d→f Energy Transfer in Ir(III)/Eu(III) Dyads: Use of a Naphthyl Spacer as a Spatial and Energetic “Stepping Stone”

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ABSTRACT: A series of luminescent complexes based on {Ir(phpy)2} (phpy = cyclometallating anion of 2-phenylpyridine) or {Ir(F2phpy)2} (F2phpy = cyclometallating anion of 2-(2,4'-difluorophenyl)pyridine) units, with an additional 3-(2-pyridyl)pyrazole (pypz) ligand, have been prepared; fluorination of the phenylpyridine ligands results in a blue-shift of the usual 3MLCT/3LC luminescence of the Ir unit from 477 to 455 nm. These complexes have pendant from the coordinated pyrazolyl ring an additional chelating 3-(2-pyridyl)-pyrazole unit, separated via a flexible chain containing a naphthalene-1,4-diyl or naphthalene-1,5-diyl spacer. Crystal structures show that the flexibility of the pendant chain allows the naphthyl group to lie close to the Ir core and participate in a π-stacking interaction with a coordinated phpy or F2phpy ligand. Luminescence spectra show that, whereas the {Ir(phpy)2(pypz)} complexes show typical Ir-based emission—albeit with lengthened lifetimes because of interaction with the stacked naphthyl group—the {Ir(F2phpy)2(pypz)} complexes are nearly quenched. This is because the higher energy of the Ir-based 3MLCT/3LC excited state can now be quenched by the adjacent naphthyl group to form a long-lived naphthyl-centered triplet (3nap) state which is detectable by transient absorption. Coordination of an {Eu(hfac)3} unit (hfac = 1,1,1,5,5,5-hexafluoro-pentane-2,4-dionate) to the pendant pypz binding site a allows for two-step d→f energy-transfer. However for the triads based on the {Ir(F2phpy)2} core, the initial Ir→3nap energy-transfer step is followed by a second, slower, 3nap→Eu energy-transfer step: transient absorption measurements clearly show the 3nap state being sensitized by the Ir center (synchronous Ir-based decay and 3nap rise-time) and then transferring its energy to the Eu center (synchronous 3nap decay and Eu-based emission rise time). Thus the 3nap state, which is energetically intermediate in the {Ir(F2phpy)2}—naphthyl—Eu systems, can act as a “stepping stone” for two-step d→f energy-transfer.

INTRODUCTION

Sensitization of lanthanide luminescence by energy-transfer from a strongly absorbing antenna group is a widely used route to populate the f-f states which are difficult to populate by direct excitation as the transitions are Laporte-forbidden. There has been much recent effort in studying the photophysical properties of d/f dyads in which this antenna group is a transition-metal complex fragment rather than an organic ligand.1−3 This requires the d-block component to have a high absorption coefficient, and an excited state which is long-lived enough such that energy-transfer to the lanthanide(III) ion is a significant deactivation pathway that competes favorably with other radiative and nonradiative deactivation processes. It also requires that the energy of the excited state of the d-block component lies sufficiently far above that of the emissive level of the lanthanide(III) ion that d→f energy-transfer has a large enough thermodynamic gradient to prevent back energy-transfer.1a

Potential applications of such d/f complexes are significant. An appropriate balance between emission colors of different components in the dyads can generate white light from a single molecule, as shown in some Ir(III)/Eu(III) systems which combine blue Ir(III)-based emission and red Eu(III)-based emission.2e,3e Given the wide interest in long-lived visible-region luminescence for cellular imaging, molecules combining two luminescent outputs at different time scales (d-block, ns to μs timescale; f-block, ms time scale) are of interest as potential new imaging agents.2f Lanthanide-based emission can be used for imaging in both the visible region [e.g., Eu(III)] because of its intensity, narrowness, and long lifetimes, and in the near-IR regions [e.g., Yb(III), Nd(III)] because long-wavelength emission can penetrate biological tissue particularly well.4

As part of this work it is essential to understand the mechanisms by which d→f energy-transfer occurs.10 We have shown in many cases that Förster-type energy-transfer is not feasible over the distances involved between the metal centers.
because the very low extinction coefficients of the f-f absorptions on the lanthanide ion, which act as the energy-acceptor levels, result in very small donor/acceptor overlap integrals and short critical transfer distances.\textsuperscript{2b,e} In contrast, Dexter-type (electron-exchange mediated) energy-transfer can occur because the low intensity of the f-f absorptions is no longer a component of the calculation of the donor/acceptor overlap integral, and conjugated bridging ligands can provide the necessary electronic coupling to facilitate the process.\textsuperscript{2b,e} In some other cases, photoinduced electron-transfer to generate a charge-separated state is the initial step after excitation,\textsuperscript{2g} and some other cases, photoinduced subtleties.\textsuperscript{1b} Based on these, the lanthanide-based emitter is accordingly nontrivial and has numerous transferred from the d-block antenna to the lanthanide(III)-is in the near-IR region. The issue of how excitation energy is collapsed of this can provide sufficient energy to sensitize luminescence from the lanthanide [Yb(III)] if the luminescence is in the near-IR region. The issue of how excitation energy is transferred from the d-block antenna to the lanthanide(III)-based emitter is accordingly nontrivial and has numerous subleties.\textsuperscript{1b}

In this paper we describe a new variant of the d→f energy-transfer theme, which is the intermediacy of an organic triplet state on a naphthyl group (hereafter abbreviated as "nap") that lies spatially and energetically between an Ir(III) unit (energy-donor) and a Eu(III) unit (energy-acceptor). The complexes concerned (Chart 1) are Ir(III)-naphthyl-Eu(III) systems, similar in principle to Ir(III)/Eu(III) dyads that we have studied before\textsuperscript{25} but with the added participation of a photophysically noninnocent naphthyl spacer in the bridging ligand. We show how, in cases where the naphthyl triplet state lies significantly below the energy of the Ir(III)-based 3MLCT/3LC state (hereafter abbreviated as "Ir"), it provides a stepping-stone for a two-step energy-transfer process (Ir→nap naphthyl and napthyl→Eu). In contrast, with a lower-energy Ir-based energy donor that lies slightly below the energy of the nap state, Ir→Eu energy-transfer occurs in a single step without the active participation of a separate nap intermediate level, although the naphthyl unit can provide a conduit for mediating the superexchange processes necessary for Dexter-type energy-transfer.

Such behavior has been demonstrated before in several examples of transition-metal based Ru(II)/Os(II) dyads which show long-range energy-transfer between metal complex termini facilitated by triplet states of bridging ligand fragments which are both spatially and energetically intermediate.\textsuperscript{5} The current contribution provides an unusual example of such behavior facilitating energy-transfer in d/f systems, and to the best of our knowledge, this is the first demonstration of d-f energy transfer by such a stepwise method. Given the current interest in dual-emissive d/f complexes for applications from display devices to cellular imaging as described above\textsuperscript{1−3} understanding the energy-transfer process which controls their luminescence behavior is of considerable importance.

## RESULTS AND DISCUSSION

### 1. Synthesis and Structural characterization of Iridium Complexes.

The Ir complexes used as the basis of the Ir/Eu dinuclear systems (Chart 1) are all based on bridging ligands which have two bidentate chelating pyrazolyl-pyridine termini.\textsuperscript{2d,e} These have several advantages for our purposes. First, when coordinated to Ir(III)/phenylpyridine units, the resulting complexes have high-energy luminescence in the blue or blue/green region from a mixed 3MLCT/3LC excited state,\textsuperscript{6} which has sufficient energy content to sensitize the emissive 3D\textsubscript{0} state of Eu(III). Second, attachment of a Eu(hfac)\textsubscript{3} unit (hfac = 1,1,1,5,5,5-hexafluoro-pentane-2,4-dionate) to the second NN-chelating site to complete the syntheses of the Ir(III)/Eu(III) dyads is trivial, and occurs in noncompeting organic solvents such as CH\textsubscript{2}Cl\textsubscript{2} rapidly according to the equilibrium in Scheme 1.\textsuperscript{1,26−7} Third, syntheses of these bridging ligands are simple, and a wide range of intermediate organic fragments separating the two pyrazolyl-pyridine termini can be used.\textsuperscript{7}

The general synthetic methods used for syntheses of complexes of this type have been described before and do not need repeating.\textsuperscript{2d,e} The significant difference for this work is that the bridging ligands all contain naphthyl units rather than phenyl units: in this work we have used the 1,4- and 1,5-disubstituted naphthyl spacer groups to give the ligands L\textsubscript{14} and L\textsubscript{15} which we have reported before.\textsuperscript{8} These ligands have been used to make the mononuclear Ir(III) complexes [Ir(phpy)\textsubscript{2}(L\textsubscript{n})][NO\textsubscript{3}] (n = 14, 15; based on unsubstituted 2-phenylpyridine) and [Ir(F\textsubscript{2}phpy)\textsubscript{2}(L\textsubscript{n})][NO\textsubscript{3}] (n = 14, 15; based on 2-(2,4'-difluorophenyl)pyridine) which have been satisfactorily characterized by standard methods. For simplicity we abbreviate these complexes as \textsuperscript{H}Ir\textsuperscript{L}\textsubscript{14} and so forth for the former series, and \textsuperscript{Fl}Ir\textsuperscript{L}\textsubscript{14} and so forth for the latter series (see Chart 1), where the superscripts "H" and "F" denote the substituents on the phenylpyridine ligands. We have also used for comparison purposes the simple mononuclear complexes \textsuperscript{H}Ir\textsuperscript{L}Me and \textsuperscript{Fl}Ir\textsuperscript{L}Me (Chart 1) which contain no pendant naphthyl groups but just a methyl substituent at the pyrazolyl N:\textsuperscript{5}

![Chart 1](Image)

![Scheme 1](Image)
Table 2. Selected Coordination-Sphere Bond Distances (Å) for the New Complexes

| Complex          | $^{10502}$IrL$^{14}$ | $^{10502}$IrL$^{15}$ |
|------------------|-----------------------|----------------------|
| $^{10502}$IrL$^{14}$ |                      |                      |
| Ir(1)−N(111)    | 2.033(3)              | Ir(1)−C(121)         | 2.035(3) |
| Ir(1)−N(131)    | 2.065(3)              | Ir(1)−N(162)         | 2.076(7) |
| Ir(1)−N(151)    | 2.079(3)              | Ir(1)−C(141)         | 2.085(3) |
| $^{10502}$IrL$^{15}$ | CH$_2$Cl$_2$       | CH$_2$Cl$_2$         |          |
| Ir(1)−C(121)    | 2.007(6)              | Ir(1)−C(141)         | 2.021(6) |
| Ir(1)−N(131)    | 2.042(5)              | Ir(1)−N(111)         | 2.047(5) |
| Ir(1)−N(162)    | 2.152(6)              | Ir(1)−N(151)         | 2.155(6) |
| $^{10502}$IrL$^{14}$ | CH$_2$Cl$_2$       | CH$_2$Cl$_2$         |          |
| Ir(1)−C(321)    | 2.012(8)              | Ir(1)−C(221)         | 2.024(8) |
| Ir(1)−N(211)    | 2.033(7)              | Ir(1)−N(311)         | 2.038(7) |
| Ir(1)−N(122)    | 2.165(7)              | Ir(1)−N(111)         | 2.169(6) |
| $^{10502}$IrL$^{15}$ | CH$_2$Cl$_2$       | CH$_2$Cl$_2$         |          |
| Ir(1)−N(311)    | 2.045(9)              | Ir(1)−N(211)         | 2.059(8) |
| Ir(1)−N(122)    | 2.169(8)              | Ir(1)−N(111)         | 2.169(7) |
| $^{10502}$IrL$^{14}$ | 2CH$_2$Cl$_2$    | 2CH$_2$Cl$_2$        |          |
| Ir(1)−C(321)    | 2.004(3)              | Ir(1)−C(221)         | 2.009(3) |
| Ir(1)−N(211)    | 2.046(2)              | Ir(1)−N(311)         | 2.049(2) |
| Ir(1)−N(111)    | 2.153(2)              | Ir(1)−N(122)         | 2.158(2) |

Figure 1 shows the crystal structures of $^{10502}$IrL$^{14}$ and $^{10502}$IrL$^{15}$; crystallographic data are summarized in Table 1, and coordination-sphere bond distances and angles in Table 2. The pseudo-octahedral geometry in each case is unremarkable with the usual trans, cis−N$_2$C$_2$ arrangement of the two phenylpyridine ligands, which means that the chelating pyrazolylpyridine ligand occupies the coordinates sites trans to the two cyclometallating phenyl rings. This arrangement of ligands is shown by all of the other structurally characterized complexes in this paper.

The crystal structures of complexes $^{10502}$IrL$^{14}$ and $^{10502}$IrL$^{15}$ are shown in Figure 2 and have the same basic core structure as shown in the previous example. A notable feature of both structures however is the disposition of the pendant naphthyl group, which lies in each case such that it is stacked with one of the F$_{ph}$py ligands with a separation of about 3.4 Å between the parallel, overlapping aromatic ligand sections. Figure 2c shows an alternative view of $^{10502}$IrL$^{14}$ emphasizing the region of overlap between the naphthyl unit and a F$_{ph}$py ligand. This stacking has important potential consequences for the photo-physical properties of the complexes as we will see later. Figure 3 shows the structure of nonfluorinated $^{10502}$IrL$^{14}$ which shows exactly similar stacking of the pendant naphthyl group with one...
of the phenylpyridine ligands; note the similarity between the structures shown in Figure 3 and Figure 2b.

2. Photophysical Properties of Ir/Naphthyl Complexes.
UV/vis absorption spectroscopic data are summarized in Table 3.

The complexes all show the usual ligand-centered $\pi - \pi^*$ transitions in the UV region, and lower-energy and less intense metal-to-ligand charge-transfer (MLCT) transitions in the region 350–400 nm.

2.1. Emission Spectroscopy of Ir/Naphthyl Complexes.
Emission spectra of the mononuclear model complexes $^1$Ir•LMe and $^1$Ir•LMe, which illustrate the emission behavior expected for these metal chromophores, are shown in Figure 4.

These spectra are characteristic of the core Ir(III) unit with two N,C-donor phenylpyridine ligands and a pyrazolyl-pyridine chelate as we reported earlier, with fluorination of the phenylpyridine ligands in the latter case resulting in a blue shift of the main emission maximum from 476 to 453 nm, a shift of approximately 1100 cm$^{-1}$.

The nonfluorinated, naphthyl-appended complexes $^1$Ir•LMe and $^1$Ir•LMe, which illustrate the emission behavior expected for these metal chromophores, are shown in Figure 4.

The luminescence lifetimes in air-equilibrated CH$_2$Cl$_2$ are 670 and 690 ns respectively with $\Phi$ = 0.31 in each case. These luminescence lifetimes are considerably longer than in the model complex bearing a methyl substituent on the pyrazolyl ring $^1$Ir•LMe ($\tau$ = 180 ns, this work) or in a complex with a pendant phenyl group in the same position ($\tau$ = 198 ns, previous work). The presence in $^1$Ir•LMe and $^1$Ir•LMe of the naphthyl group pendant from the pyrazolyl unit, which lies stacked with one of the phenylpyridine ligands, therefore increases significantly the $^1$Ir-based emission intensity and lifetime. This most likely indicates operation of the well-known “reservoir effect” arising from the fact that the Ir and Nap excited states are very similar in energy. Notwithstanding this, the emission clearly originates from the Ir(III) unit with two N,C-donor phenylpyridine ligands and a pyrazolyl-pyridine chelate as we reported earlier.

| Table 3. Summary of UV/Vis Absorption Spectra for the Complexes in CH$_2$Cl$_2$ Solution at Room Temperature |
|-----------------------------|-----------------------------|
| complex                    | $\lambda_{max}$ nm (10$^{-3}$ e, M$^{-1}$ cm$^{-1}$) |
| $^1$Ir•L$_{14}$            | 247 (61), 279 (47), 318 (17), 360 (5.9) |
| $^1$Ir•L$_{15}$            | 252 (58), 279 (45), 315 (18), 360 (5.5) |
| $^1$Ir•L$_{14}^{\text{Me}}$ | 257 (65), 269 (62), 289 (49), 382 (5.5) |
| $^1$Ir•L$_{15}^{\text{Me}}$ | 255 (62), 271 (58), 365 (41), 390 (5.1) |
| $^1$Ir•L$_{14}^{\text{Me}}$ | 256 (44), 291 (27), 341 (17), 362 (6.3), 388 (3.6) |
| $^1$Ir•L$_{15}^{\text{Me}}$ | 256 (44), 268 (41), 287 (29), 340 (9.1), 382 (5.4) |

Figure 2. Molecular structures of the complex cations of (a) $^1$Ir•L$_{14}^{\text{Me}}$ and (b) $^1$Ir•L$_{15}^{\text{Me}}$; nitrate anions, solvent molecules, and H atoms are omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. Part (c) shows an alternative view of the structure of $^1$Ir•L$_{14}^{\text{Me}}$ emphasizing the aromatic stacking interaction between the pendant naphthyl group (dark gray) and one of the coordinated phenylpyridine ligands (pale gray).

Figure 3. Molecular structure of the complex cation of $^1$Ir•L$_{14}^{\text{Me}}$; nitrate anions, solvent molecules, and H atoms are omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

Figure 4. Luminescence spectra (CH$_2$Cl$_2$, RT) of $^1$Ir•L$_{14}^{\text{Me}}$ (dashed line) and $^1$Ir•L$_{15}^{\text{Me}}$ (solid line).
from the $^3$Ir-based unit in each case as shown by the appearance of the emission spectra, and is not quenched by the naphthyl pendant unit whose lowest excited state is too high in energy to quench the $^3$Ir-based emission.

In contrast the complexes $^3$Ir(14) and $^3$Ir(15) show higher-energy luminescence with spectra qualitatively similar to that of $^3$Ir(Me) (Figure 4, solid line) with the highest energy emission component at 455 nm, as expected because of the F-atom substituents on the phenylpyridine ligands. $^6a$ However, the luminescence is—unexpectedly—very weak with quantum yield values of just 0.016 in each case. This is an order of magnitude reduction in emission intensity compared to other complexes of the $^3$Ir series which do not have naphthyl substituents pendant from the pyrazole ring. For example previously reported analogues in which the naphthyl pendant is simply replaced by a phenyl ring have emission at exactly the same wavelength but with $\phi = 0.13$. $^2e$

We ascribe the difference in behavior between these two pairs of complexes to the different energetic ordering of the $^1$Ir and $^3$nap excited states. The triplet excited state ($^3$Ir) in $^3$Ir complexes has energy of 22,200 cm$^{-1}$ whereas the energy of the $^1$Ir state in the nonfluorinated $^3$Ir complexes is 21,400 cm$^{-1}$ (determined in both cases from the highest-energy component in the 77 K emission spectra). $^2d,e$ These values may be compared to the energy of the triplet excited state of 21,200 cm$^{-1}$ for free naphthalene $^{10}$ which is approximately the same as the excited state energy of nonfluorinated $^3$Ir complexes (as required for the reservoir effect that we observed, increasing the emission lifetimes), $^9$ but significantly below the excited state energy of the fluorinated $^3$Ir complexes. In $^3$Ir(14) and $^3$Ir(15), therefore, the $^3$nap state is unable to quench the $^1$Ir state of the $^3$Ir unit; but in $^3$Ir(14) and $^3$Ir(15), the $^3$nap state acts as a quencher of the higher-energy $^1$Ir state following $^3$Ir$\rightarrow$nap energy-transfer, a process which will be facilitated by the $\pi$-stacking that brings chromophore and quencher units into close proximity (see the crystal structures in Figures 2, 3). In principle the sensitized $^3$nap state could be facilitated by the $\pi$-stacking seen in the crystal structures, must show complete quenching of Ir-based luminescence (based on the limitations of equipment) as no short-lived $^1$Ir-based decay is detectable. A small proportion of a more extended conformer, in which the naphthyl group is remote from the $^1$Ir core and does not quench the $^1$Ir emission, shows longer-lived Ir-based emission similar to that of $^3$Ir(Me). $^6a$ We note that complex decay kinetics are a common feature of conformationally flexible complexes of this type. $^2e,9$

2.2. Transient Absorption Spectroscopy of Ir/Naphthyl Complexes. The complexes have been studied further using transient absorption (TA) spectroscopy to obtain more insight about the localization and kinetic behavior of their excited states. A problem that became quickly apparent is that the $^3$Ir excited state of the $^3$Ir unit, and the $^3$nap excited state, give overlapping excited-state absorption spectra. The TA spectrum of the model complex $^3$Ir(Me), on excitation at 355 nm in degassed CH$_2$Cl$_2$ shows a broad region of excited-state absorption across the visible region with a maximum at about 420 nm. Coincidentally it is also known that the most intense feature of the TA spectrum of $^3$nap is at 420 nm, $^{11}$ which means that appearance of excited-state absorption in this region is not unambiguously diagnostic of either the $^3$Ir or the $^3$nap excited state. However time-resolved measurements allow those to be distinguished, as we will see later, because triplet states of aromatic hydrocarbon groups are much longer-lived than those of heavy metal complexes.

The kinetic behavior of the excited state decay of the mononuclear Ir complexes, as measured by decay of the TA spectrum, is surprisingly complex. This is partly because of the possibility of a mixture of conformers for the complexes $^3$Ir(14) and $^3$Ir(15) in which the pendant naphthyl groups may be close to, or remote from, the Ir core. In addition the relatively high concentrations used for TA measurements lead to aggregation effects. The resultant decays are multi-exponential but can be approximately fitted by two exponential components which indicate the excited state lifetime range in the ensemble (Table 4); correlation between these means that the two components can vary together without making much difference to the quality of the fit. These lifetime values therefore should not be overinterpreted, but taken as an indication of the range of the excited state lifetimes in this system.

For the simple model complex $^3$Ir(Me), the excited-state absorption shows biexponential decay kinetics with lifetimes of $\tau \approx 1.7$ and 2.6 $\mu$s in degassed CH$_2$Cl$_2$ (cf. single-exponential decay of 600 ns for luminescence in air-equilibrated CH$_2$Cl$_2$ at lower concentration). Longer luminescence lifetimes from a triplet state in the absence of O$_2$ are to be expected, but we see here the effects of aggregation arising from the higher concentrations used for TA spectra. In agreement with this, time-resolved luminescence measurements on the same solution used for the TA measurements could also be fitted to two lifetime components in the same range (Table 4), in good agreement with the TA spectrum. The important point is that the excited-state absorption at 420 nm therefore arises from the same excited state as does the luminescence, that is, the usual Ir-centered $^3$(MLCT/LC) state, $^6a$ and indeed we have seen similar TA spectra for related complexes in previous work. $^2e$ For the analogous nonfluorinated model complex $^3$Ir(Me), the apparent maximum in the TA spectrum is at 450 nm (Figure 5b), indicative of a slightly lower-energy $^3$Ir$\rightarrow$nap energy gap compared to $^3$Ir(Me). Again this is not a true maximum but is the strongest region of excited-state absorption that is not partially canceled by the stimulated emission peaks (which are red-shifted compared to $^1$Ir(Me)). The excited-state lifetime as determined by decay of the TA signal in degassed CH$_2$Cl$_2$ matches the luminescence measurements under the same conditions, confirming that the excited-state absorption and the luminescence arise from the same $^3$Ir excited state.

For the naphthyl-appended complexes $^3$Ir(14) and $^3$Ir(15) we find the same situation, that is, the excited-state lifetimes obtained from the TA spectra and from luminescence measurements under the same conditions are similar (Table 4, Figure 6a). The lengthening of these lifetimes to $\sim 10$ $\mu$s...
obtained in air-equilibrated CH$_2$Cl$_2$ arising from small amounts of the same conditions. Once formed, decay of the 3nap state is bi-

TA spectra in each case show the presence of a much longer-

emission is completely quenched. In agreement with this, the decay components of the reservoir emission are sensitive to the presence of O$_2$ (in air-equilibrated solution these lifetimes are reduced to 0.5 and 1.5 μs); in addition, the triplet state cannot be 3Ir as clearly shown by the luminescence behavior. Thus we are seeing a growth of 3Ir, and two slower decay components of 17 and 100 μs decay of the 3nap state following 3Ir→nap energy-transfer. 3Ir$^{15}$ shows exactly similar behavior with the excited-state absorption at 420 nm having a growth of 1.1 μs, and two slower decay components of 17 and 100 μs, consistent with the deactivation of the 3nap state (Figure 6b). The conclusion again is that the TA signal corresponds to formation and then slow decay of a 3nap excited state following 3Ir→nap energy-transfer.

To conclude this section, it is clear that 3Ir$^{14}$ and 3Ir$^{15}$ (n = 14, 15) behave differently from one another. In the former pair of complexes the excited state observed in the TA spectra is the same as the luminescent excited state and is the expected 3Ir state with a modest increase in luminescence lifetime arising from the reservoir effect. In the latter pair, there is a long-lived nonemissive triplet excited state which is clearly not the luminescent 3Ir state; it grows in (≈1 μs) and then decays slowly with lifetimes of up to 100 μs. This must be the 3nap state, generated by 3Ir→nap energy-transfer, which has become possible because of the high energy of the 3Ir state when the phenylpyridine ligands are fluorinated. Note that the excitation (at 355 nm) is in a region where naphthalene does not absorb directly, so the 3nap state can only be populated by energy-transfer from the initially generated 3Ir-based excited state of 3Ir$^{14}$ and 3Ir$^{15}$.

Table 4. Summary of Excited State Lifetimes from Luminescence and Transient Absorption Measurements$^a$

|                       | CH$_2$Cl$_2$/air-equilibrated | CH$_2$Cl$_2$/degassed | transient absorption |
|-----------------------|--------------------------------|-----------------------|---------------------|
|                       | luminescence                   | luminescence$^b$      | transient absorption |
| 3Ir$^{14}$Me          | 180 ns                         | 1.1, 2.2 μs           | 1.5, 2.4 μs         |
| 3Ir$^{14}$            | 670 ns                         | 2, 11 μs              | 6.2, 15.9 μs        |
| 3Ir$^{15}$            | 690 ns                         | 3, 8 μs               | 5.4, 10.8 μs        |
| 3Ir$^{14}$•Eu         | 160 ns, 70 ns$^b$              | 0.7 μs                | 1.0, 5.7 μs         |
|                       |                                | 5.9 μs                | 700 μs (Eu decay)   |
| 3Ir$^{15}$•Eu         | 170 ns, 60 ns$^b$              | 0.1 μs                | 0.3 μs, 2.9 μs      |
|                       |                                | 2 μs                  |                     |
|                       |                                | 700 μs (Eu decay)     |                     |
| 3Ir$^{14}$Me          | 600 ns                         | 1.4, 2.4 μs           | 1.7, 2.6 μs         |
| 3Ir$^{14}$            | ~500 ns$^d$                    | 1.4 μs                | 17 μs (3Ir decay)   |
|                       |                                |                      | 100 μs (3nap decay) |
| 3Ir$^{15}$            | ~500 ns$^d$                    | 1.1 μs                | 1.1 μs (3nap rise)  |
|                       |                                |                      | 18 μs (3nap decay)  |
|                       |                                |                      | 62 μs (3nap decay)  |
| 3Ir$^{14}$•Eu         | not measured                   | 0.8 μs ($^3$Ir decay) | 1.3 μs (3nap rise)  |
|                       |                                | 8.6 μs (Eu rise)      | 7.6 μs (3nap decay) |
|                       |                                | 560 μs (Eu decay)     |                     |
| 3Ir$^{15}$•Eu         | not measured                   | 1.1 μs ($^3$Ir decay) | 1.5 μs (3nap rise)  |
|                       |                                | 15 μs (Eu rise)       | 15 μs (3nap decay)  |
|                       |                                | 460 μs (Eu decay)     |                     |

$^a$Decays are in normal type; rise times are in bold type. $^b$Also present was a small 700 ns component (<10% of total emission intensity) ascribable to traces of the free Ir complex as part of the equilibrium in Scheme 1. $^c$Ir-based decay measured at around 500 nm (or as mentioned in the figures); Eu-based decay measured at 615 nm. $^d$Very weak Ir-based emission arising from a minor conformer in which the Ir-based emission is not quenched by the naphthyl group; the majority of the Ir-based emission is assumed to be completely quenched (see main text).

compared to 3Ir$^{14}$Me (τ ~ 2 μs) may be ascribed again to the reservoir effect as discussed earlier that is, the excited state lifetime of the 3Ir unit is lengthened by close interaction with the naphthyl unit which has a similar excited state energy. The appearance of the emission spectra of 3Ir$^{14}$ and 3Ir$^{15}$ confirm that the emissive excited state is still 3Ir in character.

The fluorinated complexes 3Ir$^{14}$ and 3Ir$^{15}$ bearing the naphthyl group however show significantly different behavior from that of their nonfluorinated analogues discussed above. As described earlier, the 3Ir luminescence intensity is largely (>90%) quenched by the presence of the naphthyl group. Emission lifetimes in degassed CH$_2$Cl$_2$ (~1 μs in each case) correspond with the very weak decay components of ≈500 ns obtained in air-equilibrated CH$_2$Cl$_2$, arising from small amounts of unquenched "open" conformers, see above. We expect there also to be a dominant folded conformer in which 3Ir-based emission is completely quenched. In agreement with this, the TA spectra in each case show the presence of a much longer-lived excited state whose lifetime does not correspond to the weak 3Ir-based luminescence (Figure 6b).

For 3Ir$^{14}$ the decay of the excited state absorption at 420 nm now shows three components with lifetimes spanning 2 orders of magnitude. The first is a grow-in of 1 μs which can be ascribed to population of the 3nap state by 3Ir→nap energy-transfer which is now possible because of the higher excited state energy of the 3Ir state arising from the fluorination of the ligands. As required, the lifetime of the grow-in matches the luminescence decay component observed for 3Ir$^{14}$ under the same conditions. Once formed, decay of the 3nap state is bi-exponential with lifetime values of τ = 17 and 100 μs, consistent with the existence of two major conformers. These long excited state lifetimes, especially the dominant 100 μs component, are entirely consistent with the values expected for triplet states of organic aromatic groups. The fact that these lifetimes are associated with a triplet excited state is confirmed by the fact that they are sensitive to the presence of O$_2$ (in air-equilibrated solution these lifetimes are reduced to 0.5 and 1.5 μs); in addition, this triplet state cannot be 3Ir as clearly shown by the luminescence behavior. Thus we are seeing a 3Ir growth and slow (17 and 100 μs) decay of the 3nap state following 3Ir→nap energy-transfer. 3Ir$^{15}$ shows exactly similar behavior with the excited-state absorption at 420 nm having a grow-in of 1.1 μs, and two slower decay components of τ = 18 and 62 μs, consistent with deactivation of the 3nap state (Figure 6b). The conclusion again is that the TA signal corresponds to formation and then slow decay of a 3nap excited state following 3Ir→nap energy-transfer.

To conclude this section, it is clear that 3Ir$^{14}$ and 3Ir$^{15}$ (n = 14, 15) behave differently from one another. In the former pair of complexes the excited state observed in the TA spectra is the same as the luminescent excited state and is the expected 3Ir state with a modest increase in luminescence lifetime arising from the reservoir effect. In the latter pair, there is a long-lived nonemissive triplet excited state which is clearly not the luminescent 3Ir state; it grows in (≈1 μs) and then decays slowly with lifetimes of up to 100 μs. This must be the 3nap state, generated by 3Ir→nap energy-transfer, which has become possible because of the high energy of the 3Ir state when the phenylpyridine ligands are fluorinated. Note that the excitation (at 355 nm) is in a region where naphthalene does not absorb directly, so the 3nap state can only be populated by energy-transfer from the initially generated 3Ir-based excited state of 3Ir$^{14}$ and 3Ir$^{15}$. 

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2.3. Luminescence Properties of Ir/Naphthyl/Eu Three-Component Complexes. As described in the introduction our motivation here was to see if the spatial and energetic intermediacy of a $^{3}$nap state between $^{3}Ir$ (energy-donor) and Eu (energy-acceptor) components facilitated the d→f energy-transfer process. We investigated this in two ways. First we performed luminescence titrations in air-equilibrated CH$_2$Cl$_2$ in which small portions of $[Eu(hfac)_3(H_2O)_2]$ were added to the samples of $^0$Ir$_n$L$_1$n and $^1$Ir$_n$L$_1$n to form $^0$Ir$_n$L$_n$•Eu and $^1$Ir$_n$L$_n$•Eu respectively ($n = 14, 15$ in both cases). During these titrations we monitored the degree of quenching by the $[Eu(hfac)_3]$ unit of the Ir-based luminescence, and also the appearance of sensitized Eu-centered emission. Plots of Ir-based emission intensity vs concentration of added $[Eu(hfac)_3]$ (showing the steady quenching during the titration), and of Eu-based emission intensity vs concentration of added $[Eu(hfac)_3]$ (showing the steady grow-in during the titration), fit to 1:1 binding isotherms and give binding constants for the equilibrium in Scheme 1 of about $2 \times 10^4$ M$^{-1}$ in agreement with previous work. Second, we performed TA measurements in deaerated CH$_2$Cl$_2$ on samples of $^0$Ir$_n$L$_1$n and $^1$Ir$_n$L$_1$n ($n = 14, 15$) to which an excess of $[Eu(hfac)_3]$ was added, to form the adducts $^0$Ir$_n$L$_n$•Eu and $^1$Ir$_n$L$_n$•Eu respectively via the equilibrium in Scheme 1.

Figure 5. Transient absorption spectra of fluorinated (a) and nonfluorinated (b) compounds recorded in CH$_2$Cl$_2$ at RT, following excitation with a 355 nm, ~7 ns laser pulse, recorded immediately after excitation. (a) Black squares, $^0$Ir$_{14}$; blue triangles, $^0$Ir$_{15}$; red circles, $^1$Ir$_{14}$; (b) Black squares, $^1$Ir$_{14}$; red circles, $^1$Ir$_{15}$; blue triangles, $^0$Ir$_{15}$. Kinetic decays for transient absorption and emission signals, as indicated, for (c) $^0$Ir$_{14}$ and (d) $^0$Ir$_{15}$; solid black lines represents the fit to the data with the parameters listed in Table 4.

Figure 6. Transient absorption spectra and associated transient absorption and emission kinetics for (a) $^0$Ir$_{14}$ (averaged between 500 and 1000 ns after excitation), and (b) $^0$Ir$_{15}$ (reconstructed excited state spectra obtained by a global fit), both in deaerated CH$_2$Cl$_2$ at RT, following a 355 nm, ~7 ns laser pulse. The solid black line represents the fit to the data with the parameters listed in Table 4. On panel (b), the two spectra shown correspond to the early time Ir-based excited state (open circles, red) and to the subsequently formed $^{3}$nap state (triangles, green). In (a) the correspondence between the relatively long luminescence and TA decay lifetimes is clear; in (b) the much shorter luminescence decay correlates with the rise time of the TA spectrum, and the slow TA decay does not have a matching luminescence component; see main text.
otherwise interfere, showed that it comprised at least three energy-transfer in the dyad.

3 equiv of [Eu(hfac)$_3$(H$_2$O)$_2$]. At this end-point the Ir-based emission by Ir resulted in a slight increase because Gd(III) does not have any low-lying excited states that changes in luminescence intensity reflect real changes in emission quantum yields. It also means that any emission seen from the {Eu(hfac)$_3$} unit can only arise from d→f energy-transfer in the intact complex HIr

of about 20% in the Ir-based emission intensity of HIr$^{15}$ following incomplete Ir→Eu energy-transfer. Strong sensitized Eu-based emission grew in during the titration as HIr$^{15}$·Eu formed. The residual 3Ir-based emission had lifetime components of about 170 and 60 ns arising from Ir→Eu energy-transfer in different conformers of HIr$^{15}$·Eu. Formation of HIr$^{15}$·Gd as a control experiment was accompanied by a slight increase (≈10%) of Ir-based emission intensity compared to free HIr$^{15}$, with a change in lifetime from 690 to 740 ns, presumably because of rigidification of the complex when {Gd(hfac)$_3$} binds, as described above.

As HIr$^{14}$·Eu formed during the titration, according to Scheme 1, the Ir-based emission in the 450–600 nm region steadily decreased, and this quenching was accompanied by appearance of intense Eu-based emission displaying the usual sequence of D$_0$ → F$_n$ components between 570 and 720 nm. No significant changes were observed after addition of about 3 equiv of [Eu(hfac)$_3$(H$_2$O)$_2$] (cf. the equilibrium in Scheme 1) will not absorb light and therefore will not interfere with the emission spectra.

As HIr$^{14}$·Eu formed during the titration, according to Scheme 1, the Ir-based emission in the 450–600 nm region steadily decreased, and this quenching was accompanied by appearance of intense Eu-based emission displaying the usual sequence of D$_0$ → F$_n$ components between 570 and 720 nm. No significant changes were observed after addition of about 3 equiv of [Eu(hfac)$_3$(H$_2$O)$_2$] (cf. the equilibrium in Scheme 1) will not absorb light and therefore will not interfere with the emission spectra.

Time-resolved measurements on the residual Ir-based luminescence, using a 475–525 nm bandpass filter to reject the intense Eu-based sensitized emission which would otherwise interfere, showed that it comprised at least three exponential components. A weak component with $\tau \approx 0.7 \mu$s can be ascribed to traces of residual HIr$^{14}$ (cf. Scheme 1). Two additional shorter components with $\tau \approx 160$ and 70 ns were needed to give a satisfactory fit to the luminescence decay curve. These may be ascribed to partial quenching of the 3Ir emission by Ir→Eu energy-transfer in two (at least) different conformers of HIr$^{14}$·Eu, with energy-transfer rate constants of the order of $10^8$ s$^{-1}$. In contrast use of (nonquenching) [Gd(hfac)$_3$(H$_2$O)$_2$] in place of [Eu(hfac)$_3$(H$_2$O)$_2$] as a control, because Gd(III) does not have any low-lying excited states that can act as energy-acceptors from either the 3Ir or 3nap states, resulted in a slight increase of about 20% in the Ir-based luminescence intensity by the end of the titration; this was accompanied by a marginal increase in the 3Ir emission lifetime from 670 to 700 ns. This presumably occurs because addition of the {Gd(hfac)$_3$} unit to the pendant pyrazolyl-pyridine site of HIr$^{14}$ to give HIr$^{14}$·Gd results in rigidification of the complex and the consequent loss of some nonradiative deactivation pathways that were associated with molecular vibrations.

Titrations of HIr$^{15}$ with [Eu(hfac)$_3$(H$_2$O)$_2$] and [Gd(hfac)$_3$(H$_2$O)$_2$] under the same conditions (6.4 × 10$^{-5}$ M in air-equilibrated CH$_2$Cl$_2$) showed exactly similar behavior. Formation of HIr$^{15}$·Eu was accompanied by 65% quenching of the 3Ir emission intensity of HIr$^{15}$ following incomplete Ir→Eu energy-transfer. Strong sensitized Eu-based emission grew in during the titration as HIr$^{15}$·Eu formed. The residual 3Ir-based emission had lifetime components of about 170 and 60 ns arising from Ir→Eu energy-transfer in different conformers of HIr$^{15}$·Eu. Formation of HIr$^{15}$·Gd as a control experiment was accompanied by a slight increase (≈10%) of Ir-based emission intensity compared to free HIr$^{15}$, with a change in lifetime from 690 to 740 ns, presumably because of rigidification of the complex when {Gd(hfac)$_3$} binds, as described above.

For both HIr$^{14}$·Eu and HIr$^{15}$·Eu, therefore, the behavior is similar to what we have observed with related Ir/Eu dyads but using simple phenyl spacers in place of naphthyl in the bridging ligand. 2e In contrast Dexter-type energy-transfer is possible over the distances required in HIr$^{15}$·Eu and HIr$^{15}$·Eu by means of a weak electronic coupling that is facilitated by π-stacking of the type that we observed in the crystal structures described earlier, 2e though here there is no evidence for a separate 3nap excited state being involved as an intermediate.

Given that Eu-based emission occurs only as a consequence of Ir→Eu energy-transfer under these conditions, we might expect to see a grow-in for the Eu-based emission in both HIr$^{14}$·Eu and HIr$^{15}$·Eu. However any grow-in of Eu-based emission at 615 nm will be masked by the decay in the tail of the residual Ir-based emission intensity at the same wavelength which must be synchronous. Accordingly time-resolved measurements at 615 nm did not reveal a grow-in associated with sensitization of Eu-based emission but this is to be expected.

(ii) HIr$^{14}$·Eu and HIr$^{15}$·Eu. Luminescence titrations using the fluorinated complexes HIr$^n$ (n = 14, 15), having a higher-energy 1Ir state, were performed in air-equilibrated CH$_2$Cl$_2$ by addition of small portions of [Eu(hfac)$_3$(H$_2$O)$_2$] in the same way as described above, until no further significant changes were observed (after addition of about 4 equiv of [Eu(hfac)$_3$(H$_2$O)$_2$]). The results using HIr$^{14}$ are shown in Figure 8. Compared to the nonfluorinated HIr$^{14}$ system the weakness of the initial Ir-based luminescence is obvious, and this is quenched further (about 30% additional reduction in intensity) as HIr$^{14}$·Eu forms. Time-resolved analysis of this residual Ir-based emission did not yield useful results, which

Figure 7. Changes in luminescence spectra ($\lambda_{\text{exc}}$ 380 nm) recorded during titration of HIr$^{14}$ (6.4 × 10$^{-5}$ M) with [Eu(hfac)$_3$(H$_2$O)$_2$] (1.4 mM; up to 3 equiv compared to HIr$^{14}$) in CH$_2$Cl$_2$ to form the HIr$^{14}$·Eu dyad, showing the decay of Ir-based emission (450–600 nm) and the rise of sensitized Eu-based emission (570–720 nm) as HIr$^{14}$·Eu forms according to Scheme 1.

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Eu(III) in a on decays on a faster time scale and is so much weaker. This rise-traces of Eu-based emission originating from the 5D1 state rather FIr signaling a3nap TA spectrum under the same conditions (see next section), emission is characteristically very long (560 the rise-time observed for sensitized Eu-based emission (15 s) for sensitized Eu-based emission of comparable intensity. Again secondary pyrazolyl-pyridine site, and the appearance of matches well the decay of the3nap state that is observed in the dominant 3Ir IR-based emission in the first place. Despite the weakness of emission from $^{3}$Ir but energy-transfer is occurring, in addition to the predominate $^{3}$Ir→nap energy-transfer which results in such weak IR-based emission in the first place.

The kinetics of the TA spectrum of $^{3}$Ir→nap energy-transfer processes that are considerably slower than the values of about $10^{7}$ s$^{-1}$ that were estimated from luminescence measurements performed during the titrations. We emphasize however that each technique may reveal different processes. Fast $^{3}$Ir→Eu energy-transfer processes based on more compact conformations of the complexes may be difficult to detect by TA measurements if these are present in only small amounts, because in this case the TA signal will be dominated by the more abundant longer-lived $^{3}$Ir component from slow energy-transfer. Conversely a slow energy-transfer process, even if it is the dominant pathway, could easily be undetectable by luminescence measurements: energy-transfer with a rate constant of $10^{5}$ s$^{-1}$ would only reduce the $^{3}$Ir-based emission lifetime from (say) 700 ns for a free Ir complex in air-equilibrated solvent to about 680 ns in a Ir/Eu dyad, a difference which is much less than the experimental uncertainty. We conclude that the combination of TA and luminescence measurements on $^{3}$Ir→Eu reveal a range of $^{3}$Ir→Eu energy-transfer processes with time scales spanning the range $10^{5}$–$10^{8}$ s$^{-1}$ in different conformers. $^{3}$IrL14•Eu shows similar behavior: on conversion of $^{3}$IrL15 to $^{3}$IrL14•Eu, the excited-state absorption at 420 nm which signals formation of the $^{3}$Ir state decays more quickly with the longest component being reduced from 11 to 3 μs in degassed CH$_2$Cl$_2$, and a similar conclusion of direct $^{3}$Ir→Eu energy-transfer applies.

The kinetics of the TA spectrum of $^{3}$IrL14 in degassed CH$_2$Cl$_2$ showed a rise-time of 1 μs for sensitization of the $^{3}$nap state, followed by slow ($\approx$ 17 and 100 μs) decays whose lifetimes had no counterpart in the weak $^{3}$Ir luminescence, consistent with formation of a nonemissive $^{3}$nap state (cf. the similar behavior of $^{3}$IrL14 illustrated in Figure 6b). In the presence of 5 equiv of [Eu(hfac)$_3$(H$_2$O)$_2$]$^-$ to generate $^{3}$IrL14•Eu in situ according to Scheme 1, the $^{3}$nap lifetime is reduced to 7.6 μs by $^{3}$nap→Eu energy-transfer, as manifested by transient absorption studies (Figure 9). Importantly, this 7.6 μs decay component for the $^{3}$nap state matches very well the 8.6 μs rise-time observed for the sensitized Eu-based emission at 615 nm, confirming the occurrence of a $^{3}$nap→Eu

Figure 8. Changes in luminescence spectra ($\lambda_{exc}$ 380 nm) recorded during titration of $^{6}$IrL14 (6.5 × 10$^{-5}$ M) with [Eu(hfac)$_3$(H$_2$O)$_2$]$^-$ (0.82 mM; up to 3 equiv compared to $^{6}$IrL14) in CH$_2$Cl$_2$ to form the $^{6}$IrL14•Eu dyad, showing the decay of the very weak IR-based emission (450–600 nm) and the rise of sensitized Eu-based emission (570–720 nm) as $^{6}$IrL14•Eu forms according to Scheme 1. The two very weak, sharp emission peaks at 535 and 664 nm (labeled *) are traces of Eu-based emission originating from the $^{3}$D$_1$ state rather than $^{3}$D$_0$.

is unsurprising given both its weakness and likely multi-

exponential behavior arising from different conformers. However from the intensity changes we can say that some additional Ir→Eu energy-transfer is occurring, in addition to the predominant $^{3}$Ir→nap energy-transfer which results in such weak IR-based emission in the first place.

2.4. Transient Absorption Measurements on Ir/ Naphthyl/Eu Three-Component Complexes. TA measurements were particularly useful at clarifying the sequential nature of the energy-transfer processes and were performed in degassed CH$_2$Cl$_2$. As mentioned earlier the excited-state absorption of $^{3}$IrL14 (arising from the $^{1}$Ir excited state) shows complex decay kinetics which can be approximated with two components having $\tau$ ≈ 6 and 16 μs under these conditions. In the presence of 5 equiv of [Eu(hfac)$_3$(H$_2$O)$_2$]$^-$, to convert $^{3}$IrL14 to $^{3}$IrL14•Eu, the TA spectrum retains a similar appearance, but the excited state absorption at 420 nm decays more quickly with $\tau$ = 1.0 and 5.7 μs, in good agreement with luminescence lifetimes measured on the same sample under the same conditions (Table 4). This is consistent with the partial quenching of the $^{3}$Ir-based emission intensity that we observed in the luminescence titration experiment. The correspondence of the excited-state lifetimes from the TA spectrum and the $^{3}$Ir-based luminescence lifetimes again implies a simple $^{3}$Ir→Eu energy-transfer process as we saw for related Ir/Eu dyads, without the intermediacy of a nonemissive $^{3}$nap state that is too high in energy to participate. From these lifetime values we can estimate $^{3}$Ir→Eu energy-transfer rates in the range 10$^{5}$–10$^{6}$ s$^{-1}$ for those conformers whose excited-state decay is clearly visible by the TA method. We can therefore detect from the TA decay kinetics for $^{3}$IrL14•Eu energy-transfer processes that are considerably slower than the values of about $10^{7}$ s$^{-1}$ that were estimated from luminescence measurements performed during the titrations. We emphasize however that each technique may reveal different processes. Fast $^{3}$Ir→Eu energy-transfer processes based on more compact conformations of the complexes may be difficult to detect by TA measurements if these are present in only small amounts, because in this case the TA signal will be dominated by the more abundant longer-lived $^{3}$Ir component from slow energy-transfer. Conversely a slow energy-transfer process, even if it is the dominant pathway, could easily be undetectable by luminescence measurements: energy-transfer with a rate constant of $10^{5}$ s$^{-1}$ would only reduce the $^{3}$Ir-based emission lifetime from (say) 700 ns for a free Ir complex in air-equilibrated solvent to about 680 ns in a Ir/Eu dyad, a difference which is much less than the experimental uncertainty. We conclude that the combination of TA and luminescence measurements on $^{3}$IrL14•Eu reveal a range of $^{3}$Ir→Eu energy-transfer processes with time scales spanning the range $10^{5}$–$10^{8}$ s$^{-1}$ in different conformers. $^{3}$IrL14•Eu shows similar behavior: on conversion of $^{3}$IrL15 to $^{3}$IrL14•Eu, the excited-state absorption at 420 nm which signals formation of the $^{3}$Ir state decays more quickly with the longest component being reduced from 11 to 3 μs in degassed CH$_2$Cl$_2$, and a similar conclusion of direct $^{3}$Ir→Eu energy-transfer applies.

The kinetics of the TA spectrum of $^{3}$IrL14 in degassed CH$_2$Cl$_2$ showed a rise-time of 1 μs for sensitization of the $^{3}$nap state, followed by slow ($\approx$ 17 and 100 μs) decays whose lifetimes had no counterpart in the weak $^{3}$Ir luminescence, consistent with formation of a nonemissive $^{3}$nap state (cf. the similar behavior of $^{3}$IrL14 illustrated in Figure 6b). In the presence of 5 equiv of [Eu(hfac)$_3$(H$_2$O)$_2$]$^-$ to generate $^{3}$IrL14•Eu in situ according to Scheme 1, the $^{3}$nap lifetime is reduced to 7.6 μs by $^{3}$nap→Eu energy-transfer, as manifested by transient absorption studies (Figure 9). Importantly, this 7.6 μs decay component for the $^{3}$nap state matches very well the 8.6 μs rise-time observed for the sensitized Eu-based emission at 615 nm, confirming the occurrence of a $^{3}$nap→Eu
energy-transfer process and the intermediacy of the \( \text{nap} \) state in the two-step \( \text{Ir} \rightarrow \text{nap} \rightarrow \text{Eu} \) energy-transfer sequence (Figure 9, 10). Further proof was obtained by repeating the above measurements after admitting air to the \( \text{CH}_2\text{Cl}_2 \) sample solution. This resulted in the \( \text{nap} \) lifetimes obtained from the TA spectrum being reduced to \( \approx 0.2 \) and 1.2 \( \mu \text{s} \) because of \( \text{O}_2 \) quenching, and also resulted in the grow-in of Eu-based emission at 615 nm being reduced to 1.5 \( \mu \text{s} \) in the time-resolved luminescence measurements. Again we have a good correspondence between the main \( \text{nap} \) decay component (1.2 \( \mu \text{s} \)) and the rise-time of sensitized Eu-based emission (1.5 \( \mu \text{s} \)). For \( ^5\text{IrL}^{14} \cdot \text{Eu} \) the sensitization of Eu emission by the \( \text{nap} \) state is equally clear. The long-lived \( \text{nap} \) state of \( ^5\text{IrL}^{15} \) (\( \approx 18, 62 \) \( \mu \text{s} \)) is shortened to 15 \( \mu \text{s} \) when \( ^5\text{IrL}^{15} \cdot \text{Eu} \) forms, and again the key point is that this decay of the \( \text{nap} \) state perfectly matches the 15 \( \mu \text{s} \) rise-time of the sensitized Eu emission.

For both \( ^5\text{IrL}^{14} \cdot \text{Eu} \) and \( ^5\text{IrL}^{15} \cdot \text{Eu} \), therefore, we can directly observe both steps of the \( \text{Ir} \rightarrow \text{nap} \rightarrow \text{Eu} \) energy-transfer sequence from the rise and decay of the intermediate \( \text{nap} \) state in the TA spectrum (Figure 9). The first (\( \text{Ir} \rightarrow \text{nap} \)) energy-transfer step is shown by quenching of \( \text{Ir} \) luminescence, and the ca. 1 \( \mu \text{s} \) grow-in of the \( \text{nap} \) state matches the residual \( \text{Ir} \) decay component. The second (\( \text{nap} \rightarrow \text{Eu} \)) energy-transfer step is again clearly shown by the grow-in of sensitized Eu-based emission which closely matches the \( \text{nap} \) decay rate. The schematic photophysical diagram summarizing two different mechanisms of energy transfer in shown in Figure 10. Remarkably, fluorination of the ancillary ligand, which only affects the energy of the energy donating antenna state by \( < 0.4 \text{ eV} \), induces a complete switch between the two mechanisms of d-f energy transfer: the one step \( \text{Ir} \rightarrow \text{Ln} \) energy transfer in the nonfluorinated complexes, and the two-step \( \text{Ir} \rightarrow \text{nap} \rightarrow \text{Eu} \) process, mediated by the naphthalene spacer, in the fluorinated complexes.

**CONCLUSIONS**

We have prepared two sets of complexes containing an \( \text{Ir} \) (phenylpyridine)/naphthyl/Eu(hfac)\(_3\) sequence of photoactive units. The energies of the naphthyl and Eu-based excited states do not change significantly between members of the series, but the \( ^5\text{Ir} \)-based excited state may lie at 22,200 \text{ cm}^{-1} \) or 21,400 \text{ cm}^{-1} \) according to whether the phenylpyridine ligands are fluorinated or not. In the nonfluorinated complexes \( ^5\text{IrL}^n \) (\( n = 14, 15 \)) the \( ^5\text{Ir} \) state is too low in energy to be quenched by the \( \text{nap} \) state, with the result that these complexes show typical \( ^5\text{Ir} \)-based luminescence and their Eu(hfac)\(_3\) adducts \( ^5\text{IrL}^n \cdot \text{Eu} \) show normal \( ^5\text{Ir} \rightarrow \text{Eu} \) energy-transfer in which the \( ^5\text{Ir} \)-based emission is substantially quenched. The Dexter-type energy-transfer process is facilitated by aromatic stacking between the components in which the naphthyl group is involved, but there is no \( \text{nap} \) intermediate state. A range of energy-transfer rate constants (\( \approx 10^6 \) to \( 10^9 \) \text{ s}^{-1} \)) detected by a combination of time-resolved luminescence and TA spectroscopic methods is consistent with a range of conformers with different \( \text{Ir} \rightarrow \text{nap} \) separations and energy-transfer pathways.

In contrast, in the fluorinated complexes \( ^5\text{IrL}^{14} \) and \( ^5\text{IrL}^{15} \) the \( ^5\text{Ir} \) state is now high enough in energy to be quenched by \( \text{Ir} \rightarrow \text{nap} \) energy-transfer generating a long-lived \( \text{nap} \) state. This means that in the Eu(hfac)\(_3\) adducts \( ^5\text{IrL}^n \cdot \text{Eu} \) and \( ^5\text{IrL}^n \cdot \text{Eu} \) there is now a two-step \( \text{Ir} \rightarrow \text{nap} \rightarrow \text{Eu} \) energy-transfer sequence, with the intermediate \( \text{nap} \) state being sensitized by the \( ^5\text{Ir} \) donor and passing its energy on to the Eu(hfac)\(_3\) unit, with the rise-time of sensitized Eu(III) luminescence matching the decay time of the \( \text{nap} \) state in each case. Thus, slightly increasing the \( ^5\text{Ir} \) energy by fluorination of the phenylpyridine ligands results in a fundamentally different energy-transfer pathway leading to sensitized Eu(III)-based emission. This finding demonstrates the first example of such a switch in d/f systems, and illustrates further how fine-tuning of electronic structure can manipulate energy transfer processes.

**EXPERIMENTAL DETAILS**

**General Details.** The following compounds were prepared according to published methods: the ligands \( ^1\text{MeL}^{14} \) and \( ^1\text{MeL}^{15} \); the dimers \( \text{Ir}(\text{phenylpyridine})(\mu\text{Cl})_2 \); based on unsubstituted 2-fluorophenylpyridine and the fluorinated analogue 2-(2,4-difluorophenyl)pyridine; \( ^3\text{IrL}^{13} \) and Eu(hfac)\(_3\)(H\(_2\text{O}\)); \( ^5\text{Ir} \) Electrospray mass spectra were recorded using a Micromass LCT instrument; \( ^1\text{H} \) NMR spectra were recorded on a Bruker Avance-2 400 MHz instrument. UV/vis

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**Figure 9.** Transient absorption spectra of \( ^5\text{IrL}^{14} \cdot \text{Eu} \) in \( \text{CH}_2\text{Cl}_2 \) at RT. (a) Transient absorption spectra at 0 and 4 \( \mu \text{s} \) after 355 nm excitation, reconstructed using global fit analysis. (b) Kinetic traces for transient absorption decay (top) and emission (bottom) at the wavelengths specified. The solid black line represents the two-exponential (TA) and the three-exponential (emission) fit to the data with the parameters listed in Table 4.

**Figure 10.** Outline photophysical scheme summarizing how the differing energy of the \( ^5\text{Ir} \) states between the \( ^5\text{Ir} \) and \( ^5\text{Ir} \) complexes results in different energy-transfer pathways to the Eu(III) center.
absorption spectra were measured on a Cary 50 spectrophotometer, and steady-state luminescence spectra on a Jobin-Yvon Fluoromax 4 fluorimeter using air-equilibrated CH2Cl2 solutions at room temperature. IR-based emission lifetimes measured during the titrations with Eu(hfac)3(H2O)2 were measured using the time-correlated single photon counting technique with an Edinburgh Instruments "Minir" luminescence lifetime spectrometer, equipped with a 405 nm pulsed diode laser as excitation source and a Hamamatsu-H8773–03 PMT detector; the lifetimes were calculated from the measured data using the supplied software. Luminescence quantum yields were calculated by comparing areas of corrected luminescence spectra, from isosbestic solutions, following the method described by Demas and Crosby15 and using fac-[(Ir(ppy))(μ-Cl)]0.040 g (33 µmol) in CH2Cl2. The mixture was heated to 50 °C overnight under N2 and in the dark. The mixture was cooled to room temperature and the solvent removed. Water and saturated KPF6 solution (20 cm3) was added, and the resulting two-phase mixture was separated; the aqueous residue was further extracted with several portions of CH2Cl2 (3 × 30 cm3). The combined organic fractions were dried with Na2SO4 and the solvent removed. The yellow powder was purified by column chromatography on silica gel using MeCN and 1% aqueous KNO3; the solvent was removed. Water and saturated KPF6 solution (20 cm3) was added to the resultant solution to dryness and affore pure [Ir(ppy)] as its nitrate salt.

**Characterization Data for [Ir(ppy)]**. 1H NMR (400 MHz, CDCl3): δ 8.69 (1H, d), 8.41 (1H, d), 8.07–8.00 (3H, m), 7.71 (1H, m), 7.59–7.48 (Sh, m), 7.46 (1H, d), 7.45 (2H, t), 7.24 (2H, q), 7.14 (1H, d), 7.03 (1H, d), 6.98–6.94 (2H, m), 6.84–6.79 (1H, t), 6.59 (1H, t), 6.45 (1H, d), 6.38 (1H, d), 6.26–6.21 (2H, m), 5.98 (1H, d), 5.82 (1H, d), 5.80 (1H, d), 5.71 (1H, d), 5.60 (1H, d), 5.51 (1H, d), 5.49 (1H, d). ESMS: m/z 943 (M − NO3). Anal. Calc. for C31H25N5IrNO3·0.5CH2Cl2: C 54.2, H 3.7, N 11.3%. Found: C 53.7, H 3.2, N 11.8%.

**Characterization Data for [Ir(ppy)]**. 1H NMR (400 MHz, CDCl3): δ 8.69 (1H, d), 8.41 (1H, d), 8.07–8.00 (3H, m), 7.95–7.92 (2H, m), 7.85 (1H, d), 7.78 (2H, m), 7.70 (1H, d), 7.59–7.48 (Sh, m), 7.42 (1H, d), 7.32 (2H, t), 7.24 (2H, q), 7.14 (1H, d), 7.03 (1H, d), 6.98–6.94 (2H, m), 6.84–6.79 (1H, t), 6.59 (1H, t), 6.45 (1H, d), 6.38 (1H, d), 6.26–6.21 (2H, m), 5.98 (1H, d), 5.82 (1H, d), 5.80 (1H, d), 5.71 (1H, d), 5.60 (1H, d), 5.51 (1H, d), 5.49 (1H, d). ESMS: m/z 943 (M − NO3). Anal. Calc. for C31H25N5IrNO3·0.5CH2Cl2: C 54.2, H 3.2, N 11.3%. Found: C 53.7, H 3.2, N 11.1%.

**Characterization Data for [Ir(ppy)]**. 1H NMR (400 MHz, CDCl3): δ 8.65 (1H, d), 8.44 (1H, d), 8.09–8.02 (2H, m), 7.79 (1H, d), 7.89–7.74 (Sh, m), 7.69 (1H, d), 7.58–7.55 (2H, m), 7.47–7.43 (3H, m), 7.32–7.20 (3H, m), 7.06 (1H, d), 6.99–6.82 (3H, m), 6.81–6.60 (4H, m), 6.32–6.25 (2H, m), 6.22 (1H, d), 5.99 (1H, d), 5.91 (1H, d), 5.78 (1H, d), 5.70 (1H, d), 5.66–5.50 (2H, m). ESMS: m/z 943 (M − NO3). Anal. Calc. for C31H25N5IrNO3·0.5CH2Cl2: C 57.2, H 3.7, N 11.3%. Found: C 57.0, H 4.0, N 12.0%.

**Characterization Data for [Ir(ppy)]**. 1H NMR (400 MHz, CDCl3): δ 8.42 (1H, d), 8.38 (1H, d), 8.31 (1H, d), 8.11 (1H, t), 8.04 (1H, d), 7.88 (2H, m), 7.75 (2H, m), 7.50 (1H, d), 7.38 (1H, d), 7.34 (1H, t), 7.26 (1H, t), 7.11 (1H, t), 6.55 (2H, m), 5.70 (1H, d), 5.60 (1H, d), 3.45 (3H, s). ESMS: m/z 733 (M − NO3). Anal. Calc. for C31H25N5IrNO3·0.5CH2Cl2: C 45.9, H 2.7, N 10.3%. Found: C 45.8, H 3.0, N 10.1%.

**Characterization Data for [Ir(ppy)]**. 1H NMR (400 MHz, CDCl3): δ 8.30 (1H, d), 8.00 (1H, t), 7.95 (2H, d), 7.90 (1H, d), 7.80 (2H, m), 7.75 (1H, d), 7.70 (1H, d), 7.65 (2H, t), 7.50 (1H, d), 7.29 (1H, d), 7.25 (1H, t), 7.15 (1H, t), 7.04 (2H, m), 6.98 (1H, t), 6.91 (1H, t), 6.87 (1H, d), 6.30 (1H, d), 6.20 (1H, d), 3.35 (3H, s). ESMS: m/z 660 (M − NO3). Anal. Calc. for C31H25N5IrNO3·0.5CH2Cl2: C 50.3, H 3.5, N 11.2%. Found: C 50.5, H 3.6, N 11.4%.

**X-ray Crystallography.** Crystals for X-ray diffraction studies were grown from CH2Cl2 solutions, either by slow evaporation or by diffusion of hexane vapor into the CH2Cl2 solution. In each case a crystal was removed from the mother liquor, coated with oil, and transferred to a stream of cold N2 on the diffractometer as quickly as possible to prevent decomposition due to solvent loss. All structural determinations were carried out on a Bruker SMART-APEX II diffractometer using graphite-monochromated Mo–Kα radiation (λ = 0.71073 Å) from a sealed tube source. After integration of the raw data, and before merging, an empirical absorption correction was applied (SADABS) based on comparison of multiple symmetry-equivalent measurements. The structures were solved by direct methods and refined by full-matrix least-squares on weighted F2 values for all reflections using the SHELX suite of programs. Pertinent crystallographic data are collected in Table 1; selected bond distances (from the metal coordination spheres) are in Table 2.

**Flash Photolysis Experiments.** Flash photolysis experiments were performed on a home-built setup. The samples were excited at 355 nm with third harmonic of a Q-switched Nd:YAG laser LS-2137U (LOTIS TII). The energy of excitation pulses delivered to the sample was about 2.5 mJ, at 10 Hz repetition rate and 7 ns pulse width. A 150 W Xe arc lamp (Hamamatsu) was used as the probe light source. The probe light was detected through a SPEX MiniMate monochromator by a custom-built detector unit, based on a FEU-118 PMT. Detector current output was coupled into Tektronix TDS 3032B digital oscilloscope and subsequently transferred to the computer. The transient absorption data were corrected for the spontaneous emission from the samples. The same setup was used for the time-resolved emission measurements in the microsecond time domain, with the only difference being a blocked probe lamp. All flash photolysis and microsecond time-resolved emission experiments were performed with the deoxygenated samples, degassed by the freeze–pump–thaw technique, unless noted otherwise. One centimeter path length quartz cells were used.

The analysis of time-resolved data to obtain decay lifetimes was performed using Igor Pro software (WaveMetrics, Inc.) or Origin 8.6 software (OriginLab Co.). The decay kinetics were fitted to the exponential decay law using a least-squares algorithm. Global fitting was applied to analyze simultaneously decay kinetics obtained for numerous spectral points, which enabled us to reconstruct the shape of transient spectra and considerably increased the reliability of the lifetime values.

### ASSOCIATED CONTENT

#### Supporting Information

X-ray crystallography data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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