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Sensitized near-infrared luminescence of Nd^{III}, Yb^{III} and Er^{III} complexes by energy transfer from a ruthenium antenna

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ABSTRACT

A series of new ruthenium–lanthanide bimetallic complexes bridged by bibenzimidazole (BibzImH₂) group were synthesized. The luminescent ruthenium bibenzimidazole complex, [(bpy)₂Ru(BibzImH₂)]²⁺, with a vacant diimine site, was used as a ‘complex ligand’ to prepare three new heterodinuclear d–f complexes by attaching a {Ln(dik)₃} fragment (Ln = Nd, Yb, or Er); (dik = tta(trifluoro theonyl acetone)) at the vacant site. All of the prepared complexes were characterized by a variety of spectral techniques. Upon excitation at the MLCT absorption band of Ru^{II}, due to efficient energy transfer, sensitized emission occurs from lanthanide centre in the near-infrared region. The lanthanide centre has low-energy f–f excited states, which are capable of accepting energy from the ³MLCT excited state of the Ru(II) centre, leading to the quenching of ³MLCT luminescence of the Ru(II) centre and subsequent sensitized lanthanide(III)-based luminescence in the near-IR region. Because BibzImH₂ is a short bridging ligand, it is able to assist in faster energy transfer from Ru(II) to Ln (III). The Nd(III) species was found to be the most effective for quenching the ³MLCT luminescence of the ruthenium component because of the high density of the f–f excited states of the appropriate energy, which make it as effective an energy-acceptor as Er(III) and Yb(III) complexes.

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1. Introduction

There has been considerable interest in the synthesis and photophysical properties of heterometallic d–f complexes, in which the strong absorption as the result of MLCT transitions associated with a d-block unit [typically Ru(II), Os(II), Re(I) or Pt(II)] is used to sensitize luminescence from lanthanide(III) ions with low-energy f–f excited states [1–3]. The use of d-block chromophores as antenna groups in this way overcomes the inherently low light absorption characteristics of lanthanide(III) ions. An extensive variety of d-block units is available, which combine the desirable characteristics of chemical and photochemical stability. They are also well characterized as having long lived excited states and absorb light strongly at more or less any desired wavelength [4–6]. Because of this, they have the ability to act as effective energy-donors. This allows the near-infrared emission from lanthanide(III) ions, to be

generated by energy-transfer from the strongly-absorbing d-block ‘antenna’ group [4–23]. These NIR emitting materials find potential applications in telecommunications [24], LED/OLED devices [25,26] and in biological imaging [27–29].

In d–f systems, it is desirable that the excited state of the d-block unit (³MLCT) has just high enough energy to act as a good energy donor, but not so high that it requires excitation in a region of the spectrum where tissue has a poor transparency [21–23]. The synthesis of such heteropolynuclear complexes, involving metal complex fragments which are kinetically inert, is generally based on a ‘complexes as ligands’ approach in which a polytopic bridging ligand has metal units that are added to its binding domains in a stepwise fashion. This requires the isolation of ‘complex ligands’ at an intermediate stage, in which the prepared metal complexes have residual vacant coordination sites that could be used as ligands in subsequent complexation steps.

Recently Chen and co-worker [3b] have presented an elegant piece of work on Ru(II) sensitized lanthanide luminescence using tetrapyrrodo [3,2-a:2',3'-c:3'',2''-h:3''',4'''-j]phenazine as the bridging ligand. These d–f bimetallic complexes have been successfully applied as NIR luminescent probe for alpha-fetal protein (AFP) which can be extended to clinical diagnosis. Advantage of

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using bis(benzimidazole) as the bridging ligand is that, the metal–metal distance in the case of homobimetallic ruthenium(II) complexes was found to be 4.5 Å [30]. Therefore upon the formation of heterobimetallic ruthenium(II)–lanthanide(III) complexes using this bis(benzimidazole) ligand the metal–metal distance would be shorter, compared to that of heterobimetallic rhenium(I)–lanthanide(III) bridged by a bipyrimidine ligand (6.23 Å, Re...Yb), as reported by Ward et al. [21]. Therefore the shorter metal–metal distance can achieve a faster energy transfer compared to that of bipyrimidine bridged complexes.

Herein we report on the synthesis of three new d–f dyads, in which the d-block donor unit and the f-block acceptor unit are bridged by a bis(benzimidazole) (BibzImH₂) ligand. The complex [(bpy)₂Ru(BibzImH₂)]²⁺ (bpy = 2,2′-bipyridine) has a vacant diimine site, which can be utilized to coordinate with the Ln(III) unit. The photophysical properties of the monometallic ruthenium complex and heterobimetallic d–f dyads were examined. Upon excitation, the luminescent Ru(II) centre acts as an antenna, and the bis(benzimidazole), by virtue of being a short bridge, permits energy transfer to rapidly occur to Ln(III), thereby resulting in sensitized NIR emission.

2. Results and discussion

2.1. Syntheses of complexes

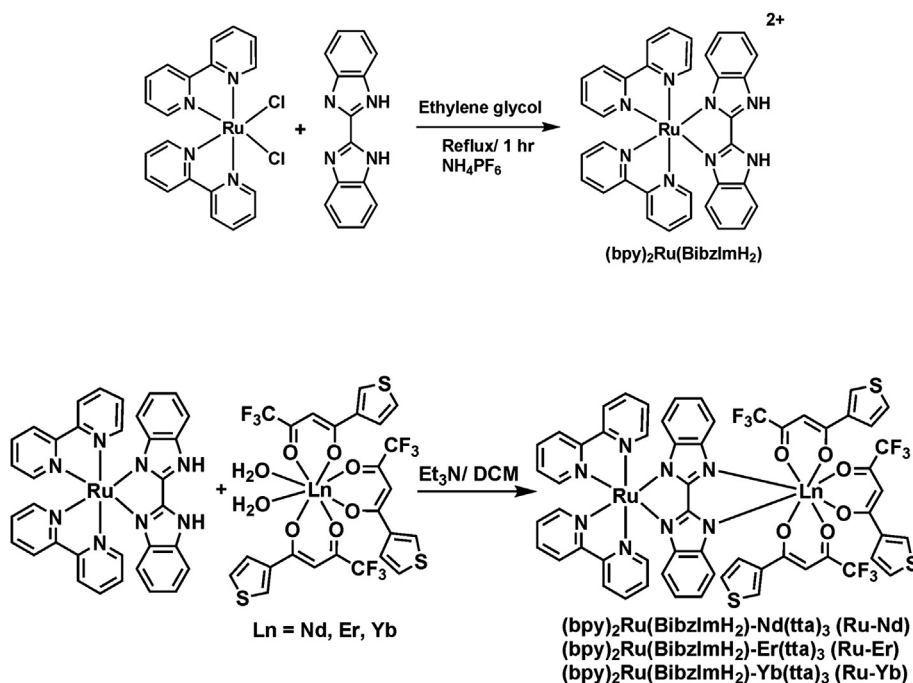
The ligand bis(benzimidazole) was prepared by reacting oxamide with *o*-phenylenediamine in ethylene glycol solution [30]. The formation and purity of the bis(benzimidazole) was confirmed by ¹H NMR and elemental analysis. The reaction of an equimolar amount of bis(benzimidazole) with Ru(bpy)₂Cl₂ in ethylene glycol, afforded the respective d-block “complex ligand” precursor [(bpy)₂Ru(BibzImH₂)]²⁺. Further reaction of the precursor with Ln(tta)₃·2H₂O in a 1:1 M ratio gave the bimetallic complexes Ru–Ln (Ln = Nd; Yb; Er) with 70–80% yield (Scheme 1). The monometallic and bimetallic complexes were characterized by various spectral techniques. The IR spectrum of Ru monometallic complex showed a

broad peak at 3350 cm^{−1} corresponding to N–H stretching frequency of bis(benzimidazole), which disappears on the formation of a heterobimetallic complex. The ¹H NMR spectrum of [(bpy)₂Ru(BibzImH₂)]²⁺ is shown in Fig. S1.

2.2. UV/vis absorption spectra

The absorption spectra of monometallic and bimetallic complexes in CH₃CN are shown in Fig. 1 and the data summarized in Table 1. The peaks at 240 and 290 nm correspond to the π–π* transition of bipyridine and peaks at 337 and 366 nm are assigned to the π–π* transition of bis(benzimidazole) and the peak at 470 nm to the dπ(Ru)–π*(BibzImH₂) ¹MLCT transition [31]. In the monometallic complex [(bpy)₂Ru(BibzImH₂)]²⁺, the presence of the bis(benzimidazole) ligand reduces the MLCT energy compared to [Ru(bpy)₃]²⁺, because of the lower LUMO energy of BibzImH₂ compared to that of bpy. Upon the formation of bimetallic complexes with Ln(III) complexes, the ¹MLCT absorption band is red-shifted substantially from 470 to 505 nm relative to that of the mononuclear complex [(bpy)₂Ru(BibzImH₂)]²⁺. The red shift is ascribed to the lowering in energy of the BibzImH₂–π* level on coordination of the electropositive lanthanide fragment to the second binding site.

When [Ln(tta)₃(H₂O)₂] (Ln = Nd, Er, Yb) was added portion-wise to a solution of [(bpy)₂Ru(BibzImH₂)]²⁺ in CH₃CN, the colour of the Ru(II) chromophore became deeper, which is associated with the ¹MLCT transition being reduced in energy and shifted more into the visible region, from 470 to 505 nm [23]. A graph of the absorbance at a wavelength of 500 nm vs. the amount of [Nd(tta)₃(H₂O)₂] added gave a smooth curve that fitted well to a 1:1 binding isotherm (Fig. 2), from which the association constant (*K*_a) for the binding of the lanthanide fragment to the diimine site could be calculated. The association constant values obtained were 5.5 (±0.2) × 10⁵ M^{−1} for **Ru–Yb**, 4.8 (±0.3) × 10⁵ M^{−1} for **Ru–Er** and 4.1 (±0.2) × 10⁵ M^{−1} for **Ru–Nd**. The order in *K*_a values for Ru(II)–Ln(III) complexes presumably reflects the order of ionic radius and the higher charge density of lanthanide ions [21].



Scheme 1. Synthesis of the Ru(II)–Ln(III) heterobimetallic complexes.

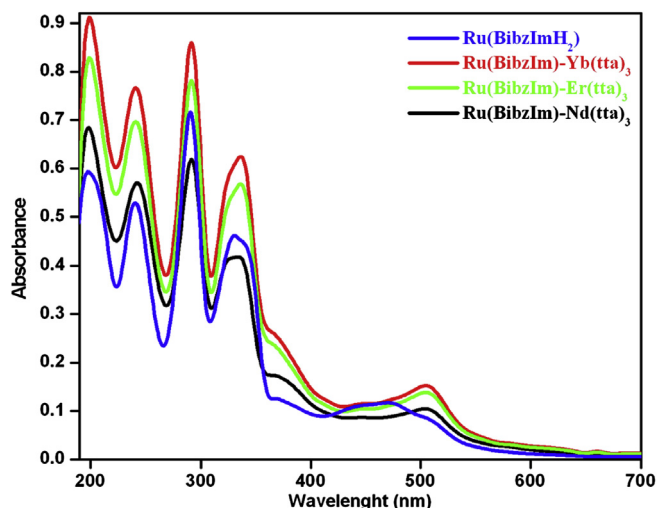


Fig. 1. Electronic absorption spectra of $[(bpy)_2Ru(BibzImH_2)]^{2+}$, **Ru–Nd**, **Ru–Er** and **Ru–Yb** in 2.5×10^{-5} M solution in CH_3CN .

2.3. Emission spectra

The luminescence spectra of the monometallic $[(bpy)_2Ru(BibzImH_2)]^{2+}$ and heterobimetallic $Ru(II)-Ln(III)$ complexes were measured in CH_3CN , by using an excitation wavelength of 470 nm and the spectra are shown in Fig. 3 and the relevant data are summarized in Table 1.

The monometallic $[(bpy)_2Ru(BibzImH_2)]^{2+}$ complex displays an emission maximum at 640 nm. The broad emission profile indicates that the emission is from the 3MLCT state. It should be noted that $\{Ln(tta)_3\}$ complexes do not show strong absorption at wavelengths longer than 400 nm, except for only very weak $f \rightarrow f$ transitions. Thus, the use of an excitation wavelength longer than this would result in essentially selective excitation of the Ru-based chromophore. The emission spectra of $Ru-Ln$ heterobimetallic complexes showed that the emission intensity of ruthenium component is quenched compared to that of monometallic ruthenium complex (Fig. 3). The measurements were performed for solutions with the same absorbance. Among the three $Ru-Ln$ complexes, quenching is more pronounced in the case of the **Ru–Nd** complex. The luminescence intensity titration of $[(bpy)_2Ru(BibzImH_2)]^{2+}$ with $Nd(tta)_3 \cdot 2H_2O$ is shown in Fig. 4. Ru^{II} -based luminescence is substantially quenched upon the addition of $Nd(tta)_3 \cdot 2H_2O$ and the emission intensity is reduced by approximately 90% compared to that of the monometallic $[(bpy)_2Ru(BibzImH_2)]^{2+}$ complex. In the case of $Ru-Ln$ complexes, the quenching of luminescence intensity of ruthenium is due to energy transfer from the $MLCT$ state of $Ru(II)$ component to Ln component, and is further evidenced by sensitized NIR emission from Ln centre (*vide infra*).

Interestingly, the excitation of $Ru(II)-Ln(III)$ complexes at 470 nm produces NIR emission (Fig. 5) that is characteristic of the

Table 1

Absorption and photophysical properties of monometallic and bimetallic ruthenium(II) complexes with 2.5×10^{-5} M concentration in CH_3CN at 298 K.

Complex	λ_{max} (nm)	$\lambda_{em, max}$ (nm)	τ (ns)
$Ru(bpy)_3^{2+}$	290, 452	615	1100
$[(bpy)_2Ru(BibzImH_2)]^{2+}$	240, 290, 337, 366, 470	640	138
Ru–Nd	240, 288, 335, 354, 508	1060	4 ^a
Ru–Er	240, 288, 334, 353, 505	980	50 ^a
Ru–Yb	240, 288, 334, 354, 505	1503	70 ^a

^a Lifetime of ruthenium component at 640 nm.

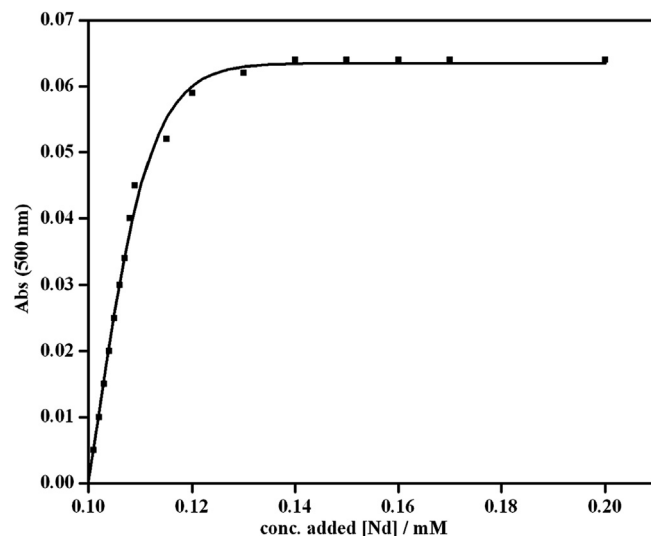


Fig. 2. Titration plots of the absorbance of 500 nm band of $[Ru(bpy)_2(BibzImH_2)]^{2+}$ for various concentrations of $Yb(tta)_3(H_2O)_2$ (dots), and fitting line to a 1:1 binding isotherm (solid line).

corresponding $Ln(III)$ ions in all cases. This clearly confirms that the $Ru(II)$ chromophore acts as a sensitizer of $Ln(III)$ luminescence, by virtue of a transfer of energy from the $Ru(II)$ chromophore to the emissive excited state of the lanthanide ions. The uncorrected excitation spectrum of **Ru–Nd** in CH_3CN recorded using an emission wavelength of 1060 nm, shown in Fig. S1 in the supporting information, closely matched the absorption spectrum, indicating that the NIR emission of Nd can be attributed to absorption by the $MLCT$ state of $Ru(II)$.

2.4. Luminescence lifetime

The photophysical behaviour of the monometallic $Ru(II)$ complex and $Ru-Ln$ heterobimetallic complexes were also examined by time-resolved measurements. The excited state lifetime of all the complexes are given in Table 1. The excited state lifetime of monometallic complex $[(bpy)_2Ru(BibzImH_2)]^{2+}$ in CH_3CN is 138 ns.

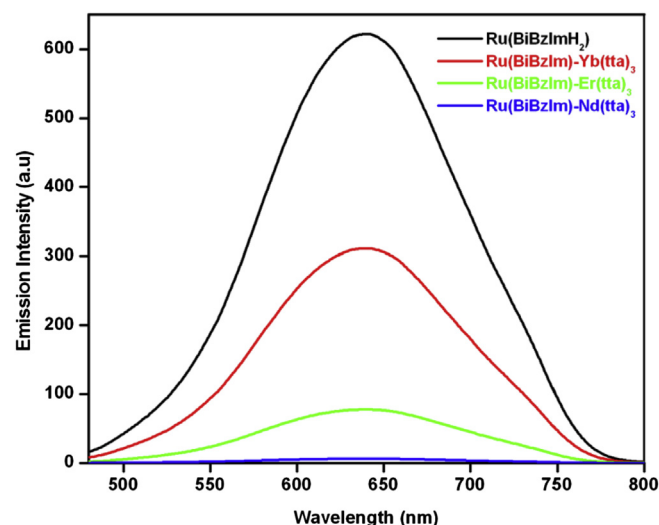


Fig. 3. Luminescence spectra of $[(bpy)_2Ru(BibzImH_2)]^{2+}$, **Ru–Nd**, **Ru–Er** and **Ru–Yb** with 2.5×10^{-5} M solution in CH_3CN .

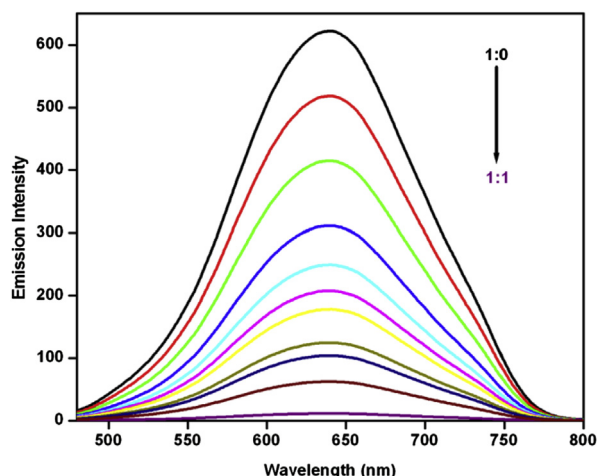


Fig. 4. Luminescence spectra of $[(bpy)_2Ru(BibzImH_2)]^{2+}$ upon addition of $Nd(tta)_3 \cdot 2H_2O$ (2.5×10^{-5} M) solution in CH_3CN .

However, in the presence of $Ln(III)$, the lifetime of the $Ru(II)$ component is quenched to a considerable extent for all the three complexes. The ruthenium component of these three heterobimetallic complexes experience a concomitant reduction in their lifetime, with values of 4, 50 and 70 ns for **Ru–Nd**, **Ru–Er** and **Ru–Yb** complexes, respectively (an uncertainty of $\pm 8\%$ is assumed for Ru^{II} -based emission lifetimes). Similar to the trend observed in the emission spectra, the excited state lifetime of **Ru–Nd** complex is substantially quenched compared to the other two complexes. When a solution of $[(bpy)_2Ru(BibzImH_2)]^{2+}$ is titrated with the $Nd(tta)_3$ complex, two luminescence components are apparent: one with a lifetime of 138 ns corresponds to $[(bpy)_2Ru(BibzImH_2)]^{2+}$ and another, with a lifetime of 4 ns, corresponds to $Nd(III)$ coordinated the $[(bpy)_2Ru(BibzIm)Nd(tta)_3]$ complex (Fig. 6). The longer component disappears and the short component becomes dominant as the titration approaches completion.

$$k_{EnT} = \tau_q^{-1} - \tau_u^{-1} \quad (1)$$

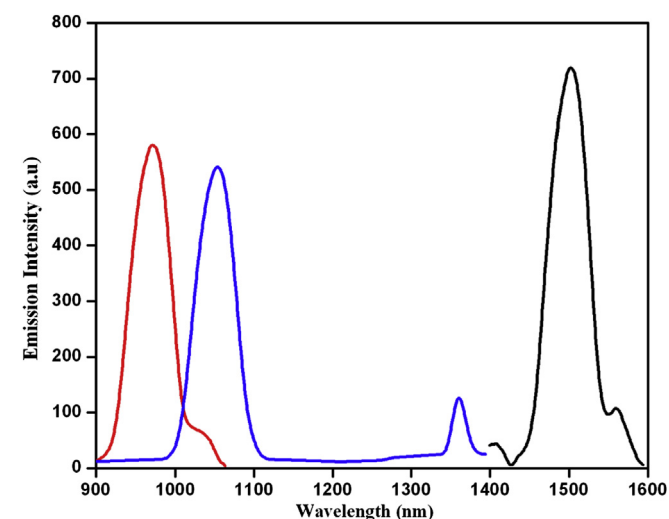


Fig. 5. Emission spectra of **Ru–Nd** (blue), **Ru–Er** (black) and **Ru–Yb** (red) 2.5×10^{-5} M solution in CH_3CN (the transitions are $^4F_{3/2} \rightarrow ^4I_{9/2}$ and $^4F_{3/2} \rightarrow ^4I_{11/2}$ for the high- and low-energy Nd^{III} emission, respectively; $^4I_{13/2} \rightarrow ^4I_{15/2}$ for Er^{III} ; $^2F_{5/2} \rightarrow ^2F_{7/2}$ for Yb^{III}). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

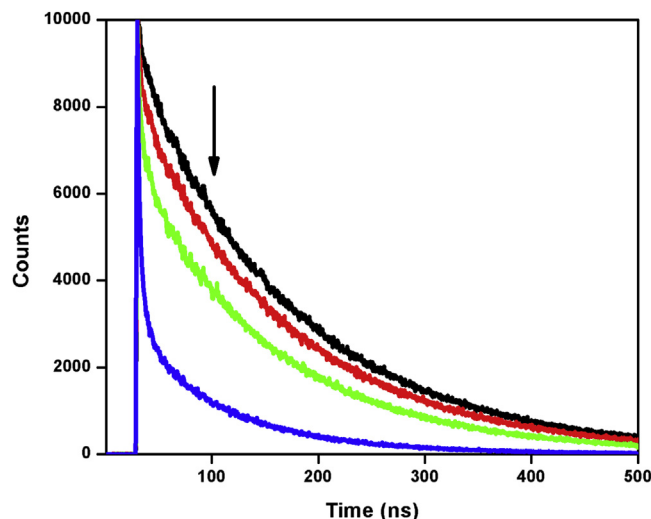


Fig. 6. Luminescence decay profiles of $Ru(BibzImH_2)$ at the start of the titration (black), and the two-component decay (mixture of free $Ru(BibzImH_2)$; and partially-quenched $Ru(BibzImH_2)$ – Nd ; (blue)) part of the way through the titration. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$\Phi_{EnT} = 1 - \tau_q/\tau_u \quad (2)$$

The energy transfer rate constant (k_{EnT}) and quantum yield (Φ_{EnT}) of $Ru \rightarrow Ln$ can be calculated from Equations (1) and (2), respectively. Here, τ_q is the “quenched” lifetime of ruthenium (with Ln) and τ_u is the “unquenched” lifetime of ruthenium (without Ln). From Equation (1) we estimated the $Ru \rightarrow Nd$ energy-transfer rate constant k_{EnT} to be $2.4 \times 10^8 s^{-1}$ ($\tau_q = 4$ ns; $\tau_u = 138$ ns). From Equation (2) we calculated the quantum yield for the $Ru \rightarrow Nd$ energy transfer to be 97%, which is consistent with the reduction of Ru^{II} -based emission intensity. In the Ru – Ln dyads, the effectiveness of the different Ln^{III} species as energy-acceptors was found to be $Nd > Er > Yb$, with residual Ru^{II} -based lifetimes. The reason for the quenching is because the donor–acceptor overlap decreases as the result of the reduced availability of f–f states on the Ln^{III} ions. This gives consistently decreasing $Ru \rightarrow Ln$ energy-transfer rates of $2.4 \times 10^8 s^{-1}$ (to Nd , $\Phi_{EnT} = 97\%$), $1.2 \times 10^7 s^{-1}$ (to Er , $\Phi_{EnT} = 63\%$) and $7.1 \times 10^6 s^{-1}$ (to Yb , $\Phi_{EnT} = 49\%$), as the donor–acceptor overlap decreases due to the reduced availability of f–f states on the Ln^{III} ions.

Ru – Ln bimetallic complexes bridged by bis(benzimidazole) verifies higher rate of energy transfer and also the quantum yields when compared to that of other systems reported by Ward and Faulkner [32]. Thus from the results obtained by Equations (1) and (2) it is clearly learnt that heterobimetallic complexes bridged by bis(benzimidazole) have lesser metal–metal distance than that bridged by bipyrimidine and 2,3 bis(pyridyl) pyrazine.

3. Discussion on $Ru \rightarrow Ln$ energy transfer

According to Dexter’s theory [33], the suitability of the energy difference between the resonance level of a Ln^{3+} ion and the triplet state of the ligand is a critical factor for efficient energy transfer [34]. If the energy difference is too large or too small, both result in a decrease in the efficiency of energy transfer from the donor to the acceptor [35]. As described above, we obtained the characteristic NIR emission of Ln^{3+} ion upon excitation at the MLCT absorption of the ruthenium component in Ru – Ln complexes. This indicates that the “complex ligand” can effectively shield Ln^{3+} ions from their

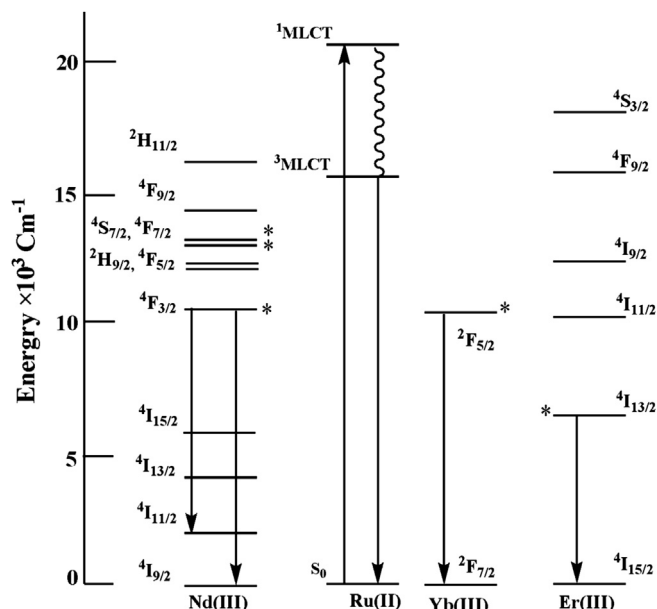


Fig. 7. Assumed energy transfer mechanism of lanthanide ions, Nd(III), Er(III) and Yb(III) via the excited Ru(II) moiety.

surroundings and transfer the absorbed energy from their triplet states to the central metal Ln^{3+} ions due to antenna effect. A plausible pathway for this energy transfer is depicted in Fig. 7.

From the energy level diagram, it is apparent that $^3\text{MLCT}$ energy level of Ru(II) is suitable for the sensitization of Nd^{III} , Er^{III} and Yb^{III} luminescence. In the case of **Ru–Nd** complex, Nd(III) has a large density of energy levels between 10,000–20,000 cm^{-1} , which allows significant overlap with the emissive state of Ru(II). Hence, in the case of the **Ru–Nd** complex, efficient energy transfer occurs from Ru(II) to Nd(III). In contrast, Yb(III) has only a single f–f transition at ca. 10,200 cm^{-1} and, because of this, it overlaps to a small extent with Ru(II) emission. So, in the **Ru–Yb** complex, due to the little overlap between Ru(II) donor and Yb(III) acceptor energy levels, the quenching of Ru(II) emission is reduced to a considerable extent, among the three complexes. The available energy levels of Er(III) is intermediate between Nd(III) and Yb(III) and, hence, in the **Ru–Er** complex, the quenching of Ru(II) emission by Er(III) is moderate [16]. Importantly, energy transfer is determined by selection rules as well. For a Förster energy transfer, $\Delta J = 2, 4$, or 6 and for a Dexter energy transfer $\Delta J = 0$ or 1, at the lanthanide. In **Ru–Nd** complex, most of the energy levels of Nd that overlap with Ru(II) emission are available for quenching. For **Ru–Yb**, the energy transfer is allowed to the singlet excited state of Yb(III). In **Ru–Er**, the energy transfer is forbidden to the $^4\text{F}_{9/2}$ and $^4\text{I}_{9/2}$ levels, and is allowed to the $^4\text{I}_{11/2}$ and $^4\text{S}_{3/2}$ levels of Er(III). Energy transfer to $^4\text{S}_{3/2}$ level of Er(III) is slightly endergonic as it lies at ca. 18,300 cm^{-1} and hence it may be inefficient due to thermally activated back energy transfer to the $^3\text{MLCT}$ state level of Ru(II).

4. Conclusions

A series of d–f dyads were prepared, in which a Ru(II) polypyridine chromophore is connected to a Ln(III) centre via a bis(benzimidazole) bridging ligand. The luminescent mononuclear Ru(II) complex acts as “complex ligand”, allowing the formation of Ru–Ln heterodinuclear complexes by the addition of a $\text{Ln}(\text{tta})_3$ unit at the second imine site. In the resulting series of Ru–Ln compounds, excitation of the $^1\text{MLCT}$ absorption of the Ru(II)

chromophore resulted in a fast Ru(II) \rightarrow Ln(III) energy transfer, which is established by the quenching of the luminescence intensity of the Ru(II) component and the sensitized NIR emission from the lanthanide unit. Among the three Ru–Ln complexes, the energy transfer for the **Ru–Nd** complex was faster and this is supported by the substantial quenching of emission intensity and the lifetime of the Ru component. Furthermore, the presence of a short bis(benzimidazole) bridge permits the energy transfer from Ru(II) to Ln(III) to be faster.

5. Experimental section

5.1. Materials

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, neodymium nitrate pentahydrate, erbium nitrate pentahydrate, ytterbium nitrate pentahydrate, theonyltrifluoroacetone were all purchased from Aldrich and used as received. Monometallic $[\text{Ru}(\text{bpy})_2(\text{BibzImH}_2)](\text{PF}_6)_2$ [36] and $\text{Ln}(\text{tta})_3(\text{H}_2\text{O})_2$ [37] were synthesized by literature procedures and characterized by NMR, mass spectrometry, and elemental analysis.

5.2. Syntheses

5.2.1. Synthesis of $[(\text{bpy})_2\text{Ru}(\text{BibzImH}_2)]^{2+}$

Bis(benzimidazole) [30] (0.11 g, 0.47 mmol) was suspended in 20 mL of ethylene glycol and the solution degassed for 15 min under nitrogen, then heated at 150 $^\circ\text{C}$ until it completely dissolved. The solution was then cooled to 120 $^\circ\text{C}$ and $\text{cis-}[\text{Ru}(\text{bpy})_2\text{Cl}_2](\text{H}_2\text{O})_2$ [38] (0.29 g, 0.47 mmol) was added. The mixture was heated at 180 $^\circ\text{C}$ for 2 h. The resulting deep red brown solution was cooled, diluted with 30 mL of water, and filtered to remove the excess bis(benzimidazole). A saturated aqueous solution of NH_4PF_6 was added dropwise to the above filtrate to precipitate the crude Ru complex. The crude material was collected on a filter and air-dried (0.17 g, crude yield: 90%). The crude product was deprotonated by treatment with NaOCH_3 /methanol to give a mixture of deprotonated and bimetallic complexes. The deprotonated form was not soluble in acetone and was separated by filtration. The pure deprotonated complex was then suspended in methanol and acidified by adding concentrated HCl to give the bis(benzimidazole) complex. Diethyl ether was added drop-wise to precipitate the $[(\text{bpy})_2\text{Ru}(\text{BibzImH}_2)](\text{PF}_6)_2$ [39]. This material was purified by dissolving it in methanol and metathesis with a saturated aqueous solution of NH_4PF_6 to convert it to the PF_6 salt of $[(\text{bpy})_2\text{Ru}(\text{BibzImH}_2)](\text{PF}_6)_2$. Yield: 81%. ^1H NMR (300 MHz $[\text{D}_6]\text{DMSO}$): δ 11.30 (b, 2H, N–H), 8.82 (d, 2H, bpy), 8.38 (d, 2H, bpy), 8.17 (t, 2H, bpy), 8.02 (t, 2H, bpy), 7.78 (d, 2H, bpy), 7.57 (d, 2H, bpy), 7.51 (d, H₈), 7.46 (t, 2H, bpy), 7.28 (t, 2H, bpy), 7.08 (t, 2H, H₇), 6.79 (t, 2H, H₆), 5.51 (d, 2H, H₅). UV–vis (CH_3CN): 469 nm, (lit. 347, 470 nm). (^1H NMR of monometallic complex is given in Fig. S2 in the supporting information).

5.2.2. General method for the preparation of the Ru(II)–Ln(III) [$\text{Ln} = \text{Nd(III)}, \text{Er(III)}$ and Yb(III)]

Equimolar amounts of $[(\text{bpy})_2\text{Ru}(\text{BibzImH}_2)]$ in CH_3CN and $\text{Ln}(\text{tta})_3(\text{H}_2\text{O})_2$ [$\text{Ln} = \text{Nd(III)}, \text{Er(III)}$ and Yb(III)] were dissolved in CH_2Cl_2 (15 mL) and Et_3N (2 mL) was added. The resulting reddish brown solution was stirred for 10 min and hexane (15 mL) was then added to the solution. Concentration of the solution resulted in the precipitation of the dinuclear complex Ru–Ln, which was isolated on a filter. In each case, the solid was collected on a filter, washed with hexane and dried under vacuum and they are air-stable and yield ranges between 70 and 80%.

Data for **Ru–Nd**: Yield: 77%. Anal. Calcd for $\text{C}_{58}\text{H}_{36}\text{F}_{21}\text{N}_8\text{NdO}_6 \cdot \text{P}_2\text{RuS}_3$: C, 39.95; H, 2.08; N, 6.45. Found: C, 39.82; H, 1.99; N, 6.39.

ESI-MS (m/z , positive mode, MeCN, found (calcd)): 872.25 (873.28) (Fig. S3 in the supporting information).

Data for **Ru–Er**: Yield: 78%. Anal. Calcd for $C_{58}H_{36}F_{21}N_8ErO_6 \cdot P_2RuS_3$: C, 39.31; H, 2.05; N, 6.32. Found: C, 39.28; H, 2.01; N, 6.26. ESI-MS (m/z , positive mode, MeCN, found (calcd)): 886.95 (888.28).

Data for **Ru–Yb**: Yield: 73%. Anal. Calcd for $C_{58}H_{36}F_{21}N_8YbO_6 \cdot P_2RuS_3$: C, 39.44; H, 2.05; N, 6.34. Found: C, 39.38; H, 2.01; N, 6.29. ESI-MS (m/z , positive mode, MeCN, found (calcd)): 882.95 (883.98) (Fig. S4 in the supporting information).

5.3. Physical measurements

All solvents used in the preparations were of reagent grade and spectral grade solvents were used for spectral measurements. UV–vis spectra were recorded on Analtikjena Specord S100 spectrophotometer and emission spectra were measured using a JASCO FP6300 spectrofluorimeter. The concentration of the solution used was 2×10^{-5} M for all the measurements. Elemental analyses (C, H, N) were performed on Perkin–Elmer 2400. Mass spectra were obtained using a Quattro LC triple quadrupole mass spectrometer (Micromass, Manchester, UK) interfaced with an (Electron Spray Ionisation) ESI source; data acquisition was done under the control of Masslynx software (version 3.2). The ESI capillary voltage was maintained between 4.0 and 4.2 kV and the cone voltage maintained at 25 V. Nitrogen was used as desolvation and nebulization gas. The source and desolvation temperatures were 100 °C. NIR emission was recorded using an Edinburgh Instrument FLS9-OP, a 450 W Xenon Arc Lamp as the light source and NIT PMT (in N_2 Flow Cooled Housing) detector. The excited state lifetime measurements were made using time correlated single photon counting technique [40].

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jorganchem.2013.04.008>.

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