

Available online at www.sciencedirect.com



POLYHEDRON www.elsevier.com/locate/poly

Polyhedron 25 (2006) 3593-3602

## Synthesis, characterization and some properties of novel bis(pentafluorophenyl)methoxyl substituted metal free and metallophthalocyanines

Metin Özer <sup>a</sup>, Ahmet Altındal <sup>b</sup>, Ali Rıza Özkaya <sup>a</sup>, Mustafa Bulut <sup>a</sup>, Özer Bekaroğlu <sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Marmara University, Faculty of Art and Science, 34722 Göztepe, Istanbul, Turkey <sup>b</sup> Department of Physics, Marmara University, Faculty of Art and Science, 34722 Göztepe, Istanbul, Turkey

> Received 26 June 2006; accepted 6 July 2006 Available online 25 July 2006

### Abstract

The preparation of some new tetrakis[bis(pentafluorophenyl)methoxyl] substituted metal free and metallophthalocyanine (MPcs) complexes were achieved by the tetramerization of 4-[bis(pentafluorophenyl)methoxy]phthalonitrile with Li metal in pentan-1-ol or metal [Co(II) or Zn(II)] acetates in DMAE, respectively. The structures of the target compounds were confirmed by elemental analysis, IR, UV–vis, <sup>1</sup>H NMR, <sup>19</sup>F NMR and mass spectroscopic methods. MPcs are soluble only in strong and medium polar solvents while the metal free one is soluble in weakly, medium and strong polar solvents. The temperature and frequency dependence of the electrical conductivities were studied on spin coated films of the compounds using dc and impedance spectroscopy techniques in the frequency range from 40 to  $10^5$  Hz and within the temperature range from 290 to 440 K. The temperature dependence of the exponent *s* and conductivity,  $\sigma_{ac}$ , were completely in agreement with the prediction of the hopping model. The redox properties of the complexes were determined by cyclic voltammetry. The nature of the redox processes was also confirmed using spectroelectrochemical measurements. © 2006 Elsevier Ltd. All rights reserved.

Keywords: Phthalocyanine; Synthesis; Bis(pentafluorophenyl)methoxyl; UV-vis spectra; Cyclic voltammetry; Spectroelectrochemistry; Impedance spectra

### 1. Introduction

For many years phthalocyanine (Pc) compounds have been widely used as organic pigments and dyestuffs. Besides the application in such traditional areas, phthalocyanines (Pcs) have been extensively studied due to their spectroscopic, electrochemical, electrical and photoelectric properties. The solubility of Pcs is very important for the investigation of their chemical and physical characteristics. The solubility of Pc can be increased by introducing different kinds of solubility-enhancing substituents such as alkyl, alkoxy, phenoxy and macrocylic groups at the peripheral and axial positions of the Pc ring [1-3].

Introducing electron donor and acceptor groups into the Pc ring also strongly affects the electrical properties of the molecule. From the viewpoint of organic semiconductors, it is known that substitution of electron donor and acceptor groups leads to p-type and n-type characteristics of the Pc ring, respectively [4,5].

Fluorinated MPcs are currently receiving a great deal of attention due to their interesting electron-transporting characteristics [6,7]. Although many studies on the chemistry of MPcs in solution, which have been limited to Pc with electron-donating substituents, have been carried out, those with electron-attracting groups, especially containing fluorine atoms, have not been extensively studied [8–11]. Recently, several workers reported on the syntheses and

<sup>&</sup>lt;sup>\*</sup> Corresponding author. Present address: Bilim Sokak, Kardesler Apt., No 6/9, Erenköy, Istanbul, Turkey. Tel.: +90 216 359 01 30; fax: +90 216 386 08 24.

E-mail address: obekaroglu@marmara.edu.tr (Ö. Bekaroğlu).

<sup>0277-5387/\$ -</sup> see front matter @ 2006 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2006.07.011

properties of some fluoro-substituted Pcs. In the case of electron-withdrawing peripheral fluorine substituents, Pcs can be dissolved even in polar aprotic solvents and become good electron donors for use as chemical sensors [9,10,12].

In this paper, we report the preparation of some new bis(pentafluorophenyl)methoxyl substituted Pc derivatives, and their spectral, electrochemical, spectroelectrochemical and electrical properties (Scheme 1).

### 2. Experimental

The starting material 4-nitrophthalonitrile 2 was synthesized by the methods described previously in the

literature [13]. Bis(pentafluorophenyl)methanol 1 was used as supplied commercially. Routine IR and UV-vis spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer as KBr pellets and a Shimadzu UV-1601 UV-vis spectrophotometer, respectively. Elemental analyses were performed by the LECO CHNS 932. Mass spectra of 4-[bis(pentafluorophenyl)methoxy]phthalonitrile 3 and Pc derivatives 4-6 were obtained by using the Agilent LC/MSD-TOF spectrometer and Micromass Quattro LC-MS/MS spectrophotometer respectively. <sup>1</sup>H NMR and <sup>19</sup>F NMR spectra were obtained on a Varian Mercury-V × 400 MHz spectrophotometer.



Scheme 1. (i) K<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>CN; (ii) a: Li, pentan-1-ol; b: Zn(CH<sub>3</sub>COO)<sub>2</sub> · 2H<sub>2</sub>O, DMAE; c: Co(CH<sub>3</sub>COO)<sub>2</sub> · 4H<sub>2</sub>O, DMAE.

### 2.1. Synthesis

### 2.1.1. 4-[Bis(pentafluorophenvl)methoxv]phthalonitrile (3)A mixture of bis(pentafluorophenyl)methanol 1 (1.00 g, 2.74 mmol), 4-nitrophthalonitrile 2 (0.47 g, 2.74 mmol) and $K_2CO_3$ (1.14 g, 8.24 mmol) was heated for 24 h, refluxing in dry acetonitrile (40 mL) under argon. The cooled reaction mixture was filtered off and the filtrate evaporated to dryness under vacuum in a rotary evaporator. After being dried under vacuum, the yellowish viscous product was isolated with column chromatography over silica gel using chloroform as the eluent. The second fraction, which is targeted, was eluted with CHCl<sub>3</sub>. On evaporation of the solvent, a white product was obtained (Scheme 1). The compound 3 is readily soluble in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, acetone, THF, MeOH and EtOH. Yield: 0.822 g (61%), m.p. 128 °C. Anal. Calc. for C<sub>21</sub>H<sub>4</sub>F<sub>10</sub>N<sub>2</sub>O: C, 51.45; H, 0.82; N, 5.71. Found: C, 51.71; H, 0.81; N, 5.69%. MS (LC/MSD-TOF, APCI), m/z: 490 [M]<sup>+</sup>, IR

(KBr pellet) v, cm<sup>-1</sup>: 3090 (Ar–H), 2923–2854 (alkyl >CH), 2233 (C=N), 1242 (C–O–C); <sup>1</sup>H NMR (*d*-CDCl<sub>3</sub>):  $\delta = 6.94$  (s, 1H, >CH), 7.24 (d, 1H, Ar–H), 7.33 (d, 1H, Ar–H), 7.76 (d, 1H, Ar–H). <sup>19</sup>F NMR (*d*-CDCl<sub>3</sub>):  $\delta$  (ppm) = -141.2 (d, *o*-fluoro), -149.9 (t, *p*-fluoro), -159.6 (q, *m*-fluoro).

### 2.1.2. Tetrakis[bis(pentafluorophenyl)methoxy]-2Hphthalocyanine (4)

Compound 3 (0.245 g, 0.5 mmol) was added to 5 mL pentan-1-ol and heated to dissolve. An excess of Li wire was subsequently added to the solution. As the Li was added, a large quantity of gas was evolved and the reaction mixture turned to dark green. The mixture was heated at reflux under nitrogen for 5 h [10]. On cooling, 30 mL of AcOH/H<sub>2</sub>O (1:1-v/v) was added to the mixture and stirred for 20 min at the room temperature. The resulting waxy green Pc phase was separated from the mixture. The Pc product which remained in the flask was washed with water three times, and the residue was dried under vacuum to give tarry green Pc (Scheme 1). The crude Pc 4 was treated with three portions of  $30 \text{ mL of (CHCl}_3/\text{H}_2\text{O} - 3:1)$  (v/v) mixture. After the separation of the CHCl<sub>3</sub> phases, the CHCl<sub>3</sub> extracts were then combined, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the total volume was evaporated to dryness using a rotary evaporator. The purification of the aimed Pc was carried out on silica gel column with CHCl<sub>3</sub>. Compound 4 is soluble in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, THF, EtOH, MeOH, DMSO and DMF. Yield: 0.085 g (34%). Anal. Calc. for C<sub>84</sub>H<sub>18</sub>F<sub>40</sub>N<sub>8</sub>O<sub>4</sub>: C, 51.39; H, 0.92; N, 5.71. Found: C, 52.02; H, 0.89; N, 5.83%. MS(LC-MS/MS, ES+) m/z: 1963 [M]<sup>+</sup>, IR (KBr pellet) v, cm<sup>-1</sup>: 3297 (NH), 3073 (Ar-H), 2948–2893 (alkyl >CH), 1236 (C–O–C). UV–vis 674(4.75), (DMSO) λ, nm  $(\log \varepsilon)$ : 700(4.72), 650(4.67), 326(5.03); <sup>1</sup>H NMR (*d*-CDCl<sub>3</sub>) δ: 7.41-7.96 (m, 3H, Ar-H), 6.99 (s,1H, CH), -8.2 (br s, 2H, NH).

### 2.1.3. Tetrakis[bis(pentafluorophenyl)methoxy]phthalocyaninato zinc(II) (5)

Compound 3 (196 mg, 0.4 mmol) and  $Zn(CH_3COO)_2$ . 2H<sub>2</sub>O (22 mg, 0.10 mmol) were mixed in dry 2-N-N-dimethylaminoethanol (DMAE) (1 mL) in a glass tube. After being degassed with a vacuum, the mixture was sealed, and heated at 150-160 °C for 5 h to give a symmetrical substituted Pc (Scheme 1). After being cooled, the reaction mixture was poured into 100 mL of ethanol and the dark green precipitate was separated by centrifuging. The product was dissolved in DMF and precipitated with a mixture of CHCl<sub>3</sub> and acetone. After filtration, the precipitate was washed successively with boiling acetic acid, water and ether, and dried under vacuum. Compound 5 is soluble in DMSO and DMF, and partly soluble in acetone, MeOH and EtOH. Yield: 0.065 g (32%). Anal. Calc. for C<sub>84</sub>H<sub>16</sub>F<sub>40</sub>N<sub>8</sub>O<sub>4</sub>Zn: C, 49.79; H, 0.80; N, 5.53. Found: C, 50.56; H, 0.83; N, 5.49%. MS(LC-MS/MS, ES+) m/z: 2026  $[M]^+$ , IR (KBr pellet) v, cm<sup>-1</sup>: 3087 (Ar–H), 2925– 2883 (alkyl CH), 1242 (C-O-C); UV-vis (DMSO) λ, nm (log ε): 698(4.84), 641(4.35), 356(4.78); <sup>1</sup>H NMR (DMSO $d_6$ ):  $\delta = 7.94-7.63$  (m, 3H, Ar–H), 6.81 (s, 1H, CH). <sup>19</sup>F NMR (DMSO- $d_6$ ):  $\delta$ (ppm) = -143.2 (d, *o*-fluoro), -156.5 (t, *p*-fluoro), -163.2 (q, *m*-fluoro).

### 2.1.4. Tetrakis[bis(pentafluorophenyl)methoxy]phthalocyaninato cobalt(II) (6)

A mixture of compound 3 (0.089 g, 0.18),  $Co(CH_3 COO_{2} \cdot 4H_{2}O$  (0.011 g, 0.045 mmol) and DMAE (0.5 mL) was heated and stirred at 150-160 °C for 6 h in a sealed glass tube under argon to afford symmetrical Pc (Scheme 1). After cooling to room temperature, the reaction mixture was treated with ethanol and a dark blue precipitate was separated by centrifuging. The product was dissolved in DMF and precipitated with a mixture of CHCl<sub>3</sub> and acetone. After filtration, the precipitate was washed several times with boiling AcOH, water and EtOH to obtain the targeted Pc. The dark blue product was dried under vacuum. Compound 6 is soluble in DMSO and DMF. Yield: 0.014 g (16%). Anal. Calc. for C<sub>84</sub>H<sub>16</sub>F<sub>40</sub>-N<sub>8</sub>O<sub>4</sub>Co: C, 49.95; H, 0.80; N, 5.55. Found: C, 49.08; H, 0.83; N, 5.62%. MS(LC-MS/MS, ES+) m/z: 2021  $[M + 1]^+$ , IR (KBr pellet) v, cm<sup>-1</sup>: 3085 (Ar–H), 2927– 2884 (alkyl CH), 1244 (C-O-C); UV-vis (DMSO) λ, nm  $(\log \varepsilon)$ : 675(4.77), 320(4.99).

# 2.2. Electrochemical and spectroelectrochemical measurements

The cyclic voltammetry (CV) and controlled potential coulometry (CPC) measurements were carried out with a Princeton Applied Research Model VersaStat 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  $0.10 \text{ cm}^2$ . The surface of the working electrode was polished with a 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. A saturated calomel electrode (SCE) was employed as the reference electrode and was separated from the bulk of the solution by a double bridge. The ferrocene/ferrocenium couple  $(Fc/Fc^+)$  was also used as an internal standard. Electrochemical grade tetrabutylammonium perchlorate (TBAP) in extra pure dimethylsulfoxide (DMSO) was employed as the supporting electrolyte at a concentration of  $0.10 \text{ mol dm}^{-3}$ . High purity N<sub>2</sub> was used for deoxygenating the solution for at least 20 min prior to each run and to maintain a nitrogen blanket during the measurements. For controlled potential chronocoulometry (CPC) studies, a Pt gauze working electrode (10.5 cm<sup>2</sup> surface area), Pt wire counter electrode separated by a glass bridge, and a SCE as a reference electrode were used. The spectroelectrochemical measurements were carried out with an Agilent Model 8453 diode array spectrophotometer equipped with a potentiostat/galvanostat and utilizing a three-electrode configuration of a 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 a SCE reference electrode, separated from the bulk of the solution by a double bridge, were used.

### 2.3. Dc and impedance spectral measurements

Spin coated thin films of the compounds were prepared on a glass substrate fitted with interdigitated (IDT) gold electrodes for electrical characterization. Before vacuum evaporation, the glass substrates were thoroughly cleaned ultrasonically and then coated with 100 Å of chromium followed by 1200 Å of gold in a Leybold Univex 450 coater system. The film was patterned photolithographically and etched to provide 10 fingers pairs of electrodes having a width of 100 µm, spaced 100 µm from the adjacent electrodes. The finger overlap distance was 5 mm. DMF was used as the solvent. The reason for using DMF as the solvent is the good solubility of the compounds in DMF. The compounds were dissolved in DMF at concentrations of  $5 \times 10^{-3}$  M for all compounds. Twenty microlitres of such solutions were added with a glass pipette onto the IDT structure held on a spinner (Speciality Coatings Systems Inc., Model P6700 Series). The substrate was spun at 2000 rpm for 20 s and then the films were dried at 60 °C under vacuum for 2 h to evaporate the solvent. Dc conductivity measurements were performed between 290 K and 440 K using a Keithley 617 electrometer. Impedance spectroscopy measurements were carried out with a Keithley 3330 LCZ meter in the frequency range  $40-10^5$  Hz, and in the temperature range 290-440 K. A close cycle liquid helium cryostat was used to allow electrical characteristics to be measured over a wide temperature range. The temperature of the samples was controlled with a Leybold LTC 60 temperature controller during the measurements. The conductivity data were recorded using an IEEE 488

data acquisition system incorporated into a personal computer.

### 3. Results and discussion

### 3.1. Synthesis

The main precursor, molecule **3**, for the synthesis of bis(pentafluorophenyl)methoxyl substituted Pcs was obtained by a nitro displacement reaction [3,14] of 4-nitrophthalonitrile (**2**) and bis(pentafluorophenyl)methanol (**1**). The peripherally substituted Pc derivatives were prepared from the phthalonitrile derivative **3** with Li in pentan-1-ol [10] or with metal acetates  $[Zn(OAc)_2 \cdot 2H_2O]$  or Co(OAc)\_2 · 4H\_2O] in DMAE by a cyclotetramerization reaction.

The central metal ions and the peripheral substituents on the Pc ring effect the solubility of the MPcs. Perfluoro-substituted compounds have a tendency for high solubility in polar solvents. This situation may be interpreted with the extreme electronegativity of the fluorine atom. Both the metal-free **4** and Zn(II) Pc **5** were soluble in strong and medium polar solvents such as DMSO, DMF, EtOH and MeOH, while the Co(II)-Pc (**6**) was soluble only in strong solvents, e.g. DMSO and DMF. On the contrary to Pcs **5** and (**6**), the metal-free one **4** also showed solubility in less polar solvents such as CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> and THF.

The IR spectra were derived from potassium bromide disks. The existence of C $\equiv$ N groups was apparent from a single peak at 2233 cm<sup>-1</sup> in the spectrum of **3**. The formation of phthalocyanines from the dinitrile derivative was verified by the disappearance of the C $\equiv$ N stretching vibration band at 2233 cm<sup>-1</sup>. The IR spectra of **4**–**6** showed similar characteristics, except for metal-free **4** which showed a peak at 3297 cm<sup>-1</sup>, assigned to NH groups of the inner core.

The UV-vis spectra of **4–6** in DMSO show characteristic absorptions between 700 and 675 nm in the Q-band region. As expected, no splitting of the Q-band in the spectra of the MPcs (M: Zn, Co) was observed while the metalfree Pc **4** showed the expected Q band splitting. The Q band observed for all Pc compounds was attributed to the  $\pi \rightarrow \pi^*$  transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring. The  $\lambda_{max}$  value of the fluorinated compounds were slightly shifted to shorter wavelengths [8–10]. The other bands in the UV region at 326 nm for **4**, 356 nm for **5** and 320 nm for **6** were observed due to transitions from the deeper  $\pi$  levels to the LUMO (Fig. 1).

The <sup>1</sup>H NMR spectra are also consistent with the proposed structures. The <sup>1</sup>H NMR spectrum of **3** in *d*-CDCl<sub>3</sub> exhibited signals for the aromatic protons around 7.24–7.76 ppm as three doublets, and a peak for the >CH proton of the aliphatic group at 6.94 ppm as a singlet. However, the aromatic and aliphatic protons in Pcs **4** and **5** appeared as multiplets at 7.96–7.41, 7.94–7.63 ppm, and as singlets at



Fig. 1. UV-vis spectra of 4-6 in DMSO.

6.99, 6.81 ppm, respectively. The internal NH protons of metal-free Pc 4 were confirmed as a broad signal at -8.2 ppm.

A close investigation of the <sup>19</sup>F NMR spectra of compounds **3** and **5** confirmed the proposed structures. These compounds displayed signals due to  $F_{2,6}$ ,  $F_4$  and  $F_{3,5}$  at  $\delta$ : -141.2, -149.9 and -159.6 ppm, and -143.2, -156.5 and -163.2 ppm, respectively. The  $F_4$  signal appeared as a triplet due to  $F_{3,5}$  coupling, the  $F_{2,6}$  signals appeared as a doublet and the  $F_{3,5}$  signals as a quartet in both compound. Thus, the <sup>19</sup>F NMR measurements provided additional support for the structures of the fluorinated compounds **3** and **5** [15].

In addition to these supportive results for the structures, the mass spectra of compounds **3–6** gave the characteristic molecular ion peaks at m/z: 490 [M]<sup>+</sup>, 1963 [M]<sup>+</sup>, 2026 [M]<sup>+</sup> and 2021 [M+1]<sup>+</sup>, respectively, from which the proposed structures were confirmed.

### 3.2. Electrochemistry and spectroelectrochemistry

Cyclic voltammetry of **4–6** was carried out on a platinum working electrode in DMSO. Controlled-potential coulometry studies showed that the redox processes monitored for these compounds generally involves the transfer of one electron. Voltammetric data of the compounds are presented in Table 1. It should be noted that as the third reductions occurred at very negative potentials, it was not possible to determine correctly the number of electrons transferred. However, on the basis of the studies reported previously for mono Pcs [16], it can be assumed that the third reduction for each compound involves the transfer of one electron.

Compound 4 displayed three quasi-reversible reduction waves at  $E_{1/2} = -0.53$  V,  $E_{1/2} = -0.93$  V and  $E_{1/2} = -1.89$  V versus SCE, with considerably high anodic to cathodic peak separations (Fig. 2). These Pc ring-based redox processes were examined as a function of potential

Table 1   Voltammetric data for 4–6						
Compound	Redox couple	$E_{1/2}^{a}$ (V) vs. SCE and Fc/Fc <sup>+b</sup>	$\Delta E_{\rm p}^{\rm c}({\rm V})$			
4	Pc(-2)/Pc(-3) Pc(-3)/Pc(-4) Pc(-4)/Pc(-5)	$\begin{array}{c} -0.53 \ (-1.03) \\ -0.93 \ (-1.43) \\ -1.89 \ (-2.39) \end{array}$	0.30 0.42 0.18			
5	Pc(-2)/Pc(-3) Pc(-3)/Pc(-4) Pc(-4)/Pc(-5)	$\begin{array}{c} -0.67 \ (-1.17) \\ -1.04 \ (-1.54) \\ -1.94 \ (-2.44) \end{array}$	0.30 0.44 0.12			
6	Co(III)/Co(II) Co(II)/Co(I) Pc(-2)/Pc(-3) Pc(-3)/Pc(-4)	$\begin{array}{c} 0.43 \ (-0.07) \\ -0.43 \ (-0.93) \\ -0.83 \ (-1.33) \\ -1.39 \ (-1.89) \end{array}$	0.06 0.30 0.54 0.06			

<sup>a</sup>  $E_{1/2} = (E_{pa} + E_{pc})/2$  at 0.100 V s<sup>-1</sup>.

<sup>b</sup> The values in parenthesis indicate the potentials vs. 
$$Fc/Fc^+$$
.

<sup>c</sup>  $\Delta E_{\rm p} = E_{\rm pa} - \hat{E}_{\rm pc}$  at 0.100 V s<sup>-1</sup>.

scan rate in order to determine the mode of mass transport. The peak currents for the processes Ic, IIc and IIIc increased in direct proportion to the square root of the scan rate between 0.025 and 1.00 V/s, thus suggesting that the relevant reactions are controlled by diffusion. Compound 5 shows similar voltammetric behaviour to 4. It also showed three one-electron, quasi-reversible reduction waves at  $E_{1/2} = -0.67 \text{ V}$ ,  $E_{1/2} = -1.04 \text{ V}$  and  $E_{1/2} =$ -1.94 V versus SCE (Fig. 3). These reduction processes are probably ligand based since zinc is not redox active in Pc complexes. The first reduction processes of 4 occur at potentials slightly less negative than those of 5. This can be attributed to the difference in the polarizing power of central metal and the hydrogens. The first two ring reduction processes for main group Pcs are generally separated by about 0.4-0.5 V. The third reduction occurs 0.8 V more negative than the second reduction. The separation between the second and the third reductions is smaller with more polarizing ions such as Zn(II) [16]. The redox potentials measured for 4 and 5 are consistent with the general



Fig. 2. Cyclic voltammogram of 4 at  $0.100 \text{ V s}^{-1}$  in DMSO/TBAP solution.



Fig. 3. Cyclic voltammogram of 5 at  $0.100\,V\,s^{-1}$  in DMSO/TBAP solution.

redox characteristics reported previously for similar Pcs. The first ring reduction potentials of 4 and 5 are less negative as compared with those given for unsubstituted Pcs in the literature [16]. This positive potential shift can be attributed to the electron withdrawing effect of the fluorine atoms in 4 and 5. Therefore, it was possible to observe the third reductions for 4 and 5, which cannot be monitored generally. On the other hand, the first oxidation could not be observed for 4 and 5, probably for the same reason, positively shifted potentials.

A typical voltammogram for **6** is shown in Fig. 4. The voltammetric behaviour of **6** is different from those of **4** and **5**. It indicates three one-electron reduction processes at  $E_{1/2} = -0.43$  V,  $E_{1/2} = -0.83$  V and  $E_{1/2} = -1.39$  V versus SCE, and a one-electron oxidation process at  $E_{1/2} = 0.43$  V versus SCE. If the transition metal ion concerned has no accessible d orbital levels lying between the HOMO and LUMO gap of a Pc species, then its redox chemistry

will appear very much like that of a main group Pc species. Nickel, copper, zinc and some other MPcs behave in this fashion, with the M(II) central ion being unchanged as the MPc unit is either oxidized or reduced. However, some species vary their electrochemical behaviour according to their environment, i.e., the oxidation of Co(II)Pc(-2) can lead to  $[Co(III)Pc(-2)]^+$  or  $[Co(II)Pc(-1)]^+$  depending on whether there are any available suitable coordinating species that would stabilize the Co(II) center. Such electrochemistry, especially of Co(II)Pc(-2) and Fe(II)Pc(-2) is split into two sections, that referring to donor solvents and that referring to non-donor solvents. The main difference lies in whether the metal or the ring is oxidized first. Donor solvents strongly favor Co(III)Pc(-2) by coordinating along the axis to form six coordinate species. If such donor solvents are absent, then oxidation to Co(III) is inhibited and ring oxidation occurs first. Thus, the first oxidation and the first reduction processes of 6 are probably metal based and correspond to Co(II)Pc(-2)/[Co(III)Pc (-2)<sup>+</sup> and Co(II)Pc(-2)/[Co(I)Pc(-2)]<sup>-</sup>, respectively, while the second and third reductions are ring based, since the voltammetric measurements were carried out in DMSO/ TBAP.

In order to provide additional support for the identification of the redox processes of **5** and **6**, spectroelectrochemistry of these complexes was also studied. Typical absorption spectra for the neutral **5** and its electrochemically generated species are shown in Fig. 5. Fig. 6a shows the UV-vis spectral changes of complex **5** during the controlled potential reduction of the complex at -0.87 V versus SCE. Upon reduction, a decrease in the absorption of the Q band centered at 700 nm and its broadening towards the red region is observed. This is accompanied by an increase in absorption at the region, 500–600 nm. Isosbestic points are observed at 337, 372, 606 and 732 nm. These spectral changes are characteristic for the formation of Zn(II)Pc(-3) species [17,18]. The well-defined spectral



Fig. 4. Cyclic voltammogram of  ${\bf 6}$  at 0.100 V  $\rm s^{-1}$  in DMSO/TBAP solution.



Fig. 5. UV-vis spectra of **5** and its electrochemically generated reduced species.



Fig. 6. UV-vis spectral changes during (a) the first reduction; (b) the second reduction of **5**.

changes during the second reduction of 5 with an applied potential of -1.40 V versus SCE are shown in Fig. 6b. Similar spectral changes continue with the formation of welldefined isosbestic points at 374, 666 and 730 nm. The appearance of a new broad absorption band with low intensity at 544 nm is also characteristic for ring reduction. The first and second reduction processes were chemically reversible on the spectroelectrochemical time scale and the nearly original spectrum of the neutral compound 5 was obtained upon reoxidation. It could be concluded that the species produced during the first and second reduction processes remained stable throughout the measurement. The final spectra obtained after the controlled potential electrolysis of 5 at -2.10 V versus SCE is given in Fig. 5. Unfortunately, the third reduction process was not chemically reversible on the spectroelectrochemical time scale although it was quasi-reversible during the cyclic voltammetric measurement. Reoxidation of the triply reduced species did not generate compound 5 with its original spectrum. This is probably due to the fact that the third reduction process occurs at considerably negative potentials, and decomposition of the complex may occur when the potential is held constant at a considerably negative potential.

Fig. 7 represents the UV-vis spectra of the neutral 6and its electro-generated species. Fig. 8a shows the UV-vis spectral changes of 6 during its first reduction at -0.70 V versus SCE. The Q band absorption at 673 nm and the intensity of the shoulder at 623 nm decrease, while a new intense band at 480 nm appears and the absorption at the red region of the Q band increases during the controlled-potential electrolysis. This reduction process has well-defined isosbestic points at 393, 568 and 703 nm. The new band at 480 nm is typical for Co(I)Pc(-2) species, and thus suggests that the first reduction of 6 occurs at the metal center [19,20]. Upon reduction at -1.2 V versus SCE, the Q band absorption goes on decreasing without shift, and the absorption of the new band also decreases (Fig. 8b). These spectral changes are accompanied by an increase in the absorption at the red region of the Q band with isosbestic point at 396, 570 and 701 nm, which is characteristic for Pc ring reduction [21]. The spectral changes observed during the third reduction process corresponding to couple III were also typical for ring reduction. The final spectra of the species electrochemically generated after third reduction is shown in Fig. 7. Although the first and second reduction, and the first oxidation processes were chemically reversible, the third reduction process was not reversible on the spectroelectrochemical timescale, and the original species could not be obtained upon reoxidation of the triply reduced species. This is also probably due to decomposition after reduction. Fig. 8c shows the spectral changes during oxidation of 6. The original Q band absorption at 673 nm increases with a clear shift to 683 nm while the absorption of the shoulder at 623 nm decreases slightly and the absorption in the 500-600 nm region increases. These spectral changes result in isosbestic points at 418, 612 and 728 nm, typical of a Co(II)Pc(-2)/Co(III)Pc(-2) redox process [20].



Fig. 7. UV-vis spectra of 6 and its electrochemically generated reduced and oxidized species.



Fig. 8. UV–vis spectral changes during (a) the first reduction; (b) the second reduction; (c) the first oxidation of 6.

#### 3.3. Dc and impedance spectral measurements

To gain more valuable information on the processes taking place in the films, the temperature dependence of the direct current conductivity was examined during heating and cooling processes. Measurements were carried out in an ambient vacuum ( $\leq 10^{-3}$  mbar). In the current–voltage (*I–V*) measurements symmetrical currents at positive and negative polarization as well as an ohmic contact behaviour were found. The conductivity values of the films were calculated from the slopes of the measured I-V characteristics. It was found that the conductivity of the films were reversible for temperature cycling. The measured dc conductivity data of the prepared films were plotted as  $\ln \sigma(T)$ versus 1/T. This plot indicated that the compounds are semiconducting in nature. A linear relationship in conductivity variations are observed for 4-6 in the temperature range 290-440 K. The slopes of these plots are determined and used to evaluate the activation energies and the data are presented in Table 2. The general trend, for the order of electrical conductivities, observed in the whole temperature range for these compounds are  $\sigma_{dc}(2H) >$  $\sigma_{\rm dc}({\rm Co}) \approx \sigma_{\rm dc}({\rm Zn})$ . The observed electrical conductivities of the compounds are found to be  $\sim 10^2$  times higher compared to their parent Pcs. Differences in the order of the electrical conductivities in this case are mainly due to the electron withdrawing effect of fluorine atoms. The electron withdrawing bis(pentafluorophenyl) substituents decreases the separation distance between the Pc macrocycles. The smaller interplanar spacing between the molecules as well as favorable intermolecular stacking are expected to lead to greater overlap between the  $\pi$ -electron orbitals of both macrocycles. This result is significant because it strongly suggests that the overlap of  $\pi$ -electron orbitals plays a major role in the electrical conduction behaviour. The highest conductivity in metal free Pc 4 indicates that the transport of charge carriers is through the ligands, and not through the metal ions.

The trend observed in the ac electrical conductivity was the same as the dc conductivity ( $\sigma_{ac}(2H) > \sigma_{ac}(Co) \approx \sigma_{ac}(Zn)$ ). Fig. 9 shows the dependence of ac conductivity on frequency for the compounds at 350 K. As can be seen from Fig. 9, the frequency has a pronounced effect on the measured ac conductivity. The frequency dependence of the conductivity follow a universal power law for all the compounds [22],

$$\sigma_{\rm ac}(\omega) = A\omega^s \tag{1}$$

where  $\omega$  is the angular frequency, A and the frequency exponent s are material dependent constants. In general, ac conductivities are not equal to dc conductivities. Several mechanisms can be operative for ac conduction in molecular materials. In the case of ac conductivity, the measured conductivity depends not only the conductivity of the material, but also on capacitance. When the impedance of the sample becomes purely resistive the ac conductivity equals the dc conductivity. The interpretation of the

Table 2			
The dc conductivity	and activation	energy values	of the compounds

Compound	$\sigma_{\rm dc290}~({\rm S/cm})$	$\sigma_{\rm dc400}~({\rm S/cm})$	$E_{\rm a}~({\rm eV})$
4	$4.4 \times 10^{-8}$	$1.3 \times 10^{-4}$	0.81
5	$1.6 \times 10^{-9}$	$5.1 \times 10^{-5}$	0.77
6	$1.2 \times 10^{-9}$	$4.0 \times 10^{-5}$	0.78



Fig. 9. The dependence of ac conductivity on frequency for 4-6 at 350 K.

measured ac conductivity data should be focused on the hopping processes. The hopping model, which was developed by Eliot, assumes that charge carriers hop between sites over the potential barrier separating them, rather than tunnelling through the barrier [23]. This model gives an ac conductivity which can be expressed to a first-order approximation as

$$\sigma_{\rm ac}(\omega,T) = \frac{n\pi^3 N^2 \varepsilon \varepsilon_0 \omega}{24} R_{\omega}^6 \tag{2}$$

where  $\varepsilon$  is the dielectric constant of the material,  $\varepsilon_0$  that of free space, N is the spatial density of defect states, n = 1 for a single electron n = 2 for hopping of two electrons and  $R_{\omega}$  is the hopping distance. The temperature dependent frequency exponent s for this model is given by,

$$s = 1 - \beta = 1 - 6k_{\rm B}T/W_{\rm M} \tag{3}$$

where  $W_{\rm M}$  is the optical band gap,  $k_{\rm B}$  is the Boltzman's constant and T is temperature. The variation of frequency exponent, s, with temperature gives information on the specific mechanism involved. The values of s have been calculated from the slope of  $\ln \sigma_{\rm ac}(\omega)$  versus  $\ln \omega$  graphs. Our calculations showed that s is definitely a function of temperature for all compounds. The comparison of the experimentally determined s values with the prediction from the hopping model suggest that the dependence of exponent s on temperature is in agreement with the prediction of the hopping model for these compounds. However, the decrease in frequency exponent s with increasing temperature is not evident for the hopping model. In addition to the behaviour of s, the temperature dependence of the measured ac conductivity has to be considered. Eq. (2) can be rewritten in the form

$$\sigma_{\rm ac}(\omega, T) = BC^{T/Q} \tag{4}$$

where  $C = 1/\omega\tau_0$ , *B* denotes all other temperature-independent parameters and  $Q = W_M/6k_B$ . According to Eq. (4), since *C* and *Q* are independent of the temperature, the



Fig. 10. The temperature dependence of the ac conductivity at a constant frequency of 15 kHz for **4**–**6**.

slope of the  $\ln \sigma_{ac}(\omega, T)$  versus T graph should be constant. Fig. 10 shows the temperature dependence of the measured ac conductivity at constant frequency (15 kHz). The linear relationship between  $\sigma_{ac}$  and T confirms that the charge carrier transport occurs via hopping processes.

### Acknowledgements

This work was supported partly by the Turkish Academy of Sciences (TUBA), The Research Fund of Marmara University (SCIENCE-YYP-290506-0130 and SCIENCE-107/020603) and Scientific and Technical Research Council of Turkey (TUBITAK) [TBAG-HD/50 (105T262)].

### References

- [1] M.J. Cook, J. Mater. Chem. 6 (1996) 677.
- [2] Ö. Bekaroğlu, Appl. Organomet. Chem. 10 (1996) 605, and literature references given therein.
- [3] M. Özer, A. Altindal, A.R. Özkaya, M. Bulut, Ö. Bekaroğlu, Synth. Met. 155 (2005) 222.
- [4] H. Yanagi, N. Tamura, S. Taira, H. Furuta, S. Douko, G. Schnurpfeil, D. Wohrle, Mol. Cryst. Liq. Cryst. 267 (1995) 435.
- [5] T. Manaka, M. Iwamoto, Thin Solid Films 438-439 (2003) 157.
- [6] Z. Bao, A.J. Lovinger, J. Brown, J. Am. Chem. Soc. 20 (1998) 207.
- [7] S. Hiller, D. Schlettwein, N.R. Armstrong, D. Wöhrle, J. Mater. Chem. 8 (4) (1998) 945.
- [8] S. Wie, D. Huang, L. Li, Q. Meng, Dyes Pigments 56 (2003) 1.
- [9] L. Gao, X. Qian, Dyes Pigments 51 (2001) 51.
- [10] T. Sugimori, S. Honike, M. Handa, K. Kasuga, Inorg. Chim. Acta 278 (1998) 253.
- [11] C.C. Leznoff, J.L.S. Sanchez, Chem. Commun. (2004) 338.
- [12] G. Winter, H. Heckmann, P. Haisch, W. Eberhardt, M. Hanack, L. Luer, H.J. Egelhaaf, D. Oelkrug, J. Am. Chem. Soc. 120 (1998) 11663.
- [13] J.G. Young, W. Onyebuago, J. Org. Chem. 55 (1990) 2155.
- [14] D. Wöhrle, G. Knothe, Synth. Commun. 19 (1989) 3231.
- [15] S.K. Shukla, A. Ranjan, A.K. Saxena, Polyhedron 25 (2006) 1415.
- [16] 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, Weinheim, 1993, p. 1.
- [17] J. Obirai, T. Nyokong, Electrochim. Acta 50 (2005) 3296.
- [18] K. Hesse, D. Schlettwein, J. Electroanal. Chem. 476 (1999) 148.

- [19] J. Obirai, N.P. Rodrigues, F. Bedioui, T. Nyokong, J. Porphyr. Phthalocya. 7 (2003) 508.
- [20] M.J. Stillman, T. Nyokong, in: C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, vol.1, VCH Publishers, Weinheim, 1993, Chapter 3.
- [21] K.J. Balkus, A.G. Gabriclov, S.I. Bell, F. Bedioui, L. Roue, J. Deevynck, Inorg. Chem. 33 (1994) 67.
- [22] N.F. Mott, E.A. Davis, Electronic Processes in Non-Crystalline Materials, 2nd ed., Clarendon Press, Oxford, 1979.
- [23] S.R. Elliot, Adv. In. Phys. 36 (1987) 135.