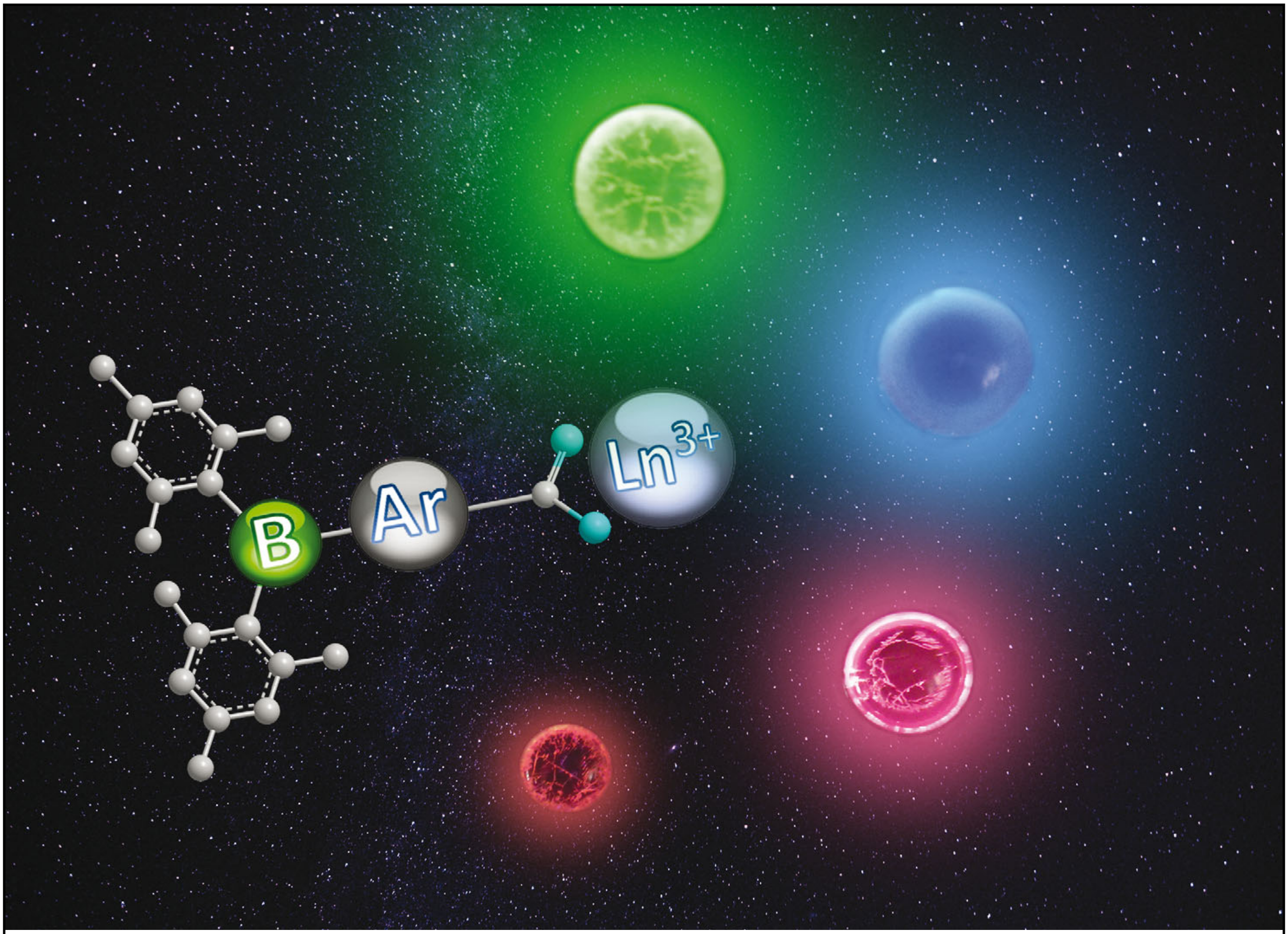

*Showcasing research from Professor Suning Wang's research group, Queen's University, Canada*

## Selective activation of lanthanide luminescence with triarylboron-functionalized ligands and visual fluoride indicators

Carboxylate-functionalized triarylboranes have been found to be highly effective in selective activation of Tb(III) or Eu(III) luminescence. Such systems are highly effective for visual and selective fluoride sensing. The triarylboron centers in these systems can be used for switching off green or red lanthanide emission and turning on ligand-based blue fluorescence by the addition of fluoride ions in solution or on a paper substrate.

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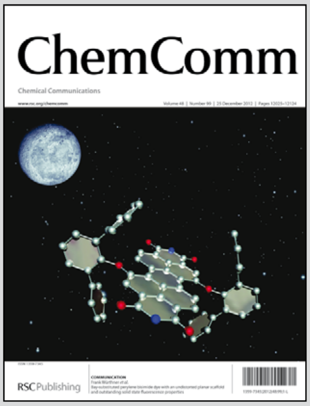
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# Selective activation of lanthanide luminescence with triarylboron-functionalized ligands and visual fluoride indicators†

**Maria Varlan, Barry A. Blight and Suning Wang***

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**Two triarylboron-functionalized carboxylate ligands have been found to be highly effective in selective activation of Tb(III) and Eu(III) emission and enable the use of the Tb(III) and Eu(III) complexes as highly effective luminescent indicators for $F^-$ and $CN^-$ in solution and on a solid substrate.**

Lanthanide-based luminescent compounds are a very attractive class of materials owing to the distinct and exceptionally narrow f → f emission bands, the long decay lifetimes and the large Stokes shifts.[1–7] However, because of the forbidden nature and the low extinction coefficients of f → f transitions, lanthanide emission is usually very weak.[1] Lanthanide emission can, however, be enhanced through the introduction of an appropriate "sensitizing" chelating ligand.[2] Sensitization of the rare earth ion is achieved through the absorption-energy transfer-emission (AETE) mechanism whereas the chelating ligand acts as an 'antenna' to harvest light and subsequently transfer the energy to a lanthanide ion, thus enhancing lanthanide emission.[3] Unlike phosphorescence of transition metal compounds that are usually very sensitive to oxygen quenching, thus limiting their use as sensors under ambient conditions,[5] lanthanide emission is much less prone to oxygen.[6] Consequently, luminescent lanthanide compounds have found use in a wide array of fields such as electroluminescent devices,[7] sensors,[8] and cellular imaging.[9] Triarylboron moieties such as $BMes_2Ar$ (Mes = mesityl) are known to be highly effective in enhancing fluorescence or phosphorescence of organic molecules and transition metal complexes.[10] The low-lying $p_\pi$ orbital on the boron center enables the use of triarylboron compounds as highly selective sensors for $CN^-$ and $F^-$ anions monitored readily by either the absorption or emission spectral change of the molecule.[11] Thus, combining the triarylboron functionality with lanthanide ions may allow us to access new functional lanthanide-based materials.

Based on these considerations, we recently initiated the development of triarylboron-functionalized luminescent lanthanide compounds. Herein we report the effective and selective activation of Tb(III) and Eu(III) ions by two $BMes_2$-functionalized carboxylate ligands **1** and **2** and the use of the lanthanide compounds in sensing applications.

The synthetic procedure of ligand **2** was reported in a recent paper from our group.[12] Ligand **1** is a new molecule and was synthesized using procedure similar to that of ligand **2** (see ESI†). These two ligands were chosen because of their distinct triplet energy for selective activation of Tb(III) or Eu(III) emission. The corresponding Tb(III) and Eu(III) compounds of **1** and **2** were obtained as colorless solids by the reaction of the potassium salt of **1** and **2** with $Tb(NO_3)_3 \cdot 6H_2O$ and $Eu(NO_3)_3 \cdot 6H_2O$, respectively, in methanol in high yield (Chart 1).

Elemental and MS analyses established that for ligand **1**, the complex has the general formula of $Ln(\mathbf{1})_3(H_2O)_x(MeOH)_y$ ($x = 0, y = 2$ for **1Tb**, $x = 2, y = 1$ for **1Eu**), while for ligand **2** the complex has the general formula of $Ln(\mathbf{2})_2(OMe)(MeOH)$ (**2Tb** and **2Eu**). Based on MS data, the lanthanide compounds are most likely oligomeric in solution and the solid state *via* either bridging carboxylate or methoxy ligands, which are commonly observed for lanthanide compounds.[13]

The impact of ligands **1** and **2** on luminescence of Tb(III) and Eu(III) is quite dramatic, as shown by the spectra and photographs of ligands and complexes in Fig. 1.

Both free ligands display weak blue fluorescence in the solid state and in solution. Complexes **1Tb**, **2Tb**, **1Eu** and **2Eu** display green, blue, red and pink luminescence, respectively, in solution and the solid state (Fig. 1, Table 1). Complex **1Tb** exhibits exceptionally bright luminescence with characteristic Tb(III) emission bands. The ligand's fluorescence band is also evident in all compounds. In the solid state, ligand **1**'s

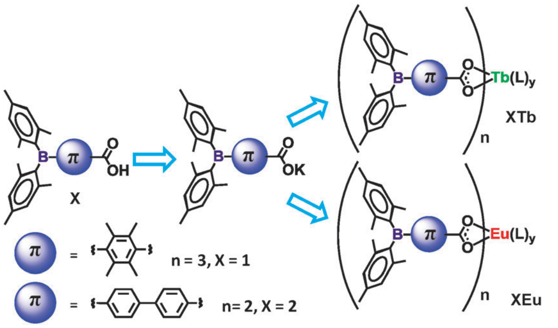

**Chart 1**

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† Electronic supplementary information (ESI) available: Synthetic details, characterization data, completed titration data. See DOI: 10.1039/c2cc36172h

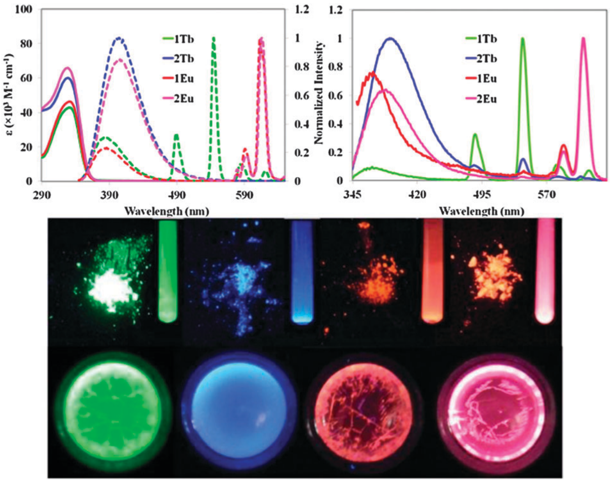

**Fig. 1** Absorption (solid line) and luminescence (dashed line) spectra of complexes in THF (top, left), luminescence spectra in PMMA (10 wt%) at r.t. (top, right), photographs of **1Tb**, **2Tb**, **1Eu** and **2Eu** in PMMA (10 wt%) (bottom), in the solid state and in THF solutions under irradiation at 365 nm (middle).

**Table 1** Photophysical properties of ligands **1** and **2** and their respective Tb(III) and Eu(III) complexes

| Compound | UV-Vis, nm ($\varepsilon$, $M^{-1}$ $cm^{-1}$) | $\lambda_{ex}$, nm THF, rt | $\lambda_{em}{}^{a}$, nm/$\tau$, ms, rt | $\Phi_{sol}{}^{b}$ | $\Phi_{ss}{}^{c}$, Total emission/ Lanthanide emission |
|---|---|---|---|---|---|
| **1** | 330 (15 997) | | 384 | 0.05 | — |
| **2** | 328 (25 031) | | 406 | 0.14 | — |
| **1Tb** | 330 (43 011) | 330 | 384, 489, 545, 585, 615/1.22(2) | — | 0.70/0.56 |
| **2Tb** | 328 (60 086) | 335 | 406 | — | 0.41/0.03 |
| **1Eu** | 330 (46 512) | 345 | 384, 579, 590, 617/0.63(1) | — | 0.14/0.04 |
| **2Eu** | 328 (65 813) | 350 | 406, 579, 590, 617/0.54(1) | — | 0.48/0.10 |

[a] In THF at $1 \times 10^{-5}$ M. [b] Relative to 9,10-diphenylanthracene in $CH_2Cl_2$. [c] Measured in the solid state in 10 wt% doped PMMA polymer films using an integration sphere.

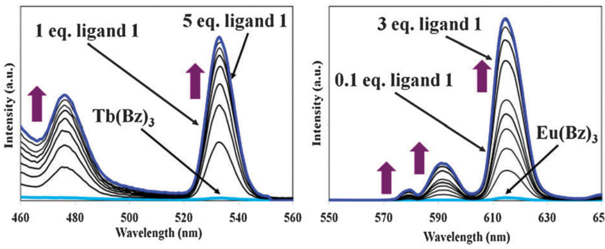

**Fig. 2** Luminescence titration spectra of $Tb(Bz)_3$ ($\lambda_{ex}$ = 300 nm, left) and $Eu(Bz)_3$ ($\lambda_{ex}$ = 330 nm, right) with **1** in THF ($1.0 \times 10^{-5}$ M) at 298 K.

contribution to the total emission of **1Tb** becomes very small, indicating very effective energy transfer from the ligand to the Tb(III) center, as shown in Fig. 1. Indeed, the quantum efficiency for **1Tb** in the solid state was found to be very impressive, 0.70 for total emission and 0.56 for Tb(III) emission bands (80% of the total emission). In contrast, **2Tb** does not display any Tb(III) emission bands in solution and shows very weak Tb(III) bands in the solid state (<10% of the total emission). These observations support that ligand **1** is highly effective in activating Tb(III) emission while ligand **2** is not.

For the **1Eu** and **2Eu** complexes, characteristic Eu(III) emission bands from the $^5D_0 \rightarrow {}^7F_n$ transitions with $n$ = 0, 1 and 2 were observed. These emission bands have moderate quantum efficiencies (0.04 for **1Eu**, 29% of the total emission; and 0.10 for **2Eu**, 21% of the total emission), indicating that ligands **1** and **2** are capable of activating Eu(III) emission, albeit much less efficient, compared to **1Tb**. The ligand's emission band contributes significantly in both Eu(III) compounds. Because of the large contribution of ligand **2**'s fluorescence, compound **2Eu** has pink luminescence while **1Eu**, with much less ligand's emission contribution, has the characteristic red emission color of Eu(III) (Fig. 1).

Since the key difference between ligands **1** and **2** and benzoate is the $BMes_2$ group, to examine the role of the $BMes_2$ group in ligands **1** and **2**, we performed the titration experiments of $Tb(Bz)_3$ and $Eu(Bz)_3$ by ligands **1** and **2**, respectively (Bz = benzoate). As shown in Fig. 2, the addition of ligand **1** to the solution of $Tb(Bz)_3$ or $Eu(Bz)_3$ led to a drastic intensity increase of the lanthanide emission bands. The exchange of ligand **1** with benzoate clearly enhances the emission of the lanthanide ions. Similar phenomenon was also observed for ligand **2** with $Eu(Bz)_3$. These experiments established that the $BMes_2$ group in ligands **1** and **2** is critical in activating Tb(III) or Eu(III) emission. The fact that ligand **1** can activate both Tb(III) and Eu(III) emission while ligand **2** can only activate Eu(III) emission may be explained by the triplet energy difference of the two ligands. It has been well established before that in order to activate lanthanide ion emission, the ligand's triplet energy should be close to and above that of the emissive state of the lanthanide ion. To determine the triplet excited energy level of the ligands, the phosphorescence spectra for **1** and **2** at 77 K were recorded in THF (see ESI†) and the $T_1$ triplet energy level was calculated[14] to be 24 398 $cm^{-1}$ and 21 563 $cm^{-1}$ respectively, which are above the lowest excited resonance levels (or the emissive states) $^5D_4$ of Tb(III) (20 500 $cm^{-1}$) and $^5D_0$ of Eu(III) (17 250 $cm^{-1}$).[15] The ineffective sensitization of the Tb(III) ion with ligand **2** may be attributed to the $T_1$ level of the ligand being too close to the lanthanide $^5D_4$ resonance level ($\Delta\nu$ = 1063 $cm^{-1}$) resulting in an inefficient energy transfer. The relatively low Eu(III) emission quantum efficiencies of **1Eu** and **2Eu** may be caused by the very large energy difference of the ligand's triplet state and the $^5D_0$ that is also known to result in low emission efficiency due to non-radiative deactivation of the lanthanide emitting state.[16]

To further probe the impact of $BMes_2$ on the lanthanide emission and the possible use of the lanthanide compounds in detecting anions such as fluoride and cyanide, we examined the absorption and luminescence spectral change of complexes **1Tb**, **1Eu** and **2Eu** in response to the addition of $NBu_4F$ (TBAF) and $NBu_4CN$ (TBACN) in THF. The complete titration data can be found in the supporting materials. For **1Tb**, the addition of TBAF or TBACN caused a general decrease of the Tb(III) emission bands and a red shift of the

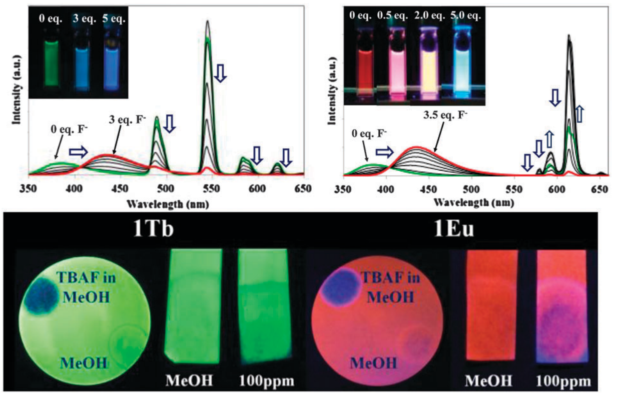

**Fig. 3** Top: Luminescence titration spectra of **1Tb** (left) and **1Eu** (right) ($1.0 \times 10^{-5}$ M in THF) by TBAF at 298 K ($\lambda_{ex}$ = 300 nm), inset: photographs showing the solution color change. Bottom: photographs showing the emission color change of **1Tb** and **1Eu** on filter papers either after the addition of one drop of TBAF (large excess) MeOH solution (left) or the dipping of the papers in MeOH of 100 ppm TBAF (right). Blank MeOH solution was used as a control.

ligand's fluorescence band from ~385 nm to 430 nm, leading to the emission color change from green to blue, as shown in Fig. 3. Because the ligand's fluorescence band change and the absorption spectral change of **1Tb** with the addition of <3.0 eq. anions resemble those of the free ligand **1** and a $Cu_2$ paddlewheel compound containing ligand **1** (see ESI†), the quenching of the Tb(III) emission bands can be attributed to the binding of the anions to the boron atom, that decreases the first excited state energy of the ligand, thus lowering of the triplet energy, leading to the diminished emission intensity of the Tb(III) ion. The decrease of the first excited energy of ligand **1** upon the addition of $F^-$ and $CN^-$ to the boron center is caused by the low energy charge transfer transition of the $BMes_2X$ group ($X = F^-$ or $CN^-$) to the carboxylate, in agreement with the behaviour of the free ligand. A control experiment with **1Tb** being titrated by TBACl shows that the Tb(III) emission did not display any appreciable quenching until more than 10 eq. of TBACl was added (see ESI†) owing to the displacement of ligand **1** from the Tb(III) center, thus further supporting that the color and spectral change of **1Tb** upon the addition of ~3 eq. $F^-$ or $CN^-$ is indeed caused by selective binding of the anion to the B center.

For **1Eu**, the addition of $F^-$ or $CN^-$ causes the luminescence of the solution to undergo multi-stage color change as shown in Fig. 3, a consequence of the combined change of the ligand-based fluorescence band and the Eu(III) emission bands. It is noteworthy that the addition of anions to the **1Eu** causes first a great increase of the Eu(III) emission peaks, and only after the addition of more than 2 eq. of the anion the Eu(III) peaks experience intensity decrease. Furthermore, the ligand's fluorescence band experiences a red shift in the same manner as that observed in **1Tb**. The initial intensity gain with the addition of ~2 eq. anions may thus be attributed to the lowering of the triplet state of the ligand after anion binding to the B atom, making the ligand more effective in Eu(III) emission activation. The subsequent quenching can be attributed to the replacement of carboxylate ligand by the anion. These experiments confirmed that the boryl group has indeed a strong impact on the emission of the lanthanide ions, which may in turn be used for anion sensing/detection by monitoring the lanthanide emission bands.

To test if the lanthanide compounds can be used for practical sensing of $F^-$, we loaded **1Tb** and **1Eu** onto filter papers. Such prepared filter papers have weak response to aqueous solutions of $F^-$. However, they do show distinct response to TBAF in MeOH (**1Tb** and **1Eu** are insoluble in MeOH), changing emission color to blue, as shown by Fig. 3 (see also ESI†), with a visual detection limit of 50–100 ppm. Similarly prepared $Tb(Bz)_3$ or $Eu(Bz)_3$ filter papers did not show any emission color change toward $F^-$. The **1Tb** and **1Eu** filter papers also respond to TBACN, albeit much less distinct color change, compared to TBAF (see ESI†).

In summary, the first examples of triarylboron functionalized Tb(III) and Eu(III) compounds have been achieved. The $BMes_2$ group has been found to be highly effective in activating Tb(III) or Eu(III) emissions and the resulting new lanthanide complexes are promising as luminescent sensors/probes for $CN^-$ and $F^-$.

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