

Iridium(III) luminophores as energy-donors for sensitised emission from lanthanides in the visible and near-infrared regions

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Supporting Information

1. Characterisation data for complexes

For complex **1**. ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 6.35 (2H, t); 6.96 (2H, td); 7.09 (4H, m); 7.38 (1H, ddd); 7.45 (1H, dd); 7.58 (1H, d); 7.62 (1H, dd); 7.68 (2H, m); 7.72 (2H, d); 7.80 (2H, t); 7.89 (1H, td); 7.94 – 8.04 (8H, m); 8.21 (1H, td); 8.47 (1H, d); 8.71 – 8.75 (2H, m); 8.76 (1H, d); 8.89 (1H, d); 8.91 (1H, d). ESMS: m/z 887 ($M - \text{PF}_6$) $^+$. Found: C, 55.3; H, 3.0; N 8.0%. $\text{C}_{48}\text{H}_{34}\text{IrN}_6\text{PF}_6$ requires: C, 55.9; H, 3.3; N 8.1%.

For complex **1^F**. ^1H NMR (400 MHz, CDCl_3): δ 9.59 (1H, d); 9.48 (1H, s); 8.79-8.74 (3H, m); 8.49 (1H, d); 8.37-8.32 (3H, m); 8.19 (2H, d); 8.02-7.84 (7H, m), 7.76 (1H, d); 7.67 (1H, d); 7.58 (1H, d), 7.52 (1H, t); 7.39 (1H, t); 7.14 (2H, t); 6.65-6.58 (2H, m); 5.75 (2H, dt). ESMS: m/z 859 ($M - \text{NO}_3$) $^+$. Found: C, 53.2; H, 2.9; N 9.0%. $\text{C}_{48}\text{H}_{30}\text{F}_4\text{IrN}_7\text{O}_3 \cdot \text{CH}_2\text{Cl}_2$ requires: C, 53.2; H, 2.9; N 8.9%.

For complex **2**. ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 2.24 (3H, s), 2.43 (3H, s), 2.85-2.95 (4H, m), 6.10 (1 H, d), 6.24 (1 H, d), 6.88 (2 H, m), 7.00 (2H, t), 7.03 (2H, t), 7.25 (1H, d), 7.33 (1H, d), 7.42 (1H, s), 7.44 (1H, d), 7.64 (4H, t), 7.67 (2H, t), 7.78 (1H, d), 7.84 (1H, d), 7.88 (1H, d), 7.98 (1H, d), 8.17 (1H, s), 8.18 (1H, d), 8.22 (1H, d), 8.43 (1H, d), 8.48 (1H, d), 8.53 (1H, d). ESMS: m/z 867.3 ($M - \text{PF}_6$) $^+$. Found: C, 54.0; H, 3.9; N 8.0%. $\text{C}_{46}\text{H}_{38}\text{F}_6\text{IrN}_6\text{P}$ requires: C, 54.6; H, 3.8; N 8.3%.

2. Data on photophysical measurements

UV/Vis absorption spectra were measured on a Cary 50 spectrometer; luminescence spectra were measured on a Jobin-Yvon Fluoromax 4 fluorimeter using air-equilibrated CH_2Cl_2 solutions at room temperature, or EtOH/MeOH glasses (4:1, v/v) at 77K. Emission spectra within a given series [*i.e.* a titration of **1**, **2** or **1^F** with a $\text{Ln}(\text{hfac})_3(\text{H}_2\text{O})_2$] were all recorded with excitation at a wavelength where all samples were isoabsorbing.

Ir-based emission lifetimes were measured using the Time-Correlated Single Photon Counting technique with an Edinburgh Instruments 'Mini- τ ' luminescence lifetime spectrometer, equipped with a 405 nm pulsed diode laser as excitation source and a cooled Hamamatsu-R928 PMT detector; the lifetimes were calculated from the measured data using the supplied software.

Near-infrared emission spectra were recorded on a home built setup. Samples were excited at 400 nm with the frequency-doubled output of a Ti:Sapphire tunable pulsed laser. The energy of excitation pulses delivered to the sample was *ca.* 1 mJ, at 10 Hz repetition rate. The Ti:Sapphire laser was pumped by the second harmonic (532 nm) of a Q-switched Nd:YAG laser LS-2137U (LOTIS TII). The detection part of the setup comprises a Bentham TMC600 spectrograph coupled with an Andor DU490-1.7 InGaAs diode array. To suppress second-order contribution of Ir(III)-based visible emission, long-pass interference filters (Thorlabs) were used in front of the entrance slit of the spectrograph. The presented emission spectra were not corrected for the spectral response of the detection system. Wavelength calibration was performed using a Ne calibration lamp.

The same excitation conditions as described above were used for the time-resolved IR emission measurements of Nd(III)-based emission. The sample emission was collected through a wide-angle lens and detected by InGaAs photodiode detector (PDA10CF, Thorlabs) with wavelength selection by means of narrow band-pass filters combined with long-pass interference filters. The detector voltage output was coupled into Tektronix TDS 3032B digital oscilloscope and subsequently transferred to a PC for analysis. The instrumental response function is estimated as *ca.* 22 ns FWHM. The analysis of time-resolved data to obtain grow-in and decay lifetimes was performed using Igor Pro software (WaveMetrics, Inc). Instrumental response deconvolution was applied when necessary to recover the fastest lifetimes.

3. Additional figures of spectra

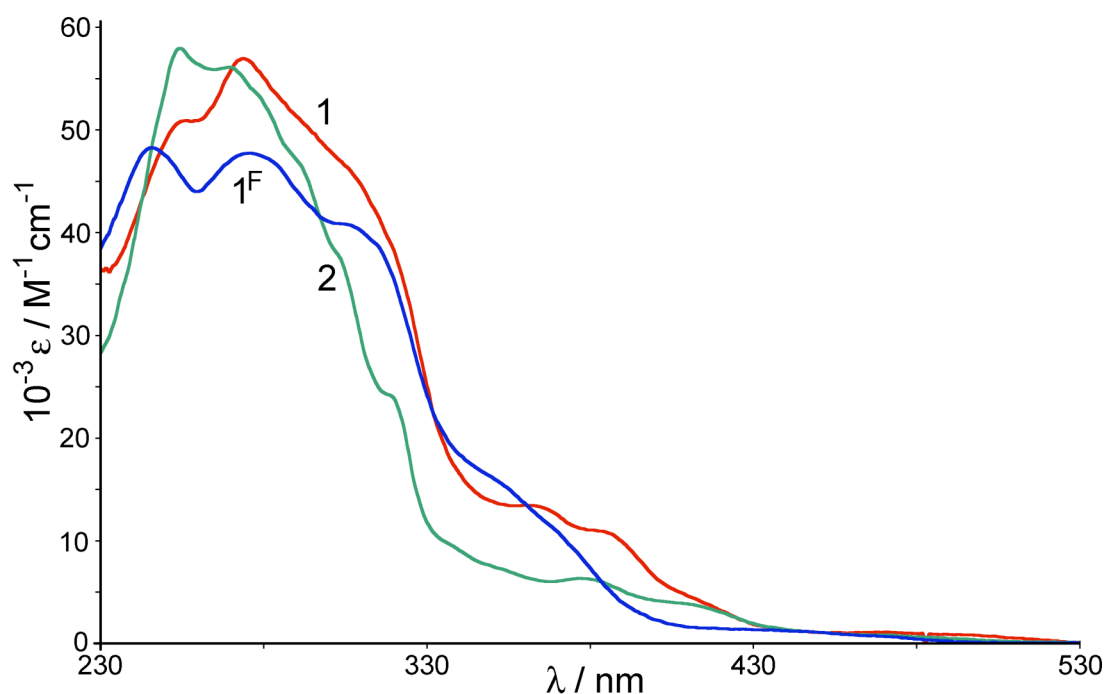


Figure S1: UV/Vis spectra of the three Ir(III) complexes in CH_2Cl_2 at room temperature

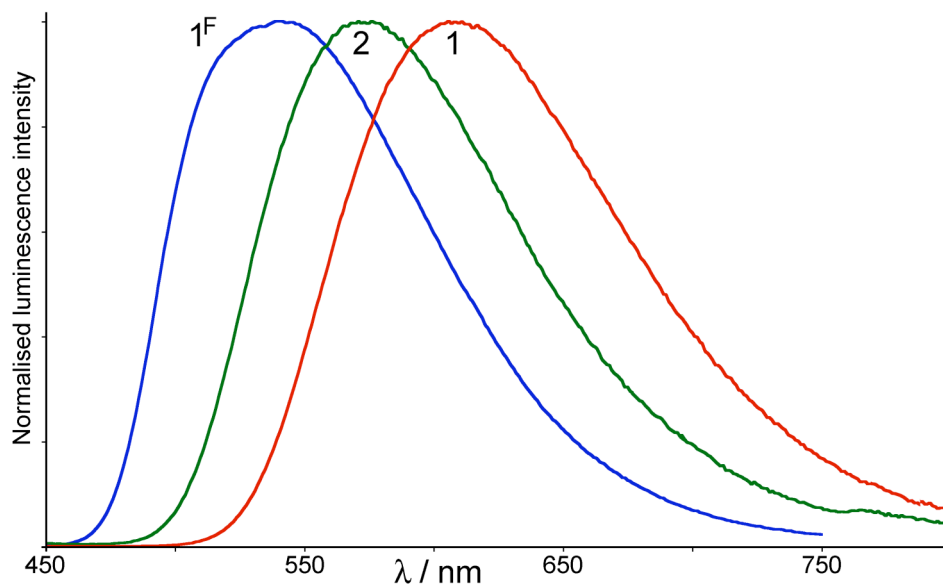


Figure S2: Normalised luminescence spectra of the three Ir(III) complexes in CH_2Cl_2 at room temperature