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Electrochemical, spectroelectrochemical characterization and electropolymerization of 2-(4-methyl-1,3-thiazol-5-yl) ethoxy-substituted manganese and indium phthalocyanines

H. Yasemin Yenilmez [a], Özgün Akdağ [a], Altuğ Mert Sevim [a], Atıf Koca [b],*, Zehra Altuntaş Bayır [a],*

[a] *Department of Chemistry, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey*
[b] *Department of Chemical Engineering, Engineering Faculty, Marmara University,34722 Goztepe, Istanbul, Turkey*

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ABSTRACT

In this study, the synthesis of novel, symmetrical, tetrasubstituted metallo-phthalocyanines (MPc; M = manganese, indium) bearing four 2-(4-methyl-1,3-thiazol-5-yl) ethoxy units has been reported. All of the synthesized compounds have been characterized by using elemental analysis, UV–Vis, FT-IR and MS spectroscopic data. Electrochemical, spectroelectrochemical and electropolymerization properties of the phthalocyanines were studied by cyclic voltammetry. Electrochemistry and spectroelectrochemistry of metallophthalocyanines (MPc) bearing redox active and polymerizable thiazole groups were introduced. **In^{III}ClPc** gave only Pc ring based reduction process, metal based and Pc based redox processes were observed for during the cathodic potential scans. However both complexes were coated on the working electrode during the oxidation reactions due to the oxidative electropolymerization of thiazole groups on the substituents of the complexes. Thiazole groups were oxidized at around 1.50 V, which triggered cationic electropolymerization reactions of the complexes. Type of the metal centers, working electrode, and solvent of the electrolytes and potential range and scan rate of the CV measurements affected the electropolymerization mechanisms of the complexes.

1. Introduction

Modifications of metallophthalocyanines (MPcs) with functional substituents extend the redox richness and versatility of their electrochemical applications in different fields, such as electrocatalytic, electrosensing and electrochromic applications [1]. For practical applications, MPcs should be coated on a substrate, thus electrode modification with different MPcs have much attention nowadays [2–5]. Although functional materials could be immobilized on different electrodes with many possible electrode modification techniques, electrode modifications with electropolymerization is frequently preferred due to the some major advantages of this technique [6–9]. It is well known that it is easily performed to control thickness, uniformity, morphology, and shape of the films coated on the substrates with changing the voltage, current, time, and scan rates of the electrochemical methods used. Therefore we intensified our studies on the electrochemical characterization and applications of MPcs bearing redox active and polymerizable substituents. For this purpose, we reported the synthesis, electrochemistry and electrochemical applications of MPcs carrying electropolymerizable thiophene [10], amines [11,12], and quinolone [13] groups. Now in this paper we have studied a new series of MPcs bearing electroactive thiazole groups.

2. Experimental

2.1. Materials

IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrometer with universal ATR module. Electronic spectra were recorded on a Scinco SD 1000 single-beam ultraviolet–visible (UV–Vis) spectrophotometer at room temperature. ^{1}H NMR spectra were recorded on Agilent VNMRS 500 MHz using TMS as the internal reference. Mass spectra were performed on Bruker Microflex MALDI-TOF/MS spectrometer. Single-mode microwave reactor (CEM Discover SP) was used for carrying out the synthesis of metallophthalocyanines. All reagents and solvents were of reagent grade quality obtained from commercial suppliers. The purity of the products was tested in each step by thin lead chromatography (TLC). All solvents were dried and purified as described by Perrin and Armarego [14]. The solvents were stored over molecular

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* Corresponding authors. Tel.: +90 212 285 32 23; fax: +90 212 285 63 86.
E-mail addresses: akoca@marmara.edu.tr (A. Koca), bayir@itu.edu.tr (Z.A. Bayır).

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sieves. 4-[2-(4-methyl-1,3-thiazol-5-yl)ethoxy] phthalo nitrile (**1**) was synthesized according to published methods [15].

2.2. Electrochemical and in situ spectroelectrochemical measurements

The cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements were carried out with Gamry Reference 600 potentiostat/galvanostat utilizing a three-electrode configuration at 25 °C. The working electrode was a Pt and/or GCE 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 TBAP in extra pure dichloromethane (DCM) or dimethylsulfoxide (DMSO) was employed as the supporting electrolyte at a concentration of 0.10 mol dm^{-3}. Ferrocene was used as universal indicator and the ΔE_p values of ferrocene were changed from 60 to 110 mV with increasing scan rates from 0.010 to 1.00 V s^{-1} in our system.

UV–Vis absorption spectra and chromaticity diagrams were measured with Ocean Optics QE65000 diode array spectrophotometer. 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 a 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 Ocean Optics QE65000 diode array spectrophotometer at color measurement mode by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell. The experiments used standard illuminant A with 2 degree observer at constant temperature in a light booth which was designed to exclude external light. 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 the final of each redox processes were reported.

2.3. Synthesis

2.3.1. [2,9,16,23-Tetrakis[2-(4-methyl-1,3-thiazol-5-yl)ethoxy] phthalocyaninato(chloro)-indium(III)] (**In^{III}ClPc, 2**)

Compound **1** (0.189 g, 0.7 mmol), anhydrous $InCl_3$ (0.040 g, 0.18 mmol), n-hexanol (2 mL) and 2–3 drops of DBU were irradiated in a quartz vessel of 10 mL by a microwave oven at 160 °C, 200 W for 5 min. After cooling to room temperature, the reaction mixture was treated with 1:1 (v/v) water/methanol mixture to precipitate the product which was filtered off. The resulting dark green solid was filtered off, washed several times with methanol and acetone. The desired compound was obtained after drying in vacuo at 75 °C. The yield:53 mg (28%); FT-IR ν_{max}/cm^{-1}: 3064 (C–H, aromatic), 2924–2869 (C–H, aliphatic), 1235 (C–O–C); UV–Vis (DMF): λ_{max}/nm (log ε, L mol^{-1} cm^{-1}): 360 (4.50), 626 (4.15), 695 (4.75); MALDI-TOF MS *m/z*: 1227.57 $[M]^+$, 1191.60 $[M-Cl]^+$; *Anal.* Calc. for $C_{56}H_{44}ClInN_{12}O_4S_4$ 1227.56 g/mol): C, 54.79; H, 3.61; N, 13.69. Found: C, 54.60; H, 3.51; N, 14.96%.

2.3.2. [2,9,16,23-Tetrakis[2-(4-methyl-1,3-thiazol-5-yl)ethoxy] phthalocyaninato(chloro)- manganese (III)] (**Mn^{III}ClPc, 3**)

Compound **1** (0.135 g, 0.5 mmol), anhydrous $MnCl_2$ (0.016 g, 0.13 mmol) and 2–3 drops of DBU were mixed in 1.5 mL of n-hexanol in a quartz vessel. The mixture was sealed and heated at 160 °C, 200 W for 5 min under N_2 to give the phthalocyanine with desired substitution. After cooling, the reaction mixture was poured into 1:1 (v/v) water/methanol mixture. The resulting dark green solid was filtered off, washed several times with acetone and methanol, and dried in vacuo at 75 °C. The yield: 63 mg (33%); FT-IR ν_{max}/cm^{-1}: 3064 (C–H, aromatic), 2925–2870 (C–H, aliphatic), 1236 (C–O–C); UV–Vis (DMF): λ_{max}/nm (log ε, L mol^{-1} cm^{-1}): 344 (4.72), 648 (4.41), 727 (4.73); MALDI-TOF MS *m/z*: 1166.96 $[M]^+$, 1131.80 $[M-Cl]^+$; *Anal.* Calc. for $C_{56}H_{44}ClMnN_{12}O_4S_4$ (1167.68 g/mol): C, 57.60; H, 3.80; N, 14.39. Found: C, 56.60; H, 3.97; N, 14.15%.

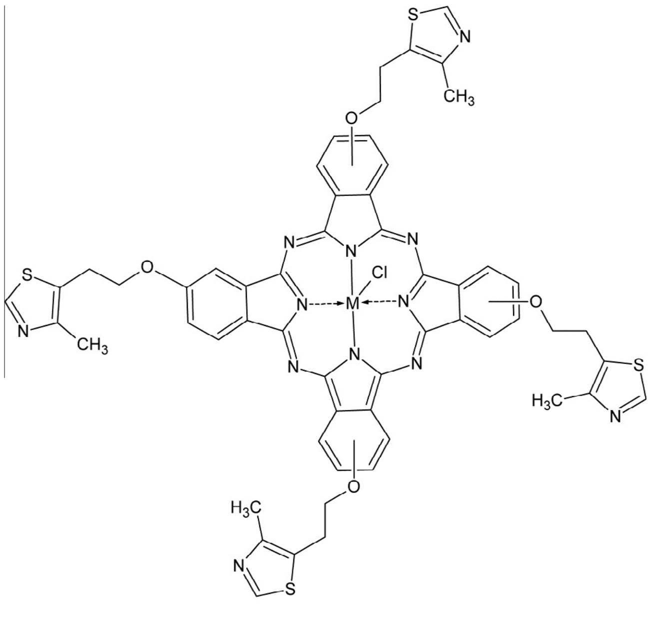
3. Results and discussion

3.1. Synthesis and characterization of macrocycles

The preparation of targeted metallophthalocyanines was originally attempted by the standard method of cyclotetramerization of 4-[2-(4-methyl-1,3-thiazol-5-yl)ethoxy]phthalonitrile in the presence of metal salts ($InCl_3$ or $MnCl_2$) and a N-donor base DBU in n-hexanol as the solvent at reflux temperature (Scheme 1). The synthesized metallophthalocyanine compounds are soluble in DMF and DMSO. They were obtained in good to adequate yields (28% for **2** and 33% for **3**) and characterized by spectral data (IR, Mass, and UV–Vis spectra). The data are consistent with the assigned structures.

After conversion into phthalocyanine derivatives, the characteristic C≡N stretch at 2226 cm^{-1} of the dinitrile 1 disappeared in the IR spectrum [16–19]. The IR spectra of the phthalocyanines are very close to each other. In the IR spectra of the phthalocyanines, aromatic groups, aliphatic groups and ether groups gave characteristic peaks at 3064, 2925–2870 and 1236 cm^{-1}, respectively. Our structural assignments were confirmed by mass spectra. The peaks for the molecular ion were found at $m/z = 1227.57$ ($[M]^+$) and 1191.60 ($[M-Cl]^+$) for **2**, 1166.96 ($[M]^+$) and 1131.80 ($[M-Cl]^+$) for **3**.

All phthalocyanines show typical electronic spectra with two strong absorptions, one of them is in the UV region at about



	M
2	In
3	Mn

Scheme 1. Structures of the metallophthalocyanines synthesized.