

## Visible-light sensitisation of Tb(III) luminescence using a blue-emitting Ir(III) complex as energy-donor

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### *Supporting information*

#### *Experimental details*

<sup>1</sup>H NMR spectra were recorded at 400 MHz on a Bruker Avance spectrometer. Electrospray mass spectra of complexes were measured on a Bruker MicroTOF mass spectrometer in positive ion mode. UV/vis absorption spectra were measured on a Cary 50 spectrophotometer and luminescence and excitation spectra on a Jobin-Yvon Fluoromax 4 fluorimeter using air-equilibrated CH<sub>2</sub>Cl<sub>2</sub> at room temperature. 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 Hamamatsu-R928 PMT detector; the lifetimes were calculated from the measured data using the supplied software.

#### *Crystallographic data collection*

A suitable crystal of each complex (grown from CHCl<sub>3</sub> for **1**, or CH<sub>2</sub>Cl<sub>2</sub> for **3**) was mounted under a stream of cold N<sub>2</sub> on a Bruker Apex-2 diffractometer equipped with a sealed-tube Mo-Kα source. Details of the crystal, data collection and refinement parameters are summarized in the footnote in the main text; selected structural parameters are in the table below. Data were corrected for absorption using empirical methods (SADABS)<sup>S1</sup> based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles. The structures were solved by direct methods and refined by full-matrix least squares on weighted *F*<sup>2</sup> values for all reflections using the SHELX suite of programs.<sup>S2</sup> Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions, refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters.

#### Selected bond distances (Å) for complex **1**:

Ir(1)-C(41)	1.992(7)
Ir(1)-C(21)	2.008(7)
Ir(1)-N(11)	2.047(6)
Ir(1)-N(31)	2.054(6)
Ir(1)-N(61)	2.158(5)
Ir(1)-N(51)	2.169(5)

#### Selected bond distances (Å) for complex **3**:

Ir(1)-C(221)	2.002(4)
Ir(1)-C(321)	2.005(4)
Ir(1)-N(311)	2.045(3)
Ir(1)-N(211)	2.059(3)
Ir(1)-N(123)	2.117(3)
Ir(1)-N(111)	2.177(3)

### *Synthesis of the complexes*

Complexes **1** – **4** were prepared as their nitrate salts using the same method; the synthesis of **1** given here is typical. A solution of the bis-pyrazolylpyridine ligand  $L^1$  (0.04 g, 85  $\mu\text{mol}$ , 2.7 equiv. with respect to Ir) was dissolved in degassed  $\text{CH}_2\text{Cl}_2$  /MeOH (3:1, v/v) under  $\text{N}_2$ . To this was added a solution of the dimer  $[\text{Ir}(2,4\text{-F}_2\text{phpy})_2(\mu\text{-Cl})_2]$  (0.04 g, 33  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$ . The mixture was heated to 50 °C overnight under  $\text{N}_2$  and in the dark. The mixture was cooled to room temperature and the solvent removed. Water and saturated aqueous  $\text{KPF}_6$  solution (20 mL) was added and the resulting two-phase mixture was separated; the aqueous residue was further extracted with several portions of  $\text{CH}_2\text{Cl}_2$ . The combined organic fractions were dried using sodium sulphate and the solvent removed. The yellow powder was purified by column chromatography on silica gel using MeCN and 1% aqueous  $\text{KNO}_3$ ; complex **1** was the second yellow band to come off the column. Fractions containing the pure product were combined and reduced in volume; excess  $\text{KNO}_3$  was precipitated by addition of  $\text{CH}_2\text{Cl}_2$  and filtered off. Evaporation of the resultant solution to dryness afforded pure **1**. Yields: 20 mg (27%). Yields of **2** – **4** were likewise in the range 20 – 30%; we were however concentrating on sample purity for photophysical analysis rather than optimising yield.

**Data for 1.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.67 (1H, s), 8.59 (1H, d), 8.25 (1H, d), 8.15-8.11 (2, m), 7.99 (1H, d), 7.83 (1H, t), 7.78-7.64 (5H, m), 7.53-7.22 (10H, m), 7.09 (2H, d), 7.01-6.97 (2H, m), 6.54 (1H, t), 6.46 (1H, t), 6.03 (2H, d), 5.68 (1H, d), 5.49-5.41 (4H, m), 5.12 (1H, d); ESMS  $m/z$  1041 ( $\text{M}+\text{H}^+$ ). UV-Vis [ $\lambda_{\text{max}}$ , nm ( $10^{-3}$   $\epsilon$ ,  $\text{M}^{-1}$   $\text{cm}^{-1}$ )] 258 (55), 284 (38), 320 (13), 363 (3.8). Elemental analysis: calcd (%) for  $\text{C}_{52}\text{H}_{36}\text{N}_8\text{F}_4\text{IrNO}_3 \cdot 0.5\text{CH}_2\text{Cl}_2$ : C 55.0, H 3.2, N 11.0; found: C 55.0, H 3.3, N 11.0.

**Data for 2.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.66 (2H, m), 8.16 (1H, t), 8.05 (1H, 2), 7.98 (1H, d), 7.61-7.52 (5H, m), 7.48 (2H, d), 7.42-7.20 (8, m), 7.15 (2H, d), 7.00 (1H, t), 6.97 (1H, d), 6.86 (1H, d), 6.42 (1H, t), 6.36 (1H, t), 6.15 (2H, d), 5.48 (2H, s), 5.40 (1H, d), 5.12 (1H, d); ESMS  $m/z$  1041 ( $\text{M}+\text{H}^+$ ). UV-Vis [ $\lambda_{\text{max}}$ , nm ( $10^{-3}$   $\epsilon$ ,  $\text{M}^{-1}$   $\text{cm}^{-1}$ )] 259 (45), 284 (32), 333 (5.9), 375 (3.2). Elemental analysis: calcd (%) for  $\text{C}_{52}\text{H}_{36}\text{N}_8\text{F}_4\text{IrNO}_3 \cdot 0.5\text{CH}_2\text{Cl}_2$ : C 55.0, H 3.2, N 11.0; found: C 55.1, H 3.4, N 11.1.

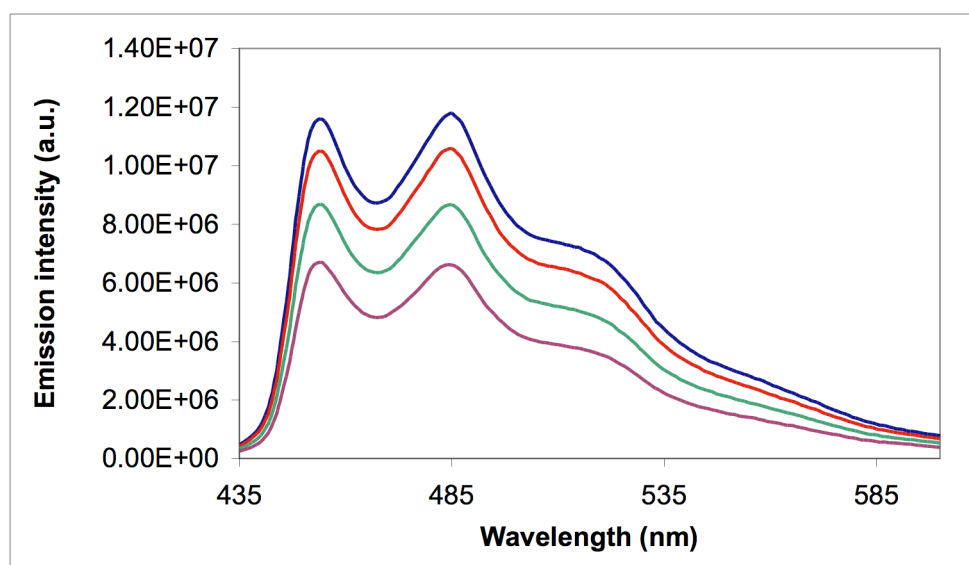
**Data for 3.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.15 (1H, s), 8.60 (1H, d), 8.55 (1H, d), 8.33 (3H, m), 8.14 (1H, d), 8.00 (1H, t), 7.84-7.75 (4H, m), 7.67 (1H, s), 7.60 (1H, d), 7.40 (1H, d), 7.37-7.29 (4H, m), 7.22 (1H, t), 7.11 (1H, t), 7.00 (1H, t), 6.57 (2H, m), 5.76-5.61 (6H, m); ESMS  $m/z$  967 ( $\text{M}+\text{H}^+$ ). UV-Vis [ $\lambda_{\text{max}}$ , nm ( $10^{-3}$   $\epsilon$ ,  $\text{M}^{-1}$   $\text{cm}^{-1}$ )] 244 (69), 279 (42), 309 (20), 361 (6.4). Elemental analysis: calcd (%) for  $\text{C}_{44}\text{H}_{30}\text{N}_{10}\text{F}_4\text{IrNO}_3 \cdot \text{CH}_2\text{Cl}_2$ : C 48.5, H 2.9, N 13.8; found: C 48.7, H 3.2, N 13.4.

**Data for 4.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.13 (1H, s), 8.65 (1H, d), 8.57 (1H, d), 8.33 (1H, s), 8.17 (1H, d), 8.00 (1H, t), 7.86-7.73 (6H, m), 7.60 (1H, s), 7.56 (1H, d), 7.40-7.22 (8H, m), 7.03 (1H, t), 6.94 (1H, t), 6.43 (2H, m), 5.65 (4H, m); ESMS  $m/z$  967 ( $\text{M}+\text{H}^+$ ). UV-Vis [ $\lambda_{\text{max}}$ , nm ( $10^{-3}$   $\epsilon$ ,  $\text{M}^{-1}$   $\text{cm}^{-1}$ )] 233 (39), 281 (23), 377 (3.2). Elemental analysis calcd (%) for  $\text{C}_{44}\text{H}_{30}\text{N}_{10}\text{F}_4\text{IrNO}_3 \cdot \text{H}_2\text{O}$ : C 47.8, H 3.0, N 13.6; found: C 47.6, H 2.8, N 13.9.

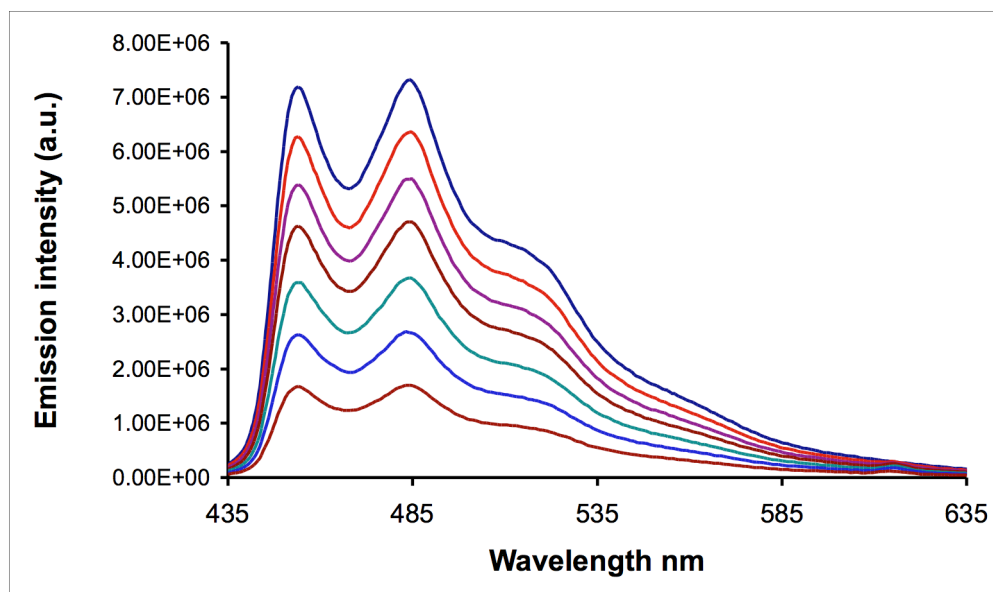
### Comments on partial quenching in Gd(III) adducts

The control experiments described in the main text involved formation of **1**•Gd, **2**•Gd, **3**•Gd and **4**•Gd by titration of [Gd(hfac)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] into solutions of **1** – **4** in CH<sub>2</sub>Cl<sub>2</sub>. Since Gd(III) cannot act as an energy-transfer quencher, minimal quenching of Ir(III)-based emission was expected, based on changes in the pattern of vibrations in the adducts which provide the main route for non-radiative decay of the Ir(III) excited state. However in some cases the partial quenching was substantial (up to 77%), see Figures S1 and S2 below. We tentatively ascribe this to photoinduced *electron*-transfer from the Ir-based excited state to the pendant pyrazolyl-pyridine or triazolyl-pyridine unit which becomes readily reducible on coordination to Gd(III). We have observed this before in anthracenyl—NN(Gd) species, in which binding of Gd(III) to the pendant diimine (NN) ligand resulted in photoinduced electron-transfer to give a short-lived (anthracenyl)<sup>•+</sup> / (diimine)<sup>•-</sup> charge-separated state.<sup>S3</sup>

In the same way, binding of the {Gd(hfac)<sub>3</sub>} unit to the pendant diimine sites of **1** – **4** will make these diimines good electron-acceptors and could allow photoinduced electron-transfer to give an [Ir]<sup>•+</sup>••(diimine)<sup>•-</sup> charge-separated state, thereby partially quenching the Ir-based emission. Ir(III) complexes of this type are well known to undergo one-electron oxidations at relatively modest potentials (ref. 5, main text) and, given their high excited-state energy, they will necessarily be able to act as electron donors in their excited state. The extent of this in each dyad will depend on the inter-component separation so it is reasonable that the presence of different conformers in the dinuclear complexes **1**•Gd, **2**•Gd, **3**•Gd and **4**•Gd, which are flexible due to the methylene spacers in the bridging ligands, will result in bi-exponential decay kinetics. Further studies on this are in progress.



**Figure S1:** Partial quenching of the Ir-based emission of **1** ( $9 \times 10^{-5}$  M in CH<sub>2</sub>Cl<sub>2</sub>) during titration with [Gd(hfac)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] to form **1**•Gd; the lines represent addition of 0, 0.5, 1.6 and 3.6 equivalents of [Gd(hfac)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] after which the changes were complete.



**Figure S2:** Partial quenching of the Ir-based emission of **3** ( $8.2 \times 10^{-5}$  M in  $\text{CH}_2\text{Cl}_2$ ) during titration with  $[\text{Gd}(\text{hfac})_3(\text{H}_2\text{O})_2]$  to form **3**•Gd; the lines represent successive addition of up to three equivalents of  $[\text{Gd}(\text{hfac})_3(\text{H}_2\text{O})_2]$  after which the changes were complete. Compare this with figure 3b (main text) showing the greater quenching in the adduct **3**•Tb (and the presence of sensitised emission from Tb).

## References

- S1 G. M. Sheldrick, SADABS: A program for absorption correction with the Siemens SMART system, University of Göttingen, Germany, 1996.
- S2 G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112.
- S3 T. Lazarides, M. A. H. Alamiry, H. Adams, S. J. A. Pope, S. Faulkner, J. A. Weinstein and M. D. Ward, *Dalton Trans.*, 2007, 1484.