Synthesis, *in situ* spectroelectrochemistry and *in situ* electrocolorimetry of electrochromic octakis(chloroethylsulfanyl) phthalocyaninatomanganese(III) chloride

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In this study, the syntheses of octakis(hydroxyethylsulfanyl) phthalocyaninatomanganese(III) chloride and its chlorinated derivative, octakis(chloroethylsulfanyl) phthalocyaninatomanganese(III) chloride, and successive electrochemical investigations of the latter were reported. The voltammetric studies of the complex revealed that it exhibits three one-electron reduction processes and a one-electron oxidation process. *In situ* spectroelectrochemical studies were performed to decide the origin of the redox processes which are assigned to $Mn^{III}Pc^{2-}/Mn^{II}Pc^{2-}$, $Mn^{II}Pc^{2-}/Mn^{I}Pc^{2-}$, $Mn^{I}Pc^{2-}/Mn^{I}Pc^{3-}$ and $Mn^{III}Pc^{2-}/Mn^{III}Pc^{1-}$ couples, respectively. The presence of oxygen significantly affected the *in situ* spectroelectrochemical behavior of the complexes due to the formation of μ-oxo MnPc species. An *in situ* electrocolorimetric method, based on the 1931 CIE (Commission Internationale de l'Eclairage) system of colorimetry, was applied to investigate the color of the electrogenerated anionic and cationic forms of the complex, which shows solvatochromic properties of the complex in solution. The possible polyelectrochromic application on solid state was suggested due to the color changes from brown to greenish blue and from brown to light yellow of a MnPc-coated thin film on ITO.

Introduction

Phthalocyanines are very versatile chemicals due to their aromatic 18-π electronic structure; this makes them very robust and stable in many instances. Phthalocyanines had firstly been used as dyes and pigments because of their blue-green colors.[1] The possibility of inclusion of more than 70 elements in the N_4 core makes phthalocyanines extremely useful chemicals, since the applications rely on the central metal atom. For example, by the inclusion of closed-shell metal ions like Zn^{2+} and Al^{3+}, one can obtain a photosensitizer operating in photodynamic therapy.[2] Similarly, if an open-shell metal ion like Fe^{2+} or Mn^{2+} is used, the macrocycle behaves as a catalytic core.[3] Phthalocyanines are also found to be used in information storage,[4] semiconductors,[1] electrochromic agents,[5] gas sensors,[6] liquid crystals,[7] molecular materials,[1] and non-linear optical materials,[8] and materials prepared as Langmuir–Blodgett films.[9]

Manganese(II) phthalocyanines are very reactive compounds to water, oxygen and protic solvents, forming the manganese(III) counterparts.[10] The reactivity is due to the open-shell configuration and their tendency to axially coordinate. Manganese phthalocyanines are found to be used in many instances in the literature, for example, as catalysts in the oxidation of nitrite and nitrate,[11–13] oxidation of L-cysteine,[14,15] reduction of molecular oxygen,[16,17] electrolysis of water,[18] aziridination of olefins,[19] also as scavengers of superoxide.[20] There are also some reports about analytical applications of manganese phthalocyanines, *e.g.*, in the determinations of vitamin B_1 in tablets[21] and triethylamine emitted from fish, utilizing the macrocycle as a gas sensor.[22] Other than the well-known lutetium sandwich phthalocyanines as electrochromic materials,[23] electrochromism of manganese phthalocyanines is investigated in a recent paper.[24] They are also used in electrochromic devices as thin films forming green to purple changes with applied potentials.[25]

As an extension to our previous research,[26–31] this article reports the synthesis and spectroscopic, electrochemical, *in situ* spectroelectrochemical and *in situ* electrocolorimetric characterization of a chlorinated manganese(III) phthalocyanine derivative. The electrochemical studies were performed in the solution to open a way to possible technological applications depending on the spectroelectrochemical and chromaticity data. This is because certain potential applications (*e.g.*, in the design of an efficient catalyst and electrochromic device) of these types of complexes will require an understanding of the nature of their redox processes. It is well known that many phthalocyanine complexes show excellent electrochromic properties[32,23] both in solution and as polymer films. Therefore, we report here the *in situ* electrocolorimetric analysis of the phthalocyanine to determine possible electrochromic application of the complex both in solution and as a thin film.

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Colorimetry is an effective and objective method to define a color giving accurate and precise description of a color. Electrocolorimetry technique provides a more precise way to define the color of the electrogenerated species.[33] The colorimetric analysis is based on a mathematical representation of a color on CIE (Commission Internationale de l'Eclairage) Yxy or L-a-b color space. Y coordinate represents brightness or luminance of a color whereas xy coordinate defines hue and saturation. After the color of the material is measured with a colorimeter on Yxy coordinates, Yxy values can be transformed to its L-a-b reciprocals throughout a computer program.

Experimental

Materials

Manganese(II) chloride was obtained from Coleman & Bell and kept in an oven at 110 °C. 1,2-Dicyano-4,5-bis(hydroxy-ethylsulfanyl) benzene (**1**) was obtained according to Bayir and co-workers.[34] Electrochemical grade tetrabutylammonium perchlorate (TBAP), extra pure dimethyl sulfoxide (DMSO), dichloromethane (DCM) and LiCl were purchased from Sigma Aldrich. UV-Vis spectra were recorded on Varian Cary spectrophotometer and Unicam UV2-100 spectrophotometer. IR analyses were performed on Perkin-Elmer Spectrum One with ATR technique. Elemental analyses were obtained on a Thermo Finnigan Flash EA 1112.

Synthesis of 2,3,9,10,16,17,23,24-octakis(hydroxyethylsulfanyl) phthalocyaninatomanganese (III) chloride (2)

Anhydrous manganese(II) chloride (0.05 g, 0.4 mmol), 1,2-dicyano-4,5-bis(hydroxyethylsulfanyl)benzene (**1**) (0.28 g, 1.0 mmol) and 0.5 mL of dry dmf were charged into a sealed tube and heated to 150 °C under nitrogen atmosphere and kept at that temperature for 24 h. The reddish-brown mixture was treated and washed with ethanol until no colored filtrate was obtained, and then washed with methanol and chloroform to remove unreacted phthalonitrile and dried *in vacuo* at 80 °C (Scheme 1). Yield: 151 mg (50%). Elemental analysis, calc. for $C_{48}H_{48}ClMnN_8O_8S_8$, C: 47.57%, H: 3.99%, N: 9.25%, found: C: 47.87%, H: 4.18%, N: 9.52%. UV (dmf), λ (log ε): 292 (5.88), 659 (5.64), 708 (5.67), 758 (5.65). IR (cm^{-1}): 3261 (ν_{O-H}), 2920, 2874 (ν_{C-H}), 1587 ($\nu_{C=N}$), 1412, 1374 (δ_{C-H}), 1323 (δ_{C-O-C}), 956, 855, 742 (γ_{Ar-H}).

Synthesis of 2,3,9,10,16,17,23,24-octakis(chloroethylsulfanyl) phthalocyaninatomanganese(III) chloride (3)

Compound (**2**) (0.15 g, 0.12 mmol) was charged to a round-bottomed flask and dissolved in 2 mL of pyridine, cooled to 0 °C and treated with 0.5 mL (0.98 g, 8.2 mmol) of thionyl chloride and flushed thoroughly with nitrogen. The flask was stoppered, and the reaction was continued for 1 h at 0 °C and 4 h at room temperature. The mixture was poured into 500 g of ice–water mixture, filtered, and dissolved in tetrahydrofuran. The solution was chromatographed over silica gel by washing with ethyl acetate and then eluting with tetrahydrofuran. The solution was evaporated to obtain the pure chlorinated phthalocyanine (**3**; see Scheme 2). Yield: 135 mg (80%).

Elemental analysis, calc. for $C_{48}H_{40}Cl_9MnN_8S_8$, C: 42.41%, H: 2.97%, N: 8.24%, found: C: 43.02%, H: 3.13%, N: 8.62%. UV (thf), λ (log ε): 292 (4.98), 756 (4.97). IR (ATR): 2950 (ν_{C-H}), 1588 ($\nu_{C=N}$), 1410 (δ_{C-H}), 742 (γ_{Ar-H}).

Voltammetric, spectroelectrochemical and electrocolorimetric measurements

The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) 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^2. 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 dimethyl sulfoxide (DMSO) was employed as the supporting electrolyte at a concentration of 0.10 mol dm^{-3}.

UV-Vis absorption spectra and chromaticity diagrams were measured by an OceanOptics QE65000 diode array spectro-photometer. *In situ* spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell at 25 °C. The working electrode was a Pt gauze. A Pt wire counter electrode separated by a glass bridge and an SCE reference electrode separated from the bulk of the solution by a double bridge were used. *In situ* electrocolorimetric measurements, under potentiostatic control, were obtained using an OceanOptics QE65000 diode array spectrophotometer at color measurement mode by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell. The standard illuminant A with 2 degree observer at constant temperature in a light booth designed to exclude external light was used. Prior to each set of measurements, background color coordinates (x, y, and z values) were taken at open-circuit, using the electrolyte solution without MPc 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 end of each redox process were reported.

Thin film formation and electrochromic measurements

ITO (indium tin oxide) quartz slides with 8–12 ohms resistance, 85% nominal transmittance and 25 × 75 mm dimensions were purchased from SPI Supplies and Structure Probe, Inc. A section of 10 × 75 mm was cut and used as bare electrode for electrochromic materials. Octakis(chloroethyl-sulfanyl) phthalocyaninatomanganese(III) chloride, MnPc (**3**), was coated on ITO quartz slide by spray-coating technique. MnPc dissolved in DCM was sprayed on ITO slide (10 × 20 mm dimensions) by N$_2$ gas. CV, spectroelectrochemical and electrocolorimetric measurements were performed in an aqueous solution of 0.10 mol dm^{-3} LiCl. The working electrode was a MnPc-coated thin film on ITO. Pt wire as the counter electrode and SCE as the reference electrode were employed and separated from the bulk of the solution by a double bridge.
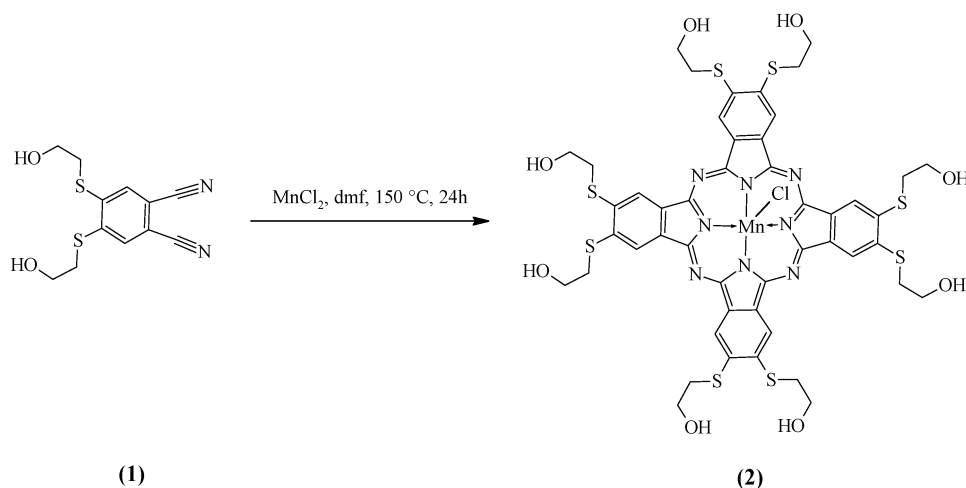
Scheme 1   Synthesis of octakis(hydroxyethylsulfanyl) phthalocyaninatomanganese(III) chloride (**2**) from the dinitrile precursor (**1**).
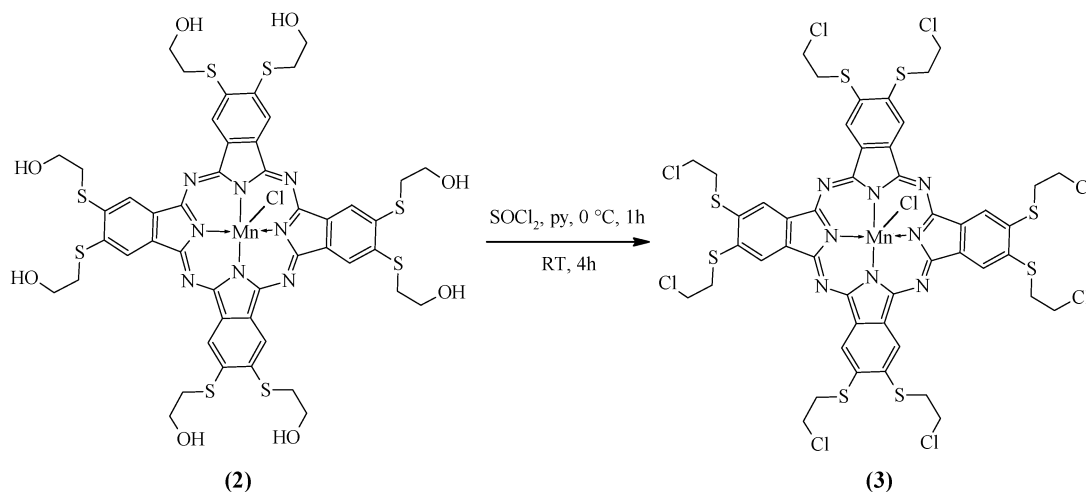
Scheme 2   Synthesis of octakis(chloroethylsulfanyl) phthalocyaninatomanganese(III) chloride (**3**).

Results and discussion

Synthesis and characterization

The synthesis and characterization of octakis(hydroxyethyl-sulfanyl) phthalocyanine compounds were reported by Bayir and co-workers.[34] The same strategy was applied to obtain the manganese(III) phthalocyanine, and it was observed that the overall solubility of the compound is similar to the solubilities of compounds synthesized earlier. The hydroxy-terminated compound is only soluble in N,N-dimethylformamide, dimethyl sulfoxide and pyridine. An additional chlorination step was required to increase the solubility. The reaction was performed with thionyl chloride and the reaction occurred almost quantitatively.[35] With column chromatography, the compound was obtained in a pure form.

The IR spectra of phthalocyanines confirmed the formation of the macrocycles, due to disappearance of the sharp triple bond signal seen in **1** at 2230 cm^{-1}. UV-Vis spectra of phthalocyanines show two characteristic bands, one of them being in the UV region (B or Soret band), while the other being in the visible region (Q band). These absorptions can be

fine-tuned by clever selection of the side groups; however, the position of the Q band is largely governed by the metal ion at the N$_4$ core. As expected, the presence of eight hydroxy- (or chloro-) ethylsulfanyl groups caused a bathochromic shift; manganese(III) ion further caused the Q band to be positioned beyond 750 nm. Similar effects were observed with titanyl(IV) groups.[27] The electronic spectrum of the hydroxy-terminated phthalocyanine compound in dimethylformamide, initially reddish-brown in color, showed three Q bands, changing rapidly into a spectrum with two Q bands and green color, which possibly suggests a redox reaction involving the formation of μ-oxo manganese(III) species from monomeric manganese(III) phthalocyanine (Fig. 1). Manganese phthalocyanine is known to form μ-oxo dimers in many solvents, including pyridine.[36] However, when the oxidation state is 3+, the reactivity is blocked.[20] This is also confirmed in our study; when we dissolved chloromanganese(III) phthalocyanine in pyridine, we observed no change of color. This suggests that the second axial position is used in the redox process (presumably by coordinating oxygen), because in pyridine, this position is filled by a pyridine ligand.
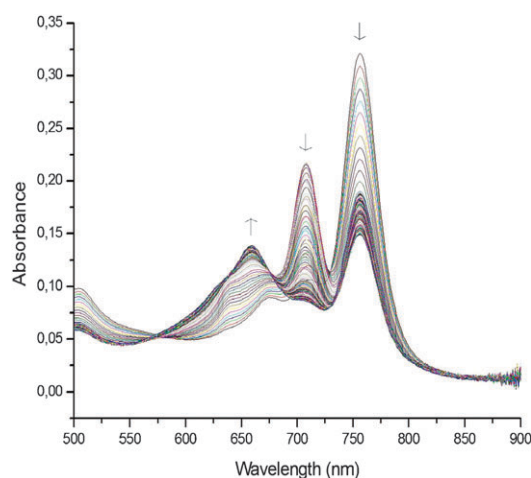
Fig. 1 UV-Vis spectrum of **2** showing three Q bands (unstable spectrum in dmf; color changed from reddish-brown to green).

Fig. 2 CV (top) and DPV (bottom) of **3** at various scan rates on Pt in DMSO/TBAP.

Voltammetric characterization

The CV and DPVs of compound **3** were obtained in deaerated DMSO/TBAP electrolyte system on a Pt working electrode. As shown in Fig. 2, within the potential window of DMSO/TBAP electrolyte system, three reduction processes, II at −0.12 V, III at −0.66 V and IV at −0.98 V, and one oxidation process, I at 0.97 V, vs. SCE at 0.100 V s^{-1} scan rate were recorded. Couple **II** was well-resolved and reversible with anodic to cathodic peak separations (ΔE) ranging from 57 to 110 mV with increasing scan rates from 10 to 500 mV s^{-1}. (ΔE_p values ranging from 60 to 100 mV were obtained for ferrocene reference.) The unity of the $I_{p,a}/I_{p,c}$ ratios at all scan rates and linear variation of the peak currents with square root of the scan rates indicated the purely diffusion-controlled mass transfer of the complexes. The reversibility of the redox process shows that axial ligand Cl$^-$, may be present as bonded to the metal center after the redox process. Alternatively, the release and bonding reaction of the ligand is so fast that it did not disrupt the reversibility of the process. However, second (**III**) and third (**IV**) reduction processes have irreversible characters at slow scan rates and become reversible with increasing scan rates. An extra peak (**IV′**) after the process **IV** is recorded at fast scan rates. These behaviors may occur due to a fast chemical reaction following the process **III**. This chemical reaction may be the release of axial ligand, Cl^{-1}. It is stated that axial ligation of Mn^{II}Pc^{2-} species is not favorable.[37]

In comparison with the MnPc complexes in the literature,[33,37–45] the first two reduction processes are assigned to the metal-based processes, Mn^{III}Pc^{2-}/Mn^{II}Pc^{2-} and Mn^{II}Pc^{2-}/Mn^{I}Pc^{2-}, and the third one is assigned to the ring-based process, Mn^{I}Pc^{2-}/Mn^{I}Pc^{3-}. Oxidation of the complex is assigned to the ring-based process, Mn^{III}Pc^{2-}/Mn^{III}Pc^{1-}. The reduction of Mn^{II}Pc^{2-} species (second reduction) has been a subject of some controversy, with some reports proposing a ring-based reduction to the Mn^{II}Pc^{3-} species and others suggesting a metal-based reduction to the Mn^{I}Pc^{2-} species. Peak separation between the first and second reduction processes (0.540 V) supports the metal-based assignments of
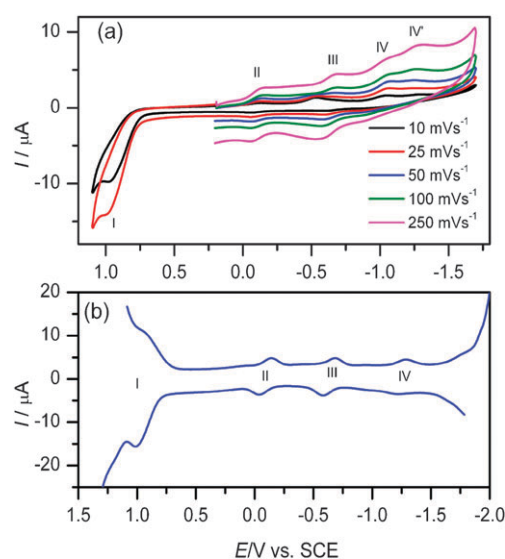
the latter, because the observed separations between 0.80 and 1.00 V are more consistent for first metal-based and second ring-based reduction processes.[33,37–45] *In situ* spectro-electrochemical results given below also confirmed these assignments.

Spectroelectrochemical and electrocolorimetric characterization in solution

In situ spectroelectrochemical experiments were employed to confirm the identities of the redox processes. *In situ* UV-Vis spectral changes and the chromaticity diagram of **3** are given in Fig. 3. Fig. 3a shows the *in situ* UV-Vis spectral changes observed upon a controlled potential reduction of **3** at −0.40 V corresponding to the couple **II**. The band at 505 nm and red-shifted Q band at 765 nm are characteristic of Mn^{III}Pc^{2-} complexes. Upon reduction, the Q band at 765 nm shifts to 698 nm, and new bands are formed at 568 and 895 nm. The formation of Mn^{II}Pc^{2-} is characterized by the shift of the Q band to shorter wavelengths and formation of new bands at MLCT region.[37–47] Clear isosbestic points at 340, 388, 447, 520, 720 and 848 nm in the spectra were recorded. These spectral changes suggest the formation of the Mn^{II}Pc^{2-} from Mn^{III}Pc^{2-}. Thus, couple **II** observed at −0.10 V is assigned to Mn^{III}Pc^{2-}/Mn^{II}Pc^{2-}.

Color changes of the complex in solution during the redox processes were recorded using *in situ* colorimetric measurement. Fig. 3d gives the chromaticity diagrams of **3** recorded simultaneously during the spectroelectrochemical measurements. Without any potential application, the solution of **3** is light brown ($Y = 41.2$, $x = 0.362$ and $y = 0.351$) (point □ in Fig. 3d). As the potential is stepped from 0 to −0.40 V color, of neutral Mn^{III}Pc^{2-} starts to change and light green color ($Y = 38.5$, $x = 0.333$ and $y = 0.349$) (point ○ in Fig. 3d) of monoanionic form, Mn^{II}Pc^{2-}, was obtained at the end of the first reduction. Fig. 3b shows further spectral changes observed during potential application at the potential of process **III**. The spectral changes are typical of metal-based
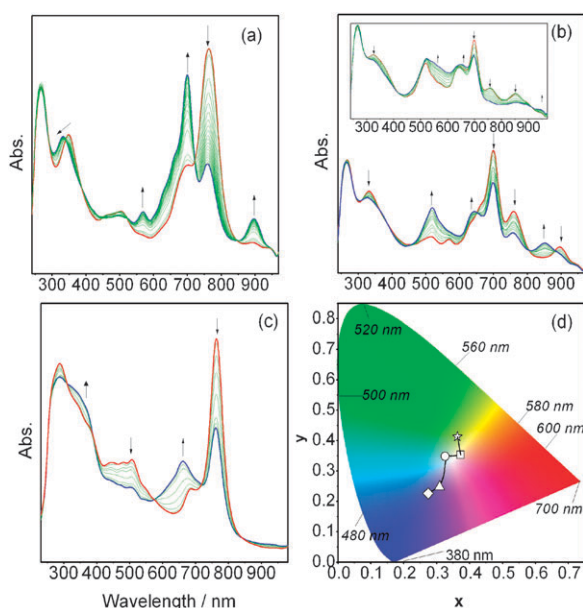
Fig. 3 *In situ* UV-Vis spectral changes of **3** in solution. (a) $E_{app} = -0.40$ V. (b) $E_{app} = -0.90$ V (inset: $E_{app} = -1.60$ V). (c) $E_{app} = 1.20$ V. (d) Chromaticity diagram of **3** (each symbol represents the color of electrogenerated species; □: $Mn^{III}Pc^{-2}$, ○: $Mn^{II}Pc^{-2}$, △: $Mn^{I}Pc^{-2}$, ◇: $Mn^{I}Pc^{-3}$, ☆: $Mn^{III}Pc^{-1}$).

reduction in MnPc complexes with the formation of a broad band at 520 nm. At the same time, while the band at 637 nm increases in intensity, the band at 895 nm shifts to 852 nm. These changes indicate that $Mn^{II}Pc^{2-}$ species is reduced to $Mn^{I}Pc^{2-}$ species at the potential of process **III**. Clear isosbestic points at 375, 460, 650, 805, and 883 nm in the spectra were recorded. The color of the dianionic species, namely $Mn^{I}Pc^{2-}$, was recorded as bluish green ($Y = 31.1$, $x = 0.304$ and $y = 0.310$) with *in situ* colorimetric measurement (point △ in Fig. 3d). The ring-reduction process upon the further reduction of the $Mn^{I}Pc^{2-}$ species is represented as an inset of the Fig. 3b. Spectral changes in this figure are characteristics of the process, $Mn^{I}Pc^{2-}/Mn^{I}Pc^{3-}$. During this process, the band at 520 nm characterizing $Mn^{I}Pc$ species is still present. Observation of a broad band between 550 and 600 nm and decrease in intensity of the Q band are typical for ring-reduction process. The color of the $Mn^{I}Pc^{3-}$ species was recorded as light blue ($Y = 26.91$, $x = 0.293$ and $y = 0.291$) (point ◇ in Fig. 3d). The original spectrum (in Fig. 3a) could be regenerated (upto >90%) by application of a positive potential, after the formation of the $Mn^{I}Pc^{3-}$ species. To confirm the origin of the oxidation process, *in situ* UV-Vis changes were recorded under controlled potential application at 1.20 V (Fig. 3c). During this process, the Q band and the band at 505 nm characterizing $Mn^{III}Pc^{2-}$ species decreased in intensity without shifting, while a new band at 662 nm increased in intensity. These spectral changes are characteristic of a ring-based oxidation process in MnPc complexes, thus the couple **I** is easily assigned to $Mn^{III}Pc^{2-}/Mn^{III}Pc^{1-}$ redox process.[37–45] Similarly, the color of the monocationic species, $Mn^{III}Pc^{1-}$, was recorded as light green ($Y = 52.3$, $x = 0.365$ and $y = 0.414$) with *in situ* colorimetric measurement (point ☆ in Fig. 3d).
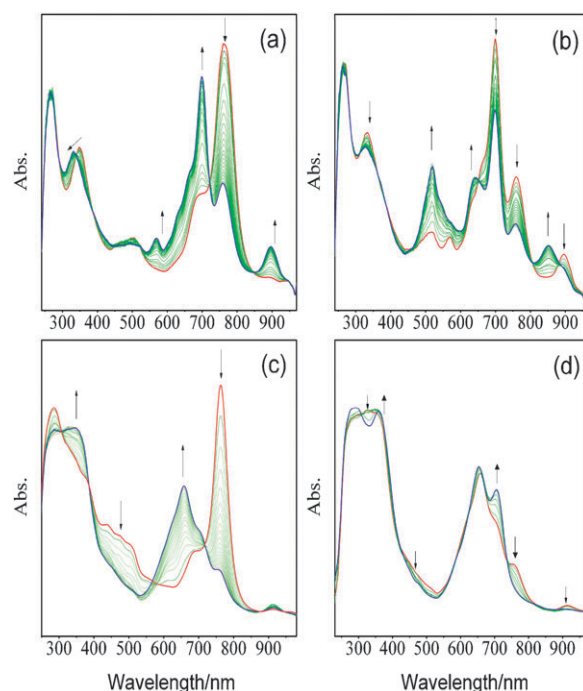

Fig. 4 *In situ* UV-Vis spectral changes of **3** in solution with and without O_2. (a) $E_{app} = -0.40$ V without O_2 (case 1, purged with N_2 gently). (b) $E_{app} = -0.90$ V without O_2 (case 1, purged with N_2 gently). (c) $E_{app} = -0.40$ V with O_2 (case 2, not purged with N_2). (d) $E_{app} = -0.90$ V with O_2 (case 2, not purged with N_2).

In order to determine the possible effects of the formation of μ-oxo MnPc species, *in situ* UV-Vis changes were recorded without purging with N_2 gas. Fig. 4 represents the spectral changes with (Fig. 4a and b; case 1) and without (Fig. 4c and d; case 2) dissolved O_2 under controlled potential reductions. When we compare the spectral changes in Fig. 4a with those in Fig. 4c, it is shown that while the complex gives three new bands at 568, 698, and 895 nm in case 1, a different band at 656 nm is recorded which characterizes the formation of the μ-oxo MnPc species in case 2 under the controlled potential application at −0.40 V. The metal to ligand charge transfer (MLCT) band of the neutral $Mn^{III}Pc^{2-}$ species recorded at 505 nm disappears in case 2, while it is present in case 1. There are also considerable spectral differences between cases 1 and 2 during the second reduction process as shown in Fig. 4b and d. While $Mn^{II}Pc^{2-}$ species is reduced to $Mn^{I}Pc^{2-}$ species at the potential of process **III** without O_2 (Fig. 4b), the process with O_2 under the application of same potential gives the reduction of μ-oxo MnPc to $Mn^{II}Pc^{2-}$. All of these spectral changes indicate the reaction of $Mn^{III}Pc^{2-}$ species with O_2 dissolved in the solution and formation of μ-oxo MnPc species (Fig. 4d). The formation of μ-oxo MnPc species was also stated by Nyokong *et al.*,[37] reporting that during the reduction processes of MnPc, new bands were recorded at around 640 nm indicating the presence of μ-oxo MnPc species in solution.

Voltammetric and electrochromic measurements of MnPc thin film

Different colors of the electrogenerated anionic and cationic forms of the complex in solution indicate possible electrochromic
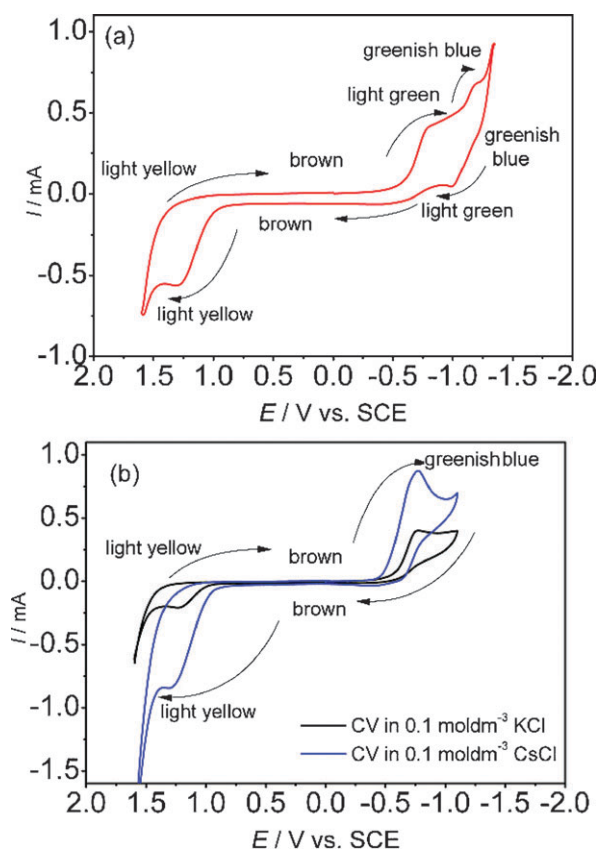
Fig. 5 CV of a thin film of **3** on ITO at 0.100 V s^{-1} scan rate (a) in 0.10 mol dm^{-3} LiCl aqueous solution; (b) in 0.10 mol dm^{-3} KCl and CsCl aqueous solutions.

application of the complex. Thus, the thin film of the complex was prepared and its electrochromic behavior was analyzed in the aqueous solutions of different alkali metal halides. It is stated that ions in the electrolyte solution were inserted into the MPc thin films as the compensated ions to maintain charge neutrality during oxidation and reduction. The sizes of ions do affect the insertion ability.[46] The same results were also found by Kahl et al.,[47] who stated that for the reversible oxidation and reduction of MgPc thin film, smaller anions allow full oxidation at faster rates, whereas larger anions inhibit oxidation. Lin et al.[25] also stated that the sizes of alkali metal ions affected the electrochromic behavior of MnPc thin film. Our results are in harmony with the results of Lin et al. The order of the reduction potentials was Li$^+$ <(−0.80 V) < K$^+$ (−0.77 V) < Cs$^+$ (−0.72 V).

Fig. 5a shows the CVs of the MnPc thin film in 0.1 LiCl solution, in which the potential was scanned between −1.35 and 1.50 V. One oxidation peak at 1.26 V and two reduction peaks at −0.80 and −1.18 V vs. SCE are recorded at 0.025 V s^{-1} scan rate. The color of the MnPc thin film switched from brown to light green and then greenish blue as the potential was scanned from 0 to −1.35 V around the peak potentials. The color of the thin film changed to light yellow when the potential was scanned positively. When the same measurements were performed in 0.1 mol dm^{-3} KCl solution, only one reduction peak at −0.77 V and one oxidation peak at 1.25 V were observed (Fig. 5b). In the case of 0.1 mol dm^{-3} CsCl

solution, these peaks shifted to −0.73 and 1.22 V, respectively. Moreover, the reduction couple is more reversible in KCl solution than the others (Fig. 5b).

In situ spectroelectrochemical and electrocolorimetric experiments were employed to determine the spectral changes during the electron transfer processes and the color coordinates of the electrogenerated species. Fig. 6a shows the *in situ* UV-Vis spectral changes of a thin film of **3** observed upon a controlled potential reduction at −1.30 V in 0.1 M LiCl solution. First of all, the band at 772 nm shifts to 727 nm (from red to purple spectrum = solid arrow) and the band at 550 nm decreases in intensity (from red to purple spectrum = solid arrow), while the bands at 410 and 476 nm decreased in intensity during this process. The color of the film changes from brown ($x = 0.354$, $y = 0.338$) to light green ($x = 0.300$ and $y = 0.350$) as shown in the chromaticity diagram in Fig. 6c. Then the band at 727 nm decreases in intensity (from purple to blue spectrum = dot arrow), while the band at 550 nm increases (from purple to blue spectrum = dot arrow). At the same time, a new band is recorded at 878 nm. The color of the film changes from light green to greenish blue ($x = 0.287$ and $y = 0.315$) (Fig. 6c). During the oxidation process, the band at 772 nm shifts to 720 nm with increasing intensity while the band at 476 nm decreases in intensity (Fig. 6b). The color of the film changes to light yellow ($x = 0.361$ and $y = 0.368$) during the oxidation process (Fig. 6c).
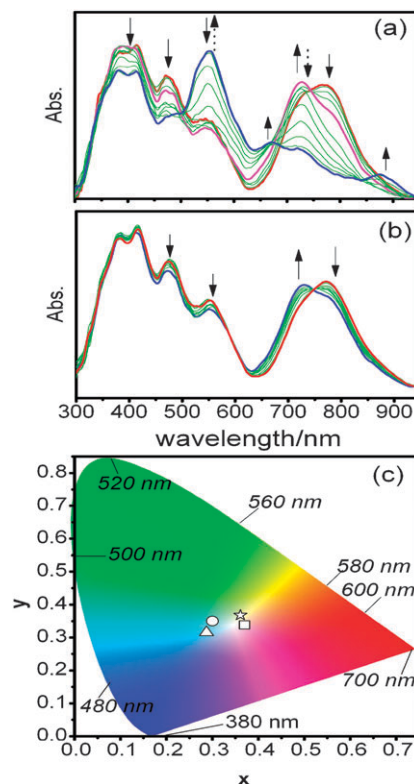

Fig. 6 *In situ* UV-Vis spectral changes of a thin film of **3** on ITO in 0.10 mol dm^{-3} LiCl aqueous solution under the applied potential at −1.30 V (a) and at 1.40 V (b). Chromaticity diagram of **3** coated on ITO (c) (each symbol represents the color of electrogenerated species; □: original film, ○: color of the first reduced form, △: color of the second reduced form, ☆: color of the oxidized form).

Conclusions

The synthetic strategy giving octakis(hydroxyethylsulfanyl) groups works well with manganese phthalocyanines along with reasonable reaction yields around 50%. Chlorination gives a product which is much more soluble than the hydroxylated counterpart, which is not soluble in chlorinated organic solvents and tetrahydrofuran, and thus, the electrochemical and spectro-electrochemical investigations were easier.

The voltammetric and spectroelectrochemical studies of the complexes showed that the complexes exhibited three reversible one-electron reduction processes, assigned to $Mn^{III}Pc^{2-}$ / $Mn^{II}Pc^{2-}$, $Mn^{II}Pc^{2-}/Mn^{I}Pc^{2-}$ and $Mn^{I}Pc^{2-}/Mn^{I}Pc^{3-}$, and one oxidation process assigned to $Mn^{III}Pc^{2-}/Mn^{III}Pc^{1-}$. The presence of O_2 in the reaction medium during the reduction of the complex causes the formation of μ-oxo MnPc species which affects the spectral changes of the species. Measurement of the xyz color coordinates of the electrogenerated anionic and cationic forms of the complex in solution and in thin film allows quantification of each color of redox species that is very important to decide their possible electrochromic application.

Acknowledgements

Notes and references

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