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Synthesis, characterization and investigation of electrical and electrochemical properties of imidazole substituted phthalocyanines

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ABSTRACT

Compound **1** has been synthesized by the reaction of 4-nitrophthalonitrile and 4,5-diphenyl-1*H*-imidazolethiole in DMSO in the presence of K₂CO₃. Compound **2** has been synthesized by heating compound **1** with metallic lithium in pentanol and hydrolyzed with hydrochloric acid (10%) and then neutralized with ammonia solution. Compound **3** and **4** have been synthesized by heating **1** with ZnCl₂ or CoCl₂ in DMF in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), respectively. The new compounds were obtained in sufficient purity after successive washing with different solvents and were characterized by elemental analysis, ¹H NMR, ¹³C NMR, UV–vis, IR and mass spectra. We also studied aggregation behavior, electrochemical and electrical properties of these phthalocyanines. Direct current (dc) and alternating current (ac) conductivity (40–100 kHz) measurements of films of **2**, **3** and **4** were performed in the temperature range of 295–523 K. Impedance spectra (IS) of the **2**, **3** and **4** were also studied. The conduction processes were discussed. Temperature dependence of dc conductivity of the films revealed that **2**, **3** and **4** show a semiconductor behavior. Results of ac measurements showed that, conduction processes of the films of the complex consisted of different mechanisms depending on temperature and frequency.

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1. Introduction

Phthalocyanines are the most studied compounds in supramolecular chemistry [1–5]. They have been used in very different areas of technology and medical applications, i.e., gas sensor [1,6,7], liquid crystal [2,8], solar cell [9,10], catalyst [2,5,11], electrochromic display [3,12], photodynamic therapy of cancer [13,14]. Phthalocyanine has been studied with many metal ions and different substituents on peripheral (β) and non-peripheral (α) positions [1–5]. The synthesis and properties of binuclear double decker, binuclear clamshell, polynuclear and dendritic phthalocyanine have also been reported [4,15,16]. As a new class of phthalocyanine, ball-type phthalocyanine has been studied during the last years [17].

On the other hand, imidazole substituted porphyrin have been used and investigated optical, electronic and catalytic properties [18–24]. Imidazole or benzimidazole substituted phthalocyanines

have been reported in a few articles [25–29]. Some of these phthalocyanines were used in photodynamic therapy [26], electron transfer processes [28] and synthesis of the phthalocyanine polymers [27,29]. Therefore, synthesis and investigation some properties of new 4,5-diphenyl-1*H*-imidazole substituted phthalocyanine could be worthwhile.

In present work, we reported synthesis and characterization of bisphenylimidazole substituted metal-free, zinc(II), cobalt(II) phthalocyanines. We also investigated aggregation behavior, electrical and electrochemical properties of these phthalocyanines.

2. Experimental

All reactions were carried out under argon atmosphere and all solvents were dried by molecular sieves or proper methods [30]. 4-Nitrophthalonitrile was prepared according to the literature [31]. IR and UV–vis spectra were recorded on an ATI Unicam-Mattson 1000 spectrophotometer using KBr pellets and Shimadzu UV–vis spectrometer, respectively. Elemental analysis were performed on LECO CHNS 932 and at Tubitak Ankara Testing and Analysis Laboratory (ATAL). ¹H NMR and ¹³C NMR spectra were



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obtained by using a Bruker 300 MHz spectrometer. Mass spectra were acquired on a Voyager-DE[™] PRO MALDI-TOF mass spectrometer (Applied Biosystems, USA) equipped with a nitrogen UV-Laser operating at 337 nm. Spectra were recorded in reflectron modes with an average of 100 shots.

2.1. Synthesis of compounds

2.1.1. 4[(4,5-Diphenyl-1H-imidazole)-2-yl-thio]phthalonitrile (1)

The 4-nitrophthalonitrile (653.0 mg, 3.77 mmol) and 4,5-diphenyl-1H-imidazolethiole (1.0 g, 3.96 mmol) were dissolved in DMSO (45 mL). Anhydrous potassium carbonate (782.0 mg, 5.66 mmol) was added to the reaction solution over period of 2 h with efficient stirring. The reaction mixture was stirred at room temperature for 5 days. Then the mixture was poured into solution of salt-water (1%), and the precipitate was filtered off, washed with water and dried in Vacuum oven at 40 °C. The crude product was dissolved in diethyl ether (300 mL) and filtered off. The ether solution was cooled at -18 °C, the precipitate was filtered off and dried in vacuum. The white solid was soluble in acetone, chloroform, EtOH, MeOH and THF. Yield 600.0 mg (42%). Mp 131 °C. ¹H NMR (300.13 MHz, Aceton- d_6 , 25 °C): δ = 12.5 (s, 1H, Im-NH, disappeared on D₂O addition); 8.0-7.9 (m, 2H, Ar-H); 7.8-7.7 (dd, 1H, Ar-H); 7.6–7.3 (m, 10H, Ar-H). ¹³C NMR (75.03 MHz, DMSO-d₆, 25 °C): δ = 145.31; 134.93; 132.34; 131.20; 131.16; 129.02; 128.12; 116.36; 115.95; 115.88; 111.95. UV-vis (DMF) λ_{max}/nm $(\log \varepsilon, dm^3 mol^{-1} cm^{-1})$ 285 (5.23). IR (KBr pellet) v (cm⁻¹) 3057; 3022; 2974; 2861; 2233; 1676; 1583; 1072; 738. Anal. Calc. for C₂₃H₁₄N₄S: C, 72.99; H, 3.73; N, 14.80; S, 8.47%. Found: C, 72.88; H, 3.61; N, 14.40; S, 8.34%.

2.1.2. [2,9,16,23-tetra{(4,5-Diphenyl-1H-imidazole)-2-yl-thio}phthalocyanine] (**2**)

Lithium metal (18.0 mg, 2.6 mmol) was heated to dissolve in pentanol (4 mL) and allowed to cool to room temperature. Compound 1 (100 mg, 0.26 mmol) was added to the above solution and was heated at 180 °C for 4 h. After cooling down to room temperature, the reaction mixture was diluted with THF (5 mL) and hydrolyzed with the hydrochloric acid (10%) and stirred at room temperature for 5 h and then neutralized with ammonia solution. This mixture was precipitated by addition of MeOH (5 mL) and filtered off and washed with water $(3 \times 5 \text{ mL})$ and MeOH $(3 \times 5 \text{ mL})$, respectively, and dried in vacuum. The dark green compound was washed in a soxhlet apparatus with acetone. Finally, the dark green compound was dissolved in a soxhlet apparatus with chloroform. The organic phase was concentrated and precipitated by addition of diethyl ether, filtered off and dried in vacuum. The metal-free phthalocyanine was soluble in chloroform, THF, DMF and DMSO. Yield 50.0 mg (50%). Mp >300 °C. ¹H NMR (300.13 MHz, DMSO d_6 , 25 °C): δ = 14.0 (br s, 4H, Im-NH, disappeared on D₂O addition); 9.0-7.0 (br m, 52H, Ar-H); -5.1 (br s, 2H, Pc-NH, disappeared on D_2O addition). MS (MALDI-TOF) m/z: 1515 $[M+H]^+$. UV-vis (DMF) $\lambda_{\text{max}}/\text{nm}$ (log ε , dm³ mol⁻¹ cm⁻¹) 710 (4.76), 681 (4.77), 650 (4.57), 616 (4.39), 345 (4.67), 295 (4.75). IR (KBr pellet) v (cm⁻¹) 3418; 3297; 3055; 3027; 1603; 1445; 1015; 764; 696. Anal. Calc. for C₉₂H₅₈N₁₆S₄: C, 72.90; H, 3.86; N, 14.78; S, 8.46%. Found: C, 72.24; H, 3.75; N, 14.30; S, 8.51%.

2.1.3. [2,9,16,23-tetra{(4,5-Diphenyl-1H-imidazole)-2-yl-thio}phthalocyaninato-zinc(II)] (**3**)

Mixtures of **1** (100.0 mg, 0.26 mmol) and $ZnCl_2$ (8.3 mg, 0.06 mmol) in DMF (3 mL) was heated at the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), at 180 °C for 8 h. After cooling, the mixture was precipitated by addition of diethyl ether, filtered off and dried in vacuum. The crude residue was washed with water (3× 5 mL) and MeOH (3× 5 mL), respectively. It was dried in vacuum. The dark green compound was washed in a soxhlet apparatus with acetone. Finally, the dark green compound was dissolved in a soxhlet apparatus with THF. The organic phase was concentrated and precipitated by addition of diethyl ether and filtered off. It was dried in vacuum. The dark green solid was soluble in THF, DMF and DMSO. Yield 30.0 mg (37%). Mp >300 °C. ¹H NMR (300.13 MHz, DMSO-*d*₆, 25 °C): δ = 13.7 (br s, 4H, Im-NH, disappeared on D₂O addition); 9.5–7.4 (br m, 52H, Ar-H). MS (MALDI-TOF) *m/z*: 1577 [M+H]⁺. UV–vis (DMF) λ_{max}/nm (log ε , dm³ mol⁻¹ cm⁻¹) 687 (5.16), 620 (4.52), 354 (4.81), 288 (4.99). IR (KBr pellet) v (cm⁻¹) 3395; 3057; 3031; 1602; 1487; 1098; 765; 697. *Anal.* Calc. for C₉₂H₅₆N₁₆S₄Zn: C, 69.97; H, 3.57; N, 14.19; S, 8.12%. Found: C, 70.18; H, 3.71; N, 14.33; S, 7.68%.

2.1.4. [2,9,16,23-tetra{(4,5-Diphenyl-1H-imidazole)-2-ylthio}phthalocvaninato-cobalt(II)] (**4**)

Mixtures of **1** (100.0 mg, 0.26 mmol) and CoCl₂ (8.0 mg, 0.06 mmol) in DMF (3 mL) were heated at the presence of DBU at 180 °C for 12 h. After cooling, the green-blue product mixture was precipitated and purified with used the same procedure explained for **3**. The dark green solid was soluble in THF, DMF and DMSO. Yield 25.0 mg (31%). Mp >300 °C. MS (MALDI-TOF) *m/z*: 1571 [M+H]⁺. UV-vis (DMF) λ_{max}/nm (log ε , dm³ mol⁻¹ cm⁻¹) 674 (5.00), 607 (4.50), 316 (4.98). IR (KBr pellet) v (cm⁻¹) 3426; 3059; 3028; 1603; 1446; 1103; 765; 696. Anal. Calc. for C₉₂H₅₆N₁₆S₄Co: C, 70.26; H, 3.59; N, 14.25; S, 8.16%. Found: C, 69.95; H, 3.70; N, 14.02; S, 8.57%.

2.2. MALDI sample preparation

MALDI matrices, α -cyano-4-hydroxycinnamic acid (CHCA) were prepared in THF at a concentration of 10 mg/mL. MALDI samples were prepared by mixing sample solutions (4 mg/mL in THF) with the matrix solution (1:10 v/v) in a 0.5 mL Eppendorf[®] micro tube. Finally 1.0 μ L of this mixture was deposited on the sample plate, dried at room temperature and then analyzed.

2.3. Electrochemistry

Electrochemical grade tetrabutylammonium tetrafluoroborate (TBAFB) (Fluka) was used as the supporting electrolyte in voltammetric measurements in non-aqueous solvents. Cyclic voltammograms (CV) and square wave voltammograms (SWV) were carried out using a Gamry Reference 600 Potentiostat/Galvanostat/ZRA. A three electrode system was used for CV and SWV measurements in DMF consisting of glassy carbon working electrode, and a platinum wire counter and platinum wire quasi-reference electrode. The ferrocene/ferrocenium couple (Fc/Fc⁺) was used as an internal standard and their potentials were reported with respect to Fc/Fc⁺ in non-aqueous solutions. Square wave voltammetric analysis was carried out at the frequency of 5 or 10 Hz, amplitude of 40 mV and step potential of 4 mV. High purity argon is used for the de-oxygenation of the cell at least 10 min prior to electrochemical measurements and the solution was protected from air by a blanket of argon during the experiments.

2.4. Electrical characterization

2.4.1. Preparation of films

Electrical measurements were performed using Interdigitated electrodes (IDTs). IDTs were fabricated onto glass substrates. Gold was selected as electrode material. Width and space between the electrodes were 100 μ m. In order to fabricate IDTs with gold electrodes, glass substrates were cleaned in acetone, isopropyl alcohol and DI-water in ultrasonic cleaner and dried with pure nitrogen blow. Cleaned glasses were placed in thermal evaporation system

and chromium and gold metals were evaporated through the glass substrates in high vacuum ambient ($<2 \times 10^{-6}$ mbar) using Edwards Auto 500 coater system. Thicknesses of the evaporated metals were 100 and 1000 Å for chromium and gold, respectively. Interdigital transducer pattern was obtained using photolithography techniques. In order to coat the synthesized molecules onto IDT, the molecules were dissolved in THF. The homogeny solutions were coated onto IDT using smearing method. The substrate temperature was kept constant at 295 K during the deposition of solution onto IDT.

2.4.2. Electrical measurements

Electrical measurements of the films were performed in two parts. (i) Direct current (dc) measurements. (ii) Alternating current (ac) measurements. Dc and ac properties of the films were determined in temperature controlled measurement chamber under vacuum ambient ($<10^{-3}$ mbar) in dark. Dc conductivity measurements were performed between the voltages of -1 and 1 V at different temperatures using Keithley model 617 Programmable Electrometer. Ac conductivity and impedance spectra (IS) measurements were performed using Keithley model 3330 LCZ meter ($40-10^5$ Hz). Measurements were done between the temperatures of 295–523 K. Both dc and ac conductivity data were recorded using an IEEE-488 data acquisition system.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis route of compounds 1-4 is summarized in Scheme 1. The starting compound, 1, was synthesized by the reaction of 4-nitrophthalonitrile and 4,5-diphenyl-1*H*-imidazolethiole in DMSO in the presence of K₂CO₃. The metal-free phthalocyanine, **2**, was synthesized by heating compound **1**, with metallic lithium in pentanol and hydrolyzed with hydrochloric acid (10%) and then neutralized with ammonia solution. Metal-containing phthalocyanines, **3** and **4**, were synthesized by heating compound **1**, with ZnCl₂ or CoCl₂ in DMF at the presence DBU, respectively (Scheme

1). UV-vis, ¹H NMR, ¹³C NMR, IR and mass spectra confirmed the proposed structure of all new compounds. The elemental analysis of the result of starting material and phthalocyanine complexes shows good agreement with calculation values.

The characteristic vibration of the $-C \equiv N$ group appear at 2233 cm⁻¹ as a single peak in the IR spectrum of compound **1**. This peak disappeared in spectrum of **2**, **3** and **4** after reaction of tetramerization. In addition, the IR spectrum of metal-free phthalocyanine, NH group inner was given an absorption at 3297 cm⁻¹ [3]. The vibration peak of imidazole NH in compound **1** appears between 3057 and 2861 cm⁻¹ which is attributed to the formation of intermolecular hydrogen bonds [5,18,20]. The IR spectra of phthalocyanine compounds **2**, **3** and **4** are shown at 3055, 3027, 3057, 3031 and 3059, 3028 cm⁻¹, respectively, peaks for NH group.

¹H NMR spectra were in good correlation with the structure of the synthesized compounds. In the ¹H NMR spectrum of compound **1** which was taken in Acetone- d_6 at room temperature, the aromatic protons appeared at 8.0–7.9 ppm (m), 7.8–7.7 ppm (dd), 7.6–7.3 (m) and imidazole –NH proton appeared at 12.5 ppm (s). NH peak disappeared on addition of D₂O. ¹³C NMR spectra were in good correlation with the structure of the compound **1**.

¹H NMR spectra of compounds **2** and **3** were taken in DMSO- d_6 at room temperature. The spectra of the **2** and **3** were almost the same, showed aromatic protons at 9.4–7.0 ppm as a broad multiplet. The NH protons of imidazole at compounds **2** and **3** appeared at 14.0 and 13.7 ppm broad singlet which disappeared with D₂O exchange. ¹H NMR measurement was precluded due to the paramagnetic nature of compound **4** [3].

The UV–vis spectra of **2–4** in DMF showed typical absorptions between 600 and 700 nm in the Q band region (Fig. 1).

The Q band absorptions of the compounds refer to the $\pi \rightarrow \pi^{*}$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring. The B band absorptions of the compounds were observed within the UV region between 300–350 nm due to the transitions from the deeper π levels to the LUMO [1]. The UV-vis spectrum of **2** in DMF gives four absorptions at 710, 681, 650 and 616 nm (shoulder) in Q band region and at 295 and 345 nm



Scheme 1. Synthesis of tetrasubstituted phthalocyanines, 2, 3, 4 (i) K₂CO₃, DMSO; (ii) (2) Li, pentanol, hydrolyzed with hydrochloric acid (10%) and then neutralized with ammonia solution. (3, 4) ZnCl₂ or CoCl₂, DBU, DMF.



Fig. 1. UV-vis spectra of **2** (-), **3** (---) and **4** (....) in DMF (*C* = 10⁻⁵ mol dm⁻³).

in B band region. Compound **2** showed aggregation. Aggregation is usually depicted as a coplanar association and is dependent of the concentration [32]. In the aggregated state, the electronic structure of phthalocyanine ring is perturbed resulting in alternation of the ground and excited state electronic structures [33]. This causes broadening and/or the split of the Q band, especially at high concentrations. The similar intensity of the Q and B band of **2** (Fig. 1) also due to the splitting of the Q band as a result of the lowering of molecular symmetry [34,35]. The aggregation behavior of **2–4** was investigated at different concentration (from 2×10^{-6} to 10×10^{-6} mol dm⁻³) in DMF (Fig. 2).

At higher concentration the aggregation was observed in compound **2**. There is no aggregation of compounds **3** and **4** at different concentrations in DMF.

3.2. Electrochemistry

The voltammetric measurements of the **2**. **3** and **4** were carried out on glassy carbon (GC) electrode in DMF, TBAFB as supporting electrolyte by cyclic voltammetry (CV) and Osteryoung square wave voltammetry (SW). A wider potential range (-2.6 to +1.1 V versus Fc/Fc⁺) was used to study electrochemical properties of all the phthalocyanine compounds. The relevant data are given in Table 1 which also includes selected data from the literature for the related compounds. The phthalocyanine complexes can undergo multiple one-electron reduction and oxidation of the conjugated macrocycle to yield anion and cation radicals, respectively. In main group phthalocyanines the redox activity is directly associated with the oxidation by the removal of the electrons from HOMO, while up to four additional electrons can be added to LUMO of phthalocvanines [3]. With the redox active metals, the oxidation and the reduction of the metal occur between the oxidation and reduction of the phthalocyanine ring such as cobalt, chromium, manganese and iron phthalocyanines.

The cyclic and square wave voltammograms of **2**, **3** and **4** are shown in Figs. 3–5, respectively. The potential values and assignments are summarized in Table 1. CV and SW voltammetric studies showed that all the phthalocyanine compounds have similar well-defined ring based redox couples up to four reductions and two oxidations labeled R_1 , R_2 , R_3 , R_4 , O_1 and O_2 .

The redox properties of **2** and **3** showed good electrochemical processes with up to two well-separated oxidation and up to four reduction waves (Figs. 3 and 4). The oxidation processes of **2** are *quasi*-reversible as can be seen from Fig. 3. The ratio of cathodic peak current to anodic peak current (i_c/i_a) is less than 1 in all of the observed redox processes.



Fig. 2. UV-vis spectra of **2** in different concentrations $(10 \times 10^{-6} (-), 8 \times 10^{-6} (---), 6 \times 10^{-6} (---), 4 \times 10^{-6} (----), 2 \times 10^{-6} (...) mol dm⁻³).$



Fig. 3. Cyclic and square wave (inset) voltammograms of 2 in DMF containing 0.1 M TBAFB, scan rate 50 mV s⁻¹.

Redox potentials of 2 , 3	4 and selected	phthalocyanines	compounds

Table 1

Compound	Solvent/supporting electrolyte	RE	02	01	R ₁	R ₂	R ₃	R ₄	ΔE_1	Ref.
2	DMF/TBAFB	Fc/Fc ⁺	0.55	0.34	-1.10	-1.44	-1.94	-2.37	1.44	tw
3	DMF/TBAFB	Fc/Fc ⁺		0.42	-1.13	-1.51	-1.94		1.59	tw
4	DMF/TBAFB	Fc/Fc ⁺	0.51	0.10	-0.75	-1.09	-1.79	-2.46	0.85	tw
H ₂ Pc	DCM/TBAP	SCE	1.14	0.82	-0.72	-0.90	-1.76		1.54	[42]
ZnPc	DCM/TBAP	SCE		0.85	-0.67	-0.98	-1.76		1.52	[43]
CoPc	DMF/TBAFB	Fc/Fc ⁺	0.44	0.01	-0.88	-2.02	-2.43		0.89	[44]

RE, reference electrode, $\Delta E_1 = O_1 - R_1$, at 10 Hz, 40 mV amplitude and 4 mV step potential; tw, this work.



Fig. 4. Cyclic and square wave (inset) voltammograms of **3** in DMF containing 0.1 M TBAFB, scan rate 50 mV s⁻¹.



Fig. 5. Cyclic and square wave (inset) voltammograms of **4** in DMF containing 0.1 M TBAFB, scan rate 50 mV s⁻¹.

Fig. 3 represents the CV and SW voltammogram of **2** displaying six redox processes, assigned to the phthalocyanine ring oxidation and reduction, labeled O_1 , O_2 , $R_1 R_2$, R_3 and R_4 . The first and the second oxidation waves were observed at 0.34 and 0.55 V and the reduction waves appeared at -1.10, -1.44, -1.94 and -2.37 V, respectively, at .050 V s⁻¹ scan rate. SW voltammogram of **2** suggest that all six redox processes have *quasi*-reversible character. The separation of the first reduction and the first oxidation processes (1.44 V) reflects the HOMO–LUMO gap of the metal-free phthalocyanine complexes and is comparable to the literature. The separation between the first reduction and the second ring reductions (ΔE_1) was found to be approximately 0.30–0.45 V and is in agreement with the reported separation of the redox processes of the reported phthalocyanine compounds [3].

The complex **3** gives (Fig. 4) three one-electron reduction and one electron-oxidation processes labeled $R_1 = -1.13$, $R_2 = -1.51$, $R_3 = -1.94$ and $O_1 = 0.42$ V versus Fc/Fc⁺ at 0.050 V s⁻¹ scan rate (Table 1). Since Zn is a redox inactive metal in the working condition, all the observed oxidation and reduction processes are all phthalocyanine ring based processes. The reduction of the phthalocyanine ring is associated with the position of the LUMO and oxidation is associated with the HOMO of the phthalocyanine

complex. Thus the difference between the potentials of the first oxidation and the first reduction processes ΔE_1 reflects the HOMO-LUMO gap of the metal-free phthalocyanines and it is closely related to the HOMO-LUMO gap of MPc species involving a redox inactive metal center. ΔE_1 and the first and the second reduction ($R_2 - R_1 = 0.38$ V) of **3** is comparable with the reported literature [3].

The compound 4 showed (Fig. 5) both the oxidation and reduction waves of metal center and phthalocyanine ring, labeled O₁ and O₂ and R₁, R₂, R₃ and R₄, with in the electrochemical window of DMF containing 0.1 M TBAFB. The first reduction and first oxidation processes are metal based in polar coordinating solvents, which is a well-known electrochemical behavior of CoPc complexes in coordinating solvents such as DMF and DMSO [36]. Therefore R_1 (-0.75 V) and O_1 (0.10 V) can be attributed to successive addition and removal of one electron to metal based orbitals of the phthalocyanine complex [37–39]. Three reductions waves labeled R_2 , R_3 and R_4 , at -1.09, -1.79 and -2.46 V with the oxidation wave labeled O₂ at 0.51 V are assigned to the ring based reduction and oxidation of the phthalocyanine, respectively. The separation between the reduction and oxidation peak potentials and the variation of the peak potentials with the scan rate for all the processes lies between 70 and 160 mV, showing their reversible or quasireversible nature. The peak currents increased linearly with the square root of the scan rates ranging from 0.050 to 0.400 V s^{-1} , indicating diffusion-controlled behavior [40]. Therefore the first oxidation and the first reduction of 4 could be assigned to $Co^{II}(Pc^{-2})/Co^{III}(Pc^{-2})$ (O₁), $Co^{II}(Pc^{-2})/Co^{I}(Pc^{-2})$ (R₁), redox couples and the second, third and fourth reductions and the second oxidation processes are phthalocyanine ring based and assigned to $Co^{I}(Pc^{-2})/Co^{I}(Pc^{-3})$ (R₂), $Co^{I}(Pc^{-3})/Co^{I}(Pc^{-4})$ (R₃), $Co^{I}(Pc^{-4})/CO^{I}(Pc^{-4})/CO^{I}(P$ $Co^{I}(Pc^{-5})(R_4)$ and $Co^{III}(Pc^{-1})/Co^{III}(Pc^{-2})(O_2)$, respectively. The separation between the reduction and oxidation processes of metal center $(O_1 - R_1 = 0.85 \text{ V})$ which reflects the HOMO-LUMO gap of the complex, is comparable with the reported cobalt phthalocyanine complexes [41]. The electrochemical reactions corresponding to all waves in the voltammograms are stepwise one electron process. The ratios of the anodic to cathodic peak currents $(i_1 \text{ to } i_c)$ for couples for all the waves except the first oxidation are close to unity, suggesting a reversible/quasi-reversible redox process but the first oxidation wave is an irreversible. There is an irreversible oxidation wave before the first oxidation wave (labeled A) shown in Fig. 5 which disappears with increasing scan speed, that could be assigned to five or six coordinated phthalocyanine complex, extra ligand coming from donor solvent molecule DMF [3].

3.3. Electrical properties

3.3.1. Dc properties

Dc conductivity studies were done on the films of **2**, **3** and **4** in temperature controlled vacuum ambient ($<10^{-3}$ mbar) in dark. Measurements were done between the voltages of -1 and 1 V at different temperatures between 295 and 523 K. Current values passing through the films were recorded versus applied voltages (*I*–*V* curves). Dc conductivity of the films was determined using Eq. (1) and the slope of the *I*–*V* curves.

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

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

Fig. 6 shows the variation of dc conductivities of the films of **2**, **3** and **4** with temperature. Conductivity of the film **2** and **3** was found as 6.7×10^{-11} and 1.0×10^{-10} S/cm at 295 K, respectively. The



Fig. 6. Temperature dependence of the dc conductivity for the films of 2, 3 and 4 between the temperatures of 295–523 K.

conductivity values increased to 5.7×10^{-7} and 6.6×10^{-7} S/cm at 523 K, respectively. Dc conductivities of the **2** and **3** increase with increasing temperature at the temperatures T < 378 K and $T \ge 438$ K. Conductivity of the **4** was found as 9.6×10^{-11} S/cm at 295 K and increased to 5.6×10^{-6} S/cm at 523 K. Generally, dc conductivity of the film **4** increases with increasing temperature. The results indicate that conductivity values of the **2** and **3** are nearly equal at the same temperatures in the measured temperature range. Film of **4** has also nearly equal conductivity values up to 378 K with **2** and **3**. After this temperature **4** has higher conductivity than that of **2** and **3**.

As seen from Fig. 6, dc conductivity behavior of the film **2** and **3** can be analyzed in three different temperature regions (I, II and III). In the first region (T < 378 K), conductivity increases linearly with increasing temperature then in the second region (378 K < $T \le \sim 438$ K) it begins to decrease. In the third region ($T \ge \sim 438$ K), linear increase in the conductivity with temperature is observed again. This behavior may be observed due to absorption of oxygen by coated films during the deposition of the films onto IDT. Similar behavior was reported for some organic molecules. The authors have ascribed this behavior to exhaustion of absorbed oxygen [45,46].

The linear relationship between the Ln dc conductivity and inverse of temperature (Arrhenius plot) shows that the films of **2**, **3** and **4** behave as intrinsic semiconductor in the third region. For the first region, behavior of Ln dc conductivity with inverse of temperature can be interpreted as extrinsic semiconductor behavior due to interpretations as mentioned above. The linear behavior indicates that the temperature dependence of dc conductivity of the film can be represented by the well-known expression (Eq. (2)) for conductivity [16].

$$\sigma_{\rm dc} = \sigma_0 \exp\left(\frac{-E_{\rm A}}{kT}\right) \tag{2}$$

where E_A is activation energy, T is temperature, k is Boltzmann's constant and σ_0 is a constant of proportionality. The activation energy values of the films which are determined from the slope of the Ln conductivity versus 1/T graph were given in Table 2. Calculated dc conductivity values of the films of **2**, **3** and **4** exhibited same or-

Table 2 Activation energies of the films for two different regions (E_{A1} for T < 378 K, E_{A2} for $T \ge \sim 438$ K).

Film	E_{A1} (eV)	
2	0.86	0.83
3	0.86	0.75
4	0.80	0.77

der of conductivity values with other reports in different phthalocyanine films such as ${\sim}10^{-12}$ S/cm at 300 K and ${\sim}10^{-8}$ S/cm at 470 K [47], and ' 10^{-12} to $\sim 10^{-6}$ S/cm between 300 < T < 400 K [48], $\sim 10^{-7}$ S/cm between 370 < T < 470 K [49]. Our activation energy values also exhibited same order of activation energy values with other reports in different phthalocyanine films such as 0.6-0.8 eV [47]. The activation energies E_{A1} corresponding to the region I is associated with a short lived charge transfer between impurity and film of complex. E_{A2} which is the activation energy corresponding to the region III, is associated with the resonant energy involved in short lived excited state. E_{A1} , corresponds to impurity conduction and E_{A2} corresponds to an intrinsic generation process [50]. The intermediate region extends from the impurity exhaustion temperature to intrinsic temperature. In this region, all impurity atoms are ionized, but the intrinsic carrier are not vet excited to a marked degree because the density of carriers remains approximately constant and equal to the impurity concentration.

3.3.2. Ac properties

Ac measurements were performed by means of conductivity and impedance measurements as a function of frequency between the frequencies 40 Hz and 100 kHz at different temperatures (295-523 K). Fig. 7 shows frequency dependence of ac conductivity for the film of 2 at indicated temperatures. As seen from Fig. 7, ac conductivity of the film increases with increasing temperature. Temperature dependence of 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). At low temperature region, conductivity of the film strongly depends on frequency. Conductivity of the film increases with increasing frequency. At high temperature region, frequency dependence of ac conductivity of the film decreases (except low frequency region above the temperature of 438 K). The σ_{ac} versus ω curves of **3** and **4** were similar to those in Fig. 7. At 295 < T < 438 K, temperature dependence of ac conductivity of the 2 at different frequencies is given in Fig. 8. It can be seen that conductivity of the film increases with increasing frequency and temperature and also approaches to each other at high temperatures in the measured frequency range.

At all temperatures frequency dependence of the measured ac conductivity of the films follows a universal power law. Universal power law is given by the Eq. (3) [16].

$$\sigma_{\rm ac} = A\omega^{\rm s} \tag{3}$$

where ω is the angular frequency, *A* and *s* are material depended constants. Investigation of the conduction mechanism involved the variation of the exponent *s* with temperature. *S* values were calculated from slope of straight portions of the σ_{ac} versus ω plot.



Fig. 7. Frequency dependence of ac conductivity of the film 2 between the temperatures of 295–523 K.



Fig. 8. Temperature dependence of ac conductivity of the film **2** at indicated frequencies ($T \le 438$ K).



Fig. 9. Temperature dependence of exponent s of the films **2**, **3** and **4** for high frequency region.

Derived values of *s* for the films **2**, **3** and **4** are around 1.0 at 295 K and decreases to 0.07 at 523 K. The variation of the *s* values of the films with temperature for high frequency region ($\ge \sim 1$ kHz) is given in Fig. 9. As seen from Fig. 9, *s* values decrease with increasing temperature. According to the band theory, the ac conductivity should be frequency independent and drops at sufficiently high frequency. Contrary to band model, in the hopping model the electrons in charged defect states hop over the coulomb barrier. This model predicts a frequency dependent ac conductivity, which increases with the increasing frequency under the condition that, the frequency exponent $s \le 1$ [51]. The Correlated Barrier Hopping (CBH) model, which was developed by Elliott, [51], predicts a temperature-dependent *s* value which is given by

$$s = 1 - \beta = 1 - \frac{6k_{\rm B}T}{W_{\rm m}} \tag{4}$$

where $k_{\rm B}$ is Boltzmann's constant and $W_{\rm m}$ is the binding energy. In this model *s* values decreases with increasing temperature. Our results showed that *s* is a function of temperature for all the films and shows a general tendency to decrease with increasing temperature (for *T* < ~438 K) over the measured frequency range. The variation of ac conductivity and variation of *s* conductivity with temperature (Figs. 7 and 9) are in agreement with the prediction of the CBH model. The same type of temperature dependence for *s* was observed in other reports in different phthalocyanine films [52,53]. However, at the temperatures *T* > ~438 K, while *s* values decrease with increasing temperature in high frequency region ($\omega \ge ~1$ kHz) as in (*T* < ~438 K), it increases with increasing temperature in low frequency region ($\omega < ~1$ kHz). In the quantum-mechanical tunneling (QMT) model [54], the exponent *s* is almost equal to 0.8 and increases slightly with temperature or independent of temperature. Because of this, QMT model is not applicable to our results. According to the overlapping-large polaron tunneling (QLPT) model [55], 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. According to the small polaron quantum-mechanical tunneling (SP) model, the exponent *s* is an increasing function of temperature [52]. It is also well known that the low values of *s* indicate multihopping process, while high values of *s* indicate single hopping process. According to these models, charge transport mechanism can be interpreted in two parts.

At low temperature region ($T < \sim 438$ K) dominant conduction mechanism can be modeled by single hopping over the measured frequency range. At high temperature region ($T > \sim 438$ K) conduction mechanism can be modeled depending on frequency region, (i) low frequency region ($\omega < \sim 1$ kHz) and (ii) high frequency region ($\omega \ge \sim 1$ kHz). In low frequency region dominant conduction mechanism can be modeled by small polaron tunneling (SP) and in high frequency region by single hopping.

Complex impedance spectroscopy is an important tool to analyze the electrical properties of a material. The complex impedance $Z(\omega)$, can be represented as a function of frequency as,

$$Z(\omega) = Z'(\omega) + jZ''(\omega)$$
(5)

where $Z'(\omega)$ and $Z''(\omega)$ are the real and imaginary parts of impedance. Fig. 10a and b show complex impedance spectrum (Nyquist plot) of the film **3** recorded at indicated temperatures. It can be seen from Fig. 10a that, the impedance spectra consist of a *quasi*-vertical line for the film **3** up to 438 K. The existence of a semicircular shaped curve in the Nyquist plot means that the impedance



Fig. 10. The cole–cole plot at temperatures (a) $T \le 438$ K; (b) T > 438 K for the film of **3**.

becomes capacitive even at relatively high frequency. The curves can be modeled as resistor parallel with a capacitor in series with another resistor [53]. Fig. 10b shows the complex impedance spectrum for the film **3** at the temperatures T > 438 K. As seen from Fig. 10b impedance spectra consist of depressed semicircles with different radius. With the examination of the Fig. 10b the effect of the temperature on impedance spectra can be seen clearly. The radius of the semicircle decreases with increasing temperature. An ideal semicircle in complex plane only appears in Debye dispersion relations for single-relaxation time process. Most of the materials show a pronounced deviation from 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 [56]. The depressed semicircles with different radius indicate deviation from Debye dispersion relation. Therefore, the equivalent circuit is modified to include a constant phase element (CPE). The series resistance in the equivalent circuit represents the 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 real axis give us an estimate of the bulk resistance of the material. It is observed that bulk resistance decreases with increasing temperature indicating semiconductor property. In addition, a straight line was observed in Fig. 10b in low frequency range. The straight line in the low frequency range indicates the presence of Warburg component [57]. The complex impedance spectrum (Nyquist plot) of the film 2 and 4 were similar to those in Fig. 10.

4. Conclusion

4,5-Diphenyl-1*H*-imidazole substituted metal-free phthalocyanine, **2**, and zinc and cobalt containing metallophthalocyanines, **3** and **4**, were synthesized. We studied aggregation behavior of phthalocyanines in different solvents and concentrations. We also studied electrochemical and electrical properties of these phthalocyanines.

The variation of dc conductivity with temperature shows that the films of 2, 3 and 4 have different activation energies in different temperature region. The activation energies E_{A1} corresponding to the region I is associated with a short lived charge transfer between impurity and complex. E_{A2} which is the activation energy corresponds to the region III, is associated with the resonant energy involved in short lived excited state. E_{A1} , corresponds to impurity conduction and E_{A2} corresponds to an intrinsic generation process. Temperature dependence of ac conductivity of the films of **2**, **3** and **4** showed that ac conductivity of the films can be characterized in two different temperature ranges. At low temperature region ($T < \sim 438$ K) dominant conduction mechanism can be modeled by single hopping over the measured frequency range. At high temperature region ($T > \sim 438$ K) conduction mechanism can be modeled depending on frequency region, (i) low frequency region (ω < ~1 kHz) and (ii) high frequency region ($\omega \ge ~1$ kHz). In low frequency region dominant conduction mechanism can be modeled by SP and in high frequency region by single hopping. Complex impedance spectrum (Nyquist plot) of the films of 2, 3 and 4 at different temperatures showed that at low temperature region $(T < \sim 438 \text{ K})$ impedance becomes capacitive even at relatively high frequency. The curves can be modeled a resistor parallel with a capacitor in series with another capacitor. At high temperature region ($T \ge \sim 438$ K), depressed semicircles with different radius indicate deviation from Debye dispersion relation. Therefore, the equivalent circuit is modified to include a CPE. It is observed that bulk resistance decreases with increasing temperature indicating semiconductor property. In this temperature region the straight line in the low frequency range indicates the presence of Warburg component.

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