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# Electrochemical and electrical properties of novel mono and ball-type phthalocyanines

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#### ABSTRACT

New mononuclear Co(II) phthalocyanine **3** and ball-type homobinuclear Cu(II)–Cu(II) and Zn(II)–Zn(II) phthalocyanines, **4** and **5** respectively, were synthesized using the corresponding metal salts and the 4,4'-(methane-5-methyl-3-(1-methylcyclohexyl)-2,2'-phenoxy)diphthalonitrile ligand **2**, which was prepared from the reaction of 4-nitrophthalonitrile with bis[2-hydroxy-5-methyl-3-(1-methylcyclohexyl)phenyl]methane (**1**). The novel compounds **3–5** have been characterized using their elemental analysis data and UV–Vis, IR, <sup>1</sup>H NMR and MALDI-TOF mass spectra. The redox properties of the complexes were investigated by cyclic voltammetry in a non-aqueous medium. The electrochemical measurements showed that complex **5** forms a mixed-valence reduction species, due to the strong intra-molecular interactions between the two phthalocyanine rings. Complex **4** displayed Pc ring-based redox signals with very high peak currents, which were attributed to the adsorption of the complex on the working electrode. Dc and ac electrical properties of films of **3**, **4** and **5** were also investigated as a function of temperature (295–523 K) and frequency (40–10<sup>5</sup> Hz). From the dc conductivity measurements, activation energy values of the films were found, being 0.70, 0.66 and 0.68 eV for films of **3**, **4** and **5**, respectively. From impedance spectroscopy measurements, it was observed that the bulk resistance decreases with increasing temperature, indicating semiconductor properties.

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### 1. Introduction

The syntheses and studies of phthalocyanines (Pcs) are among the priorities of modern Pc chemistry due to their various industrial and technological applications, such as pigments and dyes, chemical sensors, photodynamic therapy sensitizers, optical recording and non-linear optical materials, photovoltaics, catalysts, electrochromic materials and electronic device components [1–6].

Ball-type Pcs are a new class of compound, the first of which was reported in 2002 [7,8]. These studies primarily focused on their synthesis and did not make any attempt to investigate their properties. Ball-type Pcs, metal free or containing two homo or hetero-metal centers, have attracted much attention because of their intrinsic properties. These Pcs have four bridged substituents on the peripheral position of each benzene ring which connect two face to face Pc molecules. The chemical and physical characteristic of these compounds vary with the nature of bridging groups, which also determine the distance between the face to face Pc molecules, and the central metals. These Pcs can be tailored to form various types of structures. Our group has published a number of papers on ball-type Pcs with different bridging units in recent years. These compounds showed intrinsic electrochemical, electrical, gas sensing, non-linear optical and catalytic properties [9]. In one of the previous studies [10], pentaerythritol was employed to obtain a ball-type Pc, which allowed us to prepare various novel ball-type Pcs with interesting physical properties [11]. In another study, a compound with four free hydroxyl groups, 1,1,2,2-tetrakis(phydroxy-phenyl)-ethane, was used to obtain a ball-type Pc, resulting in a completely different across adjacent ring formed mono Pc [12]. Some advance reactions showed that the four hydroxyl groups are very functional to obtain unprecedented Pcs. Our continuing effort in the design of novel ball-type Pcs with potential applicability in various technological uses encouraged us to synthesize iron-iron and iron-cobalt centered ball-type Pcs. These compounds showed gas sensing properties and a remarkable electrocatalytic performance towards oxygen reduction [13,14].

In this study, the synthesis and characterization of new mononuclear Co(II) **3** and ball-type homo-dinuclear Cu(II)–Cu(II) **4** and Zn(II)–Zn(II) **5** Pcs linked with four [2,2'-methylenebis-[6-(1-methylcyclohexy)-*p*-methyl-phenoxyphthalonitrile] **2** units





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have been achieved. Their electrochemical and electrical properties were also examined.

## 2. Experimental

### 2.1. Synthesis and characterization

#### 2.1.1. Materials and methods

All reagents and solvents were used as received and were of research grade. The starting material **2** was synthesized by the method described previously in the literature [9]. Melting points were determined with a Sanyo Gallenkamp melting point apparatus using a capillary tube. IR spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer as KBr pellets. Electronic spectra were recorded on a Shimadzu 2450 UV–Vis spectrophotometer. Elemental analyses were performed by the Elementar Vario EL III instrument. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker 500 MHz Ultrashield spectrometer equipped with a 5 mm PABBO BB-inverse gradient probe. The <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported in ppm relative to tetramethylsilane or the deuterated solvent as an internal reference. Spectral splitting patterns are designated as: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

Mass spectra were acquired with the Voyager-DE<sup>TM</sup> PRO MALDI matrix cyano-4-hydroxycinnamic acid (ACCA), prepared in an ethanol:water mixture, 1:1 v/v ratio at a concentration of 10 mg/mL. MALDI samples were prepared by mixing sample solutions (2 mg/mL in a tetrahydrofuran (THF):water mixture, 1:1 v/v ratio, and in some cases, acetic acid was added to increase the solubility) with the matrix solution (1:10 v/v) in a 0.5 mL Eppendorf<sup>®</sup> micro tube. Finally 0.5 µL of this mixture was deposited on the sample plate, dried at room temperature and then analyzed with the MAL-DI-TOF mass spectrometer equipped with a nitrogen UV-laser operating at 337 nm. Spectra were recorded in the reflectron mode with an average of 100 shots.

#### 2.1.2. Synthesis

2.1.2.1. 2,2'-Methylenebis-[6-(1-methylcyclohexyl)-p-cresoylphthalonitrile] (2). A mixture of bis[2-hydroxy-5-methyl-3-(1-methylcy clohexyl)phenyl]methane (1) (1.80 g, 4.00 mmol), 4-nitrophthalonitrile (1.40 g, 8.10 mmol) and anhydrous  $K_2CO_3$  (3.50 g) in 25 mL dry dimethylformamide (DMF) was stirred at 70 °C for 70 h under a N<sub>2</sub> atmosphere. The progress of the reaction was monitored by TLC. After cooling the reaction mixture to room temperature, it was poured into 150 mL cold water and a brown precipitate was obtained. This was filtered off and the presence of two substances in it was determined by TLC. The honey-colored pure product **2** was isolated by column chromatography. Yield 0.75 g (26%). This compound is soluble in chloroform, dichloromethane (DCM), ethyl acetate and DMF. Mp: 117-120 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.63 (d, 2H, J = 8.66 Hz), 7.21 (s, 2H), 7.00 (s, 2H), 6.97 (s, 2H), 6.73 (s, 2H), 3.97 (s, 2H), 2.36 (s, 6H), 1.58–1.31 (m, 20H), 1.05 (s, 6H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 161.12, 150.88, 139.67, 137.49, 135.00, 132.78, 127.71, 127.63, 125.15, 122.83, 118.90, 117.10, 115.26, 109.60, 37.41, 33.92, 31.90, 27.80, 27.47, 22.74, 21.49. IR spectrum (KBr disk, v/cm<sup>-1</sup>): 3075 (aromatic CH), 2926-2856 (aliphatic CH), 2232 (C=N), 1594 (aromatic C=C), 1487, 1247 (Ar-O-Ar), 1200, 1165, 837. Anal. Calc. for C45H44N4O2: C, 80.33; H, 6.59; N, 8.33; O, 4.76. Found: C, 80.37; H, 6.51; N, 8.37; O, 4.71%. MALDI-TOF-MS *m*/*z*: 695 [M+Na]<sup>+</sup>.

2.1.2.2. 23,10,16,24-Tetrakis(2,2'-methylenebis-[6-(1-methylcyclohexyl-5-methyl-phenoxy-phthalonitrile]-p-cresoylphthalocyaninato Co(II) (**3**). A mixture of **2** (0.050 g, 0.074 mmol) and CoCl<sub>2</sub>· $6H_2O$  (0.037 g,

0.155 mmol) was powdered in a quartz crucible, and then transferred to a reaction tube. The mixture was heated for 10 min at 300 °C. After cooling the tube contents to room temperature, the dark-green residue was ground and washed with distilled water to remove excess of cobalt chloride. Finally, the residue was washed repeatedly with hot water, ethanol and acetone. This compound is soluble in DCM, THF, DMF, DMSO and pyridine. Mp >300 °C. Yield: 28 mg (55%). UV–Vis (DCM)  $\lambda_{max}$  (nm) (log $\varepsilon$ ): 323 (4.503), 426.5 (4.373), 455.5 (4.464), 681.5 (4.153). IR (KBr pellet)  $\nu/\text{cm}^{-1}$ : 3072 (aromatic CH), 2954, 2925 and 2862 (aliphatic CH), 2230 (C=N), 1719, 1615, 1606 (aromatic C=C), 1437, 1363, 1311, 1227 (Ar–O–Ar), 1201, 1161, 1120, 1055, 930, 883, 859, 768, 750. *Anal.* Calc. for C<sub>180</sub>H<sub>176</sub>CoN<sub>16</sub>O<sub>8</sub>: C, 78.61; H, 6.45; N, 8.15; O, 4.65. Found: C, 78.55; H, 6.50; N, 8.19; O, 4.60%. MALDI-TOF-MS *m/z*: 2748 (M+H).

2.1.2.3. 2',10',16',24'-Tetrakis[2,2'-methylenebis-(6-(1-methylcyclohexylp-cresoyl]phthalo-cyaninato Cu(II) (**4**). The synthesis of **4** was carried out using the same procedure as in the synthesis of **3**. CuCl<sub>2</sub>·2H<sub>2</sub>O (0.027 g, 0.158 mmol) was used as the copper source. It is soluble in DCM, THF, DMF, DMSO and pyridine. Mp >300 °C. Yield: 13 mg (24%). UV-Vis (DCM)  $\lambda_{max}$  (nm) (log  $\varepsilon$ ): 324 (4.336), 428 (4.693), 455.5 (4.826), 690.5 (3.877). IR (KBr pellet)  $v/cm^{-1}$ : 3073 (aromatic CH), 2954, 2928 and 2864 (aliphatic CH), 1719, 1606 (aromatic C=C), 1454, 1438, 1363, 1227 (Ar–O–Ar), 1200, 1120, 883. Anal. Calc. for C<sub>180</sub>H<sub>176</sub>Cu<sub>2</sub>N<sub>16</sub>O<sub>8</sub>: C, 76.70; H, 6.29; N, 7.95; O, 4.54. Found: C, 76.66; H, 6.31; N, 7.98; O, 4.51%. MALDI-TOF-MS *m/z*: 2815 (M+H).

2.1.2.4. 2',10',16'24'-Tetrakis[2,2'-methylenebis-(6-(1-methylcyclohexylp-cresoyl ]phthalo-cyaninato Zn(II)] (**5**). The synthesis of **5** was carried out using the same procedure as followed for **3**. Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.040 g, 0.182 mmol) was used as the zinc source. It is soluble in DCM, THF, DMF, DMSO and pyridine. Mp >300 °C. Yield: 15 mg (29%). UV-Vis (DCM)  $\lambda_{max}$  (nm) (log  $\varepsilon$ ): 335 (4.418), 623.5 (3.872), 689.5 (4.239). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.28–6.60 (m br, 40H, aromatic), 3.90–0.90 (m br, 136H, aliphatic). IR (KBr pellet)  $\nu/cm^{-1}$ : 3070 (aromatic CH), 2924 and 2855 (aliphatic CH), 1771, 1718, 1614, 1445, 1362, 1311, 1274 (Ar–O–Ar), 1222, 1041, 926, 858, 747. Anal. Calc. for C<sub>180</sub>H<sub>176</sub>N<sub>16</sub>O<sub>8</sub>Zn<sub>2</sub>: C, 76.60; H, 6.29; N, 7.94; O, 4.54. Found: C, 76.57; H, 6.27; N, 7.91; O, 4.57%. MALDI-TOF-MS *m/z*: 2817 (M+H).

#### 2.2. Electrochemical measurements

The electrochemical 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. A platinum disk, a platinum spiral wire and a SCE served as the working, counter and reference electrodes for the cyclic voltammetry measurements. The reference electrode was 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 M. 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 coulometry (CPC) studies, a Pt gauze working electrode (10.5 cm<sup>2</sup> surface area), a Pt wire counter electrode separated by a glass bridge, and a saturated calomel electrode (SCE) as a reference electrode were used. In situ spectroelectrochemical measurements were carried out by an Agilent Model 8453 diode array spectrophotometer equipped with a potentiostat/galvanostat and utilizing an optically transparent thin layer (OTTLE) cell with a three-electrode configuration at 25 °C. The working electrode was transparent Pt gauze, a Pt wire counter electrode and a SCE reference electrode separated from the bulk of the solution by a double bridge were used.

#### 2.3. Electrical characterization

An interdigital transducer (IDT) was employed as transducer in order to investigate the electrical properties of the compounds. The interdigital transducers were fabricated onto a glass substrate. The method for the fabrication of IDTs has been described previously in the literature [15]. The transducer contains 10 finger pairs of gold electrodes with a 100  $\mu$ m width. The space between the electrodes is also 100 µm. In order to obtain thin films of the synthesized compounds, the molecules were dissolved in THF using micro centrifuge tubes. The homogenous solutions were coated onto the IDT using the smearing method. The substrate temperature was kept constant at 295 K during the deposition of the solution onto the IDT. To reveal the electrical properties of the compounds, such as the dc and ac charge transport mechanism and semiconducting behavior, two types of measurements were performed. The first one was the investigation of the dc electrical properties of the compounds, and the second was of the ac properties. To do this, interdigitated gold electrodes coated with the compounds were placed into a home-made temperature controlled aluminum chamber. Electrical contacts between electrodes and measurement chamber were achieved using silver paste. Dc current values were acquired by applying dc voltages between -1 and +1 V with 50 mV steps to the films of the compounds. The data for dc conductivity were acquired using a Keithley model 617 programmable electrometer. Ac conductivity and impedance spectra (IS) measurements were performed using a Keithley model 3330 LCZ meter (40–10<sup>5</sup> Hz). All the electrical measurements were done between the temperatures of 295 and 523 K, in an ambient vacuum ( $<10^{-3}$  mbar) in the dark. The temperature was measured using a Chromel-Alumel thermocouple. Both the dc and ac conductivity data were recorded using an IEEE-488 data acquisition system.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

The starting compound **2** for the syntheses of the targeted Pcs was obtained by the reaction of bis[2-hydroxy-5-methyl-3-(1-methylcyclohexyl)phenyl]methane (**1**) with 4-nitrophthalonitrile in dry DMF in the presence of dry K<sub>2</sub>CO<sub>3</sub> under a N<sub>2</sub> atmosphere. The <sup>1</sup>H NMR, <sup>13</sup>C NMR and IR spectra and elemental analysis were used to characterize **2**. Complexes **3–5** were synthesized by heating **2** with CoCl<sub>2</sub>, CuCl<sub>2</sub> or Zn(OAc)<sub>2</sub> (Scheme 1). The melting points of compounds **3–5** were found to be higher than 300 °C. While the zinc and copper salts yielded ball-type Pcs, the cobalt salt formed only a mono Pc. Characterization of compounds **3–5** involving a combination of methods, including elemental analysis, IR, MAL-DI-TOF-MS and UV–Vis spectra, confirmed the proposed structures for the compounds.

In the FTIR spectrum of **2**, the presence of a C $\equiv$ N group was indicated by the intense stretching band at 2232 cm<sup>-1</sup>. The spectrum also showed an aromatic C–H peak at 3075 cm<sup>-1</sup>, an aliphatic C–H peak at 2926–2856 cm<sup>-1</sup>, an aromatic C=C peak at 1594 cm<sup>-1</sup> and Ar–O–Ar stretching band at 1247 cm<sup>-1</sup>.

A diagnostic feature of Pc formation is the disappearance of the sharp C $\equiv$ N vibration at 2232 cm<sup>-1</sup>. The IR spectra of **4** and **5** showed no C $\equiv$ N vibration band, whereas the IR spectra of **2** and **3** showed this vibration band at 2232 and 2230 cm<sup>-1</sup>, respectively. The rest of the spectra of **3–5** were closely similar to that of **2**. The absence of vibration bands for **4** and **5** is one of the indications for ball-type Pc formation. The IR spectra of Pcs **3–5** showed aromatic C $\equiv$ C (in phenyl rings) peaks at around 1605–1606 cm<sup>-1</sup>, aromatic CH peaks at around 3070–3075 cm<sup>-1</sup> and Ar–O–Ar peaks at around 1220–1275 cm<sup>-1</sup>. In addition, the stretching vibrations at



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**Scheme 1.** Reagents and conditions: (i) K<sub>2</sub>CO<sub>3</sub>, DMF, N<sub>2</sub>, 70 h, 70 °C; (ii) CoCl<sub>2</sub>, N<sub>2</sub>, 10 min, 300 °C; and (iii) CuCl<sub>2</sub> or Zn(OAc)<sub>2</sub>, N<sub>2</sub>, 10 min, 300 °C.

2954–2855 cm<sup>-1</sup> indicated the presence of aliphatic CH groups for Pcs **3–5**.

The <sup>1</sup>H NMR spectra also correlated well with the structures of the synthesized compounds. In the <sup>1</sup>H NMR spectrum of **2**, which was taken in chloroform, the aromatic protons appeared at 7.63 ppm as a doublet (2H), 7.21 ppm as a singlet (2H), 7.00 ppm as a singlet (2H), 6.97 ppm as a singlet (2H) and 6.73 ppm as a singlet (2H). On the other hand, the aliphatic protons appeared at 3.97 ppm as a singlet ( $-CH_2$  bridge protons, 2H), 2.36 ppm as a singlet (aromatic ring  $-CH_3$  protons, 6H), 1.05 ppm as a singlet (aliphatic cyclohexane ring  $-CH_3$  protons, 6H) and as a multiplet in the range of 1.58–1.31 ppm (20H in the cyclohexane rings). For **3** and **4**, <sup>1</sup>H NMR measurements were precluded owing to their



**Fig. 1.** Positive ion and reflectron mode MALDI-TOF-MS spectrum of **3** ( $C_{180}H_{176-}$ CoN<sub>16</sub>O<sub>8</sub>) in  $\alpha$ -cyano-4-hydroxycinnamic acid MALDI matrix using a nitrogen laser (at 337 nm wavelength) accumulating 100 laser shots. Inset spectrum shows the expanded molecular mass region of the complex.

paramagnetic nature. In the <sup>1</sup>H NMR spectrum of **5** in CDCl<sub>3</sub> the peaks are broad when compared with those of **2**. In the <sup>1</sup>H NMR spectrum of **5**, the aromatic protons appeared at 7.28–6.60 ppm (m, 40H, broad) and the aliphatic protons at 3.90–0.90 ppm (m, 136H, broad).

The UV–Vis spectra of **3–5** in DCM showed typical absorptions for Pcs between 666 and 686 nm in the Q-band region. The Qband of each complex was attributed to the transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring. The B-band absorptions in the UV region of 320-340 nm were observed due to the transitions from the deeper levels to the LUMO of all the complexes. The strong absorptions between 425 and 460 nm in the spectra of **3** and **4** arise from ligand metal charge transfer (LMCT) transitions [3]. The spectra of 3-5 showed an additional weak vibrational satellite band at ca. 600 nm. a blue shift from the normal Q-band, as a result of exciton coupling between the Pc units [16]. Depending on the bridged compounds, metals and solvent. the electronic and other properties of Pcs and ball-type Pcs change dramatically. Also the bridged substituents and the distance between the two Pc molecules of the ball-type Pcs affect considerably the degree of the interaction [17]. The intensities of the Q-bands relative to B were low for 3-5, which indicated very strong aggregation of the Pc molecules. It is also known that aggregation is enhanced by the solvent polarity and the presence of aliphatic side chains [3,18–20].

MALDI-MS spectra of all the metal complexes were recorded in  $\alpha$ -cyano-4-hydroxycinnamic acid with better intensity than other novel MALDI matrices (Figs. 1-3). For the high resolution spectra, reflectron mode positive ion MALDI-MS spectra were recorded. High values for the peak intensities could not be obtained in the reflectron mode, but highly resolved MALDI-MS spectra were obtained, which enabled comparisons between the experimental and theoretical isotopic mass distributions, thus confirming the metal complexes in detail. When the mass spectra were recorded in the linear and positive ion mode, more intense signals were obtained, but without resolution. For this reason, all mass spectra reported were obtained in the reflectron and positive ion mode. MALDI-MS spectra for all the complex compounds were evaluated and it was concluded that the compounds were perfectly purified and these metal complexes were more stable under the laser and MALDI-MS conditions in the linear mode mass spectrometer. For all the complexes, a few fragmentation peaks were observed and no other intense ions from impurities were seen in the MALDI-MS spectra. This showed that the complexes were synthesized by the experimental route given.



**Fig. 2.** Positive ion and reflectron mode MALDI-TOF-MS spectrum of **4** ( $C_{180}H_{176}$ - $Cu_2N_{16}O_8$ ) in  $\alpha$ -cyano-4-hydroxycinnamic acid MALDI matrix using a nitrogen laser (at 337 nm wavelength) accumulating 100 laser shots. Inset spectrum shows the expanded molecular mass region of the complex.



**Fig. 3.** MALDI-TOF-MS spectrum of **5** ( $C_{180}H_{176}Zn_2N_{16}O_8$ ) in  $\alpha$ -cyano-4-hydroxycinnamic acid MALDI matrix using a nitrogen laser (at 337 nm wavelength) accumulating 100 laser shots. Inset spectrum shows the expanded molecular mass region of the complex.

#### 3.2. Electrochemistry

The redox properties of 3-5 were examined by cyclic voltammetry and CPC in DMSO/TBAP. A typical voltammogram of 3 is shown in (Fig. 4). It displays an oxidation couple in addition to three reduction processes. The first reduction and the first oxidation couples are one-electron reversible and quasi-reversible processes with half-peak potentials  $(E_{1/2})$  of -0.50 V versus SCE and +0.36 V versus SCE and anodic to cathodic peak separations of 0.060 and 0.120 V, respectively. If the transition metal ion concerned has no accessible d orbital levels between the HOMO and the LUMO energies of a Pc species, then all its redox processes are Pc ring-based. The 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 [21-24]. However, the metal center in some MPcs, such as CoPc, FePc and MnPc, are redox-active due to the presence of d orbital levels within the HOMO-LUMO gap of the Pc species [21,23,24]. These species vary their electrochemical behavior according to their environment in solution and thus their electrochemistry 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



Fig. 4. Cyclic voltammogram of  $5 \times 10^{-4}$  mol dm<sup>-3</sup> 3 at 0.050 V s<sup>-1</sup> in DMSO/TBAP.



Fig. 5. Cyclic voltammogram of  $5 \times 10^{-4}$  mol dm<sup>-3</sup> 5 at 0.050 V s<sup>-1</sup> in DMSO/TBAP.

and ring oxidation occurs first. Thus, the first oxidation and the first reduction processes of **3** are probably metal-based and correspond to  $Co(II)Pc(-2)/[Co(III)Pc(-2)]^+$  and  $Co(II)Pc(-2)/[Co(I)Pc(-2)]^-$ , respectively, since the voltammetric measurements were carried out in DMSO/TBAP. In most cases, the potential difference between the metal-based first reduction and Pc ring-based second reduction processes of a CoPc is approximately 1.00 V [21]. Thus, the possibility of the correspondence of the R2 couple to the reduction of the Pc ring is excluded, and it may be attributed to the reduction of nitrile groups, while the hardly detected (due to its occurrence at very negative potentials) ill-defined R3 couple probably corresponds to the reduction of the Pc ring.

Compound **5** displayed four reductions at  $E_{1/2} = -0.37$ , -0.78, -1.05 and -1.41 V versus a saturated calomel electrode (SCE) in DMSO/TBAP. The CPC studies showed that each redox process involves the transfer of one electron. A typical cyclic voltammogram for **5** at 0.050 V s<sup>-1</sup> is shown in Fig. 5. The CPC studies of the voltammetric couples showed that the number of electrons transferred for each redox process (*p*) is equal to unity. The transfer of one electron in each of the broadly separated steps implies that the reduction of each MPc ring of **5** occurs at different potentials

as stepwise one-electron redox couples of the two cofacial Pc units, as a result of the interaction between them and thus, the splitting of the molecular orbitals. It is clear from the previous studies that the Zn<sup>II</sup> metal center is not redox-active in metallophthalocyanines and thus all the redox processes of **5** are ligand-based [21,23,24]. These processes should be associated with the presence of mixed-valence first- and second-reduced species, [Zn<sup>II</sup>Pc(-2)·Zn<sup>II</sup>-Pc(-3)]<sup>-</sup> and [Zn<sup>II</sup>Pc(-3)·Zn<sup>II</sup>Pc(-4)]<sup>3-</sup>, respectively. The mixed-valence splitting energy,  $\Delta E_s$ , values of the Pc(-2)/Pc(-3) and Pc(-3)/Pc(-4) redox processes in **5** are 0.41 and 0.36 V respectively, indicating remarkable stability of the mixed-valence species. The splitting of a redox process, i.e., Pc(-2)/Pc(-3), for **5**, due to the formation of a stable mixed-valence intermediate, [Zn<sup>II</sup>Pc(-2)·Zn<sup>II</sup>Pc(-3)]<sup>-</sup>, is a measure of the equilibrium (comproportionation) constant,  $K_c$  [21], for a reaction such as:

$$\mathbf{Zn}^{II}\mathbf{Pc}(-3)]_{2}^{2-} + \left[\mathbf{Zn}^{II}\mathbf{Pc}(-2)\right]_{2} \rightleftharpoons 2\left[\mathbf{Zn}^{II}\mathbf{Pc}(-2) \cdot \mathbf{Zn}^{II}\mathbf{Pc}(-3)\right]$$

where the mixed-valence splitting,  $\Delta E_s$  is related to  $K_c$ , via:

$$\Delta E_{\rm s} = (RT/nF)\ln(K_{\rm c}) \tag{1}$$

The values of  $K_c$  obtained for the mixed-valence species of **5**,  $[Zn^{II}Pc(-2)\cdot Zn^{II}Pc(-3)]^-$  and  $[Zn^{II}Pc(-3)\cdot Zn^{II}Pc(-4)]^{3-}$ , are  $8.56 \times 10^6$  and  $1.22 \times 10^6$ . The high  $K_c$  and  $\Delta E_s$  values of **5** give evidence of the delocalization of charge among the cofacial Pc units, and thus the formation of electrochemically reduced mixed-valence species.

Fig. 6 shows the cyclic voltammograms of 4 at various scan rates in DMSO/TBAP. Complex 4 displays two reduction and three oxidation signals. However, the first and second oxidation couples merge into one couple at high scan rates. The voltammetric behavior of **4** is considerably different from that of **5**. First of all, the peak currents of all the redox signals are much higher than those of 5. This implies that complex 4 is adsorbed on the surface of the working electrode. When the voltammograms at different scan rates were recorded with a freshly cleaned electrode and immediately after the freshly cleaned electrode had been immersed into the solution for each scan rate, the peak currents were generally proportional to the scan rate. In addition, when the voltammograms for a given scan rate were recorded with different waiting times after the freshly cleaned working electrode had been immersed into the solution, the peak currents increased with increasing waiting time and constant peak current values were reached in approximately 15 min. These observations provide strong support



**Fig. 6.** Cyclic voltammogram of  $5 \times 10^{-4}$  mol dm<sup>-3</sup> **4** in DMSO/TBAP.



**Fig. 7.** In situ UV–Vis spectral changes monitored during (A) the first reduction (at -0.90 V versus SCE) and (B) the second reduction (at -1.60 V versus SCE) processes of **4** in DMSO/TBAP.

for the idea of adsorption. It is expected that all the redox processes are Pc ring-based since Cu(II) is redox-inactive in metallophthalocyanines. However, the oxidation processes of 4 occur at less positive potentials than those of similar ball-type Pcs involving redox-inactive metal centers [25]. This may be due to the adsorption of **4** on the working electrode since the oxidation potentials of the adsorbed species are expected to be less positive than those of the species in solution. Another possibility is that the irreversible second reduction process R2 is due to demetallation of 4 and the working electrode is plated with metallic copper. Fig. 7 shows the in situ UV-Vis spectral changes observed during the first and second reduction processes of 4. The decrease in the Q band absorption without shift and the formation of a new band at 583 nm during the first reduction process (Fig. 7A), similar changes in the Q band absorption and also the appearance of a new band at 608 nm during the second reduction process (Fig. 7B) confirm that both the first and the second reduction processes are Pc ring-based. Thus, the idea that the second reduction process is related to the demetallation of 4 is excluded.

#### 3.3. Electrical measurements

Dc conductivity studies were done on films of **3**, **4** and **5** in a home-made aluminum chamber. The measurements were

$$\sigma_{\rm dc} = \left(\frac{I}{V}\right) \left(\frac{d}{(2n-1)lh}\right) \tag{2}$$

where (I/V) is slope of the *I*–*V* graph, *d* is the distance between the finger pair, *n* is the number of the finger pair, *l* is the overlap length and *h* is the thickness of the electrodes.

Fig. 8 shows the  $\ln \sigma_{dc} - 1/T$  curves of films of **3**, **4** and **5**. The conductivity of films of **3**, **4** and **5** were found to be  $3.4 \times 10^{-10}$ ,  $9.8 \times 10^{-10}$  and  $3.7 \times 10^{-10}$  S/cm at 295 K, respectively. The conductivity values increased to  $1.6 \times 10^{-5}$ ,  $8.3 \times 10^{-6}$  and  $1.2 \times$  $10^{-5}$  S/cm at 523 K. respectively. As shown in Fig. 8, the lndc conductivities of the films increase with increasing temperature in a linear form. This behavior of lndc conductivity with temperature indicates that the compounds 3, 4 and 5 are semiconductors. Further, the linear relation also shows that the compounds behave as intrinsic semiconductors in the temperature range 295-495 K. After 495 K, the slope of the **4** begins to decrease. It is well known that the structural/compositional lattice defects increases the localized states and that affects the dc conductivity. The change in behavior of the  $\sigma_{dc}$  – 1/T curve after 495 K for the film of **4** may be attributed to the occurrence of a phase transition or the presence of different crystallographic phases [26,27]. The temperature dependence of the dc conductivity can be expressed by the Arrhenius equation (Eq. (3)) [28,29]:

$$\sigma_{\rm dc} = \sigma_0 \exp\left(\frac{-E_{\rm A}}{kT}\right) \tag{3}$$

where  $E_A$  is the activation energy, T is the temperature, k is Boltzmann's constant and  $\sigma_0$  is a pre-exponent factor of dc conductivity. From the slope of straight portions of the curves in Fig. 8, the activation energies were calculated. The values were found as 0.70, 0.66 and 0.68 eV for the films of **3**, **4** and **5**, respectively. The calculated dc conductivity values of the films of **3**, **4** and **5** exhibited the same order of conductivity values as other reports on different Pc films [14]. Our activation energy values were also of the same order of magnitude as activation energy values in other reports on different Pc films, namely 0.6–0.8 eV [14,30].

Ac conductivity studies were also carried out on the films of **3**, **4** and **5** in a home-made aluminum chamber at different temperatures in the temperatures range 295–523 K in an ambient vacuum ( $<10^{-3}$  mbar) in dark, as for the dc conductivity measurements. The ac conductivity measurements were performed in the



**Fig. 8.** The variation of dc conductivity with inverse of temperature for the films of **3**, **4** and **5** between the temperatures of 295 and 523 K.



Fig. 9. Frequency dependence of the ac conductivity of the film of  ${\bf 4}$  between the temperatures of 295 and 523 K.



Fig. 10. Frequency dependence of the ac conductivity of films of 3, 4 and 5 at 523 K.

frequency range  $40-10^5$  Hz. Fig. 9 shows the variation of the ac conductivity of a film of **4** with frequency in the temperature range 295–523 K. The ac conductivity ( $\sigma_{ac}$ ) of the film increases with increasing temperature. The temperature dependence of the ac conductivity of the film can be analyzed in two parts, (i) low temperature region ( $T < \sim 438$  K) and (ii) high temperature region (*T* >  $\sim$ 438 K). In the low temperature region, the conductivity of the film strongly depends on the frequency, with different slopes in different frequency regions. The conductivity of the film increases with increasing frequency in this temperature region. In the high temperature region ( $T > \sim 438$  K) the frequency dependence of the ac conductivity of the film decreases in the measured frequency range for the film of 4. In this region, we observed different a frequency dependence of the ac conductivity for films of 3 and 5 compared to that of film 4. Fig. 10 shows this difference at 523 K. While the slope of the  $\sigma_{\rm ac}$  versus  $\omega$  curves can be analyzed in two different frequency regions  $(40-10^4 \text{ and } 10^4-10^5 \text{ Hz})$  for the film of **4**, the slopes for the films of **3** and **5** can be analyzed in four different frequency regions  $(10-10^2, 10^2-10^3, 10^3-10^4 \text{ and } 10^4-10^4)$  $10^5$  Hz). At temperatures *T* > 438 K, the slope of the curves decreases with increasing temperature in all frequency range measurements for the films of **3** and **5** (except the frequency range of  $40-10^3$  Hz). However, at all temperatures the frequency dependence of the measured ac conductivity of the films obeys the universal power law. The universal power law is given by the Eq. (4) [31]:

$$\sigma_{\rm ac} = A\omega^{\rm s} \tag{4}$$

where  $\omega$  is the angular frequency, and *A* and *s* are material dependent constants. To investigate the conduction mechanism involved,



**Fig. 11.** Temperature dependence of the exponent *s* of films of **3**, **4** and **5** in the high frequency ( $\geq \sim 1$  kHz) region.

the variation of the exponent *s* with temperature was examined. *s* values were calculated from the slope of the straight portions of the  $\sigma_{ac}$  versus  $\omega$  plot.

Calculated values of *s* for the films of **3**, **4** and **5** are around 0.9 at 295 K and decrease to 0.1 at 523 K, and the other *s* values at temperatures between 295 and 523 K are between 0.1 and 0.9. The variation of the *s* values of the films with temperature in the high frequency region ( $\ge \sim 1$  kHz) is given in Fig. 11. As seen from this figure, the *s* values decrease with increasing temperature. According to the band theory, the ac conductivity should be frequency independent and it drops at a sufficiently high frequency. On the contrary to the band model, in the hopping model the electrons in charged defect states hop over the coulomb barrier. This model predicts a frequency under the conductivity, which increases with increasing frequency under the condition that the frequency exponent *s*  $\le$  1 [32]. In the Correlated Barrier Hopping (CBH) model [32], the ac conductivity (first order approximation) is given by:

$$\sigma_{\rm ac} = \frac{1}{24} n\pi^3 N^2 \varepsilon \varepsilon_0 \omega R_\omega^6 \tag{5}$$

where *N* is the spatial density of defect states,  $\varepsilon$  and  $\varepsilon_0$  are dielectric constants of the materials and free space, respectively, n = 1 for a single electron n = 2 for hopping of two electrons and  $R_{\omega}$  is the hopping distance. The hopping distance at the frequency  $\omega$  is given by:

$$R_{\omega} = \frac{e^2}{\pi \varepsilon \varepsilon_{\rm o} [W_{\rm M} - kT \ln(1/\omega \tau_{\rm o})]} \tag{6}$$

The CBH model, which was developed by Elliot [32,33], predicts a temperature-dependent *s* value which is given by:

$$s = 1 - \beta = 1 - \frac{6k_{\rm B}T}{W_{\rm m}} \tag{7}$$

where  $k_{\rm B}$  is Boltzmann's constant,  $W_{\rm m}$  is the binding energy and *T* is temperature. In this model the *s* values decrease with increasing temperature. Our results show that *s* is a function of temperature for all the films and shows a general tendency to decrease with increasing temperature over the measured frequency range at temperatures  $T < \sim 438$  K. The variation of *s* with temperature in the high frequency region ( $\omega \ge \sim 1$  kHz) and the variation of ac conductivity with frequency (Figs. 9 and 11) are in agreement with the prediction of the hopping model. The same type of temperature dependence for *s* was observed in other reports on different Pc films [15,34]. The variation of *s* with temperature in the low frequency region ( $\omega < \sim 1$  kHz) is given in Fig. 12. As can be seen clearly from Fig. 12, while the *s* values decrease with increasing temperature for temperatures  $T < \sim 438$  K, the values increase with increasing temperature for temperatures  $T > \sim 438$  K, except for the film of **4**.



**Fig. 12.** Temperature dependence of the exponent *s* of films **3**, **4** and **5** in the low frequency ( $\leq 1$  kHz) region between the temperatures of 348 and 523 K.

In the quantum–mechanical tunneling (QMT) model [35], the exponent *s* is almost equal to 0.8 and increases slightly with temperature or is independent of temperature. Because of this, the QMT model is not applicable to our results. In the QMT model the *s* values can be calculated using (Eq. (8)) [32]:

$$s = 1 - \frac{4}{\ln(1/\omega\tau_{\rm o})} \tag{8}$$

where  $\tau_o$  is the characteristic relaxation time. According to the overlapping-large polaron tunneling (QLPT) model [33], the exponent *s* is both frequency and temperature dependent and decreases with increasing temperature to a minimum value at a certain temperature, then it increases with increasing temperature. This model is also not applicable to our results. The small polaron quantum mechanical tunneling (SP) model predicts an increase in *s* with an increase in temperature [32,33]. It is also well known that the low values of *s* indicate a multi-hopping process, while high values of *s* indicate a single hopping process.

According to these models, we can conclude that the charge transport mechanism of the film of **4** can be modeled by single hopping over all the measured frequency and temperature ranges. However, the charge transport mechanism for the films of 3 and 5 can be interpreted in two parts. In the low temperature region  $(T < \sim 438 \text{ K})$  the dominant conduction mechanism can be modeled by single hopping over the measured frequency range. In the high temperature region ( $T > \sim 438$  K) the conduction mechanism can be modeled depending on frequency region, (i) high frequency region ( $\omega > \sim 1 \text{ kHz}$ ) and (ii) low frequency region ( $\omega \leq \sim 1 \text{ kHz}$ ). In the high frequency region ( $\omega > \sim 1 \text{ kHz}$ ), the *s* values are between 0.85 and 0.06, and decrease with increasing temperature, but in the low frequency region ( $\omega \leq \sim 1 \text{ kHz}$ ), they increase with increasing temperature (for the films of **3** and **5**). We can conclude that in the high temperature region ( $T > \sim 438$  K) the dominant conduction mechanism for the films of 3 and 5 can be modeled by small polaron tunneling (SP) in the low frequency region and by single hopping in the high frequency region.

To ensure the complete characterization of the electrical properties of the compounds, the impedance spectroscopy technique was used in the frequency range  $40-10^5$  Hz. The impedance data representation is obtained by plotting  $-Z''(\omega)$  (the imaginary component of the impedance) against  $Z'(\omega)$  (the real component of the impedance)  $(Z(\omega) = Z'(\omega) \pm jZ''(\omega))$ , commonly called the Nyquist plot. Fig. 13A and B show the  $Z'(\omega)$  and  $-Z''(\omega)$  components of the impedance data plotted in the complex impedance plane for the film of **4** and Fig. 13C for the film of **5**, recorded at the indicated temperatures (in Fig. 13A the *x*-axis and *y*-axis are not drawn on the same scale to show the behavior of the curves). As seen from



**Fig. 13.** The cole–cole plot at temperatures (A)  $T \le 363$  K for the film of **4** (B)  $T \ge 458$  K for the film of **4** and (C)  $T \ge 458$  K for the film of **5**.

Fig. 13A, the impedance spectra are characterized by the appearance of semicircular shaped arcs for the film of 4 at temperatures  $T \leq 363$  K. The existence of a semicircular shaped curve in the Nyquist plot means that the impedance becomes capacitive, even at high frequencies. The curves can be modeled by a resistor parallel with a capacitor in series with another resistor [34]. Films of 3 and **5** also showed the same behavior at those temperatures. At the temperatures  $T \ge 458$  K, films of **3**, **4** and **5** showed different behavior. Fig. 13B shows the impedance spectra for the film of 4 and Fig. 13C for the film of **5** at temperatures  $T \ge 458$  K. By examining Fig. 13A and B, we can say that the semicircular arcs transform into full semicircles as the temperature rises for the film of 4. With an examination of Fig. 13B, the effect of the temperature on the impedance spectra can be seen clearly. The impedance spectra consist of depressed semicircles with different radii, the radius of a semicircle decreases with increasing temperature.

An ideal semicircle in the complex plane only appears in Debye dispersion relations for a single-relaxation time process. Most of the materials show a pronounced deviation from the Debye treatment, as in our case. In this case, the relaxation time is considered as a distribution of values, rather than a single relaxation time [36]. The depressed semicircles with different radii indicate a deviation from the Debye dispersion relation. Therefore, the equivalent circuit is modified to include a constant phase element (CPE). The series resistance in the equivalent circuit represents ohmic losses in the test fixture and electrode sheet resistance. The parallel resistance is of the coating material in parallel with that of the substrate. The intercepts of the semicircular arcs with the real axis give us information on the bulk resistance of the compounds. From the complex impedance spectra as a function of temperature, it is observed that the bulk resistance decreases with increasing temperature, indicating semiconductor properties. A monotonic decrease in this resistance suggests that the increase of temperature lowers the barrier for charge transport. For the film of **5** at temperatures  $T \ge 458$  K, in addition to Fig. 13B, a straight line was observed in the low frequency region (Fig. 13C). The straight line in the low frequency region indicates the presence of a Warburg component [37]. The complex impedance spectra (Nyquist plots) of the film of **3** at temperatures  $T \ge 458$  K were similar to those in Fig. 13C.

#### 4. Conclusions

The electrochemical measurements of the binuclear ball-type complex **5** showed the formation of electrochemically stable ligand-based mixed-valence reduction species due to intramolecular interactions between the two Pc units and the delocalization of charge amongst the cofacial MPc units. The high mixed-valence splitting values for the Pc(-2)/Pc(-3) and Pc(-3)/Pc(-4) redox couples of **5** suggested that the interactions between the two MPc units in this complex are remarkable.

The Indc conductivities of the films increase linearly with increasing temperature. This behavior of the lndc conductivity with temperature indicates that compounds 3, 4 and 5 are semiconductors. Dc conductivity values of the film of 4 were found to be greater than the other films in the measured temperature range. The calculated activation energy values were found to be 0.70, 0.66 and 0.68 eV for the films of **3**, **4** and **5**, respectively. By examining the ac measurement results, the charge transport mechanism of the film of 4 can be modeled by single hopping all over the measured frequency and temperature ranges. However, the charge transport mechanism for the films of 3 and 5 can be interpreted in two parts. In low temperature region ( $T < \sim 438$  K) the dominant conduction mechanism can be modeled by single hopping over the measured frequency range. In the high temperature region  $(T > \sim 438 \text{ K})$  the dominant conduction mechanism for the films of **3** and **5** can be modeled by small polaron tunneling (SP) in the low frequency region and by single hopping in the high frequency region. From impedance spectra results, it is observed that the bulk resistance of all the compounds decreases with increasing temperature, indicating semiconductor properties.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.09.048.

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