) and 10 µl DBU in 1 ml *n*-hexanol was heated and stirred at 147 °C in a sealed glass tube under N_2 atmosphere for 24 h. The crude suspension was purified by column chromatography on neutral alumina as the stationary phase and THF:MeOH = 1:1 as the eluent. After the column chromatography, the oily product was recrystallized from THF:hexane (1:3) mixture and the desired compound was obtained as a dark green powder.

Yield: 33 mg (24.9%); IR, γ_{max} (cm^{-1}): 2928–2764 (CH, aliphatic), 1730 (C=O), 1322 (C–O ester), 1162–1103 (C–O–C); UV–Vis ($CHCl_3$): λ_{max} (nm) (log ε): 316 (4.91), 685 (5.08), FAB-MS calc. (found) *m*/*e*: 2065.66 (2067.85) [M$^+$]. $C_{108}H_{156}N_{12}O_{16}S_4Co$. Found %: C, 62.86; H, 7.68; N, 7.97; calculated %: C, 62.80; H, 7.61; N, 8.14.

*2.3. 2,9,16,23-Tetra(dihexoxymalonyl)-3,10,17,24-tetra(2-dimethylaminoethylsulfanyl) phthalocyaninatozinc(II) (**5**)*

A mixture of dinitrile **3** (100 mg, 0.256 mmol), $Zn(CH_3COO)_2$ (11.8 mg, 0.064 mmol) and 10 µl DBU (diazabicycloundecane) in 1 ml *n*-hexanol was heated and stirred at 147 °C in a sealed glass tube under N_2 atmosphere for 24 h. The crude suspension was purified by column chromatography two times with neutral alumina as the stationary phase. DCM:MeOH (100:1) and DCM:MeOH (100:10) were used as the eluent in given order and the desired product was obtained as a dark green powder.

Yield: 25 mg, 18.8%; ^{1}H NMR ($CDCl_3$, δ, 250 MHz): 9.36–7.52 (m, 8H, aromatic H), 5.28 (s, 4H, CH–COO), 4.27–4.24 (m, 16H, COO–CH_2), 3.71–3.63 (t, 8H, S–CH_2), 3.31 (t, 8H, S–C–CH_2), 2.48 (s, 24H, S–C–C–N(CH_3)$_2$), 1.82–0.83 (m, 88H, COO–C–CH_2–CH_2–CH_2–CH_2–CH_3). IR, γ_{max} (cm^{-1}): 2925–2764 (CH, aliphatic), 1728 (C=O), 1297 (C–O ester), 1161–1074 (C–O–C); UV–Vis ($CHCl_3$): λ_{max} (nm) (log ε): 372 (4.68), 697 (5.08). $C_{108}H_{156}N_{12}O_{16}S_4Zn$, FAB-MS calc. (found) *m/e*: 2072.12 (2070.10) [M$^+$]. Found %: C, 62.69; H, 7.65; N; 7.98; calculated %: C, 62.60; H, 7.59; N, 8.11.

*2.4. 2,9,16,23-Tetra(dihexoxymalonyl)-3,10,17,24-tetra (2-trimethylaminoethylsulfanyl) phthalocyaninatocobalt(II)tetra-iodide (**6**)*

Compound **4** (30 mg, 0.014 mmol) was dissolved in CH_2Cl_2 (3.5 ml) and 51.5 mg CH_3I (0.023 ml, 0.36 mmol) was added under N_2 atmosphere and stirred at room temperature for 24 h in dark. Then, the resulting reaction mixture was evaporated to dryness under reduced pressure. The residue was washed with CH_2Cl_2 until free of any soluble reactant or side product. The hygroscopic dark blue product was dried *in vacuo*.

Yield: 23 mg, 60.13%; IR, γ_{max} (cm^{-1}): 2925–2856 (CH, aliphatic), 1720 (C=O), 1307 (C–O ester), 1171–1102 (C–O–C); UV–Vis (DMSO) λ_{max} (nm) (log ε): 345 (4.81), 680 (4.98); (H_2O) λ_{max} (nm) (log ε): 319 (4.57), 650 (4.43). $C_{112}H_{168}N_{12}O_{16}S_4I_4Co$. Found %: C, 51.14; H, 6.48; N, 6.32; calculated %: C, 51.08; H, 6.43; N, 6.38.

3. Result and discussion

3.1. Synthesis and characterization

In the synthesis of 2,9,16,23-tetra(dihexoxymalonyl)-3,10,17,24-tetra(2-dimethylaminoethylsulfanyl)phthalocyanines (**4**, **5**) was utilized 1-(2-dimethylaminoethylsulfanyl)-3,4-dicyano-6-(1,1-dicarbethoxy-methyl)benzene (**3**) as precursor. The synthetic route for 1-(2-dimethylaminoethylsulfanyl)-3,4-dicyano-6-(1,1-dicarbethoxy-methyl)benzene (**3**) is depicted in Scheme 1 which involves the nucleophilic aromatic displacement of 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxy-methyl)-benzene (**2**) with 2-dimethylaminoethanthiol hydrochloride in the presence of K_2CO_3 as the base in dry DMF at 45 °C. Similar procedures have been used in a number of other phthalonitrile derivatives [11,14,24].

The conversion of this new dinitrile (**3**) into the phthalocyanines (**4** and **5**) was achieved by cyclotetramerization in hexanol in the presence of metal salts $CoCl_2$ or $Zn(CH_3COO)_2$ and DBU. During cyclotetramerization reaction under basic conditions transesterification of diethylmalonyl groups with hexanol occurred spontaneously [24,25]. Thus, we obtained the phthalocyanines bearing four dihexoxymalonyl and four dimethylaminoethylsulfanyl groups at peripheral positions. These bulky groups are shown to be efficient to hinder the aggregation of macrocycles [11,14,24,25]. The newly synthesized phthalocyanines were isolated by column chromatography on alumina. Due to the presence of two different substituents on −4 and −5 positions of the phthalonitrile (**3**), phthalocyanines obtained from this precursor are naturally a mixture of four constitutional isomers [38]. Our attempts to separate these isomers with column chromatography and HPLC methods using different solvents are not successful. It is worth pointing out that these new phthalocyanines have high solubility in almost all organic solvents such as ethanol, methanol, THF, chloroform, DCM, DMSO.

When CoPc (**4**) was treated with an excess of methyl iodide in dichloromethane at room temperature the hygroscopic phthalocyanine with four quaternary ammonium groups (**6**) was obtained in a good yield of 60% (Scheme 1). Quaternized product was soluble in water and in DMSO but not in DCM.

All new compounds were identified through various spectroscopic techniques such as ^{1}H NMR, FT-IR, UV–Vis, FAB-MS and elemental analysis gave satisfactory data with assigned structures. IR spectrum of **3** indicated the C≡N groups at 2232 cm^{-1}, aliphatic groups at 2981–2778 cm^{-1} and ester groups at 1728 cm^{-1} (C=O), 1285 cm^{-1} (C–O), 1207–1151 cm^{-1} (C–O–C) by the intense bands. Phthalocyanines have also very similar bands for aliphatic and ester groups but they differ in the disappearance of the sharp C≡N band at 2232 cm^{-1} which signifies the cyclotetramerization of dinitrile.

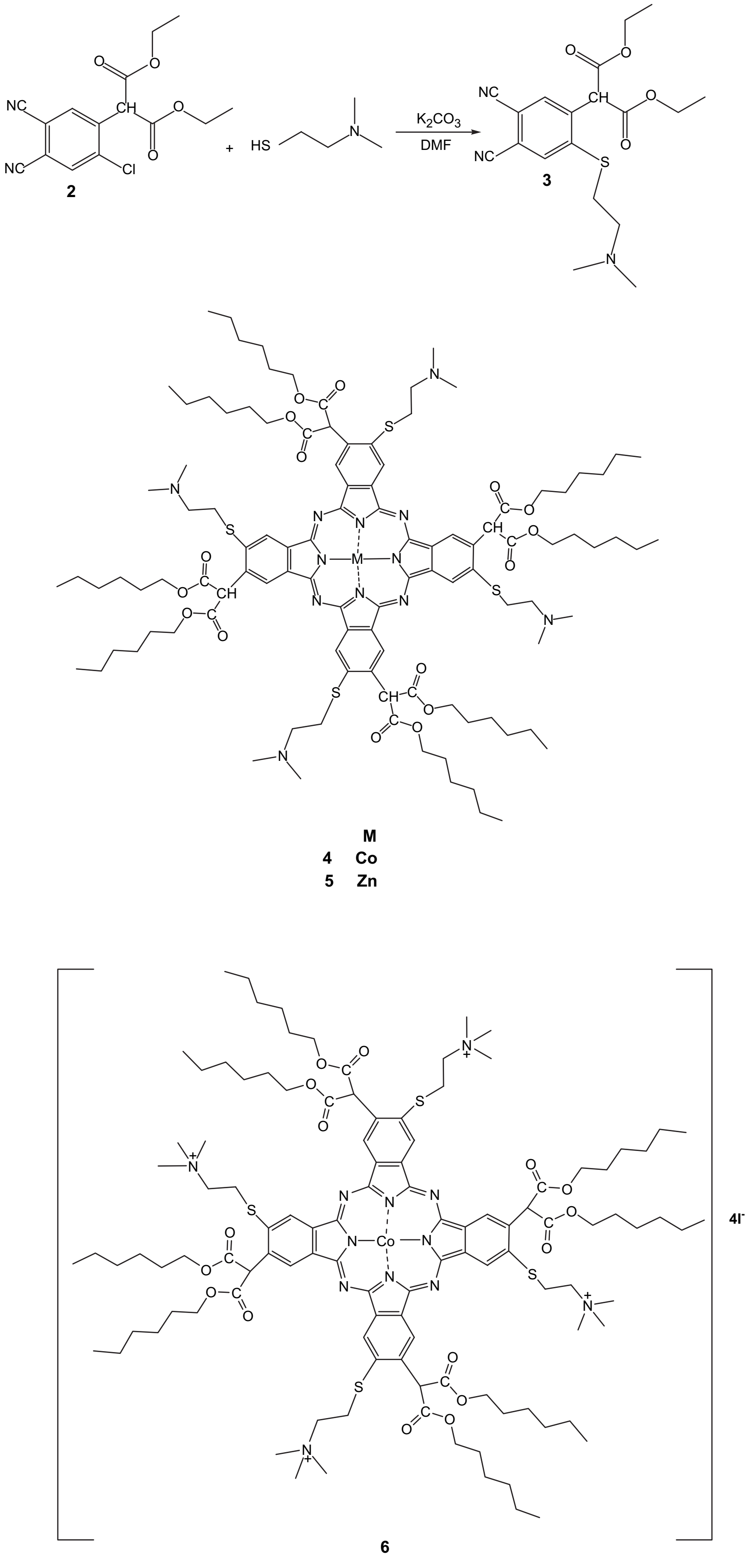
In the ^{1}H NMR spectrum of compound **3**, the typical shifts for aromatic protons can be seen at 8.15–7.78 ppm. CH proton of malonyl unit and CH_3 protons of dimethylaminoethylsulfanyl groups appear as singlets at 5.24 and 2.50 ppm, respectively. The other aliphatic CH_2 and CH_3 protons were observed in the range 4.38–1.17 ppm.

The ^{1}H NMR spectrum of zinc(II) phthalocyanine is almost identical with some small shiftings and broadenings. In addition, the chemical shift of CH proton of malonyl group can be observed as a singlet at 5.28 ppm whereas in our recent work in the case of transesterification products it was not possible to observe these aliphatic protons separately [11].

Furthermore, the FAB-MS results with convenient molecular ion peaks for compounds **3**, **4** and **5** confirm the proposed structures.

Electronic spectra are especially useful to identify the structure of the phthalocyanines. In general, phthalocyanines show characteristic electronic spectra, with two strong absorption regions around 300–350 nm (B band) and 600–700 nm (Q band). The UV–Vis spectra of the phthalocyanines are generally solvent- and concentration-dependent. At high concentrations or with solvents of high protic character, aggregates are formed. In addition, the presence of an electron donating group causes a bathochromic shift on Q bands and the bulky substituents on the periphery lead to a sharper Q band by hindering the formation of aggregated species.

Cobalt(II) (**4**) and zinc(II) phthalocyanines (**5**) exhibit B bands at 316 and 372 nm, intense Q bands at 685 and 697 nm, respectively, with a relatively sharp absorption



2

3

	M
4	**Co**
5	**Zn**

6

Scheme 1.

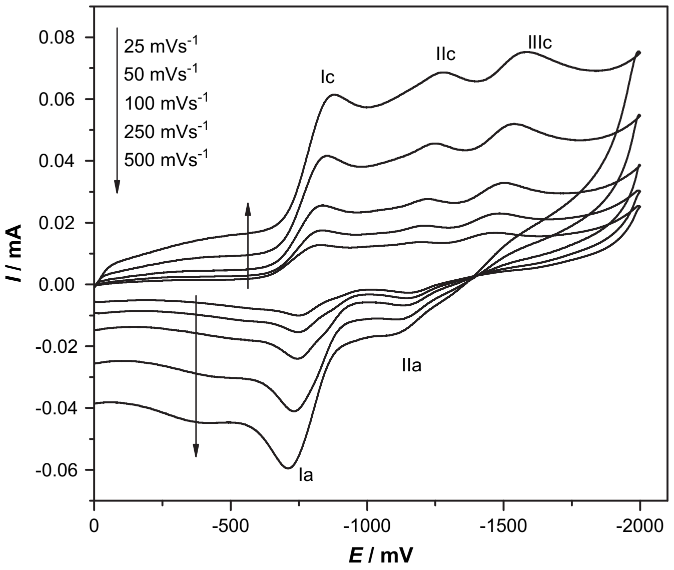


Fig. 1. CV of 5.0×10^{-4} mol dm^{-3} ZnPc in TBAP:DMSO solvent system versus SCE.

peak and almost no shoulder on the higher energy side which would correspond to aggregated species [24,25,39]. The effect of four S-substituents on the periphery of the phthalocyanine core was a shift in these intense Q bands to longer wavelengths when compared with those of unsubstituted or alkyl substituted derivatives [40]. Here, the other important outcome is the hindrance of aggregations due to the bulky substituents on the peripheral positions such as dihexoxymalonyl and aminoethylsulfanyl. Moreover, it is noteworthy that compound **6** displays a main band at 680 nm in DMSO whereas it shifts to 650 nm in water because of the solvent effect.

3.2. Electrochemical measurement

Fig. 1 shows typical cyclic voltammograms of ZnPc (**5**). Three redox processes labeled I–III are observed at −0.78, −1.18, and −1.47 V versus SCE at 0.100 V s^{-1} scan rate within the available potential range of TBAP/DMSO solvent system. In Table 1, the *CV* data are listed together with those of all complexes studied here. Since the central Zn(II) metal is redox inactive, all redox processes recorded are ring based [1]. The difference between the first and second reduction processes is 0.40 V which compares with the average value for the phthalocyanines having redox inactive metal center [1,41–44]. The anodic to cathodic peak separations (ΔE_p) of the first reduction couple (Ic/Ia) ranged between 60 and 150 mV with the increasing scan rates and unity of the anodic to cathodic peak current ratio (I_{pa}/I_{pc}) indicated the reversible peak character of the process. The anodic to cathodic peak current ratio (I_{pa}/I_{pc}) of the universal standard reference Fc/Fc^{+} ranged between 60 and 130 mV with the increasing scan rates. Second reduction process (IIc/IIa) has a *quasi*-reversible peak character with the moderately high ΔE_p and I_{pa}/I_{pc} being smaller than unity. Third reduction process is completely irreversible. The peak currents of for Ic and IIIc peaks increase linearly with the square root of the scan rates ranging from 25 to 500 mV s^{-1}, suggesting diffusion-controlled reactions. However, nonlinear change of the peak current of IIc indicates the complication of the electron transfer process with a chemical reaction.

Cyclic voltammograms of CoPc (**4**) at varying scan rates are illustrated in Fig. 2. Four redox processes labeled I–IV are recorded at −0.37, −0.78, −1.29 and 0.44 V at 100 mV s^{-1} scan rate within the available potential range of TBAP/DMSO solvent system. According to Lever et al. [1,38,41,45], only for metallophthalocyanine derivatives, such as Mn, Fe, and Co derivatives having accessible d-orbital levels lying within the *HOMO–LUMO* gap of a phthalocyanine species, the first oxidation and the first reduction processes occur on the metal center in the metal Pc depending upon whether there are any available coordinating species that would stabilize the M(II) center. While metal center oxidation takes place before the ring oxidation process in donor

Table 1
Cyclic voltammetric parameters of the complexes

Complexes	Parameters	Redox processes[d]				
		$M^{II}Pc^{-2}/M^{III}Pc^{-2}$	I^-/I_3^-	$M^{II}Pc^{-2}/M^{I}Pc^{-2}$ ($M^{II}Pc^{-2}/M^{II}Pc^{-3}$)	$M^{I}Pc^{-2}/M^{I}Pc^{-3}$ ($M^{II}Pc^{-3}/M^{II}Pc^{-4}$)	$M^{I}Pc^{-3}/M^{I}Pc^{-4}$ ($M^{II}Pc^{-4}/M^{II}Pc^{-5}$)
CoPc	$E_{1/2}$ (V)[a]	0.46		−0.37	−0.78	−1.29
	ΔE_p (mV)[b]	98		109	490	115
	I_{pa}/I_{pc}[c]	0.70		0.97	3.4	0.97
QCoPc	$E_{1/2}$ (V)[a]	0.560	0.27	−0.30	−1.20	
	ΔE_p (mV)[b]	190	270	87	73	
	I_{pa}/I_{pc}[c]	0.62	0.65	0.96	1.00	
ZnPc	$E_{1/2}$ (V)[a]			−0.78	−1.18	−1.47
	ΔE_p (mV)[b]			90	150	
	I_{pa}/I_{pc}[c]			0.95	0.70	

[a] Cathodic peak potential for reduction, anodic peak potential for oxidation for irreversible processes.

[b] $\Delta E_p = E_{pa} - E_{pc}$ at 0.100 V s^{-1} scan rate.

[c] I_{pa}/I_{pc} for reduction, I_{pc}/I_{pa} for oxidation at 0.100 V s^{-1} scan rate.

[d] Redox processes for ZnPc are given in parenthesis.

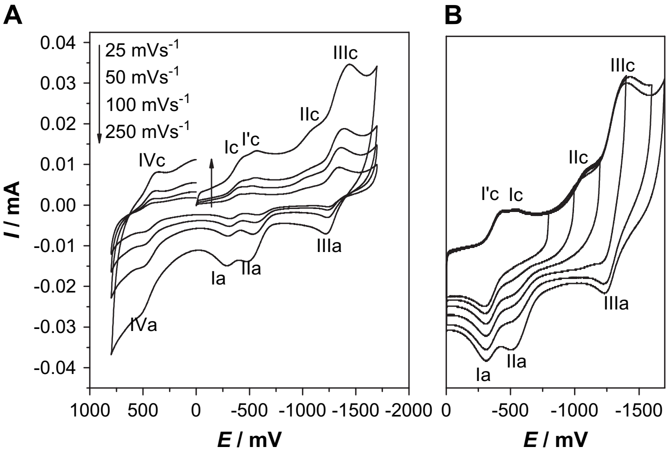


Fig. 2. (A) CV of 5.0×10^{-4} mol dm^{-3} CoPc in TBAP:DMSO solvent system versus SCE. (B) CV CoPc recorded for different switching potential at 100 mV s^{-1} scan rate.

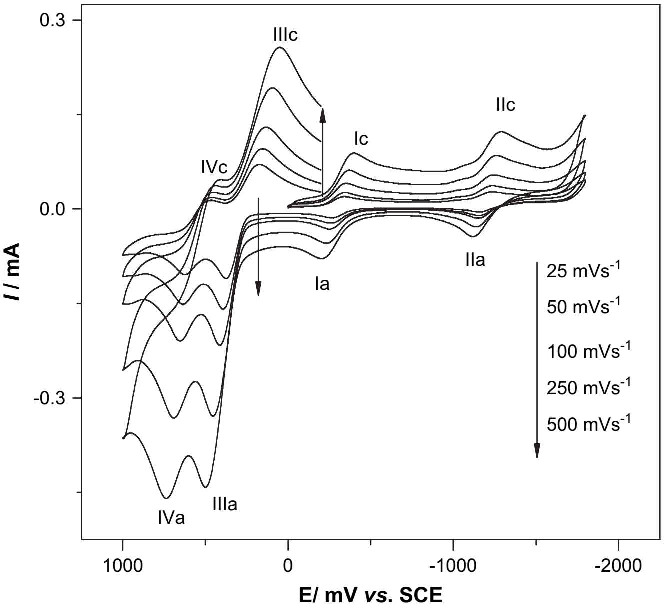


Fig. 3. Cyclic voltammograms of 5.0×10^{-4} mol dm^{-3} QCoPc in TBAP:DMSO solvent system versus SCE.

solvents strongly favoring M(III) species [1,41,9], the ring oxidation process occurs before the metal center oxidation in non-donor solvents. Likewise, the first reduction process of CoPc (**4**) recorded in this study at −0.37 V could be attributed easily to the $Co^{II}Pc^{-2}/Co^{I}Pc^{-2}$ and the first oxidation at 0.44 V to the $Co^{II}Pc^{-2}/Co^{III}Pc^{-2}$ in DMSO, a donor solvent. The second oxidation process could be attributed to the $Co^{III}Pc^{-2}/Co^{III}Pc^{-1}$ process. The difference between the first reduction and first oxidation processes corresponded to the magnitude of the energy difference between the HOMO and LUMO; it is 0.81 V, which is comparable with that of the cobalt phthalocyanines [1,42,44,45]. ΔE_p, I_{pa}/I_{pc} and $I_{pc}/\log v$ data of the voltammograms of the complex indicated that the first (Ic/Ia) and third (IIIc/IIIa) reduction couples of the complex have a quasi-reversible diffusion-controlled electron transfer mechanism. However, the very high ΔE_p value (0.490 V at 100 mV s^{-1}) of second reduction couple shows the irreversible character of the process. Considerable high value of I_{pa}/I_{pc} ratio (3.4) of the couple may have resulted from the complication of the electron transfer process with a preceding chemical reaction. Quasi-reversible electron transfer reaction of the IVa/IVc couple (ΔE_p value = 0.140 V at 100 mV s^{-1}) may also be complicated with a succeeding chemical reaction (I_{pc}/I_{pa} ratio = 0.7).

Fig. 3 shows typical cyclic voltammograms of QCoPc (**6**). Four redox processes labeled I–IV are observed at −0.30, −1.19, 0.27, and 0.56 V versus SCE at 0.100 V s^{-1} scan rate within the available potential range of TBAP/DMSO solvent system. The first reduction process of QCoPc (**6**) recorded in this study at −0.30 V could be attributed easily to the $Co^{II}Pc^{-2}/Co^{I}Pc^{-2}$ and the second oxidation at 0.56 V to the $Co^{II}Pc^{-2}/Co^{III}Pc^{-2}$ in DMSO, a donor solvent. The peak currents of the first oxidation couple recorded at 0.27 V is fourfold higher than the peak currents of other processes. This unusual behavior is not a result of the complex. Linear change of the peak current with the square root of the scan rates for the process disproves the adsorption of the complexes. CPC studies also showed that the number of electron transferred during this process is four while it is one for other processes. Addition of iodide ion to the solution increased the peak currents of this couple. Therefore, these data easily attribute this process to the oxidation of iodide belonging to the complex. This process is comparable with the oxidation of iodide ion in aprotic polar solvents [46,47]. The metal center reduction redox couple, Ic/Ia, and ring reduction couple, IIc/IIa, show reversible peak character with a ΔE_p of 70 and 73 mV at 0.100 V s^{-1} scan rate, respectively. Linearity of $I_p/v^{1/2}$ suggests diffusion-controlled electron transfer mechanism of the (Ic/Ia) and (IIc/IIa) redox processes of the complex. The oxidation processes of the complex are out of the reversible scale with respect to the ΔE_p values (270 and 190 mV at 100 mV s^{-1} scan rate), although $\Delta E_p/\Delta \log v$ values of these two couples (14 and 10 mV, respectively) are in the reversible range,. I_{pc}/I_{pa} values of these processes are considerably smaller than unity. These unusual behaviors may be a result of the complication of the electron transfer processes with a chemical reaction.

4. Conclusion

The present work announces the preparation of a novel phthalonitrile carrying two different substituents and related cobalt and zinc phthalocyanines derived from it. The presence of the bulky substituents together with quaternized ionic ones lead these phthalocyanines to show higher tendency to stay in monomeric form even in aqueous medium as observed from the electronic spectra. Electrochemical characterization of all three phthalocyanines has been carried out.

Acknowledgements

This work was supported by the Research Fund of the Technical University of Istanbul and State Planning Organization

(DPT). A.G. is grateful to Alexander von Humboldt Foundation for a senior scientist award renewed in 2006 for studies in the laboratory of Professor Markus Albrecht, Institute of Organic Chemistry, RWTH-Aachen, Aachen, Germany.

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