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## Synthesis and electrochemical and in situ spectroelectrochemical characterization of manganese, vanadyl, and cobalt phthalocyanines with 2-naphthoxy substituents

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#### A R T I C L E I N F O

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#### ABSTRACT

Metallo (Mn, Co, VO) phthalocyanines bearing peripheral 2-naphthoxy groups were synthesized by cyclotetramerisation of the corresponding phthalonitrile derivative. The phthalocyanine compounds were characterized by elemental analyses, mass, FT-IR and UV–vis spectral data. Three intense bands in the electronic spectra clearly indicate the absorptions resulting from naphthyl groups along with the Q and B bands of the phthalocyanines. Electrochemical and spectroelectrochemical measurements exhibit that incorporation of redox active metal ions, Co<sup>II</sup> and Mn<sup>III</sup>, into the phthalocyanine core extends the redox capabilities of the Pc ring including the metal-based reduction and oxidation couples of the metal. Presence of molecular oxygen in the electrolyte system affects the voltammetric and spectroelectrochemical responses of the cobalt and manganese phthalocyanies due to the interaction between the complexes and molecular oxygen. Interaction reaction of oxygen with CoPc occurs via an "inner sphere" chemical catalysis process. While CoPc gives the intermediates  $[O_2^--Co^IIPc^{-2}]^-$  and  $[O_2^2-Co^IIPc^{-2}]^2^-$ , MnPc forms  $\mu$ -oxo MnPc species. An in situ electrocolorimetric method has been applied to investigate the color of the electro-generated anionic and cationic forms of the complexes for possible electrochromatic applications.

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#### 1. Introduction

Phthalocyanines (Pcs) are  $18 \pi$ -electron macrocyclic conjugated systems which attract great interest due to their diverse applications in medicinal and materials chemistry [1]. A number of modifications can be made in the macrocycle either by introduction of different central ions or by substitution of various groups at the peripheral sites of the ring [2]. The addition of substituents to the peripheral positions of the phthalocyanine ring is expected to give enhanced solubility in numerous organic solvents [3,4] and affect the electronic spectra depending on their properties and solvents may also lead to changes in photochemical and photophysical behavior of phthalocyanines [5].

Over the years metallophthalocyanines (MPcs) have been the active site of many applications in areas such as catalysis [6], sensors [7] and photodynamic therapy (PDT) [8]. MPcs containing redox active transition metal ions such as  $Co^{2+}$ ,  $Fe^{3+}$  and  $Mn^{3+}$  are known to be effective electrocatalysts and electrochemical

sensors under homogenous and heterogeneous conditions [1,2,9]. Vanadylphthalocyanine (VOPc) has been investigated extensively as a photosensitive reagent in photo-electrophoresis, xerographic imaging techniques, and optical recording materials [10] and have been employed for polymerisation of ethylene in the presence of methyl-aluminoxane (MAO) as a co-catalyst [11]. The electrochemical properties of manganese phthalocyanine (MnPc) complexes have also generated considerable attention [12]. MnPc complexes show interesting electrochemical behavior with oxidation states of the central manganese ion ranging from Mn<sup>I</sup> to Mn<sup>IV</sup> [13], thus enhancing detection of various analytes involving multi-electron transfer processes.

The present paper reports the synthesis and characterization of metallo (Mn, Co, VO) phthalocyanines containing 2-naphthol moieties at the periphery, since the interest in MPcs having redox active metal centers which are easily reduced and/or oxidized is of importance since these complexes are well-known electrochromophores and electro-catalysts for many reactions such as electrocatalytic reduction of molecular oxygen for fuel cell applications [14–18]. The electrocatalytic mechanisms of MPcs for oxygen reduction reaction (ORR) in aqueous solution are well known [14–18]. Although ORR mechanisms in the aprotic solvents such as acetonitrile (CH<sub>3</sub>CN), dimethylsulfoxide (DMSO) and



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dichloromethane (DCM) are well known, there is no study on detailed investigation of electrocatalytic activity of MPcs for ORR in aprotic solvents. Indeed, the electrochemical reduction of  $O_2$  is an important field of research as it is the main component in alternative fuel applications. Therefore, in this study we have performed voltammetric and in situ spectroelectrochemical characterization of the newly synthesized MPc complexes and detailed investigation for the interaction of MPcs with molecular oxygen with voltammetric and in situ spectroelectrochemical measurements. We have also aimed to determine intermediate adducts with in situ spectroelectrochemical measuremetric data.

### 2. Experimental

#### 2.1. Materials and equipment

Dimethyl sulfoxide (DMSO), dichloromethane (DCM), chloroform (CHCl<sub>3</sub>), tetrahydrofuran (THF), methanol (MeOH), 1pentanol, n-hexane and toluene were purchased from Merck. Potassium carbonate, manganese chloride and cobalt chloride were purchased from Aldrich. 4-Nitrophthalonitrile was synthesized according to published methods [19]. 4-(2-Naphthoxy) phthalonitrile (1), tetrakis(2-naphthoxy)vanadylphthalocyanine (2) and tetrakis(2-naphthoxy)cobalt(II)phthalocyanine (3) were prepared as reported earlier [20,21].

IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR (ATR sampling accesory) spectrophotometer, and electronic spectra were recorded on a Scinco Neosys-2000 double-beam ultraviolet–visible (UV–vis) spectrophotometer using 1 cm path length cuvettes at room temperature. Mass spectra were performed on Ultima Fourier Transform and Varian 711 mass spectrophotometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Centre. All solvents were dried and purified according to the literature [22]. The homogeneity of the products was tested in each step by TLC (SiO<sub>2</sub>).

# 2.2. 2(3),9(10),16(17),23(24)-Tetrakis-(2-naphthoxy) phthalocyaninato manganese(III) chloride (**4**)

A mixture of compound **1** (1.00 mmol, 0.270 g) and anhydrous  $MnCl_2$  (0.25 mmol, 0.032 g) in 2.0 mL of DMF was fused in a glass tube. The mixture was heated and stirred at 145 °C for 24 h under N<sub>2</sub>. The resulting brown suspension was cooled to ambient temperature and the crude product was precipitated by addition of ethanol–water and then it was filtered off. The precipitate was washed first with water, cold ethanol, cold acetone, and hexane and then dried in *vacuo*. Finally, pure phthalocyanine complex was obtained by chromatography on silica gel using dichloromethane/ethanol (25:1) mixture as eluent. The yield was 40.10% (115 mg). Melting point: >200 °C. Anal. Calc. for  $C_{72}H_{40}ClMnN_8O_4$ : C, 73.82; H, 3.44; N, 9.56. Found: C, 73.69; H, 3.61; N, 9.75; IR (cm<sup>-1</sup>): 3054 (Ar–H), 1610–1597 (Ar C=C), 1461, 1246 (Ar–O–Ar), 1120, 964, 741; MS: *m/z* 1171.25 [M+1]<sup>+</sup>, 1135.55 [M–Cl]<sup>+</sup>.

## 2.3. Electrochemical in situ spectroelectrochemical and in situ electrocolorimetric measurements

The cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements were carried out with Gamry Reference 600 potentiostat/galvanostat controlled by an external PC and utilizing a three-electrode configuration at 25 °C. The working electrode was a Pt disc with a surface area of 0.071 cm<sup>2</sup>. A Pt wire served as the counter electrode. Saturated calomel electrode (SCE) was

employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade tetrabutylammonium perchlorate (TBAP) in extra pure DMSO and DCM was employed as the supporting electrolyte at a concentration of 0.10 mol dm<sup>-3</sup>.

UV-vis absorption spectra and chromaticity diagrams were measured by an Ocean Optics QE65000 diode array spectrophotometer. In situ spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of a guartz thin-layer spectroelectrochemical cell at 25 °C. The working electrode was a Pt gauze semitransparent electrode. Pt wire counter electrode separated by a glass bridge and a SCE reference electrode separated from the bulk of the solution by a double bridge were used. In situ electro-colorimetric measurements, under potentiostatic control, were obtained using an Ocean Optics QE65000 diode array spectrophotometer at color measurement emission mode by utilizing a three-electrode configuration of the thin-layer quartz spectroelectrochemical cell. The standard illuminant A with 2° observer at constant temperature in a light booth designed to exclude external light was used. CIE standard illuminant A is intended to represent typical, domestic, tungsten-filament lighting. Its relative spectral power distribution is that of a Planckian radiator at a temperature of approximately 2856 K. Due to the nature of the distribution of cones in the eye, the tristimulus values depend on the observer's field of view. To eliminate this variable, the CIE defined the standard (colorimetric) observer. Originally this was taken to be the chromatic response of the average human viewing through a 2°. Thus the CIE 1931 Standard Observer is also known as the CIE 1931 2° Standard Observer. Prior to each set of measurements, background color coordinates (x, y and z values) were taken at open-circuit using the electrolyte solution without the complexes under study. During the measurements, readings were taken as a function of time under kinetic control, however only the color coordinates at the beginning and final of each redox processes were reported.

Oxygen interaction experiments are followed in three cases. *Case* 1: CV responses of electrolyte system under atmospheric conditions were recorded. *Case* 2: CV responses of MPcs in the electrolyte system purged with nitrogen were recorded. *Case* 3: CV responses of MPcs in the electrolyte system bubbled gradually with oxygen were recorded.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

As used in the preparation of a variety of ether or thioethersubstituted phthalonitriles, the principle reaction to obtain 4-(2-naphthoxy)phthalonitrile (**1**) was a base-catalysed aromatic nitro displacement of 4-nitrophthalonitrile with 2-naphthol [23–25]. The base of choice in this reaction was  $K_2CO_3$  and dry DMSO was preferred as the solvent.

Conversion of 4-(2-naphthoxy)phthalonitrile into the corresponding metallo phthalocyanines (**2–4**) was accomplished in a high-boiling point solvents (DMF) in the presence of corresponding metal salts (MnCl<sub>2</sub>, VO(SO<sub>4</sub>), CoCl<sub>2</sub>). Produced MPc products were extremely soluble in various solvents such as chloroform, dichloromethane, tetrahydrofuran, and acetone and they were purified by column chromatography on silica gel with dichloromethane/ethanol (25:1) as the eluent. All compounds were identified through various spectroscopic techniques such as <sup>1</sup>H NMR, FT-IR, UV–vis, mass spectra, and elemental analysis. The results obtained were in agreement with the predicted structures given in Scheme 1. Naturally, the phthalocyanine products synthesized during this work are a mixture of positional



Scheme 1. Synthetic route of metallo phthalocyanine derivatives (2-4).

isomers while the phthalonitrile precursor carries a single substituent but the isomers were hardly separated by chromatography [26].

In the IR spectra of **4**, aromatic C–O–C peak was observed at  $1222 \text{ cm}^{-1}$  and characteristic substituted naphthalene peak was observed at about 758 cm<sup>-1</sup>. In the mass spectra of **4**, the presence of the characteristic molecular ion peaks at  $m/z = 1171.25 \text{ [M+1]}^+$  and 1135.55 [M–CI]<sup>+</sup> confirmed the proposed structure. <sup>1</sup>H-NMR measurement of the manganese phthalocyanine was precluded owing to its paramagnetic nature.

The phthalocyanines 2 and 3 show typical electronic spectra with two strong absorption regions; one of them in the UV region at about 300–400 nm (B band) arising from the deeper  $\pi$ -levels  $\rightarrow \pi^*$ transition and the other in the visible part of the spectrum around 600–700 nm (Q band) attributed to the  $\pi$ - $\pi$ \* transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc<sup>-2</sup> ring. The characteristic Q band transition of metallophthalocyanines with D<sub>4h</sub> symmetry is observed as a single band of high intensity in visible region (Fig. 1) [27]. The vanadyl phthalocyanine **2** shows the expected Q band as a single absorption at around 703 nm (Fig. 1). The observation of near-IR absorption for 2, containing V(IV) central metal, confirms that near-IR absorption is favored for MPc complexes containing central metals in a high oxidation state. The red shift is a result of the lowering of the HOMO-LUMO gap, by either destabilizing the HOMO or stabilizing the LUMO by the central metal [28].

The Q-band of complex **4** in the UV–vis spectra was red-shifted (at 718–733 nm) in different solvents (Fig. 2) relative to that of the other analogs. This observation is characteristic of manganese phthalocyanine complexes [29]. Positions of the Q bands of MPc complexes are closely related to the refractive indices of the



**Fig. 1.** UV–visible spectra of compounds **2** and **3**  $(5 \times 10^{-6} \text{ mol dm}^{-3})$  in THF.



Fig. 2. Q bands of compounds  $2-4(10^{-5} \text{ mol dm}^{-3})$  in different solvents.

solvents [30]. The higher the refractive index of the solvent, the more red-shifted the Q band of the MPc complex concerned. THF has a refractive index of 1.406 (at 718 nm), compared to 1.479 for DMSO (at 733 nm), justifying the red-shift in the Q band of the complexes in THF, relative to that in DMSO. The B-bands of **2–4** were observed at around 340–350 nm as a single band. An intense absorption due to the  $\pi$ – $\pi$ \* transition of naphthalene groups appears for **2–4** in the UV region at about 286 nm (Fig. 1) [31].

#### 3.2. Voltammetric characterization

The CVs and SWVs of VOPc (**2**), CoPc (**3**), and MnPc (**4**) were obtained in deaerated DMSO and DCM/TBAP electrolyte system on a Pt working electrode. Table 1 lists the assignments of the redox couples and estimated electrochemical parameters including the half-wave peak potentials ( $E_{1/2}$ ), ratio of the anodic to the cathodic peak currents ( $I_{p,a}/I_{p,c}$ ), peak to peak potential separations ( $\Delta E_p$ ) and difference between the first oxidation and reduction processes ( $\Delta E_{1/2}$ ).  $\Delta E_{1/2}$  reflects the HOMO–LUMO gap for metal free Pcs and it is related with HOMO–LUMO gap in MPc species having redox inactive metal center. Peak to peak separations,  $E_{1/2}$  and  $\Delta E_{1/2}$  values are in agreement with the reported data for redox processes of the metallophthalocyanine complexes [32–38].

Fig. 3 shows the CV and DPV of VOPc (2). Within the electrochemical window of DMSO/TBAP, the complex 2 illustrates two one-electron oxidation and two quasi-reversible one-electron reduction processes. For the first oxidation couple, the anodic to the cathodic peak separations ( $\Delta E_p$ ) changed from 67 to 130 mV with the scan rates from 10 to 500 mV s<sup>-1</sup> support the quasi-reversible electron transfer character of the redox process. Reversibility is illustrated by the similarity in the forward and reverse SWVs (Fig. 3b) [39]. Unity of the  $I_{pa}/I_{pc}$  ratio with the scan rates indicated the purely diffusion controlled electron transfer mechanism of the processes. Other redox processes have quasi-reversible electron transfer characters. Assignments of the redox couples are performed by spectroelectrochemical measurements given below.

Fig. 4 shows the CV and DPV of CoPc (**3**) in DCM/TBAP electrolyte. Within the electrochemical window of DCM/TBAP, the complex **3** undergoes a one-electron oxidation and two one-electron reduction processes. For the first reduction couple,  $\Delta E_p$  values changed from 61 to 115 mV with the scan rates from 10 to 500 mV s<sup>-1</sup> which supports reversible electron transfer character of the redox process. Reversibility is illustrated by the similarity in the forward and reverse SWVs (Fig. 4b) [39]. While the  $I_{pa}/I_{pc}$  ratio of first reduction couple is unity at slow scan rates, it deviates from unity with increasing scan rates, which indicate existence of a kinetic control after the first reduction process. A wave ( $R_x$ ) at -0.68 V recorded at high scan rates support existence of this kinetic control. While the  $R_x$  process is invisible at slow scan rates, its peak current increases more than that of  $R_I$  with increasing scan rates and this wave disappeared with dilution. These data indicate aggre-

#### Table 1

Voltammetric data of the complexes with the related metallophthalocyanines for comparison.

Complex	Ring oxidations		idations	$M^{III}/M^{II}$	$M^{II}/M^{I}$	Ring reductions		$^{d}\Delta E_{1/2}$	Ref.	
VOPc (in DCM)	${}^{a}E_{1/2}$ vs. SCE	1.41 <sup>e</sup>	0.90			-0.64	-0.98	-1.83	1.54	
	${}^{b}\Delta E_{p}$ (mV)	-	85			62	655	85		tw
	<sup>c</sup> I <sub>pa</sub> /Î <sub>pc</sub>	-	0.87			0.99	0.88	0.85		
CoPc (in DCM)	${}^{a}E_{1/2}$ vs. SCE		0.80		-0.32	-1.43			1.12	
	$^{b}\Delta E_{p}$ (mV)		300		70	130				tw
	<sup>c</sup> I <sub>pa</sub> /I <sub>pc</sub>		0.98		0.97	0.62				
CoPc (in DMSO)	${}^{a}E_{1/2}$ vs. SCE		0.83	0.27	-0.55	-1.49	-2.12 <sup>e</sup>		0.82	
	$^{b}\Delta E_{p}$ (mV)		105	62	75	68	-			tw
	<sup>c</sup> I <sub>pa</sub> /I <sub>pc</sub>		0.80	0.78	1.00	0.96	-			
MnPc (in DCM)	${}^{a}E_{1/2}$ vs. SCE	1.23 <sup>e</sup>	1.04	-0.16	-0.95	-1.45			1.20	
	${}^{\mathbf{b}}\Delta E_p$ (mV)	-	78	170	152	220				tw
	<sup>c</sup> I <sub>pa</sub> /I <sub>pc</sub>	-	0.85	0.99	0.91	0.55				
$OV[Pc(SC_5H_{11})_8]$	$E_{1/2}$ (in DCM)	1.02	0.68			-0.58	-0.89	-1.14		[32]
$OV[Pc(OC_6H_3(t-Bu)_2)_4]$	$E_{1/2}$ (in DCM)	1.21	0.76			-0.62	-1.12	-2.07		[33]
$OV[Pc(C_8H_{17})_4]$	$E_{1/2}$ (in DMF)		0.94			-0.51	-0.97	-1.94		[33]
$Mn-OAc[Pc()_4]$	$E_{1/2}$ (in DMF)		0.87	-0.14	-0.69	-1.46				[34]
$Mn-OAc[Pc(S(CH_2)_2OH)_8]$	$E_{1/2}$ (in DMSO)		0.97	-0.12	-0.66	-0.98				[35]
$Co[Pc(S(CH_2)_2OH)_4]$	$E_{1/2}$ (in DCM)		0.43	1.00	-0.37	-129	-1.90			[36]
$Co[Pc(OC_6H_4(OC_6F_5)_2)_4]$	$E_{1/2}$ (in DCM)		0.65	-	-0.39	-1.45				[37]
$CoPc[Pc(OCH_2(C_6F_5)_2)_4]$	$E_{1/2}$ (in DMSO)			0.43	-0.43	-0.83	-1.39			[38]

tw: this work.

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

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

<sup>c</sup>  $I_{pa}/I_{pc}$  for reduction,  $I_{pc}/I_{pa}$  for oxidation processes at 0.100 V s<sup>-1</sup> scan rate.

 $d \Delta E_{1/2} = E_{1/2}$  (first oxidation) –  $E_{1/2}$  (first reduction) = HOMO–LUMO gap for metallophthalocyanines having electro-inactive metal center (metal to ligand (MLCT) or ligand to metal (LMCT) charge transfer gap for MPc having redox active metal center.).

<sup>e</sup> The process is recorded with SWV.



**Fig. 3.** (a) CVs of VOPc (**2**)  $(5.0 \times 10^{-4} \text{ mol dm}^{-3})$  at various scan rates on Pt in DCM/TBAP. (b) SWV of VOPc, SWV parameters: pulse size = 100 mV; step size: 5 mV; frequency: 25 Hz.



**Fig. 4.** (a) CVs of CoPc (**3**)  $(5.0 \times 10^{-4} \text{ mol dm}^{-3})$  at various scan rates on Pt in DCM/TBAP (inset: CVs of CoPc recorded at different cathodic switching potentials at 0.100 V s<sup>-1</sup> scan rate). (b) SWV of CoPc, SWV parameters: pulse size = 100 mV; step size: 5 mV; frequency: 25 Hz.



Fig. 5. (a) CVs of CoPc (3)  $(5.0 \times 10^{-4} \text{ mol dm}^{-3})$  at various scan rates on Pt in DMSO/TBAP. (b) SWV of CoPc, SWV parameters: pulse size = 100 mV; step size: 5 mV; frequency: 25 Hz.

gation of the complex and aggregated species reduce at -0.68 V. Aggregation–disaggregation equilibrium is affected with the scan rate and concentration; whose responses are recorded as changing the relative peak current ratios of the R<sub>I</sub> and R<sub>x</sub> process. Differentiating the switching potential does not alter the CV responses of the complex as shown in Fig. 4a (inset). Other redox processes have quasi-reversible electron transfer characters with respect to  $\Delta E_p$ and  $I_{p,a}/I_{p,c}$  values. Assignments of the redox couples are performed by spectroelectrochemical measurements given below.

To investigate the effect of the solvent to the electrochemical properties of the complexes, CV and SWV responses of CoPc (3) are recorded in DMSO/TBAP electrolyte (Fig. 5).Within the electrochemical window of DMSO/TBAP, the complex 3 gives two one-electron oxidations and three reversible one-electron reductions. When DMSO is used instead of DCM as the solvent of electrolyte, it is obvious that redox processes get more reversible and aggregation of the complex decreases. This may be due to the coordinating feature of DMSO. It is known that CoPc complexes can coordinate with coordinating reagent, e.g. DMSO or TBAP [40]. Extension of the coordination of the cobalt center of the complex prevents interaction of the monomeric species with each other, thus diminishes aggregation of the complex. Moreover, redox processes of the complex shift to the negative potentials due to the high electron donating ability of DMSO with respect to DCM. While  $\Delta E_{1/2}$  value of CoPc is 1.21 V in DCM, it decreases to 0.82 V in DMSO. This decrease in  $\Delta E_{1/2}$  is resulted from shifting of the oxidation processes to the negative side in DMSO due to the coordination of DMSO to the Co<sup>III</sup> center of the complex. As discusses in the spec-



**Fig. 6.** (a) CVs of MnPc (**4**)  $(5.0 \times 10^{-4} \text{ mol dm}^{-3})$  at various scan rates on Pt in DMSO/TBAP (inset: CVs of MnPc recorded with different switching potentials at 0.100 Vs<sup>-1</sup> scan rate). (b) SWV of MnPc, SWV parameters: pulse size = 100 mV; step size: 5 mV; frequency: 25 Hz.

troelectrochemical measurement section below, the first oxidation process of CoPc in DMSO is a metal-based ( $[Co^{II}Pc^{-2}]/[Co^{III}Pc^{-2}]^{1+}$ ) process, while it is a ligand-based process ( $[Co^{II}Pc^{-2}]/[Co^{II}Pc^{-1}]^{1+}$ ) in DCM solvent. Due to the wide negative potential window of DMSO, it could be possible to observe the third reduction process ( $R_{III}$ ) at -2.12 V in addition to the reversible  $R_I$  process at -0.55 V and the reversible  $R_{II}$  process at -1.49 V. Assignment change of the redox couples during the oxidation processes cause to shifting of the oxidation processes to the negative side, thus two oxidation couples are clearly observed at 0.27 V ( $O_I$ ) and 0.83 V ( $O_{II}$ ).

As shown in Fig. 6, MnPc (4) displays three well-resolved reduction processes ( $R_I$  at -0.16 V,  $R_{II}$  at -0.95 V and  $R_{III}$  at -1.45 V) with CV and SWV measurements in DCM/TBAP electrolyte. Two oxidation couples are also recorded at 1.04V (O<sub>I</sub>) and at 1.23V (O<sub>II</sub>) with both CV and SWV measurements. As shown in Fig. 6a (inset), altering the cathodic switching potential influences the peak character of the reduction processes. When the potential is switched before -1.30V, the first and second reduction processes are quasi-reversible and diffusion controlled with respect to the peak separation and peak current ratio analyses. However, when the switching potential passes the third reduction potential,  $I_{p,a}/I_{p,c}$  values of the first and second reduction processes deviate from unity due to the decreasing of the anodic peak current of these processes. This deviation  $I_{p,a}/I_{p,c}$  values indicate presence of a chemical reaction succeeding the third reduction process. This chemical reaction may be removal of the axial chloride from manganese center of the complex. It is documented that decreasing



**Fig. 7.** In situ UV-vis spectral changes of VOPc (**2**) in DCM/TBAP electrolyte. (a)  $E_{app} = -0.80V$ . (b)  $E_{app} = -1.30V$ . (c)  $E_{app} = 1.00V$ . (d) Chromaticity diagram of VOPc (each symbol represents the color of electro-generated species;  $\Box: [V^{IV}OPc^{-2}]$ .  $\bigcirc: [V^{IV}OPc^{-3}]^{1-}$ ,  $\triangle: [V^{IV}OPc^{-4}]^{2-}$ ,  $\Leftrightarrow: [V^{IV}OPc^{-1}]^{1+}$ .

the oxidation state of a metal ion favors less coordination especially for CoPc and MnPc complexes [40]. SWV measurements in Fig. 6b clearly show effect of the switching potential to the electron transfer properties of the complex. As shown in this figure, when the anodic scan starts from -1.30 V (green SWV), two clear anodic waves for R<sub>I</sub> and R<sub>II</sub> processes are recorded. However, new waves are observed in addition to decreasing of the previous wave, when SWV scan starts from -1.80 V (blue SWV). These data support presence of the proposed chemical reaction.

#### 3.3. In situ spectroelectrochemical measurements

Spectroelectrochemical studies were employed to confirm the assignments of the electron transfer reactions recorded with CV and SWV measurements of MPcs. Fig. 7 represents in situ UV–vis spectral changes and in situ recorded chromaticity diagram of VOPc (**2**) in DCM/TBAP. During the first reduction process ( $E_{ap} = -0.80$  V), while the Q band at 702 nm decreases in intensity, two new bands enhance in the metal to ligand charge transfer (MLCT) regions at 590 and 882 nm. At the same time, the B band at 342 nm and the band at 410 nm decrease in intensity. These spectral changes characterize a ligand-based reduction process and assigned to the reduction of [V<sup>IV</sup>OPc<sup>-2</sup>] to [V<sup>IV</sup>OPc<sup>-3</sup>]<sup>1–</sup> species (Fig. 7a) [33,34,41]. The band at 590 nm starts to decrease under the same potential application at the end of the first reduction process. This unusual changes cause to vibration of the isosbestic point at around 613 nm while the process give clear well-defined isosbestic point at 274,

477 and 796 nm. The vibration of the isosbestic point at 613 nm and unusual change of the band at 590 nm may be due to a conformational change within the complex. As shown in Fig. 6b, under the applied potential at -1.30 V, the O band at 702 nm decreases without shift while a new broad band is recorded at 535 nm. At the same time the band at 882 nm shifts to 917 nm with increasing in intensity. Moreover the bands at 335 and 637 nm decrease in intensity. These spectral changes are characteristic of the ring-based reduction of [V<sup>IV</sup>OPc<sup>-3</sup>]<sup>1-</sup> to [V<sup>IV</sup>OPc<sup>-4</sup>]<sup>2-</sup>. Fig. 7c represents the spectral changes during the first oxidation process of the complex. During electrolysis at 1.00 V, decreasing of the Q band without shifting and increasing the bands at 533 and 865 nm indicate a Pc ringbased process and assigned to [V<sup>IV</sup>OPc<sup>-2</sup>]/[V<sup>IV</sup>OPc<sup>-1</sup>]<sup>1+</sup> process [33,34,41]. Chemical reversibility of the processes under controlled potential application was checked by applying 0.00 V after each electron transfer reactions. When 0.0 V was applied to the working electrode, while initial spectrum of VOPc was regenerated after the first reduction process, initial spectrum was not obtained after the second reduction and first oxidation reactions. These data indicate chemical reversibility of the first reduction process and irreversibility of other processes

The color change of the solution of the complexes during the redox processes were recorded using in situ colorimetric measurements. Without any potential application, the solution of  $[V^{IV}OPc^{-2}]$  is green (x = 0.287 and y = 0.372) (Fig. 7d). As the potential is stepped from 0 to -0.80 V, color of the neutral  $[V^{IV}OPc^{-2}]$  changes and light blue color (x = 0.288 and y = 0.319) for monoan-



**Fig. 8.** In situ UV-vis spectral changes of CoPc (**3**) in DMSO/TBAP electrolyte. (a)  $E_{app} = -0.40$  V. (b)  $E_{app} = -1.30$  V. (c)  $E_{app} = 0.40$  V. (d) Chromaticity diagram of CoPc (each symbol represents the color of electro-generated species;  $\Box: [Co^{II}Pc^{-2}]^{1-}$ ,  $\Delta: [Co^{IP}C^{-3}]^{2-}$ ,  $\Delta: [Co^{II}Pc^{-2}]^{1+}$ .

ionic form of  $[V^{IV}OPc^{-3}]^{1-}$  was obtained at the end of the first reduction. Similarly color of the dianionic species,  $[V^{IV}OPc^{-4}]^{2-}$ , was recorded as dark blue (*x*=0.290 and *y*=0.295) and monocationic species,  $[V^{IV}OPc^{-1}]^{1+}$ , was recorded as orange (*x*=0.362 and *y*=0.337).

Fig. 8 represents the in situ UV-vis spectral changes and in situ recorded chromaticity diagram of CoPc (3) in DMSO/TBAP. During the first reduction process, while the Q band shifts from 661 to 702 nm with increasing, a new band enhances at 469 nm. Moreover the B band shifts from 324 to 313 nm with increasing in intensity. These spectral changes characterize formation of [Co<sup>I</sup>Pc<sup>-2</sup>]<sup>1-</sup> species under the applied potential at -0.40 V (Fig. 8a) [41-45]. Well-defined isosbestic points are observed at 328, 388, 562, 679, and 742 nm. These isosbestic points demonstrate that the reduction proceeds cleanly in deoxygenated DMSO to give a single, reduced species. This process gives a color changes from light blue (x = 0.261and y=0.330) to green (x=0.351 and y=0.412) as shown in the chromaticity diagram (Fig. 8d). The process is chemically reversible, since approximately 95% of the original spectrum was obtained when 0.0 V was applied after the first reduction reaction. As shown in Fig. 8b, the Q band at 702 nm decreases without shift while a new broad band is recorded at 540 nm under the controlled potential application at -1.30 V. These spectral changes are characteristic of the ring-based reduction of [Co<sup>I</sup>Pc<sup>-2</sup>]<sup>1-</sup> species to [Co<sup>I</sup>Pc<sup>-3</sup>]<sup>2-</sup> species. Fig. 8c represents the spectral changes during the first oxidation process of the complex. During 0.40 V potential application, shifting of the Q band from 661 to 675 nm with increasing indicates the metal-based process and assigned to  $[Co^{II}Pc^{-2}]/[Co^{III}Pc^{-2}]^{1+}$ [41–45]. During the second oxidation process ( $E_{ap} = 1.00$  V), spectral changes assigned to a ring-based process was recorded. Color changes during the reduction and oxidation processes are represented in Fig. 8d.

Fig. 9 represents in situ UV-vis spectral changes and in situ recorded chromaticity diagram of MnPc (4) in DCM/TBAP. When the spectral changes (recorded under applied potential at the redox processes potential) are compared with the MnPc complexes in the literature [34,35,45-47], the first two reduction processes are easily assigned to the metal-based processes,  $[Cl-Mn^{III}Pc^{-2}]/[Cl-Mn^{II}Pc^{-2}]$  and  $[Cl-Mn^{II}Pc^{-2}]/[Cl-Mn^{IP}c^{-2}]$ and the third one is assigned to the ligand-based process, [Cl-Mn<sup>1</sup>Pc<sup>-2</sup>]/[Cl-Mn<sup>1</sup>Pc<sup>-3</sup>]. Oxidation process of the complexes is a ring-based process, [Cl-Mn<sup>III</sup>Pc<sup>-2</sup>]/[Cl-Mn<sup>III</sup>Pc<sup>-1</sup>], according to the spectral changes. Fig. 9a shows in situ UV-vis spectral changes observed upon controlled potential reduction of 4 at -0.30 V. Before any potential application, observation of a band at 524 nm and the red shifted Q band at 731 nm are characteristic of Mn<sup>III</sup>Pc<sup>-2</sup> species. During the first reduction process, the Q band at 731 nm shifts to 682 nm, while the B band at 369 shifts to 391 nm with increasing. These spectral changes are assigned to [Cl-Mn<sup>III</sup>Pc<sup>-2</sup>]/[Cl-Mn<sup>II</sup>Pc<sup>-2</sup>]<sup>1-</sup> process. The formation of [Cl-Mn<sup>II</sup>Pc<sup>-2</sup>]<sup>1-</sup> is characterized by shifting of the Q band to shorter wavelength [34,35,45-47]. To diminish the formation of  $\mu$ -oxo MnPc species the solution is purged gently with N<sub>2</sub> before the process and the solution is kept under N<sub>2</sub> atmosphere during



**Fig. 9.** In situ UV–vis spectral changes of MnPc (**4**) in DCM/TBAP electrolyte. (a)  $E_{app} = -0.30 \text{ V}$ . (b)  $E_{app} = -1.20 \text{ V}$  (inset:  $E_{app} = -1.50 \text{ V}$ ). (c)  $E_{app} = 1.00 \text{ V}$ . (d) Chromaticity diagram of MnPc (each symbol represents the color of electro-generated species;  $\Box$ : [Cl–Mn<sup>III</sup>Pc<sup>-2</sup>],  $\bigcirc$ : [Cl–Mn<sup>II</sup>Pc<sup>-2</sup>]<sup>-</sup>,  $\land$ : [Cl–Mn<sup>II</sup>Pc<sup>-2</sup>]<sup>2-</sup>,  $\bigtriangledown$ : [Cl–Mn<sup>II</sup>Pc<sup>-2</sup>]<sup>2-</sup>,  $\lor$ : [Cl–Mn<sup>II</sup>P

the process. It is well known that µ-oxo MnPc species give an absorption band at around 630 nm [34,35,45-47]. There is no band at around this wavelength during the reduction processes. Thus, all redox processes are easily assigned to the formation of electrogenerated MnPc(4) species. Color changes of the complex in solution during the redox processes were recorded by in situ electrocolorimetric measurements. Without any potential application, the solution of **4** is yellowish green (x=0.365 and y = 0.370) (Fig. 9d). As the potential is stepped from 0 to -0.30 V color of neutral Cl–Mn<sup>III</sup>Pc<sup>-2</sup> changes to bluish green (x = 0.313 and y = 0.344). The reduction of Mn<sup>II</sup>Pc<sup>-2</sup> species has been a subject of some controversy, with some reports proposing ring reduction to the Mn<sup>II</sup>Pc<sup>-3</sup> species and others suggesting metal reduction to the  $Mn^{I}Pc^{-2}$  species. During the second reduction process of 4, while two new bands are recorded at 518 and 841 nm, the Q band and the band at 682 nm decrease in intensity. The band recorded at 524 nm and decreasing of the Q band can characterize a metalbased reduction of [Cl-Mn<sup>II</sup>Pc<sup>-2</sup>]<sup>1-</sup> to [Cl-Mn<sup>I</sup>Pc<sup>-2</sup>]<sup>2-</sup> species (Fig. 9b) [34,35,45–47]. During the third reduction of the complex at -1.50 V potential application, two distinct spectral changes are recorded. First of all while a broad new band is recorded at around 570 nm, the band at 841 nm shifts to 808 nm. At the same time, the Q band at 682 nm decreases in intensity. During these changes the band at 518 nm remains as unchanged. Then the bands at 518 nm and 808 nm decrease slightly while the band at 570 nm continues to increase. In both of these two different spectral changes, increasing of the band at around 570 nm can characterize a ring-based reduction of  $[Cl-Mn^{I}Pc^{-2}]^{1-}$  to  $[Cl-Mn^{I}Pc^{-3}]^{2-}$ species (Fig. 9b, inset) [34,41-43]. These two different changes under the same potential application may be due to removing of the axial chloride ion during the third reduction process. These spectral changes are in harmony with the CV responses of the complex given above. While original spectra were obtained after the first and second reduction processes, the spectrum did not return to the original spectra after the third reduction process, when 0.0 V was applied after these processes. These data indicate irreversibility of the third reduction process. To confirm the origin of the oxidation process, O<sub>I</sub>, in situ UV-vis spectral changes were recorded under the controlled potential application at 1.20V (Fig. 9c). During this process, the Q band decreases in intensity, while a new band at 832 nm is recorded. At the same time the band characterizing Mn<sup>III</sup> metal center increases in intensity. These spectral changes are characteristics of a ring-based oxidation process for MnPc complexes, thus the couple O<sub>I</sub> is easily assigned to  $[Cl-Mn^{III}Pc^{-2}]/[Cl-Mn^{III}Pc^{-1}]^{1+}$  redox process [34,41–43]. Colors of the anionic and cationic species were given in the chromaticity diagram (Fig. 9d).

#### 3.4. Interaction of complexes with molecular oxygen

There are many studies on the redox reaction of  $O_2$  in the protic solvents, but studies in the aprotic solvents are deficient and the majorities of these are related to the mechanistic investigation of superoxide and/or peroxide formation from molecular



**Fig. 10.** (a) CVs (inset: CVs of O<sub>2</sub> in DMSO/TBAP electrolyte system with increasing amounts of O<sub>2</sub>) and (b) SWVs of CoPc (**3**) at  $0.100 \text{ V s}^{-1}$  scan rate on Pt with increasing amounts of O<sub>2</sub> in DMSO/TBAP electrolyte system. (SWV parameters: pulse size = 100 mV; step size: 5 mV; frequency: 25 Hz;  $E_i = 0.00 \text{ V}$  and  $E_f = -1.70 \text{ V}$  for SWV having cathodic currents;  $E_i = -1.70 \text{ V}$  and  $E_f = 0.00 \text{ V}$  for SWV having anodic currents).

oxygen. In this study, we have investigated the interaction of MPcs with  $O_2$  to clarify the electrocatalytic  $O_2$  reduction mechanism in the aprotic media with different electrochemical and in situ spectro-electrochemical techniques. Fig. 10a (inset) gives the CV responses of O<sub>2</sub> dissolved in DMSO/TBAP electrolyte system without MPc (case 2). Early investigations of the oxygen reduction reaction (ORR) in the aprotic solvents such as acetonitrile (ACN), dimethyl-sulfoxide (DMSO) and N,N-dimethylformamide (DMF), showed that  $O_2$  reduces via 1 e<sup>-</sup> to superoxide in the non-aqueous environment [48,49]. Similarly in this study, clear quasi-reversible oxygen/superoxide  $(O_2/O_2^-)$  couple is recorded at -1.00 V in DMSO at  $0.10 \,\text{mV}\,\text{s}^{-1}$  scan rate.  $O_2/O_2^-$  couple shifts to the negative potentials with increasing of O<sub>2</sub> concentration. Interaction of O<sub>2</sub> with MPcs was performed by bubbling of the electrolyte with O2 in which MPcs were dissolved. While VOPc did not interact with O<sub>2</sub>, and gives similar complex-based redox processes with those recorded in *case* 1 (except ORR process), presence of  $O_2$  in the CoPc and MnPc solution alters electrochemical responses of both MPcs and O<sub>2</sub> considerably. Fig. 10 represents voltammetric responses of CoPc solution bubbled with O<sub>2</sub> gradually. Electrochemical responses of O<sub>2</sub> recorded in *case* 3 with increasing O<sub>2</sub> concentration are analyzed as: (i) Redox couples of CoPc and O2 are considerably influenced with increasing O<sub>2</sub> concentration. (ii) ORR couple in case 3 shifts ca. 70 mV toward the positive direction and gets more reversible with respect to those recorded in case 2  $(\Delta E_p \text{ values of ORR couple increase from 410 to 582 mV in case 2,$  while  $\Delta E_p$  values change from 135 to 250 mV in *case* 3). (iii) While ORR couple has only one reverse peak in *case* 2, a split reverse peak is recorded with SWV in *case* 3 (Fig. 10b). Shifting of the ORR couple to the less negative potentials and increasing reversibility of the ORR process indicate the electrocatalytic activity of CoPc to the oxygen reduction reaction.

Presence of  $O_2$  in the electrolyte system also influences the electrochemical properties of CoPc. Electrochemical responses of CoPc in *case* 3 with increasing  $O_2$  concentration are recorded as: (i) both the anodic and the cathodic waves of  $R_I$  decrease gradually in current intensity, while anodic wave shifts to positive potentials. (ii) Couple IV shifts to the negative potentials with increasing in current intensity. (iii) A new wave is recorded at -0.30 V during the anodic scans. These voltammetric data indicate that CoPc interacts with  $O_2$  and this interaction affects the voltammetric behaviors of CoPc as well as  $O_2$ .

In situ spectroelectrochemical studies were employed to determine the mechanism of the interaction between CoPc and  $O_2$ . Fig. 11 represents in situ UV-vis spectral changes of CoPc in case 3in DMSO/TBAP electrolyte system. Under the open circuit potential, spectra of CoPc did not change with time in case 3. This behavior indicates that  $[Co^{II}Pc^{-2}]$  does not interact with O<sub>2</sub>. During the first reduction process (at -0.50 V), spectral changes assigned to [Co<sup>II</sup>Pc<sup>-2</sup>] to [Co<sup>I</sup>Pc<sup>-2</sup>]<sup>1-</sup> reduction reaction are observed in both case 1 (Fig. 8a) and case 3 (Fig. 11a). However final spectrum in case 3 is not completely turned to the spectrum of  $[Co^{I}Pc^{-2}]^{1-}$  recorded in case 1 (Fig. 8a). These spectral changes indicate the interaction of reduced complex  $[Co^{I}Pc^{-2}]^{1-}$  with the molecular oxygen. In this interaction, the molecular oxygen may reoxidize the reduced [Co<sup>I</sup>Pc<sup>-2</sup>]<sup>1–</sup>, and an equilibrium is established between [Co<sup>II</sup>Pc<sup>-2</sup>] and  $[Co^{I}Pc^{-2}]^{1-}$ . Different potential applications between -0.60and -0.90V were applied to observe the interaction between [Co<sup>I</sup>Pc<sup>-2</sup>]<sup>1-</sup>and molecular oxygen. During these potential applications, spectra of the complex change considerably and give the same spectra of [Co<sup>I</sup>Pc<sup>-2</sup>]<sup>1-</sup> recorded at -0.50V potential application in case 1. This change indicates that electron transfer reaction rate gets dominant at more negative potential application with respect to reoxidation of the reduced  $[Co^{I}Pc^{-2}]^{1-}$  with oxygen, thus the final spectrum reflects the  $[Co^{I}Pc^{-2}]^{1-}$  form of the complex dominantly (Fig. 11b). To observe the effects of the ORR on the spectra of the complex, spectral changes are recorded under the applied potential at -1.25 V (ORR potential). While there was no spectral change in case 1, the spectra starts to return back to the original spectrum of the neutral CoPc in *case* 3 (Fig. 11c). These spectral changes indicate the interaction of  $[Co^{1}Pc^{-2}]^{1-}$  with the reduced oxygen (superoxide,  $O_2^{-}$ ). This interaction forms an intermediate in which metal center has Co<sup>II</sup> oxidation state. At more negative applied potential, R<sub>II</sub> process could not be recorded in *case* 3, which indicates that interaction of  $[Co^{I}Pc^{-2}]^{1-}$  with the reduced oxygen gives an intermediate which does not reduce again until -1.70 V potential. Applying 0.0V after reduction reactions did not convert the spectrum to the original form in case 3, which indicates irreversibility of the reduction processes. Color change of the complex during the redox processes in case 3 is recorded using in situ colorimetric measurements. When the chromaticity diagrams of the complex in case 1 and case 3 (Fig. 11d) are compared, it is obvious that presence of  $O_2$  alters the color of the redox species differently than those in case 1, which support the interaction of complex with  $0_{2}$ .

In summary, according to the results of CV, SWV, and in situ spectroelectrochemical measurements, these are easily concluded that (i) under the applied potential at -0.50 V,  $[Co^{II}Pc^{-2}]$  species are reduced to  $[Co^{I}Pc^{-2}]^{1-}$  which is reoxidized back to  $[Co^{II}Pc^{-2}]$  with O<sub>2</sub> and form an equilibrium between electrogenerated  $[Co^{I}Pc^{-2}]^{1-}$  and reoxidized  $[Co^{II}Pc^{-2}]$ . However, the electron transfer reaction rate constant at the electrode should be bigger than the reoxida-



**Fig. 11.** In situ UV–vis spectral changes of CoPc (**3**) in DMSO/TBAP electrolyte saturated with O<sub>2</sub>. (a)  $E_{app} = -0.50$  V. (b)  $E_{app} = -0.90$  V). (c)  $E_{app} = -1.25$  V. (d) Chromaticity diagram of CoPc. (each symbol represents the color of electro-generated species after the potential applications;  $\Box$ : [Co<sup>II</sup>Pc<sup>-2</sup>] under open circuit;  $\bigcirc$ : -1.25 V;  $\triangle$ : -1.50 V.

tion rate constant of  $[Co^{I}Pc^{-2}]^{1-}$  with O<sub>2</sub>, because spectra assigned to [Co<sup>I</sup>Pc<sup>-2</sup>]<sup>1-</sup> species are dominant at this potential. (ii) Under the applied potential at -1.25 V in case 3, decreasing of the band assigned to the Co<sup>I</sup> species at around 470 nm indicate the interconversion of Co<sup>I</sup> to Co<sup>II</sup> due to reoxidation of Co<sup>I</sup> to Co<sup>II</sup> species with superoxide. Under this potential application, the final spectrum illustrates formation of  $Co^{II}$  form of the complex. (iii) Shifting of the reverse wave of  $[Co^{II}Pc^{-2}]/[Co^{I}Pc^{-2}]^{1-}$  and decreasing the peak current of R<sub>I</sub> couple in the CV and SWV of the complex may due to the interconversion of  $[Co^{I}Pc^{-2}]^{1-}$  to the intermediate in which metal center has Co<sup>II</sup> state. (iv) Shifting of the ORR process and increasing reversibility of this process support the coordination of oxygen to  $[Co^{I}Pc^{-2}]^{1-}$  and form an equilibrium between  $O_2^{-}$  and the intermediate. (v) Splitting of anodic wave of ORR reaction supports coordination of oxygen to  $[Co^{I}Pc^{-2}]^{1-}$ . According to the CV, SWV, and in situ spectroelectrochemical measurements, a homogeneous electrocatalytic ORR mechanism is proposed as given in Scheme 2. As shown in scheme, initially the active form of the catalyst  $[Co^{I}Pc^{-2}]^{-}$  is obtained (Scheme 2, Eq. (1)). Then the interaction of  $[Co^{I}Pc^{-2}]^{1-}$  with O<sub>2</sub> and the electron transfer between the active form of the catalyst and the substrate O<sub>2</sub> produced an intermediate [O<sub>2</sub><sup>-</sup>-Co<sup>II</sup>Pc<sup>-2</sup>]<sup>-</sup> (Scheme 2, Eq. (2)). The intermediate  $[O_2^--Co^{II}Pc^{-2}]^-$  is very unstable, regenerating rapidly the starting form of the catalyst  $[Co^{II}Pc^{-2}]$  and the product  $O_2^-$  (Scheme 2, Eq. (3)) or produces the second intermediate  $[O_2^{-2}-Co^{II}Pc^{-2}]^{2-}$  due to the electron transfer reaction on the working electrode (Scheme 2, Eq. (4)). This second intermediate reduced to  $[O_2^{-2}-Co^{II}Pc^{-3}]^{3-1}$ 

species if more negative potentials are scanned (Scheme 2, Eq. (5)) or regenerating the starting form of the catalyst  $[Co^{II}Pc^{-2}]$  and the product  $O_2^{2-}$  (Scheme 2, Eq. (6)). According to these results, it looks like the homogeneous catalytic ORR process occurs via an "inner sphere" chemical catalysis process. Since the intermediates  $[O_2^--Co^{II}Pc^{-2}]^-$  and  $[O_2^{-2}-Co^{II}Pc^{-2}]^{2-}$  are formed between  $O_2$  and active form of the catalyst in the solution phase, so rate constant of these interactions should affect the catalytic activity of the complex. Saveant and coworkers [50] reported that homogeneous

$$[Co^{II}Pc^{-2}] + e^{-} \qquad \underset{\scriptstyle \longleftarrow}{\overset{\scriptstyle R_I}{\longleftarrow}} \quad [Co^{I}Pc^{-2}]^{-} \tag{1}$$

$$[Co^{I}Pc^{-2}]^{-} + O_2 \iff [O_2^{-} - Co^{II}Pc^{-2}]^{-}$$
(2)

$$[O_2^- - Co^{II}Pc^{-2}]^- \longrightarrow [Co^{II}Pc^{-2}] + O_2^-$$
(3)

$$[O_2^- - Co^{II}Pc^{-2}]^- + e^- \longleftarrow [O_2^{-2} - Co^{II}Pc^{-2}]^{2-}$$
(4)

$$[O_2^{-2} - Co^{II}Pc^{-2}]^{2-} + e^{-} \stackrel{R_{II}}{\longleftarrow} [O_2^{-2} - Co^{II}Pc^{-3}]^{3-}$$
(5)

$$[O_2^{2-} - Co^{II}Pc^{-2}]^{2-} \longrightarrow [Co^{II}Pc^{-2}] + O_2^{2-}$$
(6)

**Scheme 2.** Proposed homogeneous electrocatalytic mechanism of oxygen reduction reaction.



**Fig. 12.** (a) CVs and (b) SWVs of MnPc (**4**) at  $0.100 \text{ V s}^{-1}$  scan rate on Pt with increasing amounts of O<sub>2</sub> in DCM/TBAP electrolyte system (SWV parameters: pulse size = 100 mV; step size: 5 mV; frequency: 25 Hz;  $E_i = 0.00 \text{ V}$  and  $E_f = -1.30 \text{ V}$  for SWV having cathodic currents;  $E_i = -1.30 \text{ V}$  and  $E_f = 0.00 \text{ V}$  for SWV having anodic currents).

catalysis of slow and irreversible electrochemical processes may be carried out along two conceptually different types of mechanisms. In one case, "redox catalysis", the active form of the catalyst, generated at the electrode, exchanges electrons with the reactant in an outer-sphere manner yielding the reaction products and regenerating the starting form of the catalyst. On the other hand, "chemical catalysis" involves the transient formation of an adduct between the active form of the catalyst and the reactant. The chemical bond thus formed has to be cleaved successively or after the exchange of additional electrons for eventually yielding the products and regenerating the starting form of the catalyst. The proposed mechanism given in Scheme 2 and voltammetric and spectroelectrochemical data are in harmony with the previous reported homogeneous catalytic studies [50-54]. For example, Mho and coworkers reported the homogeneous interactions of unsubstituted cobaltphthalocyanine with oxygen and proposed a conventional regenerative catalytic mechanism. They did not determine the intermediates and just predicted the possible intermediate adducts and proposed mechanism with respect to with respect to cyclic voltammetric and chronoamperometric responses of the system [54]. In this paper, we illustrate the proposed intermediates with voltammetric and in situ spectroelectrochemical measurements especially by comparing the spectroelectrochemical changes of the complexes with and without the presence of the molecular oxygen in the reaction media.



**Fig. 13.** In situ UV–vis spectral changes of MnPc (**4**) in DCM/TBAP electrolyte saturated with O<sub>2</sub>. (a)  $E_{app} = -0.50$  V. (b)  $E_{app} = -0.90$  V and then  $E_{app} = -1.25$  V. (d) Chromaticity diagram of **MPc** (each symbol represents the color of electrogenerated species after the potential applications;  $\Box$ : [Cl–Mn<sup>III</sup>Pc<sup>-2</sup>] under open circuit;  $\bigcirc$ : –1.3 V.

Fig. 12 represents the interaction of MnPc with the molecular oxygen in DCM/TBAP electrolyte system. It is well documented that  $Mn^{II}Pc^{-2}$  species reacts with  $O_2$  and form  $\mu$ -oxo MnPc species, [PcMn<sup>III</sup>–O–Mn<sup>III</sup>Pc] [55]. As shown in Fig. 12a, while MnPc gives a quasi-reversible reduction process (R<sub>I</sub>) at 0.15 V without O<sub>2</sub>, purging of the electrolyte system gradually with O<sub>2</sub> affects the redox behavior of R<sub>I</sub> couple. During this purging process, while the anodic couple of the peak decreases in the current intensity and disappears finally; two new cathodic waves are recorded at 0.12 and -0.45 V. These voltammetric data indicate that Mn<sup>III</sup>Pc<sup>-2</sup> species reduce to Mn<sup>II</sup>Pc<sup>-2</sup> at 0.15 V and Mn<sup>II</sup>Pc<sup>-2</sup> reacts immediately with O<sub>2</sub> and form [PcMn<sup>III</sup>-O-Mn<sup>III</sup>Pc] which reduces at 0.12 and -0.45 V. Due to the reaction between Mn<sup>II</sup>Pc<sup>-2</sup> and O<sub>2</sub>, concentration of Mn<sup>II</sup>Pc<sup>-2</sup> decreases with increasing oxygen, which causes disappearance of the anodic peak of  $R_I$  couple assigned to  $Mn^{II}Pc^{-2}/Mn^{III}Pc^{-2}$  process. As shown in Fig. 12, ORR couple is overlapped with the R<sub>II</sub> couple of the complex so we do not analyze ORR process. However when we compared the ORR process in case 2 (Fig. 12a, inset) with that in case 3 (Fig. 12), it is clearly shown that ORR couple in case 3 shifts ca. 300 mV toward the positive direction and gets more reversible with respect to those recorded in case 2.

In situ spectroelectrochemical studies were employed to support the interaction between MnPc and O<sub>2</sub>. Fig. 13 represents in situ UV-vis spectral changes of MnPc in case 3 in DCM/TBAP electrolyte system during the potential application at the potentials of the redox processes. Under the open circuit potential, spectra of MnPc did not change with time in case 3. This behavior indicates that  $[Cl-Mn^{III}Pc^{-2}]$  do not interact with O<sub>2</sub>.

During the first reduction process (at -0.50 V), spectral changes assigned to [Cl-Mn<sup>III</sup>Pc<sup>-2</sup>]/[Cl-Mn<sup>II</sup>Pc<sup>-2</sup>]<sup>1-</sup> process is observed in case 1 (Fig. 10a). Spectral change of MnPc is different in case 3 (Fig. 13a). Two distinct spectral changes are observed during the first reduction process in case 3. First of all, while the Q band at 730 nm decreases in intensity, a new band at 683 nm assigned to [Cl-Mn<sup>II</sup>Pc<sup>-2</sup>]<sup>1-</sup> process is observed. At the same time, the band at 519 nm decreases in intensity. These spectral changes characterize reduction of [Cl-Mn<sup>III</sup>Pc<sup>-2</sup>] to [Cl-Mn<sup>II</sup>Pc<sup>-2</sup>]<sup>1-</sup>. Then, a new band at 627 nm is recorded, while the band at 683 nm starts to decrease in intensity at the same time. It is well-known that  $\mu$ -oxo MnPc species give an absorption band at around 630 nm. These spectroscopic changes indicate that reduced [Cl-Mn<sup>II</sup>Pc<sup>-2</sup>]<sup>1-</sup> species interacts with oxygen and form µ-oxo MnPc species, which support the voltammetric data about the interaction of MnPc with molecular oxygen. Presence of the band at 683 nm assigned to  $[Cl-Mn^{II}Pc^{-2}]^{1-}$  process and the band at 630 nm assigned to  $\mu$ -oxo MnPc species ([PcMn<sup>III</sup>–O–Mn<sup>III</sup>Pc]) which indicate existence of an equilibrium between  $[Cl-Mn^{II}Pc^{-2}]^{1-}$  and  $\mu$ -oxo MnPc species.

During the potential application at -1.40 V, while spectral changes characterized [Cl-Mn<sup>I</sup>Pc<sup>-2</sup>]<sup>2-</sup> formation in case 1, any spectral changes characterizing further reduction is recorded in case 3 (Fig. 13b). Only relative intensity of the bands at 630 and 682 nm changes with time. Application of more negative potential just affects the relative intensity of these bands which support the existence of an equilibrium between  $[Cl-Mn^{II}Pc^{-2}]^{1-}$  and  $\mu$ oxo MnPc species. Fig. 13c represents the color changes during the reduction processes. When the chromaticity diagrams given in Fig. 10d and Fig. 13c are compared, it is clear that interaction of oxygen with MnPc change the spectral and color responses of the complex with respect to MnPc in case 1.

#### 4. Conclusions

Synthesis, spectroscopic, voltammetry and spectroelectrochemical characterizations of 2-naphthol substituted metallo (Mn, Co, V=O) phthalocyanine complexes are reported. Spectral, voltammetry and spectroelectrochemical properties of the complexes were influenced by the nature of central metal. The manganese derivatives showed red-shifted Q band relative to the other analogs due to the Mn<sup>III</sup> metal center of the complex. Voltammetric and spectroelectrochemical studies indicate that while vanadyl phthalocyanine gives only ring-based, multi-electron, and reversible/quasi-reversible redox processes, cobalt and manganese phthalocyanine complexes give both metal and ring-based, diffusion controlled, multi-electron, and reversible/quasi-reversible reduction processes. Solvent of the electrolyte affects the redox properties of the complexes which have redox active metal center due to the coordination ability differences of the solvents. Definite determination of the colors of the electrogenerated anionic and cationic form of the complexes with chromaticity measurements is important to decide the possible electrochromic application of the complexes. Different color of the electrogenerated species indicates their possible application in the display technologies, e.g. electrochromic and data storage application. Presence of  $O_2$  in the electrolyte system influences both the ORR and the redox couples of the complexes due to the interaction between different redox states of O<sub>2</sub> and MPcs having redox active metal center.

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