



Synthesis and electrochemical characterization of new ruthenium–terthiophene complexes



B. González*, M.A. del Valle, F.R. Díaz, C. Espinosa-Bustos, A. Ramírez, L.A. Hernández

Pontificia Universidad Católica de Chile, Facultad de Química, Departamento de Química Inorgánica, Laboratorio de Electroquímica de Polímeros (LEP), Av. V. Mackenna 4860, 7820436 Macul, Santiago, Chile

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ABSTRACT

Two new ruthenium–poly(terthiophene) complexes substituted with di-phosphines, PTA (1,3,5-triaza-7-phosphaadamantane) and mPTA (*N*-methyl-1,3,5-triaza-7-phosphaadamantane), have been chemically synthesized and characterized by multinuclear NMR spectroscopy (^1H , ^{13}C and ^{31}P), FT-IR, elemental analysis, UV–Vis and cyclic voltammetry. The latter technique allowed the electro-polymerization of the two novel complexes upon Pt disk electrodes, generating thin films whose electrochemical response could project their utility in important applications such as batteries (reversible *p*-doping/undoping response in the range between -0.3 and 0.7 V vs SCE) or analytical sensors (response as a reversible redox couple between -0.3 and -1.0 V vs SCE).

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1. Introduction

Electropolymerization is used to prepare organic polymers, e.g., polythiophenes, polyanilines, polypyrroles, among others [1], giving rise to insoluble electro-generated coatings directly on the electrode surface. Compared to saturated polymers, conducting polymers (CPs) possess a unique electronic structure, which is responsible for their electrical conductivity, low ionization potential and high electron affinity. Besides, electrochemically synthesized CPs have several advantages [2,3]: (i) the electro-polymerization can be carried out by potentiostatic, amperometric or potentiodynamic means in just a few seconds; (ii) deposition is performed at room temperature and the obtained film is limited to the size of the electrode, the shape being controlled by its design and thickness that ranges from nanometers to micrometers; (iii) polymeric film properties can be tuned by varying some of the electro-polymerization conditions [4].

However, since most synthesized CPs have been based on purely organic backbones [1,2,5,6], the possibility of incorporating metal complexes into these materials has attracted great interest. It is thus intended to combine the electronic, optical and chemical properties of the metal complex with those of the polymer backbone, to obtain novel materials with new properties [7]. One of the problems would be to determine the nature and extent of the electronic coupling between the metal and the conjugated

organic skeleton, therefore, attention is focused on the construction and study of complexes in which the metal is bonded to conjugate fragments through different bonds and to study the coupling nature of these systems.

Some CPs having in their structure an organic part combined to coordination transition metals, e.g. porphyrins [8–10], ferrocene [11–13], crown ether [14–16], Schiff base [17–19] and bipyridine [20–22], are known. However, very few have incorporated a thiophene group or derivative into its structure [23–26].

Bearing in mind the above, the growing interest that ruthenium complexes have aroused as therapeutic agents in recent years [27–31] and that polythiophene is one of the most widely studied polymers, in this paper we present the synthesis and characterization of two novel ruthenium complexes, in whose coordination sphere, there is a ligand derived from thiophene, more specifically terthiophene (TT), together with phosphine-like ligands, 1,3,5-triaza-7-phosphaadamantane (PTA) and derivatives. Subsequent to their synthesis and characterization, electropolymerization studies evidence the obtention of new polymers with quite interesting properties, that would make them not only good candidates as sensors and bio-sensors, but also for the development of batteries [32,33].

2. Experimental

2.1. Materials

All chemicals were reagent grade and, unless otherwise stated, used as received. Reactions were carried out under a pure argon

* Corresponding author.

E-mail address: beagonzalez@uc.cl (B. González).

atmosphere in freshly distilled and oxygen free solvents using standard Schlenk-tube techniques. Acetone was distilled over potassium carbonate and molecular sieves. The ligands 1,3,5-triaza-7-phosphaadamantane (PTA) and *N*-methyl-1,3,5-triaza-7-phosphaadamantane (mPTA) and the complexes, [RuClCp(PTA)₂] and [RuClCp(mPTA)₂](OSO₂CF₃)₂ were prepared as described elsewhere [34,35].

For electrochemical experiments, DMSO (Aldrich 99.7%) stored over molecular sieves and tetrabutylammonium hexafluorophosphate [(TBA)PF₆] (Aldrich 98%) previously dried at 120 °C, were used as solvent and supporting electrolyte, respectively.

2.2. General physical methods

¹H and ¹³C NMR spectra were recorded at room temperature at 400.13 and 100.62 MHz, respectively, on a Bruker Avance-400 instrument. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (¹H) or the deuterated solvent multiplet (¹³C). ³¹P NMR spectra were recorded on the same instrument operating at 161.97 MHz and the chemical shifts for ³¹P NMR were measured relative to external 85% H₃PO₄. Infrared spectra were recorded in KBr disks using a Bruker vector 22 FT-MIR spectrometer. Elemental analyses (C, N, H and S) were performed on a CE instrument EA 1108 elemental analyzer. UV–Vis adsorption spectra were registered on a Specord 40 Spectrophotometer (Analytik Jena).

Electrochemical measurements (polymerization and characterization) were performed on a Voltalab PG2100 potentiostat at room temperature (20 °C) under high purity argon atmosphere in anchor-type three-compartment electrochemical cells, using a 0.07 cm² geometric area platinum disks (Pt) as working electrode, a platinum wire coil of large geometric area as counter electrode and Ag/AgCl in tetramethylammonium chloride solution, to match the potential of a saturated calomel electrode, SCE, as reference electrode. Unless otherwise stated, all potentials quoted in the current work are referred to this electrode at room temperature.

The polymer films were deposited using potentiodynamic (cyclic voltammetry) method under the previously optimized experimental conditions: sweep window 1.0 to –1.0 V, scan rate 0.1 V·s⁻¹ (six consecutive cycles). Working solution consists of 1 × 10⁻³ mol·L⁻¹ [RuCp(TT)L]ⁿ⁺ (L = PTA, *n* = 0 or L = mPTA, *n* = 1) + 0.01 mol·L⁻¹ TBAPF₆ (supporting electrolyte) in anhydrous dimethyl sulfoxide (DMSO). Subsequently, the (Pt|p-[RuCp(TT)L]ⁿ⁺) modified electrode response was studied in 0.01 mol·L⁻¹ TBAPF₆ in DMSO.

Finally, the spectroelectrochemical characterization of the deposited films was conducted using cyclic voltammetry under the same above mentioned working conditions, but using a 1 cm² Pt mesh as working electrode in the cell coupled to the previously described spectrophotometer.

2.3. Synthesis

2.3.1. Preparation of [RuCp(TT)(PTA)₂](OSO₂CF₃) (1)

[RuClCp(PTA)₂] (**1a**) (0.20 g, 0.39 mmol) complex dissolved in water (15 mL) was added to an AgOSO₂CF₃ (0.12 g, 0.47 mmol) solution in water (2 mL). The mixture, after 1 h stirring at 50 °C, was filtered through celite to remove the formed AgCl(s) and the residue was vacuum-dried. Terthiophene (TT) (0.12 g, 0.47 mmol) solution in acetone (70 mL) was added to the oily residue and the mixture was refluxed for 12 h. The obtained precipitate was filtered, washed with acetone (2 × 2 mL) and vacuum-dried.

Yield: 0.10 g, 43.2%. *Anal. Calc.* for C₃₀H₃₇N₆F₃O₃P₂RuS₄ (*M_r* = 877.92 g·mol⁻¹): C, 41.04; H, 4.26; N, 9.57; S, 14.6. Found: C, 41.50; H, 5.03; N, 9.01; S, 14.9%. *S*_{20°C,DMSO} = 46.70 mg mL⁻¹. IR (KBr, cm⁻¹): ν(OSO) 1215.3 (s). ¹H NMR (DMSO-*d*₆) δ: 3.94–4.17

(m, 12H, PCH₂N), 4.61–4.63 (m, 12H, NCH₂N), 5.36 (s, 5H, C₅H₅), 7.18 (t, *J* = 4 Hz, 2H, H4'+H4'', terthiophene), 7.33 (s, 2H, H3'+H4, terthiophene), 7.41 (d, *J* = 4 Hz, 2H, H3'+H3'', terthiophene), 7.59 (d, *J* = 4 Hz, 2H, H5'+H5'', terthiophene). ¹³C NMR (DMSO-*d*₆) δ: 55.41 (bd, ¹*J*_{CP} = 32 Hz, PCH₂N), 71.38 (s, NCH₂N), 83.45 (s, C₅H₅), 121.06 (q, ¹*J*_{CF} = 428 Hz, OSO₂CF₃), 124.62 (s, C3'+C3'', terthiophene), 125.25 (s, C3+C4, terthiophene), 126.04 (s, C5'+C5'', terthiophene), 128.80 (s, C4'+C4'', terthiophene), 135.67 (s, C2+C5, terthiophene), 136.32 (s, C2'+C2'', terthiophene). ³¹P{¹H} NMR (DMSO-*d*₆) δ: –23.70 (s, PTA).

2.3.2. Preparation of [RuCp(TT)(mPTA)₂](OSO₂CF₃)₃ (2)

AgOSO₂CF₃ (0.065 g, 0.25 mmol) dissolved in water (2 mL), was added to [RuClCp(mPTA)₂](OSO₂CF₃)₂ (**2a**) (0.16 g, 0.23 mmol) complex in water (10 mL) and the mixture was stirred for 90 min at 50 °C, was filtered through celite and the residue was vacuum-dried. Subsequently, terthiophene (TT) (0.062 g, 0.25 mmol) solution in acetone (10 mL) was added to the oily residue in acetone (10 mL) and the mixture was refluxed for 7 h. The obtained precipitate was filtered, washed with Et₂O (2 × 4 mL) and vacuum-dried.

Yield: 0.09 g, 57.3%. *Anal. Calc.* for C₃₄H₄₃N₆F₉O₉P₂RuS₆ (*M_r* = 1206.02 g·mol⁻¹): C, 33.94; H, 3.60; N, 6.97; S, 15.05. Found: C, 34.05; H, 3.88; N, 6.62; S, 15.2%. *S*_{20°C,DMSO} = 65.82 mg mL⁻¹. IR (KBr, cm⁻¹): ν(OSO) 1228.1 (s). ¹H NMR (DMSO-*d*₆) δ: 2.82 (s, 6H, NCH₃), 3.92–4.18 (m, 8H, PCH₂), 4.33–4.79 (m, 8H, PCH₂NCH₃+NCH₂N), 4.96–5.32 (m, 8H, NCH₂NCH₃), 5.53 (s, 5H, C₅H₅), 7.11 (t, *J* = 4 Hz, 2H, H4'+H4'', terthiophene), 7.27 (s, 2H, H3'+H4, terthiophene), 7.36 (d, *J* = 3.6 Hz, 2H, H3'+H3'', terthiophene (H_C), C₁₂H₈S₃), 7.53 (d, *J* = 5.2 Hz, 2H H5'+H5'', terthiophene). ¹³C NMR (DMSO-*d*₆) δ: 48.35 (s, NCH₃), 52.24 (bd, ¹*J*_{CP} = 25.73 Hz, NCH₂P), 53.10 (bd, ¹*J*_{CP} = 29.83 Hz, NCH₂P), 63.69 (bd, ¹*J*_{CP} = 17.84 Hz, CH₃NCH₂P), 72.62 (s, NCH₂N), 79.10 (s, CH₃NCH₂N), 84.11 (s, C₅H₅), 121.68 (q, ¹*J*_{CF} = 348.78 Hz, OSO₂CF₃), 124.23 (s, C3'+C3'', terthiophene), 124.86 (s, C3+C4, terthiophene), 125.74 (s, C5'+C5'', terthiophene), 128.42 (s, C4'+C4'', terthiophene), 136.64 (s, C2+C5, terthiophene), 137.10 (s, C2'+C2'', terthiophene). ³¹P{¹H} NMR (DMSO-*d*₆) δ: –12.03 (s, mPTA).

2.4. Stability of **1** and **2** in DMSO

The compounds **1** (15 mg, 0.017 mmol) and **2** (20 mg, 0.017 mmol) were dissolved in 0.6 mL of DMSO-*d*₆ in a 5 mm NMR tube. No significant changes were observed after standing for 30 min and 24 h at room temperature and 48 h at 80 °C.

3. Results and discussion

3.1. Synthesis of the complexes

Utilizing a two-step synthesis, the two new complexes, [RuCp(TT)(PTA)₂](OSO₂CF₃) (**1**) and [RuCp(TT)(mPTA)₂](OSO₂CF₃)₃ (**2**), were obtained (Scheme 1). Mixing [RuClCp(PTA)₂] complex with one mole of AgOSO₂CF₃ in water, an AgCl precipitate was obtained. After filtration, evaporation to dryness and subsequent addition of terthiophene in acetone, the formation of **1** is produced with 43.2% yield. Likewise and starting from [RuClCp(mPTA)₂](OSO₂CF₃)₂, complex **2** was obtained with 57.3% yield.

To confirm the substitution of chlorine by terthiophene, both complexes were characterized by NMR in DMSO-*d*₆. In both cases, the ¹H and ¹³C signals fall within the characteristic region for PTA, mPTA and Cp ligands found in the starting complexes, Ru-PTA and Ru-mPTA [34–36]. It is noteworthy that signals of terthiophene coordinated to the metal atom through the central sulfur were observed at 7.18 (d), 7.33 (s), 7.41 (d) and 7.59 (d) ppm (**1**) and 7.11 (d), 7.27 (s), 7.36 (d) and 7.53 (d) ppm (**2**) in the ¹H NMR

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