

PHOTOLUMINESCENCE PROPERTIES OF Gd(III) AND Ce(III) LANTHANIDE BASED METAL ORGANIC FRAMEWORKS

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ABSTRACT

The Gd(III) and Ce(III) based-MOFs (metal organic frameworks) have been synthesized by hydrothermal method using 1,2,4,5-benzenetetracarboxylate (btcc) ligand and characterized by elemental analysis, FT-IR, UV-visible and single-crystal X-ray diffraction. The crystal structure analysis of Gd(III) complex [C₁₀H₉GdO₁₁] (**1**) and Ce (III) complex [C₁₀H₉CeO₉] (**2**) show that the central lanthanide ions are coordinated by nine oxygen atoms in which eight O atoms from btcc ligands and one O atom from water molecule for both structures. The nearest non-bonding Gd...Gd distance is 3.928 Å while Ce...Ce distance is 4.392 Å. Complex **1** and **2** bridged by oxygen atoms of btcc ligands are formed in 3D networks via strong hydrogen bonds. Additionally, solid state photoluminescence properties of **1** and **2** at room temperature have been investigated. Under the excitation of UV light, intense cyan-blue emission for complex **1** and blue emission for complex **2** are exhibited in the visible regions.

Keywords: Metal-Organic Frameworks, Lanthanide Complexes, Structural Analysis, Photoluminescence Properties

1. INTRODUCTION

In recent years, the design and synthesis of metal-organic frameworks (MOFs) as functional materials have been great deal of attention not only because of their interesting topologies, but also because of their potential applications in catalysis, gas storage, sensing, magnetism, molecular adsorption and drug delivery [1-9]. MOFs are porous materials in which metal ions or clusters are linked together by organic ligands containing N- or O-donors into 2D or 3D networks. Although there have been numerous studies on MOFs based on transition metals, lanthanide based metal organic frameworks (LnMOFs) have been quite limited [10-11]. The use of lanthanides in MOFs as metal centers is becoming quite popular in recent years due to these cations are associated with the comprising magnetism and photoluminescence, having higher coordination numbers than transition metals, their geometries and multidimensional structures leading to 2D or 3D networks [12-17]. In addition, hydrothermal synthesis technique is the most common and accomplished method to synthesis the lanthanide based porous materials [18, 19]. Although there have been numerous factors such as the structural characteristics of the ligands and metal ions, the presence of solvents, the metal-ligand ratio, the pH value and reaction temperature which play important roles to constructing the coordination polymers, the most effective way is to choose suitable organic ligands [20, 21]. The preparation of these LnMOFs can be controlled by the combination of the functionalities of the appropriate organic ligands containing N- or O-donor atoms and the geometrical preferences of the lanthanide ions [22].

In view of the importance of photoluminescence of the metal organic frameworks and our interest in the chemistry of coordination compounds involving lanthanide based complexes, two Ln⁺³ based MOFs [Ln = Gd (**1**), Ce (**2**)] have been synthesized under hydrothermal conditions with using btcc ligand. The crystal structure of complex **1** and complex **2** were previously reported at room temperature [23, 24].

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Herein, the crystal structures of complex **1** and complex **2** have been re-determined by single crystal X-ray diffraction analysis and characterized by infrared, UV-vis and photoluminescence properties of both complexes will report first time in this work.

2. EXPERIMENTAL

2.1. Materials and Instruments

Benzene-1,2,4,5-tetracarboxylic acid, $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ have been purchased from Aldrich Chemical Co. Elemental (C, H) analyses have been carried out by standard methods with a LECO, CHNS-932 analyzer. FT-IR spectra were measured with a Perkin-Elmer Spectrum 65 instrument in the range of $4000\text{--}600\text{ cm}^{-1}$. Solid state UV-visible spectra were measured at room temperature with an Ocean Optics Maya 2000Pro Spectrophotometer. Solid state luminescence spectra in the visible region were measured at room temperature with an ANDOR SR500i-BL Photoluminescence Spectrometer equipped with a triple grating and used an air-cooled CCD camera as detector. The measurements were done by using the excitation source (349 nm) of a Spectra-physics Nd:YLF laser with a 5 ns pulse width and 1.3 mJ of energy per pulse as the source.

2.2. Synthesis of Complex (1) [$\text{C}_{10}\text{H}_9\text{GdO}_{11}$]

Benzene-1,2,4,5-tetracarboxylic acid (btec) (1 mmol) were dissolved in 10 mL of distilled water and stirred for 30 min at room temperature. An aqueous solution of $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1 mmol) was added into the abovementioned solution. The reaction mixture was placed in a Parr-Teflon lined stainless steel vessel, sealed and heated at 120°C for 3 days, followed by slow cooling (5°C h^{-1}) to room temperature. After filtration and washing with H_2O , colorless crystals were collected and dried in air. Found: C, 25.62 %; H, 1.79 %. $\text{C}_{10}\text{H}_9\text{GdO}_{11}$; Calc.: C, 25.97 %; H, 1.96 %.

2.3. Synthesis of Complex (2) [$\text{C}_{10}\text{H}_5\text{CeO}_9$]

The mixture of aqueous solution of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (1 mmol) and benzene-1,2,4,5-tetracarboxylic acid (1 mmol) was sealed in a 23 mL Teflon-lined stainless steel container and heated at 120°C for 3 days. After the reactor was slowly cooled (5°C h^{-1}) to room temperature, colorless crystals of **2** were obtained. Found: C, 29.55 %; H, 1.34 %. $\text{C}_{10}\text{H}_5\text{CeO}_9$; Calc.: C, 29.34 %; H, 1.23 %.

2.4. X-ray Crystallography

Intensity data for suitable single crystals of **1** and **2** was collected using Oxford Diffraction Xcalibur-3 diffractometer equipped with a Mo K_α radiation source ($\lambda = 0.71073\text{ \AA}$ at 296 K). The data collections and data reductions were performed with the CRYCALIS CCD and CRYCALIS RED programs [25]. The structures were solved by direct methods and refined using full-matrix least-squares against F^2 using SHELXTL [26]. The crystallographic data for **1** and **2** is listed briefly in Table 1. Molecular drawings were obtained using MERCURY [27].

3. RESULTS AND DISCUSSION

3.1. Crystal Structure Description of (1)

The molecular structure of **1** with atom numbering scheme is given in Figure 1 and some selected bond lengths and angles are listed in Table 2. The X-ray structure analysis of complex **1** shows that each Gd(III) ion is nine-coordinated in which eight oxygen atoms from btec ligands with the Gd–O bond distances in the range of 2.344 (4)–2.572 (3) \AA and one oxygen atom from coordinated water molecule with the Gd–O bond distance of 2.368 (4) \AA . All bond distances and angles are comparable to similar structures [28-30]. The coordination environment around Gd(III) ion can be described as distorted monocapped square-antiprism geometry. As seen in Figure 1, the crystal structure of **1** has two crystallographically independent btec ligands which have inversion centre in the center of their

aromatic rings. In complex **1**, Gd(III) atoms have been connected by μ -oxo_{carboxylate} bridges from btc ligands to form 2D layers and these layers are further interlinked via strong O–H \cdots O hydrogen-bonding interactions resulting in 3D architecture (Figure 2).

Table 1. Crystal data and structure refinements for (1) and (2)

	1	2
Empirical formula	C ₁₀ H ₉ GdO ₁₁	C ₁₀ H ₅ CeO ₉
Formula weight	462.42 g.mol ⁻¹	409.26 g.mol ⁻¹
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1
Unit cell dimensions	a = 10.7224 (3) Å b = 7.1759 (2) Å c = 17.1658 (6) Å β = 97.183 (3)°	a = 6.4069 (5) Å b = 9.3878 (6) Å c = 9.5753 (7) Å α = 88.382 (6)° β = 74.534 (7)° γ = 76.699 (6)°
Volume	1310.42 (7) Å ³	539.84 (7) Å ³
Z	4	2
Density (calculated)	2.344 g.cm ⁻³	2.518 g.cm ⁻³
Absorption coefficient	5.12 mm ⁻¹	4.26 mm ⁻¹
θ range for data collection	3.4 to 25.7°	3.2 to 25.7°
Index ranges	-13 ≤ h ≤ 9, -8 ≤ k ≤ 4, -20 ≤ l ≤ 15	-7 ≤ h ≤ 7 -11 ≤ k ≤ 10 -6 ≤ l ≤ 11
Reflections collected	4138	2933
Independent reflections	2465 [R _{int} = 0.029]	2041 [R _{int} = 0.033]
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Goodness-of-fit on F ²	S = 1.10	S = 0.99
R indices [I > 2σ(I)]	R ₁ = 0.031, wR ₂ = 0.074	R ₁ = 0.036, wR ₂ = 0.056

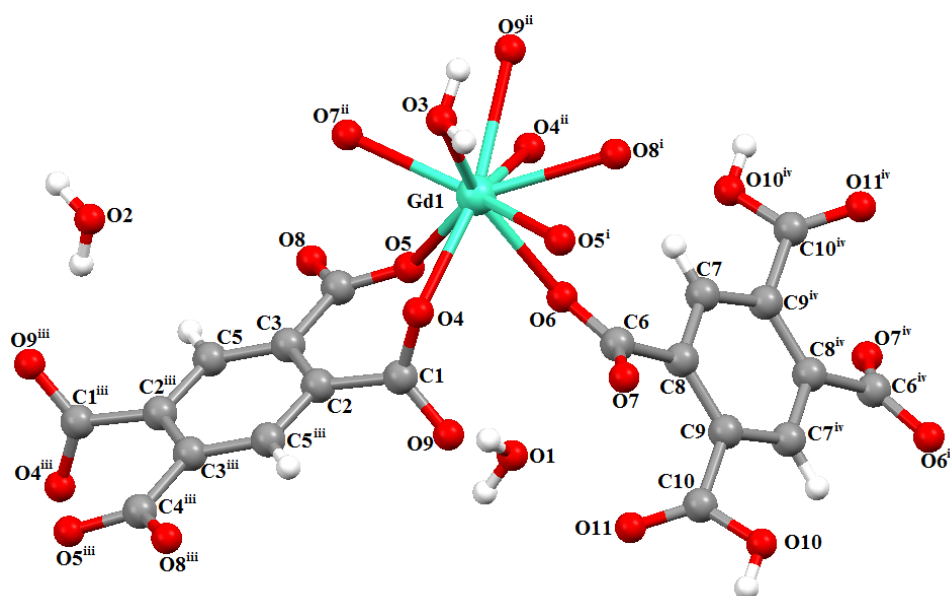


Figure 1. Part of the polymeric structure of complex **1**, showing the atom labelling scheme. [Symmetry code(s): (i) $-x+1/2, y+1/2, -z+1/2$; (ii) $-x+1/2, y-1/2, -z+1/2$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, -y+1, -z$.]

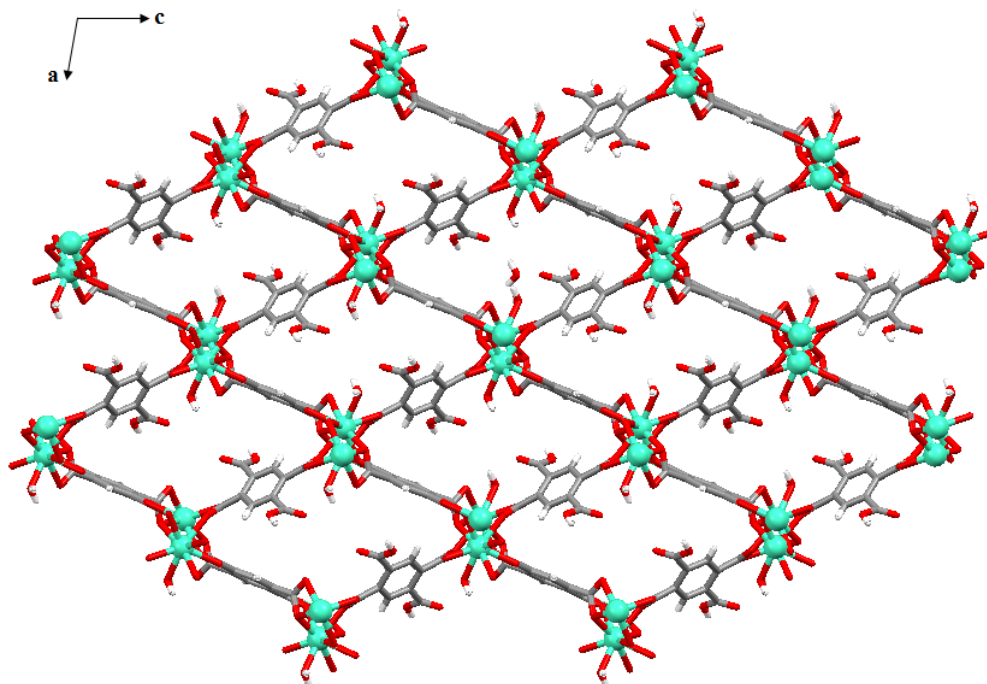


Figure 2. The molecular packing diagram of complex **1** in the *ac*-plane (H_2O molecules have been omitted for clarity)

Table 2. Some selected bond lengths [\AA] and angles [$^\circ$] for (**1**)

<i>Bond lengths</i> (\AA)			
Gd1–O3	2.368 (4)	Gd1–O6	2.344 (4)
Gd1–O4	2.367 (3)	Gd1–O7 ⁱⁱ	2.374 (4)
Gd1–O4 ⁱⁱ	2.484 (3)	Gd1–O8 ⁱ	2.478 (4)
Gd1–O5	2.417 (3)	Gd1–O9 ⁱⁱ	2.572 (3)
Gd1–O5 ⁱ	2.553 (3)		
<i>Bond Angles</i> ($^\circ$)			
O3–Gd1–O5	138.31 (15)	O6–Gd1–O5	70.68 (13)
O4–Gd1–O4 ⁱⁱ	139.39 (6)	O6–Gd1–O7 ⁱⁱ	143.71 (13)
O4–Gd1–O5	73.11 (11)	O7 ⁱⁱ –Gd1–O5	73.03 (12)
O4–Gd1–O9 ⁱⁱ	165.51 (12)	O7 ⁱⁱ –Gd1–O8 ⁱ	138.64 (13)
O5–Gd1–O5 ⁱ	133.43 (8)	O9 ⁱⁱ –Gd1–Gd1 ⁱ	148.89 (9)
O6–Gd1–O3	143.64 (14)	Gd1–O4–Gd1 ⁱ	108.10 (14)
O6–Gd1–O4	78.60 (13)	Gd1–O5–Gd1 ⁱⁱ	104.39 (12)

(Symmetry codes: (i) $-x+1/2, y+1/2, -z+1/2$; (ii) $-x+1/2, y-1/2, -z+1/2$)

3.2. Crystal Structure Description of (**2**)

The structure of complex **2** with atom numbering scheme is given in Figure 3. The X-ray structure analysis of complex **2** shows that each Ce(III) ion is coordinated by nine oxygen atoms in which eight from btec ligands with the Ce–O bond distances in the range of 2.407 (4)–2.642 (3) \AA and one from water molecule with the Ce–O bond distance of 2.476 (5) \AA . The shortest non-bonding Ce...Ce distance is 4.392 \AA . Some selected bond lengths and angles are listed in Table 3, which lie well within the range of reported values for corresponding bond lengths and angles of similar Ce(III) complexes [19, 31, 32]. Structural analysis shows that the polymeric chains of Ce(III) complex are linked with carboxylate oxygens of btec ligands to form 2D layer which lead to a 3D network via hydrogen bonding interactions (Figure 4).

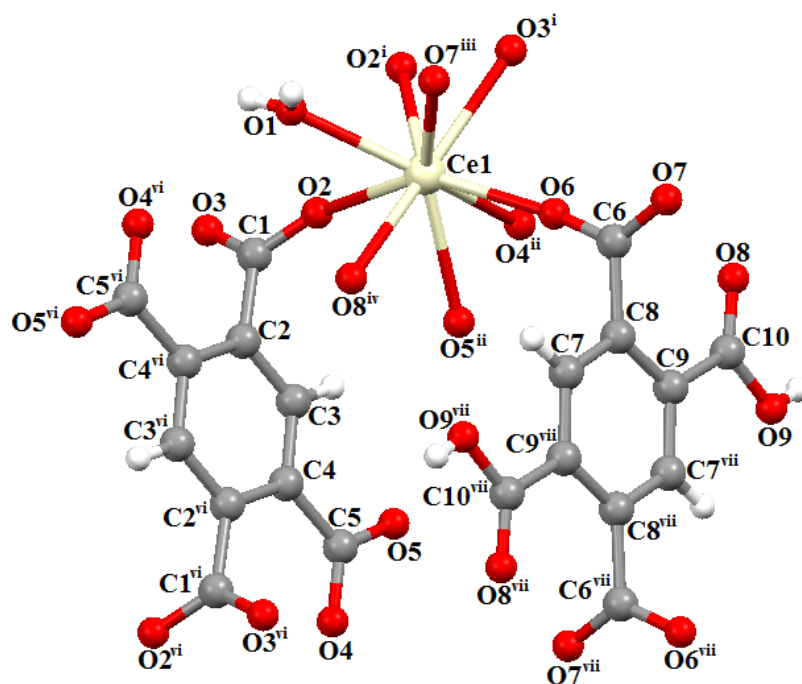


Figure 3. Part of the polymeric structure of complex **2**, showing the atom labelling scheme. [Symmetry code(s): (i) $-x+1, -y, -z+1$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+2, -y, -z$; (iv) $x-1, y, z$; (v) $x+1, y, z$; (vi) $-x, -y+1, -z+1$; (vii) $-x+2, -y+1, -z$.]

Table 3. Some selected bond lengths [\AA] and angles [$^\circ$] for (**2**)

<i>Bond lengths (\AA)</i>			
Ce1–O1	2.476 (5)	Ce1–O5 ⁱⁱ	2.571 (4)
Ce1–O2	2.642 (3)	Ce1–O6	2.407 (4)
Ce1–O2 ⁱ	2.524 (4)	Ce1–O7 ⁱⁱⁱ	2.456 (5)
Ce1–O3 ⁱ	2.534 (3)	Ce1–O8 ^{iv}	2.553 (4)
Ce1–O4 ⁱⁱ	2.589 (4)		
<i>Bond Angles ($^\circ$)</i>			
O1–Ce1–O2	70.26 (19)	O6–Ce1–O3 ⁱ	81.35 (12)
O1–Ce1–O3 ⁱ	102.48 (15)	O6–Ce1–O5 ⁱⁱ	72.38 (13)
O1–Ce1–O4 ⁱⁱ	145.99 (18)	O7 ⁱⁱⁱ –Ce1–O2	136.64 (12)
O1–Ce1–O5 ⁱⁱ	130.37 (17)	O7 ⁱⁱⁱ –Ce1–O3 ⁱ	72.54 (13)
O2–Ce1–O2 ⁱ	63.58 (13)	O7 ⁱⁱⁱ –Ce1–O5 ⁱⁱ	142.73 (13)
O2–Ce1–O3 ⁱ	112.88 (12)	O7 ⁱⁱⁱ –Ce1–O8 ^{iv}	88.18 (13)
O2–Ce1–O5 ⁱⁱ	73.19 (12)	O8 ^{iv} –Ce1–O2 ⁱ	143.19 (12)
O3 ⁱ –Ce1–O5 ⁱⁱ	122.29 (12)	O8 ^{iv} –Ce1–O4 ⁱⁱ	120.48 (12)
O3 ⁱ –Ce1–O8 ^{iv}	159.86 (15)	O8 ^{iv} –Ce1–O5 ⁱⁱ	70.37 (12)
O4 ⁱⁱ –Ce1–O2 ⁱ	74.68 (11)	O8 ^{iv} –Ce1–C1 ⁱ	162.74 (13)
O5 ⁱⁱ –Ce1–O2 ⁱ	114.15 (13)	O8 ^{iv} –Ce1–C5 ⁱⁱ	95.59 (13)
O6–Ce1–O1	140.2 (2)	C1 ⁱ –Ce1–C5 ⁱⁱ	98.93 (14)
O6–Ce1–O2	145.08 (13)	Ce1–O2–Ce1 ⁱ	116.42 (13)

[Symmetry code(s): (i) $-x+1, -y, -z+1$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+2, -y, -z$; (iv) $x-1, y, z$; (v) $x+1, y, z$; (vi) $-x, -y+1, -z+1$; (vii) $-x+2, -y+1, -z$.]

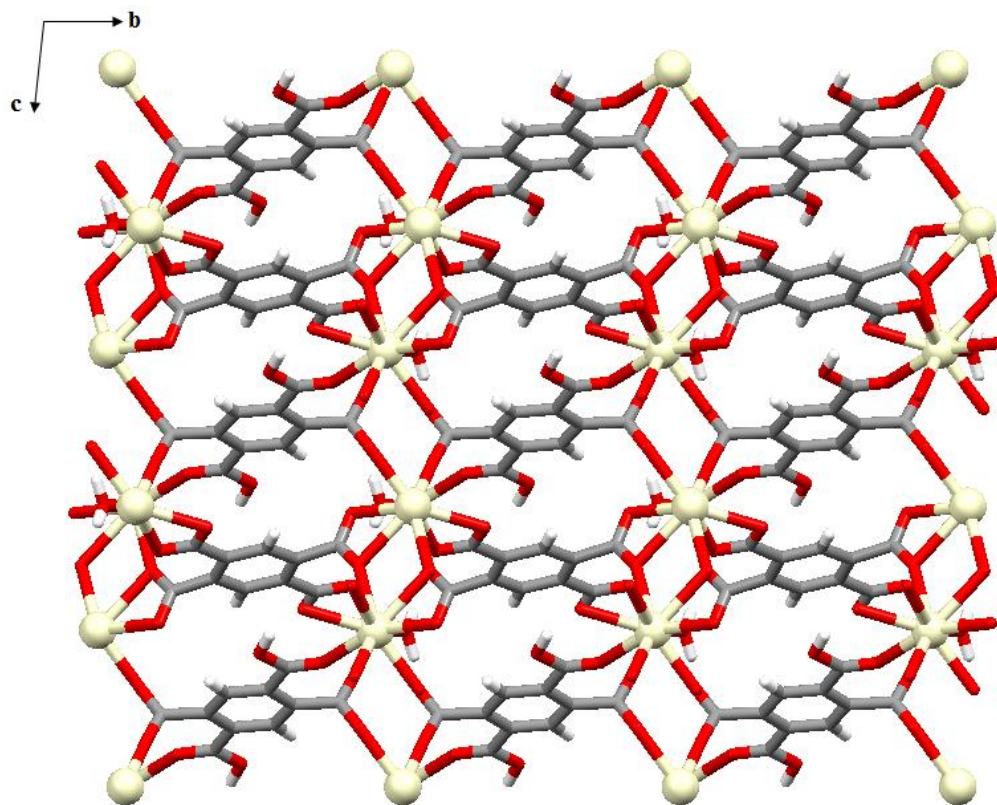


Figure 4. The molecular packing diagram of complex **2** in the *bc*-plane.

3.3. IR Spectra

The bands observed at 3400 cm^{-1} for complex **1** and 3122 cm^{-1} for complex **2** are attributed to the O–H stretching vibration of water molecules involved in extensive hydrogen bonding interactions [33]. The coordinated water also exhibits the frequencies of 655 cm^{-1} for complex **1** and 645 cm^{-1} for complex **2**, which are assigned to $\rho_r(\text{H}_2\text{O})$ [34]. The bands at 774 and 762 cm^{-1} are ascribed to O–Gd–O stretching and the harmonic frequencies of Gd–O are characteristic of 836 and 881 cm^{-1} . The observed bands at 755 and 773 cm^{-1} are assignable to the O–Ce–O stretching and the bands at 811 and 861 cm^{-1} are characteristic of Ce–O stretching vibration. The observed bands in the range of $1496\text{--}1657\text{ cm}^{-1}$ for complex **1** and $1525\text{--}1721\text{ cm}^{-1}$ for complex **2** are characteristics of carboxylic groups. Thus the infrared spectrums are found to be in good agreement with the x-ray structures of the complex **1** and **2**.

3.4 Photoluminescence Properties

The solid-state luminescent properties of the free btec ligand, complex **1** and complex **2** were investigated at room temperature in the visible regions upon excitation at $\lambda_{\text{ex}} = 349\text{ nm}$ (Figure 5). The free btec ligand shows broad emission bands at $\lambda_{\text{max}1} = 417\text{ nm}$ and $\lambda_{\text{max}2} = 504\text{ nm}$ which may be assigned to the $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ electronic transition intraligand charge transfer (ILCT) [35–37]. The emission spectrum of complex **1** indicates a wide band and intense cyan-blue emission with the maximum wavelength of 527 nm , while, two emission bands are observed of the btec ligand in the same region (Figure 5a). The metal centered (MC) electronic levels of Gd(III) are known to be located at 31000 cm^{-1} , which is well above the ligand-centered (LC) electronic levels of the btec ligand (see Figure 6). Thus, the first excited state ${}^6\text{P}_{7/2}$ of the Gd^{III} is too high to accept the energy from the triplet excited state of the btec ligand, therefore, the energy transfer from the btec ligand to the metal center

and the MC luminescence cannot be observed in complex **1**. The observed red shift of the emission maximum of complex **1** was considered to originate mainly from the influence of the coordination of the Gd(III) to the btec ligand [37-39]. In comparison of the other Gd(III) based polymers, the observed wide band emission for complex **1** is similar to the reported in literature previously [40, 41]. Complex **2** exhibits intense blue emission, and a broad band spectra can be observed from 350 to 600 nm with the maximum wavelength of 480 nm, while, two emission bands are observed of the btec ligand in the same region. The configuration of Ce(III) consist of two multiplets, the $^2F_{5/2}$ level of the ground state and the $^2F_{7/2}$ level of the excited state (see Figure 6). Mostly, the Ce(III) has a strong UV absorption [42] and may exhibit a broad band of luminescence in the blue spectral regions from the lowest crystal field level of the excited state $5d^1$ to the $^2F_{5/2}$ and $^2F_{7/2}$ levels of the ground configuration $4f^1$ [43]. So this blue emission for complex **2** may be attributed to the characteristic emission of $^2F_{5/2} \rightarrow ^2D_{3/2}$ transition of Ce(III) or combined effect of the ligand-centered (LC) fluorescence [41, 43]. In comparison of the other Ce(III) based polymers, the observed emission band for complex **2** is similar to the reported in literature previously [40, 41].

The Energy Transfer mechanism and energy level diagrams of Ce(III) and Gd(III) ions are shown in Figure 6. According to Latva's empirical rule, the suitable energy gap is $2500\text{-}4000\text{ cm}^{-1}$ for ligand to metal energy transfer process for lanthanide ions. For btec ligand, the singlet energy level (S_1) is 27000 cm^{-1} (371 nm) and the triplet lowest energy level is 24000 cm^{-1} (417 nm) (see Figure 5 and Figure 7). The energy gap $\Delta E (S_1-T_1)$ for the btec ligand is 3000 cm^{-1} . Thus, the intersystem crossing (ISC) is effective for the btec ligand [44]. For complex **2**, the experimentally observed (T_1) energy level of the btec ligand is 3200 cm^{-1} which is higher than the $^2D_{3/2}$ level of Ce(III) ion. This phenomenon indicates that the transition from the triplet energy level of the btec ligand to Ce(III) is effective.

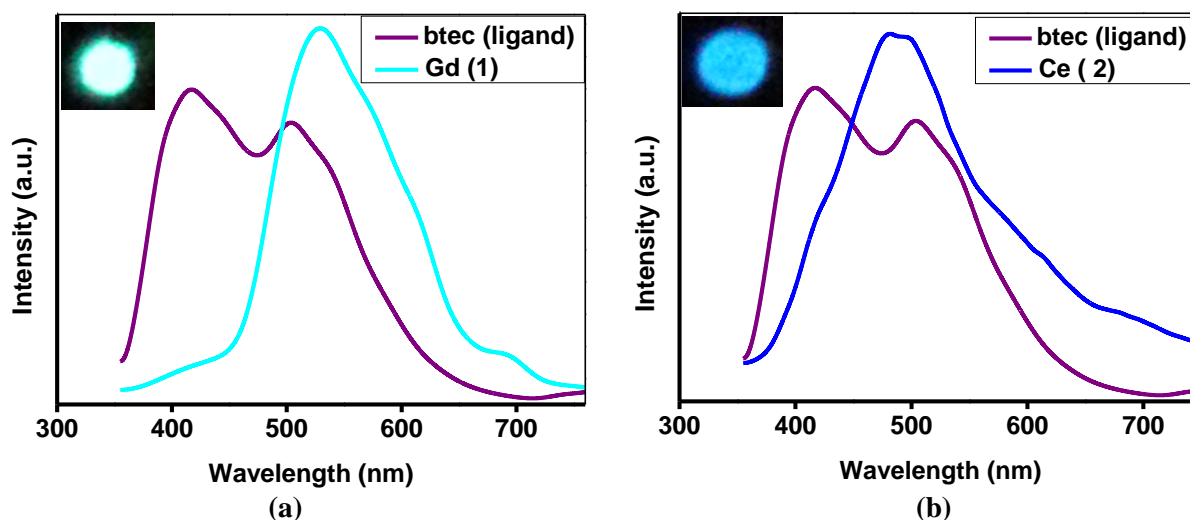


Figure 5. The emission spectrums of the free ligand (btec), complex **1** (upper) and complex **2** (bottom) in the solid samples at room temperature ($\lambda_{exc.} = 349\text{ nm}$).

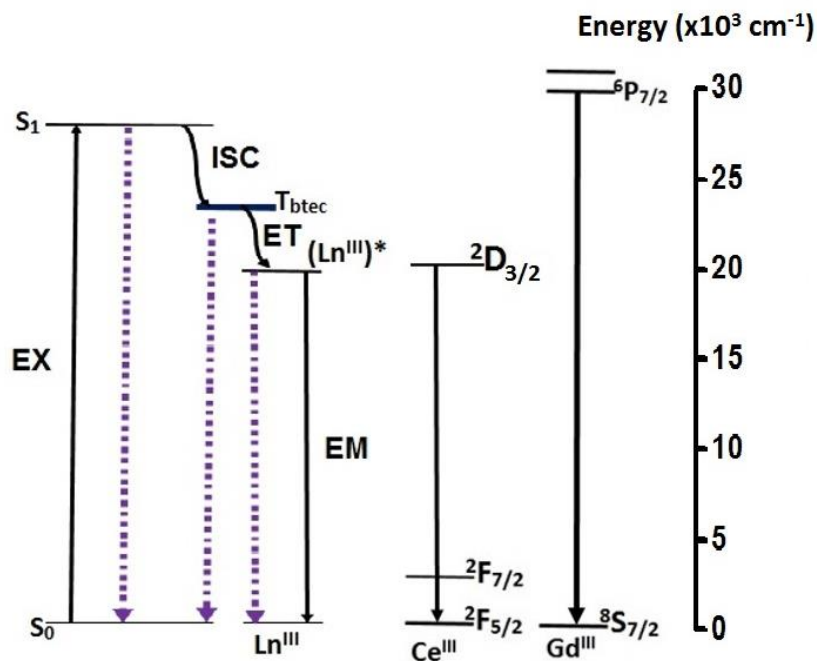


Figure 6. The Energy Transfer mechanism (left) and energy level diagrams of Ce(III) and Gd(III) ions (right)

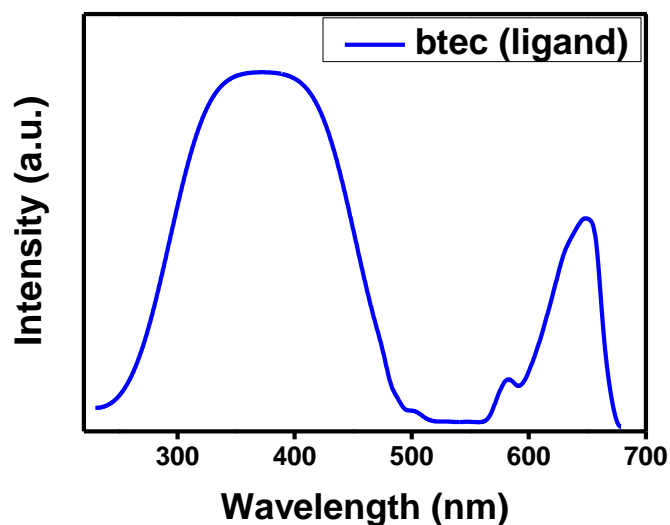


Figure 7. UV-Vis absorption spectrum of the btec ligand in solid state

4. CONCLUSIONS

Two Ln^{+3} based MOFs ($Ln = Gd, Ce$) have been synthesized successfully under hydrothermal conditions with using 1,2,4,5-benzenetetracarboxylate (btec) ligand. The crystal structures of these Ln-MOFs have been redetermined by single crystal X-ray diffraction analysis. And both complexes characterized by also elemental analysis, UV-Visible and infrared spectroscopy. Structural analysis of Gd(III) and Ce(III) complexes shows that each lanthanide ion is nine coordinated by oxygen atoms of btec ligands. For both complexes, Gd(III) and Ce(III) lanthanide ions are bridged by μ -OXO_{carboxylate}

oxygens from btec ligands to form polymeric chains which lead to 2D layers. And these layers are further interlinked via strong hydrogen bonding interactions resulting in 3D networks. In accordance with the main purpose of this study, solid-state luminescent properties have been investigated at room temperature for btec ligand, complex **1** and **2**. The solid-state photoluminescence measurements display intense cyan-blue emission for complex **1** and blue emission for complex **2** in the visible regions.

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SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1486497 for complex **1** and 1486498 for complex **2**. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).