Electrochemistry Communications 12 (2010) 905–908

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Electrogenerated chemiluminescence of poly[(2,2′-bipyridyl)(4-(2-pyrrol-1-ylethyl)-4′-methyl-2,2′-bipyridyl)$_2$]ruthenium (II) film

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ARTICLE INFO

Article history:
Received 30 March 2010
Received in revised form 12 April 2010
Accepted 21 April 2010
Available online 28 April 2010

Keywords:
Electrogenerated chemiluminescence (ECL)
Electropolymer
Poly[(2,2′-bipyridyl)(4-(2-pyrrol-1-ylethyl)-4′-methyl-2,2′-bipyridyl)$_2$]ruthenium (II)
Redox-cycling
Oxidative-reduction

ABSTRACT

Elelctrogenerated chemiluminescence (ECL) of electropolymerized films based on [(2,2′-bipyridyl)(4-(2-pyrrol-1-ylethyl)-4′-methyl-2,2′-bipyridyl)$_2$]ruthenium (II) was firstly investigated in both organic and aqueous solution. The ECL behaviors have been explained by two typical mechanisms, namely, redox-cycling type and oxidative-reduction type. For the former, no co-reactant was required and for the latter, tripropylamine (TPA) and $(NH_4)_2C_2O_4$ were selected as co-reactants in the organic and aqueous system, respectively.

1. Introduction

Electrochemical polymerization of organic monomers provides a controllable and reproducible way to functionalize conductive surfaces with molecular reagents. In addition, the quality of the electrogenerated polymer films (absence of manufacturing defects, chemical stability, and storage stability) constitutes an attractive advantage for the regularity at the molecular level of additional functionalization of the electrode via the polymer film [1].

Among conducting polymers, polypyrrole and its derivatives are most attractive due to their relative low oxidation potential, high stability and excellent electrical properties in organic and aqueous solvents [2]. In particular, the easy and versatile modification of pyrrole monomer by a large variety of molecular species leads to polymerized platforms with specific recognition, affinity, catalytic and fluorescent properties [3–12].

With the aim to confer chemiluminescent properties to polypyrrole film, luminophor group of tris(2,2′-bipyridyl)ruthenium(II) ($Ru(bpy)_3^{2+}$) was successfully bound to pyrrole monomer via carbon chain [13]. Electrogenerated chemiluminescence (ECL) systems based on $Ru(bpy)_3^{2+}$ and its derivatives have shown great importance for chemical analysis, light emitting devices and luminescent imaging due to their chemical stability, reversible electrochemical behavior and high luminescent quantum yield [14].

Thus, [(2,2′-bipyridyl)(4-(2-pyrrol-1-ylethyl)-4′-methyl-2,2′-bipyridyl)$_2$]ruthenium (II) (pyr-Ru) was electropolymerized to confer luminescent properties to the polypyrrole skeleton. To the best of our knowledge, the solid-state ECL based on electrogenerated polypyrrole substituted by ruthenium complex has never been investigated. Herein, we reported for the first time the ECL behaviors of polypyr-Ru.

2. Experimental

2.1. Materials

[(2,2′-bipyridyl)(4-(2-pyrrol-1-ylethyl)-4′-methyl-2,2′-bipyridyl)$_2$]ruthenium(II) $(BF_4)_2$ was synthesized according to the protocol reported in our previous work [13]. Its structure is shown in Fig. 1. Tripropylamine (TPA) and tetrabutylammonium perchlorate (TBAP) were purchased from Sigma-Aldrich. $LiClO_4$, $(NH_4)_2C_2O_4$ and CH_3CN were of analytical grade and obtained from Shanghai Chemical Plant. All of the aqueous solutions were prepared with doubly distilled water.

2.2. Apparatus

All electrochemical and ECL experiments were carried out in a conventional three-electrode cell. Glassy carbon electrodes (GCE) (diameter 3 mm) were polished with 0.5 μm Al_2O_3, and successively

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doi:10.1016/j.elecom.2010.04.017

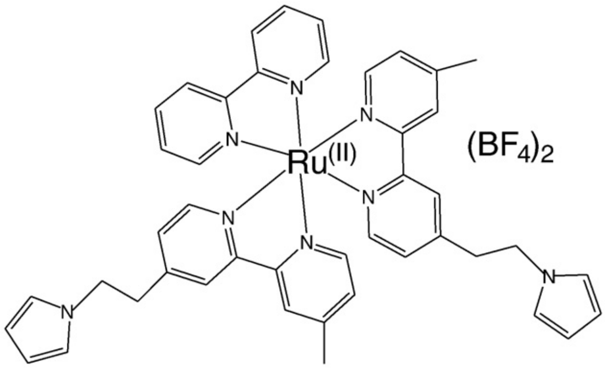

Fig. 1. Structure of [(2,2′-bipyridyl)(4-(2-pyrrol-1-ylethyl)-4′-methyl-2,2′-bipyridyl)$_2$] ruthenium(II) (BF$_4$)$_2$.

sonicated in alcohol, acetone and doubly distilled water. Before use, the resulting electrodes were dried in a desiccator. Potentials were reported relative to a Ag/Ag$^+$ (10 mM in CH$_3$CN) reference electrode or to a saturated calomel electrode (SCE) in acetonitrile electrolyte and aqueous solutions, respectively. A Pt wire, placed in a separated compartment containing the supporting electrolyte was used as counter electrode.

A CHI 760C electrochemical workstation (CH Instruments, USA) was used for all the electrochemical experiments. As previously reported, ECL was conducted by a homemade ECL system [14,15]. High voltage applied to photomultiplier tube (PMT) was −800 V, unless noted otherwise. The ECL spectra were recorded using a fluorescence spectrophotometer (RF-5301PC).

2.3. Preparation of polypyr-Ru

Polypyr-Ru films were generated on GCE by potentiostatic electropolymerization of monomer, pyr-Ru (1 mM), in CH$_3$CN containing 0.1 M TBAP under nitrogen atmosphere. The thickness of polymeric film was controlled through the integration of the electrolysis charge. All the modified electrodes were thoroughly washed with CH$_3$CN and stored in a dry state.

3. Results and discussion

3.1. Electrochemical behavior of polypyr-Ru

The polypyr-Ru-modified electrodes were prepared by controlled potential electrolysis of pyr-Ru (1 mM in CH$_3$CN + 0.1 M TBAP) at 0.9 V. The formation of a polymeric film and its sustained growth onto the GCE electrode surface was due to the continuous electropolymerization of the pyrrole groups via the ruthenium (II) centers acting as an electron relay in the film for the electro-oxidation of the monomer [9].

The apparent of surface coverage (Γ, determined from the charge integrated under the Ru$^{III/II}$ peak system) is 3.0×10^{-9}, 5.9×10^{-9} and 8.25×10^{-9} mol cm^{-2} for the electrolysis charge of 10, 20 and 3 mC cm^{-2}, respectively. This linear relationship between the apparent surface coverage and the charge passed during controlled potential electrolysis has been also observed in our previous work [9]. As expected, the thicker films show the larger ΔE_p values and the broadened waves ($\Gamma=3\times10^{-9}$ mol cm^{-2}, $\Delta E_p=32$ mV; $\Gamma=8.25\times10^{-9}$ mol cm^{-2}, $\Delta E_p=99$ mV at a scan rate of 100 mV s^{-1}). For the resulting modified electrodes, a mean electropolymerization yield of 20% was determined by dividing the charge integrated for the oxidation of the polymerized Ru(II) complexes by the charge employed for the electropolymerization and multiplying by 4.66. The latter corresponds to 2.33 electrons per pyrrole group [9]. In addition, the peak currents of polypyr-Ru/GCE vary linearly with the scan rate over the range 10 to 300 mV s^{-1}. This clearly indicates that the redox behavior of polypyr-Ru films follows a surface-controlled process.

The electrochemical stability of the polypyr-Ru film was investigated by repeatedly scanning the electrode potential in CH$_3$CN + 0.1 M TBAP at 100 mV s^{-1} over the range 0 V to +1.3 V. A slow decrease (8%) in the peak intensity of the Ru(II)/Ru(III) redox couple was recorded after 200 cycles. This slight decrease in Ru electroactivity illustrates the good mechanical stability of the polypyr Ru film due to a cross-linking process resulting from the presence of two pyrrole groups per monomer.

3.2. Electrogenerated chemiluminescence behavior of polypyr-Ru in organic solution

ECL of polypyr-Ru ($\Gamma=8.25\times10^{-9}$ mol cm^{-2}) coated on GCE was firstly investigated by cyclic voltammetry in CH$_3$CN containing 0.1 M TBAP. Fig. 2 shows the ECL–potential (E) curves for polypyr-Ru in 0.1 M TBAP + CH$_3$CN. The potential scanning was carried out in the following manner: 0 V → 1.2 V → −1.5 V → 1.2 V → −1.5 V. No ECL emission was detected upon the first positive potential scan from 0 to 1.2 V. In contrast, two different ECL signals were obtained on the reverse scan from 1.2 V to −1.5 V, the peaks being located at 1.1 V and −1.1 V. To get more useful information, the potential scanning was first initiated in the negative region: 0 V → −1.5 V → 1.2 V (data not shown). The ECL can not be observed for the first negative scan to −1.5 V. However, upon positive potential scan to 1.2 V, an ECL emission appears. Thus, we can conclude that only Ru(III) or Ru(I) produced in the film cannot generate any ECL. In contrast, both electrochemically generated Ru(III) and Ru(I) species can exist in the film for cyclic voltammogram performed at relatively high scan rate (100 mV s^{-1}) over the range 1.2 V/−1.5 V. The corresponding CVs also provide proofs to support the preceding hypothesis (inset in Fig. 2). Since no oxidizer or reductant was in solution, the irreversible shape of the redox of Ru$^{II/I}$ redox couple may indicate a reversible but very slow process (due to the film thickness, the permeation of the counter-ions was hindered inducing thus this slow process). In this case the potential scanning is so fast that both the reduction of Ru (II) at −1.2 V and its re-oxidation at 1 V led to a mixture of Ru(I) and Ru(III) in the film that may provide some ECL.

The ECL mechanism, requiring no co-reactant, is the redox-cycling type ECL where the Ru(I) and Ru(III) complexes are simultaneously produced. Then, an annihilation reaction between both species leads

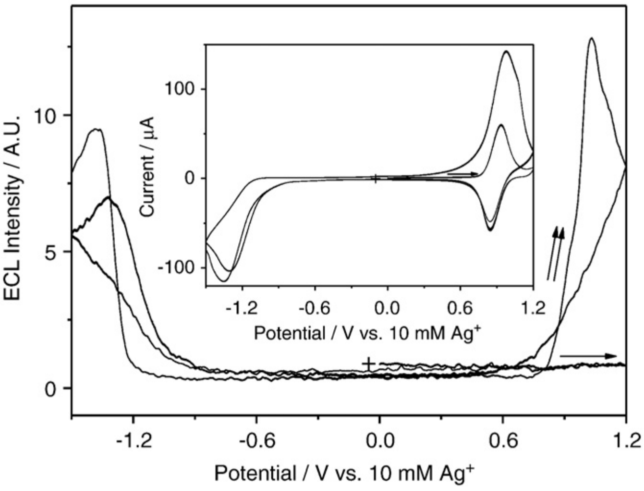

Fig. 2. ECL–E curve of polypyr-Ru/GCE in CH$_3$CN containing 0.1 M TBAP. Potential scanning starts from 0 to 1.2 V then from 1.2 to −1.5 V for 2 cycles. Inset: corresponding CVs.