Lanthanide macrocyclic quinolyl conjugates as luminescent molecular switches and logic gate functions using HO^- and O_2 as inputs†

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The design and synthesis of **1Tb**, a Tb(III) quinoline–cyclen based complex, are described. The results from the photophysical investigation of **1Tb** are compared with the results observed from its Eu(III) analogue, **1Eu**. The Tb(III) emission of **1Tb** was found to be highly pH dependent, being reversibly switched "*off–on–off*", with maximum emission intensities observed within the physiological pH range, contrary to what was observed with the Eu(III) analogue. Furthermore, the Tb(III) emission was also found to be sensitive to molecular oxygen concentration. By using a stoichiometric amount of both complexes, the changes observed in the combined lanthanide Eu/Tb-emissions (described as *output*) as a function of pH and O_2 (as ion/molecular *inputs*) can be employed in ratiometric sensing of these analytes. Furthermore, the *outputs* can also be described in molecular logic gate terms, where the emission at three different emission wavelengths can be described in terms of Boolean algebra, corresponding to the NAND, NOR and NOT logic gates functions.

Introduction

The development of luminescent signalling devices that show clear differences in their "*off*" (non-emissive) and "*on*" (emissive) states is a very active area of research within supramolecular chemistry.[1] In the past, this "*off–on*" behaviour has been used to mimic the function of logic gate operations or as mimics for molecular level devices.[2] Luminescent switches, where the emission is modulated by external inputs such as light, ions or molecules, or the combination of these, are of great current interest.[2,3] The use of lanthanide ions as luminescent reporters in such devices is particularly attractive as ions such as Eu(III), Tb(III), Nd(III) or Yb(III) emit at long wavelengths, with characteristic line-like emission bands and long lived excited state lifetimes.[4–6] For the same reason, lanthanides have also been employed in luminescent sensing, as these physical properties overcome autofluorescence and light scattering from biological media.[7,8] As the lanthanide f–f transitions are symmetry forbidden, their excited states are usually formed by indirect excitation of the lanthanide excited states through the use of sensitising chromophore (antenna).[6–9] The choice of this antenna has been shown to be crucial for the modulation of the emission properties of the lanthanide ions.[4] To demonstrate this, we[6–11] and others[12,13] have developed various examples of lanthanide-based luminescent sensors and switches, where the lanthanide emission has been modulated through the use of combined antennae–receptors, such as diaza-crown ether,[14] phenanthroline[15] or quinoline,[16] by ions and molecules.

Recently, **1Eu**, the Eu(III) complex of a quinoline derivatized cyclen (1,4,7,10-tetraazacyclododecane) **1**, was synthesised in our laboratory, and we showed that the Eu(III) emission was reversibly switched "*on–off*" in aqueous solution as a function of pH, as well as within hydrophilic polymers, hydrogels.[17] In a related study, we also demonstrated that mixed f–f metal ion complexes could be made where the emission from Eu(III) and Tb(III) was modulated within a single molecule by bis-carboxylates.[18] Similarly, Parker *et al.* developed such mixed systems for the sensing of biologically important molecules, where luminescent ratiometric sensing was achieved, by using a mixture of Eu(III) and Tb(III) complexes of the same ligand.[19] In this article, by using newly developed methodology,[20] the synthesis of **1** and the corresponding Tb(III) complex, **1Tb**, is presented and we show that contrary to that observed for **1Eu**, the Tb(III) emission is switched "*off–on–off*" as a function of pH, giving rise to a bell-shaped emission pH profile with the maximum emission output within the physiological pH range. We also show that the emission is highly sensitive to the presence of O_2[21] and that by using a 1 : 1 mixture of **1Tb** and **1Eu**, we show that the changes in their combined emission as a function of pH and O_2 (as-*inputs*) give rise to luminescent *outputs*, which can be expressed in conventional logic gate notation,[21] giving rise to three independent outputs, corresponding to the molecular logic gate functions NAND, NOR and NOT, respectively.[1,2]

Results and discussion

Synthesis of 1Tb and *q*-value determination

The synthesis of **1** was achieved in good yield by using a synthetic methodology developed in our laboratory, Scheme 1. The synthesis of the cyclen moiety **2** was achieved in 60% yield, by the selective *N*-alkylation of the cyclen by reacting

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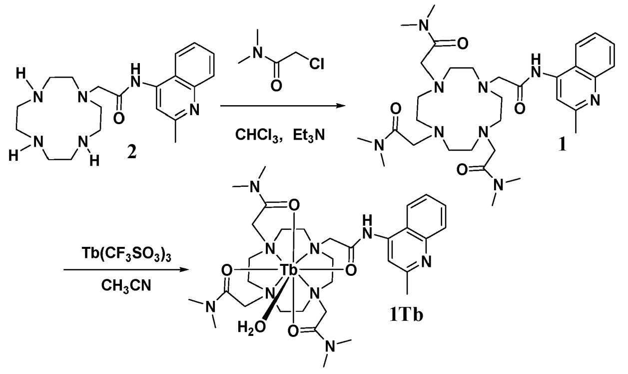

Scheme 1 Synthesis of **1** and the corresponding cationic Tb(III) complex **1Tb**.

4 equivalents of cyclen with chloro-*N*-(2-methyl-4-quinolyl)-ethanamide in $CHCl_3$ in the presence of triethylamine. The three remaining amines of the cyclen moieties were then alkylated by refluxing **2** with *N*,*N*-dimethyl-2-chloroacetamide and triethylamine in $CHCl_3$ for four days. After cooling to RT the resulting solution was recrystallised from cold diethyl ether to give **1** in 61% yield. The Tb(III) complex was then obtained in 56% yield by reacting 1.1 equivalent of $Tb(OTf)_3$ with **1** in CH_3CN for two days.

The complex was characterised using conventional methods (see Experimental) as well as by evaluating its ground, singlet excited and the Tb(III) excited state. The excitation of the quinoline antenna gave rise to Tb(III) emission at 490, 545, 586 and 622 nm for the deactivation of the $^5D_4$ excited state to the ground states ^7F_J (J = 6, 5, 4 and 3), demonstrating its ability to populate the Tb(III) excited state.

The cyclen ligand **1** has eight coordination sites, which is usually not enough to fulfil the high coordination number of 9 or 10 required for lanthanides(III). Due to the difference of quenching efficiencies of the O–H and O–D oscillators, the measurement of Tb(III) luminescence excited state lifetimes (τ) in H_2O and D_2O allows for the estimation of the number of water molecules directly bound to the metal ion. These were measured in pH/pD neutral media and under an inert atmosphere, and the excited state decays were fitted to a single exponential which gave lifetimes of 0.677 ms in H_2O and 0.795 ms in D_2O, respectively. From these, the number of metal bound water molecule, or the *q*-value for **1Tb**, was measured as 0.80 (±0.3) by using an established method,[22] indicating that one water molecule was coordinated to the Tb(III) as shown in Scheme 1.

Photophysical studies of the 1Tb complex as a function of pH

The photophysical properties of **1Tb** were then further investigated in water in the presence of tetraethylammonium perchlorate ($[Et_4NClO_4]$ = 0.1 M). The changes in the absorption spectrum as a function of pH were found to be very similar to those observed for the corresponding Eu(III) complex (see ESI†).[18] In acidic media, the main band of the absorption spectrum is displayed at 320 nm, with a shoulder at 330 nm. Upon basification, using dilute Et_4NOH solution, the absorption exhibited significant hypsochromic and hypochromic shifts, giving rise to the formation of a broad absorption band centred at 305 nm (assigned to the π–π* transition of the antenna). Two pK_as of 5.3 (±0.2) and 9.3 (±0.1) could be calculated from these spectral changes. They correlate well with the pK_as observed for **1Eu**, where the former was assigned to the protonation of the quinoline nitrogen, and deprotonation of the quinoline carboxylic amide, respectively.

The fluorescence emission spectrum of **1Tb** was also recorded after excitation at 330 nm (see ESI†), giving rise to a band centred at 366 nm in acidic media. Upon addition of base, a red shift occurred with the formation of a broad band with λ_{max} centred at 375 nm. By plotting the changes in the 366 nm transition as a function of pH it became evident that the main changes observed were those occurring within the alkaline region, with only minor changes occurring below pH 7 (see ESI†). Again, these results correlate well with those obtained for the **1Eu** analogue of this ligand, and are consistent with the fact that the absorption and fluorescence properties are mainly dependent upon the nature of the antenna.

It is not surprising that these changes seen above for **1Tb** mirror those observed for **1Eu**, as it was not expected that the choice of the lanthanide ions would have significant effect on the photophysical properties of the ground or the singlet excited state. However, we foresaw that these ions would have an effect on the ability of these complexes to modulate the possible back-energy transfer from the lanthanide excited states to T_1. The reason for this is that the sensitising antenna needs to possess a T_1 that is different from the energies of the Tb(III) excited state by *ca.* 250–260 kJ mol^{-1}, as otherwise, back-energy transfer can occur from the lanthanide excited state to T_1 which is also susceptible to quenching by O_2.[23] Hence, repopulation of the T1 state gives rise to enhanced efficiency in such quenching, and consequently, diminishing emission from the lanthanide excited state. The Eu(III) $^5D_0$ has been determined as 17 200 cm^{-1}, and the $^5D_4$ of Tb(III) as 20 500 cm^{-1}, while we determined the energies of the T_1 for **1** as 21 980 cm^{-1} in glacial ethanol.[21] Hence, the ability of the antenna to populate the excited states of Tb(III) might be affected by the presence of O_2, while for Eu(III) no significant changes would be expected. To investigate this, the changes in the Tb(III) emission as a function of pH were investigated upon excitation at 330 nm in the presence and absence of O_2.

The overall results from the titration in aerated solution are shown in Fig. 1. In acidic solution, between pH 3 and pH 5.5, only a weak emission was observed from the $^5D_4$ excited state

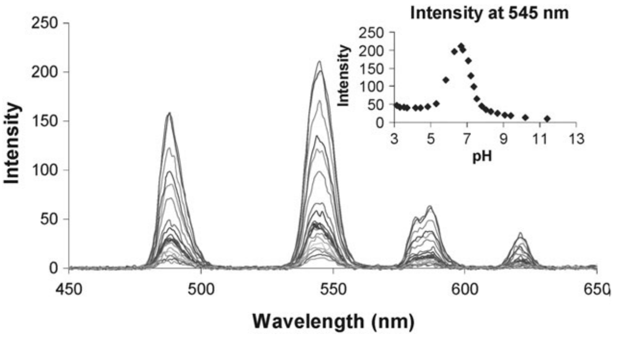

Fig. 1 Changes observed in the Tb(III) emission of **1Tb** 50 μM in aerated solution as a function of pH in water (in the presence of Et_4NClO_4 0.1 M) after excitation at 330 nm. Inset: the observed changes at 545 nm.

(see inset for the changes at 545 nm). Upon further addition of base (Et_4NOH), the Tb(III) emission was gradually enhanced, from pH 5.5 → 7.5, with a maximum emission being observed at *ca.* pH 6.6. This represents a *ca.* 5 fold luminescent enhancement. These changes can be described as a "*switching on*" of the Tb(III) emission as a function of HO^-. However, upon moving to more alkaline pH, the emission was "*switched off*" again, being almost 21 times reduced in intensity.‡ As shown as inset in Fig. 1, these overall combined luminescent changes give rise to a "bell-shaped" pH profile, with a maximum intensity *output* within the physiological pH range. This luminescence pH dependence was also found to be fully reversible upon back-titration. Such pH dependence (bell-shaped profiles) is often found in nature, for instance, many biological enzymes where the enzymatic activity is pH dependent, giving rise to high activity within a narrow pH-window.[24] Moreover, several researchers have developed supramolecular devices that function on the "*off–on–off*" luminescent principle.[9,14,25] In contrast to these results, the Eu(III) emission from the **1Eu** complex was only shown to be emissive in acidic media. Within the pH range of 4 → 7, the changes were assigned to the deprotonation of the quinoline moiety with a pK_a of 6.8, which was further confirmed by using potentiometric measurements.[17]

For the changes observed in Fig. 1, it is clear that these are significantly greater than seen in the ground or the singlet excited sates (*cf.* ESI†) which clearly demonstrate the sensitivity of the Tb(III) emission towards changes in the local environment. However, and has been discussed above, the Tb(III) emission can also be sensitive to the presence of molecular oxygen. Consequently, we investigated the changes in Tb(III) emission in degassed solution, as a function of pH (this was done by purging argon through the sample for 7 min in the spectroscopic cell).

As predicted, the Tb(III) emission was found to give rise to a "bell-shaped" pH profile similar to that seen in the inset in Fig. 1. However, here the Tb(III) was *ca.* 3 times more intense at the maximum "*output*" than seen in Fig. 1 (see ESI†). Furthermore, the emission was not fully quenched at a pH greater than 7.5, as had been observed in presence of O_2, Fig. 1. Consequently, these results demonstrate that the T_1 of the antenna is quenched by an ambient level of O_2 and that for **1Tb**, the $^5D_4$ state can participate in a back-energy transfer mechanism to this T_1 state, which leads to quenching (it should be noted that these complexes are highly hygroscopic and that accurate elemental analysis is difficult to obtain). As expected, the Eu(III) emission did not show any measurable O_2 dependence, and hence, the T_1 is not affected by back-energy transfer from the $^5D_0$ (see ESI†).

The use of a 1 : 1 mixture of 1Eu and 1Tb for achieving ratiometic sensing by internal reference channel

As described above, both Eu(III) and Tb(III) emit with line-like emission bands, where each of the lanthanide emission transitions can be independently monitored. Because of this, and the fact that the changes observed for these two complexes as a function of pH were strikingly different, the emission behaviour of a 1 : 1 mixture of **1Eu** and **1Tb** was investigated under the same conditions as before as a function of pH. As both complexes are isostructural we foresaw that the probability of addressing the excited state of **1Eu** and **1Tb** in this 1 : 1 mixture would be equally likely. Indeed, the absorption and the fluorescence spectra, as a function of pH, showed similar features as were observed for each of these complexes alone (see ESI†).

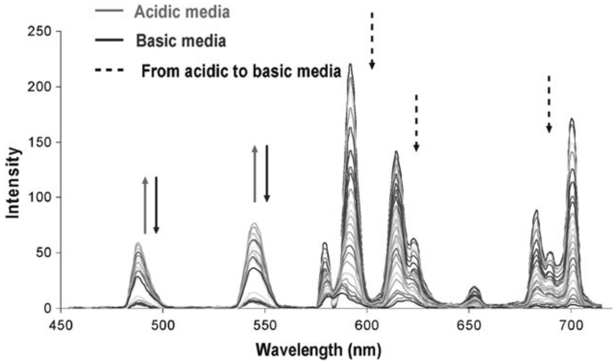

Fig. 2 Changes observed in the Tb(III) and Eu(III) emission of a degassed mixture of **1Tb** and **1Eu** (∼47 μM each) in the presence of TEAP 0.1 M as a function of pH in water after excitation at 330 nm.

The changes in the combined lanthanide emission, upon excitation of the antenna at 330 nm, as a function of pH in degassed solutions are shown in Fig. 2 (see ESI† for results from the pH titration in aerated solution). It is clear from Fig. 2 that a signal separation is achieved spatially. The emission spectra clearly show that the main characteristics of each complex are preserved, where the characteristic bands of Tb(III) occurring at 490 and 545 nm are clearly separated from the bands assigned to the Eu(III) at 654, 683 and 700 nm. However, in a window between these transitions, a mixture of overlaid Eu(III) and Tb(III) emission bands occurs at 580 and 624 nm. Despite the fact that **1Eu** and **1Tb** are present in the same quantity in solution the intensities of the Eu(III) bands are significantly greater than those of Tb(III), even in degassed solution. The relative changes in both the Eu(III) and the Tb(III) emission, as a function of pH, are shown in Fig. 3 for the 545, 700 and 622 nm transitions, respectively. In aerated solution the results clearly show that this mixed system can be used to sense pH within the pH range of 2 → 8, given the fact that at acidic pH (less than 5), the Eu(III) emission predominates the changes in the overall emission *output*. In contrast, between pH 5 and 7.5, the emission arising from **1Tb** predominates. Furthermore, in a degassed solution, the changes within the alkaline region for the Tb(III) emission are enhanced, while the Eu(III) emission remains constant (for the 700 nm transition); hence, between *ca.* pH 6 → 11 ratiometric sensing of O_2 is also possible using this system. The use of such a mixture of lanthanide complexes for determining analyte concentrations, where various emission lines can be addressed spatially and independently over a wide range of wavelengths, is of particular importance, as this allows for the development of sensing *via* internal referencing

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‡ This decrease cannot be explained by the changes observed in the absorbance at those pH; the same titration has been performed after excitation at 300 nm (at the "isosbestic point") and the same result is observed (see ESI†).

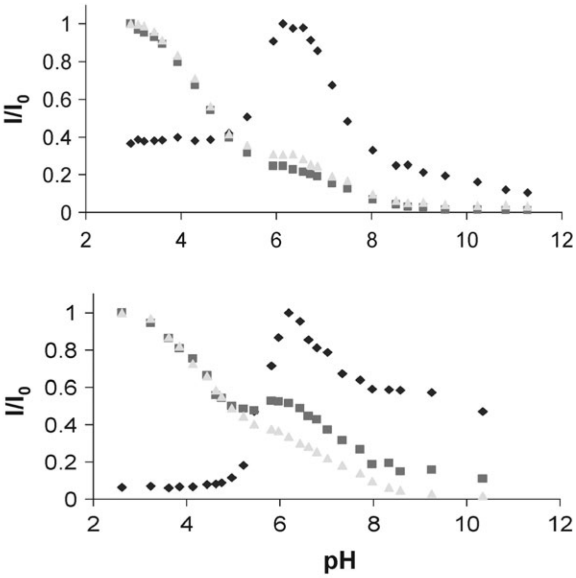

Fig. 3 The changes observed in the lanthanide emission at 545 nm (◆), 622 nm (■) and 700 nm (▲) as a function of pH for the 1 : 1 mixture of **1Eu–1Tb** in the presence of O_2 (top) and in degassed solution (bottom).

(ratiometric sensing). Furthermore, they can be employed in imaging applications, where parallel labelling or parallel processing of luminescent signals arising from biological matter can be imaged.[26]

In general, the intensity of the lanthanide emission is concentration dependent; hence, in a competitive medium a direct and exact measure of pH is not accurately possible with only one complex, without knowing the exact concentration, and/or distribution of the complex within the media. However, the changes seen in Fig. 2 and 3, respectively, allow for the development of a concentration independent method for determining pH since **1Eu** and **1Tb** are isostructural. Hence, their distribution in the environment (being solution, tissue, *etc.*) should be identical. The ratio between the emission arising from Tb(III) at 545 nm could then be used in parallel with the emission arising at 700 nm from the Eu(III) centre.

Having demonstrated that **1Eu** and **1Tb** could be used in pH sensing and that only the Tb(III) emission was sensitive to the presence of O_2, we next move towards explaining the results observed in the form of logic operations, where the two *inputs* are HO^- and O_2, respectively.

Logic gate expression of the luminescence results of 1Eu and 1Tb

In terms of logic gate functions controlled by two *inputs*, the use of Boolean algebra gives rise to 16 different logic gate functions.[1–3,27] From the perspective of expressing the above Eu(III) and Tb(III) emissions as logic gate *outputs*, the binary numbers 0 and 1 were assigned to high and low luminescent intensity, respectively.[21] For the changes observed in the 1 : 1 mixture of **1Eu** and **1Tb** above, the changes can be analysed for the two *inputs* HO^- and O_2, and their presence or absence is represented as either 1 or 0, respectively. After having analysed all the changes across the emission spectra, we set a threshold shown as absolute intensity of 1.5 a.u., in Fig. 4, for the emissions occurring at 545 nm, 622 nm and at 700 nm. Here, any emission below this threshold was considered as *output* = 0, while emission above this threshold gave the notation 1.

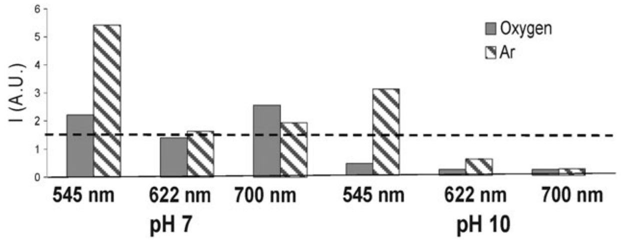

Fig. 4 Intensities of the 1 : 1 solution of **1Tb–1Eu** at neutral and basic pH with O_2 or Ar.

Inputs		Outputs		
OH$^-$	O$_2$	545 nm	622 nm	700 nm
0	0	1	1	1
0	1	1	0	1
1	0	1	0	0
1	1	0	0	0

Fig. 5 A truth table expressing HO^- and O_2 as *inputs* and the emission at three different wavelengths as *outputs*, giving rise to the parallel operations NAND, NOR and NOT molecular logic gates. See ESI† and graphical abstract for a diagram for the conventional gate notation.

To demonstrate the logic gate description of the changes occurring at 545 nm, the emission intensity is only "*switched off*" (*output* = 0) in basic media (*input* = 1) and in the presence of O_2 (*input* = 1), while any other combination of these two *inputs* gives rise to Tb(III) emission, which exceeds the threshold level, and hence results in the emission being "*switched on*." These combinations and results are shown in the corresponding truth table shown in Fig. 5 and demonstrate that the output corresponds to the NAND logic gate function. Similarly, the changes observed at 622 nm showed that the emission is only "*switched on*" in the absence of HO^- and O_2, whereas for the Eu(III) 700 nm transition, the intensity is "*switched on*" only in the absence of HO^- (independent of O_2). These results are also shown in Fig. 5, and demonstrate the output of a NOR logic gate for the changes at 622 nm, and the NOT logic gate for the changes occurring at 700 nm. Hence, using a mixture of **1Eu** and **1Tb** complexes, and only two (ionic/molecular) inputs, gives rise to the formation of three parallel molecular logic gate functions.

Conclusions

Herein, we have presented the synthesis and the photophysical evaluation of a new Tb(III) complex, **1Tb**, that displays a bell-shaped luminescent "*off–on–off*" switching as a function of pH in water, with maximum emission occurring at pH *ca.* 6.5. The lanthanide emission arising from **1Tb** was shown to be also sensitive to O_2. In contrast to this, the emission arising from the Eu(III) complex of **1**, **1Eu**, was however only dependent on pH. Consequently, using a 1 : 1 mixture of the **1Eu** and **1Tb** complexes allowed for the development of ratiometric sensing of both pH and O_2, as well as the construction of a molecular logic gate device corresponding to the three independent NAND, NOR and NOT logic functions. We are currently exploring the use of such combined lanthanide luminescent complexes in the construction of novel sensing devices and with the aim of developing integrated logic gate devices.

Experimental

General

Starting materials were obtained from Sigma-Aldrich and used without further purification. Solvents used were HPLC grade unless otherwise mentioned. Water was purified with a Waters Milli-Q system to give a specific resistance < 15 MΩcm and was then boiled for 30 min to remove CO_2 and allowed to cool in flasks fitted with soda lime tubes. ^1H NMR spectra were recorded at 400 MHz using a Bruker Spectrospin DPX-400. 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.

Synthesis of 2-{4,7-bis-dimethylcarbamoylmethyl-10-[(2-methyl-quinolin-4-ylcarbamoyl)-methyl]-1,4,7,10-tetraazacyclododecayl}-*N*,*N*-dimethyl-acetamide (1)

[(2-Methyl-quinolin-4-ylcarbamoyl)-methyl]-1,4,7,10-tetraazacyclododecyl (**2**) (0.447 g, 1.2 mmol), triethylamine (0.407 g, 3.99 mmol) and 2-chloro-*N*,*N*-dimethylacetamide (0.484 g, 3.99 mmol) were added to $CHCl_3$ (50 mL). The mixture was heated at 90 °C under inert atmosphere for 72 h. The solvent was then removed under reduced pressure. A dark orange viscous residue was obtained (0.487 g, 0.78 mmol) and then purified from diethyl ether to give **1** as a brown solid in 65% yield. Calculated for $C_{32}H_{51}N_9O_4$ $(M + H)^+$: $m/z = 626.4064$; found $m/z = 626.4142$. δ_H (400 MHz, $CDCl_3$): 10.5(1H, s, N*H*), 8.75(1H, d, $J = 8.5$, Ar-*H*), 7.93 (1H, d, $J = 8.5$, Ar-*H*), 7.89 (1H, d, $J = 8.5$, Ar-*H*), 7.57 (1H, t, $J = 6$, Ar-*H*), 7.43 (1H, t, $J = 6$, Ar-*H*), 3.86 (2H, s, $HNCOCH_2$), 2.70 (40H, m, N–CH_3, $CH_2CON(CH_3)_2$, cyclen CH_2). δ_C (100 MHz, $CDCl_3$): 172.1, 170.4, 170.3, 158.3, 148.0, 141.8, 128.7, 127.7, 124.6, 123.4, 119.7, 112.6, 57.6, 54.5, 54.4, 35.7, 35.6, 35.0, 28.8, 26.5, 25.2.

Synthesis of Tb(III) complex of 1, 1Tb

2-{4,7-Bis-dimethylcarbamoylmethyl-10-[(2-methyl-quinolin-4-ylcarbamoyl)-methyl]-1,4,7,10-tetraazacyclododecayl}-*N*,*N*-dimethyl-acetamide (**1**) (0.163 g, 0.26 mmol) and Tb(III) trifluoromethanesulfonate (0.17 g, 0.287 mmol) were added to MeCN (25 mL). The mixture was heated at 90 °C under inert atmosphere for 48 h. The solvent was removed under reduced pressure. A brown powder was obtained and dissolved in MeOH. It was then added dropwise to dry diethyl ether (100 mL) while stirring. The resulting precipitate was isolated to give **1Tb** as a pale orange solid in 60% yield. Calculated for $C_{32}H_{51}TbN_9O_4{\cdot}3CF_3SO_3{\cdot}12H_2O{\cdot}2CHCl_3{\cdot}0.5C_4H_{10}O$: C. 27.22, H. 4.85, N. 7.30. Found: C. 26.90, H. 4.50, N. 7.15. (It should be noted that these complexes are highly hygroscopic and that accurate elemental analysis is difficult to obtain.) Calculated for $C_{32}H_{51}TbN_9O_4$ $[M + 2CF_3SO_3]^+$: $m/z = 1082.2358$; found $m/z = 1082.2411$, $([M + CF_3SO_3]/2)^+$, 466.7. δ_H (400 MHz, D_2O): 8.32, 7.96, 7.76, 7.62, 7.49, 7.14, 6.51, 5.34, 4.12, 3.85, 3.51, 3.22, 3.1, 2.95, 2.85, 2.79, 2.48, 2.21, 2.10, 1.94.

Luminescence titrations

Solutions were all made in 0.1 M Et_4NCl and pH was adjusted by adding either $HClO_4$ or Et_4NOH. UV-Vis spectra were recorded on a Varian UV-Vis spectrophotometer from 250 to 400 nm using excitation and emission slit width of 1 nm with a medium scan speed. Luminescence spectra and lifetimes were measured on a Varian Carey Eclipse Fluorescence spectrophotometer.

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