

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

A highly luminescent and highly oxygen-sensitive Tb(III) complex with a tris-aryloxyde functionalised 1,4,7-triazacyclononane ligand†

Cite this: DOI:
10.1039/x0xx00000x

H. Nakai,^{*ab} T. Goto,^a K. Kitagawa,^{ac} K. Nonaka,^{ac} T. Matsumoto^{abc} and S. Ogo^{*abc}

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

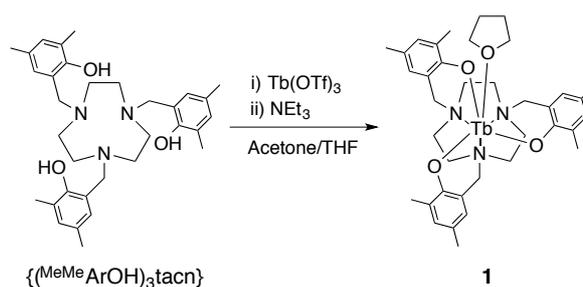
This paper presents a new terbium(III) complex that shows the highest luminescence quantum yield in the oxygen-sensitive lanthanide complexes ($\Phi = 0.91$ under N_2 , $\Phi = 0.054$ under Air).

Luminescent lanthanide complexes have attracted considerable interest because of their potential applications to probes for sensing in biological and environmental systems.¹ To date, various ligands as sensitizers for lanthanide f–f emission have been developed to obtain the lanthanide complexes which are stable, luminescent and/or responsive to stimulations (H^+ , temperature, O_2 , etc.). However, it is still difficult to design the ligands for the lanthanide complexes with desired functions: for instance, the lanthanide complexes with high luminescence quantum yield ($\Phi = \text{photons emitted/photons absorbed} > 0.9$) are still extremely rare despite the Φ is one of the important parameters for optical sensing applications.²

Macrocyclic polyamines such as 1,4,8,11-terazacyclotetradecane (cyclam), 1,4,7,10-terazacyclododecane (cyclen) and 1,4,7-triazacyclononane (tacn) are widely employed as useful frameworks to construct functional chelating ligands in coordination chemistry.³ In this context, tacn-based tris-aryloxyde ligands ($\{(RR'ArO)_3tacn\}^{3-}$ (R, R' = Me (methyl), tBu (*tert*-butyl), Ad (adamantyl), etc.)) allow easy derivatisation of the *ortho* (R) and *para* (R') positions of the phenolate ring and have been successfully utilised in f-element chemistry.⁴ Although the ligands of this class would have a potential as tunable sensitizers suitable for the lanthanide f–f emission, their luminescent lanthanide complexes have not been reported so far.

We have now found that the tacn-based tris-aryloxyde ligand, $\{(MeMeArO)_3tacn\}^{3-}$, efficiently sensitises f–f emission of Tb^{3+} ion ($\Phi = 0.91$ under N_2 in THF) and unexpectedly found that the emission is highly oxygen-sensitive ($\Phi = 0.054$ under Air). To the best of our knowledge, the terbium(III) complex with

$\{(MeMeArO)_3tacn\}^{3-}$, [$\{(MeMeArO)_3tacn\}Tb^{III}(THF)$] (**1**, Scheme 1), shows the highest luminescence quantum yield in the oxygen-sensitive lanthanide complexes.⁵ Herein, we report the synthesis, structure and oxygen-sensitive luminescence properties of **1**.



Scheme 1 Preparation of the highly luminescent and highly oxygen-sensitive terbium(III) complex **1** with the tris-aryloxyde functionalised 1,4,7-triazacyclononane ligand.

Reaction of 1,4,7-tris(3,5-dimethyl-2-hydroxybenzyl)-1,4,7-triazacyclononane $\{(MeMeArOH)_3tacn\}$ ⁶ with $Tb(OTf)_3$ in Acetone/THF (100/1) in the presence of NEt_3 at room temperature led to the formation of the terbium(III) complex **1** as a white powder (77%, Scheme 1, see ESI†). Colorless crystals suitable for X-ray diffraction analysis were grown from a saturated AcOEt/THF (9/1) solution of **1** at room temperature. The solid-state molecular structure of **1** is depicted in Fig. 1, along with selected interatomic data (Table S1, ESI†). The trivalent terbium ion in **1** is coordinated by the three nitrogen and four oxygen atoms. The coordination polyhedron of the seven-coordinate Tb^{3+} ion can be described as monocapped octahedron, in which the oxygen atom of THF caps the triangular face formed by the oxygen atoms of the $\{(MeMeArO)_3tacn\}^{3-}$ ligand (O1, O2 and O3).⁷ The observed

geometry of **1** is similar to those of the previously reported seven-coordinate lanthanide and uranium complexes with tacn-based N_3O_3 -hexadentate ligands.^{4b,8}

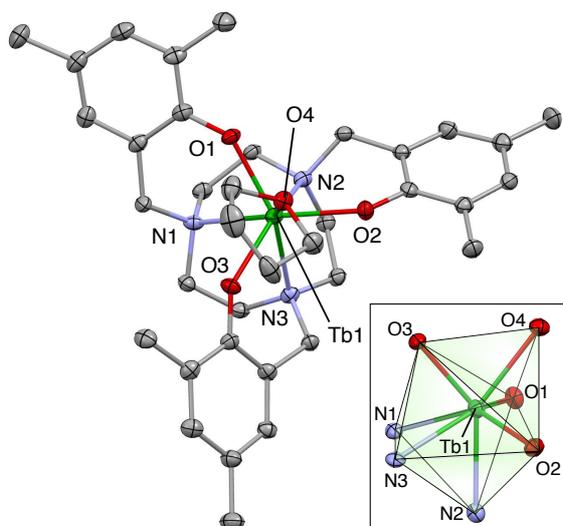


Fig. 1 An ORTEP drawing of terbium(III) complex **1** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Tb1–N1 = 2.557(4), Tb1–N2 = 2.527(5), Tb1–N3 = 2.535(5), Tb1–O1 = 2.189(3), Tb1–O2 = 2.193(3), Tb1–O3 = 2.186(3), Tb1–O4 = 2.458(4), O1–Tb1–O4 = 79.98(13), O2–Tb1–O4 = 80.90(14), O3–Tb1–O4 = 75.87(13). Inset: the coordination polyhedron of Tb^{3+} ion in **1**.

The UV-vis absorption spectrum of **1** in THF at room temperature is shown in Fig. 2, black. The absorption band at 302 nm ($\epsilon = 15 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) is contributed to the $\pi \rightarrow \pi^*$ transition of the phenolato moieties ($^{\text{MeMe}}\text{ArO}^-$) and is slightly red-shifted relative to that of $\{(\text{MeMeArOH})_3\text{tacn}\}$ (287 nm, $\epsilon = 7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, Fig. S1, ESI†).⁹

The luminescence spectrum ($\lambda_{\text{ex}} = 300 \text{ nm}$) of **1** under N_2 in THF at room temperature is shown in Fig. 2, red. As expected, **1** shows the f–f emission of the Tb^{3+} ion. The seven bands at 490, 547, 588, 622, 653, 673 and 679 nm are assigned to the $^5D_4 \rightarrow ^7F_J$ transitions ($J = 6, 5, 4, 3, 2, 1$ and 0, respectively).^{1c,1d} The absence of broad luminescence arising from the $\{(\text{MeMeArO})_3\text{tacn}\}^{3-}$ indicates that the ligand-centred excited state was almost completely quenched by the Tb^{3+} ion. Furthermore, the excitation spectrum monitored at 547 nm ($^5D_4 \rightarrow ^7F_5$ transition) was identical to the absorption spectrum of **1** (Fig. S2, ESI†). These findings support that an efficient intramolecular energy transfer occurs from the phenolato moieties ($^{\text{MeMe}}\text{ArO}^-$) to the Tb^{3+} ion.

The luminescence quantum yield (Φ) of **1** was determined to be 0.91 under N_2 in THF at room temperature using quinine bisulfate in 0.5 M H_2SO_4 ($\Phi = 0.60$) as a reference.^{5,10} The emission lifetime (τ) of **1** was determined to be 840 μs under N_2 in THF (Fig. S3, ESI†): the radiative rate constant ($k_r = \Phi/\tau$) of **1** is calculated to be $1.08 \times 10^3 \text{ s}^{-1}$, which is relatively high among the highly luminescent lanthanide complexes.¹¹ Since the asymmetric environment of lanthanide(III) ions is known to

promote f–f radiative transition and thereby provide high quantum yield,¹² the seven-coordinate environment of Tb^{3+} ion in **1** (*vide supra*, Fig. 1) would dominantly contribute to the high quantum yield of **1**.¹³

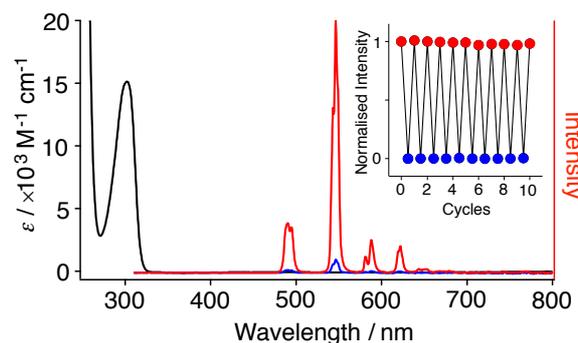


Fig. 2 UV-vis absorption (black) and corrected luminescence spectra (under N_2 (red) and Air (blue), $\lambda_{\text{ex}} = 300 \text{ nm}$) of **1** in THF at room temperature. Inset: reversible responses of the luminescence intensity of **1** ($2.0 \times 10^{-6} \text{ M}$) to alternating Air and N_2 exposures. The luminescence was monitored at 547 nm.

Unexpectedly, the luminescence of **1** is highly oxygen-sensitive ($\Phi = 0.054$ and $\tau = 40 \mu\text{s}$ under Air, Fig. 2, blue). The luminescence intensities of **1** reversibly respond to alternating changes of oxygen concentration (under Air (21%) and N_2 (0%)) (Fig. 2, inset). This indicates that **1** has reversible oxygen quenching and nitrogen recovering properties without any degradation at least ten cycles.

The oxygen-sensing properties of **1** were further characterised by the Stern–Volmer quenching constant (K_{sv}) obtained from the following equation: $I_0/I = 1 + K_{\text{sv}}[\text{O}_2]$ (I_0 and I are the luminescence intensities at 0.00 M of O_2 concentration (under N_2) and at the indicated O_2 concentrations, respectively; $[\text{O}_2]$ is oxygen concentration). The Stern–Volmer plot (I_0/I vs. $[\text{O}_2]$) of **1** exhibits good linearity ($R^2 = 0.9989$) in the O_2 concentration range of 0.00 M (under N_2) to $1.01 \times 10^{-2} \text{ M}$ (under O_2) in THF (Fig. 3). The K_{sv} of **1** (8300 M^{-1}) is comparable to that of the ruthenium(II) polypyridyl complex (10352 M^{-1}) which is the most frequently studied class of oxygen-sensitive transition-metal complexes.^{14,15} Thus, the terbium(III) complex **1** has attractive features for oxygen sensing applications.

It is noteworthy that the lowest triplet energy of the phenolato moieties ($^{\text{MeMe}}\text{ArO}^-$) in **1** is 26460 cm^{-1} , which is estimated from the phosphorescence spectrum of the corresponding gadolinium(III) complex, $\{(\text{MeMeArO})_3\text{tacn}\} \text{Gd}^{\text{III}}(\text{THF})$, in 2-MeTHF at 77 K (Fig. S4, ESI†).^{11,16} Thus, the energy gap (ΔE) between the lowest ligand-centred ($^{\text{MeMe}}\text{ArO}^-$) and metal-centred (Tb^{3+} , 5D_4 : 20490 cm^{-1} , which is estimated from the luminescence spectrum of **1** in 2-MeTHF at 77 K (Fig. S5, ESI†)) levels in **1** is found to be 5970 cm^{-1} . This value is much higher than those found in the previously reported oxygen-sensitive terbium(III) complexes ($< 3500 \text{ cm}^{-1}$): the oxygen-responsive mechanism of **1** can not be explained by the well-known mechanism that involves the thermally activated back-energy transfer.^{5,17} This intriguingly suggests that the

lowest triplet excited state of $^{\text{MeMe}}\text{ArO}^-$ in **1** should have long lifetime intrinsically. Further studies to elucidate the oxygen-responsive mechanism of **1** are now in progress.

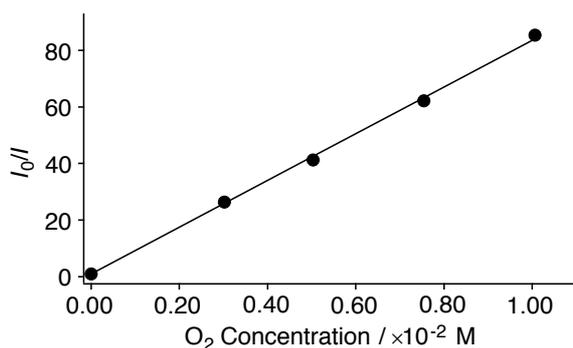


Fig. 3 Stern-Volmer plot of the luminescence intensity (I_0/I) against the oxygen concentration $[\text{O}_2]$ for **1** (4.1×10^{-6} M). The I_0 and I are the luminescence intensities at 0.00 M of O_2 concentration (under N_2) and at the indicated O_2 concentrations, respectively.

In conclusion, we have demonstrated that tacn-based tris-aryloxy is useful ligand to construct the oxygen-sensitive luminescent terbium(III) complex. The essential properties for optical sensing applications are high luminescence and high sensitivity. Our findings offer attractive new insight into the development of not only highly luminescent lanthanide complexes but also highly oxygen-sensitive materials.

This work was supported by grants-in aid: 26000008 (Specially Promoted Research), 26410074, 26810038 and 24109016 (Scientific Research on Innovative Areas "Stimuli-responsive Chemical Species") and the World Premier International Research Centre Initiative (WPI Program) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) (Japan).

Notes and references

^a Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan.

E-mail: nakai@mail.cstm.kyushu-u.ac.jp; Fax: +81-92-802-2823; Tel: +81-92-802-2822

^b Centre for Small Molecule Energy, Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan

^c International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan

† Electronic Supplementary Information (ESI) available: Experimental details, Table S1 and Fig. S1–S4. CCDC 1026622 (**1**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x

- (a) M. C. Heffern, L. M. Matosziuk and T. J. Meade, *Chem. Rev.*, 2014, **114**, 4496; (b) J. Lehr, P. D. Beer, S. Faulkner and J. J. Davis, *Chem. Commun.*, 2014, **50**, 5678; (c) L. Armelao, S. Quici, F. Barigelletti, G. Accorsi, G. Bottaro, M. Cavazzini and E. Tondello, *Coord. Chem. Rev.*, 2010, **254**, 487; (d) S. V. Eliseeva and J.-C. G. Bünzli, *Chem. Soc. Rev.*, 2010, **39**, 189; (e) D. Parker, *Coord. Chem. Rev.*, 2000, **205**, 109.
- (a) S. D. Pietro, D. Imbert and M. Mazzanti, *Chem. Commun.*, 2014, **50**, 10323; (b) M. Hasegawa, H. Ohtsu, D. Kodama, T. Kasai, S.

- Sakurai, A. Ishii and K. Suzuki, *New J. Chem.*, 2014, **38**, 1225; (c) M. Starck, P. Kadjane, E. Bois, B. Darbouret, A. Incamps, R. Ziessel and L. J. Charbonnière, *Chem. Eur. J.*, 2011, **17**, 9164; (d) T. Fiedler, M. Hilder, P. C. Junk, U. H. Kynast, M. M. Lezhnina and M. Warzala, *Eur. J. Inorg. Chem.*, 2007, 291; (e) E. Brunet, O. Juanes, R. Sedano and J.-C. Rodríguez-Ubis, *Photochem. Photobiol. Sci.*, 2002, **1**, 613.
- (a) S. Shinoda, *Chem. Soc. Rev.*, 2013, **42**, 1825; (b) R. E. Mewis, S. J. Archibald, *Coord. Chem. Rev.*, 2010, **254**, 1686.
- (a) A.-C. Schmidt, F. W. Heinemann, W. W. Lukens, Jr. and K. Meyer, *J. Am. Chem. Soc.*, 2014, **136**, 11980; (b) P. Benndorf, S. Schmitt, R. Köppe, P. Oña-Burgos, A. Scheurer, K. Meyer and P. W. Roesky, *Angew. Chem. Int. Ed.*, 2012, **51**, 5006; (c) O. P. Lam and K. Meyer, *Polyhedron*, 2012, **32**, 1; (d) I. Castro-Rodríguez and K. Meyer, *Chem. Commun.*, 2006, 1353.
- The quantum yield of **1** (0.91) is considerably higher than those found in the previously reported oxygen-sensitive lanthanide complexes (< 0.55). Selected examples: (a) S. Quici, M. Cavazzini, G. Marzanni, G. Accorsi, N. Armaroli, B. Ventura and F. Barigelletti, *Inorg. Chem.*, 2005, **44**, 529; (b) S. Quici, G. Marzanni, M. Cavazzini, P. L. Anelli, M. Botta, E. Gianolio, G. Accorsi, N. Armaroli and F. Barigelletti, *Inorg. Chem.*, 2002, **41**, 2777.
- D. A. Moore, P. E. Fanwick and M. J. Welch, *Inorg. Chem.*, 1989, **28**, 1504.
- A systematic analysis of the coordination geometry of the Tb^{3+} in **1** was performed using the SHAPE program for the stereochemical analysis of molecular fragments by means of continuous shape measures (CSM). The monocapped octahedron geometry is suggested by the low CSM value: 0.907 and 2.276 for the monocapped octahedron and monocapped trigonal prism, respectively (Table S2, ESI†). *SHAPE, version 2.1*, M. Llunell, D. Casanova, J. Cirera, P. Alemany and S. Alvarez, Barcelona, 2013.
- (a) H. Nakai, K. Kitagawa, H. Nakamori, T. Tokunaga, T. Matsumoto, K. Nozaki and S. Ogo, *Angew. Chem. Int. Ed.*, 2013, **52**, 8722; (b) I. Castro-Rodríguez, K. Olsen, P. Gantzel and K. Meyer, *J. Am. Chem. Soc.*, 2003, **125**, 4565.
- M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, *Handbook of Photochemistry, 3rd Ed.*, CRC Press, 2006.
- K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H. Ishida, Y. Shiina, S. Oishi and S. Tobita, *Phys. Chem. Chem. Phys.*, 2009, **11**, 9850.
- T. Yatabe, H. Nakai, K. Nozaki, T. Yamamura and K. Isobe, *Organometallics*, 2010, **29**, 2390.
- (a) Y. Hasegawa, Y. Wada and S. Yanagida, *J. Photochem. Photobiol., C*, 2004, **5**, 183; (b) Y. Hasegawa, M. Yamamuro, Y. Wada, N. Kanehisa, Y. Kai and S. Yanagida, *J. Phys. Chem. A*, 2003, **107**, 1697.
- The positive-ion electrospray ionisation mass spectrum of **1** shows a signal at m/z 760.3 (relative intensity (I) = 100% in the range m/z 200–2000), which has a characteristic isotopic distribution that matches well the calculated isotopic distribution for $[\text{1} + \text{H}]^+$ (Fig S6, ESI†). Thus, even in solution, the Tb^{3+} ion in **1** retains the seven-coordinate structure found in the crystalline state.
- H. Komatsu, K. Yoshihara, H. Yamada, Y. Kimura, A. Son, S. Nishimoto and K. Tanabe, *Chem. Eur. J.*, 2013, **19**, 1971.
- The detection limit for oxygen concentration is calculated to be 3.6×10^{-7} M ($= 0.003/K_{sv}$): X. Wang and O. S. Wolfbeis, *Chem. Soc. Rev.*, 2014, **43**, 3666.
- (a) D. Parker and J. A. G. Williams, *Chem. Commun.*, 1998, 245; (b) L. Prodi, M. Maestri, R. Ziessel and V. Balzani, *Inorg. Chem.*, 1991, **30**, 3798.
- Selected publications: (a) Z. Dou, J. Yu, Y. Cui, Y. Yang, Z. Wang, D. Yang and G. Qian, *J. Am. Chem. Soc.*, 2014, **136**, 5527; (b) Y. Amao, Y. Ishikawa, I. Okura and T. Miyashita, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 2445; (c) A. Beeby, D. Parker and J. A. G. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1565; (d) F. J. Steemers, W. Verboom, D. N. Reinhoudt, E. B. van der Tol and J. W. Verhoeven, *J. Am. Chem. Soc.*, 1995, **117**, 9408.