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The synthesis and electrochemical study of novel phthalocyanines substituted with a crown ether and alkyl chains

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ABSTRACT

A new class of soluble unsymmetrically substituted metallophthalocyanines (M = Zn, Ni, Co) bearing a crown ether and six alkylthio substituents was synthesized and their electrochemical and spectroelectrochemical properties studied. Cyclic and square wave voltammetry revealed well-defined ligand-based oxidation and reduction processes within the complexes. Assignment of the redox processes was performed by in-situ spectroelectrochemical measurements. The disappearance of the redox processes for the monomeric species and the observation of new waves indicated that intermolecular dimer formation occurred during the potentiometric titration of the complexes with K^+ and Na^+ ions.

1. Introduction

Phthalocyanines (PC's) and their substituted derivatives continue to attract research interest because of their many applications which benefit from the ease of tuning the properties of the ring system [1,2]. The substituents and the central metal ions play a critical role in the design, solubility and properties of PC's. Their solubility is of fundamental importance in terms of both synthesis and purification stages as well as their properties. The solubility of phthalocyanines can be improved by introducing various peripheral substituents, such as crown ethers, alkyl, alkoxy and alkylthio chains [3–8].

Crown ethers also enjoy applications in molecular electronic devices owing to their remarkable recognition and metal-binding features. Phthalocyanines substituted by crown ether rings play a key role in the charge transfer properties of stacked Pcs with extended π-conjugation and show potential for use as ion-conducting channels or heavy metal extraction agents. The attachment of polar side chains such as oligo-(ethyleneoxy) moieties and crown ether rings to large aromatic macrocycles is also of interest in the construction of supramolecular wires and ion-conducting channels [9–16].

Phthalocyanines with two or more different substituents at the exterior of the ring system offer potential for use in second-order nonlinear optics, thin-film electronics, Langmuir–Blodgett (LB) film formation, liquid crystals and photodynamic therapy of cancer [17–26].

Several synthetic strategies can be used to prepare unsymmetrical phthalocyanines, namely, a statistical condensation route, subphthalocyanine route and polymeric support method or solid phase synthesis [23–26]. However, whilst each strategy has a number of disadvantages, the most common method employed is the statistical condensation of two differently substituted dinitriles or diiminoisoindolines followed by chromatographic separation of the resulting mixture.

The present authors have previously reported the synthesis and characterization of unsymmetrically substituted phthalocyanines [27–31] and, as an extension of this work, this paper concerns the preparation and structural determination of unsymmetrically substituted metallophthalocyanines which carry six alkylthio groups and a benzo-15-crown-5 unit through oxy bridges. Voltammetric and spectroelectrochemical studies of phthalocyanines and complexation with alkali metal ions are also described.

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2. Experimental

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrophotometer (ATR sampling accessory), electronic spectra were collected on a Unicam UV2-100 spectrophotometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Center. ^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrometer using TMS as an internal reference, and mass spectra were obtained on a VG Zabspec GC–MS spectrometer. All reagents and solvents were dried and purified as described by Perrin and Armarego [32]. Purity of the products was tested in each step by TLC. 1-{[(benzo-15-crown-5)-4-yl]oxy}phthalonitrile (**1**) [13] and 4,5-bis(hexylthio)-1,2-dicyanobenzene (**2**) [33] were synthesized according to published methods, by a multi-step reaction sequence.

Cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements were carried out with a Gamry Reference 600 potentiostat/galvanostat controlled by an external PC and utilizing a three-electrode configuration at 25 °C. The working electrode was a Pt disc with a surface area of 0.071 cm^2. Surface of the working electrode was polished with a diamond suspension before each run. A Pt wire served as the counter electrode. Saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Ferrocene was used as an internal reference. Electrochemical grade tetrabutylammonium perchlorate (TBAP) in extra pure dichloromethane (DCM) was employed as the supporting electrolyte at a concentration of 0.10 mol dm^{-3}. High purity N_2 was used to remove dissolved O_2 at least 15 min prior to each run and to maintain a nitrogen blanket during the measurements. IR (current × resistance) compensation was also applied to the CV scans to further minimize the potential control error.

Spectroelectrochemical measurements were carried out with an Ocean Optics QE65000 diode array spectrophotometer equipped with the potentiostat/galvanostat utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell at 25 °C. The working electrode was transparent Pt gauze. A Pt wire counter electrode separated by a glass bridge and an SCE reference electrode, separated from the bulk of the solution by a double bridge, were used.

*2.1. 2-{[(Benzo-15-crown-5)-4-yl]oxy}-9,10,16,17,23,24-hexakis(hexylthio)phthalocyaninatozinc (II) (**3**)*

A mixture of **1** (0.21 g, 0.5 mmol), **2** (0.54 g, 1.5 mmol) and anhydrous Zn(OAc)$_2$ (0.10 g, 0.5 mmol) in anhydrous DMF (1.5 mL) was heated under reflux with stirring under a nitrogen atmosphere for 24 h. The mixture was allowed to cool and then poured into MeOH/H_2O, 2:1 (200 mL), whereby a green solid precipitated. The precipitate was collected by centrifugation and dried *in vacuo*. The crude product was isolated on an alumina column by performing two consecutive column chromatographic separations. In the first column, the mobile phase was $CHCl_3$. The desired ZnPc (AAAB) was present in the first fraction together with octakis(alkylthio)-substituted ZnPc (AAAA), while the second fraction contained the other ZnPc isomers (AABB, ABAB, ABBB, BBBB). This first fraction was purified by subsequent column chromatography (alumina, $CHCl_3$/MeOH, 20:1). The first fraction contained traces of the symmetrical phthalocyanines; the second fraction was the desired product. The dark green compound was soluble in CH_2Cl_2, $CHCl_3$, ethyl acetate, and diethyl ether. Yield: 0.09 g, 12%. Mp. > 200 °C. IR, ν (cm^{-1}): 2953–2854 (aliph. CH), 1591,1505,1404,1371,1255–1216 (Ar–O–C), 1128–1085 (C–O–C), 988, 943, 869 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ: 8.59–7.55 (m, 9H, Ar-H), 6.98–6.82 (m, 3H, Ar-H), 4.22 (m, 4H, O–CH_2), 3.99 (m, 4H, O–CH_2), 3.82–3.71 (m, 8H, O–CH_2), 3.40 (t, 12H, S–CH_2), 1.94 (t, 12H), 1.74 (m, 12H), 1.46 (m, 12H), 1.24 (m,12H), 0.96 (t, 18H); MS(ESI$^+$) m/z: 1557 [M]$^+$; UV–VIS λ_{max} (nm) (log ε) in $CHCl_3$: 332 (4.19), 662 (4.12), 709 (4.88). Anal. Calc. for $C_{82}H_{106}N_8O_6S_6Zn$: C, 63.23; H, 6.86; N, 7.19%. Found: C, 63.21; H, 6.79; N, 7.05%.

*2.2. 2-{[(Benzo-15-crown-5)-4-yl]oxy}-9,10,16,17,23,24-hexakis(hexylthio)phthalocyaninatonickel (II) (**4**)*

A mixture of **1** (0.16 g, 0.4 mmol), **2** (0.43 g, 1.2 mmol), anhydrous $NiCl_2$ (0.065 g, 0.5 mmol), and anhydrous DMF (1.5 mL) were mixed in a glass tube which was sealed under nitrogen and heated and stirred at 155 °C for 30 h. The dark green mixture was cooled to room temperature and diluted with MeOH/H_2O, 1:1, until a crude green product precipitated. The precipitate was filtered and washed several times with ethanol to remove unreacted materials. The desired product was isolated by two chromatographic separations carried out successively on neutral alumina. In the first column, the mobile phase was $CHCl_3$ while $CHCl_3$/MeOH (15:1) were used as a mobile phase in the second column. Yield: 0.05 g, 8%. Mp. > 200 °C. IR, ν (cm^{-1}): 2953–2853 (aliph. CH), 1596, 1505, 1453, 1256–1219 (Ar–O–C), 1130–1099 (C–O–C), 987, 966, 862 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ: 8.19–7.34 (m, 9H, Ar–H), 7.08–6.97 (m, 3H, Ar-H), 4.24–4.22 (m, 4H, O–CH_2), 4.00–3.95 (m, 4H, O–CH_2), 3.84–3.81 (m, 8H, O–CH_2), 3.24 (m, 12H, S–CH_2), 1.98 (t, 12 H), 1.69 (m, 12H), 1.36–1,31 (m, 12H), 1.31–1.23 (m,12H), 0.99 (t, 18H); MS (ESI$^+$) m/z: 1550 [M]$^+$; UV–VIS λ_{max} (nm) (log ε) in $CHCl_3$: 321 (4.26), 666 (4.22), 702 (4.92). Anal. Calc. for $C_{82}H_{106}N_8O_6S_6Ni$: C, 63.51; H, 6.89; N, 7.23%. Found: C, 63.37; H, 6.78; N, 7.13%.

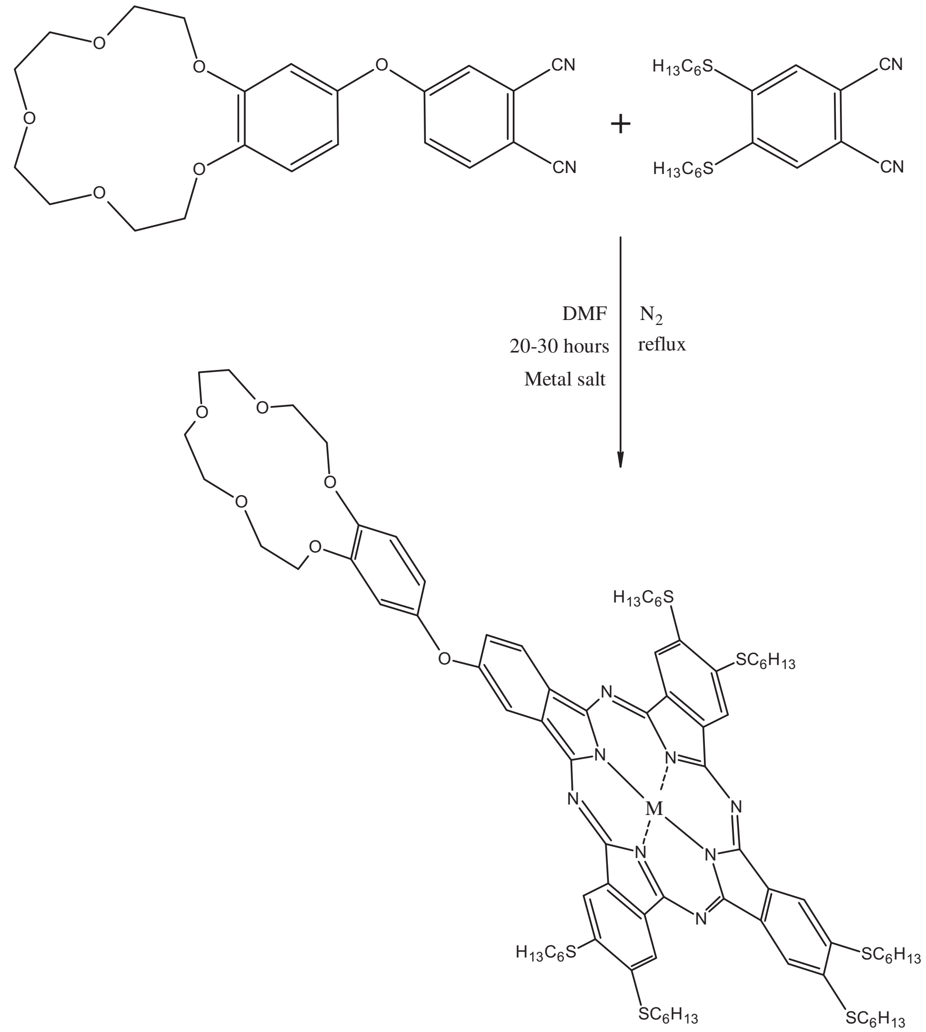
*2.3. 2-{[(Benzo-15-crown-5)-4-yl]oxy}-9,10,16,17,23,24- hexakis(hexylthio)phthalocyaninatocobalt (II) (**5**)*

A mixture of **1** (0.14 g, 0.3 mmol), **2** (0.29 g, 0.9 mmol) and anhydrous DMF (1 mL) were fused in the presence of anhydrous $CoCl_2$ (0.063 g, 0.48 mmol) in a glass tube under nitrogen at 160 °C for 20 h. After cooling, the residue was washed well with water and methanol to remove unreacted materials and further isolation of the mixture was carried out using two successive column chromatographic separations on neutral alumina. The first column was eluted with $CHCl_3$ while $CHCl_3$/MeOH (7:1) were used as eluent in the second column. Yield: 0.07 g, 15%. Mp. > 200 °C. IR, ν (cm^{-1}): 2953–2853 (CH aliph.), 1596, 1505, 1453, 1256–1219 (Ar–O–C), 1130–1099 (C–O–C), 987, 966, 862 cm^{-1} MS (ESI$^+$) m/z: 1551 [M]$^+$; UV–VIS λ_{max} (nm) (log ε) in $CHCl_3$: 331 (4.36), 662 (4.25), 710 (4.89). Anal. Calc. for $C_{82}H_{106}N_8O_6S_6Co$: C, 63.50; H, 6.89; N, 7.22%. Found: C, 63.41; H, 6.68; N, 7.08%.

3. Results and discussion

3.1. Synthesis and characterization

The 1-{[(benzo-15-crown-5)-4-yl]oxy}phthalonitrile (**1**) was condensed with 4,5-bis(hexylthio)-1,2-dicyanobenzene (**2**) to form the desired unsymmetrical metallophthalocyanines (**3**–**5**) according to the statistical method. The reaction mixture of one equivalent of **1**, three equivalents of **2**, together with a metal salt (Zn(OAc)$_2$, $NiCl_2$ or $CoCl_2$) and anhydrous DMF was stirred in a glass tube which was sealed under nitrogen (Scheme 1). When the resulting crude product was subjected to TLC analysis, it showed five separable spots. Purification by column chromatography enabled the separation of these compounds. The first fraction contained the undesired symmetrical octaalkylphthalocyanine (AAAA) compound, which



	3	4	5
M	Zn^{2+}	Ni^{2+}	Co^{2+}

Scheme 1. Synthesis of the unsymmetrical phthalocyanine **3**–**5**.

was identified by TLC comparison against an authentic sample [33], along with the desired 3:1 (AAAB) metallophthalocyanine derivative (**3, 4** or **5**). The mixture was re-chromatographed using $CHCl_3$/MeOH at different ratios as the eluent. The first fraction from this second separation was eliminated. The second fraction showed one spot on TLC, with no evidence of the presence of the symmetrical octaalkylphthalocyanine.

All phthalocyanines **3**–**5** show good solubility in common organic solvents, *e.g.*, dichloromethane, chloroform, and DMF. The pure compounds obtained were characterized by IR, ^1H NMR, ESI^+ MS and UV–Vis spectral data along with elemental analysis.

The IR spectra of **3**–**5** clearly indicated the presence of alkyl groups and crown ether moieties and characteristic frequencies of the crown ether moieties and alkyl groups were observed at around 2953–2854 (C–H), 1258–1216 (Ar–O–C) and 1128–1081 cm^{-1} (C–O–C), respectively.

The new unsymmetrically substituted metallophthalocyanines showed electronic spectra typical of MPc complexes with Q and B bands. The Q band absorptions in the UV–Vis absorption spectra of the phthalocyanines **3**–**5** were observed as a single high intensity band due to $\pi-\pi^*$ transitions at 709, 702 and 710 nm, respectively. The B bands of these phthalocyanines appeared in the UV region at 332, 321 and 331 nm, respectively. A hypsochromic shift was observed by increasing the number of crown ethers on the peripheral positions of phthalocyanine macrocycle. UV–Vis spectra of zinc phthalocyanines substituted with four, three and one crown ether moieties yielded different Q bands in UV–Vis region at 690 [13], 696 [30] and 709 nm, respectively (Table 2). The bathochromic shift of the Q band of the Pc increases in parallel with the number of S-donor moieties.

The ^1H NMR spectra of the unsymmetrical metallophthalocyanines **3** and **4** are in excellent agreement with the proposed structures. In the ^1H NMR spectra of **3** and **4**, the aromatic protons were observed between δ 8.59 and 7.34 ppm. The aromatic protons of crown ether moiety appeared at δ 7.08–6.82 ppm. The methyleneoxy protons of the crown ether group ($-OCH_2CH_2O$) were observed between δ 4.24–3.81 ppm while the protons of alkyl groups ($-SC_6H_{13}$) were observed between δ 3.40–0.96 ppm.

Table 1
Voltammetricdata of the complexes with the related metallophthalocyanines for comparison.

Complex		Redox processes					$^{d}\Delta E_{1/2}$	Reference
		I	II	III	IV	V		
NiPc (4)	$E_{1/2}$ (V vs. SCE)^{a}	1.53^{e}	1.03 (0.74)^{f}	(−0.82)	−1.09	−1.53^{e}	1.56	tw*
	ΔE_p (mV)^{b}	–	–	85	93	–		
	I_{pa}/I_{pc}^{c}	–	–	0.93	0.90	–		
ZnPc (3)	$E_{1/2}$ (V vs. SCE)	1.54^{e}	0.75	−0.90 (−0.80)^{f}	(1.28)^{f}−1.44	–	1.55	tw*
	ΔE_p (mV)	–	090	–	–	–		
	I_{pa}/I_{pc}	–	0.94	–	–	–		
ZnPc^{g}	$E_{1/2}$ (SCE) in DMSO	0.78	0.78 (0.61)^{f}	−0.82	−1.24	−1.55	1.43	[13]
CuPc^{h}	$E_{1/2}$ (SCE) in DCM		0.82	−0.86	−1.25	–	1.68	[30]
ZnPc^{i}	$E_{1/2}$ (SCE) in DCM	1.36	0.65	−0.98	−1.31	−1.63	1.63	[34]
NiPc^{i}	$E_{1/2}$ (SCE) in DCM	1.51	0.89 (0.65)^{f}	−0.86	−1.25	–	1.51	[34]
CuPz^{j}	$E_{1/2}$ (Fc^{+}/Fc) in DCM		0.48	−0.46	−0.85	−1.31	0.98	[35]
H_2Pz^{k}	$E_{1/2}$ (Ag^{+}/Ag) in DCM		1.11	−0.94	−1.23	–	2.05	[36]

***tw:** this work.

[a] $E_{1/2} = (E_{pa} + E_{pc})/2$ at 0.100 Vs^{-1} scan rate (E_{pc} for reduction, E_{pa} for oxidation for irreversible processes).

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

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

[d] $\Delta E_{1/2} = \Delta E_{1/2}$ (first oxidation) − $\Delta E_{1/2}$ (first reduction).

[e] Recorded by square wave voltammetry (SWV).

[f] Assigned to the aggregated species(II^{a}).

[g] :Substituted with four{[(benzo-15-crown-5)-40-yl]oxy} groups [13].

[h] Substituted with 2-nitro-9,16,23-tri{[(benzo-15-crown-5)-40-yl]oxy} groups [30].

[i] Substituted with four flexible 18-crown-6(1,4,7,10,13,16-hexaoxacyclooctadecane) groups [34].

[j] Substituted with eight crown ether substituents groups [35].

[k] Substituted with TTF-tetrathiacrown ether units [36].

In addition, the assignment of the product to a 3:1 combination of the reactant was made on the basis of elemental analyses and mass spectral data, confirming the proposed structures. The molecular ion peaks of **3**–**5** at m/z 1557, 1550 and 1551 respectively were obtained by ESI^{+} MS.

3.2. *Voltammetric and spectroelectrochemical measurements*

The electrochemical behaviour of the complexes **3** (ZnPc) and **4** (NiPc) were investigated with the cyclic voltammetry (CV) and square wave voltammetry (SWV) on a platinum working electrode in DCM. Table 1 lists the redox potentials of the complexes studied here and related complexes from the literature [13,30,34–36] for comparison. As shown in the table, the complexes bearing different numbers of benzo-15-crown-5 units give similar redox processes with a small potential shift due to the number of benzo-15-crown-5 units, the metal center and the solvent of electrochemical measurements. Compounds **3** and **4** display very similar voltammetric behaviour with small potential differences and different aggregation tendency of the complexes, thus, CV and SWV of **4** are given in Fig. 1 and are representative of the complexes. Within the electrochemical window of TBAP/DCM, **4** undergoes two quasi-reversible one-electron oxidations at 1.03 and 1.53 V and three quasi-reversible one-electron reduction processes at −0.82, −1.09 and −1.53 V vs. SCE at 0.100 Vs^{-1} scan rate. SWV of the complex clearly confirms the recorded redox processes. Reversibility is illustrated by the similarity in the forward and reverse SWV scans (Fig. 1B) [37,38]. CV and SWV show the aggregation character of the complex. For the couples III and IV, anodic to cathodic peak separations (ΔE_p) varied from 70 to 150 mV with the increasing scan

Table 2
Electronic spectra of the phthalocyanines.

Complex	Solvent	λ_{max}, nm (logε)
ZnPc (3)	$CHCl_3$	332 (4.19), 662 (4.12), 709 (4.88)
ZnPc [13]	$CHCl_3$	351 (4.79), 616 (4.45), 690 (4.99)
ZnPc [30]	$CHCl_3$	377 (4.59), 675 (4.87), 696 (4.82)

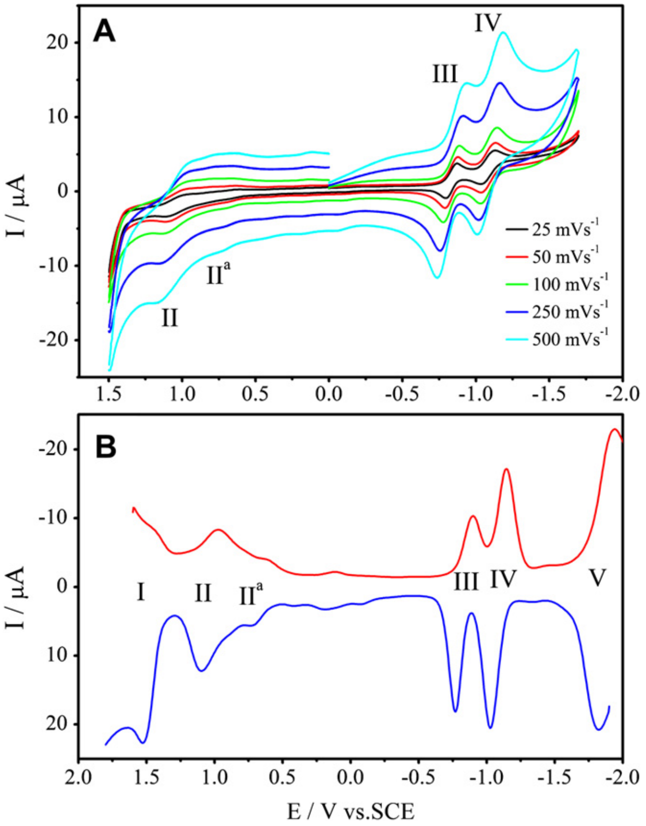


Fig. 1. A) Cyclic voltammograms of NiPc (**4**) (5.0 10^{-4} mol dm^{-3}) at various scan rates on Pt in DCM/TBAP. B) Square wave voltammograms of **4** (5.0 10^{-4} mol dm^{-3}) pulse width: 50 ms; pulse height: 100 mV, step height: 5 mV, step time: 100 ms, scan rate:50 mVs^{-1}. (for red SWV, E_i = 1.7 V and E_f = −2 V and for blue SWV, E_i = −2 V and E_f = 1.7 V). For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.

rates (ΔE_p values of60–110 mV, were obtained for a ferrocene reference) support quasi-reversible electron transfer. While the values of $I_{p,a}/I_{p,c}$ for the couples III is unity at all scan rates in the CVs, whereas $I_{p,a}/I_{p,c}$ were less than unity in SWV (Square wave voltammetry). This difference may due to the different time scales of these techniques. The different time scale affects the amount of aggregated or disaggregated species at any instant potential. When the SWV is scanned from negative potential to the positive potentials (with the parameters E_i = -2 V and E_f = 1.7 V), the high negative potential causes the disaggregation of the aggregated species. The anodic wave of the first reduction couple assigned to the reoxidation of the monomeric species has a higher current than the cathodic one. But the values of $I_{p,a}/I_{p,c}$ for IV couple of the complex are close to unity and the peak current increased linearly with the square root of the scan rate for scan rates ranging from 10 to 500 mVs^{-1}, indicating purely diffusion-controlled mass transfer of the species. The first oxidation couple splits into two waves due to the aggregation–disaggregation equilibrium during the anodic scans. Due to the close coincidence of peaks resulting from monomeric (II) and aggregated species (II^a), analysis of the oxidation peaks could not be further carried out. Because of redox-inactive nickel center of the complex **4**, all of these processes are attributed to successive removal of electrons from, or addition of electrons to, the macrocycle orbitals [39]. The separation between the first and second ring reductions was found to be 0.27 V for the complex. The peak separation and HOMO–LUMO gap value (1.56 V) are in agreement with the reported separations for redox processes in metallophthalocyanine complexes [40–44].

Spectroelectrochemistry was used to confirm some of the assignments in the CV of **4** (Fig. 2). Due to the aggregation of the complex, the Q band is broad at the beginning of the process. During the controlled potential reduction of **4** at −0.90 V *vs.* SCE, while the absorption of Q band at 684 nm and its shoulder at 652 nm decrease in intensity, the bands in the metal to ligand charge-transfer region (MLCT) at 595 and 820 nm increase in intensity. Moreover, while the B band increases in intensity with a hypsochromic shift from 316 to 307 nm a new band appears at 366 nm (Fig. 2A). Decrease in intensity of the Q band without shifting the absorption maxima and observation of new bands at 595 and 820 nm (MLCT), are characteristic of ligand-based processes and assign the couple III to [Ni^{II}Pc^{-2}]/[Ni^{II}Pc^{-3}]$^{-1}$ for both aggregated and monomeric species at the same potential. During electrochemical reduction, well-defined isosbestic points are observed at 263, 313, 345, 400, 467, 620, and 747 nm, which demonstrate that the reduction proceeds cleanly in deoxygenated

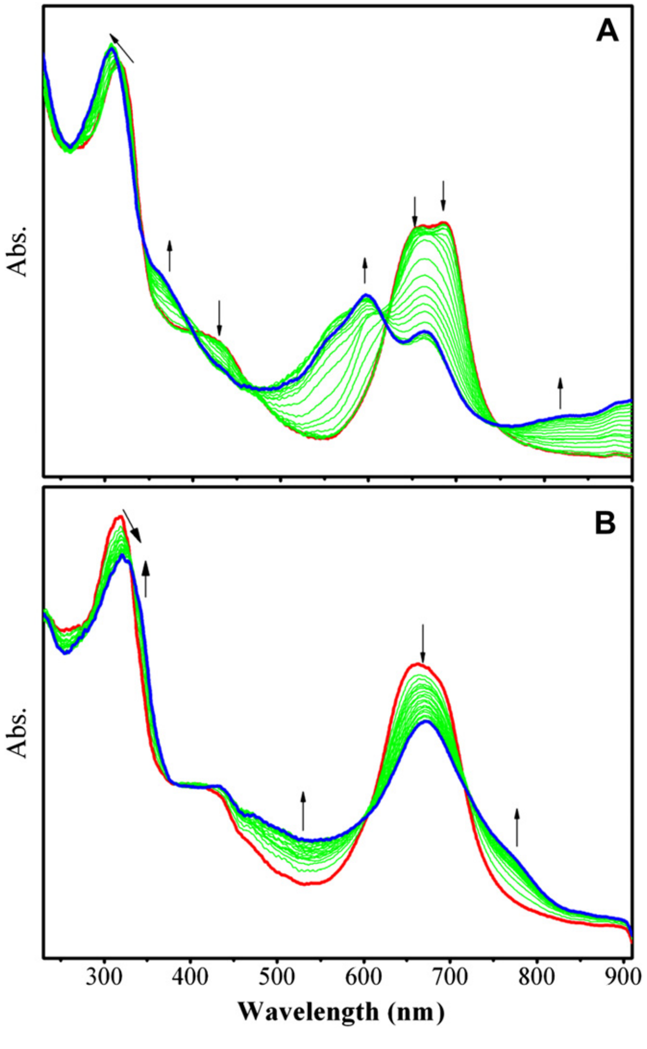


Fig. 2. In-situ UV–vis spectral changes of NiPc (**4**) ($1.0 \cdot 10^{-4}$ mol dm^{-3}). A) E_{app} = −0.90 V. B) E_{app} = 1.15 V.

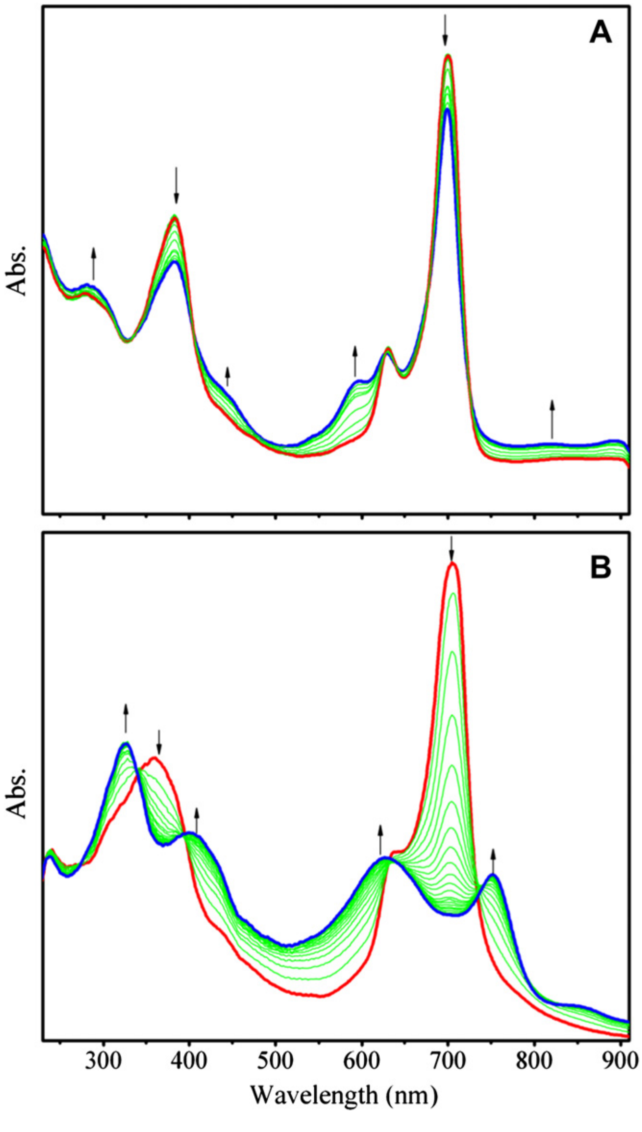


Fig. 3. In-situ UV–vis spectral changes of ZnPc (**3**) ($1.0 \cdot 10^{-4}$ mol dm^{-3}). A) E_{app} = −1.00 V. B) E_{app} = 1.00 V.

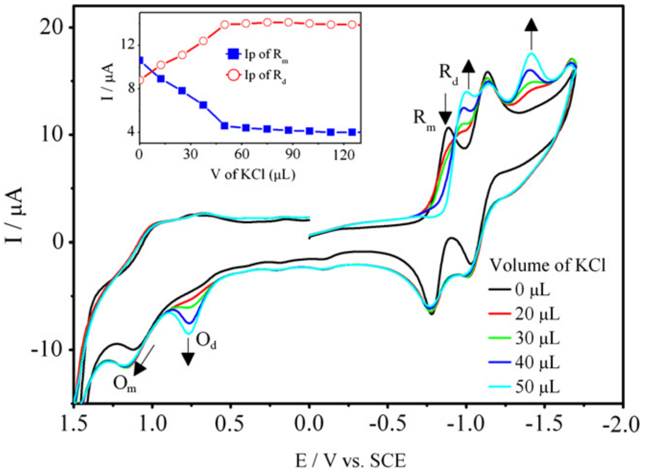
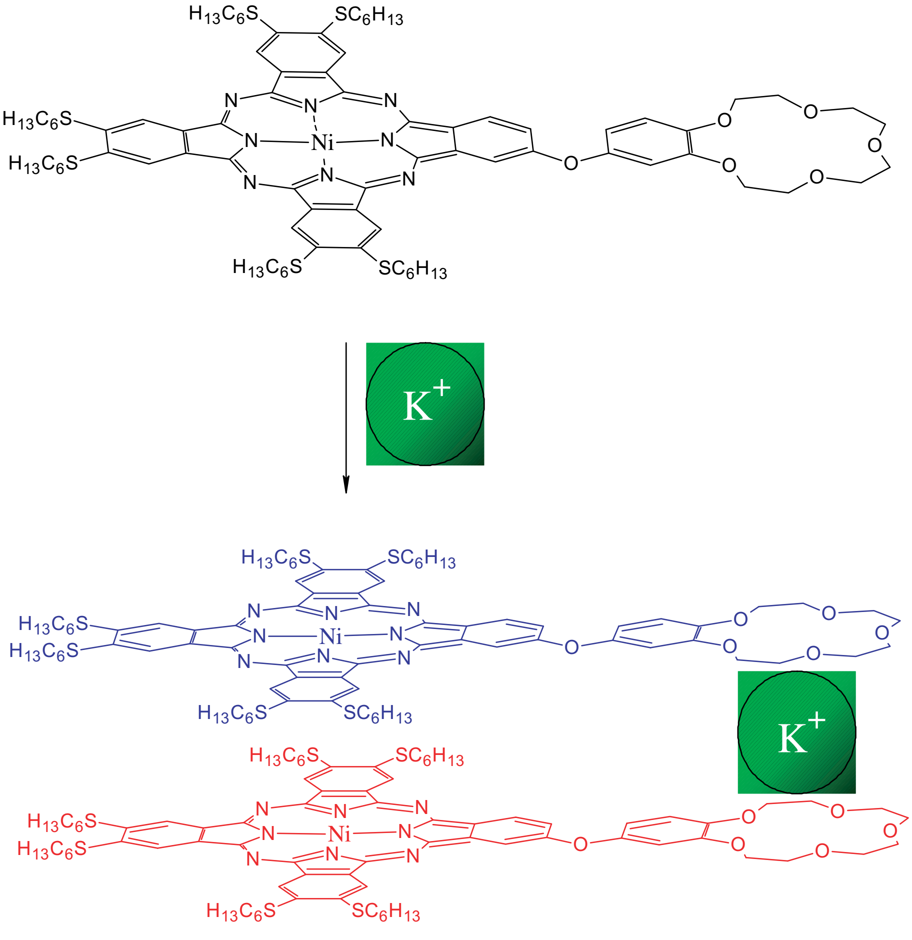


Fig. 4. Cyclic voltammetric changes of 5.0 ml NiPc (**4**) ($5.0 \cdot 10^{-4}$ mol dm^{-3}) titrated with K$^+$ ions ($2.5 \cdot 10^{-3}$ mol dm^{-3}) at 100 mVs^{-1} scan rate on Pt in DCM/TBAP. (Inset: current changes of R$_m$ and R$_d$ peaks with respect to increasing K$^+$ concentration).

DCM to give a single, reduced nickel (I) species (Fig. 2A). During the controlled potential oxidation of **4** (Fig. 2B) at 1.15 V *vs.* SCE, while the absorption of the Q band at 684 nm decreases in intensity, a new band appears in the MLCT region at 773 nm with an increase in the absorption at ca. 525 nm (MLCT) in intensity. These changes are typical of the ring-based oxidation of MPc complexes [40–47]. This process occurred with clear isosbestic points at 275, 330, 415, 602, and 720 nm in the spectra.

The complex **3** (ZnPc) gave very similar voltammetric behaviour to **4** accompanied by the small negative potential shift and less degrees of aggregation due to the different metal center. Within the electrochemical window of TBAP/DCM, **3** gave two one-electron oxidation processes at 0.75 and 1.54 V and two one-electron reductions at −0.90 and −1.44 V *vs.* SCE at 0.100 Vs^{-1} scan rate. Because of the presence of the electro-inactive zinc center, all of these processes are attributed to successive removal of electrons from, or addition of electrons to, the macrocyclic orbitals [39]. In-situ spectroelectrochemistry was also used to confirm some of the assignments in the CV of **3** (Fig. 3). Spectral changes during the controlled potential reduction of **3** at −1.00 V and oxidation at 1.00 V *vs.* SCE shows the ring-based electron transfer of the complexes during these processes. The spectral changes during the reduction in Fig. 3A show a decrease in the intensity of the Q band without any wavelength shift and the observation of a new band at 593 nm metal to ligand charge transfer (MLCT), which are characteristic of a ligand-based reduction process [40–47]. The process gives clear isosbestic points at 326, 406, 487, 626, and 727 nm in the spectra. During the controlled potential oxidation of **3** (Fig. 3B), while the absorption of the Q band at 670 nm decrease in intensity, two new bands appear in the MLCT region at 625 and 752 nm. These changes are typical of a ring-based oxidation for MPc complexes [41,42,47–51]. This process occurred with clear isosbestic points at 274, 340, 394, 633, and 735 nm in the spectra.



Scheme 2. Dimerization of the NiPc complex (**4**) with K$^+$ ions.

3.3. *Potentiometric titration of the complexes with alkali metal ions*

The combination of cyclic voltammetry coupled with potentiometric titrations constitutes an effective method for the characterization of the dimerization behaviour of MPcs bearing crown ether moieties in the presence of alkali metal ions [13,35,48–50]. The attachment of either oxa-, aza- or thio- crowns to tetrapyrrolic macrocycles, such as phthalocyanines (Pcs) or porphyrazines (Pzs), allow for metal ion selectivity and dimer stability to be enhanced through changing the number and types of crown ether donors. These compounds either display solvent and metal ion induce aggregation behaviour or can self-assemble in solution to form supramolecular structures [50–52]. Up to now, metal ion induce aggregation behaviour of the complexes were monitored by spectroscopic titration. Thus, here 5.0 mL of **4** was titrated with K^+ and Na^+ ions and the metal ion interaction of the complex **4** was monitored by following CV responses of the system by potentiometry. Higher concentration of alkali metal ions ($0.025\ \text{mol dm}^{-3}$) with respect to the concentration of MPcs ($5.0\ 10^{-3}\ \text{mol dm}^{-3}$) was employed to diminish the peak current change due to dilution. As shown in Fig. 4, while the cathodic peak currents of the reduction processes of the monomeric complex (R_m) decrease; two new peaks appear just after the reduction processes. These new peaks may be due to the reduction of dimeric species produced by dimerization of the complex with K^+ ions. The oxidation couples of the complexes are split into two peaks due to the oxidation of the dimers with monomers. Potentiometric titration results (inset in Fig. 4) show 2:1 interaction of **4** with both K^+ and Na^+ ions. Dimerization with Na^+ ion showed similar voltammetric changes. It has been reported that different alkali metal ions can form intermolecular sandwich complexes with MPc having crown ether units; the highest affinity for potassium ion was observed in the case of the MPc derivative having 5-crown ethereal units in solvent extraction experiments [53,54]. Dimerization of the Pc units in the presence of alkali metal ions, especially with those which have a tendency to form sandwich type complexes (Scheme 2), affects the electron withdrawing ability of the complexes, thus changes the potentials of the redox processes [32,35,49,54].

4. Conclusion

Three asymmetrically substituted metallophthalocyanines have been obtained by a statistical condensation between two different phthalonitriles. Measurement of their electrochemical and spectroelectrochemical properties revealed that zinc and nickel phthalocyanines give common Pc ring-based oxidation–reduction processes. Potentiometric titration of the new complexes with both sodium and potassium ions resulted in observation of a new redox wave instead of the peak of the monomeric species which indicated intermolecular dimer formation.

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