

## Supporting Information

### Spectro-electrochemical Study of Iron and Ruthenium Bis-terpyridine Complexes with Methyl Viologen-like Subunits as Models for Supramolecular Polymers

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#### Experimental section

##### General

All reagents and solvents were obtained from commercial suppliers (VWR, Fisher Scientific, Acros or Merck) and used as received unless stated otherwise. For experiments under microwave irradiation, a Biotage Initiator or a Discover SP microwave synthesizer were used. The ligand tolyltpy (4'-tolyl-2,2':6',2''-terpyridine) and 6'-(pyridine-2-yl)-2,2':4',4''-terpyridine **1** were prepared according to a published procedure.<sup>[1]</sup> The precursor 4'-(-p-aminophenyl)2,2':6',2''-terpyridine **2** is synthesized according to a published procedure.<sup>[2]</sup> The synthesis of the heteroleptic complexes was carried out as a two-step procedure with [Ru(tolyltpy)]Cl<sub>3</sub> as an intermediate adapted from the literature.<sup>[3]</sup>

##### Instrumentation details

NMR experiments were performed on a Bruker AV-400 (<sup>1</sup>H: 400 MHz and <sup>13</sup>C{<sup>1</sup>H}: 101 MHz, Montréal, Canada) spectrometer, a Fourier 300 (<sup>1</sup>H: 300 MHz and <sup>13</sup>C{<sup>1</sup>H}: 75 MHz, Bruker Biospin, Rheinstetten, Germany) spectrometer, or a Bruker Avance 500 (<sup>1</sup>H: 500 MHz and <sup>13</sup>C{<sup>1</sup>H}: 126 MHz, Montréal, Canada) spectrometer at 295 K. The chemical shifts are reported in ppm relative to the residual peak of the solvent as the internal standard. High-resolution mass spectrometry (HR-MS) were recorded either on a SYNAPT G2-Si spectrometer from Waters or a Bruker Daltonics microTOF focus. Samples were ionized by electrospray ionization (ESI). UV-vis absorption spectra were recorded on an Agilent Cary 5000 UV-vis-NIR spectrometer.

Electrochemical measurements were carried out in a three-electrode set-up with a glassy carbon disk (d=3mm) working electrode (WE), a platinum wire as counter electrode (CE) and a silver wire as pseudo-reference (RE), using ferrocene as internal

standard. Potentials are reported vs the internal standard ferrocenium/ferrocene couple. Measurements were carried out using a Gamry Interface1010 potentiostat. Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) was used as electrolyte in a concentration of 0.1 M. The concentration of the analyte was 0.5 mM. The samples were purged with argon before each measurement. The cyclic voltammograms were recorded with a sweep rate of 100 mV/s in dried acetonitrile or dimethyl sulfoxide.

Spectro-electrochemical experiments were carried out in a quartz glass cell with 1 mm path length or 1 cm path length. The three-electrode set-up consisted of a platinum mesh WE, a platinum wire CE, and a silver wire as RE (organic electrolyte) or Ag/AgCl reference electrode (aqueous electrolyte). Measurements were conducted in argon-purged dry acetonitrile or dimethyl sulfoxide with 0.1 M TBAPF<sub>6</sub> or 1 M KCl in water as supporting electrolyte. The sample concentration was chosen to yield an absorptivity between 0.5 and 1. The potential was controlled by a Gamry Interface1010 potentiostat. The voltage was changed in 0.1 V steps, then kept constant while the UV-vis spectrum was recorded by an Agilent Cary 5000 UV-vis-NIR spectrometer.

## Synthesis

### S.I.1.1.1. **N''-(2,4-dinitrophenyl)-6'-(pyridine-2-yl)-[2,2':4',4''-terpyridin]-N''-ium chloride I3**

Under inert-gas atmosphere, a solution of 6'-(pyridin-2-yl)-2,2':4',4''-terpyridine (450 mg, 1.45 mmol, 1 eq) and 2,4-dinitrochlorobenzene (1.47 g, 7.25 mmol, 5 eq) in 100 mL ethanol was heated to reflux for four days. The solvent was reduced, and diethyl ether was added. The precipitate was filtered off and washed with diethyl ether to yield the product as a yellow solid (300 mg, 585  $\mu$ mol, 40%).

<sup>1</sup>H-NMR (500 MHz, CD<sub>3</sub>OD):  $\delta$  = 9.47 (d, <sup>3</sup>J = 7.0 Hz, 2H), 9.33 (d, <sup>4</sup>J = 2.4 Hz, 1H), 9.06 (s, 2H), 8.97 (m, 3H), 8.76 (m, 4H), 8.39 (d, <sup>3</sup>J = 8.6 Hz, 2H), 8.08 (td, <sup>3</sup>J = 7.8 Hz, <sup>4</sup>J = 1.6 Hz, 2H) and 7.57 ppm (m, 2H). <sup>13</sup>C{<sup>1</sup>H}-NMR (126 MHz, CD<sub>3</sub>OD):  $\delta$  = 158.7, 158.6, 156.1, 151.3, 150.5, 147.8, 144.7, 144.6, 140.0, 139.2, 132.7, 131.2, 127.1, 126.3, 123.3, 123.1 and 120.4 ppm. ESI-MS: m/z [M]<sup>+</sup> calcd for C<sub>26</sub>H<sub>17</sub>N<sub>6</sub>O<sub>4</sub>: 477.13058; found: 477.13194; difference: 2.8 ppm.

#### **S.I.1.1.2. N''-phenyl-6'-(pyridin-2-yl)-[2,2':4',4''-terpyridin]-N''-ium chloride L1**

Under inert gas atmosphere, a solution of N''-(2,4-dinitrophenyl)-6'-(pyridin-2-yl)-[2,2':4',4''-terpyridin]-N''-ium chloride **1** (100 mg, 495  $\mu\text{mol}$ , 1 eq) and aniline (100  $\mu\text{L}$ , 102 mg, 1.10 mmol, 5.6 eq) in 10.0 mL ethanol was heated to reflux over night. Diethyl ether was added, and the precipitate was filtered off and washed with diethyl ether to yield the product as a yellow solid (70.0 mg, 166  $\mu\text{mol}$ , 85%).

$^1\text{H-NMR}$  (500 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  = 9.42 (d,  $^3\text{J}$  = 6.8 Hz, 2H), 9.03 (s, 2H), 8.82 (d,  $^3\text{J}$  = 6.7 Hz, 2H), 8.74 (m, 4H), 8.39 (d,  $^3\text{J}$  = 8.6 Hz, 2H), 8.08 (t,  $^3\text{J}$  = 7.6 Hz, 2H), 7.98 (m, 2H), 7.81 (m, 3H) and 7.56 ppm (m, 2H).  $^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  = 158.6, 156.6, 156.3, 150.5, 146.6, 145.0, 144.2, 139.1, 133.0, 131.9, 127.2, 126.2, 125.5, 123.1 and 120.2 ppm. ESI-MS:  $m/z$   $[\text{M}]^+$  calcd for  $\text{C}_{26}\text{H}_{19}\text{N}_4$ :387.16042; found:387.16035; difference: 0.2 ppm.

#### **S.I.1.1.3. 1''-(4-([2,2':6',2''-terpyridin]-4'-yl)phenyl)-6'-(2-pyridinyl)-[2,2':4',4''-terpyridin]-1''-iumchlorid L2**

Under inert gas atmosphere, a suspension of **I2** (791 mg, 1.54 mmol, 1 eq) and **I3** (500 mg, 1.54 mmol, 1 eq) in 100 mL degassed ethanol was heated to reflux for four days. After cooling to room temperature, diethyl ether is added. The formed precipitate was collected by filtration and washed with diethyl ether to yield the product as a yellow-brown solid (589 mg, 856  $\mu\text{mol}$ , 56%).

ESI-MS:  $m/z$   $[\text{M}]^+$  calcd for  $\text{C}_{41}\text{H}_{28}\text{N}_7$ : 618.24007; found: 618.24145; difference: 2.2 ppm.

#### **S.I.1.1.4. $[\text{FeCl}_3(\text{tolyltpy})]$**

As solution of tolyltpy (500 mg, 1.55 mmol, 1 eq) in 40.0 mL warm acetonitrile was added slowly to a solution of iron(III) chloride in 25.0 mL acetonitrile. The solution was stirred at room temperature for five minutes and the resulting precipitate was isolated as a yellow solid via filtration (579 mg, 1.19 mmol, 77%). The compound was used without further purification.

#### S.I.1.1.5. [Ru(L1)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub> Ru1

A suspension of ruthenium(III) chloride (80.0 mg, 355  $\mu$ mol, 1 eq) and **L1** (300.0 mg, 709  $\mu$ mol, 2 eq) in 15.0 mL ethylene glycol was heated to 180 °C for 40 minutes using microwave irradiation. After cooling to room temperature, tetrahydrofuran was added, and the deep red precipitate was isolated via filtration. Ethylene glycol residues were removed by washing with tetrahydrofuran and diethyl ether (129 mg, 127  $\mu$ mol, 36%). Ion exchange of the counter ion was performed by dissolving the complex in a small volume of methanol and adding aqueous potassium hexafluoride solution.

<sup>1</sup>H-NMR (300 MHz, CD<sub>3</sub>CN)  $\delta$  = 9.29 (d, <sup>3</sup>J = 6.7 Hz, 4H), 9.23 (s, 4H), 8.95 (d, <sup>3</sup>J = 6.8 Hz, 4H), 8.75 (d, <sup>3</sup>J = 8.1 Hz, 4H), 8.03 (dd, <sup>3</sup>J = 11.4 Hz, <sup>4</sup>J = 4.4 Hz, 4H), 7.88 (m, 10H), 7.49 (d, <sup>3</sup>J = 5.4 Hz, 4H) and 7.27 ppm (m, 4H). <sup>13</sup>C-NMR (75 MHz, CD<sub>3</sub>CN)  $\delta$  = 158.3, 157.0, 154.3, 153.6, 146.3, 143.4, 141.6, 139.6, 132.9, 131.6, 129.0, 127.3, 126.1, 125.5 and 123.3 ppm. ESI-MS: m/z [M+3PF<sub>6</sub>]<sup>+</sup> calcd for C<sub>52</sub>H<sub>38</sub>F<sub>18</sub>N<sub>8</sub>P<sub>3</sub>Ru: 1311.11938; found: 1311.11338; difference: 4.6 ppm. Anal. calc. for C<sub>52</sub>H<sub>38</sub>F<sub>24</sub>N<sub>8</sub>P<sub>4</sub>Ru, H<sub>2</sub>O: C, 42.38; H, 2.74; N, 7.60. Found: C, 42.49; H, 2.89; N, 7.63.

#### S.I.1.1.6. [Fe(L1)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub> Fe1

The synthesis was carried out under inert-gas atmosphere. Iron(II) chloride (45.0 mg, 355  $\mu$ mol, 1 eq) is added to a solution of **L1** (300 mg, 709  $\mu$ mol, 2 eq) in 25.0 mL dry methanol. The solution is stirred at room temperature over night. Diethyl ether is added, and the dark blue precipitate is isolated via filtration (226 mg, 232  $\mu$ mol, 66%). Ion exchange of the counter ion was performed by dissolving the complex in little methanol and adding aqueous potassium hexafluoride solution.

<sup>1</sup>H-NMR (300 MHz, CD<sub>3</sub>CN):  $\delta$  = 9.40 (s, 4H), 9.35 (d, <sup>3</sup>J = 6.2 Hz, 4H), 9.04 (d, <sup>3</sup>J = 6.4 Hz, 4H), 8.72 (d, <sup>3</sup>J = 8.0 Hz, 4H), 7.96 (m, 14H) and 7.19 ppm (m, 8H). <sup>13</sup>C-NMR (75 MHz, CD<sub>3</sub>CN)  $\delta$  = 162.2, 158.3, 154.4, 154.1, 146.5, 143.9, 143.6, 140.3, 133.1, 131.8, 129.0, 127.7, 125.6, 125.6 and 123.1 ppm. ESI-MS: m/z [M+3PF<sub>6</sub>]<sup>+</sup> calcd for C<sub>52</sub>H<sub>38</sub>F<sub>18</sub>FeN<sub>8</sub>P<sub>3</sub>: 1265.14998; found: 1256.15604; difference: 4.8 ppm. Anal. calc. for C<sub>52</sub>H<sub>38</sub>F<sub>24</sub>FeN<sub>8</sub>P<sub>4</sub>, 2H<sub>2</sub>O: C, 43.17; H, 2.93; N, 7.75. Found: C, 43.30; H, 2.79; N, 7.67.

#### S.I.1.1.7. [Ru(tolyItpy)(L1)](PF<sub>6</sub>)<sub>3</sub> Ru2

A suspension of [RuCl<sub>3</sub>(tolyItpy)] (49.9 mg, 93.9 μmol, 1 eq) and **L1** (50.0 mg, 93.9 μmol, 1 eq) in 15.0 mL ethylene glycol was heated to 150 °C for 15 minutes using microwave irradiation. After cooling to room temperature, 1-2 mL hydrazine, water and aqueous potassium hexafluoride solution were added to the solution and the precipitate was filtered off over celite. After washing with water, it was dissolved in acetonitrile, dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, MeCN: KNO<sub>3(aq)</sub> 12:1 to 9:1) to yield a dark red solid (38.0 mg, 30.5 μmol, 33%).

<sup>1</sup>H-NMR (500 MHz, CD<sub>3</sub>CN): δ = 9.27 (d, <sup>3</sup>J = 7.0 Hz, 2H), 9.21 (s, 2H), 9.04 (s, 2H), 8.95 (d, <sup>3</sup>J = 7.0 Hz, 2H), 8.74 (d, <sup>3</sup>J = 7.9 Hz, 2H), 8.67 (d, <sup>3</sup>J = 7.8 Hz, 2H), 8.13 (d, <sup>3</sup>J = 8.1 Hz, 2H), 8.02 (td, <sup>3</sup>J = 7.9, <sup>4</sup>J = 1.4 Hz, 2H), 7.97 (td, <sup>3</sup>J = 7.9, <sup>4</sup>J = 1.5 Hz, 2H), 7.90 (m, 3H), 7.85 (m, 2H), 7.60 (d, <sup>3</sup>J = 7.8 Hz, 2H), 7.52 (dd, <sup>3</sup>J = 5.6 Hz, <sup>4</sup>J = 0.7 Hz, 2H), 7.40 (dd, <sup>3</sup>J = 5.6 Hz, <sup>4</sup>J = 0.7 Hz, 2H), 7.27 (m, 2H), 7.18 (m, 2H) and 2.55 ppm (s, 3H). <sup>13</sup>C{<sup>1</sup>H}-NMR (126 MHz, CD<sub>3</sub>CN): δ = 158.9, 158.5, 157.5, 155.7, 154.4, 153.5, 153.4, 150.2, 146.2, 143.4, 142.1, 140.4, 139.3, 139.2, 134.7, 132.9, 131.6, 131.2, 128.9, 128.6, 128.4, 127.2, 125.8, 125.6, 125.4, 123.0, 122.4 and 21.3 ppm. ESI-MS: m/z [M]<sup>2+</sup> caclcd for C<sub>48</sub>H<sub>36</sub>N<sub>7</sub>Ru: 405.60385; found: 405.60538; difference: 3.8 ppm. Anal. calc. for C<sub>48</sub>H<sub>36</sub>F<sub>18</sub>N<sub>7</sub>P<sub>3</sub>Ru: C, 46.24; H, 2.91; N, 7.86. Found: C,46.06; H, 3.15; N, 7.90.

#### S.I.1.1.8. [Fe(tolyItpy)(L1)](PF<sub>6</sub>)<sub>3</sub> Fe2

The synthesis was carried out under inert-gas atmosphere. Fe(tolyItpy)Cl<sub>3</sub> (57.4 mg, 118 μmol, 1 eq) is added to a solution of **L1** (50.0 mg, 118 μmol, 1 eq) in methanol. The solution was heated to reflux for two hours. After cooling to room temperature, aqueous potassium hexafluoride solution and water were added, and the precipitate was filtered off over celite. The dark blue solid was dissolved in acetonitrile, dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, MeCN: KNO<sub>3(aq)</sub> 9:1) to yield a dark red solid (32.0 mg, 26.6 μmol, 23%).

<sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>CN) δ = 9.36 (s, 2H), 9.33 (d, <sup>3</sup>J = 6.6 Hz, 2H), 9.22 (s, 2H), 9.03 (d, <sup>3</sup>J = 6.7 Hz, 2H), 8.69 (d, <sup>3</sup>J = 8.0 Hz, 2H), 8.64 (d, <sup>3</sup>J = 8.0 Hz, 2H), 8.25 (d, <sup>3</sup>J = 8.1 Hz, 2H), 7.94 (m, 6H), 7.86 (m, 3H), 7.65 (d, <sup>3</sup>J = 8.0 Hz, 2H), 7.18 (m, 6H),

7.09 (dd,  $^3J = 9.5$  Hz,  $^4J = 3.6$  Hz, 2H) and 2.58 ppm (s, 3H).  $^{13}\text{C}$ -NMR (101 MHz,  $\text{CD}_3\text{CN}$ )  $\delta = 162.8, 160.5, 158.9, 158.3, 154.4, 154.1, 153.9, 152.3, 146.4, 143.5, 142.7, 142.6, 140.0, 139.9, 134.6, 133.0, 131.7, 131.4, 128.8, 128.7, 128.3, 127.4, 125.5, 125.2, 125.0, 122.7, 122.5$  and 21.4 ppm. ESI-MS:  $m/z$   $[\text{M}+2\text{PF}_6]^+$  calcd for  $\text{C}_{48}\text{H}_{36}\text{F}_{12}\text{FeN}_7\text{P}_2$ : 1056.16652; found: 1056.16927; difference: 2.5 ppm. Anal. calc. for  $\text{C}_{48}\text{H}_{36}\text{F}_{18}\text{FeN}_7\text{P}_3 \cdot 5.5\text{H}_2\text{O}$ : C, 44.32; H, 3.64; N, 7.54. Found: C, 44.29; H, 3.33; N, 7.30.

#### **S.I.1.1.9. $\text{Ru}_n(\text{L}2)_n(\text{OAc})_{2n}$ Ru-L2-MEPE**

A solution of ruthenium(III) chloride (500 mg, 2.41 mmol) in 10.0 mL dimethyl sulfoxide (DMSO) was heated to reflux for 30 min. After cooling to room temperature, acetone was added. The formed precipitate was collected via filtration and washed with diethyl ether and acetone. The product,  $\text{RuCl}_2(\text{DMSO})_2$ , was used without further purification.

Under inert gas atmosphere, a solution of **L2** (250 mg, 380  $\mu\text{mol}$ , 1 eq) and  $\text{RuCl}_2(\text{DMSO})_2$  (185 mg, 380  $\mu\text{mol}$ , 1 eq) in 40.0 mL degassed ethylene glycol was heated to 180  $^\circ\text{C}$  for 27 hours. After cooling to room temperature, tetrahydrofuran (THF) was added and the formed precipitate was collected via filtration and washed with acetone and diethyl ether. The product was dissolved in water and lyophilized to remove remaining traces of solvent, yielding the product as purple solid in quantitative yield.

#### **S.I.1.1.10. $\text{Fe}_n(\text{L}2)_n(\text{OAc})_{2n}$ Fe-L2-MEPE**

Under inert gas atmosphere, iron powder (21.4 mg, 380  $\mu\text{mol}$ , 1 eq) was heated to reflux in 20.0 mL degasses acetic acid (75%) for two hours until it was fully dissolved. A solution of **L2** (250 mg, 380  $\mu\text{mol}$ , 1 eq) in 20.0 ml acetic acid (75%) was added to the iron solution and the reaction mixture was stirred at room temperature for two days. The solvent was removed under vacuum, yielding a blue solid. The product was dissolved in water and lyophilized to remove remaining traces of acetic acid, yielding the product as blue solid in quantitative yield.



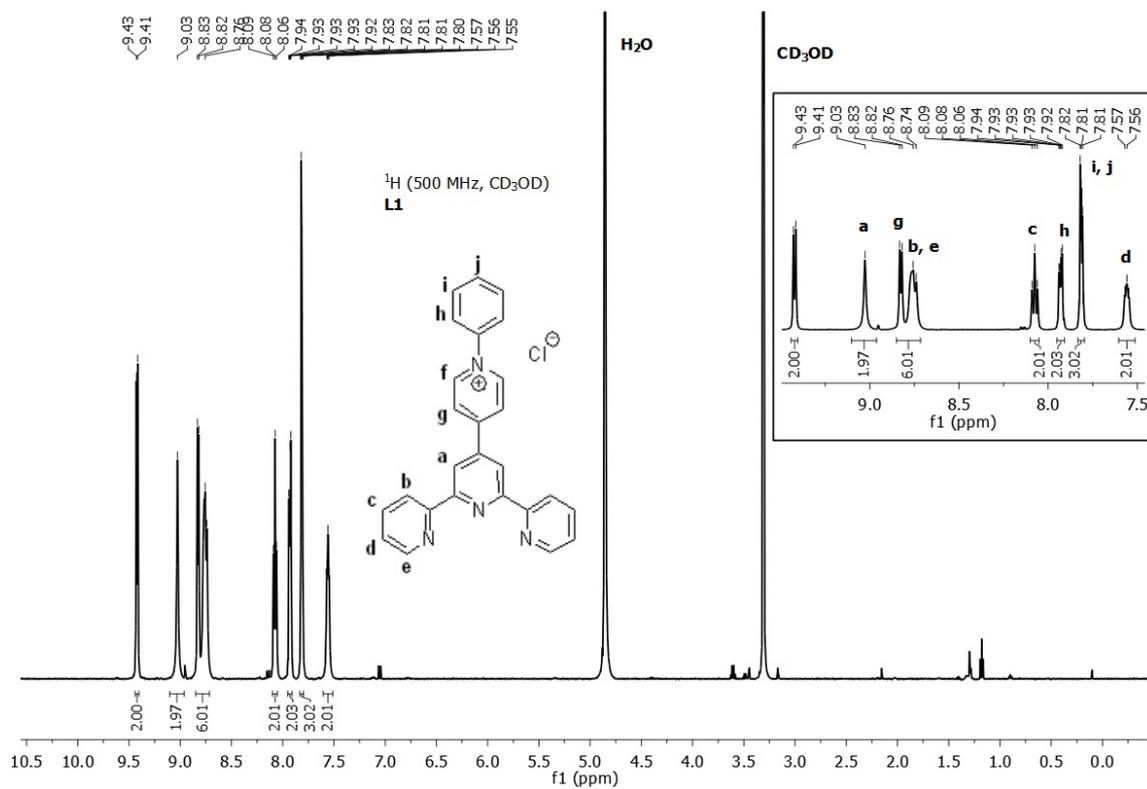


Figure S 3. <sup>1</sup>H-NMR spectrum (500 MHz, CD<sub>3</sub>OD) of **L1**.

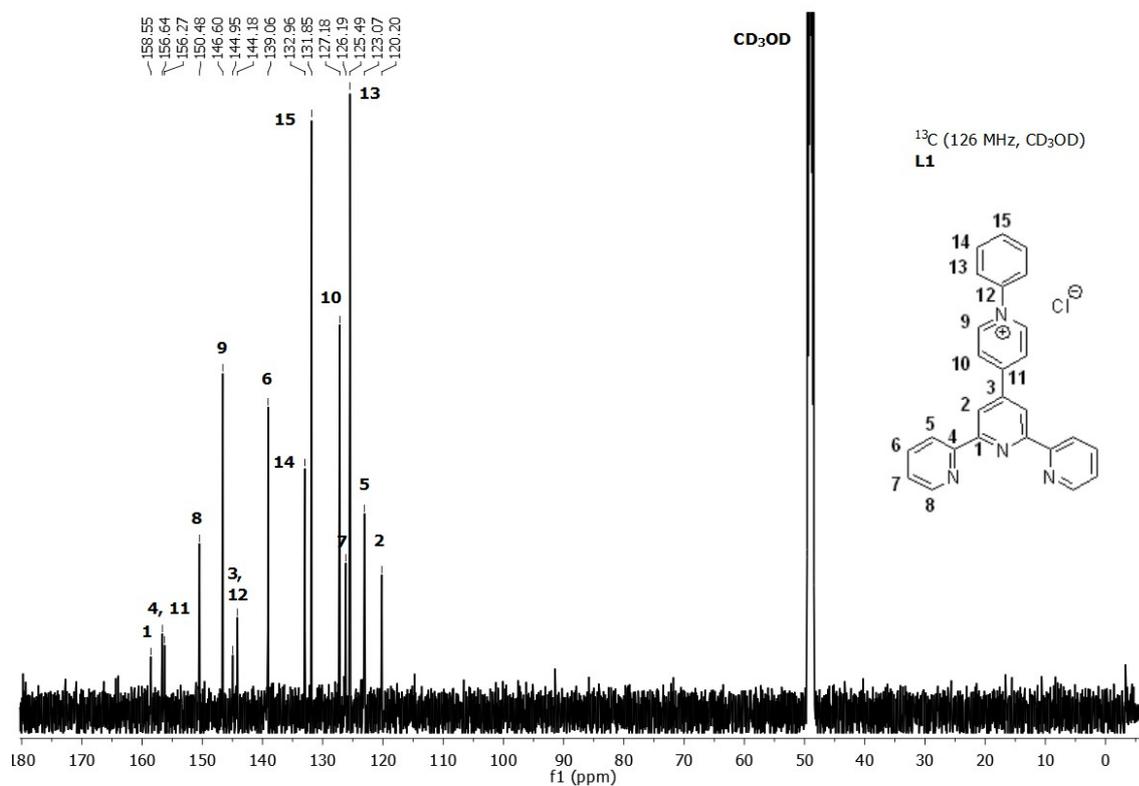


Figure S 4. <sup>13</sup>C-NMR spectrum (126 MHz, CD<sub>3</sub>OD) of **L1**.

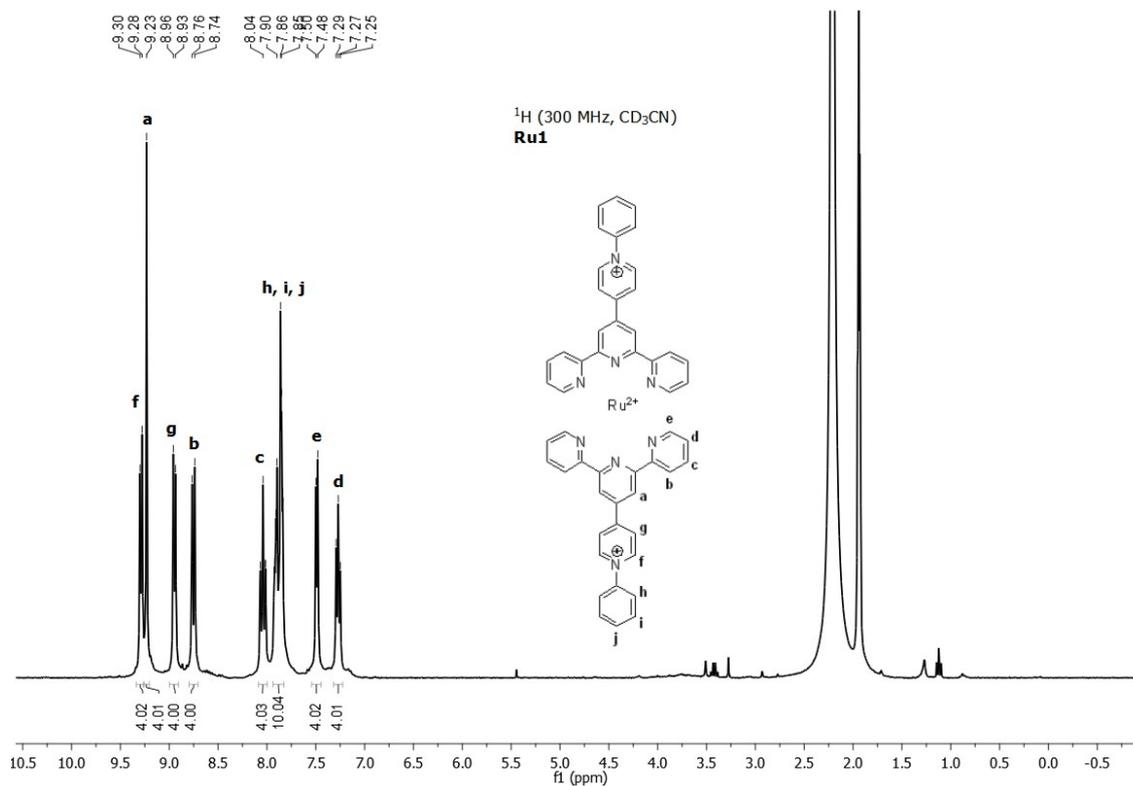


Figure S 5. <sup>1</sup>H-NMR spectrum (300 MHz, CD<sub>3</sub>CN) of Ru1.

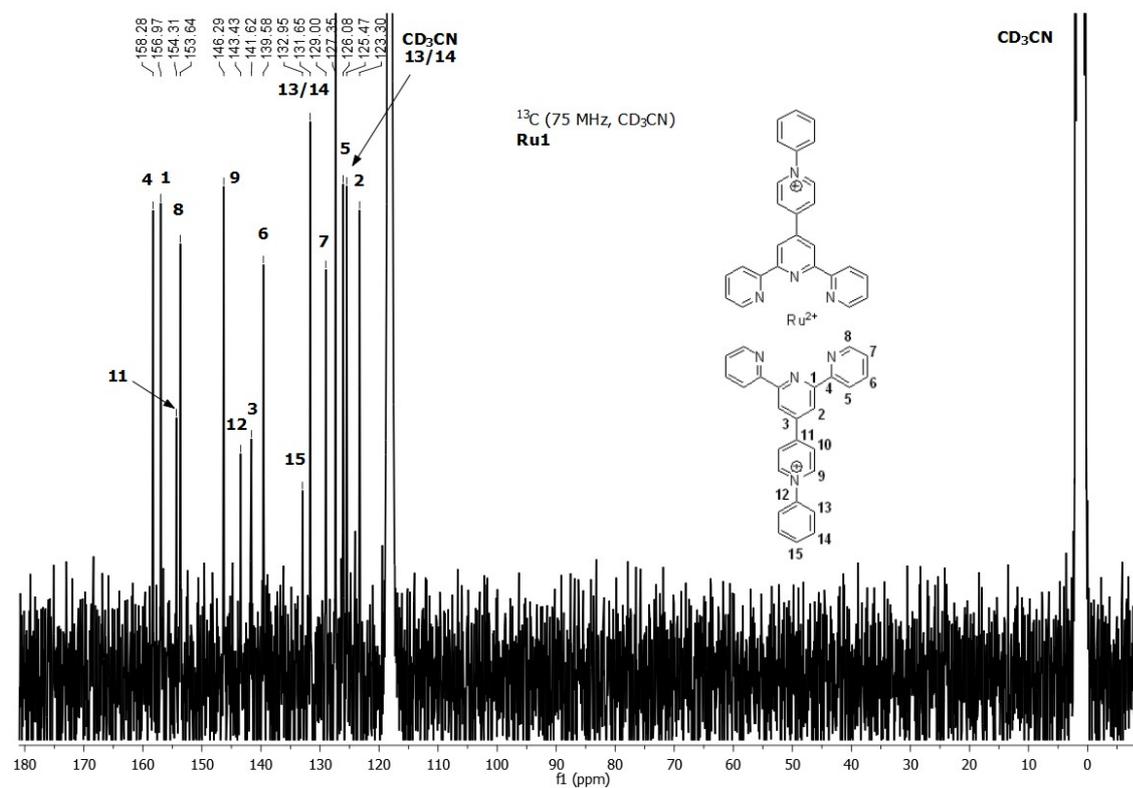


Figure S 6. <sup>13</sup>C-NMR spectrum (75 MHz, CD<sub>3</sub>CN) of Ru1.

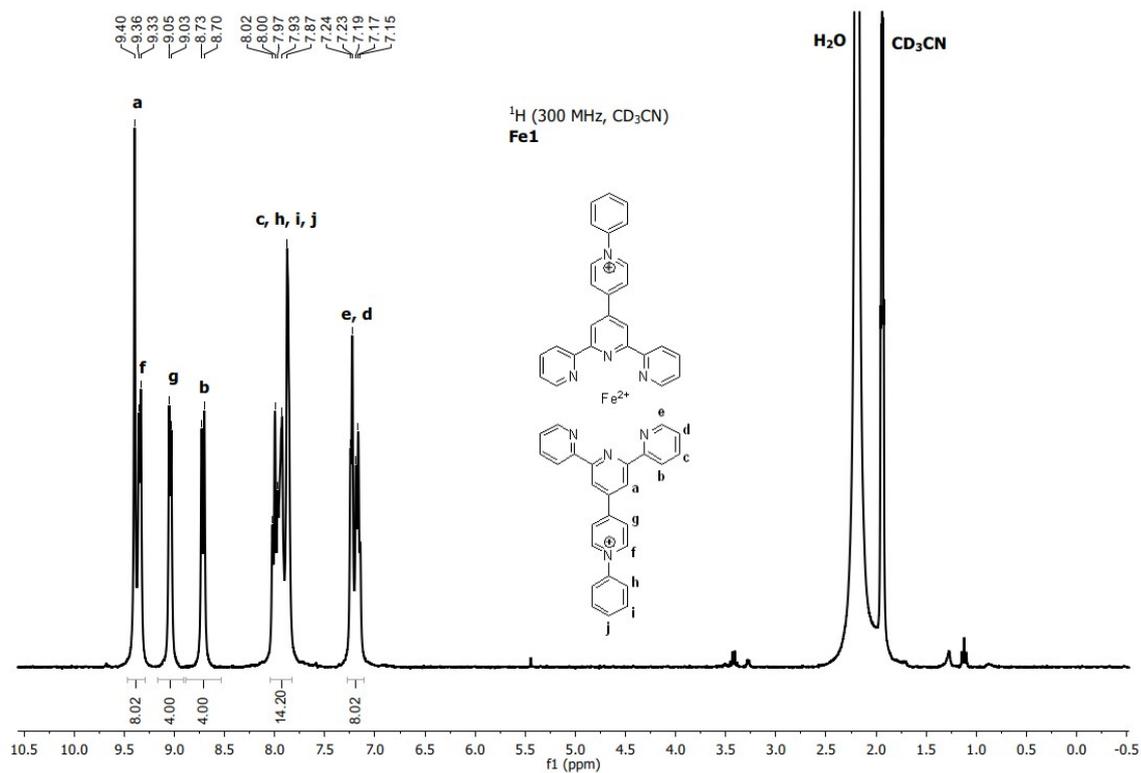


Figure S 7. <sup>1</sup>H-NMR spectrum (300 MHz, CD<sub>3</sub>CN) of **Fe1**.

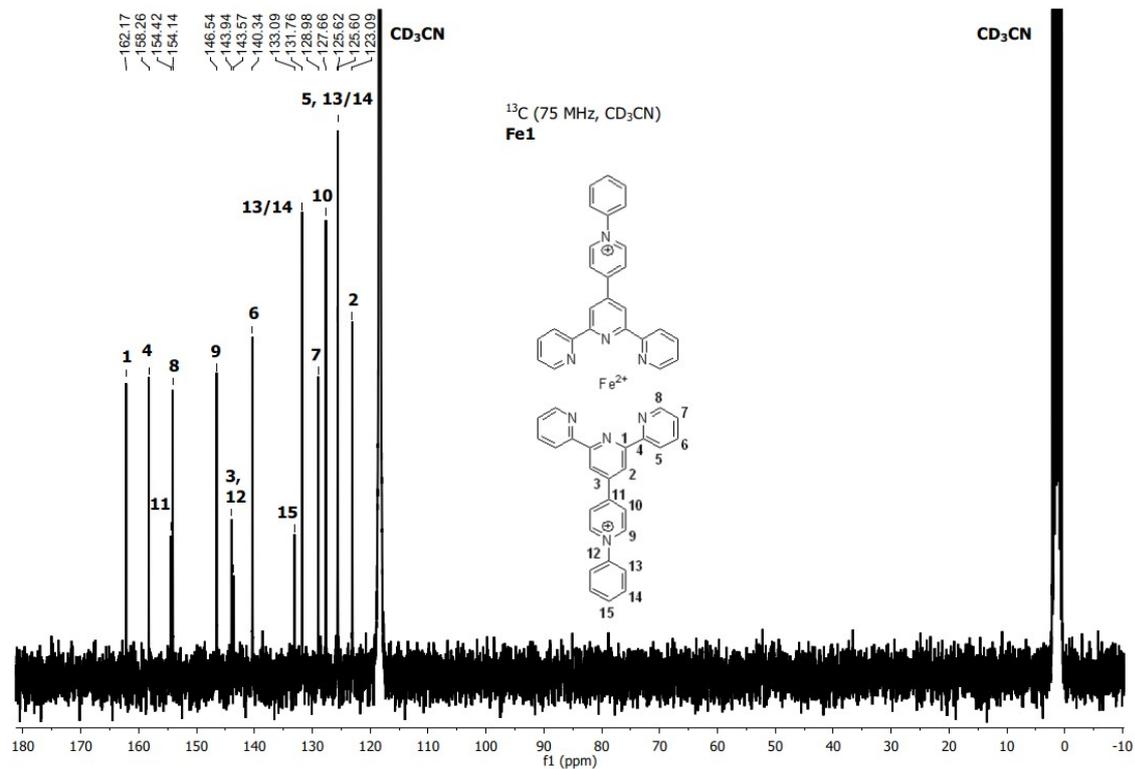


Figure S 8. <sup>13</sup>C-NMR spectrum (75 MHz, CD<sub>3</sub>CN) of **Fe1**.

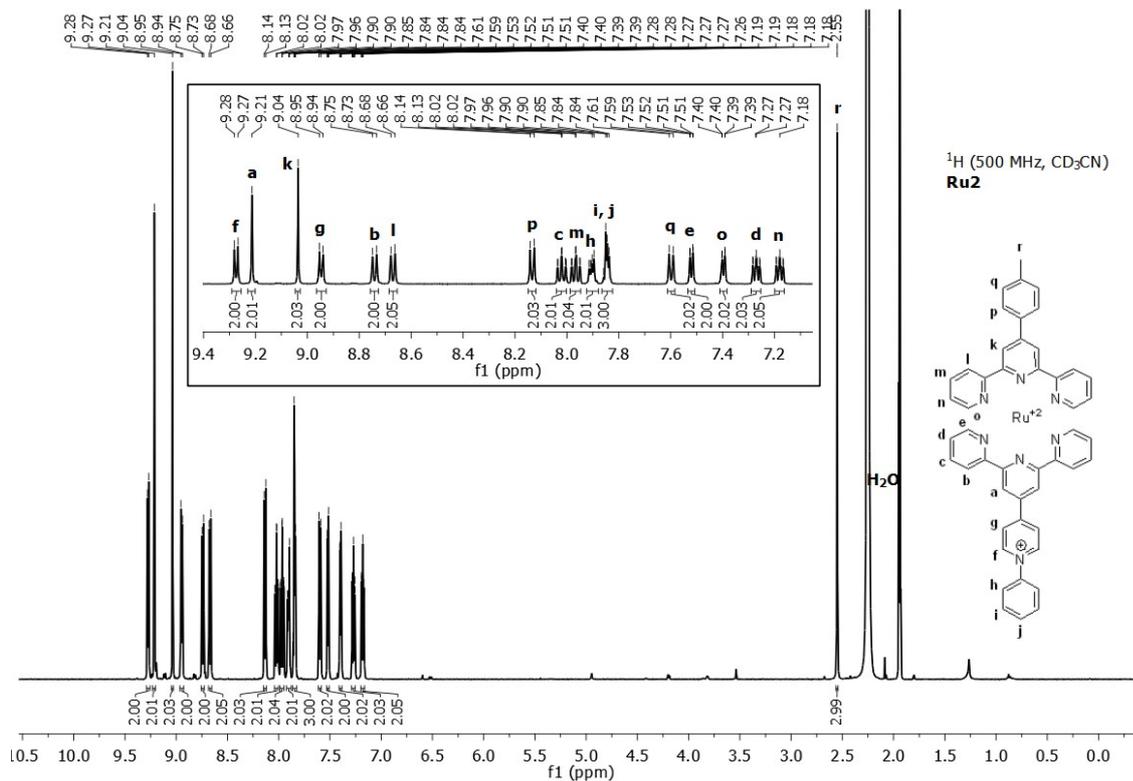


Figure S 9. <sup>1</sup>H-NMR spectrum (500 MHz, CD<sub>3</sub>CN) of Ru<sub>2</sub>.

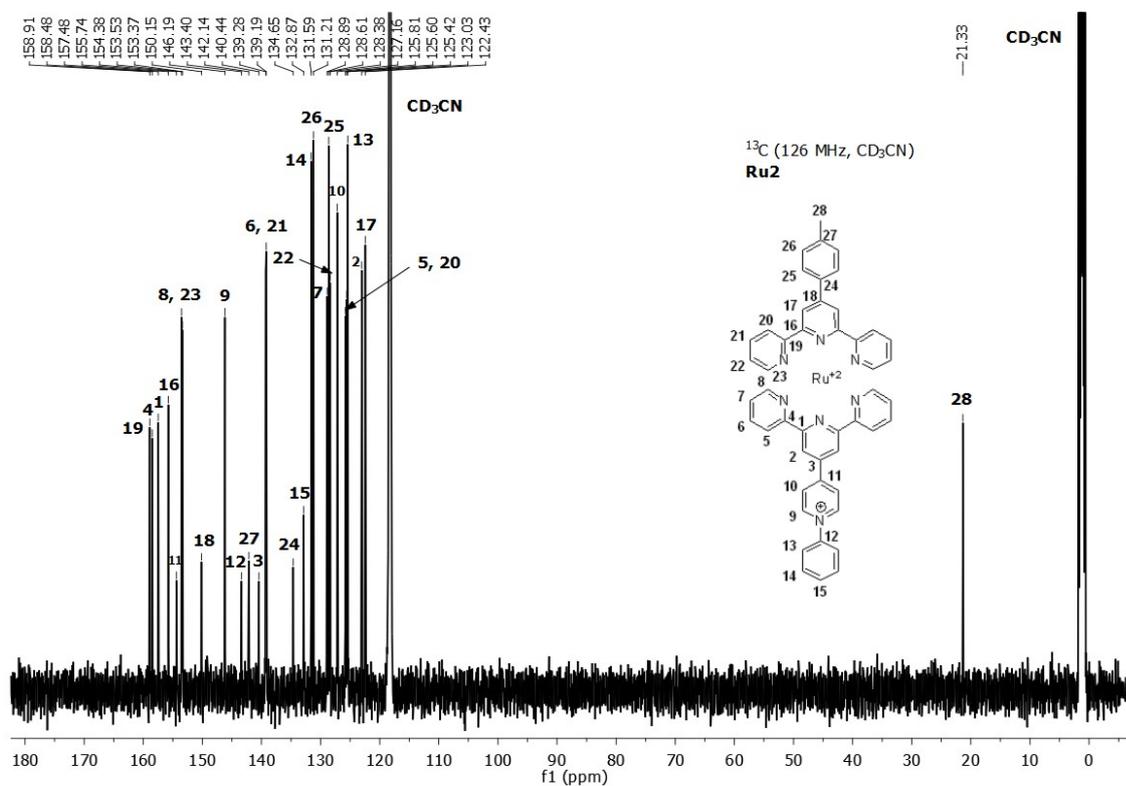


Figure S 10. <sup>13</sup>C-NMR spectrum (126 MHz, CD<sub>3</sub>CN) of Ru<sub>2</sub>.

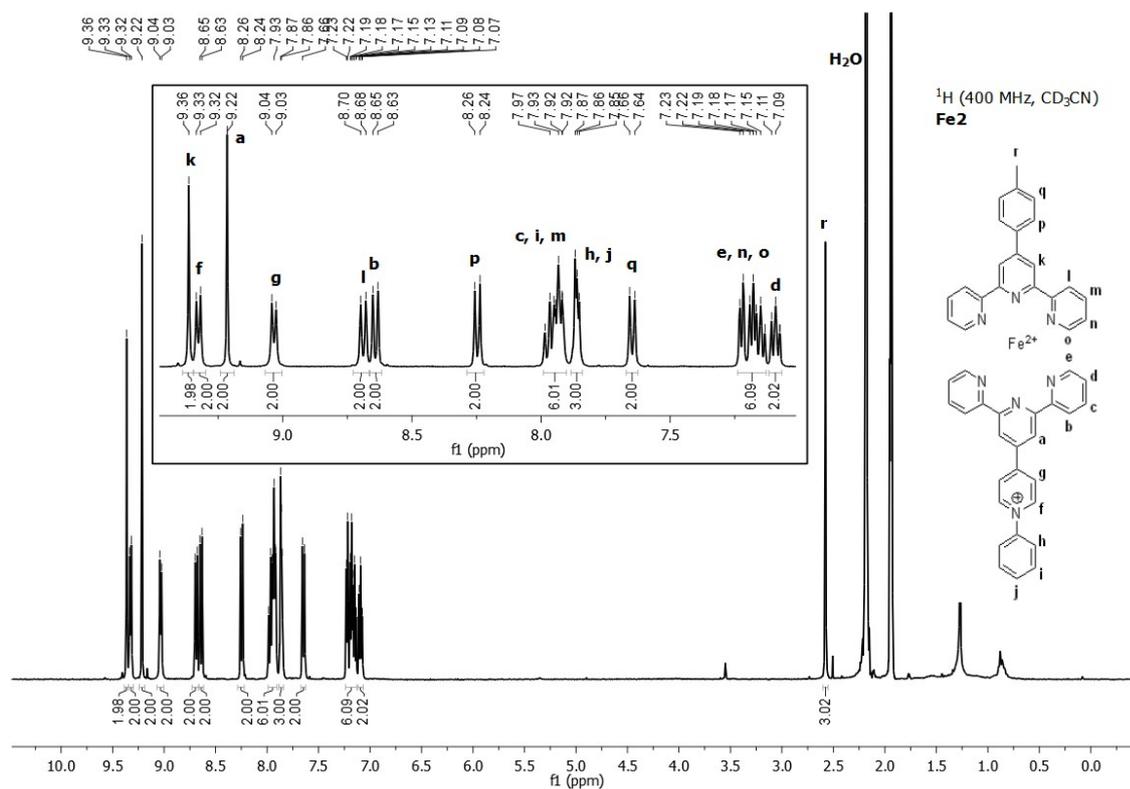


Figure S 11. <sup>1</sup>H-NMR spectrum (400 MHz, CD<sub>3</sub>CN) of Fe<sub>2</sub>.

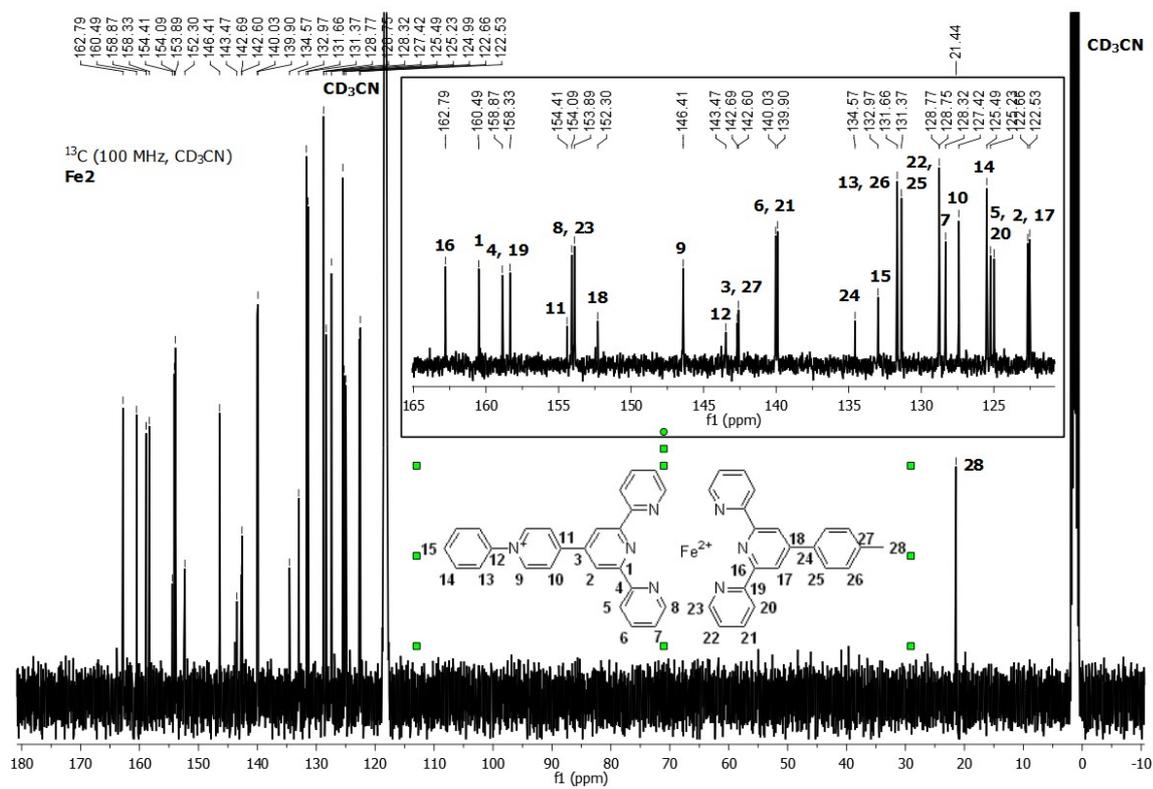


Figure S 12. <sup>13</sup>C-NMR spectrum (100 MHz, CD<sub>3</sub>CN) of Fe<sub>2</sub>.

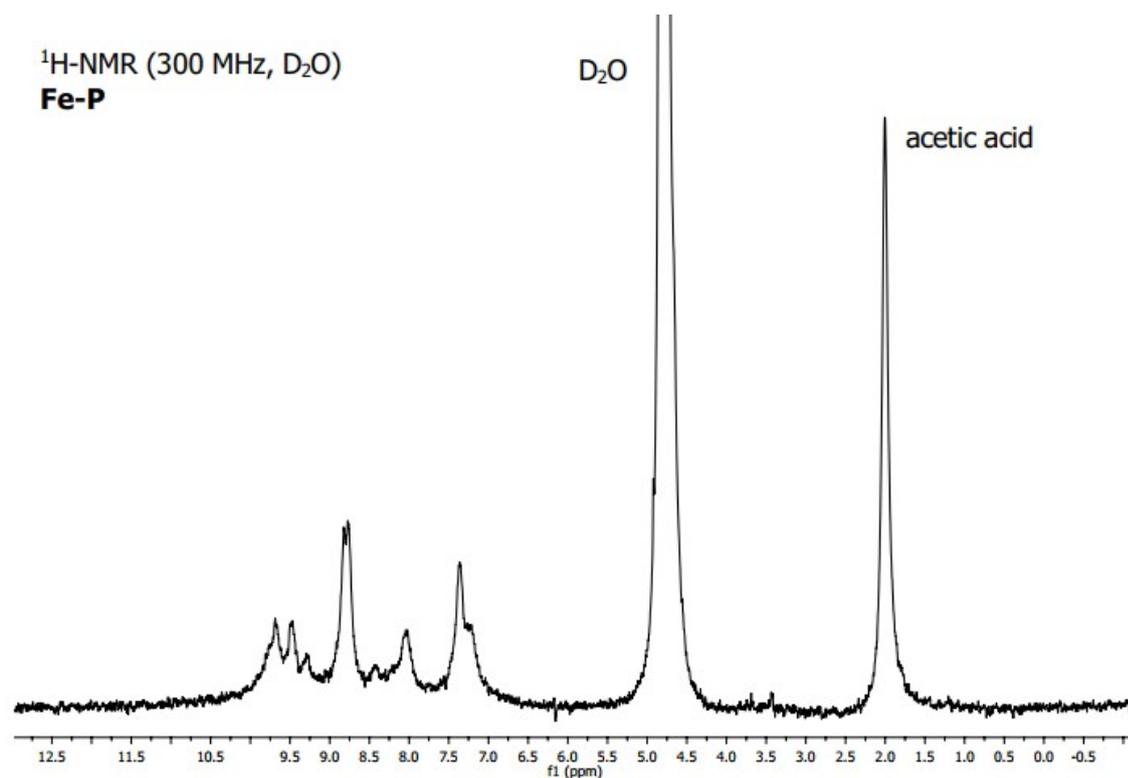


Figure S 13. <sup>1</sup>H-NMR spectrum (300 MHz, D<sub>2</sub>O) of **Fe-L2-MEPE**.

## Mass spectrometry

MS Spectrum

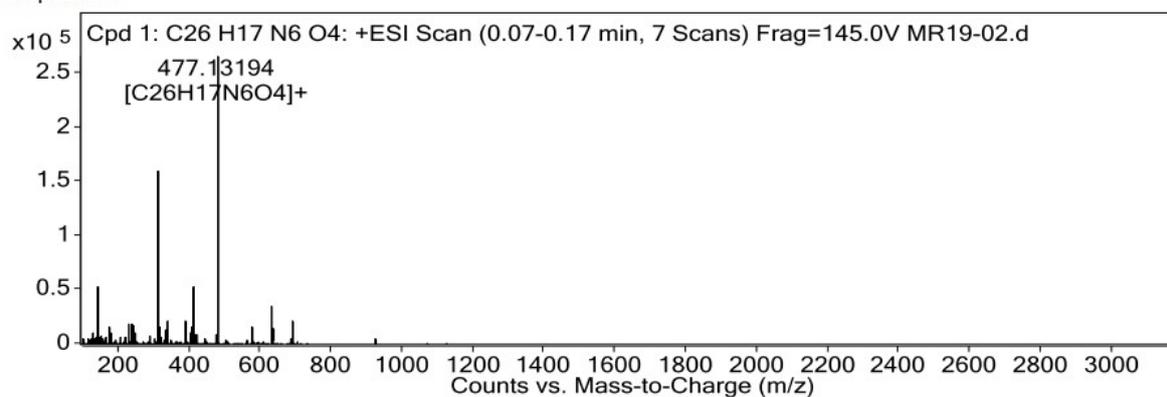


Figure S 14. High-resolution mass spectrum of **13**. The strongest peak at 477.13194 m/z corresponds to **13** without its chloride counterion (caclcd for C<sub>26</sub>H<sub>17</sub>N<sub>6</sub>O<sub>4</sub>: 477.13058). Difference: 2.8 ppm.

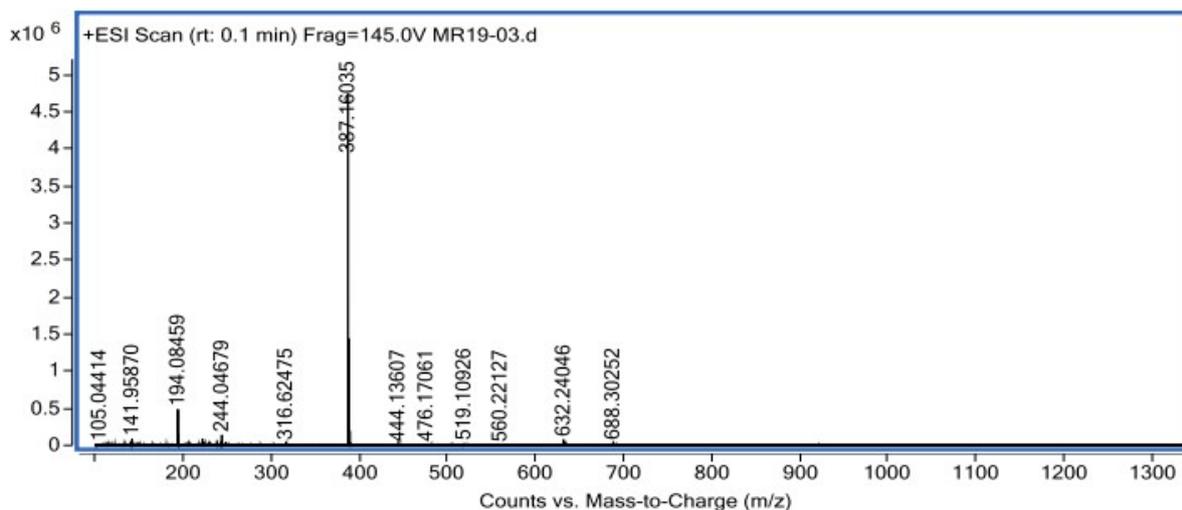


Figure S 15. High-resolution mass spectrum of **L1**. The strongest peak at 387.16035 m/z corresponds to **L1** without its chloride counterion (cacl'd for  $C_{26}H_{19}N_4$ : 387.16042). Difference: 0.2 ppm.

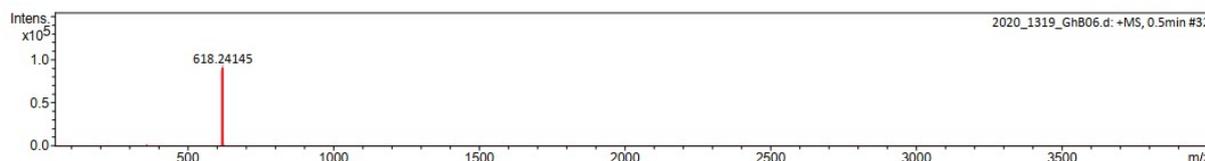


Figure S 16. High-resolution mass spectrum of **L2**. The strongest peak at 618.24145 m/z corresponds to **L2** without its chloride counterion (cacl'd for  $C_{41}H_{28}N_7$ : 618.24007). Difference: 2.2 ppm.

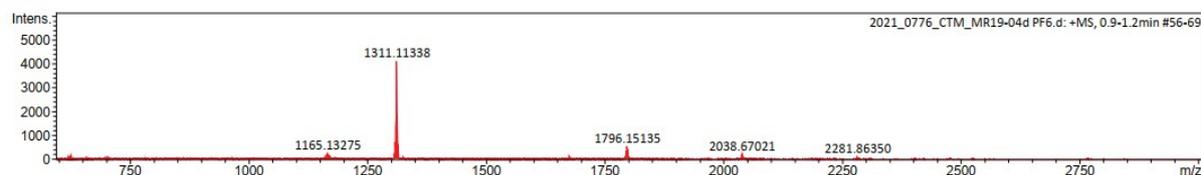


Figure S 17. High-resolution mass spectrum of **Ru1**. The strongest peak at 1311.11338 m/z corresponds to **Ru1** with three hexafluoro phosphate counterions (cacl'd for  $C_{52}H_{38}F_{18}N_8P_3Ru$ : 1311.11938). Difference: 4.6 ppm.

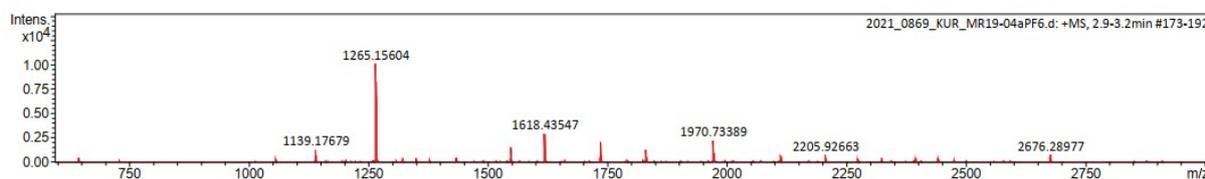


Figure S 18. High-resolution mass spectrum of **Fe1**. The strongest peak at 1265.15604 m/z corresponds to **Fe1** with three hexafluoro phosphate counterions (cacl'd for  $C_{52}H_{38}F_{18}FeN_8P_3$ : 1265.14998). Difference: 4.8 ppm.

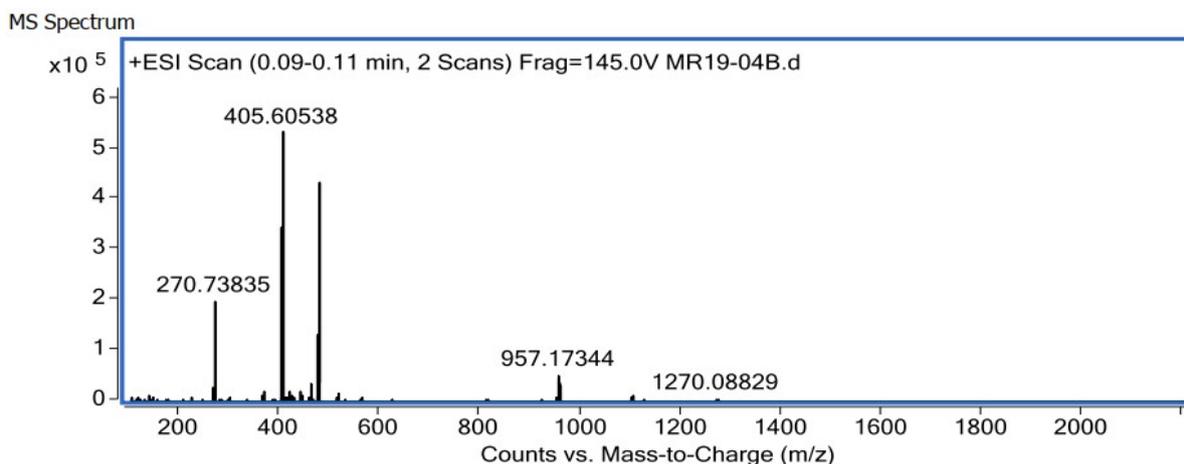


Figure S 19. High-resolution mass spectrum of **Ru2**. The strongest peak at 405.60538 m/z corresponds to **Ru2** without any counterions (cacl'd for  $C_{48}H_{36}N_7Ru$ : 405.60385). Difference: 3.8 ppm.

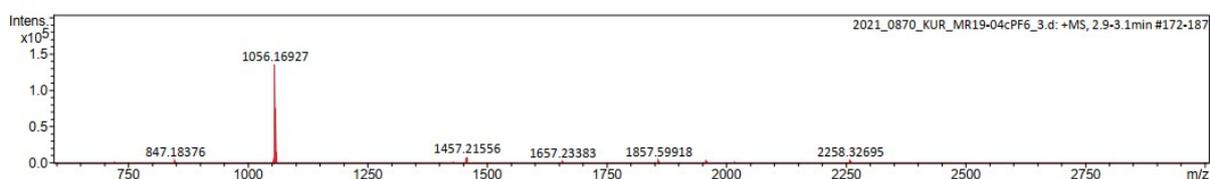


Figure S 20. High-resolution mass spectrum of **Fe2**. The strongest peak at 1056.16927 m/z corresponds to **Fe2** with two hexafluoro phosphate counterions (cacl'd for  $C_{48}H_{36}F_{12}FeN_7P_2$ : 1056.16652). Difference: 2.5 ppm.

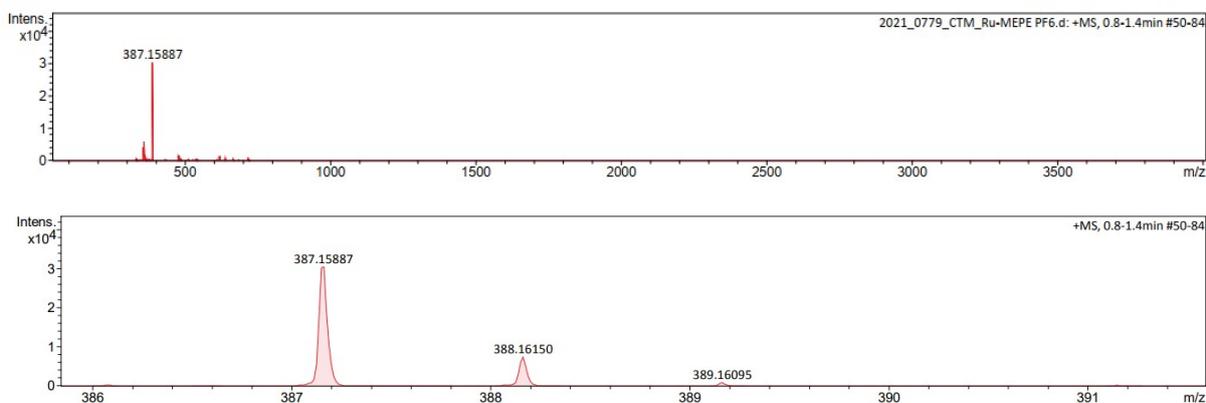


Figure S 21. High-resolution mass spectrum of **Ru-L2-MEPE**. The strongest peak at 387.15887 m/z corresponds roughly to protonated **L2** complexed with one Ru ion and one chloride counterion, plus one  $H_2O$  molecule (cacl'd for  $C_{41}H_{31}ClN_7ORu$ : 387.06556). Difference: 241 ppm. The bottom spectrum shows a zoom-in on the largest peak.

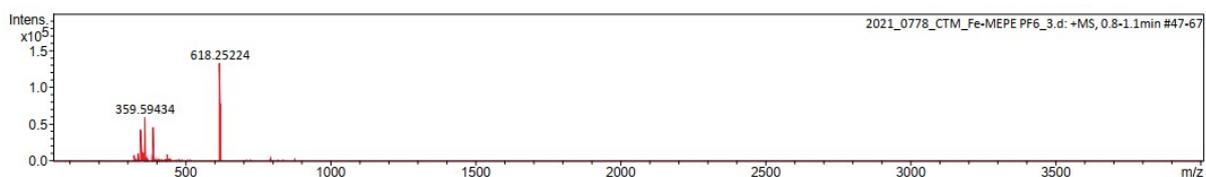


Figure S 22. High-resolution mass spectrum of **Fe-L2-MEPE**. The strongest peak at 618.25224 m/z corresponds to free **L2** (cacl'd for  $C_{41}H_{28}N_7$ : 618.24007). Difference: 2.0 ppm. The cluster of peaks around 360 m/z presumably corresponds to different variations of **L2** complexed with Fe ions, e.g., two

**L2**, complexed with two Fe ions, with one acetate counter ion and two water molecules (calcd for  $C_{84}H_{63}Fe_2N_{14}O_4$ : 360.84584).

## Electrochemistry

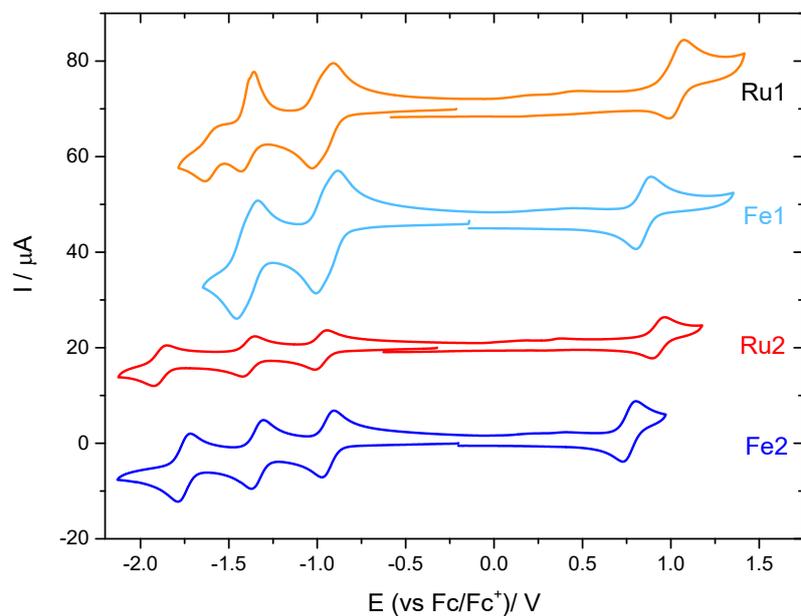


Figure S 23. Cyclic voltammograms of complexes **Ru1** (0.5 mM), **Fe1** (0.5 mM), **Ru2** (0.25 mM), and **Fe2** (0.5 mM) in dry acetonitrile under inert gas atmosphere, with 0.1 M  $TBAPF_6$ ; scan rate 100 mV/s; scans start at 0 V vs. open circuit potential in cathodic direction first. Potentials are corrected vs the internal standard  $Fc/Fc^+$  couple.

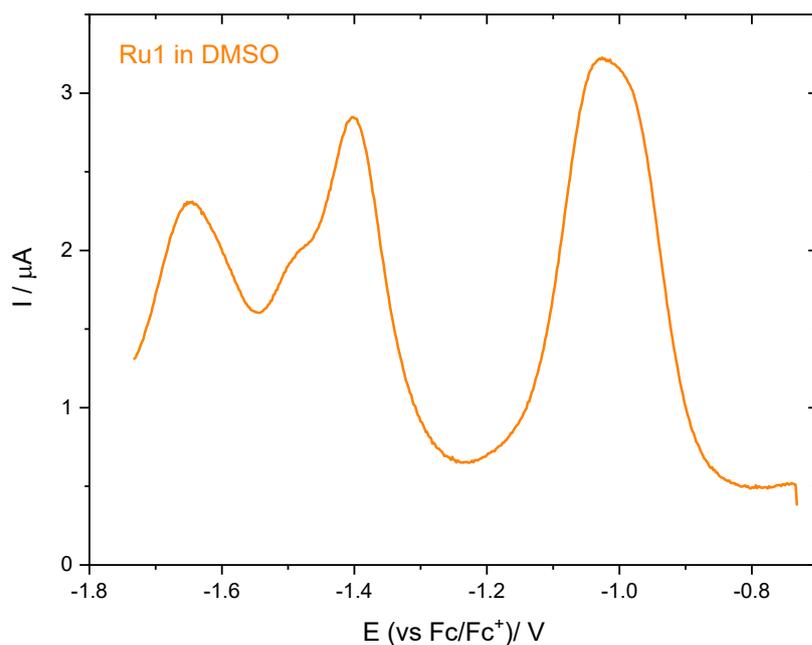


Figure S 24. Square wave voltammogram of complex **Ru1** (chloride salt, 0.5 mM) in DMSO under inert gas atmosphere, with 0.1 M TBAPF<sub>6</sub>; scan rate 100 mV/s; scans start at 0 V vs. reference electrode in cathodic direction. Potentials are corrected vs the internal standard Fc/Fc<sup>+</sup> couple.

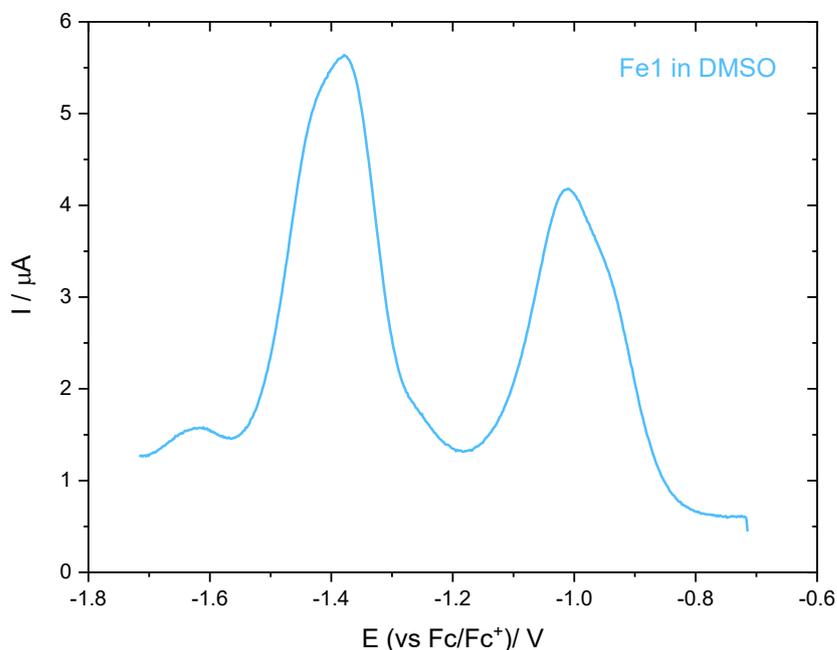


Figure S 25. Square wave voltammogram of complex **Fe1** (chloride salt, 0.5 mM) in DMSO under inert gas atmosphere, with 0.1 M TBAPF<sub>6</sub>; scan rate 100 mV/s; scans start at 0 V vs. reference electrode in cathodic direction. Potentials are corrected vs the internal standard Fc/Fc<sup>+</sup> couple.

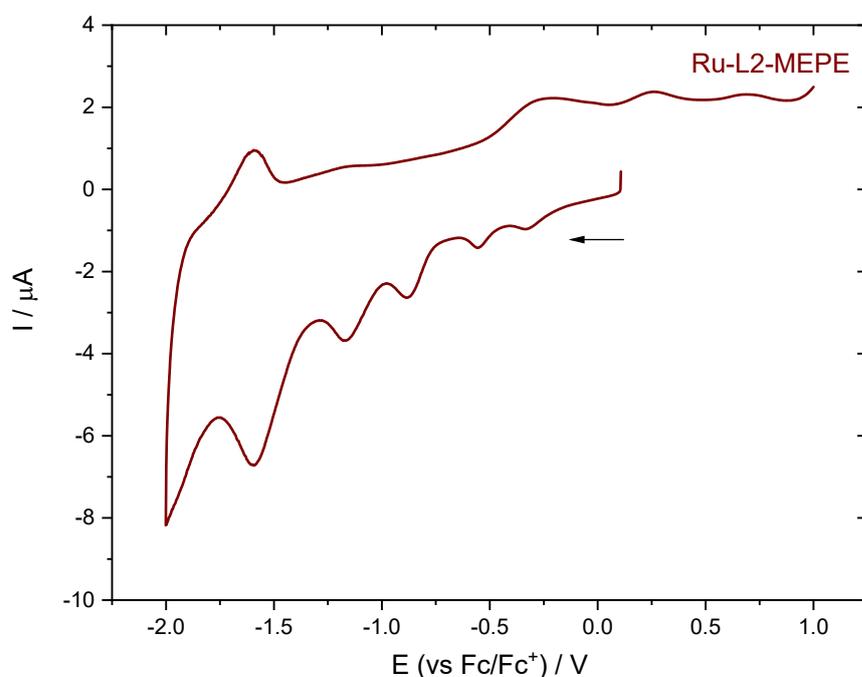


Figure S 26. Cyclic voltammogram of **Ru-L2\_MEPE** (chloride salt, 0.5 mM) in DMSO under inert gas atmosphere, with 0.1 M TBAPF<sub>6</sub>; scan rate 100 mV/s; scans start at 0 V vs. open circuit potential. Potential is uncorrected and reported as obtained using a silver wire as a pseudo-reference electrode.

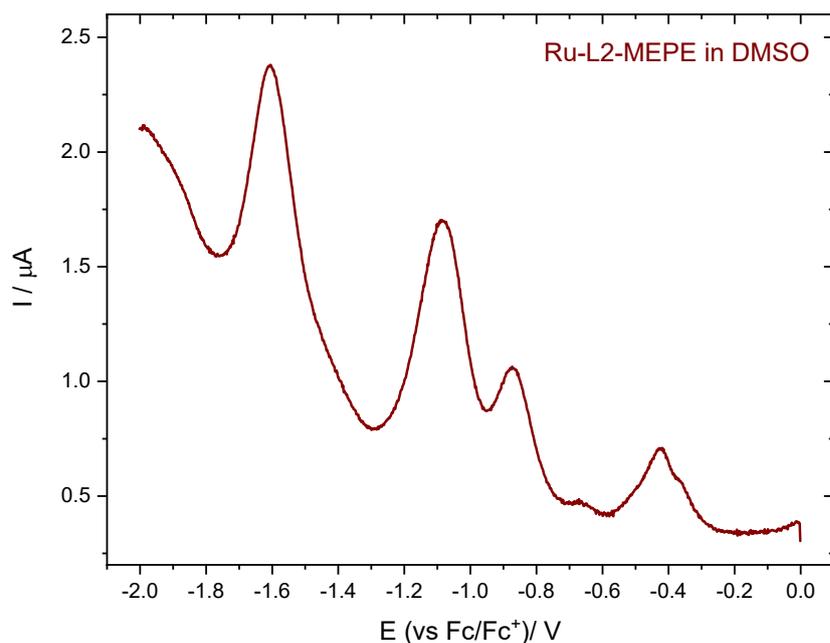


Figure S 27. Square wave voltammogram of **Ru-L2-MEPE** (chloride salt, 0.5 mM) in DMSO under inert gas atmosphere, with 0.1 M TBAPF<sub>6</sub>; scan rate 100 mV/s; scans start at 0 V vs. reference electrode in cathodic direction. Potentials are corrected vs the internal standard Fc/Fc<sup>+</sup> couple.

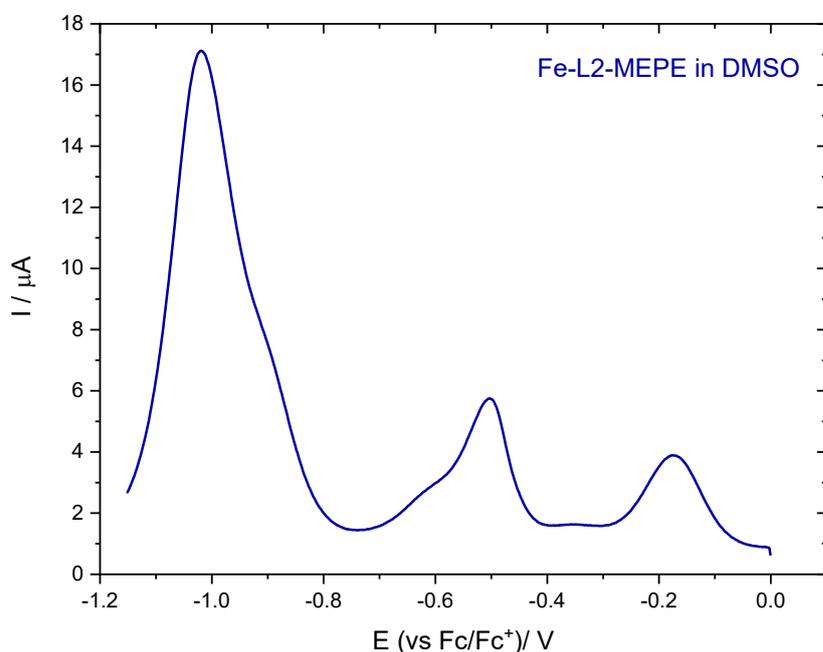


Figure S 28. Square wave voltammogram of **Fe-L2-MEPE** (acetate salt, 0.5 mM) in DMSO under inert gas atmosphere, with 0.1 M TBAPF<sub>6</sub>; scan rate 100 mV/s; scans start at 0 V vs. reference electrode in cathodic direction. Potentials are corrected vs the internal standard Fc/Fc<sup>+</sup> couple.

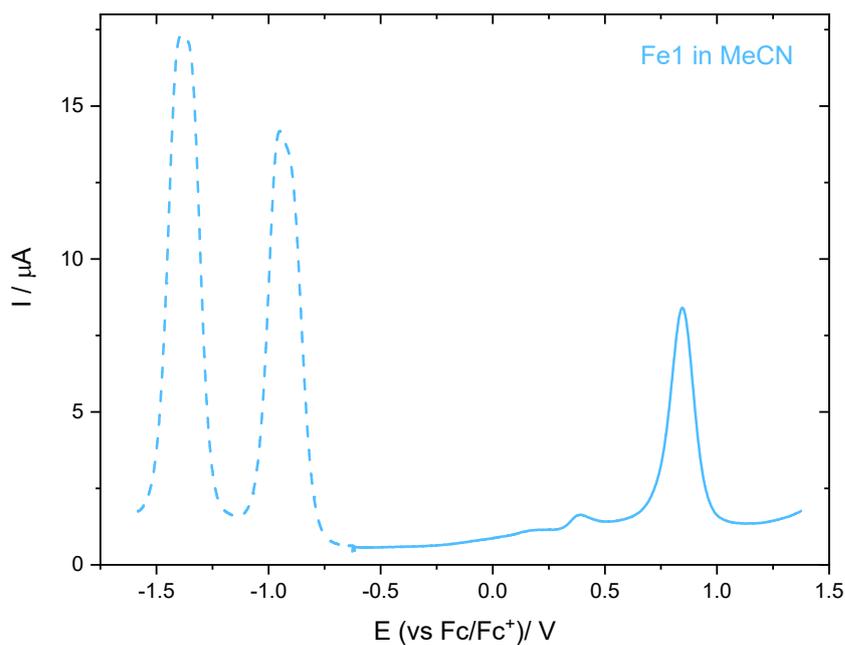


Figure S 29. Square wave voltammogram of complex **Fe1** (0.5 mM) in dry acetonitrile under inert gas atmosphere, with 0.1 M TBAPF<sub>6</sub>; scan rate 100 mV/s; scans start at 0 V vs. reference electrode in both anodic (solid line) and cathodic (dashed line) direction. Potentials are corrected vs the internal standard Fc/Fc<sup>+</sup> couple.

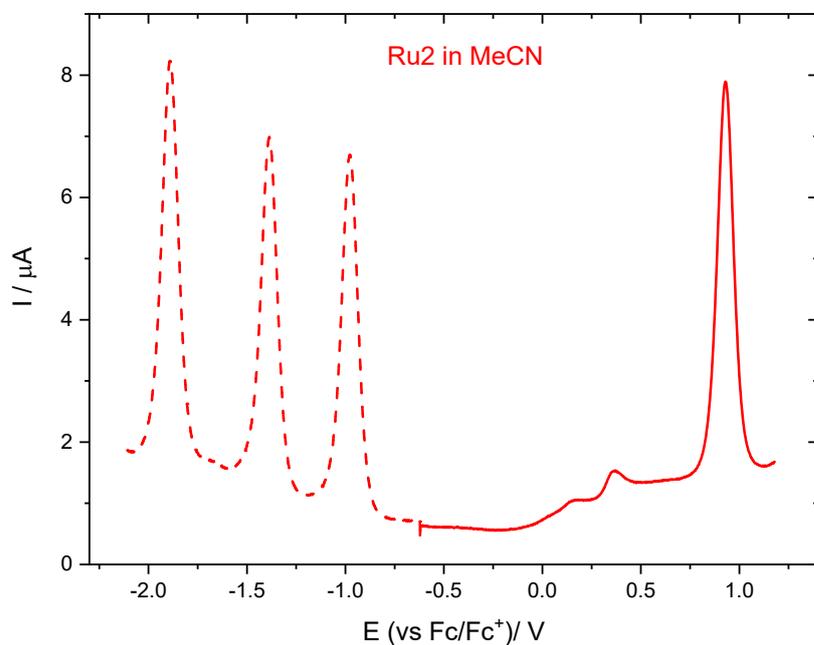


Figure S 30. Square wave voltammogram of complex **Ru2** (0.25 mM) in dry acetonitrile under inert gas atmosphere, with 0.1 M TBAPF<sub>6</sub>; scan rate 100 mV/s; scans start at 0 V vs. reference electrode in both anodic (solid line) and cathodic (dashed line) direction. Potentials are corrected vs the internal standard Fc/Fc<sup>+</sup> couple.

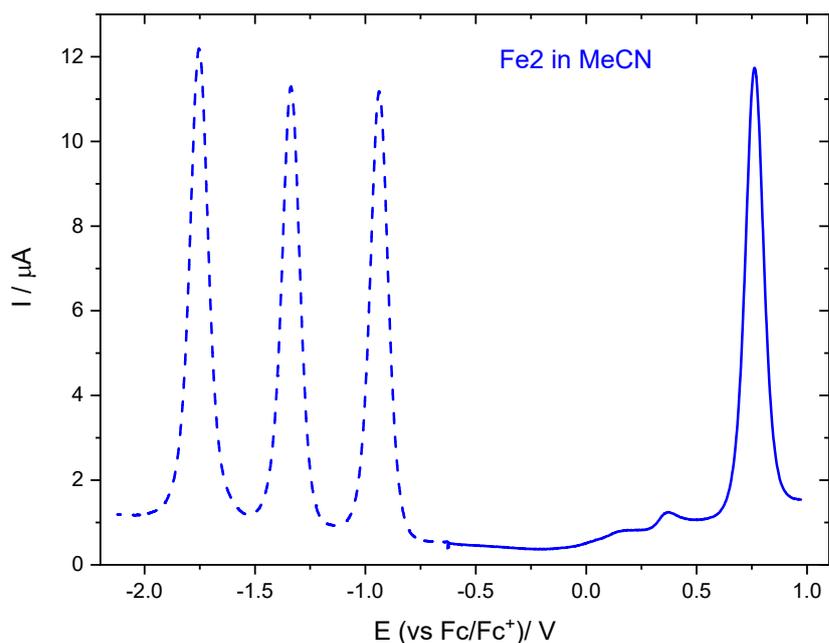


Figure S 31. Square wave voltammogram of complex **Fe2** (0.5 mM) in dry acetonitrile under inert gas atmosphere, with 0.1 M TBAPF<sub>6</sub>; scan rate 100 mV/s; scans start at 0 V vs. reference electrode in both anodic (solid line) and cathodic (dashed line) direction. Potentials are corrected vs the internal standard Fc/Fc<sup>+</sup> couple.

Table S 1. Summary of the anodic to cathodic current ratio; current ratios are determined in acetonitrile unless state otherwise.

complex	E <sub>ox</sub>	E <sub>red</sub>			
Ru1	0.92	1.12*		0.83	1.20
		1.14* <sup>a</sup>		1.11 <sup>a</sup>	1.05 <sup>a</sup>
Fe1	1.17	0.99*		0.99*	
		1.06* <sup>a</sup>		0.89* <sup>a</sup>	
Ru2	1.08	1.00		1.03	0.96
Fe2	0.99	1.10		1.33	1.00
Ru-L2-MEPE	0.12 <sup>b</sup>	n.d.	n.d.	n.d.	n.d.
Fe-L2-MEPE	0.80 <sup>b</sup>	1.05 <sup>ac</sup>		0.92 <sup>ac</sup>	0.95 <sup>ac</sup>

\*Two closely spaced one-electron processes as determined by square wave voltammetry. <sup>a</sup>Samples measured in DMSO instead of acetonitrile. <sup>b</sup>Data obtained from PET-ITO foils coated with **Ru-L2-MEPE** or **Fe-L2-MEPE**. <sup>c</sup>Values taken from square wave voltammetry of **Ru-L2-MEPE** in DMSO (see SI); <sup>e</sup>data taken from Rupp et al.<sup>[3b]</sup> n.d.: not determined as reduction and oxidation potentials were obtained from square wave voltammetry.

## Spectro-electrochemistry

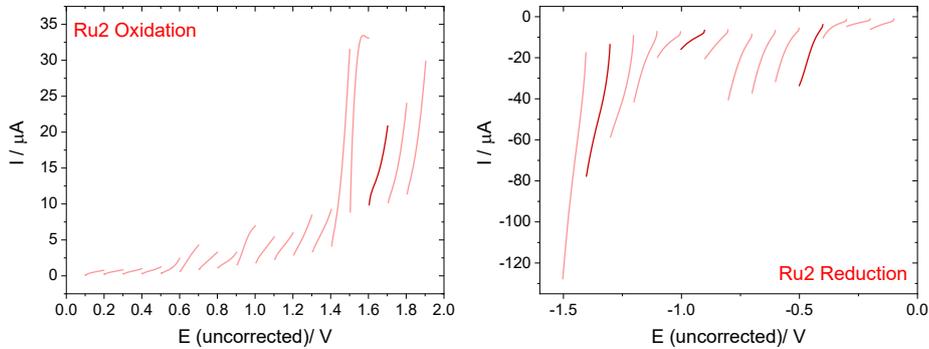


Figure S 32. Linear sweep voltammograms obtained during spectroelectrochemical experiments using complex **Ru2** in dry acetonitrile under inert gas atmosphere, with 0.1 M TBAPF<sub>6</sub>; sweep rate 100 mV/s; pause between scans 130 s; darker traces highlight where UV-vis absorption spectra reported in the main manuscript were recorded. **Left:** Oxidation. **Right:** Reduction. Potentials are reported as obtained using a silver wire as pseudo-reference electrode.

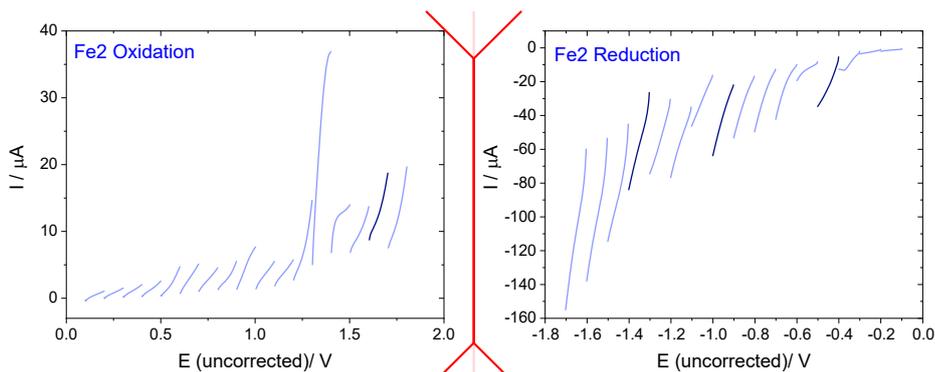


Figure S 33. Linear sweep voltammograms obtained during spectroelectrochemical experiments using complex **Fe2** in dry acetonitrile under inert gas atmosphere, with 0.1 M TBAPF<sub>6</sub>; sweep rate 100 mV/s; pause between scans 130 s; darker traces highlight where UV-vis absorption spectra reported in the main manuscript were recorded. **Left:** Oxidation. **Right:** Reduction. Potentials are reported as obtained using a silver wire as pseudo-reference electrode.

**Comment [MG]:** In diesen Graphen die Skala auf der X-Achse einheitlich anpassen

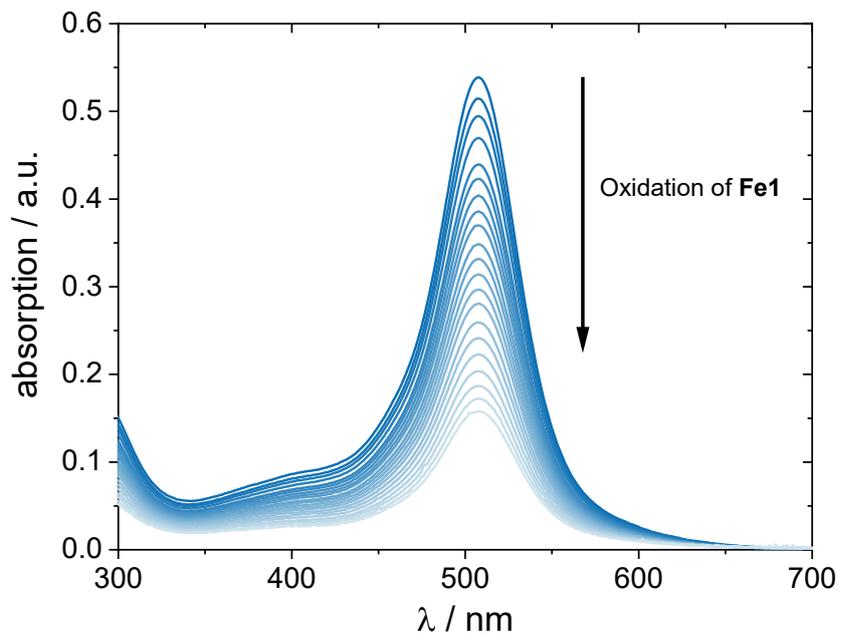


Figure S 34. UV-vis absorption spectra recorded during electrochemical oxidation of Fe1 in aqueous solution KCl (1 M) electrolyte under inert gas atmosphere. The potential is set to 1.5 V vs Ag/AgCl reference electrode, scan rate 100 mV/s, and kept at 1.5 V for 40 minutes; path length 1 cm. The arrow highlights the most significant changes upon oxidation.

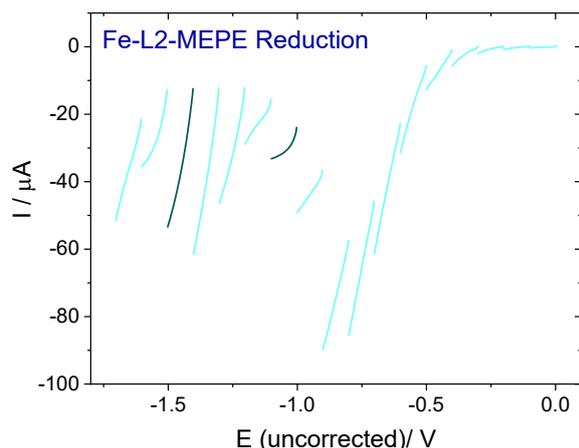


Figure S 35. Linear sweep voltammograms obtained during spectroelectrochemical experiments using complex **Fe-L2-MEPE** in DMSO under inert gas atmosphere, with 0.1 M TBAPF<sub>6</sub>; sweep rate 100 mV/s; pause between scans 130 s; darker traces highlight where UV-vis absorption spectra reported in the main manuscript were recorded. Potentials are reported as obtained using a silver wire as pseudo-reference electrode.

## Layer-by-layer coating

Layer-by-layer self-assembly of **Ru-L2-MEPE** and **Fe-L2-MEPE** on glass substrates as well as ITO-coated PET foil was carried out according to literature procedures.<sup>[4]</sup> In short, the glass substrate was primed in an aqueous polyethyleneimine (PEI, 10 mM) solution for several hours. Both the glass substrate and the PET-ITO foil were then coated by dipping in an aqueous polystyrene sulfonate (PSS, 10 mM) solution for 3 minutes, rinsed gently with water, then dipped in a solution of **Ru-L2-MEPE** or **Fe-L2-MEPE** (0.5 mM) in methanol for 3 minutes and rinsed with water again. This procedure is then repeated. For the glass substrate, each cycle leads to the formation of two bilayers (one on each side of the substrate) while the PET-ITO foil is protected on the non-ITO side, hence leading to only one bilayer per cycle. After the last bilayer coating, the substrates were dipped again in the PSS solution, rinsed, and then dried.

Electrochemical measurements were carried out using the PET-ITO foils, contacted with copper for better conductivity, as working electrode, a platinum mesh as counter electrode, and a Ag/AgCl reference electrode. An aqueous solution of 1 M potassium chloride was used as electrolyte. Measurements were carried out using a Gamry Interface1010 potentiostat and under inert-gas atmosphere.

For the spectroelectrochemical experiment depicted in Figure S40, the coated PET-ITO foil was used as working electrode, a platinum wire as counter electrode, and

potassium chloride (1 M) as electrolyte. The potential was increased stepwise and UV-vis spectra were measured after each 100 mV step.

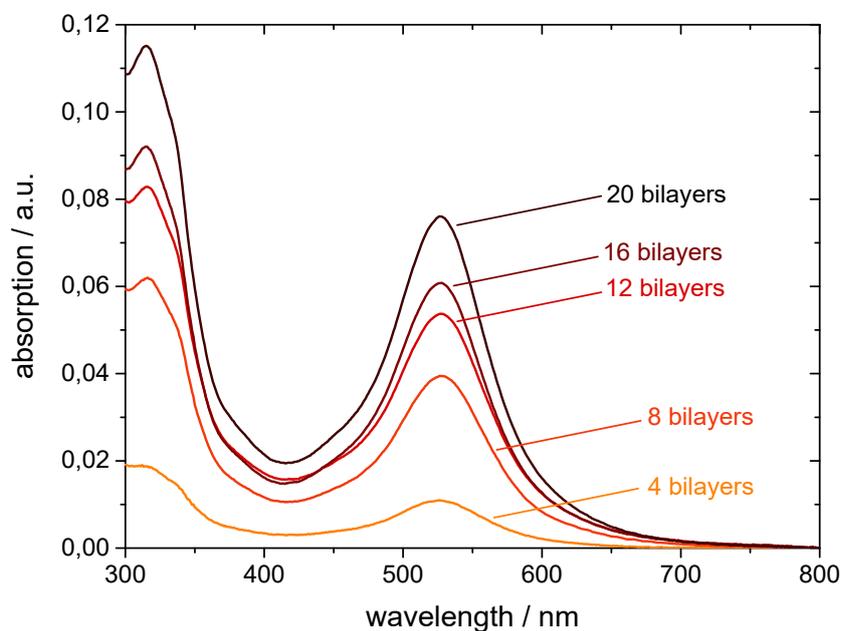


Figure S 36. UV-vis absorption spectra of **Ru-L2-MEPE** coated on a glass substrate with a different number of **PSS-Ru-L2-MEPE** bilayers.

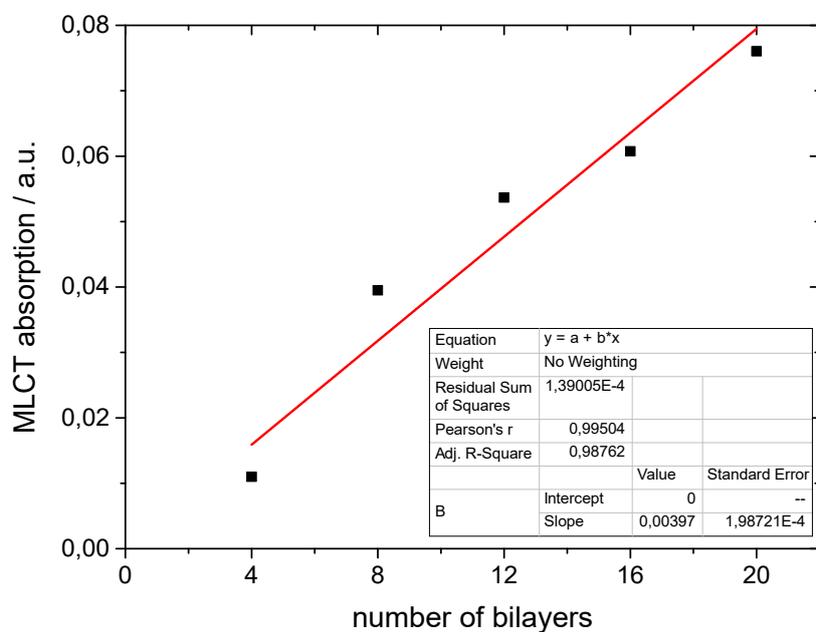


Figure S 37. MLCT absorption maximum depending on the number of **PSS-Ru-L2-MEPE** bilayers coated on a glass substrate. The linear fit shows an even growth of absorptivity with growing number of bilayers.

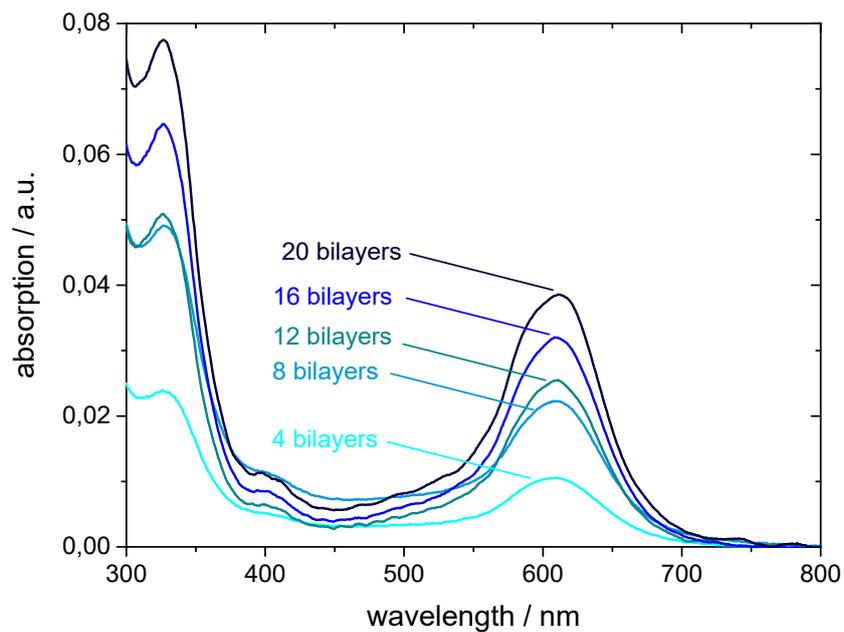


Figure S 38. UV-vis absorption spectra of **Fe-L2-MEPE** coated on a glass substrate with a different number of **PSS-Fe-L2-MEPE** bilayers.

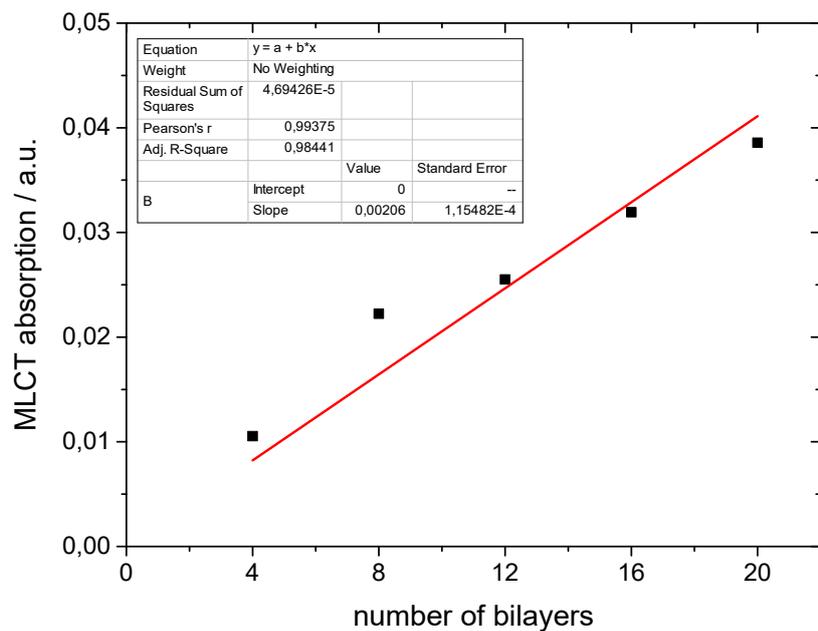


Figure S 39. MLCT absorption maximum depending on the number of **PSS-Fe-L2-MEPE** bilayers coated on a glass substrate. The linear fit shows an even growth of absorptivity with growing number of bilayers.

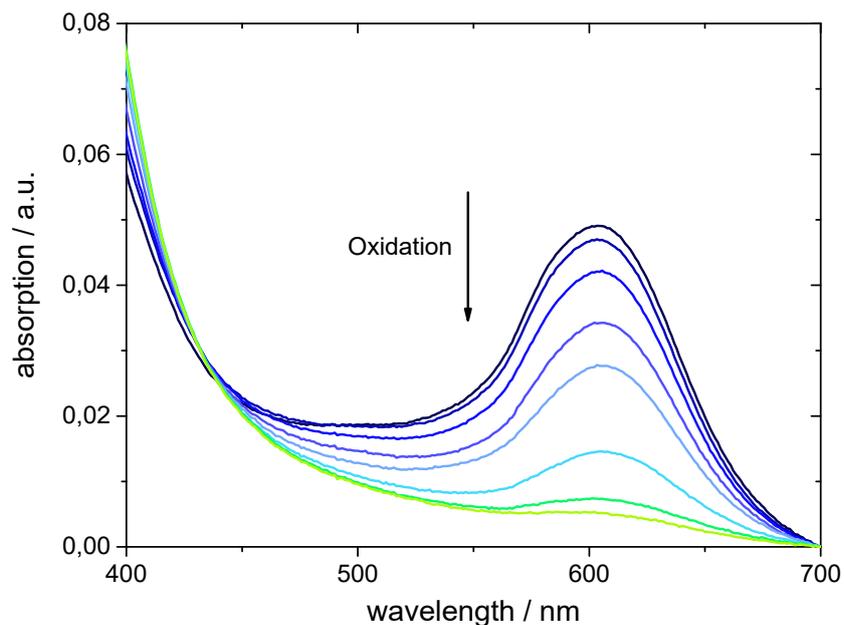


Figure S 40. UV-vis absorption spectra were recorded during the electrochemical oxidation of a PET-ITO foil coated with **Fe-L2-MEPE** (20 bilayers) in an aqueous potassium chloride (1 M) electrolyte under inert gas atmosphere. The arrow highlights the most significant changes upon oxidation.

## Literature

- [1] J. Wang, G. S. Hanan, *Synlett* **2005**, 1251-1254.
- [2] Y. Qian, H. Yang, Y. Wang, *Dyes and Pigments* **2020**, 176, 108251.
- [3] a) R.-A. Fallahpour, M. Neuburger, M. Zehnder, *New J. Chem.* **1999**, 23, 53-61; b) M. Rupp, T. Auvray, E. Rousset, G. M. Mercier, V. Marvaud, D. G. Kurth, G. S. Hanan, *Inorg. Chem.* **2019**, 58, 9127-9134.
- [4] M. Schott, M. Beck, F. Winkler, H. Lormann, D. G. Kurth, *J. Chem. Educ.* **2015**, 92, 364-367.