SUPPORTING INFORMATION

DOI: 10.1002/ejic.201300366

Title: An Electrochemical and Raman Spectroscopy Study of the Surface Behaviour of Mononuclear Ruthenium and Osmium Polypyridyl Complexes Based on Pyridyl- and Thiophene-Based Linkers

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Synthesis and characterisation

2-(3-thio)imidazo[1,10-phenanthroline (thimphen)

Thimphen was synthesised using literature procedures. \(3.50 \text{ g (17 mmol) 1,10-phenanthroline-5,6-dione and 11.55 g (150 mmol) of ammonium acetate were dissolved in 150 cm}^3 \text{ of glacial acetic acid. The reaction mixture was warmed and 1.56 cm}^3 \text{ (17 mmol) 3-thiophene carboxaldehyde was added dropwise. The reaction mixture was heated to 90 °C for 5 h, cooled to room temperature, poured onto 500 cm}^3 \text{ of } \text{H}_2\text{O and neutralised with conc. ammonia. The resulting brown precipitate was filtered, washed with water and dried with diethyl ether. This crude product was recrystallized from hot methanol. Yield: 50% (2.60g).}

\[
\text{Elem. Anal: } \text{C: 44.2, H: 2.6, N: 11.1; Calculated: C: 44.2, H: 2.6, N: 11.1}
\]

\(\text{[Ru(D}_{\text{thimphen})\text{]}(\text{PF}_6)\text{]}^{2+}\)

374 mg (1.2 mmol) of thimphen was dissolved in 25 cm\(^3\) ethanol:water and heated to reflux temperature. 500 mg (0.96 mmol) Ru(bpy)\(_2\)Cl\(_2\) and 2H\(_2\)O was added to the reaction mixture over 1 h. The resulting mixture was heated at reflux for 5 h. The ethanol was removed from the mixture by rotary evaporation. The remaining solution was allowed to cool to room temperature and a saturated aqueous solution of NH\(_4\)PF\(_6\) was added. The orange mixture was left at 5 °C overnight, filtered and the resulting solid was columned on alumina with CH\(_3\)CN and recrystallized from acetonitrile: water 50:50. Yield: 33% (318.9 mg); \(^1\)H NMR: \(D_2\)-DMSO \(\delta \) 9.90 (dd, 2H, \text{H}_3, \text{J} = 4.8 Hz), 8.82 (dd, 4H, \text{H}_4^\text{a}, \text{J} = 7.6 Hz), 8.39 (dd, \text{H}_4^\text{b}, \text{J} = 4.0 Hz), 8.20 (t, \text{H}_4^\text{a}, \text{J} = 8 Hz, \text{H}_5^\text{a}, \text{J} = 8 Hz), 8.09 (t, \text{H}_4^\text{b}, \text{J} = 8.4 Hz, \text{H}_5^\text{b}, \text{J} = 8.4 Hz), 8.05 (d, \text{H}_2^\text{a}, \text{J} = 5.2 Hz), 7.93-7.89 (m, 3H, \text{H}_2^\text{b}, \text{J} = 4.0 Hz), 7.85-7.83 (m, \text{H}_3, \text{J} = 8 Hz), 7.61-7.56 (m, 4H, \text{H}_5^\text{a}, \text{J} = 6.4 Hz, \text{H}_5^\text{b}, \text{J} = 6.8 Hz). Mass spec: Observed m/z: 303.2 \([\text{M}]+\); Calc m/z = 302.37; Elem. Anal.: C\(_{14}\)H\(_8\)N\(_4\)S\(_{10}\)O\(_3\)PF\(_6\): Observed: C: 57.8, H: 3.8 N: 15.6; S 9.5 Calculated: C: 57.4, H: 4.4, N: 15.7, S 9.0.

\(\text{[Os(bpy)}_2\text{thimphen)](PF}_6\text{)}_2\)

61 mg (0.20 mmol) thimphen was dissolved in 5 cm\(^3\) ethylene glycol at 100 °C. 100 mg (0.17 mmol) [Os(bpy)_2Cl_2] treated with thimphen and 11.55 g (150 mmol) of ammonium acetate were dissolved in 150 cm\(^3\) of glacial acetic acid. The reaction mixture was warmed and 1.56 cm\(^3\) (17 mmol) 3-thiophene carboxaldehyde was added dropwise. The reaction mixture was heated to 90 °C for 5 h, cooled to room temperature, poured onto 500 cm\(^3\) of H\(_2\)O and neutralised with conc. ammonium. The resulting brown precipitate was filtered, washed with water and dried with diethyl ether. This crude product was recrystallized from hot methanol. Yield: 50% (2.60g). \(\text{[Os(bpy)}_2\text{thimphen)](PF}_6\text{)}_2\): Observed m/z: 805.2 \([\text{M}]+\); Calc m/z = 805.0 \(\text{m/z: 402.5} \) \text{calc \[M-2PF}_6\text{]}^{2+} \text{m/z = 402.5}

Elem. Anal: \(\text{C}_{33}\text{H}_{26}\text{N}_{10}\text{O}_{5}\text{S}_{10}\text{PF}_{4}\_2\): Found: C: 38.8, H: 2.3, N: 8.8;

\(\text{[Ru(D}_{2-bpy)}_2\text{thimphen)](PF}_6\text{)}_2\)

54 mg (0.18 mmol) thimphen ligand was dissolved in 25 cm\(^3\) 2:1 ethanol:water and heated to reflux temperature. 75 mg (0.15 mmol) \(\text{[Ru(D}_{2-bpy)}_2\text{Cl}_2\) in 25 cm\(^3\) 2:1 ethanol:water was added to the reaction mixture and heated to reflux for 5 h. The ethanol was removed from the mixture by rotary evaporation. The remaining solution was allowed to cool to room temperature and a
saturated solution of NH₄PF₆ was added. The orange mixture was left at 5 °C overnight, filtered and the resulting solid was columned on alumina with CH₂Cl₂;CHCN 50:50. Yield: 31% (48 mg). ¹H NMR: D₆-DMSO ³H δ = 9.03 (d, 2H, H6), 8.38 (dd, H5, J = 1.6 Hz), 8.06 (d, 2H, H2, J = 4.4 Hz), 7.94-7.89 (m, 3H, H3+H6'), 7.86-7.82 (m, H2')

[Ru(bpy)₂(phendione)](PF₆)₂

The complex was prepared by a literature procedure. 300 mg (0.34 mmol) [Ru(bpy)₂](phen)](PF₆)₂ was dissolved in 7 cm³ H₂SO₄ with stirring. 349 mg (3.39 mmol) NaBr was added, followed by 5.5 cm³ 70% HNO₃. The resulting mixture was heated to 110 °C for 20 min, cooled to room temperature and poured onto 50 cm³ cold saturated KPF₆ (aq) solution. This mixture was placed in a fridge overnight, filtered and washed with water. This solid used in the next step without further purification.

[Ru(bpy)₂(pyrophen)](PF₆)₂

312 mg (0.34 mmol) [Ru(bpy)₂(phendione)](PF₆)₂ was dissolved in 9 cm³ dry glacial acetic acid with 523 mg (6.78 mmol) ammonium acetate. This mixture was heated to 100 °C and 0.03 cm³ (0.34 mmol) 4-pyridyl carboxaldehyde was added dropwise. The resulting mixture was heated to 100 °C for 1 h. After cooling to room temperature 20 cm³ acetonitrile was added and the product was precipitated by addition of a saturated aqueous solution of KPF₆. The crude product was filtered, dried at the pump and purified by column chromatography on alumina using acetonitrile as an eluent, followed by recrystallization from 1:1 acetonitrile: water. Yield: 153 mg (45.1%) ¹H NMR: D₆-DMSO δ: 9.13 (2H, d, H4, H2), 8.93 (2H, d, H6), 8.89-8.84 (4H, dd, H6'), 8.30 (2H, d, H7, Hz), 8.24-8.21 (4H, m, H3, H2), 8.12(2H, t, H4''), 8.02 (dd, 2H, H3''), 7.84 (2H, d, H3'), 7.64-7.59 (4H, m, H5'), 7.37-7.32 (2H, m, H4') Mass spec; Observed m/z: 857.4 (90) [M-PF₆]⁺ calc 855.8; m/z 356 (100) [M-2PF₆]²⁺ calc m/z = 355.40. Elem: Anal: [C₃8H₁₇N₄Ru](PF₆)₂.2H₂O Calculated: C: 44.0, H: 3.0, N: 12.1; Found: C: 44.0, H: 2.6, N: 10.6;

[Ru(D₆-bpy)₂(pyrophen)](PF₆)₂

This compound was prepared as outlined above for the non-deuterated analogue. 256 mg (0.28 mmol) [Ru(D₆-bpy)₂(phen)](PF₆)₂ was dissolved in 5 cm³ H₂SO₄ with stirring. 292 mg (2.80 mmol) NaBr was added, followed by 3.5 ml 70% HNO₃. The resulting mixture was heated to 110°C for 20 min, cooled to room temperature and poured onto 25 cm³ cold saturated KPF₆ (aq) solution. This mixture was placed in the fridge overnight, filtered and washed with water. This solid was used in the next step without further purification. 229 mg (0.24 mmol) [Ru(D₆-bpy)₂(phendione)](PF₆)₂ was dissolved in 10 cm³ dry glacial acetic acid with 374 mg (4.85 mmol) ammonium acetate. This mixture was heated to 100 °C and 0.02 cm³ (0.24 mmol) 4-pyridyl carboxaldehyde was added dropwise. The resulting mixture was heated to 100 °C for 1 h. After cooling to room temperature 50 cm³ acetone was added and the resulting solution was added to a large amount of diethyl ether with stirring. The resulting suspension was filtered and the orange solid was dried at the pump. The crude product was purified by column chromatography on alumina using acetonitrile as an eluent. Yield: 60 mg (25 %) ¹H NMR: D₆-DMSO δ: 9.15 (2H, d, H4, H2), 8.98 (2H, d, H6, J = 7.2 Hz), 8.33 (2H, d, H5, J = 7.2 Hz), 8.24 (2H, d, H2, J = 7.8), 8.06-8.01 (2H, m, H3')

[Os(bpy)₂(phendione)](PF₆)₂

[Os(bpy)₂(phendione)](PF₆)₂: 400 mg (0.70 mmol) [Os(bpy)₂Cl₂].2H₂O and 166 mg (0.84 mmol) 1,10-phenanthroline was placed in 10 cm³ ethylene glycol and heated to reflux for 4 h. The resulting mixture was cooled to room temperature and added slowly to a 50 cm³ aqueous saturated NH₄PF₆ solution. The resulting suspension was left at 4 °C overnight and filtered. The green/black solid obtained was recrystallised from acetonewater:water 50:50. Yield: 499 mg (73.6 %) ¹H NMR: D₆-DMSO δ: 8.96 (2H, d, H6), 8.96-8.81 (6H, m, H4, H6, H5'), 8.32 (2H, d, H7), 8.16 (2H, d, H2), 8.03(2H, t, H4''), 7.95-7.90 (4H, m, H3, H5'), 7.75 (2H, d, H3'), 7.63-7.220 (2H, m, H4')(Os(bpy)₂(phendione)](PF₆)₂. This reaction was carried out as for [Ru(bpy)₂(phendione)](PF₆)₂, using 500 mg [Os(bpy)₂(phendione)](PF₆)₂ (0.51 mmol) and 529 mg NaBr (5.14 mmol) in 7.5 cm³ H₂SO₄ and 5.5 cm³ 70% HNO₃. This reaction was also assumed to occur in quantitative yield and was used immediately in the next reaction.

[Os(bpy)₂(pyrophen)](PF₆)₂

515 mg (0.51 mmol) [Os(bpy)₂(phendione)](PF₆)₂ was dissolved in 15 cm³ dry glacial acetic acid with 792 mg (10.28 mmol) ammonium acetate. This mixture was heated to 100 °C and 0.049 cm³ (0.51 mmol) 4-pyridyl carboxaldehyde was added dropwise. The resulting mixture was heated to 100 °C for 1 h. After cooling to room temperature 40 cm³ acetonitrile was added and
the resulting solution was added to a large amount of diethyl ether with stirring. The resulting suspension was filtered and the orange solid was dissolved in a small volume of acetone. This solution was diluted to twice its volume with water and the product was precipitated by addition of a saturated aqueous solution of KPF$_6$. This crude product was filtered, dried at the pump and purified by column chromatography on alumina using acetonitrile as an eluent followed by recrystallization from 1:1 acetone: water. Yield: 33mg (29.5%) $^1$H NMR: D$_2$-DMSO $\delta$: 8.96 (2H, d, H$_6$), 8.96-8.81 (6H, m, H$_4$, H$_7$), 8.32 (2H, d, H$_2$), 8.16 (2H, d, H$_2$), 8.03 (2H, t, H$_4$), 7.95-7.90 (4H, m, H$_3$, H$_3'$), 7.75 (2H, d, H$_1$), 7.263-7.220 (2H, m, H$_4$). Mass spec: Observed m/z: 947 (100) [M-PF$_6$]$^+$ Calc m/z = 944.94; Observed: m/z 801 (25) [M-2PF$_6$]$^+$; Calculated: 799 [M]$^-$; m/z 401 (95) [M-2PF$_6$]$^{2+}$ calc 399.5 Elem. Anal. [C$_{38}$H$_{27}$N$_9$Os](PF$_6$)$_2$.$2$H$_2$O; Calculated: C: 40.5, H: 2.8, N: 11.1, Found: C: 41.9, H: 3.2, N: 8.2;

$^1$H NMR spectroscopy

![Figure S1 Labelling scheme used for assignment of $^1$H NMR spectra of thimphen and pyrphen.](image-url)
Figure S2 $^1$H NMR spectra of (a) thimphen (b) [Ru(D$_8$-bpy)$_2$(thimphen)]$^{2+}$ and (c) [Ru(bpy)$_2$(thimphen)]$^{2+}$ in D$_6$-DMSO.
Figure S3 $^1$H NMR spectra of (upper) [Ru(bpy)$_2$(pyrphen)]($\text{PF}_6$)$_2$ and (lower) [Os(bpy)$_2$(pyrphen)]($\text{PF}_6$)$_2$ in D$_6$-DMSO.
UV/Vis absorption spectroscopy

Figure S4 UV/vis absorption spectra for [Ru(bpy)$_2$(thimphen)]($\text{PF}_6$)$_2$ as a function of pH in the range from pH 2 to pH 12.

Figure S5 UV/vis absorption spectra for [Ru(bpy)$_2$(thimphen)]($\text{PF}_6$)$_2$ as a function of pH in the range from pH 1 to pH 5.
Figure S6 UV/vis absorption spectra for [Ru(bpy)$_2$(thimphen)]([PF$_6$])$_2$ as a function of pH in the range from pH 5 to pH 12 and pH dependence of the absorbance of [Ru(bpy)$_2$(thimphen)]([PF$_6$])$_2$ at 367 nm.
Figure S7 pH dependence (pH 2 to 13.5) of the absorbance of [Ru(bpy)$_2$(pyphen)](PF$_6$)$_2$ at 350 nm.
Figure S8 Resonance Raman spectra of (i) [Ru(bpy)₂(thimphen)]²⁺, (ii) [Os(bpy)₂(thimphen)]²⁺, (iii) [Ru(bpy)₂(pyroph)]²⁺, (iv) [Os(bpy)₂(pyroph)]²⁺ and (v) [Ru(bpy)₃]²⁺ in acetonitrile at λₖₑᵢₙ (a) 355 nm, (b) 449 nm and (c) 473 nm. Spectra are baseline corrected and solvent subtracted.
Preparation of electrodes for monolayer formation and SERS spectroscopy

Pt electrodes were prepared by manually polishing with 1.0, 0.3 or 0.05 µm alumina slurries (CH Instruments, Inc.) followed by sonication in Millipore water after each successive grade and finally in the appropriate electrolyte solvent. Prior to sonication in the electrolyte solvent, the Pt electrode was cleaned electrochemically by cycling in 0.5 M H$_2$SO$_4$ (Aldrich, 99.999%). The Au bead electrode was manually cleaned by connecting it to a 3 V battery and dipping it into 0.5 M H$_2$SO$_4$, followed by immersion in 1 M HCl (Aldrich) when a rusty orange/brown colour forms. The bead is then cleaned electrochemically following the procedure described for Pt above. For the formation of monolayers, the Pt and Au electrodes were immersed in a solution (500 µM) of the surface active molecule for a minimum period of 24 hours. A mixture of DMF (Aldrich, spectrophotometric grade, 99.8%) and H$_2$O (1:1) was used as the deposition solvent for the [M(bpy)$_2$(pyrphen)]$^{2+}$ complexes with EtOH (Breanntag, GPR grade) used for the [M(bpy)$_2$(thimphen)]$^{2+}$ complexes. Lithium perchlorate (LiClO$_4$, Aldrich, 99.99 %) in H$_2$O (Millipore) or tetrabutylammonium perchlorate (TBAClO$_4$, Fluka, electrochemical grade ≥ 99.0 %) in acetonitrile were used as electrolyte/solvent systems for surface confined measurements.

The surface coverage of each of the monolayers are shown in Table 3 and have been calculated using

\[ \Gamma = \frac{Q}{nFA} \]

where \(\Gamma\) represents the surface coverage in mol cm$^{-2}$, \(Q\) is the Faradaic charge, \(n\) is the number of electrons involved in the redox process, \(F\) is the Faraday constant and \(A\) is the real surface area of the electrode. Using the values obtained for the surface coverage, the average area that each molecule occupies, \(A_{\text{molec}} \) (Å$^2$) can be calculated from Eq. 2.

\[ A_{\text{molec}} = \frac{10^{16}}{N_A \Gamma} \]

where \(N_A\) is the Avogadro constant.

Gold bead electrodes, formed by melting gold wire in a butane flame, were cleaned electrochemically in 0.5 M H$_2$SO$_4$ by cycling between -0.4 – 1.2 Volts vs Hg/HgSO$_4$, with a Pt-wire counter electrode. Subsequently electrochemical stripping was carried out using sweep-step functions in 0.1 M KCl(aq), with a Pt-wire counter electrode and a SCE reference electrode. The potential was increased from -0.3 to 1.2 V (vs. SCE) at 1 V/s. The gold electrode was held at 1.2 V for 30 s. Then the potential was swept back to -0.3 V at 0.5 V/s and held at -0.3 V for 1.2 s. This procedure was repeated 24 times after which the surface of the gold electrode appeared rusty brown. The beads were immersed overnight in a 1 mg/mL solution of the complex in question in ethanol. Prior to measurements the beads for dipped in fresh ethanol three times. The Raman spectra obtained using Au beads were recorded in air.

**Figure S9** Cyclic voltammetry of a monolayer of Os(pyrphen) (top) on a Pt macro electrode (electrochemical surface area = 0.0698 cm$^2$) following immersion overnight in a 500 µM solution of the complex in DMF/H$_2$O (1:1), vs. SCE, using 0.1 M LiClO$_4$ in H$_2$O as the supporting electrolyte. A linear relation between the peak current, $i_p$, and scan rate was obtained (anodic $R^2 = 0.9984$ and cathodic $R^2 = 0.9964$).
### Table S1. Percentage contributions of selected parts of [Ru(II)pyrphen]^{2+} to selected frontier orbitals.

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### Table S2. Percentage contributions of selected parts of [Ru(II)thimphen]^{2+} to selected frontier orbitals.

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### Table S3. Percentage contributions of selected parts of [Os(II)pyrphen]^{2+} to selected frontier orbitals.

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Table S4. Percentage contributions of selected parts of [Os(II)thimphen]^{2+} to selected frontier orbitals.

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Table S5. Percentage contributions of selected parts of [Ru(III)pyrphen]⁺ to selected frontier orbitals.

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Table S6. Percentage contributions of selected parts of [Ru(III)thimphen]⁺ to selected frontier orbitals.

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Table S10. Percentage contributions of selected parts of the deprotonated [Ru(II)thimphen]$^{1+}$ to selected frontier orbitals.

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