

Luminescent sensing and formation of mixed $f-d$ metal ion complexes between a Eu(III)-cyclen-*phen* conjugate and Cu(II), Fe(II), and Co(II) in buffered aqueous solution†

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The synthesis and photophysical properties of the Eu(III) complex **1.Eu**, based on the use of 1,10-phenanthroline (*phen*) as a combined sensitizing antenna and a transition metal ion coordinating ligand, is described. The long-wavelength Eu(III) emission from this complex was found to be highly pH sensitive, giving rise to a 'off-on-off' pH profile with maximum emission occurring within the physiological pH range. This allowed for the use of **1.Eu** as a luminescent sensor for transition metal ions, where the titration with ions such as Cu(II), Co(II) and Fe(II) gave rise to the formation of mixed $f-d$ nuclear complexes, with concomitant changes in the photophysical properties of **1.Eu**. Here, changes in both the ground and the singlet excited state properties of the *phen* antenna were observed, but the largest changes were observed for the delayed Eu emission, which was fully quenched upon titration with these ions in aqueous pH 7.4 buffered solutions. In comparison, no changes were observed in the Eu(III) emission upon titration with ions such as Zn(II) or group I and II ions. From these changes, we were able to demonstrate the binding stoichiometry and the binding constant for the formation of novel supramolecular complexes between **1.Eu** and Cu(II), Co(II) and Fe(II), which showed that either two or three equivalents of **1.Eu** complexed to each of these transition metal ions, giving rise to the formation either linear $f-d-f$ or branched f_3-d based mixed nuclear complexes in solution.

Introduction

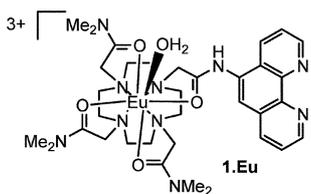
The use of metal-directed synthesis, using transition metal ions (d -block) and organic ligands, has become a very powerful tool in the formation of two- or three-dimensional supramolecular structures.¹⁻⁴ More recently, the use of the f -metal ions to dictate the outcomes of such synthesis has also become a popular choice and several examples of lanthanide based coordination networks^{5,6} as well as single supramolecular structures⁷⁻¹¹ have been developed to date. The advantage of using the lanthanides in such metal-directed synthesis also lies in the fact that they possess unique magnetic¹² and photophysical¹³⁻¹⁵ properties that are generally modulated upon formation of such architectures. Furthermore, the organic ligands employed in such synthesis are often aromatic based and can be used as sensitizing chromophores, or antennae, for the population of the lanthanide excited states.¹⁵ Hence, by simply observing the changes in the intensity of the lanthanide emission, lifetimes and quantum yields, useful information about the thermodynamics and the kinetics of such supramolecular formation can be obtained, as well as potential insight into the structural aspects of such structures in solution.¹⁶⁻²⁰

We have recently demonstrated that by using simple acyclic chiral ligands and lanthanide ions such as Eu(III), Tb(III) and Nd(III), chiral lanthanide-directed self-assemblies could be formed where these luminescent properties were used to quantify both the stability and the stoichiometry of the resulting self-assembly structures.²¹ Furthermore, the chiroptical properties of the resulting assembly were probed by using circular polarized luminescence, where we demonstrated that the chirality of the ligands (*R* or *S*) dictated the overall chirality (Δ vs. Λ) of the resulting assemblies. Concurrently, we^{22,23} and others,²⁴⁻²⁶ have also explored the use of mixed $f-d$ metal ions in the synthesis of such supramolecular structures in solution.²⁷ Of these, the luminescence arising from the lanthanides was directly modulated by the presence of the d -metal ions. Hence, a direct relationship between luminescence sensing and self-assembly formation was achieved.

The use of lanthanide luminescence in optical sensing is also highly attractive, particularly for use in *in vivo* sensing and for biological imaging, an area that has become a highly active field of research in recent times.^{28,29} This is due to the nature of the lanthanide excited states, which gives rise to long-wavelength emission and long-lived excited state lifetimes, which overcomes auto-fluorescence and light scattering from biological matter.³⁰ In this article, we give a full account of our investigation into the use of **1.Eu**, a cationic Eu(III) based cyclen complex possessing a 1,10-phenanthroline (*phen*)³¹ moiety as a combined sensitizing antenna and a d -metal ion coordinating ligand, that can be employed in both sensing and for the construction of supramolecular structures.^{22,32}

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We demonstrate that the Eu(III) emission from **1.Eu** is significantly modulated as a function of pH and that the changes observed in the luminescence emission upon titration with Cu(II), Fe(II) or Co(II) (using non-linear regression analysis) can be used to quantify the stoichiometry, and hence the supramolecular structures, formed in solution upon binding of these *d*-metal ions to the *phen* moiety of **1.Eu**, which gives rise to the formation of linear tri-nuclear *f*-*d*-*f* or tetra-nuclear *f*₃-*d* complexes. The stability of these various structures was determined by fitting the changes in the ground and the excited state of the *phen* antenna and the Eu(III) emission using a non-linear regression analysis program.

Experimental

General procedures

All ¹H NMR spectra were recorded at 400 MHz using a Bruker Spectrospin DPX-400 instrument. ¹³C NMR were recorded at 100 MHz using a Bruker Spectrospin DPX-400 instrument. Mass spectrometry was carried out using HPLC grade solvents. Mass spectra were determined by detection using Electrospray on a Micromass LCT spectrometer. High resolution mass spectra were determined relative to a standard of leucine enkephaline. Elemental analysis was performed in the Microanalytical Laboratory, University College Dublin. Starting materials were obtained from Sigma Aldrich, Strem Chemicals and Fluka and used as received. High-grade solvents (methanol and acetonitrile) were used for the synthesis of the ligand and complex. Columns were run using Aluminium Oxide (activated, Neutral, Brockmann I STD grade 150 mesh). All luminescent spectra were recorded on a Cary Eclipse Varian fluorimeter in phosphorescent mode with a gate time of 10 ms and slit widths of 2.5 or 5 nm.

Synthesis and characterization

2-Chloro-*N*-[1,10]-phenanthroline-5-yl-acetamide, 2. 5-Amino-[1,10]-phenanthroline (0.30 g, 1.54 mmol) was placed in a round bottomed flask under argon. THF (dry, 55 mL) and triethylamine (0.16 g, 1.58 mmol, 0.22 mL) were added and the suspension was stirred for thirty minutes. The mixture was cooled to 0 °C before chloroacetyl chloride (0.213 g, 1.89 mmol, 0.15 mL, 1.2 equivalents) in THF (5 mL) was added drop-wise. The mixture was left stirring overnight at room temperature. The solution was washed with 5% NaHCO₃. The organic layer was collected, evaporated and the residue washed with water and diethyl ether to yield **2** as a beige solid (0.24 g, 59%) (Found: C, 60.84; H, 3.71; N, 14.84. Calc. for C₁₄H₁₀N₃OCl: C, 61.89; H, 3.71; N, 15.47%). δ_H(400 MHz, CDCl₃) 9.27 (d, 1H, *J* = 4.0 Hz), 9.18 (d, 1H, *J* = 4.0 Hz), 8.91 (s broad, 1H, NH), 8.39 (s, 1H), 8.33 (d, 1H, *J* = 8.52 Hz), 8.27 (d, 1H, *J* = 8.04 Hz), 7.74 (dd, 1H, *J* = 4.02 Hz, *J* = 8.03 Hz), 7.67 (dd, 1H, *J* = 4.02 Hz, *J* = 7.78 Hz), 4.43 (s, 2H, CH₂). δ_C(100 MHz, CDCl₃) 164.2, 150, 149.8, 146.1, 144.2, 138.9,

137.2, 135.6, 128.5, 127.6, 123.2, 122.6, 119.2, 26.5. Calculated for C₁₄H₁₁N₃OCl ([M + H]): *m/z* = 272.0579. Found: *m/z* = 272.0591. IR (ν_{max}/cm⁻¹) 1687, 1541, 1422, 1318, 1250, 1153, 1130, 896, 804, 739, 653.

***N*-[1,10]-Phenanthroline-5-yl-2-(4,7,10-tris-dimethylcarbamoylmethyl-1,4,7,10-tetraaza-cyclododec-1-yl)-acetamide, 1.** 2-(4,7-Bis-dimethylcarbamoylmethyl-1,4,7,10-tetraazacyclododec-1-yl)-*N,N*-dimethylacetamide (0.23 g; 0.53 mmol), 2-chloro-*N*-[1,10]-phenanthroline-5-yl-acetamide (0.17 g, 0.64 mmol) and Cs₂CO₃ (0.21 g, 0.64 mmol) were dissolved in DMF (10 mL) and refluxed overnight under argon. The mixture was allowed to cool and then filtered. The solvent was then evaporated under reduced pressure and the resulting brown oil purified by alumina column chromatography using gradient elution of CH₂Cl₂ : MeOH (0–10%), giving a pale brown solid (0.135 g, 38%). Calculated for C₃₄H₅₁N₁₀O₄ ([M + H]): *m/z* = 663.4069. Found: *m/z* = 663.4095. δ_H(400 MHz, CDCl₃) 11.12 (s, 1H, NH), 9.09 (d, 1H, *J* = 8.2 Hz), 8.98 (m, 2H), 8.04 (m, 2H), 7.45 (m, 2H) 3.86 (br s, 2H, CH₂), 3.02–2.05 (br m, 42H, CH₂, CH₃). δ_C(100 MHz, CDCl₃) 172.2, 170.5, 170.4, 149.1, 148.6, 145.7, 144.2, 135.0, 133.9, 132.6, 127.9, 122.3, 121.8, 119.2, 56.4, 54.4, 54.3, 52.9, 51.2, 50.5, 50.0, 35.5, 34.9. Calculated for ([M + H]): *m/z* = 663.4. Found: *m/z* = 663.4. IR (ν_{max}/cm⁻¹) 3413, 2968, 2825, 2361, 1647, 1536, 1507, 1456, 1408, 1347, 1299, 1262, 1226, 1151, 1104, 1062, 1004, 951, 901, 828, 742, 630.

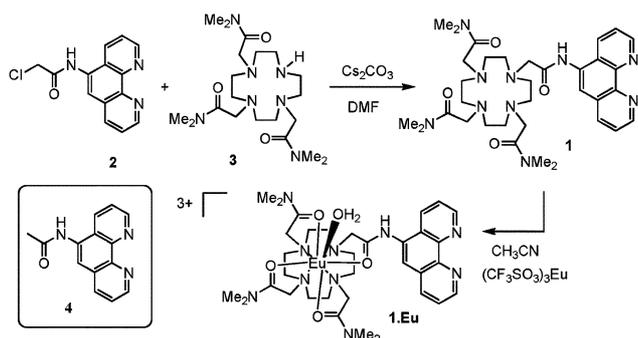
Eu(III) complex of ligand 1, 1.Eu

Compound **1** (16 mg, 24.1 μmol) and Eu(CF₃SO₃)₃ (15.9 mg, 26.5 μmol) were dissolved in acetonitrile (5 mL). The solution was freeze-thawed twice in order to remove any gasses. The reaction was refluxed under argon overnight. The complex was precipitated from diethyl ether and then from DCM before being collected by filtration and dried under vacuum to give **1.Eu** (27.6 mg, 90%). Calculated for ([M + H]⁺): *m/z* = 813.8. Found: *m/z* = 406.9 [M⁺/2], 481.8 [M + Triflate/2]. δ_H(400 MHz, D₂O) 28.3, 9.1, 8.1, 7.6, 3.21, 2.8, 1.0, 0.2, -3, -8, -12, -15. IR (ν_{max}/cm⁻¹) 3362, 2945, 2833, 1656, 1449, 1414, 1278, 1257, 1114, 1028.

Results and discussion

Synthesis and characterization of 1 and 1.Eu

The synthesis of **1** was achieved in a single step from the tri-amide-modified cyclen structure **3**³³ and 2-chloro-*N*-[1,10]-phenanthroline-5-yl-acetamide **2**, which was formed as a beige solid in 59% yield from the commercially available 5-amino-[1,10]-phenanthroline, by refluxing the two compounds together in DMF in the presence of Cs₂CO₃ for 12 hours under argon, Scheme 1. The resulting brown oil was purified by alumina column chromatography (using gradient elution (100→90 : 10; CH₂Cl₂ : MeOH) to give the desired product *N*-[1,10]-phenanthroline-5-yl-2-(4,7,10-tris-dimethylcarbamoylmethyl-1,4,7,10-tetraaza-cyclododec-1-yl)-acetamide, **1**, as a pale brown solid in 38% yield, and was characterized by using conventional methods. For comparison studies, the acetamide derivative of 5-amino-[1,10]-phenanthroline, **4**, was also formed in a single step by reacting the amine with acetic anhydride. The ¹H NMR spectrum of **1** (see Fig. S1 in ESI[†]), showed the presence of a



Scheme 1 The synthesis of **1** and the corresponding Eu(III) complex **1.Eu**, and the model compound **4**.

single NH proton at 11.35 ppm as well as the seven aromatic resonances, while the cyclen moieties and the methylene protons of the pendent arms were observed as a broad signal at ~ 2.57 ppm due to the dynamic exchange of several conformations in solution. The Eu(III) complex of **1**, **1.Eu**, was formed by refluxing **1** with 1.1 equivalents of $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ under argon in CH_3CN for 18 hours. The complex was precipitated from diethyl ether and then from CH_2Cl_2 before being collected by filtration and dried under vacuum to give a brown solid in 90% yield, and characterized using conventional methods (see Fig. S2 and S3 in ESI for the ^1H NMR and the ESMS, respectively). The ^1H NMR analysis (400 MHz, D_2O) showed a broad spectrum that was significantly shifted due to the paramagnetic nature of the Eu(III) ion and hence its fast relaxation properties.³⁴

However, characteristic resonances were observed at 28, -3 , -8 , -12 , and -15 ppm, respectively, which is characteristic for the shifted axial and equatorial CH_2 protons of the cyclen moiety and usually indicative of mono-capped square antiprismatic geometry in solution, where the axial position is occupied by a metal-bound water molecule.³⁵ The ESMS for the complex also confirmed its formation, with a $m/z = 406.9$ corresponding to the $\text{M}^+/2$ species, and a second peak at 481.8 which corresponds to the $\text{M} + \text{Triflate}/2$ species. Both of these matched the calculated isotopic distribution pattern for these masses. The mono-capped nature of **1.Eu** was further confirmed by measuring the excited state lifetime of the Eu(III) in H_2O and D_2O , respectively, by direct excitation of the Eu(III) ion at 395 nm, and calculating the hydration state, q , using established methods.³⁶ The excited state decay for Eu(III) was best fitted to a single exponential, giving lifetimes of 0.33 ms ($k = 3.05 \text{ m s}^{-1}$) and 0.52 ms ($k = 1.89 \text{ m s}^{-1}$), for H_2O and D_2O , respectively. From these results, a q value of $1 (\pm 0.3)$ was determined, confirming the mono-capped nature of the complex in solution.

Spectroscopic investigation of **1.Eu** and the role of pH

The *phen* ligand has been a popular choice in inorganic photochemistry of the *d*-block, but has also recently been employed as sensitizers for lanthanide ions.³⁴ The absorption spectrum of **1.Eu** was recorded in water at pH 7.4 (buffered with 0.1 M HEPES) under ambient conditions, and showed a broad band with two maxima at 266 nm ($\log \epsilon = 3.66$) and 230 nm ($\log \epsilon = 3.90$), respectively assigned to the *phen* antenna. Upon excitation at 266 nm, a broad fluorescent band was observed with a λ_{max}

at 425 nm. Furthermore, using time gating, we were able to clearly observe the Eu(III) luminescent spectrum of **1.Eu** at long wavelength with characteristic emission bands appearing at 581, 593, 615, 624, 654, 686 and 702 nm, respectively, for the deactivation of the $^5\text{D}_0$ excited state to the ground states $^7\text{F}_J$ ($J = 0, 1, 2, 3$ and 4) (e.g. Fig. 1B). This showed that the antenna was indeed able to sensitize the Eu(III) excited state and that the Eu(III) was 'switch on' at pH 7.4. To investigate this sensitization process further, the changes in the ground, the singlet and the $^5\text{D}_0$ excited states were recorded as a function of pH.

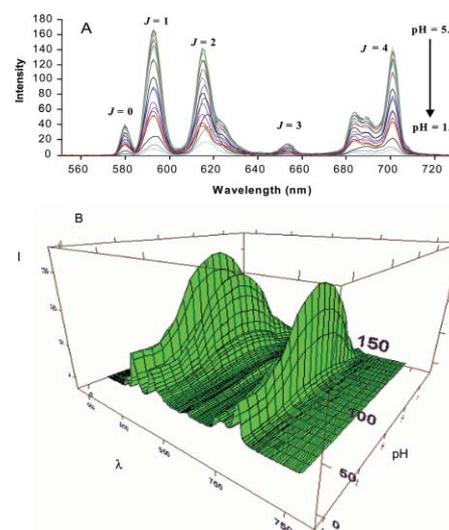


Fig. 1 (A) Changes in the Eu(III) emission as a function of pH within the pH range of 1.3–5.5. (B) The luminescence–pH profile for the titration of acid→base and the corresponding back-titration, showing that all the transitions gave rise to the same changes in their pH dependence.

Only small changes were seen in the absorption spectrum of the *phen* antenna of **1.Eu** as a function of pH, where in acidic media the 266 nm band was slightly shifted to 278 nm (see ESI,† Fig. S4, for the changes observed as a function of pH for these two wavelengths). When the complex was irradiated at 266 nm, the intensity of the 425 nm band was reduced by ca. 38% (see ESI, Fig. S5) where the emission–pH profile from pH 2→10, gave rise to a 'bell-shaped' profile, with a pH maximum at ca. pH 5. In contrast to these results, the changes in the Eu(III) emission were dramatic. The results of this investigation are shown in Fig. 1. The changes occurring from pH 5.5→1.3 are shown in Fig. 1A, demonstrating that significant quenching was observed in the Eu(III) emission as a function of pH. Similarly, for the titrations from pH 5.5→12, the emission was also quenched. The changes observed for all the transitions are shown in Fig. 1B as a function of their overall pH titration and demonstrate that the overall pH profile for the titrations is bell-shaped, where an 'off-on-off' profile is observed for all of the transitions, with a maximum emission occurring at ca. pH 6, which is similar to that observed in the fluorescence titration. It is interesting to note that in related work developed for the sensing of Na^+ and K^+ , using Tb(III) based cyclen-crown ether conjugates, the luminescent–pH profile observed gave rise to an 'on-off-on' dependence within the same pH range.³⁷ From the results shown in Fig. 1, we were able to determine two $\text{p}K_{\text{a}}$ values as $\text{p}K_{\text{a}1} = 4.1 (\pm 0.2)$, assigned to the protonation of the *phen*

nitrogen moiety,³⁸ and $pK_{a2} = 8.2 (\pm 0.2)$, which we assigned to the deprotonation of the *phen*-amide moiety. To verify this, we made **4**, the acetamide derivative of the antenna (the absorption spectrum in water, which showed two bands at 231 nm ($\log \epsilon = 4.51$) and 267 nm ($\log \epsilon = 4.44$), and an emission centered at 427 nm upon excitation of the 267 nm band) and monitored the changes in the ground and the singlet excited states as a function of pH. As was observed for **1.Eu**, two pK_{a} s could be determined from the changes in the ground state of **4** (see Fig. S6 in ESI). The results correlate quite well with that observed for **1.Eu** above, and the pK_{a} s were calculated as $4.6 (\pm 0.2)$ and $9.3 (\pm 0.2)$, which we assigned to the protonation of the *phen* nitrogen moiety and the deprotonation of the amide, respectively.

We also investigated the effect of pH on the hydration state of **1.Eu** (see Table S1 in ESI†) which demonstrates that *q* remained as *ca.* 1 within the entire pH range. It is important to note that within the physiological pH range, the changes observed in the Eu(III) of **1.Eu** are only minor and, essentially, the Eu(III) emission is 'switched on' within this range. Hence, we foresaw that titrations using various transition metal ions within this pH range would potentially give rise to measurable changes in the Eu(III) emission that could be quantitatively analyzed. Consequently, we carried out a series of titrations on **1.Eu** using various transition metal ions.

Changes in the ground state of **1.Eu** upon titration with Cu(II), Fe(II) and Co(II)

The absorption spectra of **1.Eu** (35.8 μ M) were first monitored upon titrations with Cu(II), Fe(II) and Co(II), in water at pH 7.4 (buffered with 0.1 M HEPES) using the chloride salts of these ions, in the presence of 0.1 M tetrabutylammonium chloride solution to maintain constant ionic strength. The changes observed in the spectra of **1.Eu** upon titration with CuCl₂ are shown in Fig. 2, and clearly demonstrate the formation of a complex between Cu(II) and **1.Eu**, where the absorption centered at 266 nm is red shifted to 276 nm with the formation of a 'pseudo' isosbestic point at *ca.* 271 nm. The changes in three different wavelengths (248, 266 and 290 nm) are shown as the inset in Fig. 2, and demonstrate that the stoichiometry between Cu(II) and **1.Eu** is not a simple 1 : 2 stoichiometry. Indeed, fitting these changes, using the non-linear regression analysis program SPECFIT, gave a good fit (see Fig. S7 in ESI†) from which several binding constants could be determined (later represented as $\log \beta$). The results demonstrated that, in general, three main species were formed in solution corresponding to the formation of *f-d*, *f₂-d* and *f₃-d* nuclear complexes (shown below as **ML**, **ML₂** and **ML₃**, where the **1.Eu** = **L**, or *f*) in solution:

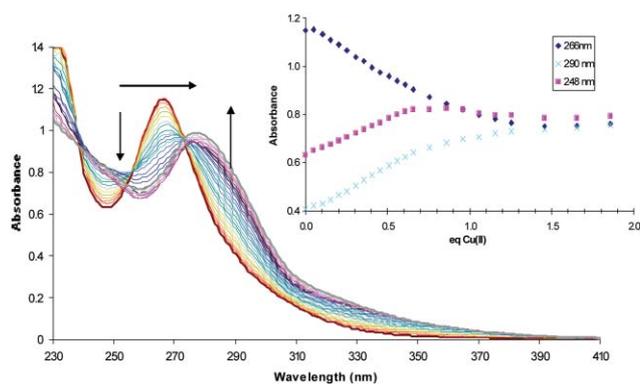
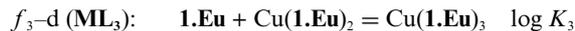
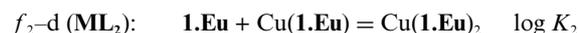
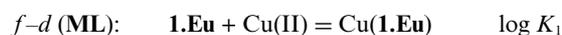


Fig. 2 Changes in the absorption spectra of **1.Eu** (35.8 μ M) upon titration with CuCl₂ at pH 7.4. *Inset:* The changes observed at 248, 266 and 290 nm, respectively as a function of added equivalents of Cu(II).



within the concentration range of $0 \rightarrow 4 \times 10^{-5}$ M of Cu(II), with $\log \beta = 6.49 (\pm 0.22)$, $11.61 (\pm 0.32)$ and $16.07 (\pm 0.53)$ for the formation of these species. These values are summarized in Table 1. The speciation distribution diagram (see Fig. S8 in ESI†) for this titration demonstrated that the **ML₂** stoichiometry was the major species, formed in *ca.* 45%, within this concentration range. The formation of the mixed *f-d* based **ML₂** and **ML₃** are shown in a cartoon format in the graphical abstract of this article.

Similarly, the titration of **1.Eu** with Co(II) under identical conditions, gave rise to the same trend as seen for the titration of Cu(II); however, the overall changes were smaller (see Fig. S9 in ESI†). Similarly by fitting these data, a good fit was observed which again showed the presence of three species, all of which gave rise to similar $\log \beta$ values as seen for Cu(II), with an **ML₂** contribution of *ca.* 50%. The binding constants for these titrations are summarized in Table 1, which shows similar $\log \beta$ for the formation of **ML₂** as seen for Cu(II).

In contrast to these results the titration of **1.Eu** with Fe(II) gave rise to significant changes in the ground state, where the 266 nm transition was red shifted by *ca.* 10 nm, with the formation of a shoulder at *ca.* 330 nm and the formation of a new band at long wavelengths, centered at 518 nm, assigned to the formation of a MLCT transition, Fig. 3. By plotting the changes at this wavelength as a function of Fe(II) concentration, rapid changes up to 0.5 equivalents of Fe(II) were observed, clearly establishing

Table 1 Binding constants (expressed as $\log \beta$) obtained by fitting the changes in the ground state (abs.), singlet excited state (fluor.) and the delayed Eu(III) emission (Eu(III)) using the non-linear regression analysis program SPECFIT, for the formation of **ML**, **ML₂** and **ML₃** upon titration of **1.Eu** with Cu(II), Co(II) and Fe(II) in pH 7.4 buffered solution (*I* = 0.1 M TMACl). All the measurements were repeated several times

M	Log β (abs.)			Log β (fluor.)			Log β (Eu(III))		
	ML	ML ₂	ML ₃	ML	ML ₂	ML ₃	ML	ML ₂	ML ₃
Cu(II)	6.49 (± 0.22)	11.61 (± 0.32)	16.07 (± 0.53)	6.58 (± 0.33)	11.35 (± 0.29)	16.03 (± 0.33)	7.10 (± 0.26)	12.06 (± 0.25)	15.74 (± 0.37)
Co(II)	5.71 (± 0.40)	11.64 (± 0.34)	16.84 (± 0.50)	7.10 (± 0.49)	11.64 (± 0.48)	17.08 (± 0.49)	6.00 (± 0.12)	11.38 (± 0.07)	15.39 (± 0.19)
Fe(II)	5.94 (± 0.51)	11.84 (± 0.56)	17.04 (± 0.71)	6.14 (± 0.44)	11.56 (± 0.34)	16.56 (± 0.38)	5.96 (± 0.23)	11.78 (± 0.25)	17.18 (± 0.37)

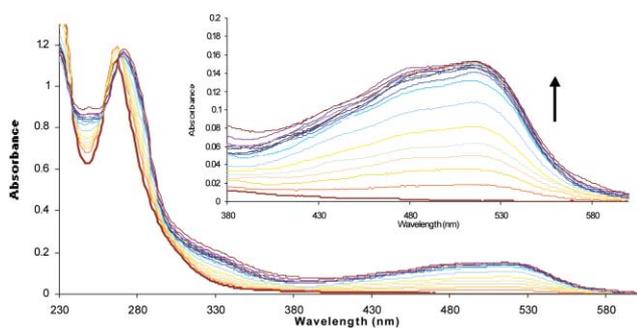


Fig. 3 The changes in the absorption spectra of **1.Eu** upon titration with Fe(II) at pH 7.4. *Inset*: The concomitant formation of the MLCT band upon addition of Fe(II).

the formation of the self-assembly system. As before, no clear isosbestic points were observed in the absorption spectra at shorter wavelengths, indicating the formation of several species in solution. This was confirmed by fitting the changes in the absorption spectra, which showed the formation of three main species in solution (see Fig. S10 in ESI†), from which binding constants $\log \beta$ of 6.49 (± 0.22), 11.61 (± 0.32) and 16.07 (± 0.53) were determined, respectively. The resulting speciation distribution diagram showed, however, that unlike that seen for either Cu(II) or Co(II), then the dominant species in solution between *ca.* 0 and 2×10^{-5} M of Fe(II) was in fact the **ML**₃ species. These results clearly indicate that these transition metal ions are coordinating to the *phen* antenna, resulting in the formation of mixed *f-d* supramolecular complexes, and are in general in good agreement with stoichiometries observed for simple or unmodified *phen* ligands for these ions.

Changes in the singlet excited state of **1.Eu** upon titration with Cu(II), Fe(II) and Co(II)

Having investigated the changes in the ground state of **1.Eu** upon titration with Cu(II), Fe(II) and Co(II), titrations were also carried out where the fluorescence arising from the *phen* antenna was monitored by exciting at 266 nm and 274 nm, respectively. We had foreseen that ions such as Cu(II) would, through an electron transfer mechanism, quench the excited state of **1.Eu** upon formation of the mixed *f-d* assembly. This was indeed found to be the case as shown in Fig. 4A, where the fluorescence was >90% ‘switched off’ as a function of increasing Cu(II) concentration upon excitation at 266 nm (same behavior was observed upon excitation at 274 nm). This quenching was also accompanied by a small blue shift in the λ_{max} . The changes at 400 nm (when excited at 266 nm) are shown in Fig. 4B, and demonstrate that the emission was rapidly quenched by *ca.* 70% upon the addition of 0 \rightarrow 0.5 equivalents of Cu(II). From these changes we were able to obtain a good fit that demonstrated the formation of both the **ML**₂ and the **ML**₃ conjugates in solution (see the speciation distribution diagram as the inset in Fig. 4) in addition to the formation of the **ML** species at higher concentrations. From these changes, binding constants $\log \beta$ of 6.14 (± 0.44), 11.56 (± 0.34) and 16.56 (± 0.38) were determined for the formation of **ML**, **ML**₂ and **ML**₃, respectively. These results correlate well with that observed for the ground state titrations discussed above and are summarized in Table 1. Furthermore, as the changes in the fluorescence emission

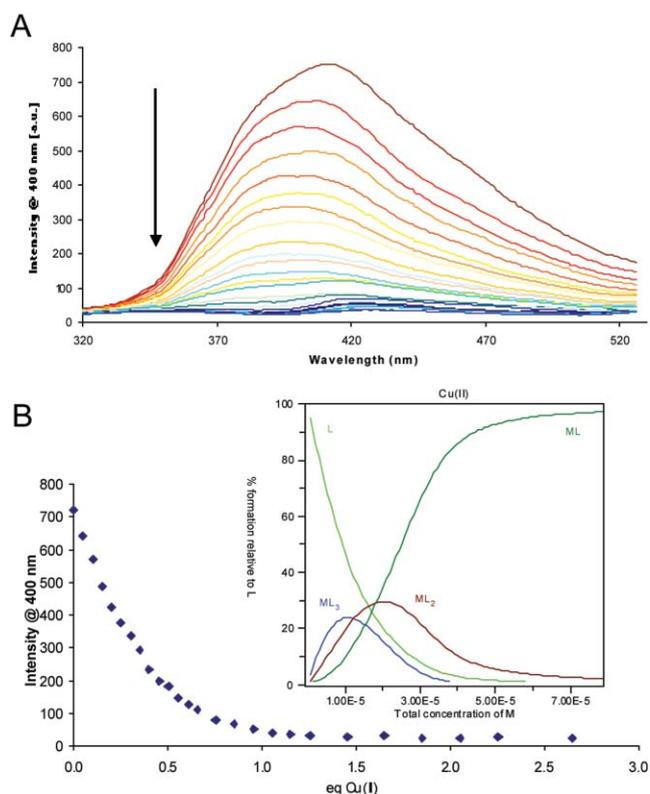


Fig. 4 (A) The changes in the fluorescence emission of **1.Eu** upon titration with Cu(II) at pH 7.4. (B) the changes observed at 400 nm. *Inset*: The speciation distribution diagram for the binding of Cu(II), generated from the results obtained by fitting the changes in the fluorescence emission using the non-linear regression analysis program SPECFIT.

spectra are significant, being almost fully ‘switched off’, it is possible to use these changes for quantitative analysis, *e.g.* sensing of Cu(II) in competitive media, as the changes observed in Fig. 4, overlap with that of the physiological concentration of Cu(II).

Having established the formation of the mixed *f-d* assemblies for Cu(II), we next examined the changes in the fluorescence of **1.Eu** caused by Co(II) and Fe(II) (Fig. S11 and S12 respectively in ESI†). As before, the fluorescence of **1.Eu** (centered at 396 nm) was quenched upon titration with these ions. Furthermore, similar binding isotherms were observed from the changes observed at 396 nm as seen for Cu(II) above (see inset in Fig. S11 and S12). Fitting these changes using SPECFIT gave rise to a good fit of the experimental data which again indicated the formation of several structures in solution, which showed that for Co(II) the **ML**₃ self-assembly dominated, with $\log \beta$ of 17.08, while a small contribution of the **ML**₂ was also observed within the $1 \rightarrow 4 \times 10^{-5}$ M concentration range. Above this concentration, the **ML** complex was exclusively observed. Similarly, upon titration with Fe(II), both the **ML**₂ and **ML**₃ were initially formed, with $\log \beta$ of 11.56 and 16.56 for the formation of these two species, respectively (see Fig. S13 and S14, respectively in the ESI for the speciation distribution); however, the **ML**₃ complex was formed in higher yield. We also carried out titrations on **1.Eu** using Fe(III). However, only very minor changes were observed in the ground and the singlet excited state or in the Eu(III) emission of **1.Eu**, and these changes were not analyzed further.

Changes in the lanthanide luminescence of 1.Eu upon titration with Cu(II), Fe(II) and Co(II)

Having investigated the formation of the mixed $f-d$ metal self-assemblies by observing the changes in the ground and the excited state of the *phen* ligand, we next monitored the changes in the Eu(III) emission. As before, at pH 7.4, the excitation at the antenna at 272 nm, gave rise to sensitized emission from the 5D_0 excited state. From the results obtained from the singlet excited state, we anticipated that the Eu(III) emission would be quenched upon formation of the ML , ML_2 and ML_3 systems since the singlet excited state was on all occasions quenched. This was indeed found to be the case as is shown in Fig. 5A for the titration of Cu(II). Here, the Eu(III) emission was quenched up to *ca.* one equivalent of Cu(II), Fig. 5B, showing similar results to that obtained above for the singlet excited state changes. Furthermore, this same effect was seen for all of the ΔJ transitions Fig. 5B. These results clearly demonstrate that the energy transfer process from the S_1 of the antenna to the 5D_0 excited state, *via* the T_1 of the antennae, is blocked upon binding of the Cu(II) to the *phen* moiety, which is due to the electron transfer quenching of the S_1 of the antenna by Cu(II). Hence, these changes demonstrate the sensitivity of the Eu(III) emission to changes in the local environment of 1.Eu, *i.e.* the coordination of the *phen* antenna to Cu(II).

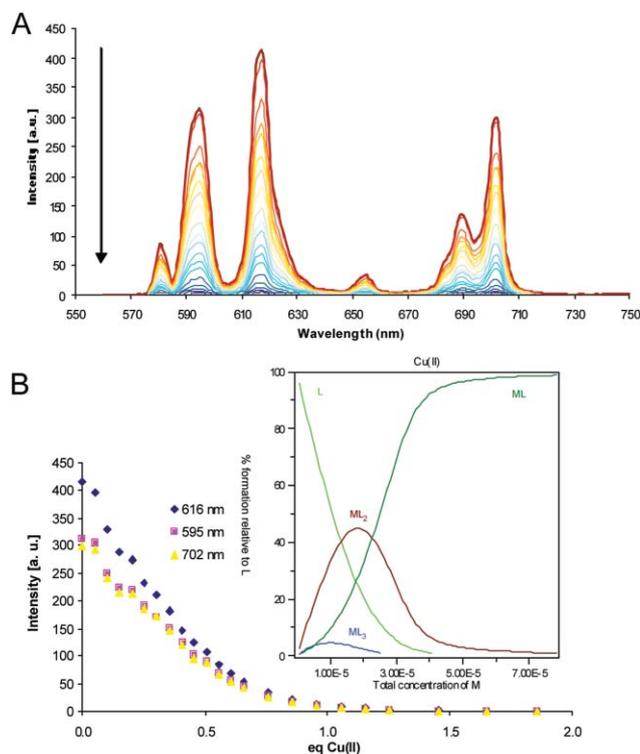


Fig. 5 (A) The changes in the Eu(III) emission upon titration with Cu(II). (B) The changes in the 595, 616 and 702 nm transitions as a function of added Cu(II). *Inset:* The speciation distribution diagram for the same titration, generated from the results obtained by fitting the changes in the Eu(III) emission using the non-linear regression analysis program SPECFIT.

We also investigated the changes in the Eu(III) emission against various Cu(II) mole fractions, and analyzed the changes using Jobs plot analysis. The results of these changes were, however, not

conclusive, but indicated that ML_3 systems were formed. However, by fitting the changes in Fig. 5A using SPECFIT, a good fit was observed, from which the formation of all three stoichiometries could be seen, with $\log \beta$ values of $7.10 (\pm 0.26)$, $11.56 (\pm 0.34)$ and $16.56 (\pm 0.38)$ for ML , ML_2 and ML_3 , respectively. Again, these correlate well with that observed and discussed above for the changes in the ground and the singlet excited states. From these analyses, a speciation distribution diagram was also constructed, which is shown as the inset in Fig. 5B, and demonstrates that, again, the use of Cu(II) mostly gave rise to the formation of the ML_2 stoichiometry within the concentration range of $0 \rightarrow 5 \times 10^{-5}$ M, and that ML_3 is only formed as a minor product within that same range.

With the aim of evaluating the reversibility of this binding, which is important for sensing applications, 10 equivalents of EDTA were added to the Cu(II) solution containing ML_2 and ML_3 . This had a significant effect on the Eu(III) emission (as well as the fluorescence emission), which was re-instated, indicating that EDTA was able to extract the Cu(II) and, hence, break up the $f-d$ assemblies.

The above titrations were also carried out by using Co(II) and Fe(II). For both titrations, similar changes were observed in the Eu(III) emission, as seen for the Cu(II) titrations above, as shown in Fig. 6, for the titration of 1.Eu using Fe(II), where the emission was almost fully quenched upon formation of the $f-d$ mixed systems. As before, the titration of Co(II) gave mostly rise to the formation of the ML_2 system (see Table 1 for details and Fig. S15 in ESI†).

In contrast to these results, the changes in the Eu(III) emission upon titration of Fe(II) showed that within the concentration range of $0 \rightarrow 1 \times 10^{-5}$ M, the ML_3 was formed as the major product, and that above 2×10^{-5} M, ML_2 dominated, Fig. 6B. Again, from these changes, binding constants of $\log \beta = 5.96 (\pm 0.23)$, $11.78 (\pm 0.25)$ and $17.18 (\pm 0.37)$ were determined for the formation of ML , ML_2 and ML_3 , respectively. These results clearly show that the changes in the Eu(III) emission can be used to monitor the formation of a complex between the *phen* antenna and these transition metal ions. As in the case of Co(II), the Eu(III) emission was quenched, upon binding to Fe(II), and demonstrates the sensitivity of the Eu(III) emission to changes in the local environment. However, this quenching is most likely due to energy transfer from the $^5D_0 \rightarrow ^3MLCT$ upon binding to Fe(II), rather than electron transfer quenching as in the case of Cu(II). All of the binding constants obtained in this investigation are summarized in Table 1.

From Table 1, it is clear that the binding constants obtained for the fitting of the changes in the ground, the singlet excited and the lanthanide emission correlate well within experimental error. Of these three techniques, the results obtained from the fitting of the lanthanide emission generally gave rise to the best fit and to the lowest error. This we assign to the nature of the Eu(III) emission, which is a delayed emission, occurring in the millisecond time-frame as demonstrated above, and at long wavelengths (with over 300 nm Stokes' shift). Moreover, the characteristic line-like emission bands can be addressed spatially and independently over a wide range of wavelengths which is of particular importance, as this allows for the development of sensing, as it gives rise to a significantly improved signal-to-noise ratio. Furthermore, the attractiveness of monitoring the Eu(III) emission upon formation

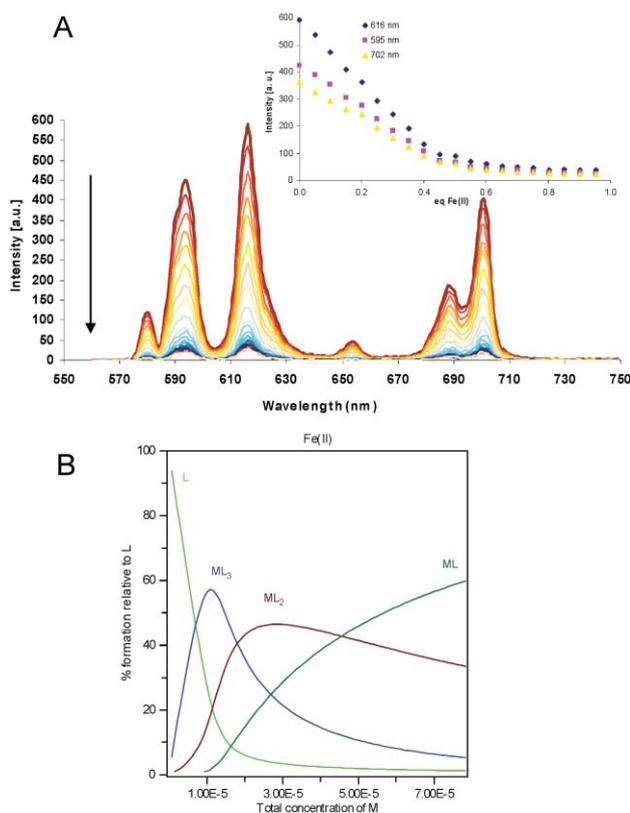


Fig. 6 (A) The changes in the Eu(III) emission upon titration with Fe(II). *Inset:* The changes in the 595, 616 and 702 nm transitions as a function of added Fe(II). (B) The speciation distribution diagram for the same titration, generated from the results obtained by fitting the changes in the Eu(III) emission using the non-linear regression analysis program SPECFIT.

of the $f-d$ self-assemblies, over that of the ground and the singlet excited state, lies in the fact that the changes are significantly larger and the Eu(III) ion is an *impartial luminescent reporter*, as it does not participate directly in the binding to these ions. However, it is worth pointing out that it is clear from Table 1 that poor selectivity is obtained for the ‘sensing’ of these ions by **1.Eu**. Nevertheless, in the context of sensing of these ions within their physiological concentration ranges, the sensing of free Cu(II) by **1.Eu** falls within that range, as previously discussed. With the aim of investigating the selectivity of the sensing of **1.Eu** further, we carried out luminescent titrations using ions such as Na⁺, K⁺, Ca(II), Mg(II) and Zn(II), which are all commonly found in human blood or serum. None of these ions gave rise to changes in the Eu(III) emission of **1.Eu**. Consequently, we carried out a Cu(II) titration for **1.Eu** in a buffered pH 7.4 solution containing a simulated biological ‘ionic’ background, using a solution consisting of 150 mM NaCl, 10 mM KCl, 5 mM CaCl₂ and 5 mM MgCl₂. As was observed above, the Eu(III) emission was gradually quenched upon addition of Cu(II), indicating the binding of Cu(II) to the *phen* moiety even in this competitive media; moreover, both the overall changes in the Eu(III) emission as well as the resulting binding profile were identical to that observed for the titration of Cu(II) shown in Fig. 5. Hence, these results clearly demonstrate that lanthanide conjugates such as **1.Eu**, which possess a combined antenna/*d*-block receptor, can

be used in both luminescent sensing applications as well as in the construction of mixed supramolecular $f-d$ self-assemblies, which are currently under investigation in our laboratory.

Conclusion

We have developed a method for forming tri- and tetra-nuclear mixed $f-d$ metal systems from **1.Eu**, a cyclen-conjugated *phen* Eu(III) based complex. We showed that the *phen* antenna is capable of sensitizing the Eu(III) ⁵D₀ excited state within the physiological pH range, and that the emission is also highly modulated as a function of pH, being quenched in both acidic and basic media.

The changes in the ground, the singlet excited state and the Eu(III) emission were all monitored at pH 7.4, upon titrating **1.Eu** with Cu(II), Co(II) and Fe(II) with the aim of forming novel, mixed $f-d$ nuclear complexes, and to explore the possibility of using **1.Eu** as a delayed luminescent sensor for these ions at physiological pH. In the case of Cu(II) and Co(II) only minor changes were observed in the absorption spectra, which were red shifted upon addition of these ions, while for Fe(II), the formation of a MLCT band at longer wavelength signified the formation of the mixed $f-d$ metal systems in solution. In contrast to these results the fluorescence emission arising from the *phen* moiety was almost fully quenched upon titration of these ions. Consequently, we anticipated that the delayed Eu(III) emission would also be quenched upon formation of the mixed $f-d$ nuclear assemblies, as the population of the Eu(III) ⁵D₀ excited state is achieved by an energy transfer mechanism from the S₁ of the antenna *via* the antenna T₁. We also demonstrated that the addition of EDTA to a fully quenched solution of these mixed nuclear complexes re-instated the Eu(III) emission (as well as the absorption and fluorescence emission), indicating that dissociation of the self-assembly in this competitive media had occurred. The addition of EDTA reversed these changes, demonstrating that these self-assemblies were formed in a reversible manner.

Analysis of the spectral changes observed for the above titrations were carried out using non-linear regression analysis, which showed that, on all occasions, a mixture of linear tri-nuclear $f-d-f$ and branched f_3-d tetra-nuclear complexes was formed (depicted in a cartoon in graphical abstract). In the case of Cu(II) and Co(II) the formation of the linear ML₂ system dominated, while for Fe(III) the formation of ML₃ was the main species in solution.

In summary, we have developed novel means of forming mixed $f-d$ nuclear self-assembly systems (complexes) where the formation of these assemblies can be monitored by observing the changes in the ground and the excited state of a sensitizing *phen* ligand, or by monitoring the changes in the delayed lanthanide emission, occurring at long wavelength within the millisecond time-frame. We are currently developing other such mixed $f-d$ complexes for use as responsive biological probes and sensors.

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