



Homoleptic Ru(II) complex with terpyridine ligands appended with terthiophene moieties: Synthesis, characterization and electropolymerization

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ABSTRACT

A new Ru(II) complex, [Ru(TTT)₂][PF₆]₂ (TTT = 4'-[(2,2':5',2''-terthien-3'-yl)methoxy]-2,2':6',2''-terpyridine) has been synthesized and characterized by ¹H NMR and UV–Vis spectroscopy and by cyclic voltammetry. The electrosynthesis of the corresponding conductive polymer, P[Ru(TTT)₂], is reported, as well as its voltammetric and spectroelectrochemical characterization. The comparison between [Ru(TTT)₂][PF₆]₂ and TTT voltammetric data shows that the presence of the metal ion makes easier the oxidation and the polymerization of the organic framework. On the other hand, UV–Vis data confirm that the presence of the –O–CH₂– spacer between coordinating and polymerizing unit (terpyridine and terthiophene, respectively) reduces the electronic delocalization among these moieties, analogously to that observed in the TTT ligand alone. As far as P[Ru(TTT)₂] is concerned, the voltammetric characterization evidences the so-called ‘charge-trapping’ phenomena, already observed also in PTTT, too. Moreover, spectroelectrochemical characterization shows a likely overlapping of the π–π* polymer and MLCT complex absorption bands, causing a bathochromic shift with respect to PTTT.

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1. Introduction

Polypyridyl-Ru(II) complexes with N-donor ligands, such as bipyridine, 1,10-phenanthroline and terpyridine, have attracted a great interest over the past three decades, due to their peculiar photophysical, photochemical and electrochemical features [1–4]. Such properties make these species appealing in the fields of photocatalysis, dye sensitized solar cells (DSSCs) and artificial photosynthesis [5–8]. Especially Ru(II) complexes with bidentate ligands have shown excellent photophysical properties, starting from the highly emissive [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine) [9]. However, the main trouble of this class of compounds lies in the fact that they afford chiral complexes, leading to mixtures of diastereomers hard to resolve. On the other hand, the bis-terdentate complex [Ru(tpy)₂]²⁺ (tpy = 2,2':6',2''-terpyridine) shows a very weak emission and a short-lived excited state, preventing its application for photochemical devices [10]. Nevertheless, tpy ligand can be easily functionalized in the 4' position of the central ring, leading to achiral assemblies and allowing the tuning of the photochemical properties of the related complexes. A successful way to properly modify the structure of the tpy ligand consists of the introduction of electron-donating or electron-withdrawing groups in the 4' position.

Especially, five-membered heterocyclic rings, such as thiophene, furane and pyrrole, lead to a more extended delocalization, stabilising the ³MLCT (metal-to-ligand charge transfer) states relative to non-emissive ³MC (metal centred) states, mostly in systems where the heterocyclic ring facilitates a co-planar arrangement [11]. Furthermore, such substitution allows the obtainment of a molecule with two different functions: a coordinating one, due to the tpy fragment, and a polymerizing one, due to the heterocyclic ring. The corresponding multifunctional metal-containing π-conjugated polymers form a very interesting class of materials: the simultaneous presence of a polymer backbone and a metal complex, performing different roles, induces a mishmash of the conductivity deriving from the conjugated framework with the optical, electronic and catalytic function of the metal complex. Models for charge transfer in conducting polymers and metallopolymers were developed since 1990's [12–16], accounting for the electronic conduction in the polymer backbone and the ionic conduction in the ionic pores. If the metal complex is characterized by a strong absorption in the visible region, the resulting metallopolymer shows a higher photosensitivity [17]. Moreover, combining Ru(II)-polypyridyl fragments with thiophene-based oligomers allows to obtain mono- or multimetallic arrays suitable for optoelectronic applications and sensitizers for DSSCs [18].

In a previous work [19] we reported the synthesis and the electrochemical characterization of a novel species (4'-[(2,2':5',

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2''-terthien-3'-yl)methoxy]-2,2':6',2''-terpyridine, TTT), where the polymerizing terthiophene framework was linked to a terpyridine unit, able to coordinate transition metal ions. The electrochemistry and UV–Vis spectroscopy of the corresponding electro-generated polymer, PTTT, was also reported.

In the present paper we describe the synthesis, the spectroscopic characterization and the electrochemistry of a new homoleptic complex of TTT with Ru(II) ion, $[\text{Ru}(\text{TTT})_2][\text{PF}_6]_2$ (Scheme 1).

2. Experimental

2.1. Materials and methods

All reagents used for the synthesis were purchased from Aldrich and used without prior purification. ^1H NMR spectra were recorded on a Varian VXR 300 spectrometer, working at 300 MHz, in CD_3CN solution, using the solvent residual signal (1.94 ppm) as internal standard [20]. QTOF/MS spectra were recorded on a QTOF2 instrument by WATERS. Elemental analyses were recorded using a Perkin Elmer 240B elemental analyzer. Electrochemical characterizations were performed with an Autolab PGSTAT 12 system interfaced with a PC under GPES software. All electrochemical measurements were carried out in a three-electrode cell, under Ar atmosphere, at room temperature. A Pt disk electrode (diameter 2 mm) and a double junction, aqueous Ag/AgCl (both from AMEL) were the working and the reference electrodes, respectively, and a graphite bar was the auxiliary electrode. The working electrode was polished subsequently with 0.3 and 0.05 μm alumina powder, then rinsed with distilled water and acetone and thoroughly dried before use. All the experiments were carried out in CH_3CN (Prolabo, anhydrous, +99.8%, packaged under nitrogen) solvent, using 0.1 M tetraethylammonium hexafluorophosphate (TEAPF_6 for electrochemical analysis, $\geq 99\%$, Fluka) as supporting electrolyte. Spectroelectrochemical measurements were carried out by coupling the electrochemical instrument with a Perkin-Elmer Lambda 650 UV–Vis spectrophotometer, working in the wavelength range 190–900 nm. The spectroelectrochemical cell was directly constructed in a conventional quartz cuvette, using an ITO glass as working electrode, a Pt wire as auxiliary electrode and a non-aqueous Ag/AgCl as reference electrode. All potential values are referred to the half-wave potential of the ferrocene/ferricinium (Fc/Fc^+) ion redox couple.

2.2. Syntheses

2.2.1. TTT

The synthesis of 4'-[(2,2':5',2''-terthien-3'-yl)methoxy]-2,2':6',2''-terpyridine (TTT) was reported by us elsewhere [19]. ^1H NMR (CD_3CN , ppm): δ = 8.69 (d, 2H, H6 + H6'' terpyridine, J = 4.8 Hz), 8.64 (d, 2H, H3 + H3'' terpyridine, J = 7.9 Hz), 8.08 (s, 2H, H3' + H5' terpyridine), 7.96 (ddd, 2H, H4 + H4'' terpyridine, J = 7.8, 7.9, 1.7 Hz), 7.51 (dd,

1H, H5 or H5'' terthiophene, J = 5.1, 1.0 Hz), 7.45 (m, 2H, partially overlapping with H4', H5 + H5'' terpyridine), 7.44 (s, 1H, H4' terthiophene), 7.39 (dd, 1H, H5 or H5'' terthiophene, J = 5.1, 1.0 Hz), 7.33 (dd, 1H, H3 or H3'' terthiophene, J = 3.6, 1.0 Hz), 7.31 (dd, 1H, H3 or H3'' terthiophene, J = 3.6, 1.0 Hz), 7.16 (dd, 1H, H4 or H4'' terthiophene, J = 5.1, 3.6 Hz), 7.08 (dd, 1H, H4 or H4'' terthiophene, J = 5.1, 3.6 Hz), 5.38 (s, 2H, CH_2).

2.2.2. $\text{Ru}(\text{DMSO})_4\text{Cl}_2$

$\text{Ru}(\text{DMSO})_4\text{Cl}_2$ was obtained according to Ref. [21]. $\text{RuCl}_3 \cdot 2\text{H}_2\text{O}$ (0.1480 g, 5.66×10^{-4} mol) was refluxed in DMSO (2.5 ml) under stirring until the solution resulted yellow in colour. The volume was then reduced to half under reduced pressure to give a yellow precipitate. The precipitation was completed adding acetone. The yellow complex was filtered off and subsequently washed with acetone and diethyl ether. Elemental Anal. Calc. for $\text{C}_8\text{H}_{24}\text{Cl}_2\text{O}_4\text{RuS}_4$: C, 19.83; H, 4.96. Found: C, 19.80; H, 4.85%. Yield 65%.

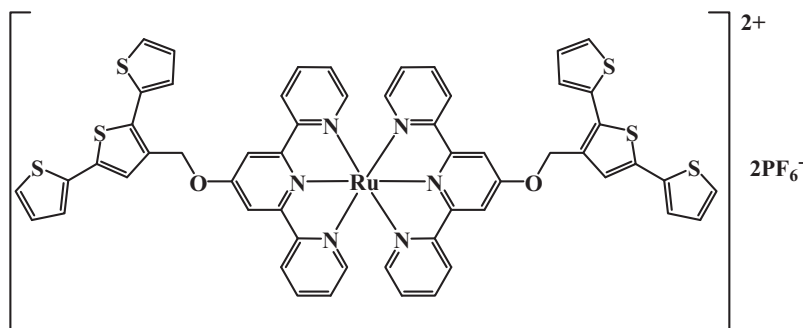
2.2.3. $[\text{Ru}(\text{TTT})_2][\text{PF}_6]_2$

$\text{Ru}(\text{DMSO})_4\text{Cl}_2$ (0.0524 g, 1.08×10^{-4} mol) was added to a solution of TTT (0.1061 g, 2.08×10^{-4} mol) in CH_3OH (25 mL). The reaction mixture was refluxed for 1 h, then the solvent was evaporated under reduced pressure and the residue dissolved in CH_3CN , filtered off and a saturated KPF_6 aqueous solution was added. The red precipitate was filtered off and washed with CHCl_3 and Et_2O . Elemental Anal. Calc. for $\text{C}_{56}\text{H}_{38}\text{N}_6\text{F}_{12}\text{O}_2\text{P}_2\text{RuS}_6$: C, 47.69; H, 2.70; N, 5.96. Found: C, 47.22; H, 2.76; N, 5.99%. Yield: 80%. ^1H NMR (CD_3CN , ppm) (Fig. 1): δ = 8.40 (d, 2H, H3 + H3'' terpyridine, J = 7.8 Hz), 8.36 (s, 2H, H3' + H5' terpyridine), 7.91 (td, 2H, H4 + H4'' terpyridine, J = 7.8, 1.5 Hz), 7.61 (dd, 1H, H5 or H5'' terthiophene, J = 5.1, 1.1 Hz), 7.59 (s, 1H, H4' terthiophene), 7.45 (m, 2H partially overlapping, H5 or H5'' terthiophene (J = 5.1, 1.1 Hz) + H3 or H3'' terthiophene), 7.38 (m, 3H partially overlapping, H6 + H6'' terpyridine + H3 or H3'' terthiophene), 7.25 (dd, 1H, H4 or H4'' terthiophene, J = 5.1, 3.6 Hz), 7.17 (ddd, 2H, H5 + H5'' terpyridine, J = 7.8, 5.6, 1.4 Hz), 7.14 (dd, 1H, H4 or H4'' terthiophene, J = 5.1, 3.6 Hz), 5.64 (s, 2H, CH_2). QTOF/MS: m/z = 560.01 [$\text{M}-2\text{PF}_6^{2-}$] $^{2+}/2$ requires m/z = 560.20.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of $[\text{Ru}(\text{TTT})_2][\text{PF}_6]_2$ was first attempted by us starting from RuCl_3 and TTT, according to the approach described by Husson et al. [22], based on the extraction of chlorides with AgBF_4 and on the subsequent anion exchange of BF_4^- with a saturated aqueous solution of KPF_6 . The synthetic route proposed by Newkome and He [23] was then explored: TTT and RuCl_3 mixture



Scheme 1.

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