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COMMUNICATION

A macrocyclic tetraamine bearing four phenol groups: a new class of heptadentate ligands to provide an oxygen-sensitive luminescent Tb(III) complex with an extendable phenol pendant arm†

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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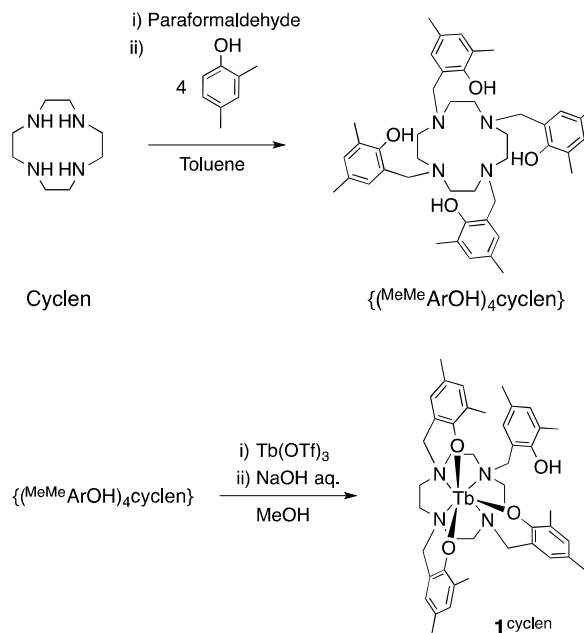
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This paper presents a 1,4,7,10-tetraazacyclododecane-based tetrakis-phenol as a protonated ligand precursor and its oxygen-sensitive luminescent terbium(III) complex with an extendable phenol pendant arm ($\Phi = 0.91$ under N_2 , $\Phi = 0.031$ under air), in which the potentially N_4O_4 -octadentate ligand unprecedentedly coordinates to the Tb^{3+} ion with N_4O_3 -heptadentate fashion.

Macrocyclic polyamines such as 1,4,8,11-tetraazacyclotetradecane (cyclam), 1,4,7,10-tetraazacyclododecane (cyclen) and 1,4,7-triazacyclononane (tacn) are fascinating frameworks to construct functional chelating ligands in coordination chemistry.^{1–8} Especially, the ligands of these classes have been successfully utilised in luminescent lanthanide chemistry.² In this context, we have recently reported that a tacn-based tris-aryloxide, $\{(^{MeMe}ArO)_3tacn\}^{3-} = \{(CH_2(CH_3)_2C_6H_2O)_3C_6H_{12}N_3\}^{3-}$, is useful ligand to construct the highly luminescent terbium(III) complex, $[\{(^{MeMe}ArO)_3tacn\}Tb^{III}(THF)]$ ($\mathbf{1}^{tacn}$, $\Phi = 0.91$ under N_2), with high oxygen-sensitivity ($\Phi = 0.054$ under air).³ This complex not only represents a rare example of the oxygen-sensitive lanthanide complexes but also shows the highest luminescence quantum yield among the oxygen sensitive lanthanide complexes. We presume that the aryloxide moieties ($^{MeMe}ArO^-$) in $\mathbf{1}^{tacn}$ play a key role in the oxygen-sensitive luminescence properties.

In our efforts to extend this intriguing terbium(III) chemistry, we have newly designed and prepared a cyclen-based tetrakis-phenol, $\{(^{MeMe}ArOH)_4cyclen\}$, as a protonated ligand precursor (Scheme 1). Surprisingly, the potentially N_4O_4 -octadentate ligand coordinates to the Tb^{3+} ion with N_4O_3 -heptadentate fashion and provides an oxygen-sensitive luminescent terbium(III) complex with an extendable phenol pendant arm ($^{MeMe}ArOH$), $[\{(^{MeMe}ArOH)(^{MeMe}ArO)_3cyclen\}Tb^{III}]$ ($\mathbf{1}^{cyclen}$). Recently,

numerous efforts have been devoted to synthesise luminescent lanthanide complexes with the functional and/or extendable pendant arm to further applications: the dominant class of complexes is 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid (DO3A)-based lanthanide complexes.⁴ However, almost all methodologies involve multi-step and/or troublesome synthesis to introduce the pendant arm.^{4,5} Herein, we report the syntheses, structures and properties of the readily preparable protonated ligand $\{(^{MeMe}ArOH)_4cyclen\}$ and its extendable oxygen-sensitive luminescent terbium(III) complex $\mathbf{1}^{cyclen}$.



Scheme 1 Preparation of the cyclen-based tetrakis phenol $\{(\text{MeMeArOH})_4\text{cyclen}\}$ and the terbium(III) complex with the extendable phenol pendant arm $\{(\text{MeMeArOH})(\text{MeMeArO})_3\text{cyclen}\}\text{Tb}^{\text{III}}$ ($\mathbf{1}^{\text{cyclen}}$).

The new cyclen-based tetrakis phenol, $\{(\text{MeMeArOH})_4\text{cyclen}\} = 1,4,7,10\text{-tetrakis}(3,5\text{-dimethyl-2-hydroxybenzyl})\text{-}1,4,7,10\text{-tetraazacyclododecane}$, was synthesised through a Mannich reaction of cyclen with 2,4-dimethylphenol and was isolated in 64% yield (Scheme 1, see ESI†). Colorless crystals suitable for X-ray diffraction analysis were obtained from a saturated AcOEt/EtOH (3/1) solution of $\{(\text{MeMeArOH})_4\text{cyclen}\}$ at room temperature. The solid-state molecular structure of $\{(\text{MeMeArOH})_4\text{cyclen}\}$ is depicted in Fig. 1, along with selected interatomic data (Table S1, ESI†). As is observed in the tacn-based analogue $\{(\text{MeMeArOH})_3\text{tacn}\}$,⁶ the $\{(\text{MeMeArOH})_4\text{cyclen}\}$ exhibits intramolecular hydrogen bonding between the phenolic protons and the amine nitrogens ($\text{N1-H1} = 1.916 \text{ \AA}$).

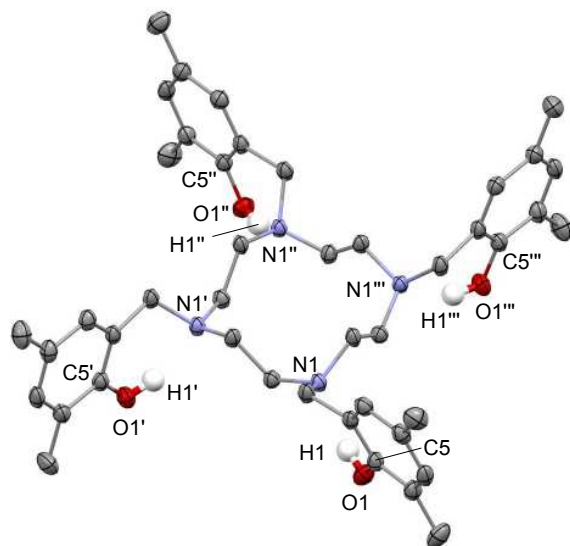


Fig. 1 An ORTEP drawing of the cyclen-based tetrakis phenol $\{(\text{MeMeArOH})_4\text{cyclen}\}$ with 50% probability ellipsoids. Hydrogen atoms, except O-H, and co-crystallised solvents are omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: $\text{C5-O1} = 1.369(5)$, $\text{C5-O1-H1} = 109.475$.

Reaction of $\{(\text{MeMeArOH})_4\text{cyclen}\}$ with $\text{Tb}(\text{OTf})_3$ in MeOH in the presence of NaOH at room temperature led to the formation of the terbium(III) complex $\mathbf{1}^{\text{cyclen}}$ as a white powder (65%, Scheme 1, see ESI†). Colorless crystals suitable for X-ray diffraction analysis were obtained from a saturated MeOH solution of $\mathbf{1}^{\text{cyclen}}$ at room temperature. The solid-state molecular structure of $\mathbf{1}^{\text{cyclen}}$ is depicted in Fig. 2, along with selected interatomic data (Table S1, ESI†). The trivalent terbium ion in $\mathbf{1}^{\text{cyclen}}$ is coordinated by the four nitrogen and three oxygen atoms. The coordination polyhedron of the seven-coordinate Tb^{3+} ion can be described as monocapped trigonal prism, in which one of the oxygen atoms (O3) caps the square face formed by the two oxygen atoms (O1 and O2) and the two nitrogen atoms (N3 and N4).⁹ Thus, the potentially N_4O_4 -

octadentate ligand unprecedentedly coordinates to the Tb^{3+} ion with N_4O_3 -heptadentate fashion and provides the terbium(III)-encapsulating complex with the extendable phenol pendant arm.⁷ This is in contrast to the tacn-based analogue $\mathbf{1}^{\text{tacn}}$,³ in which the $\{(\text{MeMeArO})_3\text{tacn}\}^{3-}$ ligand coordinates to the Tb^{3+} ion with N_3O_3 -hexadentate fashion and provides the seven-coordinate (N_3O_4) complex with one THF molecule: the coordination chemistry of the cyclen-based tetrakis-aryloxide ligand is different from that of the tacn-based analogues.⁸

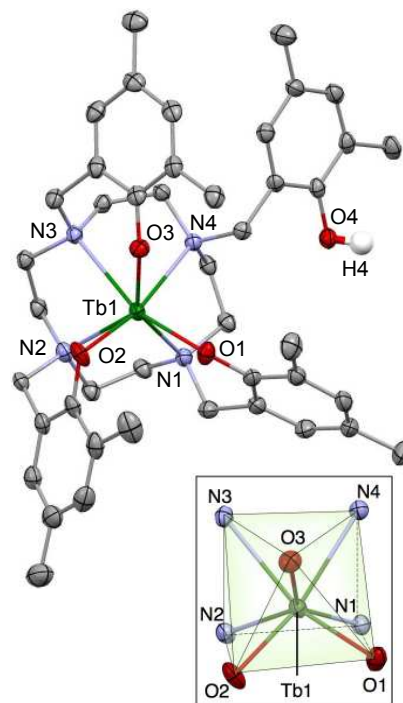


Fig. 2 An ORTEP drawing of $\mathbf{1}^{\text{cyclen}}$ with 50% probability ellipsoids. Hydrogen atoms, except O-H, and co-crystallised solvents are omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: $\text{Tb1-N1} = 2.660(3)$, $\text{Tb1-N2} = 2.641(3)$, $\text{Tb1-N3} = 2.650(3)$, $\text{Tb1-N4} = 2.667(3)$, $\text{Tb1-O1} = 2.147(3)$, $\text{Tb1-O2} = 2.224(3)$, $\text{Tb1-O3} = 2.171(3)$, $\text{O1-Tb1-O2} = 93.52(11)$, $\text{O1-Tb1-O3} = 94.80(11)$, $\text{O2-Tb1-O3} = 86.91(11)$, $\text{N1-Tb1-N2} = 69.13(10)$, $\text{N2-Tb1-N3} = 69.60(10)$, $\text{N3-Tb1-N4} = 68.63(10)$, $\text{N4-Tb1-N1} = 67.23(10)$. Inset: the coordination polyhedron of the Tb^{3+} ion in $\mathbf{1}$.

The UV-vis absorption spectrum of $\mathbf{1}^{\text{cyclen}}$ in THF at room temperature shows an absorption band corresponding to the $\pi \rightarrow \pi^*$ transition of the phenolato (MeMeArO^-) moieties and the phenol (MeMeArOH) pendant arm ($\lambda_{\text{max}} = 299 \text{ nm}$, $\epsilon = 15 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, Fig. 3, black).¹⁰ The band is the same as that observed in $\mathbf{1}^{\text{tacn}}$ ($\lambda_{\text{max}} = 302 \text{ nm}$, $\epsilon = 15 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)³ and is slightly red-shifted relative to that of $\{(\text{MeMeArOH})_4\text{cyclen}\}$ ($\lambda_{\text{max}} = 285 \text{ nm}$, $\epsilon = 10 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, Fig. S1, ESI†).

The luminescence spectrum ($\lambda_{\text{ex}} = 300 \text{ nm}$) of $\mathbf{1}^{\text{cyclen}}$ under N_2 in THF at room temperature shows the seven bands at 496, 543, 585, 621, 659, 671 and 680 nm corresponding to the $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 6, 5, 4, 3, 2, 1$ and 0, respectively) transitions of the Tb^{3+} ion (Fig. 3, red).^{2c,2d} The effective intramolecular energy transfer from the ligand to the Tb^{3+} ion in $\mathbf{1}^{\text{cyclen}}$ is supported by

(i) the absence of ligand-centred emission (Fig. 3, red)¹¹ and (ii) the identical excitation spectrum with the absorption spectrum (Fig. S2, ESI†). The luminescence quantum yield (Φ) and lifetime (τ) of $\mathbf{1}^{\text{cyclen}}$ were determined to be 0.91 and 1070 μs , respectively (Fig. S3, ESI†). As expected, the luminescence of $\mathbf{1}^{\text{cyclen}}$ is highly oxygen-sensitive ($\Phi = 0.031$ and $\tau = 40 \mu\text{s}$ under air, Fig. 3, blue) and its intensities reversibly respond to alternating changes of oxygen concentration (under air (21%) and N_2 (0%)) (Fig. 3, inset).¹² In addition, the Stern-Volmer quenching constant (K_{sv}) of $\mathbf{1}^{\text{cyclen}}$ was determined to be 12600 M^{-1} (Fig. S4, ESI†). The observed luminescence and oxygen-sensing properties of $\mathbf{1}^{\text{cyclen}}$ are comparable to those of the tacn-based analogue $\mathbf{1}^{\text{tacn}}$ ($\Phi = 0.91$ and $\tau = 840 \mu\text{s}$ under N_2 , $\Phi = 0.054$ and $\tau = 40 \mu\text{s}$ under air, $K_{\text{sv}} = 8300 \text{M}^{-1}$).³ These results support that the oxygen-sensitive luminescence properties of $\mathbf{1}^{\text{cyclen}}$ and $\mathbf{1}^{\text{tacn}}$ are mainly attribute to the aryloxy moieties ($^{\text{MeMe}}\text{ArO}^-$).¹¹

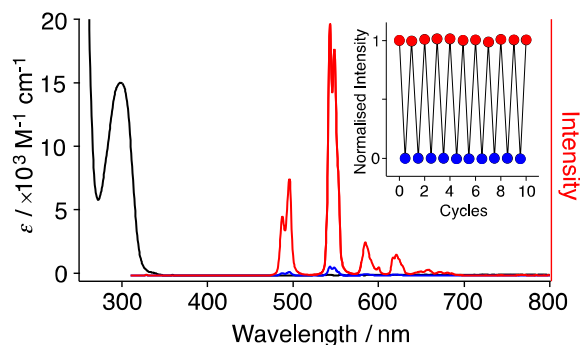


Fig. 3 UV-vis absorption (black) and corrected luminescence spectra (under N_2 (red) and air (blue), $\lambda_{\text{ex}} = 300 \text{ nm}$) of $\mathbf{1}^{\text{cyclen}}$ in THF at room temperature. Inset: reversible responses of the luminescence intensity of $\mathbf{1}^{\text{cyclen}}$ ($1.6 \times 10^{-6} \text{ M}$) to alternating air and N_2 exposures. The luminescence was monitored at 543 nm.

The number of solvent molecules bound in the inner coordination sphere of the Tb^{3+} ion (q) can be estimated by using the well-established Horrocks' equation: $q = A(1/\tau_{\text{H}} - 1/\tau_{\text{D}})$, where $A = 8.4$ for the Tb^{3+} ion in CH_3OH .¹³ The lifetimes (τ) of $\mathbf{1}^{\text{cyclen}}$ in CH_3OH and CD_3OD were determined to be 1350 and 1360 μs , respectively (Fig. S5, ESI†): the q for $\mathbf{1}^{\text{cyclen}}$ is calculated to be 0.00.¹⁴ Thus, even in solution, the Tb^{3+} ion in $\mathbf{1}^{\text{cyclen}}$ retains the seven-coordinate structure found in the crystalline state (*vide supra*).¹⁵

It is worthy to note that the phenol pendant arm ($^{\text{MeMe}}\text{ArOH}$) of $\mathbf{1}^{\text{cyclen}}$ can work as the extendable functional group. In order to examine the reactivity of the phenol pendant arm, the methylation of phenol by dimethyl sulfate (Me_2SO_4) was selected as a typical reaction.¹⁶ The reaction of $\mathbf{1}^{\text{cyclen}}$ with Me_2SO_4 at room temperature afforded an *o*-methylation product [$\{(^{\text{MeMe}}\text{ArOMe})(^{\text{MeMe}}\text{ArO})_3\text{cyclen}\}\text{Tb}^{\text{III}}$] ($\mathbf{2}^{\text{cyclen}}$) which was characterised by UV-vis and luminescence spectroscopy, electrospray ionisation mass spectrometry and X-ray crystallography (Fig. 4, Table S1 and Fig. S6–S10, ESI†). The positive-ion electrospray ionisation mass spectrum of $\mathbf{2}^{\text{cyclen}}$

dissolved in CsOH/MeOH shows a signal at m/z 1011.4 (relative intensity (I) = 100% in the range m/z 200–2000), which has a characteristic isotopic distribution that matches well with the calculated isotopic distribution for $[\mathbf{2}^{\text{cyclen}} + \text{Cs}]^+$. These data are depicted in Fig. 4, together with the data obtained from $\mathbf{1}^{\text{cyclen}}$. The luminescence and oxygen-sensing properties of $\mathbf{2}^{\text{cyclen}}$ ($\Phi = 0.90$ and $\tau = 1060 \mu\text{s}$ under N_2 , $\Phi = 0.031$ and $\tau = 40 \mu\text{s}$ under air, $K_{\text{sv}} = 11400 \text{M}^{-1}$) are identical to those of $\mathbf{1}^{\text{cyclen}}$ (*vide supra*). These results indicate that the phenol pendant arm of $\mathbf{1}^{\text{cyclen}}$ is extendable without any change of the luminescence and oxygen-sensing properties.

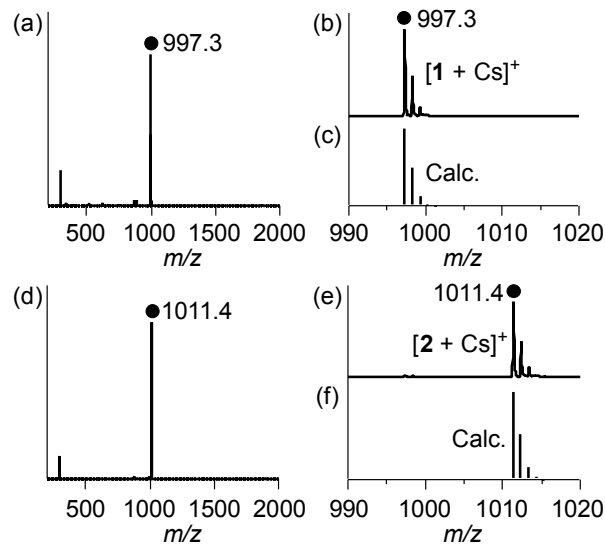


Fig. 4 Positive-ion electrospray ionisation mass spectra of (a) $\mathbf{1}^{\text{cyclen}}$ and (d) $\mathbf{2}^{\text{cyclen}}$ dissolved in CsOH/MeOH . The signal at (b) m/z 997.3 corresponds to $[\mathbf{1}^{\text{cyclen}} + \text{Cs}]^+$ and (e) m/z 1011.4 corresponds to $[\mathbf{2}^{\text{cyclen}} + \text{Cs}]^+$. Calculated isotopic distribution for (c) $[\mathbf{1}^{\text{cyclen}} + \text{Cs}]^+$ and (f) $[\mathbf{2}^{\text{cyclen}} + \text{Cs}]^+$.

In conclusion, we have demonstrated that the macrocyclic tetraamine bearing four phenol groups is useful ligand precursor to construct not only the *expected* oxygen-sensitive luminescent terbium(III) complex but also the *unexpected* seven-coordinate lanthanide complex with the extendable phenol pendant arm. We believe that our findings offer attractive new insight into not only the construction of novel oxygen sensors in biological/environmental systems but also the synthetic strategies for introduction of the extendable pendant arm in f-element chemistry. Further works are currently in progress on the basis of these approaches.

This work was supported by grants-in aid: 26000008 (Specially Promoted Research), 26410074, 26810038 and 15H00953 (Scientific Research on Innovative Areas “Stimuli-responsive Chemical Species”) and the World Premier International Research Center Initiative (WPI Program) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) (Japan).

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† Electronic Supplementary Information (ESI) available: Experimental details, Table S1–S2 and Fig. S1–S10. CCDC 1041014 ($\{(\text{Me}^{\text{Me}}\text{ArOH})_4\text{cyclen}\}$), 1041015 (1^{cyclen}) and 1041016 (2^{cyclen}). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x

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Text: The potentially N_4O_4 -octadentate ligand unprecedentedly coordinates to the Tb^{3+} ion with N_4O_3 -heptadentate fashion and provides the highly luminescent and highly oxygen-sensitive terbium(III) complex.

