



Titanyl phthalocyanines: Electrochemical and spectroelectrochemical characterizations and electrochemical metal ion sensor applications of Langmuir films



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ABSTRACT

Electrochemical and spectroelectrochemical characterizations of titanyl phthalocyanines, which were peripheral (α -TiOPc) and nonperipheral (β -TiOPc) tetra and octa substituted (**octa-TiOPc**) with 3,4-(methylenedioxy)-phenoxy moieties were performed to determine their possible applications in different electrochemical technologies. Voltammetric and *in situ* spectroelectrochemical measurements illustrate that position and number of 3,4-(methylenedioxy)-phenoxy substituents affect the redox behavior of the complexes. While α -TiOPc gives up to four reduction processes, β -TiOPc and **octa-TiOPc** gives up to three reduction processes. While **octa-TiOPc** gives metal–metal–ring–ring reductions, α -TiOPc and β -TiOPc complexes give metal–ring–ring–metal reduction mechanism. Solvent of the media also alter the electrochemical behavior of the complexes. *In situ* electrocolorimetric measurements shows distinct color differences among the electrogenerated anionic and cationic redox species, which indicates their possible applications in display technologies. Multiple and reversible, diffusion controlled and multi-electron redox reaction indicate possible usage of the complexes especially in electroensing applications. The complexes sense Ag^+ and Pd^{2+} ions in the solution and in the solid states.

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1. Introduction

Phthalocyanine (Pc) complexes are of great interest due to their various important applications in modern science and technology such as photodynamic therapy, chemical sensors, non-linear optics, liquid crystals [1–5]. Their semi-conducting properties are exploited for applications such as photoconductors [6], solar cells [7] as well as gas sensors [8] and their electrochemical properties [9,10] are utilized for electrochemical applications such as electrocatalytic [11,12], electroensing [13,14] and electrochromic fields [15]. Various phthalocyanines have been investigated for the relevant applications. Although all transition metals can coordinate to Pc ligands, only a few of them (Zn, Ti, Pd) can form highly photoactive complexes, such as titanyl phthalocyanine (TiOPc), owing to the closed shell nature of the electronic configuration of Ti^{4+} , similar to that of main group metal ions [16–18]. Although TiOPc have found many more important applications in especially high sensitive photoconductors in laser printing and photocopying, now a days, the studies are condensed to the sensor applications of TiOPc complexes [8]. In our previous papers, we reported electrochemical properties and electrocatalytic activities of various TiOPc com-

plexes [19–21]. However the related studies for the electrochemical application of TiOPc and its derivatives are still rare in the literature [19–24], and the correlation of electrochemical properties with their chemical structures is much less explored compared to the case of other MPcs. In literature, Nyokong and her coworkers [22,23] and our research group have studies on the electrochemistry and electrochemical applications of TiOPcs. On the basis of our previous reports on the electrochemical, electropolymerization, electrochromic, electroensing, and electrocatalytic properties of MPcs [19–21,25–29], we now extend our studies with the synthesis, characterization and application studies of TiOPcs and their derivatives. Thus in this paper, we have investigated the electrochemical and spectroelectrochemical properties of TiOPc synthesized and published by our research group [29] (Scheme 1). We have also performed detailed investigation for the possible sensor and electroelectrocatalytic applications of TiOPc. It was found in this study that TiOPcs has potential to use as electroensors for heavy metal ions.

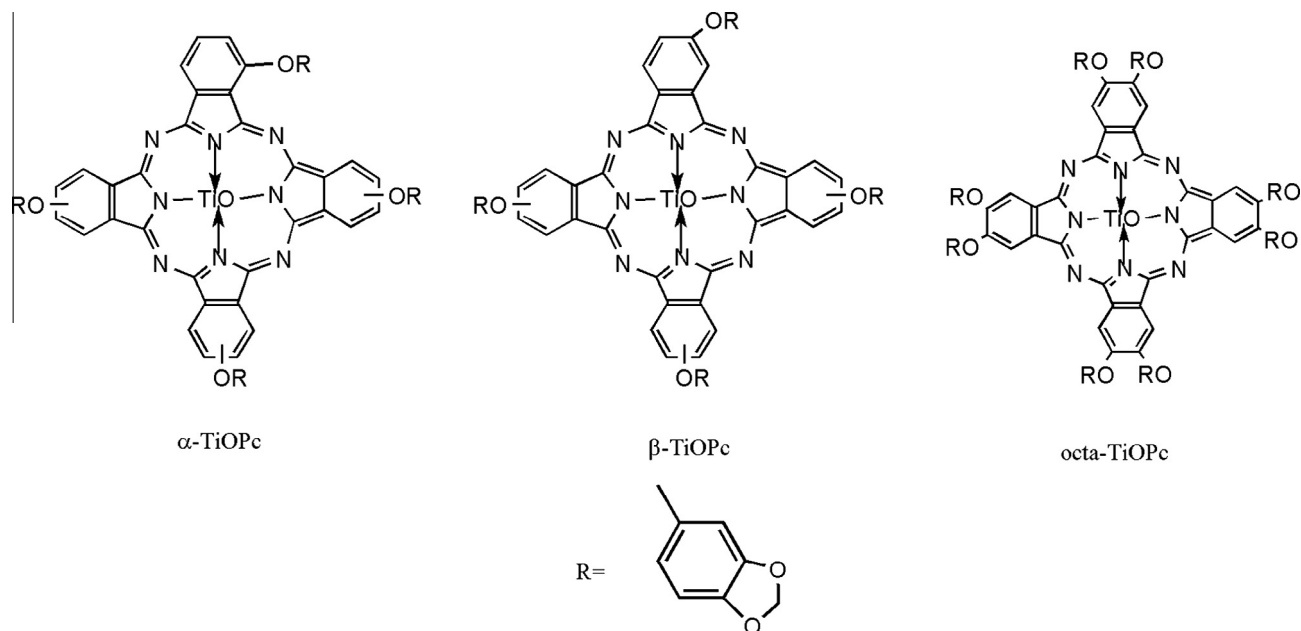
2. Experimental

2.1. Electrochemical and *in situ* spectroelectrochemical measurements

The cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements were carried out with Gamry Reference

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Scheme 1. Structure of TiOPc complexes. β -TiOPc: titanyl phthalocyanine nonperipherally tetra substituted with 3,4-(methylenedioxy)-phenoxy moieties; α -TiOPc: Titanyl phthalocyanine peripherally tetra substituted with 3,4-(methylenedioxy)-phenoxy moieties; octa-TiOPc: Titanyl phthalocyanine peripherally octa substituted with 3,4-(methylenedioxy)-phenoxy moieties.

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 cm². 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) and dimethylsulfoxide (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 Ocean Optics QE65000 diode array spectrophotometer. *In situ* spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of thin-layer quartz thin-layer spectroelectrochemical cell at 25 °C. The working electrode was a semipermeable Pt sheet. 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 an Ocean Optics QE65000 diode array spectrophotometer at color measurement mode by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell.

2.2. Langmuir Blodgett film preparation

Langmuir experiments were carried out using a KSV/Nima 5000. 0.1 M CdCl₂ dissolved ultrapure water (resistivity greater than 18M_{cm}) from a Milli-Q Millipore system was used as the subphase (pH 5.9). LB films were prepared by spreading chloroform solution of the compounds (1 mg of TiOPcs or a mixture of 1 mg of the TiOPcs 1 mg of SA) on subphase. A 100 μ l aliquot of the spreading solution was uniformly spread over the aqueous subphase by adding small drops at different locations on the water surface. A time period of 15 min was allowed for the solvent to evaporate before the area enclosed by the barriers was reduced. The π -A isotherm was recorded using a compression speed of barriers of 10 mm min⁻¹. A surface pressure (π) versus molecular area isotherm was measured to characterize the quality of the monolayer on the subphase. The surface pressure was measured by the

Wilhelmy method. After 30 min waiting for the stabilization of the monolayer, a vertical dipping procedure was performed at the selected surface pressure with a speed of 5 mm min⁻¹ for both the down and up strokes to transfer the monolayer on the ITO substrates. LB film samples were left to dry after each up stroke. Twenty monolayers were transferred to the ITO glass by Y-type deposition. Langmuir coated electrodes are abbreviated as ITO/TiOPc(LB) and ITO/TiOPc + SA(LB). To characterize the coating ability of the LB film, a transfer ratio was calculated by dividing the area of deposited film by the area of substrate.

2.3. Sensor measurements

First of all, to find out the possible interaction of TiOPcs with transition metal ions, CV and SWV of TiOPcs in DMSO/TBAP electrolyte system was carried out without metal ions and with gradual addition of 1.0 mmol dm⁻³ metal ions. Then sensor measurements of the modified electrodes (ITO/TiOPcs) were carried out in aqueous solution with the CV and SWV techniques. During the measurements in solid state, first of all, an adequate number of SWV cycles were applied to reach the steady state and then, metal ion solutions were added to the aqueous solution gradually. After an efficient stirring, SWVs and CVs were recorded.

3. Results and discussion

3.1. Voltammetric measurements

Electrochemical analyses of the complexes were investigated in solution to propose possible applications of the complexes in electrochemical technologies. For this purpose, the CV and SWV of the complexes (2–5) were recorded in DCM and DMSO/TBAP electrolyte system on a Pt working electrode. Table 1 lists the assignments of the redox couples and estimated electrochemical parameters including the half-wave peak potentials ($E_{1/2}$), ratio of anodic to cathodic peak currents ($I_{p,a}/I_{p,c}$), peak to peak potential separations (ΔE_p), and difference between the first oxidation and reduction processes ($\Delta E_{1/2}$).

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