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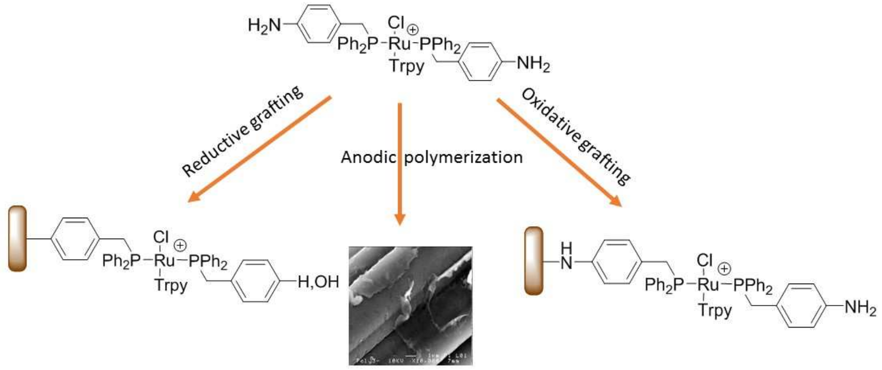
Reductive grafting
Anodic polymerization
Oxidative grafting
H,OH
NH2

Multi-modal surface grafting of [*trans*-bis(aminodiphenylphosphine) terpyridine-Ru(II)Cl]$^{+}$Cl^{-} complex onto glassy carbon electrode

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Abstract: The design of a ruthenium-terpyridine complex having 4-aminobenzyl-diphenylphosphine as remote ligands in a *trans* arrangement ([Ru(*trans*-PN)$_2$(trpy)Cl]$^{+}$Cl^{-} , [trans-bis(aminodiphenylphosphine) terpyridine-Ru(II)Cl]$^{+}$Cl^{-}) is shown to be a highly versatile approach for the immobilization of the organometallics at a carbon surface. Three distinct strategies could be then successfully employed to achieve the grafting of the complex, namely i) the electroreduction of the corresponding *in situ* produced diazonium cation, ii) the electrooxidation of the aromatic amine moiety in the presence of a base and iii) an anodic electropolymerisation in the absence of base. The modified surfaces were characterized by electrochemical or Scanning Electron Microscopy (SEM) studies. The reported approach allows a clean modulation of film thickness and anchoring modes, particularly useful for a given design of ruthenium containing films dedicated to a given application. In this context, the polymer films which contain the largest surface concentration of active ruthenium were employed as immobilized catalyst for oxidation of benzyl alcohol in water, allowing a test of the catalytic activity of the complexes as grafted materials.

Keywords: Ru complexes, diazonium grafting, oxidation grafting, anodic polymerization

1. Introduction

Ruthenium complexes have been extensively considered as building blocks with regards to applications as photosensitizer units, [1],[2] as redox-active components in molecular electronics [3],[4],[5],[6], and in catalysis[7],[8],[9],[10]. Ruthenium polypyridyl complexes are particularly interesting due to their facile synthetic tailoring, high charge-transfer kinetics, rich optical properties, high luminescence yield and high stability depending on the structure and ligand environment[11],[12],[13],[14]. To fully exploit these desirable properties in applications, the ruthenium complexes could be advantageously immobilized at a surface. Various approaches have been implemented to achieve the immobilization of Ru complexes. They have been deposited as thin films using spin coating[15], or using layer by layer assembly[16]. Interestingly, anodic or cathodic electropolymerization have been used to prepare metallopolymer films through incorporation of a ruthenium complex in a conducting polymer matrix [17],[18],[19],[20],[21],[22]. The resulting materials have been shown to be particularly interesting because the primary electronic, optical or catalytic properties of the metal complexes remain accessible while incorporating in an electrically conducting polymer film that can be deposited on a substrate in a controlled fashion. For some applications, ultra-thin films are more desirable, and the most popular strategy is the self-assembly of Ru complex having thiols anchoring units[23],[24]. However, Ru polypyridyl complexes usually exhibit quite high oxidation potential (> 0.9 V vs SCE) which could be unsuitable for gold-thiols self-assembled monolayers (SAMs), prone to deleterious oxidation at high oxidative potentials[25]. Moreover, strong robust interface is demanded for applications. In this context, electrografting methods including the reduction of diazonium cations or the oxidation of amine terminal group are particularly relevant[26]. These strategies do not necessarily lead to monolayers but ultrathin layers (equivalent to a few monolayers) are generally obtained. A few examples of Ru complexes equipped with an aromatic unit that have been attached through diazonium electroduction have been reported in the literature, allowing grafting on different substrates such as carbon nanotubes [27], boron-doped-diamond [28], Highly Oriented pyrolytic Graphite (HOPG) and Indium Tin oxide (ITO) surfaces[29]. Amine electrooxidation has been even more rarely employed with metal complexes, but successful immobilization onto carbon surfaces has been described with polypyridyl Ru-complexes or ferrocene bearing an aromatic amine, [30] [31] and with Os-complexes bearing an aliphatic amine group[32]. In all these examples, the anchoring unit was specifically targeted to a chosen grafting method. However, it could be of great interest to design a molecular system allowing distinct grafting modes. In a previous work, we have reported that aromatic aminophosphine ligands could be covalently bound to surface of glassy carbon electrode through radical species produced either from electrooxidation of the aromatic amine group or from electroreduction of the corresponding diazonium cations, showing the high versatility of the aminophenyl group as anchoring unit[33].

In this work, we have designed a new ruthenium-terpyridine complex having 4-aminobenzyl-diphenylphosphine as remote ligands in a *trans* arrangement ([Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ = [*trans*-bis(aminobenzyldiphenylphosphine)(terpyridine)Ru(II)Cl]$^+$Cl$^-$). The symmetrical structure of the complex and of the amine *termini* of the ligand advantageously allow the multi-modal grafting of the complex as successfully demonstrated. Three distinct strategies highlighted in Fig. ***1*** are used for immobilizing the ruthenium complex. Formation of (Sub-)monolayer of the ruthenium complex at carbon surface could be achieved either through the reduction of *in situ* produced diazonium cations or directly through the oxidation of amine *termini* in the presence of base. Interestingly, in the absence of base, an anodic polymerization occurs, allowing the preparation of a thick layer (a few 100-nm). Such a result evidences an unprecedented control of the grafting route thanks to addition of base.

It is worth noting that the choice of phosphine ligands for the ruthenium complex is also a parameter of high relevance. As compared to polypyridyl complexes, immobilization of ruthenium compounds having phosphine ligands has been hardly explored in literature [34]. Yet, phosphine ligands can modify both the steric and electronic properties of the system, broadening the interest of the materials for optoelectronics and catalytic applications[35],[36],[37]. Thus, combining terpyridine with two phosphine-ligands could generate new Ru-complex types with high electrocatalytic activity for oxidation reaction of numerous types of organic compounds including benzyl alcohol, cyclohexene, 1-pentanol, cyclohexanol, 1,2- and 1,4-butadiol [34] [38]. In this connection, exploratory experiments were performed to test the electrocatalytic activity of immobilized complexes towards oxidation of benzyl alcohol chosen as model reaction. Thick layers were preferentially targeted because they contain the highest surface concentration of active ruthenium moieties. Results demonstrate that the complexes retain catalytic properties when grafted and suggest the facile transformation of [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ $^-$ to its corresponding aqua complexes.

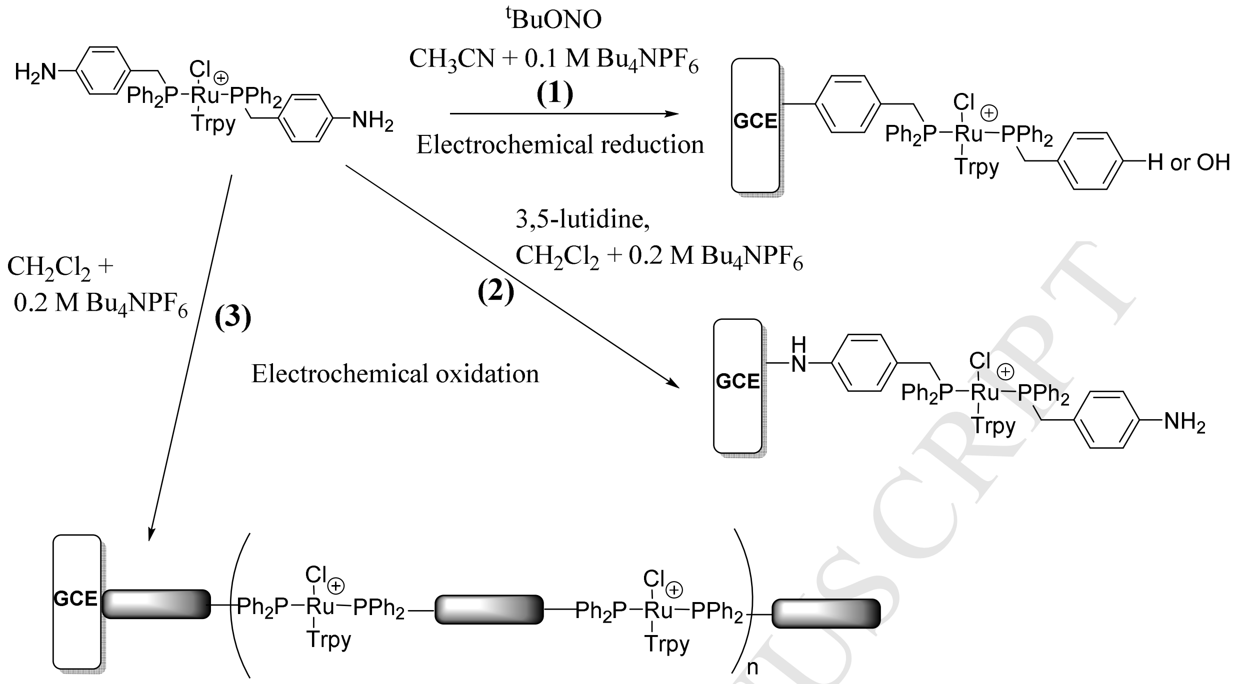

Fig. 1: Three strategies for surface functionalization at a glassy carbon electrode (GCE). (1) electrochemical reduction of diazonium salt produced from 1 mM Ru-complex in CH_3CN + 6 mM of t-BuONO, (2) electrochemical oxidation of 1 mM Ru-complex in CH_2Cl_2 + 50 mM of 3,5-lutidine and (3) electropolymerisation of 1 mM Ru-complex in CH_2Cl_2

2. Experimental

2.1.Materials

Chemicals and solvents were purchased from Acros, Sigma-Aldrich and VWR. Acetonitrile (CH_3CN), toluene and dichloromethane (CH_2Cl_2) were distilled prior to use. Bu_4NPF_6 (Acros) used in electrochemical measurements was of electrochemical grade.

2.2.Synthesis.

NMR spectra were measured on Bruker Avance 500 MHz (Cryoprobe) and Bruker Avance 300 MHZ equipments. High-resolution mass spectra (HRMS) were recorded in Rennes at the CRMPO (centre Régional de mesures Physiques de l’Ouest) on a ZabSpecTOF (LSIMS at 4 kV). These large molecules contain inclusion solvents, precluding any satisfactory elemental analysis. Therefore, ^{1}H, ^{31}P and ^{13}C NMR spectra are provided in the Supporting Information.

Synthesis of (4-aminobenzyl)diphenylphosphine ligand, [(H_2NPhCH_2)Ph_2P] = (PN). PN ligand was obtained from the corresponding borane-protected compound [(H_2NPhCH_2)Ph_2P$\rightarrow$$BH_3$] using a deprotection procedure using diazabicyclo[2.2.2]octane (DABCO) [33]. [(H_2NPhCH_2)Ph_2P$\rightarrow$$BH_3$] was synthesized according to a previously described procedure [39]. A mixture of [(H_2NPhCH_2)Ph_2P$\rightarrow$$BH_3$] (200 mg, 0.65 mmol) and DABCO (74 mg, 0.65 mmol) was stirred in freshly distilled toluene (10 mL) for 4 h at 55^0C under Ar atmosphere. After solvent evaporation, dissolution in diethyl ether and filtration on silica gel, 170 mg of a yellow oil (90 % yield) is finally obtained.

^{1}H NMR (300 MHz, $CDCl_3$) δ /ppm = 7.40 (*m*, 4H), 7.30 (*m*, 6H), 6.84 (*dd*, *J*= 8.3 Hz, 1.6 Hz, 2H), 6.52 (*d*, *J*= 8.3 Hz, 2H), 3.48 (*brd*, 2H), 3.31 (*s*, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ /ppm = 144.29 (*d*, 1C, *Cq*-NH_2), 138.51 (*d*, 2C, *Cq*), 132.94 (*d*, 4C, CH), 130.13 (*d*, 2C, *C*H), 128.56 (*s*, 2C, *C*H), 128.28 (*d*, 4C, *C*H), 127.08 (*d*, 1C, *Cq*), 115.20 (*d*, 2C, *C*H), 35.00 (*d*, 1C, *C*H_2).
^{31}P NMR (121 MHz, $CDCl_3$) δ /ppm: -10.9 (*m*, 1P).

Synthesis of {Ru[trans-bis(4-aminobenzyl)diphenylphosphine](trpy)Cl}$^+$Cl$^-$ complex {[Ru(trans-PN)$_2$(terpy)Cl]$^+$Cl$^-$}. [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ complex (Fig. 2A) was prepared following a procedure similar to that described by Sussuchi *et al.* [38]. A mixture of PN ligand (220 mg, 0.76 mmol), Ru(trpy)Cl_3 (130 mg, 0.30 mmol), LiCl (76 mg, 1.78 mmol) and Et_3N (0.24 mL) was heated under reflux in $ClCH_2CH_2Cl$:EtOH (3:1 v/v) for 3h under Ar atmosphere. This procedure uses LiCl to promote the second substitution of the Ru center with the PN ligand. However, a purple precipitate corresponding to Ru(PN)(trpy)Cl_2 compound was also generated but was easily separated from the targeted diphosphine complex by hot filtration (80 mg of a purple solid). After solvent evaporation of the filtrate, followed by recristallization in CH_2Cl_2 (10 mL), the diphosphine compound was obtained as a brown solid powder (95 mg, 40 % yield). Complete details of the X-ray analyses reported herein have been deposited at the Cambridge Crystallographic Data Center (CCDC 1549033).

^{1}H NMR (300 MHz, DMSO-d$_6$) δ/ppm = 9.14 (*d*, *J* = 5.6 Hz, 2H), 8.10 (*d*, *J* = 8.1 Hz, 2H), 7.95 (*t*, *J* = 7.6 Hz, 2H), 7.63 (*d*, *J* = 7.8 Hz, 4H), 7.31 (t, *J* =7.3 Hz, 1H), 7.16 (*t*, *J* = 7.4 Hz, 4H), 6.94 (*t*, *J* = 7.5 Hz, 8H), 6.73 (*m*, 8H), 5.93 (*m*, 8H), 4.71 (*br*, 4H), 3.58 (*m*, 4H).
^{13}C NMR (75.4 MHz, DMSO-*d*$_6$) δ = 158.11, 156.29, 154.54, 146.94, 137.28, 132.14, 131.21, 129.78, 128.24, 127.39, 125.40, 123.45, 122.52, 120.24, 115.26.

^{31}P NMR (121 MHz, DMSO-d$_6$) δ/ppm = + 27.5 (*m*, 2P).
HRMS (ESI): *m/z* calcd for $C_{53}H_{47}N_5ClP_2Ru$ [M]$^+$: 952.2033; found, m/z 952.2038

Synthesis of Ru(4-aminobenzyl)diphenylphosphine](trpy)Cl$_2$ complex = [Ru(PN)(trpy)Cl$_2$]. A mixture of PN ligand (70 mg, 0.24 mmol), Ru(trpy)Cl$_3$ (53 mg, 0.12 mmol), and Et_3N (1.0 mL) was heated under reflux in $CHCl_3$ (20 mL) for 1.5 h under Ar atmosphere following a previously published procedure [40]. A purple solid was precipitated. Hot filtration leads to 58 mg of the product (70 % yield).

^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ = 8.58 (*dd*, *J* = 8.1, 1.1 Hz, 2H), 8.45 (*m*, 2H), 8.05 (*t*, *J* = 8.0 Hz, 1H), 7.87 (*td*, *J* = 8.4, 1.4 Hz, 4H), 7.73 (*td*, *J* = 7.8, 1.5 Hz, 2H), 751 – 7.29 (*m*, 8H), 6.75 – 6.62 (*m*, 4H), 6.13 (*d*, *J* = 8.4 Hz, 2H), 4.80 (*br*, 2H), 4.21 (*d*, *J* = 8.1 Hz, 2H).
^{13}C NMR (75.4 MHz, DMSO-*d*$_6$) δ = 160.14, 158.36, 158.22, 147.10, 138.21, 137.82, 136.05, 135.11, 132.33, 129.65, 128.16, 124.95, 122.95, 122.22, 121.49, 113.75, 45.56
^{31}P NMR (121 MHz, $CDCl_3$): δ /ppm = 34.26 (*s*, 1P).
HRMS (ESI): *m/z* calcd for ($C_{34}H_{29}N_4Cl_2PRu$) [M]$^+$: 696.0550; found, m/z 696.0544

2.3.Instrumentation

X-ray Diffraction. Data were collected using an APEX II diffractometer Bruker-AXS, Mo-Kα radiation (λ = 0.71073). The structure was solved by direct methods using the SIR97 program, [41] and then refined with full-matrix least-square methods based on F^2 (SHELXL-97) [42] with the aid of the WINGX program [43]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions.

Scanning Electron Microscopy. A JEOL JSM-6031-F scanning electron microscope (Scan-MAT CMEBA, Rennes) was used to analyze the morphology of carbon felt coated with films of [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$. The SEM microscope is equipped with a field-emission gun working under vacuum condition at 10^{-9} Torr. Electron beam was accelerated through a tension of 7 kV and spectroscopic resolution was reached to a value of 15 Å.

Electrochemistry. Cyclic voltammetry or chronoamperometric experiments were performed in freshly distilled and thoroughly degassed CH_2Cl_2 or CH_3CN containing NBu_4PF_6 as supporting salt under an Ar blanket. A Pt foil served as counter electrode and a SCE reference electrode, equipped with a salt bridge containing the CH_3CN or CH_2Cl_2-based electrolyte, was used. Glassy carbon disk electrodes (0.07 cm^2, GCE) and carbon felt (0.7 m^2.g^{-1}, RVG 4000 Le Carbon

Lorraine) were used as working electrodes (GCE) for analyzing the electrochemical behavior of the complexes or as substrates (GCE and carbon felt) for surface functionalization. GCE surfaces were thoroughly polished with DP-Nap polishing paper 1 µm (Struers) and Al_2O_3 slurry 0.3 µm (Struers). Electrochemical signals were recorded using an Autolab electrochemical analyzer (PGSTAT 30, EcoChemie BV).

2.4 Surface functionalization protocols

Reductive diazonium grafting. Diazonium salt of Ru complex was prepared *in situ* from 1 mM $[Ru(\textit{trans}\text{-PN})_2(trpy)Cl]^+Cl^-$ in CH_3CN solution containing 0.1 M NBu_4PF_6 and in the presence of 3 equivalents of *tert*-butylnitrite (t-BuONO) [44]. We added the solution of $[Ru(\textit{trans}\text{-PN})_2(trpy)Cl]^+Cl^-$ on the *tert*-butylnitrite solution. The concentrations above are the final concentrations in the electrochemical cell. The final solution was stirred for 10 min under Ar bubbling prior to electrochemical reduction. Electrochemical reduction of the produced diazonium cations was performed by sweeping the potential between 0 to -1.35 V for 5 successive scans.

Oxidative grafting. Grafting of the Ru-complex (1 mM) was carried out in CH_2Cl_2 + 0.2 M Bu_4NPF_6 in the presence 50 equivalents of 3,5-lutidine (3,5-dimethylpyridine) by holding the potential at 0.86 V for 5 min [28],[31].

Electrochemical polymerization. Anodic polymerization was achieved in CH_2Cl_2 + 0.2 M Bu_4NPF_6 upon oxidation of 1 mM $[Ru(\textit{trans}\text{-PN})_2(trpy)Cl]^+Cl^-$ by 10 repeated successive potential cycling between 0 and 1.20 V.

Modified electrodes and carbon felt were sonicated in CH_2Cl_2 for 5 minutes for removing residual unreacted species, then thoroughly rinsed with acetone and dried under an argon flow. They will be then transferred in an electrochemical cell containing CH_2Cl_2 + 0.2 M Bu_4NPF_6 for further characterization. The surface concentration of electroactive Ru complex was estimated from Faraday's law $\Gamma = Q/nFA\rho$ where Q is the charge, n is the number of electron exchanged (here n= 1), F the Faraday constant (96500 $C.mol^{-1}$), A the geometric surface area of the electrode (0.07 cm^2) and ρ is the roughness factor of the electrode varying between 4 and 8 [45]. Q is evaluated through the numerical integration of the area under the voltammetric peaks at low scan rates using the integration function of the Origin® software. Polynomial baselines can be solved and subtracted prior to curve integration.

3. Results and discussion

3.1.Synthesis and characterization of [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$

[Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ was prepared from mixing PN ligand with Ru(trpy)Cl$_3$ (Fig. 2A). The isolated product was characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. Estimated integration of the total number of protons from ^{1}H NMR spectrum is found equal to 47, in agreement with the expected structure of the Ru center which is coordinated with two PN (36) and one terpyridine ligands (11). The broad signal at 4.71 ppm is characteristic for protons of the terminal NH$_2$ groups. ^{31}P RMN signal is positively shifted as compared with the corresponding PN ligand, from -10.9 to +27.5 ppm, indicating the coordination of PN to the Ru(trpy) unit. In addition, the observation of a single resonance peak in the ^{31}P NMR spectrum suggests a *trans* arrangement on the ruthenium centers in the complex as proposed in Fig. **2**A. To further ascertain for the *trans* conformation, **[Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$** was recristallized after anion-exchange with PF$_6^-$ counter-ions, thus orange crystals of **[Ru(*trans*-PN)$_2$(trpy)Cl]$^+$PF$_6^-$** were obtained through slow diffusion of ether in an acetonitrile solution containing the Ru complex. X-ray diffraction analysis shows that the Ru complex displays a *trans* conformation, with two equivalent PN ligands perpendicular with respect to the Ru-trpy molecular plan (Fig. **2**B). Interestingly, [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$ has two pendant amine groups available as anchoring group for surface grafting.

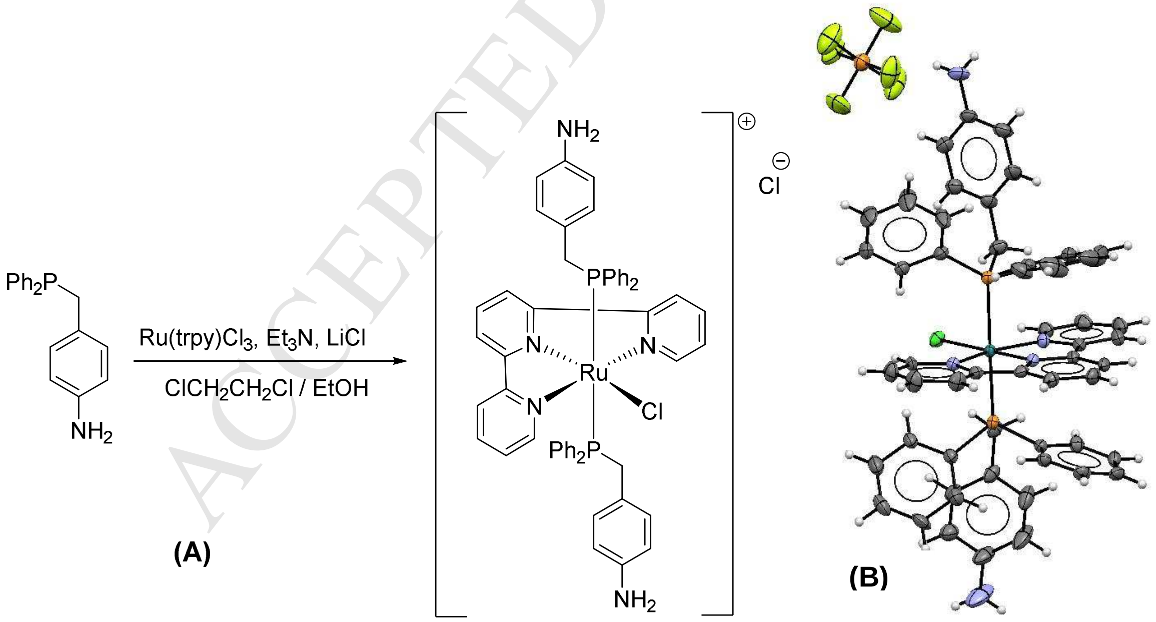

Fig. 2. (A) Scheme for the synthetic pathway yielding [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ complex and (B) X-ray diffraction solid-state structure of [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$PF$_6^-$ obtained from

recrystallization of [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$after anion exchange. Thermal ellipsoid plot at the 50% probability level Hydrogen atoms are drawn as spheres of arbitrary radius.

The electrochemical behavior of the [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ complex was studied in dichloromethane containing 0.2 M NBu$_4$PF$_6$ using cyclic voltammetry (Fig. 3). A reversible redox system at $E_{1/2}$ = 0.91 V vs SCE exhibiting a peak-to-peak separation (ΔEp) of 60 mV is observed together with an irreversible shoulder-like oxidation peak at E_{pa} = 0.84 V vs SCE. For sake of comparison, cyclic voltammetry of [Ru(*trans*-PPh$_3$)$_2$(trpy)Cl]$^+$Cl$^-$ was also recorded and only displays a reversible redox system at $E_{1/2}$ =0.93 V (ΔEp= 80 mV). Thus, the reversible signal at 0.91 V vs SCE was confidently assigned to the reversible one-electron oxidation of the metallic center (Ru(II) / Ru (III) couple) while the shoulder at 0.84 V vs SCE was attributed to the oxidation of the aniline *termini* of the PN ligand. Indeed, the electrochemical signal of the borane-protected ligand gave an irreversible peak at 0.85 V (figure S6).

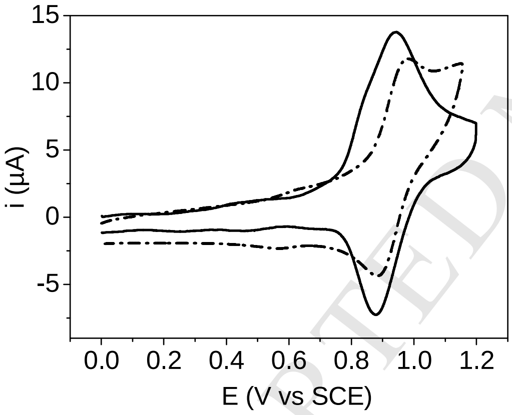

Fig. 3. Cyclic voltammetry of a millimolar solution of [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ (—) and [Ru(*trans*-PPh$_3$)$_2$(trpy)Cl]$^+$Cl$^-$ (– • –) in CH$_2$Cl$_2$ + 0.2 M NBu$_4$PF$_6$ at a GC electrode. v= 100 mV s^{-1}

The redox potential value for the Ru(III)/Ru(II) couple is fully characteristic for cationic Ru complexes with phosphine ligands [37]. Interestingly, analogous monophosphine Ru complex (Ru(*trans*-PN)(trpy)Cl$_2$) exhibits a reversible monoelectronic oxidation at much more negatively shifted potential, $E_{1/2}$ = 0.41 V vs SCE (ΔEp = 60 mV) (Figure S7), in line with the easier oxidation of the neutral complex as compared to the electron-deficient cationic one.

3.2.Surface functionalization

Importantly, the presence of remote aniline ligands offers three different strategies for immobilizing the ruthenium complex at carbon surfaces.

The electrochemical reduction of *in situ* produced aryldiazonium cations is now a recognized method to strongly bind organic layer onto carbon surface through the formation of a C-C bond [26]. Firstly, *in situ* diazotation of Ru-complex was achieved in CH_3CN containing $^tBuNO_2$ rather than in acidic aqueous solution containing $NaNO_2$ due to the lack of solubility of the complex in the latter medium. The potential was swept between 0 and -1.35 vs SCE for 5 cycles. Even if the irreversible reduction peak of diazonium reduction cannot be clearly identified, we still observe the characteristic behaviour of diazonium electrografting with a gradual decrease of the intensity of the cathodic current during consecutive scans (Fig. 4). After ultrasonicating the electrode in CH_3CN and CH_2Cl_2 in order to remove any unreacted species, the electrode was transferred in an electrochemical cell containing CH_2Cl_2 + 0.2 M NBu_4PF_6.

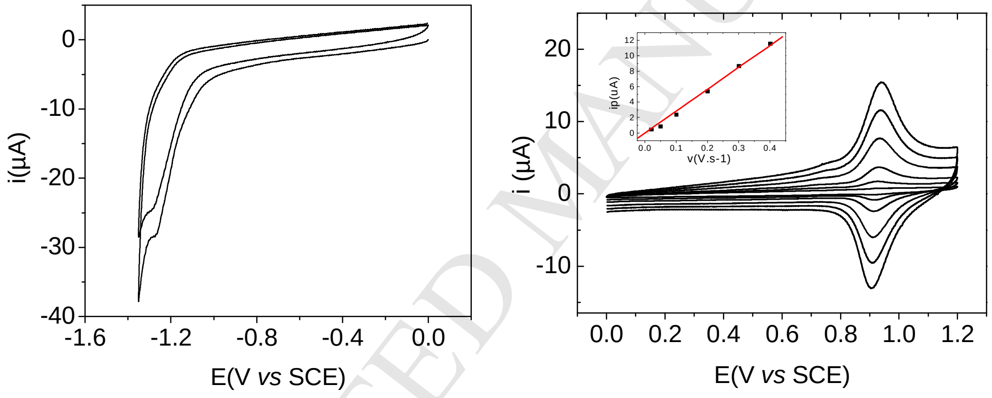

Fig. 4. (left) cyclic voltammetry of diazonium cations produced *in situ* from [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ in CH_3CN (+0.1 M NBu_4PF_6) in the presence of 3eq. $tBuNO_2$ at a GC electrode (v = 100 mV s^{-1}). (right) Electrochemical behavior of the resulting GC electrode in CH_2Cl_2 (+ 0.2 M NBu_4PF_6) at different scan rates (0.02 to 0.4 Vs^{-1}). Insert: linear variation of the anodic peak current intensity of the modified electrode as a function of the scan rates.

The modified electrode exhibits a well-defined electrochemical response at 0.92 V vs SCE characteristic to the grafted Ru complex (Fig. 4). While the peak-to-peak separation is equal to 20 mV, the peak currents were found to vary linearly as a function of the scan rates, as expected for surface-confined electroactive species. Note that this behavior corresponds to Nernstian reaction under Langmuir isotherm conditions, i.e. for a thin layer associated with a fast electron-transfer. These observations indicate the successful immobilization of the Ru-complex as thin film through diazonium electrografting.

The surface functionalization of carbon surfaces through electrochemical oxidation of amines is a well-documented procedure, namely for aliphatic amines, since the 1990s [45],[46],[47],[48],[49],[50],[51]. More recently, this strategy has been successfully extended to aromatic amines [52],[53],[54],[55],[56]. Mechanistic studies have shown that the radical cation [-NH$_2$]$^{•+}$ formed upon oxidation deprotonates to yield an aminyl radical [-NH•] able to covalently bind the carbon surface [49]. It was demonstrated that an excess of organic base such as 2,4,6-collidine [28],[31], 3,5-lutidine could promote the deprotonation step, thus significantly enhances the grafting efficiency [33]. Addition of 50 equivalents of 3,5-lutidine leads to a strong increase of the electrochemical signal of [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ (Fig. 5) while 3,5-lutidine does not display any oxidation peak in this potential range. A similar behavior has been observed by Buriez *et al.* with an amino-ferrocifen complex [31]. It could be explained by the reaction of the base with the electrochemically produced cation radical to form the aminyl radical, which speeds up the amine oxidation process.

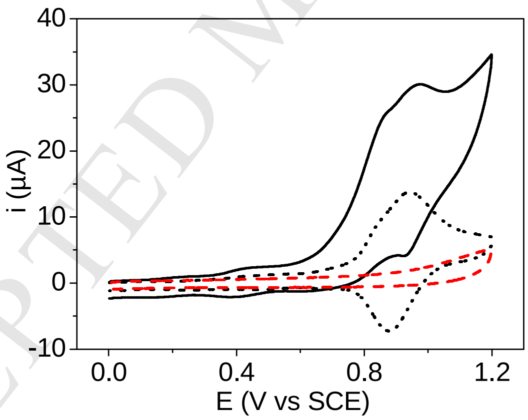

Fig. 5. Cyclic voltammetries of [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ in CH$_2$Cl$_2$ + 0.2 M NBu$_4$PF$_6$ in the absence (dotted line) and in the presence (solid line) of 50 eqs. 3,5-lutidine. Signal of 3,5-lutidine alone (red dashed line) is provided for sake of comparison. Scan rate is 100 mV s^{-1}.

Upon repetitive scans between 0 and 1.20 V, a gradual diminution of the amine peak current at 0.86 V is observed and becomes hardly identified after 5 scans (Fig. 6A). Similarly, after holding the potential at 0.86 V for 5 min, no peak could be further detected for amine oxidation process (Fig. 6B). In sharp contrast, the signal corresponding to Ru(II)/Ru(III) oxidation is always persistent.

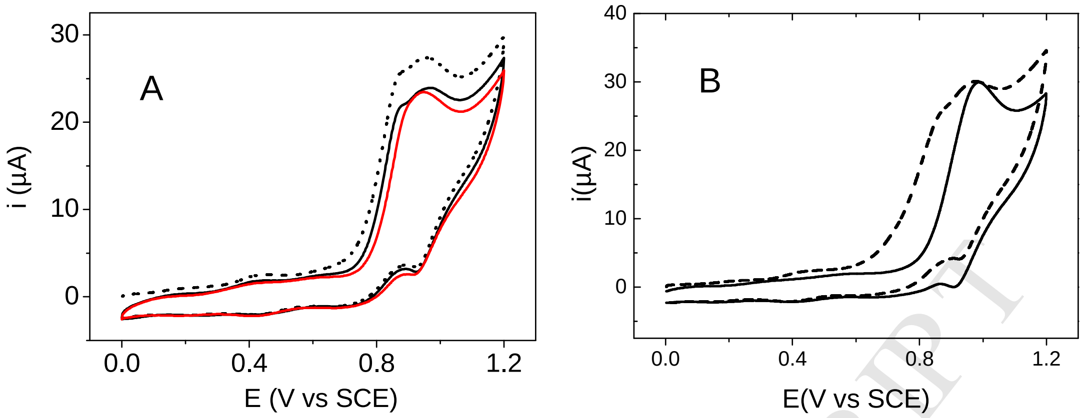

Fig. 6. Cyclic voltammograms of [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ in CH_2Cl_2 + 0.2 M NBu_4PF_6 at a glassy carbon surface in the presence of 50 eqs. of 3,5-lutidine **A**) 1st (dotted line), 2nd (black solid line), 5th (red solid line) scans and **B**) before (dashed line) and after (solid line) controlled-potential electrolysis at 0.86 V. Scan rate is 100 mV s^{-1}.

After ultrasonication in CH_2Cl_2 and drying under an argon flow, the electrodes were examined in CH_2Cl_2 + 0.2 M NBu_4PF_6 electrolyte. Characteristic signals at 0.92 V/SCE with a peak-to-peak separation of ≈ 30 mV are observed while linear variations of the intensity of the peak current as a function of scan rates are obtained (Fig. 7). These results indicate that the Ru-complex is immobilized at the carbon electrodes as a thin layer.

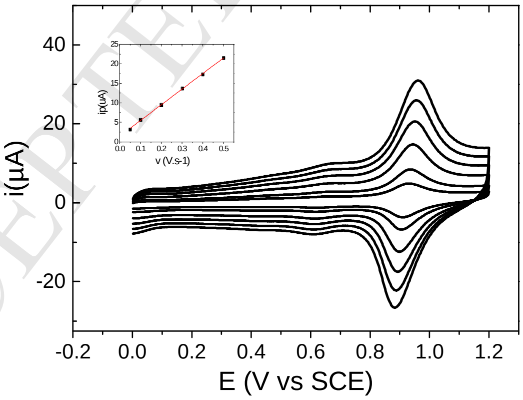

Fig. 7. Electrochemical behavior in CH_2Cl_2 (+ 0.2 M NBu_4PF_6) of an electrode modified through oxidation of [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ in the presence of 50 eqs. 3,5-lutidine at different scan rates (0.05 to 0.5 Vs^{-1}). Insert: linear variation of the anodic peak current intensity of the modified electrode as a function of the scan rates.

By comparing the results obtained through reductive or oxidative electrochemical grafting, it could be noted that the nature of covalent bonds C-C/C-N does not cause any effect on the peak potential value corresponding to the Ru metallic center. Moreover, the potentials values for immobilized complexes correspond to those obtained in solution. The surface concentration of the electroactive Ru-complex was estimated from the integration of the electrochemical signals. The corresponding values gathered in table 1 are found to vary between 0.4 and 2.3×10^{-10} mol cm^{-2} when corrected from the carbon surface roughness. Considering the X-ray diffraction structure, the [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$ complex presents an external diameter of 7.6 Å, the theoretical surface concentration for the closest packing of the complex as hexagonal compact arrangement of disks is estimated to 3.3×10^{-10} mol cm^{-2}. Electrooxidation at constant potential of Ru-complex or electroreduction of its corresponding diazonium cation lead to the formation of a (sub-)-monolayer, with similar surface concentrations. However, electrooxidation with 5 repeated potential scans produces less thick and/or compact films than the controlled-potential electrolysis.

Table 1. Electrochemical data and surface concentration (Γ) of Ru-complex immobilized at GC electrodes

	Electrochemical reduction grafting	**Electrochemical oxidation grafting**		**Electro-polymerization**
		Controlled-potential electrolysis for 5 min	5 successive scans	
$E^{\circ\prime}$(V/SCE)/ΔE_p	0.92 (20 mV)	0.92 (34 mV)	0.92 (28 mV)	0.91 (110 mV)
10^{-10} Γ (mol cm^{-2})[a]	0.8-1.6	1.1-2.3	0.4-0.8	200-900[b]

[a] These values were obtained from 3 different experiments (averaging) and corrected from surface roughness (4 < roughness factor < 8). [b] Rough estimations from thickness

In the absence of 3,5-lutidine, the electrochemical oxidation of [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ complex with successive scans between 0 and 1.20 V/SCE leads to a gradual increase of peak current intensity of the reversible Ru(II)/Ru(III) system along with the disappearance of the oxidation peak of the amine terminal group (Fig. 8A). After 10 scans, a deposit at the electrode surface is discernible with naked eyes. The electrochemical behavior of the modified electrode is studied in CH_2Cl_2 containing 0.2 M NBu_4PF_6 at different scan rates between 0.05 to 0.5 V s^{-1}. As already observed in Fig. 4 and Fig. 7, a clear electroactivity due to the oxidation of the metallic center is recorded but in that case, the peak-to-peak separation ΔEp is equal to 60 mV and the intensity of the peak currents varies linearly as a function of the square root of the scan rates.

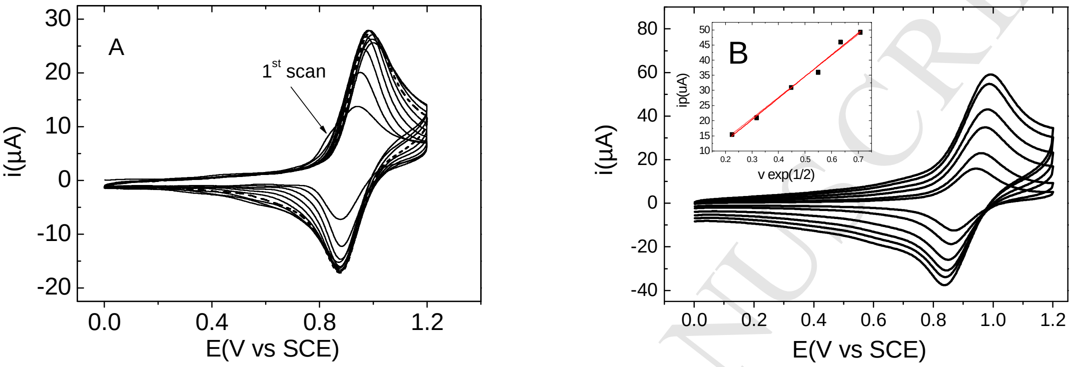

Fig. 8. A) Cyclic voltammetry of [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$in CH_2Cl_2 (+ 0.2 M NBu_4PF_6) at a carbon disk electrode in the absence of 3,5-lutidine, 10 successive scans (1st scan is denoted by an arrow). Scan rate is 100 mV s^{-1}. B) Electrochemical response of the resulting modified electrode in CH_2Cl_2+ 0.2 M NBu_4PF_6 for scan rates varying between 0.05 and 0.5 V s^{-1}. Insert: linear variation of the intensity of the peak current with the square root of scan rates.

This behavior is fully characteristic of relatively thick films and suggests that repeated oxidation cycles of [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ complex, in the absence of 3,5-lutidine, allows an anodic electropolymerization to occur [57],[58]. Carbon felt was subsequently used as carbon substrate to achieve the electrooxidation of the Ru-complex under the same experimental conditions. By comparing with blank carbon felt, SEM images of the carbon fibers clearly demonstrated the presence of a polymer film deposited at the surface of the fibers (Fig. 9). Note that the term polymer refers here as generic term and the organic film could be formed from oligomers. By measuring the profile width of the deposit on the SEM image at different points when a profile is available, the deposit thickness could be estimated to 0.1-0.5 µm. Such a value is fully consistent with the linear variation of intensity of the peak currents with the square root of the scan rates as observed in Fig. 8B. Considering that a close-packing monolayer of [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ exhibits a theoretical thickness around 17-18 Å and leads to a surface concentration equal to 3.3×10^{-10} mol cm^{-2}, we could estimate that the deposit obtained from electropolymerization roughly correspond to a surface concentration equal to 2-9 × 10^{-8} mol cm^{-2}.

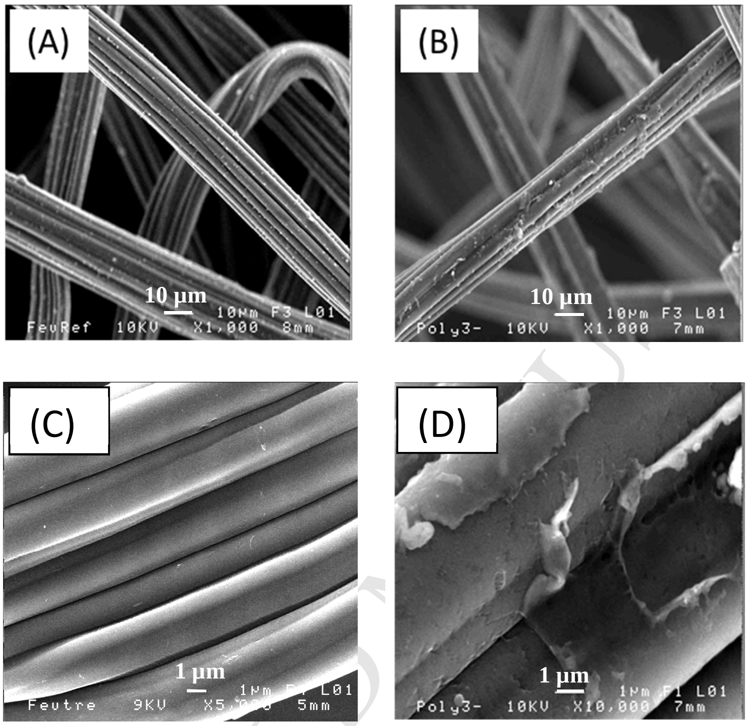

Fig. 9. SEM images of (A,C) blank carbon felt; (B, D) Ru-polymer deposited onto the fibers constituting the carbon felt.

Worth is to outline that this behavior is very unique to the [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ complex, having two pendant *para*-aminobenzyl terminal groups. Thus, anodic electropolymerizations involving the corresponding analogous monophosphine Ru complex (Ru(*trans*-PN)(trpy)Cl$_2$), the protected PN ligand (PN-BH$_3$) or the Ru complex [Ru(*trans*-PPh$_3$)$_2$(trpy)Cl]$^+$Cl$^-$ were unsuccessful. Similarly, surface functionalization with {Ru[4-(4-aminophenyl)-2,2'-bipyridine]bis(2,2'-bipyridine-*N,N'*)}$^{2+}$2[PF$_6$]$^-$ complex was also reported to fail in the absence of 2,4,6-collidine compound, suggesting only one possible immobilization route based on oxidative grafting with one pendant aminophenyl group [28].

Importantly, in the present study, the addition of base (or not) clearly allows a control of the fate of the oxidation reaction, to form either an ultra-thin film or a thick polymeric deposit. Such a situation has not been reported yet. Indeed, Ruthenium complexes containing polypyridyl ligands functionalized with amine substituents were reported to undergo oxidative electropolymerization [59]. As in our study, at least two amine ligands are required to observe the film deposit but, in sharp contrast, addition of base is also needed, except for a Ru complex containing three amino ligands (i.e. 5-amino-1,10-phenantroline) [59].

A full understanding of the anodic polymerization of [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ complex is beyond the scope of this paper but we may speculate that known mechanism for anodic electropolymerization of aniline [59], mainly involving C-N bonds formation [60], could be involved. More precisely, in our case, regarding the *para* substitution of the aminobenzyl group, mechanistic studies concerning the polymerization of *para*-phenylene diamine are particularly relevant to consider [61] [62] [63]. The key steps for the reported mechanisms are the formation of radical cations upon oxidation which is followed by a cleavage of the C-N bond, leading to the formation of primary carbocation. The carbocation is subsequently attacked by another ω-amine, forming a C-N bond, and after proton expulsion, the resulting dimer could undergo similar steps for the chain growth [63]. The presence of two remote aminobenzyl ligands would then sustain polymerization around the ruthenium metallic center (Fig. 10).

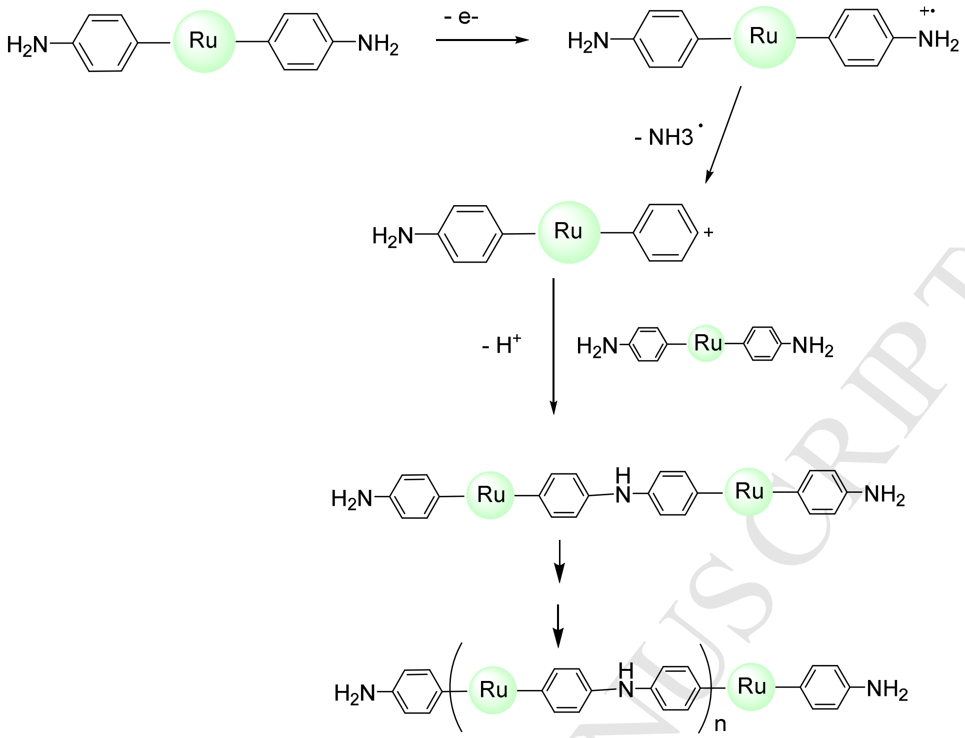

Fig. 10. Scheme of mechanistic pathways proposed for oxidative electro-polymerization of [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ complex.

On the whole, the oxidative electropolymerization of [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ constitutes a versatile and simple-to-process strategy to obtain a thick metallopolymer incorporating a ruthenium center that can be deposited onto surfaces, potentially useful for photophysical, optical or catalytic applications. In particular, electropolymerization leads to immobilized layers with the highest surface concentration of ruthenium moieties as compared to the two other grafting routes (Table 1), making this strategy much more relevant for applications in catalysis. At this stage, it would be interesting to test a possible catalytic activity of the ruthenium complexes when grafted. Ruthenium oxo/aqua complexes containing polypyridyl ligands have been shown to be efficient electrocatalysts for a wide range of organic substrates including aromatic hydrocarbons, olefins, alcohols and ketones [38],[64],[65],[66],[67],[68],[69]. Thus, the complexes allow the oxidation in water of primary and secondary alcohols to aldehyde and carboxylic acid [38],[66]. The high reactivity of the Ru(IV)=O polypyridyl species is generally demonstrated to play a key role in the catalysis, promoting complex mechanisms involving proton-coupled electron transfer [38],[67]. This species could be produced at pH =7 from electrochemical oxidation of Ru(II) aqua complex as a result of a comproportionation reaction of the corresponding Ru(III) complex [67]. Following this, the electrocatalytic activity of the film obtained by oxidative electropolymerization of [Ru(*trans*-PN)$_2$(trpy)Cl]$^+$Cl$^-$ has been tested with oxidation of benzyl alcohol as model reaction in a mixture of phosphate buffer and *tert*-butanol (70/30). Fig. 11A shows the electrochemical signal of the Ru-polymer film (black line) in this mixture, being less defined than in CH_2Cl_2. Addition of 10 mM of benzyl alcohol leads to a significant increase of the anodic current together with a loss of reversibility of the redox system (Fig. 11A, red line) due to the metallopolymer while the benzyl alcohol itself does not give any remarkable oxidation peak in the potential range (Fig. 11A, dotted line). This behavior is fully characteristic of an electrocatalytic activity associated to the ruthenium aqua complexes. Importantly, the Ru-polymer immobilized at the carbon electrode was examined in CH_2Cl_2 containing 0.2 M NBu_4NPF_6 before and after the catalytic test (Fig. 11B). The electrochemical signal due to the Ru-polymer considerably decreased after the electrocatalytic experiment. A ligand exchange Cl→H_2O has probably occurred in the phosphate buffer- *tert*-butanol electrolyte during the course of the experiment. Indeed, the electrochemical behavior of aqua complex shows two very weak systems for Ru(II)/Ru(II) and Ru(III)/Ru(IV) in CH_2Cl_2 (figure S8), which could be overlapped by the signal of residual chloro complex, precluding any observation of new peaks due to the aqua complex.

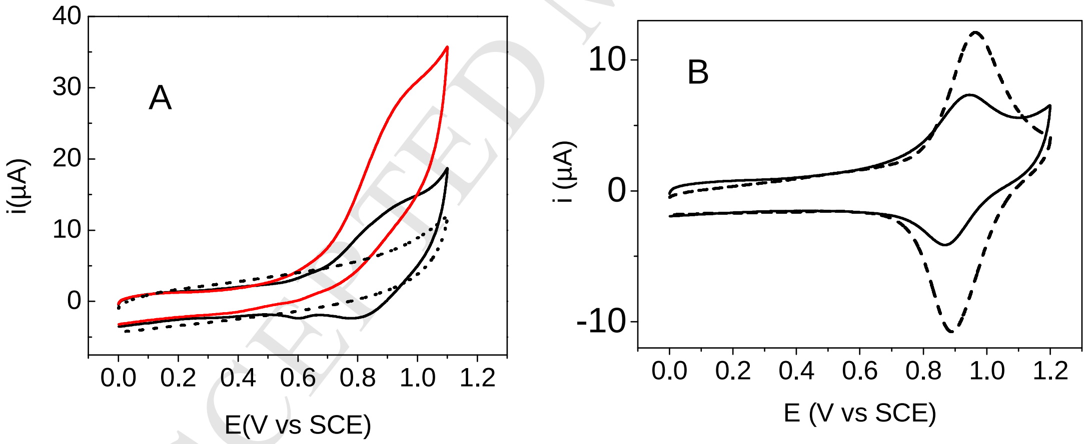

Fig. 11. Cyclic voltammetry at v = 100 mV s^{-1} (A) in 0.25 M phosphate buffer/*t*-BuOH (70/30) of a glassy carbon electrode modified with the Ru-polymer before (black solid line) and after addition of 10 mM of benzyl alcohol (red solid line). Dotted line is the signal for 10 mM benzyl alcohol at a bare carbon electrode. (B) in CH_2Cl_2 + 0.2 M NBu_4PF_6 of a glassy carbon electrode modified with the Ru polymer before (dashed line) and after (solid line) the experiments performed in A.

4. Conclusion

A terpyridine-ruthenium complex equipped with two 4-aminobenzyl-diphosphine (PN) ligands was designed for multimodal surface grafting onto carbon surface. The XRD structure of the ruthenium complex demonstrates the *trans* arrangement of the PN ligand with respect to the metallic center. The aromatic amine pendant groups offer distinct and versatile strategies for immobilizing the ruthenium complex at a carbon surface. Electroreduction of the corresponding *in situ* produced diazonium cation or electrooxidation in the presence of 3,5–lutidine allows surface immobilization of the complex as (sub-)monolayer. In the absence of 3,5-lutidine, the electrochemical oxidation leads to an anodic polymerization yielding a thick (100-500 nm) polymeric or oligomeric deposit at the electrode surface, as shown with SEM and electrochemical analyses. It is shown that this strategy could be easily transferred to high area-to-volume ratio surface like carbon felt, potentially useful for catalytic applications. In terms of applications, preliminary results using the oxidation of benzyl alcohol in water as a model reaction showed a promising electrocatalytic activity of the ruthenium complex immobilized as a polymeric or oligomeric film onto a carbon surface thanks to its versatile transformation to aqua complexes. The presented approach shows high versatility, allowing modulation of the film thickness and anchoring modes which are suitable properties for using the ruthenium complex as materials in optical, electronic or catalytic applications.

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AppendixA. Supplemementary data Supporting Information

Supplementary data associated with this article can be found in XXX.

References

[1] Sauvage, J. P.; Collin, J. P.; Chambron, J. C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. Ruthenium(II) and Osmium(II) Bis(terpyridine) Complexes in Covalently-Linked Multicomponent Systems: Synthesis, Electrochemical

Behavior, Absorption Spectra, and Photochemical and Photophysical Properties. Chem. Rev. 94(1994)993-1019.

[2] Forster, R. J.; Keyes, T. E. Photonic interfacial supramolecular assemblies incorporating transition metals. Coord. Chem. Rev. 253(2009)1833-1853.

[3] Winter, A.; Hoeppener, S.; Newkome, G. R.; Schubert, U. S. Terpyridine-Functionalized Surfaces: Redox-Active, Switchable, and Electroactive Nanoarchitecturesgland. Adv. Mat. 23(2011)3484-3498.

[4] Blum, A. S.; Ren, T.; Parish, D. A.; Trammell, S. A.; Moore, M. H.; Kushmerick, J. G.; Xu, G.-L.; Deschamps, J. R.; Pollack, S. K.; Shashidhar, R. Ru2(ap)4(σ-oligo(phenyleneethynyl)) Molecular Wires: Synthesis and Electronic Characterization. J. Am. Chem. Soc. 127(2005)10010-10011.

[5] Grelaud, G.; Gauthier, N.; Luo, Y.; Paul, F.; Fabre, B.; Barrière, F.; Ababou-Girard, S.; Roisnel, T.; Humphrey, M. G. Redox-Active Molecular Wires Derived from Dinuclear Ferrocenyl/Ruthenium(II) Alkynyl Complexes: Covalent Attachment to Hydrogen-Terminated Silicon Surfaces. J. Phys. Chem. C 118(2014)3680-3695.

[6] Mulas, A.; Hervault, Y.-M.; He, X.; Di Piazza, E.; Norel, L.; Rigaut, S.; Lagrost, C. Fast Electron Transfer Exchange at Self-Assembled Monolayers of Organometallic Ruthenium(II) σ-Arylacetylide Complexes. Langmuir 31(2015)7138-7147.

[7] Jia, W.; Chen, X.; Guo, R.; Sui-Seng, C.; Amoroso, D.; Lough, A. J.; Abdur-Rashid, K. Aminophosphine ligands R2P(CH2)nNH2 and ruthenium hydrogenation catalysts RuCl2(R2P(CH2)nNH2)2. Dalton Trans., DOI:10.1039/B911459A 10.1039/B911459A(2009)8301-8307.

[8] Liao, W.-M.; Zhang, J.-H.; Hou, Y.-J.; Wang, H.-P.; Pan, M. Visible-light-driven CO2 photo-catalytic reduction of Ru(II) and Ir(III) coordination complexes. Inorg. Chem. Commun. 73(2016)80-89.

[9] Ishizuka, T.; Kotani, H.; Kojima, T. Characteristics and reactivity of ruthenium-oxo complexes. Dalton Trans. 45(2016)16727-16750.

[10] Tong, L.; Thummel, R. P. Mononuclear ruthenium polypyridine complexes that catalyze water oxidation. Chem. Sci. 7(2016)6591-6603.

[11] Vergeer, F. W.; Chen, X.; Lafolet, F.; De Cola, L.; Fuchs, H.; Chi, L. Ultrathin luminescent films of rigid dinuclear ruthenium (II) trisbipyridine complexes. Adv. Funct. Mat. 16(2006)625-632.

[12] Zhang, J.; Chu, B. W.-K.; Zhu, N.; Yam, V. W.-W. Synthesis, Characterization, Langmuir− Blodgett Film-Forming Property, and Second-Order Nonlinear Optical Study of Rhenium (I) and Ruthenium (II) Diimine Complexes. Organomet. 26(2007)5423-5429.

[13] Coe, B. J. Switchable nonlinear optical metallochromophores with pyridinium electron acceptor groups. Acc. Chem. Res. 39(2006)383-393.

[14] Astruc, D. *Electron transfer and radical processes in transition-metal chemistry*; Wiley-VCH, 1995.

[15] Gao, F. G.; Bard, A. J. Solid-state organic light-emitting diodes based on tris (2, 2 ‘-bipyridine) ruthenium (II) complexes. J. Am. Chem. Soc. 122(2000)7426-7427.

[16] Nagashima, T.; Suzuki, T.; Ozawa, H.; Nakabayashi, T.; Oyama, M.; Ishida, T.; Haga, M.-a. Electrochemical Behavior of Sequentially Assembled Homo and Heterolayer Molecular Films Based on Dinuclear Ruthenium Complexes. Electrochim. Acta 204(2016)235-244.

[17] Cui, B.-B.; Nie, H.-J.; Yao, C.-J.; Shao, J.-Y.; Wu, S.-H.; Zhong, Y.-W. Reductive electropolymerization of bis-tridentate ruthenium complexes with 5, 5′′-divinyl-4′-tolyl-2, 2′: 6′, 2′′-terpyridine. Dalton Trans. 42(2013)14125-14133.

[18] Zhu, X. J.; Holliday, B. J. Electropolymerization of a Ruthenium (II) Bis (pyrazolyl) pyridine Complex to Form a Novel Ru-Containing Conducting Metallopolymer. Macromol. Rapid Commun. 31(2010)904-909.

[19] Friebe, C.; Görls, H.; Jäger, M.; Schubert, U. S. Linear Metallopolymers from Ruthenium (II)-2, 6-di (quinolin-8-yl) pyridine Complexes by Electropolymerization–Formation of Redox-Stable and Emissive Films. Eur. J. Inorg. Chem. 2013(2013)4191-4202.

[20] Friebe, C.; Schulze, B.; Görls, H.; Jäger, M.; Schubert, U. S. Designing Cyclometalated Ruthenium (II) Complexes for Anodic Electropolymerization. Chem. Eur. J. 20(2014)2357-2366.

[21] Zhang, H.-T.; Yan, S. G.; Subramanian, P.; Skeens-Jones, L. M.; Stern, C.; Hupp, J. T. On the mechanism of oxidative electropolymerization and film formation for phenanthroline-containing complexes of ruthenium. J. Electronal. Chem. 414(1996)23-29.

[22] Fang, Z.; Keinan, S.; Alibabaei, L.; Luo, H.; Ito, A.; Meyer, T. J. Controlled electropolymerization of ruthenium (II) vinylbipyridyl complexes in mesoporous nanoparticle films of TiO2. Angew. Chem. Int. Ed. 53(2014)4872-4876.

[23] Eckermann, A. L.; Feld, D. J.; Shaw, J. A.; Meade, T. J. Electrochemistry of redox-active self-assembled monolayers. Coord. Chem. Rev. 254(2010)1769-1802.

[24] Smalley, J. F.; Finklea, H. O.; Chidsey, C. E.; Linford, M. R.; Creager, S. E.; Ferraris, J. P.; Chalfant, K.; Zawodzinsk, T.; Feldberg, S. W.; Newton, M. D. Heterogeneous electron-transfer kinetics for ruthenium and ferrocene redox moieties through alkanethiol monolayers on gold. J. Am. Chem. Soc. 125(2003)2004-2013.

[25] Vericat, C.; Vela, M.; Benitez, G.; Carro, P.; Salvarezza, R. Self-assembled monolayers of thiols and dithiols on gold: new challenges for a well-known system. Chem. Soc. Rev. 39(2010)1805-1834.

[26] Bélanger, D.; Pinson, J. Electrografting: a powerful method for surface modification. Chem. Soc. Rev. 40(2011)3995-4048.

[27] Jousselme, B.; Bidan, G.; Billon, M.; Goyer, C.; Kervella, Y.; Guillerez, S.; Hamad, E. A.; Goze-Bac, C.; Mevellec, J.-Y.; Lefrant, S. One-step electrochemical modification of carbon nanotubes by ruthenium complexes via new diazonium salts. J. Electronal. Chem. 621(2008)277-285.

[28] Sandroni, M.; Volpi, G.; Fiedler, J.; Buscaino, R.; Viscardi, G.; Milone, L.; Gobetto, R.; Nervi, C. Iridium and ruthenium complexes covalently bonded to carbon surfaces by means of electrochemical oxidation of aromatic amines. Cat. Today 158(2010)22-28.

[29] Nguyen, V. Q.; Sun, X.; Lafolet, F. d. r.; Audibert, J.-F.; Miomandre, F.; Lemercier, G.; Loiseau, F. d. r.; Lacroix, J.-C. Unprecedented Self-Organized Monolayer of a Ru (II) Complex by Diazonium Electroreduction. J. Am. Chem. Soc. 138(2016)9381-9384.

[30] Agnès, C.; Arnault, J.-C.; Omnès, F.; Jousselme, B.; Billon, M.; Bidan, G.; Mailley, P. XPS study of ruthenium tris-bipyridine electrografted from diazonium salt derivative on microcrystalline boron doped diamond. PCCP 11(2009)11647-11654.

[31] Buriez, O.; Labbé, E.; Pigeon, P.; Jaouen, G.; Amatore, C. Electrochemical attachment of a conjugated amino–ferrocifen complex onto carbon and metal surfaces. J. Electronal. Chem. 619(2008)169-175.

[32] Kumar, R.; Leech, D. Immobilisation of alkylamine-functionalised osmium redox complex on glassy carbon using electrochemical oxidation. Electrochim. Acta 140(2014)209-216.

[33] Tran, Q. T.; Bergamini, J.-F.; Mangeney, C.; Lagrost, C.; Pellon, P. Grafting of borane-protected aliphatic and aromatic aminophosphine ligands to glassy carbon electrodes. Electrochem. Commun. 13(2011)844-847.

[34] Sussuchi, E. M.; de Lima, A. A.; De Giovani, W. F. Synthesis and electrochemical, spectral and catalytic properties of diphosphine–polypyridyl ruthenium complexes. Polyhedron 25(2006)1457-1463.

[35] Dixon, I. M.; Lebon, E.; Sutra, P.; Igau, A. Luminescent ruthenium–polypyridine complexes & phosphorus ligands: anything but a simple story. Chem. Soc. Rev. 38(2009)1621-1634.

[36] Kumar, P.; Singh, A. K.; Pandey, R.; Pandey, D. S. Bio-catalysts and catalysts based on ruthenium (II) polypyridyl complexes imparting diphenyl-(2-pyridyl)-phosphine as a co-ligand. J. Organomet. Chem. 696(2011)3454-3464.

[37] Leising, R. A.; Grzybowski, J. J.; Takeuchi, K. J. Synthesis and characterization of six-coordinate ruthenium (II) complexes that contain trans spanning diphosphine ligands. Inorg. Chem. 27(1988)1020-1025.

[38] Sussuchi, E. M.; de Lima, A. A.; De Giovani, W. F. Effect of the cis-and trans-[1, 2-bis (diphenylphosphino) ethylene] ligands in the properties of diphosphine–polypyridyl complexes of ruthenium (II): Application to electrocatalytic oxidations of organic compounds. J. Mol. Cat. A 259(2006)302-308.

[39] Brisset, H.; Gourdel, Y.; Pellon, P.; Le Corre, M. Phosphine-borane complexes; direct use in asymmetric catalysis. Tet. Lett. 34(1993)4523-4526.

[40] Sullivan, B. P.; Calvert, J. M.; Meyer, T. J. Cis-trans isomerism in (trpy)(PPh3) RuC12. Comparisons between the chemical and physical properties of a cis-trans isomeric pair. Inorg. Chem. 19(1980)1404-1407.

[41] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G.; Polidori, G.; Spagna, R. SIR97: a new tool for crystal structure determination and refinement. J. Appl. Cryst. 32(1999)115-119.

[42] Sheldrick, G. M. Crystal structure refinement with SHELXL. Acta Cryst. C 71(2015)3-8.

[43] Farrugia, L. J. WinGX suite for small-molecule single-crystal crystallography. J. Appl. Cryst. 32(1999)837-838.

[44] Baranton, S.; Bélanger, D. In situ generation of diazonium cations in organic electrolyte for electrochemical modification of electrode surface. Electrochim. Acta 53(2008)6961-6967.

[45] Chrétien, J. M.; Ghanem, M. A.; Bartlett, P. N.; Kilburn, J. D. Covalent tethering of organic functionality to the surface of glassy carbon electrodes by using electrochemical and solid-phase synthesis methodologies. Chem. Eur. J. 14(2008)2548-2556.

[46] Barbier, B.; Pinson, J.; Desarmot, G.; Sanchez, M. Electrochemical bonding of amines to carbon fiber surfaces toward improved carbon-epoxy composites. J. Electrochem. Soc. 137(1990)1757-1764.

[47] Deinhammer, R. S.; Ho, M.; Anderegg, J. W.; Porter, M. D. Electrochemical oxidation of amine-containing compounds: a route to the surface modification of glassy carbon electrodes. Langmuir 10(1994)1306-1313.

[48] Adenier, A.; Chehimi, M. M.; Gallardo, I.; Pinson, J.; Vila, N. Electrochemical oxidation of aliphatic amines and their attachment to carbon and metal surfaces. Langmuir 20(2004)8243-8253.

[49] Liu, J.; Dong, S. Grafting of diaminoalkane on glassy carbon surface and its functionalization. Electrochem. Commun. 2(2000)707-712.

[50] Geneste, F.; Moinet, C. Electrochemically linking TEMPO to carbon via amine bridges. New J. Chem. 29(2005)269-271.

[51] Ghilane, J.; Martin, P.; Randriamahazaka, H.; Lacroix, J.-C. Electrochemical oxidation of primary amine in ionic liquid media: Formation of organic layer attached to electrode surface. Electrochem. Commun. 12(2010)246-249.

[52] Liu, J.; Cheng, L.; Liu, B.; Dong, S. Covalent modification of a glassy carbon surface by 4-aminobenzoic acid and its application in fabrication of a polyoxometalates-consisting monolayer and multilayer films. Langmuir 16(2000)7471-7476.

[53] Yang, G.; Shen, Y.; Wang, M.; Chen, H.; Liu, B.; Dong, S. Copper hexacyanoferrate multilayer films on glassy carbon electrode modified with 4-aminobenzoic acid in aqueous solution. Talanta 68(2006)741-747.

[54] Li, X.; Wan, Y.; Sun, C. Covalent modification of a glassy carbon surface by electrochemical oxidation of r-aminobenzene sulfonic acid in aqueous solution. J. Electronal. Chem. 569(2004)79-87.

[55] Yang, G.; Liu, B.; Dong, S. Covalent modification of glassy carbon electrode during electrochemical oxidation process of 4-aminobenzylphosphonic acid in aqueous solution. J. Electronal. Chem. 585(2005)301-305.

[56] Cougnon, C.; Mauzeroll, J.; Bélanger, D. Patterning of Surfaces by Oxidation of Amine-Containing Compounds Using Scanning Electrochemical Microscopy. Angew. Chem. Int. Ed. 48(2009)7395-7397.

[57] Volkov, A.; Tourillon, G.; Lacaze, P.-C.; Dubois, J.-E. Electrochemical polymerization of aromatic amines: IR, XPS and PMT study of thin film formation on a Pt electrode. J. Electroanal. Chem. Interf. Electrochem. 115(1980)279-291.

[58] Wnek, G.; Skotheim, T. Handbook of Conducting Polymers. Ed. TA Stotheim, Marcel Dekker, Inc. NY (1986).

[59] Ellis, C. D.; Margerum, L. D.; Murray, R. W.; Meyer, T. J. Oxidative electropolymerization of polypyridyl complexes of ruthenium. Inorg. Chem. 22(1983)1283-1291.

[60] Breitenbach, M.; Heckner, K.-H. Untersuchungen zur Kinetik der anodischen Oxydation von Anilin in Azetonitril an der rotierenden Platinelektrode. J. Electroanal. Chem. Interf. Electrochem. 29(1971)309-323.

[61] Mazloum-Ardakani, M.; Sheikh-Mohseni, M.; Benvidi, A. Electropolymerization of thin film conducting polymer and its application for simultaneous determination of ascorbic acid, dopamine and uric acid. Electroanal. 23(2011)2822-2831.

[62] Sayyah, S.; Abd El-Rehim, S.; El-Deeb, M.; Kamal, S.; Azooz, R. Electropolymerization of p-phenylenediamine on Pt-electrode from aqueous acidic solution: Kinetics, mechanism, electrochemical studies, and characterization of the polymer obtained. J. Appl. Polym. Sci. 117(2010)943-952.

[63] Lakard, B.; Herlem, G.; Lakard, S.; Fahys, B. Ab initio study of the polymerization mechanism of poly (p-phenylenediamine). J. Mol. Struct. (theochem) 638(2003)177-187.

[64] Geneste, F.; Moinet, C.; Jezequel, G. First covalent attachment of a polypyridyl ruthenium complex on a graphite felt electrode. New J. Chem. 26(2002)1539-1541.

[65] Stultz, L. K.; Huynh, M. H. V.; Binstead, R. A.; Curry, M.; Meyer, T. J. Allylic Oxidation of Cyclohexene and Indene by cis-[RuIV (bpy) 2 (py)(O)] 2+. J. Am. Chem. Soc. 122(2000)5984-5996.

[66] Farrer, B. T.; Thorp, H. H. Redox pathways in DNA oxidation: kinetic studies of guanine and sugar oxidation by para-substituted derivatives of oxoruthenium (IV). Inorg. Chem. 39(2000)44-49.

[67] Geneste, F.; Moinet, C. Electrocatalytic oxidation of alcohols by a [Ru (tpy)(phen)(OH 2)] 2+-modified electrode. J. Electronal. Chem. 594(2006)105-110.

[68] Geneste, F.; Moinet, C.; Ababou-Girard, S.; Solal, F. Stability of [RuII (tpy)(bpy)(OH2)] 2+-modified graphite electrodes during indirect electrolyses. Inorg. Chem. 44(2005)4366-4371.

[69] Geneste, F.; Moinet, C. Electrocatalytic activity of a polypyridyl ruthenium-oxo complex covalently attached to a graphite felt electrode. New J. Chem. 28(2004)722-726.

Highlights:

- A new ruthenium-terpyridine complex with 4-aminobenzyl-diphenylphosphine as remote ligands.
- A *trans* arrangement of the ligands allows multi-modal grafting onto carbon surface
- Base addition simply controls the thickness and the anchoring mode of the layers