

Synthesis and electrochemical properties of purple manganese(III) and red titanium(IV) phthalocyanine complexes octa-substituted at non-peripheral positions with pentylthio groups

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Abstract

The synthesis and electrochemical characterisation of octapentylthiophthalocyaninato manganese(III) acetate (**4**) and octapentylthiophthalocyaninato titanium(IV) oxide (**5**) complexes are reported. The complexes have an unusual purple (**4**) and red (**5**) colouration since the Q-band is shifted to the near infra red region with Q-band maxima at 893 nm and 808 nm in dichloromethane for **4** and **5**, respectively. The structures of the complexes were confirmed by elemental analysis and interpretation of their spectroscopic data, including 2D NMR. The cyclic voltammetry (CV) of the Mn complex (**4**) showed four quasi reversible couples. The reduction processes are attributed to $\text{Mn}^{\text{III}}\text{Pc}^{-2}/\text{Mn}^{\text{II}}\text{Pc}^{-2}$ and $\text{Mn}^{\text{II}}\text{Pc}^{-2}/\text{Mn}^{\text{I}}\text{Pc}^{-3}$ and the oxidation processes to $\text{Mn}^{\text{IV}}\text{Pc}^{-2}/\text{Mn}^{\text{III}}\text{Pc}^{-2}$ and $\text{Mn}^{\text{IV}}\text{Pc}^{-1}/\text{Mn}^{\text{IV}}\text{Pc}^{-2}$. The processes were confirmed by spectroelectrochemistry. A well-defined spectrum of the rare $\text{Mn}^{\text{IV}}\text{Pc}^{-2}$ species is reported. The CV of the Ti complex (**5**) showed two well-resolved reduction processes due to $\text{Ti}^{\text{IV}}\text{Pc}^{-2}/\text{Ti}^{\text{III}}\text{Pc}^{-2}$ and $\text{Ti}^{\text{III}}\text{Pc}^{-2}/\text{Ti}^{\text{II}}\text{Pc}^{-2}$. However, oxidation processes of the complex revealed adsorption behaviour and resulted in decomposition on electrolysis using spectroelectrochemistry.

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1. Introduction

Properties of metallophthalocyanine (MPc) macrocycles can be tailored through substitution on the peripheral or non-peripheral positions and at the same time, their solubility is enhanced such that many applications are facilitated. The choice of metals and substituents strongly influence the electrochemical and other properties of the MPc macrocycles. Substitution at the non-peripheral (α) positions causes red shifting of the Q-band [1,2] and also reduces aggregation tendencies to a greater extent than substitution at the peripheral (β) positions. The presence of electron donating sulphur groups in addition to substitution at the non-peripheral positions, will result in the

shift of the Q-band to even longer wavelengths. Pc complexes containing Mn as a central metal, in particular, show a highly red-shifted Q-band [2]. Hence in this work we present the synthesis and electrochemistry of MnPc and TiPc complexes octa-substituted at the non-peripheral positions with pentylthio groups (Scheme 1). The electrochemical data will be compared with those of other thiol derivatised MnPc and TiPc complexes shown in Fig. 1a. The electrochemistry of both complexes has received less attention compared to other 1st row transition metal phthalocyanines such as CoPc and FePc. The thiol substituted MPc complexes show red-shifted spectra and often show complicated electrochemistry involving the central metal, the Pc ring and the Pc ring substituents.

Manganese phthalocyanine complexes have very interesting electrochemistry due to the fact that the manganese

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