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 was both referenced to δH 3.31 (H) and δC 49.05 (C). Methanol was referenced to δH 3.31 (H) and δC 48.34 (C). Acetonitrile was referenced to δH 1.94 (H) and δC 1.24 (C). Ethanol was referenced to δH 3.31 (H) and δC 48.34 (C).

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 using 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 (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 Univeq 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(phenindione)[PF6]2 | pyridine-2-carboxyhydrazonamide,2 | [Co(en)2(O Tf)]OTf,1 and [Co(tren)(OTT)2](OTf)3 | were synthesized according to literature methods.

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

0.5 g [(bpy)2Ru(phenindione)] [PF6]2. H2O was dissolved in 15 ml of CH3CN. 0.076 g of pyridine-2-carboxyhydrazonamide 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. 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 CD CN) 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)4]3), 362.32 ([M-2(PF6)2]3).
UV-vis (CH$_3$CN): $\lambda_{\text{max}} = 440.0$ nm.

$\left[\text{bpy}\right]_2\text{Ru(pytp)}\text{Co(tren)}\left[\text{PF}_6\right]_5$

0.0586 g of $\left[\text{bpy}\right]_2\text{Ru(pytp)}^{2+}$ and 0.0377 g [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 PF$_6^-$ salt by drop wise addition to a stirred solution of 60 ml water and 3 ml of saturated solution of NH$_4$PF$_6$ in methanol. Yield 0.0515g. $^1$H NMR (500MHz; solvent CD$_2$CN) $\delta$ 9.856 (dd, 1 H), 9.589 (dd, 1 H), 9.333 (dd, 1 H), 8.880 (dd, 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 – 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, tren), 4.115 (m, 4 H), 3.166 (m, 6 H). $^{13}$C NMR (75 MHZ; solvent CD$_2$CN) $\delta$ 165.166, 159.777, 158.013, 157.818, 157.818, 157.785, 155.528, 154.595, 153.096, 152.991, 152.466, 151.849, 148.527, 147.127, 144.772, 144.772, 143.259, 139.280, 139.259, 139.217, 139.058, 138.058, 136.405, 135.046, 132.958, 130.379, 128.679, 128.630, 128.583, 127.814, 127.766, 125.403, 65.248, 61.879, 47.856, 44.969. Anal. Calc. for C$_{44}$H$_{42}$N$_{13}$P$_6$CoRu$_2$H$_2$O (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-(PF$_6$)$_4$]), 362.32 ([M-2(PF$_6$)]$^{2+}$). UV-vis (CH$_3$CN): $\lambda_{\text{max}} = 445$ nm.

$\left[\text{bpy}\right]_2\text{Ru(pytp)}\text{Co(en)}\left[\text{PF}_6\right]_5$

0.0586 g of $\left[\text{bpy}\right]_2\text{Ru(pytp)}^{2+}$ and 0.0377 g [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 was precipitated out as the PF$_6^-$ salt by drop wise addition to a stirred solution of 60 ml water and 3 ml of saturated solution of NH$_4$PF$_6$ in methanol. Yield 0.0515g. $^1$H NMR (500MHz; solvent CD$_2$CN) $\delta$ 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 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), 7.588 (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 C$_{44}$H$_{42}$N$_{13}$P$_6$CoRu$_2$H$_2$O (1627.70): C 30.99, H 2.60, N 12.05%; found: C 30.32, H 3.26, N 11.59. UV-vis (CH$_3$CN): $\lambda_{\text{max}} = 445$ nm.

Notes and references