Highly luminescent lanthanide complexes sensitised by tertiary amide-linked carbostyril antennae†

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Carbostyrils are among the most widely used sensitising antennae for luminescent lanthanides; they afford bright complexes with Eu and Tb, and can also sensitise the emissions of the less commonly used Sm, Dy, Yb and Nd. Systematic studies on the effect of structural variations on the photophysical properties and lanthanide sensitising abilities of carbostyrils can therefore have a large impact. We replaced the secondary amide linker that connects the metal binding site to the antenna with a carboxymethyl-substituted tertiary amide. Eight Tb and Eu complexes were prepared. All had higher lanthanide luminescence quantum yields (Φ_{Ln}) than their secondary amide analogues; three Tb emitters had Φ_{Tb} > 40%. Eu complexes had Φ_{Eu} up to 11.6%. The antenna singlet and triplet excited states are slightly shifted, while the metal coordination sphere is unchanged by the introduction of the carboxymethyl group.

The development of new emitters is a lengthy and high-risk task. Therefore, there are substantial efforts directed towards the optimization of already reported luminescent Ln complexes, which encompass the understanding of the energy transfer mechanism and, if possible, elimination of quenching pathways. A well-known Ln excited state quenching pathway involves X–H overtones (X = O, N, C)16,17 but can be avoided by the saturation of the Ln inner coordination sphere with a multidentate ligand, and, in some cases, by ligand deuteration.18,19

The quenching of the antenna excited state by atmospheric oxygen21–23 and biologically relevant reductants has also been studied.4,24,25 These quenching processes could be harnessed for the construction of responsive probes, or environmentally-activated Ln-based theranostics.23,26–28

Carbostyrils (quinolin-2(1H)-ones) are among the most widely used antennae for the sensitisation of Eu and Tb, of which the most commonly used one is cs124 (Scheme 1, 2a).29–37 Some are even effective for Sm and Dy,38 as well as the near infrared (NIR) emitting Yb and Nd.39 A variety of substituted carbostyrils have been reported (Fig. 1a).38,40 Many were evaluated as antennae, even though in-depth photophysical characterizations are rare.39 Most of the structural variations were limited to the peripheral substituents, usually in the 3 and 4 (R1 and R2, respectively in Fig. 1) positions. There are also a few examples of core N-substitutions (alkylations).34 The effects of exocyclic N-alkylations on Ln sensitization have not been studied in detail, presumably because changes were expected to be small.

We hypothesised that the removal of the N–H bond may have a measurable effect on the Ln emission quantum yield, at

Introduction

Lanthanide (Ln)-based emitters occupy a unique niche among luminescent compounds. They have long emission lifetimes, narrow emission bands, are often highly photostable, and have negligible phototoxicities.1–6 These properties are in sharp contrast to the rapid degradation, broad emission profiles and short lifetimes of organic emitters, or the toxicity of transition metal-based phosphorescent dyes or quantum dots. Ln(II) emission results from Laporte-forbidden f–f-transitions, and direct Ln(II) excitation is inefficient. Sensitisation by a light-harvesting antenna is common, and bypasses the small extinction coefficients of the Ln(III). Energy transfer (ET) from the antenna to the Ln can be efficient, and in the most successful cases, bright luminescent complexes are obtained.2,7 The brightness of Ln(III) emitters (B = ε·Φ; ε: molar decadic absorption coefficient at λ_{εmax}, Φ: dye’s fluorescence quantum yield) depends on several factors, e.g. the number of absorbing and emitting units,8–11 the efficiency of the antenna absorption and of the energy transfer,12,13 the intrinsic quantum yield of the Ln(III), and the quenching processes that deplete the antenna and Ln(III) excited states.14,15
least for the more sensitive Eu complexes. The majority of the reported carbostyril-appended Ln-emitters retain this N–H bond. Parker and Williams have prepared the tetraamide shown in Fig. 1b. However, the methylamide arms bring further N–H oscillators into the proximity of the Ln. Furthermore, the +3 charge of this complex facilitates photoinduced electron transfer (PeT) from the excited antenna to the Eu by destabilizing Eu\(^{3+}\). For most of the sensitised Eu(III) emitters, PeT quenches the luminescence. Because of the combination of detrimental processes the evaluation of the contribution of the N-alkylation to the photophysics of the complex shown in Fig. 1b difficult. Here, we investigate the role of exocyclic N-alkylation in carbostyril-sensitised DO3A-type Ln complexes (Fig. 1c, DO3A = 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetracetic acid). Surprisingly, we found that N-alkylation with a carboxymethyl group afforded a dramatic increase in Ln emission for both Eu and Tb emitters. We attempt to explain these results based on spectroscopic and structural analyses.

Results and discussion

Synthesis

The DO3A-derived ligands were synthesised as shown in Scheme 1. For the Ln complex numbers see Fig. 1c. The general procedure was amenable to the preparation of all four ligands without significant adjustments in the protocols. Briefly, the carbostyrils 2a–d were N-alkylated with tert-butyl bromoacetate in the presence of DIPEA. Acylation of secondary amines of 3a–d was performed with 2,6-di-tert-butylypyridine.
base. Other, less hindered and more nucleophilic bases (e.g. Et$_3$N) could not be used, as they got acylated by chloroacetyl chloride faster than the modestly nucleophilic carbostyril amines. The chloroacetylated derivatives 4a-d were obtained in at least 72% yield after column chromatography on silica gel. Monoalkylation of cyclen yielded 5a-d along with small amounts of di- and trialkylated side-products, which were readily removed upon purification. Less side-product was seen than in similar reactions of secondary amide carbostyrils, as due to the better solubilities of 4a-d in CHCl$_3$ much less DMF co-solvent was needed, which improved the selectivity.

The secondary amines in 5a–d were alkylated in DMF in the presence of DIPEA base. These conditions minimise the formation of the by-products that are N- or O-alkylated in the carbostyril core. The drawback of these conditions is that the DIPEA-HBr co-elutes with the product on silica gel in CHCl$_3$/acetone/MeOH systems. Therefore, the protected ligands 6a–c required several chromatographic purification steps, and the purified products still contained varying amounts of DIPEA-HBr and DMF. For 6d CHCl$_3$/acetone/EtOH eluent worked best, and an analytically pure sample was isolated after a single chromatographic step. However, a large amount of the product co-eluted with the DMF residues of the reaction mixture, which diminished the yield. Other bases (e.g. Na$_2$CO$_3$) afforded the N- or O-alkylated by-products. Finally, the tert-butyl esters were cleaved with a 1:1 mixture of CH$_2$Cl$_2$ and nitrile at 70 °C in the presence of Na$_2$CO$_3$ (Scheme 2). After layer separation, the reaction mixture to Et$_2$O). After layer separation, the aqueous phase was purified by column chromatography on silica gel. It was crucial to keep the stationary phase short. Elution from a longer column required the addition of aqueous ammonia to the eluent, which resulted in partial loss of the lanthanide ion.

Chemical characterisation

The identities of 2–7 were confirmed by $^1$H and $^{13}$C NMR spectroscopy and high resolution mass spectrometry (see ESI† for details). We were able to grow X-ray quality crystals from 5a (Fig. 2, S1†). The cyclen moiety is disordered over two positions in the free ligand, which was modeled as a positional disorder without any geometric constraints of the two units. The site occupation factors are 0.592 and 0.408 for the major and the minor components, respectively.

The complexes were shown to be pure by HPLC-MS analysis (see ESI†). High resolution mass spectrometry (HR-MS) of the Ln complexes showed the deprotonated, singly negatively

![Scheme 2](image_url)

**Scheme 2** Attempted alternative syntheses of the N-alkylated ligands.

**Fig. 2** Crystal structure of 5a. Thermal ellipsoids are shown at the 30% (cyclen) probability levels. For clarity, only one of the disordered cyclen parts is shown.
charged molecule ions with the expected isotope distribution pattern. Further support for the identities of the metal complexes was provided by their photophysical properties (vide infra). Briefly, Eu and Tb complexes displayed the characteristic red and green Ln emissions, respectively, while Gd complexes only had antenna-based photophysical activities.

We could obtain crystals from a Dy complex of the non-N-alkylated analogue of the 1d ligand (Dy9d, Fig. 3). This structure shows a different configuration of the antenna-linking amide compared to that found in the current ligands, which may impact the photophysical properties (vide infra). The Dy center shows a classical monocapped square antiprismatic arrangement typical of this type of complexes. The four carboxylic oxygen and four nitrogen atoms form two near ideal planes that are almost coplanar; the angle between the least square planes is only 0.63(8)°. One additional water molecule caps the face spanned by O4 to O7. The O–Dy distances fall into two regimes: 2.300(2)–2.332(2) Å and 2.423(2)–2.433(2) Å. The two longer distances are found for the amide oxygen (O7-Dy) and capping water (O3-Dy1). The Dy–N distances are in the range from 2.600(2) to 2.657(2) Å.

In the Dy-complex, a significant void with ill-defined solvent molecules was identified. The best solution was found with ten positions with high electron density in this void. However, the diffuse nature of these contributions prompted us to treat this cavity using the solvent masking algorithm implemented in OLEX2. We identified a void centered on the crystallographic position –0.282 0.000 0.500 of approx. 693 Å³ containing ca. 197 electrons. In the final solution after solvent masking, only the coordinated water (O3) has been refined.

Absorption and emission spectroscopy

The photophysical characterisation of Ln1a–d was done on [Ln1a–d] = 3 × 10⁻⁵ M solutions in 0.01 M aqueous PIPES buffer at pH 6.5. These conditions were chosen because previously we observed that Ln complexes with trifluoromethylated carbostyril antennae showed a reversible loss in Ln emission at pH > 7. Analysis of the spectral shape of such Eu complexes showed no changes in the coordination environment, suggesting that deprotonation occurred in a non-coordinated group. As we could not exclude the loss of the core N–H proton, we have decided to do our experiments at a pH where deprotonation is not significant.

The absorption and emission data are summarised in Tables 1–4. All absorption and emission spectra are given in the ESI (Fig. S3–S13f). Compared to the non-alkylated Ln9a–d, the new complexes had slightly blue-shifted absorption and emission maxima (by 5–6 and 1–2 nm, respectively). The exception was the emission of Ln1b, which was red-shifted by 3 nm. In all cases, the change was small. The complexes had appreci-

*Table 1* Antenna and Ln emissions in Ln1a–d, and comparisons with Ln9a–d

| Ligand | Ln | Φ₁<sup>b</sup> | Φ₁<sub>Ln</sub><sup>b</sup> |
|-------|----|---------|-----------------|
| 1a    | Eu | 1.5 (<3<sup>c</sup>) | 6.0 (<1.94<sup>d</sup>) |
|       | Tb | 5.9 (<1.05<sup>c</sup>) | 43.4 (<1.23<sup>d</sup>) |
|       | Gd | 6.8 (<0.88<sup>c</sup>) | — |
| 1b    | Eu | 2.7 (<1.6<sup>c</sup>) | 11.6 (<1.47<sup>d</sup>) |
|       | Tb | 3.1 (<0.69<sup>c</sup>) | 15.9 (<5.3<sup>d</sup>) |
|       | Gd | 3.2 (<0.65<sup>c</sup>) | — |
| 1c    | Eu | 2.5 (<6.25<sup>c</sup>) | 8.9 (<1.89<sup>d</sup>) 9.2<sup>d</sup> |
|       | Tb | 4.5 (<8.2<sup>c</sup>) | 45.1 (<1.96<sup>d</sup>) 47.9<sup>d</sup> |
|       | Gd | 5.1 (<0.74<sup>c</sup>) | — |
| 1d    | Eu | 1.7 (<4.05<sup>c</sup>) | 5.85 (<2.1<sup>d</sup>) 5.5<sup>d</sup> |
|       | Tb | 7.1 (<1.11<sup>c</sup>) | 41.7 (<4.2<sup>d</sup>) 39.9<sup>d</sup> |
|       | Gd | 7.7 (<0.87<sup>c</sup>) | 7.7<sup>d</sup> |

<sup>a</sup> In pH 6.5 PIPES buffer, [Ln1] = 3 × 10⁻⁵ M; λ<sub>ex</sub> = 336 (Ln1a), 348 (Ln1b), 338 (Ln1c,d) nm.  Using quinine sulfate as the reference.

<sup>b</sup> Fold increase compared to Ln9 reference compound, calculated from data from ref. 39. Unbuffered solutions, pH 6–7, see ref. 39. Quantum yields have an error of 10%. Values given in italics were recorded in a second set of independent measurements.

<sup>c</sup> In water, measured under the same conditions as reported for Tb9d.

Fig. 3 Crystal structure of Dy9d (top), and side (middle) and top views (bottom) of the metal coordination sphere. Thermal ellipsoids are shown at the 50% probability levels.
In pH 6.5 PIPES buffer, [Gd1] = 3 × 10⁻⁵ M. In parentheses: change from Gd9a–d, calculated from ref. 39.

Table 4 Emission lifetimes and hydration numbers of Ln1–d

| Ligand | Ln  | τ_H2O/ns | τ_D2O/ns | q  |
|--------|-----|----------|----------|----|
| 1a     | Eu  | 0.65     | 2.18     | 1.0|
|        | Tb  | 1.91     | 3.11     | 0.7|
| 1b     | Eu  | 0.66     | 2.16     | 1.0|
|        | Tb  | 0.7      | 1.34     | —  |
| 1c     | Eu  | 0.66     | 2.17     | 1.0|
|        | Tb  | 1.81     | 2.92     | 0.8|
| 1d     | Eu  | 0.65     | 2.16     | 1.0|
|        | Tb  | 1.56     | 2.47     | 0.9|

*λ_ex = 336 (Ln1a), 348 (Ln1b), 338 (Ln1c, d) nm; λ_em = 615 nm (Eu), 545 nm (Tb), initial delay: 0.05 ms; increments were adjusted between 0.2–10 μs depending on the lifetime. Lifetimes are reported as the average of three independent measurements. Calculated as in ref. 17.

state in Ln9a–d than in Ln1a–d. This is consistent with the slightly higher Φ_l in Ln9a–d, although the changes are small (Table 1).

All Eu and Tb complexes had robust Ln-centred emission upon antenna excitation. The Ln1 absorption spectra and the Eu and Tb excitation spectra were similar, as expected for sensitised Ln emission (Fig. 4 and S3–S10†). Ln emissions were at 490, 545, 580, 620, 650, 667 and 680 nm for Tb and at 580, 590, 615, 655 and 700 nm for Eu, corresponding to the 5D4 → 7F_J (J = 6–0) transitions, respectively (Fig. 5). In all Eu complexes the major transition was the 5D4 → 7F_J one, as in the Ln9a–d complexes. Every single one of the N-alkylated Eu and Tb complexes had higher Ln emission quantum yields than their non-alkylated analogues, Ln9 (Table 1). Tb1, with the exception of Tb1b, had Φ_Ln > 40%. The best result was obtained for MOM-functionalised Tb1c, Φ_Ln = 43%. Tb1c had a fourfold higher Φ_Ln than Tb9c, while for Tb1b a 5.3-fold increase was noted (to 15.9%) from non-N-alkylated Tb9b. Eu1 were less efficient than Tb1, with Φ_Ln in the 5.9–11.6% range; still, these values are in some cases twice as high as in the analogous Eu9 complexes.

Antenna triplet states obtained from the phosphorescence bands at 77 K were located at 23100–23900 cm⁻¹ in Gd1 (Table 2). Trifluoromethylated Gd1b had the lowest-lying antenna triplet, at 23100 cm⁻¹. The triplet states were 400–700 cm⁻¹ higher in energy than in Gd9a–d. Tb and Eu have excited states at 20 400 (Tb), 19 000 (5D4, Eu) and 17 200 (5D0, Eu) cm⁻¹. A general rule is that good triplet-mediated absorptions at 337 nm, which is beneficial for laser-excitation without causing excessive damage to biomolecules.

The carbostyril emissions (Φ_u) in Gd1a–d were weaker than in the non-alkylated complexes Gd9a–d (Table 1). While we did not have crystals of Ln1, in its precursor 5a, which has a tertiary amide, the least squares planes (l.s.pl.) of the amide and the chromophore deviate by 86.72°. This is reduced to 29.30° in Dy9d, which has a secondary amide linker. Thus, there is essentially no orbital overlap between the tertiary amide and the heterocycle. In Dy9d (Fig. 3, synthesised previously, crystal structure not reported) the amide and the heterocycle are more co-planar, which should be beneficial for the charge transfer excited state. The more efficiently electron-donating substituent of Ln9a–d yields a more polar emitting

Table 3 Radiative lifetimes, intrinsic quantum yields and sensitisation efficiencies of Eu1a–d and Eu9a–d

| Ligand | r_rad/µs | r_ab/µs | Φ_Eu | Φ_Eu/sens | Φ_Eu/sens | η_Eu | η_Eu/sens |
|--------|----------|---------|-------|-----------|-----------|------|----------|
| 1a     | 0.65     | 2.18    | 1.0   | 0.65      | 2.18      | 1.0  | 0.65     |
| 9a     | 0.66     | 2.16    | 1.0   | 0.66      | 2.16      | 1.0  | 0.66     |
| 1b     | 0.66     | 2.17    | 1.0   | 0.66      | 2.17      | 1.0  | 0.66     |
| 9b     | 0.66     | 2.18    | 1.0   | 0.66      | 2.18      | 1.0  | 0.66     |
| 1c     | 0.66     | 2.17    | 1.0   | 0.66      | 2.17      | 1.0  | 0.66     |
| 9c     | 0.66     | 2.18    | 1.0   | 0.66      | 2.18      | 1.0  | 0.66     |
| 1d     | 0.66     | 2.17    | 1.0   | 0.66      | 2.17      | 1.0  | 0.66     |
| 9d     | 0.66     | 2.18    | 1.0   | 0.66      | 2.18      | 1.0  | 0.66     |

*Calculated according to ref. 45. Values taken from or calculated based on data reported in ref. 39. Ratio of the intrinsic quantum yields of Eu9 and Eu1. Ratio of the overall quantum yields of Eu9 and Eu1. Calculated as in ref. 17.
sensitisation requires an antenna triplet-Ln excited state energy gap of 2500–3500 cm\(^{-1}\). Previous studies have shown that a minimal energy gap of 2000–2500 cm\(^{-1}\) is required to avoid energy back transfer; energy transfer is then improved with an increasing energy gap until ~24000 cm\(^{-1}\) for Tb. The presence of multiple acceptor levels in Eu makes the energy gap relation more complicated. Thus, 1a–d should be excellent sensitising ligands for both Eu and Tb, with the possible exception of 1b, which may be too low-lying for Tb.

In the case of the Eu complexes the increased \(\Phi_{\text{Ln}}\) appears to be in large part due to improved sensitisation efficiencies for all the antennae (Table 3). Quantum yield determinations carry ~10% relative error, and \(\Phi_{\text{Ln}}\) should therefore be compared cautiously. Still, \(\Phi_{\text{Eu}}\) of Eu1a–d are within experimental error (~0.1 ms) of those of Eu9a–d. This is expected based on the similarities of the coordination spheres (Fig. S11†). The observed lifetimes and the intrinsic quantum yield are identical within experimental error within the group of Eu1a–d. Interestingly, in a previous study, an Eu complex with the same Ln binding site and a tertiary amide-linked 7-amidocoumarin antenna had a very similar observed lifetime, 0.65 ms, while an non-alkylated analogue had \(\tau_{\text{obs}} \approx 0.6\) ms. Thus, N-alkylation indeed increases the Eu lifetime and the intrinsic quantum yield, probably because of the removal of the N–H oscillator.

Most of the gain in overall quantum yield comes from the better sensitisation efficiency, \(\eta_{\text{sens}}\). This is the product of the population of the feeding level (here, the antenna triplet), and the efficiency of the energy transfer. The triplet population is dependent on the efficiency of intersystem crossing, which will be affected by the S\(^1\)–T\(^1\) energy gap, which was calculated in both Gd1a–d and Gd9a–d (Table 2). The differences are small, typically within experimental error, and are thus unlikely to have substantially benefited ISC; a possible exception is trifluoromethylated Ln1b. Energy transfer is dependent on the spectral overlap, on orientation factors, and on the donor–acceptor distance. In solution, the latter two are difficult to pin down, despite observations in the solid state. However, the small blue shifts of the Gd1a–d T\(^1\) states compared to Gd9a–d may allow for a better spectral overlap.

The increased Ln emission is not caused by a decrease in the number of inner sphere solvent (water) molecules, which would increase the intrinsic quantum yield (Table 4). This is not surprising. The added carboxylate is not well disposed for Ln coordination, as that would form an unfavoured 8-membered ring. The shape of the Eu1 and Eu9 emission spectra are very similar, as expected for complexes with similar metal coordination environments (Fig. S11†). The \(q\)-values determined for Eu1 are the same as the values obtained for their Eu9 analogues within experimental error (1.0 vs. 1.0–1.1). For Tb complexes the \(q\)-values were lower than for the Eu species, which is consistent with Tb(III) being the smaller ion. The exception was Tb1b, for which an unrealistic result \((q = 5)\) was obtained. As the antenna triplet in Tb1b is only 1800 cm\(^{-1}\) above the Tb excited state, this is likely due to energy back transfer. Substantial non-X–H–caused quenching makes the determination of \(q\) unreliable. In the case of back energy transfer the antenna triplet is repopulated, which in turn can be quenched by e.g. atmospheric oxygen.

The Ln complexes had modest antenna fluorescence emissions \((\Phi_z)\). In Tb1a–d \(\Phi_z\) were 87–97% of those in Gd1a–d (Table 1), which may be due to ET from the carbostyril singlet excited state to the Tb. This has been seen before in both coumarin and carbostyril sensitised species. Tb and Gd may also have different heavy atom effects, although these are usually assumed to be similar. PeT can be excluded for Tb and Gd complexes.

The drop in \(\Phi_z\) was larger in Eu1a–d than in Tb1a–d. Antennae retained only 22–84% of the \(\Phi_z\) of the appropriate Gd1a–d complexes. PeT and singlet ET could both contribute to this decrease. PeT from the excited carbostyril antennae to Eu\(^{3+}\) was found to be an efficient quenching pathway in Eu9. The \(\Phi_z\) decrease was smaller in Eu1a–d than in Eu9a–d, which may reflect decreased PeT due to the increased overall negative charge, or less efficient singlet ET. However, it is important to emphasize that the observed changes in \(\Phi_z\) in Tb1a–d and Eu1a–d compared to Gd1a–d do not support a substantial singlet mediated ET, and the contribution of the singlet state to Ln emission is small.
Experimental

Materials and methods

General procedures. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a JEOL 400 MHz instrument, respectively. Chemical shifts were referenced to residual solvent peaks and are given as follows: chemical shift (δ, p.p.m.), multiplicity (s, singlet; br, broad; d, doublet, t, triplet; q, quartet; m, multiplet), coupling constant (Hz), integration. LC-MS analysis was carried out using Agilent 1100 and 1200. Bruker D8 APEX-II equipped with a CCD camera. The structure was solved by direct methods (SHELXS-2014) and refined by full-matrix least-squares techniques against F² (SHELXL-2018). The non-hydrogen atoms were refined with anisotropic displacement parameters. The H-atom positions were calculated geometrically and treated as fixed isotropic displacement parameters.

Compounds 1a–46, 1b–36, 1c–47, 1d–40 and 8c–39 were synthesised following literature methods. All other chemicals were from commercial sources and used as received.

Chromatography. Preparative chromatography was carried out on silica gel [Norsil 60 chromatographic silica media (40–63 micron)]. Thin layer chromatography was performed on silica-coated (60G F254) glass plates from Merck. Samples were visualised by UV-light (254 and 365 nm).

HPLC-analysis was performed on a RP-HPLC performed on a Dionex UltiMate 3000 system using a Phenomenex Gemini® C18 TMS end-capped 150 mm × 4.6 mm HPLC column with water (0.05% formic acid): CH₃CN (0.05% formic acid) eluent system: 0–10 min: 10% → 90% CH₃CN, 0–12 min: 10% → 50% CH₃CN, 0–8 min: 10% → 20% & 8–12 min: 20% iso CH₃CN. Flow rate: 0.5 mL min⁻¹, UV- (UltiMate 3000 Photodiode Array Detector) and ESI-MS detections (LCQ DECA XP MAX) were used.

Spectroscopy. All measurements were performed in PIPES buffered distilled water at pH 6.5. [Ln] was 0.05 M, CH₃CN (0.05% formic acid) eluent system: 0–10 min: 10% → 90% CH₃CN, 0–12 min: 10% → 50% CH₃CN, 0–12 min: 10% → 20% & 8–12 min: 20% iso CH₃CN. Flow rate: 0.5 mL min⁻¹, UV- (UltiMate 3000 Photodiode Array Detector) and ESI-MS detections (LCQ DECA XP MAX) were used.

Low temperature measurements were done in quartz capillaries at 77 K by immersion in a liquid N₂-filled quartz Dewar and with addition of glycerol (1 drop) to the solutions (9 drops) measured at room temperature.

X-ray diffraction data. Measurements were performed using graphite-monochromatised Mo Kα radiation at 150 K using a Bruker D8 APEX-II equipped with a CCD camera. The structure was solved by direct methods (SHELXS-2014) and refined by full-matrix least-squares techniques against F² (SHELXL-2018). The non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms of the CH₃/CH groups were refined with common isotropic displacement parameters for the H atoms of the same group and ideal...
ised geometry. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealised staggered geometry; one methyl group is modelled as a disordered staggered configuration.

**Specific for 5a.** NH protons are located on the difference map or placed at idealised positions. The cyclen ring shows a positional disorder which is modelled with an occupancy of 0.53 and 0.47 of the two different orientations, respectively.

**Specific for Dy9d.** Solvent accessible voids were treated using the solvent masking algorithm implemented in OLEX2 accounting for a 197 electrons in a 693 Å³ large void. In addition a structure refinement prior to applying solvent masking is attached.

CCDC 1832851 and 1833918 contain the supplementary crystallographic data for this paper.

**Synthetic procedures**

**General procedure for synthesis of compounds 3a–d.** The appropriate carbostyril (2a–d) was dissolved in DMF (250 mM). DIPEA (3.0 equiv.), and then the alkyllating agent (tert-butyl bromoacetate, 1.2 equiv.) were added. The reaction mixture was stirred at room temperature, and the progress of the reaction was monitored by TLC analysis. A further 2.4 equiv. of alkyllating agent was added in each case to drive the reaction to completion. When necessary, more base was also added. Once TLC analysis indicated the completion of the reaction, the mixture was poured into a separation funnel, and CH₂Cl₂ and H₂O were added. The phases were separated, and the aqueous phase was extracted again with CH₂Cl₂. The combined organic phases dried over MgSO₄, filtered, and the filtrate was concentrated at reduced pressure. Residual DMF was co-evaporated with toluene. The crude products were purified by column chromatography on silica gel using the following eluent mixtures: CH₂Cl₂:AcOEt:PrOH (6:4:0 → 6:3:1) for 3a, CH₂Cl₂:Et₂O:acetone (8:2:0 → 7:3:0 → 7:1.5:1.5) for 3b, CH₂Cl₂:Et₂O:EtO (3:2 iso) for 3c, CH₂Cl₂:Et₂O:acetone (8:2:0 → 5:5:0 → 5:3:2) for 3d.

**3a.** 1.057 g (61% → 41% after recrystallization +20% after col. chromat. on the filtrate); ¹H NMR (400 MHz, DMSO-d₆) δ ppm 1.43 (3, 9H), 2.29 (s, 3H), 3.79 (d, J = 6.3 Hz, 2H), 5.99 (s, 1H), 6.25 (d, J = 2.1 Hz, 1H), 6.52 (dd, J = 8.8 Hz, 2.2 Hz, 1H), 6.64 (t, J = 6.1 Hz, 1H), 7.39 (d, J = 8.8 Hz, 1H), 11.22 (s, 1H); ¹³C NMR (101 MHz, DMSO-d₆) δ ppm 18.4 (CH₃), 27.7 (CH₃), 45.0 (CH₃), 80.8 (C₆H₅), 94.8, 109.4, 110.8, 115.2, 125.4, 140.7, 147.9, 162.3, 169.9; RP-HPLC τᵣ = 6.13 min (10 min method 10% → 90%); ESI-MS obsd 289.02; HR-ESI-MS obsd 311.1373, calcld 311.1366 [(M + Na)⁺, M = C₉H₁₀N₂O₄].

**3b.** 1.302 g, (43% → 34% after recrystallization +9% after col. chromat. on the filtrate); ¹H NMR (400 MHz, DMSO-d₆) δ ppm 1.43 (3, 9H), 2.83 (d, J = 4.7 Hz, 2H), 6.34 (d, J = 1.9 Hz, 1H), 6.49 (s, 1H), 6.65 (dd, J = 9.0, 2.2 Hz, 1H), 7.04 (brd, 1H), 11.92 (s, 1H); ¹³C NMR (101 MHz, DMSO-d₆) δ ppm 27.7 (CH₃), 44.8 (CH₃), 81.0 (C₆H₅), 94.8 (CH₃), 104.0 (CH₃), 111.1 (CH₃), 114.2 (CH), 122.9 (C₆H₅), 124.2 (C₆H₅), 136.7 (C₆H₅), 142.1 (C₆H₅), 151.0 (C₆H₅), 160.8 (C₆H₅), 169.5 (C₆H₅); ¹⁹F NMR (376 MHz, DMSO-d₆) δ ppm −62.3; RP-HPLC τᵣ = 6.97 min (10 min method 10% → 90%); ESI-MS obsd 342.99; HR-ESI-MS obsd 365.1075, calcld 365.1083 [(M + Na)⁺, M = C₉H₁₂N₂F₂N₂O₄].

**3c.** 1.954 g (84% → 49% after recrystallization +35% after col. chromat. on the filtrate); ¹H NMR (400 MHz, DMSO-d₆) δ ppm 1.42 (s, 9H), 3.36 (s, 3H), 3.79 (d, J = 6.4, 2H), 4.54 (s, 2H), 6.13 (s, 1H), 6.27 (d, J = 2.2 Hz, 1H), 6.51 (dd, J = 8.8, 2.2 Hz, 1H), 6.67 (t, J = 6.4 Hz, 1H), 7.37 (d, J = 8.8 Hz, 1H), 11.35 (s, 1H); ¹³C NMR (101 MHz, DMSO-d₆) δ ppm 28.2 (CH₃), 45.0 (CH₃), 58.0 (CH₃), 70.5 (CH₃), 80.8 (C₆H₅), 108.4 (CH₃), 109.6 (C₆H₅), 113.3 (CH₃), 124.9 (CH₃), 141.0 (C₆H₅), 147.3 (C₆H₅), 150.2 (C₆H₅), 162.4 (C₆H₅), 169.9 (C₆H₅); RP-HPLC τᵣ = 6.03 min (10 min method 10% → 90%); ESI-MS obsd 318.65; HR-ESI-MS obsd 341.1469, calcld 341.1472 [(M + Na)⁺, M = C₁₀H₁₁N₂O₃].

**3d.** 3.72 g (76%); ¹H NMR (400 MHz, CDCl₃) δ ppm 1.25 (t, J = 7.1 Hz, 1H), 1.51 (s, 9H), 2.43 (s, 3H), 3.80 (s, 2H), 3.88 (s, 2H), 4.17 (q, J = 7.1 Hz, 2H), 6.38 (d, J = 2.3 Hz, 1H), 6.62 (d, J = 8.9, 2.3 Hz, 1H), 7.54 (d, J = 8.9 Hz, 1H), 11.59 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ ppm 140.7, 147.9, 162.3, 169.9; RP-HPLC R = 6.73 min (10 min method 10% → 90%); ESI-MS obsd 374.71; HR-ESI-MS obsd 397.1730, calcld 397.1724 [(M + Na)⁺, M = C₁₀H₁₂N₂O₄].

**General procedure for synthesis of compound 4a–d.** Samples of 3a–d were dissolved in 1:1 mixture of DMF and distilled CH₂Cl₂ (125 mM). The solutions were cooled to 0 °C and 2,6-di-tert-butyl-pyridine (3.0 equiv.) was added followed by the addition of chloroacetyl chloride (1.2 equiv.). The reaction mixtures were then allowed to warm to room temperature. When TLC analysis indicated the completion of the reaction, the mixture was diluted with H₂O and EtOAc. The phases were separated, and the aqueous layer was extracted with EtOAc. The combined organic phases were dried over MgSO₄, filtered, and the filtrate was concentrated at reduced pressure. The crude products were purified by column chromatography on silica gel using the following eluent mixtures: CH₂Cl₂:Et₂O:PrOH (8:2:0 → 8:1:1) for 4a, CHCl₃:Et₂O:EtOH (9:5:0.5 → 8:2:0 → 8:1.6:0.4) for 4b, CHCl₃:Et₂O:EtOH:PrOH (9:1:0:1 → 8:5:1:5 → 8:5:1:5) for 4c, CH₂Cl₂:Et₂O:EtOH (9:5:0:5:0 → 8:2:0 → 8:1:6:0.4) for 4d.
13C NMR (101 MHz, DMSO-d6) δ ppm 27.7 (CH3), 41.9 (CH2), 52.2 (CH2), 81.6 (Cq), 112.6 (Cq), 115.0 (CHAr), 121.0 (CHAr), 122.3 (CH), 122.4 (q, J = 7.5 Hz, Cq), 125.7 (CHAr), 136.2 (q, J = 32.2 Hz, Cq), 140.6 (Cq), 144.0 (Cq), 160.2 (Cq), 165.7 (Cq), 167.6 (Cq). 13C NMR (101 MHz, DMSO-d6) δ ppm 1.48 (s, 9H), 2.18 (s, 3H), 3.72 (s, 2H), 4.07 (q, J = 6.8 Hz, 1H), 11.92 (s, 1H). 13C NMR (101 MHz, DMSO-d6) δ ppm 11.92 (s, 1H), 19.2 (CH3), 26.0 (Cq), 45.7 (CH2), 46.5 (CH2), 46.6 (CH2), 51.1 (CH2), 52.7 (CH2), 54.4 (CH2), 55.3 (CH2), 81.4 (Cq), 119.5 (CHAr), 121.0 (Cq), 125.4 (CHAr), 126.6 (CHAr), 136.2 (Cq), 142.4 (Cq), 144.1 (Cq), 161.4 (Cq), 165.7 (Cq), 166.7 (Cq), 170.4 (Cq). RP-HPLC tR = 6.83 min (10 min method 10% → 90%); ESI-MS obsd 543.01; HR-ESI-MS obsd 543.1446, calcld 543.1450 [M + Na]+, M = C22H17ClN6O6.

5d. 2.84 g (89%); 1H NMR (400 MHz, DMSO-d6) δ ppm 1.18 (t, J = 7.1 Hz, 3H), 1.42 (s, 9H), 2.40 (s, 3H), 3.72 (s, 2H), 4.07 (q, J = 0.7 Hz, 2H), 4.14 (s, 2H), 4.30 (s, 2H), 7.25 (d, J = 8.1 Hz, 1H), 7.33 (s, 1H), 7.86 (d, J = 8.6 Hz, 1H), 11.92 (s, 1H), 119.5 (Cq), 121.0 (Cq), 125.4 (CHAr), 126.6 (CHAr), 136.2 (Cq), 142.4 (Cq), 144.1 (Cq), 161.4 (Cq), 165.7 (Cq), 166.7 (Cq), 170.4 (Cq). RP-HPLC tR = 6.83 min (10 min method 10% → 90%); ESI-MS obsd 543.01; HR-ESI-MS obsd 543.1446, calcld 543.1450 [M + Na]+, M = C22H17ClN6O6.
volume of TFA was added (45 mM). The mixture was stirred overnight at room temperature. Full conversion was observed the following day by TLC analysis. The volatile components were evaporated under reduced pressure, and the TFA-residues were removed by repeated co-evaporation with toluene. The resulting viscous orange residue was dissolved in acetonitrile containing a small amount of water, and the solution was loaded onto a silica gel column that had been conditioned with acetonitrile: H2O (9:1). Elution with acetonitrile: H2O (9:1 → 7:3) yielded the ligands as white (6a,e) and yellowish-white (6b,d) solids.

7a. 208 mg (81%); 1H NMR (400 MHz, D2O) δ ppm 1.25–1.35 (m, 1.02H DIPA), 1.84–4.65 (m, 29.3H 29H product, 0.3H DIPA)), 6.31 (s, 1H), 7.27 (d, J = 8.4 Hz, 1H), 7.37 (s, 1H), 7.71 (d, J = 8.4 Hz, 1H); 13C NMR (101 MHz, D2O) δ ppm 16.3 (CH3), 45.7–45.8 (CH2), 52.2–53.2 (CH2), 54.1 (CH2), 56.5 (CH2), 58.7 (CH2), 58.9 (CH2), 114.3 (CH2), 119.4 (CAr), 120.3 (CAr), 121.8 (CH2), 126.8 (CH2), 137.7 (Cq), 143.0 (Cq), 146.1 (Cq), 174.0 (Cq), 174.7 (Cq), 180.2 (Cq); RP-HPLC tR = 3.02–7.12 min (16 min method: 0–12 min 10% → 50%); ESI-MS obsd 619.27; HR-ESI-MS obsd 655.2068, calc 655.2046 ([M + Ca – 3H], M = C29H37N6O10). 7b. 434 mg (92%); 1H NMR (400 MHz, D2O) δ ppm 1.85–4.68 (m, 26H), 6.94 (m, 1H), 7.38 (d, J = 8.7 Hz, 1H), 7.51 (m, 1H), 7.87 (d, J = 7.4 Hz, 1H); 13C NMR (101 MHz, D2O) δ ppm 51.4 (CH2), 56.6 (CH2), 58.8 (CH2), 58.9 (CH2), 114.2 (CAr), 114.9 (CH2), 120.8 (CH2), 121.6 (CAr), 122.0 (q, J = 275 Hz, Cq), 126.8 (CH2), 138.5 (q, J = 32.2 Hz, Cq), 139.3 (CAr), 143.9 (CAr), 162.6 (Cq), 174.1 (Cq), 174.6 (Cq), 180.2 (Cq); 19F NMR (376 MHz, CDCl3) δ ppm −63.4 RP-HPLC tR = 5.60–9.72 min (16 min method: 0–12 min 10% → 50%); ESI-MS obsd 673.32; HR-ESI-MS obsd 709.1779, 731.1559, calc 709.1763, 731.1583, [M + Ca – 3H], M = C29H37N6O10F3; [M + Ca + Na – 4H], M = C29H37N6O10F3.

7c. 477 mg (quant.); 1H NMR (400 MHz, D2O) δ ppm 1.80–4.71 (m, 31H), 7.31 (d, J = 8.6 Hz, 1H), 7.43 (s, 1H), 7.73 (d, J = 8.6 Hz); 13C NMR (101 MHz, D2O) δ ppm 54.2 (CH2), 56.6 (CH2), 58.4 (CH2), 58.8 (CH2), 70.3 (CH2), 114.5 (CH2), 118.0 (CAr), 118.3 (CH2), 122.0 (CH), 126.0 (CH2), 138.3 (Cq), 143.2 (Cq), 148.8 (CAr), 164.0 (Cq), 174.1 (Cq), 174.9 (Cq), 180.1 (Cq), 180.2 (Cq); RP-HPLC tR = 2.95–7.02 min (16 min method: 0–12 min 10% → 50%); ESI-MS obsd 649.29; HR-ESI-MS obsd 685.2175, 707.1980, calc 685.2152, 707.1971, [M + Ca – 3H], M = C29H37N6O10F3; [M + Ca + Na – 4H], M = C29H37N6O10F3.
General procedure for Ln complexation. A sample of the ligand (50 mg) was placed into a 4 mL vial equipped with a stirring bar. A 1:1 mixture of H$_2$O and EtOH was added (c = 0.05 M) into the vial using a micropipette, followed by the appropriate (2.4 equiv.) lanthanide salt [EuCl$_3$-6H$_2$O, TbCl$_3$ (anhydrous), or GdCl$_3$ (anhydrous)]. The vials were sealed with a screw-cap and parafilm. The mixtures were sonicated to ensure full dissolution. The reaction mixtures were stirred overnight at 45 °C in an alumina bath. The following day the mixture was sonicated again, and then it was transferred drop-wise to a 20 mL vial filled with Et$_2$O. The phases were separated, (the organic phase was removed from the top), and the aqueous layer was loaded onto a silica gel chromatography column (0 1 cm, $h$ = 3 cm). Elution with acetonitrile : H$_2$O (8 : 2 → 6 : 4) yielded the Ln complexes as yellowish-white (ivory) solids. The final products contain a small amount of silica because of the polar conditions applied on the silica column.

Most of the residual silica can be removed through membrane filtration (0.2 µm) of the concentrated solution of the complexes using a syringe. It is important to leave the solution standing for about a day (or at least for several hours) before filtration to allow the silica to precipitate out.

**EuA.** 8 mg (43%); RP-HPLC $t_R = 5.85$ min (16 min method: 0–8 min: 10 → 20% & 8–12 min: 20% iso); ESI-MS obsd 769.20; HR-ESI-MS obsd 767.15435, calcld 767.15568, [(M − H)$^+$, M = C$_{28}$H$_{35}$N$_6$O$_{10}$Eu$]$. 54 mg (87%); RP-HPLC $t_R = 5.43$ min (16 min method: 0–8 min: 10 → 20% & 8–12 min: 20% iso); ESI-MS obsd 803.16896, calcld 803.17010, [(M − H)$^+$, M = C$_{28}$H$_{37}$N$_6$O$_{12}$Eu$].

**GdA.** 10 mg (53%); RP-HPLC $t_R = 5.67$ min (16 min method: 0–8 min: 10 → 20% & 8–12 min: 20% iso); ESI-MS obsd 774.18; HR-ESI-MS obsd 772.15725, calcld 772.15896, [(M − H)$^+$, M = C$_{28}$H$_{37}$N$_6$O$_{10}$Gd$]. 35 mg (58%); RP-HPLC $t_R = 5.25$ min (16 min method: 0–8 min: 10 → 20% & 8–12 min: 20% iso); ESI-MS obsd 855.15; HR-ESI-MS obsd 853.19253, [(M − H)$^+$, M = C$_{28}$H$_{37}$N$_6$O$_{12}$Gd$].

**TbA.** 7 mg (37%); RP-HPLC $t_R = 5.87$ min (16 min method: 0–8 min: 10 → 20% & 8–12 min: 20% iso); ESI-MS obsd 775.30; HR-ESI-MS obsd 773.15826, calcld 773.15953, [(M − H)$^+$, M = C$_{28}$H$_{37}$N$_6$O$_{12}$Tb$].

**EuB.** 36 mg (59%); RP-HPLC $t_R = 10.80$ min (16 min method: 0–8 min: 10 → 20% & 8–12 min: 20% iso); ESI-MS obsd 823.17; HR-ESI-MS obsd 821.12580, calcld 821.12879, [(M − H)$^+$, M = C$_{28}$H$_{37}$N$_6$O$_{10}$Eu$].

**GdB.** 35 mg (57%); RP-HPLC $t_R = 10.73$ min (16 min method: 0–8 min: 10 → 20% & 8–12 min: 20% iso); ESI-MS obsd 828.16; HR-ESI-MS obsd 826.12879, calcld 826.13069, [(M − H)$^+$, M = C$_{28}$H$_{37}$N$_6$O$_{10}$Gd$].

**TbB.** 44 mg (71%); RP-HPLC $t_R = 10.75$ min (16 min method: 0–8 min: 10 → 20% & 8–12 min: 20% iso); ESI-MS obsd 829.26; HR-ESI-MS obsd 827.12989, calcld 827.13127, [(M − H)$^+$, M = C$_{28}$H$_{37}$N$_6$O$_{12}$Tb$].

**EuC.** 52 mg (85%); RP-HPLC $t_R = 5.78$ min (16 min method: 0–8 min: 10 → 20% & 8–12 min: 20% iso); ESI-MS obsd 799.18; HR-ESI-MS obsd 797.16485, calcld 797.16626, [(M − H)$^+$, M = C$_{28}$H$_{37}$N$_6$O$_{12}$Eu$].

**GdC.** 33 mg (53%); RP-HPLC $t_R = 5.45$ min (16 min method: 0–8 min: 10 → 20% & 8–12 min: 20% iso); ESI-MS obsd 804.26; HR-ESI-MS obsd 802.16777, calcld 802.16956, [(M − H)$^+$, M = C$_{29}$H$_{37}$N$_6$O$_{12}$Gd$].

Conclusions

In conclusion, four new ligands and their Tb, Eu and Gd complexes were synthesised and characterised. The ligands have carbostyril sensitising antennae decorated with 4-Me, 4-CF$_3$, 4-MOM or 3-CH$_3$CO$_2$Et and 4-Me substituents. Antennae are attached to the ligand-binding DOTA framework through a tertiary amide linker, which carries a negatively charged carboxy-methyl group. The Tb and Eu complexes had greatly increased quantum yields compared to analogous species wherein the linker was a secondary amide. The increased $\Phi_{en}$ is due to an enhanced sensitisation efficiency, based on the analysis of the Eu spectra, and, to a much smaller extent, due to a slightly increased intrinsic quantum yield possibly caused by the removal of the amide N–H oscillator from the proximity of the Ln.

The reasons for the improved photophysical properties are likely to be multiple. The blue-shifted antenna triplets should allow for better overlap with the Tb excited states, and thus allow for a more efficient energy transfer. In the case of Eu, a reduction in PeT may contribute; this effect would be smallest for the electron-poor trifluoromethylated antenna. Factors that are difficult to evaluate are: better ISC due to the larger heavy atom effect of the N-alkyl group, and the removal of the NH oscillator that may quench the triplet as well as the Ln excited state. Finally, the Ln-antenna distance and orientation may differ in complexes with secondary and with tertiary amide linkers.

Conflicts of interest

There are no conflicts to declare.

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