



Cyclic voltammetry and spectroelectrochemistry of a novel manganese phthalocyanine substituted with hexynyl groups

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ARTICLE INFO

Article history:

Received 14 August 2010

Accepted 22 November 2010

Available online 27 November 2010

Keywords:

Manganese phthalocyanine

Cyclic voltammetry

Alkyne

Spectroelectrochemistry

ABSTRACT

We report here on the synthesis of a new manganese phthalocyanine complex, namely Mn tetrakis(5-hexyn-oxo) phthalocyanine (**3**), specifically designed to possess an alkyne moiety for its potential use in controlled immobilization on electrodes *via* the so called “click” chemistry reaction. The electrochemical activity of complex **3** was investigated by cyclic voltammetry and the nature of the observed redox couples was elucidated by spectroelectrochemistry. This work has also shown that the reduction of Mn(III)Pc complex to Mn(II)Pc is accompanied by the formation of MnPc μ -oxo species. Further reduction results in the formation of Mn(II)Pc(−3) rather than Mn(I)Pc(−2).

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Phthalocyanines (Pcs) have attracted a lot of interest in research because of their diverse properties which are harnessed in a variety of applications, including their use in non-linear optical devices, oncology, sensors and security printing industry [1–5]. The properties of phthalocyanines can be tuned by the introduction of substituents on the periphery of the molecule. The presence of electron donating groups results in the shift of the Q band to longer wavelengths. Alkynyl substituted MPc complexes are known [6–9]; they were found to be more soluble in common organic solvents (such as dichloromethane, chloroform and tetrahydrofuran) when compared with alkylthiophthalocyanines [7]. MPc complexes containing Mn as a central metal show a highly red-shifted Q band [10]. The alkyne substituted MPc complexes reported in the literature so far are either unmetallated or contain electrochemically inactive central metals such as Cu or Zn [6–9]. Also alkyne substituted MPc complexes containing a long alkyl chain and which terminate with a triple bond carbon are unknown. These types of complexes have the potential of being attached covalently to an electrode surface bearing azide groups by “click” chemistry. Click chemistry is an emerging attractive and efficient method of immobilization of molecular moieties on solid material. “Click” chemistry involving alkyne complexes uses the Sharpless copper(I) catalyzed azide–alkyne cycloaddition reaction to produce stable immobilized layers on electrodes [11,12]. Thus the synthesis of MPc complexes bearing terminal alkyne groups, which are also separated from the ring by long alkyl chains is of importance.

This work reports on the synthesis and electrochemistry of tetra-5-hexyn-oxo substituted MnPc derivative (complex **3**, Scheme 1). The first reduction in Mn^{III}Pc^{−2} complexes has been a subject of some controversy, with some reports proposing ring reduction to the Mn^{II}Pc^{−3} species and others suggesting metal reduction to the Mn^IPc^{−2} species. The former species has been reported by us and other authors [13–15], and the latter has rarely been observed [16]. The formation of Mn^IPc^{−2} or Mn^{II}Pc^{−3} species is highly dependent on the ring substituents.

Complex **3** (Scheme 1) was prepared by the template reaction of 4-hex-5-ynoxyphtalonitrile (compound **2**) precursor with manganese (II) acetate in the presence dimethylaminoethanol (DMAE). The details are supplied as Supplementary data. The complex was characterized by spectroscopic methods and elemental analyses. With the aid of 2 dimensional nuclear magnetic resonance (NMR) spectroscopy experiments such as correlation spectroscopy (COSY), heteronuclear multiple bond correlation (HMBC) and heteronuclear single quantum coherence (HSQC), the structure of complex **3** was confirmed. The presence of the triple bond was confirmed by a correlation from the $\text{C}\equiv\text{CH}$ proton to the quaternary carbon in the HMBC experiment.

A mixture of four possible structural isomers is expected for complex **3**. The four probable isomers can be designated by their molecular symmetry as C_{4h} , C_{2v} , C_s and D_{2h} , and they are known to occur in an expected statistical mixture of 12.5% C_{4h} , 25% C_{2v} , 50% C_s and 12.5% D_{2h} for peripherally substituted complexes [17]. The isomers are difficult to separate and no attempt was made to separate them in this work.

The Q band of complex **3** at 732 nm in DMF is red shifted compared to unsubstituted MnPc in DMF (at 716 nm) [18], confirming that the presence of the electron donating 5-hexyn-oxo group results in red-

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