

## Two novel isostructural Ln (III) 3D frameworks supported by 3,6-dibromobenzene-1,2,4,5-tetracarboxylic acid and in situ generated oxalate: Syntheses, characterization and photoluminescent property

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### ABSTRACT

Two isostructural lanthanide complexes,  $[\text{Ln}(\text{dbtec})_{0.5}(\text{ox})_{0.5} \cdot 3\text{H}_2\text{O}]_n$ ,  $[\text{Ln} = \text{Dy} (\mathbf{1}), \text{Yb} (\mathbf{2})]$  ( $\text{H}_4\text{dbtec} = 3,6$ -dibromobenzene-1,2,4,5-tetracarboxylic acid;  $\text{H}_2\text{ox} = \text{oxalic acid}$ ), have been synthesized under the hydrothermal method and characterized by single-crystal X-ray diffraction, X-ray powder diffraction (PXRD), thermogravimetric analysis (TGA) and elemental analysis (EA) and IR spectra. Complex  $\mathbf{1}$  and  $\mathbf{2}$  present a 2-nodal (4,6)-connected 3D fsc network. The  $^{13}\text{C}$  NMR of  $\text{H}_4\text{dbtec}$  indicates ox in  $\mathbf{1}$  and  $\mathbf{2}$  is generated by the in situ decomposition of  $\text{H}_4\text{dbtec}$ . Additionally, the photoluminescent properties of  $\mathbf{1}$  and  $\mathbf{2}$  are also discussed.

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The rational design and synthesis of functional metal-organic frameworks (MOFs) is a more and more fascinating field due to their interesting topologies and potential applications in gas adsorption, nonlinear optics, magnetism, luminescence, molecular recognition, etc. [1–3]. Organic carboxylate ligand is currently a good candidate to construct MOFs, because it can not only provide a number of coordination sites to coordinate to metal ions through coordinative bonds, but also act as hydrogen-bonding acceptors or donors to further extend low-dimensional frameworks to high-dimensional architectures through hydrogen-bonding interactions [4]. Meanwhile, the utilization of polynuclear metal clusters as secondary building units (SBUs) to construct high-connected frameworks has been proved to be an effective method [5]. In addition, lanthanide elements were selected to construct network, owing to their high 8–12 coordination numbers and flexible Ln–O bond lengths, which allow forming new topological and interesting fluorescent properties [6]. At the same time, in hydro- or solvothermal reactions, some unexpected in situ ligand reactions may occur involving organic ligand in the presence of metal ion, which makes accurately predicting final structures more difficult [7]. In fact, oxalate in situ generation under several conditions is quite widespread and investigated and has been used to generate coordination compounds and MOFs with a variety of transition metal and lanthanide ions. The mechanism of in situ formation of oxalic acid is also being studied. Considering these in mind, we constructed two isostructural lanthanide complexes,  $[\text{Ln}(\text{dbtec})_{0.5}(\text{ox})_{0.5} \cdot 3\text{H}_2\text{O}]_n$ ,  $[\text{Ln} = \text{Dy} (\mathbf{1}), \text{Yb} (\mathbf{2})]$  [ $\text{H}_4\text{dbtec} = 3,6$ -dibromobenzene-1,2,4,5-tetracarboxylic acid

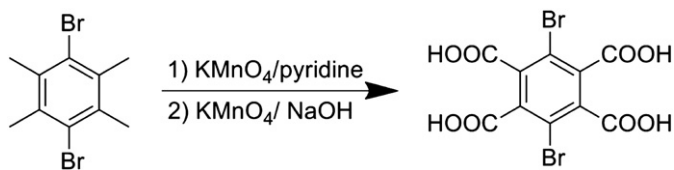
(Scheme 1);  $\text{H}_2\text{ox} = \text{oxalic acid}$ ], which were constructed from  $\text{H}_4\text{dbtec}$  and in situ generated ox ligand.

Single-crystal X-ray analysis of  $\mathbf{1}$  and  $\mathbf{2}$  indicates that they are isostructural, so the structure of  $\mathbf{1}$  is described representatively here in detail. Complex  $\mathbf{1}$  was synthesized by the reaction of  $\text{Dy}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$  and  $\text{H}_4\text{dbtec}$  through the conventional hydrothermal method [8] in a pressure-resistant glass tube. X-ray single-crystal diffraction reveals [9] that compound  $\mathbf{1}$  is a three-dimensional framework and crystallizes in triclinic  $P\bar{1}$  space group. The asymmetric unit contains one crystallographic independent Dy (III) ion, half dbtec ligand, half ox ligand, and three coordinated water molecules. As shown in Fig. 1, Dy1 is eight coordinated by three carboxylate oxygen atoms ( $\text{O}2^{\text{ii}}, \text{O}3^{\text{i}}, \text{O}4$ ) from three different dbtec ligands, three oxygen atoms ( $\text{O}1\text{W}, \text{O}2\text{W}, \text{O}3\text{W}$ ) from three coordinated water molecules and two oxygen atoms ( $\text{O}5, \text{O}6$ ) from one ox ligand molecular, exhibiting a slightly distorted square antiprism configuration. The bond distances of  $\text{Dy}-\text{O}_{\text{dbtec}}$ ,  $\text{Dy}-\text{O}_{\text{water}}$  and  $\text{Dy}-\text{O}_{\text{ox}}$  are in the ranges of 2.286 (7)–2.373 (6) Å, 2.374 (7)–2.442 (7) Å, and 2.374 (6)–2.451 (6) Å, respectively (Table S1). The bromide atoms and benzene ring in dbtec ligand are essentially planar, with mean deviations of 0.034 (1) Å, from the least-squares plane defined by C1/C2/C3/C4/Br atoms. The dihedral angles formed by carboxylate group ( $\text{O}1/\text{O}2^{\text{ii}}/\text{C}1, \text{O}3^{\text{i}}/\text{O}4/\text{C}5$ ) and central benzene ring range from 65.536 (19)° to 78.251 (26)°. All of bond lengths and angles are comparable to those reported dysprosium complexes [10] (symmetry codes: (i)  $1-x, 1-y, -z$ ; (ii)  $2-x, 1-y, 1-z$ ).

For the coordination mode of ox ligand, it is in a  $\mu_2$ -bridging mode to link two Dy ions (Fig. 2a). As for btec ligand, four carboxylate groups of each btec adopts two kinds of coordination modes: one pair of the inversion-related carboxylate groups of one btec exhibit a  $\mu_1\text{-}\eta^1\text{-}\eta^1$

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Scheme 1. The synthesis route of H<sub>4</sub>dbtec.

mode, and the other couple inversion-related carboxylate groups display a  $\mu_2\text{-}\eta^1\text{-}\eta^1$  bridging mode, and so the dbtec ligand exhibits  $\mu_6\text{-}\eta^1\text{-}\eta^0\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1\text{-}\eta^0$  bridging fashion linking six Dy ions (Fig. 2b). So dbtec ligand were linked by four dinuclear Dy (III) SBUs to form a 2D layer and then the neighboring layer was further connected by ox ligand to form the whole 3D crystal structure of **1** (Fig. 2c). The intramolecular hydrogen bonds between uncoordinated O atom of carboxylate group and coordinated water molecules stabilized the final structure. To better understand the complicated structure of compound **1**, the topological analysis of complex **1** has been performed by the TOPOS software [11]. Each dbtec linking four dinuclear Dy (III) SBUs unit is defined as a 4-connected node (Fig. 3a), and each dinuclear Dy (III) SBUs was linked by two adjacent dinuclear Dy (III) SBUs and four dbtec ligand, forming a 6-connected node (Fig. 3b). The whole three-dimensional net can be represented as a 2-nodal (4,6)-connected **fsc** network (Fig. 3c) with the Schlafli symbol of  $\{4^4.6^{10}.8\}\{4^4.6^2\}$  identified and categorized by O'Keeffe et al., and structures containing **fsc** topological network have been reported rarely. As far as we know, **cor** network is one of representation of (4,6)-connected 3D topology network with the style of corundum ( $\text{Al}_2\text{O}_3$ ) [12], where the geometries of 4- and 6-connected nodes are tetrahedron and octahedron, respectively. But **fsc** topology features square 4-connected node and octahedron 6-connected node, which makes an important difference between each other. The first **fsc** topology was observed in a coordination polymer, namely,  $[(\text{Cu})_7(\text{DABCO})_{2.5}]_n$  (DABCO = 1,4-diazabicyclo[2.2.2]octane) [13]. Subsequently, the interpenetrated **fsc** networks was also observed in  $[\text{Cu}(\text{bbi})_2(\text{H}_2\text{O})]$  ( $\beta\text{-Mo}_8\text{O}_{26}$ )<sub>0.5</sub> (bbi = 1,1'-(1,4-butanediyl)bis(imidazole)) [14]. Recently, an unusual trinodal **fsc** network was discovered in a mixed-ligand coordination polymer [15].

To prove the origination of ox ligand in **1** and **2**, the <sup>13</sup>C NMR (Fig. S4) of H<sub>4</sub>dbtec was performed. By identification of <sup>13</sup>C NMR of H<sub>4</sub>dbtec, we ensured the purity of H<sub>4</sub>dbtec and no trace of H<sub>2</sub>ox exists in the starting materials. So we deduced that H<sub>2</sub>ox originated from the in situ decomposition of H<sub>4</sub>dbtec under the hydrothermal reaction. In situ ligand

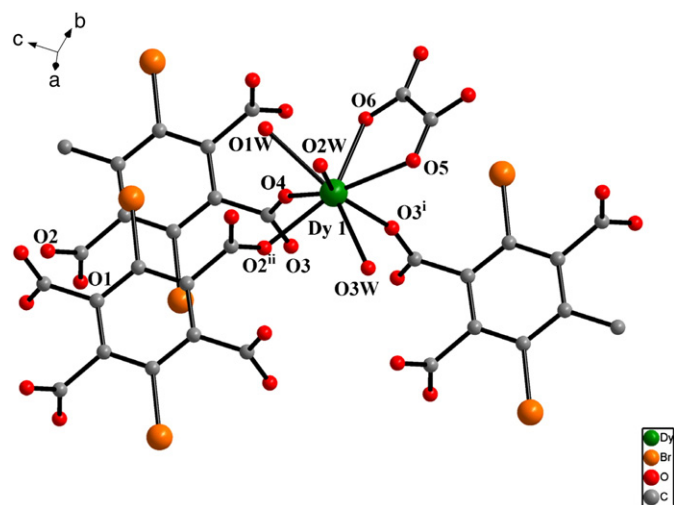


Fig. 1. The coordination environment around Dy(III) ions in **1**; all hydrogen atoms are omitted for clarity (symmetry codes: (i)  $1-x, 1-y, -z$ ; (ii)  $2-x, 1-y, 1-z$ ).

formation has largely been a serendipitous process. Because of C–C bond formation or cleavage, oxidation, and decarboxylation, among many others, the organic starting material may undergo a variety of reactions, so the products of these reactions are not always intuitive [16]. Recently, a research paper “Exploring the mechanism of in situ formation of oxalic acid for producing mixed fumarato-oxalato lanthanide (Eu, Tb and Gd) frameworks” has been published. Based on the mechanisms mentioned in that paper together with the <sup>13</sup>C NMR of H<sub>4</sub>dbtec, we concluded that ox ligand in **1** and **2** was formed by in situ hydrolysis of H<sub>4</sub>dbtec ligand for  $\text{Ln}^{3+}$  followed by oxidation and decarboxylation steps, which paved the way for understanding the dual role of  $\text{Ln}^{3+}$  ions and the nature of the oxidant in forming the frameworks [17].

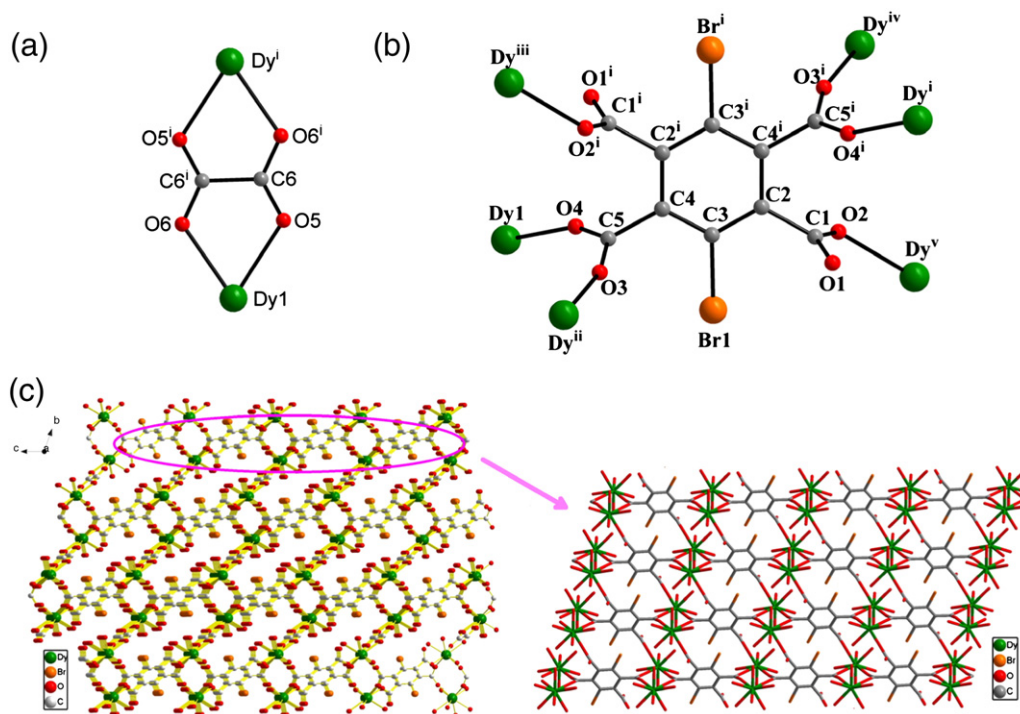
The powder X-ray diffraction (PXRD) pattern of **1** and **2** was also investigated. The simulated and experimental PXRD patterns of **1** and **2** are shown in Fig. S1 indicating the phase purity of the products. The most peak positions of simulated and experimental patterns are in good agreement with each other; the differences in intensity may be due to the preferred orientation of the powder samples [18].

In **1** and **2**, the observed broad peak at  $3500\text{ cm}^{-1}$  in the FT-IR spectrum (Fig. S2) is attributed to the O–H stretching vibration of the coordinated water molecules, and the sharp bands in the ranges of  $1690\text{--}1605$  and  $1440\text{--}1330\text{ cm}^{-1}$  are attributed to asymmetric and symmetric stretching vibrations of carboxylic group, respectively [19].

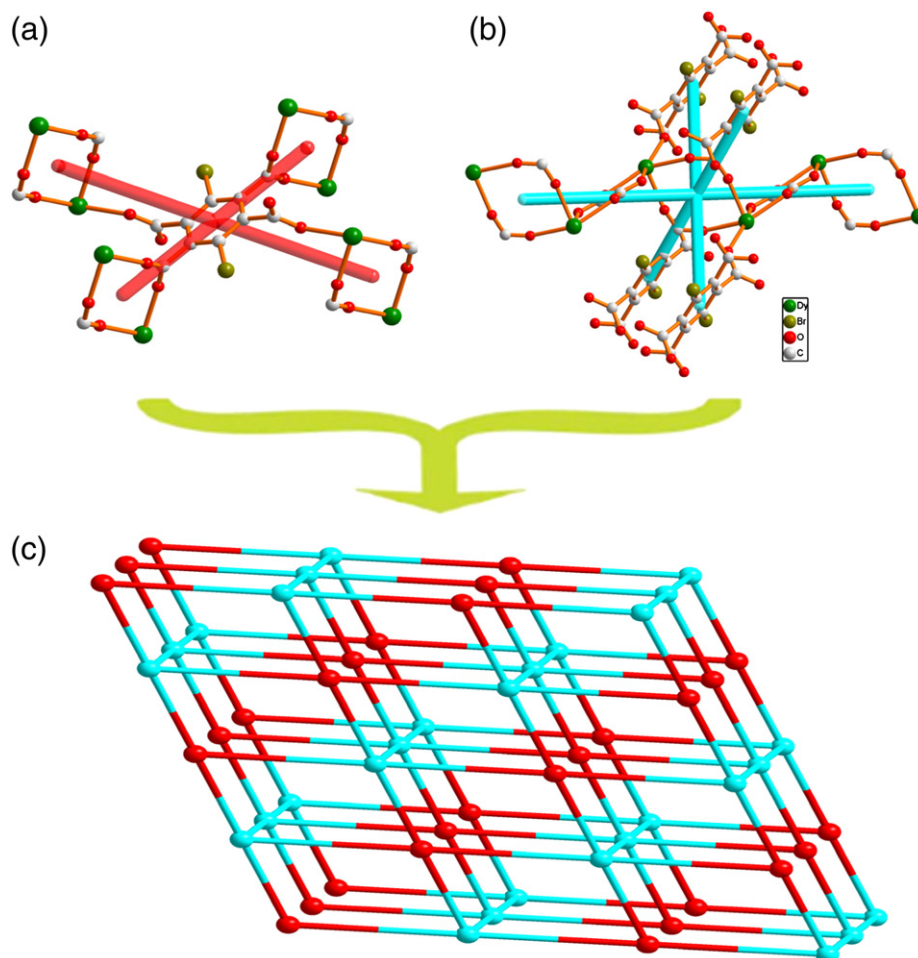
To better understand the coordinated water and the thermal stability of **1** and **2**, thermal gravimetric analysis (TGA) was performed. Thermogravimetric analysis of **1** and **2** was carried out under a nitrogen-flow atmosphere with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  in the temperature region of  $30\text{--}800\text{ }^\circ\text{C}$ . Because of the isostructure of **1** and **2**, the two compounds exhibited similar thermal stability as shown in Fig. S3, and the TG curve displays mainly two steps of weight loss processes. TGA indicates that **1** and **2** are stable up to ca.  $430\text{ }^\circ\text{C}$ . A loss weight of 12.01% observed between 150 and  $300\text{ }^\circ\text{C}$  for **1** and 11.51% observed for **2** corresponds to the full release of lattice water molecules (calcd: 11.65% for **1** and 11.39% for **2**). The second process began from ca.  $410\text{ }^\circ\text{C}$ , corresponding to the decomposition of dbtec organic ligands as well as ox ligand, which is nearly in agreement with the single-crystal analysis.

The solid-state luminescent spectrum of **1**, **2** and free ligand was also investigated at room temperature. As shown in Fig. 4, the ligand displays emission peak at 470 nm upon excitation at 302 nm, which can be attributed to the  $\pi^*\text{--}\pi$  transition of the p electrons of the aromatic rings. Compound **1** displays luminescent emission bands at 481, 572, 665 nm ( $\lambda_{\text{ex}} = 302\text{ nm}$ ), respectively, which are attributed to the characteristic emission for  ${}^4\text{F}_{9/2}\text{--}{}^6\text{H}_J$  ( $J = 15/2, 13/2, 11/2$ ) transition of the Dy (III) ion. The luminescence spectrum shows that the blue emission intensity of the  ${}^4\text{F}_{9/2}\text{--}{}^6\text{H}_{15/2}$  transition is similar with the yellow emission intensity of the  ${}^4\text{F}_{9/2}\text{--}{}^6\text{H}_{13/2}$  transition, and the intensity of the  ${}^4\text{F}_{9/2}\text{--}{}^6\text{H}_{11/2}$  transition is much weaker. Compared with the emission peak of the free ligand and compound **1**, the photoluminescence absence of ligand-based emission suggests efficient energy transfer from the ligands to the lanthanide centers upon excitation [20]. Compound **2** displays luminescent emission bands at 447 nm ( $\lambda_{\text{ex}} = 302\text{ nm}$ ). Compared with the emission peak of the free ligand and compound **2**, the luminescent behavior of compound **2** is blue shift 23 nm which tentatively ascribed to weaker interlumophore interactions that occur relative to the free ligand to different extents in their low-density crystal structures [21].

In summary, the syntheses and characterization of two new Ln (III) compounds are described. Both **1** and **2** are (4,6)-connected 3D **fsc** topology framework, in which ox ligand (in situ reaction generated) plays an important role in determining the 3D frameworks. The luminescent behavior of compound **1** displays the characteristic emission of Dy (III) ion, and compound **2** displays the emission peak of the free ligand upon excitation at 302 nm.



**Fig. 2.** (a) The coordination modes of ox ligand [symmetry codes: (i)  $1-x, 2-y, -z$ ]. (b) The coordination modes of and btec ligand in **1** [symmetry codes: (i)  $1-x, 1-y, 1-z$ ; (ii)  $1-x, 1-y, -z$ ; (iii)  $-1+x, y, z$ ; (iv)  $x, y, 1+z$ ; (v)  $2-x, 1-y, 1-z$ ]. (c) Perspective view of the 3D structure of **1**.



**Fig. 3.** (a) Each dbtec linking four dinuclear Dy (III) SBU unit is defined as a 4-connected node. (b) Each dinuclear Dy (III) SBU was linked by two adjacent dinuclear Dy (III) SBU and four dbtec ligand, forming a 6-connected node. (c) A schematic representation of (4,6)-connected fsc net of **1**.

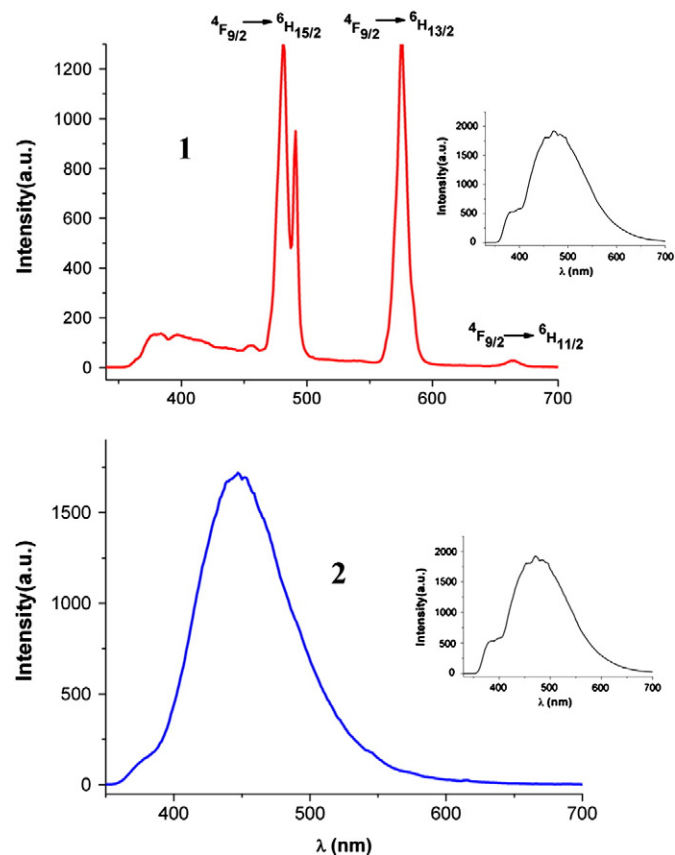


Fig. 4. Solid-state excitation spectra of complexes **1** and **2** at room temperature and the insert are free ligand.

## Acknowledgments

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## Appendix A. Supplementary material

CCDC 891409 and 891410 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB 21EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found in the online version. Supplementary materials related to this article can be found online at <http://dx.doi.org/10.1016/j.inoche.2012.09.023>.

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- (8) [Dy (dbtec)<sub>0.5</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>0.5</sub> 3H<sub>2</sub>O]<sub>n</sub> (**1**). A mixture of Dy (NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O (2 mg, 0.0058 mmol), H<sub>4</sub>dbtec (1 mg, 0.0024 mmol) and H<sub>2</sub>O (1 ml) were sealed in a pressure-resistant glass tube and put into a programmed oven, slowly heated to 120 °C from room temperature in 600 min, kept at 120 °C for 3000 min. After slowly cooled to 30 °C in 800 minutes colorless block crystals of **1** were separated in 52.1% yield based on ligand. Elemental analysis: Anal. Calc. for C<sub>6</sub>H<sub>5</sub>BrDyO<sub>9</sub>: C 15.52, H 1.09%. Found: C 15.40, H 1.00%. IR (KBr, cm<sup>-1</sup>): 3556 m, 1687 s, 1605 s, 1433 m, 1329 m, 1140 m, 893 w, 811 s, 757 w, 718 w 560 w, 502 w. [Yb (dbtec)<sub>0.5</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>0.5</sub> 3H<sub>2</sub>O]<sub>n</sub> (**2**). A mixture of Yb (NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (2 mg, 0.0045 mmol), H<sub>4</sub>dbtec (1 mg, 0.0024 mmol), H<sub>2</sub>O (1 ml) and 1 drop dilute HCl (1 mol/l) were sealed in a pressure-resistant glass tube and put into a programmed oven, slowly heated to 120 °C from room temperature in 600 min, kept at 120 °C for 3000 min. After slowly cooled to 30 °C in 800 minutes colorless block crystals of **2** were separated in 47.6% yield based on ligand. Elemental analysis: Anal. Calc. for C<sub>6</sub>H<sub>5</sub>BrYbO<sub>9</sub>: C 15.19, H 1.06%. Found: C 14.98, H 1.10%. IR (KBr, cm<sup>-1</sup>): 3560 m, 3456 m, 1690 s, 1610 s, 1436 s, 1330 s, 1141 m, 815 m, 560 m.
- (9) Crystal data for **1**: triclinic P-1 space group, a = 6.265(4) Å, b = 9.327(6) Å, c = 9.926(6) Å, α = 108.325(8) ° β = 107.268(9) ° γ = 90.577(9) ° V = 522.3(6) Å<sup>3</sup>, Z = 2, ρ = 2.915 g/cm<sup>3</sup>, F(000) = 418, μ = 11.012 mm<sup>-1</sup>, 2865 reflection measured, 2168 unique (Rint = 0.000), final R1 = 0.0433, wR2 = 0.1183 for all data; **2**: triclinic P-1 space group, a = 6.1925(13) Å, b = 9.2427(19) Å, c = 9.845(2) Å, α = 108.222(3) ° β = 107.484(3) ° γ = 90.664(3) ° V = 507.02(18) Å<sup>3</sup>, Z = 2, ρ = 3.092 g/cm<sup>3</sup>, F(000) = 432, μ = 13.200 mm<sup>-1</sup>, 2450 reflection measured, 1739 unique (Rint = 0.000), final R1 = 0.0405, wR2 = 0.1328 for all data; data collection of **1** and **2** were performed with MoKα radiation (Kα = 0.71073 Å) on a Bruker APEX-II diffractometer. The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F<sub>2</sub> using the SHELXTL program.
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