

# A Dinuclear Lanthanide Complex for the Recognition of Bis(carboxylates): Formation of Terbium(III) Luminescent Self-Assembly Ternary Complexes in Aqueous Solution

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The synthesis and photophysical properties of a coordinatively unsaturated cationic dinuclear terbium complex,  $2 \cdot \text{Tb}_2$ , that can detect the presence of mono- or bis(carboxylates) in buffered aqueous solution at physiological pH is described. Full ligand synthesis and structural characterization of  $2 \cdot \text{Na}_2$  are also described. Spectroscopic measurements determined that each Tb(III) metal center has two metal-bound water molecules ( $q = 2$ ). The recognition or sensing of *N,N*-dimethylaminocarboxylic acid, **4**, and the bis(carboxylate) terephthalic acid, **5**, which can also function as sensitizing antennae, was found to occur through the binding of these carboxylates to the metal center via the displacement of the metal bound water molecules. This gave rise to the formation of luminescent ternary complexes in solution in 2:1 or 1:1 (ion: $2 \cdot \text{Tb}_2$ ) stoichiometry, respectively. Aliphatic bis(carboxylates) also bind to  $2 \cdot \text{Tb}_2$  where the selectivity for the ion recognition and stoichiometry was dictated by the structure of the anion, being most selective for pimelic acid, **6**. Binding of either L- or D-tartaric acid gave rise to the formation ternary complex formation, with 2:1 stoichiometry, where the ion recognition resulted in quenching of the lanthanide emission.

## Introduction

The recognition of ions and molecules is of great current interest in supramolecular photochemistry.<sup>1,2</sup> Over the years some excellent examples of luminescent and colorimetric sensors for cations have been developed, where the ion recognition/sensing gives rise to modulations in various photophysical properties such as absorption and emission wavelengths, lifetimes, and quantum yields, polarization, and isomerization.<sup>3,4</sup> Luminescent sensors that show so-called

“off–on” or “on–off” emission changes as a function of analyte concentration are particularly attractive as chemosensors for in-vivo application.<sup>5,6</sup> For such practical applications, luminescent sensors should ideally have good selectivity and sensitivity to a specific analyte, emit at long wavelengths, and possess long-lived excited-state lifetimes ( $> 10$  ns), with the aim of overcoming autofluorescence and light scattering from competitive biological matter.<sup>7,8</sup> The lanthanide ions such as Tb(III) and Eu(III) are particularly attractive as luminescent emitters. Despite the fact that these ions have excited states ( $^3\text{D}_0$  and the  $^5\text{D}_4$  for Eu(III) and Tb(III), respectively) that are produced by Laporte-forbidden

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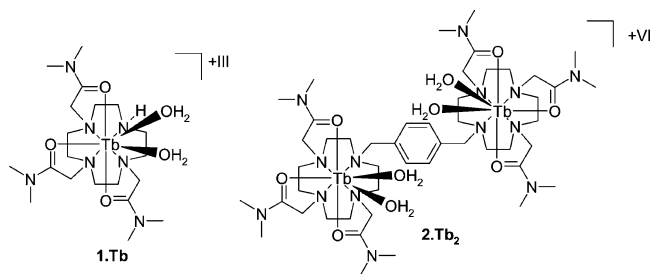
f–f transitions and, hence, have low extinction coefficients, they have found use as biological probes as they possess long-lived excited-state lifetimes (in ms or  $\mu$ s time scale) and emit at long wavelengths (in the green and red for Tb(III) and Eu(III), respectively) with characteristic linelike emission bands.<sup>9–11</sup> Moreover, the excited states of these ions can be populated indirectly, via an energy transfer pathway using a sensitizing chromophore or “antenna”.<sup>2,7,8,11</sup> The use of synthetically modified chromophores as ion and molecular receptors that are covalently incorporated into macrocyclic structures such as functionalized cyclen (1,4,7,10-tetraazacyclododecane) that can form kinetically and thermodynamically stable complexes with lanthanide ions has led to the development of delayed lanthanide luminescence sensors.<sup>11,12</sup> In general, the Tb(III) or Eu(III) complexes of such hepta- or octadentate cyclen ligands adopt square antiprismatic geometries in solution and the solid state.<sup>13,14</sup> Generally, the lanthanide ions prefer high coordination environments (usually of 8–10), and in the cases where these high coordination requirements are not met, the remaining coordination sites are usually occupied by counterions and/or labile solvent molecules.<sup>15</sup> Parker et al. have demonstrated that such coordinatively unsaturated cyclen complexes, bearing covalently attached antennae, can be designed to have two metal bound water molecules in aqueous solution and that these can be displaced by more strongly coordinated ligands such as  $\text{HCO}_3^-$  in water.<sup>16</sup> As the lanthanide excited states are quenched by O–H oscillators, such complexes are poorly emissive prior to the ligand exchange.<sup>17</sup> In a similar manner,

we have demonstrated that the combination of aromatic carboxylates such as *N,N*-dimethylaminobenzoic acid, **4**, and Tb(III) complexes such as **1**•Tb resulted in the formation of **1**•Tb•**4** through self-assembly to yield a highly luminescent complex in buffered water (pH 7.4), following the excitation of the aromatic carboxylate antenna.<sup>18</sup> Indeed, we demonstrated the use of such complexes for the selective detection of salicylic acid in the presence of the prodrug aspirin.<sup>19</sup> For these, the complexes incorporating Tb(III) were found to bind the antennae with binding constants that were 1 order of magnitude stronger than those measured for the Eu(III) complexes. The Eu(III) complexes were also less emissive as the energy transfer from the antenna to the Eu(III) centers was found to be thermodynamically unfavorable. Faulkner et al. have also developed similar, using NIR emitting analogues, using antennae that absorb at long wavelength and Nd(III) and Yb(III) as the NIR emitting ions,<sup>20</sup> while Li et al. have developed related complexes for MRI and luminescent applications.<sup>21</sup> With the aim of further exploring the use of such complex formation for luminescent sensing and in particular for sensing biologically important aromatic or aliphatic dicarboxylates we have developed the coordinatively unsaturated dinuclear<sup>22</sup> Tb(III) complex, **2**•Tb<sub>2</sub>. Dicarboxylate ion recognition is of great biological and medicinal relevance, as many dicarboxylates take part in metabolic processes and energy storage.<sup>23</sup> The strategy behind the design of **2**•Tb<sub>2</sub> was that by simply connecting two **1**•Tb complexes together via a (short) semirigid bridge would allow each of the lanthanide ions to coordinate bidentate anions in conjunction. However, such 1:1 complex formation would only be possible provided that anions are capable of bridging the distance between the two lanthanide ion centers as well as being able to displace both of the coordinated water molecules on each of the metal ion centers. As proof of principle, **2**•Tb<sub>2</sub> was also designed to incorporate

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an integrated antenna, e.g. the xylene spacer, which could be used to populate the Tb(III) excited state when evaluating the recognition of aliphatic dicarboxylates, that lack the sensitizing antenna. Herein, we give a full account of our investigation.

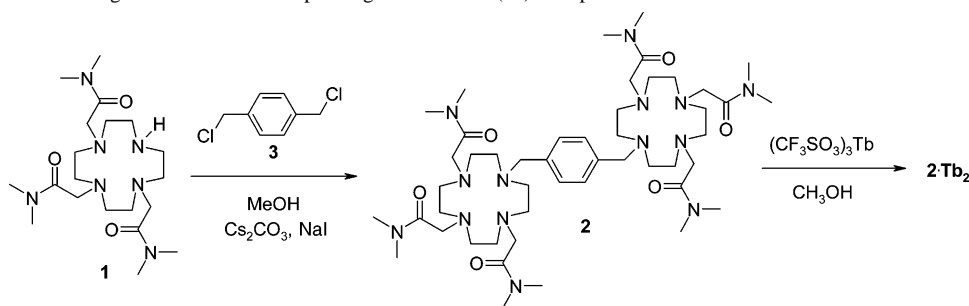


## Experimental Section

**General Procedures.** Melting points were determined using an Electrothermal IA9000 digital melting point apparatus. Infrared spectra were recorded on a Mattson Genesis II FTIR spectrophotometer. Samples were dispersed in KBr and recorded as clear pressed disks. <sup>1</sup>H NMR spectra were recorded at 400 MHz using a Bruker Spectrospin DPX-400 instrument. <sup>13</sup>C NMR were recorded at 100 MHz using a Bruker Spectrospin DPX-400 instrument. Mass spectrometry was carried out using HPLC grade solvents. Mass spectra were determined by detection using electrospray on a Micromass LCT spectrometer. High-resolution mass spectra were determined relative to a standard of leucine enkephaline. Elemental analysis was performed in the Microanalytical Laboratory, University College Dublin. Starting materials were obtained from Sigma Aldrich, Strem Chemicals, and Fluka and used as received. High-grade solvents (methanol and acetonitrile) were used for the synthesis of the ligand and complex. Columns were run using aluminum oxide (activated, neutral, Brockmann I STD grade 150 mesh). All luminescent spectra were recorded on a Cary Eclipse Varian fluorometer in phosphorescent mode with a gate time of 10 ms and slit widths of 2.5 or 5 nm.

**Synthesis.** 2-[4,7-Bis((dimethylcarbamoyl)methyl)-10-[4-(4,7,10-tris((dimethylcarbamoyl)methyl)-1,4,7,10-tetraazacyclododec-1-ylmethyl)benzyl]-1,4,7,10-tetraazacyclododec-1-yl]-*N,N*-dimethylacetamide (**2**). Compound **1** (0.22 g, 0.51 mmol),  $\alpha,\alpha$ -dichloro-*p*-xylene (**3**) (0.04 g, 0.24 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.12 g, 0.37 mmol), and NaI (0.07 g, 0.49 mmol) were dissolved in MeOH (25 mL) and refluxed for 120 h. The solvent was evaporated, and the residue was then suspended in CHCl<sub>3</sub> and filtered. The volume was then reduced and the solution was left to stand. The resulting crystals were filtered off and washed with cold CHCl<sub>3</sub>. The desired product was isolated as off-white crystals, 0.04 g, 10%. Mp: dec above 118 °C. Calcd for C<sub>48</sub>H<sub>90</sub>N<sub>14</sub>O<sub>6</sub>, [M + 2H]: *m/z* = 958.7168.

**Scheme 1.** Synthesis of the Ligand **2** and the Corresponding Dinuclear Tb(III) Complex **2·Tb<sub>2</sub>**



**Table 1.** Crystallographic Data for **2·Na<sub>2</sub>**

chem formula	Na <sub>2</sub> C <sub>56</sub> H <sub>100</sub> N <sub>14</sub> O <sub>8</sub> Cl <sub>2</sub> I <sub>2</sub>
fw	2248.08
cryst system	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	14.7450(5)
<i>b</i> /Å	14.8471(5)
<i>c</i> /Å	21.8612(8)
$\alpha$ /deg	90
$\beta$ /deg	96.124(1)
$\gamma$ /deg	90
<i>V</i> /Å <sup>3</sup>	4755.3(3)
<i>Z</i>	2
<i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.570
$\mu$ (Mo K $\alpha$ )/mm <sup>-1</sup>	1.397
<i>F</i> (000)	2268
$\theta$ range (deg)	1.66–25.01
unique reflns	8370
no. of params	484
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	0.0428
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	0.0935

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

Found: *m/z* = 958.7117 (−5.3 ppm).  $\delta_H$  (400 MHz, D<sub>2</sub>O): 7.30 (s, 4H, Ar), 3.95 (s, 4H, Ar–CH<sub>2</sub>), 3.22 (s, 4H, CH<sub>2</sub>), 2.99 (s, 8H, CH<sub>2</sub>), 2.79 (bm, 68H, cyclen + CH<sub>3</sub>).  $\delta_C$  (100 MHz, D<sub>2</sub>O): 172.5, 172.1, 136.5, 129.8, 57.7, 54.5, 53.8, 50.8, 50.3, 49.7, 48.3, 35.5, 35.1, 34.8. IR  $\nu_{max}$  (cm<sup>-1</sup>): 3442, 2937, 2829, 1639, 1507, 1453, 1404, 1348, 1262, 1102, 1006, 819, 631.

**2·Tb<sub>2</sub>** The ligand **2** (26.00 mg, 27.2  $\mu$ mol) and Tb(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (33.00 mg, 54.4  $\mu$ mol) were dissolved in MeOH (15 mL) and heated at reflux overnight. The solution was filtered, and the solvent was then removed. The residue was triturated with CH<sub>2</sub>Cl<sub>2</sub> (3  $\times$  20 mL). The residue was then dissolved in MeOH (5 mL) and added dropwise to ether (150 mL). The resulting precipitate was filtered, allowing the collection of a pale yellow solid, 24.00 mg, 41%. Mp: dec above 170 °C. Anal. Calcd for C<sub>47</sub>H<sub>93</sub>N<sub>14</sub>O<sub>6</sub>Tb<sub>2</sub>·6CF<sub>3</sub>SO<sub>3</sub>·2H<sub>2</sub>O·4CH<sub>2</sub>Cl<sub>2</sub>: C, 27.06; H, 3.86; N, 7.75. Found: C, 26.68; H, 3.74; N, 7.59.  $\delta_H$  (400 MHz, D<sub>2</sub>O): 120.25, 85.41, 74.99, 72.99, 59.79, 34.95, 31.35, 19.33, 13.33, 7.48, 5.44, 3.54, 3.31, 3.12, 1.17, −14.75, −15.76, −20.76, −37.78, −46.99, −61.40, −98.04, −106.25, −122.88. Mass spectrum (MeOH, ES<sup>+</sup>; *m/z*): found, 573.5 [M + 3 triflate]/3. IR  $\nu_{max}$  (cm<sup>-1</sup>): 3460, 2939, 1624, 1508, 1458, 1409, 1259, 1165, 1082, 959, 826, 639, 574, 517, 468.

**Crystallographic Structure Determination.** Crystallographic data and experimental details are summarized in Table 1. Single-crystal analyses were performed at 153 K with a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.710 73 Å) using the  $\omega$  scan method. Data were collected, processed, and corrected for Lorentz and polarization effects using SMART and SAINT-NT software. The structures were solved using direct methods and refined with the SHELXTL

program package. All non-hydrogen atoms were refined anisotropically. Aromatic hydrogen atoms were assigned to calculated positions with isotropic thermal parameters fixed at 1.2 times that of the attached carbon atom. Water hydrogen atoms could not be located from difference maps due to rotational disorder and were therefore not included in the refinement.

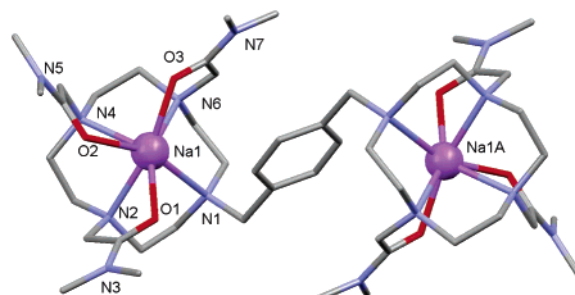
## Results and Discussion

### Synthesis and Characterization of **2**, **2**·Na<sub>2</sub>, and **2**·Tb<sub>2</sub>.

With the aim of achieving the selective recognition of anions having two binding sites, using the modulation of lanthanide luminescence, we designed ligand **2**. Having successfully demonstrated that Tb(III) complexes, such as **1**·Tb,<sup>19</sup> could be employed to bind anions such as arylacetates through the displacement of metal-bound water molecules, we decided on building our target sensor modifying this previous design by simply linking two **1**·Tb complexes together via a short covalent spacer. We have previously demonstrated that the fluorescent PET sensing of anions such as bis(carboxylates) and pyrophosphate can be achieved in DMSO using a 9,10-dimethylanthracene bridge in a 1:1 binding stoichiometry giving rise to quenching of the anthracene emission.<sup>24</sup> For such 1:1 binding the anions would have to bridge the anthracene spacer. Consequently, we decided on using a similar type spacer for the study herein, e.g. the xylene molecule. This spacer would potentially (a) provide the correct geometry for such bidentate anions to bridge across the two metal ion centers and bind to the Tb(III) ions by the displacement of their bound water molecules, respectively, (b) enable the successful population of the Tb(III) excited state via the antenna effect, and (c) be easily synthetically introduced.

The synthesis of the ligand **2** was carried out as outlined in Scheme 1. The reaction of a methanolic solution of **1**<sup>25</sup> with  $\alpha,\alpha$ -dichloro-*p*-xylene (**3**), in a 2:1 molar ratio in the presence of Cs<sub>2</sub>CO<sub>3</sub> and NaI, gave **2** as a crystalline solid following workup. The <sup>1</sup>H NMR spectrum of **2** (400 MHz, D<sub>2</sub>O) reflected the high degree of symmetry inherent in the molecule, with the four aromatic proton resonances at 7.30 ppm, while the four benzyl protons appeared as a singlet at 3.95 ppm. The <sup>13</sup>C NMR (D<sub>2</sub>O, 100 MHz) spectrum also showed two carbonyl resonances at 172.5 and 172.1 ppm. The aromatic carbon atoms appeared at 136.5 (quaternary) and 129.8 ppm, while seven methylene carbon atom resonances appeared at 57.7, 54.5, 53.8, 50.8, 50.3, 49.7, and 48.3 ppm. Moreover, the methyl groups of the acetamide arms resonate at 35.5, 35.1, and 34.8 ppm due to a syn and anti relationship with the amide carbonyl group.

The crystals isolated above were found to be of sufficient quality for a single-crystal X-ray diffraction study.<sup>26</sup> The



**Figure 1.** Molecular structure of **2**·Na<sub>2</sub> showing the atomic labeling scheme. Hydrogen atoms, solvent of crystallization, and iodide anions have been omitted for the sake of clarity.

structure showed that the desired ligand had been successfully synthesized. However, the study also revealed that it was not the free ligand, **2**, but instead that of the corresponding disodium complex, **2**·Na<sub>2</sub>, the sodium atoms presumably complexed during synthesis. The structure of **2**·Na<sub>2</sub> is shown in Figure 1. Sodium is known to have a coordination geometry similar to that of many lanthanide ions, and we and others have used it as a lanthanide ion mimic for crystal structure analysis.<sup>27,28</sup> As might have been anticipated (and by virtue of its seven-coordinate nature), the sodium ion adopts a pseudo-square antiprism geometry. This geometry is also commonly found for octadentate lanthanide cyclen complexes.<sup>13,14,29</sup> The sodium ion is coordinated to four cyclen ring nitrogen atoms as well as three amide oxygen atoms of the pendant arms, with average Na···N and Na···O distances of 2.55 and 2.45 Å, respectively. The across dimer Na···Na distance is ca. 8.68 Å.

The corresponding Tb(III) complex was formed by refluxing a methanolic solution of **2** with 2 molar equiv of Tb(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> to give **2**·Tb<sub>2</sub> in 41% yield following workup. The <sup>1</sup>H NMR spectrum (400 MHz, D<sub>2</sub>O) was consistent with complex formation as evidenced by the large shift in the proton signals due to the presence of the paramagnetic metal ions. The ES mass spectrum contained a peak at *m/z* = 573.5 corresponding to the [M + 3 triflate]/3 species indicating the presence of two metal ions within this structure. The IR spectrum showed that the carbonyl stretching frequency decreased from 1639 cm<sup>-1</sup> in **2** to 1624 cm<sup>-1</sup> in **2**·Tb<sub>2</sub>, which is characteristic for such complex formation. Previously we established via X-ray crystallography that **1**·Tb formed as a nine-coordinated complex, with seven coordination sites occupied by the ligand akin to that seen above in **2**·Na<sub>2</sub> and the remainder by two coordinated water molecules. Consequently, we anticipate that each Tb(III) center in **2**·Tb<sub>2</sub> also possesses two metal bound water molecules. To confirm this, the excited-state lifetime ( $\tau$ ) of the complex was measured in both H<sub>2</sub>O and D<sub>2</sub>O, respectively, upon direct excitation of the Tb(III) ion at 395 nm. These lifetimes obtained were

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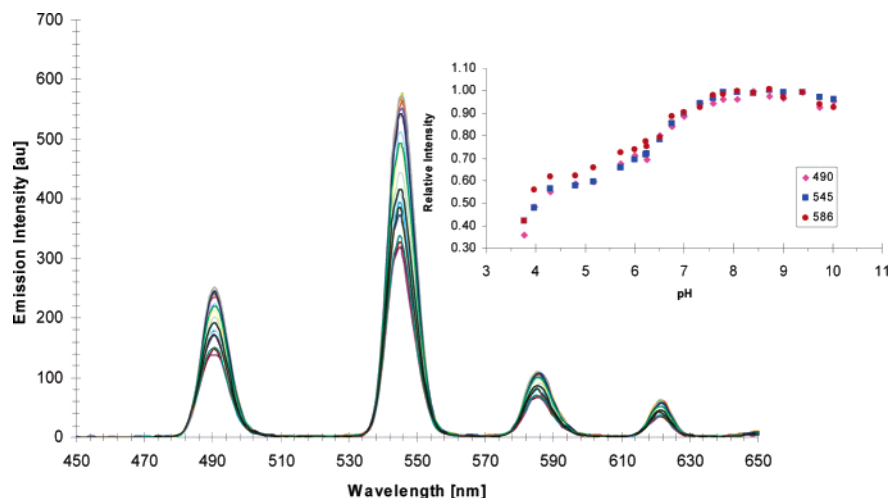
(25) Gunnlaugsson, T.; Leonard, J. P.; Mulready, S.; Nieuwenhuyzen, M. *Tetrahedron* **2003**, *59*, 3231.

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(29) Parker, D.; Puschmann, H.; Batsanov, A. S.; Senanayake, K. *Inorg. Chem.* **2003**, *42*, 8646.



**Figure 2.** Changes in the Tb(III) luminescence of  $2\cdot\text{Tb}_2$  upon excitation of the xylene bridge as a function of pH. Insert: Relative emission changes for three of the wavelengths.

then used to determine the hydration state of the complexes (the  $q$  value) using eq I.<sup>30</sup>

$$q[\text{Tb(III)}] = 5\{[1/\tau(\text{H}_2\text{O}) - 1/\tau(\text{D}_2\text{O})] - 0.06\} \quad (\text{I})$$

The results of these measurements, where the luminescence decays in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  were fitted to a single-exponential decay, indicated that each center had two metal-bound water molecules,  $q \sim 2$ . Interestingly, the decay lifetimes and rate constants determined from these studies were similar to those observed for the corresponding mononuclear complex,  $1\cdot\text{Tb}$  ( $\tau_{\text{H}_2\text{O}} = 0.720$  ms;  $\tau_{\text{D}_2\text{O}} = 0.92$  ms), with single-exponential decay lifetimes of 0.73 ms and 0.93 ms ( $\pm 10\%$ ) in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , respectively ( $k_{\text{H}_2\text{O}} = 1.37$  ms<sup>-1</sup> and  $k_{\text{D}_2\text{O}} = 1.08$  ms<sup>-1</sup>). This would indicate that there was no communication between the two metal ions, as the results were best fitted to a single-exponential decay. Consequently in  $2\cdot\text{Tb}_2$  each metal possesses two metal-bound water molecules that presumably could be displaced in a manner similar to that observed previously for  $1\cdot\text{Tb}$ .

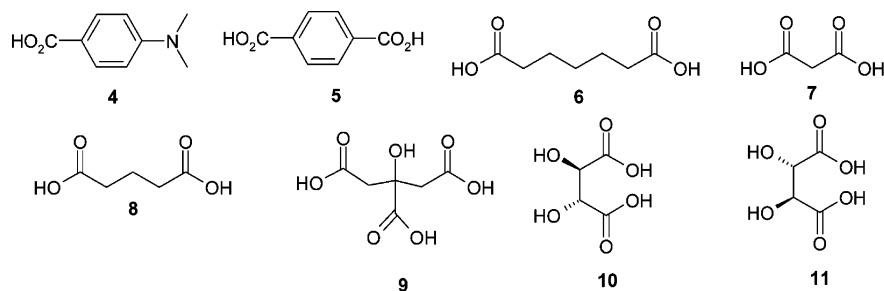
**Photophysical Evaluation of  $2\cdot\text{Tb}_2$  in Aqueous Solutions upon Addition of Anions.** Having established the hydration state for  $2\cdot\text{Tb}_2$  as two for each of the metal ions, we set out to investigate the formation of the potential luminescent ternary complexes with mono- and bidentate anions in competitive media with  $2\cdot\text{Tb}_2$ . This was done by evaluating the changes in the ground and the singlet excited states as well as the changes in the intensity and lifetime of the Tb(III) emission (in water and in TRIS buffer at pH 7.4 solution) as a function of added anions.

When recorded in water,  $2\cdot\text{Tb}_2$  had a  $\pi$ - $\pi$  absorption band in the UV-visible spectrum with  $\lambda_{\text{max}}$  at 237 nm, which was structurally typical of that observed for xylene. Upon excitation at this wavelength a fluorescence emission characteristic for the xylene chromophore was observed. More-

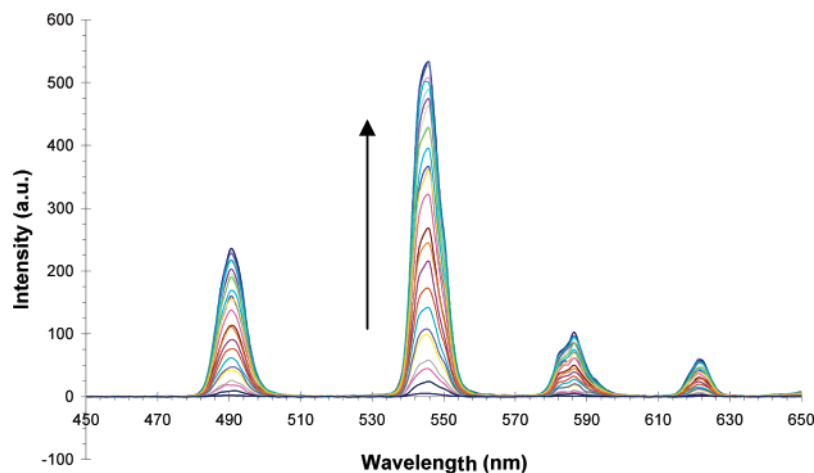
over, a characteristic Tb(III) emission was also observed upon time gating at 491.5, 547.5, 588.0, and 623 nm for the deactivation of the  $^5\text{D}_4 \rightarrow ^7\text{F}_J$  ( $J = 6, 5, 4,$  and  $3$ ) bands, showing that the xylene bridge acted as an efficient antenna and populated the  $^5\text{D}_4$  excited-state effectively (Figure 2). However, even though this emission was not quantified (it was too weak) as it would be expected that the lanthanide excited state would be quenched by the metal-bound water molecules through vibrational coupling to the O-H oscillators. As our main aim was to employ  $2\cdot\text{Tb}_2$  as an anion sensor in competitive media under physiological conditions, the pH dependence of the Tb(III) emission was also investigated, by carrying out a pH titration in water between pH 3.5–11, in the presence of 0.1 M tetramethylammonium chloride [(TMA)Cl] to maintain constant ionic strength, and observing the concomitant changes in the Tb(III) emission. Here, the Tb(III) emission was indeed found to be pH dependent, being reversibly switched “on–off”. These emission changes occurred mainly between pH 5.5–7.5, which we assign to two effects: (i) the possible deprotonation of metal bound water molecules; (ii) conformational changes occurring at lower pH. Most importantly, above pH 7.5, the changes were only minor. This is desirable as any additional luminescent changes that occur above this pH, on the addition of any coordination anions, such as **4–11**, Figure 3, can be directly assigned to the formation of the desired ternary complexes. Because of this, all anion recognition studies were carried out at pH 7.4, which would also ensure that all carboxylic acids employed in this study would be fully ionized to their corresponding carboxylate anions.

Having determined the pH independence at higher pH, we first carried out titrations of  $2\cdot\text{Tb}_2$  using *N,N*-dimethylaminobenzoic acid (**4**) in pH 7.4 buffered aqueous solution [0.1M TRIS,  $I = 0.1$  M (TMA)Cl]. This coordinated antenna was previously used by us for the formation of the luminescent ternary complex of  $1\cdot\text{Tb}$ , in a 1:1 stoichiometry, whereas for binding to  $2\cdot\text{Tb}_2$  a 2:1 stoichiometry would be expected. The overall changes observed in the Tb(III) emission are shown in Figure 4. Upon excitation at 300 nm, in

(30) Beeby, A.; Clarkson, I. M.; Dickins, R. S.; Faulkner, S.; Parker, D.; Royle, L.; de Sousa, A. S.; Williams, J. A. G.; Woods, M. *J. Chem. Soc., Perkin Trans. 2* **1999**, 493. This equation is based on the work of Horrocks et al.: (a) Horrocks, W. D.; Sunick, D. R. *Acc. Chem. Res.* **1981**, *14*, 384. (b) Supkowski, R. M.; Horrocks, W. D. *Inorg. Chim. Acta* **2002**, *340*, 44.



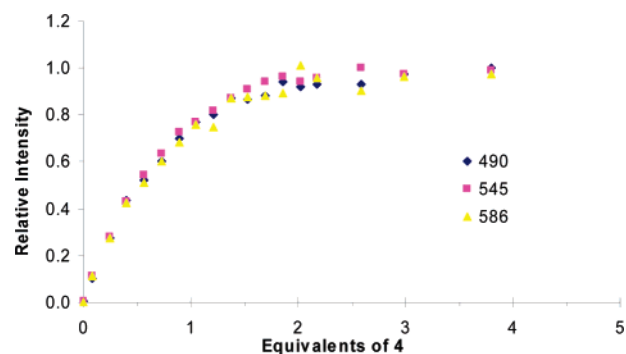
**Figure 3.** Coordinating carboxylic acids used in this study.



**Figure 4.** Luminescence spectrum of  $2 \cdot \text{Tb}_2$  ( $16 \mu\text{M}$ ) showing increase in luminescent intensity upon addition of increasing concentration of **4** upon excitation at 300 nm.

the absence of **4**,  $2 \cdot \text{Tb}_2$  ( $16 \mu\text{M}$ ) was found to be only weakly luminescent as previously stated (e.g. 5 au on the scale shown in Figure 4). However, upon addition of **4** (which has an absorption band at 300 nm, assigned to the ICT character of the molecule) the Tb(III) emission was clearly enhanced at 491.5, 547.5, 588.0, and 623 nm, respectively. These luminescent enhancements represent an efficient sensitization of the lanthanide  $^5\text{D}_4$  excited state by the coordinating carboxylate antenna, indicating the formation of the desired luminescent ternary complex. This is due to two features; first, the displacement of the metal bound water molecules brings the antenna into close proximity to the metal ion center, which facilitates efficient energy transfer from the antenna, and second, the aforementioned quenching of the Tb(III) excited state by O–H oscillators is removed.

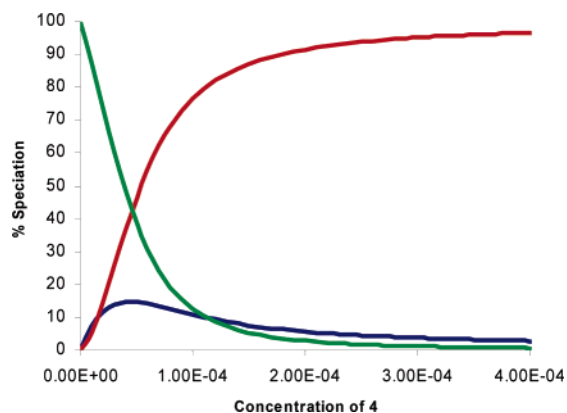
Analyzing the changes in the intensity for any of the  $^5\text{D}_4 \rightarrow ^7\text{F}_j$  transitions in Figure 4 showed that the Tb(III) emission was highly dependent on the concentration of **4** and that the emission intensity reached a maximum after the addition of 2 equiv of **4**, Figure 5. This indicates that each of the metal ion centers is operating independently in the presence of such monocoordinating antenna; each binding **4** giving a  $4:2 \cdot \text{Tb}_2$  stoichiometry equal to 2:1. Moreover, Figure 5 clearly shows that all the transitions give rise to identical luminescent enhancements upon anion coordination. [It is possible that the complex can be formed in 2:2 geometry which would give rise to a molecular square, with four Tb(III) centers. However, analysis of such binding using nonlinear least-squares regression analysis did not give satisfactory results.



**Figure 5.** Relevant intensity changes in the Tb(III) emission of  $2 \cdot \text{Tb}_2$  at three different wavelengths as a function of [**4**] in pH 7.4 solution [ $I = 0.1 \text{ M (TMA)Cl}$ ].

We do thus not propose that such a structure is formed in solution. The formation of coordination polymers could also be envisioned; however, the analysis of the binding constant also excludes such binding as, at high concentration of the anion, the 2:1 would be expected to dominate.]

We also employed luminescent lifetime measurements to further verify the binding of the two equivalents of **4** to  $2 \cdot \text{Tb}_2$ . As discussed above,  $q$  was determined to be 2 in the absence of the antenna. However, upon the addition of 2 equiv of **4**, the luminescence lifetimes were significantly increased being 1.315 and 1.504 ms in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , respectively. From these results we determine that  $q = 0.18$ ; e.g., the two water molecules have been removed from each Tb(III) center. The significant enhancement in the lumines-



**Figure 6.** Speciation variation of  $2\cdot\text{Tb}_2$  upon titration with **4** in pH 7.4 solution: green,  $2\cdot\text{Tb}_2$ ; blue, 1:1 ( $4:2\cdot\text{Tb}_2$ ); red, 2:1 ( $4:2\cdot\text{Tb}_2$ ).

cence lifetimes in both solvents also indicated the suppression of any quenching by the metal-bound water molecules through O–H vibrational deactivation. Using the nonlinear least-squares regression program SPECFIT, we also evaluated the stoichiometry by fitting the overall luminescence changes seen in Figure 4. This fitting also evaluated the binding affinity of  $2\cdot\text{Tb}_2$  for **4**. The binding constants  $\log K_1 = 4.07 (\pm 0.01)$  and  $\log K_2 = 4.98 (\pm 0.10)$  were determined for the 1:1 and the 2:1 complex formations, respectively. The speciation distribution diagram in Figure 6 for this titration also clearly shows that the 2:1 stoichiometry dominates.

We next investigated the ability of  $2\cdot\text{Tb}_2$  to form self-assembly complexes using aromatic bis(carboxylates) with the anion functioning as an antenna for the sensitization of the Tb(III) centers. Terephthalic acid, **5**, was first chosen as its geometry is complementary to the *p*-xylene spacer of  $2\cdot\text{Tb}_2$ , and it is known to have a suitable triplet energy state to enable sensitization of  $^5\text{D}_4$  of Tb(III). Luminescence studies were conducted in a manner identical to that described above. However, bis(carboxylate) **5** has an absorption band centered at  $\lambda_{\text{max}} = 240$  nm, close to the  $\lambda_{\text{max}}$  of  $2\cdot\text{Tb}_2$  itself (237 nm), which would make it difficult to directly address the anion selectivity as  $2\cdot\text{Tb}_2$  self-sensitizes the lanthanide excited state. Nevertheless, upon addition of one equivalent of **5** to  $2\cdot\text{Tb}_2$ , a significant 26-fold enhancement was observed in the Tb(III) emission, signifying binding of the anion to the Tb(III) ion, Figure 7A. Indeed, the emission intensity was highly dependent on the concentration of **5**, reaching a maximum at ca. 1 equiv (Figure 7B), indicating the formation of a luminescent ternary complex with 1:1 stoichiometry i.e. with the anion bridging between the two metal centers, Figure 8.

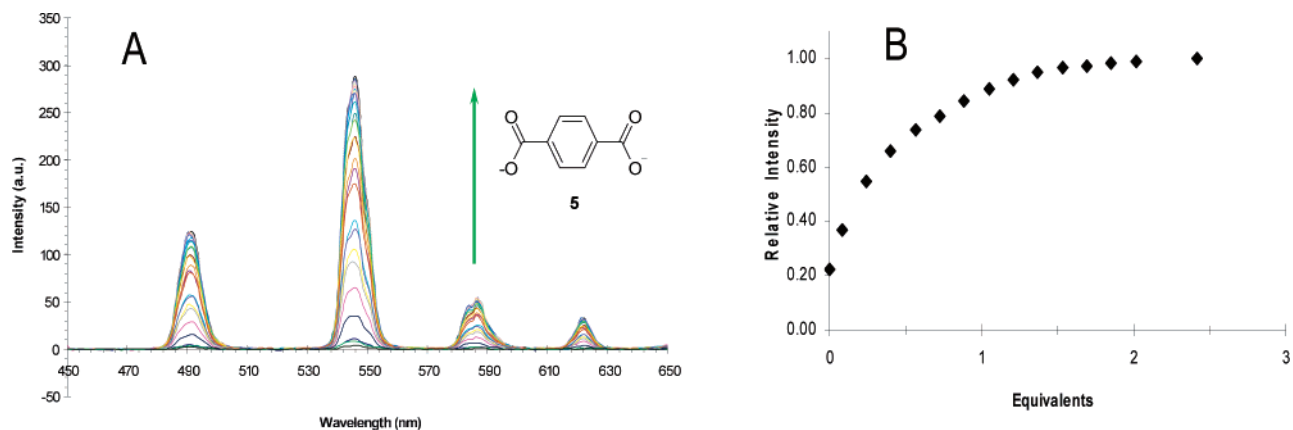
Conceivably the bis(anions) may interact with  $2\cdot\text{Tb}_2$  independently and bind with the bis(anion) bridging between each metal center with an anion: $2\cdot\text{Tb}_2$  stoichiometry of 1:1 (A) or at one metal center with 1:1 stoichiometry (B) or bind at each metal in 2:1 stoichiometry (C), Figure 8. To verify the binding stoichiometry, we carried out several analyses of the above titration results. Binding modes A and C would have similar *q*-values as each does not have any metal-bound water molecules to quench the luminescence. Of these, mode C can be discounted as no substantial luminescence enhance-

ments were observed after the addition of more than 1 equiv of **5** (Figure 7B). In the case of the 1:1 binding mode B, the Tb(III) emission intensity would be expected to be smaller than that observed for the 1:1 binding mode A, as the antenna would only be populating one of the two Tb(III) centers. The metal-bound water molecules would still be present on the second Tb(III) center. Hence, for such binding, the *q* value would be expected to be higher than zero.

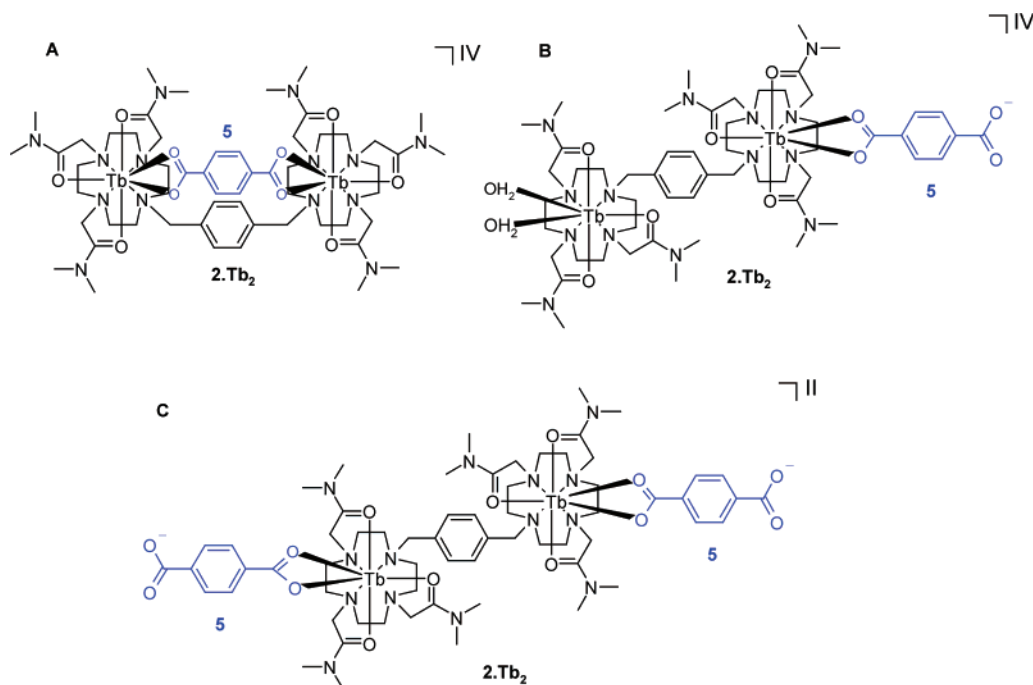
To determine the correct binding mode for this complex, the Tb(III) excited-state lifetimes were measured in H<sub>2</sub>O and D<sub>2</sub>O in the presence of 1 equiv of **5**, by direct excitation into the Tb(III) center at 360 nm rather than exciting the antenna. This yields information about the changes in the coordination environment of the Tb(III) center. The Tb(III) luminescence decay in both solvents was fitted to a single-exponential decay, giving  $\tau_{\text{H}_2\text{O}} = 1.73$  ms and  $\tau_{\text{D}_2\text{O}} = 1.99$  ms, with an associated *q* value of 0.08, clearly indicating that both metal centers have no bound water molecules. These results support the formation of the 1:1 stoichiometry and the formation of the ternary complex mode A in solution. This hypothesis was further confirmed by using nonlinear least-squares regression analysis of the luminescence changes observed in Figure 7. Here, a  $\log K_1 = 5.42 (\pm 0.21)$  was determined for 1:1 binding, where the speciation distribution diagram (not shown) indicated the instantaneous formation of the 1:1 self-assembly. These are, to the best of our knowledge, the first examples of such luminescent ternary complexes in aqueous solution formed from self-assembly of bis(carboxylates) and dinuclear lanthanide complexes made from kinetically and thermodynamically stable lanthanide complexes.

With the confirmation of the 1:1 binding of **5** to  $2\cdot\text{Tb}_2$ , a range of other bis(carboxylates), such as pimelic acid, **6**, malonic acid, **7**, glutaric acid, **8**, citric acid, **9**, L-tartaric acid, **10**, and D-tartaric acid, **11**, were investigated, Figure 3. These each would potentially be able to bridge the distance between the two Tb(III) centers in  $2\cdot\text{Tb}_2$ . In contrast to that observed for **4** and **5** above, **6–11** do not contain an antenna. Therefore, the *p*-xylene spacer was used as the antenna by exciting the chromophore at 240 nm. In the case of pimelic acid, **6**, the Tb(III) emission showed a 13% luminescent enhancement. This is due to the fact that the population of the Tb(III) excited state is achieved far less efficiently via the xylene antenna. For these titrations, the maximum intensity was reached at 1 equiv of **6**. Fitting the changes in the Tb(III) emission using nonlinear least-squares regression analysis gave a  $\log K_1 = 6.62 (\pm 0.22)$  for 1:1 stoichiometry. This indicates that **6** shows stronger binding affinity than **5** for  $2\cdot\text{Tb}_2$ . The speciation variation diagram also showed the instantaneous formation of the desired 1:1 self-assembled product as seen for **5**. Lifetime measurements of  $2\cdot\text{Tb}_2$  in the presence of 1 equiv of **6** also indicated that *q*  $\sim$  0. These results suggest that the formation of a self-assembled ternary complex similar to that seen for **5** has been achieved, i.e. binding mode A, Figure 8.

Titration with **7**, which is the shortest of the dicarboxylates investigated, gave rise to a 25% increase in the Tb(III) luminescence, reaching a maximum after the addition of 2 equiv.



**Figure 7.** (A) Luminescence spectrum of  $2 \cdot \text{Tb}_2$  ( $16 \mu\text{M}$ ), showing increase in luminescent intensity upon addition of **5**, when excited at 240 nm. (B) Relevant intensity changes in three different conditions.



**Figure 8.** Three possible binding modes A (1:1 stoichiometry), B (1:1 stoichiometry), and C (2:1 stoichiometry), following the interaction between  $2 \cdot \text{Tb}_2$  and **5**. The formation of a polymeric network is also possible at higher concentrations of the anion; however, we do not have any evidence for such a formation in this case.

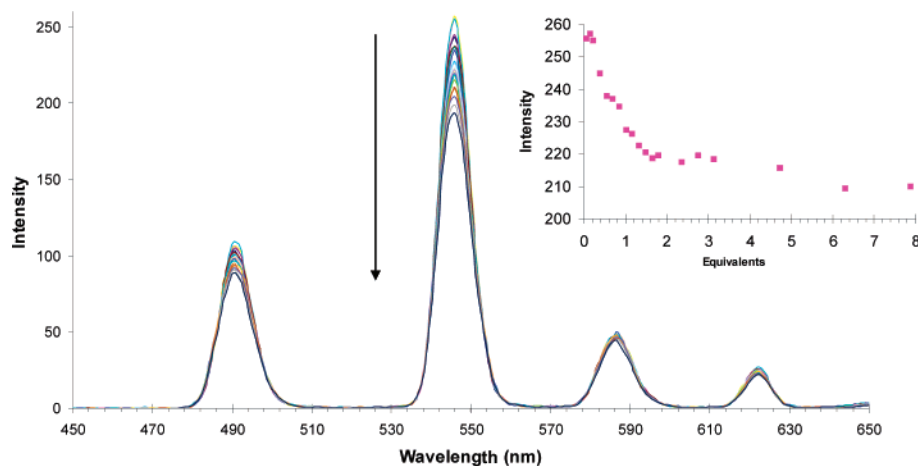
Analysis of the Tb(III) excited-state lifetimes showed that  $q \sim 0$ , confirming that indeed both Tb(III) centers were involved in coordination to **7**. Nonlinear least-squares regression analysis was used to determine the binding constants. Two stability constants were evident; however, only the second could be determined with any accuracy,  $\log K_2 = 8.43 (\pm 0.11)$ . This indicates that the 2:1 stoichiometry dominates and that **7** binds to  $2 \cdot \text{Tb}_2$  with a binding mode reminiscent of mode C as shown in Figure 8. This would indicate that **7** is too short to span the *p*-xylene bridge and therefore two molecules interact independently with the Tb(III) centers. In contrast to these results, the titration of  $2 \cdot \text{Tb}_2$  with either **8** or **9** did not result in any significant changes in the lanthanide luminescence.

The titration of  $2 \cdot \text{Tb}_2$  with either **10** and **11** (L- and D-tartaric acid, respectively) resulted in some interesting results, as the Tb(III) luminescence was quenched by ca. 15%

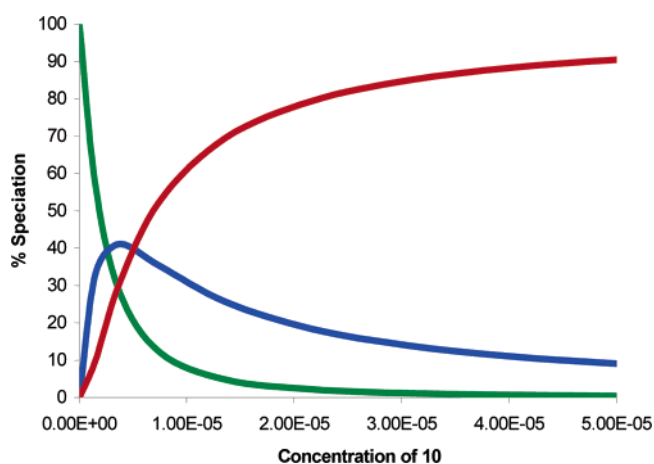
after the addition of 2 equiv of either, which is in contrast to that observed for the other anions tested, Figure 9. No enantioselective binding was observed as similar titration spectra resulted from **10** and **11**.<sup>31</sup> It is also worth noting that for the binding of **10** and **11** the largest changes in the spectra were observed for the deactivation of the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition. Using nonlinear least-squares regression analysis of the luminescence changes observed yielded  $\log K_1 = 5.59 (\pm 0.34)$  and  $\log K_2 = 5.30 (\pm 0.24)$  for the 1:1 and the 2:1 complex formations, respectively, for the D-tartaric acid, with complementary results being observed for the L-isomer. The species distribution diagram, Figure 10, shows that both the

(31) Examples of selective fluorescent sensing of tartaric acid include the following: (a) Zhao, J. Z.; Fyles, T. M.; James, T. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 3461. (b) Zhao, J. Z.; Davidson, M. G.; Mahon, M. F.; Kociok-Kohn, G.; James, T. D. *J. Am. Chem. Soc.* **2004**, *126*, 16179.





**Figure 9.** Change in intensity of the Tb(III) emission upon titration of  $2 \cdot \text{Tb}_2$  with **10** upon excitation at 240 nm. Inset: Changes at 545 nm (the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition), with respect to the added equivalents of **10**.



**Figure 10.** Speciation variation of  $2 \cdot \text{Tb}_2$  upon titration with **10**, in pH 7.4 solution: green,  $2 \cdot \text{Tb}_2$ ; blue, 1:1 ( $10:2 \cdot \text{Tb}_2$ ); red, 2:1 ( $10:2 \cdot \text{Tb}_2$ ).

1:1 and 2:1 stoichiometries were initially observed but at higher concentrations the 2:1 stoichiometry predominates. The nature of the luminescence quenching is worth commenting on, as it is most likely due to the presence of the extra OH oscillators in the structure of the tartaric acid leading to (i) additional vibrational quenching of the Tb(III) excited state, even after the displacement of the metal bound water molecules, or (ii) quenching of the excited state of *p*-xylene spacer. Hence, even though, selective binding of either L- or D-tartaric acid was not observed, it can be distinguished from the binding of the remaining carboxylates, as it gave rise to luminescent quenching rather than enhancement.

The above results indicate that despite the structural simplicity of  $2 \cdot \text{Tb}_2$  selective anion recognition is possible. The binding selectivity can be viewed as being in the order of  $7 > 6 > 5$ . All of the ternary complexes exhibit sensitized luminescence, in which the carboxylic acids give rise to large changes in the Tb(III) luminescence upon anion binding. This can be attributed to the efficiency of the sensitization process, which is significantly better by those antennae that bind directly to the metal ion center. Hence, this simple structure can also distinguish between aliphatic and aromatic car-

boxylates. In contrast, while tartaric acids are strongly bound, the anion recognition gives rise to luminescent quenching.

### Conclusion

We have developed a novel ligand **2** from the reaction of a cyclen amide with  $\alpha, \alpha$ -dichloro-*p*-xylene. The ligand was characterized by several methods such as NMR spectroscopy and as the structure of  $2 \cdot \text{Na}_2$  determined by X-ray crystallography. The coordinatively unsaturated binuclear Tb(III) complex  $2 \cdot \text{Tb}_2$  was found to have two metal-bound water molecules on each of the Tb(III) metal ion centers. Upon excitation of the *p*-xylene bridge in  $2 \cdot \text{Tb}_2$ , which can function as an antenna for sensitizing the  $^5\text{D}_4$  excited state of Tb(III), a weak Tb(III) emission was observed. This emission was greatly enhanced upon addition of several carboxylate anions such as *N,N*-dimethylaminobenzoic acid, **4**, terephthalic acid, **5**, and pimelic acid, **6**, at pH 7.5, due to the binding of these carboxylates to the Tb(III) centers which occurred through the displacement of the metal-bound water molecules. This gave rise to the formation of self-assembly ternary complexes between these carboxylates and  $2 \cdot \text{Tb}_2$ . Fitting the lanthanide luminescence changes, using nonlinear least-squares regression analysis, enabled us to further verify the stoichiometry and the binding affinity of this molecular recognition. The titration of  $2 \cdot \text{Tb}_2$ , in water at pH 7.4, with **4** gave rise to 2:1 binding stoichiometry, whereas the titration using **5** gave rise to the formation of 1:1 stoichiometric self-assembly. Several aliphatic bis(carboxylates) were also found to modulate the Tb(III) luminescence upon binding in either 1:1 or 2:1 stoichiometry. For the aliphatic carboxylates, the changes in the Tb(III) emission were significantly smaller than for the aromatic once. In the case of tartaric acid, both the 1:1 and 2:1 stoichiometries were observed (in a stepwise manner). However, the Tb(III) emission was quenched upon recognition of these ions, possibly due to O–H quenching, induced by the anions themselves upon binding to the Tb(III) centers.

In summary, a new binuclear lanthanide conjugate  $2 \cdot \text{Tb}_2$  for the detection of aromatic carboxylates such as *N,N*-dimethylaminobenzoic acid, **4**, and terephthalic acid, **5**, has been developed. The recognition of these ions occurs through

the formation of self-assembled ternary complexes which give rise to significant enhancements in the Tb(III) emission. In the presence of tartaric acid, the binding was found to be in 2:1 stoichiometry and the Tb(III) emission was quenched. We are currently improving this design principle to achieve more selective anion binding and achieving such sensing as well as using near-infrared emissive lanthanide ions such as Nd(III), Yb(III), and Er(III).

**Acknowledgment.** We thank Trinity College Dublin, Enterprise Ireland, IRCSET, Center for Synthesis and Chemical Biology, and Kinerton Ltd. for financial support.

**Supporting Information Available:** X-ray crystal data (CIF file) for  $2 \cdot \text{Na}_2$  (CCD No. = 622414). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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