Available online at www.sciencedirect.com

ScienceDirect

Electrochimica Acta 53 (2008) 4599–4605

ELECTROCHIMICA Acta

www.elsevier.com/locate/electacta

The influence of poly(2-methoxyaniline-5-sulfonic acid) on the electrochemical and photochemical properties of a highly luminescent ruthenium complex

Lynn Dennany [a,b], Emmet J. O'Reilly [a], Peter C. Innis [b], Gordon G. Wallace [b], Robert J. Forster [a,*]

[a] *Biomedical Diagnostics Institute, National Centre for Sensor Research, School of Chemical Sciences, Dublin City University, Dublin 9, Ireland*

[b] *ARC Centre of Excellence for Electromaterials Science and Intelligent Polymer Research Institute, University of Wollongong, Northfields Avenue, Wollongong, NSW, Australia*

Received 26 September 2007; received in revised form 7 November 2007; accepted 11 November 2007

Abstract

Immobilisation of a luminescent material on an electrode surface is well known to substantially modulate its photophysical and electrochemical properties. Here a positively charged ruthenium metal complex ($[Ru(bpy)_3]^{2+}$) is immobilised on all electrode surface by ion paring with a sulfonated conducting polymer poly(2-methoxyaniline-5-sulfonic acid), (PMAS). Significantly, our study reveals that the electron transport between the ruthenium metal centres can be greatly enhanced due to the interaction with the conducting polymer when both are surface confined. Charge transfer diffusion rates in the present system are an order of magnitude faster than those found where the metal centre is immobilised within a non-conducting polymeric matrix. Electron transport appears to be mediated through the PMAS conjugated structure, contrasting with the electron hopping process typically observed in non-conducting metallopolymers. This increased regeneration rate causes the ruthenium-based electrochemiluminescence (ECL) efficiency to be increased. The impact of these observations on the ECL detection of low concentrations of disease biomarkers is discussed.

Keywords: Electrochemiluminescence; Conducting polymers; Luminescence; $Ru(bpy)_3{}^{2+}$; Electropolymerisation

---

1. Introduction

Chemically modified electrodes have been of interest because of their potential in electrocatalysis and other applications where deliberate control of the electrode–solution interface is desirable. The use of polymers as supports for confining transition metals at the electrode–solution interface is well known [1,2]. Polypyrroles containing coordinated metal complexes are an attractive approach to forming interfacial metallopolymer films since the π conjugated backbone can provide a rapid electron transfer pathway between the metal complex and the electrode [2–5]. Here we explore an alternative approach that simply involves the incorporation of the ruthenium metal centre by ion pairing with sulfonate groups of poly(2-methoxyaniline-5-sulfonic acid), (PMAS).

Sulfonated self-doped polyaniline has been extensively studied due to its unique electrochemical properties, water solubility, improved processability and potential industrial applications [6–8]. PMAS is a fully sulfonated conducting polymer that has been synthesised by chemical and electrochemical polymerisation of 2-methoxyaniline 5-sulfonic acid, MAS [9,10]. In-depth characterisation of the electrochemical and photochemical properties of these two distinctive fractions have also been reported [11].

The ability of conjugated linkages to provide an effective pathway for the electron transfer between metal centres has been demonstrated in a number of polymeric systems. Zotti et al. [12] have shown that electron transfer rates between metal centres in substituted polythiophenes, with pendant ferrocene moieties, is enhanced when a conjugated linkage is used.

---

[*] Corresponding author. Tel.: +353 1 7005943; fax: +353 1 7005503.
E-mail address: Robert.Forster@dcu.ie (R.J. Forster).

0013-4686/$ – see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.electacta.2007.11.025

Cameron and Pickup [4,5] have also shown that coordination of ruthenium moieties to a conjugated polybenzimidazole provides a rapid electron transfer pathway by superexchange interactions between metal centres. However, this increased electron transfer did not translate into enhanced luminescence of the ruthenium moiety, presumably due to the energy/electron transfer processes from the excited state of the metal complex to the polymer represents a competing radiationless decay pathway.

Significantly, PMAS can form novel composites via the anionic SO_3^- functionality ion pairing with the cationic $[Ru(bpy)_3]^{2+}$ fluorophore. Earlier studies have focused upon luminescent $[Ru(bpy)_2]^{2+}$ moieties covalently bound to a poly(4-vinyl-pyridine) backbone at statistical separations of the order of 50 Å [13]. Unlike these PVP-based metallopolymers, the PMAS–$[Ru(bpy)_3]^{2+}$ composites offer greater synthetic flexibility as well as increased charge transport rates due to both physical diffusion and the electronically conducting properties of the backbone. These properties uniquely enable the development of advanced diagnostic devices based on the luminescent detection of analytes including proteins and DNA biomarkers since more rapid electrochemical production of the Ru^{3+} state ought to produce a greater total emission intensity per unit time [14]. ECL represents a powerful analytical approach that combines simple equipment with inherent sensitivity, selectivity, and a wide linear dynamic range for amine containing analytes, such as alkylamines, NADH, hydrazine, amino acids, biomolecules and a variety of pharmaceutical compounds [15–19]. ECL usually involves the reaction of electrogenerated species that react to form excited states, usually via an energetic redox reaction [19]. Thus, ECL can also be utilised to probe electron and energy transfer processes at electrified interfaces [20,21]. Consequently, increasing and improving the ECL efficiency could advance the sensitivity ranges and expand the dynamic range of current ECL systems.

We have recently reported that oxidation of guanines in DNA by electrochemically generated $[Ru(bpy)_2(PVP)_{10}]^{2+}$ in ultrathin films leads to photoexcited $[Ru(bpy)_2]^{2+*}$ sites in the film, generating an ECL signal upon relaxation back to the ground state [22]. This thin-film ECL approach has been exploited to detect DNA damage induced by styrene oxide. The reaction was initiated by an electrochemical catalytic oxidation of guanine sites in DNA in a way that is similar to that reported by Thorp and co-workers [23] for $Ru(bpy)_3{}^{2+}$ in solution. By enhancing the ECL or luminescent efficiency of the ruthenium moiety through interactions with a conducting polymer, the sensitivity of this type of ECL sensors could be dramatically improved. Within this contribution, however, we will focus on the production of light from the reaction of ruthenium metal centres with oxalate, similar to that described by Hogan and co-workers [13,24].

It is known that when $[Ru(bpy)_3]^{2+}$ is oxidized in a solution containing $C_2O_4{}^{2-}$ the following reaction takes place and ECL is observed [25,26]:

$$Ru(bpy)_3{}^{2+} \rightarrow Ru(bpy)_3{}^{3+} + e^- \quad (1)$$

$$Ru(bpy)_3{}^{3+} + C_2O_4{}^{2-} \rightarrow Ru(bpy)_3{}^{2+} + CO_2 + CO_2{}^{\bullet -} \quad (2)$$

$$Ru(bpy)_3{}^{2+} + CO_2{}^{\bullet -} \rightarrow Ru(bpy)_3{}^{+} + CO_2 \quad (3)$$

$$Ru(bpy)_3{}^{3+} + Ru(bpy)_3{}^{+} \rightarrow Ru(bpy)_3{}^{2+*} + Ru(bpy)_3{}^{2+} \quad (4)$$

$$Ru(bpy)_3{}^{3+} + CO_2{}^{\bullet -} \rightarrow Ru(bpy)_3{}^{2+*} + CO_2 \quad (5)$$

$$Ru(bpy)_3{}^{2+*} \rightarrow Ru(bpy)_3{}^{2+} + h\nu \quad (6)$$

Similar processes occur within metallopolymer films deposited on metallic electrodes containing pendant $Ru(bpy)_2{}^{2+}$ centres [13]. The $[Ru(bpy)_2(PVP)_{10}]^{2+}$ films contain ruthenium centres that are electrochemically isolated, while in a PMAS–$Ru(bpy)_2{}^{2+}$ composite an electrochemically active backbone provides a mechanism for communication between adjacent ruthenium centres absence in the systems discussed above. The effect of an electronically conducting polymer on the ECL response, charge transport and photochemical properties of a metal centre are examined in this contribution.

2. Experimental

2.1. Materials and reagents

$[Ru(bpy)_3]^{2+}$ was synthesised according to a literature method [27]. The metallopolymer, $[Ru(bpy)_2PVP_{10}](ClO_4)_2$, was prepared as described previously [28]. PMAS synthesis has been reported previously for both chemical and electrochemical synthesis methods [9]. MAS was provided by Mitsubishi Rayon, Japan and purified by acid base crystallisation before polymerisation.

2.2. Apparatus

Absorbance and photo-luminescence were recorded using a Shimadzu UV-1601 spectrophotometer and a JY Spex fluorescence spectrophotometer, respectively. Fluorescence lifetime studies were made on a PicoQuant PDL-800B pulsed diode laser controller and FluoTime 100 time-correlated single photon counting system (TCSPC) with 280, 370 and 450 nm pulsed laser sources with cut-on filters of 400, 475 and 530 nm. TCSPC analysis was preformed using PicoQuant FluoFit software. Samples were deoxygenated for approximately 20 min with nitrogen prior to analysis. All other electrochemical experiments were carried out using a 3 or 2 mm diameter platinum or glassy carbon working electrode in a conventional three-electrode assembly. Potentials are quoted versus Ag/AgCl and all measurements were made at room temperature.

Cyclic voltammetry analysis was made with a CH Instruments Model 660 electrochemical analyser. All potentials were made with respect to a 3 M Ag/AgCl reference electrode unless otherwise stated. Measurements involving simultaneous detection of light and current utilised a model 273 (Princeton) potentiostat and an Oriel 70680 photomultiplier tube (PMT) equipped with a high voltage power supply, (Oriel, model 70705), which was used at a bias of −850 V, and amplifier/recorder (Oriel, model 70701). During experiments the cell was placed inside a specially constructed holder, where the working electrode is positioned in a reproducible manner directly opposite the face of a fibre optic bundle, the other end of which was coupled to the PMT. The entire electrode assem-