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Research paper

# The synthesis and electrochemical characterization of new metallophthalocyanines containing 4-aminoantipyrine moieties on peripherally positions



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### ABSTRACT

The electrochemical characterization and synthetic procedures of novel metallophthalocyanines (Co, Cu and Mn) **5**, **6** and **7** fused eight *N*-(2,3-dihydro-1,5-dimethyl-3-oxo-2-phenyl-1*H*-pyrazol-4-yl)-4-methylbenzenesulfonamide groups connected to ethylmercapto arms on peripherally positions were reported in this work. The metal complexes **5**, **6** and **7** were prepared by a tetramerization reaction of the phthalonitrile derivative **4** with corresponding metal salts and materials. The characterization of new products was made by a combination of elemental analysis, FT–IR, MALDI–TOF mass spectral data, UV–Vis, <sup>1</sup>H NMR and <sup>13</sup>C NMR. Electrochemical characterization of metallophthalocyanines was determined by using cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques. Copper(II) phthalocyanine showed Pc based electron transfer processes because of redox inactive metal center. On the other hand, Mn<sup>III</sup> and Co<sup>II</sup> metal ions behave as redox active cations in the core of the phthalocyanines. Therefore, Mn<sup>III</sup>CIPc and Co<sup>II</sup>Pc gave metal and ligand based reduction reactions as expected.

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## 1. Introduction

Phthalocyanines (Pcs) are versatile and stable compounds. Structurally, Pcs are similar to porphyrins, but they are synthetic macrocyclic derivatives. Pcs have found numerous applications in materials science such as gas and chemical sensors, molecular solar cells, industrial catalytic systems, electrochromic display devices, optical switching, nanotechnology and light-emitting devices in recent years [1]. The optical and electronic properties of the phthalocyanine (Pc) macrocycle make it suitable for a wide range of technological applications such as photoconductors in xerographic machines [2], electrochromic displays [3], photovoltaic materials in solar cells [4,5], systems for fabrication of light emitting diodes (LED) [6], optical limiters [7], dyes at recording layers in recordable digital versatile discs (DVDs) [8], liquid crystalline [9], organic conductors [10] diverse catalytic systems [11], photocatalysts [12], photosensitizers in the cancer treatment [13], the photoinactivation of bacteria and viruses [14], semiconductor devices [15] and in routine diagnostic procedure [16]. It has been also reported antioxidant properties of some phthalocyanine compounds [17].

Metallophthalocyanines (MPcs) are composed of a central metal atom that is bound to a  $\pi$ -conjugated ligand. The physicochemical characteristics of the MPcs can be precisely changed by modifying the central metal atom and the peripheral substituents. MPcs create one of the most studied categories of organic functional materials with potential application in many diverse areas since they have interesting and varied properties. Metal phthalocyanines have become a very popular choice of materials owing to their various electrochemical activity [18–20].

The electrochemistry of metallophthalocyanines (MPcs), especially those involving redoxactive metal centers such as Co(II), Fe (II) and Mn(II) or Mn(III), have received great interest due to their rich ligand- and metal-based redox properties and colour changes, leading to potential applicability especially in the areas of electrocatalysis [21,22] and electrochromism [23]. The redox properties of MPcs with redox active metal centers are strongly affected by various factors such as the nature of the solvent and supporting electrolyte, the presence or absence of oxygen, and peripheral or non-peripheral substituents, due to their ability to coordinate axial ligands [24]. The redox properties of Pcs are generally determined by voltammetric methods such as cyclic voltammetry, differential pulse voltammetry and square wave voltammetry [25,26].



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Antipyrine derivatives have elicited great interest particularly in medicine due to their wide range of pharmacological activities and clinical applications, including antifungal, antibacterial, antipyretic, analgesic, anti-inflammatory as well as antitumoractivity [27,28]. 4-Aminoantipyrine has been utilized as a key intermediate for the synthesis of heterocycles bearing biologically active moieties [29–32]. In addition, it is used as a reagent for biochemical reactions producing peroxides or phenols [33,34] and is also be used to detecting phenols in environment [35,36].

In view of great importance of 4-aminoantipyrine derived compounds, its wide range of applications in various fields, we focused on synthesizing the octa substituted 4-aminoantipyrine containing phthalocyanine complexes with transition metal ions such as Co (II), Cu(II) and Mn(III) and also we purposed to investigate the electrochemical characterization and possible applications in various electrochemical technologies such as electrocatalytic, electrosensing and electrochromic fields.

## 2. Experimental

#### 2.1. Materials

Reactions were performed under an atmosphere of nitrogen and new phthalocyanine derivatives were synthesized by using standard Schlenk techniques. 1,2-bis(2-tosyloxyethylmercapto)-4,5dicyanobenzene **3** was prepared according to the literature procedure [37]. Following the similar procedure [38], *N*-(2,3-dihydro-1,5-dimethyl-3-oxo-2-phenyl-1*H*-pyrazol-4-yl)-4-methylbenzenesulfonamide (**2**) was synthesized as white crystals starting from 4aminoantipyrine and *p*-toluenesulfonyl chloride. All other reagents and solvents were of reagent grade quality from commercial suppliers and were dried before use as described in the literature [39]. Column chromatography was carried out on silica gel (70– 230 mesh) and Merck 90 active neutral alumina columns with the indicated eluents.

#### 2.2. Equipment

A Perkin Elmer Spectrum One FT–IR spectrometer was used to record the infrared spectra. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian XL–400 NMR spectrometer with CDCI<sub>3</sub>/DMSO-d<sub>6</sub> and chemical shifts were reported ( $\delta$ ) relative to Me<sub>4</sub>Si (tetramethylsilane) as the internal standard. Melting points were determined by an electrothermal apparatus and were uncorrected. Mass spectra were measured with Bruker Microflex LT MALDI-TOF–MS and Micromass Quattro LC-MS/MS spectrometer. Electronic absorption (ultraviolet–visible) spectrum was recorded with a Perkin Elmer Lambda 25 UV/Vis spectrophotometer by using a 1 cm pathlength cuvette at room temperature. Elemental analysis of the compounds was determined on a LECO TruSpec Micro instrument.

#### 2.3. Electrochemical measurements

All electrochemical measurements were carried out with Gamry Interface 1000 potentiostat/galvanostat utilizing a three–electrode configuration at 25 °C. The working electrode was a Pt disc. A Pt wire was served as the counter electrode and saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade tetrabutylammonium perchlorate (TBAP) in extra pure dichloromethane (DCM) was employed as the supporting electrolyte at a concentration of 0.10 mol dm<sup>-3</sup>.

#### 2.4. Synthesis

#### 2.4.1. N-(2,3-dihydro-1,5-dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-yl)-4-methylbenzenesulfonamide (2)

4-Aminoantipyrine (1) (1.5 g, 7.38 mmol) was dissolved in dry pyridine (10 mL) inside a two-necked round bottomed flask under nitrogen atmosphere and degassed several times on a vacuum line. p-Toluenesulfonyl chloride (1.547 g, 8.11 mmol) in dry pyridine (10 mL) was added dropwise within 1 h to the reaction mixture at -5 °C. The colour of the flask content was changed from orange to claret. After the addition of *p*-toluenesulfonyl chloride solution, it was stirred at the same temperature under N<sub>2</sub> atmosphere for 4 h and then kept stirring at room temperature for overnight. Thereafter, 200 g of crushed ice was added and stirred at room temperature for 2 h. Conc. HCl (75 mL) was added dropwise within 1 h to acidify the mixture. A distinct change in colour was observed from claret to pale vellow. Pale vellow solid was then filtered off and dried in vacuo. The solid residue was crystallized from ethanol yielding as white crystals. Yield: 0.72 g (27%), m.p. 225-228 °C. Elemental analysis: Calc. (%) for C<sub>18</sub>H<sub>19</sub>N<sub>3</sub>O<sub>3</sub>S: C, 60.49; H, 5.36; N, 11.76; S, 8.97, Found C, 59.67; H, 5.10; N, 10.98; S, 8.40. FT-IR: v<sub>max</sub>  $(cm^{-1}) = 3266$  (N–H), 3099–3028 (C–H aromatic), 2922–2823 (CH<sub>3</sub>), 1654 (C=O), 1592 (C=C), 1322-1140 (SO<sub>2</sub>-tosyl group), 1295, 1055 (N–H) and 694 (C–S). <sup>1</sup>H NMR (ppm, CDCl<sub>3</sub>):  $\delta$  = 7.65–7.63 (d, 2H, Tosyl, Ar–H), 7.42–7.38 (d, 2H, Tosyl, Ar–H), 7.29 (broad s, 1H, N-H), 7.25-7.11 (m, 5H, N-Ar-H), 3.06 (s, 3H, N-CH<sub>3</sub>), 2.34 (s, 3H, Tosyl, CH<sub>3</sub>), 2.31 (s, 3H, C=C-CH<sub>3</sub>). <sup>13</sup>C NMR (ppm, CDCl<sub>3</sub>):  $\delta$  = 161.99 (C=O), 153.79, 143.35, 136.92, 134.43, 129.24, 127.36, 127.16, 124.44, 106.66, 35.63 (N-CH<sub>3</sub>), 21.60 (Tosyl,  $-CH_3$ ), 11.28 (C=C-CH<sub>3</sub>). MALDI-TOF-MS m/z: Calculated: 357.43, Found: 358 [M+H]<sup>+</sup>.

# 2.4.2. N,N'-(((4,5-dicyano-1,2-phenylene)bis(sulfanediyl))bis(ethane-2,1-diyl))bis(N-(2,3-dihydro-1,5-dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-yl)-4-methylbenzenesulfonamide (4)

A 100-mL two necked round-bottomed flask containing 40 mL of dry acetonitrile and fitted with a condenser was evacuated. refilled three times with nitrogen gas and connected to a vacuum line. The flask was charged with compound **2** (0.7 g, 1.96 mmol), finely ground anhydrous Na<sub>2</sub>CO<sub>3</sub> (1.04 g, 9.81 mmol) and 1,2-bis (2-tosyloxyethylmercapto)-4,5-dicyanobenzene 3 (0.577 g, 0.98 mmol). Under the nitrogen atmosphere, the reaction mixture was refluxed at 95 °C for 6 days. The reaction was monitored by TLC using chloroform:petroleum ether:methanol (7:2:1). After cooling to room temperature, the residue was dissolved in 150 mL of chloroform and extracted with  $(3 \times 20 \text{ mL})$  water. The combined organic extract was dried over MgSO<sub>4</sub>, filtered and the solvent was removed by evaporation. The purification of the crude product was made by column chromatography on neutral alumina with chloroform: ethanol (100:1 v/v) to give the phthalonitrile derivative **4** as a brown viscous oily product. Yield: 0.96 g (61%). Elemental analysis: Calc. (%) for C<sub>48</sub>H<sub>46</sub>N<sub>8</sub>O<sub>6</sub>S<sub>4</sub>: C, 60.10; H, 4.83; N, 11.68; S, 13.37, Found C, 60.51; H, 4.42; N, 10.77; S, 12.82. FT-IR:  $v_{max}$  (cm<sup>-1</sup>) = 3068–3030 (C–H aromatic), 2922–2853 (CH<sub>2</sub>, CH<sub>3</sub>), 2229 (C≡N), 1660 (C=O), 1593 (C=C), 1333–1155 (SO<sub>2</sub>-tosyl groups), 1290, 695 and 663 (C–S). <sup>1</sup>H NMR (ppm, CDCl<sub>3</sub>):  $\delta$  = 8.48 (s, 2H, Ar-H), 8.07 (d, 4H, Tosyl, Ar-H), 7.76-7.63 (d, 4H, Tosyl, Ar-H), 7.19-6.89 (m, 10H, N-Ar-H), 3.87 (t, 4H, N-CH<sub>2</sub>), 3.83 (t, 4H, Ar-S-CH<sub>2</sub>), 1.73 (s, 6H, N-CH<sub>3</sub>), 1.44 (s, 6H, Tosyl, CH<sub>3</sub>), 1.23 (s, 6H, C=C-CH<sub>3</sub>). <sup>13</sup>C NMR (ppm, DMSO- $d_6$ ):  $\delta$  = 161.75 (C=O), 153.16, 138.46, 136.84, 135.53, 133.38, 130.49, 124.02, 122.40, 121.68, 120.31, 118.55, 115.78 (C=N), 113.46, 109.49, 56.15 (N-CH<sub>2</sub>), 40.39 (S-CH<sub>2</sub>) 35.41 (N-CH<sub>3</sub>), 22.08 (Tosyl, -CH<sub>3</sub>), 12.04 (C=C-CH<sub>3</sub>). MALDI-TOF-MS m/z: Calculated: 959.19, Found: 959.95 [M]<sup>+</sup>.

#### 2.4.3. Synthesis of phthalocyaninato cobalt(II) (5)

Compound 4 (0.2 g, 0.208 mmol) was dissolved in 5 mL of dry npentanol into a Schlenk tube under a nitrogen atmosphere. Anhydrous CoCl<sub>2</sub> (14 mg, 0.108 mmol) and 3 drops of 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) were added. The reaction mixture was heated at 160 °C for 5 h. After cooling to room temperature, the blue reaction mixture was diluted and the product was precipitated by adding 10 mL of ethanol. The resulting precipitate was filtered off, washed with EtOH and H<sub>2</sub>O separately and dried in vacuo. Afterwards, it was dissolved in minimum amount of chloroform and eluted on neutral alumina using chloroform:ethanol (100:1) as eluent. The extract was evaporated to dryness and dried under vacuum to give blue coloured compound 5. Yield: 70 mg (35%), m.p.>300 °C. Elemental analysis: Calc. (%) for C<sub>192</sub>H<sub>184</sub>N<sub>32</sub>O<sub>24</sub>S<sub>16</sub>Co: C, 59.20; H, 4.76; N, 11.51; S, 13.17, Found C, 58.62; H, 4.60; N, 10.74; S, 12.43. FT–IR:  $v_{max}$  (cm<sup>-1</sup>) = 3044 (C–H aromatic), 2921– 2851 (CH<sub>2</sub>, CH<sub>3</sub>), 1662 (C=O), 1638 (C=N), 1521, 1494, 1335-1156 (SO<sub>2</sub>-tosyl groups), 1287, 695 and 664 (C-S). UV-Vis (chloroform),  $\lambda_{max}$ , nm (log $\epsilon$ ): 702 (5.00), 663 (4.66) and 384 (4.83). MALDI-TOF-MS m/z: Calculated: 3895.69, Found: 3182.34 [M-4Ts-6CH<sub>3</sub>-3H]<sup>+</sup>, 2823.39 [M-6Ts-9CH<sub>3</sub>-6H]<sup>+</sup>, 2497.50 [M-8Ts-10CH<sub>3</sub>-7H]<sup>+</sup>, 2465.31 [M-8Ts-12CH<sub>3</sub>-9H]<sup>+</sup>, 2439.40 [M-8Ts- $14CH_3 - 5H]^+$ .

#### 2.4.4. Synthesis of phthalocyaninato copper(II) (6)

Under N<sub>2</sub> atmosphere, a standard Schlenk tube was charged with compound 4 (0.21 g, 0.219 mmol), anhydrous CuCl<sub>2</sub> (15 mg, 0.112 mmol), 5 mL of dry n-pentanol and 4-5 drops of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) and heated at 160 °C by stirring for 4 h. At the end of this period, the mixture was cooled to room temperature, filtered off and washed with methanol and water to remove any unreacted organic residue. The crude product was dissolved in minimum amount of chloroform and launched into a column and eluted on neutral alumina using chloroform as eluent. The extract was evaporated to dryness and 5 mL of ethanol was added and stirred for 30 min. The green product 6 was filtered and dried in vacuo. Yield: 69 mg (33%); m.p. > 300 °C. Elemental analysis: Calc. (%) for  $C_{192}H_{184}N_{32}O_{24}S_{16}Cu$ : C, 59.13; H, 4.75; N, 11.49; S, 13.15, Found C, 58.48; H, 4.93; N, 10.67; S, 12.36. FT-IR: v<sub>max</sub> (cm<sup>-1</sup>) = 3066 (C–H aromatic), 2921–2851 (CH<sub>2</sub>, CH<sub>3</sub>), 1663 (C=O), 1640 (C=N), 1593 (C=C), 1493, 1334-1156 (SO<sub>2</sub>-tosyl groups), 1289, 695 and 664 (C–S). UV–Vis (chloroform),  $\lambda_{max}$ , nm (logε): 713 (5.04), 655 (4.51) and 321 (4.99). MALDI-TOF-MS m/ z: Calculated: 3900.30, Found: 3900.95 [M]<sup>+</sup>.

#### 2.4.5. Synthesis of phthalocyaninato manganese(III) chloride (7)

A well-stopped Schlenk tube was charged with phthalonitrile derivative **4** (0.21 g, 0.219 mmol), anhydrous MnCl<sub>2</sub> (14 mg, 0.111 mmol), 5 mL of dry n-pentanol and 4 drops of DBU (1,8-diazabicyclo[5.4.0] undec-7-ene) under nitrogen gas. The reaction mixture was refluxed at 160 °C for 4 h and then it was diluted and precipitated with 10 mL of methanol and stirred for 30 min after cooling to room temperature. The resulting precipitate was filtered off, washed with methanol, water and diethyl ether and afterwards it was dissolved in minimum amount of chloroform and eluted on neutral alumina using chloroform:ethanol (100:1) as eluent. The extract was evaporated to dryness under vacuum and 5 mL of ethanol was added and stirred for 45 min. The compound 7 was filtered and dried in vacuo. Yield: 62 mg (29%); m.p. > 300 °C. Elemental analysis: Calc. (%) for  $C_{192}H_{184}N_{32}O_{24}S_{16}MnCI$ : C, 58.72; H, 4.72; N, 11.41; S, 13.06, Found C, 58.19; H, 4.72; N, 10.63; S, 12.17. FT-IR:  $v_{max}$  (cm<sup>-1</sup>) = 3098–3082 (C–H aromatic), 2921–2851 (CH<sub>2</sub>, CH<sub>3</sub>), 1663 (C=O), 1642 (C=N), 1592 (C=C), 1494, 1326-1154 (SO<sub>2</sub>-tosyl groups), 1288, 695 and 663 (C-S). UV-Vis (chloroform),  $\lambda_{max}$ , nm (log $\varepsilon$ ): 769 (5.01), 688 (4.38), 529 (4.61) and 468 (4.68). MALDI–TOF–MS *m*/*z*: Calculated: 3927.14, Found: 3891.74 [M–CI]<sup>+</sup>.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

The synthetic route of **4–7** is exhibited in Scheme 1. Herein, we report the synthesis and electrochemical characterization of a series of novel metallophthalocyanines **5–7**. The verification of the synthesized new compounds was made by using FT–IR, UV–Vis, MALDI–TOF mass spectral data, elemental analysis, <sup>1</sup>H NMR and <sup>13</sup>C NMR.

We synthesized the compound 2 by adopting the synthetic procedure described in the literature [38] by the reaction of 4aminoantipyrine **1** and *p*-toluenesulfonyl chloride in the presence of dry pyridine at  $-5 \,^{\circ}$ C with the yield of 27% after crystallized from ethanol. In the <sup>1</sup>H NMR spectrum of **1**, the signal corresponding to the NH<sub>2</sub> group disappeared and a new broad signal related to the N–H proton at  $\delta$  = 7.29 ppm was observed for the compound **2**. The resonance peaks were in a good agreement with the proposed structure in the <sup>1</sup>H NMR spectrum of **2**, being at  $\delta$  = 7.65–7.63 and 7.42-7.38 ppm (Tosyl, Ar-H); 7.25-7.11 ppm (N-Ar-H); 3.06, 2.34 and 2.31 ppm (methyl protons). The characteristic <sup>13</sup>C NMR signals of aromatic carbon atoms at  $\delta$  = 153.79, 143.35, 136.92, 134.43, 129.24, 127.36, 127.16, 124.44, 106.66; carbonyl carbon atom at  $\delta$  = 161.99 and carbon atoms belonging to methyl groups at  $\delta$  = 35.63, 21.60 and 11.28 ppm, supported the structure. The FT– IR spectrum of 2 was easily verified with the disappearance of the NH<sub>2</sub> group of **1** and the presence of stretching vibrations of **2** associated with the N-H group at 3266-1055 cm<sup>-1</sup> (stretchingbending) and the tosyl group at 1322–1140 cm<sup>-1</sup> which indicated that the tosylation reaction was clearly accomplished. Other FT-IR stretching vibrations of **2** were similar to compound **1** with slight changes. This compound demonstrated the molecular ion peak at m/z = 358 indicating the formation of  $[M+H]^+$ . The result of elemental analysis was also in accord with the proposed formula.

The phthalonitrile derivative 4 was synthesized by 2:1 substitution reaction of compound 2 with 1,2-bis(2-tosyloxyethylmercapto)-4,5-dicyanobenzene **3** in the presence of anhydrous Na<sub>2</sub>CO<sub>3</sub> and dry acetonitrile at 95 °C for 6 days under the nitrogen as a brown viscous oily product. The crude product was purified by column chromatography on neutral alumina with chloroform: ethanol (100:1 v/v) to give **4** in 61% yield. In the infrared spectrum of **2**, the signals at 3266 and 1055  $\text{cm}^{-1}$  which were for the N–H bond vanished and a new peak arose in the IR spectrum of 4 at 2229 cm<sup>-1</sup> that was attributed to the dicyano groups. The N-H proton signal observed in the <sup>1</sup>H NMR spectrum of precursor compound **2** at  $\delta$  = 7.29 ppm was disappeared and also other characteristic signals were seen for the N-CH<sub>2</sub> and Ar-S-CH<sub>2</sub> protons at  $\delta$  = 3.87 and 3.83 ppm respectively, in the case of product **4**. In addition, aromatic protons of compound 4 were observed at  $\delta$  = 8.48, 8.07, 7.76–7.63, 7.19–6.89 ppm. Methyl protons were seen at  $\delta$  = 1.73, 1.44 and 1.23 ppm in the <sup>1</sup>H NMR spectrum of **4**. The proton-decoupled <sup>13</sup>C NMR spectrum of this compound also clearly indicated signals of carbonyl groups; dicyano groups; N-CH<sub>2</sub>; Ar–S–CH<sub>2</sub> and methyl carbons at  $\delta$  = 161.75; 115.78; 56.15; 40.39; 35.41, 22.08, 12.04 ppm, respectively. In addition to the result of elemental analysis, MALDI-TOF mass spectrum of 4, which showed a molecular ion peak at m/z = 959.95 [M]<sup>+</sup>, confirmed the proposed chemical structure.

Metallophthalocyanines **5**, **6** and **7** were prepared from the dicyano derivative **4** and the appropriate metal salts in dry *n*-pentanol under inert atmosphere in yields of 35%, 33% and 29%, respectively. A comparison of the IR spectra obtained for **4** with **5**, **6** and **7** 



Mn<sup>III</sup>CIPc

Scheme 1. Synthesis of phthalocyaninato Co (II), Cu (II) and Mn(III) chloride.

confirmed the conversion of the C $\equiv$ N groups into the characteristic skeleton of phthalocyanine. The C $\equiv$ N band at 2229 cm<sup>-1</sup> of compound **4** disappeared and C=N stretching vibrations of the inner core of the metallophthalocyanines **5**, **6** and **7** appeared at 1638, 1640 and 1642 cm<sup>-1</sup>, respectively. The molecular ion cluster

for metallophthalocyanine **6** was observed at m/z: 3900.95 [M]<sup>+</sup>. Phthalocyaninato manganese(III) chloride **7** were found together with a reasonable fragment ion at m/z: 3891.74 [M–CI]<sup>+</sup>. The mass spectrum of Co phthalocyanine **5** was obtained with some fragmentation ions at m/z: 3182.34 [M–4Ts–6CH<sub>3</sub>–3H]<sup>+</sup>, 2823.39



Fig. 1. Electronic absorption spectra of  $Mn^{III}CIPc,$  CuPc and CoPc  $(1.00\times10^{-5}\,M)$  in CHCl\_3.

 $[M-6Ts-9CH_3-6H]^+$ , 2497.50  $[M-8Ts-10CH_3-7H]^+$ , 2465.31  $[M-8Ts-12CH_3-9H]^+$ , 2439.40  $[M-8Ts-14CH_3-5H]^+$ . The data related with elemental analyses of all the metallophthalocyanine complexes **5–7** were consistent with the proposed structures.

The electronic absorption (ultraviolet-visible) spectrum of the cobalt(II) 5 and copper(II) 6 phthalocyanine complexes demonstrated the expected absorptions (Fig. 1), with the main peaks of the Q and B bands appearing at  $\lambda_{max} = 702$  (log $\varepsilon = 5.00$ ), 663 (4.66) and 384 nm (log $\varepsilon$  = 4.83); 713 (log $\varepsilon$  = 5.04), 655 (log $\varepsilon$  = 4.51) and 321 nm (log $\varepsilon$  = 4.99), respectively. This result is typical of metal complexes of substituted and unsubstituted metallophthalocyanines with  $D_{4h}$  symmetry [40,41], where a single band of high intensity in the visible region is observed. The main peaks of the Q and B bands of phthalocyaninato manganese(III) chloride complex **7** appeared at  $\lambda_{max} = 769$  (log $\varepsilon = 5.01$ ) and 688 nm  $(\log \epsilon = 4.38)$  (Fig. 1). Besides, Mn<sup>III</sup>ClPc **7** displayed the new absorption bands at around 400-550 nm in addition to the B band [42-44] at  $\lambda_{max}$  = 529 nm (log $\varepsilon$  = 4.61) and 468 nm (log $\varepsilon$  = 4.68), respectively. These new bands are sometimes observed, which can be ascribed to metal-to-ligand charge-transfer or ligand-to-metal charge-transfer transitions because metal ions have partially filled d orbitals [45].

#### 3.2. Electrochemical studies

Electrochemical characterization of phthalocyanines was performed with CV and SWV measurements in dichloromethane

#### Table 1

Voltammetric data of the phthalocyanines. All voltammetric data were given versus SCE.



**Fig. 2.** (a) CV of  $Mn^{III}$ CIPc at various scan rates (ranging from 25 to 500 mV s<sup>-1</sup>) on a Pt working electrode in DCM/TBAP. (b) SWV of  $Mn^{III}$ CIPc recorded at 0.100 Vs<sup>-1</sup> scan rate on a Pt working electrode in DCM/TBAP electrolyte.

(DCM)/tetrabutylammonium perchlorate (TBAP) electrolyte system on a Pt working electrode. Basic electrochemical parameters, the assignments of the redox couples and estimated electrochemical parameters including the half-wave potentials ( $E_{1/2}$ ), peak to peak potential separations ( $\Delta E_p$ ), ratio of anodic to cathodic peak currents ( $I_{p,a}/I_{p,c}$ ) and difference between the first oxidation and reduction processes ( $\Delta E_{1/2}$ ), were derived from the analyses of the complexes and these data were tabulated in Table 1.

Fig. 2 shows CV and SWV responses of  $Mn^{III}$ CIPc in DCM/TBAP. Mn<sup>III</sup>CIPc gave two quasi reversible reduction processes at -0.17 V (R<sub>1</sub>) and -0.96 V (R<sub>2</sub>) and one irreversible reduction process at

Complexes	Redox processes	<sup>a</sup> E <sub>1/2</sub>	${}^{\mathrm{b}}\varDelta E_{\mathrm{p}} (\mathrm{mV})$	<sup>c</sup> I <sub>p,a</sub> /I <sub>p,c</sub>	$^{\mathbf{d}} \varDelta E_{1/2}$
MnClPc	$\begin{array}{l} \textbf{R_1} \rightarrow [\text{Cl-}Mn^{II}\text{Pc}^{-2}]/[\text{Cl-}Mn^{II}\text{Pc}^{-2}]^{-1} \\ \textbf{R_2} \rightarrow [Mn^{II}\text{Pc}^{-2}]/[Mn^{IP}\text{C}^{-2}]^{-1} \\ \textbf{R_3} \rightarrow [\text{Cl-}Mn^{II}\text{Pc}^{-2}]^{-1}/[\text{Cl-}Mn^{II}\text{Pc}^{-3}]^{-2} \\ \textbf{O_1} \rightarrow [\text{ Cl-}Mn^{III}\text{Pc}^{-2}]/[\text{Cl-}Mn^{III}\text{Pc}^{-1}]^{+1} \end{array}$	-0.17 -0.96 -1.44 1.02	139 147 205 130	0.69 0.66 0.51 0.71	1.19
СоРс	$\begin{array}{l} \textbf{R_1} \rightarrow [Co^{ll}Pc^{-2}]/[Co^{l}Pc^{-2}]^{-1} \\ \textbf{R_2} \rightarrow [Co^{l}Pc^{-2}]^{-1}/[Co^{l}Pc^{-3}]^{-2} \\ \textbf{O_1} \rightarrow [Co^{ll}Pc^{-2}]/[Co^{ll}Pc^{-1}]^{+1} \end{array}$	-0.21 -1.32 0.76	78 96 148	0.93 0.91 0.67	0.97
CuPc	$\begin{array}{l} \textbf{R_1} \rightarrow [Cu^{ll}Pc^{-2}]/[Cu^{ll}Pc^{-3}]^{-1} \\ \textbf{R_2} \rightarrow [Cu^{ll}Pc^{-3}]^{-1}/[Cu^{ll}Pc^{-4}]^{-2} \\ \textbf{O_1} \rightarrow [Cu^{ll}Pc^{-2}]/[Cu^{ll}Pc^{-1}]^{+1} \end{array}$	-0.79 -1.12 0.84	147 150 145	0.72 0.70 0.69	1.63

 $E_{1/2}$  values (( $E_{pa} + E_{pc}$ )/2) were given versus SCE at 0.100 Vs<sup>-1</sup> scan rate.

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

 $I_{p,a}^{c} I_{p,a}^{p} I_{p,c}^{p}$  for reduction,  $I_{p,c}/I_{p,a}$  for oxidation processes.

<sup>d</sup>  $\Delta E_{1/2} = E_{1/2}$  (first oxidation)- $E_{1/2}$  (first reduction).

-1.44 V ( $R_3$ ) respectively. First two reduction processes and oxidation process were quasi reversible characters and last reduction process was irreversible with respect to  $I_{p,a}/I_{p,c}$ , and  $\Delta E_p$  values. With respect to the positions of the redox processes, the first two redox couple ( $R_1$  at -0.17 V and  $R_2$  at -0.96 V) were proposed to the reduction of Mn<sup>III</sup> to Mn<sup>II</sup> and then Mn<sup>II</sup> to Mn<sup>I</sup> oxidation states. The remaining reduction ( $R_3$  at -1.44 V) was proposed to Pc based process. These assignments are in agreements with the MnPcs in the literature [46–48]. Also, during the cathodic scan, Mn<sup>III</sup>CIPc gave one quasi-reversible oxidation  $O_1$  at 1.02 V within the potential window of DCM/TBAP electrolyte system ( $\Delta E_p = 130$  mV).

CoPc complexes generally give a metal based reduction process at around 0 V due to the electron gaining to the empty d orbitals of Co<sup>II</sup> center located between the HOMO and LUMO orbitals of the Pc ring. Fig. 3 represents CV and SWV responses of CoPc in DCM/TBAP electrolyte on a Pt working electrode. CoPc underwent two reduction reactions. at -0.21 V and -1.32 V, and one oxidation reaction at 0.76 V within the potential window of DCM/TBAP electrolyte system. CoPc gave two reversible reductions, R1 at -0.21 V ( $\Delta E_{\rm p}$  = 78 mV), R<sub>2</sub> at -1.32 V ( $\Delta E_{\rm p}$  = 96 mV) and one quasi-reversible oxidation reaction  $O_1$  at 0.76 V ( $\Delta E_p = 148 \text{ mV}$ ) within the potential window of DCM/TBAP electrolyte system. These reduction processes were seemed reversible with respect to  $I_{p,a}/I_{p,c}$ , and  $\Delta E_p$  values. Since while  $I_{p,a}/I_{p,c}$  values of these couples were approximately unity at all scan rates,  $\Delta E_{\rm p}$  values are ranged between 60 and 110 mV with respect to scan rates ranging from 25 to 500 mV s<sup>-1</sup> scan rates. Electrochemical behaviors of CoPc is in agreement with the similar CoPc complexes reported in the lit-



**Fig. 3.** (a) CV of CoPc at various scan rates (ranging from 25 to 500 mV s<sup>-1</sup>) on a Pt working electrode in DCM/TBAP. (b) SWV of  $Co^{II}Pc$  recorded at 0.100 Vs<sup>-1</sup> scan rate on a Pt working electrode in DCM/TBAP electrolyte.



**Fig. 4.** (a) CV of  $Cu^{II}Pc$  at various scan rates (ranging from 25 to 500 mV s<sup>-1</sup>) on a Pt working electrode in DCM/TBAP. (b) SWV of  $Cu^{II}Pc$  recorded at 0.100 Vs<sup>-1</sup> scan rate on a Pt working electrode in DCM/TBAP electrolyte.

erature [49,50], which support the proposed structure of the complex synthesized here. Also, HOMO–LUMO gap of CoPc ( $\Delta E_{1/2} = 0.97$  V) is in compliance with the CoPc reported in the literature [51].

MPc complexes having redox inactive metal centers, such as Ni, Cu and Zn, can give only Pc based redox reactions, since the energy level of the d orbitals of these metal ions are placed out of the HOMO-LUMO energy levels [52]. Fig. 4 represents CV and SWV responses of CuPc in DCM/TBAP electrolyte on a Pt working electrode. CuPc gave two reduction reactions,  $R_1$  at -0.79 V and  $R_2$  at -1.12 V during the cathodic potential scans. These reduction reactions were quasi-reversible reductions,  $R_1$  at -0.79 V ( $\Delta E_p = 147$  mV), R<sub>2</sub> at -1.12 V ( $\Delta E_p$  = 150 mV). Furthermore, one quasireversible oxidation reaction,  $O_1$  at 0.84 V ( $\Delta E_p = 145$  mV), was observed during the anodic potential scans. Two reduction processes and oxidation process were quasi reversible characters with respect to  $I_{p,a}/I_{p,c}$ , and  $\Delta E_p$  values. Electrochemical behaviors of CuPc are in harmony with the general characters of CuPcs reported in the literature [53,54]. Especially the first reduction and first oxidation processes of Co<sup>II</sup>Pc were observed at very small potentials with respect to those of CuPc, since these processes were proposed as metal-based electron transfer processes. Also, the peak currents increased linearly with the square root of the scan rates for scan rates ranging from 25 to 500 mV s<sup>-1</sup> (Fig. 2a for Mn<sup>III</sup>ClPc, Fig. 3a for CoPc, Fig. 4a for CuPc), respectively.  $\Delta E_{1/2}$  of the complexes (1.19 V for Mn<sup>III</sup>CIPc, 0.97 V for Co<sup>II</sup>Pc, 1.63 V for Cu<sup>II</sup>Pc) reflected the energy band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

This result is in harmony with the reported Mn<sup>III</sup>ClPc, Co<sup>II</sup>Pc, Cu<sup>II</sup>Pc complexes [55–57].

4. Conclusion

In conclusion, we reported the synthetic procedures and electrochemical characterization of a new series of phthalocyanine derivatives substituted with eight N-(2,3-dihydro-1,5-dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-yl)-4-methylbenzenesulfonamide groups through ethylmercapto bridges by using proper materials and equipments. MALDI-TOF mass spectral data. UV-Vis. elemental analysis, FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR were used to characterize all these novel compounds. Electrochemistry of Mn<sup>III</sup>CIPc, Co<sup>II</sup>Pc and Cu<sup>II</sup>Pc were studied in solution with voltammetric measurements. Electrochemical responses of the phthalocyanines supported the proposed structure of the metallophthalocyanines. While Cu<sup>II</sup>Pc gave Pc ring based redox processes, Mn<sup>III</sup>ClPc and Co<sup>II</sup>-Pc gave metal based electron transfer reactions in addition to the Pc based redox reactions, which enriched the possible usage of the complex in various electrochemical technologies. Also, rich redox activities of cobalt and manganese phthalocyanines indicated their possible usage in especially electrocatalytic and electrochromic applications.

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