Combined two-photon excitation and d→f energy-transfer in Ir/lanthanide dyads with time-gated selection from a two-component emission spectrum

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Supporting Information:

Experimental information for the Two-photon absorption (TPA) spectroscopy

The two-photon cross-section of $[Ir(F_2ppy)_2(py\text{-}pz)]^+$ was measured using the femtosecond TPA induced fluorescence method. A mode-locked, cavity dumped (APE Pulse switch) Ti:sapphire laser (Coherent MIRA) was pumped by the 2nd harmonic (532 nm) of a CW Nd:YAG laser (Coherent Verdi V6) at a power of 4.5 W to create a pulsed excitation source. The pulse characteristics were: a temporal full width at half maximum (FWHM) of ~150 fs, average power 10 mW at a repetition rate of ~2.5 MHz and an energy of 4 nJ $pulse^{-1}$. A variable ND filter (Edmund Optics) mounted on a translation stage was used to control the light intensity incident on the sample, with the power monitored by splitting the beam to a photodiode of known response, calibrated against a free standing power meter. Gold mirrors, highly reflective of NIR radiation, were used with a 20x objective (Olympus LWD C A20) to focus the source onto the sample. A 55 μM sample of the nitrate salt of the complex in aerated dichloromethane was prepared in a 1 cm path length quartz cuvette. Two-photon excited photoluminescence spectra were collected with a dichroic mirror (Semrock FF735) and detected with a 100 μm core fibre optic cable coupled CCD spectrograph (Avantes Avaspec 2048FT) fitted with a 700 nm shortpass filter to remove extraneous laser light. The TPA cross section (σ_2) was measured relative to fluorescein as a reference, as per the standard methodology of Webb *et al.*,[1] using the equation:

$$\sigma_2^S = \frac{\sigma_2^R \Phi_P^R c^R n^S F^S(\lambda)}{\Phi_P^S c^S n^R F^R(\lambda)}$$

The superscripts *R* and *S* refer to the reference and sample respectively, Φ_P is the one photon photoluminescence quantum yield, *c* is the concentration, *n* is the solvent refractive index and $F(\lambda)$ is the integrated two-photon emission spectrum. The sample and reference were recorded under identical pulse conditions. The concentration of the reference fluorescein was measured by UV-visible spectroscopy using $\varepsilon_{(492\ nm)}$ = 88,000 $dm^3\ mol^{-1}\ cm^{-1}$, and a literature value[1] for fluorescein of σ_2 = 37 GM at 780 nm in 0.1 M $NaOH_{(aq)}$ with Φ_P = 0.9 was used. The system was calibrated to correct for the dark noise of the detector and the photoluminescence spectrum was averaged over 100

measurements of 250 ms integration time. In-house software was used for data collection and analysis. Estimated error ± 20%.

The time-gated two-photon excited photoluminescence spectra were acquired with a lower repetition rate of 25 kHz and energy of 30 nJ pulse^{-1}. The emission was detected using a photomultiplier tube (Hamamatsu H10682-01) attached to a dual-grating scanning monochromator (Princeton Instruments Acton SP2150). The TTL signal from the detector was gated using an AND logic gate with the timing being achieved using a variable duration TTL pulse synchronised with the laser cavity dumper driver. Spectra were recorded at 1 nm intervals with a 1 second integration time and are the average of 16 scans. Spectra are corrected for spectral response and dark background.

1. M. A. Albota, C. Xu and W. W. Webb, *Appl. Opt.*, 1998, **37**, 7352; C. Xu and W. W. Webb, *J. Opt. Soc. Am. B*, 1996, **13**, 481.

To confirm that a two-photon process had been observed, the integrated two-photon induced emission spectrum of the Ir complex was recorded as a function of laser intensity. To achieve this, a variable ND filter (Edmund Optics), mounted on a translation stage, was used to control the light intensity incident on the sample, with the power monitored by a free standing power meter whilst a series of spectra were recorded. The result is shown below (Fig. S1): the log(intensity) *vs.* log(power) graph is linear with a slope of 1.9 ± 0.1 (R^2 = 0.99), as required for a two-photon process.

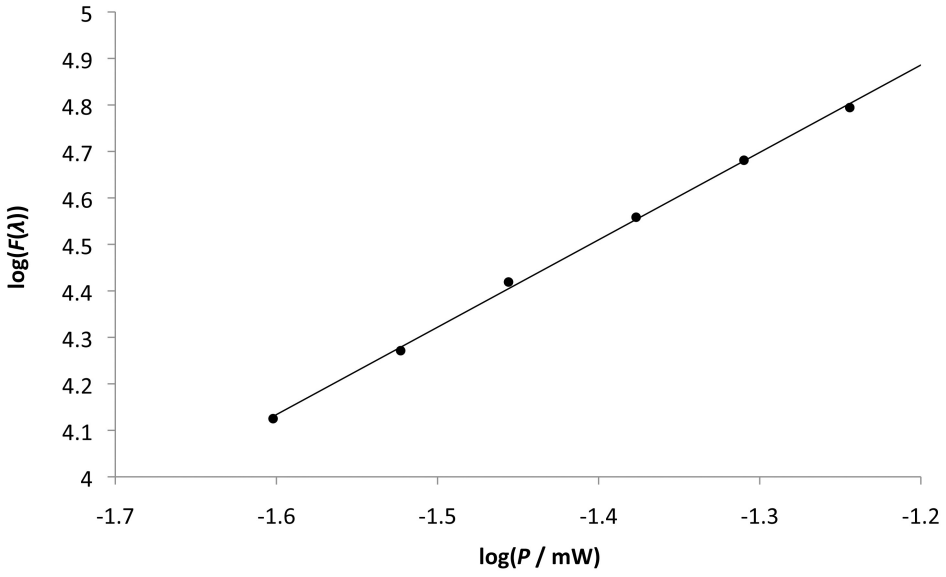

Fig. S1. Relationship of emission intensity from the Ir complex as a function of laser intensity at 780 nm, confirming the presence of a two-photon excitation process.