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Characterization of multi-walled carbon nanotube electrodes functionalized by electropolymerized tris(pyrrole-ether bipyridine) ruthenium (II)

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ABSTRACT

We synthesized new electropolymerizable $[Ru(bpy)_nL_m](PF_6)_2$ (L = 4,4 bis(3-pyrrol-1-ylpropyloxy) bipyridyl) derivatives. The introduction of electron donating ether groups in the bipyridine ligand induced a negative shift of the Ru(III)/(II) redox couple. The electrochemical behavior of complex **Ru1** ($n = 2$, $m = 1$) and complex **Ru2** ($n = 0$, $m = 3$) were compared using platinum and Multi-Walled Carbon Nanotube (MWCNT) electrode. Higher polymerization yields and surface concentrations were obtained at MWCNT electrodes. Furthermore, MWCNT electrodes increase polymer permeability and decrease the charge trapping phenomenon involved in the oxidation and reduction of the polypyrrolic skeleton of the Ru(II) functionalized polymers.

1. Introduction

Carbon nanotube (CNT)-based electrodes show promising properties in the field of electrochemical sensors, thanks to their great conductivity, wide surface area and stability. Electrochemistry on CNTs takes the advantage of high-area, three-dimensional nanoporous electrodes and envisages future perspectives in the construction of nanoelectrodes. A challenging area in this field is the combination of CNTs and conducting polymers forming novel hybrid electrodes. The electropolymerization process, indeed, leads to the simple and reproducible formation of organic films with precise spatial resolution over surfaces, whatever their size and geometry. In particular, redox polymers awoke great interest as functional materials for energy conversion, sensing or molecular electronics [1–3]. In addition to synergetic effects created by the combination of CNTs and conductive polymers, the functionalization of these nanocomposites with redox species is aimed at designing redox nanocomposites with biosensing properties [4–7].

Metallopolymers based on polypyridinyl ruthenium(II) are particularly interesting for promising applications in photoelectrochemical sensors based on photogenerated current [8] and electrogenerated chemiluminescence (ECL) [9,10]. With the aim to develop ECL transduction in water for immunosensors and DNA sensors, an attractive perspective may be the concept of electrogenerated $[Ru(bpy)_3]^{2+}$ films exhibiting a less positive potential for the Ru(III)/(II) system. In addition, these films should present a good accessibility to the redox sites as well as an efficient permeability for the electro-oxidation of co-reactants necessary for ECL.

For this purpose, the electrochemical properties of novel redox-active nanocomposites formed with Multi-Walled Carbon Nanotubes (MWCNT) and new Ru(II)-functionalized polypyrroles were investigated. In this work, we describe a new route to synthesize polypyrrole tris-bipyridinyl Ru(II) complexes via an ether-oxide linkage acting as an electron donating group for modulating the potential of the Ru(III)/(II) redox couple. Two ruthenium complexes were thus prepared: complex **Ru1** containing two pyrroles at one bipyridine ligand and complex **Ru2** exhibiting six pyrroles, two at each bipyridine ligand. The electrochemistry of the corresponding electrogenerated metallopolymers **poly-Ru1** and **poly-Ru2** was compared using Pt and MWCNT electrodes. Pt electrodes were chosen as a model for a planar electrode exhibiting high electron transfer rate. Moreover, MWCNT-doped metallopolymers were characterized by Scanning Electron Microscopy (SEM) and cyclic voltammetry (CV), focusing on the charge trapping effects in these redox polymers.

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Table 1
Redox potentials (V) and spectral data for complexes **Ru1** and **Ru2** (in MeCN–TBAP 0.1 M at 0.1 V s^{-1}, potential vs Ag/10 mM AgNO$_3$).

Complex	λ_{max} (nm)	ε (dm^3 mol^{-1} cm^{-1})	$E^{red}_{1/2}$ (V)	$E^{red}_{1/2}$ (V)	$E^{red}_{1/2}$ (V)	$E^{ox}_{1/2}$ (V)	$E^{ox}_{1/2}$ (V)
Ru1	460	11300	−2.26	−1.87	−1.67	0.81	0.9
Ru2	478	4900	−2.33	−2.05	−1.78	0.59	0.9

2. Experimental

2.1. Methods and instrumentation

NMR spectra were recorded on a Bruker AVANCE 400 operating at 400.0 MHz for ^{1}H. ESI mass spectra were recorded with a Bruker APEX-Qe ESI FT-ICR mass spectrometer.

The electrochemical experiments were carried out in a three-electrode electrochemical cell under an argon dry atmosphere in a glove box using an Autolab pgstat100 potentiostat. The preparation of the working electrodes is described below. A platinum wire placed in a separated compartment was used as counter electrode and the Ag/AgNO$_3$ 10^{-2} M couple served as reference electrode. All potentials given in this work are referred to the (Ag/AgNO$_3$) reference electrode.

The experiments were conducted in anhydrous acetonitrile with tetrabutylammonium perchlorate [Bu$_4$N]ClO$_4$ (TBAP) as the supporting electrolyte.

The morphology of, in particular, the modified MWNT electrodes was investigated by SEM using an ULTRA 55 FESEM based on the GEMENI FESEM column with beam booster (Nanotechnology Systems Division, Carl Zeiss NTS GmbH, Germany) and tungsten gun.

2.2. Preparation of MWCNT electrodes

Commercial grade thin Multi-walled Carbon Nanotubes (9.5 nm diameter, purity >95%,) obtained from Nanocyl were used as received, without any purification step. MWCNT films were prepared using a modified procedure from [11]. MWCNTs (10 mg) were dispersed in pure water (250 mL) and sonicated during 30 min. The solution was carefully decanted overnight and the remaining supernatant (80 mL) was then filtered over cellulose nitrate filter (Sartorius, 0.45 μm, Ø 3.5 cm) resulting in the deposition of ~0.02 mg of MWCNTs. The obtained membrane was deposited on a platinum electrode (surface area 0.2 cm^{-2}) and dissolved by washings with acetone. All such prepared electrodes were further heated at 100 °C for 5 h.

2.3. Electropolymerization

Pt and MWNT electrodes were used as working electrodes in a three-electrode cell in the presence of ruthenium-based complexes (0.25 mM) in degassed and anhydrous MeCN 0.1 M Bu$_4$NClO$_4$ (TBAP) solution. Electropolymerization was performed through oxidation of pyrroles either using controlled potential coulometry at E = 0.70 V vs Ag/AgNO$_3$ or cyclic voltammetry (recording 5, 10 or 20 cycles at 100 mV s^{-1} between 0 V and 1 V vs Ag/AgNO$_3$). The electrodes are then rinsed with MeCN and acetone.

2.4. Synthesis

All reagents and chemicals were purchased from Aldrich. Reagents and chemicals were used as received until it was mentioned. 4-4′-Bishydroxy-2-2′-bipyridine and 1-(3-bromopropyl)-pyrrole were prepared according to previously described procedures [12,13].

2.4.1. 4,4′-Bis(3-pyrrol-1-ylpropyloxy)-2,2′-bipyridine (L)

A solution of bipyridine (0.79 g, 4.3 mmol), bromopropylpyrrole (2 g, 10.6 mmol,), 18-crown-6 (0.84 g, 3.2 mmol) and K$_2$CO$_3$ (1.65 g, 10.6 mmol) in dried acetone (15 mL) was refluxed for 48 h. K$_2$CO$_3$ was removed by filtration. Solvent was evaporated and the crude product was dissolved in a minimum of MeCN and precipitated by Et$_2$O. The solid was purified by chromatography on silica gel with CH$_2$Cl$_2$ 9/1 as the eluant to give **L** as a white powder (830 mg, 2.1 mmol, 52%). RMN ^{1}H (CDCl$_3$) δ/ppm (J/Hz): 2.25 (q, 4H, ^3J = 6.4), 4.06 (t, 4H, ^3J = 6.4), 4.13 (t, 4H, ^3J = 6.4), 6.14 (s, 4H), 6.65 (s, 4H), 6.82 (dd, 2H, ^3J = 6.4, ^3J = 2.8), 7.95 (dd, 2H, ^3J = 2.8), 8.46 (d, 2H, ^3J = 6.4).

2.4.2. [Bis-(2,2′-bipyridine)(4,4′-bis(3-pyrrol-1-ylpropyloxy)bipyridyl)] ruthenium(II) hexafluorophosphate (*Ru1*)

A solution of 4,4′-bis(3-pyrrol-1-ylpropyloxy)-2,2′-bipyridine (75 mg, 0.19 mmol) and Ru(bipy)$_2$Cl$_2$ (80 mg, 0.16 mmol) were refluxed in 30 mL isopropanol under argon in the dark for 48 h. The precipitate was filtrated and solvent was removed under vacuum. 10 mL of H$_2$O was added and the aqueous phase was washed two times with 10 ml CH$_2$CL$_2$. 150 mg NH$_4$PF$_6$ was added and the aqueous phase was extracted two times with 10 mL CH$_2$Cl$_2$. Solvent was removed under vacuum. The solid was purified by chromatography over silica gel with MeCN/H$_2$O/KNO$_3$ $_{sat,}$ ratio: 20/3/1 giving **Ru1** (90 mg, 0.081 mmol, 51%) as the PF$_6$$^-$ salt. RMN ^{1}H (CD$_3$CN) δ/ppm (J/Hz): 2.23 (m, 4H), 4.08 (m, 8H), 6.02 (s, 4H), 6.67 (s, 4H), 6.88 (dd, 2H, ^3J = 6.4, ^3J = 2.8), 7.35 (m, 2H), 7.42 (m, 4H), 7.70 (d, 2H, ^3J = 5.2), 7.80 (d, 2H, ^3J = 5.2), 7.91 (d, 2H, ^3J = 2.8), 8.04 (m, 4H), 8.47 (m, 4H). MS (ESI+): 408.1 (M-2PF$_6$$^{2+}$), 961.2 (M-PF$_6$$^+$). UV/vis λ_{max} (MeCN)/nm: 460 (ε = 11,300 dm^3 mol^{-1} cm^{-1})

2.4.3. Tris[4,4 bis(3-pyrrol-1-ylpropyloxy)bipyridinyl)] ruthenium(II) hexafluorophosphate(*Ru2*)

A solution of 4,4′-bis(3-pyrrol-1-ylpropyloxy)-2,2′-bipyridine (100 mg, 0.25 mmol) and RuCl$_3$·3H$_2$O (20 mg, 0.077 mmol) in 20 mL isopropanol was refluxed under argon, in the dark, for 96 h. The precipitate was filtrated and solvent was removed under vacuum. 10 mL of H$_2$O and 100 mg NH$_4$PF$_6$ was added and the aqueous phase was extracted two times with 10 mL CH$_2$Cl$_2$. The solvent was removed under vacuum. The solid was purified by chromatography over silica gel with MeCN/H$_2$O/KNO$_3$ $_{sat,}$ ratio: 20/3/1 giving **Ru2** (70 mg, 0.044 mmol, 57%) as the PF$_6$$^-$ salt. RMN ^{1}H (CD$_3$CN)) δ/ppm (J/Hz): 2.23 (m, 12H), 4.09 (m, 24H), 6.03 (s, 12H), 6.68 (s, 12H), 6.91 (m, 6H), 7.48 (m, 6H), 7.90 (m, 2H). MS (ESI+): 654.3 (M-2PF$_6$$^{2+}$), 1453 (M-PF$_6$$^+$). UV/vis λ_{max} (MeCN)/nm: 478 (ε = 4900 dm^3 mol^{-1} cm^{-1})

3. Results and discussion

3.1. Synthesis and electrochemical characterization of the ruthenium monomers

The **Ru1** and **Ru2** complexes, depicted in Fig. 1, were prepared in several steps. Ligand **L** was synthesized by reaction of 4-4′-bishydroxy-2-2′-bipyridine with 1-(3-bromopropyl)-pyrrole and further characterized by NMR and mass spectroscopy. The reaction of one equivalent of **L** with [Ru(bipy)$_2$]Cl$_2$ gives complex **Ru1** while the reaction of three equivalents of **L** with RuCl$_3$.H$_2$O leads to complex **Ru2**. These derivatives were