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Metal ion sensing multi-functional differently octasubstituted ionophore chiral metallophthalocyanines: Synthesis, characterization, spectroscopy, and electrochemistry

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Abstract

Multi-functional, differently octasubstituted ionophore chiral metallophthalocyanines (MPc's where M = Ni, Cu, Co and Zn), bearing reactive functionalities on the periphery, propane 1,2-diolsulfanyl moieties, which facilitated solubility in polar solvents and metal ion binding, were prepared from the corresponding anhydrous metal salts and differently substituted 4-(1,2-propanediolsulfanyl)-5-chlorobenzene-1,2-dicarbonitrile compound. The reactivity of the peripheral groups of the synthesized MPc's towards several metal ions was determined spectrophotometrically resulting in the formation of polynuclear phthalocyanine complexes. In all ionophore phthalocyanines, peripheral 1,2-propanediolsulfanyl moieties serve as exocyclic binding sites for a number of metal ions for further reactions after phthalocyanine formation, and also provide solubility of the phthalocyanines in protic solvents. The newly synthesized ligand and MPc's were characterized by elemental analysis, FTIR, ^{1}H NMR, ^{13}C NMR, MS (EI and FAB), UV/Vis and Atomic Absorption Spectroscopy. The electrochemical behaviours of the complexes have also been investigated. Electrochemical studies reveal that cobalt phthalocyanine indicated two metal-based and three ligand-based redox processes while nickel phthalocyanine and copper phthalocyanine showed three ligand-based reduction and one ligand-based oxidation processes.

Keywords: Phthalocyanines; Phthalonitrile; Chiral; Sensor; Ionophore; Electrochemistry

1. Introduction

Functional chiral phthalocyanines have interesting self-assembling and self-organizing behaviour and have been shown to assemble into a variety of molecular materials, ranging from liquid crystals to fibrous assemblies [1–8]. Such materials are receiving increasing attention as potential components in optical, electronic, and magnetic devices [9–12]. Crown-ether derivatized phthalocyanines have also been found to possess particularly interesting self-assembly properties which can be influenced by metal ions. The strength of these assemblies can be tuned by the introduction of H-bonding groups or substituents on the periphery of the phthalocyanine macrocycle which increase π–π stacking. Various modifications on the peripheral positions of phthalocyanines carrying multiple binding sites for various metal ions have been carried out with the aims of tuning and optimizing their performance as advanced materials [13–25]. Even small chemical modifications can lead to large differences in molecular packing and in π–orbital interactions and, thus, in their properties, especially in thin films [22,26–31]. To date, a great variety of symmetrical or pseudosymmetrical mononuclear phthalocyanines have been comprehensively studied. Nevertheless, there have been a limited number of reports on functional phthalocyanines [15,20,21,24,32–35], mainly because of the difficulties for preparation and purification. Phthalocyanines appended ionophore moieties, such as ether and amide moieties on the periphery, exhibit selectivity towards alkaline,

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alkaline earth and soft metal cations. While the hard ether–oxygen containing macrocycles show binding preference towards "hard" alkaline and alkaline earth cations, the incorporation of sulfide, amine or amide moieties on the periphery shifts their preference towards "soft" heavy metals. Of these peripheral moieties, crown ethers are particularly noteworthy, as they permit metal ion selectivity and complex stability to be enhanced through changing the numbers and/or types of crown donor atoms. This makes this family of reactive phthalocyanine molecules an interesting target for the development of new further chemical reactions on the phthalocyanine complexes [13–18,20,21,24–30,36,37].

As an extension of our previous research [16,17,20,24,25,32], this paper reports the synthesis and characterization of 4,5-differently substituted functional phthalonitrile, [4-(1,2-propanediolsulfanyl)-5-chlorobenzene-1,2-dicarbonitrile], and its chiral ionophore metallophthalocyanines, 2,3,9,10,16,17,23,24-[tetrakis(1,2-propandiolsulfanyl)-tetrachloro] substituted metallophthalocyanines (M = Ni, Cu, Co and Zn). The functions of metallophthalocyanine derivatives are almost all based on their electron transfer properties. Thus, in this study, electrochemical analysis of the complexes was also studied using cyclic voltammetric measurement.

2. Result and discussion

The synthesis of the target ionophore metallophthalocyanines (**2**–**5**) undertaken in this work is shown in Scheme 1. The new ligand (**1**), [4-(1,2-propanediolsulfanyl)-5-chlorobenzene-1,2-dicarbonitrile], was prepared according to published methods [38]. All final products were obtained as pure samples after numerous purifications via column chromatography on silica gel. Nucleophilic aromatic displacement of one of the two chloro atoms of the 4,5-dichloro-1,2-dicyanobenzene with –SH function of 3-mercapto-1,2-propandiol was employed, as this was preferable to the use of –OH nucleophiles at reflux temperature in THF in the presence of K_2CO_3 (Scheme 1).

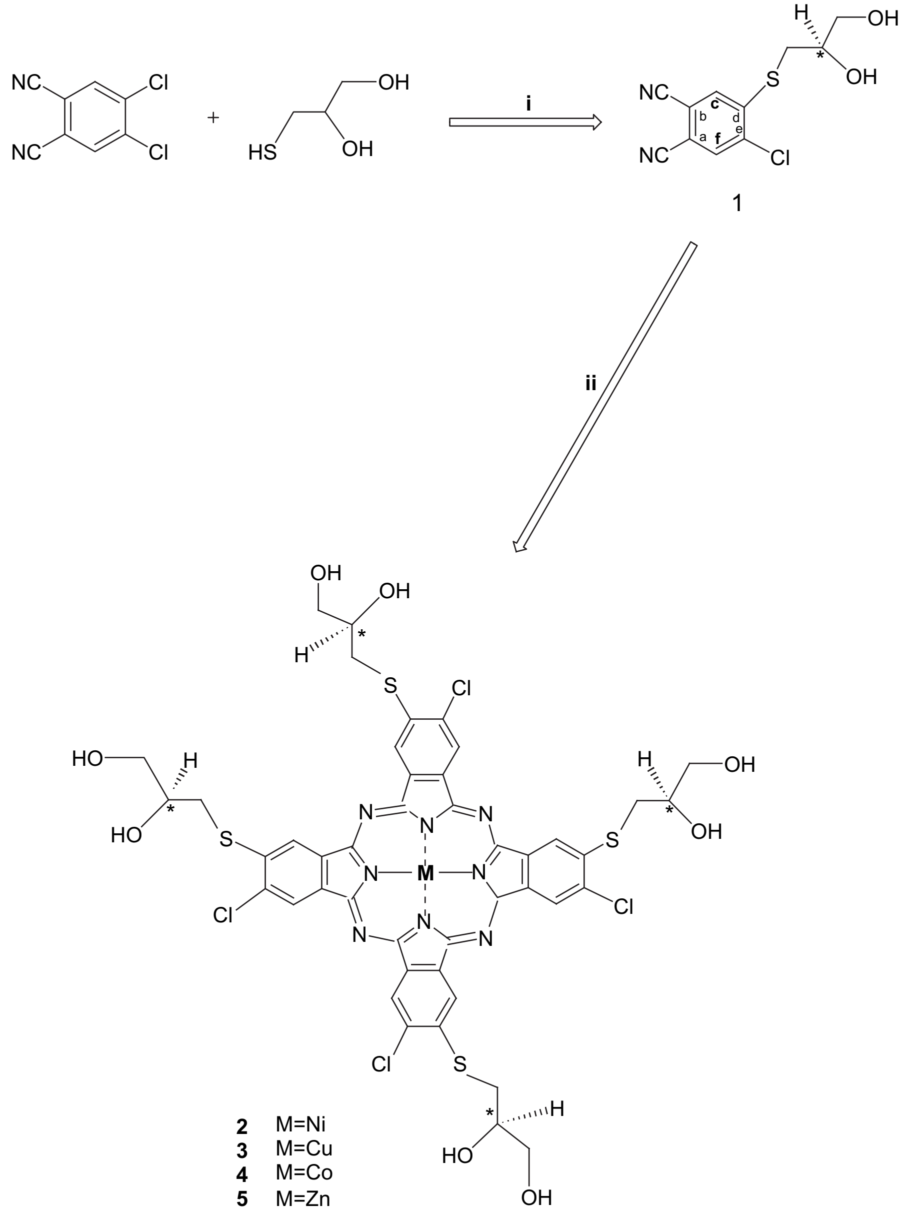
The preparation of phthalocyanine derivatives from aromatic dinitriles can be carried out under different reaction conditions [39]. The desired phthalocyanines (**2**–**5**) were prepared by the reaction of the corresponding substituted phthalonitrile with anhydrous metal salts ($NiCl_2$, $CuCl_2$, $CoCl_2$, $Zn(O_2CMe_2)_2$) in hexanol or quinoline at reflux. The blue-green cyclotetramerization MPc products (M = Ni, Cu, Co and Zn) were purified by column chromatography in moderate yield (26.23% for **2**, 13.29% for **3**, 12.07% for **4**, and 17.56% for **5**). The four polar peripheral substituents conferred upon these macromolecules good solubility in polar solvents, such as DMF, DMSO and DMAA. Differently octasubstituted metallophthalocyanines were prepared as the structural positional isomer mixtures. Therefore, purification steps were tedious because of peripheral reactive end-group. The reactive substituent, 3-mercapto-1,2-propanediol, attached to peripheral positions on the phthalocyanine molecule, offers the possibility of binding various metal ions and functional organic groups for further reactions [40]. The structure of each phthalocyanine was verified using elemental analysis, IR, ^{1}H NMR, UV/Vis and mass spectroscopic methods, as well as by elemental analysis. All the analytical and spectral data were consistent with the predicted structures.

In the IR spectrum of **1**, both the strong –CN, primary and secondary aliphatic –OH peaks at around 2234, 3240–3339 cm^{-1} and the remainder of the spectra were easily diagnosed. The most instinctive indicators for **1** were the signals belonging to the *ortho* aromatic protons to the cyano group in the lower field region of the ^{1}H NMR and six different aromatic carbon atoms between 110–145 ppm in ^{13}C APT spectrum. In compound **1** bearing two different substituents in 4,5-positions, the *ortho* aromatic protons to the cyano group appeared at 7.88–8.10 ppm as two slightly broad singlets in the down field of the ^{1}H NMR spectrum while two different broad deuterium exchangeable –OH protons came out at 4.65 and 5.07 ppm, respectively. Also, the presence of **1** was confirmed by mass spectra (EI and FAB) which showed molecular ion peaks at *m/z*: 268.7 [M$^+$]; the major fragment ions corresponding to the loss of Cl $[M-35]^+$, $M-H_2O$ $[M-18]^+$, $M-2\times H_2O$ $[M-36]^+$, and $M-CH_2OH$ $[M-31]^+$ were easily identified.

The ^{1}H NMR spectra of phthalocyanines **2** and **5** were almost identical to the starting compound **1** except for small shifts; the broad signals in **2** and **5** were probably due to the chemical exchange associated with aggregation–disaggregation equilibria which occurred at the high concentrations used in the NMR measurements [41,42]. The substitution of the phthalocyanines with different moieties results in the formation of positional isomers, which causes splitting of the signals for the peripheral aromatic protons in the down field of the aromatic region. Slightly broad signals for primary and secondary aliphatic –OH exchangeable protons of the phthalocyanines appeared at 5.20, 4.65 and 5.10, 4.73 ppm, respectively and disappeared after the addition of D_2O. Weak broad aromatic signals of **2** and **5** at 7.73 and 7.90 ppm, respectively, in the down field of the spectrum were another indication of the positional isomers.

The mass spectra of **2**, **3** and **5** confirmed the proposed structures; molecular ions were easily identified at *m/z*: 1131, $[M-2]^+$ for **2**, at *m/z*: 1143.1 $[M-1]^+$ for **3**, and at *m/z*: 1132.0 $[M-1]^+$ for **5**.

The UV/Vis spectra of the phthalocyanine complexes (**2**–**5**) exhibited characteristic Q and B bands, one in the visible region at ca. 600–750 nm (Q-band) attributed to the π–π* transition from HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital) of the pthalocyanine ring, and the other in the UV region at ca. 300–400 nm (B-band) arising from the deeper π–π* transitions (Table 1). In the UV/Vis absorption spectra of all phthalocyanines, the Q-band absorptions were observed as a single band of high intensity at 688, 682, 672, and 679 nm. There was also a shoulder at slightly higher energy side of the Q band for each phthalocyanine. In the phthalocyanines bearing sulfanyl substituted moieties on the periphery, the Q band absorption is shifted to lower energy side as a result of the electron-donating thioether substituents than that of phthalocyanines bearing oxa substituted moieties, whereas the position of the soret-like π–π* bands of all



Scheme 1. i, Na_2CO_3, THF; ii, anhydrous quinoline or ethyleneglycol, anhydrous $NiCl_2$, $CuCl_2$, $CoCl_2$, $Zn(O_2CMe)_2$.

phthalocyanines are slightly shifted [14–17,24,28,32,43]. Any increase in concentration results in the aggregation of the phthalocyanine molecules, which is accompanied by a blue shift of the Q-band with a decrease in intensity (ε_{max}). The extent of aggregation was slightly stronger for the phthalocyanines bearing tetrasubstituents on the periphery than for the octasubstitued derivatives [27,30,43].

2.1. Spectroscopic metal ion binding titrations

It has been shown previously that macrocyclic metal complexes (MPc's) with heteroatoms fused directly to the periphery are optically sensitive to metal ions when the peripheral heteroatoms are able to interact with the metals [6,14–18,24,35,43,44]. A mixed set of S and O donor atoms on the periphery of the phthalocyanines imparts a preference for the coordination of heavy metal ions [14–18,24]. Therefore, we employed UV/Vis spectroscopic titrations to monitor the capability of the synthesized MPc's for sensing/coordinating transition metal ions of different sizes. Each titration experiment was carried out using DMF/THF solutions of the MPc (10/90, v/v) to ensure complete dissolution of the analyte salts, $AgNO_3$ and Na_2PdCl_4 dissolved in MeOH. Here the concentration of each MPc and the metal salt was ca. 10^{-5} and 10^{-3} mol dm^{-3}, respectively. The reason for the higher concentration of the metal salt was to produce negligible changes by dilution after its addition to the phthalocyanine solution.

The room temperature and gradual addition (μl) of Ag^I to the solution of **3** caused a gradual color change, from blue-green to green, suggesting complex formation of **3** with Ag^I. Fig. 1 shows that Ag^I binding to the donor atoms of **3** resulted in pronounced effects in the Q and B bands, as well as in the n–π*

Table 1
Electronic spectral data for the phthalocyanine complexes in dimethylformamid

Compound	λ_{max} (nm)		
	Q-band region	Shoulder	Soret region
2	688	635	344
3	682	634	322
4	672	615	350
5	679	637	347

transitions; this observation agrees with that of reported studies [14–18,43,44]. During the titration, an intractable dark blue-black precipitate that could not be isolated was formed. The addition of Ag^I to **3** caused a decrease in the intensities of the Q-band at 682 nm and the B band at 322 nm, and a notable increase in the intensity of the shoulder of the Q band at 638 nm, which can be attributed to the transition of the non-bonding sulfur electron (n) to the π* pc orbital. These spectroscopic changes indicate the coordination of Ag^I by the donor atoms of the phthalocyanines. A decrease in the intensity of the Q-band at 682 nm was attributed to a decrease in the concentration of the monomers, whereas the increase in the concentration of the oligomeric aggregates increased the absorption at 638 nm.

The titration of **4** with Ag^I showed similar spectroscopic behaviour to that of **3**. While the intensities of the Q- and B-band absorptions at 672 and 350 nm, respectively, decreased, the intensity of the shoulder of Q-band absorption at 615 nm increased. On the other hand, the titration of **4** with Pd^{II} gave very different spectra (Fig. 2). The intensity of the Q-band at 672 nm was not changed much; its shoulder disappeared first, and then a new shoulder appeared at longer wavelength. This type of spectroscopic behaviour probably results from the effect of Pd^{II} on the aggregation–disaggregation equilibrium [43,44].

2.2. Electrochemical measurements

The voltammetric properties of the complexes (**2–4**) were studied in DMSO solution containing TBAP (0.1 mol dm^{-3}). Fig. 3 is the typical cyclic voltammograms of **2**, showing four well-defined redox couples (I–IV) at 100 mV s^{-1} scan rate; the redox potentials of the complexes are given in Table 2. Since the central Ni^{II} metal is redox inactive, all redox couples are ring-based processes. The redox processes I, II and III showed a reversible behaviour in that the anodic to cathodic peak currents (I_{pa}/I_{pc}) were unity and ΔE_p values ranged within the reversible peak character with increasing scan rate. The peak currents for these processes increased linearly with the square root of scan rates, suggesting diffusion-controlled electron transfer reactions. The redox process IV was found to be irreversible because it did not have the corresponding anodic couple during the reverse scan even at very high scan rates. The difference between the first and second reduction processes is 0.21 V, which compares with the average value for the first and second reduction processes of non-transition metal phthalocyanine complexes. The difference between the second and third reduction processes is 0.90 V, a value that perfectly agrees with literature values of various MPc complexes. The potential difference between the first reduction and first oxidation, 1.57 V, is within the range (1.5–1.7 V) for the HOMO–LUMO gap of the Pc complexes, and comparable with the reported values [2,22,25,32,45–47].

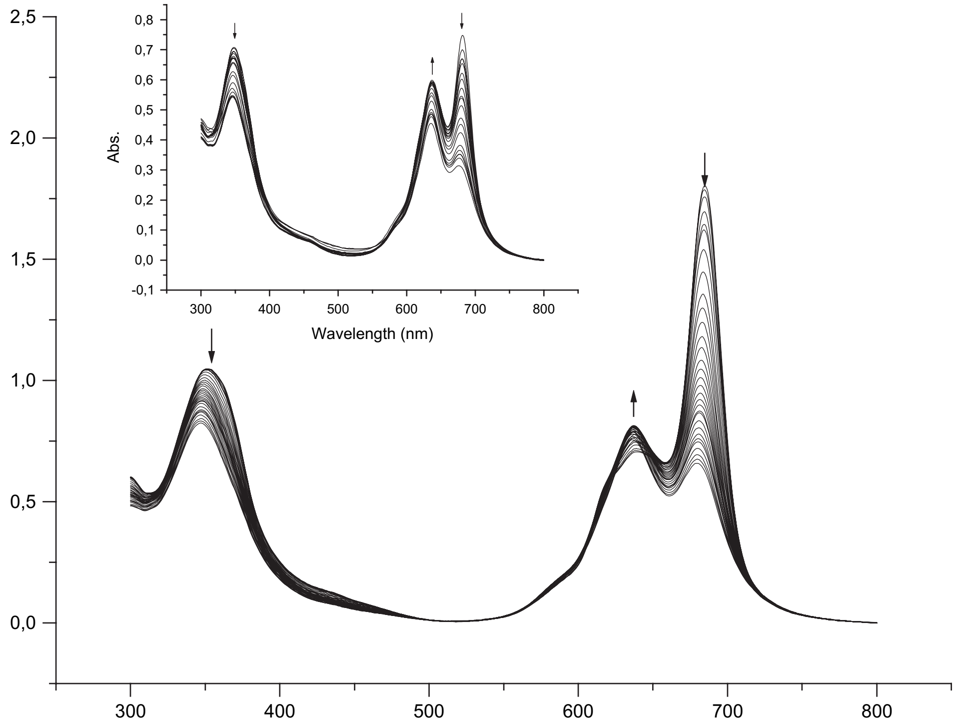


Fig. 1. UV/Vis spectra during titration by Ag^I of **3**; Inset: titration end point spectra of **3** with Ag^I.

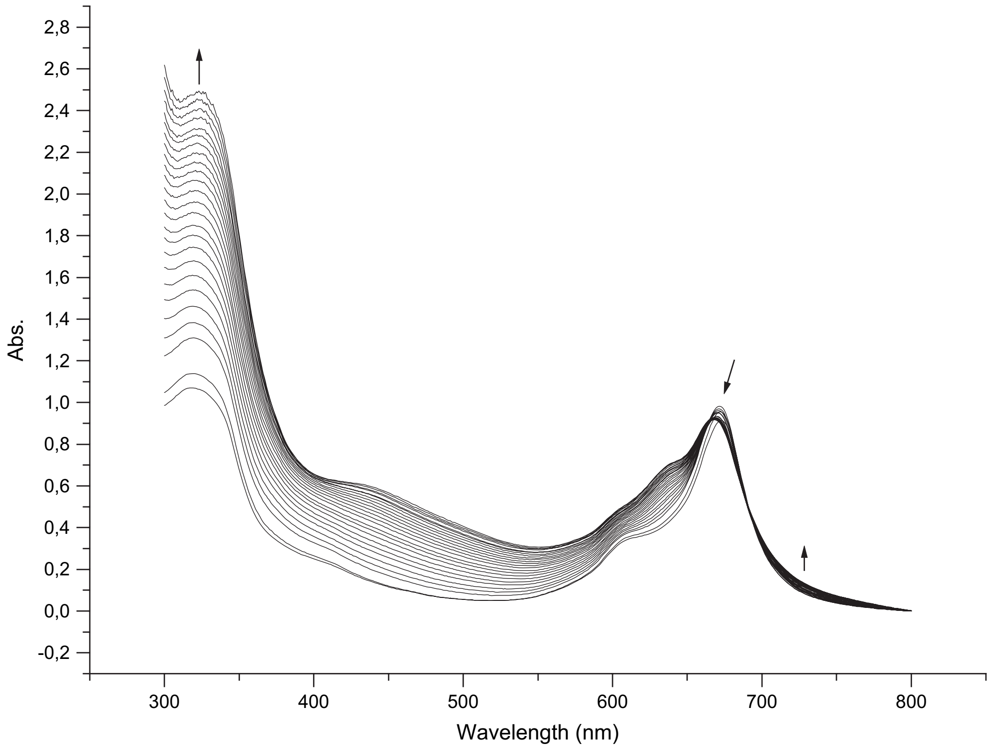


Fig. 2. UV/Vis spectra during titration by Pd^{II} of **4**.

Fig. 4 represents the CV of **3** showing four well-defined redox processes labelled as I–IV. The first reduction process (II) at -1.35 V at 100 mV s^{-1} scan rate has a *quasi*-reversible character. Its cathodic wave shifted towards negative potential side with increasing scan rates and coalesced with the second reduction process. Differently, the oxidation process (I) of the complex was observed at less positive potentials with respect to **2**. This probably arises from the adsorption of the complex on the electrode surface during the cathodic scan since at slow scan rates an extra oxidation peak (AP) was recorded before the usual oxidation process.

While complexes **2** and **3** have three, one-electron ring reductions and a one-electron ring oxidation, complex **4** has both metal-based and ligand-based redox processes. The cyclic voltammograms of **4** in Fig. 5 display four redox couples within the available potential range of the TBAP/DMSO solvent system used. It has been well established that for Ni, Cu and Zn phthalocyanines, redox processes take place on the Pc ring and the first oxidation and the first reduction processes occur on the metal centre in the MPc only for Mn, Fe and Co derivatives in polar solvents [2,22,25]. The voltammetric results recorded in this study concur with the reported common phthalocyanines. It can be proposed that the first oxidation and the first reduction processes of **4** recorded at -0.28 and -1.00 V are attributable to the Co^{II}/Co^{I} and Co^{II}/Co^{III} redox couples, respectively, and the reductions at -1.47 and -1.80 V correspond to the phthalocyanine ring (Pc^{-2}/Pc^{-3} and Pc^{-3}/Pc^{-4}). The separation between the metal centre reduction and oxidation processes ($\sim$0.70 V), which reflects the HOMO–LUMO gap of the complexes, is comparable with the reported CoPc papers [2,22,25].

3. Experimental

All organic solvents were dried and distilled before use. All reagents were freshly distilled or recrystallized and dried under reduced pressure before use. Melting points were determined using a Buchi melting apparatus. ^{1}H and ^{13}C NMR spectra with tetramethylsilane as internal standard were recorded on both a Varian Gemini 300 MHz and a Varian Inova 500 MHz spectrometer; mass spectra (IE and FAB) were recorded on a VG Zab-spectrometer. FTIR (thin film) was recorded on a Perkin Elmer 598 spectrophotometer and

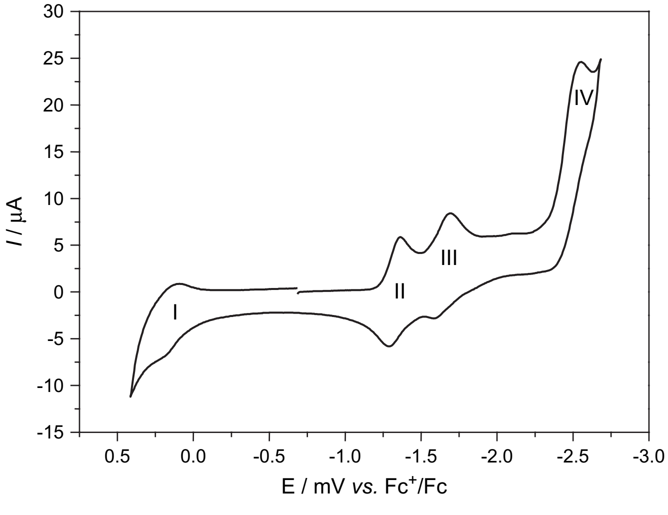


Fig. 3. Cyclic voltammograms of **2** in 0.10 mol dm^{-3} TBAP/DMSO at 0.100 V s^{-1} scan rate.

Table 2
Cyclic voltammetric parameters of the complexes

Complexes	Parameters	Redox processes			
		$Co^{II}Pc^{-2}/Co^{III}Pc^{-2}$	$Co^{II}Pc^{-2}/Co^{I}Pc^{-2}$	$Co^{I}Pc^{-2}/Co^{I}Pc^{-3}$	$Co^{I}Pc^{-3}/Co^{I}Pc^{-4}$
CoPc (**4**)	$^{a}E_{1/2}$ (V)	−0.28	−1.00	−1.47	−1.80
	$^{b}\Delta E_p$ (mV)	280	195	93	105
	$^{c}I_{pa}/I_{pc}$	0.92	1.00	0.98	0.89
		$M^{II}Pc^{-2}/M^{II}Pc^{-1}$	$M^{II}Pc^{-2}/M^{II}Pc^{-3}$	$M^{II}Pc^{-3}/M^{II}Pc^{-4}$	$M^{II}Pc^{-4}/M^{II}Pc^{-5}$
NiPc (**2**)	$^{a}E_{1/2}$ (V)	0.14	−1.43	−1.64	−2.54
	$^{b}\Delta E_p$ (mV)	90	67	93	–
	$^{c}I_{pa}/I_{pc}$	0.90	0.98	0.87	–
CuPc (**3**)	$^{a}E_{1/2}$ (V)	−0.35	−1.35	−1.56	−2.40
	$^{b}\Delta E_p$ (mV)	280	140	70	
	$^{c}I_{pa}/I_{pc}$	0.84	0.89	1.01	–

[a] Cathodic peak potential for reduction, anodic peak potential for oxidation for irreversible processes. Potential are given versus Fc^+/Fc internal reference electrode.

[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.

UV/Vis absorption spectra were recorded on a Unicam 2401 PC spectrophotometer. Chromatography was performed using silica gel (Merck grade 60 and Sephadex) obtained from Aldrich. Elemental analysis (C, H, and N) was performed at the Instrumental Analysis Laboratory of TUBITAK Gebze Research Center. The metal contents of the complexes were determined using a Hitachi 180-80 atomic absorption spectrophotometer in solution prepared by decomposition of the compounds in conc. HCl and conc. HNO_3 (3:1) solution followed by the dilution in water. The homogeneity of the products was tested in each step by TLC (SiO_2, $CHCl_3$, DMF, and methanol).

CV measurements were carried out with a Princeton Applied Research Model Versostat II potentiostat, controlled by an external PC, utilizing a three-electrode configuration at 25 °C. A spiral Pt wire served as the counter electrode. Ag/Ag^+ in acetonitrile was employed as the reference electrode and was separated from the bulk of the solution by a glass bridge. Ferrocene/ferrocenium was used as an internal reference and potential is reported versus Fc^+/Fc couple. The working electrode was a Pt with an area of 0.12 cm^2. The surface of working electrode was polished with an H_2O suspension of Al_2O_3 before each run. Electrochemical grade 0.1 mol dm^{-3} tetrabutylammonium perchlorate (TBAP) in extra pure DMSO was employed as the supporting electrolyte. High purity N_2 was used for deaeration and to maintain a N_2 blanket for at least 15 min prior to each run. For controlled potential coulometric (CPC) studies, platinum gauze working electrode (10.5 cm^2 surface area), Pt wire counter electrode separated by a glass bridge, and Ag/Ag^+ in acetonitrile as a reference electrode were used.

All reagents and solvents were of commercial quality and were distilled or dried when necessary using standard procedures. 3-Mercapto1,2-propanediol and 4,5-dicholoro-1,2-benzenedicarboxylic acid were purchased from Merck and Aldrich and were used as received. The synthesis of the

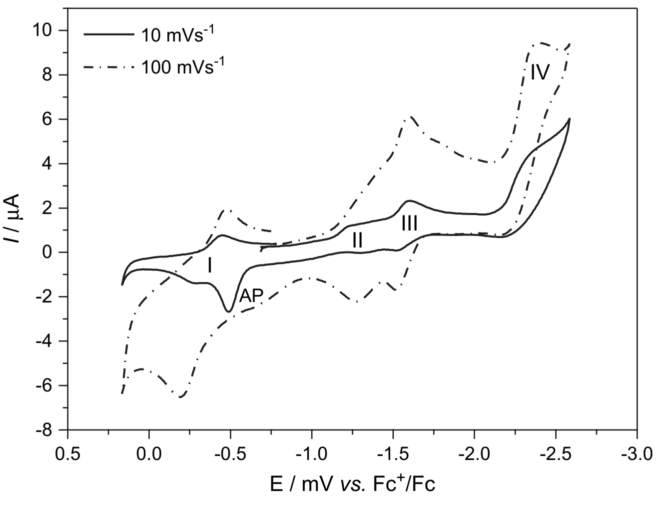


Fig. 4. Cyclic voltammograms of **3** in 0.10 mol dm^{-3} TBAP/DMSO at (·—·—·—) 0.010 and (——) 0.100 V s^{-1} scan rates.

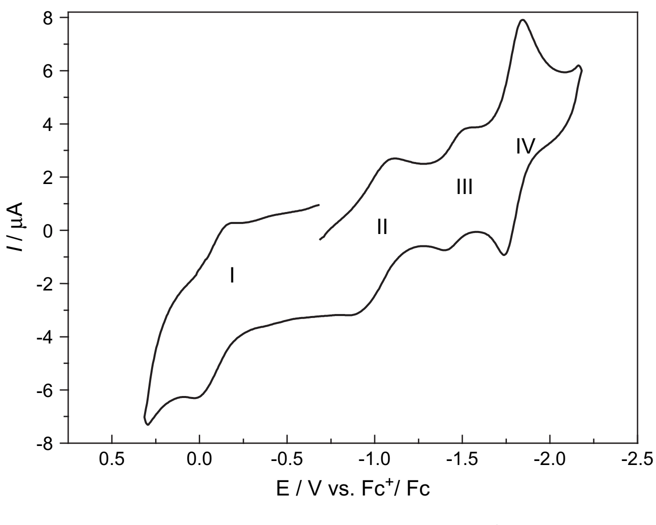


Fig. 5. Cyclic voltammograms of **4** in 0.10 mol dm^{-3} TBAP/DMSO at 0.100 V s^{-1} scan rate.

precursor of our target compounds, 4,5-dichloro-1,2-dicyanobenzene, was according to the reference procedure [38] by a multi-step reaction sequence.

*3.1. 4-(1,2-Propanediolsulfanyl)-5-chloro-benzene-1,2-dicarbonitrile (**1**)*

3-Mercapto-1,2-propandiol (1.15 g, 10.64 mmol) was dissolved in 30 cm^3 dry tetrahydrofuran under nitrogen. Finely ground anhydrous potassium carbonate ($\sim$1.5 g) was added to this solution. After efficient stirring for 0.5 h, 1.0 g (5.07 mmol) 4,5-dichloro-1,2-dicyanobenzene in tetrahydrofuran ($\sim$20 cm^3) was added dropwise at room temperature. After the reaction mixture was kept at reflux under nitrogen atmosphere for 12 h, the solution was cooled to room temperature. The solvent was removed under reduced pressure; water was added and decanted to separate any inorganic residues. The crude compound was dissolved in tetrahydrofuran again and dried with anhydrous sodium sulfate. Having removed the solvent to dryness, it was treated with diethylether several times to remove unreacted starting compounds. The target yellow compound was obtained without further purification.

1: 1.12g (82.42%), m.p.: 190 °C. Anal. calc. for $C_{11}H_9ClN_2SO_2$: C, 49.16; H, 3.35; N, 10.43. Found: C, 48.33; H, 3.31; N, 10.01. IR (thin film, disc) ν: 3339–3240 (CH–*OH* and CH_2*OH*); 2234 (–CN). ^{1}H NMR (500) DMSO-d_6) δ: 8.10 (s, 1H, *ortho* to Cl group), 7.88 (s, 1H, *meta* to Cl), 5.07 and 4.65 (s, br, 1H, CH–*OH*, D_2O-exchangeable and s, br, 1H, $-CH_2$*OH*, D_2O-exchangeable), 2.90 (d, S*CH*$_2$), 3.50 (m, *CH*–OH, 3.64 (m, *CH*$_2$OH). ^{13}C NMR (APT) (DMSO-d_6): δ 38.3 ($S-CH_2$), 40.6 (*CH*$_3$, DMSO), 64.61 (CH_2*OH*), 69.70 (CH–*OH*), 114.14–115.25 (aromatic C≡N), 129.94, 133.24 (aromatic C), 134.39, 135.38 (aromatic CH), 137.36, 139.00 (aromatic C–Cl), 146.61 (aromatic C–S) ppm. EI/MS: *m/z* (%): 267.5 (17) [$M^+ - 1$], 266.6 [$M^+ - 2$], 250.3 [$M^+ - 18$], 236.3 [$M^+ - 31$; $M - CH_2{=}OH^+$], 222.4 [$M^+ - 46$], 249.1, 207.6 [M − 61], 197.4 $[M - 71]^+$, 107.7, 75.1.

*3.2. 2,3,9,10,16,17,23,24-[Tetrakis-(1,2-propandiolsulfanyl)-tetrachloro] substituted-nickel (II) phthalocyanine (**2**)*

0.2 g (0.74 mmol) of **1** was dissolved in 0.2 cm^3 of dry quinoline in a sealed tube in the presence of DBU (0.05 cm^3). Anhydrous $NiCl_2$ (0.012 g excess) was added to the reaction mixture under nitrogen atmosphere at 120 °C. The mixture was heated and stirred gently at 120 °C for about 1 h under nitrogen atmosphere until the sealed tube got rid of the moisture and then covered. After stirring and heating for about another 3 h at 175–180 °C, the mixture was cooled to room temperature. Then hexane was added to the mixture in order to precipitate the crude product. The filtrated blue product was washed several times with ethanol–hexane mixture (1:3 or 1:2 v/v) to precipitate and purify crude compound and then successively 2-propanol, diethylether to remove unreacted inorganic and organic impurities. Finally, precipitates were collected on function filtrate, washed with 2-propanol, and dried in vacuo.

2: 0.055 g (26.23%), m.p. >200 °C. Anal. calc. for $C_{44}H_{36}Cl_4N_8O_8S_4Ni$: C, 46.60; H, 3.17; N, 9.88. Found: C, 45.03; H, 3.04; N, 8.96. IR (thin film) ν: 3372–3245 cm^{-1} (Aliph-CH*OH*, CH_2*OH*); 3080 (Ar-H), 2973, 2924, 2853 (Aliph-H), 1726 (w, H-Bonding), 1557, 1559, 1531, 1409, 1345, 1252, 1218, 1135, 1075, 996, 885, 784, 744, 708, 661. ^{1}H NMR DMSO-d_6) δ: 8.13 (s, 4H, *ortho* to Cl group), 7.90 (s, 4H, *meta* to Cl), 5.11 and 4.67 (s, br, 4H, CH–*OH*, D_2O-exchangeable and $-CH_2$*OH*, D_2O-exchangeable), 2.92 (d, 8H, S*CH*$_2$), 3.54 (m, 4H, *CH*–OH, 3.63 (m, 8H, *CH*$_2$OH). MS (FAB) *m/z* (%): 1131.0 (7) $[M - 2]^+$, 1113.2 (5) [M − 18], 1102.5 [M − 31; ($CH_2{=}OH^+$, $M - H_2S$)] (7), 1096.1 (4) $[M - Cl \text{ or } M - 2H_2O]^+$, 1071.0 (5) [M $- 2\times CH_2{=}OH^+$ or M − 59], 1063 (6) $[M - 2\times Cl]^+$, 990.3 (7) $[M - 3\times Cl]^+$, 847.5 (10) [$M - 4\times CH_2CHOHCH_2OH$)].

*3.3. 2,3,9,10,16,17,23,24-[Tetrakis-(1,2-propandiolsulfanyl)-tetrachloro] substituted copper (II) phthalocyanine (**3**)*

A mixture of compound **1** (0.2 g, 0.74 mmol), anhydrous $CuCl_2$ (0.012 g, excess) and anhydrous quinoline (0.4 cm^3) were heated and stirred at 170 °C in a sealed tube under nitrogen atmosphere for 6–7 h. The color of the mixture turned into green-blue during the course of time. Then, the green-blue product was cooled to room temperature. The subsequent procedure was the same as described for **2**.

4 Yield: 0.028 g (13.29%). m.p. >200 °C. Anal. calc. for $C_{44}H_{36}Cl_4N_8O_8S_4Cu$: C, 46.42; H, 3.16; N, 9.84. Found: C, 45.44; H, 3.02; N, 9.19. 3240–33370 cm^{-1} (Aliph-CH*OH*, CH_2*OH*); 3010 (Ar-H), 2941, 2877 (Aliph-H), 1715 (w, H-Bonding), 1655, 1456, 1414, 1377, 1254, 1204, 1150, 1082, 1010, 945, 881, 852, 653. MS (FAB): *m/z* (%): 1143.1 (5) $[M - 1]^+$, 1141.1 [M − 3], 1124.7 [M − 18], 1112.3 [M − 31; ($CH_2{=}OH^+$, $M - H_2S$)] (6), 1106.3 (8) [M − Cl or $M - 2H_2O]^+$ (7), 1081.0 [$M - 2\times CH_2{=}OH^+$] (5), 1072 $[M - 2\times Cl]^+$, 1050 [$M - 3\times CH_2{=}OH^+$].

*3.4. 2,3,9,10,16,17,23,24-[Tetrakis-(1,2-propandiolsulfanyl)-tetrachloro] substituted cobalt(II) phthalocyanine (**4**)*

Compound **1** (0.2 g, 0.74 mmol) and anhydrous $CoCl_2$ (0.012 g, excess) were dissolved in 15 cm^3 of anhydrous ethylene glycol in two neck round bottomed flask under nitrogen atmosphere. The reaction was continued at 180 °C for about 6 h. The dark green-blue product formed during the reaction was poured into diethylether (40 cm^3) after cooling to room temperature to precipitate the desired product. The green-blue product was filtered off and then washed successively with water, 2-propanol, and several times with diethylether. The precipitates formed were centrifuged and washed with 2-propanol and dried in vacuo. The compound is slightly soluble in MeOH, EtOH, THF and soluble DMF, DMSO, quinoline.

4: 0.012 g (12.07%). m.p. >200 °C. Anal. calc. for $C_{44}H_{36}Cl_4N_8O_8S_4Co$: C, 46.88; H, 3.27; N, 10.19. Found: C, 45.84; H, 3.19; N, 9.59. IR (thin film) ν: 3375–3245 cm^{-1}

(Aliph-CH*OH*, CH_2*OH*); 3075 (Ar-H), 2924, 2853 (Aliph-H), 1726 (w, H-Bonding), 1655, 1456, 1414, 1377, 1254, 1204, 1150, 1082, 1010, 945, 881, 852, 653. MS (FAB) *m/z* (%): 1132.0 (4) $[M-1]^+$, 1129.1 $[M-3]$, 1115.2 (5) $[M-18]$, 1102.5 $[M-31;\ (CH_2{=}OH^+,\ M-H_2S)]$ (7), 1096.1 (4) $[M-Cl \text{ or } M-2H_2O]^+$, 1071.0 (5) $[M-2{\times}CH_2{=}OH^+]$, 1063 (6) $[M-2{\times}Cl]^+$, 990.3 (7) $[M-3{\times}Cl]^+$.

*3.5. 2,3,9,10,16,17,23,24-[Tetrakis-(1,2-propandiolsulfanyl)-tetrachloro] substituted zinc (II) phthalocyanine (**5**)*

Compound **1** (0.2 g, 0.74 mmol), and anhydrous $Zn(AcO)_2$ (0.012 g, excess) and anhydrous quinoline were heated and stirred under nitrogen in a sealed tube at 170−180 °C for 12 h. The dark green-blue product formed during the reaction was poured into diethylether (40 cm^3) after cooling to room temperature to precipitate the desired product. The green-blue product was filtered off and then washed successively with water, 2-propanol, and several times with diethylether. The precipitates formed were centrifuged and washed with 2-propanol and dried in vacuo. The compound is slightly soluble in MeOH, EtOH, THF and soluble DMF, DMSO, quinoline.

5: 0.012 g (17.56%). m.p.>200 °C. Anal. calc. for $C_{44}H_{36}Cl_4N_8O_8S_4Zn$: C, 46.36; H, 3.16; N, 9.83. Found: C, 45.579; H, 3.14; N, 9.40. IR (thin film) ν: 3391−3245 cm^{-1} (Aliph-CH*OH*, CH_2*OH*); 3030 (Ar-H), 2970, 2928 (Aliph-H), 1736 (w, H-Bonding), 1656, 1503, 1410, 1379, 1254, 1216, 1158, 1087, 1046, 944, 889, 780, 741, 660.

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