

Sensitized Near-Infrared Luminescence From Nd^{III}, Yb^{III} and Er^{III} Complexes by Energy-Transfer From Ruthenium 1,3-Bis([1,10]Phenanthroline-[5,6-d]-Imidazol-2-yl)Benzene

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Abstract The luminescent ruthenium 1,3-bis([1,10]phenanthroline-[5,6-d]-imidazol-2-yl)benzene (bpibH₂) complex, a potentially useful bridging ligand with a vacant diimine site, has been used as ‘*metallo ligand*’ to make heterodinuclear d–f complexes by attachment of a {Ln(dik)₃} fragment (dik=1,3-diketonate) at the vacant site. When Ln=Nd, Yb, or Er the lanthanide centre has low-energy f–f excited states capable of accepting energy from the ³MLCT excited state of the Ru(II) centre, there is quenching in the ³MLCT luminescence of the Ru(II) centre, that affords sensitized lanthanide(III) based luminescence in the near-IR region. Nd(III) was found to be the most effective at quenching the ³MLCT luminescence of the ruthenium component because of the high density of f–f excited states of the appropriate energy which make it as effective energy-acceptor compared to Er and Yb complexes.

Keywords Ruthenium · Lanthanides · Energy transfer · NIR Luminescence · 1,3-bis([1,10]phenanthroline-[5,6-d]-imidazol-2-yl)benzene

Introduction

Near-infrared (NIR) luminescence from lanthanides such as Yb(III), Er(III), Pr(III) and Nd(III) has become an area of intense interest in the past few years because of its relevance to applications as diverse as luminescent probes in biological

media[1–6] and optical amplification in fiber optic telecommunications systems.[7–10] Very often, ligand centered π - π^* transitions in the UV region have been used to sensitize lanthanide luminescence following a ligand-to metal energy transfer; this overcomes the problem that f–f transitions are very weak, so direct excitation is difficult.[11–15] However, d-block complexes with strong charge-transfer transitions are emerging as effective sensitizer units, for a variety of reasons.[16–23] The high extinction coefficients associated with fully allowed charge-transfer transitions mean efficient absorption by the light-harvesting unit; relatively long-lived excited states mean that an energy transfer to the lanthanide ions can occur before the excited state collapses; the wide tunability of metal-to-ligand charge transfer (MLCT) transitions by varying the metal ion, ancillary ligands, and the ligand substituent means that a sensitizing chromophore can be chosen to have an ideal excited-state energy content to match with the energy receiving level on the lanthanide ion; and the broad luminescence bands characteristic of d-block luminophores maximize the necessary spectral overlap with the sharp, weak lanthanide f–f absorption bands. [8]

Ward et al., have used the mononuclear d-block complexes based on bridging ligands such as bipyrimidine and 2,3-bis(2-pyridyl)-pyrazine, containing vacant *N,N'*-bidentate sites. [24–27] The addition of lanthanide tris-diketonate units to the second diimine site results in d–f dyads with short metal-metal separations and an unsaturated bridging ligand, both of which make d→f energy transfers fast and efficient. In many of these complexes, a mononuclear, kinetically inert d-block complex fragment was prepared with a peripheral, vacant diimine binding site; reaction of the “complex ligand” with a lanthanide tris-(diketonate) dihydrate [Ln(dik)₃(H₂O)₂] resulted in an immediate attachment of the {Ln(dik)₃} fragment to the vacant *N,N'*-bidentate site of the d-block complex to give the heterodinuclear species. The syntheses are facile and high-yielding, and the method is very general, allowing a wide range of d-block chromophores and f-block luminophores to be combined.

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In this paper, we describe studies on the series of d-f complexes, based on a {Ru(bpy)(diimine)} unit as an energy donor, with BpibH₂ (1,4-bis(1,10-phenanthroline-[5,6-d]imidazol-2-yl)-benzene) as the bridging ligand connecting the two metal sites to facilitate energy transfer.

Materials and Methods

The synthesis of ligand BpibH₂ 1,3-bis([1,10]phenanthroline-[5,6-d]-imidazol-2-yl)benzene [28], tris lanthanide diketonate[29] and the parent ruthenium complex(I) were synthesized utilizing the literature methods and characterized using ¹H NMR and mass spectrometry, and elemental analysis (Figs S1 and S2). The observed δ and mass values are close to the reported values.[30] RuCl₃·3H₂O, neodymium nitrate pentahydrate, erbium nitrate pentahydrate, ytterbium nitrate pentahydrate, theonyl trifluoro acetone and 2-amino-5-nitroanisole were purchased from Aldrich and used as received. All solvents used for the synthesis were of reagent grade and for spectral measurements spectral grade was used. UV-vis absorption spectra were recorded on Analtikjena Specord S100 spectrophotometer and emission spectra in JASCO FP6300 spectrofluorimeter. The elemental analyses (C, H, N) were performed on Perkin-Elmer 2400. Mass spectra using a Quattro LC triple quadrupole mass spectrometer (Micromass, Manchester, UK) interfaced to an (Electron Spray

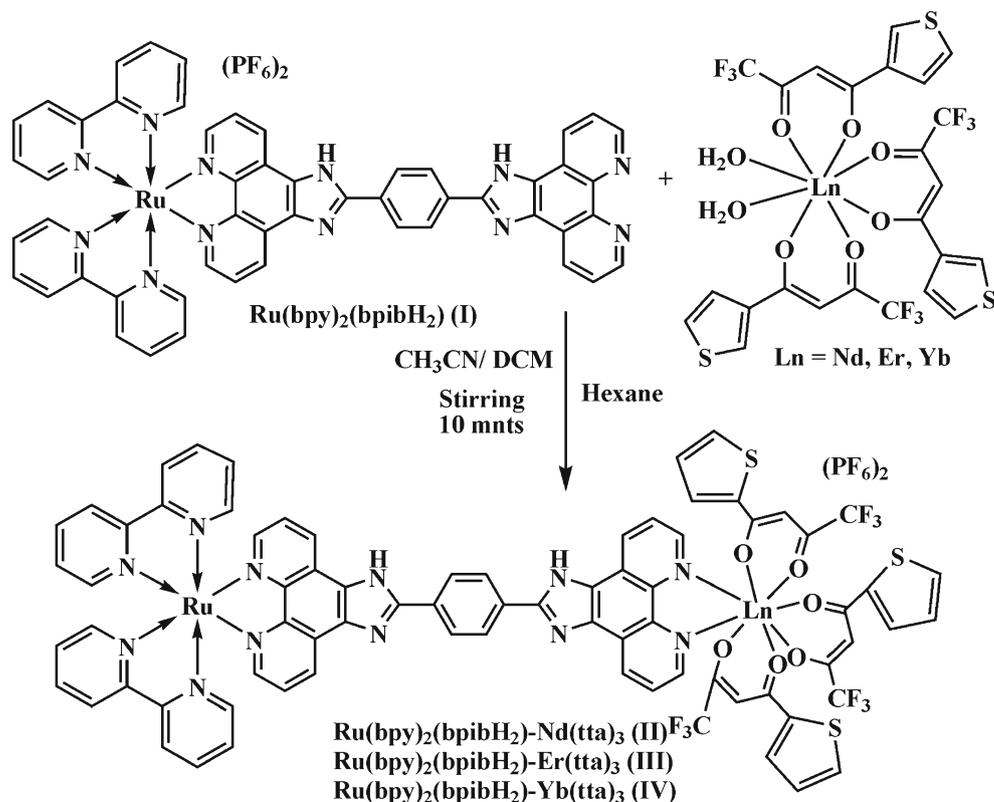
Ionisation). The ESI capillary voltage was maintained between 4.0 kV and 4.2 kV and the cone voltage kept at 25 V. Nitrogen was used as desolvation and nebulization gas. The source and desolvation temperatures were 100 °C. NIR emission was recorded using Edinburgh Instrument FLS9-OP, 450 W Xenon Arc Lamp as light source and NIT PMT(in N₂ Flow Cooled Housing) detector. The excited state lifetime of all the complexes at 298 K are measured using a laser flash photolysis set up with the third harmonic ($\lambda=355$ nm) of a Nd:YAG laser (Quanta-Ray). The transient absorption changes are monitored perpendicular to the laser beam by a 150 W pulsed xenon arc lamp. The transient signals are detected by Hamamatsu R-928 PMT. The PMT output was digitized with 500 MHz storage oscilloscope (Agilent Infiniium) interfaced to a computer. All reported lifetime measurements are averages of at least three measurements which typically agreed to ± 8 %.

Results and Discussion

Synthesis of the Ru(II)–Ln(III) Heterobimetallic Complexes [Ln=Nd(III), Er(III) and Yb(III)][23]

Equimolar amount of [Ru(bpy)₂(bpibH₂)] in CH₃CN and Ln(tta)₃(H₂O)₂ [Ln=Nd(III), Er(III) and Yb(III)] were dissolved in CH₂Cl₂ (5 cm³), the resulting reddish brown solution was stirred for 30 min. Hexane(15 cm³) was added

Chart 1 Synthesis of the lanthanide-ruthenium bimetallic complexes



to the solution. Concentration of the solution resulted in the precipitation of the dinuclear complex Ru-Ln, which was filtered. In each case, the solid was collected by filtration, washed with hexane and dried under vacuum and they are air-stable and yield ranges between 70 % and 80 %. The synthesis of the lanthanide-ruthenium bimetallic complexes is shown in Chart 1. All the complexes formed were confirmed by the jobs plot and it is shown in Fig S3.

1. Data for Ru(bpy)₂(bpibH₂)-Nd(tta)₃ (**II**): Yield: 77 %. Anal. Calcd for C₇₆H₄₆F₂₁N₁₂NdO₆P₂RuS₃: C, 44.86; H, 2.19; N, 8.14; Found: C, 45.06; H, 2.29; N, 8.30. ESI-MS(*m/z*, positive mode, MeCN, found (calcd)): 866.48(867.88) ([M-2PF₆-H⁺]²⁺). The mass spectrum is shown in Fig S4.
2. Data for Ru(bpy)₂(bpibH₂)-Er(tta)₃ (**III**): Yield: 78 %. Anal. Calcd for C₇₆H₄₆F₂₁N₁₂ErO₆P₂RuS₃: C, 44.16; H, 2.14; N, 8.11; Found: C, 44.56; H, 2.26; N, 8.20. ESI-MS(*m/z*, positive mode, MeCN, found (calcd)): 881.95(882.28) ([M-2PF₆-H⁺]²⁺). The mass spectrum is shown in Fig S5.
3. Data for Ru(bpy)₂(bpibH₂)-Yb(tta)₃ (**IV**): Yield: 73 %. Anal. Calcd for C₇₆H₄₆F₂₁N₁₂YbO₆P₂RuS₃: C, 44.23; H, 2.16; N, 8.08; Found: C, 44.43; H, 2.26; N, 8.18. ESI-MS(*m/z*, positive mode, MeCN, found (calcd)): 882.95(883.98) ([M-2PF₆-H⁺]²⁺).

Absorption Spectra

The absorption spectra of mono and bimetallic ruthenium-lanthanide complexes are shown in Fig. 1. All the monometallic complexes display peaks at 240 and 288 nm corresponding to the π - π^* of bipyridine and peak at 344 nm to the π - π^* of

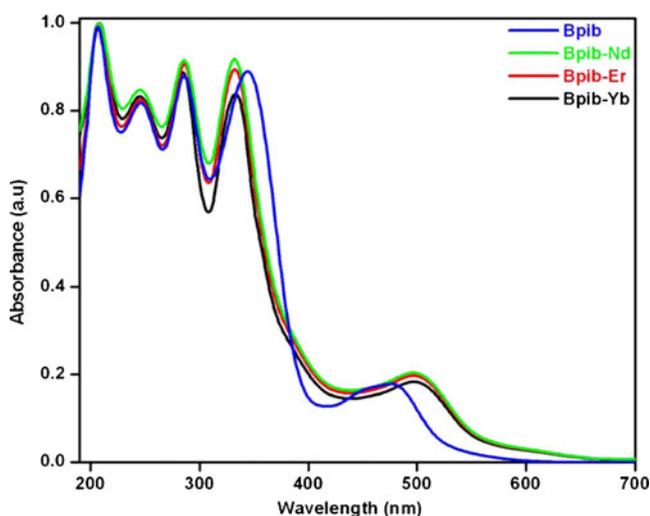


Fig. 1 Overlay absorption spectra of Ru(bpy)₂(bpibH₂)²⁺, Ru(bpy)₂(bpibH₂)-Nd(tta)₃, Ru(bpy)₂(bpibH₂)-Er(tta)₃ and Ru(bpy)₂(bpibH₂)-Yb(tta)₃ in CH₃CN with 1 × 10⁻⁵ concentration

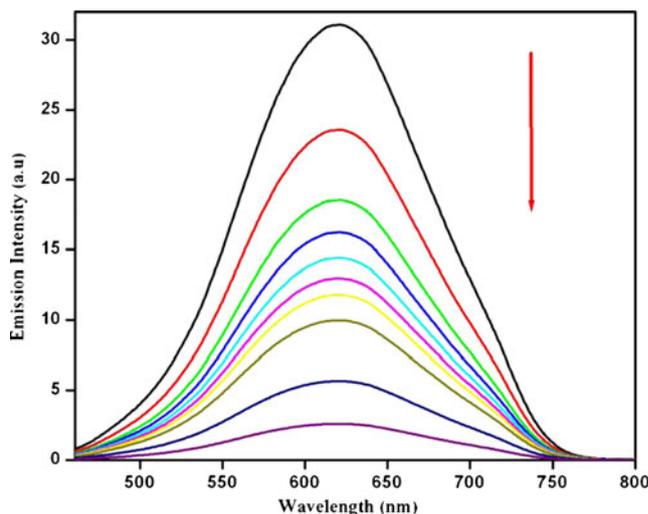


Fig. 2 Change in the luminescence spectrum of [Ru(bpy)₂(bpibH₂)]²⁺ upon addition of Er(tta)₃ (0–2 × 10⁻⁵) concentration in CH₃CN

bridging ligand and the peak in the region 450–480 nm meant for $d\pi(\text{Ru})-\pi^*(\text{BpibH}_2)$ MLCT transition. Upon formation of bimetallic complexes with lanthanide diketonates, the MLCT transition is red-shifted to 507 nm relative to that of mononuclear complex [Ru(bpy)₂(bpibH₂)]²⁺. The red shift is ascribed to the lowering in energy of the bpibH₂- π^* level on coordination of the electropositive lanthanide fragment to the second binding site.[31] A graph of absorbance at a wavelength of 500 nm versus the amount of [Yb(tta)₃(H₂O)₂] added gave a smooth curve that fitted well to a 1:1 binding isotherm (Fig S6), from which the association constant for binding of the lanthanide fragment to the diimine site could be determined,

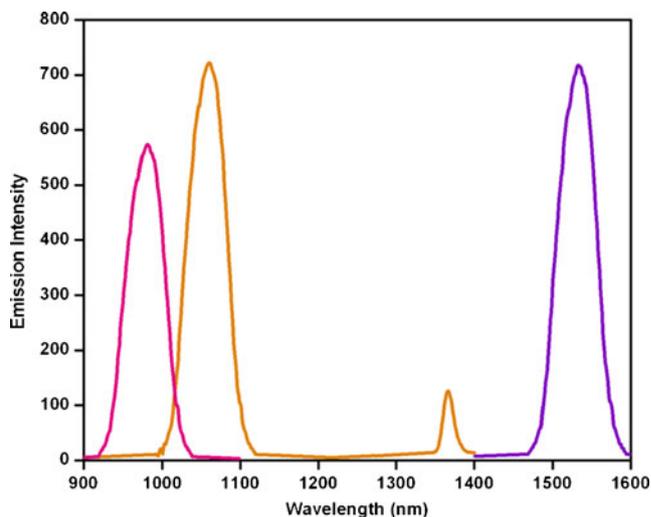
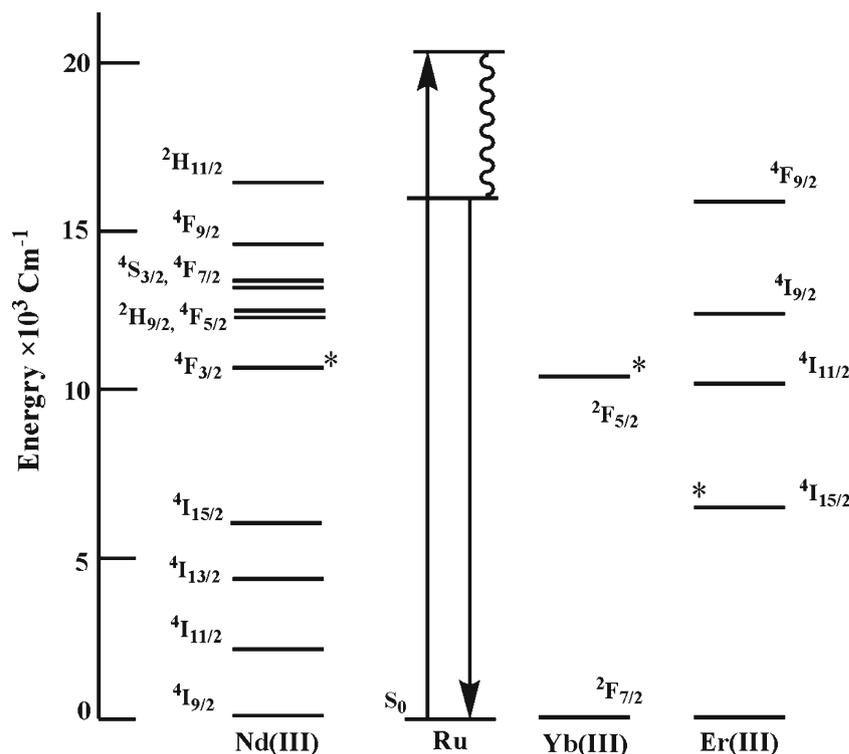


Fig. 3 Emission spectral profiles of Er (pink), Yb (rose) and Nd (orange) (the transitions are ⁴I_{13/2} → ⁴I_{15/2} for Er^{III}; ²F_{5/2} → ²F_{7/2} for Yb^{III}; and ⁴F_{3/2} → ⁴I_{9/2} and ⁴F_{3/2} → ⁴I_{11/2} for the high- and low- energy Nd^{III} emission lines respectively) in CH₃CN

Fig. 4 Approximate energy levels for Nd(III), Er(III) and Yb(III) complexes



the values obtained are $4.5 \times 10^5 \text{ M}^{-1}$ for Ru-Yb, $3.1 \times 10^5 \text{ M}^{-1}$ for Ru-Er and $2.4 \times 10^5 \text{ M}^{-1}$ for Ru-Nd.

Emission Spectra

The luminescence spectra of the heterobimetallic complexes were measured in CH_3CN , by using the excitation wavelength of 478 nm for complexes **II**, **III** and **IV** (Fig. 2). The emission spectra collected in Fig S6, show that the Ru^{II} -based luminescence at 616 nm is substantially quenched upon addition of $\text{Ln}(\text{tta})_3$, and the luminescence intensity is reduced substantially compared to that of monometallic $\text{Ru}(\text{bpibH}_2)$ complex. The details of quenching in the luminescence intensity of $[\text{Ru}(\text{bpy})_2(\text{bpibH}_2)]^{2+}$ upon addition of different concentration of $\text{Er}(\text{tta})_3$ are collected in Fig S7.

Excitation of these heterobimetallic complexes at 478 nm produces the NIR emission (Fig. 3) characteristic

of the lanthanide ions in all cases. In this way we could see the characteristic luminescence of Nd(III) (${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ at 1,060 nm), Yb(III) (${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ at 980 nm) and Er(III) (${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ at 1,510 nm). This clearly confirms that the Ru chromophore acts as a sensitizer of lanthanide luminescence, following energy transfer from the Ru centered chromophore to the emissive excited state of the lanthanide ion. The uncorrected excitation spectrum of heterobimetallic complex **IV** is given in Fig S8 and it is similar to that of the absorption spectrum of the bimetallic complex confirming that the complex is very stable under the irradiation of UV-vis light.

Excited State Lifetime Measurements

These heterobimetallic complexes also experience a concomitant reduction in the lifetime from 146 ns to 46 ns (an uncertainty of $\pm 8\%$ is assumed for Ru^{II} -based emission lifetimes). Upon formation of bimetallic complexes the lifetime of the monometal is quenched for all the three complexes. As the titration proceeds two luminescence components are apparent that is, both 146 ns and 46 ns lifetime components from $\text{Ru}(\text{bpy})_2(\text{bpibH}_2)$ [32] and bound $\text{Ru}(\text{bpibH}_2)\text{-Yb}$, with the longer component disappearing and the short component becoming dominant as the titration approaches completion.

$$k_{\text{EnT}} = \tau_{\text{q}}^{-1} - \tau_{\text{u}}^{-1} \quad (1)$$

$$\Phi_{\text{EnT}} = 1 - \tau_{\text{q}} / \tau_{\text{u}} \quad (2)$$

Table 1 The rate of energy transfer k_{EnT} and quantum efficiency Φ_{EnT} of heterobimetallic Ru(II)-Nd(III) complexes in CH_3CN at 298 K

Complex	$k_{\text{EnT}} \text{ s}^{-1}$	$\Phi_{\text{EnT}} \%$ [ref]
II	3.2×10^7	83
$[(\text{Ln}_2\text{-Ru})\text{I}]^{2+}$	1.1×10^6	–[16]
$\text{Ru}^{\text{II}}(\text{bpy})_2(\text{L}_1)\text{Nd}^{\text{III}}(\text{L}^2)^+$	3.5×10^5	31[19]
$\text{Ru-CH}_2\text{CH}_2$	2.2×10^6	46[33]
RuPh	1.9×10^7	91[33]
RuPh_2	1.7×10^7	44[33]
Calix[4] arene- $[\text{Ru}(\text{bpy})_3]^{2+}$	2.4×10^6	30[34]

Equation (1) gives Ru→Nd energy-transfer rate, k_{EnT} , of $3.3 \times 10^7 \text{ s}^{-1}$ (τ_q is the “quenched” lifetime, here 25 ns; τ_u is the “unquenched” lifetime, here 146 ns), Ru→Er energy-transfer rate k_{EnT} of $2.3 \times 10^7 \text{ s}^{-1}$ (τ_q is the “quenched” lifetime, here 34 ns; τ_u is the “unquenched” lifetime, here 146 ns), Ru→Yb energy-transfer rate k_{EnT} of $1.4 \times 10^7 \text{ s}^{-1}$ (τ_q is the “quenched” lifetime, here 46 ns; τ_u is the “unquenched” lifetime, here 146 ns). From Eq. (2) we calculate the quantum efficiency for Ru^{II}→Nd^{III} energy transfer and the value is 83 %, quantum efficiency for Ru^{II}→Er^{III} energy transfer is 76 %, quantum efficiency for Ru^{II}→Yb^{III} energy transfer is 68 %. These quantum efficiency values are in agreement with the reduction of Ru^{II}-based emission intensity. The rate of energy-transfer k_{EnT} for these lanthanides follows the order Nd>Er>Yb, and it is attributed to the energy level of these lanthanide ions.

Discussion on the Energy-Transfer Process

Nd^{III} has numerous electronically excited states that would be energetically appropriate for sensitization by the Ru^{II} chromophores, excitation to which is allowed by one of the selection rules (e.g., $^4\text{F}_{5/2}$, $^2\text{H}_{11/2}$, $^2\text{H}_{9/2}$, $^4\text{F}_{7/2}$ and $^4\text{F}_{9/2}$ lie between 13,000 cm^{-1} and 15,000 cm^{-1} from the $^4\text{I}_{9/2}$ ground state). The short metal-metal distance and the conjugated bridging ligand, which provide an orbital coupling pathway, mean that both Förster and Dexter energy-transfer mechanisms are perfectly feasible. Together with the large number of possible energy-acceptor levels on Nd(III), it is not surprising that the Ru(II)-diimine ³MLCT donor state is completely quenched by Nd(III).

For Er^{III} the $^4\text{I}_{11/2}$, $^4\text{I}_{9/2}$ and $^4\text{F}_{9/2}$ levels (lying between 10,000 cm^{-1} and 16,000 cm^{-1}) would be energetically appropriate, although population of only the first of these is allowed by the Förster mechanism. Dexter energy transfer is allowed only to the low-lying $^4\text{I}_{13/2}$ level at 6,500 cm^{-1} , for which the energy-transfer rate would be very slow, because of the large gap between donor and acceptor energy levels, but the rate of energy transfer is faster, but it is much slower than that of Ru(II)-Nd(III). Yb^{III} is a more unusual case as it has only a single excited state, $^2\text{F}_{5/2}$, which is 10,200 cm^{-1} Dexter-allowed ($|\Delta J|=1$ with respect to the ground state). Possible energy transfer path way is dissipated in Fig. 4.

Discussion on Rate of Energy Transfer and Quantum Efficiency

The rate of energy transfer, k_{EnT} , and quantum efficiency, Φ_{EnT} , of heterobimetallic Ru(II)-Nd(III) complexes synthesized in the present study and some of the heterobimetallic Ru(II)-Nd(III) complexes reported by other authors are collected in Table 1.

The rate of energy transfer decreases with an increase in the distance of energy transfer. When we compare our data

with the data already reported by other authors on similar systems we arrive at the following conclusion. The observed rate of energy transfer is much higher with the systems carrying conjugated bridging ligands than in d-f heterobimetallic systems where there is no conjugated bridging system and also it is higher when compared to that of bridging system reported by Ward et. al.[31] The reported energy transfer for Ru^{II}→Nd^{III} occurs at 9 Å with the rate $2.3 \times 10^6 \text{ s}^{-1}$, where as in ligand mediated Ru^{II}→Nd^{III} exchange energy transfer rate is $1.9 \times 10^7 \text{ s}^{-1}$ over a distance of 15.6 Å.[33]

Conclusions

A series of d-f dyads has been prepared, in which Ru(II) polypyridine-type chromophore is connected to a Ln(III) centre via 1,4-bis(1,10-phenanthroline-[5,6-d]imidazol-2-yl)-benzene bridging ligand. The luminescent mononuclear Ru(II) complex acts as “*metallo ligands*”, allowing the formation of Ru(II)-Ln(III) heterodinuclear complexes by the addition of a Ln(tta)₃ unit at the second imine site. In the resulting series of heterobimetallic Ru(II)-Ln(III) compounds, excitation of the ³MLCT absorption of the d-block chromophore results in fast energy transfer from Ru(II)→Nd(III) with concomitant sensitized NIR luminescence from the lanthanide unit.

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