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Introduction

Luminescence from lanthanide complexes has proved to be an effective tool in both assay and imaging.^{1–4} The long-lived lanthanide luminescence is easily separated from fluorescence and scatter by time-gating methods,^{2,5,6} giving rise to very low detection limits in assay and high signal: noise ratios in imaging.⁷ The low molar absorptivities associated with f-f transitions dictate that the use of lanthanides in such applications must generally rely upon sensitizing the formation of the lanthanide state by energy transfer from another chromophore.⁸ For most lanthanides such energy transfer occurs *via*

†This paper is dedicated to the memory of Dr Gerald Bernardinelli.

Ln₂M complexes (M = Ru, Re) derived from a bismacrocyclic ligand containing a 4,4'-dimethyl-2,2'bipyridyl bridging unit†‡

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Homodinuclear lanthanide complexes derived from a ligand featuring two DO3A chelating sites linked by a 4,4'-dimethyl-2,2'-bipyridyl spacer were prepared and characterized. The bipyridyl coordination site of **1** was used to introduce Ru(Bpy)₂ and Re(CO)₃Cl moieties, leading to the formation of heterometallic d–f₂ complexes with general formulae $[Ln_2 \cdot \mathbf{1} \cdot Ru(Bpy)_2]^{2+}$ (Ln = Nd, Eu, Tb, Yb and Lu) and $[Ln_2 \cdot \mathbf{1} \cdot Re (CO)_3Cl]$ (Ln = Nd, Yb and Lu). The luminescence properties of the complexes were investigated by means of absorption spectroscopy and steady-state and time-resolved luminescence spectroscopy covering the visible and NIR regions. Both Ru and Re chromophores were shown to act as efficient sensitizers of the NIR emission of Yb and Nd in aqueous solutions. We also consider the unsaturated coordination spheres of the Ln cations in the Ln₂·**1** complexes, which form ternary complexes with bidentate anions without showing particular synergistic effects for polyanionic species.

the ligand triplet state,⁹ though a sequential electron transfer mechanism has been implicated in energy transfer in some ytterbium complexes.¹⁰

For many years, aryl chromophores were used as sensitizing antennae. However more recently there has been a surge of interest in the use of d-block transition metal complexes as sensitizers in so-called d–f hybrid arrays. The effective formation of triplet metal-to-ligand charge transfer states (³MLCT states) by such systems can lead to very effective energy transfer,¹¹ and has been widely exploited. Energy transfer can, in principle, occur by Forster energy transfer or by Dexter exchange. In general, the former predominates where the chromophore and the lanthanide are separated from one another (*e.g.* by an alkyl spacer),^{12,13} while the latter predominates where there is a direct link between the chromophore and the lanthanide, or where superexchange can occur through the ligand skeleton.¹³

We recently showed that metal bipyridyl complexes can be linked to cyclen derived complexes, and that efficient sensitization of the metal centre is observed.^{14–17} Furthermore, we observed that ytterbium containing systems can be sensitized effectively without perturbing the ³MLCT state in such systems. We now report the results of a study on Ln_2M systems in which transition metal bipyridyl complexes are used to sensitize lanthanide luminescence.

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 $[\]pm$ Electronic supplementary information (ESI) available: HR-MS of Eu₂·1, ¹H NMR spectrum of Yb₂·1, excitation spectra of $[Ln_2·1·Ru(Bpy)_2]^{2+}$ complexes (Ln = Eu, Tb), optimized geometry of Yb₂·1·2H₂O obtained from DFT calculations and optimized Cartesian coordinates obtained from HF and DFT calculations. See DOI: 10.1039/c2dt32660d



Results and discussion

Synthesis

Our synthetic strategy is shown in Scheme 1. Reaction between the well-known triester,18 2, and 4,4'-bis(bromomethyl)-2,2'bipyridine (3) yielded 4. Subsequent deprotection with trifluoroacetic acid yielded H₆·1. Complexation was achieved by reaction with lanthanide trifluoromethane sulfonate salts, yielding $Ln_2 \cdot 1$ (Ln = Nd, Eu, Tb, Yb, Lu). The high-resolution mass spectra of the complexes (ESI⁺) show intense peaks due to the $[Ln_2 \cdot H_2 \mathbf{1}]^{2+}$ entities, which unambiguously confirms the formation of the desired complexes (Fig. S1, ESI[‡]). The ¹H-NMR spectrum of the paramagnetic Yb complex (Fig. S2, ESI[‡]) shows broadened and shifted resonances that unambiguously signal the coordination of the ligand to the metal ion. The presence of four resonances associated with the most shifted axial protons of the cyclen ring (observed at 134.3, 126.4, 119.3 and 109.9 ppm) indicates a lack of symmetry about the DO3A unit. However, the presence of only four signals (instead of eight) for these protons suggested that both metal cations possess identical coordination environments. This is in contrast to the situation observed for the analogous dinuclear lanthanide complexes based on a 6,6'-substituted Bpy linker, for which different coordination environments were observed for the two metal ions.¹⁷ The chemical shift values observed for the resonances of axial protons are similar to those reported for other cyclen-derived systems with a broken symmetry,¹⁹⁻²¹ and point to a square antiprismatic coordination around the metal ion. Intriguingly, the diastereoisomers of both complexes appear to be in slow exchange on the NMR timescale, suggesting that these DO3A binding sites differ from what might normally be expected as other DO3A derivatives show much more flexibility and fluxionality.¹⁹ The Nd complex exhibited highly broadened lines in the ¹H NMR spectra, suggesting that the larger size of the neodymium ion facilitates interconversion between isomers.

Stable d–f hybrid complexes were prepared by reaction with labile transition metal complexes. Reaction of $Ln_2 \cdot 1$ with rhenium pentacarbonyl chloride in THF yielded $Ln_2 \cdot 1 \cdot Re$ (CO)₃Cl, while the $[Ln_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ complexes were prepared by reaction of $Ln_2 \cdot 1$ with *cis*-Ru(Bpy)₂Cl₂. Alternatively, the synthesis of $[Ln_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ complexes can be also achieved by reaction of the protected precursor 4 with *cis*-Ru(Bpy)₂Cl₂, followed by deprotection of the *tert*-butyl esters with trifluoroacetic acid. Subsequent reaction of 5 with two equivalents of the corresponding lanthanide triflate in the presence of triethylamine resulted in the formation of the desired heterometallic complexes. The high-resolution mass spectra of the complexes (ESI⁺) show intense peaks due to the doubly charged species $[Ln \cdot 1 \cdot Ru(Bpy)_2]^{2+}$, thereby confirming the formation of the heterometallic compounds (Fig. 1).

Photophysical properties of the complexes

The photophysical properties of the $Eu_2 \cdot 1$ and $Tb_2 \cdot 1$ complexes are summarized in Table 1. The UV-vis absorption spectra recorded in 0.1 M TRIS buffered aqueous solutions (pH 7.4) are presented in Fig. 2. Both spectra display a broad absorption band with a maximum at 286 nm ($\varepsilon = 11700 \text{ M}^{-1} \text{ cm}^{-1}$ for Eu₂·1; ε = 13 600 M⁻¹ cm⁻¹ for Tb₂·1), which is typical of $n \to \pi^*$ and $\pi \to \pi^*$ transitions centred on the bipyridine unit.²² Noteworthy, the energy level of the lowest energy absorption band is a very sensitive probe of the cis to trans isomerization process of 2,2'-bipyridyl compounds,²³ with a ca. 20 nm low energy shift from the trans to the cis isomer. Regarding the values of the literature for similar compounds,²⁴ a maximum absorption at 286 nm suggests an intermediate conformation in the complexes. This intermediate situation appears surprising as it is generally observed that, in the absence of protons or chelating metals, the lone pair repulsions of the nitrogen atoms clearly favour the trans isomer. Upon excitation into the absorption band in the UV-vis domain, the complexes display typical emission patterns characteristic of the ${}^{5}D_{0} \rightarrow {}^{7}F_{I}$ (J = 0–4) and ${}^{5}D_{4} \rightarrow {}^{7}F_{I} (J = 6-3)$ transitions of the Eu^{III} and Tb^{III} ions, respectively (Fig. 2).25 Interestingly, in both cases, no residual fluorescence of the ligand could be observed.



Fig. 1 Observed (top) and theoretical (bottom) mass spectral isotopic distribution for the fragment [Eu·1·Ru(Bpy)₂]²⁺.

Table 1 Selected photophysical data for Ln₂·1 and [Ln₂·1·Ru(Bpy)₂]²⁺ complexes (Ln = Eu or Tb) in aqueous solution (TRIS/HCl, 0.1 M, pH 7.4)

	$\phi_{\mathrm{H_2O}} \ (\%)$	$\phi_{\mathrm{Ru, H_2O}}^{a}$ (%)	$\phi^{{ m Ln}b}_{{ m Ln}}$ (%)	$ au_{\mathrm{H_2O}} \ (\mu\mathrm{s})$	$\begin{array}{c}\tau_{\rm H_2O}{}^c\\\left(\mu s\right)\end{array}$	$\left(\substack{ \tau_{\mathrm{D}_{2}\mathrm{O}}^{d} \ (\mu\mathrm{s}) } \right)^{d}$	q^e
Eu ₂ ·1	8.4		13	560	540	1680	0.8
$Tb_2 \cdot 1$	25		_	1440	1400	2540	1.3
$\left[\mathrm{Eu}_{2}\cdot1\cdot\mathrm{Ru}(\mathrm{Bpy})_{2}\right]^{2+}$		3.4	12	348	373	1496	2.1
$[Tb_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$		3.9	—	732	724	1199	2.4

 $^{a}\lambda_{exc}$ = 450 nm. b According to ref. 28. c H₂O, pH 7.4. d D₂O, pD 7.4. ^e According to ref. 29. Estimated errors: ±10% on lifetimes, ±15% on quantum yields.

The excitation spectra recorded upon metal-centred emission are very similar to the corresponding absorption spectra, which suggest an efficient ligand-to-metal energy transfer following the antenna effect (Fig. 2). The sensitised emission quantum yields ($\phi_{H,O}$) were determined in 0.1 M TRIS buffered aqueous solutions (pH 7.4) using $[Ru(Bpy)_3]Cl_2 (\phi_{H_2O} = 4.0\%)^{26}$ in non-degassed water as a reference for $Eu_2 \cdot 1$ and rhodamine 6G ($\phi_{\rm H_2O}$ = 76%) in water²⁷ for Tb₂·1. The values obtained $[\phi_{\rm H_2O} = 8.4 \ ({\rm Eu}_2 \cdot 1) \text{ and } 25\% \ ({\rm Tb}_2 \cdot 1)]$ point to a relatively efficient sensitization of the two metal ions, particularly in the case of $Tb_2 \cdot 1$.



 $\epsilon / L \cdot mol^{-1} \cdot cm^{-1}$

ε / L·mol⁻¹·cm⁻¹

0

300

250

450 500

Fig. 2 UV-vis absorption spectra, excitation spectra (dotted lines, $\lambda_{em} = 616$ nm (Eu) and 545 nm (Tb)) and high resolution emission spectra (λ_{exc} = 286 nm) recorded for Eu₂·1 (red, bottom) and Tb₂·1 (green, top) complexes in 0.1 M TRIS buffered aqueous solutions (pH 7.4, 7×10^{-5} M).

600 650 700 750

550

 λ / nm

The hydration state of the $Ln_2 \cdot 1$ complexes (Ln = Eu, Tb) was studied by comparison of their luminescence lifetimes in H₂O and D₂O solutions.²⁹ All observed lifetimes can be correctly fitted with mono-exponential decays, pointing to single species in solutions or mixtures of species in rapid equilibrium. The emission lifetimes measured in water (τ_{H_2O}) for $Tb_2 \cdot 1$ complexes are longer than the one previously observed by Pope et al. for bis-aquo dinuclear complexes linked by a xylyl spacer ($\tau_{\rm H_2O}$ = 360 µs for the Eu^{III} complex and $\tau_{\rm H_2O}$ = 1340 µs for Tb^{III}).³⁰ Furthermore, the observed lifetimes (Table 1) are in agreement with the presence of one coordinated water molecule in the first coordination sphere of each metal centre. This is somewhat surprising, since DO3A lanthanide complexes usually behave as di-aqua complexes, and for instance an averaged hydration number of q = 1.8 has been determined for $[Ln(DO3A)(H_2O)_q]$ (Ln = Eu or Tb) complexes.³¹ In some instances a lower hydration number could be partially related to the aggregation of the complexes in solution. Indeed, a hydration of q = 1 was established for xylenecored Gd^{III}-DO3A derivatives as a result of self-aggregation of the complexes in aqueous solution.³² A preliminary relaxometric study on the $Gd_2 \cdot 1$ complex and other related systems

Table 2 Photophysical properties of Yb and Nd complexes in aqueous solution a

	MLCT emission			Lanthanide emission			
	λ _{em} / nm	$ au_{\mathrm{D_2O}}/$ ns	$ au_{ m H_2O}/ m ns$	$\frac{\lambda_{\rm em}}{\rm nm}$	$ au_{ m D_2O}/ m ns$	$ au_{ m H_2O}/ m ns$	$q_{ m Yb}$
$Yb_2 \cdot 1$	_	_	_	980	4870	2135	0.2
$Nd_2 \cdot 1$	_		_	1055	408	200	
Yb ₂ ·1·Re(CO) ₃ Cl	600	8.9	5.5	980	5166	1410	0.4
$Nd_2 \cdot 1 \cdot Re(CO)_3 Cl$	600	9.2	5.5	1055	303	76	
Lu ₂ ·1·Re(CO) ₃ Cl	600	16.7	14.5	_	_	_	
$[Yb_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$	800	407	280	980	5368	644	1.3
$[Nd_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$	800	311	113	1055	335	73	
$[Lu_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$	800	591	401	—	_	—	

^{*a*} Lifetimes are given with an error of $\pm 10\%$. For the heterometallic complexes, the lanthanide centred signal is convoluted with the detector response and the tail of the MLCT emission. The lifetimes given were obtained by iterative reconvolution to a double exponential where one value was fixed to the lifetime determined for the ³MLCT state outside the range of lanthanide emission.

points to the formation of aggregates in solution, presumably through the coordination of bridging carboxylate groups. However, a full relaxometric characterization of these complexes exceeds the purpose of the present paper, and will be reported elsewhere.

The $Ln_2 \cdot 1$ complexes (Ln = Nd, Yb) were studied in H₂O and D₂O (Table 2). In the case of the ytterbium complexes, the observed luminescence lifetimes were used to probe the solvation at the lanthanide, and the number of inner sphere water molecules (*q*) was calculated using the equation

$$q = 1.0(\tau_{\rm H_2O} - \tau_{\rm D_2O} - 0.1) \tag{1}$$

where $\tau_{\rm H_2O}$ and $\tau_{\rm D_2O}$ are the lifetimes in water and deuterium oxide respectively.²⁹ The calculated value of q for $Yb_2 \cdot 1$ is 0.2: very low for a complex in which the lanthanide is bound by a heptadentate ligand, implying that the formation of aggregates in solution, or the presence of intramolecular carboxylate bridging units, prevents the coordination of inner-sphere water molecules. While relationships between q and lifetime have been suggested for neodymium complexes, the profound variation in luminescence lifetime with the number of C-H oscillators in the ligand backbone makes their application limited.^{7a} That said, the luminescence lifetime observed for $Nd_2 \cdot 1$ in H_2O is very long for a complex with a heptadentate ligand, suggesting that q < 1 in this system also; literature values for aminocarboxylate ligands with neodymium would lead us to expect a lifetime of less than 100 ns with coordinated inner sphere water in the lanthanide coordination sphere.33

The UV-vis absorption spectra of the $[Ln_2 \cdot 1 \cdot Ru(Bpy)_2]^{2^+}$ complexes (Ln = Eu, Tb) in 0.1 M TRIS buffered aqueous solutions (at pH 7.4) are presented in Fig. 3. Both spectra display a broad absorption band with a maximum at 288 nm (ε = 72 700 M⁻¹ cm⁻¹ for Eu^{III}; ε = 66 500 M⁻¹ cm⁻¹ for Tb^{III}), which is typical of $\pi \to \pi^*$ transitions centred on the bipyridine units in *cis* conformation.²³ Moreover, a broad absorption



Fig. 3 UV-vis absorption spectra and emission spectra ($\lambda_{exc} = 288$ nm) recorded for $[Eu_2 \cdot \mathbf{1} \cdot Ru(Bpy)_2]^{2+}$ (red) and $[Tb_2 \cdot \mathbf{1} \cdot Ru(Bpy)_2]^{2+}$ (green) complexes in 0.1 M TRIS buffered aqueous solutions (pH 7.4, 2 × 10⁻⁵ M). Inset: Phosphorescence emission spectra of $[Tb_2 \cdot \mathbf{1} \cdot Ru(Bpy)_2]^{2+}$ recorded under the same conditions (delay time 0.05 ms).

band is also observed at 456 nm ($\varepsilon = 15000 \text{ M}^{-1} \text{ cm}^{-1}$ for Eu^{III} and $\varepsilon = 14000 \text{ M}^{-1} \text{ cm}^{-1}$ for Tb^{III}), which is attributed to the characteristic metal-to-ligand charge transfer bands observed in polypyridyl Ru^{II} complexes.³⁴

Excitation into the absorption band due to the bipyridyl units at 288 nm resulted in broad emission spectra (Fig. 3) characteristic of the fluorescence of the Ru^{II} centre. In the case of $[Tb_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ an additional pattern which accounts for Tb^{III} emission is also observed. The typical emission patterns characteristic of the Eu^{III} and Tb^{III} ions could be clearly observed in the time-resolved luminescence mode, with a 50 µs delay (Fig. 3). These results indicate that both the Ru^{II} and the Ln^{III} centres are sensitized upon excitation in the bipyridyl units. The excitation spectra recorded by monitoring the Ru^{II}centered emission at 641 nm, a region devoid of Eu or Tb emission, for both the Eu^{III} and Tb^{III} complexes, display two bands with maxima at 286 nm and 456 nm, showing that Ru^{II} sensitization occurs from the $\pi \to \pi^*$ transitions centred on the bipyridine units and the ¹MLCT transition (Fig. S3, ESI[‡]). Similar excitation patterns have been recorded for λ_{em} = 616 nm, which is a combination of Ru^{II} and Eu^{III} excitation, as well as for $\lambda_{em} = 545$ nm, which is mostly Tb^{III} excitation. The emission spectrum recorded upon excitation in the MLCT band at 450 nm did not show Ln-centered emission, indicating the lack of photosensitization of Eu or Tb by the $[Ru(Bpy)_3]^{2+1}$ chromophore.

The Ru^{II} MLCT emissive quantum yields of $[Eu_2 \cdot 1 \cdot Ru (Bpy)_2]^{2+}$ ($\phi_{H_2O} = 3.4\%$) and $[Tb_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ ($\phi_{H_2O} = 3.9\%$) were determined in 0.1 M TRIS buffered aqueous solutions (pH 7.4) upon excitation into the ¹MLCT absorption band, using $[Ru(Bpy)_3]Cl_2$ ($\phi_{H_2O} = 4.0\%$)²⁶ in non-degassed water as a reference. These results are all very similar to one another, showing that the Ru^{II} emission is weakly affected by the presence of the Ln₂·1 unit, which suggests that the Ru^{II} coordination environment in $[Ln_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ is very similar to that in $[Ru(Bpy)_3]^{2+}$. The lifetime of the Ru^{II} centred emission has

also been measured in TRIS-buffered aqueous solutions, upon excitation at 303 nm with a LED source. For both complexes, the coordination sphere of Ru^{II} is unchanged and, as expected, the same value has been measured for the lifetime ($\tau_{Ru} = 384$ ns). This value is significantly shorter than the one previously reported for the [Ru(Bpy)₃]²⁺ complex in aerated water ($\tau_{Ru} =$ 580 ns),³⁵ but in good agreement with that measured for the parent Lu complex ($\tau = 401$ ns, Table 2).

The hydration state of $[Ln_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ complexes was studied by comparison of the luminescence lifetimes of the lanthanide-centered emission in H₂O and D₂O solutions. For the Eu complex τ_{H_2O} and τ_{D_2O} (Table 1) are significantly shorter than those measured for $Eu_2 \cdot 1$, and point to the presence of two metal-bound water molecules per Eu^{III} ion. The luminescence lifetime measured for $[Tb_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ is also shorter than that measured for $Tb_2 \cdot 1$ (Table 1). However, the luminescence lifetime in heavy water was significantly affected by the presence of the [Ru(Bpy)₃] unit (τ_{D_2O} = 1199 and 2540 µs for $[Tb_2 \cdot \mathbf{1} \cdot Ru(Bpy)_2]^{2+}$ and $Tb_2 \cdot \mathbf{1}$, respectively). Moreover, the lifetime in H₂O is significantly shorter than the one reported by Pope for a similar Tb^{III} complex ($\tau_{H_{2}O} = 1340 \text{ }\mu\text{s}$).³⁰ These results suggest the presence of an energy transfer from the Tb^{III} to the Ru^{II} centre, which would also be in agreement with the higher Ru^{II} quantum yield observed for the Tb complex in comparison to the Eu analogue. On the basis of the shortening of the Tb lifetime in the presence of the Ru acceptor, the Tb to Ru energy transfer efficiency may be estimated by

$$\phi_{\rm ent} = 1 - \frac{\tau_{\rm TbRu}}{\tau_{\rm Tb}} = 48\% \tag{2}$$

One may also have expected an influence of such a transfer on the Ru lifetime, with a contribution containing an increased lifetime due to the long lived excited donor,³⁶ but this effect is expected to be weak compared to direct excitation of the Ru centre by the bipyridyl antennae, and could not be observed with our experimental setup.

Excitation of the bipyridyl chromophore in $Ln_2 \cdot 1 \cdot Re(CO)_3 Cl$ and $[Ln_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ complexes (Ln = Nd or Yb) gives rise to long lived lanthanide luminescence. Thus, time-resolved measurements were used to probe the structure at the lanthanide centre, and probe energy transfer from the chromophore to the lanthanide. Key photophysical properties are shown in Table 2.

The rhenium complexes $Ln_2 \cdot 1 \cdot Re(CO)_3 Cl$ (Ln = Nd or Yb) display luminescence from both the rhenium MLCT state and the lanthanide excited state. In both cases, the tail of the emission from the ³MLCT state overlaps with the lanthanide centred emission, as can be seen from the time-resolved emission spectrum of Nd₂·1·Re(CO)₃Cl shown in Fig. 4.

The luminescence lifetimes of the lanthanide centred luminescence in H₂O are significantly shorter than those observed for the analogous $Ln_2 \cdot 1$ complexes. For Yb₂·1·Re-(CO)₃Cl, *q* was calculated to be 0.4, while the lifetimes observed for the neodymium centred luminescence in Nd₂·1·Re(CO)₃Cl are certainly consistent with hydration at the



Fig. 4 Time-resolved emission spectrum of $Nd_2 \cdot 1 \cdot Re(CO)_3 CI$ following laser excitation at 337 nm in D_2O .

metal centre, and comparable to values reported for systems in which there are one or two water molecules.

In these complexes, the luminescence lifetime of the ³MLCT state reflects the efficiency of energy transfer from the triplet to the lanthanide. The lifetime of the ³MLCT state in Lu₂·1·Re(CO)₃Cl, which has no excited states available in the f-electron manifold in consequence of the 4f¹⁴ configuration of each lutetium ion, can be used as a standard, and the efficiency of energy transfer, ϕ_{ent} , calculated from the equation

$$\phi_{\text{ent}} = 1 - \left(\tau_{\text{MLCT}(\text{Ln})} / \tau_{\text{MLCT}(\text{Lu})}\right) \tag{3}$$

where $\tau_{MLCT(Lu)}$ is the lifetime of the MLCT state in the lutetium complex, and $\tau_{MLCT(Ln)}$ the lifetime of the same state in the Ln complex.¹³ Applying this equation, we find that the efficiency of energy transfer to neodymium (0.62) in water is the same as that to ytterbium. In D_2O , the efficiency is significantly reduced as a consequence of less efficient dissipation of excess energy through the solvent vibrational manifold, but both values are again within error of one another. Importantly, the changes in ³MLCT lifetimes between the lutetium complex and the others clearly implicate triplet mediated energy transfer in both the neodymium and ytterbium complexes. By contrast, in one of our earlier studies, we observed negligible contribution of the triplet pathway in the case of energy transfer to Yb·L·Re(CO)3Cl.¹⁶ Given the similarities between the donor and acceptor chromophores in these molecules, the difference in behaviour is rather surprising. The donor chromophore is much closer to the lanthanide centres in the case of $Yb_2 \cdot 1 \cdot Re(CO)_3 Cl$, and it is clear that the structure of the whole complex must be taken into account, but it is far from clear why these differences arise.

The story is similar in the case of the $[Ln_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ complexes. Once again, the time-resolved emission spectra



Fig. 5 Time-resolved emission spectra of $[Yb_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ in D₂O following laser excitation at 337 nm.

reveal how the emission from the ³MLCT state overlaps with that from the lanthanide centres (Fig. 5 shows the timeresolved emission spectrum for $[Yb_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$). The luminescence lifetimes of $[Nd_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ are very similar to those of $Ln_2 \cdot 1 \cdot Re(CO)_3 Cl$. Given the similarity between the structures of these two complexes, it is safe to deduce that both have very similar local structures at the neodymium centres. However, the luminescence lifetimes of $[Yb_2 \cdot 1 \cdot Ru-(Bpy)_2]^{2+}$ equate to $q_{Yb} = 1.3$, indicating a much greater degree of hydration at the metal sites, as observed for the analogous Eu and Tb complexes. It is clear that the increased bulkiness of the ruthenium chromophore influences the structure at the lanthanide centre, presumably preventing aggregation, and thus giving rise to an increased hydration.

As with $Ln_2 \cdot 1 \cdot Re(CO)_3 Cl$, the $[Ln_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ complexes all exhibit shorter luminescence lifetimes for the ³MLCT state when Ln = Yb or Nd compared to the lutetium complex, and the efficiency of energy transfer is (once again) greater in H₂O than in D₂O. In H₂O, the efficiency of energy transfer to neodymium in $[Nd_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ can be calculated to be 0.72, which is comparable to the efficiency of energy transfer in Nd₂·1·Re(CO)₃Cl. However, energy transfer to ytterbium in $[Yb_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ ($\phi_{ent} = 0.3$) is much less efficient than the same process in Yb₂·1·Re(CO)₃Cl, despite the much greater spectral overlap between the ³MLCT state of the ruthenium chromophore and the ²F_{5/2} state of ytterbium. This dramatic change bears out the change in structure implied by the calculation of q and shows, once again, the importance of considering the molecule or ion as a whole when describing its properties.

DOSY spectra and theoretical calculations

In order to investigate the possible formation of aggregates in the Ln_2 ·1 complexes, we have performed DOSY (diffusion-

ordered NMR spectroscopy) experiments on the diamagnetic analogues $Lu_2 \cdot 1$ and $[Lu_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$. These experiments provided diffusion coefficients D at 298 K for the Lu_2 ·1 and $[Lu_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ systems amounting to 1.78×10^{-10} and 2.31 $\times 10^{-10}$ m² s⁻¹. These data imply that the $[Lu_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+1}$ complex diffuses faster in solution than the $Lu_2 \cdot 1$ one, in line with the formation of aggregates in solution in the latter case. These self-diffusion coefficients depend on the solution viscosity η , the van der Waals radius of the complex a, and a translational microviscosity factor that accounts for the discrete nature of the solution through the Stokes-Einstein equation for translation.³⁷ The Stokes–Einstein equation assumes a spherical shape for the molecule being measured by diffusion. Assuming spherical volumes for Lu₂·1 and $[Lu_2 \cdot \mathbf{1} \cdot Ru(Bpy)_2]^{2+}$, the Stokes–Einstein equation provides hydrodynamic radii of 7.7 and 10.0 Å for $[Lu_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ and $Lu_2 \cdot 1$, respectively. A hydrodynamic radius of 5.4 Å has been recently determined from diffusion measurements for a mononuclear Lu complex.38 Thus, the hydrodynamic radius determined for $[Lu_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ is compatible with the presence of discrete complexes in solution. In the case of $Lu_2 \cdot 1$ the diffusion coefficient suggests the formation of relatively small aggregates, or the formation of larger aggregates in equilibrium with discrete $Lu_2 \cdot 1$ entities.

Attempts to grow single crystals of the homo- and heterobimetallic complexes presented in this work were unsuccessful. Furthermore, a striking feature of the family of complexes presented here is the low hydration numbers determined for $Yb_2 \cdot 1$ and $Yb_2 \cdot 1 \cdot Re(CO)_3 Cl$ complexes in comparison to the $[Yb_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ one. Thus, aiming to obtain information concerning the structure of these complexes we turned our attention to theory. Due to the relatively large size of the $[Yb_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ complex we performed theoretical calculations at the HF level. The lanthanide was described by using the quasi-relativistic effective core potential (ECP) of Dolg et al.³⁹ and the related [5s4p3d]–GTO valence basis set. This ECP includes the 4f electrons in the core, as they are not expected to provide a substantial contribution to chemical bonding. For the ligand atoms and Ru we used the standard 3-21G and LanL2DZ basis sets, respectively. Although small, HF calculations employing the 3-21G basis set in combination with the f-in-core ECP of Dolg were shown to provide molecular geometries of Ln^{III} DOTA-like complexes in good agreement with the experimental structures observed by single-crystal X-ray diffraction studies.⁴⁰ Given the hydration number determined for $[Yb_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ (1.3, Table 2), calculations were performed on the $[Yb_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+} \cdot 2H_2O$ system, which includes one inner-sphere water molecule for each of the two Yb centers. The minimum energy conformation obtained from these calculations was then fully optimized by using DFT calculations (B3LYP model) and a better basis set for the ligand atoms (6-31G(d)).

The optimized geometry obtained for the $[Yb_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+}$ complex shows a nearly undistorted C_2 symmetry, with the symmetry axis bisecting the 4,4'-substituted bipyridyl unit and containing the Ru^{II} ion (Fig. 6). The average Yb–O_{carboxylate} and

Yb–N distances amount to 2.21 and 2.70 Å, respectively, while the calculated Yb–O_{water} distance is 2.41 Å. These distances are in excellent agreement with those observed in the solid state for the Lu^{III}–DOTA complex.⁴¹ The calculated Ru–N distances (average at 2.116 Å) are very close to those observed in the solid state for [Ru(Bpy)₃]²⁺ (2.056 Å).⁴²

Theoretical calculations were also performed on the $Yb_2 \cdot 1 \cdot 2H_2O$ system. The minimum energy geometry obtained (Fig. S4, ESI[‡]) presents two nine-coordinated Yb^{III} ions, which are bound to the four nitrogen atoms of the cycle *n* unit, three oxygen atoms of the acetate groups of the DO3A cage, one inner-sphere water molecule, and an oxygen atom of an acetate group of the neighboring DO3A that is bridging the two metal ions. These results suggest that the low q values determined for this compound in comparison to other mononuclear Ln^{III}-DO3A complexes may be related to the presence of similar intra- or inter-molecular bridging carboxylate groups. A similar effect is probably responsible for the low q values determined for Yb₂·1·Re(CO)₃Cl. Thus, our DFT calculations provide additional support to the formation of aggregates in solution, in agreement with the NMR data presented above. In the case of $\left[Ln_2{\cdot}{\bf 1}{\cdot}Ru(Bpy)_2\right]^{2+}$ complexes, the presence of a bulkier $[Ru(Bpy)_2]^{2+}$ unit, together with the higher positive charge of the complex, probably disrupts the formation of acetate bridging units.



Fig. 6 Optimized geometry of $[Yb_2 \cdot 1 \cdot Ru(Bpy)_2]^{2+} \cdot 2H_2O$ obtained from DFT calculations (B3LYP). Hydrogen atoms are omitted for the sake of simplicity.

Anion binding studies

The unusually low values of q observed for the Ln₂·1 complexes, related to the presence of either inter- or intramolecular carboxylate bridging groups, lead us to believe that anion binding in these systems should be considerably inhibited in comparison to mononuclear DO3A derivatives. Thus, the interaction of $Eu_2 \cdot 1$ with selected anions (acetate, lactate, glutamate, citrate, carbonate and phosphate) was monitored spectrophotometrically by following the changes in the emission spectra upon addition of anions (as their sodium salts) in a 0.1 M TRIS buffered aqueous solution (pH = 7.4). In each case, the addition of anions gave rise to significant changes in the emission spectral patterns together with an increase of the overall emission intensity. This is in line with anion coordination to the Eu^{III} ion with replacement of inner-sphere water molecules and/or carboxylate bridging groups. Following procedures of the literature,43 these spectral changes were fitted, using the non-linear regression analysis program SPECFIT,44,45 with two distinct models: the first one corresponds to the formation of a 1:1 complex to anion species, while the second one takes into account the formation of an additional 1:2 species. Results obtained from the second model have been reported only when a significant improvement of the quality of the fitting was observed in comparison to the 1:1 binding model. It is worth mentioning that anion addition did not provoke significant changes in the absorption spectrum of the complex.

Addition of acetate, lactate or glutamate to solutions of Eu₂·1 led to an increase of the overall emission intensity, together with significant changes in the ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_4$ transitions, pointing to the formation of new species in solution with different coordination environments around the Eu^{III} cation.⁴⁶ Moreover, noticeable changes were observed in the ${}^5D_0 \rightarrow {}^7F_0$ transition, with its maximum shifting from 578.5 nm to *ca.* 579.0 nm and the formation of an isosbestic point, indicative of the presence of a 1:1 species in solution. These spectral changes could be unambiguously fitted to a 1:1 binding model, which provided the association constants shown in Table 3. Addition of citrate and carbonate provoked also significant changes in the splitting of the ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_4$ transitions, as well as a shift (~0.5 nm) of the maximum due to the ${}^5D_0 \rightarrow {}^7F_0$ transition to longer

Table 3 Association constants for the interaction of Eu₂·1 with selected anions in aqueous solution (pH 7.4, 0.1 M TRIS/HCI) and photophysical properties of the ternary adducts formed

	$\log K_{11}$	$\log K_{12}$	$\phi_{ m H_{2}O}^{1:1}{}^{a}$ %	$\phi^{2:1}_{ m H_2O}{}^a$ %	$\left(\frac{I_{0\to 2}}{I_{0\to 1}}\right)_{1:1}$	$\left(\frac{I_{0\to2}}{I_{0\to1}}\right)_{2:1}$	$ au_{\mathrm{H_{2}O}}{}^{b}\left(\mu\mathrm{s}\right)$
Acetate	1.573(9)	_	23.5	_	4.5		773
Carbonate	2.90(3)	2.86(3)	14.3	23.5	4.1	4.9	820
Citrate	2.82(5)	1.64(8)	14.3	24.4	7.1	4.1	910
Glutamate	1.72(2)		19.3	_	4.5		721
Lactate	2.76(2)		16.0	_	3.5		824
Phosphate	2.28(3)		10.9	—	2.9		674

 ${}^{a}\lambda_{exc} = 286 \text{ nm}. {}^{b}[\text{Anion}] > 2300 [\text{Eu}_{2} \cdot \mathbf{1}].$



Fig. 7 Top: Changes observed in the emission spectrum of Eu₂·1 ($\lambda_{exc} = 286 \text{ nm}, 10^{-5} \text{ M}$ in 0.1 M TRIS buffer, pH 7.4) upon addition of aliquots of a solution of sodium hydrogen carbonate (*ca.* 0.2 M in 0.1 M TRIS buffer, pH 7.4; 0–3500 equiv.). Inset: Detail of the spectral changes observed for the ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{0}$ transition upon anion addition. Bottom: Emission spectra of 1:0 (green), 1:1 (blue) and 1:2 (red) species (Eu:anion) as calculated from the fitting of the titration data.

wavelengths (Fig. 7). However, for these anions the titration data could not be fitted satisfactorily with a 1:1 binding model, while considering a model involving the formation of both 1:1 and 1:2 (Eu^{III} : anion) ternary species provided good fits of the experimental data with the association constants listed in Table 3.

The addition of sodium hydrogen phosphate resulted in a modest increase of the emission intensity at 616 nm (Fig. 8). However, no changes were observed in the position of the maximum of the ${}^5D_0 \rightarrow {}^7F_0$ transition, while two isosbestic points were observed in the ${}^5D_0 \rightarrow {}^7F_1$ transition at 587 nm and 591 nm. Indeed, whereas only two components were observed in the ${}^5D_0 \rightarrow {}^7F_1$ transition of Eu₂·1 (with their maxima at 590 nm and 596 nm), the ternary adduct formed upon interaction with phosphates displayed three components centred at 587, 592.5 and 595.5 nm. This emission pattern strongly suggests the formation of a complex species with low local symmetry around the Eu^{III} ion.

The analysis of the titration data allowed the calculation of the emission spectra of the ternary complexes with each



Fig. 8 Changes observed in the emission spectrum of Eu₂·1 (10⁻⁵ M in 0.1 M TRIS buffer, pH 7.4, λ_{exc} = 286 nm) upon addition of aliquots of a solution of phosphate (*ca.* 0.2 M in 0.1 M TRIS buffer, pH 7.4). Inset: Detail of the spectral changes observed for the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition upon anion addition.

anion. In those cases where the spectral changes were fitted considering the formation of 1:1 and 1:2 species (carbonate and citrate) the spectra of the two ternary complexes were obtained. From these calculated spectra we estimated the emission quantum yields of the ternary adducts, which range between 10.9 and 24% for the 1:1 complexes, and are close to 24% for the 1:2 species formed upon carbonate or citrate binding. These values are clearly higher than that determined for the parent complex (8.4%), which can be attributed to the replacement of inner-sphere water molecules upon anion binding. This is confirmed with the emission lifetimes measured at the end of each titration, which vary from 674 for phosphate to 910 µs for citrate (560 µs for the unbound complex). These lifetimes are actually weighted values of the emission lifetimes of each species present in solution, and therefore do not correspond to the lifetimes of the ternary complexes, as in most cases anion binding is rather weak and at the end of the titration the Eu^{III} complex is not in the fully bound form. Nevertheless, the lifetimes determined at the end of each titration are longer than that determined for the unbound Eu^{III} complex (560 µs), thereby confirming the replacement of inner-sphere water molecules by the anion in the ternary complexes.

The reconstituted luminescence spectra of the ternary complexes show that the relative intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transitions also increases upon anion binding, with the noticeable exception of phosphate (Table 3). It has been demonstrated that the nature and polarizability of the group occupying a position on or close to the principal axis of the complex affects the relative intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition.^{46,47} The more polarizable the axial donor atom is, the greater the relative intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ emission band. Thus, the increase of the relative intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition upon anion binding is attributed to the substitution of a coordinated water molecule by a more polarizable anion.

The binding constant shown in Table 3 indicates a relatively weak binding of the investigated anions to the $Eu_2 \cdot 1$ complex.

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The binding strength of the anions investigated varies in the following order: carbonate ~ citrate > lactate > phosphate > glutamate > acetate. However, no particularly high selectivity was observed for any of these anions.

Conclusions

Introduction of $[Ru(Bpy)_2]^{2+}$ and $Re(CO)_3Cl$ chromophores into $Ln_2 \cdot 1$ systems provides an efficient sensitization of lanthanide luminescence in the NIR region. The ³MLCT state centered in the d metals moiety states are clearly implicated in the energy transfer process, even for the ytterbium complex. We have previously observed that sensitization of ytterbium by similar chromophores does not implicate the triplet state when the chromophore is held at a greater distance from the metal centre. It is clear that the whole structure of the complex, and not just the nature of the donor and acceptor must play a key role in determining the pathway for sensitization.

The compact structure of these complexes also exerts considerable control over their behaviour, with differences in the bridging substituent giving rise to profound changes in hydration at the lanthanide centres. When not coordinated, the central Bpy core allows for some flexibility that resulted in the formation of carboxylate bridging units, as evidenced by the rather low hydration numbers. Whether this is due to interactions between the coordinating units of the two vicinal lanthanide cations or to more complicated interactions such as aggregation is not yet clear. Whatever the interaction, the income of added anions did not result in significant binding as demonstrated by the fluorescence titrations. In contrast, the coordination of the Ru(Bpy)₂ units are characterized by a large increase of the hydration numbers, possibly as a result of the breaking of the presumed interactions, resulting in two independent Ln(DO3A) units.

Experimental

General

Elemental analyses were carried out on a ThermoQuest Flash 1112 elemental analyzer. ESI-TOF mass spectra were recorded using an LC-Q-q-TOF Applied Biosystems QSTAR Elite spectrometer in the positive mode. IR spectra were recorded using a Bruker Vector 22 spectrophotometer equipped with a Golden Gate Attenuated Total Reflectance (ATR) accessory (Specac). ¹H and ¹³C NMR spectra were run on a Bruker Avance 500 spectrometer equipped with a dual cryoprobe or on a Bruker Avance 300 spectrometer. Chemical shifts are reported in δ values. For measurements in D₂O *tert*-butyl alcohol was used as an internal standard with the methyl signal calibrated at $\delta = 1.2$ (¹H) and 31.2 ppm (¹³C). Diffusion coefficients from DOSY experiments were referenced by using a value of 1.92×10^{-9} m² s⁻¹ for the DHO signal in D₂O at 298 K.⁴⁸

Photophysical measurements on Nd, Yb and Lu complexes

All luminescence spectra in the visible region of the spectrum were obtained using a Perkin Elmer LS55 fluorimeter.

Luminescence measurements in the NIR region were conducted on a custom-made set-up that uses excitation by a pulsed nitrogen laser (PTI-3301, 337 nm). Luminescence from the sample was collected at right angles to the incident beam and focused onto the slits of a monochromator (PTI-120). The growth and the decay of the luminescence at selected wavelengths were detected by using a germanium photodiode (Edinburgh Instruments, EI-P) and were recorded using a digital oscilloscope (Tektronix TDS220) before being transferred to a PC for analysis. 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-centred luminescence, using a spreadsheet running in Microsoft Excel. Time-resolved emission spectra (TRES) in the NIR region were obtained by measuring the growth and decay of the luminescence at each of a series of wavelengths.

Time-resolved luminescence measurements in the visible part of the spectrum were obtained using an Edinburgh Instruments mini-Tau system through time-correlated single photon counting. Lifetimes were obtained by either tail fit on the data obtained or by reconvoluting the observed decay with the instrument response signal. In both cases the quality of fit was judged by minimization of reduced chi-squared and residuals squared.

Photophysical measurements on Eu and Tb complexes

UV-visible absorption spectra were recorded on a Specord 205 (Analytik Jena) spectrometer. Emission and excitation spectra in the UV-vis range were recorded in a 1 cm path length quartz Suprasil cell by using a Fluorolog® 3-22 spectrometer from Horiba Jobin Yvon working with a 450 W Xe lamp in the steady state mode or with a pulsed Xe lamp (fwhh < 4 μ s) for time-resolved luminescence experiments. Detection was performed with a Hamamatsu R928 photomultiplier. All spectra were corrected for the instrumental functions. When necessary, a 399 nm cut-off filter was used to eliminate the second generation harmonic artefacts. Phosphorescence lifetimes were measured on the same instrument (working in the phosphorescence mode), with a 50 µs delay time and a 100 ms integration window. The ruthenium emission lifetimes were measured in time-resolved mode, which were made by monitoring the decay at the maxima of the emission spectra using a Jobin Yvon FluoroHub single photon counting controller, fitted with a 303 nm Jobin Yvon NanoLED. The decays were analyzed with DataStation v2.4 or with the FAST program from Edinburgh Instruments. Luminescence quantum yields were measured according to conventional procedures, with diluted solutions (optical density < 0.05), using [Ru(Bpy)₃]Cl₂ in non-degassed water ($\phi = 4.0\%$),²⁶ or rhodamine 6G in water $(\phi = 76.0\%)^{27}$ as references. Estimated errors are ±15%.

Hydrations numbers, q, were obtained using eqn (4),²⁹ where $\tau_{\rm H_2O}$ and $\tau_{\rm D_2O}$ respectively refer to the measured luminescence decay lifetimes (in ms) in water and deuterated water, using $A_{\rm Eu} = 1.2$ and $B_{\rm Eu} = 0.25$ for Eu and $A_{\rm Tb} = 5.0$ and $B_{\rm Tb} = 0.06$ for Tb.

$$q = A_{\rm Ln} (1/\tau_{\rm H_2O} - 1/\tau_{\rm D_2O} - B_{\rm Ln})$$
(4)

Anion binding studies were performed by following the changes of the emission spectra of the Eu₂·1 complex. In a typical experiment, a 0.1 M TRIS buffered (pH 7.4) 10^{-5} M solution of the complex was titrated with *ca.* 0.2 M solution of the corresponding anion (as the sodium salt) in 0.1 M TRIS (pH 7.4). After the addition of each aliquot, the absorption and emission spectra of the solution were recorded. The factor analysis and the mathematical treatment of the spectrophotometric data were performed with the SPECFIT program.^{44,45} The models used consisted in the fitting of the equilibria (5) (*model 1*) or (5) and (6) (*model 2*), to which was added protonation equilibria corresponding to the acid-base reactions of the anion potentially occurring around pH 7.0 (5.0 < pK_a < 9.0). Constants corresponding to the successive formation are reported.

$$[\operatorname{Eu}_{2}\operatorname{L}] + \operatorname{X}^{n-} \leftrightarrow [\operatorname{Eu}_{2}\operatorname{LX}]^{n-} \quad \beta_{11} = \frac{[\operatorname{Eu}_{2}\operatorname{LX}]}{[\operatorname{Eu}_{2}\operatorname{L}][\operatorname{X}]} \tag{5}$$

$$[\mathrm{E}\mathbf{u}_{2}\mathrm{L}] + 2\mathrm{X}^{n-} \leftrightarrow [\mathrm{E}\mathbf{u}_{2}\mathrm{L}\mathrm{X}_{2}]^{2n-} \quad \beta_{12} = \frac{[\mathrm{E}\mathbf{u}_{2}\mathrm{L}\mathrm{X}_{2}]}{[\mathrm{E}\mathbf{u}_{2}\mathrm{L}][\mathrm{X}]^{2}} \tag{6}$$

Synthesis

All new compounds were found to be air-stable both in the solid state and in the solution. Inert-atmosphere techniques were utilized however due to the hygroscopic nature of the lanthanide complexes and the pro-ligand.

All NMR spectra were run at ambient probe temperature, unless otherwise stated.

5,5'-Bis(bromomethyl)-2,2'-bipyridine (3)

Bis(hydroxymethyl) bipyridine⁴⁹ (0.450 g, 2.08 mmol) was dissolved in a mixture of 48% HBr (20 mL) and concentrated H₂SO₄ (6.7 mL). The resulting solution was heated to reflux for 6 hours and then allowed to cool to room temperature. To this solution, H₂O (40 mL) was added and the solution neutralised with 1 M NaOH solution and the resulting precipitate filtered, washed with H₂O and dried. The product was then dissolved in CHCl₃ and filtered. The solvent was removed under reduced pressure and dissolved in Et₂O. This was filtered and the solution was evaporated to dryness yielding a white solid (0.300 g, 42%). Found: C, 42.68; H, 2.86; N, 7.95; Br, 45.81%. Calc. for C₁₂H₁₀N₂Br₂: C, 42.13; H, 2.93; N, 8.19; Br, 46.75%. $\delta_{\rm H}$ (CDCl₃, 25 °C) 8.71 (2H, d, ³J_{HH} = 4.98 Hz), 8.48 (2H, s), 7.41 (2H, dd, ³J_{HH} = 4.98, ⁴J_{HH} = 1.76 Hz) and 4.53 (4H, s) ppm.

Cis-Ru(Bpy)₂Cl₂·2H₂O

Following the literature procedure, a solution of $RuCl_3 \cdot 3H_2O$ (1.95 g, 7.46 mmol), 2,2'-bipyridine (2.35 g, 15.0 mmol) and

LiCl (2.10 g, 49.5 mmol) in DMF (15 ml) was heated under reflux in a N₂ atmosphere for 6 hours. The dark purple reaction mixture was cooled to room temperature and H₂O (25 ml) was added to produce a precipitate. This was cooled to 0 °C for 1 hour and the crude solid was collected by filtration and washed several times with H₂O (5 × 10 ml). This was dried to yield a dark brown solid. The product was dissolved in CH₂Cl₂ and 2% MeOH and passed through an alumina column (CH₂Cl₂, 2% MeOH). The solvent was removed by rotary evaporation and the dry black solid was mobilized by addition of Et₂O and collected by filtration. This was air dried and isolated as a black solid (2.26 g, 58%). $\delta_{\rm H}$ (300 MHz, DMSO, 25 °C) 9.96 (2H, m), 8.70 (2H, d, ${}^{3}_{J\rm HH}$ = 7.6 Hz), 8.56 (2H, d, ${}^{3}_{J\rm HH}$ = 7.9 Hz), 8.13 (2H, t, ${}^{3}_{J\rm HH}$ = 7.8 Hz), 7.80 (2H, m), 7.71 (2H, t, ${}^{3}_{J\rm HH}$ = 7.3 Hz), 7.49 (2H, m) and 7.18 (2H, m) ppm.

{4,7-Bis-*tert*-butoxycarbonylmethyl-10-[4'-(4,7,10-tris-*tert*butoxycarbonylmethyl-1,4,7,10-tetraaza-cyclododec-1-yl)-[2,2']bipyridinyl-4-yl]-1,4,7,10-tetraaza-cyclododec-1-yl}-acetic acid *tert*-butyl ester (4)

1,4,7-Tris(tert-butoxycarbonylmethyl)-1,4,7,10-tetraazacyclododecane, hydrobromide salt (2) (0.174 g, 0.290 mmol) was dissolved in MeCN (2 mL) and Cs₂CO₃ (0.190 g, 0.583 mmol) was added. To this stirred solution, 4,4'-bis(bromomethyl)-2,2'bipyridine (3) (0.05 g, 0.146 mmol) was added, and the mixture was heated to reflux for 3 days. The solvent was then removed and the crude residue was re-dissolved in CH₂Cl₂. This was washed with H_2O (3 × 50 mL), and the CH_2Cl_2 layer collected and the solvent removed. The product was purified by column chromatography on alumina (CH₂Cl₂/MeOH gradient 0-2%). This gave a white solid (0.070 g, 40%). Found: C, 62.17; H, 8.89; N, 11.33; Na, 0.46%. Calc. for C₆₄H₁₀₉N₁₀O₁₂·0.25NaBr: C, 62.49; H, 8.85; N, 11.39; Na, 0.37%. $\delta_{\rm H}$ (CDCl₃, 25 °C) 8.53 (2H, d, ${}^{3}J_{\rm HH}$ = 5.2 Hz), 8.20 (2H, s), 7.48 (2H, d, ${}^{3}J_{HH}$ = 5.2 Hz, ${}^{4}J_{HH}$ = 1.2 Hz), 3.57 (4H, s), 3.21 (4H, s), 3.15 (8H, s), 2.78 (24H, br s), 2.57 (8H, m), 1.39 (22H, s) and 1.34 (32H, s) ppm. δ_c (CDCl₃, 25 °C) 171.3, 171.1, 156.0, 150.0, 149.0, 124.0, 121.0, 80.7, 80.6, 59.3, 56.5, 56.4, 53.4, 52.5, 52.4, 52.3, 51.9, 28.3 and 28.7 ppm. $\nu_{\text{max}}/\text{cm}^{-1}$ 2973 and 2813 (CH), 1727 and 1598 (CO). ES-MS m/z 606 $[M + 2H]^{2+}$, 1210 [M]⁺.

$\label{eq:constraint} $$ \{4,10\mbox{-}ls-carboxymethyl-7-[4'-(4,7,10\mbox{-}tris-carboxymethyl-1,4,7,10\mbox{-}tetraaza-cyclododec-1-ylmethyl}]-[2,2'] bipyridinyl-5-ylmethyl]-1,4,7,10\mbox{-}tetraaza-cyclododec-1-yl}-acetic acid (H_6\cdot1) $$$

The bipyridine cyclen triester derivative (4) (0.200 g, 0.162 mmol) was dissolved in CH₂Cl₂ (5 ml) and TFA (5 ml) was added drop wise and stirred for 24 hours. All volatiles were removed under reduced pressure and the residue washed and evaporated with CH₂Cl₂ (5 × 10 mL) and MeOH (5 × 10 mL). The residue was then dissolved in the minimum amount of MeOH and Et₂O added to afford a precipitate. The solid was collected using a Schlenk filter apparatus to yield a hygroscopic pink solid (0.130 g, 87%). $\delta_{\rm H}$ (D₂O, 25 °C) 8.65 (2H, d, ³J_{HH} = 5.3 Hz), 8.37 (2H, s), 7.94 (2H, d, ³J_{HH} = 5.2 Hz) and 4.3–2.9 (48H, m) ppm. $\nu_{\rm max}/\rm cm^{-1}$ 1668 (CO). MALDI-MS

(α -MeOH) m/z 872 [M]⁺. UV-vis (H₂O) λ_{max} (ε /mol⁻¹ dm³ cm⁻¹) = 294 nm (8300).

$\label{eq:constraint} $$ \{4,10\mbox{-}Bis\mbox{-}carboxymethyl-7-[4'-(4,7,10\mbox{-}tris\mbox{-}carboxymethyl-1,4,7,10\mbox{-}tetraaza\mbox{-}cycloddec\mbox{-}1\mbox{-}ylmethyl]\mbox{-}[2,2']bipyridinyl-5-ylmethyl]\mbox{-}1,4,7,10\mbox{-}tetraaza\mbox{-}cycloddec\mbox{-}1\mbox{-}yl\mbox{-}acetic acid hexatrifluoroacetate} (H_6\mbox{-}1\mbox{-}6\mbox{-}F_3\mbox{-}COOH) $$$

A solution of compound 4·2CH₂Cl₂ (0.510 g, 0.370 mmol) in a 1:1 CH₂Cl₂: TFA mixture (10 mL) was stirred at room temperature for 24 h. The mixture was concentrated to dryness and the resulting oil was dissolved in methanol (~1 mL). Addition of diethyl ether resulted in the formation of a pale pink solid that was collected by filtration and dried under vacuum. (0.420 g, 70%). Found: C, 38.49; H, 4.96; N, 8.60%. Calc. for C₄₀H₆₀N₁₀O₁₂·6CF₃COOH·3H₂O: C, 38.76; H, 4.50; N, 8.69%. $\delta_{\rm H}$ (500 MHz, D₂O, 25 °C, ^tBuOH, pD = 1.8) 8.71 (2H, d, ³*J* = 5.5 Hz), 8.44 (2H, s), 7.99 (2H, d, ³*J* = 5.5 Hz) and 4.09–2.84 (48H, m) ppm. $\delta_{\rm C}$ (125.8 MHz, D₂O, 25 °C, ^tBuOH, pD = 1.8) 176.5, 176.0, 171.0, 155.7, 149.2, 147.7, 129.9, 127.9, 67.6, 58.3, 57.3, 57.1, 55.2, 54.7, 53.4, 52.1, 50.7, 49.8, 49.3 and 43.9 ppm. ES-MS *m*/*z* 873 [M]⁺. $\nu_{\rm max}$ /cm⁻¹ 3417 (OH), 1669, 1634 and 1601 (CO), 1461 and 1391 (π(ArH)).

{4,10-Bis-carboxymethyl-7-[4'-(4,7,10-tris-carboxymethyl-1,4,7,10-tetraaza-cyclododec-1-ylmethyl)-[2,2']bipyridinyl-4ylmethyl]-1,4,7,10-tetraaza-cyclododec-1-yl}-acetic acid ytterbium complex (Yb₂·1)

The deprotected cyclen derivative (H₆·1) (0.050 g, 0.057 mmol) and Yb(OTf)₃ (0.036 g, 0.057 mmol) were dissolved in MeOH (15 mL) and heated to 50 °C for 24 hours. The solution was then evaporated to dryness, redissolved in MeOH and Et₂O was layered on top and the solution left at 0 °C overnight. The resultant precipitate was filtered using a Schlenk apparatus (0.061 g, 88%). $\delta_{\rm H}$ (300 MHz, D₂O, 25 °C, ^{*t*}BuOH, pD = 7.0) 134.3, 126.4, 119.3, 109.9, 40.0, 30.3, 24.6, 14.5, 11.3, -0.6, -3.6, -10.1, -14.4, -57.7, -61.2, -68.0, -70.8, -76.2, -80.0 and -97.8 ppm. $\nu_{\rm max}/\rm{cm}^{-1}$ 1596 (CO). MALDI-MS (α-MeOH) m/z 1236 [M + Na]⁺. HRES-MS m/z 608.1420. Calc. for [M + 2H]²⁺ 608.1422. UV-vis (H₂O) $\lambda_{\rm max}$ ($\varepsilon/\rm{mol}^{-1}$ dm³ cm⁻¹) = 290 nm (8500). Emission: $\lambda_{\rm em}$ = 980 nm, $\tau_{\rm D_2O}$ = 4870 ns, $\tau_{\rm H_2O}$ = 2135 ns, q = 0.2.

{4,10-Bis-carboxymethyl-7-[4'-(4,7,10-tris-carboxymethyl-1,4,7,10-tetraaza-cyclododec-1-ylmethyl)-[2,2']bipyridinyl-4ylmethyl]-1,4,7,10-tetraaza-cyclododec-1-yl}-acetic acid neodymium complex (Nd₂·1)

Prepared by an analogous procedure using Nd(OTf)₃ (0.034 g, 0.057 mmol). The product was isolated as a pink solid (0.060 g, 91%). $\nu_{\text{max}}/\text{cm}^{-1}$ 1584 (CO). MALDI-MS (α -MeOH) m/z 1154 [M - H]⁺. UV-vis (H₂O) λ_{max} ($\varepsilon/\text{mol}^{-1}$ dm³ cm⁻¹) = 291 nm (9000). Emission: $\lambda_{\text{em}} = 1054$ nm, $\tau_{\text{D}_2\text{O}} = 408$ ns, $\tau_{\text{H}_2\text{O}} = 200$ ns, q = 0.3.

$\label{eq:constraint} $$ \{4,10\mbox{-}Bis\mbox{-}carboxymethyl-7-[4'-(4,7,10\mbox{-}tris\mbox{-}carboxymethyl-1,4,7,10\mbox{-}tetraaza\mbox{-}cyclododec\mbox{-}1\mbox{-}ylmethyl]\mbox{-}[2,2']bipyridinyl-4-ylmethyl]\mbox{-}1,4,7,10\mbox{-}tetraaza\mbox{-}cyclododec\mbox{-}1\mbox{-}yl\mbox{-}acetic acid lutetium complex (Lu_2\mbox{-}1) $$$

Prepared by an analogous procedure using Lu(OTf)₃ (0.036 g, 0.057 mmol). The product was isolated as a pink solid (0.063 g, 91%). $\delta_{\rm H}$ (500 MHz, D₂O, 25 °C, ^{*i*}BuOH, pD = 7.0) 8.65 (2H, m), 7.98 (2H, m), 7.48 (2H, m) and 4.1–2.8 (48H, m) ppm. $\delta_{\rm C}$ (125.8 MHz, D₂O, 25 °C, ^{*i*}BuOH, pD = 7.0) 183.0, 182.5, 181.4, 156.8, 150.9, 143.8, 129.6, 127.2, 67.9, 67.3, 58.0, 57.8, 56.9, 56.8, 56.4, 55.0, 53.7 and 47.3 ppm. $\nu_{\rm max}/{\rm cm}^{-1}$ 1596 (CO). MALDI-MS (α -MeOH) m/z 1217 [M]⁺. HRES-MS m/z 609.1426. Calc. for [M + 2H]²⁺ 609.1441. UV-vis (H₂O) $\lambda_{\rm max}$ (ε /mol⁻¹ dm³ cm⁻¹) = 290 nm (11 000).

$\label{eq:4.10-Bis-carboxymethyl-7-[4'-(4,7,10-tris-carboxymethyl-1,4,7,10-tetraaza-cyclododec-1-ylmethyl)-[2,2']bipyridinyl-4-ylmethyl]-1,4,7,10-tetraaza-cyclododec-1-yl}-acetic acid europium complex hexahydrate (Eu_2·1·6H_2O)$

A mixture of H₆·1·6CF₃COOH (0.100 g, 0.062 mmol), triethylamine (0.075 g, 0.744 mmol) and Eu(OTf)₃ (0.074 g, 0.124 mmol) in 2-propanol (10 mL) was heated to reflux for 24 h. The reaction was allowed to cool to room temperature, which resulted in the formation of a pink solid. This was isolated by filtration, washed with 2-propanol and diethyl ether, and dried under vacuum. A second portion of the complex was obtained by concentration of the filtrate to about a half of the initial volume and cooling the mixture to 4 °C for several days. The solid formed was again isolated by filtration, washed with 2-propanol and diethyl ether, and dried under vacuum (0.055 g, 69%). Found: C, 37.73; H, 5.35; N, 10.72%. Calc. for C₄₀H₅₄Eu₂N₁₀O₁₂·6H₂O: C, 37.56; H, 5.20; N, 10.95%. HRES-MS m/z 587.1248. Calc. for $[M + 2H]^{2+}$ 587.1246. $\nu_{max}/$ cm⁻¹ 1587 (CO). UV-vis (H₂O) λ_{max} (ϵ/mol^{-1} dm³ cm⁻¹) = 286 nm (11 700). Emission: λ_{em} = 616 nm, $\tau_{D,O}$ = 1680 µs, τ_{H_2O} $= 540 \ \mu s, q = 0.8.$

{4,10-Bis-carboxymethyl-7-[4'-(4,7,10-tris-carboxymethyl-1,4,7,10-tetraaza-cyclododec-1-ylmethyl)-[2,2']bipyridinyl-4-ylmethyl]-1,4,7,10-tetraaza-cyclododec-1-yl}-acetic acid terbium complex hexahydrate (Tb₂·1·6H₂O)

Prepared following the same procedure described for the europium analogue using Tb(OTf)₃ (0.075 g, 0.124 mmol) to give 0.059 g of the desired product (74%). Found: C, 36.90; H, 4.92; N, 10.72%. Calc. for C₄₀H₅₄N₁₀O₁₂Tb₂·6H₂O: C, 37.16; H, 5.15; N, 10.83%. HRES-MS *m/z* 593.1281. Calc. for [M + 2H]²⁺ 593.1287. ν_{max} cm⁻¹ 1591 cm⁻¹ (CO). UV-vis (H₂O) λ_{max} (ϵ /mol⁻¹ dm³ cm⁻¹) = 286 nm (13 600). Emission: λ_{em} = 545 nm, $\tau_{\text{D}_2\text{O}}$ = 2540 µs, $\tau_{\text{H}_2\text{O}}$ = 1400 µs, *q* = 1.3.

Rhenium(I) [{4,10-bis-carboxymethyl-7-[4'-(4,7,10-tris-

carboxymethyl-1,4,7,10-tetraaza-cyclododec-1-ylmethyl)-[2,2']bipyridinyl-4-ylmethyl]-1,4,7,10-tetraaza-cyclododec-1-yl}-acetic acid ytterbium complex] tricarbonyl chloride (Yb₂·1·Re(CO)₃Cl) [Re(CO)₅Cl] (0.010 g, 0.027 mmol) was heated to reflux in THF (5 mL) with the Yb^{III} bipyridine complex (0.034 g, 0.027 mmol) for 48 hours, under a N₂ atmosphere. The yellow solution was allowed to cool, and the solvent was removed. The complex was stirred in warm toluene (5 mL) and extracted into H₂O (3 × 5 mL). The H₂O was then removed and the orange solid was recrystallised from MeOH (0.020 g, 49%). ν_{max} /cm⁻¹ 2019, 1900, 1596 (CO). MALDI-MS (α-MeOH) *m*/z 1481 [M - Cl⁻]⁺. UV-vis (H₂O) λ_{max} (ε/mol⁻¹ dm³ cm⁻¹) = 360 nm (1600), 301 nm (9000), 246 nm (12 700). Emission: λ_{max} = 600 nm, lifetime (χ^2): τ_{D_2O} = 8.9 ns (1.4), τ_{H_2O} = 5.5 ns (1.4). λ_{em} = 980 nm, τ_{D_2O} = 5166, 34 ns, τ_{H_2O} = 1410, 43 ns, *q* = 0.4.

$\label{eq:response} \begin{array}{l} Rhenium(l) \left[\{4,10\mbox{-}bis\mbox{-}carboxymethyl\mbox{-}7\mbox{-}[4'\mbox{-}(4,7,10\mbox{-}tris\mbox{-}carboxymethyl\mbox{-}1,4,7,10\mbox{-}tetraaza\mbox{-}cyclododec\mbox{-}1\mbox{-}yl\mbox{-}bipyridinyl\mbox{-}4\mbox{-}ylmethyl\mbox{-}1,4,7,10\mbox{-}tetraaza\mbox{-}cyclododec\mbox{-}1\mbox{-}yl\mbox{-}etric acid neodymium complex} \right] tricarbonyl chloride (Nd_2\mbox{-}1\mbox{-}Re(CO)_3Cl) \end{array}$

Prepared using Nd₂·1 (0.032 g, 0.027 mmol). Product isolated as orange solid (0.022 g, 56%) $\nu_{\text{max}}/\text{cm}^{-1}$ 2015, 1867, 1600 (CO). MALDI-MS (α-MeOH) *m*/z 1428 [M - Cl⁻]⁺. UV-vis (H₂O) λ_{max} (ε/mol⁻¹ dm³ cm⁻¹) = 355 nm (1700), 305 nm (10 600), 254 nm (14 200). Emission: λ_{max} = 600 nm, lifetime (χ^2): $\tau_{\text{D}_2\text{O}}$ = 9.2 ns (1.4), $\tau_{\text{H}_2\text{O}}$ = 5.5 ns (1.5). λ_{em} = 1054 nm, $\tau_{\text{D}_2\text{O}}$ = 303 ns, $\tau_{\text{H}_2\text{O}}$ = 76 ns, λ_{em} = 1340 nm, $\tau_{\text{D}_2\text{O}}$ = 303 ns, *q* = 1.

Rhenium(1) [{4,10-bis-carboxymethyl-7-[4'-(4,7,10-triscarboxymethyl-1,4,7,10-tetraaza-cyclododec-1-ylmethyl)-[2,2']bipyridinyl-4-ylmethyl]-1,4,7,10-tetraaza-cyclododec-1-yl}-acetic acid lutetium complex] tricarbonyl chloride (Lu₂·1·Re(CO)₃Cl)

Prepared using Lu₂·1 (0.034 g, 0.027 mmol). Product isolated as orange solid (0.016 g, 39%). $\nu_{\text{max}}/\text{cm}^{-1}$ 2020, 1899, 1590 (CO). UV-vis (H₂O) $\lambda_{\text{max}}(\epsilon/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}) = 350 \text{ nm}$ (1700), 304 nm (11000), 259 nm (18000). Emission: $\lambda_{\text{max}} = 600 \text{ nm}$, lifetime (χ^2): $\tau_{\text{D}_2\text{O}} = 16.7 \text{ ns}$ (1.6), $\tau_{\text{H}_2\text{O}} = 14.5 \text{ ns}$ (1.7).

cis-[Ruthenium(II) bis(bipyridine)] [{4,10-Bis-carboxymethyl-7-[4'-(4,7,10-tris-carboxymethyl-1,4,7,10-tetraaza-cyclododec-1ylmethyl)-[2,2']bipyridinyl-4-ylmethyl]-1,4,7,10-tetraazacyclododec-1-yl}-acetic acid ytterbium complex](PF₆)₂ [Yb₂·1·Ru(Bpy)₂](PF₆)₂

 $[Ru(Bpy)_2Cl_2]$ (0.013 g, 0.026 mmol) was added to a stirred solution of AgOTf (0.013 g, 0.051 mmol) in acetone under an inert N₂ atmosphere and in the dark. The solution was stirred for 24 hours overnight and filtered through celite to remove AgCl. The dark red solution was evaporated to dryness and redissolved in an EtOH: H₂O (1:1) mix. The Yb^{III} complex (0.026 g, 0.021 mmol) was then added and the solution heated to reflux for a further 24 h and monitored by TLC. The solution was allowed to cool and EtOH was removed and H₂O added. The solution was washed with CH₂Cl₂ and EtOAc to remove any of the ruthenium bipyridine starting material. The H₂O was removed under reduced pressure and the dark orange solid was recrystallised from MeCN/Et₂O to give the desired product (0.022 g, 55%). $\delta_{\rm H}$ (500 MHz, D₂O, 25 °C) 137.9, 128.7, 116.4, 111.1, 41.0, 38.3, 32.2, 31.8, 26.5, -18.8, -62.3, -66.4, -73.7, -76.8, -83.0 and -102.0 ppm. $\nu_{\rm max}/{\rm cm}^{-1}$ 1600 (CO). MALDI-MS (α -MeOH) *m*/*z* 1628 [M]⁺, 1816 [M + α -MeOH]⁺. UV-vis (H₂O) $\lambda_{\rm max}$ (ε /mol⁻¹ dm³ cm⁻¹) = 458 nm (1600), 288 nm (57 000), 245 nm (21 000). Emission: $\lambda_{\rm max}$ = 627 nm, $\tau_{\rm D_2O}$ = 407 ns, $\tau_{\rm H_2O}$ = 280 ns. $\lambda_{\rm em}$ = 980 nm, $\tau_{\rm D_2O}$ = 5638, 408 ns, $\tau_{\rm H_2O}$ = 664, 280 ns, *q* = 1.3.

$[Nd_2 \cdot 1 \cdot Ru(Bpy)_2](PF_6)_2$

Nd₂·1 (0.022 g, 0.019 mmol), [Ru(Bpy)₂Cl₂] (0.012 g, 0.023 mmol) and AgOTf (0.012 g, 0.046 mmol). Product isolated as a dark orange solid (0.019 g, 53%). ν_{max}/cm^{-1} 1602 (CO). MALDI-MS (α-MeOH) m/z 1564 [M]⁺, 1716 [M + OTf]⁺, 1755 [M + α-MeOH]⁺. UV-vis (H₂O) λ_{max} (ε /mol⁻¹ dm³ cm⁻¹) = 461 nm (11 600), 287 nm (66 500), 243 nm (24 000). Emission: λ_{max} = 627 nm, $\tau_{D,O}$ = 311 ns, τ_{H_2O} = 113 ns.

$[Lu_2 \cdot 1 \cdot Ru(Bpy)_2](PF_6)_2$

Lu₂·1 (0.020 g, 0.016 mmol), [Ru(Bpy)₂Cl₂] (0.010 g, 0.020 mmol), AgOTf (0.010 g, 0.040 mmol). Product isolated as a dark orange solid (0.023 g, 53%). $\delta_{\rm H}$ (500 MHz, D₂O, 25 °C, ^tBuOH, pD = 7.0) 8.50 (6H, m), 8.00 (4H, m), 7.77 (6H, m), 7.33 (6H, m) and 4.19–2.55 (48H, m) ppm. $\nu_{\rm max}/{\rm cm^{-1}}$ 1601 (CO). MALDI-MS (α -MeOH) m/z 1630 [M]⁺. UV-vis (H₂O) $\lambda_{\rm max}$ ($\epsilon/{\rm mol^{-1}}$ dm³ cm⁻¹) = 457 nm (11 500), 288 nm (63 000), 245 nm (23 000). Emission: $\lambda_{\rm max}$ = 627 nm, $\tau_{\rm D_2O}$ = 591 ns, $\tau_{\rm H_2O}$ = 401 ns.

cis-[Ruthenium(II) bis(bipyridine)] [{4,10-Bis-carboxymethyl-7-[4'-(4,7,10-tris-carboxymethyl-1,4,7,10-tetraaza-cyclododec-1ylmethyl)-[2,2']bipyridinyl-4-ylmethyl]-1,4,7,10-tetraazacyclododec-1-yl}-acetic acid](CF₃COO)₂ (5)

Compound 4 (0.510 g, 0.370 mmol) and [Ru(Bpy)₂Cl₂] (0.206 g, 0.370 mmol) were dissolved in ethanol (50 mL) and the mixture was heated to reflux under an argon atmosphere over a period of 24 h. Evaporation of the solvent gave a red residue that was purified by column chromatography on SiO₂ with a CH_3CN : saturated aqueous KNO_3 : H_2O (14:2:1) mixture as an eluent. The fractions containing the product were concentrated to eliminate the acetonitrile, and the resulting aqueous solution was extracted with CH_2Cl_2 (5 × 100 mL). Evaporation of the organic extracts gave the tert-butoxycarbonyl protected intermediate as a red solid (0.490 g, 62%). Found: C, 50.64; H, 6.41; N, 9.24%. Calc. for C₈₄H₁₂₄Cl₂N₁₄O₁₂Ru·5CH₂Cl₂: C, 50.46; H, 6.38; N, 9.26%. HRES-MS m/z 811.4243. Calc. for $[M + 2H]^{2+}$ 811.4277. ν_{max}/cm^{-1} 1726 and 1665 (CO), 1462 and 1367 (π(ArH)). δ_H (500 MHz, CDCl₃, 25 °C) 8.68 (4H, m), 8.05 (4H, m), 7.78-7.45 (10H, m), 7.29 (4H, m), 4.50-2.04 (48H, m) and 1.53-1.43 (54H, m) ppm. A solution of the ester derivative (0.490 g, 0.231 mmol) in a 1:1 CH₂Cl₂: TFA mixture (10 mL) was stirred at room temperature for 24 h. The mixture was concentrated to dryness and the resulting oil was dissolved in

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methanol (~1 mL). Addition of diethyl ether resulted in the formation of a pink solid that was collected by filtration and dried under vacuum (0.371 g, 75%). Found: C, 41.80; H, 3.85; N, 9.46%. Calc. for $C_{64}H_{76}F_6N_{14}O_{16}Ru\cdot5CF_3COOH\cdot3H_2O$: C, 41.60; H, 4.10; N, 9.18%. HRES-MS *m*/*z* 643.2394. Calc. for $[M + 2H]^{2+}$ 643.2399. ν_{max}/cm^{-1} 1668 (CO), 1464 and 1421 (π (ArH)). $\delta_{\rm H}$ (D₂O, 500 MHz, 25 °C, ^{*t*}BuOH, pD = 1.6) 8.48 (6H, m), 7.99 (4H, m), 7.76 (6H, m), 7.32 (6H, m) and 4.35–2.84 (48H, m) ppm.

General procedure for the preparation of the [Ln₂·1·Ru(Bpy)₂]-(CF₃SO₃)₂·8H₂O complexes

A mixture of compound 5 (0.100 g, 0.047 mmol), triethylamine (0.052 g, 0.517 mmol) and $Ln(OTf)_3$ (0.094 mmol, Ln = Eu, Tb, Yb or Lu) in methanol (10 mL) was heated to reflux for 24 h under an argon atmosphere. Evaporation of the solvent gave a red oil, and subsequent addition of THF (5 mL) resulted in the formation of a red solid that was isolated by filtration. The solid was then suspended in THF (10 mL) and the mixture stirred at room temperature for 24 h to remove inorganic salts. The solid was isolated by filtration, washed with THF and diethyl ether, and dried under vacuum.

$$\begin{split} & [\text{Eu}_2 \cdot 1 \cdot \text{Ru}(\text{Bpy})_2](\text{CF}_3\text{SO}_3)_2 \cdot 8\text{H}_2\text{O}. \ (0.075 \ \text{g}, \ 79\%). \ \text{Found:} \\ & \text{C}, \ 36.62; \ \text{H}, \ 4.04; \ \text{N}, \ 9.31\%. \ \text{Calc. for} \ \ \text{C}_{62}\text{H}_{86}\text{Eu}_2\text{F}_6\text{N}_{14}\text{O}_{26}\text{RuS}_2\text{:} \\ & \text{C}, \ 36.75; \ \text{H}, \ 4.28; \ \text{N}, \ 9.68\%. \ \text{HRES-MS} \ m/z \ 793.1393. \ \text{Calc. for} \\ & [\text{M} + 2\text{H}]^{2^+} \ 793.1377. \ \nu_{\text{max}}/\text{cm}^{-1} \ 1599 \ (\text{CO}). \ \text{UV-vis} \ (\text{H}_2\text{O}) \ \lambda_{\text{max}} \\ & (\epsilon/\text{mol}^{-1} \ \text{dm}^3 \ \text{cm}^{-1}) = 288 \ (72\ 700), \ 456 \ \text{nm} \ (15\ 000). \ \text{Emission:} \\ & \lambda_{\text{em}} = 545 \ \text{nm}, \ \tau_{\text{D}_2\text{O}} = 1496 \ \mu\text{s}, \ \tau_{\text{H}_2\text{O}} = 373 \ \mu\text{s}, \ q = 2.1. \end{split}$$

$$\label{eq:constraint} \begin{split} & [\text{Tb}_2 \cdot 1 \cdot \text{Ru}(\text{Bpy})_2](\text{CF}_3\text{SO}_3)_2 \cdot 8\text{H}_2\text{O}. \ (0.079 \ \text{g}, \ 82\%). \ \text{Found:} \\ & \text{C}, \ 36.41; \ \text{H}, \ 4.35; \ \text{N}, \ 9.52\%. \ \text{Calc. for} \ \text{C}_{62}\text{H}_{86}\text{F}_6\text{N}_{14}\text{O}_{26}\text{Ru}\text{S}_2\text{Tb}_2: \\ & \text{C}, \ 36.49; \ \text{H}, \ 4.25; \ \text{N}, \ 9.61\%. \ \text{HRES-MS} \ m/z \ 799.1452. \ \text{Calc. for} \\ & [\text{M} + 2\text{H}]^{2^+} \ 799.1418. \ \nu_{\text{max}}/\text{cm}^{-1} \ 1593 \ (\text{CO}). \ \text{UV-vis} \ (\text{H}_2\text{O}) \ \lambda_{\text{max}} \\ & (\varepsilon/\text{mol}^{-1} \ \text{dm}^3 \ \text{cm}^{-1}) = 288 \ (66 \ 500), \ 456 \ \text{nm} \ (14 \ 000). \ \text{Emission:} \\ & \lambda_{\text{em}} = 545 \ \text{nm}, \ \tau_{\text{D}_2\text{O}} = 1199 \ \mu\text{s}, \ \tau_{\text{H}_2\text{O}} = 724 \ \mu\text{s}, \ q = 2.4. \end{split}$$

[Yb₂·1·Ru(Bpy)₂](CF₃SO₃)₂·8H₂O. (0.076 g, 78%). Found: C, 36.26; H, 4.35; N, 9.22%. Calc. for C₆₂H₈₆F₆N₁₄O₂₆RuS₂Yb₂: C, 36.00; H, 4.19; N, 9.48%. HRES-MS *m*/*z* 814.1546. Calc. for [M + 2H]²⁺ 814.1553. ν_{max} /cm⁻¹ 1600 (CO).

 $\label{eq:Lu2-1-Ru(Bpy)_2](CF_3SO_3)_2\cdot8H_2O. (0.085 g, 87\%). Found: C, 36.12; H, 4.07; N, 9.35\%. Calc. for C_{62}H_{86}F_6Lu_2N_{14}O_{26}RuS_2: C, 35.93; H, 4.18; N, 9.46\%. HRES-MS$ *m*/*z* $815.1564. Calc. for <math>[M + 2H]^{2+}$ 815.1572. ν_{max}/cm^{-1} 1600 (CO).

Computational methods

All calculations were performed with the Gaussian 09 package (Revision A.02).⁵⁰ Relativistic effects were considered through the use of relativistic effective core potentials (ECP). Different computational studies on Ln^{III} complexes have shown that the 4f orbitals do not participate in bonding because of their contraction into the core.⁵¹ Thus, full geometry optimizations of the Yb₂·1·2H₂O and [Yb₂·1·Ru(Bpy)₂]²⁺·2H₂O systems were performed *in vacuo* at the HF level by using the ECP of Dolg *et al.* and the related [5s4p3d]-GTO valence basis set for the lanthanides, and the 3-21G basis set for C, H, N and O atoms. The RECP of Dolg *et al.*³⁹ includes 46 + 4fⁿ electrons in the core for the lanthanide, leaving the outermost 11 electrons to

be treated explicitly, in line with the non-participation of 4f electrons in bonding. For the Ru atoms we used the standard LanL2DZ, which includes the ECP of Hay and Wadt and its associated [3s3p2d]-GTO valence basis set for Ru.⁵² The stationary points found on the potential energy surfaces as a result of the geometry optimizations have been tested to represent energy minima rather than saddle points via frequency analysis. The relative free energies of the different conformations calculated for these systems include non-potentialenergy contributions (that is, zero point energy and thermal terms) obtained by frequency analysis. Selected geometries optimized at the HF level were subsequently fully optimized by using hybrid DFT with the B3LYP exchange-correlation functional,⁵³ and the standard 6-31G(d) basis set for the ligand atoms. Due to the considerable computational effort involving the calculation of second derivatives at this level the optimized geometries were not characterized by using frequency analysis.

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