In situ monitoring of metallation of metal-free phthalocyanine *via* UV-Vis and steady-state fluorescence techniques. Thin-layer UV-Vis and fluorescence spectroelectrochemistry of a new non-aggregating and electrochromic manganese(3+) phthalocyanine

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A new non-aggregating and electrochromic manganese(3+) phthalocyanine, (acetato)[2(3),9(10),16(17),23(24)-tetrakis(4-(1-naphthoxy-4-sulfonic acid sodium salt))phthalocyaninato]manganese(3+) [NhtMn(3+)PcL] (where Nht and L indicate naphthoxy-4-sulfonic acid sodium salt and acetate ion, respectively), was synthesized by reaction of the metal-free phthalocyanine (NhtH$_2$Pc) and manganese(2+) acetate (Mn(OAc)$_2$) in methanol. The formation of the complex was monitored by both *in situ* UV-Vis and fluorescence techniques based on the change of the symmetry and the quenching of the fluorescence-probe molecule as a result of the insertion of the metal into the cavity of the macrocycle. The electro-spectrochemical behavior of [NhtMn(3+)PcL] was investigated with thin-layer UV-Vis and fluorescence spectroelectrochemical methods in DMSO solution. The electrochemical studies revealed that [NhtMn(3+)PcL] exhibited two reversible one-electron reductions which were assigned to Mn(2+)Pc(2−)/Mn(3+)Pc(2−) and Mn(2+)Pc(3−)/Mn(2+)Pc(2−) reversible couples based on the metal and phthalocyanine ring reductions, respectively. All redox processes were accompanied with a change of color from dark green to green and purple which are clearly monitored on the surface of the light transparent platinum gauze working electrode in the thin-layer cell. *In situ* UV-Vis and fluorescence spectroelectrochemical methods were also applied to determine the $E_{1/2}$ (half-wave potential) and n (number of electrons) of the first reduction process, both of which confirmed the reversible one-electron [Mn(3+)Pc(2−)L] + e → [Mn(2+)Pc(2−)L]$^-$ reduction process.

Introduction

Phthalocyanines have attracted considerable interest for many decades because of their remarkable thermal stability, chemical resistance, strong colors and negligible vapor pressure at room temperature.[1] This class of compounds exhibits a wide range of qualities in the area of dyes and photoconducting agents in photocopying devices,[2] chemical sensors,[3] electrochromism agents,[4] molecular metals,[5] electrocatalyst,[6] liquid crystals,[7] optical limiting and nonlinear optics,[8] and photosensitizers in PDT (photodynamic therapy).[9] Especially, the tetrasulfonated phthalocyanines are well-known with great theoretical and practical significances due to their high solubility in aqueous solution in a wide range of pH and their easy preparation.[10–13] Therefore, the introduction of naphthoxy-sulfonated groups with bulky electron rich units on the macrocycle core is not only expected to improve their solubility in protic and aprotic solvents but also to enhance photophysical or electrochemical properties of phthalocyanines in solution or film states. Manganese phthalocyanines have been currently studied for electrocatalytic and electrochromic applications.[14] Among these applications, the usages as electrochromic devices have been realized during the last two decades. Metal phthalocyanines possess great potential in electrochromic applications due to their good chemical stability and rich color changes. Early research focused on double-decker lanthanide metal phthalocyanines because their redox reactions are accompanied with substantial color changes and reversibility.[15] Recent studies show that electrochemical factors affect the electrochromic behavior of manganese phthalocyanine and reaction reversibility can be improved by altering the operating potential or electrolytic conditions.[16] This result created a new field of use for metal phthalocyanines in electrochromic applications. Manganese(3+) phthalocyanine can be reduced to mono-, di-, tri-, tetra-anionic and more anionic species based on phthalocyanine ring and metal centre, all of which can be accompanied with absorbance changes and multi color response.

Herein, we report the *in situ* monitoring of the metallation of a metal-free phthalocyanine *via* UV-Vis and fluorescence techniques leading to the formation of a new non-aggregating manganese(3+) phthalocyanine [NhtMn(3+)PcL], where Nht and L indicate naphthoxy-4-sulfonic acid sodium salt and acetate ion, respectively. Although UV-Vis

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spectrophotometry is frequently used to characterize metal phthalocyanines[17] there is no report on the *in situ* monitoring of metallation of metal-free phthalocyanines by use of UV-Vis or fluorescence techniques.

The first aim of this study is to monitor the complexation reaction taking place between metal-free phthalocyanine ($NhtH_2Pc$) and manganese(3+) acetate using the *in situ* UV-Vis and steady-state fluorescence techniques in methanol solution. Thus, the methods allowed us to complete the reaction with a high yield. It is known that electrochemical and spectroelectrochemical studies of phthalocyanines are also important with regard to their possible usage as electrochromic materials, where several colors are displayed depending on the potential applied to the electrode surface. [4,15,18–21] The second aim of this study is to provide a best documentation on the electrochemical and spectroelectrochemical behavior of the (acetato)[2(3),9(10),16(17),23(24)-tetrakis(4-(1-naphthoxy-4-sulfonic acid sodium salt)) phthalocyaninato]manganese(3+) complex, thereby revealing the polyelectrochromic response of the complex. In addition, an application of the *in situ* UV-Vis and fluorescence spectroelectrochemical methods allows determination of $E_{1/2}$ (half-wave potential) and n (the number of electrons) with the spectra of fully oxidized and reduced species in one unified experiment.[18–21,22] On the other hand, the spectrofluorescence method has higher sensitivity and can provide multi-parameter information such as excited and emission spectra, fluorescence intensity and efficiency. Although, there have been known a few reports on the *in situ* fluorescence electrochemistry in the literature[22b,23] there are no reports on the application of this technique for phthalocyanine or porphyrin molecules. Finally, the third aim of this study is to present for the first time an application of *in situ* fluorescence spectroelectrochemistry on the phthalocyanine molecule, in addition to the detailed study of the *in situ* UV-Vis spectroelectrochemistry.

Experimental

Chemicals and reagents

1-Naphthol-4-sulfonic acid sodium salt (Merck, 70%) was purified by column chromatography (silica gel, $MeOH–CH_2Cl_2$, 5 : 1) before use. DMSO was dried over molecular sieve of 4 Å. 4-Nitrophthalonitrile was prepared and purified according to the methods described in the literature.[24] 2(3),9(10),16(17),23(24)-Tetrakis(4-(1-naphthoxy-4-sulfonic acid sodium salt)) phthalocyanine ($NhtH_2Pc$) was prepared and purified according to our previous work.[25] Briefly, ($NhtH_2Pc$) was synthesized from 4-(1-naphthoxy-4-sulfonic acid sodium salt)phthalonitrile which was prepared by the reaction of 4-nitrophthalonitrile and 1-naphthol-4-sulfonic acid sodium salt in the presence of Na_2CO_3 in dry DMSO at 45 °C under nitrogen atmosphere. Electrochemical grade tetrabutylammonium perchlorate (n-Bu_4NClO_4, TBAP, Fluka Chemical Company), (0.1 mol dm^{-3}) was employed as the supporting electrolyte.

Instrumentation

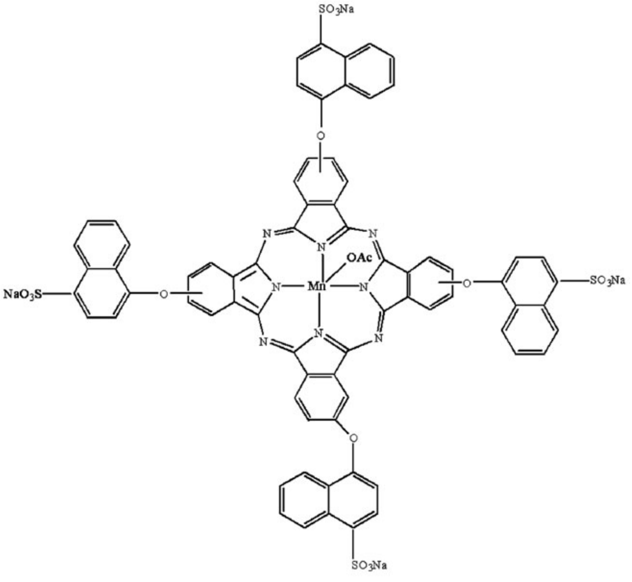
^1H NMR spectra were recorded on a Bruker 250 MHz spectrometer. FTIR spectra were recorded on Perkin-Elmer FTIR spectrophotometer where samples were dispersed in KBr. UV-visible spectra were recorded on Agilent Model 8453 diode array spectrophotometer. Cyclic voltammograms (CV) measurements were carried out with Princeton Applied Research Model 2263 potentiostat controlled by an external PC. A three-electrode system (BAS model solid cell stand) consisting of a 2 mm sized platinum disc electrode as working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode, was used for CV measurements in DMSO. The reference electrode was separated from the bulk solution by a fritted-glass bridge filled with the solvent/supporting electrolyte mixture. The ferrocene/ferrocenium couple (Fc/Fc^+) was used as an internal standard but all potentials in the paper are referenced to the Ag/AgCl reference electrode. Solutions containing [NhtMn(3+)PcL] were deoxygenated by a stream of high purity nitrogen for at least 5 min before running the experiment and the solution was protected from air by a blanket of nitrogen during the experiment. Controlled potential electrolysis (CPE) was performed with Princeton Applied Research Model 2263 potentiostat/Galvanostat. An BAS model electrolysis cell with a fritted glass to separate the cathodic and anodic portions of the cell was used for bulk electrolysis. The sample and solvent were placed into the electrolysis cell under nitrogen. UV-Vis spectroelectrochemical experiments were performed with a home-built thin-layer cell that utilized a light transparent platinum gauze working electrode.[26] A platinum wire counter electrode, and Ag/AgCl reference electrode were used for spectroelectrochemical cell. Potentials were applied and monitored with a Princeton Applied Research Model 2263 potentiostat. Time- and applied-resolved UV-visible spectra were recorded on Agilent Model 8453 diode array spectrophotometer. The steady-state fluorescence (SSF) measurements were carried out using a Varian Carry Eclipse Fluorescence Spectrophotometer at 90° position. *In situ* fluorescence electrochemical experiments were performed with a home-built thin-layer cell that utilized a light transparent platinum gauze working electrode, a platinum wire counter electrode, and Ag/AgCl reference electrode. Potentials were applied and monitored with a Princeton Applied Research Model 2263 potentiostat.

Synthesis of (acetato)[2(3),9(10),16(17),23(24)-tetrakis(4-(1-naphthoxy-4-sulfonic acid sodium salt))phthalocyaninato]manganese(3+). [NhtMn(3+)PcL]: $NhtH_2Pc$ (50 mg, 0.033 mmol) and manganese(2+) acetate (5.8 mg, 0.033 mmol) were refluxed in 25 ml of methanol for 24 h under nitrogen atmosphere. The mixture was cooled to ambient temperature and then filtered off. The filtrate was evaporated to collect the crude product. The product was successively washed with ethanol, methanol and acetone, respectively. The crude product was purified by column chromatography (silica gel, $MeOH–CH_2Cl_2$, 10 : 1). This compound is soluble in water methanol and DMSO. Yield: 44 mg (94%). Anal. Calc. for $C_{74}H_{43}Na_4N_8O_{18}S_4Mn$ (MW: 1607.3): C, 55.30; H, 2.70; N, 6.97. Found: C, 55.01; H, 2.74; N, 7.01%. IR [(KBr) ν_{max}/cm^{-1}]: 3073 (ArH), 2928 (CH), 1705 $\nu_{as}(CO_2)$, 1590, 1574 (Ar), 1375 $\nu_s(CO_2)$, 1285 (Ar–O–Ar), 1080 (O–S–O), 763, 688. UV/Vis (DMSO): λ_{max}/nm (log $\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) = 300 (5.14), 330 (5.07), 605 (3.80), 667 (5.15).

Results and discussion

Synthesis and characterization

Metal phthalocyanines are generally prepared by the reaction of a convenient phthalonitrile derivative with metal salts in an alcohol having a high boiling point in the presence of catalytic amount of a strong organic base such as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). In this method, the purification process is difficult because of the side products formed during the reaction. Metal phthalocyanines can also be prepared by the complexation of the metal-free phthalocyanines with a convenient metal salt in certain organic solvents.[17] The main obstacle of the latter procedure is the low solubility of metal free-phthalocyanines in common solvents. Therefore, the number of metal phthalocyanines obtained using this method is limited compared to the first method. However, the main advantage of the latter procedure is the possibility to monitor formation of complexes by using some spectrophotometric methods such as *in situ* UV-Vis and fluorescence techniques. In the present study, metal-free phthalocyanine, 2(3),9(10),16(17),23(24)-tetrakis(4-(1-naphthoxy-4-sulfonic acid sodium salt))phthalocyanine ($NhtH_2Pc$), which is highly soluble in methanol, was subjected to the complexation reaction with $Mn(OAc)_2$. Thus, 2(3),9(10),16(17),23(24)-tetrakis(4-(1-naphthoxy-4-sulfonic acid sodium salt)) phthalocyanine [NhtMn(3+)PcL] could be prepared by the reaction of ($NhtH_2Pc$) and $Mn(OAc)_2$ in methanol with a high yield (Scheme 1). A detailed discussion on the *in situ* monitoring of the metallation of the metal-free phthalocyanine *via* UV-Vis and fluorescence techniques is reported below. Column chromatography with methanol–dichloromethane (10 : 1) as eluent on silica gel was employed to obtain pure product. The product was soluble in water and DMSO due to the introduction of the naphthoxysulfonic acid sodium salt having hydrophilic character on the peripheral position of phthalocyanine ring. Elemental analysis and spectroscopic data confirmed the assigned structure for [NhtMn(3+)PcL]. The structure of the complex [NhtMn(3+)PcL] was also verified by the disappearance of the characteristic NH stretching absorption of the inner core of the metal-free phthalocyanine. A carboxylate ion, RCO_2^-, can be coordinated to a metal in one of the modes of unidentate, chelating bidentate, free carboxylate, and bridging complexes. Unidentate complexes exhibit Δ values ($\nu_{as}(CO_2) - \nu_s(CO_2)$) that are markedly greater than those in the ionic complexes, 164–171 cm^{-1}. Chelating bidentate complexes and/or bridging complexes exhibit Δ values that are significantly less than those in the ionic complexes.[27]



[NhtMnPcL]

Scheme 1 Manganese(3+) phthalocyanine [NhtMnPcL].

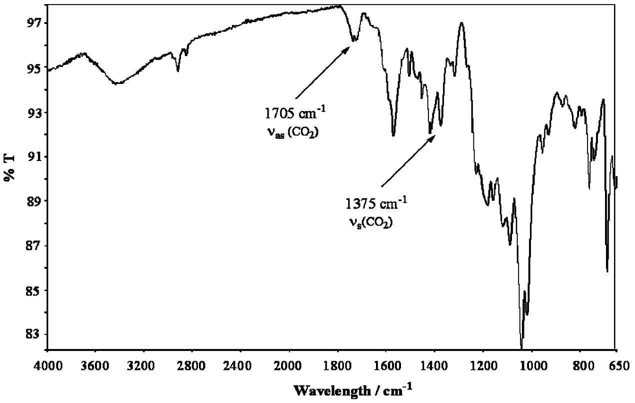


Fig. 1 IR spectrum of [NhtMnPcL].

In the present study, the acetate ion is axially bound to the central metal, which is confirmed with the appearance of new bands at 1705 and 1375 cm^{-1} corresponding to $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$, respectively. The Δ values ($\nu_{as}(CO_2) - \nu_s(CO_2)$) of the complex is 330 cm^{-1}, which is assigned to the unidentate coordination of the acetate to the central metal atom. The complex also exhibited characteristic absorption bands at 2928 (CH), 1285 (Ar–O–Ar) and 1080 cm^{-1} (O–S–O) as expected (Fig. 1).

In situ monitoring of the complexation of metal-free phthalocyanine *via* UV-Vis and fluorescence techniques

In this study, the complexation reaction taking place between metal-free phthalocyanine ($NhtH_2Pc$) and $Mn(OAc)_2$ could easily be monitored by UV-Vis spectrophotometer. Fig. 2 shows the characteristic electronic absorption spectra of the $NhtH_2Pc$ (dotted line) and [NhtMn(3+)PcL] (solid line with highest intensity of Q band). $NhtH_2Pc$ shows the main split intense bands (Q_1 and Q_2 bands) at 703 nm and 660 nm, and B (Soret bands) at 340 nm. In addition, $NhtH_2Pc$ shows the characteristic band at 290 nm corresponding to $\pi \rightarrow \pi^*$ transition due to the existence of the naphthalenyl group on the molecule.[25,28] These characteristic split intense bands corresponding to $NhtH_2Pc$ changed into the main Q band appearing at 732 nm during the formation of the complex (Fig. 2, solid line with highest intensity of Q band). Fig. 3 shows the UV-Vis spectra of the complex in methanol (dotted line), DMSO (dashed line), and water (solid line) where the inset represents the UV-Vis spectrum of 1-naphthol-4-sulfonic acid sodium salt in methanol. It is seen that although the Q band position is the same in both methanol and DMSO (732 nm), it shifts to longer wavelength in water (741 nm). The molecules

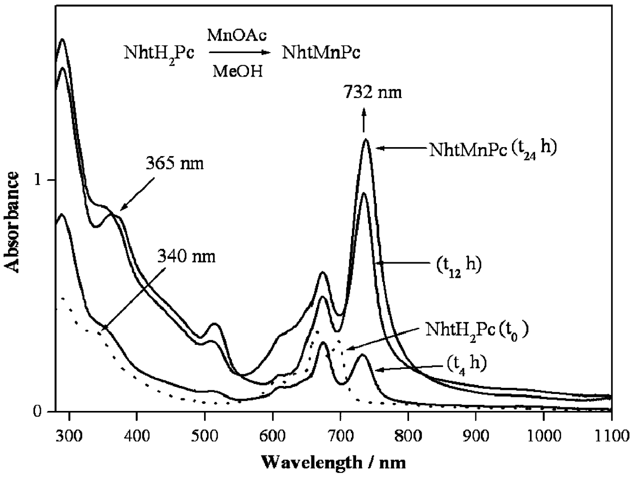


Fig. 2 UV-Vis spectral changes during formation of [NhtMnPcL].

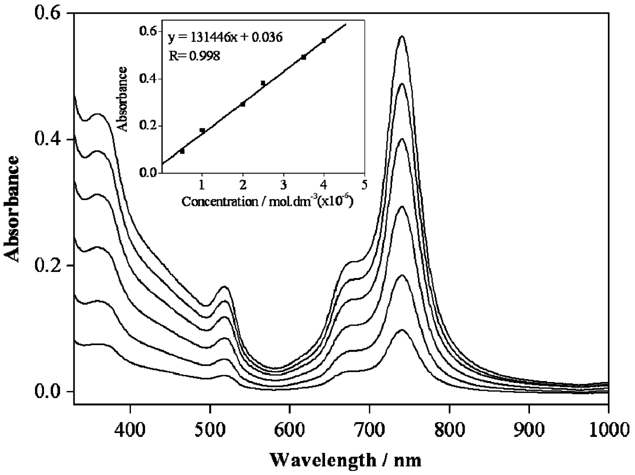


Fig. 4 Absorption spectra of [NhtMnPcL] in water at different concentrations ranging from 4 × 10^{-6} to 0.5 × 10^{-6} mol dm^{-3}. The inset represents the plot of absorbance *vs.* concentration.

remain almost as non-aggregating species in all solvent media. The UV-Vis spectra of [NhtMn(3+)PcL] in water (Fig. 4) shows that Beer–Lambert law is obeyed for the complex in the concentration range from 4 × 10^{-6} to 0.5 × 10^{-6} mol dm^{-3} (inset to Fig. 4). It is known that phthalocyanine molecules tend to aggregate especially in aqueous media. The non-aggregating behavior of [NhtMn(3+)PcL] is due to the existence of bulky naphthalenyl groups and axial ligand on the macrocycle which reduces π–π interaction between the two macrocycle units in the solvents. Synthesis and characterization of the manganese phthalocyanines are, generally, more complicated than those of the other metal phthalocyanines. This is because three forms of manganese phthalocyanines, namely manganese(2+) phthalocyanine ([Mn(2+)Pc]), manganese(3+) phthalocyanine ([Mn(3+)PcX]), where X is an axial ligand coordinated on metal center such as Cl$^-$, OAc$^-$ or OH$^-$, and μ-oxo-manganese(3+) phthalocyanines ([Mn(3+)Pc–O–PcMn(3+)]), can be formed depending on the reaction conditions.[29] The UV-Vis spectral information of the complexes is very distinctive to confirm the related structure. The characteristic band observed around 630 nm is assigned to the [Mn(3+)Pc–O–PcMn(3+)] complex and the band centered about 680 nm is ascribed to the [Mn(2+)Pc] complex, while a transition appearing at lower energy (λ_{max} > 700 nm) with respect to those of [Mn(3+)Pc–O–PcMn(3+)] and [Mn(2+)Pc] complexes is ascribed to the [Mn(3+)PcX] complex.[29,30] Even if the oxygen adduct manganese phthalocyanine [(Mn(2+)PcO$_2$] is expected in the reaction process, the species are not stable and requires special reaction condition to obtain it.[31] The related *in situ* monitoring of the complexation of metal-free phthalocyanine *via* UV-Vis technique is presented in Fig. 2 exhibiting the characteristic band at 732 nm which is clearly assigned to manganese(3+) phthalocyanine [NhtMn(3+)PcL]. The green color of the solution was changed into dark green color during the complexation reaction. Surprisingly, no other manganese complexes were formed during the course of the reaction, as seen from Fig. 2. This observation is due to the fact that the UV-Vis spectral changes did not show any characteristic bands related with Mn(II)Pc or ([Mn(3+)Pc–O–PcMn(3+)]), and only one spot corresponding to the product was also observed when the reaction was also monitored by thin layer chromatography (TLC). This makes the [NhtMn(3+)PcL] complex easier to purify and characterize. By monitoring the complexation with the spectral changes of NhtH$_2$Pc, the reaction was completed when [NhtMn(3+)PcL] exhibits only the main Q band in methanol solution. [NhtMn(3+)PcL] also shows the characteristic band at 514 nm which is attributed to LMCT (ligand-to-metal charge transfer).[29c] The B band corresponding to NhtMnPc was red-shifted by 25 nm compared to that of NhtH$_2$Pc. The π→π* transitions of the naphthalenyl groups appended on phthalocyanine ring were observed at 290 nm.[28] It shows that the complex formation does not affect the π→π* transitions of the naphthalenyl groups. In spite of appending of π-electrons of naphthalenyl substituent on phthalocyanine system, no large shift toward the near IR region for Q and B bands in the UV-Vis spectrum of [NhtMn(3+)PcL] was observed compared with that of unsubstituted Mn(3+)Pc.[32]

It is known that the interaction of a fluorescence probe with a molecule is realized on the changes of the fluorescence

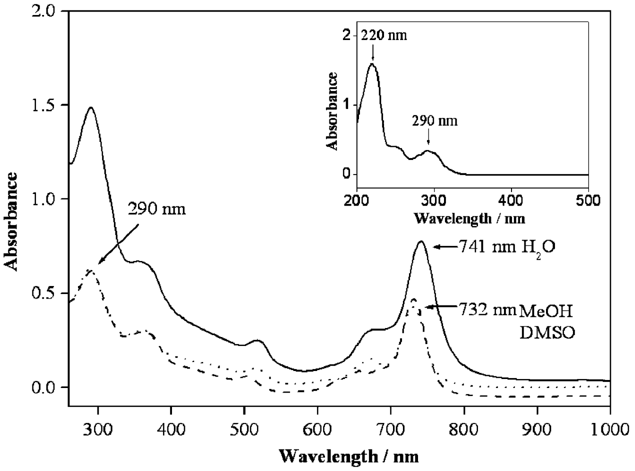


Fig. 3 UV-Vis spectra of [NhtMnPcL] in methanol (dotted line), DMSO (dashed line), and water (solid line), inset: UV-Vis spectrum of 1-naphthol-4-sulfonic acid sodium salt in methanol.

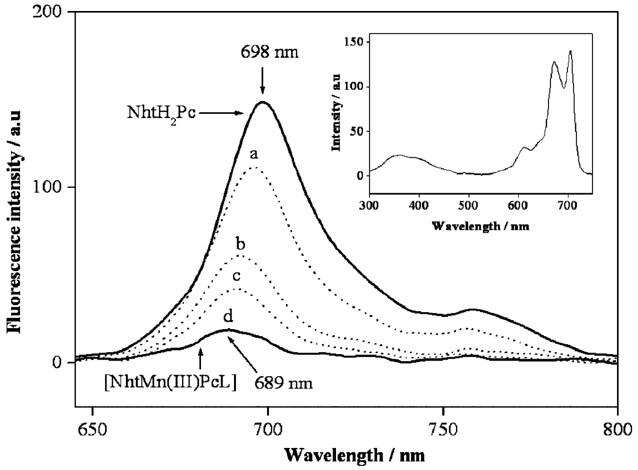


Fig. 5 Fluorescence spectral changes during formation of [NhtMnPcL] where the inset represents the excitation spectrum of [$NhtH_2Pc$] (*a*: after 4 h; *b*: 12 h: 18 h; 24 h).

characteristic of the aromatic molecule.[33,34] First, it may be a binding process where aromatic molecules, such as pyrene, naphthalene or their derivatives, bind chemically or physically to the molecules, thereby causing a shift in their fluorescence spectra or a change in the fluorescence intensity. The second process may be the change in the spectra or intensity of the aromatic molecules due to dynamic or static interactions with the molecules concerned, or with by-products formed during a reaction. Thirdly, the fluorescence characteristic of a fluorescence probe-bonded-molecule may be changed due to the interaction of this molecule with by-products formed during a reaction. Thus, the change in the emission spectra of a fluorescence probe during a synthesis process may be related to the stages of a reaction. In our previous study, a new technique based on fluorescence quenching of a chromophore, pyranine (8-hydroxypyrene-1,3,6-trisulfonic acid, trisodium salt) was developed for monitoring of the synthesis of the pyranine-substituted phthalonitrile derivative.[33] A similar technique was for the first time applied to the monitoring of the metallation of a metal-free phthalocyanine. Fig. 5 shows the changes in fluorescence emission during the complexation reaction in methanol where the inset figure exhibits the excitation spectrum of $NhtH_2Pc$ in methanol. It is seen that $NhtH_2Pc$ shows fluorescence emission at 698 nm when excited at 610 nm. The fluorescence intensity decreases during the reaction and remains unchanged after 24 h. Also, the band shifts by 9 nm to shorter wavelength. The decrease of the fluorescence intensity and shift to shorter wavelength are likely due to the heavy metal effect, the paramagnetic nature of the central metal ion and perturbation of π-conjugation of the macrocycle by insertion of metal into the cavity of the macrocycle. As seen from the UV-Vis spectra of the metallation of metal-free phthalocyanine (Fig. 2, dotted line), the Q band of the metal-free phthalocyanine is split as a result of D_{2h} symmetry of molecule. For the metal phthalocyanine, electronic transition to the S_1 state ($^1(a_{1u}e_g)$) gives rise to a single Q band where the a_{1u} and e_g orbitals denote the HOMO (π) and LUMO (π*) of the phthalocyanine ligand.[35] Since the LUMOs (e_g) are degenerate in metal-phthalocyanines with D_{4h} symmetry, S_1 and S_2, states are degenerate. But for the metal-free phthalocyanines, the LUMOs (e_g) and also S_1 and S_2 are not degenerate in metal-free phthalocyanine with D_{2h} symmetry, which is responsible for splitting of the Q band in the UV-Vis spectrum of the molecule. However, the fluorescence spectrum of the metal-free phthalocyanine exhibits a single Q band (not split) because fluorescence emission occurs only from S_1 state to S_0 and is not affected by the non-degenerate states. Finally, as seen from Fig. 5, the Q band of the unmetallated complex is not split as a result of emission from S_1 state to S_0.

Electrochemistry

The electrochemical behavior of [NhtMn(3+)PcL] was investigated using cyclic voltammetric (CV) technique in DMSO solution containing 0.1 M TBAP. The data obtained in this work and some selected data from the literature are given in Table 1. Fig. 6 shows the CV of [NhtMn(3+)PcL] at 0.100 V s^{-1} scan rate. [NhtMn(3+)PcL] exhibited three reduction waves in DMSO containing Ag/AgCl electrode system, but we did not observe any clean oxidation wave out to +0.9 V *vs.* Ag/AgCl. The first and second waves displayed two one-electron reductions with convenient values of the cathodic to the anodic peak separation for the first reduction process (0.100 V) and for the second reduction process (0.070 V) at 0.100 V s^{-1} scan rate, which is assigned to the reversible character for the mono- and doubly-reduced species in DMSO solution. In addition, the peak cathodic and peak anodic current ratios, i_{pc}/i_{pa} for the first and the second reduction waves approached almost unity, which indicated that these electrochemical reactions were not accompanied by any other physical or chemical processes throughout the electrochemical timescale. The third reduction wave has corresponding anodic wave with a small ratio of the anodic to cathodic peak current (i_{pc}/i_{pa}) and the large peak potential between two waves in the scan rate between 0.010 and 0.250 V s^{-1}, indicative of an irreversible process. It is known that the first reduction of Mn(3+)Pc in solution or film states is expected to be a metal-

Table 1 The electrochemical half-wave potentials of [NhtMn(3+)PcL] and some selected manganese phthalocyanines from literature

Complex	Solvent	Mn(2+)Pc(4−)/ Mn(2+)Pc(3−): $E_{1/2}$/V	Mn(2+)Pc(3−)/ Mn(2+)Pc(2−): $E_{1/2}$/V	Mn(2+)Pc(2−)/ Mn(3+)Pc(2−): $E_{1/2}$/V	ΔE^c/V	Ref.
[NhtMnPc]	DMSO	−1.310[d]	−0.670 (0.070)[b]	−0.055 (0.100)	0.615	This work
MnPc	DMSO	−1.390	−0.755	−0.080	0.675	37, 38
[$(SO_3)_4$MnPc]	DMF	−1.360	−0.720			37, 39

[a] $E_{1/2}/V = E_{pa} + E_{pc}/2$. [b] $\Delta E_p = (E_{pa} - E_{pc})$. [c] $\Delta E = E_{1/2}(red_1) - E_{1/2}(red_2)$. [d] Cathodic peak potential.

Table 2 UV-visible spectral data of [NhtMn(3+)PcL])^n in DMSO containing 0.2 M TBAP

Charge, *n*	Species	λ/nm (log ε/dm^3 mol^{-1} cm^{-1})
0	[NhtMn(3+)PcL]	290 (5.32), 365 (5.03), 501 (4.58), 641 (4.64), 732 (5.14)
−1	[NhtMn(2+)Pc(2−)L]$^-$	293 (5.30), 346 (5.08), 630 (4.87), 684 (5.04), 889 (4.28)
−2	[NhtMn(2+)Pc(3−)L]$^{2-}$	293 (5.30), 360 (5.00), 527 (4.88), 630 (4.76), 684 (4.71), 856 (4.41)
−3	[NhtMn(2+)Pc(4−)L]$^{3-}$	293 (5.31), 364 (4.91), 531 (4.94), 558 (4.90), 863 (4.28)

based process because of the electroactive nature of manganese metal coordinated to the macrocycle unit.[36,37] On the other hand, it is noted from literature that there is a confusion whether the second reduction of Mn(3+)Pc(2−) is based on the phthalocyanine ring or metal. However, the *in situ* spectroelectrochemical study provides useful information to confirm the nature of the reduction process.[36,37] It is clear that the first reduction observed in our study is based on the manganese with Mn(2+)Pc(2−)/Mn(3+)Pc(2−) couples while the second reduction process is based on the phthalocyanine ring with Mn(2+)Pc(3−)/Mn(2+)Pc(2−) couples as seen from Fig. 6, Table 1 and Scheme 2. This conclusion can be deduced from the comparison of the half-wave potentials of [NhtMn(3+)PcL] and unsubstituted phthalocyanine MnPc under the same experimental condition from Table 1. The half-wave potentials of [NhtMn(3+)PcL is consistent with those of MnPc and MnPc derivatives previously studied.[37,38] The first and second reduction processes based on the metal and phthalocyanine ring were clearly confirmed with the *in situ* spectroelectrochemical study, which will be discussed in detail in the section of UV-visible and fluorescence spectra of electro-oxidized and electro-reduced complexes. In this way, an agreeable verification was presented on the nature of the second reduction process of the complex. The CV of the [NhtMn(3+)PcL] looks perfectly normal and reversible and would then be consistent with the acetate remaining bound to the manganese atom during the first two reduction processes as seen from Scheme 2. If the acetate ion was released upon the first reduction process, the first reduction wave would be accompanied with an EC process, which was observed in literature.[30a] The electrochemical half-wave potentials of the first and the second reduction processes are located at $E_{1/2}$ = −0.055 V and $E_{1/2}$ = −0.670 V *vs.* Ag/AgCl. On the other hand, a cathodic peak potential of the third reduction process was displayed at E_{pa} = −1.310 V *vs.* Ag/AgCl. The potential values of [NhtMn(3+)PcL] and some selected manganese(3+) phthalocyanines from literature[37–39] are given in Table 1. The potential difference between the first and second reduction waves of [NhtMn(3+)PcL] is 0.615 V (ΔE), which refers to an average separation for the first and second reduction processes of Mn(3+)Pc(2−).[37,38] This potential difference is almost the same with those of Mn(3+)Pc(2−) and some substituted manganese(3+) phthalocyanines.[37,38] The electrode processes were found to be diffusion controlled as demonstrated by the linearity of a plot of peak current *vs.* square root of scan rate for scan rate ranging from 0.010 to 0.250 V s^{-1}.[40] The controlled potential coulometric (CPC) study indicated that the number of electrons transferred for electrochemical reactions of the complex was one for each reduction process. The proposed electron-transfer mechanism of [NhtMn(3+)PcL] on the electrode surface is given by Scheme 2.

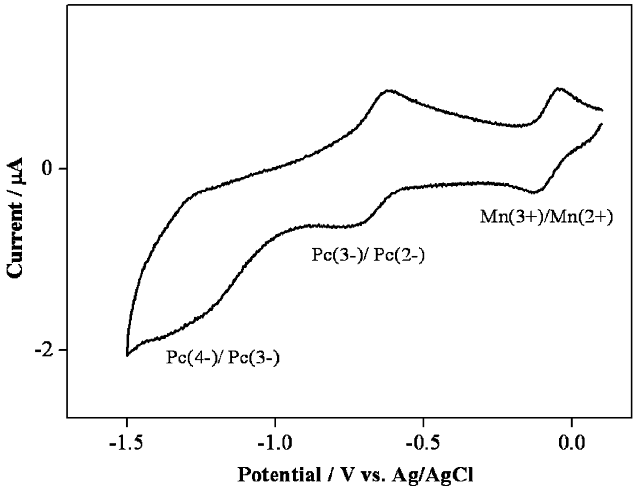
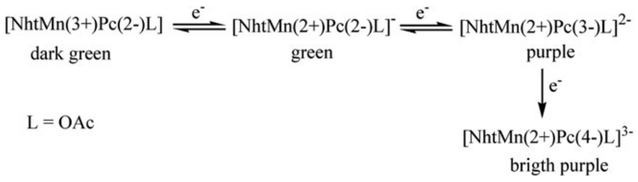


Fig. 6 Cyclic voltammograms of [NhtMnPcL] in DMSO solution containing 0.1 M TBAP. Scan rates = 0.100 V s^{-1} and concentration = 1.24 × 10^{-4} M.

UV-visible and fluorescence spectra of electro-oxidized and electro-reduced complexes

The spectroelectrochemical studies of [NhtMn(3+)PcL] were performed by using *in situ* UV-Vis and fluorescence spectroelectrochemical techniques in DMSO solution containing 0.2 M TBAP. The UV-Vis and fluorescence spectral changes for the reduced species of [NhtMn(3+)PcL] were obtained in a thin-layer cell during applied potentials. The data obtained in these experiments are given in Table 2.

[NhtMn(3+)PcL] was stepwise reduced in the thin-layer cell with the applied potentials and the resulting UV-Vis spectra were measured as a function of time. The UV-Vis spectral changes upon the first reduction of [NhtMn(3+)PcL] showed that the main Q band at 732 nm (Fig. 7, solid line) disappeared in the course of reduction process and some new bands appeared at 684 in high intensity and 889 and 630 nm in low intensity (Fig. 7, dashed line for the final spectrum of [NhtMn(2+)Pc(3−)L]$^-$ and Fig. 8 (the time-resolved UV-Vis spectral changes)). The band observed at 684 is the characteristic Q band[41] and the 889 nm-band is probably due to MLCT transitions (metal-to-ligand charge transfer) of the



Scheme 2

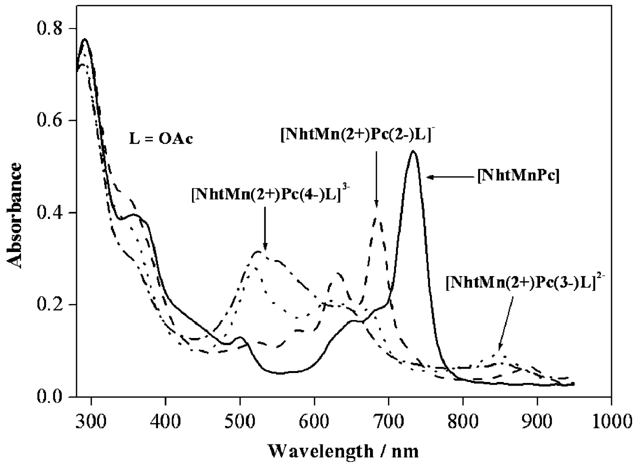


Fig. 7 UV-Vis spectra of [NhtMnPcL] (solid line), [NhtMn(2+)Pc(2−)L]$^-$ (dashed line), [NhtMn(2+)Pc(3−)L]$^{2-}$ (dotted line) and [NhtMn(2+)Pc(3−)L]$^{3-}$ (dash-dot line) in DMSO containing 0.2 M TBAP.

mono-reduced species, [NhtMn(2+)Pc(2−)L]$^-$. Even if the band at 630 nm falls into the region of ([Mn(3+)Pc–O–PcMn(3+)] complex, formation of the μ-oxo-manganese(III)phthalocyanine complex during applied potential under nitrogen atmosphere are not expected. Thus, the band refers to an aggregation phenomenon of [NhtMn(2+)Pc(2−)L]$^-$ in DMSO. The B band which belongs to [NhtMn(2+)Pc(2−)L]$^-$ was also shifted to higher energy with respect to that of [NhtMn(3+)PcL]. The final spectrum of [NhtMn(2+)Pc(2−)L]$^-$ is given in Fig. 7 (dashed line), which is a typical of a monoanionic form, [Mn(2+)Pc(2−)X]$^-$.[*30a*] It is concluded from the UV-Vis spectral changes upon the first reduction of [NhtMn(3+)PcL] that the mono-reduced form, [NhtMn(2+)Pc(2−)L]$^-$, is assigned to one-electron reduction process based on the metal center. The dark green color of the solution of the neutral complex changed to green when the first reduction process was completed. As also seen from Fig. 8, the isosbestic points of the UV-Vis spectral changes were found at 361, 701 and 780 nm, confirming that the electrode reaction proceeds in a quantitative fashion and therefore in the absence of any coupled chemistry.[18,20,42] It could be deduced from the monitoring of the redox reaction that the first reduction process was reversible on the spectroelectrochemical timescale and the original spectrum (and the color) of the compound was obtained upon re-oxidation. This indicated that the reduced phthalocyanine remained fully stable throughout the experiment, which also confirmed the acetate ligand was not released from the manganese atom during the reduction process.

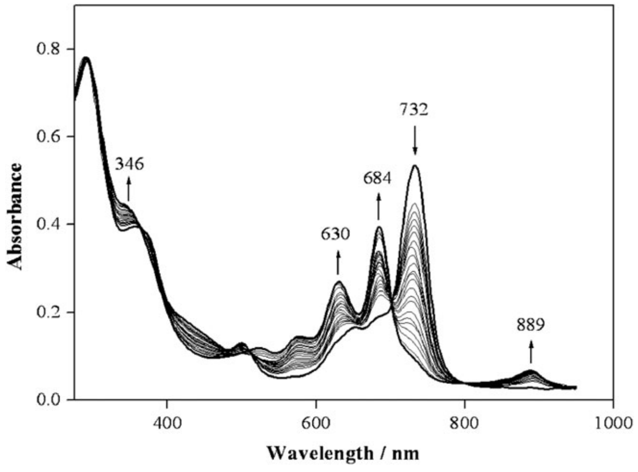


Fig. 8 Time-resolved UV-Vis spectral changes of [NhtMnPcL] during the first reduction at E_{app} = −0.35 V in DMSO solution containing 0.2 M TBAP.

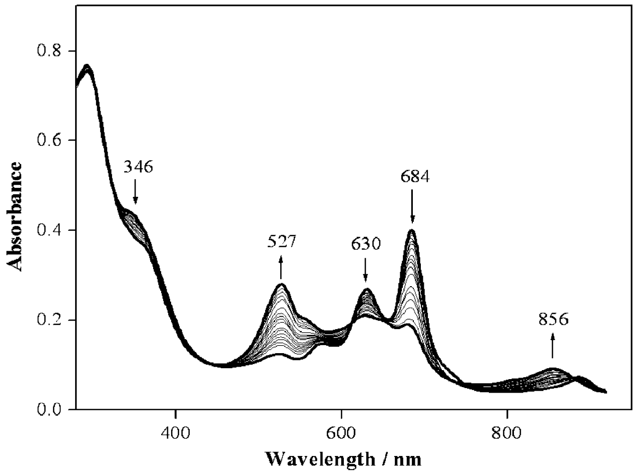


Fig. 9 Time-resolved UV-Vis spectral changes of [NhtMnPcL] during the second reduction at E_{app} = −1.00 V in DMSO solution containing 0.2 M TBAP.

The well defined UV-Vis spectral changes during the second reduction of [NhtMn(3+)PcL] are shown in Fig. 7 (dotted line) for the final spectrum of [NhtMn(2+)Pc(3−)L]$^{2-}$ and Fig. 9 (the time-resolved UV-Vis spectral changes). The second reduction product results in a color change from green to purple. Isosbestic points are observed at 611, 747 and 882 nm, which confirmed the formation of the doubly-reduced species. The intensity of the Q and B band with respect to that of the first reduction product decreased and a new band in moderate intensity formed at 527 nm. This observation is due to the rearrangement of molecular orbitals on addition of one electron into the phthalocyanine ring. If the second reduction proceeded through metal center (as Mn(+)Pc(2−) couples), a red-shift Q and a new CT (charge transfer) band in a moderate intensity around 470 nm would be probably observed (as observed for Co(1+)Pc species).[42] On the contrary, the spectral changes observed for the second reduction of [NhtMn(3+)PcL] are assigned to a ligand-based reduction species NhtMn(2+)Pc(3−)L]$^{2-}$. The observation is similar to those mentioned for metal-phthalocyanines based on the first ring reduction.[18,42] It is concluded that the *in situ* spectroelectrochemical study clearly verifies a ring-based second reduction process of [NhtMn(3+)PcL], which can not be understood using the CV technique only. Re-oxidation at a positive potential of second reduced species generated the first reduced species [NhtMn(2+)Pc(2−)L]$^-$ with almost the same band intensity. It showed that the electron transfer reaction for the second reduction process was reversible on the

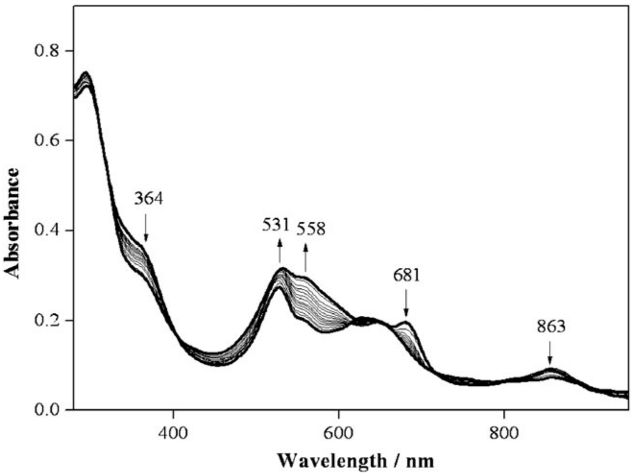


Fig. 10 Time-resolved UV-Vis spectral changes of [NhtMnPcL] during the oxidation at $E_{app} = -1.43$ V in DMSO solution containing 0.2 M TBAP.

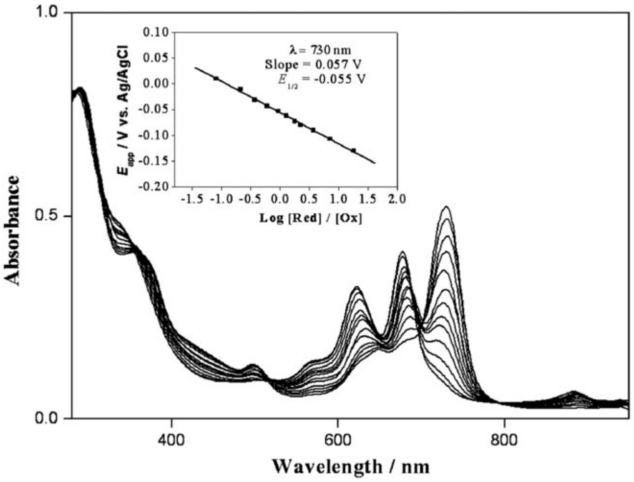


Fig. 11 Potential-resolved UV-Vis spectral changes of [NhtMnPcL] during the first reduction in DMSO solution containing 0.2 M TBAP where the inset shows the plot of E_{app} *vs.* log[R]/[O].

spectroelectrochemical timescale and the original spectrum (and the color) of the compound was obtained upon the re-oxidation. Thus, the doubly-reduced phthalocyanine species $[\text{NhtMn}(2+)\text{Pc}(3-)\text{L}]^{2-}$ remained stable throughout the experiment. UV-Vis spectral changes upon the third reduction of [NhtMn(3+)PcL] are shown in Fig. 7 and 10 (dash-dot line) for the final spectrum of $[\text{NhtMn}(2+)\text{Pc}(4-)\text{L}]^{3-}$. An increase in the intensity of the bands at 531 and 558 nm and a decrease in the intensity of the B bands at 681 and 863 nm were observed during the third reduction process. However, no drastic color change was observed. Isosbestic points are observed at 402, 661, 716 and 801 nm. The final spectrum (Fig. 7, dash-dot line) of $[\text{NhtMn}(2+)\text{Pc}(3-)\text{L}]^{2-}$ is similar to that of the triply-reduced forms of phthalocyanines.[32,40] Re-oxidation at a positive potential of the trianionic species did not generate dianionic species, indicating that the third reduced species $[\text{NhtMn}(2+)\text{Pc}(4-)\text{L}]^{3-}$ did not remain stable throughout the experiment. These results indicate that the new non-aggregating manganese(3+) phthalocyanine presents a multi-color response upon the applied potentials which is important for electrochromic applications.

Besides the electro-spectrochemical studies discussed above, we realized an application of the *in situ* UV-Vis and fluorescence spectroelectrochemical methods to determine the $E_{1/2}$ and n for the first reduction process of [NhtMn(3+)PcL]. Although the first technique was well-known and applied in our previous studies,[20] the second was realized for the first time for phthalocyanines to understand changes in fluorescence emission of the reduced species and to determine $E_{1/2}$, and n under applied potential. In the experiments, a series of potentials was applied to the optically transparent thin-layer cell in DMSO, and individual spectra were measured after equilibrium was attained at each potential as monitored by current decay to a small, essentially zero value. Fig. 11 and 12 (potential-resolved spectra) show the results. The changes in the absorbance and fluorescence intensities at a given wavelength (732 nm for the former and 689 nm for the latter) can be related to the concentration ratio of reduced to oxidized species using the equation.

$$[\text{R}]/[\text{O}] = (A_2 - A_3)/(A_1 - A_2) \qquad (1)$$

Here A_2 is the absorbance of the mixture of oxidized and reduced forms, A_1 is the absorbance of the totally reduced form, and A_3 is the absorbance of the totally oxidized form. The Nernst equation,

$$E_{app} = E_{1/2} - (0.059)/n)\log([\text{R}]/[\text{O}]) \qquad (2)$$

indicates that a plot of E_{app} *vs.* log[R]/[O] should be linear with a slope 59/n mV and an intercept of $E_{1/2,}$ assuming Nernstian reversibility. For the $[\text{Mn}(3+)\text{Pc}(2-)\text{L}] + \text{e} \rightarrow [\text{Mn}(2+)\text{Pc}(2-)\text{L}]^{-}$ process, $E_{1/2} = -0.055$ V and $n = 1.04$ electron (slope = 0.057 V, correlation coefficient = 0.998 for plot) were found (Fig. 11, inset). Fig. 12 shows the potential-resolved fluorescence spectra obtained during the reduction process in the thin-layer cell where the inset represents the plot of E_{app} *vs.* log[R]/[O]. As seen, the fluorescence intensity of the neutral complex [NhtMn(3+)PcL] during the applied potentials decreased due to the formation of negatively charged complex molecules which probably cause a fluorescence quenching of fluorescence-probe molecule. When the E_{app} is plotted against log[R]/[O], $E_{1/2} = -0.065$ V and $n = 0.88$ electron (slope = 0.067 V, correlation coefficient = 0.997 for plot) were found. As seen, these results are in agreement with those obtained from the *in situ* UV-Vis electrochemical method and both techniques confirmed reversible one-electron $[\text{Mn}(3+)\text{Pc}(2-)\text{L}] + \text{e} \rightarrow [\text{Mn}(2+)\text{Pc}(2-)\text{L}]^{-}$ reduction process. It is deduced from the result that the *in situ* fluorescence spectroelectrochemistry may be favored over the *in situ* UV-Vis spectroelectrochemistry for some purposes such as understanding of optical spectra of electro-oxidized or reduced species and determination of $E_{1/2}$ and n during the redox processes because of its higher sensitivity. In many cases, the phthalocyanine molecules, for instance, exist as aggregated forms in the solutions used during the UV-Vis spectrochemical measurements, which lead to preclude monitoring of spectral changes during the redox process. However, this handicap can be overcome by studying of the *in situ* fluorescence

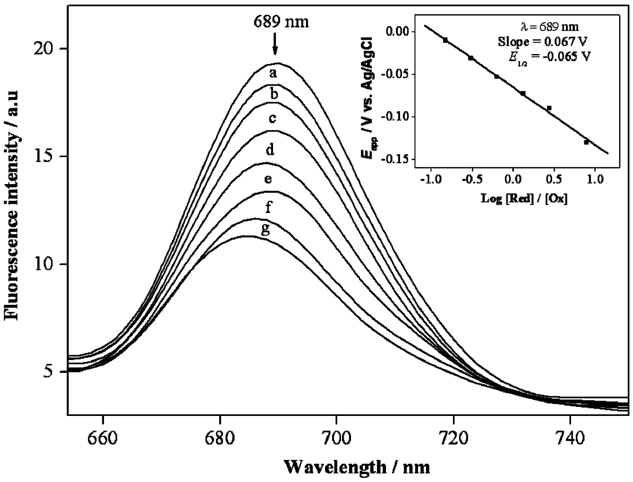


Fig. 12 Potential-resolved fluorescence spectral changes of [NhtMnPcL] during the first reduction in DMSO solution containing 0.2 M TBAP (applied potentials: *a*: 0.01 V; *b*: −0.01 V: *c*: −0.03 V; *d*: −0.05 V; *e*: −0.07 V; *f*: −0.09 V; *g*: −0.11 V) where the inset shows the plot of E_{app} *vs.* log[R]/[O].

spectroelectrochemistry in lower concentration where the molecules appear in non-aggregating forms.

Conclusion

In the present study, first, we report the *in situ* monitoring of the metallation of a metal-free phthalocyanine *via* UV-Vis and fluorescence techniques, which allow us to prepare a new non-aggregating and electrochromic manganese(3+) phthalocyanine [NhtMn(3+)PcL] in a high yield. These techniques are based on the change of the symmetry and the quenching of the fluorescence-probe molecule as a result of the insertion of the metal into the cavity of the macrocycle. Although UV-Vis is frequently applied to the monitoring of preparation of metal phthalocyanines, the fluorescence technique has not been used so far for *in situ* monitoring of metallation of a phthalocyanine macrocycle. So the metal insertion into the macrocycle could be followed by the *in situ* fluorescence technique as well as UV-Vis technique.

Second, this study presents a detailed knowledge for the electro-spectrochemical properties of [NhtMn(3+)PcL], which is important with regard to its possible usage as electrochromic material, where several colors are displayed depending on the potential applied to the electrode surface. All redox processes of [NhtMn(3+)PcL] are accompanied with a change of color from dark green to green and purple which are clearly monitored on the surface of the light transparent platinum gauze working electrode in the thin-layer cell. Thus, new manganese(3+) phthalocyanine presents multicolor response upon the applied potentials in the thin-layer cell.

Moreover, our study describes herein the application of the *in situ* UV-Vis and fluorescence spectroelectrochemical methods to determine $E_{1/2}$ and *n* with the spectra of fully oxidized and reduced species in one unified experiment. The spectrofluorescence method has higher sensitivity and can provide multi-parameter information such as excited and emission spectra, fluorescence intensity and efficiency. However, there have been known only a few reports on the *in situ* fluorescence electrochemistry in the literature and there is no report on the application of this technique for phthalocyanine molecules. Finally, The *in situ* fluorescence spectroelectrochemistry could be for the first time applied to determine $E_{1/2}$ and *n* for the phthalocyanine molecule in this study.

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