

ESI to accompany

Homoleptic complexes of a porphyrinatozinc(II)–2,2':6',2''-terpyridine ligand

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Preparation of $[\text{Zn}(\text{ttol})_2][\text{PF}_6]_2$

The complex $[\text{Zn}(\text{ttol})_2][\text{PF}_6]_2$ was prepared following the method used for analogous zinc(II) complexes.¹ The ^1H NMR spectrum has previously been reported.² ^{13}C NMR (126 MHz, CD_3CN) δ/ppm : 157.3 ($\text{C}^{\text{B}4}$), 150.8 ($\text{C}^{\text{B}2}$), 149.0 ($\text{C}^{\text{A}6+\text{A}2}$), 143.0 ($\text{C}^{\text{C}4}$), 142.2 ($\text{C}^{\text{A}4}$), 134.2 ($\text{C}^{\text{C}1}$), 131.3 ($\text{C}^{\text{C}3}$), 129.0 ($\text{C}^{\text{C}2}$), 128.5 ($\text{C}^{\text{A}5}$), 124.2 ($\text{C}^{\text{A}3}$), 122.2 ($\text{C}^{\text{B}3}$), 21.5 (C^{Me}).

Figures:

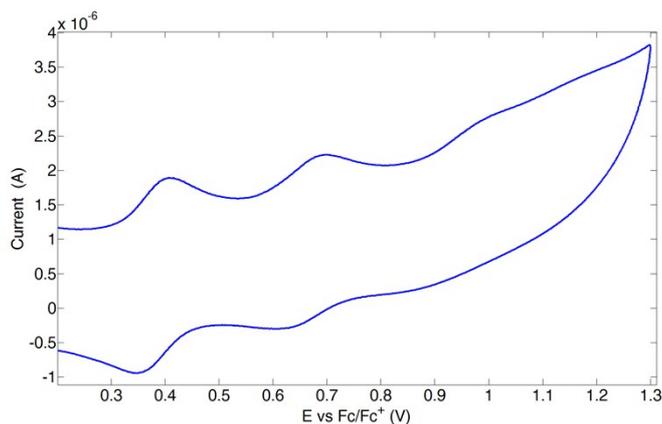


Fig. S1. Oxidative processes in the cyclic voltammogram of $[\text{Zn}(\mathbf{1})_2][\text{PF}_6]_2$ (in MeCN). For conditions, see Table 1.

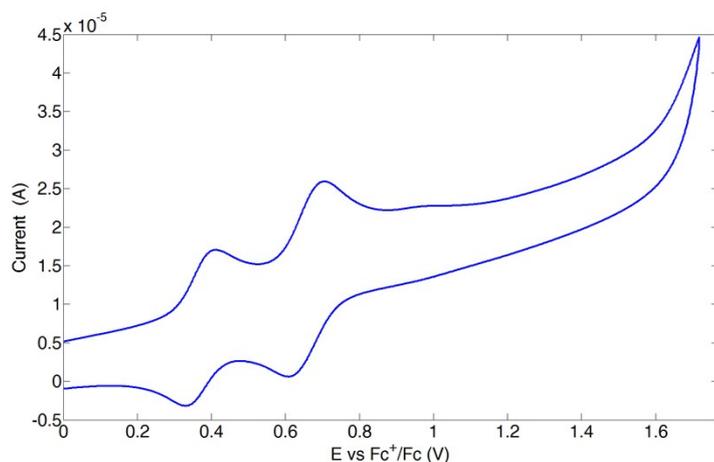


Fig. S2. Oxidative processes in the cyclic voltammogram of $[\text{Fe}(\mathbf{1})_2][\text{PF}_6]_2$ (in MeCN). For conditions, see Table 1.

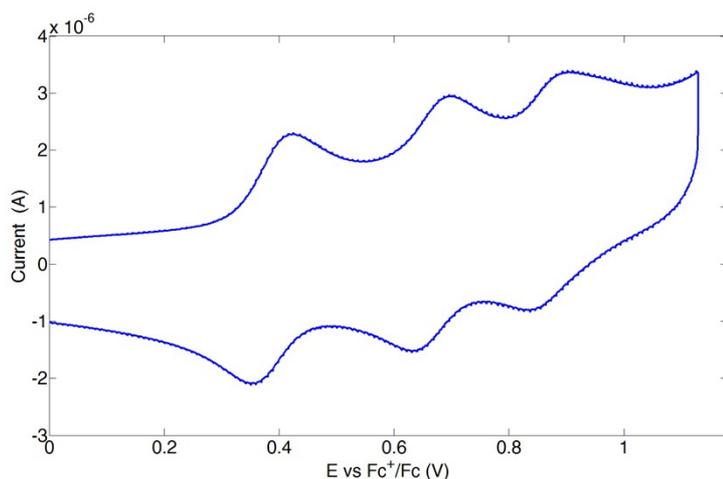
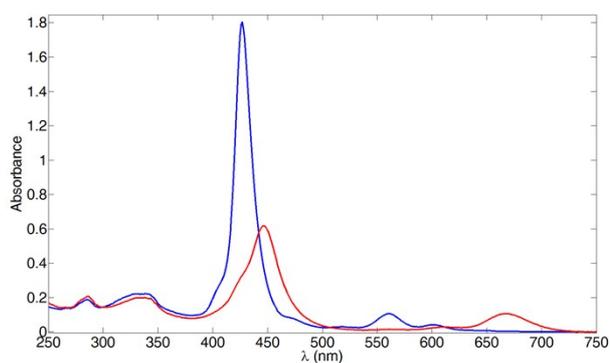
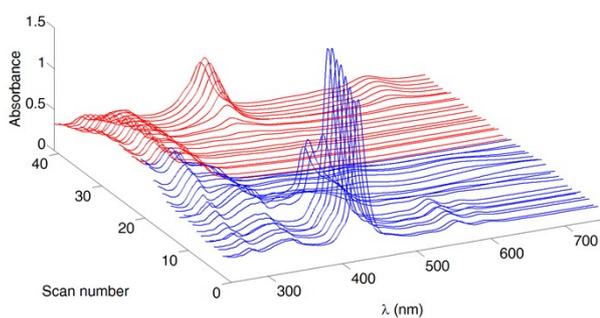


Fig. S3. Oxidative processes in the cyclic voltammogram of $[\text{Ru}(\mathbf{1})_2][\text{PF}_6]_2$ (in MeCN). For conditions, see Table 1.

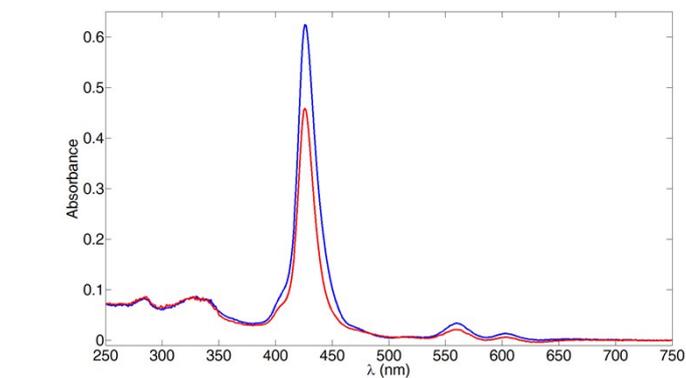


(a)

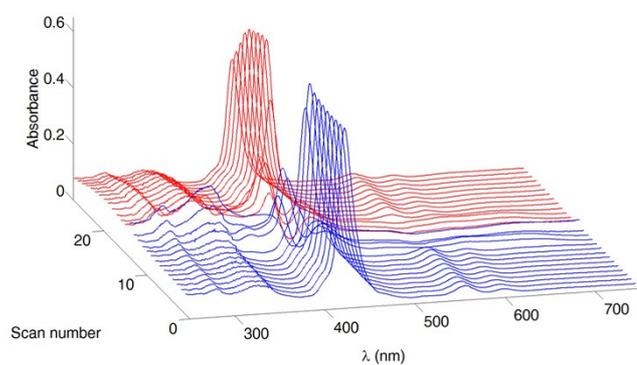


(b)

Fig. S4 Spectroelectrochemical data for the oxidative cycle of $[\text{Zn}(\mathbf{1})_2][\text{PF}_6]_2$ (~ 1 mM in MeCN, $[\text{nBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte). (a) Absorption spectra before (blue line) and after (red line) the oxidative cycle. (b) A spectrum was recorded every 0.1 V, starting from 0 V (first blue line at the front) to +2 V (last blue line) and back from +2 V (first red line) to 0 V (last red line). The potential is referenced with respect to the Fc/Fc^+ redox couple with the same cell under the same experimental conditions.

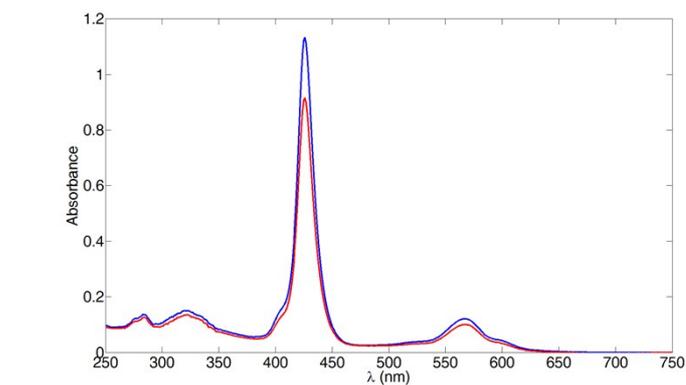


(a)

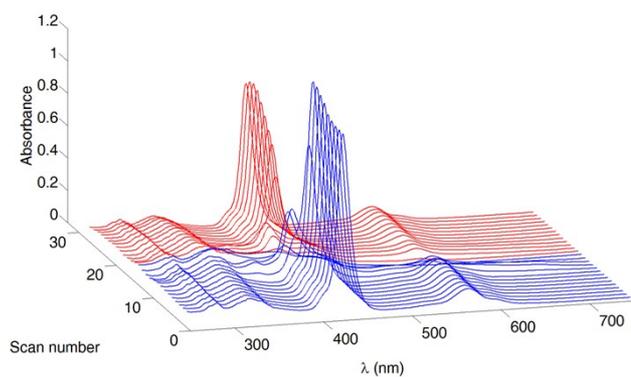


(b)

Fig. S5. Spectroelectrochemical data for the oxidative cycle of $[\text{Zn}(\mathbf{1})_2][\text{PF}_6]_2$ (≈ 0.3 mM in MeCN, $[\text{nBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte). (a) Absorption spectra before (blue line) and after (red line) the oxidative cycle. (b) A spectrum was recorded every 0.1 V, starting from 0 V (first blue line at the front) to +1.3 V (last blue line) and back from +1.3 V (first red line) to 0 V (last red line). See caption to Fig. S4 for referencing to Fc/Fc^+ .

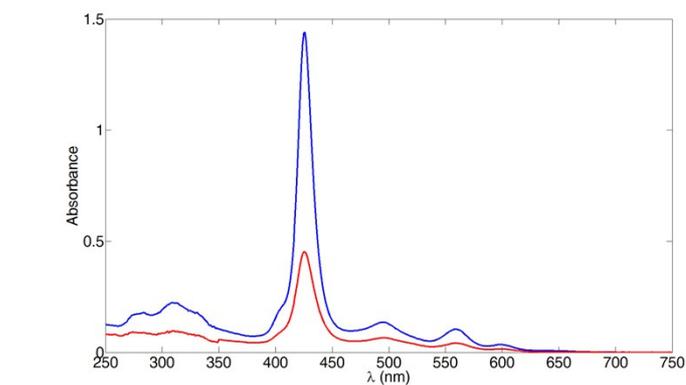


(a)

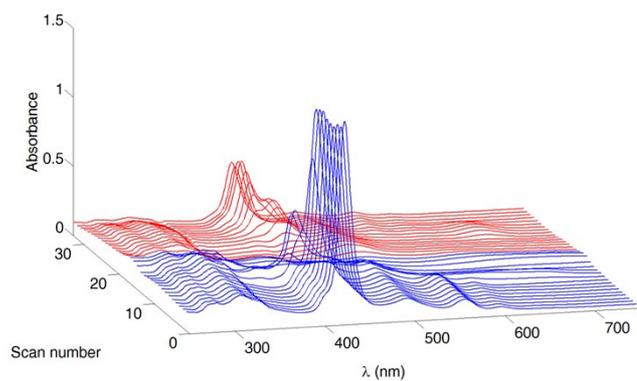


(b)

Fig. S6. Spectroelectrochemical data for the oxidative cycle of $[\text{Fe}(\mathbf{1})_2][\text{PF}_6]_2$ (≈ 0.6 mM in MeCN, $[\text{nBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte). (a) Absorption spectra before (blue line) and after (red line) the oxidative cycle. (b) A spectrum was recorded every 0.1 V, starting from 0 V (first blue line at the front) to +1.3 V (last blue line) and back from +1.3 V (first red line) to 0 V (last red line). See caption to Fig. S4 for referencing to Fc/Fc⁺.

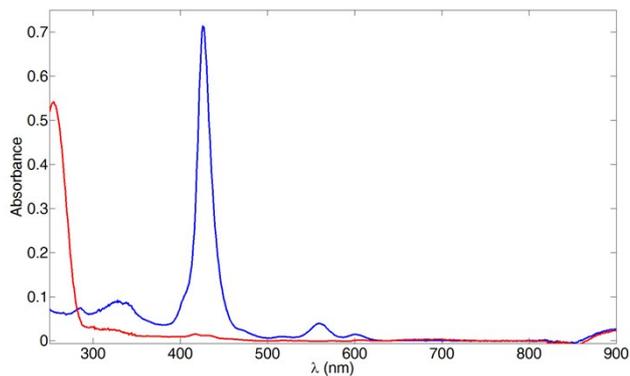


(a)

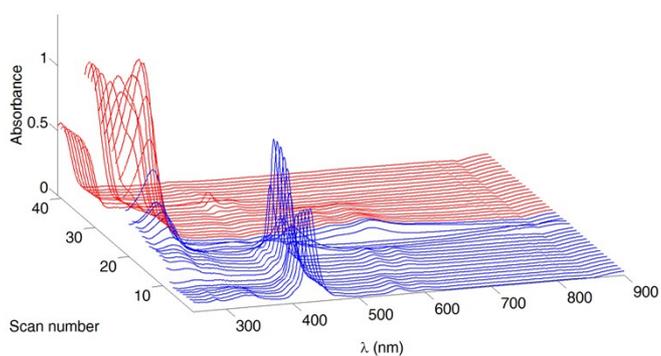


(b)

Fig. S7. Spectroelectrochemical data for the oxidative cycle of $[\text{Ru}(\mathbf{1})_2][\text{PF}_6]_2$ (≈ 0.5 mM in MeCN, $[\text{nBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte). (a) Absorption spectra before (blue line) and after (red line) the oxidative cycle. (b) A spectrum was recorded every 0.1 V, starting from 0 V (first blue line at the front) to +1.6 V (last blue line) and back from +1.6 V (first red line) to 0 V (last red line). See caption to Fig. S4 for referencing to Fc/Fc^+ .



(a)



(b)

Fig. S8. Spectroelectrochemical data for the reductive cycle of $[\text{Zn}(\mathbf{1})_2][\text{PF}_6]_2$ (≈ 1 mM in MeCN, $[\text{nBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte). (a) Absorption spectra before (blue line) and after (red line) the reductive cycle. (b) A spectrum was recorded every 0.1 V, starting from 0 V (first blue line at the front) to -2.0 V (last blue line) and back from -2.0 V (first red line) to 0 V (last red line). See caption to Fig. S4 for referencing to Fc/Fc^+ .

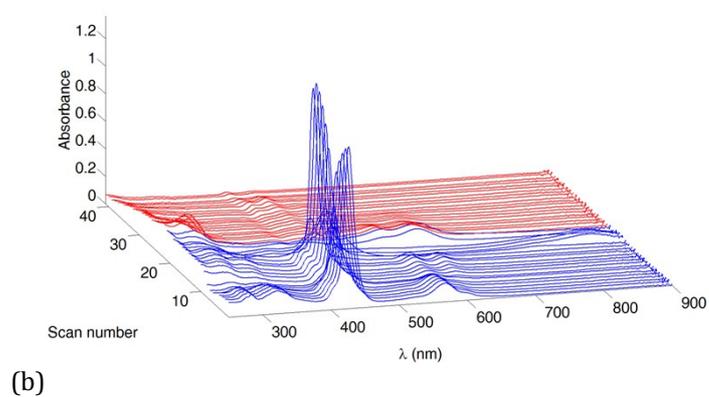
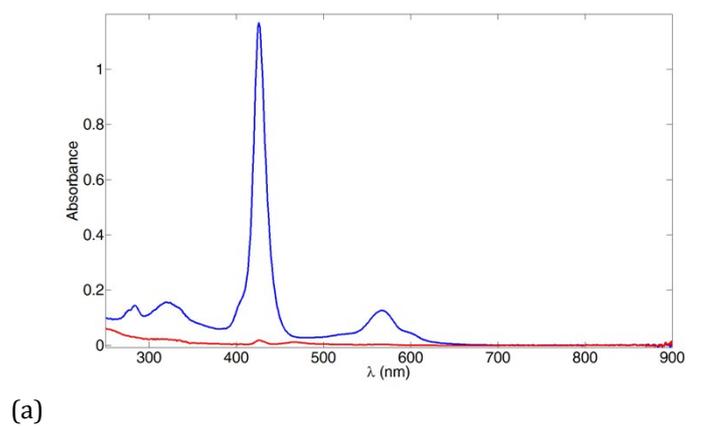
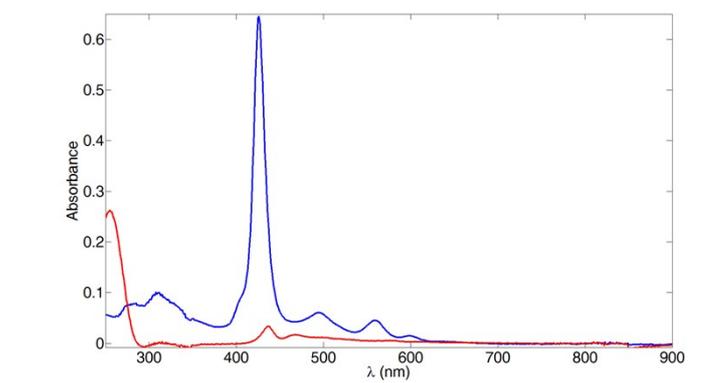
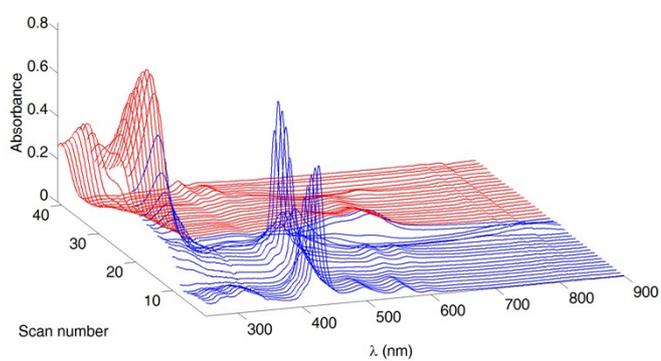


Fig. S9. Spectroelectrochemical data for the reductive cycle of $[\text{Fe}(\mathbf{1})_2][\text{PF}_6]_2$ (≈ 1 mM in MeCN, $[\text{nBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte). (a) Absorption spectra before (blue line) and after (red line) the reductive cycle. (b) A spectrum was recorded every 0.1 V, starting from 0 V (first blue line at the front) to -2.0 V (last blue line) and back from -2.0 V (first red line) to 0 V (last red line). See caption to Fig. S4 for referencing to Fc/Fc^+ .



(a)



(b)

Fig. S10. Spectroelectrochemical data for the reductive cycle of $[\text{Ru}(\mathbf{1})_2][\text{PF}_6]_2$ (≈ 1 mM in MeCN, $[\text{nBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte). (a) Absorption spectra before (blue line) and after (red line) the oxidative cycle. (b) A spectrum was recorded every 0.1 V, starting from 0 V (first blue line at the front) to -2.0 V (last blue line) and back from -2.0 V (first red line) to 0 V (last red line). See caption to Fig. S4 for referencing to Fc/Fc^+ .

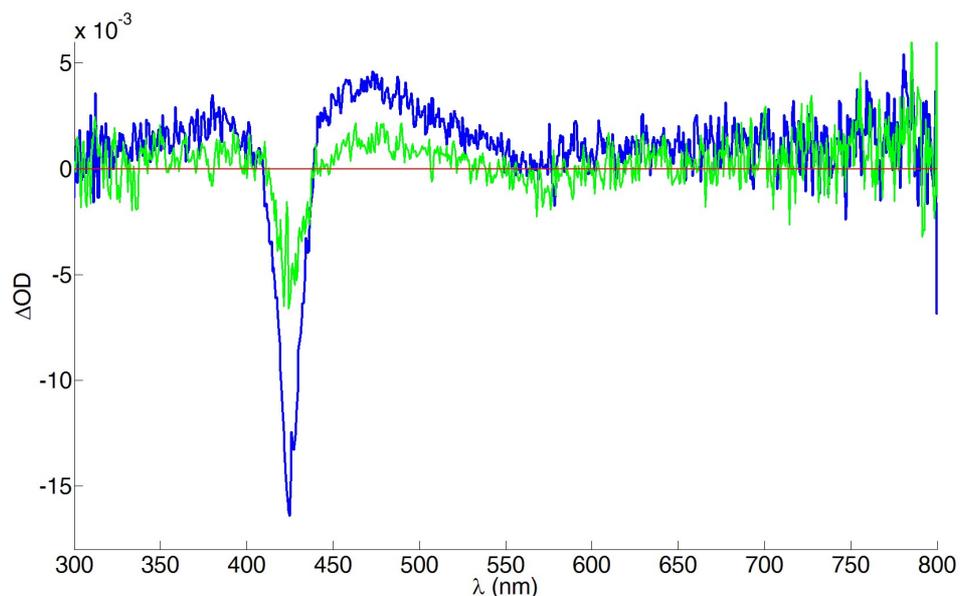


Fig. S11. Transient absorption spectrum of $[\text{Fe}(\mathbf{1})_2][\text{PF}_6]_2$ (MeCN, $\approx 2 \times 10^{-6}$ M, room temperature), $\lambda_{\text{ex}} = 550$ nm. Acquisition time 200 ns, 5 acquisitions. Blue line, deaerated solution; green line, air equilibrated solution.

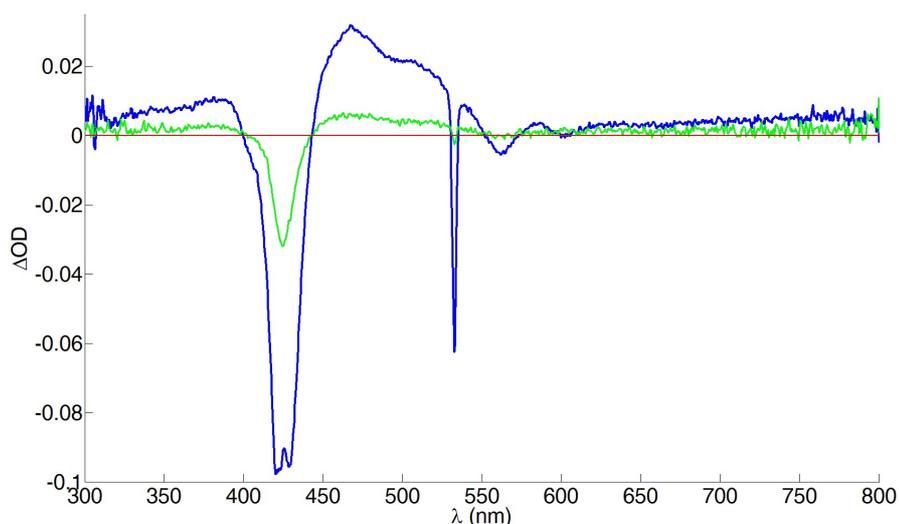


Fig. S12 Transient absorption spectrum of $[\text{Ru}(\mathbf{1})_2][\text{PF}_6]_2$ (MeCN, $\approx 2 \times 10^{-6}$ M, room temperature), $\lambda_{\text{ex}} = 532$ nm. Acquisition time 200ns, 5 acquisitions. Blue line deaerated solution (the Soret band is doubled due to a slightly over-concentrated solution), green line air equilibrated solution. Different intensities are due to different concentration of the samples. Sharp peak at 532 nm in the figure is due to stray laser light.

References

- 1 E.C. Constable, C.E. Housecroft, N.S. Murray and Z.A. Zampese, *Polyhedron*, 2013, **54**, 110.
- 2 B. Bozic-Weber, E. C. Constable, N. Hostettler, C. E. Housecroft, R. Schmitt and E. Schönhofer, *Chem. Commun.*, 2012, **48**, 5727.