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

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5 Jérôme Husson*, Abdeslam Et Taouil and Laurent Guyard,

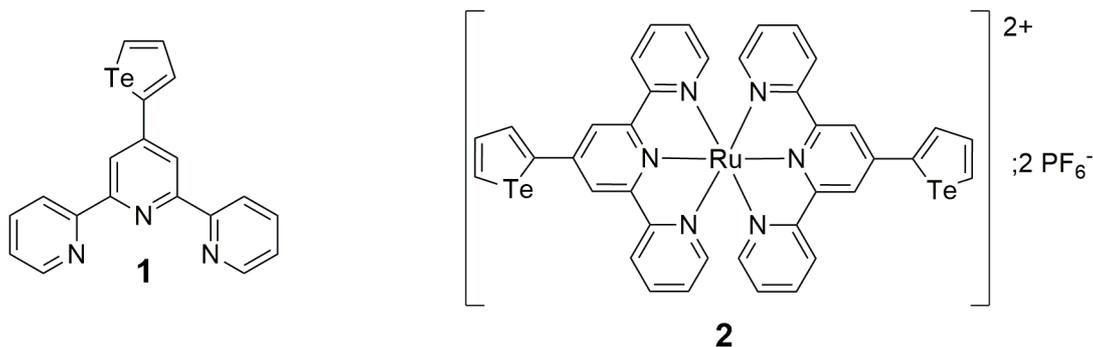
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13
14 **Abstract:** The new terpyridine derivative 4'-(tellurophen-2-yl)-2,2':6',2''-terpyridine and its
15 homoleptic Ru(II) complex have been prepared and characterized by different techniques
16 (NMR, UV-Vis, mass spectrometry). Additionally, a thin polymer film was obtained through
17 electrochemical oxidation and coupling of tellurophene moieties. The obtained organic
18 coating showed very interesting electrochemical and electrochromic properties, thanks to its
19 Ru(terpy)₂ groups.

20
21 **Keywords:** Oligopyridine; Tellurophene; Electroactive metallopolymer; Electrochromism.

22
23 **1. Introduction:** 2,2':6',2''-Terpyridine derivatives and their complexes have been widely
24 studied [1]. This can be explained by the important number of compounds that can be
25 prepared by varying the substitution pattern onto the terpyridine scaffold and the nature of the
26 complexed metal. Terpyridines and their complexes have found a vast range of applications
27 such as sensitizers in solar cells [2], catalysts [3], electrochromic materials [4] or as
28 chromophores [5] just to name a few. Terpyridine complexes that are substituted with five-
29 membered heterocycles such as pyrrole, furan or thiophene are interesting compounds as they
30 can be electrochemically polymerized onto electrodes as metal-containing polymer films.
31 These materials can find applications in sensors [6] or as electrochromic layers [7] for
32 example. While terpyridines substituted with chalcogenophene heterocycles such as furan [8],
33 thiophene [9] and selenophene [10] have been already described, to the best of our knowledge
34 the tellurophene-substituted one has not been reported yet. In fact, tellurophene derivatives
35 are much less studied than other chalcogenophene. For example, a bibliographic research
36 performed onto Web of Science™ (2019.06.12) using the term tellurophene returned 212
37 references while it was 1139, 49354 and 41125 references for selenophene, thiophene and
38 furan respectively. This article follows one of our previous works on [Ru(terpy)₂
39 selenophene]-based polymer film [10] and describes the preparation of the new 4'-
40 (tellurophen-2-yl)-2,2':6',2''-terpyridine (**1**) and its homoleptic Ru(II) complex (**2**) (Fig. 1).
41 These new compounds have been characterized by different techniques (NMR, UV-Vis, Mass
42 spectrometry). Electrochemical oxidation and coupling of tellurophene moieties in complex **2**
43 were carried out to enable formation of a thin polymer film which exhibited very interesting
44 properties.



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

47
48
49 **2. Experimental**

50
51 *2.1. Chemicals and apparatus*

52
53 All reagents were purchased from commercial suppliers and used as received unless otherwise
54 stated. Tellurophene was prepared according to literature [11]. Tellurophen-2-aldehyde was
55 prepared using a slightly modified literature [12] procedure (see supplementary material).
56 Column chromatography was carried out onto silica gel (40-63 μm). ^1H and ^{13}C NMR were
57 recorded on a Bruker Avance 400 spectrometer at 400 MHz and 100 MHz respectively.
58 Melting point was recorded on a Stuart SMP 3 melting point apparatus and is uncorrected.
59 UV-Vis spectra of complex **2** ($5 \cdot 10^{-3}$ M solution in acetonitrile) and of the film onto FTO
60 were recorded onto an Agilent Technologies Cary 300 spectrometer. HR-MS spectra were
61 recorded at Wellience (Dijon, France). SEM and EDX experiments were realized with a MEB
62 FEB TESCAN apparatus. Electrochemical measurements were carried out using a
63 PGSTAT30 AUTOLAB potentiostat and a classical three-electrode setup consisting of a
64 Ag/AgCl/KCl (3M) reference electrode (-36mV/SCE), a platinum wire counter-electrode and
65 a working electrode on which the deposit was realized. The working electrode was a platinum
66 disk (0,071 cm^2) or a Fluorine-doped Tin Oxide plate (1.5 x 1.5 cm).

67
68 *2.2. Synthesis of 4'-(tellurophen-2-yl)-2,2':6',2''-terpyridine (1)*

69
70 To a solution of 2-acetylpyridine (1.51 g; 12.5 mmol) in ethanol (33 mL) are successively
71 added tellurophene-2-aldehyde (1.30 g; 6.2 mmol), 85% potassium hydroxide pellets and 25%
72 aqueous ammonia solution (19 mL). The solution is stirred at room temperature for 24 hours.
73 The precipitate is then filtered and washed with ice cold 50% ethanol until washings are
74 colourless. The product is dried under vacuum over phosphorus pentoxide. Crude **1** is
75 sufficiently pure (>98 % by quantitative ^1H NMR [13]) to be used in next step without
76 purification. Light brown solid (0.82 g; 32 %) mp=196-200°C (dec.). ^1H NMR (CDCl_3 , 400
77 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,
78 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,
79 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
80 = 7.4, 4.8, 1.2 Hz, H5,5''). ^{13}C NMR (CDCl_3 , 100 MHz), δ (ppm) = 156.1 ; 156.0 ; 149.1 ;
81 149.0 ; 146.9 ; 138.8 ; 136.8 ; 136.1 ; 128.7 ; 123.9 ; 121.4 ; 118.5. HR-MS: calc. for
82 $[\text{C}_{19}\text{H}_{13}\text{N}_3\text{Te} + \text{H}]^+$ 414.02445, found 414.02376.

88 2.3. Synthesis of $[Ru(\mathbf{1})_2]PF_6$ ($\mathbf{2}$):

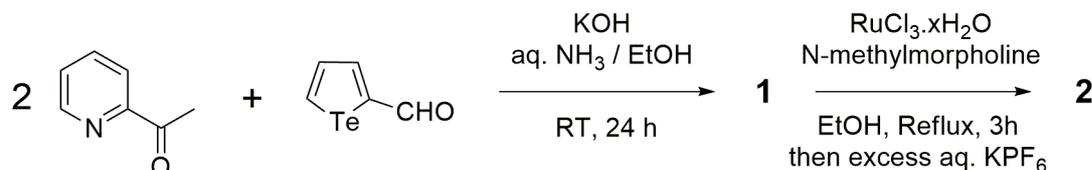
89
90 To a mixture of ligand $\mathbf{1}$ (0.795 g; 1.9 mmol), $RuCl_3 \cdot xH_2O$ (0.283g; 1.3 mmol) in ethanol
91 (140 mL) is added N-methylmorpholine (10 drops of Pasteur pipette). The reaction mixture is
92 refluxed for 3 hours. After cooling to room temperature, the deep red solution is poured onto a
93 saturated KPF_6 aqueous solution and ethanol is removed on a rotary evaporator. The resulting
94 precipitate is filtered, washed with water and dried under vacuum over phosphorus pentoxide.
95 This crude product is purified by column chromatography (silica gel; eluent:
96 acetone/water/saturated aqueous KNO_3 100:0:0 to 70:30:0.1 v:v:v). Fractions containing the
97 product are poured onto saturated KPF_6 aqueous solution and acetone is removed on a rotary
98 evaporator. The precipitate is filtered, washed with water and diethyl ether and dried under
99 vacuum over phosphorus pentoxide. This afford pure $\mathbf{2}$ as a red solid (0.595 g; 51%). 1H
100 NMR (CD_3CN , 400 MHz), δ (ppm) = 9.39 (d, 1H, J = 6.4 Hz, Ha), 8.80 (s, 2H, H3',5'), 8.73
101 (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''),
102 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
103 MHz), δ (ppm) = 158.6 ; 155.9 ; 153.0 ; 148.3 ; 144.8 ; 139.8 ; 139.4 ; 138.5 ; 133.8 ; 128.0 ;
104 125.2 ; 121.4. HR-MS: calc. for $[C_{38}H_{26}N_6RuTe_2]^{2+}$ 463.96843, found 463.96816.
105
106
107

108 **3. Results and discussion:**

109
110 3.1. Synthesis and characterization of ligand $\mathbf{1}$ and complex $\mathbf{2}$.

111
112 Terpyridine $\mathbf{1}$ is prepared by reacting tellurophene-2-aldehyde and 2-acetylpyridine with
113 potassium hydroxide in a mixture of ethanol and aqueous ammonia according to the protocol
114 of Wang and Hanan [13] (Fig. 2). At this point, although obtained in a relatively low yield
115 (32%), the compound is sufficiently pure (> 98% by quantitative 1H NMR [14]) to be used for
116 the preparation of complex $\mathbf{2}$ without purification.

117 The latter was prepared by reacting ligand $\mathbf{1}$ with $RuCl_3$ in refluxing ethanol in the presence
118 of N-methylmorpholine and after precipitation in excess aqueous hexafluorophosphate salt
119 (potassium for instance), according to a classical protocol for the preparation of homoleptic
120 bis-terpyridine complexes [6, 10, 15].
121



125 **Fig. 2.** Synthetic pathway to ligand $\mathbf{1}$ and complex $\mathbf{2}$.

126 1H and ^{13}C NMR spectra are in agreement with the proposed structures for compounds $\mathbf{1}$ and
127 $\mathbf{2}$. Their identification was further confirmed by mass spectrometry, since the molecular ion
128 peaks as well as the isotopic distribution agree with the proposed formulas. Moreover,
129 complex $\mathbf{2}$ was characterized by UV-Vis spectroscopy. Especially, the spectrum of $\mathbf{2}$ exhibit a
130 MLCT (Metal to Ligand Charge Transfer) band in the visible region ($\lambda_{max}=504$ nm), a
131 phenomenon that account for a bis-terpyridine $Ru(II)$ complex formation as described
132 previously, especially for chalcogenophene-functionalized terpyridine complexes [16].
133

134 3.2. Electrochemistry

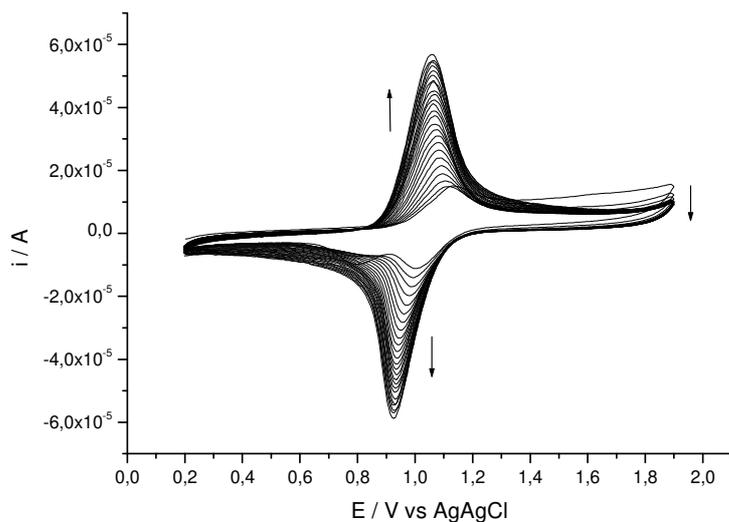
134 Fig. 3 shows cyclic voltammogram obtained after 25 cycles in trifluoroborate etherate (TFBE)
135 solution containing 1 mM of compound **2** on platinum (Pt) electrode. Irreversible oxidation
136 wave of tellurophene moiety is slightly visible as a current shouldering at a potential of about
137 1.63 V vs Ag/AgCl but only on the first cycle. As noticed in previous studies, oxidation
138 potential of such pendant moieties decreases with heteroatom electronegativity. Indeed, for
139 similar molecules, it was lower with selenophene, thienyl and furyl moieties [10,16]. For
140 following cycles, tellurophene oxidation signal decreases with potential cycling. This is due to
141 polymer growth on the surface getting polymerization process more and more difficult after
142 each cycle as film's quality gets poorer and poorer. As fully described in the literature [17-24]
143 for such heteroaromatic compounds, polymerization mechanism starts with tellurophene
144 moieties oxidation to form radical cations which rapidly couple together (due to their unstable
145 nature) leading to dimers after loss of protons. Oligomers oxidation being easier than
146 oxidation of monomers, polymerization process occurs to enable growing of the film.
147 Reversible signal of Ru(terpy)₂²⁺/Ru(terpy)₂³⁺ is centered at about 1 V vs Ag/AgCl.
148 Continuous increase in anodic and cathodic current with potential scanning shows
149 accumulation of an electroactive film at the electrode surface. Indeed, after 25 cycles, an
150 adherent deep red coating is present on platinum electrode.

151 It was also possible to get a film of good quality on glassy carbon in the same conditions
152 (results not shown). Polymerization was also successful on gold, but the obtained coating had
153 poor adherence. However, in acetonitrile, no deposit was obtained probably due to too high
154 solubility of oligomers in this solvent. Even if irreversible oxidation of tellurophene was well
155 visible, the voltammogram only showed diffusional signal for Ru(terpy)₂²⁺/Ru(terpy)₂³⁺ couple
156 and the surface was unchanged after the experiment.

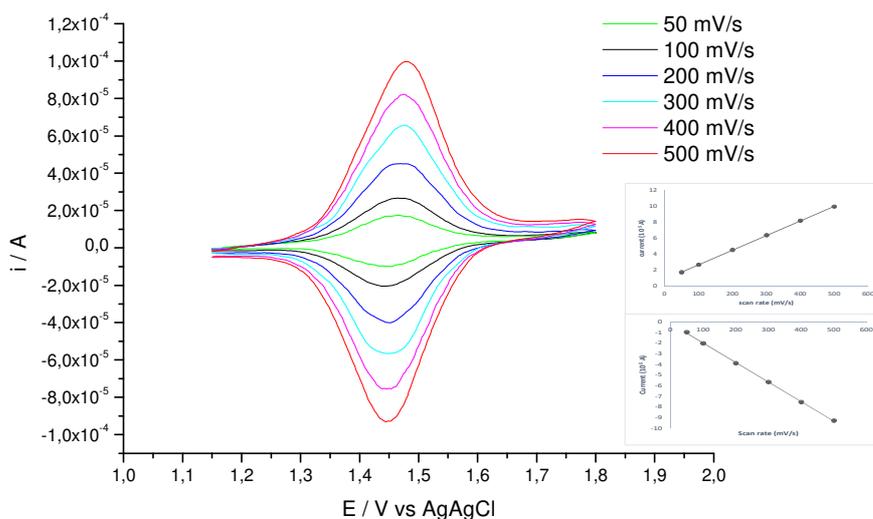
157 Electroactivity of the polymer film grown on Pt was investigated in monomer free 0.5 M
158 tetraethylammonium tetrafluoroborate (TEABF₄) acetonitrile solution after abundant rinsing
159 of the electrode with acetonitrile. Typical adsorbed Ru(terpy)₂^{2/3+} reversible behavior was
160 observed with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

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

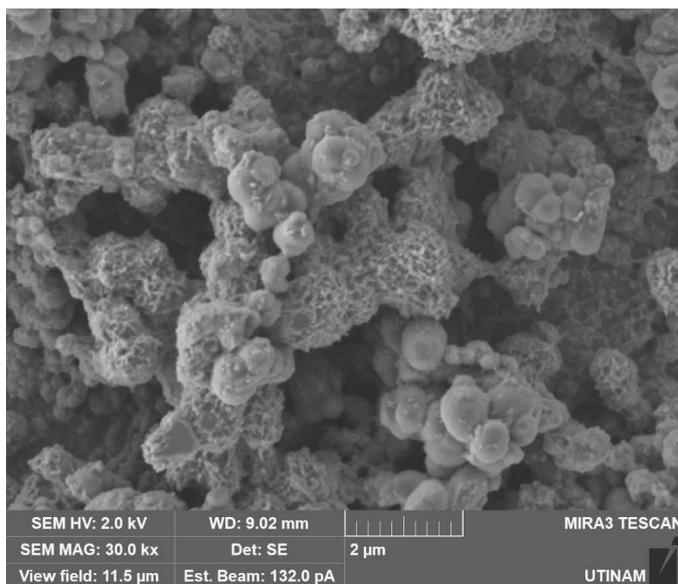
167 To investigate eventual electrochromic properties of poly-**2** film, deposits were grown on
168 FTO substrates from 1 mM and 3 mM of compound **2** in TFBE solution using cyclic
169 voltammetry in the same conditions that in Fig. 3 (25 cycles). It was not possible to work at
170 higher concentration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



184
 185 **Fig. 3.** Cyclic voltammogram (50 mV/s) of 1 mM of compound **2** in trifluoroborate etherate
 186 (TFBE) on platinum disk (0.071 cm²). The arrows indicate current evolution with potential
 187 scanning.
 188



189
 190 **Fig. 4.** Cyclic voltammogram at different scan rates of poly-**2** modified platinum electrode
 191 (0.071 cm²). Experiments were carried out in monomer free 0.5 M tetraethylammonium
 192 tetrafluoroborate (TEABF₄) acetonitrile solution. The curves on bottom right represent anodic
 193 and cathodic peaks current evolution with scan rate.
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Fig. 5. Scanning Electron Microscopy images of poly-2 modified platinum electrode.



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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.

209
210

4. Conclusions

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

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

221

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223

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