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Photoinduced Ligand Release in a Ruthenium(II)-Cobalt(III) Heterodinuclear System

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General Experimental

¹H NMR spectra were recorded on either a Varian INOVA 500 spectrometer at 23°C, operating at 500 MHz or a Varian UNITY 300 NMR spectrometer at 23°C operating at 300 MHz. gCOSY, HSQCAD and gHMBC experiments were all performed on a Varian INOVA 500 spectrometer at 23°C, operating at 500 MHz. ¹³C NMR spectra were recorded on either a Varian INOVA 500 spectrometer at 23°C operating at 125 MHz or a Varian UNITY 300 NMR spectrometer at 23°C operating at 75 MHz. The INOVA was equipped with a variable temperature and inverse-detection 5 mm probe or a triple-resonance indirect detection PFG probe. The UNITY was equipped with a variable temperature direct broadband 5 mm probe. Chemical shifts are expressed in parts per million (ppm) on the δ scale and were referenced to the appropriate solvent peaks, TMS or TMPS. DMSO-d₆ referenced to CD₃(CHD₂)SO at δH 2.50 (¹H) and (CD₃)₂SO at δC 39.43 (¹³C). Acetonitrile-d₃ referenced to CHD₂CN at δH 1.94 (¹H) and CD₃CN at δC 1.24 (¹³C). Methanol-d₄ referenced to CHD₂OD at δH 3.31 (¹H) and CD₃OD at δC 49.05 (¹³C). TMS and TMPS were both referenced to δH 0 (¹H) and δC 0 (¹³C). Electrospray Ionisation Mass Spectra were recorded on a Micromass LCT spectrometer using a probe voltage of 3200 V, an operating temperature of 150°C and a source temperature of 80°C. The carrier solvent was 1:1 CH₃CN/H₂O at 20 μL min⁻¹. Typically, 10 μL of a 10 μL mL⁻¹ solution was injected. Leucine enkephalin was used as the lock mass internal standard.

UV-visible spectra were recorded on a Varian CARY Probe 50 UV-vis spectrophotometer or a Varian CARY 100 UV-vis spectrophotometer.

Steady state absorption measurements were performed using an absorption spectrometer (Cary Bio50, Varian). Steady state emission spectra were acquired with an emission spectrometer (Cary Eclipse, Varian). Quantum yield measurements were performed using the optically dilute method, using [Ru(bpy)₃]Cl₂ in aqueous solution as a standard (φ_{ref} = 4.2%). Time resolved emission lifetime experiments were performed using a nanosecond laser setup. The 355 nm tripled output of a Q-switched Nd:YAG (Continuum NY-61-10, Coherent) was used to drive an OPO system (Casix BBO, Shanghai Uniwave Technologies) which was tuned to 440 nm, and this output was focused on the

sample using all quartz optics. Emission was collected perpendicular to the excitation, collimated then refocused onto the entrance port of a 0.3 m triple grating monochromator (SpectraPro 300i, Acton Instruments) for spectral selection at 630 nm. The detector was a PMT tube (R928P, Hamamatsu), the output of which was sampled directly using a 500 MHz digital oscilloscope (TDS520, Tektronix). The instrument response function (IRF) for this setup was measured using scattered excitation to be ca. 8 ns at FWHM. Each resulting trace contained at least 1000 data points, and was averaged over 1000 shots. Data analysis was performed using a commercially available software package (Igor, Version 6.1.2.1, Wavemetrics). The quality of the fit was assessed using the reduced chi-squared χ² function and by an inspection of the weighted residuals.

Elemental analyses were performed by the Campbell Microanalytical Laboratory at the University of Otago.

[(bpy)₂Ru(phen)](PF₆)₂,¹ pyridine-2-carbohydrazonamide,² [Co(en)₂(OTf)₂](OTf)₃,³ and [Co(tren)(OTf)₂](OTf)₃³ were synthesized according to literature methods.

[(bpy)₂Ru(pytp)](PF₆)₂

[(bpy)₂Ru(pytp)](PF₆)₂ was synthesised by a modification of the literature method of Liu.⁴

0.5 g [(bpy)₂Ru(phen)](PF₆)₂·H₂O was dissolved in 15 ml of CH₃CN. 0.076 g of pyridine-2-carbohydrazonamide was dissolved in 5 ml of EtOH and then added to the acetonitrile solution. The reaction mixture was heated at reflux for 1 h after which it was filtered over celite and taken to dryness. The pure product was obtained by column chromatography on silica gel, eluting with an EtOH and 10% NaCl H₂O solution (50:50). The major red band was collected and the ethanol removed under vacuum. The addition of a few drops of a methanolic saturated solution of NH₄PF₆ precipitated out the product which was filtered and washed with 0 °C water, 0 °C EtOH and ether. Yield 0.30 g (52 %). ¹H NMR (500MHz; solvent CD₃CN) δ 9.806 (dd, 1 H, phen), 9.721 (dd, 1 H, phen), 8.963 (d, 1 H, py), 8.927 (d, 1 H, py), 8.543 (m, 4 H, bpy), 8.302 (dd, 1 H, phen), 8.263 (dd, 1 H, phen), 8.140 (m, 1 H, py), 8.127 (m, 2 H, bpy), 8.030 (m, 2 H, bpy), 7.957 (m, 2 H, py), 7.848 (d, 2 H, bpy), 7.717 (d, 1 H, py), 7.682 (m, 2 H, bpy), 7.475 (m, 2 H, bpy), 7.269 (m, 2 H, bpy). ESI-MS: m/z (fragment) 869.38 ([M-(PF₆)]⁺), 362.32 ([M-2(PF₆)]²⁺).

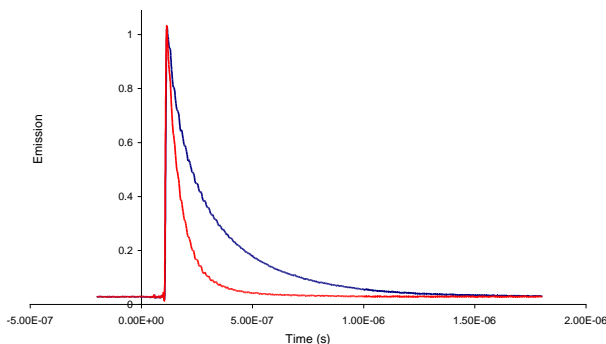
UV-vis (CH₃CN): λ_{max} = 440.0 nm.

[(bpy)₂Ru(pytp)Co(tren)](PF₆)₅

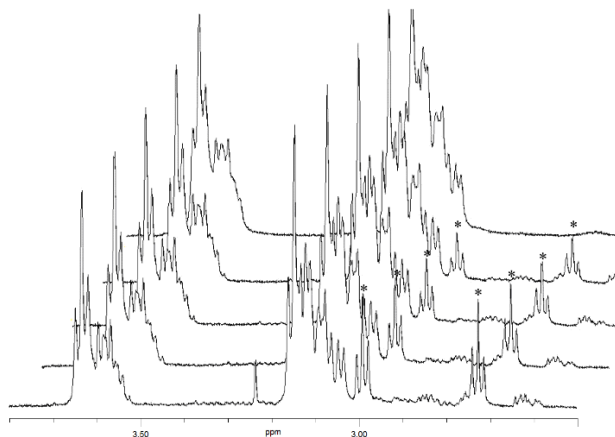
0.0586 g of [(bpy)₂Ru(pytp)]²⁺ and 0.0377g
 5 [Co(tren)(OTf)₂](OTf) were placed in a 25 ml round bottom
 flask. The flask was wrapped in aluminium foil and 2 ml of
 acetonitrile added. The flask was then stoppered and the
 solution stirred for 3 hours at room temperature. The product
 was precipitated out as the PF₆⁻ salt by drop wise addition to a
 10 stirred solution of 60 ml water and 3 ml of saturated solution
 of NH₄PF₆ in methanol. Yield 0.0515g ¹H NMR (500MHz;
 solvent CD₃CN) δ 9.856 (dd, 1 H), 9.589 (dd, 1 H), 9.333 (dd,
 1 H), 8.880 (d, 1 H), 8.693 (t, 1 H), 8.562 (m, 4 H), 8.490 (dd,
 1 H), 8.409 (dd, 1 H), 8.232 (m, 1 H), 8.143 (m, 2 H), 8.092 –
 15 8.032 (m, 4 H, phen), 7.846 (m, 2 H), 7.750 (dd, 1 H), 7.689
 (dd, 1 H), 7.490 (m, 2 H), 7.294 (m, 2 H), 5.299 (br s, 2 H,
 tren), 4.637 (m, 2 H), 4.364 (br s, 2 H), 4.115 (m, 2 H), 3.637
 (m, 4 H), 3.166 (m, 6 H). ¹³C NMR (75 MHz; solvent
 20 CD₃CN) δ 165.166, 159.777, 158.013, 157.818, 157.785,
 155.528, 154.595, 153.096, 152.991, 152.466, 151.849,
 148.527, 147.127, 144.772, 139.280, 139.259, 139.217,
 139.187, 136.405, 135.046, 132.958, 130.379, 128.679,
 128.630, 128.583, 127.814, 127.766, 125.403, 65.248, 61.879,
 47.867, 44.969. Anal. Calc. for C₄₄H₄₄F₃₀N₁₄P₅CoRu.H₂O
 25 (1653.74): C 31.96, H 2.68, N 11.86%; found: C 31.70, H
 3.50, N 11.05. ESI-MS: m/z (fragment) 1509.31 ([M-(PF₆)]⁺),
 362.32 ([M-2(PF₆)]²⁺). UV-vis (CH₃CN): λ_{max} = 445 nm.

[(bpy)₂Ru(pytp)Co(en)](PF₆)₅

30 0.0586 g of [(bpy)₂Ru(pytp)]²⁺ and 0.0377g
 [Co(en)(OTf)₂](OTf) were placed in a 25 ml round bottom
 flask. The flask was wrapped in aluminium foil and 2 ml of
 acetonitrile added. The flask was then stoppered and the
 solution stirred for 3 hours at room temperature. The product
 35 was precipitated out as the PF₆⁻ salt by drop wise addition to a
 stirred solution of 60 ml water and 3 ml of saturated solution
 of NH₄PF₆ in methanol. Yield 0.0515g ¹H NMR (500 MHz;
 solvent CD₃CN) δ 9.851 (m, 1 H), 9.781 (m, 1 H), 9.304 (d, 1
 H), 8.830 (d, 1 H), 8.714 (t, 1 H), 8.554 (m, 4 H), 8.470 (m, 1
 40 H), 8.412 (m, 1 H), 8.268 (m, 1 H), 8.144 (m, 2 H), 8.061 (m,
 4 H), 7.842 (m, 2 H), 7.742 (t, 1 H), 7.688 (t, 1 H), 7.489 (m,
 2 H), 7.300 (m, 2 H), 3.156 (m, 4 H), 3.758 (m, 4 H). Anal.
 Calc. for C₄₂H₄₂F₃₀N₁₄P₅CoRu.H₂O (1627.70): C 30.99, H
 2.60, N 12.05%; found: C 30.32, H 3.26, N 11.59. UV-vis
 45 (CH₃CN): λ_{max} = 445 nm.



50 **Fig. S1** Lifetime measurements for [(bpy)₂Ru(pytp)]²⁺ (blue) and
 [(bpy)₂Ru(pytp)Co(tren)]⁵⁺ (red)



55 **Fig. S2** Photoinduced release of tren from [(bpy)₂Ru(pytp)Co(tren)]⁵⁺
 (from top to bottom: 0, 1, 2, 3, 4, 5 hr irradiation time); the peaks
 assigned to free tren are marked with an asterisk

Notes and references

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