ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Dyes and Pigments 68 (2006) 151–157

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Synthesis and solution properties of phthalocyanines substituted with four crown ethers

Esin Hamuryudan*

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

Revised 4 January 2005; accepted 28 January 2005
Available online 24 March 2005

Abstract

Metal-free and metal phthalocyanines (M = Ni, Zn, Co) substituted with four benzo-15-crown-5 units through oxy-bridges have been synthesized from a new phthalonitrile derivative, 1-{[(benzo-15-crown-5)-4′-yl]oxy}phthalonitrile (**3**). The newly prepared compounds have been characterized by elemental analyses, IR, ^{1}H NMR, MS and UV–Vis spectroscopy. Alkali metal interactions of the crown ethers on the zinc phthalocyaninato (**6**) are shown to form intermolecular adduct. The electrochemical properties of ZnPc were investigated by using cyclic voltammetry and controlled potential coulometry.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Phthalocyanine complexes; Crown ether; Alkali metal extraction; Electrochemistry

1. Introduction

Phthalocyanine compounds are very important class of organic materials. For many years various substituted phthalocyanines (Pcs) have been developed for use as commercial dyes and pigments. During the past 30 years, increasing investigation of the magnetic, catalytic and photochemical properties of Pcs has resulted in potential or new applications outside of traditional areas, such as non-linear optics, liquid crystals, catalysis, gas sensors, photosensitizers and semi-conductive materials [1–5].

A disadvantage of metal-free and metallo phthalocyanines is their limited solubility in aqueous media and common organic solvents. One of the important aims of research on the chemistry of phthalocyanines is to enhance their solubility in various solvents. The stable phthalocyanine core should be amenable to modifications, which can be accomplished either by changing the central metal ion or by adding functional groups on the periphery. Peripheral substitution with bulky groups [6–8], long alkyl chains [9–11] or polyether moieties [12–14] leads to phthalocyanine derivatives soluble in common organic solvents.

Since their first appearance in the literature about four decades ago, crown ethers have taken a key role to understand supramolecular interactions and novel applications for heteromacrocycles emerged from there in many areas of chemistry and biology. These might include their use in the fields of phase transfer catalysis, ion selectivity, iono electronics, etc.

A combination of these two potentially promising units (i.e. phthalocyanines and crown ethers) has yielded products showing interesting properties. Phthalocyanines with crown ethers fused to peripheral positions have resulted with materials showing extreme sensitivity towards the presence of alkali metal ions on aggregation behavior [12,15,16]. "Ionoelectronics" have been defined by Simon from this effect observed in Lu-bis(phthalocyanine) derivatives [17]. One or two crown ether units attached to the periphery of phthalocyanines through

---

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

0143-7208/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2005.01.018

thia, aza or methylene oxy-bridges resulted with supramolecular entities showing intermolecular or intramolecular interactions when alkali metal ions were present in the same medium [18–21]. The nature of interaction was rather easily verified by following the changes occurring in the Q absorption maximum of phthalocyanine core. Another common contribution of crown ether substitution has been the enhanced solubility of phthalocyanines in common organic solvents.

When tetra- and octa-substituted phthalocyanines have been carefully examined, tetrasubstituted macrocycles exhibit usually a higher solubility than octasubstituted derivatives. The greater solubility of these tetrasubstituted phthalocyanines results not only from the steric bulk of the substituents preventing aggregation, but also from the presence of the very similar isomers [1,22–24].

In the present work, the objective is the preparation and characterization of metal-free and metallo phthalocyanines (Ni, Zn, Co) containing four benzo-15-crown-5 moieties on the periphery through oxy bridges. The aggregation behavior of crown ether substituted phthalocyanines in different solvents and in the presence of various alkali metal salts has been investigated. Electrochemical analysis of ZnPc was also carried out by cyclic voltammetry.

2. Experimental

Routine IR spectra were recorded on an ATI Unicam-Mattson 1000 FTIR spectrophotometer using KBr pellets, electronic spectra on a Unicom UV–Vis spectrophotometer UV2. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TÜBİTAK Marmara Research Centre. ^{1}H NMR spectra were recorded on a Bruker 200 MHz spectrometer, mass spectra on a VG Zabspec GC–MS spectrometer. 4′-Hydroxybenzo-15-crown-5 (**1**) [25] and 4-nitrophthalonitrile (**2**) [26] were synthesized according to the literature methods, by a multi-step reaction sequence. 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 [27]. The homogeneity of the products was tested in each step by TLC.

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 degassing 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, a SCE as reference electrode, and a model 377/12 Synchronous stirrer were used.

2.1. 1-{[(Benzo-15-crown-5)-4′-yl]oxy} phthalonitrile (**3**)

4′-Hydroxybenzo-15-crown-5 (**1**) (1.642 g, 5.78 mmol) was dissolved in anhydrous DMF (6 ml) under nitrogen and 4-nitrophthalonitrile (**2**) (1.0 g, 5.78 mmol) was added. After stirring 10 min of additional nitrogen purging, finely ground anhydrous potassium carbonate (1.19 g, 8.67 mmol) was added in portions at 0.5 h intervals over a 4 h period with efficient stirring. The reaction mixture was stirred under nitrogen at 30 °C for 48 h. Then the reaction mixture was poured slowly into a stirred mixture of ice water. The aqueous phase was extracted with chloroform (3 × 10 ml). The combined extracts were treated first with sodium carbonate solution (5%), then with distilled water followed by drying over anhydrous sodium sulfate. The solvent was evaporated to dryness. The crude product was washed several times with hot diethyl ether. Finally, the pure product was obtained by column chromatography with alumina (MeOH/$CHCl_3$, 1:50 v/v). Yield of **3**, 1.78 g (75.1%); m.p. 123 °C; Calcd. for $C_{22}H_{22}O_6N_2$: C, 64.39; H, 5.36; N, 6.83%. Found: C, 64.01; H, 5.45; N, 6.75%. IR (KBr) ν_{max} (cm^{-1}): 3060, 2960–2890 (CH aliph.), 2220 (C≡N), 1600, 1510, 1460, 1270–1235 (Ar–O–C), 1105–1060 (C–O–C), 980, 830, 635. ^{1}H NMR ($CDCl_3$) δ: 7.71–7.15 (m, 3H, Ar–H), 6.92–6.57 (m, 3H, Ar–H), 4.17–3.67 (m, 16H, O–CH_2).

2.2. Synthesis of metal-free phthalocyanine (**4**)

A solution of **3** (0.3 g, 0.732 mmol) in dry 2-(dimethylamino) ethanol (1.5 ml) was stirred and heated in a sealed glass tube at 140 °C for 16 h. After cooling the mixture was poured into a mixture of H_2O: MeOH (1:1), (20 ml) and centrifuged. The precipitate was washed with MeOH (5×) and dried. The residue was then further purified by column chromatography with alumina (eluent chloroform/methanol, 7:1 v/v). Yield 0.10 g (35%); Calcd. for $C_{88}H_{90}N_8O_{24}$: C, 64.31; H, 5.48; N, 6.82%. Found: C, 64.27; H, 5.61; N, 6.63%. IR (KBr) ν_{max} (cm^{-1}): 3310 N–H), 3050

(CH arom.), 2930–2875 (CH aliph.), 1626, 1525, 1470, 1268–1242 (Ar–O–C), 1140–1115 (C–O–C), 1010; ^{1}H NMR ($CDCl_3$) δ: 9.20–7.62 (m, 12H, Ar–H), 7.18–6.35 (m, 12H, Ar–H), 4.27–3.82 (m, 64H, O–CH_2), −4.91 (s, 2H); MS (FAB) *m*/*z*: 1643 (M^+); UV–Vis (THF), λ_{max}(10^{-4} ε/L mol^{-1} cm^{-1}), (nm): 341(5.01), 610 (2.82), 636 (3.10), 668 (9.98), 702 (9.92).

2.3. Nickel (II) phthalocyaninate (**5**)

A mixture of **3** (0.5 g, 1.22 mmol), anhydrous $NiCl_2$ (0.040 g, 0.31 mmol) and anhydrous dimethylformamide (2 ml) was mixed in a glass tube which was sealed under nitrogen. The reaction mixture was heated and stirred at 150 °C for 21 h. After cooling to room temperature the mixture was treated with methanol (4 ml) and the product was filtered off and washed with the same hot solvent several times. The crude green product was purified by column chromatography with alumina (eluent chloroform/methanol, 7:1 v/v). Yield 0.13 g (25%); Calcd. for $C_{88}H_{88}N_8O_{24}Ni$: C, 62.16; H, 5.18; N, 6.59%. Found: C, 61.97; H, 5.30; N, 6.27%. IR (KBr) ν_{max} (cm^{-1}): 2930–2875 (CH aliph.), 1625, 1525, 1470, 1268–1242 (Ar–O–C), 1137–1111 (C–O–C), 1012, 957; ^{1}H NMR ($CDCl_3$) δ: 9.42–7.71 (m, 12H, Ar–H), 7.15–6.33 (m, 12H, Ar–H), 4.19–3.64 (m, 64H, O–CH_2); UV–Vis (THF), λ_{max} (10^{-4} ε/L mol^{-1} cm^{-1}), (nm): 338 (3.85), 609 (1.41), 635 (1.55), 675 (6.21).

2.4. Zinc (II) phthalocyaninate (**6**)

A mixture of **3** (0.5 g, 1.22 mmol), anhydrous zinc acetate (0.055 g, 0.3 mmol) and absolute dimethylformamide (2.4 ml) was mixed in a glass tube which was sealed under nitrogen. The mixture was heated at 150 °C for 24 h. After cooling to room temperature, ethanol (5 ml) was added in order to precipitate the product. The dark blue-greenish product was filtered off and then washed with hot ethanol several times. It was further purified on an alumina column with chloroform/methanol (7:1 v/v) as the eluent. Yield 0.23 g (44.4%); Calcd. for $C_{88}H_{88}N_8O_{24}Zn$: C, 61.92; H, 5.16; N, 6.56%. Found: C, 61.54; H, 5.37; N, 6.25%. IR (KBr) ν_{max} (cm^{-1}): 2925–2870 (CH aliph.), 1727, 1625, 1472, 1268–1242 (Ar–O–C), 1114–1089 (C–O–C), 1063, 961; ^{1}H NMR ($CDCl_3$) δ: 9.48–7.73 (m, 12H, Ar–H), 7.20–6.38 (m, 12H, Ar–H), 4.24–3.74 (m, 64H, O–CH_2); MS (FAB) *m*/*z*: 1706 (M^+); UV–Vis ($CHCl_3$) λ_{max} (10^{-4} ε/L mol^{-1} cm^{-1}), (nm): 351 (6.24), 616 (2.86), 690 (14.35).

2.5. Cobalt (II) phthalocyaninate (**7**)

A mixture of **3** (0.4 g, 0.96 mmol), anhydrous $CoCl_2$ (0.032 g, 0.25 mmol) and dry 2-(dimethylamino) ethanol (2 ml) was heated and stirred at 135 °C in a sealed glass tube for 24 h under nitrogen. After cooling to room temperature, blue-green suspension was treated with H_2O:MeOH (1:1) (20 ml) and centrifuged. The precipitate was washed several times with MeOH and dried. It was further purified on an alumina column with chloroform/methanol (7:1 v/v) as the eluent. Yield 0.120 g (29%); Calcd. for $C_{88}H_{88}N_8O_{24}Co$: C, 62.15; H, 5.17; N, 6.59%. Found: C, 61.97; H, 4.99; N, 6.32%. IR (KBr) ν_{max} (cm^{-1}): 2927–2873 (CH aliph.), 1625(C=N), 1472 (arom. C=C), 1268–1242 (Ar–O–C), 1120–1095 (C–O–C), 1057, 963; MS (FAB) *m*/*z*: 1700 (M^+); UV–Vis (THF), λ_{max} (10^{-4} ε/L mol^{-1} cm^{-1}), (nm): 332 (4.51), 604 (2.27), 666 (8.73).

3. Results and discussion

3.1. Synthesis and characterization

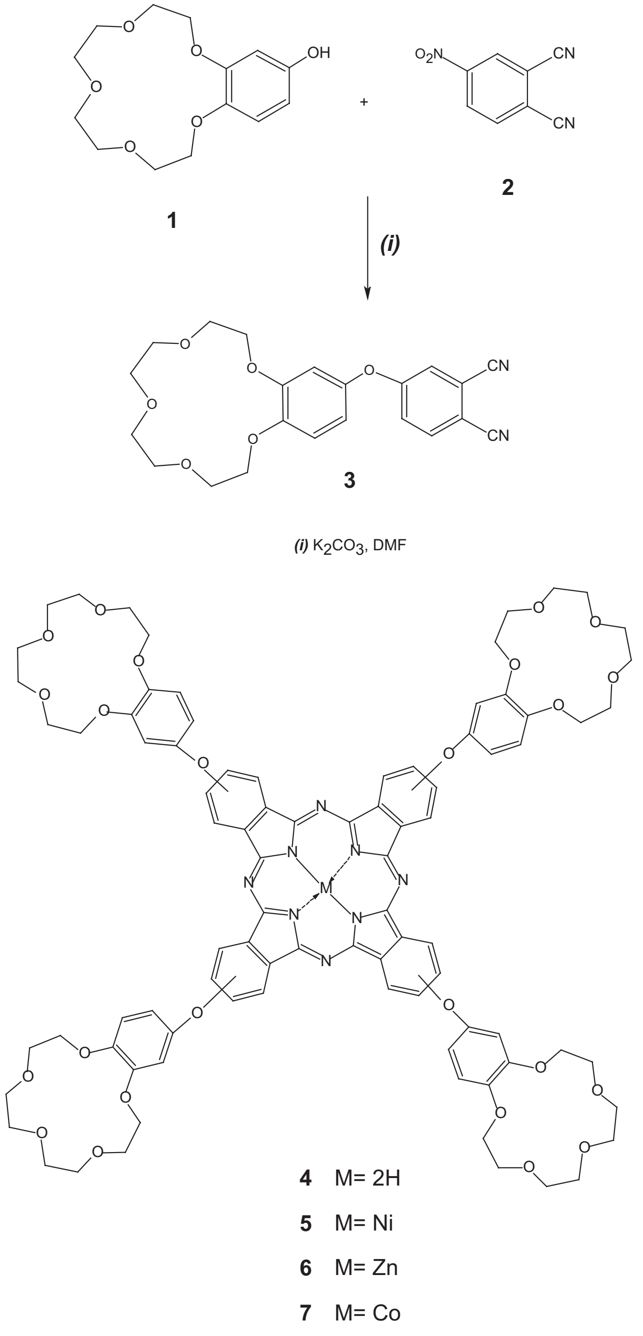
Starting from 4′-hydroxybenzo-15-crown-5 (**1**) and 4-nitrophthalonitrile (**2**), the general synthetic route for the synthesis of new phthalocyanines is given in Scheme 1. 1-{[(Benzo-15-crown-5)-4′-yl]-oxy}phthalonitrile (**3**) was obtained in 75% yield by the base-catalyzed nucleophilic aromatic nitro displacement of **2** with **1** [28,29]. The reaction was carried out in a single step synthesis by using the K_2CO_3 as the nitro-displacing base at 30 °C in dry dimethylformamide under N_2 atmosphere.

Cyclotetramerization of the phthalonitrile derivative **3** to the metal-free phthalocyanine **4** was accomplished in 2-(dimethylamino)ethanol (DMAE) at 140 °C in a sealed tube. The metal phthalocyanines **5–7** were obtained from the dicyano derivative and the corresponding metal salts [$NiCl_2$, $Zn(O_2CMe)_2$ or $CoCl_2$] in suitable anhydrous solvents (e.g. dimethylformamide or 2-(dimethylamino)ethanol). The yields were satisfactory and depended upon the transition metal ion.

The intense green tetrasubstituted phthalocyanine products were soluble in a number of solvents such as chloroform, dichloromethane, tetrahydrofuran, acetone and were chromatographed on neutral alumina to give elemental analysis consistent with the proposed structure. Tetrakis-(crown ether)-substituted phthalocyanine compounds were characterized by IR, Mass, ^{1}H NMR and UV–Vis spectral techniques.

In the IR spectra of **3**, the intense absorption band at 2220 cm^{-1} corresponds to the C≡N groups. This spectrum exhibits characteristic frequencies at 3060 (C–O–H), 2960–2890 (C–H), 1270–1235 (Ar–O–C) and 1105–1060 (C–O–C) cm^{-1}. In the ^{1}H NMR spectrum of **3**, the aromatic protons appear at δ 7.71–6.57 and the aliphatic ether protons at δ 4.17–3.62.

Cyclotetramerization of the dinitriles (**3**) to the phthalocyanine, **4–7** was confirmed by the disappearance



Scheme 1. Synthesis of the phthalocyanines **4–7**.

of the sharp C≡N vibration at 2220 cm^{-1}. IR bands characteristic of the metal-free phthalocyanine ring is an N–H stretching at 3310 cm^{-1} [30]. The IR spectra of metal-free (**4**) and metallo (**5–7**) phthalocyanines are very similar, except these υ (NH) vibrations of the inner phthalocyanine core in the metal-free molecule. These protons are also very well characterized by the ^1H NMR spectrum which shows a peak at δ −4.91 ppm, as a result of the 18 π-electron system of the phthalocyanine ring. In the ^1H NMR spectrum of **4**, the aromatic protons of the phthalocyanine core appear at lower field around 9.20–7.62 ppm while those of benzo-15-crown-5 moiety appear at 7.18–6.35 ppm. The ether protons of the crown ether group are observed between 4.27 and 3.82 ppm. The only difference between the ^1H NMR spectra of metal-free phthalocyanine **4** and the metallo-derivatives **5** and **6** is the lack of broad chemical shifts of inner core NH protons in the latter group.

In addition to the elemental analysis results, mass spectra will be definitive. The mass spectral studies by the fast atom bombardment technique on the newly synthesized compounds exhibited molecular ion peaks for **4**, **6** and **7**. Values of the molecular ions show good agreement with the calculated values for metal-free phthalocyanine **4** (m/z 1643), zinc phthalocyanine **6** (m/z 1706) and cobalt phthalocyanine **7** (m/z 1700).

The phthalocyanines **4–7** show typical electronic spectra with two strong absorption regions, one of them in the UV region at about 300–350 nm (B band) and the other in the visible part of the spectrum around 600–700 nm (Q band). In extremely dilute solutions (ca. 10^{-6} M) the phthalocyanines behave as monomers [31]. Increasing the concentration leads to aggregation, which is easily observed by the values of the Q bands, which shift to higher energies by a parallel decrease in the molar absorption coefficient. On the other hand metal-free derivatives with D_{2h} symmetry show two intense absorptions in the visible region, that having D_{4h} symmetry gives only a single band in this region. These two absorptions around 700 nm are due to the π–π* transition of the fully conjugated 18 π electron system. Tetrasubstitution with oxygen or sulfur bridged groups causes a shift (10–15 nm) of the intense Q band to longer wavelengths when compared with the unsubstituted derivatives [21,28,29]. A typical spectrum of the metal-free phthalocyanine (**4**) in THF showed a doublet in the Q band region at 668 and 702 nm while the metallo-phthalocyanines each gave an intense single band at 675, 690 and 666 nm for the corresponding compounds **5**, **6** and **7**, respectively.

3.2. Alkali metal interaction of crown ether appending on phthalocyanines

The effect of alkali metal cations on the aggregation behavior of the phthalocyanine crowns was investigated through UV–Vis measurements in chloroform/ethanol. A 1×10^{-5} M solution of ZnPc (**6**) was prepared by dissolving it in chloroform and the metal salt (NaSCN, KSCN) dissolved in ethanol (10^{-3} M) was added to this solution in small portions (15×10 μl to 3 cm^3 of **6** solution). The alkali metal concentration was preferred to be higher in order to prevent any effect arising from the dilution after addition of metal salt to phthalocyanine solution. When the changes in the Q band absorption spectra of **6** due to addition of NaSCN

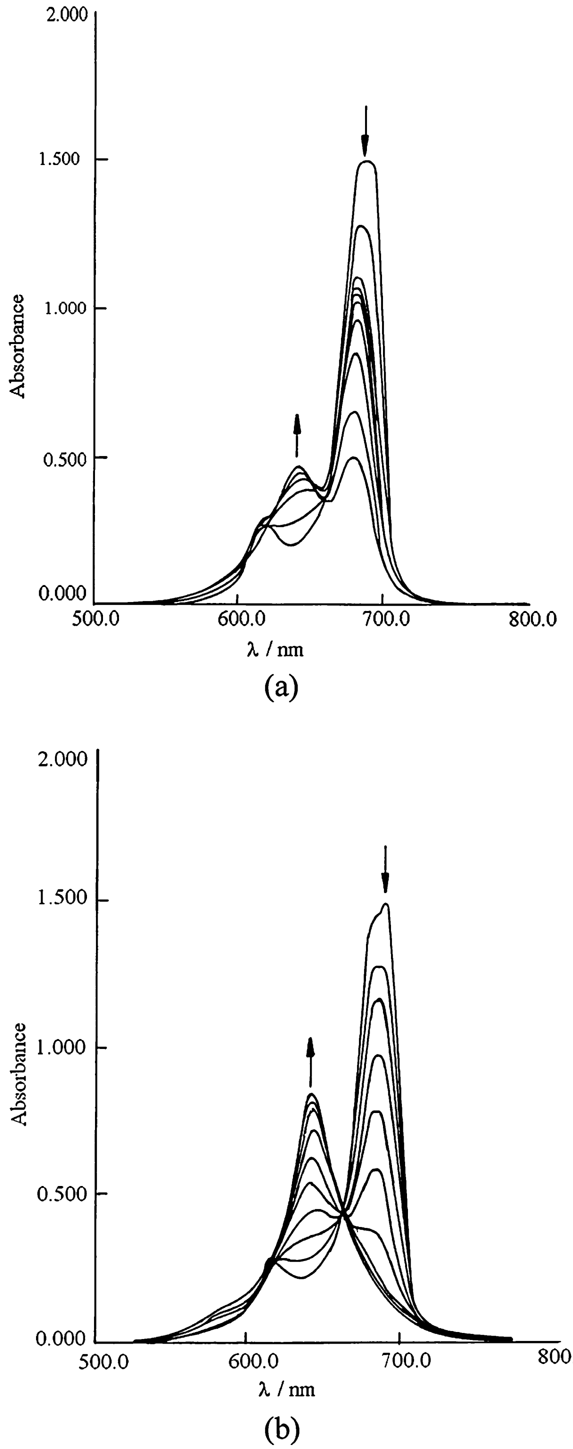


Fig. 1. Changes in absorption spectrum of **6** upon addition of (a) NaSCN solution and (b) KSCN solution.

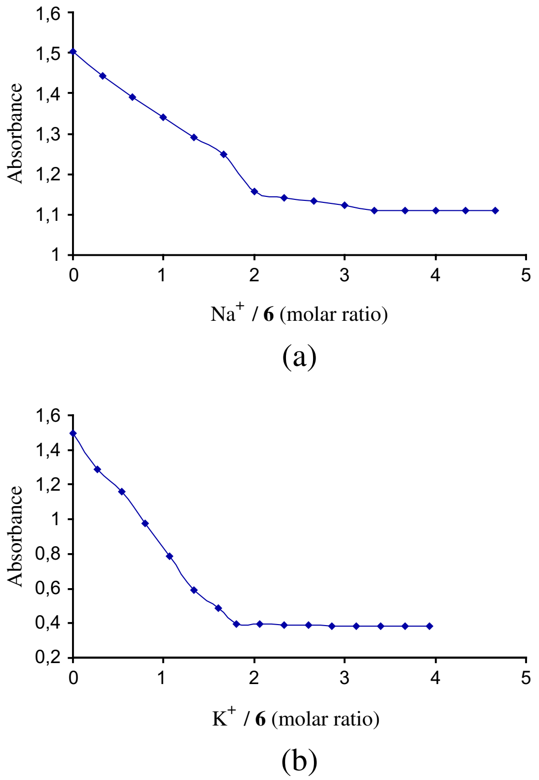


Fig. 2. Changes in the Q band absorption maximum of **6** with respect to addition of (a) NaSCN and (b) KSCN.

(Fig. 1(a)) and KSCN (Fig. 1(b)) are compared, the latter appears to be completely shifted to aggregated species [15,32,33]. Also as observed in Fig. 2(a) and (b), the minimum has been reached when M^+/**6** ratios is about 2 when M^+ is Na^+ or K^+. This corresponds to an intermolecular sandwich complex formation between crown ether moieties of two-phthalocyanine molecule and sodium or potassium ion.

The alkali ion binding capability of the ZnPc (**6**) having four crown ether units was estimated by alkali-picrate extraction experiments from aqueous phase to organic phase (chloroform). Picrate salts of Li^+, Na^+, K^+ and Rb^+ (7.5×10^{-5} M) were prepared in aqueous solutions and the absorbance of the aqueous layer before and after treatment with chloroform solution of **6** (1.875×10^{-5} M) was measured [16,34]. Here the ratio of [alkali metal picrate]/[phthalocyanine] were taken to be 4:1. Even though fully interaction of all crown ethers with the metal ions has not been expected in these extraction experiments, sufficient amount of alkali metal ion was supplied for each of four crown ether units attached to the phthalocyanine core in **6**. A parallel test with blank solutions was also carried out. The percentage extraction of alkali metal picrate was calculated to be 0.2, 3.58, 14.76 and 9.51% for Li^+, Na^+, K^+ and Rb^+ ions, respectively. The results indicate that the highest affinity is observed for potassium ion among the order $K^+ > Rb^+ > Na^+ > Li^+$ and these findings closely comply with the earlier data reported in the case of other extraction experiments with 15-crown-5 substituted compounds [20,34]. In this case a sandwich complex between two ZnPc and four potassium ion must be assumed to explain the higher selectivity for this cation.

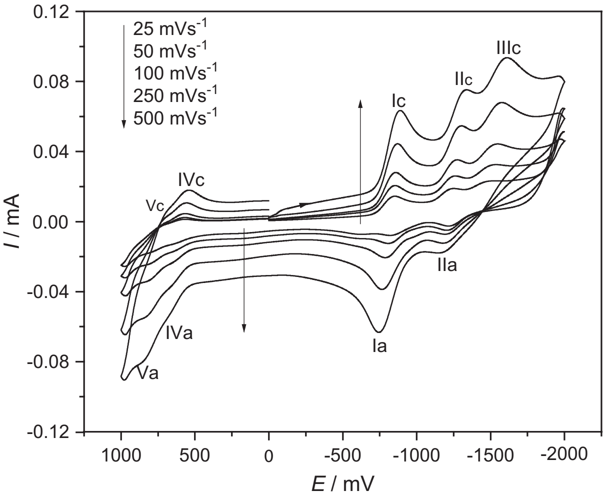


Fig. 3. Cyclic Voltamograms of 5.0×10^{-4} mol dm^{-3} ZnPc in DMSO/TBAP vs. SCE.

3.3. Electrochemical measurements

The electrochemical properties of ZnPc (**6**) were studied by cyclic voltammetry (CV) and controlled potential coulometry (CPC). The cyclic voltammograms of **6** exhibited five redox processes in the $+1.0$ to -2.0 V available range of the DMSO/TBAP solvent system as shown in Fig. 3. Upon scanning cathodically, ZnPc shows three cathodic peaks at 0.825, -1.235, and -1.545 V and two anodic peaks at 0.607 and 0.780 V vs. SCE at 0.1 V s^{-1} scan rates. Peak separation (ΔE) of the first reduction couple (Ic/Ia) is 64 mV at 0.1 V s^{-1} scan rate and increase slightly with increasing scan rates and has an $\delta E_{pc}/\delta \log v$ value of 75 mV. These data show that while Ic/Ia redox couple is reversible at low scan rate it behaves *quasi*-reversible at higher scan rates. IIc/IIa redox couples have similar characters with ΔE value of 57 mV at 0.1 V s^{-1} scan rates and $\delta E_{pc}/\delta \log v$ of 67 mV. The IIIc peak has no anodic couple during the reverse scan even at very high scan rates and has a 177 mV value of $\delta E_{pc}/\delta \log v$. The reduction and oxidation behavior of metallophthalocyanine derivatives is due to the interaction between the phthalocyanine ring and the central metal. The redox properties of metallophthalocyanines have been studied by many authors [1,35–38]. First-row transition metal phthalocyanines differ from those of the main-group metal phthalocyanines due to the fact that metal ‘d’ orbitals may be positioned between the HOMO and LUMO of the phthalocyanine (Pc-2) ligand [36–38]. According to these studies, the first oxidation and first reduction processes occur on the metal center in the metal phthalocyanines only for Mn, Fe and Co derivatives. For Ni, Cu and Zn phthalocyanines, redox processes take place on the phthalocyanine ring. According to these studies, ZnPc investigated in this study behaved in this fashion with the M (II) central ion being unchanged as the MPc unit is either oxidized or reduced. Therefore, all redox processes recorded with ZnPc (**6**) are easily assigned to successive ring reductions and oxidations of the bulk species.

The linear dependence of the I_{pc} of Ic and IIc to $v^{1/2}$ suggests diffusion-controlled processes for these redox processes recorded with ZnPc, However, I_{pc} of IIIc does not increase linearly with $v^{1/2}$ indicating the effect of kinetic control to the mass transfer process of this redox reaction. Existence of the kinetic effect is well established with the peak current ratios (I_{pa}/I_{pc}) of these processes. I_{pa}/I_{pc} ratio of Ic/Ia redox couple is nearly unity at all scan rates while I_{pa}/I_{pc} ratio of IIc/IIa redox couple is approximately 0.5 and unchanged with increasing scan rates. These indicated that first redox couple is a simple electron transfer reaction however second one is followed with an irreversible chemical reaction. The CPC studies indicated that the number of electrons transferred for all these electron transfer reactions is one.

Acknowledgements

The author is grateful to Dr. Atif Koca for cyclic voltammetry measurements. This work was supported by the Research Fund of Technical University of Istanbul.

References

[1] Leznoff CC, Lever ABP. Phthaolcyanines: properties and applications, vols. 1–4. Weinheim: VCH; 1989–1996.
[2] Gregory P. High technology applications of organic colorants. New York: Plenum; 1991.
[3] Clarkson GJ, Mc Keown NB, Treacher KE. Chem Soc Perkin Trans 1995;1817–23.
[4] Wöhrle D, Meissner D. Adv Mater 1991;3:129–38.
[5] Simon JJ, Andre HJ. Molecular semiconductors. Berlin: Springer; 1985.
[6] Mc Keown NB. Phthalocyanine materials synthesis structure and function. Cambridge: Cambridge University Press; 1998.
[7] Hamuryudan E, Bekaroglu Ö. J Chem Res (S) 1993;460–1.
[8] Hamuryudan E, Bayır ZA, Bekaroğlu Ö. Dyes Pigments 1999;43:77–81.
[9] Hamuryudan E, Merey Ş, Bayır ZA. Dyes Pigments 2003;59:263–268.
[10] Bakboord JV, Cook MJ, Hamuryudan E. J Porphyrins Phthalocyanines 2000;4:510–7.
[11] Gürsoy S, Bayır ZA, Hamuryudan E, Bekaroğlu Ö. Monatsh Chem 2000;131:287–92.
[12] Koray AR, Ahsen V, Bekaroğlu Ö. J Chem Soc Chem Commun 1986;932–3.
[13] Bilgin A, Gök Y. Tetrahedron Lett 2002;43:5343–7;
Kandaz M, Bekaroğlu Ö. J Porphyrins Phthalocyanines 1999;3:339–45.
[14] Koçak M, Okur AI, Bekaroğlu Ö. J Chem Soc Dalton Trans 1994;323–6;
Musluoğlu E, Ahsen V, Gül A, Bekaroğlu Ö. Chem Ber 1991;124:2531–6.

[15] Sielcken OE, van Tilborg MM, Roks MFM, Hendriks R, Drenth W, Nolte RJM. J Am Chem Soc 1987;109:4261–5.

[16] Ahsen V, Yılmazer E, Ertaş M, Bekaroğlu Ö. J Chem Soc Dalton Trans 1988;401–6.

[17] Bardin M, Bertounesque E, Plichon V, Simon J, Ahsen V, Bekaroğlu Ö. J Electroanal Chem 1989;271:173–80.

[18] Cooper SR, editor. Crown compounds: toward future applications. New York: VCH; 1992.

[19] Sarıgül S, Bekaroğlu Ö. Chem Ber 1989;122:291–2.

[20] Okur AI, Gül A, Cihan A, Tan N, Bekaroğlu Ö. Synth React Inorg Met Org Chem 1990;20:1399–412;
Gürol I, Ahsen V. J Porphyrins Phthalocyanines 2000;4:620–5.

[21] Musluoğlu E, Bekaroğlu Ö. J Chem Res (S) 1994;420–1.

[22] Leznoff CC, Marcuccio SM, Greenberg S, Lever ABP, Tower KB. Can J Chem 1985;63:623–31.

[23] Leznoff CC, Hu M, Arthur CR, Qin Y, Van Lier JE. Can J Chem 1994;72:1990–8.

[24] Hanack M, Meng D, Beck A, Sommerauer M, Subramanian LRJ. Chem Soc Chem Commun 1993;58–60.

[25] Wada F, Arata R, Goto T, Kikukawa K, Maksuda T. Bull Chem Soc Jpn 1980;53:2061–3.

[26] Young JG, Onyebuagu W. J Org Chem 1990;55:2155–9.

[27] Perrin DD, Armarego WLF. Purification of laboratory chemicals. 2nd ed. Oxford: Pergamon; 1980.

[28] Snow AW, Griffith JR, Marullo NP. Macromolecules 1984;17:1614–24.

[29] Wöhrle D, Eskes M, Shigehara K, Yamada A. Synthesis 1993;194–6.

[30] Snow AW, Jarvis NLJ. Am Chem Soc 1984;106:4706–11.

[31] Hirsch A, Hanack M. Chem Ber 1991;124:833–9.

[32] Xu H, Xiong GJ. Photochem Photobiol A Chem 1995;92:35.

[33] Kobayashi N, Lever ABP. J Am Chem Soc 1987;109:7433–41.

[34] Sağlam Ö, Gül A. Polyhedron 2001;20:269–75;
Haines AH, Hodgkisson I, Smith C. J Chem Soc Perkin Trans I 1983;311–8.

[35] Baumann TF, Nasir MS, Sibert JW, White AJP, Olmstead MM, Williams DJ, et al. J Am Chem Soc 1996;118:10479–86.

[36] Kadish KM, Moninot G, Hu Y, Dubois D, Ibnifassi A, Barbe JM, et al. Am Chem Soc 1993;115:8153–66.

[37] Özkaya AR, Hamuryudan E, Bayır ZA, Bekaroğlu Ö. J Porphyrins Phthalocyanines 2000;7:689–97.

[38] Koca A, Sağlam ÖG, Gül A. Monatsh Chem 2003;134:11–21.