Letter

First covalent attachment of a polypyridyl ruthenium complex on a graphite felt electrode

Florence Geneste,*[a] Claude Moinet[a] and Guy Jezequel[b]

[a] *UMR 6509, Laboratoire d'Electrochimie et Organométalliques de l'Université de Rennes 1, Institut de Chimie de Rennes, Campus de Beaulieu, 35042, Rennes cedex, France*
[b] *UMR 6627, Laboratoire de Physique des Atomes, Lasers, Molécules et Surfaces de l'Université de Rennes 1, Campus de Beaulieu, 35042, Rennes cedex, France*

Received (in London, UK) 7th July 2002, Accepted 24th September 2002
First published as an Advance Article on the web 15th October 2002

A bipyridine carboxylate ligand has been grafted to a graphite felt electrode by an electrochemical process and the synthesis of $[Ru^{II}(tpy)(bpy^*)(OH_2)]^{2+}$, where bpy* is the grafted bipyridine, has been achieved.

Polypyridyl ruthenium–oxo complexes are of particular interest as efficient oxidants for a wide variety of organic substrates, including aromatic hydrocarbons, olefins, alcohols, and ketones.[1] Among them, $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$, where bpy is 2,2′-bipyridine and tpy is 2,2′:6′,2″-terpyridine, has been widely studied because of its substitutional stability[1b] and its catalytic reactivity. It can be prepared by electrochemical oxidation of $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ in aqueous medium.[2] The mechanism of this reaction involves a disproportionation reaction (eqn. 3):[3]

$$Ru^{II}(tpy)(bpy)(OH_2)^{2+} \rightleftharpoons Ru^{III}(tpy)(bpy)(OH)^{2+} + H^+ + e^- \quad (1)$$

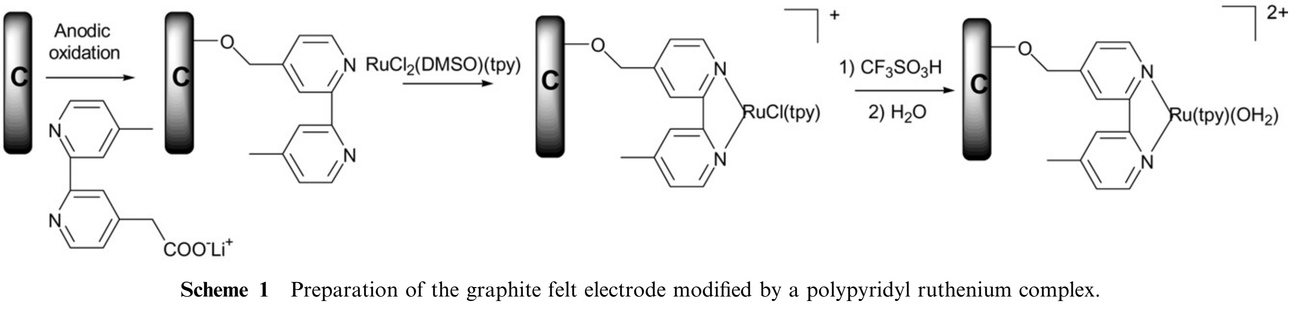
$$Ru^{III}(tpy)(bpy)(OH)^{2+} \rightleftharpoons Ru^{IV}(tpy)(bpy)(O)^{2+} + H^+ + e^- \quad (2)$$

$$2Ru^{III}(tpy)(bpy)(OH)^{2+} \rightleftharpoons Ru^{II}(tpy)(bpy)(OH_2)^{2+} + Ru^{IV}(tpy)(bpy)(O)^{2+} \quad (3)$$

Moreover, Gallagher and Meyer[4] revealed the interesting catalytic activity of $[Ru(tpy)(bpy(PO_3H_2)_2)(OH_2)]^{2+}$ ($bpy(PO_3H_2)_2$ = 2,2′-bipyridyl-4,4′-diphosphonic acid) adsorbed on thin films of TiO_2 nanoparticles on glass. The immobilized $Ru^{II}–OH_2^{2+}$ species was first oxidized to its $Ru^{IV}=O^{2+}$ form by $Ce^{IV}(NH_4)_2(NO_3)_6$. For surfaces with small amounts of the complex attached, they observed that the oxidation was limited to two successive monoelectronic transfers, as illustrated by the major formation of cyclohexanol during the oxidation of cyclohexene, whereas cyclohexanone was obtained as the major product in homogeneous catalysis.[5] The loss of translational mobility of the oxidant prevents the disproportionation reaction and the formation of $Ru^{III}–OH^{2+}$ species, formation that is responsible for the oxidation of cyclohexanol to cyclohexanone. This result emphasizes why it is of interest to immobilize polypyridyl ruthenium complexes on electrodes for application in indirect electrolysis. This immobilization can be achieved through electroactive metallopolymer films on electrodes. Studies dealt with the electropolymerisation of Ru^{II} complexes with bipyridine ligands containing vinyl or pyrrol groups,[6] and with the adsorption of $[Ru(bpy)_3]^{2+}$ on the surface of zeolite or its encapsulation inside their aluminosilicate supercages.[7] However, to our knowledge, the solid covalent attachment of polypyridyl complexes to electrodes has never been realized.

We have previously shown that stable covalent bonding of aryl species to high-surface felt electrodes could be achieved by anodic oxidation of arylacetate compounds in aqueous medium.[8] We report here that this grafting process can be applied to bipyridine ligands containing a carboxylate group and gives rise to the synthesis of $[Ru^{II}(tpy)(bpy^*)(OH_2)]^{2+}$, where bpy* is the grafted bipyridine.

The lithium salt of 4′-methyl-(2,2′-bipyridine)-4-acetic acid was prepared by reaction of the monolithiated 4,4′-dimethyl-2,2′-bipyridine with carbon dioxide according to a previously described procedure.[9] This bipyridine ligand was covalently attached to the electrode by anodic oxidation (300 mA) of 100 mg of the lithium salt in 100 ml of phosphate buffer pH 2.2 (NaH_2PO_4 0.25 M; H_3PO_4 0.25 M) using a flow reactor,[10] with graphite felt as the working electrode[8] (Scheme 1). The grafted felt was refluxed in ethanol for 18 h with an excess of $Ru^{II}Cl_2(DMSO)(tpy)$ prepared from $Ru^{II}Cl_2(DMSO)_4$[11] and terpyridine in refluxing ethanol. Further reaction[12] with



Scheme 1 Preparation of the graphite felt electrode modified by a polypyridyl ruthenium complex.

DOI: 10.1039/b206414f

CF_3SO_3H followed by addition of water led to $[Ru^{II}(tpy)(bpy^*)(OH_2)]^{2+}$. $[Ru^{II}(tpy)(dmbpy)(OH_2)]^{2+}$ (dmbpy = 4,4′-dimethyl-2,2′-bipyridine) was also prepared by the same reaction sequence for comparison with grafted ruthenium species in cyclic voltammetry.

The cyclic voltammetry analyses of $[Ru^{II}(tpy)(bpy^*)(OH_2)]^{2+}$ and $[Ru^{II}(tpy)(dmbpy)(OH_2)]^{2+}$ were performed in phosphate buffer pH 7.2 (NaH_2PO_4 0.25 M; Na_2HPO_4 0.25 M) in an analytical cell[8] and on graphite carbon, respectively. Only the $Ru^{III/II}$ couple at 0.51 ± 0.01 V_{SCE}[13] (saturated calomel electrode: SCE) was observed in the case of the grafted complex, whereas both $Ru^{III/II}$ (0.51 ± 0.01 V_{SCE}) and $Ru^{IV/III}$ (0.62 ± 0.01 V_{SCE}) waves appeared with $[Ru^{II}(tpy)(dmbpy)(OH_2)]^{2+}$ in solution (Fig. 1).

The charge corresponding to the one-electron reduction of the $Ru^{III/II}$ couple was obtained by integrating the cyclic voltammograms.[14] Thus, the volume concentration of grafted molecules calculated from the Faraday law was 1.9×10^{-8} mol cm^{-3} (Table 1).

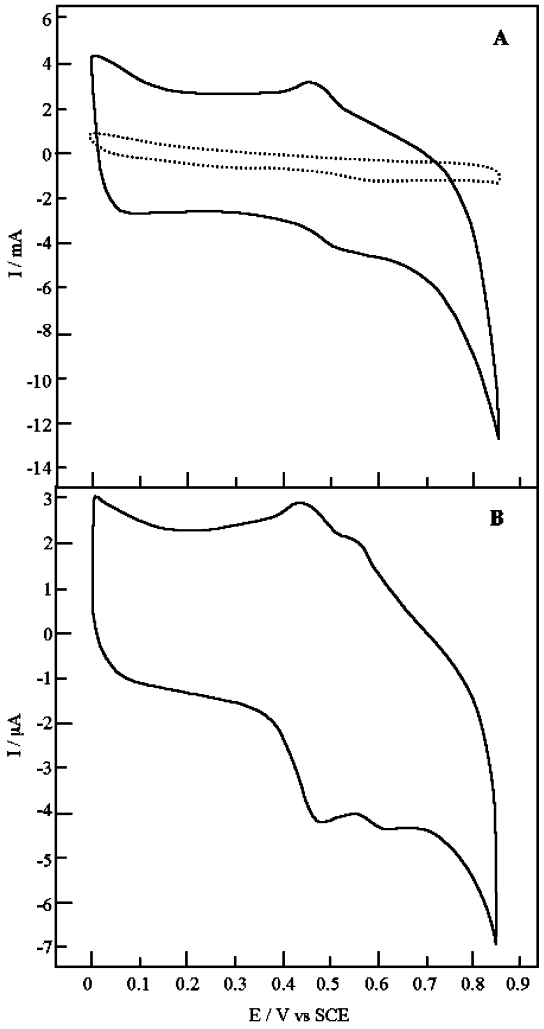


Fig. 1 A Cyclic voltammogram of a fresh felt (·········) and of a grafted felt (——) in phosphate buffer pH 7.2 (0.25 M). Scan rate: 20 mV s^{-1}. B Cyclic voltammogram of $[Ru^{II}(tpy)(dmbpy)(OH_2)]^{2+}$ (2.4 mM) in phosphate buffer pH 7.2 (0.25 M) on a graphite carbon electrode.

Table 1 Characteristics of the grafted felt

	Volume concentration/ mol cm^{-3}	Double-layer capacity[a]/ µF cm^{-2}	Surface concentration/ mol cm^{-2}	XPS analysis: peak at 467 eV (%)[c]
Grafted felt	1.9×10^{-8}	260 (35)[b]	0.4×10^{-11}	8.2×10^{-3}

[a] $C_{dl} = (Ia - Ic)/2Av$ where Ia and Ic are the anodic and cathodic current measured at 0.7 V_{SCE}, A is the initial electrode surface area and v is the scan rate.[8] [b] The C_{dl} of a fresh felt is given in parentheses. [c] Ru/carbon ratio.

The surface concentration of the grafted felt was more difficult to estimate. Indeed, during the grafting process, the graphite was also oxidized, leading to the increase of the surface area of the electrode as previously shown by scanning electronic microscopy.[8] This larger surface could be explained by the intercalation of anions (A^-) coming from the electrolyte and the solvent (solv) in the graphite lattice (eqn. 4):[8]

$$[C_x] + y(A^-, \mathrm{solv}) \rightleftharpoons [C_x{}^{y+}, y(A^-, \mathrm{solv})] + ye^- \qquad (4)$$

$$[C_x{}^{y+}, y(A^-, \mathrm{solv})] + yH_2O \rightleftharpoons [C_x(OH)_y] + yAH + y\mathrm{solv} \qquad (5)$$

A subsequent nucleophilic attack of water, probably responsible for the formation of C–O functionalities at the graphite surface, modified the graphite lattice. However, the double-layer capacity, corresponding to the capacitor formed at the electrode/solution interphase by the charged electrode and the attracted opposite charges coming from the electrolyte solution, depends on the electrode surface. Thus, the comparison of the C_{dl} of a grafted felt with that of a fresh felt can give a rough estimation of the variation of the surface area.[8] The double-layer capacity was calculated from the cyclic voltammograms (Table 1). The ratio of the grafted felt C_{dl} to the fresh felt C_{dl} was about 7, showing that the surface area of the grafted felt was about 7 times that of a fresh felt. The surface concentration was then estimated to be 0.4×10^{-11} mol cm^{-2}. The presence of the ruthenium complex at the electrode surface was also confirmed in XPS analysis by the peak at 467 eV corresponding to Ru $3p_{3/2}$(Table 1).

Although the grafting process of the lithium salt of 4′-methyl-(2,2′-bipyridine)-4-acetic acid was not optimized, the volume concentration (higher than 1.9×10^{-8} mol cm^{-3}, *i.e.* a concentration of catalyst higher than 1.9×10^{-5} mol l^{-1} if one considers that 1 cm^3 of felt contains less than 1 cm^3 of solution) seems sufficient for future applications in indirect electrolysis, where the substrate is in 5- to 2000-fold excess over catalyst.[1] Moreover, the absence of the $Ru^{IV/III}$ wave in the cyclic voltammogram of the grafted felt could be explained by the inhibition of the direct oxidation of $Ru^{III}–OH^{2+}$ to $Ru^{IV}=O^{2+}$ and by the larger distance between the immobilized molecules, so that the disproportionation reaction did not occur.[3] Indeed the surface concentration (0.4×10^{-11} mol cm^{-2}) was lower than the value (0.8×10^{-10} mol cm^{-2}) previously reported for monolayer coverage of adsorbed $[Ru(tpy)(bpy(PO_3H_2)_2)(OH_2)]^{2+}$ at an ITO electrode.[3] This discrepancy was due to the formation of oxides at the graphite surface during the grafting process, resulting from the nucleophilic attack of water on oxidized graphite (eqn. 5).

This grafting process leads to a stable covalent bonding of isolated polypyridyl ruthenium complex at graphite felt and presents great interest for application in heterogeneous catalysis.[4] The catalytic activity of the immobilized compound and its further application in indirect electrolysis should be investigated.

Experimental

The graphite felt was obtained from Le Carbone Lorraine (RVG 4000, specific area: 0.7 m^2 g^{-1}; volume density: 0.088 g cm^{-3}).

The electrochemical procedure was performed using a disc of graphite felt (5.2 cm diameter, 1.2 cm thickness) in a flow cell with 100 mg of the lithium salt of 4′-methyl-(2,2′-bipyridine)-4-acetic acid, dissolved in 100 ml of phosphate buffer pH 2.2 (NaH_2PO_4 0.25 M; H_3PO_4 0.25 M). The same buffer was used in the cathodic and anodic compartments. The current intensity for the electrolysis was 300 mA, distributed in 200 mA for the upstream electrical circuit and 100 mA for the downstream one. The electrolyte flowed through the porous electrode for 1 h with recycling (5 ml $\mathrm{min^{-1}}$).

Chloro(4,4′-dimethyl-2,2′-bipyridine)(2,2′:6′,2″-terpyridine)ruthenium(II) chloride, [Ru(tpy)(dmbpy)Cl]Cl

$RuCl_2(DMSO)_4$ (100 mg; 0.2 mmol) and 2,2′:6′,2″-terpyridine (51 mg; 0.2 mmol; 1.0 equiv) were refluxed in 3 ml of ethanol for 3 h. 4,4′-Dimethyl-2,2′-bipyridine (37 mg; 0.2 mmol; 1.0 equiv.) was added and the solution was refluxed for 18 h. The ethanol was evaporated and 3 ml of water were added. The mixture was allowed to cool and the resulting precipitate was filtered, washed with HCl 1 M, water, ether and dried at the pump leading to 61.5 mg (0.1 mmol; 52%) of $[\mathrm{Ru^{II}Cl(tpy)(dmbpy)}]^+\mathrm{Cl}^-$. ^{1}H NMR (300 MHz, CD_3CN), δ: 9.99 (d, $J = 5.8$ Hz, 1 H, H-6′ bpy); 8.49 (d, $J = 8.1$ Hz, 2 H, H-3′ and H-5′ tpy); 8.48 (s broad, 1 H, H-3′ bpy); 8.38 (ddd, $J = 8.1$, 1.3, 0.8 Hz, 2 H, H-3 and H-3″ tpy); 8.19 (s broad, 1 H, H-3 bpy); 8.05 (t, $J = 8.1$ Hz, 1 H, H-4′ tpy); 7.86 (ddd, $J = 8.1$, 7.6, 1.5 Hz, 2 H, H-4 and H-4″ tpy); 7.78 (dm, $J = 5.8$ Hz, 1 H, H-5′ bpy); 7.67 (ddd, $J = 5.5$, 1.5, 0.8 Hz, 2 H, H-6 and H-6″ tpy); 7.26 (ddd, $J = 7.6$, 5.5, 1.3 Hz, 2 H, H-5 and H-5″ tpy); 7.07 (d, $J = 5.9$ Hz, 1 H, H-6 bpy); 6.77 (dm, $J = 5.9$ Hz, 1 H, H-5 bpy); 2.74 (s, 3 H, CH_3); 2.31 (s, 3 H, CH_3). ^{13}C NMR (75 MHz, CD_3CN) 159.75, 159.15, 159.07, 156.69, 152.96 (C-6 and C-6″ tpy), 152.61 (C-6′ bpy), 152.09 (C-6 bpy), 149.75, 148.97, 137.75 (C-4 and C-4″ tpy), 134.15 (C-4′ tpy), 128.62 (C-5′ bpy), 128.11 (C-5 and C-5″ bpy), 127.87 (C-5 bpy), 125.02 (C3′-bpy), 124.92 (C-3 bpy), 124.40 (C-3 and C-3″ tpy), 123.33 (C-3′ and C-5′ tpy), 21.42 (CH_3 bpy), 20.87 (CH_3 bpy). FAB-MS, m/z: found for $[\mathrm{M}]^+$, 554.0688; simulated monoisotopic mass for $C_{27}H_{23}N_5ClRu$, 554.0690.

Aqua(4,4′-dimethyl-2,2′-bipyridine)(2,2′:6′,2″-terpyridine)ruthenium(II) trifluoromethanesulfonate, [Ru(tpy)(dmbpy)OH$_2$]2OTf

[Ru(tpy)(dmbpy)Cl]Cl (61.5 mg; 0.1 mmol) was dissolved in 5 ml of anhydrous dichloromethane and several drops of trifluoromethanesulfonic acid were added. The mixture was refluxed for 5 h. Water (3 ml) was added and the dichloromethane was evaporated. The mixture was cooled and the resulting precipitate was filtered, washed with cold water and dried. 21.4 mg (0.03 mmol; 30%) of $[\mathrm{Ru^{II}(tpy)(dmbpy)OH_2}]^{2+}2\mathrm{Tf}^-$ were obtained. ^{1}H NMR (300 MHz, CD_3CN), δ: 9.39 (d, $J = 5.8$ Hz, 1 H, H-6′ bpy); 8.54 (d, $J = 8.2$ Hz, 2 H, H-3′ and H-5′ tpy); 8.48 (s broad, 1 H, H-3′ bpy); 8.41 (ddd, $J = 8.0$, 1.2, 0.6 Hz, 2 H, H-3 and H-3″ tpy); 8.27 (t, $J = 8.2$ Hz, 1 H, H-4′ tpy); 8.22 (s broad, 1 H, H-3 bpy); 7.99 (ddd, $J = 8.0$, 7.7, 1.5 Hz, 2 H, H-4 and H-4″ tpy); 7.79 (dm, $J = 5.8$ Hz, 1 H, H-5′ bpy); 7.68 (ddd, $J = 5.6$, 1.5, 0.6 Hz, 2 H, H-6 and H-6″ tpy); 7.35 (ddd, $J = 7.7$, 5.6, 1.2 Hz, 2 H, H-5 and H-5″ tpy); 7.06 (d, $J = 6.0$ Hz, 1 H, H-6 bpy); 6.90 (dm, $J = 6.0$ Hz, 1 H, H-5 bpy); 2.75 (s, 3 H, CH_3); 2.36 (s, 3 H, CH_3). The H_2O was exchanged with the solvent CD_3CN molecules and was thus not observed. ^{13}C NMR (75 MHz, CD_3CN) 159.31, 158.63, 157.92, 156.32, 153.81, 152.56, 151.07, 150.92, 139.29, 137.38, 129.12, 128.71, 128.30, 125.65, 125.13, 125.12, 124.31, 124.00, 21.33 (CH_3 bpy), 20.90 (CH_3 bpy). FAB-MS, m/z: found for $[\mathrm{M - H_2O - H}]^+$, 518.0925; simulated monoisotopic mass for $C_{27}H_{22}N_5Ru$, 518.0926.

The grafted polypyridyl ruthenium complex was prepared from the grafted bipyridine ligand according to a similar procedure.

Acknowledgements

We are grateful to Dr H. Le Bozec for discussions and to J.-P. Guegan for recording NMR spectra.

References

1 (*a*) M. S. Thompson and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 5070; (*b*) B. A. Moyer, M. S. Thompson and T. J. Meyer, *J. Am. Chem. Soc.*, 1980, **102**, 2310; (*c*) M. S. Thompson, W. F. De Giovani, B. A. Moyer and T. J. Meyer, *J. Org. Chem.*, 1984, **49**, 4972; (*d*) M. Navarro, W. F. De Giovani and J. R. Romero, *J. Mol. Catal. A: Chem.*, 1998, **135**, 249; (*e*) M. Navarro, W. F. De Giovani and J. R. Romero, *Synth. Commun.*, 1990, **20**, 399; J. M. Madurro, G. Chiericato Jr., W. F. De Giovani and J. R. Romero, *Tetrahedron Lett.*, 1988, **29**, 765.

2 K. J. Takeuchi, M. S. Thompson, D. W. Pipes and T. J. Meyer, *Inorg. Chem.*, 1984, **23**, 1845.

3 S. A. Trammell, J. C. Wimbish, F. Odobel, L. A. Gallagher, P. M. Narula and T. J. Meyer, *J. Am. Chem. Soc.*, 1998, **120**, 13 248.

4 L. A. Gallagher and T. J. Meyer, *J. Am. Chem. Soc.*, 2001, **123**, 5308.

5 L. K. Stultz, M. H. V. Huynh, R. A. Binstead, M. Curry and T. J. Meyer, *J Am. Chem. Soc.*, 2000, **122**, 5984.

6 (*a*) C. E. Williams, R. B. Lowry, J. Braven and S. T. Belt, *Inorg. Chim. Acta*, 2001, **315**, 112; (*b*) P. D. Beer, O. Kocian, R. J. Mortimer, C. Ridgway and N. R. Stradiotto, *J. Electroanal. Chem.*, 1996, **408**, 61; (*c*) R. M. Leasure, T. Kajita and T. J. Meyer, *Inorg. Chem.*, 1996, **35**, 5962; (*d*) A. Deronzier, D. Eloy, P. Jardon, A. Martre and J.-C. Moutet, *J. Electroanal. Chem.*, 1998, **453**, 179.

7 V. Ganesan and R. Ramaraj, *Langmuir*, 1998, **14**, 2497 and references therein.

8 F. Geneste, M. Cadoret, C. Moinet and G. Jezequel, *New J. Chem.*, 2002, **26**, 1261.

9 L. D. Ciana, I. Hamachi and T. J. Meyer, *J. Org. Chem.*, 1989, **54**, 1731. The procedure was modified as follows: the monoanion of 4,4′-dimethyl-2,2′-bipyridine was prepared with lithium diisopropylamine in tetrahydrofuran at −78 °C and CO_2 gas dried over sulfuric acid was then bubbled through the reaction medium for 15 min. A yellow precipitate formed immediately. It was filtered, washed with ether, dried and used without further purification.

10 C. Moinet, *J. Phys. IV*, 1994, **4**, C1–175.

11 I. P. Evans, A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, 204.

12 T. Ben Hadda and H. Le Bozec, *Inorg. Chim. Acta*, 1993, **204**, 103.

13 The potential was calculated as follows: $(E_c - E_a)/2$, where E_c and E_a are the cathodic and anodic potentials respectively.

14 Only the top of the $\mathrm{Ru^{III/II}}$ wave was considered in order to eliminate the charge due to the capacitive current.