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Journal Name

COMMUNICATION

## Solvent polarity and oxygen sensitivity, rather than viscosity, determine lifetimes of biaryl-sensitised terbium luminescence<sup>†</sup>

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**In a macrocyclic terbium complex incorporating a biaryl sensitiser, the observed variation of emission lifetime is shown to be determined by the solubility of oxygen in the solvent system and the relative energy of the chromophore excited state, rather than any dependence on solvent viscosity.**

Emissive lanthanide complexes whose lifetime and emission profiles vary as a function of their chemical and physical environment continue to be explored in depth.<sup>1-4</sup> During the course of studies directed towards the synthesis of cation-selective luminescent probes, we have come across the unusual spectroscopic behaviour of a biaryl lanthanide complex that exhibits a strong dependence of metal-based emission with variation of solvent and degree of aeration. Such properties are not unusual *per se*,<sup>5,6</sup> but in this case they help to rationalise the properties of related systems that have been promulgated very recently as millisecond viscosity probes.<sup>7,8</sup> Indeed, it is suggested that such probes are best considered as being sensitive primarily to dissolved oxygen in the medium, and are therefore not viscosity probes at all. The solvatochromism of the biaryl complexes of Eu<sup>3+</sup> and Tb<sup>3+</sup> has been examined in six solvents of varying viscosity, under both aerated and degassed conditions. Solvent viscosity is not a function of its degree of aeration.

The biaryl complexes **LnL**<sup>1</sup> were synthesised in a multi-step reaction sequence from the *tert*-butyl ester of DO3A (DO3A = 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid). The synthesis of the intermediate boronate ester, **2**, was achieved using the Miyaura borylation reaction, from **1** and bis(pinacolato)diboron (B<sub>2</sub>pin<sub>2</sub>) in a microwave reactor, adapting a procedure from Dehaen.<sup>9</sup> The boronate formed quickly within 2 h and was isolated in moderate yield, after purification by silica gel column chromatography. A palladium-catalysed Suzuki cross-coupling reaction of **2** and 4-bromo-2-(hydroxymethyl)pyridine afforded the alcohol **3** in a mixture of

dimethoxyethane (DME) and water at 85°C (Scheme 1). Treatment of **3** with PBr<sub>3</sub> in dichloromethane formed the benzylic bromide **4** that was used directly to alkylate the DO3A-*tert*-butyl ester, followed by *tert*-butyl ester hydrolysis using TFA in dichloromethane. Lanthanide complexation to form **LnL**<sup>1</sup> was carried out at pH 5.5 and purification was achieved by reverse phase HPLC.

The absorbance spectrum of **TbL**<sup>1</sup> (Fig. 1) reveals the presence of the aryl-pyridyl chromophore with an absorbance wavelength maximum of 280 nm in aqueous solution, arising from a localised  $\pi$ - $\pi^*$  excited state transition in the chromophore. A weak shoulder to lower energy (around 340 nm in water) is probably associated with an intramolecular charge-transfer (ICT) transition within the aryl-pyridyl unit.

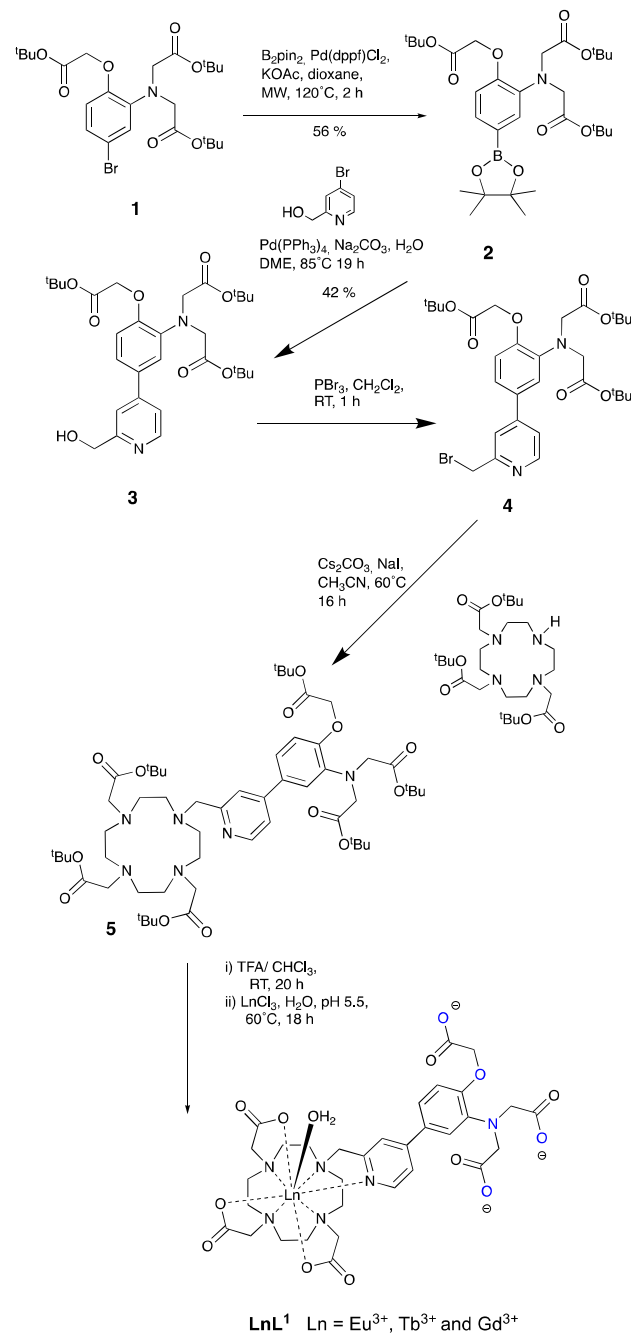
In less polar alcoholic solvents, *i.e.* MeOH, <sup>i</sup>PrOH and <sup>t</sup>BuOH, a bathochromic shift in the main absorbance band was observed. A 5 nm shift of the  $\pi$ - $\pi^*$  wavelength maximum was seen in methanol and a 10 nm red shift in isopropanol, ethanol and *tert*-butanol. The solvatochromic behaviour implies that the ground state is somewhat stabilised by dipolar interactions, and is lowered in energy.<sup>4,11</sup>

Sensitised lanthanide luminescence was observed following excitation into the  $\pi$ - $\pi^*$  band at 280 nm and, in water, also into the ICT transition at around 340 nm (Table 1). Emission from the metal ion in **EuL**<sup>1</sup> was weak ( $\Phi_{em} < 0.03\%$ ), consistent with the presence of competitive charge transfer from the singlet excited state to Eu<sup>3+</sup>. Values of the europium lifetime were insensitive to degassing of the solvent, and the lifetimes measured in H<sub>2</sub>O and D<sub>2</sub>O were consistent with the presence of one coordinated water molecule ( $q = 1$ ). The energy of the ligand triplet excited state was estimated by studying the phosphorescence spectrum of **GdL**<sup>1</sup> at 77 K, in an EtOH glass. The energy of the 0,0 component of the  $^3\pi$ - $\pi^*$  transition was estimated to be 22,250 cm<sup>-1</sup>, which is sufficiently high to permit efficient energy transfer to Tb in **TbL**<sup>1</sup> (ESI Fig S1). A broad ICT excited state was also observed centred around 25,000 cm<sup>-1</sup> but extending beyond 22,000 cm<sup>-1</sup>, suggesting that the system may be prone to thermally activated back-energy transfer from Tb (energy of <sup>5</sup>D<sub>4</sub> = 20500 cm<sup>-1</sup>) to repopulate the

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<sup>†</sup> Electronic Supplementary Information (ESI) available: Synthetic methods, compound characterisation, additional spectra. See DOI: 10.1039/x0xx00000x

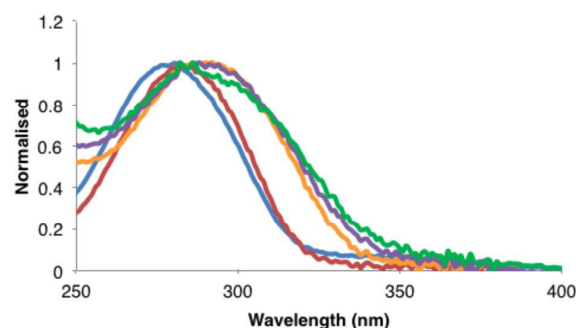
ICT excited state (or indeed even the  $^3\pi-\pi^*$ ). In such cases, terbium luminescence will be sensitive to the presence of dissolved oxygen through its effect in quenching the excited state of the sensitiser. Thus, the terbium excited state can be indirectly quenched by dissolved triplet oxygen, shortening its excited state lifetime.



**Scheme 1** Synthetic route to  $\text{LnL}^1$  complexes.

The terbium complex  $\text{TbL}^1$  displayed much brighter emission and a much longer excited state lifetime in deoxygenated samples, in both  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . A 1.6-fold

increase in the total luminescence emission intensity was observed with a 3.6- and 3.2-fold increase in the excited state lifetime in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  respectively. Such behaviour is characteristic of the reduction of quenching of a triplet-character chromophore excited state by  $^3\text{O}_2$ , and strongly suggests that back energy transfer from the  $^5\text{D}_4$  excited state of  $\text{Tb}^{3+}$  to the triplet excited state of the chromophore occurs at room temperature. This complex therefore, could be considered as an emission and lifetime-based  $\text{pO}_2$  sensor, and should show temperature dependent emission.<sup>11,12</sup>



**Figure 1** Normalised absorbance spectra of  $\text{TbL}^1$  in  $\text{H}_2\text{O}$  (blue); MeOH (red); EtOH (orange);  $i\text{PrOH}$  (purple);  $t\text{BuOH}$  (green) at 298 K.

**Table 1** Photophysical data for  $\text{LnL}^1$  (298 K; lifetimes  $\tau$  are given in milliseconds, estimated uncertainty  $\pm 10\%$ ; air-equilibrated and degassed solutions as indicated; glycerol value under air-equilibrated conditions)

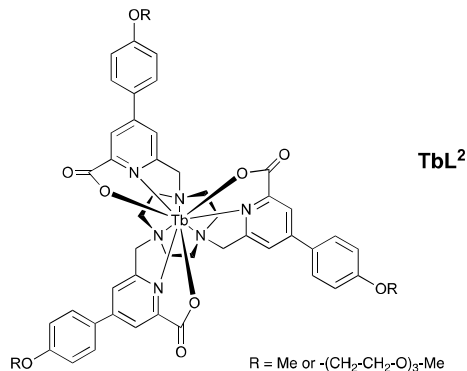
	$[\text{EuL}^1]$	$[\text{TbL}^1]^b$
$\lambda_{\text{abs}} / \text{nm}$ ( $\epsilon / \text{M}^{-1}\text{cm}^{-1}$ ) <sup>a</sup>	280 (6000)	280 (6000)
	345 (250)	345 (200)
$\tau \square \text{H}_2\text{O}$ (air-equil.)	0.50	0.42
$\tau \square \text{H}_2\text{O}$ (degassed)	0.56	1.52
$\tau \square \text{D}_2\text{O}$ (air-equil.)	1.70	0.72
$\tau \square \text{D}_2\text{O}$ (degassed)	1.82	2.30
$\tau \square$ glycerol)	0.77	1.13
$\Phi \square \text{H}_2\text{O}$ (air-equil.)	< 0.03%	3.4%
$\Phi \square \text{H}_2\text{O}$ (degassed)	< 0.03%	5.4%

<sup>a</sup> In  $\text{H}_2\text{O}$ . <sup>b</sup> The hydration number,  $q$ , determined under degassed conditions is  $q = 0.9$ .  $q$  is independent of concentration, indicating no significant intermolecular interactions between chromophore carboxylates and  $\text{Tb}^{3+}$ .

Increasing the viscosity of the solution was found to increase the lifetime of the excited state in both  $\text{EuL}^1$  and  $\text{TbL}^1$ , where a 1.5- and 2.7-fold increase was observed in glycerol compared to water respectively. Differences in behaviour between water and glycerol solutions were recently observed in lanthanide systems by Bui *et al.*, and millisecond-scale viscosity probes containing biaryl chromophores such as  $\text{TbL}^2$  have been postulated.<sup>7,8</sup>

The terbium complexes studied in that work displayed sub-millisecond lifetimes in methanol, with 3.7-fold increase in the excited state lifetime in glycerol (0.24 to 0.89 ms).<sup>8</sup> This behaviour was attributed to the perturbation of carbon-carbon bond rotation of the biaryl unit in more viscous solutions, reducing the energy lost by non-radiative relaxation pathways. Unlike  $\text{EuL}^1$ , however, europium analogues were found to be

insensitive to changes in viscosity. It was suggested that back energy transfer from the  $^5D_4$  state was essential to viscosity sensitivity of **TbL**<sup>2,7,8</sup>. An energy gap of less than about 1800  $\text{cm}^{-1}$  is typically required for back energy transfer to occur, and is therefore much more commonly observed with  $\text{Tb}^{3+}$ , as its emitting  $^5D_4$  state at 20,500  $\text{cm}^{-1}$  is higher in energy than the  $^5D_0$  level of  $\text{Eu}^{3+}$  at 17,200  $\text{cm}^{-1}$ .<sup>4,13</sup>



Measurements of the Tb excited state lifetime for **TbL**<sup>1</sup> were made in degassed solution for a variety of solvents and in every case the lifetime increased dramatically. For example, lifetimes were 0.23 ms in EtOH and 0.43 ms in water and increased to 1.70 and 1.52 ms, respectively, in the absence of dissolved oxygen (Table 2). No well-defined correlation exists between the observed Tb excited state lifetime and the viscosity of the solvent, or the Reichardt solvent polarity parameter (ESI Figs S2 and S3).<sup>14</sup> The slightly longer Tb emission lifetime in glycerol can simply be attributed to the known lower solubility of oxygen in glycerol. Indeed, Schumpe has reported the solubility of oxygen in a range of aqueous alcohol solutions, and found that as the mole fraction of glycerol increased, there was a large and proportionate decrease in oxygen solubility.<sup>15,16</sup>

**Table 2** Excited-state lifetimes for **TbL**<sup>1</sup> in a range of solvents of varying viscosity and polarity (Reichardt's solvent polarity parameter,  $E_T^N$ )<sup>14</sup> at 298 K in air-equilibrated and in degassed solutions ( $\lambda_{\text{ex}} = 280 \text{ nm}$ ,  $\lambda_{\text{em}} = 544 \text{ nm}$ ).<sup>a</sup>

Solvent	Viscosity cP at 298 K	Lifetime / ms		$E_T^N$
		air-equil.	degassed	
H <sub>2</sub> O	0.89	0.43	1.52	1.000
Methanol	0.54	0.59	1.87	0.765
Ethanol	1.02	0.23	1.70	0.655
<i>t</i> -Butanol	4.31	0.85	1.51	0.602
<i>i</i> -Propanol	2.04	0.67	1.33	0.552
Glycerol	934	1.13	<sup>b</sup>	–

<sup>a</sup> The solubilities of oxygen in these solvents, expressed as mole fractions at 298 K and 101.3 kPa, are H<sub>2</sub>O ( $2.29 \times 10^{-5}$ ), MeOH ( $4.15 \times 10^{-4}$ ), EtOH ( $5.71 \times 10^{-4}$ ), <sup>1</sup>PrOH ( $6.76 \times 10^{-4}$ ), <sup>4</sup>BuOH ( $8.34 \times 10^{-4}$ , value for 2-butanol); glycerol ( $4.8$  to  $5.5 \times 10^{-6}$ ).<sup>15,16</sup> <sup>b</sup> No excited-state lifetime measured for deoxygenated glycerol.

Such behaviour is quite different from that reported in the structurally related Tb bi-aryl complex, **TbL**<sup>2</sup>, where solvent viscosity was hypothesised to determine the Tb emission lifetime, as it was thought that aryl-aryl bond rotation might favour non-radiative relaxation, and this motion is sensitive to

viscosity variation. The presence of a back energy transfer process was also mentioned as being essential in **TbL**<sup>2</sup> for the hypothesised sensitivity of terbium emission lifetime to solvent viscosity, though without further proof.<sup>7,8</sup>

In the work with **TbL**<sup>2</sup>, luminescence lifetimes were only measured in MeOH / glycerol mixtures of varying proportions; such solutions display a wide range of viscosities.<sup>7,8</sup> A linear increase in the Tb emission lifetime was reported for MeOH / glycerol solutions of increasing viscosity. Notwithstanding very similar complex structures, Tb excited state lifetimes and ligand triplet energies, such a dependence on solution viscosity is not found here (ESI) for **TbL**<sup>1</sup>, suggesting that the mechanism for quenching of the excited state lifetime is *not* associated with non-radiative vibrational relaxation, via aryl-aryl bond rotation. Solvent viscosity remains unchanged in aerated and deoxygenated environments, so perturbation of the rate of intramolecular aryl-aryl bond rotation cannot simply explain the reduced lifetime.<sup>‡</sup> The variation in lifetime in this earlier work, examining MeOH / glycerol mixtures only, could be reasonably ascribed to decreased oxygen solubility in solution as the mole fraction of glycerol is increased.

Here, varying oxygen solubilities combine with the change in the excited state energy of the chromophore, as the solvent polarity is varied (Figures S2 and S3 in ESI). Indeed, the effect of solvent polarity and viscosity on the energy of chromophore charge-transfer excited states has been the subject of related studies, in systems with pyridyl and alkynyl *p*-chromophores of varying conjugation length.<sup>17</sup> Such behaviour reduces the extent of triplet oxygen quenching of the chromophore excited state, increasing the Tb luminescence lifetime. The solubility of oxygen in glycerol is two orders of magnitude lower than in simple alcohols, and is 4 to 5 times lower in water (Table 2 footnote).

In summary, these studies cast considerable doubt on the utility of **TbL**<sup>2</sup> and related systems as millisecond viscosity probes. It is suggested that the reported sensitivity of Tb emission intensity and lifetime to environment is a combination of the intrinsic sensitivity to oxygen quenching and to the differential solvation of the organic chromophore's ground and excited states. The degree and nature of excited state solvation modulates the energy of the triplet and ICT states and hence changes the energy gap between the chromophore excited state and the Tb  $^5D_4$  excited state.<sup>18</sup> Hence, it affects the rate of back energy transfer and influences the degree of oxygen sensitivity of the observed terbium emission lifetime. Such excited state solvation effects could be addressed in future by time-resolved, triplet absorption spectroscopy.

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## Notes and references

‡ A variable-temperature <sup>1</sup>H NMR study of the protonated biaryl intermediate, **3**, carried out in CD<sub>3</sub>OD from 295 to 183 K, showed no evidence for spectral change associated with the onset of restricted rotation about the aryl-pyridyl bond, suggesting that the barrier to rotation is < 30 kJ mol<sup>-1</sup> and that, at 295 K, the rate of rotation must

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