Contents lists available at ScienceDirect

### Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

# Synthesis, characterization, spectroscopic and electrochemical properties of phthalocyanines substituted with four 3-ferrocenyl-7-oxycoumarin moieties

Meryem Çamur<sup>a</sup>, A. Aslı Esenpınar<sup>a</sup>, A. Rıza Özkaya<sup>b</sup>, Mustafa Bulut<sup>b,\*</sup>

<sup>a</sup> Kırklareli University, Department of Chemistry, 39100 Kırklareli, Turkey
<sup>b</sup> Marmara University, Department of Chemistry, 34722 Goztepe-Istanbul, Turkey

#### ARTICLE INFO

Article history: Received 6 January 2011 Received in revised form 17 February 2011 Accepted 23 February 2011

Keywords: Phthalocyanine Coumarin (2H-1-benzopyran-2-one) Ferrocene Fluorescence Electrochemistry

#### ABSTRACT

The synthesis, spectroscopic and electrochemical properties of the tetra-(3-ferrocenyl-7-oxycoumarin)substituted zinc (II) and cobalt (II) phthalocyanines (**3** and **4**) are reported for the first time. The synthesis of novel 3-ferrocenyl-7-hydroxycoumarin (**1**) was performed according to Perkin reaction, and the ligand, 7-(3,4-dicyanophenoxy)-3-ferrocenylcoumarin (**2**), was synthesized by the reaction of 3-ferrocenyl-7-hydroxycoumarin with 4-nitrophthalonitrile in the presence of K<sub>2</sub>CO<sub>3</sub> as the base in dry dimethylformamide. The preparation of the corresponding zinc (II) and cobalt (II) metallo phthalocyanines (**3** and **4**) substituted with 3-ferrocenyl-7-oxycoumarin moieties at  $\beta$ -positions of the phthalocyanine ring was achieved by the cyclotetramerization of the coumarin ligand (**2**) with relevant metal(II) acetates in dry 2-dimethylaminoethanol. The new compounds have been characterized by elemental analyses, FT-IR, <sup>1</sup>H NMR, Mass and electronic spectroscopy. The fluorescence property of the zinc metallo phthalocyanine (**3**) is strongly affected by the presence of ferrocenyl moiety. The ferrocenyl moieties were very efficient in quenching the excited state of **3**, which show very poor fluorescent intensity. The electrochemical properties of the complexes were also investigated by cyclic and differential pulse voltammetry techniques in non-aqueous medium. It was found that the redox-active ferrocene substituents are reduced concurrently at one potential.

© 2011 Elsevier B.V. All rights reserved.

#### 1. Introduction

Phthalocyanines (Pcs) have been an area of increasing research for several years, due to their applicability in a variety of fields, such as liquid crystals, semiconductors, non-linear optics and electron transfer, among others. Pcs are compounds of special interest for their unique redox and photophysical properties [1-3]. Many derivatives of these compounds can be prepared not only by changing the nature of the central metal atom, but also by formally fusing additional aromatic rings to the central core; or by forming planar or linear groups [4]. Pc-based multicomponent systems have been explored, including porphyrins [5], ferrocenes [6,7], crown ethers [8,9], tetrathiafulvalenes, oligopyridyl-metal complexes, dendrimers, and C<sub>60</sub> [10–12]. Furthermore, Pcs have long been known to undergo electron transfer reactions, both to and from their excited states, and strong electron donors such as ferrocene are able to quench the Pc fluorescence by intermolecular electron transfer [13,14]. Many ferrocene derivatives are of considerable interest in various areas [15], like asymmetric catalysis, non-linear optics [16] and electrochemistry [17] due to the quasi-reversible oxidation of iron(II).

Coumarin (2H-1-benzopyran-2-one) and its derivatives are a group of lactones derived from o-hydroxycinnamic acids: alternately stated, a coumarin ring system is formed by the fusion of a benzene and a 1,2-pyrone ring [18]. Coumarins belong to an important class of fluorescent compounds having interesting photophysical properties and a wide range of applications in laser dyes [19], photosensitizers [20], pesticides [21] etc. Materials containing a coumarin component are useful in many fields due to their characteristics of high emission yield, excellent photostability and extended spectral range, such as fluorescent images [22,23], non-linear optical materials [24], liquid crystals [25] and fluorescent labels for fluorescence energy transfer experiments [26]. 7-Hydroxy-4-methylcoumarin (7-HMC) is a derivative of coumarin, who's ground- and excited state, photophysical properties have been the subject of many studies. It is used as an important fluorescent indicator for pH measurements [27-31].

Recently, we have successfully prepared Pcs substituted with coumarin skeleton, which exhibited excellent fluorescence properties with quantum yield of almost unity [32–34]. In this paper,



<sup>\*</sup> Corresponding author. Tel.: +90 216 3479641/1370; fax: +90 216 3478783. *E-mail address:* mbulut@marmara.edu.tr (M. Bulut).

<sup>0022-328</sup>X/\$ – see front matter @ 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.jorganchem.2011.02.029

our aim has been to prepare and characterize novel zinc (II) ( $\mathbf{3}$ ) and cobalt (II) ( $\mathbf{4}$ ) metallo Pcs substituted with 3-ferrocenyl-7-oxycoumarin. We also investigated the change of fluorescence properties of  $\mathbf{3}$  which is substituted with ferrocene moiety at the 3-position of coumarin. The electrochemical properties of the complexes were also presented.

#### 2. Experimental

#### 2.1. Materials and equipment

Infrared Spectra (IR) were recorded on a Shimadzu FTIR-8300 Fourier Transform Infrared Spectrophotometer using KBr pellets, electronic spectra on a Shimadzu UV-2450 UV-VISIBLE Spectrophotometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Centre. <sup>1</sup>H NMR spectra were recorded on a Varian Mercury-VX 500 MHz spectrometer using TMS as an internal standard. Mass spectra were performed on a Bruker Autoflex III MALDI-TOF spectrometer. A 2,5-dihydroxybenzoic acid (DHB) (20 mg/mL in THF) matrix was used. MALDI samples were prepared by mixing the complex [2 mg/mL in tetrahydrofuran (THF)] with the matrix solution (1:10 v/v) in a 0.5 mL Eppendorf micro tube. Finally, 1  $\mu$ L of this mixture was deposited on the sample plate, dried at room temperature and then analyzed. Fluorescence excitation and emission spectra were recorded on a HITACHI F-7000 Fluorescence Spectrophotometer using 1 cm pathlength cuvettes at room temperatures. 4-Nitrophthalonitrile was prepared according to the reported procedure [35] and ferroceneacetic acid was purchased from Aldrich Chemical Company, and was used as purchased. All reagents and solvents were of reagent-grade quality obtained from commercial suppliers. All solvents were dried, purified and stored over molecular sieves (4 Å). The homogeneity of the products was tested in each step using TLC (SiO<sub>2</sub>).

#### 2.2. Synthesis

#### 2.2.1. 3-Ferrocenyl-7-hydroxycoumarin (1)

Ferroceneacetic acid (0.900 g, 3.688 mmol), 2,4-dihydroxybenzaldehyde (0.509 g, 3.688 mmol), sodium acetate (1.2095 g, 14.75 mmol) and anhydrous acetic anhydride (8 mL) were heated for 9 h at 160 °C. After cooling to room temperature, water was added and the mixture stirred overnight. The resulting solid, 7-acetoxy-3-ferrocenylcoumarin, was filtered, washed with water. The crude product was suspended in methanol. A 10% aq HCl solution was added to adjust the pH to 3 and ensuing mixture was heated and stirred at 65 °C for 24 h under vacuum. The product, 3-ferrocenyl-7-hydroxycoumarin, was washed with water after the removal of methanol and dried. The compound was purified on a silica gel column using chloroform as eluent. Yield: 0.945 g (66%); m.p.:>300 °C. Anal. calcd. for C<sub>19</sub>H<sub>14</sub>O<sub>3</sub>Fe: C, 65.90; H, 4.05%. Found: C, 65.86; H, 3.99. UV-vis (CHCl<sub>3</sub>):  $\lambda_{max}$ , nm (log  $\epsilon$ ) 468 (3.28, ferrocene, Fc), 344 (4.25, coumarin). <sup>1</sup>H NMR (500 MHz; DMSO):  $\delta_{H}$ , ppm 9.89 (s, 1H, OH), 8.12 (s, 1H, lactone 4–H), 7.50 (d, J = 8Hz, 1H, Ar–H), 6.76 (dd, 1H, Ar–H), 6.70 (d, J = 3Hz, 1H, Ar–H), 4.94 (s, 2H, Fc), 4.36 (s, 2H, Fc), 4.07 (s, 5H, Fc). IR  $\nu$ (cm<sup>-1</sup>): 3200 (OH), 3015-3060 (Ar-H), 1700 (C=O lactone), 1450-1620 (C=C). MS (MALDI-TOF): *m*/*z* 346 [M]<sup>+</sup>, 347 [M + 1]<sup>+</sup>.

#### 2.2.2. 7-(3,4-Dicyanophenoxy)-3-ferrocenylcoumarin (2)

3-Ferrocenyl-7-hydroxycoumarin (1) (0.900 g, 2.60 mmol) was dissolved in 20 mL of dry DMF and 4-nitrophthalonitrile (0.450 g, 2.60 mmol) was added. After stirring for 10 min finely ground anhydrous  $K_2CO_3$  (0.542 g, 2.60 mmol) was added and the reaction mixture was stirred at 50 °C for 48 h under vacuum. Then the

mixture was poured into 150 mL ice—water. The resulting solid was collected by filtration and washed with water. The crude product was purified on a silica gel column using chloroform as eluent. Yield: 1.05 g (86%); m.p.: 250 °C. Anal. calcd. for  $C_{27}H_{16}N_2O_3Fe: C$ , 68.64; H, 3.39; N, 5.93%. Found: C, 68.86; H, 3.14; N, 5.82. UV—vis (CHCl<sub>3</sub>):  $\lambda_{max}$ , nm (log  $\epsilon$ ) 495 (3.26, Fc), 335 (4.27, coumarin). <sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>):  $\delta_{H}$ , ppm 7.78 (dd, 1H, Ar–H), 7.75 (s, 1H, lactone 4–H), 7.55 (d, *J* = 8Hz, 1H, Ar–H), 7.33 (dd, 1H, Ar–H), 7.37 (d, *J* = 3Hz, 1H, Ar–H), 7.04 (d, *J* = 3Hz, 1H, Ar–H), 6.97 (d, *J* = 8Hz, 1H, Ar–H), 4.97 (s, 2H, Fc), 4.46 (s, 2H, Fc), 4.16 (s, 5H, Fc). IR  $\nu$  (cm<sup>-1</sup>): 3040–3090 (Ar–H), 2200 (–C $\equiv$ N), 1770 (C=O lactone), 1475–1600 (C=C), 1250 (C–O–C). MS (MALDI-TOF): *m/z* 472 [M]<sup>+</sup>, 473 [M + 1]<sup>+</sup>.

## 2.2.3. 2(3),9(10),16(17),23(24)-Tetrakis(3-ferrocenyl-7-oxycoumarin)phthalocyaninato zinc (II) (**3**)

A mixture of 2 (0.100 g, 0.212 mmol), Zn(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O (0.0116 g, 0.053 mmol) in 2-dimethylaminoethanol (1.5 mL) was heated and stirred at 155 °C for 6 h under N2 atmosphere. After cooling to room temperature, the reaction mixture was precipitated by the addition of methanol (5 mL) and green precipitate was filtered off. It was treated with boiling ethanol, methanol, ethyl acetate and acetone several times to dissolve the unreacted started materials and decomposition product. Furthermore this product was purified with preparative thin layer chromatography using (silicagel) THF-MeOH (10:1) solvent system. Yield: 0.047 g (45%); m.p.: >300 °C. Anal. calcd. for C<sub>108</sub>H<sub>64</sub>N<sub>8</sub>O<sub>12</sub>Fe<sub>4</sub>Zn: C, 66.36; H, 3.28; N, 5.74%. Found: C, 66.45; H, 3.21; N, 5.76. UV–vis (DMF): λ<sub>max</sub>, nm  $(\log \epsilon)$  675 (4.83), 606 (4.05), 485 (3.88), 343 (4.68). IR  $\nu(cm^{-1})$ : 3050-3080 (Ar-H), 1760 (C=O lactone), 1440-1600 (C=C), 1280 (C-O-C). MS (MALDI-TOF): m/z 1953  $[M]^+$ , 1954  $[M + 1]^+$ , 1955  $[M + 2]^+$ , 1956  $[M + 3]^+$ , 1957  $[M + 4]^+$ .

## 2.2.4. 2(3),9(10),16(17),23(24)-Tetrakis(3-ferrocenyl-7-oxycoumarin)phthalocyaninato cobalt (II) (**4**)

Compound **4** was prepared and purified according to the procedure described for **3**, starting from 0.100 g (0.212 mmol) **2**, 0.0132 g (0.053 mmol) Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O and 2-dimethylaminoethanol (1.5 mL). Yield: 0.052 g (51%); m.p.: >300 °C. Anal. calcd. for C<sub>108</sub>H<sub>64</sub>N<sub>8</sub>O<sub>12</sub>Fe<sub>4</sub>Co: C, 66.56; H, 3.29; N, 5.75%. Found: C, 66.24; H, 3.12; N, 5.50. UV–vis (DMF):  $\lambda_{max}$ , nm (log  $\epsilon$ ) 661 (4.69), 598 (4.24), 489 (3.88), 334 (4.88). IR  $\nu$ (cm<sup>-1</sup>): 3065–3075 (Ar–H), 1754 (C=O lactone), 1448–1603 (C=C), 1284 (C–O–C). MS (MALDI-

#### 2.3. Electrochemistry

TOF): *m*/*z* 1947 [M]<sup>+</sup>, 1948 [M + 1]<sup>+</sup>.

The cyclic voltammetry, differential pulse voltammetry, and controlled potential chronocloumetry (CPC) measurements were carried out with a Princeton Applied Research Model Versostat II potentiostat/galvanostat controlled by an external PC and utilizing a three-electrode configuration at 25 °C. The working electrode was a Pt plate with a surface area of 0.10 cm<sup>2</sup>. The surface of the working electrode was polished with H<sub>2</sub>O suspension of Al<sub>2</sub>O<sub>3</sub> before each run. The last polishing was done with a particle size of 50 nm. 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. Electrochemical grade tetrabutylammonium perchlorate (TBAP) in extra pure DMSO was employed as the supporting electrolyte at a concentration of 0.10 mol dm<sup>-3</sup>. High purity N<sub>2</sub> was used for deoxygenating the solution at least 20 min prior to each run and to maintain a nitrogen blanket during the measurements. For CPC studies, Pt gauze working electrode (10.5 cm<sup>2</sup> surface area), Pt wire counter electrode separated by a glass bridge, and SCE as a reference electrode were used.

#### 3. Results and discussion

The synthetic procedures of the 3-ferrocenyl-7-oxycoumarin substituted phthalonitrile derivatives (2) and Pc complexes (3 and 4) are given in Scheme 1. 3-Ferrocenyl-7-hydroxycoumarin (1) was synthesized by the reaction of ferroceneacetic acid with 2,4-dihydroxybenzaldehyde via Perkin reaction [36]. 7-(3,4-Dicyanophenoxy)-3-ferrocenylcoumarin (2) was synthesized through basecatalyzed aromatic nitro displacement of 4-nitrophthalonitrile with 1 using K<sub>2</sub>CO<sub>3</sub> as the base in dry DMF. The reaction was carried out at 50 °C for 48 h under N<sub>2</sub> atmosphere. Zinc(II) and cobalt(II) metallo Pcs (3 and 4) were synthesized by reaction of 2 with Zn(CH<sub>3</sub>COO)<sub>2</sub>,2H<sub>2</sub>O and Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O in 2-dimethylaminoethanol for 6 h at 155 °C under N<sub>2</sub> atmosphere. The Pc complexes were purified by preparative thin layer chromatography using THF-MeOH (10:1) solvent system. The structures of the target compounds were confirmed using elemental analysis, FT-IR, <sup>1</sup>H NMR, UV–Vis and MALDI-TOF methods. The analyses are consistent with the predicted structures.

Comparison of the FT-IR spectral data clearly indicated the formation of compound **1** by the appearance of new absorption bands at 3200 cm<sup>-1</sup> (OH), 3015–3060 cm<sup>-1</sup> (Ar–H), 1700 cm<sup>-1</sup> (C=O lactone) and 1450–1620 cm<sup>-1</sup> (C=C). After conversion of the **1** into dinitrile derivative (**2**) the broad peak for the –OH band disappeared and the characteristic vibrations of the –C=N appear at 2200 cm<sup>-1</sup>. <sup>1</sup>H NMR spectrum of **1** indicated the –OH proton at  $\delta$  9.89 ppm as a singlet, the aromatic protons at the range of  $\delta$  6.70–7.50 ppm as doublets and the proton of coumarin at position

4 at  $\delta$  8.12 ppm as a singlet. The ferrocenyl protons were observed at  $\delta$  4.94, 4.36 and 4.07 ppm as singlets. In the <sup>1</sup>H NMR analysis of **2** in CDCl<sub>3</sub>, the proton of coumarin at position 4 appeared as a singlet at  $\delta$  7.75 ppm, the aromatic protons as dublets at  $\delta$  6.97–7.78 ppm, ferrocenyl protons as singlets at  $\delta$  4.97, 4.46 and 4.16 ppm. The MALDI-TOF mass spectra of compounds **1** and **2** confirmed the proposed structures; molecular ions were easily indentified at *m*/*z*: 346 [M]<sup>+</sup> for **1** and *m*/*z*: 472 [M]<sup>+</sup> for **2**.

In the FT-IR spectra of **3** and **4**, the lactone C=O bands of the coumarins and aromatic C=C bands appear at 1760, 1440–1600 cm<sup>-1</sup> for **3** and 1754, 1448–1603 cm<sup>-1</sup> for **4**, respectively. In the mass spectra of compounds **3** and **4**, the presence of molecular ion peaks at m/z: 1953 [M]<sup>+</sup> (Fig. 1) and 1947 [M]<sup>+</sup> respectively, confirmed the proposed structures.

The ground state electronic spectra of the Pc complexes showed characteristic absorption in the Q band region at 675 nm for **3** and 661 nm for **4**. The B band region was observed at 343 nm for **3** and 334 nm for **4**. The spectra showed monomeric behavior evidenced by a single Q band, typical of metalled Pc complexes for **3** and **4** in DMF which depict the monomeric nature of these complexes (Fig. 2). It was found that the Q band of **3** is red shifted (14 nm) as compared with that of **4** in DMF. A broad absorption band at *ca*. 485 nm originates from the presence of ferrocene units on the periphery. Due to the ferrocenyl moieties, the Q band (675 nm in DMF) is substantially blue-shifted (14 nm) by comparing with the 2 (3),9(10),16(17),23(24)-tetrakis(7-oxy-4-methylcoumarin)phthalocvaninato zinc(II) (**5**) (689 nm in DMF) (Fig. 3) [37].

Fig. 4 shows the fluorescence emission spectra for compounds **3** and **5**. The Pc **4** does not show fluorescence at excitation wavelength. In DMF, emission peaks were observed at 689 nm for **3** and 692 nm



Scheme 1. Synthetic procedures of 3-ferrocenyl-7-oxycoumarin substituted phthalonitrile derivatives (1 and 2) and Pc complexes (3 and 4).



Fig. 1. Mass spectrum of zinc(II) metallo Pc (3).

for 5. The excitation spectra were similar to absorption spectra and both were mirror images of the fluorescence spectra [38]. The fluorescence property of coumarin chromophore system is significantly altered by appropriate substituents at the 3- and the 7-position. Electron donors such as amino, hydroxyl and methoxy groups at the 7-position and electron acceptor heterocyclic rings such as benzthiazole, benzoxazole and benzimidazole at the 3-position impart pronounced bathochromicity and strong fluorescence [39]. Fluorescence property of the 7-oxy-4-methylcoumarin substituted Pc (5) is strongly affected by the presence of ferrocenyl substituents. Pc 5 possesses high fluorescence intensity, while the ferrocenesubstituted Pc 3 shows very poor fluorescent intensity. In fact, it has been reported that covalently linked ferrocenes substantially quenched the fluorescence emission of other chromophores, for example; porphyrins, through an intramolecular electron-transfer process [40,41]. Our fluorescence studies indicated that the phthalocyanine fluorescence was guenched to a greater extent in phthalocyanine-coumarin-ferrocene conjugates because of photoinduced electron transfer from ferrocene to coumarin substituted phthalocyanine.

The solution redox properties of the Pc complexes **3** and **4** were studied using cyclic voltammetry, differential pulse voltammetry and controlled potential chronocoulometry in DMSO on platinum electrode. Complete electrolysis of each Pc solution at the working electrode at a suitable constant potential for the first reduction and

first oxidation processes of 3 was achieved, and the time integration of the electrolysis current was recorded with the controlled potential coulometry studies. The charge, Q, at the end of electrolysis was calculated using the current-time response of solution and Faraday's law was used to estimate the number of electrons transferred. The number of electrons was found to be one for the mentioned redox processes of 3. The comparison of the peak currents of these processes with those of others suggested that the number of electrons is also one for the other redox processes except the second oxidation couple of **3**. Figs. 5 and 6 show typical cyclic and differential pulse voltammograms of 3 and 4, respectively, in DMSO containing TBAP. The peak currents of the second oxidation couple (O2) of **3** are approximately four times those of its reduction couples (R1-R4) and first oxidation couple (O1). The situation was similar for the comparison of the peak currents of the first oxidation couple of **4** with those of its reduction couples (R1-R3),







Fig. 3. 2(3),9(10),16(17),23(24)-Tetrakis(7-oxy-4-methylcoumarin)phthalocyaninato zinc(II) (5).



**Fig. 4.** (A) Emission spectra of **3** and **5** in DMF, excitation wavelengths: 640 nm for **3**, 650 nm for **6**, (B) Excitation spectra of **3** and **5** in DMF.

implying strongly that the second oxidation couple (O2) of **3** and the first oxidation couple of **3** correspond to the oxidation of ferrocene substituents simultaneously at one potential. Voltammetric data and the assignment of the redox couples recorded for the complexes are listed in Table 1. The ferrocene substituents of both **3** and **4** are oxidized at the same potential, 0.51 V vs. SCE, probably due to the fact that the metal centers in **3** and **4** does not influence the electron density on ferrocene substituents considerably.

Complex 3 gives three one-electron reduction processes labelled as  $R_1$  at -0.78 V,  $R_2$  at -1.12 V and  $R_3$  at -1.40 V, and a four-electron oxidation process labelled as  $O_1$  at 0.51 V vs. SCE at 0.050 Vs<sup>-1</sup> scan rate (Fig. 5 and Table 1). All the one-electron reduction processes of 3 are Pc ring based since zinc(II) metal center behaves as redoxinactive in Pcs [42-45]. Reduction of the Pc ligand is associated to the position of LUMO whereas its oxidation is associated to the position of the HOMO. Thus, the difference between the potentials of the first oxidation and the first reduction processes ( $\Delta E_{1/2}$ ) reflects the homo-lumo gap for metal free Pcs and it is closely related with the HOMO-LUMO gap in MPc species involving redoxinactive metal center.  $\Delta E_{1/2}$  values within the range of 1.50–1.70 V were reported in the literature [42]. Thus, the first oxidation couple of **3** (01) is due to the oxidation of ferrocene substituents and Pc ring-based first oxidation couple of 3 is probably out of the solventlimited potential range, and cannot be observed. The peak currents ratios at different scan rates for all redox couples of 3 are usually close to unity, suggesting the absence of coupled chemical reactions. Anodic to cathodic peak separations  $(\Delta E_p)$  changed from 0.050 to 0.180 V within the scan rates from 0.010 to 0.500 Vs<sup>-1</sup> ( $\Delta E_p$ changed from 0.060 to 0.140 V for ferrocene), indicating the occurrence of quasi-reversible electron transfer reactions. The peak currents increased linearly with the square root of scan rates, indicating the purely diffusion-controlled behavior [46].

The redox potentials of **4**, especially its first reduction and first oxidation potentials are highly different as compared with those of **3** (Figs. 5 and 6, and Table 1). Within the electrochemical window of

TBAP/DMSO, the complex **4** undergo two oxidations, the first one with reversible transfer of one electron and the second one with quasi-reversible transfer of four electrons, and four one-electron reversible or quasi-reversible reductions, with anodic to cathodic peak separations ( $\Delta E_p$ ) changed from 0.050 to 0.160 V within the scan rates from 0.010 to 0.500 Vs<sup>-1</sup>. The peak currents increased linearly with the square root of scan rates, indicating the purely diffusion-controlled behavior [46]. The difference in the voltammetric behaviour of **4** as compared with that of **3** is due to the fact that metallo phthalocyanines, such as MnPc, CoPc and FePc, having a metal that possesses energy levels lying between the HOMO and the LUMO of the Pc ligand, in general exhibit redox processes centered on the metal [42, 47-50]. For CoPc complexes, the first oxidation and first reduction processes occur on the metal center in polar solvent such as DMF and DMSO; however the first oxidation process occurs on the Pc ring in nonpolar solvent such as DCM and THF. Therefore, the first reduction and the first oxidation processes of **4** could be assigned easily to the  $[Co(II)Pc(-2)]/[Co(I)Pc(-2)]^{-1}$ and  $[Co(II)Pc(-2)]/[Co(III)Pc(-2)]^+$  redox couples and the other reduction processes to the Pc ring. The separation between the first oxidation and the first reduction potentials of the metal center for 4 (0.65 V) is comparable with the relevant values in the literature [1,6–9], and does not reflect the HOMO-LUMO gap.



Fig. 5. (A) Cyclic and (B) differential pulse voltammograms of  $5.0 \times 10^{-4}$  M 3 in TBAP/DMSO.



Fig. 6. (A) Cyclic and (B) differential pulse voltammograms of  $5.0\times10^{-4}$  M 4 in TBAP/ DMSO.

#### Table 1

The electrochemical data of the Pc complexes (3 and 4).

Complex	Redox processes	$E_{1/2}$ (V vs. SCE) <sup>a</sup>	$\Delta E_{p}\left(V\right)^{b}$	Ipa/Ipc <sup>c</sup>	$\Delta E_{1/2} \left( V \right)^d$
3	01	0.51	0.080	1.00	1.29
	R1	-0.78	0.080	0.97	
	R2	-1.12	0.060	0.98	
	R3	-1.40	0.080	0.98	
4	02	-0.37	0.100	1.05	
	01	0.48	0.090	0.98	0.91
	R1	-0.43	0.060	1.05	
	R2	-0.82	0.120	0.97	
	R3	-1.11	0.060	1.00	
	R4	-1.40	0.080	1.02	

<sup>a</sup>  $E_{1/2} = (E_{pa} + E_{pc})/2$  at 0.050 Vs<sup>-1</sup>.

<sup>b</sup>  $\Delta E_{\rm p} = E_{\rm pa} - E_{\rm pc}$  at 0.050 Vs<sup>-1</sup>.

 $^{c}~I_{pa}/I_{pc}$  for reduction,  $I_{pc}/I_{pa}$  for oxidation processes at 0.050  $Vs^{-1}.$ 

 $^d$   $\Delta E_{1/2} = E_{1/2}(first oxidation) - E_{1/2}(first reduction). These values do not reflect the HOMO-LUMO gap for$ **3**and**4**.

#### Acknowledgement

We are thankful to the Reseach Foundation of Marmara University, Commission of Scientific Research Project (BAPKO) [FEN-A-090909-0302].

#### References

- C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, vols. 1–4, Weinheim: VCH, New York, 1989, 1993, 1996.
- [2] N.B. McKeown, Phthalocyanines Materials, Synthesis, Structure and Function. Cambridge University Press, Cambridge, 1998.
- [3] G. Torre, P. Vazquez, F. Agullo-Lopez, T. Torres, J. Mater. Chem. 8 (1998) 1671–1683.
- [4] M. Nicolau, B. Cabezon, T. Torres, J. Org. Chem. 66 (2001) 89-93.
- [5] H. Akkuş, A. Gül, Transit. Met. Chem. 26 (2001) 689–694.
- [6] K.W. Poon, W. Liu, P.K. Chan, Q. Yang, T.W.D. Chan, T.C.W. Mak, D.K.P. Ng, Org. Chem. 66 (2001) 1553–1559.
- [7] K.W. Poon, Y. Yan, X. Li, D.K.P. Ng, Organometallics 18 (1999) 3528-3533.
- [8] V. Ahsen, E. Yilmazer, M. Ertas, ÖBekaroğlu, J. Chem. Soc. Dalton Trans. (1988) 401–406
- [9] C.F. van Nostrum, S.J. Picken, A.J. Schouten, R.J.M. Nolte, J. Am. Chem. Soc. 117 (1995) 9957–9965.
- [10] N. Kobayashi, T. Ohya, M. Sato, S. Nakajima, Inorg. Chem. 32 (1993) 1803-1808.
- [11] M.J. Cook, G. Cooke, A. Jafari-Fini, J. Chem. Soc. Chem. Commun. (1995) 1715–1716.
- [12] M. Kimura, T. Hamakawa, T. Muto, K. Hanabusa, H. Shira, N. Kobayashi, Tetrahedron Lett. 39 (1998) 8471–8474.
- [13] J.A. Delaire, J. Delouis, J. Zakrzewski, Formation and quenching of the photoexcited triplet state of tetrasulfonated zinc phthalocyanine, ZnPcS<sub>4</sub><sup>4–</sup> by azaferrocene and ferrocene, J. Photochem. Photobiol. A 141 (2001) 169–173.
- [14] Z. Jin, K. Nolan, C.R. McArthur, A.B.P. Lever, C.C. Leznoff, J. Organomet. Chem. 468 (1994) 205–212.
- [15] A. Togni, T. Hayashi, Ferrocenes. VCH, New York, 1995.
- [16] I.R. Whittall, A.M. McDonagh, M.G. Humphrey, M. Samoc, Adv. Organomet. Chem. 42 (1998) 291–362.
- [17] D. Astruc, Electron Transfer and Radical Processes in Transition-Metal Chemistry. VCH, New York, 1995.
- [18] S.M. Sethna, N.M. Shah, Chem. Rev. 36 (1) (1945) 1-62.
- [19] S.C. Haydon, Spectrosc. Lett. 8 (1975) 815-892.
- [20] N. Kitamura, S. Kohtani, R. Nakagaki, J. Photochem. Photobiol. C 6 (2005) 168–185.
- [21] G. Matlocsy, M. Nadasy, V. Andriska, Pesticide Chemistry, Studies in Environmental Science. Elsevier, Budapest, 1998, pp. 32.
- [22] M. Frenette, C. Coenjarts, J.C. Scaiano, Macromol. Rapid Commun. 25 (2004) 1628–1631.
- [23] B. YanWang, X.Y. Liu, Y.L. Hu, Z.X. Su, Polym. Int. 58 (2009) 703-709.
- [24] C.R. Moylan, J. Phys. Chem. 98 (1994) 13513-13516.
- [25] Y. Tian, E. Akiyama, Y. Nagase, A. Kanazawa, O. Tsutsumi, T. Ikeda, Macromol. Chem. Phys. 201 (2000) 1640–1652.
- [26] J. Kwon Oh, V. Stöeva, J. Rademacher, R. Farwaha, M.A. Winnik, J. Polym. Sci. A 42 (2004) 3479–3489.
- [27] E. Bardez, P. Boutin, B. Valeur, Chem. Phys. Lett. 191 (1992) 142-148.
- [28] J. Seixas de Melo, A.L. Maçanita, Chem. Phys. Lett. 204 (1993) 556-562.
- [29] J. Seixas de Melo, R.S. Becker, A.L. Macanita, J. Phys. Chem. 98 (1994) 6054-6058.
- [30] K. Setsukinai, Y. Urano, K. Kikuchi, T. Higuchi, T. Nagano, J. Chem. Soc. Perkin Trans. 2 (2000) 2453–2457.
- [31] J. Seixas de Melo, P.F. Fernandes, J. Mol. Struct. 565-566 (2001) 69-78.
- [32] H. Çakıcı, A.A. Esenpınar, M. Bulut, Polyhedron 27 (2008) 3625-3630.
- [33] M. Çamur, M. Bulut, M. Kandaz, O. Güney, Polyhedron 28 (2009) 233–238.
- [34] M. Çamur, M. Bulut, M. Kandaz, O. Güney, Supramol. Chem. 21 (7) (2009) 624–631.
- [35] J.G. Young, W. Onyebuagu, J. Org. Chem. 55 (1990) 2155-2159.
- [36] M. Çamur, M. Bulut, Dyes Pigm. 77 (2008) 165–170.
- [37] A.A. Esenpinar, M. Bulut, Dyes Pigm. 76 (2008) 249-255.
- [38] N. Kobayashi, H. Ogata, N. Nonaka, E.A. Lukyanets, Chem. Eur. J. 9 (2003) 5123-5124.
- [39] A.R. Jagtap, V.S. Satam, R.N. Rajule, V.R. Kanetkar, Dyes Pigm. 82 (2009) 84–89.
   [40] R. Giasson, E.J. Lee, X. Zhao, M.S. Wrighton, J. Phys. Chem. 97 (1993) 2596–2601.
- [41] N.B. Thornton, H. Wojtowicz, T. Netzel, D.W. Dixon, J. Phys. Chem. B. 102 (1998) 2101–2110.
- [42] A.B.P. Lever, E.R. Milaeva, G. Speier, in: C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, vol. 3, VCH Publishers, New York, 1993, pp. 1–63.
- [43] T. Ceyhan, A. Altındal, A.R. Özkaya, Ö Çelikbıçak, B. Salih, M.K. Erbil, Ö Bekaroğlu, Polyhedron 26 (2007) 4239–4249.
- [44] Z. Odabaş, A. Altındal, A.R. Özkaya, M. Bulut, B. Salih, Ö Bekaroğlu, Polyhedron 26 (2007) 3505–3512.
- [45] D. Kulaç, M. Bulut, A. Altındal, A.R. Özkaya, B. Salih, ÖBekaroğlu, Polyhedron 26 (2007) 5432–5440.
- [46] A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, second ed., Wiley, New York, 2001.
- [47] M. Özer, A. Altındal, A.R. Özkaya, M. Bulut, Ö Bekaroğlu, Polyhedron 25 (2006) 3593–3602.
- [48] A.R. Özkaya, E. Hamuryudan, Z.A. Bayır, Ö Bekaroğlu, J. Porphyrins Phthalocyanines 7 (2000) 689–697.
- [49] M. Kandaz, A.R. Özkaya, Ö Bekaroğlu, Monats. Chem. 132 (2001) 1013–1022.
- [50] A. Koca, A.R. Özkaya, M. Selçukoğlu, E. Hamuryudan, Electrochim. Acta 52 (2007) 2683–2690.