



A missing member in the family of chalcogenophene-substituted 2,2':6',2 -terpyridine: 4'-(tellurophen-2-yl)-2,2':6',2 -terpyridine, its Ru(II) complex and its electropolymerization as a thin film

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A missing member in the family of chalcogenophene-substituted 2,2':6',2''-terpyridine: 4'-(tellurophen-2-yl)-2,2':6',2''-terpyridine, its Ru(II) complex and its electropolymerization as a thin film.

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Abstract: The new terpyridine derivative 4'-(tellurophen-2-yl)-2,2':6',2''-terpyridine and its homoleptic Ru(II) complex have been prepared and characterized by different techniques (NMR, UV-Vis, mass spectrometry). Additionally, a thin polymer film was obtained through electrochemical oxidation and coupling of tellurophene moieties. The obtained organic coating showed very interesting electrochemical and electrochromic properties, thanks to its Ru(terpy)₂ groups.

Keywords: Oligopyridine; Tellurophene; Electroactive metallopolymer; Electrochromism.

1. Introduction: 2,2':6',2''-Terpyridine derivatives and their complexes have been widely studied [1]. This can be explained by the important number of compounds that can be prepared by varying the substitution pattern onto the terpyridine scaffold and the nature of the complexed metal. Terpyridines and their complexes have found a vast range of applications such as sensitizers in solar cells [2], catalysts [3], electrochromic materials [4] or as chromophores [5] just to name a few. Terpyridine complexes that are substituted with five-membered heterocycles such as pyrrole, furan or thiophene are interesting compounds as they can be electrochemically polymerized onto electrodes as metal-containing polymer films. These materials can find applications in sensors [6] or as electrochromic layers [7] for example. While terpyridines substituted with chalcogenophene heterocycles such as furan [8], thiophene [9] and selenophene [10] have been already described, to the best of our knowledge the tellurophene-substituted one has not been reported yet. In fact, tellurophene derivatives are much less studied than other chalcogenophene. For example, a bibliographic research performed onto Web of Science™ (2019.06.12) using the term tellurophene returned 212 references while it was 1139, 49354 and 41125 references for selenophene, thiophene and furan respectively. This article follows one of our previous works on [Ru(terpy)₂ selenophene]-based polymer film [10] and describes the preparation of the new 4'-(tellurophen-2-yl)-2,2':6',2''-terpyridine (**1**) and its homoleptic Ru(II) complex (**2**) (Fig. 1). These new compounds have been characterized by different techniques (NMR, UV-Vis, Mass spectrometry). Electrochemical oxidation and coupling of tellurophene moieties in complex **2** were carried out to enable formation of a thin polymer film which exhibited very interesting properties.

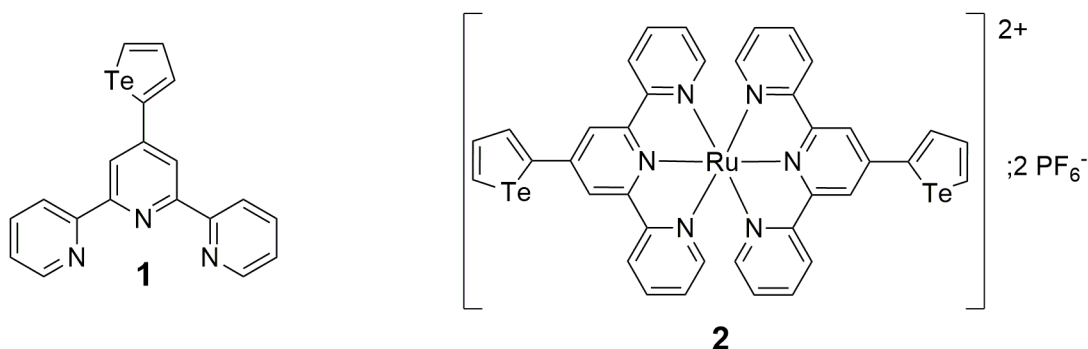


Fig. 1. Chemical structures of terpyridine **1** and its homoleptic Ru(II) complex **2**.

2. Experimental

2.1. Chemicals and apparatus

All reagents were purchased from commercial suppliers and used as received unless otherwise stated. Tellurophene was prepared according to literature [11]. Tellurophen-2-aldehyde was prepared using a slightly modified literature [12] procedure (see supplementary material). Column chromatography was carried out onto silica gel (40-63 μm). ^1H and ^{13}C NMR were recorded on a Bruker Avance 400 spectrometer at 400 MHz and 100 MHz respectively. Melting point was recorded on a Stuart SMP 3 melting point apparatus and is uncorrected. UV-Vis spectra of complex **2** (5.10^{-3} M solution in acetonitrile) and of the film onto FTO were recorded onto an Agilent Technologies Cary 300 spectrometer. HR-MS spectra were recorded at Wellience (Dijon, France). SEM and EDX experiments were realized with a MEB FEB TESCAN apparatus. Electrochemical measurements were carried out using a PGSTAT30 AUTOLAB potentiostat and a classical three-electrode setup consisting of a Ag/AgCl/KCl (3M) reference electrode (-36mV/SCE), a platinum wire counter-electrode and a working electrode on which the deposit was realized. The working electrode was a platinum disk (0,071 cm^2) or a Fluorine-doped Tin Oxide plate (1.5 x 1.5 cm).

2.2. Synthesis of 4'-(tellurophen-2-yl)-2,2':6',2''-terpyridine (**1**)

To a solution of 2-acetylpyridine (1.51 g; 12.5 mmol) in ethanol (33 mL) are successively added tellurophene-2-aldehyde (1.30 g; 6.2 mmol), 85% potassium hydroxide pellets and 25% aqueous ammonia solution (19 mL). The solution is stirred at room temperature for 24 hours. The precipitate is then filtered and washed with ice cold 50% ethanol until washings are colourless. The product is dried under vacuum over phosphorus pentoxide. Crude **1** is sufficiently pure (>98 % by quantitative ^1H NMR [13]) to be used in next step without purification. Light brown solid (0.82 g; 32 %) mp=196-200°C (dec.). ^1H NMR (CDCl_3 , 400 MHz), δ (ppm) = 8.95 (dd, 1H, J = 6.8, 1.1 Hz, Ha), 8.65 (ddd, 2H, J = 4.8, 1.7, 0.8 Hz, H6,6''), 8.56 (d, 2H, J = 8.0 Hz, H3,3''), 8.48 (s, 2H, H3',5'), 8.26 (dd, 1H, J = 4.1, 1.1 Hz, Hc), 7.83 (dd, 1H, J = 6.8, 4.1 Hz, Hb), 7.79 (td, 2H, J = 7.7, 1.8 Hz, H4,4''), 7.27 (ddd, 2H, J = 7.4, 4.8, 1.2 Hz, H5,5''). ^{13}C NMR (CDCl_3 , 100 MHz), δ (ppm) = 156.1 ; 156.0 ; 149.1 ; 149.0 ; 146.9 ; 138.8 ; 136.8 ; 136.1 ; 128.7 ; 123.9 ; 121.4 ; 118.5. HR-MS: calc. for $[\text{C}_{19}\text{H}_{13}\text{N}_3\text{Te} + \text{H}]^+$ 414.02445, found 414.02376.

2.3. Synthesis of $[Ru(\mathbf{1})_2]PF_6$ (**2**):

To a mixture of ligand **1** (0.795 g; 1.9 mmol), $RuCl_3 \cdot xH_2O$ (0.283g; 1.3 mmol) in ethanol (140 mL) is added N-methylmorpholine (10 drops of Pasteur pipette). The reaction mixture is refluxed for 3 hours. After cooling to room temperature, the deep red solution is poured onto a saturated KPF_6 aqueous solution and ethanol is removed on a rotary evaporator. The resulting precipitate is filtered, washed with water and dried under vacuum over phosphorus pentoxide. This crude product is purified by column chromatography (silica gel; eluent: acetone/water/saturated aqueous KNO_3 100:0:0 to 70:30:0.1 v:v:v). Fractions containing the product are poured onto saturated KPF_6 aqueous solution and acetone is removed on a rotary evaporator. The precipitate is filtered, washed with water and diethyl ether and dried under vacuum over phosphorus pentoxide. This afford pure **2** as a red solid (0.595 g; 51%). 1H NMR (CD_3CN , 400 MHz), δ (ppm) = 9.39 (d, 1H, J = 6.4 Hz, Ha), 8.80 (s, 2H, H3',5'), 8.73 (br, 2H, H3,3''), 8.66 (d, 1H, J = 7.8 Hz, Hc), 8.15 (br, Hb), 7.96 (t, 2H, J = 7.4 Hz, H4,4''), 7.46 (d, 2H, J = 4.4 Hz, H6,6''), 7.21 (t, 2H, J = 5.8 Hz, H5,5''). ^{13}C NMR (CD_3CN , 100 MHz), δ (ppm) = 158.6 ; 155.9 ; 153.0 ; 148.3 ; 144.8 ; 139.8 ; 139.4 ; 138.5 ; 133.8 ; 128.0 ; 125.2 ; 121.4. HR-MS: calc. for $[C_{38}H_{26}N_6RuTe_2]^{2+}$ 463.96843, found 463.96816.

3. Results and discussion:

3.1. Synthesis and characterization of ligand **1** and complex **2**.

Terpyridine **1** is prepared by reacting tellurophene-2-aldehyde and 2-acetylpyridine with potassium hydroxide in a mixture of ethanol and aqueous ammonia according to the protocol of Wang and Hanan [13] (Fig. 2). At this point, although obtained in a relatively low yield (32%), the compound is sufficiently pure (> 98% by quantitative 1H NMR [14]) to be used for the preparation of complex **2** without purification.

The latter was prepared by reacting ligand **1** with $RuCl_3$ in refluxing ethanol in the presence of N-methylmorpholine and after precipitation in excess aqueous hexafluorophosphate salt (potassium for instance), according to a classical protocol for the preparation of homoleptic bis-terpyridine complexes [6, 10, 15].

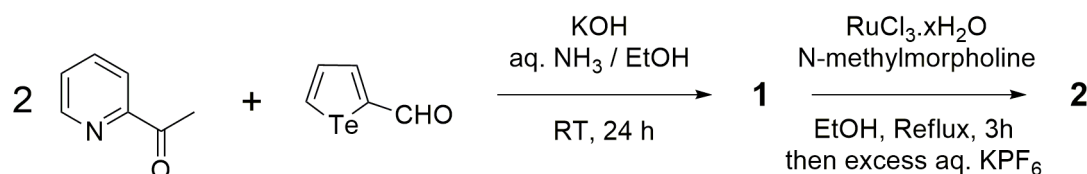


Fig. 2. Synthetic pathway to ligand **1** and complex **2**.

1H and ^{13}C NMR spectra are in agreement with the proposed structures for compounds **1** and **2**. Their identification was further confirmed by mass spectrometry, since the molecular ion peaks as well as the isotopic distribution agree with the proposed formulas. Moreover, complex **2** was characterized by UV-Vis spectroscopy. Especially, the spectrum of **2** exhibit a MLCT (Metal to Ligand Charge Transfer) band in the visible region (λ_{max} =504 nm), a phenomenon that account for a bis-terpyridine $Ru(II)$ complex formation as described previously, especially for chalcogenophene-functionalized terpyridine complexes [16].

3.2. Electrochemistry

Fig. 3 shows cyclic voltammogram obtained after 25 cycles in trifluoroborate etherate (TFBE) solution containing 1 mM of compound **2** on platinum (Pt) electrode. Irreversible oxidation wave of tellurophene moiety is slightly visible as a current shouldering at a potential of about 1.63 V vs Ag/AgCl but only on the first cycle. As noticed in previous studies, oxidation potential of such pendant moieties decreases with heteroatom electronegativity. Indeed, for similar molecules, it was lower with selenophene, thienyl and furyl moieties [10,16]. For following cycles, tellurophene oxidation signal decreases with potential cycling. This is due to polymer growth on the surface getting polymerization process more and more difficult after each cycle as film's quality gets poorer and poorer. As fully described in the literature [17-24] for such heteroaromatic compounds, polymerization mechanism starts with tellurophene moieties oxidation to form radical cations which rapidly couple together (due to their unstable nature) leading to dimers after loss of protons. Oligomers oxidation being easier than oxidation of monomers, polymerization process occurs to enable growing of the film. Reversible signal of $\text{Ru(terpy)}_2^{2+}/\text{Ru(terpy)}_2^{3+}$ is centered at about 1 V vs Ag/AgCl. Continuous increase in anodic and cathodic current with potential scanning shows accumulation of an electroactive film at the electrode surface. Indeed, after 25 cycles, an adherent deep red coating is present on platinum electrode.

It was also possible to get a film of good quality on glassy carbon in the same conditions (results not shown). Polymerization was also successful on gold, but the obtained coating had poor adherence. However, in acetonitrile, no deposit was obtained probably due to too high solubility of oligomers in this solvent. Even if irreversible oxidation of tellurophene was well visible, the voltammogram only showed diffusional signal for $\text{Ru(terpy)}_2^{2+}/\text{Ru(terpy)}_2^{3+}$ couple and the surface was unchanged after the experiment.

Electroactivity of the polymer film grown on Pt was investigated in monomer free 0.5 M tetraethylammonium tetrafluoroborate (TEABF₄) acetonitrile solution after abundant rinsing of the electrode with acetonitrile. Typical adsorbed $\text{Ru(terpy)}_2^{2/3+}$ reversible behavior was observed with perfect linear dependence of peak current with scan rate, proving immobilization of the redox couple on the surface (Fig. 4). Peaks integration indicated a surface coverage of $(0.74 \pm 0.06) \cdot 10^{-8}$ mol/cm² for $\text{Ru(terpy)}_2^{2/3+}$ groups.

Morphology of the polymer film was observed using Scanning Electron Microscopy (Fig. 5). Images show typical nodular structure with nodules size varying between 100 to 1000 nm, approximatively. Energy-dispersive X-ray spectroscopy confirmed presence of C, N, Ru and Te elements as expected for such material.

To investigate eventual electrochromic properties of poly-**2** film, deposits were grown on FTO substrates from 1 mM and 3 mM of compound **2** in TFBE solution using cyclic voltammetry in the same conditions that in Fig. 3 (25 cycles). It was not possible to work at higher concentration as saturation is rapidly reached. As for the curve obtained on Pt, growing of the electroactive polymer film is evidenced through the increase in $\text{Ru(terpy)}_2^{2/3+}$ redox signal all along potential scanning (figure not shown). In both cases, a polymer film is clearly present on the FTO surface after cyclic voltammetry experiment. However, the film obtained from 3 mM solution was thicker and macroscopically more homogeneous. The electrode was then well rinsed with acetonitrile and plunged in monomer free 0.5 M TEABF₄ acetonitrile solution. Potential was varied from 1V to 2 V vs Ag/AgCl and changes in color for the polymer film were clearly visible when shifting from reduced to oxidized form of $\text{Ru(terpy)}_2^{2/3+}$ groups. Indeed, as shown in Fig. 6, for the deposit obtained in 1 mM solution, the polymer surface goes from pink/purple for reduced form to brown/beige for oxidized form. For the thicker film grown in 3 mM solution, it turns from dark red to brown/yellow color. The UV-Vis spectrum of the film onto FTO (supplementary material) exhibits a slightly red-shifted maximum ($\lambda_{\text{max}}=513$ nm). This further accounts for the formation of poly-**2** resulting in an increased conjugation and therefore in a higher absorption wavelength [25].

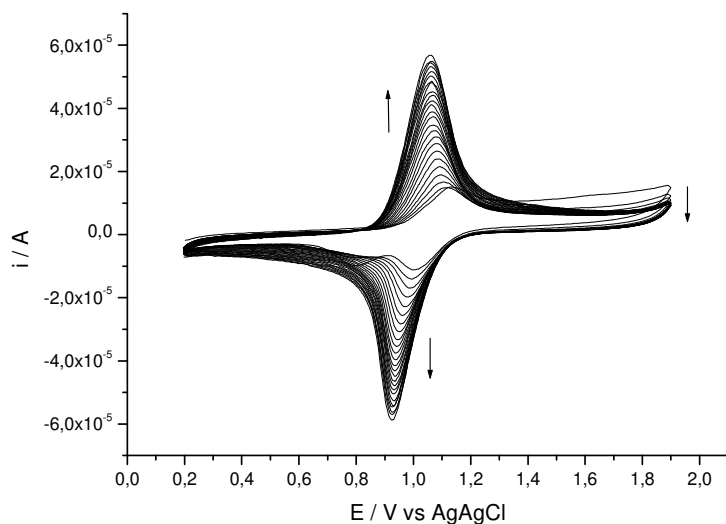


Fig. 3. Cyclic voltammogram (50 mV/s) of 1 mM of compound **2** in trifluoroborate etherate (TFBE) on platinum disk (0.071 cm²). The arrows indicate current evolution with potential scanning.

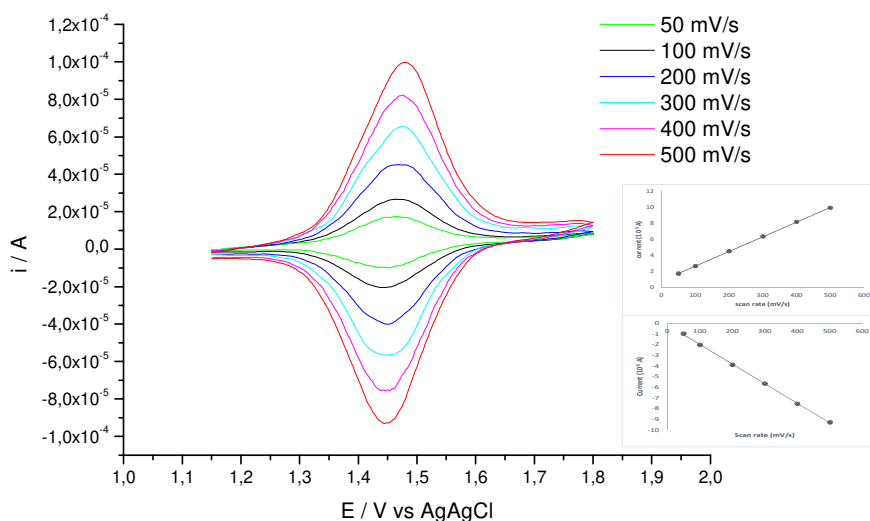


Fig. 4. Cyclic voltammogram at different scan rates of poly-**2** modified platinum electrode (0.071 cm²). Experiments were carried out in monomer free 0.5 M tetraethylammonium tetrafluoroborate (TEABF₄) acetonitrile solution. The curves on bottom right represent anodic and cathodic peaks current evolution with scan rate.

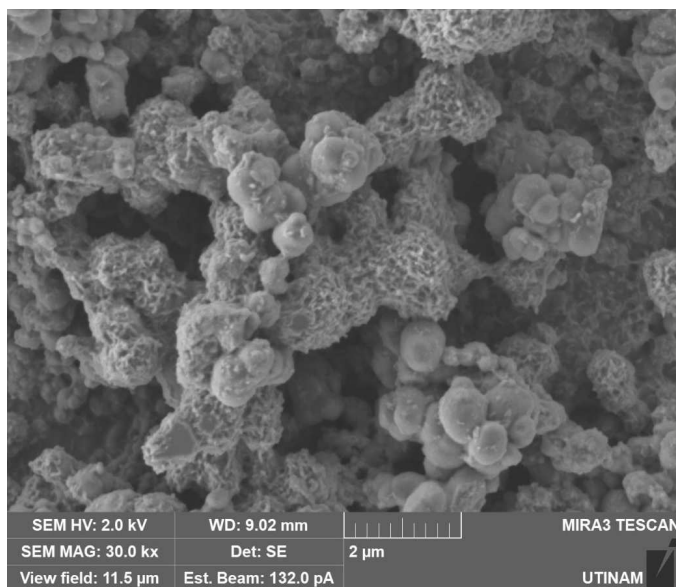


Fig. 5. Scanning Electron Microscopy images of poly-2 modified platinum electrode.



Fig. 6. Pictures of FTO substrates modified with poly-2 grown in (top) 1 mM and (bottom) 3 mM solution in (left) reduced form at 1 V vs Ag/AgCl and (right) oxidized form at 2 V vs Ag/AgCl. Potential variation was made in 0.5 M tetraethylammonium tetrafluoroborate (TEABF₄) acetonitrile solution.

4. Conclusions

In conclusion, a new ruthenium-containing metallocopolymer thin film was grown by the mean of electrochemical polymerization of a bis-terpyridine complex. The use of TFBE as solvent was necessary to enable deposition of an adherent film. The originality of this metal-containing polymer is the presence of tellurophene units, a heterocycle that is very uncommon. Polymerization mechanism consisted in electrochemical oxidation and coupling of these adjacent tellurophene groups. This new material was thoroughly characterized by different techniques such as electrochemistry, SEM imaging and EDX. Moreover, this new polymer exhibits very interesting electrochromic properties. Future work will focus on

exploiting this kind of tellurium and ruthenium containing-material in various applications (e.g. sensors).

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