D ? f energy transfer in heteronuclear Ir(III)/Ln(III) near-infrared luminescent complexes

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abstract

A series of d/f dinuclear complexes Ir Ln [where Ln = Eu(III), Gd(III), Yb(III) and Nd(III)] are reported. The core structure consists of a rigid skeleton containing two different types of receptor site in a single molec-ular motif designed to combine a transition metal ion [Ir(III)] and a lanthanide ion [Ln(III)] in different binding sites at either end of fully conjugated bridge to facilitate d ? f energy-transfer following pho-toexcitation of the Ir(III)-based antenna unit. Steady state and time-resolved photophysical experiments on these compounds revealed that the energy-transfer is feasible only in case of Ir Yb and Ir Nd systems, affording sensitized emission from the Yb(III) or Nd(III) centres. Such EnT is not possible in the Ir Eu dyad as the excited state energy of the Ir(III) unit is insufficient to sensitise the excited state of the Eu(III) centre.

1. Introduction

In recent years significant attempts have been made to develop new luminophores which are potentially useful for two-photon induced fluorescence microscopy (TPFM) [1], in vivo fluorescence lifetime imaging microscopy (FLIM) [2] and dual modal imaging [3]. In this context, phosphorescent metal complexes with long-lived triplet excited states are of particular interest [4–6] because they offer substantial advantages compared to the more traditional organic fluorophores. These advantages include tunability of absorption and emission maxima over a wide range by using sim-ple ligand substitutions for the metal coordination site, and long-lived ($>10^{7}$ s) luminescence which allows rejection of short-lived autofluorescence and also provides large, easy to detect variations in emission lifetime for lifetime-based imaging.

In parallel, the use of transition metal luminophores to sensitize luminescence from lanthanide ions in heterometallic d/f com-plexes has attracted recent attention from various groups [3b,7,8] with such complexes having potential applications in areas from white-light emission for lighting devices [7a] to dual-luminescent probes for imaging purposes [7b]. This activity has resulted in the preparation of a wide range of d/f complexes in which one or more phosphorescent d-block antennae is/are connected to one or more lanthanide units [3b,7]. The long lifetimes typical of d-block antenna units with triplet excited states make them excellent energy donors whose excited-state energy can be tuned by proper substituents Several straightforward synthetic methods exist to combine d-block and f-block units in ligand skeletons which provide the distinct binding sites that these different types of metal ion require [8].

In particular, amongst such d/f hybrids the extensive family of cyclometallated Ir^{3+}-complexes with their high energy and long-lived triplet excited states, that often afford blue or green lumines-cence [9], have proven to be effective energy-donors for sensitisa-tion of the luminescent excited states of lanthanides such as Eu(III), Tb(III), Yb(III) and Nd(III) in Ir Ln dyads [10,11]. Ir Ln dyads have potential value in phosphorescence lifetime imaging microscopy (PLIM) for cell imaging applications [3g,3h,5a,6a,7b]. Moreover, use of Gd(III) as a highly paramagnetic partner for an Ir(III) luminophore provides a basis for developing probes for dual modal imaging (phosphorescence + MRI) [3g].

We report herein a new series of rigid Ir(III)/Ln(III) dyads based on a fully conjugated framework connecting the two metal centres [3g], providing the necessary through-bond coupling for d ? f Dexter energy-transfer which is the main energy-process that operates in such dyads [8c]. Steady-state and time-resolved photophysical studies have been performed to evaluate the inter-component d ? f energy-transfer in these systems.

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2. Results and discussion

2.1. Synthesis

The chemical structures of the compounds under study are given in Scheme 1. The bridging ligand skeleton is based on that reported in previous papers [3g,3h]; it contains a phenanthroline binding site for the Ir(III) ion and a heptadentate poly (amino)carboxylate binding site for the Ln(III) ions, with the two sites connected by an alkynyl spacer. The Ir Ln complexes containing Ir(III) and Ln(III) were then synthesized by following the stepwise methodology summarised in Scheme 1 [3g,3h]; Scheme 1 also depicts related compounds of interest which are referred to in this paper. The novel features of the complexes in this work are that (i) the $\{Ir(ppy)_2\}^+$ unit, coordinated to the phenanthroline terminus of the bridging ligand, is different from the one used before in that the ppy ligands are not fluorinated, resulting in a lower-energy excited state which will accordingly have different energy-transfer capabilities; and (ii) the lanthanide ions include members of the near-IR emitting type [Yb(III) and Nd(III)].

Fig. 1. UV/Vis absorption spectra of the Ir Ln complexes in MeCN solution.

2.2. Steady-state absorption spectra and associated computational studies

The Ir Ln dyads all have similar absorption spectra to one another, whose main features are those associated with the Ir(III) core, viz. ligand-centred π-π' transitions in the UV region and a weaker transition which appears as a shoulder at ca. 400 nm (see Fig. 1). Cyclometallated Ir(III) complexes of this class can have excited states displaying different proportions of ligand-centred

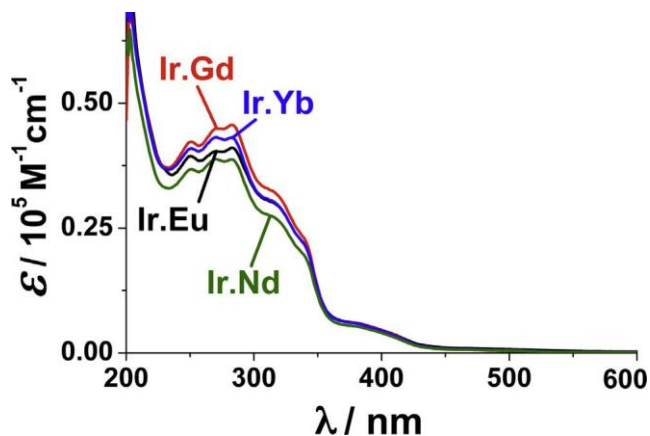and MLCT character according to the ligand substituents, so to clar-ify the nature of the lowest-excited state (and hence the absorption and luminescence properties) we performed DFT calculations on the precursor Ir(III) complex Ir A using the Gaussian 09 program suite [12]. For simplicity we used the mononuclear Ir(III) complex for these calculations with no lanthanide centre present.

The calculations revealed that the conjugated phenanthroline-based ligand with an alkyne substituent in Ir A is planar, as would be expected. Moreover, there is a moderate (0.053 eV) reduction of energy gap (ΔE) between the HOMO and LUMO on moving from corresponding fluorinated derivative ^{F}Ir A (ΔE = 2.630 eV) [3h] to the nonfluorinated derivative Ir A, (ΔE = 2.577 eV). This can be attributed to the stabilization of the HOMO of ^{F}Ir A that results
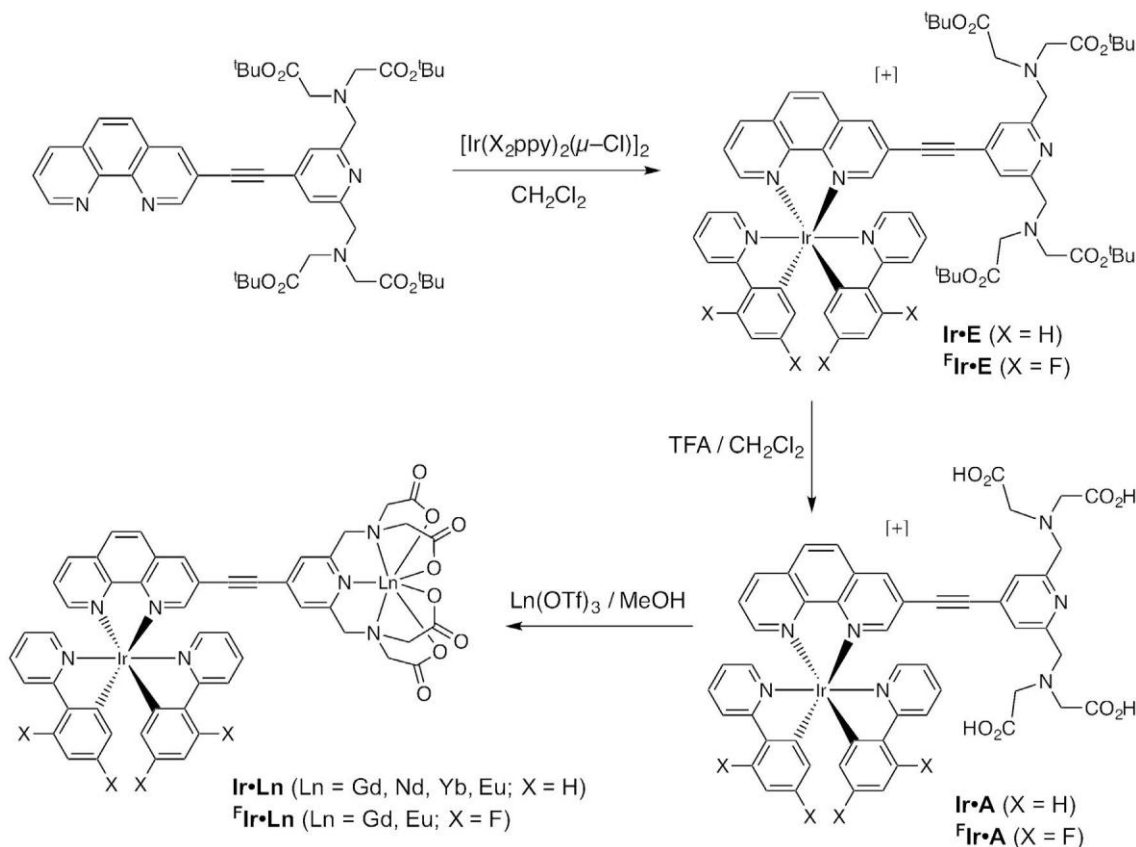
Scheme 1. Preparation and structures of the new complexes Ir Ln (this work) and their fluorinated analogues ^{F}Ir Ln (Ref. [3g]).

from the inductive effect of the four highly electronegative 'F' atoms. This finding is fully in agreement with the observed red shift of the $\pi \to \pi'$ absorption bands of **Ir A** in the UV–Vis region, in comparison to ^{F}**Ir A**.

Molecular orbital energy-level diagrams from HOMO 10 to LUMO + 10 were constructed to explain the spectroscopic features. In the case of **Ir A**, the HOMO is mainly concentrated on the Ir(III) ion as well as the two anionic, cyclometallating phenylpyridine ligands. In contrast the LUMO is located throughout the phenan-throline/alkyne based conjugated fragment ligand (Fig. 2). On this basis, we assign the lowest-energy absorption band observed in the visible region of **Ir A** as having a combination of Ir $\to$ phen MLCT and phenylpyridine $\to$ phen LLCT character. Time-dependent DFT simulations of the electronic spectra of **Ir A** were also carried out; the TD-DFT stick spectrum obtained from this analysis are in good agreement with the experimental spectrum (cf. Fig. S16, Table S1 in ESI) in the frontier orbital region.

2.3. Luminescence spectra and photoinduced energy-transfer

The complexes **Ir Gd** and **Ir Eu** show very similar luminescence spectra (Fig. 3), with a broad and featureless emission band in MeCN at 640 nm which corresponds to emission from the ^{3}MLCT/^{3}LLCT excited state of the Ir(III) centre [9]. The lumines-cence lifetimes (main component, ca. 55 ns) and quantum yields (ca. 0.15) are likewise similar for the two complexes (see Table 1).

The similarity between these two emission spectra, and in par-ticular their lifetimes and quantum yields, implies that no Ir $\to$ Eu energy-transfer is occurring in **Ir Eu**: this must be a consequence of the relatively low excited-state energy of the $\{Ir(N-C)_2(phen)\}^+$ unit (where 'N-C' denotes a cyclometallating phenyl pyridine ligand), which is unable to effect photoinduced energy-transfer to the Eu(III) centre whose emissive $^5D_0$ excited state lies at ca.
17,500 cm $^{-1}$. For such energy-transfer to be complete at room temperature the excited state energy of the $\{Ir(NC)_2(phen)\}^+$ unit would have to be ca. 19,500 cm $^{-1}$ to give a sufficient energy-trans-fer gradient, [13] corresponding to onset of luminescence at ca. 510 nm for the Ir(III) unit which is clearly not the case here. Thus, in **Ir Gd** and **Ir Eu** the Gd(III) and Eu(III) centres act in the same way, as triply-charged substituents that are otherwise photophys-ically innocent with respect to their effect on the Ir(III) core. This is illustrated in Fig. 4 which emphasises the different behaviour of these two **Ir Ln** dyads compared to the previously-studied exam-ples ^{F}**Ir Ln**, which have a much higher-energy Ir-based excited state (luminescence at 560 nm in solution) arising from use of flu-orinated phenylpyridine ligands [3g]. The result of this was that in ^{F}**Ir Eu** the occurrence of Ir $\to$ Eu energy-transfer resulted in partial
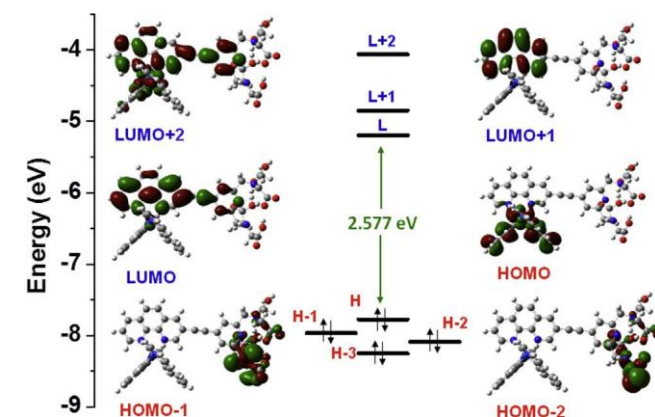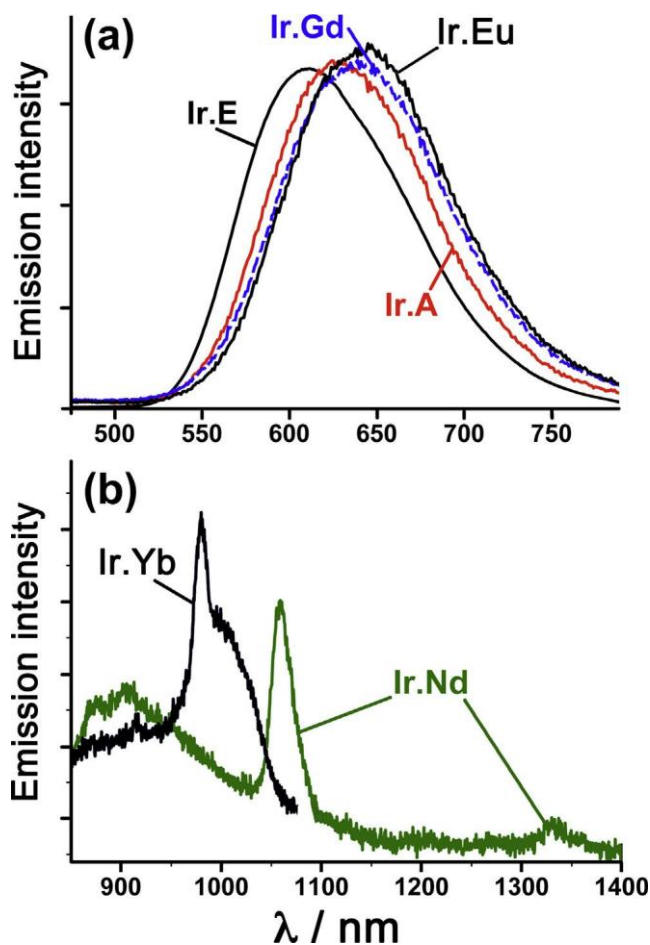

Fig. 3. (a) Luminescence spectra in MeCN of some complexes in the visible region showing the Ir-based luminescence; (b) luminescence spectra in the near-IR region showing sensitised lanthanide-based emission from **Ir Yb** and **Ir Nd**.

Table 1
Summary of steady-state and time-resolved luminescence data in MeCN at 298 K.

Compound	k_{em}/nm	τ		
Ir Gd	620	54 ns [a]		
Ir Eu	620	55 ns [a]		
Ir Nd	620	33 ns [a]		
	1060	25 ns (9%),	170 ns (95%) [b]	
	1340	170 ns [b]		
Ir Yb	620	63 ns [a]		
	980	66 ns,	7.4 μs [b]	

[a] Ir-based luminescence.
[b] Lanthanide-based luminescence.

quenching of Ir-based emission and appearance of sensitised Eu-based emission [3g], neither of which occurs in **Ir Eu**.

The relatively low excited-state energy of **Ir Gd** and **Ir Eu** compared to ^{F}**Ir Gd** and ^{F}**Ir Eu** however does not prevent them from sensitising Nd(III) and Yb(III), which have much lower energy excited states with luminescence in the near-IR region. In **Ir Nd** and **Ir Yb** we can see again the main Ir-based ^{3}MLCT/^{3}LLCT emission band at 640 nm. For **Ir Yb** there is no detectable loss of intensity compared to the control compound **Ir Gd** indicating that any quenching of the Ir-based emission component by Ir $\to$ Yb energy-transfer is small. This is confirmed by time-resolved measurements which show that this emission component has a lifetime of 63 ns: the same, within experimental error, as the life-times measured for luminescence from **Ir Gd** and **Ir Eu** (ca. 55 ns
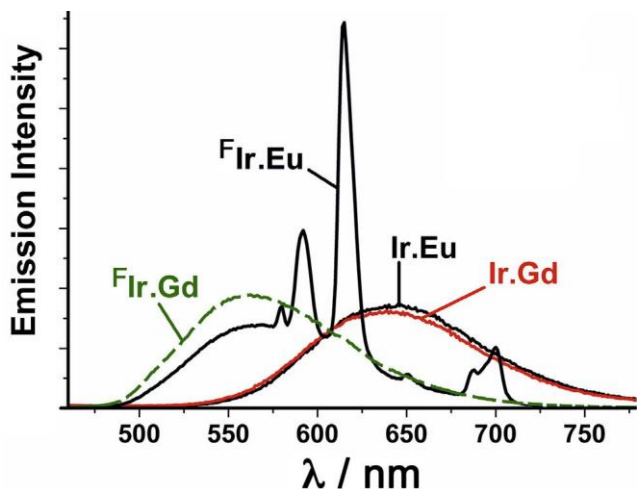

Fig. 2. Frontier molecular orbitals of **Ir A**.

Fig. 4. Comparison of luminescence spectra of Ir Gd and Ir Eu (this work) with those of ^{F}Ir Gd and ^{F}Ir Eu (Ref. [3g])..

each). However, the fact that Ir ? Yb energy-transfer does occur to some extent is apparent from the presence of a weak luminescence feature at 980 nm (Fig. 3b): this is the $^{2}F_{5/2}$? $^{2}F_{7/2}$ luminescence from Yb(III), which can only have arisen from Ir ? Yb energy-transfer as the excitation at 355 nm was into the Ir-based absorp-tion band. Time-resolved measurements at 980 nm revealed a short-lived decay component with a lifetime of 66 ns which is the long-wavelength tail of residual Ir-based emission, and a much longer-lived component with a lifetime of 7.4 ls which is charac-teristic of Yb-based decay; this lifetime corresponds to a quantum yield of 3.7 10^{3} for the Yb-based emission based on a natural radiative lifetime of 2 ms [14].

In Ir Nd the quenching of the Ir-based luminescence compo-nent is greater, with a lifetime for residual Ir-based emission of 33 ns, significantly smaller than for the control complex Ir Gd (54 ns). From this difference, using Eq. (1) [where s and s$_q$ are the unquenched (in Ir Gd) and partially quenched (in Ir Nd) life-times, respectively], we can calculate the rate of Ir ? Nd energy-transfer to be 1 10^{7} s^{1}.

$$k_{EnT} \; \frac{1}{4} \; 1=s_q \quad 1=s \qquad \delta 1 Þ$$

The observation that this is clearly much faster than the rate of Ir ? Yb energy-transfer in Ir Yb arises from the fact that the Nd (III) ion has a large number of f–f absorptions in the visible region which overlap with the region where the Ir-based luminescence is intense; in contrast, the Yb(III) ion has a solitary f–f absorption at 980 nm in the region where the Ir-based emission has almost decayed to the baseline. Thus, the spectroscopic overlap (between the emission from the donor and absorption of the acceptor) that is necessary for energy-transfer is inevitably much higher in the Nd (III)-containing dyad, and this is consistent with other examples of d/f dyads in which energy-transfer to Nd(III) is faster than it is to Yb(III) for the same reason [15].

The sensitised Nd(III)-based emission arising from Ir ? Nd energy-transfer can be seen in the form of weak signals at 1060 and 1330 nm in the near-IR region, superimposed on the low-energy tail of the residual Ir-based emission decay (Fig. 3b). These two signals correspond to the $^{4}F_{3/2}$? $^{4}I_n$ transitions (n = 11/2, 13/2) respectively. Of these the 1060 nm peak ($^{4}F_{3/2}$? $^{4}I_{11/2}$) is the more intense. Time-resolved emission measurements at this wavelength reveal two decay components of ca. 25 ns (minor) and 170 ns (major); the former corresponds to a trace of residual Ir-based emission and corresponds approximately with the figure of 33 ns that was measured for the 640 nm emission maximum

in the visible region. To avoid this interference from the Ir-based emission which still has non-zero intensity by 1060 nm, the lumi-nescence decay was also measured at 1340 nm giving a single decay component, again of 170 ns, corresponding to the Nd-based decay. The much smaller value of this luminescence lifetime com-pared to what we observed for Yb in Ir Yb (7.4 ls) is characteristic of Nd(III) for which the lower-energy luminescence is more easily quenched by molecular vibrations compared to Yb(III) [16]. The Nd (III) emission lifetime of 170 ns corresponds to a quantum yield of 6.8 10^{4} for the Nd-based emission, based on a natural radiative lifetime of 0.25 ms [14].

3. Conclusions

In a set of d/f dyads based on a fully conjugated ligand skeleton connecting the two metal centres, photoinduced energy-transfer was observed from an {Ir(N-C)$_2$(phen)}$^{+}$ unit to Yb(III) and Nd(III) centres which demonstrated sensitised luminescence in MeCN. The energy of the excited state of the {Ir(N-C)$_2$(phen)}$^{+}$ unit was, however, too low to permit sensitisation of luminescence from Eu(III) – in contrast to the situation when fluorinated {Ir(N-C)$_2$-(phen)}$^{+}$ units with higher-energy excited states were used [3g].

4. Experimental

4.1. Materials and instrumentation

^{1}H NMR spectra (400 MHz) and ^{13}C NMR spectra (100 MHz) were recorded on a Bruker Avance-3 spectrometer at 298 K using residual solvent signals as internal standards. ESI mass spectra were recorded with a Micromass LCT instrument. UV–Vis-NIR spectra were recorded on a Varian Cary 50 spectrophotometer in anhydrous MeCN at room temperature. Luminescence spectra were measured on a Jobin Yvon Fluoromax 4 fluorimeter in MeCN at room temperature. The Ir(III)-based emission lifetimes were measured using the time correlated single photon counting (TCSPC) technique with an Edinburgh Instruments ''Mini S'' lumi-nescence lifetime spectrometer, equipped with a 410 nm pulsed diode laser as an excitation source and a Hamamatsu H577303 photomultiplier tube (PMT) detector. The lifetimes were calculated from the measured data using the supplied software. All near-IR photophysical data were obtained on a JobinYvon–Horiba Fluo-rolog-3 spectrometer fitted with a Hamamatsu R5509-73 detector (cooled to 80 LC using a C9940 housing). For the near-IR lifetimes the pulsed laser source was a Continuum Minilite Nd:YAG config-ured for 355 nm output. Near-IR luminescence lifetime profiles were obtained using the JobinYvon–Horiba FluoroHub single pho-ton counting module and the data fits yielded the lifetime values using the provided DAS6 deconvolution software.

All calculations were performed using Gaussian 09 [12] with the density functional theory (DFT) method, using the Becke three-parameter hybrid exchange functional and the Lee–Yang-Parr correlation functional (B3LYP) [17], employing a basis set of 6-31G' for non-metals and LanL2DZ [18] for Ir(III) ions.

4.2. Synthesis of Ir E

A mixture of the ligand L (see Scheme 1; 0.398 g, 0.5 mmol) and [Ir(ppy)$_2$(l–Cl)$_2$] (ppy = cyclometallating anion of 2-phenylpyri-dine) (0.268 g, 0.25 mmol) was heated to reflux in dry degassed CH$_2$Cl$_2$/MeOH (50 cm^3; 4:1, v/v) for 16 h. After cooling the reaction mixture, NH$_4$PF$_6$ (1.22 g, 7.5 mmol) was slowly to the reaction mix-ture whilst stirring was continued. After 6 h this reaction mixture was evaporated near to dryness and CH$_2$Cl$_2$ (5 cm^3) was added to it to completely dissolve the organic substances. Residual NH$_4$PF$_6$

was removed by filtration and the dark organic solution was con-centrated under vacuum. The crude reaction mixture was then subjected to column chromatography on Al_2O_3 [Eluent: (1) CH_2Cl_2,

(2) 2% MeOH in CH_2Cl_2] to furnish 0.475 g of the title compound as a deep yellow crystalline material in 60% yield. ^1H NMR (500 MHz, $CDCl_3$, 298 K): d = 1.48 (36 H, s); 3.50 (8H, s); 4.06 (4H, s); 6.38 (1H, d, J = 8 Hz); 6.42 (1H, d, J = 8 Hz); 6.97–7.01 (4H, m); 7.08–7.13 (2H, m); 7.37 (1H, d; J = 6 Hz); 7.43 (1H, d, J = 6 Hz); 7.68 (2H, m); 7.73–7.78 (4H, m); 7.87–7.90 (1H, m); 7.95–7.98 (2H, m); 8.17 (1H, d, J = 8 Hz); 8.26 (1H, d, J = 4 Hz); 8.30 (1H, s); 8.37 (1H,

d, J = 8 Hz); 8.67   (1H, br s); 8.78   (1H,   d, J = 8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$,   298 K): d = 28.2,   55.9,   59.5, 81.2,   87.0,   94.6, 119.7,   122.9,   123.3,   123.6,   124.8,   125.0,   127.2,   127.8,   130.2, 130.7,   130.9,   131.8,   132.2,   134.5,   138.3,   139.4,   140.8,   143.4, 143.6,   145.7,   146.3,   148.5,   148.8,   151.2,   151.9,   159.5,   167.7, 170.4. ESI-MS: m/z calcd. for $C_{67}H_{73}N_7O_8Ir$, 1296.5. Found: 1296.0 (100%, M)$^+$.

4.3. Synthesis of Ir A

A sample of Ir E (0.130 g, 0.1 mmol) was dissolved in CH_2Cl_2 (2 cm^3) and placed in an ice bath under an atmosphere of argon. An excess of cold trifluoroacetic acid (3 cm^3) was added dropwise to this cold solution. The resulting mixture was kept in an ice bath and stirred for 12 h under argon. The solvents and other volatile substances were removed under vacuum without heating. The residue was triturated with ether (3 5 cm^3) and finally filtered to afford the tetracarboxylic acid Ir A as a yellow mass. The com-pound was then dried under high vacuum for overnight before characterization. Yield: 80%. ^1H NMR (500 MHz, CD_3OD, 298 K): d = 3.80 (8H, s); 4.37 (4H, s); 6.41 (1H, d, J = 8 Hz), 6.43 (1H, d, J = 8 Hz), 6.93–7.00 (4H, m); 7.07–7.13 (2H, m), 7.48 (1H, d, J = 5 Hz), 7.58 (1H, d, J = 5 Hz); 7.79–7.97 (7H, m); 8.15–8.18 (2H, m); 8.33–8.41 (4H, m); 8.81 (1H, d, J = 8 Hz); 9.04 (1H, s). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): d = 56.5, 58.3, 79.5, 92.5, 121.2, 122.4, 124.0, 124.6, 126.1, 126.4, 128.5, 128.9, 129.3, 130.0, 130.8, 131.8, 132.2, 132.8, 133.1, 133.8, 136.2, 139.9, 140.1, 143.2, 145.5, 147.7, 150.1, 150.3, 150.5, 152.7, 153.2, 156.7, 169.2, 173.6. ESI-MS: m/z calcd for $C_{51}H_{41}N_7O_8Ir$, 1072.1. Found: 1072 (100%, M$^+$).

4.4. Synthesis of Ir Ln complexes

These were all prepared in the same way: the example given for Ir Eu is typical. A mixture of Ir A (0.043 g, 0.04 mmol) and Eu (OTf)$_3$ (0.024 g, 0.04 mmol) in anhydrous MeOH under Ar was stir-red for 30 min. To this was slowly added a solution of NaOH (1 M in MeOH) such that the apparent pH was maintained at 5. The reac-tion mixture was then heated to 50 $^{\circ}$C with constant stirring for 48 h. After cooling the reaction mixture the solvent was evapo-rated under reduced pressure. The residue was dissolved in mini-mum amount of MeOH and re-precipitated by the gradual addition of ether. This dissolution/re-precipitation process was repeated several times and the light yellow solid mass was col-lected by filtration to give Ir Eu in 60–70% yield. ESI-MS: m/z calcd. for $C_{51}H_{37}N_7O_8IrEu$, 1220.1. Found: m/z 1220.0 (10%, M$^+$) and 634 (100%; M/2+Na)$^+$. Purity of the compound was confirmed by the presence of a single peak in analytical HPLC trace (see ESI). For mass spectra and HPLC traces of the other Ir Ln dyads (Ln = Gd, Yb, Nd), see ESI.

Appendix A. Supplementary data

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