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1-D Chain and 3-D grid green luminescent terbium(III) coordination polymers: $\{Tb(O_2CPh)_3(CH_3OH)_2(H_2O)\}_n$ and $\{Tb_2(O_2CPh)_6(4,4'\text{-bipy})\}_n$

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Two lanthanide coordination polymers $\{Tb(O_2CPh)_3(CH_3OH)_2(H_2O)\}_n$ **1** and $\{Tb_2(O_2CPh)_6(4,4'\text{-bipy})\}_n$ **2** have been identified and isolated from a methanol solution **A** of $Tb(OAc)_3{\cdot}4H_2O$, benzoic acid and 4,4′-bipyridine in a 1 : 3 : 2 ratio. Their structures have been determined by single-crystal X-ray diffraction analyses, which revealed that **1** has a covalent, 1-D linear chain structure while **2** has a covalent, 3-D grid architecture. When irradiated by UV light, **1** and **2** are brightly green luminescent, facilitated by a ligand (benzoate or 4,4′-bipy) to Tb^{III} inter-system energy transfer process. Solution **A** has been found to be suitable for the formation of transparent films containing terbium(III) ions by spin coating. The polymeric structures of **1** and **2** and their co-existence are believed to be responsible for the good film forming property of solution **A**. The amorphous film produced by using solution **A** and spin coating has a green emission similar to those of **1** and **2**.

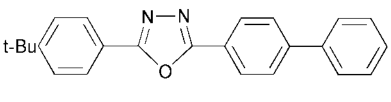
Introduction

As a unique group of elements, lanthanides and their chemistry have fascinated scientists for decades. Coordination compounds of lanthanides have found a variety of applications in materials science including superconductors, magnetic materials, luminescent probes and catalysts.[1] Recently it has been demonstrated that luminescent lanthanide compounds have the potential as emitters in electroluminescent (EL) devices.[2] The potential advantages of lanthanide emitters over fluorescent organic emitters in EL applications are that (a) lanthanide ions have sharp emission bands with colors ranging from blue to red, and (b) EL devices using lanthanide compounds as emitters may have a much higher device efficiency than those using fluorescent organic emitters.[2,3] However, the emission intensity of lanthanide ions is usually very weak, hindering their applications in EL displays. By using appropriate ligands, one can enhance the $f \longrightarrow f$ emission intensity substantially,[4] but the complexes often do not have the volatility required for EL device fabrication by vacuum deposition methods, due to the high coordination number of lanthanides. An alternative way to process lanthanide compounds for EL devices is spin coating. To achieve the desired viscosity and homogeneity for spin coating, lanthanide compounds are often blended with or doped into organic polymers, which limits the performance of the EL device.[2,3] Alternatively, one could achieve the desired spin-coating solution by adding organic ligands that cannot only enhance the emission intensity of lanthanide ions, but also cross-link lanthanide ions so that they can be deposited on the substrate with common organic solvents. The key to the successful choice of the cross-linking organic ligand for spin coating of lanthanide compounds is to have a good understanding of the chemistry, luminescence and structural relationship between the ligand and the lanthanide. 4,4′-Bipyridine (4,4′-bipy) has widely and successfully been used as a bridging ligand in a variety of transition metal coordination oligomers and polymers.[5] In addition, 4,4′-bipy has excitation and emission bands centered at $\lambda = 325$ and 385 nm, respectively, making it a possible activator for lanthanide luminescence. We report herein a novel green-luminescent terbium(III) complex, $\{Tb_2(O_2CPh)_6(4,4'\text{-bipy})\}_n$ **2**, which is a three-dimensional coordination polymer and the related compound $\{Tb(O_2CPh)_3(CH_3OH)_2(H_2O)\}_n$ **1** and their roles in spin coating of terbium(III) thin films.

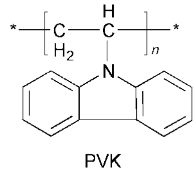
Results and discussion

Structures

We have found that the addition of 4,4′-bipy and benzoic acid to a methanol solution of $Tb(OAc)_3$ in a 2 : 3 : 1 ratio leads to formation of a homogeneous and brightly luminescent solution **A** that, upon heating and concentration, has a sufficient viscosity for spin coating to form an uniform and amorphous film on a polymer substrate (*e.g.* PVK). In the absence of 4,4′-bipy and benzoic acid the luminescence of the methanol solution of $Tb(OAc)_3$ is very weak. To understand the role of 4,4′-bipy and benzoic acid in the film formation and luminescence of solution **A** we investigated possible species from solution **A**. Two coordination polymers, $\{Tb(O_2CPh)_3(CH_3OH)_2(H_2O)\}_n$ **1** and $\{Tb_2(O_2CPh)_6(4,4'\text{-bipy})\}_n$ **2** from solution **A** have been identified. Compound **1** can also be synthesized directly from the reaction of benzoic acid with $Tb(OAc)_3$ hydrate in methanol in a 3 : 1 ratio. The structures of **1** and **2** were determined by single-crystal X-ray diffraction analyses. Selected bond lengths and angles are given in Table 1.



PBD



PVK

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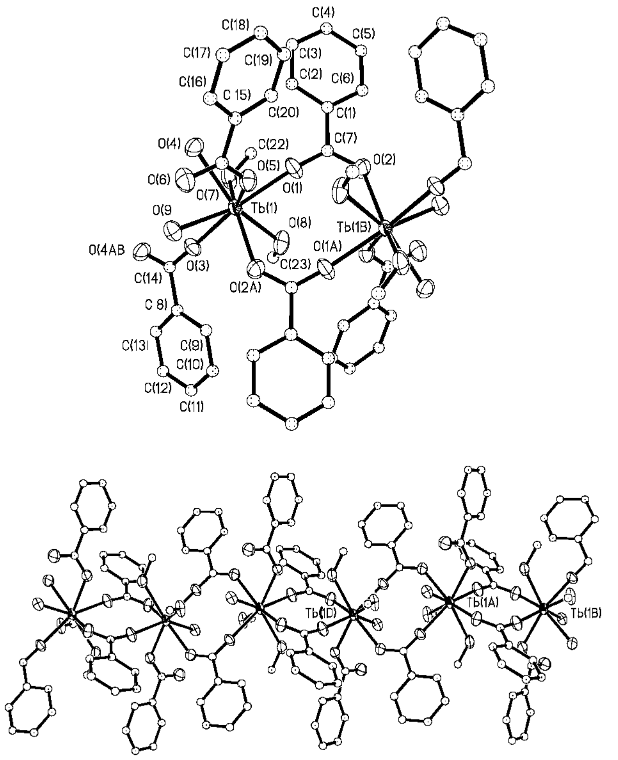

Fig. 1 Top: the dimer unit and the coordination environment around the Tb(1) ion in compound **1** with a labeling scheme. For clarity, all carbon atoms are shown as isotropic spheres. Bottom: the 1-D chain of **1**.

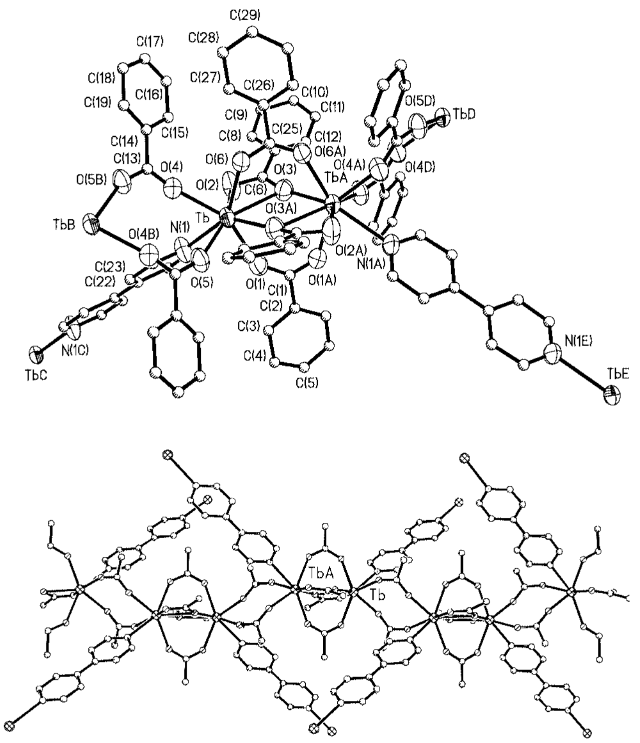

Fig. 2 Top: the Tb(B)–Tb–Tb(A) unit and the coordination environment around the Tb in compound **2** with a labeling scheme. For clarity, all carbon atoms are shown as isotropic spheres. Bottom: the 1-D chain of **2**.

As shown in Fig. 1, the Tb^{III} in compound **1** is coordinated by eight oxygen atoms, two from two methanol ligands, one from a H_2O ligand (O(9)), and five from the benzoates. Two of the benzoate ligands function as bidentate bridging, resulting in the formation of a 1-D covalent chain with the separations between two neighboring Tb^{III} being 4.907(1) and 5.038(1) Å, respectively. The Tb(1D)–Tb(1A)–Tb(1B) angle is 166.0°, thus the structure of **1** can be described as a linear chain. The third benzoate ligand is terminal and forms an intramolecular and an inter-chain hydrogen bond with the coordinated H_2O as indicated by the O(6)···O(9′) distance of 2.604 (intramolecular) and 2.923 Å (inter-chain), leading to a hydrogen-bound 2-D network.

In the asymmetric unit of compound **2** there is one Tb^{III}, one half of 4,4′-bipy, and three benzoate ligands. A crystallographically imposed C_2 axis bisects two benzoate groups (C(26) and C(2) rings) with C(1), C(2), C(5), C(25), C(26) and C(29) lying on the axis. As shown in Fig. 2, the Tb^{III} is coordinated by 7 oxygen atoms of benzoate and one nitrogen atom of 4,4′-bipyridine. The Tb–O bond lengths vary considerably, 2.242(5)–2.635(4) Å, but they are not uncommon for lanthanide compounds.[1,6] All benzoate ligands in **2** function as bridging/chelating ligands to link Tb^{III} together, forming a one dimensional chain. However, unlike compound **1**, where none of the bridging benzoate ligands is chelated to the Tb^{III}, the Tb and Tb(A) ions in **2** are linked by four benzoate ligands, two bridging and two bridging and chelating, resulting in the Tb···Tb(A) distance of 3.9184 (6) Å, much shorter than those of **1**. The Tb and Tb(B) ions, on the other hand, are linked by two bridging benzoate ligands in a similar manner to that found in **1** and with a comparable separation of 5.478(1) Å. With the alternating Tb···Tb′ distances and the 145.1(1)° Tb(B)–Tb–Tb(A) angle, the benzoate linked 1-D array in **2** can best be described as a zigzag chain. Unlike **1**, where the 1-D chains are inter-linked by hydrogen bonds, the 1-D chains in **2** are inter-linked by covalent bonds *via* 4,4′-bipy ligands. The 4,4′-bipy ligands on the 1-D chain are oriented approximately at right angles with respect to each other and are bridged to Tb^{III} in four neighboring chains, leading to the formation of a grid architecture perpendicular to the benzoate 1-D chains, as shown in Fig. 3. Compound **2** is therefore a 3-D coordination polymer. The Tb···Tb separation linked by the 4,4′-bipy ligand is 12.32(1) Å, thus the approximate dimensions of the square channels occupied by the phenyl groups of the benzoate ligands are 12 × 12 Å^2. The 1-D chain of **1** is most likely a precursor of **2**, if we consider that the terminal benzoate in **1** becomes the bridging and chelating benzoate in **2**, thus effectively replacing the H_2O and one of the methanol ligands in **1**, and that the second methanol ligand in **1** is replaced by one of the nitrogen donors of 4,4′-bipy in **2**. 4,4′-bipy linked 1-D ladder and 2-D grid architectures are abundant among transition metal compounds.[5] To our best knowledge, the 3-D

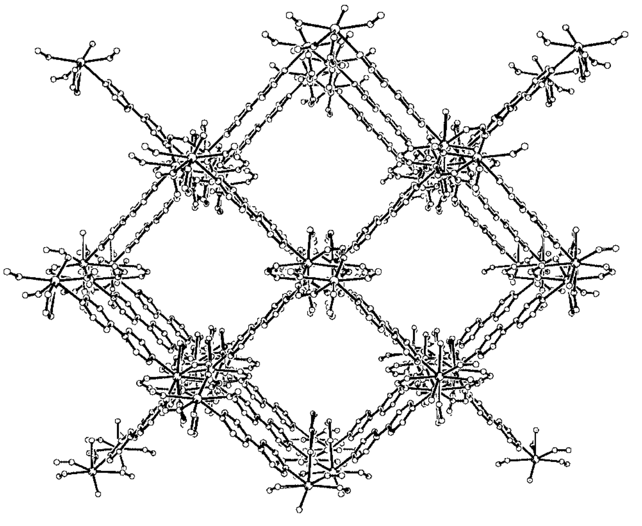

Fig. 3 The grid structure of compound **2** projected down the 1-D chain. For clarity the phenyl groups of the benzoate ligands are omitted.

Table 1 Selected bond lengths [Å] and angles [°]

Compound **1**			
Tb(1)–O(1)	2.276(2)	O(5)–Tb(1)–O(7)	135.69(9)
Tb(1)–O(3)	2.283(2)	O(4)–Tb(1)–O(8)	144.05(9)
Tb(1)–O(2A)	2.322(2)	O(5)–Tb(1)–O(8)	129.66(7)
Tb(1)–O(4)	2.333(2)	O(1)–Tb(1)–O(9)	145.85(10)
Tb(1)–O(5)	2.410(2)	O(7)–Tb(1)–O(9)	123.37(8)
Tb(1)–O(7)	2.436(3)	O(8)–Tb(1)–O(9)	133.59(11)
Tb(1)–O(8)	2.474(3)	O(1)–Tb(1)–O(3)	144.92(9)
Tb(1)–O(9)	2.481(3)	O(1)–Tb(1)–O(2A)	104.30(8)
		O(3)–Tb(1)–O(4)	100.80(8)
		O(2A)–Tb(1)–O(4)	141.33(9)
		O(3)–Tb(1)–O(5)	142.46(8)
		O(2A)–Tb(1)–O(7)	143.42(9)
Compound **2**			
Tb–O(5)	2.242(5)	O(4)–Tb–O(1)	145.66(17)
Tb–O(4)	2.281(5)	O(5)–Tb–O(6)	114.77(18)
Tb–O(1)	2.299(5)	O(1)–Tb–O(6)	137.29(15)
Tb–O(6)	2.336(5)	O(4)–Tb–O(3A)	133.35(18)
Tb–O(3A)	2.354(5)	O(5)–Tb–O(2)	151.67(17)
Tb–O(2)	2.374(5)	O(3A)–Tb–O(2)	127.45(15)
Tb–N(1)	2.621(6)	O(6)–Tb–N(1)	144.9(2)
Tb–O(3)	2.635(4)	O(3A)–Tb–N(1)	142.2(2)
		O(5)–Tb–O(3)	151.38(16)
		O(4)–Tb–O(3)	123.45(17)
		N(1)–Tb–O(3)	115.35(18)
		Tb–O(3)–Tb	103.36(17)

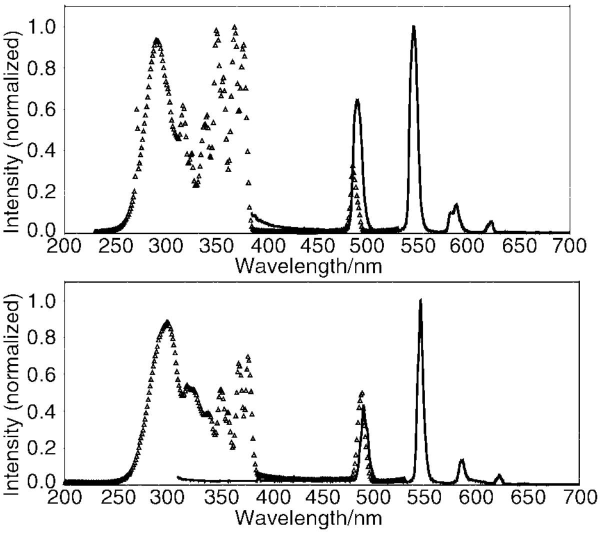

Fig. 4 Excitation (triangles) and emission (solid line) of compounds **1** (top) and **2** (bottom) in the solid state.

grid architecture of **2** based on coordination bonds of 4,4′-bipy is unprecedented. We believe that the polymeric structures of **1** and **2** and their co-existence are most likely to be responsible for the formation of the uniform and amorphous film by solution **A**.

Luminescence

Both compounds **1** and **2** emit a bright green color in solution and the solid state. Their emission spectra are essentially identical as shown in Fig. 4. However, the broad excitation band at $\lambda = 300$ nm of **2** is much more intense than that of **1** due to the contribution of 4,4′-bipy. In fact the brightest emission for **2** was achieved when excited at $\lambda = 300$ nm. In contrast, there is no significant difference in emission intensity for **1** whether the molecule is excited at $\lambda = 300$ or 368 nm. Fig. 4 shows unequivocally that the excitation of the terbium(III) ion in **1** and **2** is by an indirect process, *i.e.* a ligand to metal inter-system energy transfer. Owing to the insoluble nature of **1** and **2**, we have not been able to determine the quantum efficiency of emission from these two compounds (a 100% quantum yield has been reported for anhydrous terbium(III) benzoate[1i]). The two intense emission bands at 490 and 545 nm correspond to $^5D_4 \longrightarrow {}^7F_6$ and $^5D_4 \longrightarrow {}^7F_5$ transitions while the two weak emission bands at 587 and 624 nm are from $^5D_4 \longrightarrow {}^7F_4$ and $^5D_4 \longrightarrow {}^7F_3$ transitions, respectively.[4] No emission bands from the ligands were observed, indicating that the ligands transfer the excitation energy efficiently to the Tb^{III}. Furthermore, the 490 nm emission band was also observed as an excitation band when the emission wavelength was set at 545 nm. In fact, the 545, 587 and 624 nm emission bands can be obtained by direct excitation of compounds **1** and **2** at $\lambda = 490$ nm, but the emission intensity is much lower than those obtained by indirect excitation. Both 4,4′-bipy and benzoate clearly function as activators in the luminescence of **1** and **2**, which explains why $Tb(OAc)_3$ is a very weak emitter while **1** and **2** are bright emitters. The bright green luminescence of solution **A** can, therefore, be attributed to the presence of species such as **1** and **2**. Oligomeric species are also likely present and contribute to the properties of solution **A**, but we have not been able to isolate any of them directly from **A**.

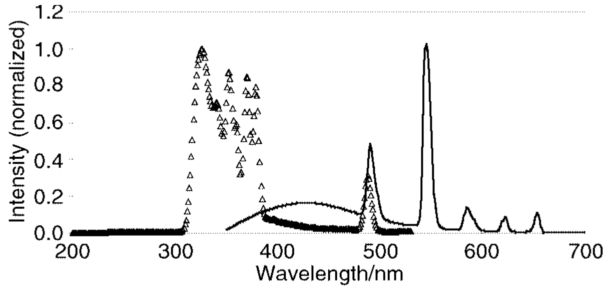

Fig. 5 The excitation and emission spectra of a composite film of PVK(500 Å)/Tb^{III} (300 Å) from solution **A**.

Transparent thin films (300 Å thickness) of Tb^{III} obtained by using solution **A** and spin coating have excitation and emission spectra similar to those of compounds **1** and **2**. We attempted to fabricate electroluminescent devices of Tb^{III} by using solution **A** (in the absence of 4,4′-bipyridine, the solution does not have the viscosity to form homogeneous films by spin coating). Three types of device structures were used. The first type is a single-layer device with the terbium(III) layer (300 Å) sandwiched between cathode (Mg/Ag) and anode (ITO, indium–tin–oxide). The second type is a two-layer device, ITO/PVK/Tb^{III}/(Mg/Ag), where PVK (500 Å) was deposited by spin coating on to the ITO substrate and used as the hole transport layer. The third type is a three-layer device, ITO/PVK/Tb^{III}/PBD/(Mg/Ag), where PVK (500 Å) and PBD (300 Å, vacuum deposited) were used as the hole transport and electron transport layers, respectively. The photoluminescent spectra of the single-, the double- and the triple-layer films are all dominated by the emission peaks of Tb^{III} (the emission band at 655 nm is from the $^5D_4 \longrightarrow {}^7F_2$ transition). The double- and triple-layer films have a weak broad emission band ranging from 400 to 500 nm, attributable to the PVK film (Fig. 5). Unfortunately, electroluminescence of Tb^{III} was not observed in all devices. The most likely cause for the failure of the EL devices is the mismatch of energy levels between the different layers. Efforts to replace PVK and PBD by other hole transport and electron transport materials in the above EL devices are being undertaken.

In summary, a novel 3-D terbium(III) coordination polymer **2** with a grid architecture has been identified, which is structurally related to the 1-D coordination polymer **1**. Both **1** and **2** are likely responsible for the thin-film formation of Tb^{III} on using solution **A** and spin coating. The bright green emission and readily attainable uniform films by the 4,4′-bipy and terbium(III) benzoate system make it a promising candidate for green electroluminescent devices but further research is required to fabricate a working EL device.

Experimental

All starting materials were purchased from Aldrich Chemical Co. Reagent-grade solvents were used without further purification. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada. Melting points were measured on a Fisher–Johns melting point apparatus. Excitation and emission spectra were recorded on a Photon Technologies International QuantaMaster Model C-60 spectrometer. The thickness of spin-coated films was measured by a Talystep instrument manufactured by Taylor-Hobson.

Synthesis

Compound 1. Benzoic acid (0.0909 g, 0.735 mmol) and $Tb(OAc)_3 \cdot 4H_2O$ (0.100 g, 0.245 mmol) were dissolved and mixed well in 10 mL of methanol. The solution was allowed slowly to evaporate at ambient temperature under air, yielding colorless needle crystals of compound **1** in 76% yield. Calc. for $C_{23}H_{25}O_9Tb$: C 45.71, H 4.17. Found: C 45.35, H 4.01%.

Compound 2. Terbium(III) acetate tetrahydrate (0.102 g, 0.25 mmol) and benzoic acid (0.092 g, 0.75 mmol) were dissolved in 10 mL of methanol. 4,4′-Bipyridine (0.078 g, 0.50 mmol) was dissolved in 10 mL of benzene. The reactants were combined using a solvent layering method in a 40 mL vial, with the benzene/4,4′-bipy solution at the bottom, followed by 10 mL of benzene, 10 mL of methanol, and finally the methanol solution of $Tb(OAc)_3 \cdot 4H_2O$ and benzoic acid. The solution was allowed to evaporate slowly at ambient temperature, affording colorless crystals of compound **2**. Crystals of **1** were also obtained. Satisfactory elemental analysis could not be achieved for **2** due to the co-existence of **1** in the sample.

Device fabrication

ITO was deposited on to a glass substrate by vacuum deposition. PVK (500 mg) was dissolved in 9 : 1 THF–toluene solution (25 mL) to produce a 20 g L^{-1} solution. A thin film (500 Å) of PVK was spin coated on the ITO patterned glass substrate by placement of 1 mL of solution to cover the substrate, then spinning at 1000 rpm for 30 seconds. $Tb(OAc)_3 \cdot 4H_2O$ (0.204 g, 0.50 mmol), benzoic acid (0.184 g, 1.50 mmol) and 4,4′-bipy (0.156 g, 1.00 mmol) were dissolved and mixed well in 9 : 1 methanol–toluene (20 mL). This solution was concentrated by heating on a hot plate to about 10 mL, resulting in homogeneous and clear solution **A**. A thin film (300 Å) using solution **A** was obtained by spin coating onto either patterned ITO glass or a thin layer of PVK. The PBD layer (300 Å) and the Mg/Ag cathode layer were deposited onto the terbium(III) layer by vacuum deposition.

X-Ray crystallographic analysis

All crystals were obtained from a concentrated methanol solution and mounted on glass fibers. The data for compounds **1** and **2** were collected on a Siemens Smart CCD 1000 X-ray diffractometer with graphite-monochromated Mo-Kα radiation. No significant decay was observed during the data collection. The structural solution and refinement were performed on a PC using Bruker AXS Window NT SHELXTL software package (Version 5.10). Empirical absorption corrections were applied to all crystals. Neutral atom scattering factors were taken from Cromer and Waber.[7] The crystallographic data are given in Table 2.

CCDC reference number 186/2271.

See http://www.rsc.org/suppdata/dt/b0/b007866m/ for crystallographic files in .cif format.

Table 2 Crystallographic data for compounds **1** and **2**

	1	**2**
Formula	$C_{23}H_{25}O_9Tb$	$C_{26}H_{19}NO_6Tb$
M	604.35	600.45
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a/Å	8.8547(16)	16.2103(14)
b/Å	9.8709(16)	17.7707(16)
c/Å	14.718(3)	17.6211(13)
α/°	92.620(3)	
β/°	95.352(3)	108.247(2)
γ/°	113.621(3)	
V/Å^3	1168.6(4)	4820.8(7)
Z	2	8
T/°C	23	23
μ/cm^{-1}	30.76	29.75
Reflections measured	8470	12319
Reflections used	5395	3485
Parameters	314	310
Final $R1$, $wR2$ ($I > 2\sigma(I)$)	0.0275, 0.0482	0.0356, 0.0708

Acknowledgements

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