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PAPER

Synthesis of luminescent homo-dinuclear cationic lanthanide cyclen complexes bearing amide pendant arms through the use of copper catalysed (1,3-Huisgen, CuAAC) click chemistry†

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The design and synthesis of dinuclear-lanthanide complexes possessing triazole-based bridges, formed by using copper catalysed 1,3-cycloaddition reactions between heptadentate alkyne functionalised cyclen europium or terbium complexes and di-azides (CuAAC reactions), are described. While this click reaction worked well for the formation of the homo-Eu(III) and Tb(III) bis-tri-arm cyclen *N*,*N*-dimethyl acetamide complexes, **2Eu** and **2Tb**, and for the homo-Eu(III) chiral *N*-methylnaphthalene based complexes **3Eu** (*S*,*S*,*S*) and **4Eu** (*R*,*R*,*R*), the formation of the Eu(III) complex of the primary amide analogue of **2**, namely **1Eu**, was not successful, clearly demonstrating the effect that the nature of the pendant arms has on this reaction. Furthermore, the click reactions between the free alkyne cyclen bis-derivatives (**5–8**) and the di-azide were unsuccessful, most likely due to the high affinity of the cyclen macrocycles for Cu(II). The Eu(III) complexes of **2–4** and **2Tb** all gave rise to sensitised metal ion centred emission upon excitation of the triazole or the naphthalene antennae in methanol solution, and their hydration states were determined, which showed that while the Eu(III) mono-nuclear complexes had $q \sim 2$, the click products all had $q \sim 1$. In the case of **3Eu** (*S*,*S*,*S*) and **4Eu** (*R*,*R*,*R*), the circular polarised emission (CPL) was also observed for both, demonstrating the chiral environment of the lanthanide centres.

Introduction

The development of luminescent sensors, switches and molecular imaging agents is a fast growing field of research.[1–3] The development of such systems that possess long excited state lifetimes is of particular current interest, not least for their use in time-resolved imaging of biological matter.[4,5] The visibly emitting lanthanides Eu(III), Tb(III), Sm(III) and the NIR emitting ions Nd(III) and Yb(III) are excellent candidates for such applications, due to their long lived exited states, and their line-like emission bands, which are the cause of their spin forbidden transitions.[6,7] For this reason, the generation of their excited states is best achieved by using sensitised excitation by organic chromophores or metal-complexes as antennae.[8–10]

To date, many examples of mono-nuclear lanthanide luminescence have been developed for the aforementioned applications,[11,12] furthermore, development of higher order systems, such as those possessing two[13,14] three[15,16] or more[17,18] lanthanide ion centres, have been reported. Recently, we have developed bis-lanthanide complexes by joining together, *via* aromatic or aliphatic spacers, two lanthanide complexes based on the use of the 1,4,7,10-tetraazacyclododecane (cyclen) that have been functionalised with amide based pendant arms.[19] While in general, the synthesis of these complexes resulted in the formation of the desired targets in good yields, our approach had several limitations or disadvantages, such as involving several steps, complicated

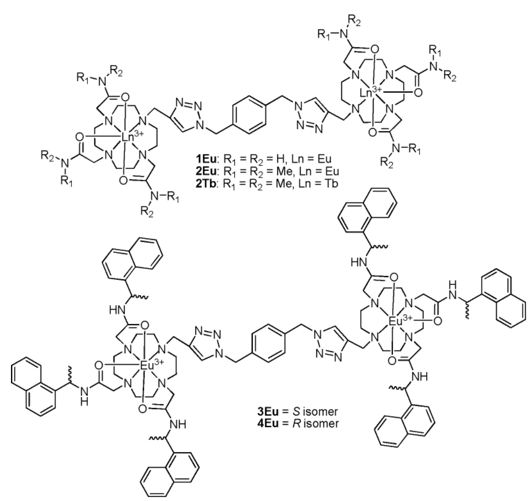

Fig. 1 Structures **1-4Ln** (Ln = Eu(III) or Tb(III)) developed in this study.

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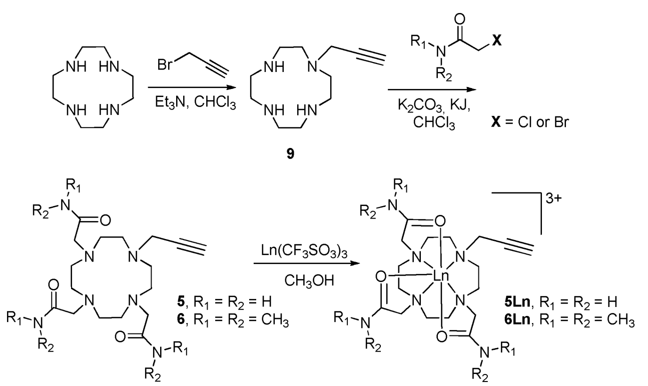
isolations and limitations to the nature of the starting materials. Due to these drawbacks, we embarked on exploring the use of alternative synthetic methods, such as click chemistry, by employing Cu(I) catalysed 1,3-cycloaddition reactions[20] between appropriate cyclen functionalised azides and alkyl derivatives, with the view of initially forming bis-lathanide complexes, and further extending such synthesis to polymetallic macrocyclic analogues. To the best of our knowledge, only a few examples of the use of the copper-catalysed click chemistry for the formation of lanthanide complexes have been reported to date.[21] Concurrently to our work, Hulme,[22] as well as Faulkner and Lowe,[23] worked on a similar synthetic strategy for the development of mono- and di-metallic lanthanide complexes, functionalised with *carboxylate pendant arms*. The latter was published in a joint contribution by Faulkner and Lowe,[23] indicating that the formation of the cyclen-based triazole systems was quite troublesome; this being further emphasised in a later publication by Lowe.[24] Herein, we present our results in this area, which show that the 1,3-Huisgen reaction can be successfully employed in the synthesis of di-lanthanide complexes possessing achiral (**2Eu** and **2Tb**) or chiral amide functionalities (**3Eu** and **4Eu**) and that this reaction works well for secondary and tertiary amides, but fails when primary amides (**1Eu**) are employed as pendant arms.

Results and discussion

Design, synthesis and characterisation of the mono-nuclear complexes 5Eu–8Eu and 6Tb

The 1,3-Huisgen reaction, when catalysed with Cu(I), has been shown to give rise to the formation of products in high yield and purity.[20] Our strategy was to click together the lanthanide cyclen complexes **5Ln–8Ln**, with the xylene di-azide **10**, to yield **1Ln–4Ln**, respectively (Fig. 1). We foresaw that due to the high affinity of such modified cyclen derivatives for copper, the free ligands, **5–8**, of these complexes could not be used, and hence it would be necessary to use the complexes themselves. This, in fact, would extend the scope of this method to the synthesis of heteronuclear systems; a research area currently under investigation in our laboratory.[25]

The synthesis of the alkyne precursors **5–8**, was achieved in a good yield in few steps. The first synthetic target, **5**, Scheme 1, possessed a single alkyne and three acetamide arms. The initial



Scheme 1 Synthesis of the ligands **5** and **6** and the corresponding Eu(III) and Tb(III) complexes **5Eu**, **6Eu** and **6Tb**.

synthesis involved the formation of **9**, by monoalkylation of cyclen with 3-bromopropyne, using a method developed in our group,[26] by refluxing the mixture of four equivalents of cyclen with 3-bromopropyne and triethylamine in $CHCl_3$ under argon overnight, followed by washing with 1 M aqueous KOH solution and after with distilled water. This resulted in **9**, as a yellow oil in 94% yield; the successful formation of which was also confirmed by conventional means (see Experimental) including the use of HRMS, which gave a peak at m/z = 211.1917. Compound **9** was functionalised with 2-bromoacetamide over a period of 7 days under reflux in the presence of 3.3 equivalents of K_2CO_3 in $CHCl_3$. After cooling to room temperature and removal of any inorganic salts through suction filtration, the solvent was removed under reduced pressure, the product redissolved in a minimal amount of methanol and precipitated from diethyl ether. This gave compound **5** as a yellow oil in 55% yield, the formation of which was confirmed by using HRMS with m/z = 382.1940 for $C_{17}H_{32}N_7O_3$, and was further confirmed by ^1H NMR ($CDCl_3$, 400 MHz) analysis, indicating the appearance of the cyclen CH_2 protons at 2.5 ppm, with the NH resonances visible at 5.7 ppm and 8.2 ppm, respectively, Fig. 2.

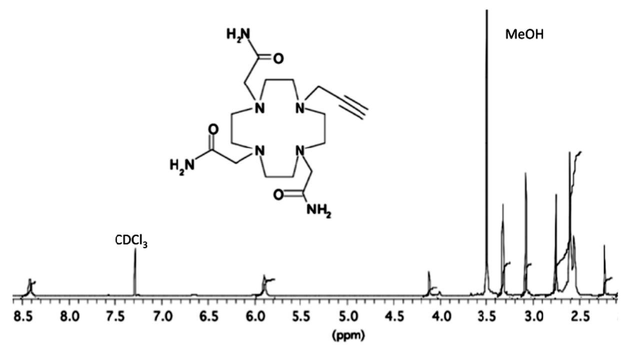


Fig. 2 The ^1H NMR ($CDCl_3$, 400 MHz) of the ligand **5**.

The complexation of **5** with Eu(III) was carried out with 1.1 equivalents of $Eu(CF_3SO_3)_3$, stirring in CH_3OH at 65 °C overnight, and after initial workup (see Experimental) the desired product was precipitated out of diethyl ether to give the product, **5Eu**, as a yellow oil. The ^1H NMR (CD_3OD, 400 MHz) spectrum of **5Eu**, showed the expected shifts in the axial and equatorial protons due to the paramagnetic nature of the europium ion, commonly seen for twisted square antiprismatic complexes. In a similar manner **6** was formed in a multiple step synthesis from **9**, Scheme 1, which was alkylated with α-chloro-*N*,*N*-dimethyl acetamide in the presence of K_2CO_3 and KI under reflux over 7 days, followed by filtration through a plug of celite and basic aqueous workup, yielding the desired product as a yellow oil in 58% yield. The ^1H NMR ($CDCl_3$, 400 MHz) spectrum of the ligand again showed the alkyne proton and cyclen protons as seen before, with the CH_3 and CH_2 of the arms shown among the protons of the macrocycle. Also, the formation of **6** was confirmed by using HRMS with m/z = 466.3500 for $C_{23}H_{44}N_7O_3$.

The lanthanide complexation was carried out in an identical manner using both $Eu(CF_3SO_3)_3$ and $Tb(CF_3SO_3)_3$, giving **6Eu** and **6Tb**, respectively. The ^1H NMR spectrum (CD_3OD, 400 MHz) of **6Eu** (Fig. 3) shows the shifting in the equatorial protons of the cyclen ring and those of the pendant arms. The presence of

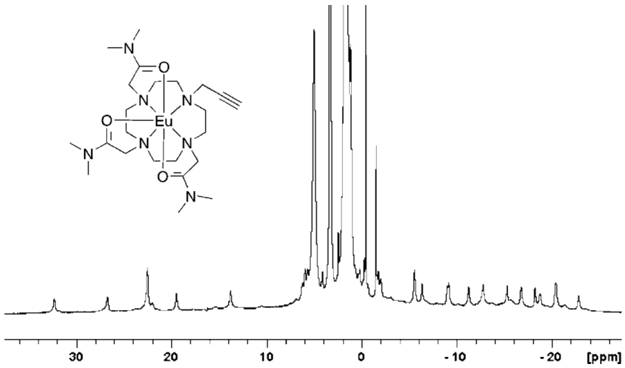
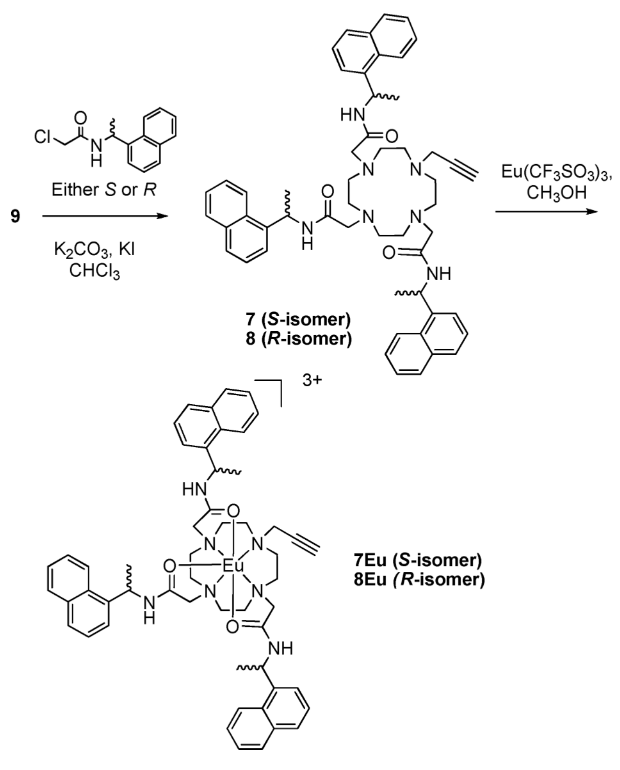


Fig. 3 The [1]H NMR (CD_3OD, 400 MHz) of the cationic complex **6Eu** at room temperature.

diastereoisomers, that are in slow mutual exchange on the NMR timescale, causes the number of resonances to be larger than expected.[27] The [1]H NMR spectrum (CD_3OD, 400 MHz) of the **6Tb** complex was also observed and due to the paramagnetic nature of the Tb(III) ion caused much more dramatic shifting of the complex in the [1]H NMR. The ESMS observed for both **6Eu** and **6Tb**, also demonstrated the formation of the desired complexes, with the isotopic distribution patterns matching that of the calculated one (See ESI†).



Scheme 2 Synthesis of the ligands **7** and **8** and the corresponding Eu(III) and Tb(III) complexes **7Eu** (*R*,*R*,*R*) and **8Eu** (*S*,*S*,*S*).

The synthesis of **7Eu** and **8Eu** is shown in Scheme 2, and these structures are based on the design of Parker *et al.*[28] who employed the tri-substituted cyclen analogues for the sensing of anions. The synthesis was carried out in a similar manner to that discussed above, commencing with the formation of **9**, which was reacted with 3.3 equivalents of (*R* or *S*) 2-chloro-*N*-(1-(naphthalen-1-yl)ethyl)acetamide, in $CHCl_3$ in the presence of K_2CO_3 and KI under reflux overnight. After filtration of any inorganic salts, the crude material (both *S* and *R* enantiomers) were purified using column chromatography on alumina (CH_2Cl_2/CH_3OH 95 : 5 as gradient), to yield the desired products, **7** (the *S*-isomer, *S*,*S*,*S*) and **8** (the *R*-isomer, *R*,*R*,*R*) as brown oils in 40 and 37% yields, respectively. The [1]H NMR spectrum ($CDCl_3$, 400 MHz) of these ligands confirmed the formation of the desired products; with the naphthyl protons resonating between 8.5–7 ppm, while the stereogenic methine and the CH_2 protons of the pendant arms occurred in a 1 : 2 ratio demonstrating the presence of a C_2 symmetry (See ESI†). This symmetry was further confirmed in the [13]C NMR. The optical activity of the two ligands was also investigated using Circular Dichroism (CD) in CH_3OH, which showed a distinctive bisignate profile for these ligands, with a strong $\pi\pi^*$ transition for each compound which were of equal and opposite magnitude, indicating that **7** and **8** were obtained as pair of enantiomers (See ESI†), similar to that seen in the work of Parker and co-workers for the tetraamide analogues.[29]

The Eu(III) complexes of **7** and **8** were formed as discussed above, by refluxing 1.1 equivalents of $Eu(CF_3SO_3)_3$ under argon in CH_3CN for 18 h. The complexes were then precipitated from swirling diethyl ether and dried under vacuum to yield **7Eu** and **8Eu** as brown oils in quantitative yields. As above, the complexes were analysed using both NMR (See ESI†) and MALDI HRMS, Fig. 4, for **8Eu**, which showed the correct isotopic distribution pattern for both complexes, while the CD spectra (See ESI for 7†) also showed the complexes with equal and opposite signs, which is consistent with the formation of single stereoisomers for these complexes, respectively, in solution. Moreover, the CD showed that the Eu(III) complexes displayed at room temperature large exciton coupling particularly at high energy.

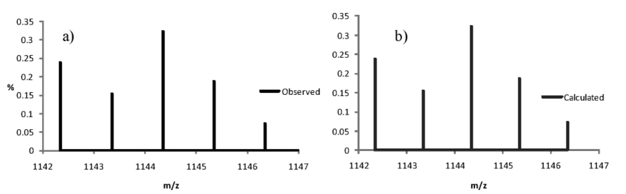


Fig. 4 The observed and the calculated isotopic distribution patterns for **8Eu**, for HRMS (*m*/*z*–MALDI). Found *m*/*z* 1144.344 for $[M\text{-}H^+ + CF_3SO_3^-]^+$ Calculated *m*/*z*: 1144.349.

Photophysical studies of 5Eu–8Eu and 5Tb

The photophysical properties of the complexes were investigated in methanol, at 1×10^{-5} M concentration. The spectra observed for **6Eu** and **6Tb** are shown in Fig. 5, recorded upon excitation at 250 nm (log ε = 4.17); into a transition assigned to the alkynyl moiety. The Eu(III) emission spectrum (Fig. 5 left), shows the deactivation of the $^5D_0$ excited state to ^7F_J (J = 0–4 respectively) occurring at 575, 593, 616, 651 and 695 nm, respectively, while the Tb(III) is typical of deactivation occurring from $^5D_4 \rightarrow {}^7F_J$ (J = 6–3). The presence of the ΔJ = 0 transition in the Eu(III) emission, is often observed for octa- or heptadentate lanthanide cyclen complexes possessing square antiprismatic geometry in solution. In a similar manner the emission spectra of **5Eu** was recorded in CH_3OH, showing an identical spectrum to that seen for **6Eu** above, while the emission spectra for **7Eu** and

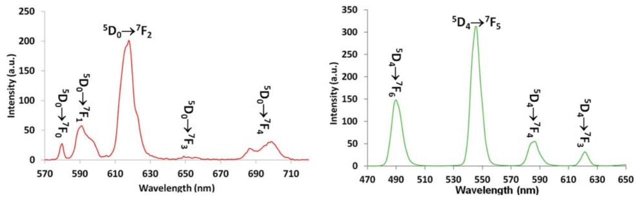


Fig. 5 The Eu(III) emission (left) and the Tb(III) emission spectra (right) of **6Eu** and **6Tb** (λ_{ex} = 250 nm, CH_3OH).

8Eu were recorded after excitation into the ππ* transition of the naphthalene antenna at 281 nm (log ε = 5.07). Once more, the appearance of the typical line-like emission bands due to the deactivation of the $^5D_0$ excited state to ^7F_J (J = 0–4) was observed.

The hydration state (q), or the number of metal bound water molecules, of the Eu(III) complexes formed above was evaluated by either direct excitation of the Eu(III) centre, as in the case of **5Eu** and **6Eu**, in H_2O and D_2O, or by excitation of the naphthalene antenna in **7Eu** and **8Eu**, in CH_3OH and CD_3OD (due to low solubility in water) and using the modified equation q Eu(III) = $A\cdot[(1/\tau_{O\text{-}H} - 1/\tau_{O\text{-}D}) - 0.25 - 0.075x]$ (where A = 1.2, 2.4 for measurements in H_2O/D_2O and CH_3OH/CD_3OD respectively; x = number of carbonyl-bound amide NH oscillators with Eu) developed by Parker *et al.*[30] Similarly, q values of Tb(III) complexes were determined in H_2O and D_2O using the following equation: q Tb(III) = $5\cdot[(1/\tau_{H2O} - 1/\tau_{D2O}) - 0.06]$. Table 1 summarises the excited state lifetimes determined for these complexes (which were best fitted to mono-exponential decay), which demonstrated that all the complexes had $q \sim 2$, which is to be expected for such heptadentate cyclen complexes. In contrast, only a single metal bound water molecule was found to be coordinated to **6Tb**.

Synthesis of the di-nuclear 1Ln–4Ln complexes using CuAAC reactions

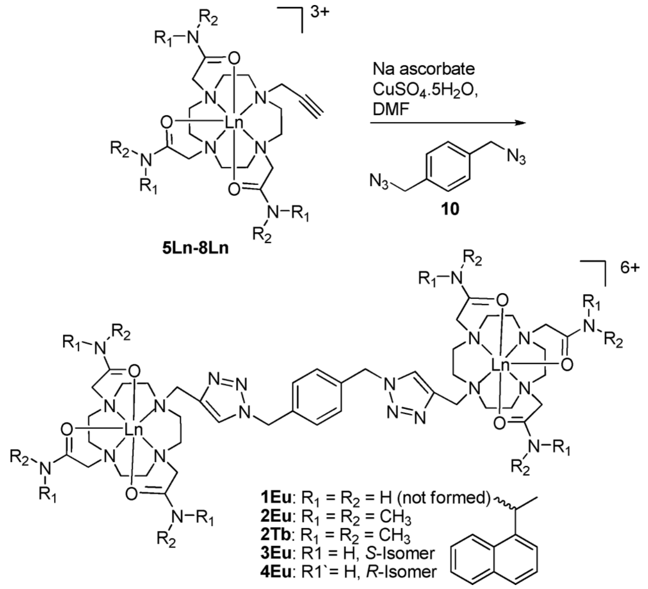
The synthesis of **1Ln–4Ln** is shown in Scheme 3. In each case, the mono-nuclear complexes developed above were reacted with the azide **10**, which was synthesised from 1,4-bis(bromomethyl)benzene in DMF followed by the addition of NaN_3, and the resulting mixture was stirred overnight to ensure the complete formation of the azide.

Initially the synthesis of compound **1Eu** was undertaken. The Eu(III) complex, **5Eu**, was dissolved in a minimal amount of DMF followed by the addition of $CuSO_4\cdot5H_2O$ and sodium ascorbate,

Table 1 Lifetimes and q values of **5Eu–8Eu** and **6Tb**

Complex	$\tau_{O\text{-}H}$ (ms)	$\tau_{O\text{-}D}$ (ms)	q (± 0.5)
5Eu[a]	0.40	1.50	1.4 (1.9)[c]
6Eu[a]	0.41	1.47	1.8
7Eu[b]	0.57	1.67	1.4 (1.9)[c]
8Eu[b]	0.56	1.69	1.5 (2.0)[c]
6Tb[a]	1.41	1.91	0.6

[a] Measured in H_2O and D_2O; [b] measured in CH_3OH and CD_3OD; [c] q-calculated without the correction factor for N–H vibrations.



Scheme 3 Attempted synthesis of **1Eu**, and the synthesis of **2Eu–4Eu** and **2Tb** using click chemistry.

and the resulting mixture was stirred at room temperature for three days, after which the solvent was removed under reduced pressure, giving an oily residue. Analysis of this product did not confirm the formation of the desired product. Consequently, the synthesis of **1Eu** was attempted by employing number experimental procedures; including changing the amount of the copper catalyst or ascorbate used, solvents (such as using toluene, or mixtures of DMF/H_2O or C_2H_5OH/H_2O) and varying the reaction temperature from room temperature to 120 °C. However, on all occasions, the reactions did not lead to the formation of **1Eu**. Consequently, it was concluded that the primary amide of the pendant arms could possibly interfere with the catalytic activity of the copper catalyst, and hence, we attempted the synthesis of **2Eu**.

As above, the azide **10** was synthesised *in situ* using DMF, after which the complex, **6Eu** and sodium ascorbate, were added, followed by the addition of $CuSO_4\cdot5H_2O$ in H_2O. The resulting mixture was stirred for 48 h, followed by washing with diethyl ether, to remove any unreacted azide, and precipitation out of swirling diethyl ether, which yielded **2Eu** in moderate 46% yield as a yellow oil. Analysis of this product was carried out using ^1H NMR (CD_3OD, 400 MHz), HRMS and IR, with the sharp stretch at 1600 cm^{-1} assigned to the triazole and as such, verifying the successful formation of the dinuclear click complex.

In a similar manner, the Tb(III) analogue **2Tb** was also formed using this method, in 51% yield as an oil. The product was analysed by using ^1H NMR (CD_3OD, 400 MHz) and HRMS which showed the formation of the desired product, where the observed isotopic distribution pattern matched that of the calculated spectra.

Both **3Eu** and **4Eu** were formed, by *in situ* preparation of the azide **10** in DMF, followed by the addition of **7Eu** or **8Eu**, respectively, $CuSO_4\cdot5H_2O$ and sodium ascorbate. In the case of **3Eu**, the reaction mixtures were refluxed overnight, after which it was washed with H_2O giving the desired product as brown oil

Table 2 Lifetimes and q values of **2Eu–4Eu** and **2Tb**

Complex	τ_{O-H} (ms)	τ_{O-D} (ms)	q (± 0.5)
2Eu[a]	0.86	1.60	0.4
3Eu[a]	0.72	0.82	−0.4 (−0.1)[c]
4Eu[b]	0.69	0.87	−0.4 (0.1)[c]
2Tb[a]	1.36	1.89	0.7

[a] Measured in H_2O and D_2O; [b] Measured in CH_3OH and CD_3OD; [c] q-calculated without the correction factor for N–H vibrations; for both q can be taken as 0.

in 55% yield. Similarly, **4Eu** was formed in 51% yield. Both were analysed using ^{1}H NMR (See ESI†), IR and ESMS‡.

As for the mono-nuclear complexes above, the hydration states of the dinuclear complexes, formed using the click chemistry, were determined. On all occasions, their excited state decays were best fitted to a monoexponential decay function. The results from these measurements (Table 2) show that the hydration state for all of the Eu(III) complexes has been reduced from *ca.* 2 to ~1, suggesting a change in the coordination environment of the Eu(III) ions, most likely due to coordination of one of the triazole nitrogens, as suggested originally by Lowe *et al.*[24] for such mono-nuclear analogues.

Photophysical studies of 2Eu–4Eu and 2Tb

The UV-Vis absorption spectra of **2Eu**, in CH_3OH ($c = 1 \times 10^{-5}$ M) showed the presence of two broad bands occurring at 250 nm and at *ca.* 450 nm, corresponding to the weak absorption of the phenyl and the triazole linker of these dinuclear complexes, respectively, Fig. 6. For **2Eu** and **2Tb**, excitation at 250 nm gave rise to metal centred emission for both complexes; moreover, the excitation at 450 nm, assigned to the triazole, also gave metal centred emission for the **2Tb** complex.

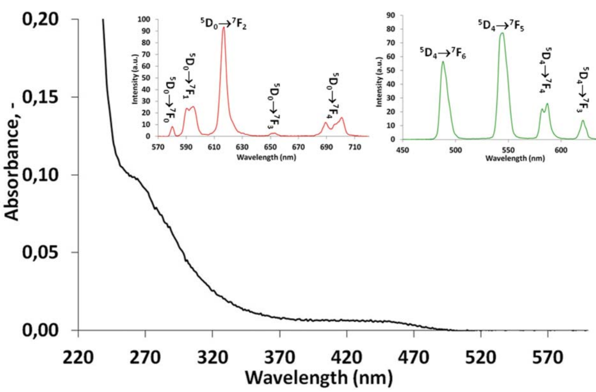


Fig. 6 The UV-Vis absorption spectrum of **2Eu**. *Inset*: The emission spectra of **2Eu** (left) and **2Tb** (right) (λ_{ex} = 250 nm, CH_3OH).

Similarly, the photophysical properties of **3Eu** and **4Eu** were evaluated in H_2O or CH_3OH. In the case of **3Eu**, the UV-Vis absorption spectrum displayed the expected ππ* transition attributed to the naphthalene groups which overlap with the absorption of the central triazole-based spacer. As before, the two complexes were also analysed by recording the CD-spectra of the two enantiomers, which showed that the chirality of the two was preserved during the Cu(I) catalysed click synthesis. Excitation into the antennae gave rise to fluorescence emission, Fig. 7a, which showed the dominance of the naphthalene emission and a smaller broader emission band at longer wavelength, assigned to eximer formation between the antennae, which can correspond to changes in the coordination environment of the complex after the click reaction, as such broadening was absent for the mono-nuclear complexes.

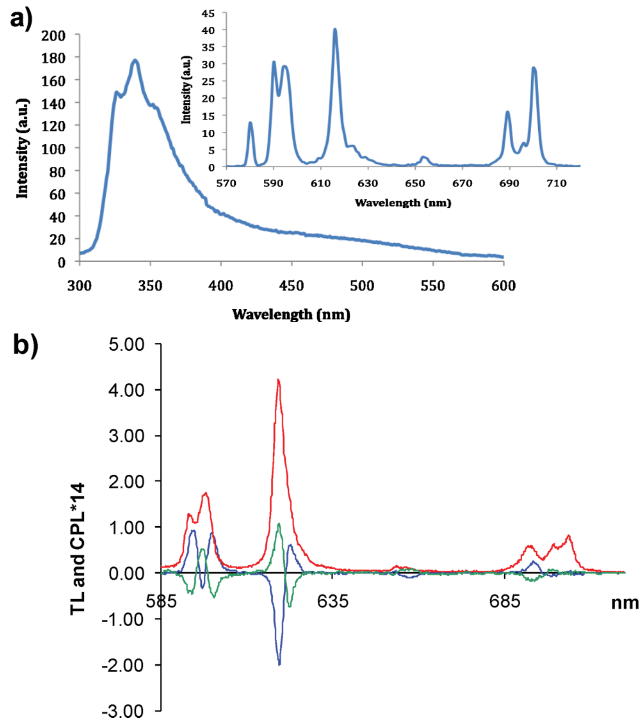


Fig. 7 a) The fluorescence emission spectrum of **3Eu**. *Inset*: the corresponding Eu(III) emission spectrum. b) The total luminescence of **4Eu** (in red) and the circular polarised (CPL) emission spectra of both **3Eu** (green) and **4Eu** (blue) (λ_{ex} = 281 nm, CH_3OH).§.

Excitation into the antennae at 281 nm also gave rise, on both occasions, to the Eu(III) centred emission, which had a strong contribution from the ΔJ = 0 band, Fig. 7a inset, for **3Eu**. The Eu(III) spectrum looks similar to that observed for the mono-complex but upon closer inspection there are some differences, particularly for the ΔJ = 2 and 4, both of which are hypersensitive and sensitive to change in the local coordination environment of the metal ion; possibly indicating that the triazole antenna was coordinating to the metal centre, as had been confirmed by the q-values determined above (*cf.* Table 1 and 2). Due to the presence of the chiral antennae in **3Eu** and **4Eu**, we also probed the chiral emission arising from the Eu(III) ions in these complexes.[28] The enantiomeric nature of the complexes was evident from their CPL spectra shown in Fig. 7b, upon excitation of the antennae in CH_3OH solution. As expected, the CPL signals were of opposite sign,§ moreover, the magnitude of the dissymmetry factors ($2\Delta I/I$) was calculated as g_{em} = −0.063 for the ΔJ = 2 transition of **4Eu**, which is similar in magnitude to that reported by Parker *et al.*

‡ These complexes were analysed by both ESMS as well as MALDI MS. Fragmentation was observed for both **3Eu** and **4Eu**, both of which showed the fragmentation of the bimetallic cyclen complexes into the mono-nuclear species **M1**$^+$ and **M2**$^+$ (see experimental above). We were unable to obtain HR-MS of compund **5Eu**.

for both C_3 (reported as $g_{em} = -0.06$) and C_4 symmetrical related phenyl based tri-[28b] and tetra-amide[30] complexes.

Conclusions

Herein, we have presented the synthesis and the photophysical evaluations of several new Eu(III) and Tb(III) dinuclear-lanthanide complexes. All possess triazole-based bridges, formed by using copper catalysed 1,3-cycloaddition reactions between a heptadentate alkyne functionalised cyclen Eu(III) or Tb(III) complex and the azide **10**. We demonstrated that for such systems, the prerequisite is the formation of the lanthanide complexes prior to the use of the Cu(I) catalysed 1,3-cycloaddition reactions, due to the high affinity of the cyclen macrocycle for Cu(II).

We also show that the nature of the acetamide arms has a significant influence on the outcome of the click reaction, where the use of the acetamide **5Eu** did not give rise to the successful coupling, while the *N*,*N*-dimethyl analogues **6Eu** and **6Tb** did result in the successful formation of the di-nuclear complexes **2Eu** and **2Tb** in 46 and 51% yields, respectively. Similarly, we showed that the use of antenna appended to the acetamide arms also resulted in the successful formation of such di-nuclear complexes (*e.g.* **3Eu** and **4Eu**). Moreover, we confirmed, using excited state lifetimes measurements in H_2O and D_2O (or CH_3OH and CD_3OD), that the triazole moiety participates in the direct coordination of the lanthanides ions within these di-nuclear complexes, where the hydration state of the Eu(III) complexes **2Eu–4Eu** changed from ~2 to ~1 for each metal centre. Furthermore, we demonstrated that on all occasions, these dinuclear complexes gave rise to metal centred emission upon excitation of the triazole or, in the case of **3Eu** and **4Eu**, the naphthalene antennae, the latter also giving rise to CPL, which demonstrated the metal-centred chiral emission.

We are currently in the process of exploring the use of the Cu-catalysed 1,3-Huisgen reaction in alternative lanthanide based complexes and for the formation of novel ligands for the use in lanthanide directed synthesis of lanthanide luminescent self-assembly structures.

Experimental

General

Starting materials were obtained from Sigma-Aldrich and used without further purification. Solvents used were HPLC grade unless otherwise mentioned. ^{1}H NMR spectra were recorded at 400 MHz using a Bruker Spectrospin DPX-400. Electrospray mass spectra (ES-MS) were measured on a Micromass LCT spectrometer calibrated using a leucine enkephaline standard. MALDI Q-Tof mass spectra were carried out on a MALDI Q-Tof Premier (Waters Corporation, Micromass MS technologies, Manchester, UK) and high-resolution mass spectrometry was performed using Glu-Fib as an internal reference (peak at *m*/*z* 1570.677).

All photophysical studies were performed at 298 K in methanol or water solutions. UV-visible absorption spectra were measured in 1 cm quartz cuvettes on a Varian Cary 50 spectrophotometer. Baseline correction was applied for all spectra. Emission (fluorescence, phosphorescence) spectra and lifetimes were recorded on a Varian Cary Eclipse Fluorimeter. Quartz cells with a 1 cm path length from Hellma were used for these measurements. The temperature was kept constant throughout the measurements by using a thermostated unit block. CD spectra were recorded on a Jassco J-810-150S spectrometer.

1-(Prop-2-ynyl)-1,4,7,10-tetraazacyclododecane (9)

1,4,7,10-tetraazacyclododecane (1.16 g, 6.72 mmoles, 4 eq.) was dissolved in $CHCl_3$ with Et_3N (0.23 mL, 6.72 mmoles, 4 eq.). 3-Bromopropyne (0.15 mL, 1.68 mmoles, 1 eq.) was added slowly drop wise and the solution was refluxed overnight at 61 °C. The resulting solution was then washed with 1 M aqueous KOH (5 × 15 mL) solution and distilled H_2O (2 × 15 mL), dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure to yield a yellow oil 0.334 g in 94% yield. HRMS (*m*/*z*-ES+) Found for $C_{11}H_{23}N_4$: 211.1974, Calculated: 211.1923; δ_H ($CDCl_3$, 400 MHz): 3.67 (2H, s, CH_2), 2.69–2.65 (m, 16H, CH_2), 2.11 (1H, CH, alkyne). δ_C ($CDCl_3$, 100 MHz): 76.34 (CH), 72.2 (CH), 49.5 (CH_2), 46.4 (CH_2), 45.7 (CH_2), 44.1 (CH_2), 42.7 (CH_2). ν_{max} (neat sample)/cm^{-1}: 3431, 3372, 3284, 3239, 3183, 2921, 2841, 2820, 2311, 2092, 1648, 1613, 1550, 1461, 1401, 1343, 1263, 1257, 1155, 1122, 1054, 985, 901, 814.7, 807, 735.

2,2′,2″-(10-(prop-2-ynyl)-1,4,7,10-tetraazacyclododecane-1,4,7-triyl)triacetamide (5)

Compound **9** (0.17 g, 0.80 mmoles, 1 eq.), K_2CO_3 (0.34 g, 2.47 mmoles, 3.1 eq.) and KI (0.41 g, 2.47 mmoles, 3.1 eq.) were dissolved in $CHCl_3$. 2-Bromoacetamide (0.34 g, 2.47 mmoles, 3.1 eq.) was added drop wise over 10 min and the resulting mixture was refluxed over 7 days. The mixture was filtered through a plug of celite. The solvent was removed under reduced pressure and the residue was dissolved in 1 mL of CH_3OH and precipitated out of swirling diethyl ether to give a yellow oil, 0.167 g in 55% yield. HRMS (*m*/*z*-ES+) Found for $C_{17}H_{32}N_7O_3$: 382.1940, Required 382.2567; δ_H ($CDCl_3$, 400 MHz): 8.20 (2H, s, NH_2), 5.80 (4H, s, NH_2), 3.30 (4H, s, CH_2), 3.1 (4H, s, CH_2), 2.53–2.58 (16H, cyclen CH_2), 2.19 (1H, Alkyne CH); δ_C (CD_3OD, 100 MHz): 175.1 (q), 72.9 (q), 61.8 (CH), 58.9 (CH), 53.4 (CH_2), 53.0 (CH_2), 50.9 (CH_2), 50.7 (CH_2), 43.5 (CH_2), 31.1 (CH). ν_{max} (neat sample)/cm^{-1}: 3348, 2949, 2837, 1672, 1450, 1248, 1226, 1172, 1117, 1019.

5Eu. Ligand **5** (0.04 g, 0.11 mmoles, 1 eq.) was dissolved in CH_3OH (10 mL) and $Eu(CF_3SO_3)_3$ (0.075 g, 0.13 mmoles, 1.2 eq.) added slowly to the solution and refluxed overnight at 65 °C. The solvent was reduced to 1 mL under reduced pressure and precipitated from swirling diethyl ether (100 mL) to yield yellow oil, 0.059 g, in quantitative yield. δ_H (CD_3OD, 400 MHz): 30.2, 26.7, 22.5, 19.5, 13.8, 5.99, 5.69, 4.17, 2.48, 0.24, −0.28, −1.73, −1.98, −5.53, −6.33, −9.12, −11.2, −12.72, −15.25, −16.73, −18.18, −18.71, −20.41, −22.77. ν_{max} (neat sample)/cm^{-1}: 3348, 2949, 2837, 1672, 1450, 1248, 1226, 1172, 1117, 1019.

2,2′-(4-(2-(methylamino)-2-oxoethyl)-10-(prop-2-ynyl)-1,4,7,10-tetraazacyclododecane-1,7-diyl)bis(*N*,*N*-dimethyl-acetamide) (6)

Compound **9** (0.33 g, 1.59 mmoles, 1 eq.) was dissolved in CH_3CN and KI (0.80 g, 5.25 mmoles, 3.3 eq.) and K_2CO_3 (0.726 g, 5.25 mmoles, 3.3 eq.) were added to the solution. α-Chloro-*N*, *N*-dimethyl acetamide (0.64 g, 5.25 mmoles, 3.3 eq.) was added slowly to the solution and the solution was stirred at 85 °C for 7 days. The solution was filtered and the product was extracted into $CHCl_3$, washed with 1 M KOH (5 × 15 mL) and H_2O (2 × 15 mL), dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure to yield a yellow oil, 0.43 g in 58% yield. HRMS (*m*/*z*-ES+): Found for $C_{23}H_{44}N_7O_3$: 466.3484, Required: 466.3506; δ_H ($CDCl_3$, 400 MHz): 3.38–2.66 (m, 34 CH_2 and CH_3, CH_2), 2.13 (m, 1H, alkyne CH). δ_C ($CDCl_3$, 100 MHz): 170.9 (q) 72.59 (q), 72.5 (q), 57.9 (CH_2), 57.3 (CH_2), 52.6 (CH_2), 52.38 (CH_2), 51.98 (CH_2), 51.9 (CH_2), 51.6 (CH_2), 43.1 (CH_2), 42.3 (CH_2), 37.2 (CH_3), 37.0 (CH_3), 35.5 (CH). ν_{max} (neat sample)/cm^{-1}: 3455, 3302, 3231, 2935, 2815, 2237, 1635, 1503, 1457, 1398, 1360, 1263, 1104, 1060, 1008, 924, 803, 751, 729, 694.

6Eu. Ligand **6** (0.26 g, 0.57 mmoles, 1 eq.) was dissolved in CH_3OH and $Eu(CF_3SO_3)_3$ (0.37 g, 0.62 mmoles, 1.1 eq.) added slowly and the solution was stirred overnight at 65 °C, after which the solvent was reduced to 1 mL and the product was precipitated from swirling diethyl ether (100 mL) to yield a yellow oil 0.50 g, quantitative yield. HRMS (*m*/*z*-ES+) Found for $C_{24}H_{42}N_7O_6F_3SEu$: 766.2103, Required: 766.2081; δ_H (CD_3OD, 400 MHz): 19.21, 18.08, 16.43, 11.90, 5.56, 4.01, 2.52, 1.70, 0.73, −1.79, −7.69, −8.62, −13.28, −16.66, −18.96. ν_{max} (neat sample)/cm^{-1}: 3454, 3232, 2926, 1618, 1505, 1459, 1414, 1409, 1249, 1215, 1153, 1078, 1026, 957, 906, 823, 756.

6Tb. Ligand **6** (0.30 g, 0.645 mmoles, 1 eq.) was dissolved in CH_3OH (25 mL) with $Tb(CF_3SO_3)_3$ (0.52 g, 0.71 mmoles, 1.1 eq.) and refluxed overnight. The solvent was removed under reduced pressure and redissolved in 1 mL of CH_3OH with further precipitation out of swirling diethyl ether (150 mL) to yield yellow oil 0.40 g, quantitative yield. HRMS (*m*/*z*-ES+) Found 772.2144 for $C_{24}H_{42}N_7O_6F_3STb$, Required: 772.2123; δ_H (CD_3OD, 400 MHz): 432.6, 391.9, 376.1, 295.1, 287.2, 247.0, 215.1, 192.9, 177.2, 145.2, 129.2, 109.6, 96.9, 89.9, 86.9, 82.2, 53.1, 16.2, 1.35, −7.4, −11.8, −12.2, −18.5, −27.9, −31.1, −2.0, −7.6, −12.5, −18.9, −28.1, −31.5, −49.6, −53.5, −55.4, −82.2, −86.9, −89.6, −94.8, 106.7, −107.3, −119.5, −148.1, −150.7, −174.8, −186.5, −219.7, −242.8, −260.6, −318.2, −338.1, −366.2, −372.3, −608.0; ν_{max} (neat sample)/cm^{-1}: 3485, 1620, 1462, 1248, 1155, 1079, 1026, 958, 824.

2Eu. 1,4-Bis(bromomethyl)benzene (0.04 g, 0.16 mmoles, 1 eq.) was dissolved in DMF (5 mL) and sodium azide (0.03 g, 0.48 mmoles, 3 eq.) was added to the solution and stirred overnight at 25 °C. The complex **6**.**Eu** (0.20 g, 0.32 mmoles, 2 eq.) was then added with sodium ascorbate (0.003 g, 0.02 mmoles, 0.1 eq.) and $CuSO_4{\cdot}5H_2O$ (0.04 g, 0.02 mmoles, 0.1 eq.) and stirred for a further 48 h before extracting the solution with ether to remove excess xylene starting material. The solvent was removed from the aqueous layer and the product redissolved in CH_3OH and triturated with ether to yield a green solid. This was then purified using column chromatography on neutral alumina with CH_2Cl_2:MeOH(5%) gradient as eluent, giving the product as a yellow hygroscopic solid (R_f 0.66), 0.11 g in 46% yield. HRMS (*m*/*z*-MALDI+) Found: 944.3231 for $C_{57}H_{95}Eu_2F_9N_{20}O_{16}S_3^{2+}$, Required: 944.2339. δ_H (CH_3OH, 400 MHz): 36.40, 34.90, 30.56, 29.01, 27.46, 26.78, 25.41, 22.43, 21.27, 19.34, 17.99, 16.92, 14.79, 13.63, 12.38, 9.28, 8.12, 7.54, 6.77, 5.03, 4.54, 3.58, 2.90, 2.20, 1.45, 0.48, −0.58, −1.35, −2.80, −3.26, −4.45, −5.22, −6.00, −7.64, −9.57, −10.73, −11.41, −12.76, −13.44, −14.31, −16.64, −18.57, −19.15, −20.02. ν_{max} (neat sample)/cm^{-1}: 3415, 2141, 2060, 1621, 1610, 1449, 1283, 1234, 1183, 1155, 1131, 1032, 767, 638.

2Tb. 1,4–Bis(bromomethyl)benzene (0.04 g, 0.02 mmoles, 1 eq.) was dissolved in DMF (5 mL) and sodium azide (0.02 g, 0.03 mmoles, 2 eq.) was added to the solution and stirred overnight at 25 °C. The complex **6Tb** (0.19 g, 0.30 mmoles, 2 eq.) was then added with sodium ascorbate (0.003 g, 0.02 mmoles, 0.1 eq.) and $CuSO_4{\cdot}5H_2O$ (0.004 g, 0.02 mmoles) and stirred for a further 48 h before extracting the solution with ether to remove excess xylene starting material. The aqueous layer was evaporated and the resulting product was re-dissolved in CH_3OH and triturated with ether to yield yellow oil 0.11 g in 51% yield. HRMS (*m*/*z*-MALDI+): Found: 2031.413 for $C_{58}H_{93}N_{20}O_{18}F_{12}S_4Tb_2$, Required: 2031.417; δ_H (CD_3OD, 600 MHz): 306.7, 254.7, 174.3, 167.0, 150.8, 99.9, 85.0, 82.6, 65.6, 63.6, 61.0, 45.7, 4.83, 3.69, 3.33, 1.32, 0.92 −19.73, −16.44. ν_{max} (neat sample)/cm^{-1}: 3659, 3556, 3475, 2942, 2923, 2850, 2091, 1619, 1540, 1500, 1458, 1406, 1374, 1255, 1231, 1169, 1035, 958, 907, 821, 823, 765, 698.

2,2′-(4-(2-(1-(naphthalen-1-yl)ethylamino)-2-oxoethyl)-10-(prop-2-ynyl)-1,4,7,10-tetraazacyclododecane-1,7-diyl)bis(*N*-methyl-*N*-(1-(naphthalen-1-yl)ethyl)acetamide)

7(*S*,*S*,*S*). Ligand **9** (0.11 g, 0.50 mmoles, 1eq.) was dissolved in CH_3CN with K_2CO_3 (0.23 g, 1.66 mmoles, 3.3 eq.) and KI (0.28 g, 1.66 mmoles, 3.3 eq.). (*S*)-2-chloro-*N*-(1-(naphthalen-1-yl)ethyl)acetamide (0.41 g, 1.66 mmoles, 3.3 eq.) was added and the solution was refluxed over 7 days. The solution was filtered through a plug of celite and the solvent was removed under vacuum. The compound was redissolved in $CHCl_3$ and extracted with 0.1 M KOH solution. The organic layers were combined, dried over $MgSO_4$, filtered and the solvent was removed to yield a cream oil which was purified by column chromatography on neutral alumina using 95 : 5 CH_2Cl_2/CH_3OH to yield 0.1588 g, 37% yield. HRMS (*m*/*z*-ES+) Found for $C_{53}H_{62}N_7O_3$: 844.4911, Required: 844.4914; δ_H ($CDCl_3$, 400 MHz): 7.29–8.1 ppm (br, m, 21 CH naphthyl), 5.7–5.9 ppm (m, 3 H, CH-naphthyl), 1.28–3.0 ppm (br m, 34H, CH_2-Cyclen, CH_3, CH-alkyne). δ_C ($CDCl_3$, 100 MHz): 170.40 (q) 169.90 (q), 169.19 (q), 137.9 (q), 137.6 (q), 133.8 (q), 133.81 (q), 131.5(q), 131.3(q), 128.7 (CH), 128.6 (CH), 128.5 (CH), 126.7 (CH), 126.6 (CH), 126.5 (q), 126.0 (CH), 125.9 (CH), 125.5 (CH), 125.2 (CH), 125.0 (CH), 123.6 (CH), 123.4 (CH), 122.8 (CH), 122.6 (CH), 78.0 (CH), 77.2 (CH), 77.0 (CH), 76.7 (CH), 73.1 (CH), 72.5 (CH), 58.6 (CH_2), 56.1 (CH_2), 55.2 (CH_2), 54.9 (CH_2), 54.6 (CH_2), 52.6 (CH_2), 51.8 (CH_2), 51.7 (CH_2), 51.6 (CH_2), 50.8 (CH_2), 43.8 (CH), 43.7 (CH_2), 43.5 (CH), 43.4 (CH_2), 19.9 (CH_3), 19.7 (CH_3), 19.5 (CH_3). ν_{max} (neat sample)/cm^{-1}: 3280, 3040, 2966, 2927, 2810, 2235, 1646, 1597, 1508, 1446, 1396, 1368, 1323, 1293, 1246, 1237, 1170, 1107, 1101, 1087, 1000, 961, 905, 799, 777, 724.

8(*R*,*R*,*R*). Ligand **9** (0.10 g, 0.48 mmoles, 1 eq.) was dissolved in CH_3CN with K_2CO_3 (0.22 g, 1.57 mmoles, 3.3 eq.) and KI (0.26 g, 1.57 mmoles, 3.3 eq.). (*R*)-2-chloro-*N*-(1-(naphthalen-1-yl)ethyl)acetamide (0.39 g, 1.57 mmoles, 3.3 eq.) was added and the solution was refluxed over 7 days. The solution was filtered through a plug of celite and the solvent was removed under vacuum. The compound was redissolved in $CHCl_3$ and extracted with 0.1 M KOH solution. The organic layers were combined, dried over

$MgSO_4$, filtered and the solvent was removed, followed by column chromatography on neutral alumina using 95 : 5 CH_2Cl_2/CH_3OH to yield light brown oil, 0.19 g, 47% yield. HRMS (*m*/*z*-ES+) Found for $C_{53}H_{62}N_7O_3$: 844.4932, Required: 844.4914; δ_H ($CDCl_3$, 400 MHz): 7.28– 8.1 ppm (br, m, 21 CH-naphthyl), 5.7–5.9 ppm (m, 3 H, CH-naphthyl), 1.28– 3.0 ppm (br m, 34H, CH_2-Cyclen, CH_3, CH-alkyne). δ_C ($CDCl_3$, 100 MHz): 170.4 (q) 169.9 (q), 169.2 (q), 138.0 (q), 137.5 (q), 133.9 (q), 133.81 (q), 131.5(q), 131.3(q), 128.7 (CH), 128.6 (CH), 128.5 (CH), 126.7 (CH), 126.6 (CH), 126.5 (q), 126.0 (CH), 125.8 (CH), 125.5 (CH), 125.2 (CH), 125.1 (CH), 123.6 (CH), 123.4 (CH), 122.8 (CH), 122.6 (CH), 78.0 (CH), 77.2 (CH), 77.0 (CH), 76.7 (CH), 73.6 (CH), 73.1 (CH), 58.6 (CH_2), 56.1 (CH_2), 55.2 (CH_2), 54.9 (CH_2), 54.6 (CH_2), 52.6 (CH_2), 52.1 (CH_2), 51.7 (CH_2), 51.6 (CH_2), 50.8 (CH_2), 43.8 (CH), 43.7 (CH_2), 43.5 (CH), 43.4 (CH_2), 20.0 (CH_3), 19.6 (CH_3), 19.5 (CH_3). v_{max} (neat sample)/cm^{-1}: 3510, 3275, 3118, 2931, 2881, 1617, 1581, 1535, 1463, 1367, 1243, 1233, 1165, 1082, 1028, 959, 903, 830, 804, 780.

7Eu(*S*,*S*,*S*). Ligand **7** (0.046 g, 0.053 mmoles, 1eq.) was dissolved in CH_3OH with $Eu(CF_3SO_3)_3$ (0.035 g, 0.058 mmoles, 1.1 eq.) and refluxed overnight. The product was isolated by precipitation from ether to give a clear oil 0.0573 g in quantitative yield; HRMS (*m*/*z*-MALDI+): Found 1144.343 for $C_{54}H_{60}EuF_3N_7O_6S$ ([M-H$^+$+$CF_3SO_3^-$]), Required 1144.349 δ_H (CD_3OD, 400 MHz) 19.21, 18.42, 9.76, 9.52, 9.39, 9.13, 8.38, 8.23, 8.15, 7.74, 7.69, 7.45, 7.43, 7.07, 6.65, 6.49, 6.30, 6.02, 5.73, 5.52, 3.66, 3.50, 3.16, 3.09, 2.48, 2.28, 2.18, 1.59, 1.42, 1.31, 1.20, 0.97, 0.00, –0.41, –2.26, –4.51, –4.96, –5.88, –7.01, –7.99, –9.12, –9.64, –10.36, –11.35, –12.20, –12.98, –15.19, –19.62, –20.00. v_{max} (neat sample)/cm^{-1}: 3494.9, 3253.9, 3095, 2977, 2870, 1615, 1575, 1511, 1454, 1379, 1362, 1261, 1237, 1162, 1079, 1027, 957, 927, 899, 861, 801, 779, 731.

8Eu(*R*,*R*,*R*). Ligand **8** (0.164 g, 0.194 mmoles, 1 eq.) was dissolved in CH_3OH with $Eu(CF_3SO_3)_3$ (0.128 g, 0.213 mmoles, 1.1 eq.) and refluxed overnight. The product was isolated by precipitation from swirling diethyl ether to give a clear oil 0.20 g quantitative yield. HRMS (*m*/*z*-MALDI+): Found 1144.343 for $C_{54}H_{60}EuF_3N_7O_6S$ ([M-H$^+$+$CF_3SO_3^-$]), Required 1144.349 δ_H (CD_3OD, 400 MHz) 19.21, 18.42, 9.76, 9.52, 9.39, 9.13, 8.38, 8.23, 8.15, 7.74, 7.69, 7.45, 7.43, 7.07, 6.65, 6.49, 6.30, 6.02, 5.73, 5.52, 3.66, 3.50, 3.16, 3.09, 2.48, 2.28, 2.18, 1.59, 1.42, 1.31, 1.20, 0.97, 0.00, –0.41, –2.26, –4.51, –4.96, –5.88, –7.01, –7.99, –9.12, –9.64, –10.36, –11.35, –12.20, –12.98, –15.19, –19.62, –20.00. v_{max} (neat sample)/cm^{-1}: 3494.9, 3253.9, 3095, 2977, 2870, 1615, 1575, 1511, 1454, 1379, 1362, 1261, 1237, 1162, 1079, 1027, 957, 927, 899, 861, 801, 779, 731.

3Eu(*S*,*S*,*S*). 1,4-Bis(bromomethyl)benzene (0.028 g, 0.15 mmoles, 1 eq.) was dissolved in DMF (5 mL) and sodium azide (0.02 g, 0.30 mmoles, 2 eq.) was added to the solution and stirred overnight at 25 °C. The complex **7*S*** (0.30 g, 0.30 mmoles, 2 eq.) was then added with sodium ascorbate (0.003 g, 0.02 mmoles, 0.1 eq.) and $CuSO_4{\cdot}5H_2O$ (0.004 g, 0.02 mmoles) and stirred for a further 48 h before washing the solution with ether to remove excess xylene starting material. The solvent was removed from the aqueous layer and the product re-dissolved in CH_3OH and triturated with ether to yield green oil 0.17 g in 51% yield. HRMS (*m*/*z*-ESMS+): **M1$^+$**, calculated 1054.340, found: 1054.708 for the chemical formula $C_{50}H_{59}EuN_7O_7S$ and **M2$^+$**, calculated 1039.421; found: 1039.688 for the chemical formula: $C_{53}H_{62}EuN_{10}O_3$;‡ δ_H (CD_3OD, 600 MHz): 306.7, 254.7, 174.3, 167.0, 150.8, 99.9, 85.0, 82.6, 65.6, 63.6, 61.0, 45.7, 4.83, 3.69, 3.33, 1.32, 0.92 –19.73, –16.44. v_{max} (neat sample)/cm^{-1}: 3279, 3118, 2989, 2928, 1746, 1617, 1599, 1516, 1484, 1461, 1413, 1365, 1244, 1166, 1081, 1027, 960, 903, 829, 803, 780, 735.

4Eu(*R*,*R*,*R*). 1,4-Bis(bromomethyl)benzene (0.05 g, 0.26 mmoles, 1 eq.) was dissolved in DMF (5 mL) and sodium azide (0.03 g, 0.52 mmoles, 2 eq.) was added to the solution and stirred overnight at 25 °C. The complex **7*R*** (0.52 g, 0.52 mmoles, 2 eq.) was then added with sodium ascorbate (0.005 g, 0.03 mmoles, 0.1 eq.) and $CuSO_4{\cdot}5H_2O$ (0.004 g, 0.02 mmoles, catalytic) and stirred for a further 48 h before extracting the solution with ether to remove excess xylene starting material. The solvent was removed from the aqueous layer and the product was re-dissolved in CH_3OH and triturated with ether to yield yellow oil 0.30 g in 53% yield. HRMS (*m*/*z*-ESMS+): **M1$^+$**, calculated 1054.340, found: 1054.708 for the chemical formula $C_{50}H_{59}EuN_7O_7S$ and **M2$^+$**, calculated 1039.421; found: 1039.688 for the chemical formula: $C_{53}H_{62}EuN_{10}O_3$;‡ δ_H (CH_3OH, 600 MHz): 27.49, 25.51, 24.20, 22.77, 22.38, 9.93, 9.22, 8.78, 8.45, 8.07, 7.79, 7.57, 7.08, 6.80, 6.53, 6.09, 5.60, 5.43, 4.94, 4.44, 3.84, 3.40, 3.13, 2.91, 2.30, 1.87, 1.43, 1.10, 0.05, –0.06, –1.65, –2.63, –3.24, –4.17, –5.49, –7.19, –8.17, –8.72, –9.93, –11.16, –11.62, –12.74, –14.93, –15.75, –16.92, –17.88. v_{max} (neat sample)/cm^{-1}: 3419, 2997, 2909, 2061, 1617, 1540, 1463, 1387, 1254, 1171, 1083, 1031, 957, 901, 804, 780.

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