

Study of the Structure and the Luminescence Properties of the Tb Compound

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Abstract: A lanthanide-organic frameworks Tb (C₂O₄)(HCOO) (1) is synthesized via. hydrothermal methods (autogenous pressure) at temperature around 200°C over a period of a week. Obtained single crystals are characterized by Elemental Analysis (EA), Single Crystal Powder X-Ray Diffraction SCPXRD as well as optical measurements were categorized by Photoluminescence (PL) experiments. The results showed crystals are pure and they exhibit the peak of crystalline orthorhombic Pnma group space. The PL emission spectrum has been monitored at 325 nm (pulsed laser He-Cd). Resulted green luminescence spectrum for the green luminescence emission for compound 1 was located at 544 nm attributed to (⁵D₄•⁷F₅) electronic transition. The noticeable emission intensity for the compound 1 indicated that the lanthanide organic frameworks are good candidate materials for electro-optical devices, Field Emission Displays (FEDs) and they have a potential application in solid-state light.

Key words: Lanthanide organic framework, photoluminescence, hydrothermal method, single crystal, rare earth, solid-state light

INTRODUCTION

Lanthanide-Organic Frameworks (LOFs) are certain types of materials which have a potential application in the fields of sensitive devices, biology, chemistry, medicine and optoelectronics like optical displays panels and Light-Emitting Diodes (LEDs) due to their special chemical and physical properties (Zhang *et al.*, 2008, 2011; Feng *et al.*, 2010; Dai *et al.*, 2010; Klein *et al.*, 2009; Zhu *et al.*, 2007; Mahata *et al.*, 2007; Maspoeh *et al.*, 2007; Zhao *et al.*, 2009; Cheng *et al.*, 2007). The hybrid frameworks are composed by an organic ligand and a metal ion within a porous structure establishing an extensive range of emissive phenomena, for instance linker-based luminescence (Du *et al.*, 2007; Lan *et al.*, 2007; Lu *et al.*, 2007; Wang *et al.*, 2007) metal-based emission (Sonnaner *et al.*, 2007; Gandara *et al.*, 2007; Serre *et al.*, 2004) or antennae effects (De Lill *et al.*, 2017; McManus *et al.*, 2007; Chen *et al.*, 2006; Wagner *et al.*, 2002). Both the inorganic and the organic moieties can provide the platforms to produce luminescence, typically the origin of luminescence emission widely observed in lanthanide MOFs via. the so-called (antenna effect) which is often referred to as (LMCT), since, the strongly absorbing ligand acts as a receiving antenna for the bond metal ion. In addition, the cooperative functionalities of permanent porosity and luminescence property qualified

luminescent MOFs as a very attractive new class of sensing materials (Hatanaka *et al.*, 2017; Rossin *et al.*, 2012).

Trivalent lanthanide Ln (•••) ions produce attractive optical properties. Recently the luminance studies of rare earths metals that are synthesized with various organic ligands have been conducted. Ln (•••) chelates provide narrow band emissions and very pure luminescence using UV/VIS excitation (Latva *et al.*, 1997). This sensitized luminescence of the lanthanide compounds are commonly used for the optical materials, biological applications, electroluminescent devices, optical amplifier or laser and sensors (Bunzli and Piguet, 2005; Cui *et al.*, 2014).

Luminescence of compound Terbium (Tb³⁺) take the tending due to the narrow f-f transitions have attracted a lot of attention because of their good sensitization luminescence that can be carried out through the antenna effect as well as the line of emission spectra look mostly sharp as it depends on the crystal field around the metal ions. Furthermore, a great attention has been paid to the luminescence of Tb³⁺ ions owing to the ability of acting as phosphors and progress of materials (Vicentini *et al.*, 2000). It is well-known that Rare Earth Organic Frameworks (REOFs) have attracted comprehensive interest over the past few years because not only their interesting applications but also their luminescence which originated from intra 4f or 4f-5d transitions (Robin and

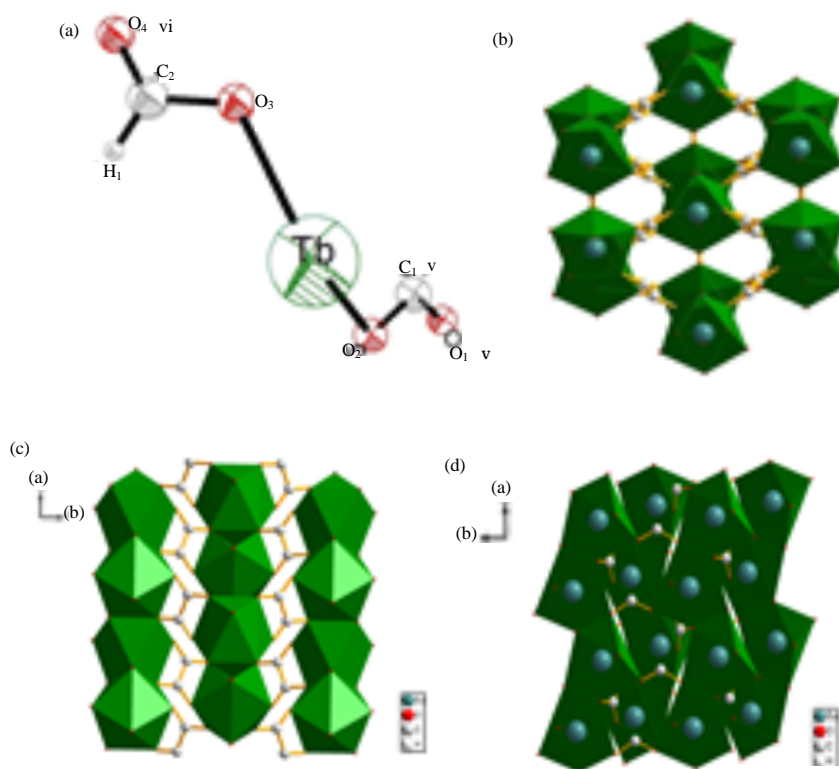


Fig. 1: Illustration of the crystal structure of the $\text{Tb}(\text{C}_2\text{O}_4)(\text{HCOO})$ 1 hybrid framework with asymmetric unit: a) Typical single crystal morphology (habit) and its low index face and b-d) Views perpendicular to the (100), (010) and (001) planes, respectively, hydrogen atoms have been deleted for clarity

Fromm, 2006; Chandler *et al.*, 2016; Pretsch *et al.*, 2006; Yeung *et al.*, 2006; Gu and Xue, 2016; Sun *et al.*, 2006; Gheorghe *et al.*, 2006; Zhu *et al.*, 2007; Huang *et al.*, 2007; Gandara *et al.*, 2007; Zimmermann *et al.*, 2007; Shi *et al.*, 2008; Pompidor *et al.*, 2008; Lunstroot *et al.*, 2009). This specific luminescence is characterized by high luminescence quantum yield, narrow bandwidth, long life time, large Stokes shifts and ligand dependent luminescence sensitization (Shang *et al.*, 2012, Sun *et al.*, 2007).

Here in, we show crystalline framework materials incorporated both inorganic and organic moieties are attracting candidates because of their wide chemical and structural variety that propose opportunities for making many technologically relevant properties (Cheetham *et al.*, 2006; Rao *et al.*, 2008; Kurmoo, 2009; Allendorf *et al.*, 2009; Jain *et al.*, 2008). Notably, the dense hybrid systems usually incorporated with infinite inorganic connectivity, like Metal-Oxygen-Metal (M-O-M) arrays that present the topological characteristics desired for certain types of physical properties (Rao *et al.*, 2004). The synthesized compound 1 was first successfully synthesized by hydrothermal method where compound 1

and 2 consist of lanthanide organic frameworks with an orthorhombic crystal structure, as previously prepared by Romero *et al.* (1996). In Fig. 1, we illustrated the crystal structure of compound 1, we can notice that the three basic building blocks are the inorganic M-O-M chains and the two organic bridging ligands, namely the oxalate ($\text{C}_2\text{O}_4^{2-}$) and the formate (HCOO^-) ions which are effectively oriented perpendicular to one another as well, it is also known that oxalate is structurally more rigid than formate.

In the present research, compound 1 is successfully prepared by hydrothermal method, the crystal structure and the optical properties have been described in details. The results showed that compound 1 exhibited strong green luminescence the characteristics luminescence of Tb^{3+} ions indicating that the compound 1 are a perfect experimental probe of the crystalline environment.

MATERIALS AND METHODS

Materials and measurements: All starting materials and solvents are reagent grade commercially available the

Table 1: Crystallographic data of compound 1

Variables	Values
Compound	1
Formula sum	C ₃ H ₄ O ₈ Tb ₁
Formula weight	291.96 g/mole
Crystal system	Orthorhombic
Space-group	Pnma
Cell parameters	a = 7.0138(3) Å
	b = 10.6077(4) Å
	c = 6.66021(6) Å
•	90
•	90
•	90
V(Å ³)	491.198
D _c (g cm ⁻³)	3.948
Z	4

Table 2: Atomic parameters of compound 1

Atom	x/a	y/b	z/c
Tb1	0.20372(4)	0.13266(4)	0.25000(4)
O1	-0.0863(5)	0.1464(4)	0.1234(3)
O2	0.2361(5)	-0.0205(6)	0.4562(3)

materials provided by Aldrich. All materials were used as received without further purification. PXRD patterns for complex 1 was collected on (Empyrean, PANalytical V. V., 40 kV, 40 mA) diffractometer, using (Cu-Kα) (1.540598 Å) radiation in the angular range $2\theta = 5-80^\circ$. Single crystal X-ray data of 1 were collected at room temperature using OXFORD diffraction Rigaku. XtalABmin™ diffractometer. EA test was performed using an Elementar Vario Micro Cube EL *** elemental analyzer. Optical measurements were performed using pulsed laser He-Cd (325 nm) (Horiba Jobin Yvon) at room temperature.

Synthesis of Tb (C₂O₄)(HCOO): We prepared the title compounds was carried out in a Pyrex-lined steel bomb (autogenous pressure) at the temperature around 200 coover a period for a week, single crystals were obtained by heating an aqueous suspension of Tb oxalate decahydrate Tb₂(C₂O₄) 10 H₂O, 0.5 mmol of Tb oxalate decahydrate and 15 mmol of acid oxalic dihydrate in 10 mL of water for a week. By varying the heating time less or more than 7 days, it has been observed that no single crystals were developed. The final product, consisting of single crystals of compound 1 were recovered by filtration, washed with water and ethanol and then dried in air.

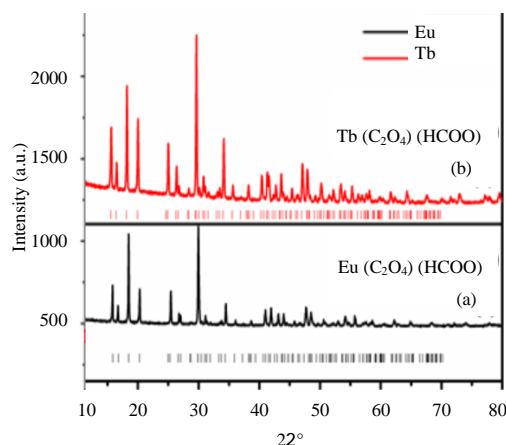
Structure determination: Table 1 and 2 present a summary of the crystal data, data collection and refinement parameters for the compound 1. Figure 2 shows the XRD pattern of the as-formed samples through hydrothermal method. Crystallographic data were collected with oxford diffraction Rigaku. XtalABmin™ diffractometer and all data indicates that the compounds Tb(C₂O₄)(HCOO) are pure and exhibited

Table 3: Selected geometric information of compound 1

Atoms	U ₁₁	U ₂₂	U ₃₃
Tb1	0.00933(16)	0.00875(14)	0.00791(16)
O1	0.0160(15)	0.0158(13)	0.0098(14)
O2	0.0164(15)	0.0294(18)	0.0162(17)
Atoms 1, 2	d 1, 2 [Å]	Atoms 1, 2	d 1, 2 [Å]
Tb1-O ₁ ⁱ	2.465(3)	Tb1-O ₃	2.493(4)
Tb1-O ₁ ⁱⁱ	2.491(3)	Tb1-O ₃ ⁱ	2.442(5)
Tb1-O ₁ ⁱⁱⁱ	2.465(3)	Tb1-O ₄	2.472(5)
Tb1-O ₁ ^{iv}	2.491(3)	O1-C ₂	1.274(5)
Tb1-O ₂ ⁱ	2.436(3)	O2-C ₂ ^v	1.238(5)
Tb1-O ₂	2.436(3)	C2-C ₂ ^{iv}	1.545(8)
Tb1-C ₂ ^{iv}	3.230(4)	O3-C ₃	1.293(7)
Tb1-C ₂ ^v	3.230(4)	C3-O ₄ ^{vi}	1.216(8)

Table 4: Selected bond length (Å) and angles (deg.) for compound 1

Atoms 1, 2, 3	Angle 1, 2, 3 [°]	Atoms 1, 2, 3	Angle 1, 2, 3 [°]
O ₁ ⁱⁱ -Tb1-O ₁	66.56(15)	O ₃ -Tb1-O ₁ ⁱ	76.57(11)
O ₁ ⁱⁱ -Tb1-O ₁	100.38(11)	O ₃ -Tb1-O ₂ ⁱⁱ	114.33(9)
O ₁ ⁱⁱ -Tb1-O ₁ ⁱ	100.38(11)	O ₃ ⁱ -Tb1-O ₂ ⁱⁱ	78.52(10)
O ₁ ⁱⁱⁱ -Tb1-O ₁ ⁱ	65.75(15)	O ₃ ⁱ -Tb1-O ₂	78.52(10)
O ₂ ⁱⁱ -Tb1-O ₁	66.32(11)	O ₃ -Tb1-O ₂	114.33(9)
O ₂ -Tb1-O ₁ ⁱ	72.49(12)	O ₃ -Tb1-C ₂ ^{iv}	102.14(9)
O ₂ -Tb1-O ₁ ⁱⁱⁱ	132.86(11)	O ₃ ⁱ -Tb1-C ₂ ^{iv}	97.88(9)
O ₂ ⁱⁱ -Tb1-O ₁ ⁱⁱⁱ	72.49(12)	O ₃ ⁱ -Tb1-C ₂ ^v	97.88(9)
O ₂ ⁱⁱ -Tb1-O ₁ ⁱ	132.86(11)	O ₃ -Tb1-C ₂ ^v	102.14(9)
O ₂ -Tb1-O ₁	126.17(12)	O ₄ -Tb1-O ₁	70.70(12)
O ₂ -Tb1-O ₁ ⁱⁱ	66.32(11)	O ₄ -Tb1-O ₁ ⁱⁱⁱ	142.29(9)
O ₂ ⁱⁱ -Tb1-O ₁ ⁱⁱ	126.17(12)	O ₄ -Tb1-O ₁ ⁱⁱ	70.70(12)
O ₂ ⁱⁱ -Tb1-O ₂	129.30(19)	O ₄ -Tb1-O ₁ ⁱ	142.29(9)
O ₃ ⁱ -Tb1-O ₁ ⁱ	64.80(11)	C ₂ ^{iv} -C ₂ -O ₁	115.1(5)
O ₃ ⁱ -Tb1-O ₁ ⁱⁱ	144.72(8)	C ₂ ^{iv} -C ₂ -O ₂ ^{vii}	118.7(5)
O ₃ ⁱ -Tb1-O ₁	144.72(8)	C ₃ -O ₃ -Tb1	122.3(4)
O ₃ -Tb1-O ₁ ⁱⁱ	64.46(10)	C ₃ -O ₃ -Tb1 ^{viii}	134.2(5)
O ₃ -Tb1-O ₁ ⁱⁱⁱ	76.57(11)	O ₄ ^{vi} -C ₃ -O ₃	125.6(7)
O ₃ ⁱ -Tb1-O ₁ ⁱⁱⁱ	64.80(11)	C ₃ ^{ix} -O ₄ -Eu1	129.0(5)
O ₃ -Tb1-O ₁	64.46(10)	-	-

Fig. 2: The PXRD patterns of the as-synthesized Tb(C₂O₄)(HCOO)

the peak of pure crystalline orthorhombic group Pnma (62) which was well consistent with the created CIF file (Xpert HIGH SCORE PLUS) as shown in Fig. 2. Crystallographics and the selected, bond lengths and angles are listed in Table 1-4.

RESULTS AND DISCUSSION

Structure description: In this research, the single crystal X-ray diffraction study revealed that compound 1 have asymmetric unit as illustrated in Fig. 1. It is also, observed that the structure of compound 1 is orthorhombic and it may be described in the following way. The structures of 1 is 3-D hybrid frameworks which are Pnma (62) space group. The dimensionality of its inorganic and organic connectivities are 1 and 2-D, respectively. The 1-D inorganic chains contain of 9 coordinated europium polyhedra that participate their faces to form infinite zigzag chains along the (100) direction. To form the 2-D organic connectivity, europium chains are bridged by formate ligands along the (010) direction to form infinite 2-D layers, nearby layers are subsequently bridged by the oxalate ligands along the (001) direction to make a 3-D framework structure.

Finally, the structures for the two compounds **1** is built up from Eu, Tb oxalate shared all their oxygen atoms with oxalate and formate ligands, thus take the shape of a 3D framework structure as shown in Fig. 1.

Luminescent property: Photoluminescence experiment results were measured using an excitation wavelength of the pulsed ultraviolet He-Cd laser 325 nm at room temperature. Notably compound 1 show emissions intensity in the range of 300-800 nm as displayed in Fig. 3. The emission spectra of compound 1 gave the characteristics of Tb^{3+} transitions, respectively. The resonance energy levels of terbium ions are presented in Table 5 along with the various luminescence transitions.

Figure 3 illustrates the photoluminescence spectra for compound 1, there are four very strong characteristic emission bands for the Tb^{3+} ion in the visible region. The spectrum is dominated by the major sharp peak at 544 nm due to $^5D_4 \rightarrow ^7F_5$ transition which give strong green emission as well as the other emission bands are: $^5D_4 \rightarrow ^7F_6$ at 486 nm and $^5D_4 \rightarrow ^7F_4$ at 583 nm and $^5D_4 \rightarrow ^7F_3$ at 620 nm, respectively. These transitions which are allowed by Electric Dipole (ED) and supersensitive to surrounding in the vicinity of Tb^{3+} ion, is very intense, emitting strong green luminescence (Bunzli *et al.*, 2007).

Symmetry operators:

$$\begin{aligned} &0.5+x, 0.5-y, 0.5-z, x, y, 0.5-z, 0.5+x, 0.5-y, z \\ &-x, -y, -z, -x, -y, 0.5+z, x, 1+y, z, -x, -y, -0.5+z \\ &-0.5+x, 0.5-y, 0.5-z, x, -1+y, z \end{aligned}$$

The PXRD patterns of the as-synthesized $Tb(C_2O_4)(HCOO)$ was shows in Fig. 2.

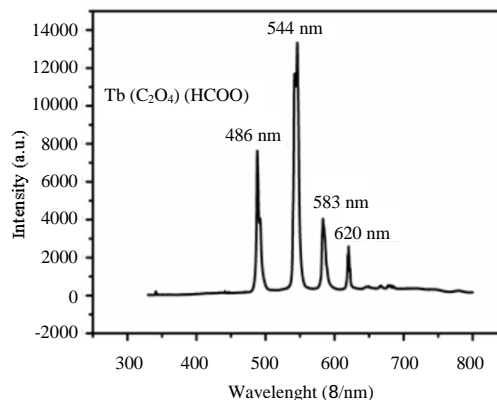


Fig. 3: PL spectra from compound of Tb compound

Table 5: Energy levels and luminescence transition for europium (18 and 19) and terbium (20)

Upper energy levels (energy cm^{-1})	Lower levels	• (nm)
$Tb^{3+}D_3(26250)$	$^7F_6, ^7F_5, ^7F_4, ^7F_3$	490, 545, 587, 622,
$^5D_4(20500)$	$^7F_6, ^7F_5, ^7F_4$	650, 671, 681

CONCLUSION

In the presented research, 3-D hybrid framework 1 was successfully prepared through hydrothermal method and characterized by SCPXRD. Single crystal structure of compound 1 has asymmetric unit and the spectrum of UV laser induced photoluminescence shows that compound 1 gave a strong strong green emission at 544 nm, respectively. Measurements indicate that the luminescence behavior demonstrates that Rare Earth Organic Framework (REOFs) of compound 1 has excellent potential application in solid state light, Field Emission Displays (FEDs).

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