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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 TbH**L** potentially is a good phosphor for WLED.

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-hydroxyisophthalate 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 $[Tb(HL)(H_2O)_2]_n$ (TbHL) were obtained from a hydrothermal reaction of $TbCl_3$ with H_4L. The asymmetric unit of TbH**L** 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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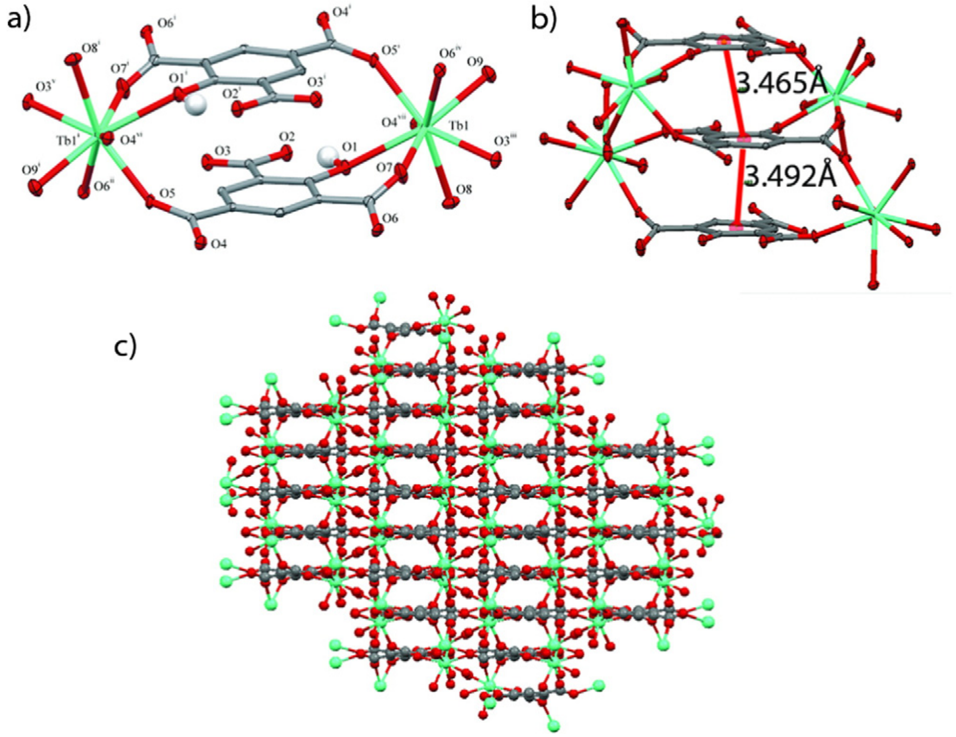

Fig. 1. Crystal structure of $[Tb(HL)(H_2O)_2]_n$ a) projection of part of the structure of TbH**L** with the atomic numbering; b) view of the π-stacking interactions, including the ligand-ligand distance; c) projection of the structure of TbH**L** along the *c* axis. Green = terbium, red = oxygen, gray = 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 $\{4^5 \cdot 6^5\}$ [40]. An overview of other structures reported

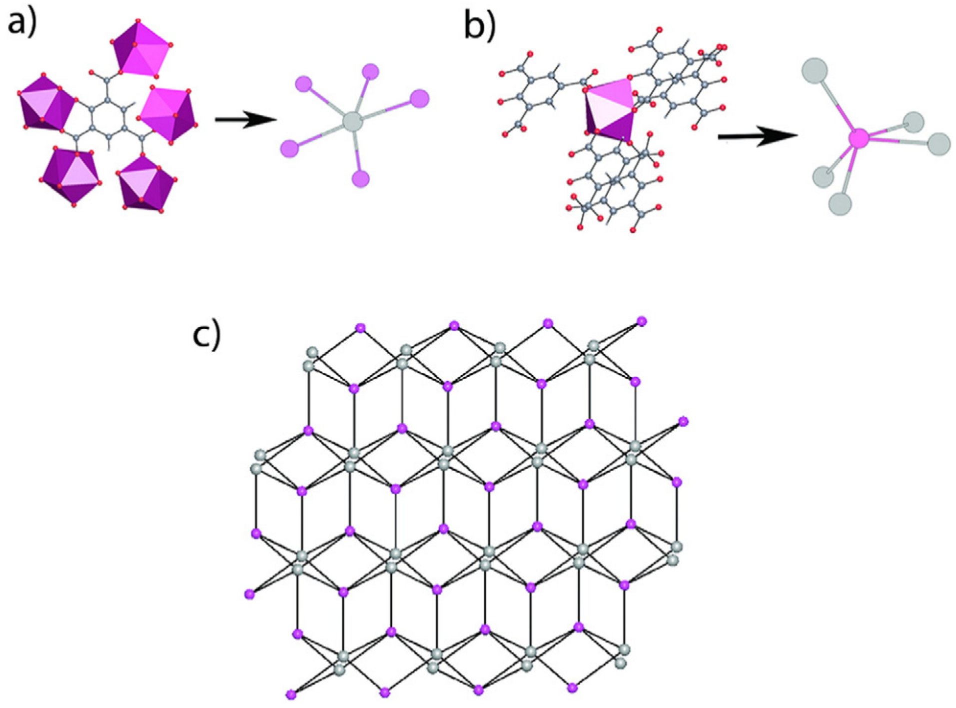

Fig. 2. Topology structure of TbH**L**: (gray) ligand HL^{3-}; (pink) Tb(III). a) the Tb(III) ion is linked by five ligands HL^{3-}; b) the ligand HL^{3-} is linked by five Tb(III) ions; c) topology structure.