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Synthesis, electrochemical and spectroelectrochemical properties of novel phthalocyanine complexes of manganese, titanium and indium

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ABSTRACT

The new tetra peripheral 3,5-bis(trifluoromethyl)phenylethynyl substituted metallophthalocyanines (MPc) have been synthesized and their aggregative properties were investigated in different concentrations. Voltammetric and in situ spectroelectrochemical characterization of MPcs bearing metal centers with higher oxidation states In^{III}, Mn^{III}, and Ti^{IV} were performed in solution. While $In^{III}ClPc$ gave only Pc ring based reduction process, $Mn^{III}ClPc$ and $Ti^{IV}OPc$ showed metal based reduction reactions in addition to Pc-based redox processes. The presence of redox active metal centers like $Mn^{III}Cl$ and $Ti^{IV}O$ in the core of Pc ring increases the electrochemical activity of the complexes. The redox responses of the complexes confirmed the submitted structure of the complexes. During the electrochemical measurements, it was noticed that the presence of molecular oxygen in the electrolyte system considerably influenced the redox responses of the complexes due to the interaction of MPcs with O_2, which indicated the electrocatalytic and/or electrochemical sensing activities of the complexes for O_2 sensing. Electrocatalytic oxygen reduction and oxygen sensing measurements were performed in solution and in solid states as Langmuir-Blodgett multilayer thin films. While $In^{III}ClPc$ did not give any voltammetric signal for the interaction with molecular oxygen, square wave voltammetric (SWV) responses of $Mn^{III}ClPc$ and $Ti^{IV}OPc$ show electrocatalytic activities of the complexes for oxygen reduction reactions (ORR). Moreover, interaction of O_2 with these complexes gave extraordinary anodic SWV signals in both of aprotic and protic solvents, which indicate possible usage of the complexes as molecular oxygen sensor.

1. Introduction

As an example of tetrapyrrolic macrocycles, phthalocyanines (Pcs) are also promising materials for applications in catalysts, sensors, and optical limiting devices [1,2]. Peripheral substitution with long alkyl chains, bulky groups and crown ethers leads to Pc derivatives soluble in common organic solvents [3–8], which can beat the solubility barrier on the applications of Pcs. Due to the presence of fluoro groups at the periphery of Pcs, the solubility dramatically increases in a range of polar and apolar solvents, including the protic ones. Tetrapyrrolic macrocycles having a metal ion at the core and fluorinated moieties at the periphery are interesting materials due to their advantageous electron transport features [9–13]. It is well documented in the literature that altering the substituent environment and core metal ion of MPcs affects the redox activity of the complexes considerably as well as their basic chemical, physical, and thermal properties [14–18].

Although, synthesis and electrochemistry of numerous MPcs have been reported in literature, most of these reported complexes have M^{II} Pc core, such as Co^{II}, Zn^{II}, Cu^{II}, and Ni^{II} due to the ease synthesis, purification and high yield of these type complexes [1,19,20]. MPcs having higher oxidized metal center are not much in number and have potentiality for more applications because of their redox richness [21–29]. Thus, in this paper, we reported the synthesis and spectral, and electrochemical characterizations and the electrocatalytic and the electro sensing applications of $In^{III}ClPc$, $Mn^{III}ClPc$, and $Ti^{IV}OPc$ bearing (3,5-bis(trifluoromethyl)phenyl)ethynyl substituents. Since the metal centers of MPcs studied here have 3+ and 4+ oxidation states, each metal center has an axial ligand and forms $In^{III}Cl$, $Mn^{III}Cl$, and $Ti^{IV}O$. Binding ability of an axial ligand to the central metal ion of MPc donates it to behave as a possible functional material for the electrocatalytic reduction/oxidation and electrochemical sensing applications. These type of complexes bind the target species to the axial position of metal center and

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this interaction affects the electron transfer properties of MPcs and the target species. For this reason, we have chosen **$In^{III}ClPc$, $Mn^{III}ClPc$,** and**$Ti^{IV}OPc$** complexes for the usage as electrocatalyst and electrosensor for molecular oxygen. Indeed, the electrocatalytic reduction of O_2 is important in electrochemical energy field as it is a major reaction in fuel cell applications and metal-air battery technologies. So the results of this study may open a way for the application of the complexes in these fields.

2. Experimental

2.1. Materials

UV-Vis spectra were obtained at room temperature with a Scinco SD-1000 diode array, single-beam spectrophotometer by using cuvettes having 1 cm path length. FT-IR spectra were recorded with a Perkin-Elmer Spectrum One FT-IR spectrometer with UATR sampling system. ^1H- and ^{19}F-NMR spectra were obtained with a Agilent VNMRS 500 MHz Nuclear Magnetic Resonance Spectrometer by utilizing TMS as an internal reference. Mass spectra of the compounds were recorded on a Bruker Microflex MALDI-TOF mass spectrometer for metallophthalocyanines and Perkin-Elmer Clarus 500 GC-EI-MS for the precursor ligands. In every phase of the experimental setup, thin layer chromatography on silica gel-coated aluminum sheets was used to assess the purity of the samples. For the reactions, we have used either dry or appropriately dried solvents purged with nitrogen after use. Drying the solvents commonly includes introducing activated molecular sieves into the solvent and keeping overnight before use. No water content determination was made as per Karl-Fischer titration. All reagents and solvents used were of reagent grade purity as supplied by the chemical vendors (Sigma Aldrich, Merck, etc.). Tetraiodophthalocyanine compounds (**1a-c**) were prepared according to an existing literature procedure along with some minor adjustments [30].

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 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) 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's of ferrocene were changed from 60 to 110 mV with increasing scan rates from 0.010 to 1.00 Vs^{-1} in our system.

UV-Vis absorption spectra and chromaticity diagrams were measured with Oceanoptics 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* electro colorimetric measurements, under potentiostatic control, were obtained using 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 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.

MPcs were coated on ITO electrode with Langmuir-Blodgett technique using KSV NIMA Langmuir-Blodgett monolayer coating device. $CdCl_2.H_2O$ solution was prepared with ultrapure water at a concentration of 1 mg/1 mL that is used as a sub-phase in the trough of the device. To form well defined monolayer and controllable homogenous coating on ITO substrates, stearic acid (SA) solution was prepared (1 mg/mL) with chloroform solvent and mixed with MPCs solution (1:1 by volume). Then 1 mg/1 mL chloroform solutions of MPcs and SA mixtures were spread on the sub-phase solution drop by drop until the surface pressure rose up to 0.5 mN/m. Surface pressure (π)-area isotherm was recorded and the ideal surface pressure was detected as 35 mN/m for the formation of monolayers on the sub-phase. Finally MPc monolayers were transferred on the ITO substrates with 5 mm s^{-1}"up stroke" and "down stroke" rate of ITO substrate. The LB films of the complexes were abbreviated as ITO/**$Mn^{III}ClPc$** and ITO/**$Ti^{IV}OPc$.**

Oxygen interaction experiments were followed in three cases. *Case* 1: SWV responses of MPcs free electrolyte system bubbled gradually with molecular oxygen were recorded. *Case* 2: SWV responses of MPcs in the electrolyte system purged with nitrogen were recorded. *Case* 3: SWV responses of MPcs in the electrolyte system bubbled gradually with oxygen were recorded. During the oxygen sensing measurements, CV technique was used to obtain a calibration line for oxygen sensing. Amount of dissolved oxygen in aqueous and/or organic solutions were determined with following the peak current change of oxygen reduction reaction wave at different scan rates in an electrolyte containing known amount of oxygen. Then by using the equation ($I_p = (2.99 \times 10^5) n[(\alpha) n_a]^{1/2} C^*_{O_2} D^{1/2}_{O_2} \nu^{1/2} A$). Slope of a graph of I_p vs. $\nu^{1/2}$ was used to determine unknown concentration of oxygen in an electrolyte. For the quantification of dissolved oxygen ($C^*_{O_2}$), oxygen concentration was changed gradually by purging the electrolyte with oxygen and I_p vs.[O_2] changes were followed. The results of these analyses (I_p vs. $\nu^{1/2}$ at constant O_2 concentration and I_p vs. [O_2] at constant scan rate) were used for the quantification of dissolved oxygen. Oxygen concentration quantified with voltammetric measurements were also confirmed with an oxygen meter.

2.3. Synthesis

2.3.1. [2,9,16,23-Tetrakis(3,5-bis(trifluoromethyl)phenylethynyl) phthtalocyaninato oxotitanium (IV)] ($Ti^{IV}OPc$, 2a)

[2(3),9(10),16(27),23(24)-tetraiodophthalocyaninato]oxotitanium(IV) (**1a**) (0.1096 g, 0.1 mmol) was reacted with 1-ethynyl-3,5-bis(trifluoromethyl)benzene (0.238 g, 1 mmol) in the presence of bis(triphenylphosphine) palladium(II) chloride (1 μmol) and copper(I) iodide (0.5 μmol) in a mixture of freshly distilled diethylamine (4 mL) and THF (2 mL). The resulting mixture was allowed to react at ambient temperature for 16 hours with the exclusion of air by generously purging with nitrogen. A green color was formed, and methanol-water (3:1, v:v) mixture was used to obtain the desired precipitates. After discarding the liquid phase, the solid was washed several times with ethanol and methanol to purify it. The green colored product was loaded onto a column filled with silica gel and eluted with chloroform, and then THF, followed by washing with hot acetonitrile, methanol, and n-hexane. The yield was 0.08 g (55%). m.p. > 300 °C. IR (υ, cm^{-1}): 3096 (C-H, aromatic), 2200 (C≡C), 1612, 1464, 1381 (C-F), 1124, 1089, 967 (Ti = O) 772. ^1H NMR (250 MHz; $(CD_3)_2CO$; Me_4Si): δH, ppm 8.56-7.81 (24H,