Sensitized near-infrared emission from ytterbium(III) *via* direct energy transfer from iridium(III) in a heterometallic neutral complex[†]

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A tetrametallic iridium-ytterbium complex has been synthesised that shows sensitized near-infrared emission ($\lambda_{max} =$ 976 nm) upon excitation of the iridium unit in the visible region (400 nm) due to efficient energy transfer from the iridium units to the Yb(III) ion. The iridium phosphorescence is quenched nearly quantitatively while the ytterbium ion emits brightly in the NIR.

Introduction

The luminescent properties of near-infrared (NIR) emitting lanthanide ions [Ln(III)] are widely studied due to possible applications for optical amplification in lasers1 as well as in telecommunications² and bioimaging.³ Lanthanide complexes often display narrow emission spectra, long excited-state lifetimes, and large energy differences between absorption and emission.⁴ Direct excitation of Ln(III) ions is however difficult because the optical transitions in the 4f subshell are parity forbidden, yielding absorption coefficients on the order of 1-10 M⁻¹cm⁻¹.⁴ Therefore, lanthanide ions are generally excited via light-harvesting antenna or sensitizing groups that transfer energy to the excited states of the emitting ion, typically organic molecules.⁴ Near-infraredemitting lanthanides such as Er(III) and Pr(III) are standards in telecommunications as dopants into the glass cores of fiber optic amplifiers.² The amplifiers are required to 'regenerate' the signal due to intrinsic losses that occur as it propagates through the fiber; currently, the amplifiers are pumped optically with a laser.²

Recently, a number of complexes with d-block transition metals have been used as sensitizers for Ln(III) ions.⁵ However, to the best of our knowledge, the only example of an Ir(III)–Ln(III) complex has been published by our group.⁵ Iridium(III) complexes are highly tunable over the entire visible and NIR spectra, generally with relatively small changes to the coordinating ligands, and are commonly used in electroluminescent applications due to their excellent redox properties.⁶ Therefore, we sought to combine the properties of the lanthanides with those of Ir(III) complexes in a single molecule. The advantage would be the possibility to electrically populate the excited states of the lanthanide ions, which themselves have poor redox properties (limited oxidation state range), using an iridium compound as a sensitizer. With a redoxactive antenna, NIR emission could be achieved *via* electrical excitation of Ln(III) ions in a light-emitting diode (LED) type configuration. In addition, the use of transition metal complexes as sensitizers for lanthanides extends the ability to photoexcite the systems throughout the visible and into the near-infrared.^{5a}

Previously, we reported a ligand system wherein three monoanionic bipyridine carboxylates coordinate one Ln(III) ion to yield neutral, nine-coordinate complexes with excellent photophysical properties.⁷ By exploiting this binding motif, we can attach different units to the bipyridine core. Here we report the synthesis, characterization, and photophysical properties of a tetrametallic Ir–Yb complex (**Ir₃Yb**), bearing three iridium units around a central Yb(III) core. The photoinduced electronic energy transfer from the excited Ir(III) moiety to the Yb(III) unit is also described.

Results and discussion

The synthesis of Ir_3Yb is shown in Scheme 1. Ir-COOEt was prepared by a Suzuki coupling of Ir-Br with the pinacolatoboronate derivative of ethyl phenylbipyridine carboxylate (see ESI[†]). After saponification of the ester with NaOH and neutralization of the solution, the resulting product Ir-COOH was dissolved in H₂O– Et₃N, and, upon addition of a solution of YbCl₃·6H₂O in water, a precipitate formed that was washed and dried to give Ir₃Yb in 80% yield.

High-resolution electrospray ionization mass spectrometry confirmed the formation of **Ir**₃**Yb** (Fig. S1 and S2[†]), and comparison of molar absorptivity values proved the tetrametallic nature of the complex (Fig. 1; *vide infra*). The precursors were characterized by mass spectrometry, elemental analysis and NMR spectroscopy (see ESI[†]). **['Bu-COO]**₃**Yb** (Fig. 2, inset) was synthesized (Scheme S1[†]) and investigated as reference for the multimetallic



Fig. 1 Absorption and emission spectra in degassed CH₂Cl₂ ($\lambda_{esc} = 400$ nm). The intensities of the emissions of Ir-COOH and Ir₃Yb are multiplied by a factor of 5 for clarity.

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[†] Electronic supplementary information (ESI) available: Synthesis of ['Bu-COO]₃Yb, experimental details, excitation spectrum of Ir₃Yb, mass spectra of Ir₃Yb, isoabsorptive emission spectra of Ir₃Yb and ['Bu-COO]₃Yb and normalized emission spectra in the visible region. See DOI: 10.1039/b800162f



Scheme 1 Synthetic procedure for the preparation of Ir₃Yb.



Fig. 2 Normalized Yb(III) emission of Ir_3Yb ($\lambda_{exc} = 400$ nm) and ['**Bu-COO**]₃Yb ($\lambda_{exc} = 301$ nm) in CH₂Cl₂.

system, in order to understand the role of the iridium moiety in the Ir_3Yb system.

The absorption spectra of compounds Ir-Br, Ir-COOEt, Ir-COOH, Ir₃Yb and ['Bu-COO]₃Yb are shown in Fig. 1. All the compounds investigated display bands assigned to $\pi - \pi^*$ transitions at energies greater than 320 nm due to the phenylene and pyridine units. The iridium-containing complexes also show bands in the visible region that are assigned to singlet metal-toligand charge transfer transitions (¹MLCT) and, at lower energy, spin-forbidden ³MLCT absorptions. It should be noted that at energies lower than 26 000 cm⁻¹ (380 nm) the absorption is almost exclusively due to the iridium moiety, and therefore virtually selective excitation is possible at these energies in this system. The molar absorptivity for the Ir₃Yb complex is about three times higher than in the iridium ligands, as is expected due to the presence of three chromophoric moieties in the molecule. All the compounds possessing the diphenyl-bipyridine-carboxylate show an intense absorption between 350 and 400 nm. We attribute these transitions to conjugation in these systems in which the bipyridine moiety is also involved. The absorption spectrum of ['Bu-COO]₃Yb has been used as a reference to understand the contribution of the iridium moiety to the absorption spectrum of Ir₃Yb.

Fig. 1 also shows the room-temperature visible emission of **Ir-Br**, **Ir-COOEt**, **Ir-COOH** and **Ir**₃**Yb** in degassed CH_2Cl_2 . For iridium cyclometallated systems or in heteroleptic complexes, the emission in the visible region originates from the ³MLCT state, which can be mixed with the ligand-centred triplet (³LC)

state.⁶ The degree of mixing depends on the relative energy of the ³MLCT state with respect to the triplet excited states of the ligand, which are strongly effected by the extent of conjugation and of substituents (ref. 8(a) and vide infra). The emission spectra reported here all have the same shape and maxima (Fig. 1 and S5[†]), but the emission quantum yields and excited-state lifetimes are dramatically different.^{9a} The emission of Ir-COOH ($\Phi_{vis} =$ 0.06) is about 7 times lower in intensity compared with Ir-COOEt $(\Phi_{vis} = 0.39)$ or Ir-Br ($\Phi_{vis} = 0.42$). Ir-COOEt phosphoresces with a remarkably long excited-state lifetime for an iridium complex (127 µs) when compared to the typical lifetimes for similar complexes ($\sim 1-5 \ \mu s$),⁶ such as that of Ir-Br (1.5 μs). Ir-COOH has an excited-state lifetime of 20 µs, and while still long, it is one order of magnitude less than the ester. As already indicated by the absorption spectra, the aromatic rings lead to a conjugated system with an approximate triplet energy (³LC) of 18 900 cm⁻¹.^{8b} Therefore, strong mixing between the ³MLCT state (20 576 cm⁻¹)^{8c} and the low-lying ³LC states of the ligands was envisaged.^{8d}

The iridium emission is drastically quenched when complexed to ytterbium in Ir_3Yb ($\Phi_{vis} = 0.006$), compared to that of the iridium precursors (Fig. 1). This indicates that electronic energy transfer from the iridium fragment to the ytterbium moiety, upon excitation into the MLCT state of the iridium, is taking place. The iridium emission in the Ir_3Yb complex is quenched by 95% when compared to Ir-COOEt,¹⁰ which was chosen as a model for the donor system, under identical conditions (Fig. 1).¹¹ In addition, we find a shortened lifetime of 2 µs, which indicates a 98% quenching.¹¹ Due to the uninterrupted conjugation between the iridium unit and the ytterbium ion, we propose a throughbond, Dexter mechanism for the energy transfer, which is fully allowed ($\Delta J = 1$) with respect to the ²F_{7/2} ground state of the ytterbium ion.^{5c,d}

The energy transfer leads to typical Yb(III) luminescence in the near infrared with a maximum at 976 nm assigned to the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition and broader vibronic components at longer wavelengths (Fig. 2). The near-infrared emission spectrum was recorded after excitation at 400 nm, where the MLCT states of the iridium moieties absorb, and direct population of the π -states of the ligand directly bound to the ytterbium ion is negligible (see Fig. 1; *vide supra*). We can therefore conclude that the ytterbium emission is due to an efficient electronic energy transfer from the excited iridium moiety to the ${}^{2}F_{5/2}$ level of the Yb ion. Further confirmation that energy transfer originates from the MLCT states of the iridium is found in the excitation spectrum recorded upon monitoring the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ emission at 976 nm of Yb(III) (Fig. S3†). The excitation spectrum overlaps the absorption spectrum in the MLCT region between ~350–450 nm, proving that the energy originates from these states.

Thus far, we have determined that the iridium units in Ir₃Yb are quenched nearly quantitatively (>95%) and that energy can be transferred to the Yb(III) ion under selective excitation of the iridium moiety (400 nm). To determine the efficiency of the energy transfer and to rule out other possible quenching pathways (e.g., electron transfer), we have determined the degree of sensitization of the ytterbium by measuring the NIR emission spectra of ['Bu-COO₃Yb and Ir₃Yb upon excitation at an isoabsorptive point (370 nm). Unfortunately, we cannot excite both complexes at 400 nm because the ['Bu-COO]₃Yb complex used as reference does not absorb at this wavelength (vide supra). However, at 370 nm most of the excitation light is absorbed by the iridium moiety (\sim 95% based on Fig. 1). The integrals of the emission spectra (Fig. S4[†]) reveal that the energy is transferred with an efficiency of ~65% in Ir_3Yb relative to ['Bu-COO]₃Yb. In other words, there is a non-radiative loss mechanism upon excitation of the iridium unit that does not exist when the sensitizer bound to the ytterbium ion is directly excited. The incomplete energy transfer upon excitation of the iridium moiety seems to indicate that a competitive process occurs, leading to quenching of the iridium emission and to a loss of electronic energy. We do not have a good explanation for this behavior but suggest that it could be related to an electron transfer process, which has been postulated for other ytterbium complexes.12 As discussed above, the emissive states of the iridium complex have energies near $\sim 20\,000$ cm⁻¹, while the ²F_{5/2} state of Yb(III) lies at 10 200 cm⁻¹—this large gap between donor and acceptor levels would suggest inefficient energy transfer by a Dexter mechanism and therefore hint at the possibility of other processes.5c,d

The ytterbium emission in the Ir₃Yb complex has a quantum yield of 0.7% when excited at 300 nm,^{9b} which is relatively high for near-infrared emitters, equivalent to ['Bu-COO]₃Yb ($\Phi_{\rm NIR} = 0.7\%$) and a related system ($\Phi_{\rm NIR} = 0.7\%$) previously reported.⁷ This is likely due to the fact that the three bipyridine-carboxylate ligands occupy nine coordination sites around the ytterbium ion, leaving no positions free for vibronically deactivating solvent molecules.⁴ To the best of our knowledge, the highest quantum yield values for ytterbium complexes in solution were reported by Imbert et al.^{13a} with an emission quantum yield of 0.8% in deuterated water and by Puntus et al.^{13b} who measured a quantum yield in toluene of 1.1%. The fact that Ir₃Yb and ['Bu-COO]₃Yb have identical quantum yields ($\Phi_{\text{NIR}} = 0.7\%$) upon excitation in the UV (300 nm), further suggest that there is an additional decay pathway open upon selective excitation of the iridium units as evidenced by the lower efficiency upon excitation of Ir₃Yb at 400 nm (vide supra).

The nine coordination in Ir₃Yb also leads to a long excited-state lifetime of 17.7 μ s of Yb(III).¹⁴ This is also in good agreement with other ytterbium complexes measured in solution: *e.g.*, the reference compound ['Bu-COO]₃Yb has an excited-state lifetime of 18.3 μ s, and in the literature ytterbium complexes with excited-state lifetimes of 12.0 μ s^{13b} up to 23.2 μ s^{13c} have been reported. One outstanding example of a 1.1 ms lifetime for an Yb(III) complex has been reported recently by Glover *et al.*¹⁵

Conclusions

In conclusion, we have prepared an iridium complex containing a conjugated phenylene bridge able to coordinate lanthanide ions in a 3:1 stoichiometry to give an overall neutral complex. Upon selective excitation of the iridium to the MLCT states, a strong quenching (\geq 95%) of the iridium emission is observed along with intense infrared emission from the ytterbium ion at 976 nm. The Ir₃Yb complex has a quantum yield of 0.7% ($\lambda_{exc} = 300$ nm), which is high for emitters in the near-infrared and likely due to the exclusion of solvent molecules from the inner coordination sphere of the lanthanide ion, which is a result of the nine coordination sites occupied by the bipyridine-carboxylate ligand.

These findings open up interesting possibilities for the sensitization of lanthanide ions with metal complexes and perhaps with electrical excitation in systems containing such electroluminescent metal complexes. In addition, the iridium precursors have interesting photophysical properties such as long (>100 μ s) excited-state lifetimes that are currently being investigated further and will be published in a forthcoming full paper.

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- 9 (a) Quantum yields in the visible region were measured versus quinine bisulfate in 1 N H₂SO₄ ($\phi_{ref} = 0.546$) as reference compound ($\lambda_{exc} = 400$ nm); (b) NIR quantum yields were measured versus Yb(TTA)₃ in toluene (TTA = thenoyltrifluoroacetylacetonate, $\Phi = 0.35\%$) ($\lambda_{exc} = 300$ nm). It was not possible to excite at 400 nm, due to the lack of absorbtion of Yb(TTA)₃ at this wavelength; S. B. Meshkova, Z. M. Topilova, D. V. Bolshov, S. V. Beltyukova, M. P. Tsvirko and V. Y. Venchikov, Acta Phys. Pol., A, 1999, **95**, 983–990.
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