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Mixed d−f_3 Coordination Complexes Possessing Improved Near-Infrared (NIR) Lanthanide Luminescent Properties in Aqueous Solution

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The cyclen-based ligand **1**, possessing a [1,10]-phenanthroline moiety as a pendant arm, has been used as a ditopic ligand for the complexation of d- and near infrared (NIR) emitting (and) f-metal ions. This ligand forms kinetically stable complexes, **1·Ln**, with lanthanide ions such as Ln = ytterbium, neodymium, and lutetium (formed as a non-IR emitting reference compound), the synthesis and photophysical properties of which are described herein in detail. These **1·Ln** complexes were then used as building blocks for the formation of mixed d−f heteropolymetallic self-assemblies, where the phen moiety was used to complex a ruthenium (Ru(II)) ion, giving the d−f_3 complexes **Ru·Ln$_3$** (Ln = Nd(III), Yb(III), Lu(III)). The formation of these supramolecular coordination conjugates was studied by using absorption and luminescence spectroscopy, while the solution structure of the **Ru·Lu$_3$** was elucidated by ^{1}H NMR in D_2O and H_2O. Of these conjugates, both **Ru·Nd$_3$** and **Ru·Yb$_3$** displayed an intense NIR-emission in H_2O at pH 7.4 (with Q^{L}_{Yb} = 0.073% and Q^{L}_{Nd} = 0.040%) and in D_2O (with Q^{L}_{Yb} = 0.23% and Q^{L}_{Nd} = 0.10%). By comparison with their monometallic analogues **Ln·1** (Ln = Nd(III), Yb(III)), we demonstrate that our new design possesses an enhanced sensitization efficiency for lanthanide metal centered sensitization upon using the [Ru(phen)$_3$] moiety (d → f energy transfer) as a visibly exciting antenna, and we demonstrate that the intensity of the Ru(II)-based luminescence strictly correlates to the efficiency of the d → f energy transfer processes.

Introduction

Because of their unique magnetic and photophysical properties, the design and synthesis of lanthanide-containing supramolecular structures have received growing interest in recent time. More specifically, the development of novel near infrared (NIR)-emitting lanthanide complexes, or assemblies, has gained significant momentum, because of their potential application in various optical and medical devices.[1,2] While their applications in chemical sensing[3−5] and imaging[6] have been shown to be very promising, achieving efficient sensitization of the NIR-emissive lanthanides (Nd(III), Yb(III), and Er(III)) in competitive media, such as in water, is still a challenge that needs to be overcome if such NIR emitting devices are to be of commercial use, particularly in medical application such as in vivo imaging. The lanthanides possess Laporte-forbidden 4f → 4f transitions, which makes direct excitation of their excited states inefficient. Moreover, the low excited levels are particularly sensitive to nonradiative quenching by the vibrational harmonics of O−H oscillators of water. To date, a large variety of UV-absorbing organic chromophores has been used as antennae to populate the Ln(III) excited states of ions such as Eu(III)

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and Tb(III).[7] While the use of these ions requires excitation within the UV regions, NIR emitting lanthanide ions can be sensitized using visibly absorbing antennae.[8,9] The use of d-metal ion complexes, such as those possessing strongly absorbing metal to ligand charge transfer (MLCT) absorption bands, as such visible absorbing antennae has been demonstrated,[9,10] and shown to be more adapted for luminescent imaging purposes. The use of such relatively low energetic excitation wavelengths is generally less damaging for biological material, as these long excitation wavelengths are often not easily absorbed by biological tissue.[10] Even though several examples of such d-metal ion based antennae systems have been reported to date, these conjugates often suffer from low water solubility, relatively weak luminescence, or even poor stability in water, which is a real drawback for their use in sensing of imaging in biological media.[11−14] With the aim of addressing these drawbacks, we have recently described two examples of water-soluble NIR-emissive f−d dyads made from Nd(III) and Yb(III)-based tetraamide-functionalized cyclen complexes bearing a [1,10]-phenanthroline unit, which were complexed to a Ru(II)(bpy)$_2$ (bpy = 2,2′-bipyridine) and a Ru(II)(phen)$_2$ (phen = 1,10-phenanthroline) core, respectively.[4] Herein, we describe the controlled synthesis of larger polymetallic conjugates where three of these Ln(III) cyclen-based complexes have been assembled around a single Ru(II) metal center, resulting in the formation of $d-f_3$ metal ion (self-assembly) complexes. While similar strategies, based on the use of other kinetically inert building blocks, have been successfully used for the synthesis of high relaxivity Gd(III)-based MRI contrast agents,[15] and for the in situ formation of luminescent ruthenium d−f, $d-f_2$, and $d-f_6$ calix[4]arene-based conjugates in acetonitrile solution,[16] these assemblies have never been isolated nor fully characterized. In this contribution, the synthesis of three $d-f_3$ metal ion self-assembly complexes, based on the use of Ru(II) and the NIR emitting Nd(III) and Yb(III) ions as well as Lu(III), which was formed for comparison studies, is discussed as well as the detailed study of their photophysical properties in water. The structural investigation of these complexes is also presented, which was carried out using ^{1}H NMR (on the Lu(III) complex **Ru·Lu$_3$**) in D_2O/H_2O. We show that our systems are dual emitters, giving rise to both visibly Ru(II) centered (MLCT) emission and NIR emission, where the efficiency of the lanthanide sensitization process is greatly enhanced by the presence of the Ru(II) center.

Experimental Section

General Procedures. All solvents and starting materials were purchased from Aldrich and Fluka and used without further purification. Cyclen was purchased from CheMatech. THF was distilled over Na-benzophenone and triethylamine over KOH before use. The ^{1}H NMR spectra were recorded at 400 MHz using a Bruker Spectrospin DPX-400 instrument. The ^{13}C NMR spectra were recorded at 100 MHz using a Bruker Spectrospin DPX-400 instrument. Chemical shifts are reported in ppm with the deuterated solvent as the internal reference. Mass spectrometry was carried out using HPLC grade solvents. Electrospray mass spectra were determined on a Micromass LCT spectrometer and high resolution mass spectra were determined relative to a standard of leucine enkephaline. Maldi-Q-Tof mass spectra were carried out on a MALDI-Q-TOF-Premier (Waters Corporation, Micromass MS technologies, Manchester, UK) and high resolution mass spectrometry was performed using Glu-Fib with an internal reference peak of m/z 1570.6774. Elemental analysis was performed in the Microanalytical Laboratory, University College Dublin. Thin layer chromatography (TLC) and flash chromatography were performed on neutral aluminum oxide 60 F254 (Merck).

Spectroscopic Measurements. All UV−visible absorption spectra were recorded on Varian Cary 50 spectrophotometer. The UV−visible emission and excitation spectra were recorded on a Cary Eclipse fluorimeter equipped with a 1 cm path length quartz cell. The quantum yields of the Ru(II) emission were determined relative to the Φ value of $[Ru(bpy)_3]^{2+}$ in air-equilibrated water ($\Phi = 0.028$).[17] Other low-resolution luminescence measurements (spectra in the near-infrared range and lifetimes) were recorded on a Fluorolog 3-22 spectrometer from Horiba-Jobin-Yvon with double grating emission and excitation monochromators, and a R5509-73 photomultiplier. For measurements in

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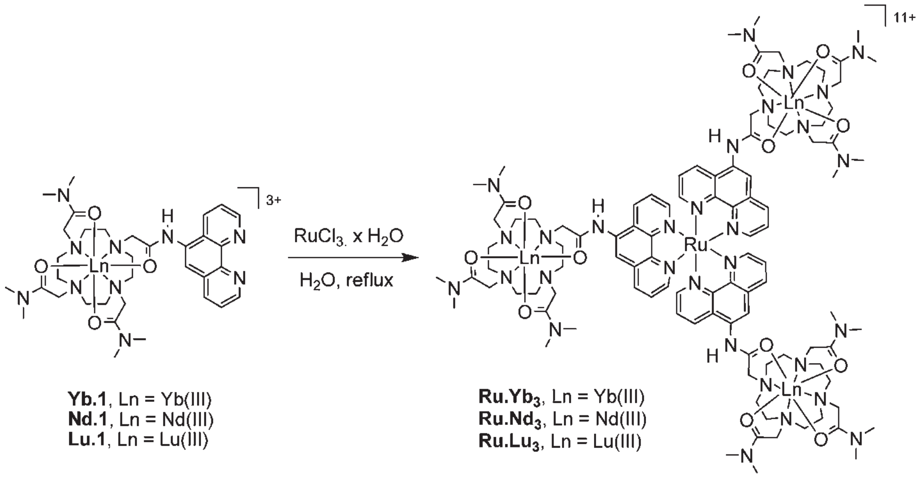
Scheme 1. Synthesis of the Mixed d−f_3 Conjugates **Ru·Yb$_3$**, **Ru·Nd$_3$**, and **Ru·Lu$_3$** from the Corresponding Yb(III), Nd(III), and Lu(III) Complexes **Ln·1**



Yb.1, Ln = Yb(III)
Nd.1, Ln = Nd(III)
Lu.1, Ln = Lu(III)

Ru.Yb$_3$, Ln = Yb(III)
Ru.Nd$_3$, Ln = Nd(III)
Ru.Lu$_3$, Ln = Lu(III)

the NIR spectral range, light intensity was measured by a C9940-22 detector from Hamamatsu, cooled to 77 K (range 800−1700 nm) coupled to a Jobin Yvon SpectrAcq v5.20 data acquisition system. All spectra were corrected for the instrumental functions. For the measurement of the Nd(III) and Yb(III)-based luminescence lifetimes, the samples were excited using a pulsed nitrogen laser (PTI-3301, 337 nm) or a nitrogen pumped dye laser (PTI-330, 435 nm), operating at 10 Hz. Light emitted right angles to the excitation beam was focused onto the slits of a monochromator (PTI120), which was used to select the appropriate wavelength. The growth and decay of the luminescence at selected wavelengths were detected using a germanium photodiode (Edinburgh Instruments, EI-P) and recorded using a digital oscilloscope (Tektronix TDS220) before being transferred to a PC for analysis. Time-resolved emission spectra were obtained by measuring the growth and decay of the luminescence at each of a series of wavelengths. Luminescence lifetimes were obtained by iterative reconvolution of the detector response (obtained by using a scatterer) with exponential components for growth and decay of the metal centered luminescence, using a spreadsheet running in Microsoft Excel. The details of this approach have already been previously discussed.[18] Unless otherwise stated, fitting to a double exponential decay yielded no improvement in fit as judged by minimization of residual squared and reduced chi squared. Quantum yields ($Q^{\mathrm{L}}_{\mathrm{Ln}}$) of the complexes were determined in both water and D_2O at pH 7.4 (PBS buffer), relative to the one of [Yb(tta)$_3$(phen)] in toluene, $Q^{\mathrm{L}}_{\mathrm{Ln}}$ = 1.10%,[19] at room temperature.

Synthesis and Characterization. Lanthanide Complexes of Ligand 1, Ln·1 (Ln = Nd(III), Yb(III), Lu(III)). The appropriate lanthanide triflate salt Ln(CF_3SO_3)$_3$ (1.1 equiv) and **1** (1.0 equiv) were dissolved in acetonitrile (5 mL) under argon. The mixture was then refluxed overnight. The complexes **1·Yb**, **1·Nd**, and **1·Lu** were isolated by precipitation in diethyl ether and triturated several times with dichloromethane to give pale brown solids (**1·Yb**: 37.7 mg, 91%; **1·Nd**: 178.9 mg, 100%; **1·Lu**, 84.4 mg, 86%): **1·Yb**: ES-MS (ES$^+$) Calculated for $YbC_{35}H_{50}N_{10}O_7F_3S$ [M + 1(CF_3SO_3)$^-$]: *m*/*z* = 492.642, found: *m*/*z* = 492.6768; MALDI-MS Calculated for $YbC_{34}H_{50}N_{10}O_4$ [M^{3+}]: *m*/*z* = 834.340, found: *m*/*z* = 834.326. **1·Nd**: ES-MS (ES$^+$) Calculated for $NdC_{35}H_{50}N_{10}O_7F_3S$ [M + 1(CF_3SO_3)$^-$]2+: *m*/*z* = 477.6307, found: *m*/*z* = 477.6076; MALDI-MS Calculated for $NdC_{34}H_{50}N_{10}O_4$ [M^{3+}]: *m*/*z* = 804.310, found: *m*/*z* = 804.298. **1·Lu**: ES-MS Calculated for $LuC_{34}H_{49}N_{10}O_4$ [M − H]: *m*/*z* = 418.1673 found: *m*/*z* = 418.1659. ^{1}H NMR (D_2O, 600 MHz, 27 °C, ppm): 9.11 (t, 1H, *J* = 4.6 Hz, H$_{\mathrm{ar}}$), 9.13 (t, 1H, *J* = 4.6 Hz, H$_{\mathrm{ar}}$), 8.55 (d, 1H, *J* = 8.8 Hz, H$_{\mathrm{ar}}$), 8.50 (d, 1H, *J* = 8.8 Hz, H$_{\mathrm{ar}}$), 8.16 (s, 1H, H$_{\mathrm{ar}}$), 7.90 (m, 1H, H$_{\mathrm{ar}}$), 7.87 (m, 1H, H$_{\mathrm{ar}}$), 4.4−2.5 (m, 42H, $CH_2 + CH_3$).

Tetrametallic Coordination Conjugates Ru·Ln$_3$ (Ln = Nd(III), Yb(III), and Lu(III)). The corresponding lanthanide complex **Ln·1** (Ln = Yb(III), Nd(III), and Lu(III)) (23−39 μmol, 3.0 equiv) and ruthenium tris-chloride (8.5−15 μmol, 1.1 equiv) were dissolved in degassed mQ water (10 mL) and refluxed overnight under argon. After the solvent was evaporated to dryness, the resulting black solid was purified by a size exclusion column on lipophilic Sephadex LH20, eluting with methanol. The pure complexes **Ru·Ln$_3$** were obtained as dark yellow compounds (**Ru·Nd$_3$**: 13.6 mg, 41%; **Ru·Yb$_3$**: 20.6 mg, 74%; **Ru·Lu$_3$**: 23.8 mg, 100%): **Ru·Nd$_3$**: Elemental analysis calculated for **Ru·Nd$_3$**. 2 Cl$^-$. 9 OTf$^-$. 12 H_2O: C, 32.12; H, 4.23; N, 10.12; Found: C, 31.80; H, 3.81; N, 9.77. **Ru·Yb$_3$**: Elemental analysis calculated for **Ru·Yb$_3$**. 2 Cl$^-$. 9 OTf$^-$. 10 H_2O: C, 31.73; H, 4.08; N, 10.00; Found: C, 31.73; H, 3.89; N, 9.74. **Ru·Lu$_3$**: Elemental analysis calculated for **Ru·Lu$_3$**. 2 Cl$^-$. 9 OTf$^-$. 2 TfOH. 3 CH_3OH: C, 31.54; H, 3.80; N, 9.43; Found: C, 31.48; H, 3.74; N, 9.07.

Results and Discussion

Synthesis and Spectroscopic Characterization of the d−f_3 Coordination Conjugates Ru·Ln$_3$. Ligand **1** was obtained in good yield from 2-chloro-*N*,*N*-dimethyl-acetamide[20] and 2-chloro-*N*-[1,10]-phenanthrolin-5-yl-acetamide,[21] according to a previously published procedure.[22] The lanthanide complexes of ligand **1**, **Ln·1** (Ln = Nd(III), Yb(III), and Lu(III)) were prepared in quantitative yields by refluxing overnight equimolar amounts of **1** and of the appropriate Ln(III) triflate salt in acetonitrile. The synthesis of the d-f_3 tetrads, Scheme 1, was then achieved by refluxing the corresponding lanthanide complexes **Ln·1** in degassed water overnight with ruthenium trichloride ($RuCl_3$) hydrade. The desired products were obtained in good yields as dark yellow solids after purification by size-exclusion column chromatography on Sephadex LH20. The successful complexation of the [1,10]-phenanthroline unit by the Ru(II) was verified from the changes

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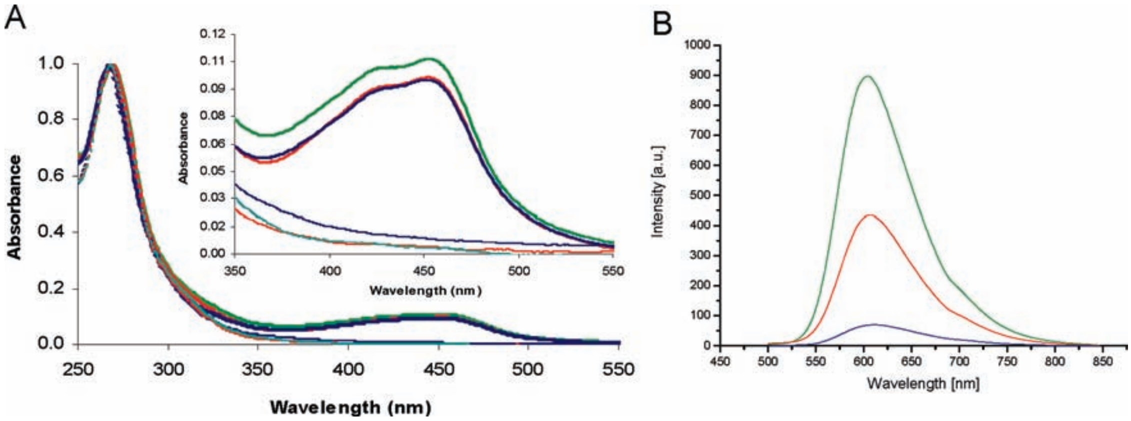

Figure 1. (A) Absorption spectra of the three **Ru·Ln$_3$** conjugates (—) and of the **Ln·1** complexes (---) in a 10 mM phosphate buffer at pH 7.4. Ln = Yb(III) in red, Nd(III) in blue, and Lu(III) in green. Inset: The corresponding MLCT absorptions. (B) The corresponding fluorescence emission spectra of **Ru·Yb$_3$** (in red), **Ru·Nd$_3$** (in blue), and **Ru·Lu$_3$** (in green) showing the characteristic MLCT emission.

in the ground state of **Ru·Ln$_3$** in comparison to their corresponding **Ln·1** starting materials.

The absorption spectra of the six complexes, **Yb·1**, **Nd·1**, **Lu·1**, **Ru·Yb$_3$**, **Ru·Nd$_3$**, and **Ru·Lu$_3$** are shown in Figure 1A. They all display the characteristic band cantered at ca. 267 nm, assigned to the [1,10]-phenanthroline chromophore. Moreover, **Ru·Yb$_3$**, **Ru·Nd$_3$**, and **Ru·Lu$_3$** exhibit an additional band at ca. 435 nm, which represents the Ru(II) MLCT transition (log $\varepsilon = 3.85$). Exciting the **Ru·Ln$_3$** conjugates into this new band gave rise to the formation of Ru(II) based MLCT emission at long wavelengths, with $\lambda_{\max}$ at ca. 605 nm, Figure 1B. Furthermore, the relative intensities of the MLCT emission spectra of the three conjugates differ greatly, as demonstrated in Figure 1B, where an intense red emission was observed for **Ru·Lu$_3$**, while the emission arising from the Ru(II) was only half of that for **Ru·Yb$_3$** and significantly lower for **Ru·Nd$_3$**, which was almost 80% less emissive than **Ru·Lu$_3$**. These results are indicative of effective intramolecular *n*d → 4f energy transfer processes occurring from the Ru(II) center MLCT excited state to the excited states of both the Yb(III) and Nd(III) moieties. In contrast, such an energy transfer would not be possible in **Ru·Lu$_3$**, where the Lu(III) possesses a higher excited state energy than that of the MLCT state. Hence, these results demonstrate that for **Ru·Yb$_3$** and **Ru·Nd$_3$**, a sensitized NIR emission should be expected to be observed for these complexes.

Molecular Structure of Ru·Lu$_3$. The formation of the mixed d−f$_3$ tetrads was also investigated by using ^{1}H NMR spectroscopy of the diamagnetic **Ru·Lu$_3$** conjugate in solution. The ^{1}H NMR spectrum of the corresponding starting material **Lu·1** in D$_2$O at 27 °C displays one set of signals, in agreement with the presence of C_1 symmetric species in solution. Seven resonances were observed for the phenanthroline moiety: two triplets at 9.11 and 9.13 ppm ($J_{HH} = 4.6$ Hz), two doublets ($\delta = 8.55$ and 8.50 ppm, $J_{HH} = 8.8$ Hz), one singlet at 8.16 ppm and two multiplets at 7.90 and 7.87, respectively. The cyclen framework and the methylene protons of the dimetylacetamide pendant arms give rise to broad multiplets occurring between 2.5 and 4.4 ppm whereas four singlets were observed at $\delta = 3.22$, 3.18, 3.04, and 3.00 ppm, for the methyl groups, respectively. After reacting the ligand with ruthenium(III) chloride, the ^{1}H NMR spectrum of the isolated **Ru·Lu$_3$** conjugate in a D$_2$O solution at 27 °C displays a similar pattern. The ^{1}H NMR spectra of **Lu·1** and **Ru·Lu$_3$** is shown in Figure 2, and clearly shows that the resonances of the phenanthroline protons are shifted downfield upon complexation to the Ru(II) center. The phenanthroline unit also displayed four quadruplets at 9.27 and 9.23 pm ($J_1 = 4.9$ Hz, $J_2 = 1.6$ Hz) and at $\delta = 8.92$ and 8.81 ppm ($J_1 = 8.7$ Hz, $J_2 = 1.3$ Hz), one singlet at 8.41 ppm and two multiplets at 8.19 and 8.12, respectively. The cyclen framework and the dimetylacetamide pendant arms give rise to broad multiplets between 4.4 and 2.6 ppm. It is worth pointing out that these complexes should be formed as racimic mixture of complexes. Moreover, contribution from the helical chirality of the lanthanide center could be expected. Nevertheless, the ^{1}H NMR spectra of does indicate that on the NMR time scale, **Ru·Lu$_3$** is seen as a single species, but broader resonances are also observed, and these we assign to the presence of other minor diastereoisomers in solution, which exists possibly in less than 20%.

The presence of the pollymetallic assembly was confirmed by carrying out a diffusion NMR experiment (See Supporting Information, Figures S1−S3). The self-diffusion coefficients of **Lu·1** and **Ru·Lu$_3$** were measured in D$_2$O at 27 °C.[23] The diffusion coefficients of the **Ru·Lu$_3$** species were found to be 2.0 to 2.8 smaller than the one measured for the starting material, **Lu·1** ($D = 1.82(3) \times 10^{-6}$ cm s^{-1}), which is in agreement with the formation of a larger species in solution. Indeed, a diffusion coefficient of $D = 9.35(5) \times 10^{-7}$ cm s^{-1}) was measured for the major species, whereas $D \sim 6.5 \times 10^{-7}$ cm s^{-1} was calculated for the minor species. Moreover, neither the proportion of the two species nor their self-diffusion coefficients were affected after refluxing the sample with an excess of RuCl$_3$, in agreement with the presence of fully complexed **Ru·Lu$_3$** in solution.

Sensitization of Lanthanide-Centered NIR Emission Arising in the Ru·Ln$_3$ (Ln = Yb, Nd) Complexes. We have demonstrated in our previous investigations that the [Ru(phen)$_3$]$^{2+}$ moiety can be used effectively for the sensitization of the excited states of the NIR-emitting lanthanide

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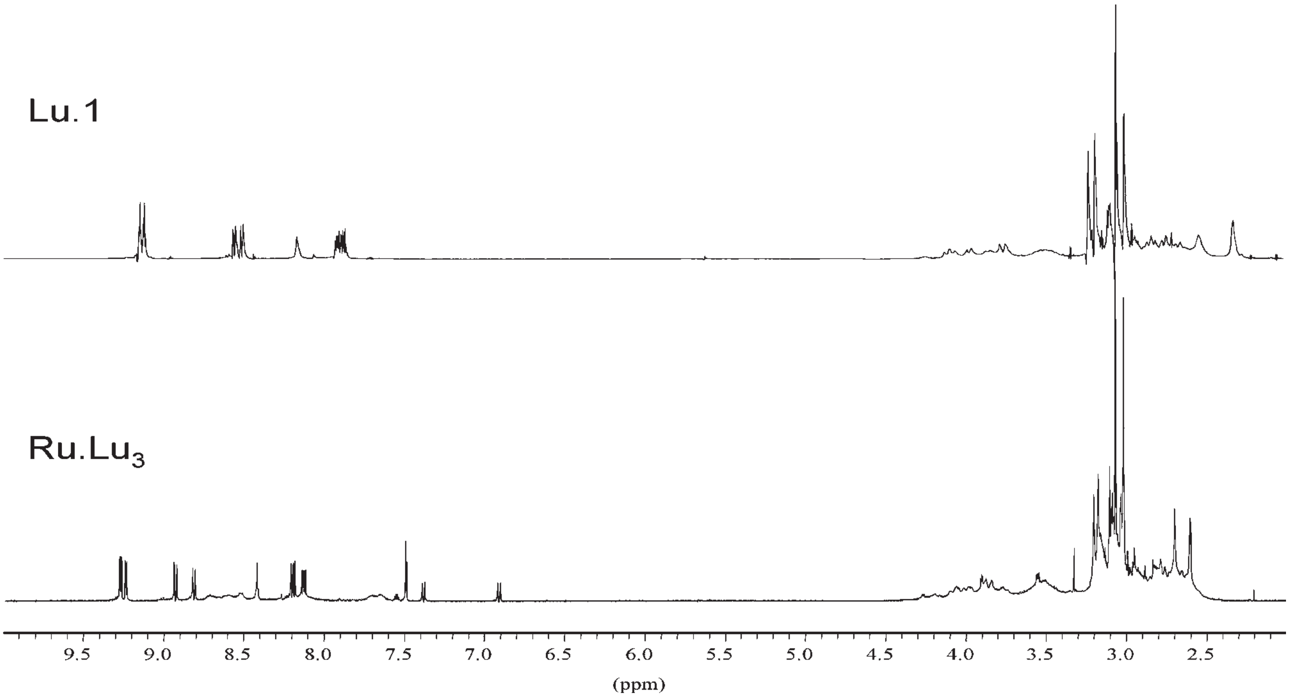

Figure 2. The ^{1}H NMR spectra of the Lu(III) complexes, in D_2O, at 600 MHz and 27 °C, with watergate solvent suppression. Top: **Lu·1**, bottom: **Ru·Lu$_3$**.

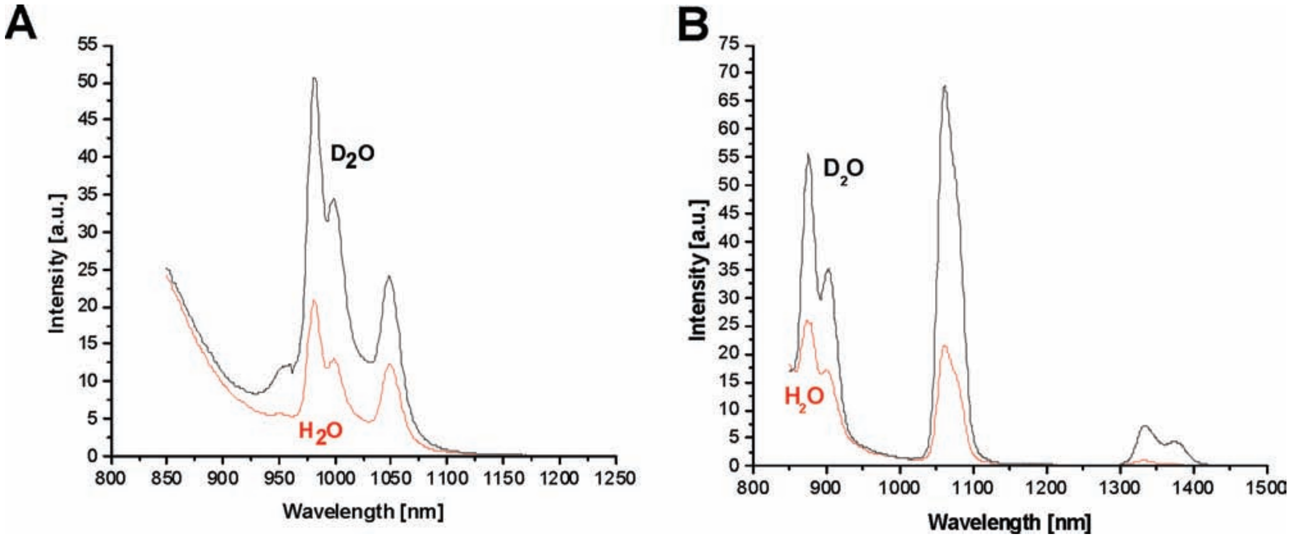

Figure 3. Emission spectra of **Ru·Ln$_3$** in the NIR region, at room temperature in buffered solutions (PBS 10 mM, pH 7.4) in water (in red) and D_2O (in black). (A) Ln = Yb(III), (B) Ln = Nd(III).

ions Yb(III) and Nd(III).[4] In the current study, the excitation into the Ru(II) centered MLCT transition of **Ru·Yb$_3$** and **Ru·Nd$_3$** at 447 nm resulted in the formation of lanthanide ion centered emission occurring in the NIR region for both complexes, with characteristic line-like emission bands, corresponding to the expected f−f transitions, Figure 3. While the Yb(III) complex emitted within the 930−1140 nm range, with a sharp band at 978 nm assigned to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition and a broader vibronic component at longer wavelength, the Nd(III) conjugate gave rise to three bands within the 850−1460 nm range; the main emission band occurring between 1022 and 1150 nm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$), with a maximum at 1062 nm, while the two other bands occurred between 857 and 870 nm ($^4F_{3/2} \rightarrow {}^4I_{9/2}$) and 1280−1456 nm ($^4F_{3/2} \rightarrow {}^4I_{13/2}$), respectively. The sensitizitation process was further examined by varying the excitation wavelength and observing the evolution of both the Nd(III) and Yb(III) center NIR emissions. As an example, an excitation−emission profile for the changes observed for **Ru·Nd$_3$** is shown in Figure 4, and clearly demonstrated that while the Nd(III) $^4F_{3/2}$ excited state can be probed at varieties of wavelength, the most efficient sensitization of the excited state was achieved upon excitation at λ_{max} of the Ru(II) MLCT transition. For both complexes, a residual emission was also observed from the Ru(II) center, a phenomenon previously seen in our investigations. However, the emission from the ^{3}MLCT is of much lower

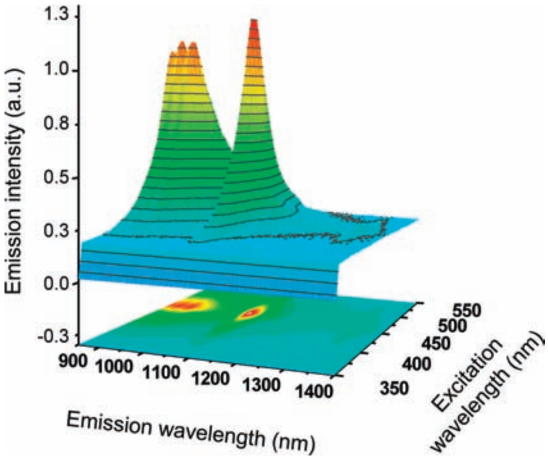

Figure 4. Excitation−emission profile of **Ru·Nd$_3$** in 10 mM phosphate buffer at pH 7.4, using a 580 nm filter.

Table 1. Metal Ion Centered Lifetimes (τ/μs) for Nd($^4F_{3/2}$) and Yb($^2F_{5/2}$) in **Ru·Ln$_3$** at pH = 7.4 (PBS Buffer) in Water/D$_2$O Solutions and the Corresponding Number of Inner Sphere Water Molecules q

	λ_{ex}:λ_{an}/nm	τ_{H_2O}/μs	τ_{D_2O}/μs	q^a
Ru·Yb$_3$	337:978	2.68	0.083 6.44	0.0
	435:978	1.88		
Ru·Nd$_3$	337:870	0.200	0.166 0.587	0.0
	337:1060	0.190	0.056 0.340	−0.1
	337:1340	0.297	0.059 0.351	−0.3
	435:870	0.073 0.117		
	435:1060	0.092 0.102		

[a] From eqs (1) and (2). From ref 27.

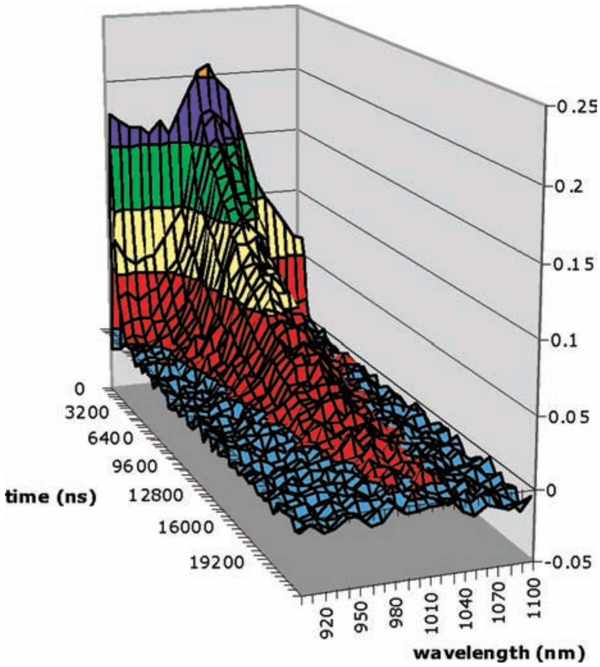

Figure 5. Time-resolved emission spectrum of **Ru·Yb$_3$** after excitation at 337 nm, showing sensitized lanthanide-based luminescence with residual Ru(II) emission. Lifetimes (Table 1) were obtained by deconvoluting these traces from the detector response function.

intensity in **Ru·Nd$_3$** than seen for **Ru·Yb$_3$**, while the emission is quite pronounced in the **Ru·Lu$_3$** analogues which is indicative of participating in an energy transfer process from the Ru(II) to the lanthanide ions. The emission spectra of **Ru·Nd$_3$** and **Ru·Yb$_3$** were also recorded in 10 mM phosphate buffer in D$_2$O leading to the same emission pattern as seen above, where on all occasions, the NIR centered emissions were much larger in intensity than seen in water, due to the absence of effective O−H quenching oscillators, Figure 3.

From the deactivation of the NIR emission, we were able to determine the lifetimes of the Nd($^4F_{3/2}$), and Yb($^2F_{5/2}$) excited states in phosphate buffered H$_2$O and D$_2$O solutions at pH 7.4 (see Supporting Information, Figures S4−S15). The luminescence decays were recorded upon excitation at 337 nm and of the Ru(II) MLCT at 435 nm using a nitrogen pulsed laser and a dye-laser, respectively. The corresponding values are summarized in Table 1. The luminescence decay of **Ru·Yb$_3$** in water was found to be monoexponential, and the corresponding lifetime ($\tau_{H_2O} \sim 2.28$ μs) is close in value to the lifetime previously measured for **Yb·1** (2.4 μs) (See the emission spectra of **Yb·1** and **Nd·1** in Supporting Information, Figure S17 upon excitation at 339 nm.). As expected, the lifetime is appreciably longer in D$_2$O and a double-exponential decay has been observed with a short component of $\tau = 83$ ns and a major component of $\tau = 6.44$ μs, which is again similar to the lifetime of **Yb·1** in D$_2$O (6.4 μs). As previously mentioned, these complexes exist in solution as mixture of isomers, where contributions from the phen moiety as well as the usual helical chirality on all the lanthanide centers and the ruthenium core all play a potential part here, which could potentially affect the photophysical properties of these systems. Despite this structural complexity, the spectra shown above themselves do not reflect this complexity, and the above results suggest that there is not much photophysical difference between these possible isomers in solution.

The time-resolved emission spectrum of **Ru·Yb$_3$**, in D$_2$O, is shown in Figure 5. For the Nd(III) conjugates, the luminescence decays of the three transitions, $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$, and $^4F_{3/2} \rightarrow {}^4I_{13/2}$, have been monitored at 870, 1060, and 1340 nm, respectively. Excitation at 337 nm gave rise to monoexponential decays with $\tau = 195(5)$ ns, whereas the decays recorded upon excitation at 435 nm were best fitted to double exponential functions, with $\tau_{\text{rise time}} = 0.08(1)$ μs and $\tau = 110(7)$ ns, in water. Consistent lifetimes were obtained by monitoring the changes at 1340 nm, although the fitting of these results were less accurate due to a lower intensity. Values of $\tau_{\text{rise time}} = 0.06(1)$ μs and $\tau = 345(5)$ ns have been measured by monitoring the decay of the two last transitions in deuterated water, upon excitation at 337 nm. Significantly longer lifetimes were, however, obtained for the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ deactivation, probably due to the contribution of the Ru(III) emission. Similar values had been previously reported for **Nd·1** in water ($\tau_{\text{rise time}} = 30$ ns and $\tau = 209$ ns), although the lifetime of **Ru·Nd$_3$** in D$_2$O is significantly longer than for **Nd·1** in D$_2$O ($\tau_{\text{rise time}} = 197$ ns and $\tau = 210$ ns). The lifetimes determined for the Nd(III) and Yb(III) emissions are within the same range as

Table 2. Metal Ion Centered Emission Absolute Quantum Yields for Nd($^4F_{3/2}$) and Yb($^2F_{5/2}$) in **Ru·Ln$_3$** and in **Ln·1** (Ln = Yb, Nd) at pH = 7.4 (PBS Buffer) in H_2O and in D_2O Solutions (Corrected for pD)

	λ_{ex} / nm	Q^{L}_{Ln}/%	
		H_2O	D_2O
Yb·1	339	0.074	0.29
Ru·Yb$_3$	339	0.071	0.25
	447	0.074	0.21
Nd·1	339	0.010	0.044
Ru·Nd$_3$	339	0.043	0.102
	447	0.037	0.099

those recently published for polymetallic cyclen-based complexes.[24]

From the lifetimes measured above, we were able to determine the number of inner-sphere water molecules by using eqs 1 and 2,[25,26] for Nd(III) and Yb(III), respectively.

$$\text{for Nd(III)} \quad q = A(\Delta k_{obs}) - C \qquad (1)$$

$$\text{For Yb(III)} \quad q = A(\Delta k_{obs} - B) \qquad (2)$$

Here, $A = 130$ ns for Nd(III) and 1 μs for Yb(III), $C = 0.4$, and $B = 0.2\ \mu s^{-1}$, while $k_{obs} = 1/\tau_{obs}$, is expressed in μs^{-1} and ns^{-1} for Yb(III) and Nd(III), respectively, and $\Delta k_{obs} = k_{obs}(H_2O) - k_{obs}(D_2O)$. The results are summarized in Table 1 and clearly indicate that there is no water molecule coordinated to either of the lanthanide ions within these complexes, though q value determination for neodymium complexes has a very high uncertainty owing to the contribution of C−H oscillators to non-radiative quenching.

The absolute quantum yields of the Nd(III) and Yb(III) centers in the tetrads were also determined in phosphate buffered solutions in H_2O and D_2O, at pH 7.4, upon excitation in the Ru(II) MLCT band at 447 nm, and are summarized in Table 2. For that purpose, the quantum yields of the monometallic systems, **Yb·1** and **Nd·1**, have been determined relative to [Yb(tta)$_3$(phen)] in toluene ($Q_{Yb} = 1.10\%$),[28] upon excitation at 339 nm, and are used as secondary references. Moreover, since the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition is overlapping with residual Ru(II) emission, a good approximation of the quantum yield of **Ru·Nd$_3$** has been obtained by considering only the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition.

Table 3. Quantum Yields for the Ru(II) Based MLCT Emission in the **Ru·Ln$_3$** (Ln = Lu, Nd, Yb) Complexes at pH = 7.4 (PBS Buffer) in Water and in D_2O Solutions (λ_{ex} = 447 nm)

	Q_{Ru,H_2O}%	Q_{Ru,D_2O}%
Ru·Lu$_3$	0.043	0.050
Ru·Yb$_3$	0.018	0.021
Ru·Nd$_3$	0.004	0.004

The quantum yields of **Yb·1** and **Nd·1** in water at pH 7.4 were calculated as 0.074 and 0.010% for Yb(III) and Nd(III), respectively. As expected from the lifetimes measured, the quantum yields are significantly higher in deuterated water with a 4-fold increase (0.29% for Yb(III) and 0.044% for Nd(III), respectively, which is indicative of a large quenching effect due to vibrational processes. Although these values are low in comparison to the best NIR-emitters to date ($Q_{Yb} = 0.90\%$ and $Q_{Nd} = 0.18\%$[29] in D_2O), the measured quantum yields are double those previously reported for similar complexes with a diethylenetriamine tetracarboxylic unit connected to a [1,10]-phenanthroline antenna.[30] This could be explained by a combination of both vibrational quenching processes and an inefficient sensitization of the lanthanide, resulting from a large energy difference between the MLCT stated (and possibly the triplet state of the phenanthroline ($E_T \sim$ 21 640 cm^{-1})) and the acceptor levels of the lanthanide ions ($^2F_{5/2}$: 10 230 cm^{-1}, $^4F_{3/2}$: 11 670−10 540 cm^{-1}). To further support this, the efficiency of the overall ligand-to-metal energy transfer η_{sens} was calculated according to eq 3 where Q^{L}_{Ln} and

$$Q^{L}_{Ln} = \eta_{sens} Q^{Ln}_{Ln} = \eta_{sens}\frac{\tau_{H_2O}}{\tau_{rad}} \qquad (3)$$

Q^{Ln}_{Ln} are the absolute and the intrinsic quantum yield of the complex, respectively. Q^{Ln}_{Ln} was obtained by calculating the ratio between the luminescence lifetime in H_2O, and the radiative lifetime. We can consider, with good approximation, that τ_{rad} is independent of the lanthanide coordination sphere and is equal to the constants proposed for the corresponding Ln(III) aqua-ions (0.42 ms for Nd(III)[31] and 2 ms for Yb(III)).[32] Taking those values into account, we were able to calculate $\eta_{sens} = 0.6$ and 0.2 for **Yb·1** and **Nd·1**, respectively. The excitation of phosphate buffered aqueous solutions of **Ru·Yb$_3$** at 339 nm gave $Q_{Yb} = 0.071\%$ in H_2O and $Q_{Yb} = 0.25\%$ in D_2O, which is similar to that determined for **Yb·1**. Consistent values have also been obtained upon excitation in the Ru(II)-centered MLCT at 447 nm ($Q_{Yb} = 0.074\%$ in H_2O and $Q_{Yb} = 0.21\%$ in D_2O). From these values, the overall sensitization efficiency was estimated to be around $\eta_{sens} = 0.6$.

From this investigation, the most interesting results were, however, obtained for the **Ru·Nd$_3$** tetrads. Here, an intense Nd(III) emission was observed in water upon excitation of the ligand at 339 nm ($Q_{Nd} = 0.043\%$) or upon excitation of the MLCT transition at 447 nm ($Q_{Nd} = 0.037\%$). This is a further evidence for the presence of a fully complexed species in solution, which is formed in high purity. Moreover, the intensity of the Nd(III) NIR-emission was increased by a factor of 2.5 when recorded in D_2O ($Q_{Nd} = 0.102\%$ with $\lambda_{ex} = 339$ nm; $Q_{Nd} = 0.099\%$ with $\lambda_{ex} = 447$ nm). These values have the same order of magnitude to those recently published for other Nd(III)

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complexes.[8,9] Furthermore, these results are in agreement with an efficient energy transfer process from the Ru(II) MLCT to the $^4F_{3/2}$ acceptor level, with $\eta_{sens} = 0.95$ (by assuming that $\tau_{rad} = 0.42$ ms). This behavior could be related to a better overlap between the energy levels of the ^{3}MLCT state (~14 500 cm^{-1}) and of the Nd(III) excited states, in comparison to the Yb(III) excited states.

To further investigate the energy transfer processes in these tetrads, we also determined the quantum yields for the Ru(II) based MLCT emission in the **Ru·Ln$_3$** coordination conjugates (Ln(III) = Lu, Yb, Nd), Table 3. Here, **Ru·Lu$_3$**, for which no energy transfer to the Lu(III) occurs, was used as a model compound. The quantum yield for the Ru(II) emission has been calculated as 4.3%, using aerated solution of $[Ru(bpy)_3]^{2+}$ ($Q_{Ru} = 2.8\%$) as a reference. This value is significantly higher than the one reported for $[Ru(phen)_3]^{2+}$ ($Q_{Ru} = 3.2\%$)[33] and could be explained by a shielding effect of the Ru(II) center by the macrocyclic lanthanide complexes. Indeed, a similar quantum yield has recently been reported for a $[Ru(phen)_3]^{2+}$ derivative covalently bound to silica nanoparticles via an acetamide spacer ($Q_{Ru} \sim 4.0\%$).[34]

However, when the Lu(III) was replaced by Yb(III), the red emission of the Ru(II) center was quenched ca. 58% (with a $Q_{Ru,Yb} = 1.8\%$), as expected from the NIR luminescence measurements ($\eta_{sens} \sim 0.6$). A much larger quenching (91%) was, however, observed for the Nd(III) conjugate, for which a quantum yield of 0.4% was determined. This is in agreement with a very efficient energy transfer from the d-metal complex to the Nd(III) center ($\eta_{sens} \sim 0.95$). However, only minor changes were observed in the Ru(II) emission in D_2O solutions, indicating that while the O−H oscillators are strongly affecting the Ln(III) luminescent lifetimes, they do not influence the efficiency of the Ru → Ln energy transfer process. All these results indicate that the use of the $[Ru(phen)_3]$ core as an antenna is more suitable for the sensitization of Nd(III) than Yb(III). Similar observations have been seen in other $[Ru(phen)_3]$-based heterobimetallic complexes[35] and in particular in the bimetallic analogues **Ln·1·Ru·phen** (Ln = Yb, Nd).[4] This preference for Nd(III) has been assigned to a better overlap between the Ru(II) ^{3}MLCT state and the Nd(III) acceptor levels in comparison to that of Yb(III); that is, whereas seven levels (^4F_J, $J = 3/2, 5/2, 7/2, 9/2$; ^2H_J, $J = 8/2, 11/2$ and $^4S_{3/2}$) are available for Nd(III), Yb(III) has only one emissive excited state ($^2F_{5/2}$).

Overall, the above studies clearly demonstrate that kinetically stable heterobimetallic tetrads can be synthesized, which are highly NIR-emissive in water and present a well-defined coordination sphere with no inner-sphere water molecule.

Conclusion

We have developed a method for the synthesis of a series of mixed supramolecular d−f$_3$ self-assemblies with NIR-emissive lanthanide ions such as Yb(III) and Nd(III). A cyclen-based ligand featuring a [1,10]-phenanthroline moiety has been designed for the formation of lanthanide complexes that are easily assembled around the Ru(II) ion. The formation of the diamagnetic Lu(III)−Ru(II) tetrads has been demonstrated by using ^{1}H NMR spectroscopy and by carrying out NMR based diffusion experiments. These results indicated the formation of a high symmetry species (expected as a C_3-symmetric). In the case of Yb(III) and Nd(III), both the $[Ru(phen)_3]^{2+}$ core and the Ln(III) complexes are luminescent allowing the monitoring of the photophysical properties upon formation of the coordination conjugates. The adduct formation is clearly shown in the absorption spectra with the presence of a characteristic MLCT band within the visible region.

The formation of the mixed d−f metal systems also affects the ruthenium luminescence, which is strongly quenched by Nd(III) and moderately quenched by Yb(III). This quenching occurs via energy transfer to the Nd(III) and Yb(III) ions, as demonstrated by using a Lu(III) analogue, and both **Ru·Nd$_3$** and **Ru·Yb$_3$** display sizable NIR-luminescence quantum yields in water and at physiological pH (Q_{Yb} = 0.073% and Q_{Nd} = 0.040%). Moreover, these results further show that the use of $[Ru(phen)_3]^{2+}$ as a sensitizing antenna is particularly well-suited for the population of the Nd(III) acceptor levels, with a sensitization efficiency higher than 90%, which is, to the best of our knowledge, among the highest reported in the literature. Future work will be directed at tuning the ligand properties in order to increase the overall luminescence efficiency by minimizing the nonradiative processes and the second-sphere interactions.

In summary, the Yb(III)- and Nd(III)-based conjugates **Ru·Yb$_3$** and **Ru·Nd$_3$** are dual emitting probes that emit both within the visible and the NIR regions, in water and at physiological pH, upon excitation of their antennae using visible excitation wavelengths. Hence, these systems are therefore well-suited for use in biomedical analysis and as probes. We are currently developing other d−f coordination conjugates with potential applications as biological probes and sensors that are based on the design discussed herein. Moreover, this approach could be extended to systems containing different lanthanide ions with potential applications for multimodal imaging, an area currently being pursued in our laboratories.[36−38]

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Supporting Information Available: Figures S1−S17. This material is available free of charge via the Internet at http://pubs.acs.org.

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