Short communication

A novel coordination network of Tb(III) with 2-hydroxy-trimesic acid showing very intense photoluminescence

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ABSTRACT

A novel coordination network consisting of Tb(III) ions and 2-hydroxy-trimesic acid (H_4**L**) has been prepared and characterized using infrared spectroscopy, elemental analysis, thermogravimetric analysis and single crystal X-ray crystallography. The structure forms a rigid three-dimensional network, which is described by the formula $[Tb(H\mathbf{L})(H_2O)_2]_n$. The compound shows emission lines characteristic for Tb(III) when excited with near-UV radiation. The quantum yield of this process is 67%, showing that the ligand acts as a highly efficient antenna for sensitizing Tb(III) emission and that the complex Tb**HL** potentially is a good phosphor for WLED.

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The advances made in the early 1990s in the field of In:GaN based LED chips emitting in the near-UV and blue spectral region have sparked active research to the development of efficient Solid State Lighting (SSL) devices, both by industry and academia. SSLs have the potential to become much more energy efficient than the currently used lamps and thus can aid in the reduction of energy consumption and the emission of carbon dioxide [1,2]. LEDs generate light by radiative recombination of electrons and holes at the PN-junction of a suitable semiconductor. Thus, electricity is converted into light directly and potentially with high efficiency. An important drawback of LEDs, owing to their semiconductor nature, is their intrinsically monochromatic emission that is determined by the band gap. Although this allows for LEDs to be used as signal lamps, general household illumination requires warm white light. Several approaches have been developed to establish white light using LEDs [3,4]. For example, a near-UV In:GaN LED, emitting at 370 nm, can be used to pump a coating of blue, green and red emitting phosphors. This requires phosphors that can be efficiently excited in the near-UV region. As a result, the development of novel phosphor materials forms a challenging research task. In this respect, lanthanoid coordination compounds are highly attractive. Direct excitation of the lanthanoid ion is inefficient due to the parity and often spin-forbidden nature of the intra-4f transitions. Efficient population of 4f excited states is possible *via* the antenna effect; that is, by excitation of the ligand's excited state, followed by ligand-to-lanthanoid energy transfer [5–7]. This principle allows the complexes to be tuned

to the excitation source by introduction of subtle changes in the ligand structure.

In the past decade, lanthanoid-based coordination compounds have become very important multifunctional luminescent materials due to their special photophysical properties, such as the high quantum yields, long lifetime and sharp line emissions [8–12]. Various *Ln* coordination polymers have been established for *e.g.* sensing of small organic molecules, temperature sensing, gas storage, gas separation, proton conduction and heterogeneous catalysis [8,12–35].

Our previous research has shown the ligand 5-*tert*-butyl-2-hydroxy-isophthalate to be an efficient sensitizer for Tb(III)-centered luminescence, giving rise to a complex that exhibits a photoluminescent quantum yield of 52% [36]. In this study, we report a new Tb(III)-based coordination network using the similar ligand 2-hydroxy-trimesic acid (H_4**L**).

Pale yellow crystals of $[Tb(H\mathbf{L})(H_2O)_2]_n$ (Tb**HL**) were obtained from a hydrothermal reaction of $TbCl_3$ with H_4**L**. The asymmetric unit of Tb**HL** contains a single Tb(III) ion, one trianionic ligand and two molecules of water (Fig. 1, Table S1). The Tb(III) ion is eight coordinated by five carboxylate O atoms from carboxylate groups of five different ligand molecules, one O atom from a hydroxyl group and two O atoms from water molecules. The geometry around the Tb(III) ion is best described as a distorted biaugmented triangular prism. Tb–O bond lengths range from 2.255(2) to 2.435(3) Å, which can be considered normal for this type of bonds. Each ligand H$\mathbf{L}^{3-}$ links five Tb(III) ions with $(\eta^1:\eta^1):(\eta^1:\eta^0):\eta^1:(\eta^1:\eta^1):\mu_5$ connectivity. The three-dimensional structure of the network consists of puckered layers of ligand molecules, and the ligands of adjacent layers are connected by Tb(III) centers. The framework is further stabilized by hydrogen bonds (Table S2).

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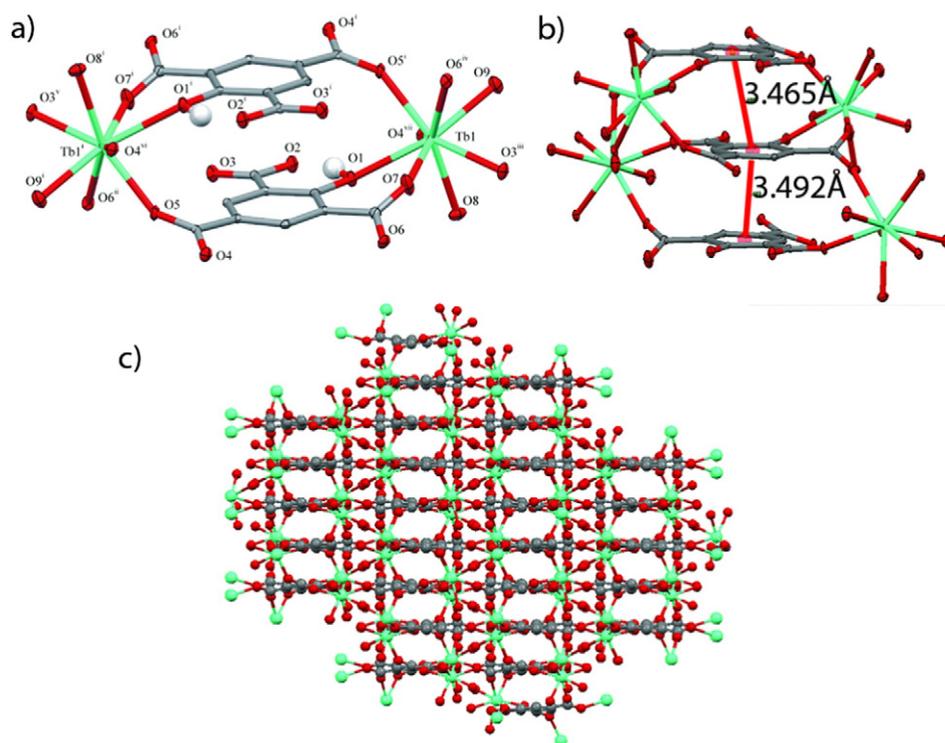 *E-mail address:* bouwman@chem.leidenuniv.nl (E. Bouwman).

Fig. 1. Crystal structure of [Tb(HL)(H$_2$O)$_2$]$_n$ a) projection of part of the structure of TbH**L** with the atomic numbering; b) view of the π-stacking interactions, including the ligand-ligand distance; c) projection of the structure of TbH**L** along the *c* axis. Green = terbium, red = oxygen, gray = carbon, white = hydrogen.

Between adjacent layers π-stacking interactions are present at distances of 3.465(2) Å and 3.492(2) Å between the ring centroids. Altogether, the three-dimensional structure results in a highly dense packing with a calculated density as high as 2.995 g cm^{-3}.

A better insight into the framework can be obtained by the application of a topological approach. The free software TOPOS was used to

analyze the connectivity in the network [37–39]. Each Tb(III) ion is linked by five ligands HL^{3-} and each ligand HL^{3-} is linked by five Tb(III) ions (Fig. 2). Both Tb(III) and HL^{3-} can thus be considered as a five-connected node. The structure can be considered as a rare derived 5,5-connected binodal net named as nia-5, 5-P2$_1$/c. The point symbol of this topology is {4^5·6^5} [40]. An overview of other structures reported
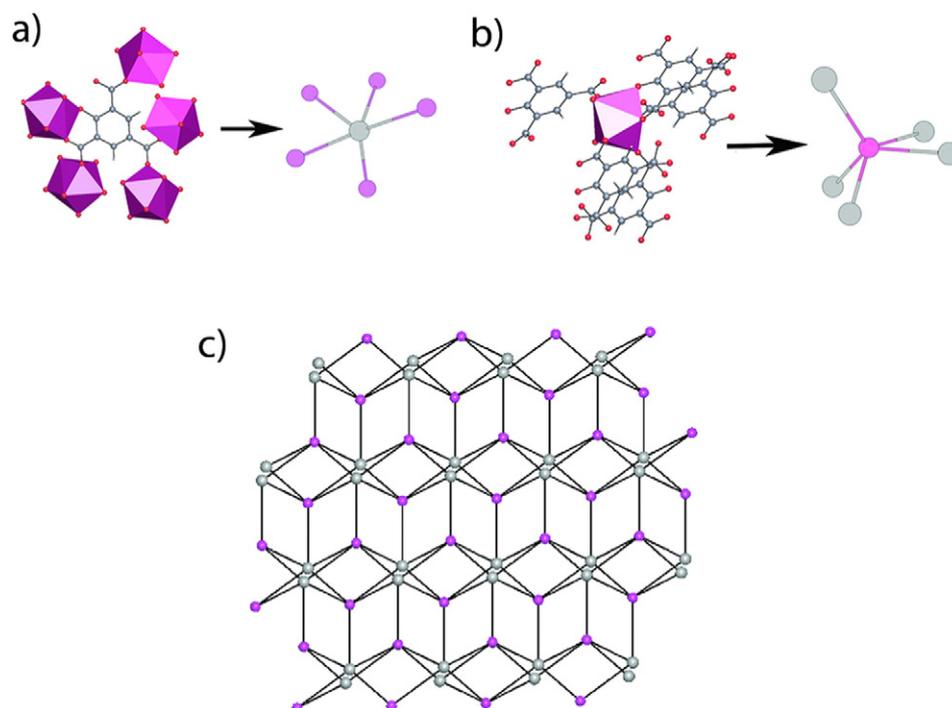

Fig. 2. Topology structure of TbH**L**: (gray) ligand HL^{3-}; (pink) Tb(III). a) the Tb(III) ion is linked by five ligands HL^{3-}; b) the ligand HL^{3-} is linked by five Tb(III) ions; c) topology structure.
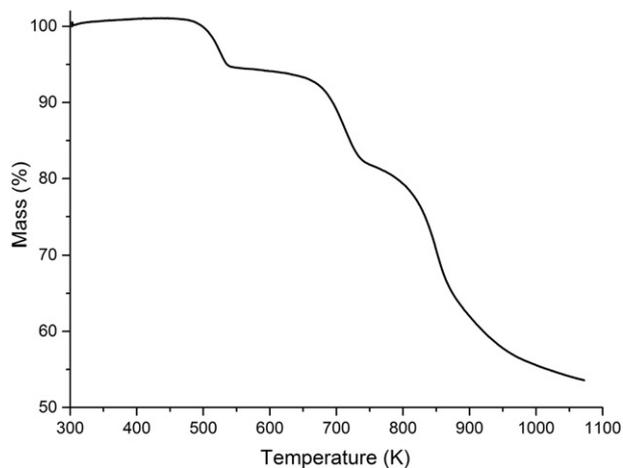
Fig. 3. TGA curve of TbH**L**.

Fig. 5. Phosphorescence spectrum of GdH**L** at 77 K and its deconvolution using Gaussians. Black: experimental phosphorescence spectrum; red: Gaussian components of phosphorescence spectra; green: sum curve of components.

before to have the same topology is provided in Table S3; two of these are lanthanoid coordination networks comprising lanthanum and either the ligand 5-sulfoisophthalic acid that is rather similar to trimesic acid, or {4-[3,5-bis-(1-carbonylmethyl-1H-triazol-4-yl)phenyl]-triazol-1-yl}acetic acid, which also comprises a trisubstituted benzene fragment [41–43].

To test the thermostability of TbH**L**, TGA was performed under an argon atmosphere at a heat rate of 3 K/min in the temperature range of 300–1070 K. The TGA curve is shown in Fig. 3. The compound TbH**L** starts to lose the coordinated water at 470 K (7.6%, calcd 8.6%). Subsequently, the water-free compound starts to decompose at 650 K with loss of one carboxylate group (10.9%, calcd 10.3%), and finally further decomposes at 750 K.

Upon illumination of TbH**L** by a standard laboratory UV lamp emitting at 366 nm, it exhibits intense green luminescence as shown in Fig. S1. The photoluminescence spectrum recorded in the solid state for TbH**L** is provided in Fig. 4. The excitation spectrum of TbH**L** shows a broad band in the near UV region with a maximum at 380 nm, which is typical for ligand-centered excitation. The emission spectrum is characteristic of the Tb(III) ion, with transitions from the $^5D_4$ level to the ^7F_J manifold appearing as emission lines at 492 nm ($J = 6$), 548 nm ($J = 5$), 588 nm ($J = 4$) and 622 nm ($J = 3$). No emission from the ligand is observed, indicating a very efficient energy transfer from the ligand to the Tb(III) ion. The $^5D_4 \rightarrow {}^7F_5$ transition dominates
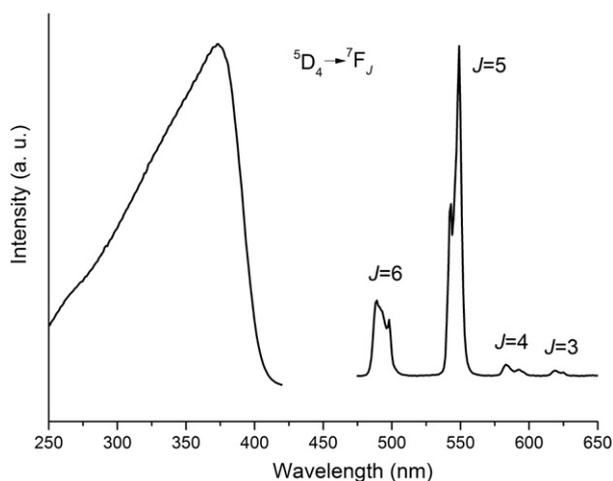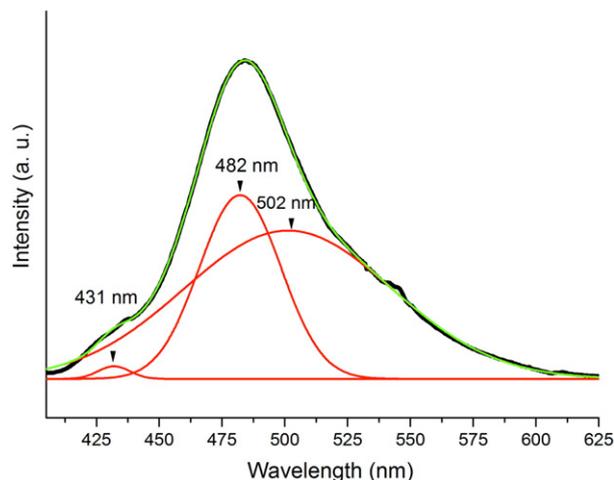
the emission spectrum, contributing over 70% to the total emission intensity. The emission lines are visibly split as a result of crystal field splitting. The photoluminescence quantum yield determined for this compound is 67% upon excitation at 380 nm, which makes the compound a good potential phosphor. This quantum yield is remarkably high, even higher than the value reported for the Tb(III) complex with 5-*tert*-butyl-2-hydroxy-isophthalate as a ligand (52%) or the Tb(III) complexes with 2-hydroxy-phthalimide ligands (59 and 61%) [36,44]. The luminescence lifetime of TbH**L** has also been studied; the decay spectrum is shown in Fig. S2. The compound exhibits mono-exponential decay behavior and the lifetime of TbH**L** emission is 0.4 ms.

The triplet energy level of the ligand has been estimated from the zero-phonon transition in the phosphorescence spectrum of the corresponding Gd(III) complex recorded at 77 K (Fig. 5) [45–49]. The energy difference between the triplet state of the ligand (around 23,200 cm^{-1}, 431 nm) and the Tb(III) $^5D_4$ level (at 20,500 cm^{-1}) is 2700 cm^{-1}, which indicates that the energy back transfer from the $^5D_4$ level to the ligand is most likely prohibited [45].

In summary, 2-hydroxytrimesic acid has been reacted with TbCl$_3$·6-H$_2$O under hydrothermal conditions, giving a novel and high-density coordination network with the formula [Tb(H**L**)(H$_2$O)$_2$]$_n$. This compound exhibits very efficient photoluminescence characteristic for the Tb(III) ion upon excitation of the ligand-centered absorption band by near-UV radiation. The quantum yield for this process is 67%. Based on its high quantum yield, long excitation wavelength, and high thermal stability, TbH**L** is an ideal candidate for a green phosphor material for application in LEDs.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2015.08.020.

Fig. 4. Excitation (left, $\lambda_{em} = 548$ nm) and emission (right, $\lambda_{exc} = 380$ nm) spectra of TbH**L**.

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