doi:10.20944/preprints201811.0244.v1

Article

Synthesis, structure and luminescence property of a 3D coordination polymer based on La(III) and terephthalic acid

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Abstract: One new La (III) based coordination polymer , namely, [La(1,4-bdc)(H_2O)].(H_2O) (**1**) (tpa = terephthalic acid) has been synthesized through the solvothermal synthesis using terephthalic acid. Structural analysis reveals that compound **1** has a 3-D network with a cube topology. The solid state photolumienescence study shows that compound **1** has a strong emission peak at 680 nm upon excitation at 220 nm . The emission peak is characteristic of the red light emission in the visible region of the electromagnetic spectrum.

Keywords: polymers; terephthalic acid; solvothermal; crystal structure; topology; photoluminescence

1. Introduction

Metal organic frameworks (MOFs) are remarkable class of hybrid organic-inorganic compounds, synthesised from the coordination of metal ions or clusters with organic ligands [1-2]. These crystalline or hybrid organic-inorganic compounds have received great research interest because of their functional properties and potential applications in numerous scientific fields such as gas adsorption/delivery, catalysis, magnetism, luminescent materials, drug delivery, etc [3-5]. The properties of MOFs are related to their structure topology; however, the structure of the MOFs can be affected and get distorted by many factors, thus the control synthesis to obtain MOFs with desired structures and properties is always challenging [6]. In this study, we focus on the design, synthesis and characterisation of coordination polymers from terephthalic acid and lanthanum metal atom. This is because the terephthalic acid ligand can be used as the building block in the construction of MOFs or coordination polymers architectures of various sizes and shapes [7]. The coordination polymers having 2D or 3D structures with high surface area, chemical stability, thermal stability and acceptable voids have wide applications in selective separations, sensing, luminescence and hosting of guest molecules [8]. Carboxylates ligands form stable MOFs, thus the use of rigid organic ligands such carboxylates make it possible to predict the structure of the MOFs. This is because these types of organic ligands can chelate the metal ion and lock them into the M-O-C clusters [9]. The advantage of using rigid organic ligands is more on the outcome of often forming MOFs with permanent porosity. Terephthalic acid ligand will be used because is one type of carboxylates with various coordination modes, thus it can coordinate metal ions to form rigid and multidimensional structures [10-13]. The choice of using terephthalic acid ligand for MOFs or coordination polymer synthesis is also based on the practical evidence that it can be used to tune the luminescence property and generate permanent porous nature in MOFs [14]. This occurs because carboxylates ligands often possess a C_2 symmetry, which makes it possible to synthesise porous MOFs with highly ordered networks. The metal ions can be coordinated in different forms with the carboxylates, hence different structures and topologies can be obtained. This makes it easy to tune the luminescence property of MOFs [15].

The synthesis of MOFs has been done using transition metals such as Zn^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Cu^{2+}, lanthanide ions, etc [16]. In this study, we have chosen the La^{3+} metal ion for the construction of a coordination polymer. The selection of lanthanum metal ion in this study is because this metal ion belongs to the lanthanide ions. The lanthanide ions have good luminescence property, and this is supported by them showing increased brightness and high emission quantum yield [17]. The coordination of La with the organic ligands, particularly 1,4-benzenedicarboxylate (1,4-bdc) is because this organic ligand plays a major role in determining the final structure and topology of the MOF. Its geometry and nature are suitable for coordinating it with metal ions such as lanthanides. The La cation has affinity for the carboxylate oxygen atoms found in 1,4-benzenedicarboxylate [18-20].

2. Experimental section

2.1 Solvothermal synthesis

1,4-benzenedicarboxyate (0.033 g, 0.2 mmol) and $LaCl_3.7H_2O$ (0.08 g, 0.2 mmol) were added to a mixture of water (10.0 mL) and acetonitrile (2.0 mL) and stirred for few minutes. The resultant solution was heated at 160^0C in a feflon lined 23 mL stainless steel autoclave for over three days. The resulted colourless crystals were collected by filtration and washed with distilled water. Colourless block-shaped single crystals were obtained. FT-IR (KBr pellet, cm^{-1}): 3424.57 (1b), 1609.20 (s), 1583.72 (s), 1526.92 (s), 1504.03 (s), 1310.57 (s).

2.2 Single Crystal X-Ray Diffraction Studies

Single crystal X-ray diffraction data of complex **1** was collected on a Bruker SMART APEX2 area detector diffractometer. A suitable crystal of 0.22 x 0.16 x 0.12 mm^3 was selected and mounted on a MITIGEN holder in paratone of the diffractometer. To ensure an appropriate capture of data, the crystal was kept at a steady temperature of 100(2) K during data collection, using a Bruker SMART APEX2 area detector diffractometer. The data was measured with ω and ϕ scans using MoK_α radiation. The maximum resolution that was achieved was $\Theta = 28.219^{\circ}$ (0.75 Å). The structure was solved using Charge Flipping program and refined by least squares using ShelXL. The positions of all atoms were measured by direct methods. All non-hydrogen atoms were refined anisotropically. In X-ray diffraction, the measurements depend upon the presence of electron density, that are derived from an atom. The heavy atoms possess more electron density; thus, they have more effect on the diffraction pattern. A heavy metal ion such as lanthanum also play a role in diffracting the X-rays. During the radiation, constructive interference is obtained when electromagnetic radiation wave with wavelength comparable to the space between atoms are radiated upon a crystalline sample. This makes the X-rays to be scattered in a specular fashion by the atoms present in the complex [21].

2.3 Infrared spectrum

The IR data were collected at room temperature using FTIR Perkin Elmer 1000 Spectrometer from KBr pellets. The spectrum was collected over the range 4000-400 cm^{-1} by averaging 16 scans at a maximum resolution of 5 cm^{-1}.

2.4 Thermal analysis

The Perkin Elmer TGA was used for the thermal analysis in nitrogen dynamic atmosphere at a heating rate of 10^0C/min. The sample was heated from 50^0C to 1000^0C, whereby the temperature was held for 5 minutes at 1000^0C.

2.5 Photoluminescence Studies

Room temperature excitation and emission spectrum was measured using a Perkin Elmer LS 55 Fluorescence spectrometer. The sample was placed between two quartz plates such that the angle between the sample holder, incident beam and the detector is 45^0 degrees. The sample was excited at 220 nm. The optical image of the sample was obtained upon excitation at 220 nm and detection at 680 nm

by using an automated optical microscope Olympus CAST2 for transmission and fluorescence studies equipped with a motorized stage and a high-resolution digital camera.

3. Results

3.1 Description of the Crystal Structures

The coordination polymer **1** crystallizes in the triclinic *P*-1 space group as revealed by single-crystal X-ray diffraction studies. The crystallographic and structural refinement are presented in Table 1. Table 2 shows selected bond lengths and angles for coordination polymer **1**.

Table A1: Crystal data, data collection and refinement details of coordination polymer **1.**

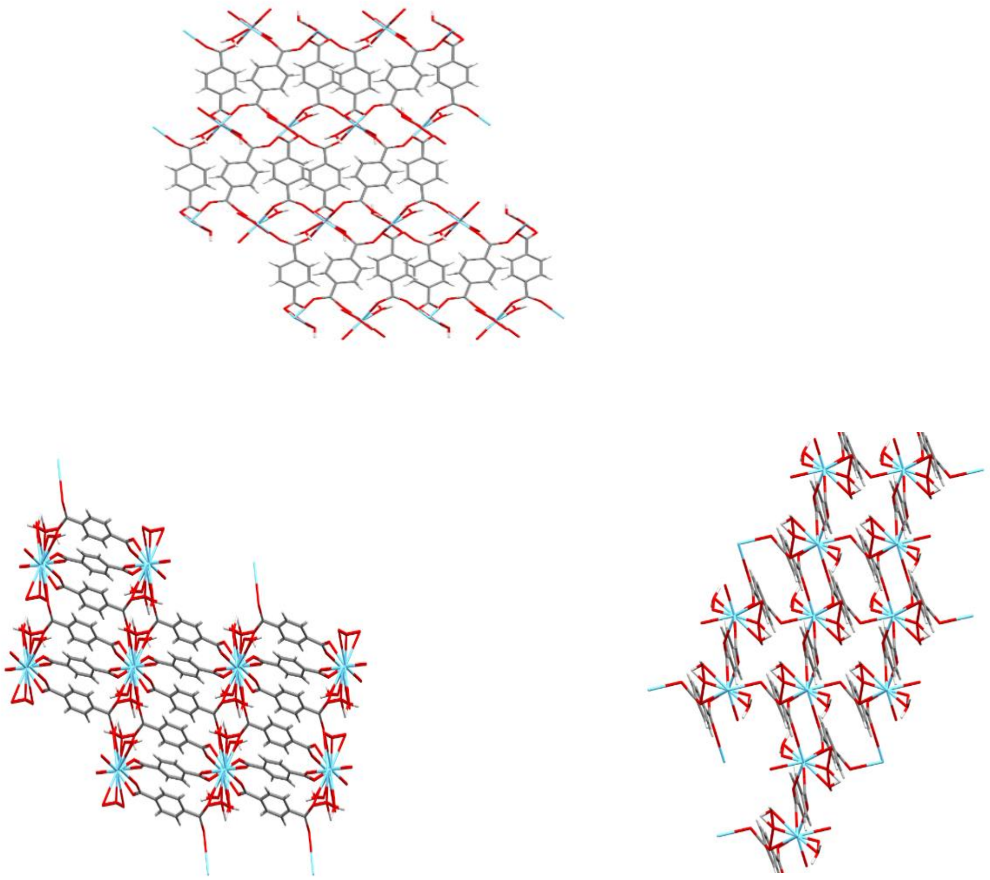
Compound	**[La(1,4-bdc)(H_2O)]**
Empirical formula	$C_{12}H_{10}LaO_{10}$
Formula weight	454.50 g/mol
T/K	100
Wavelength/Ǻ	0.71073
Space group	P-1
Crystal system	Triclinic
a/Ǻ	6.2160(6)
b/Ǻ	10.2282(9)
c/Ǻ	10.2529(9)
α/°	102.613(4)
β/°	101.956(5)
γ/°	91.727(4)
V/Ǻ3	620.39(10)
Z	2

Z’	1
Radiation type	MoKα
Θmin/°	2.086
Θmin/°	28.219
Measured Refl.	2792
Independent Refl.	2792
Reflections with I>	2067
Parameters	96
Restrains	0
Largest peak	5.942
Deepest hole	-7.471
GooF	1.297
wR2(all data)	0.3216
wR2	0.3157
R1(all data)	0.1434
R1	0.1240

Table A2: Selected bond lengths (Å) and angles (°) for coordination polymer **1**.

La-O1	**2.364**	**O-La-O2**	**141.9**
La-O1	**2.364**	**O1-La-O3**	**68.7 (6)**
La-O1AA	**2.424**	**O1-La-O1AA**	**95.4 (6)**
La-O3	**2.621**	**O1-La-O5**	**142.4 (6)**
La-O3AA	**2.429**	**O2-La-O5**	**131.9 (5)**
La-O5	**2.592**	**O3AA-La-O3**	**74.9 (6)**
		O3-La-O1	**141.4 (6)**
		O3-La-O5	**74.1 (6)**
		O1AA-La-O3	**143.5 (6)**
		O1AA-La-O5	**72.9 (5)**
		O5-La-O3	**138.9 (4)**

The single crystal structural analysis reveals that compound **1** crystallizes in a triclinic system with the space group *P*-1. The symmetric unit of **1** contains one crystallography independent La(III) metal ion, one 1,4-bdc and one coordinated water molecule. The crystal data and refinement details are presented in table 1. As shown in scheme 1, three coordination sites of 1,4-bdc namely monodentate-, bidentate chelating- and bidentate bridging modes are involved in bonding with La(III) ions. The X-ray diffraction structural analysis of **1** reveals that La(III) atoms are in the square antiprismatic coordination environments. It is coordinated to ten oxygen atoms. As shown in figure 1b, ten coordination sites of a La(III) atom are occupied by ten oxygen atoms.



(a)

(b) (c)

Figure A1: Three-dimensional structure of **1** projected along (**a**) a-axis, (**b**) b-axis and (**c**) c-axis. Where red sticks indicate oxygen atoms, blue balls indicate La(III) atoms and grey balls indicate hydrogen atoms.

3.2 IR Analysis

The FT-IR revealed the following absorption bands for coordination polymer 1. A broad absorption band is observed at 3424.57 cm^{-1}, it shows the presence of the O-H band stretching vibrations of the guest solvent molecules (H_2O). The characteristic bands for the assymetric (v(COO)asym) and symmetric stretching vibrations (v(COO)sym) of the carboxylate groups showed up at 1310 cm^{-1}, which is within 1210-1320 cm^{-1} region. The medium absorption bands which appear in the region 1400-1600 specify the presence of the C=C stretching vibrations.

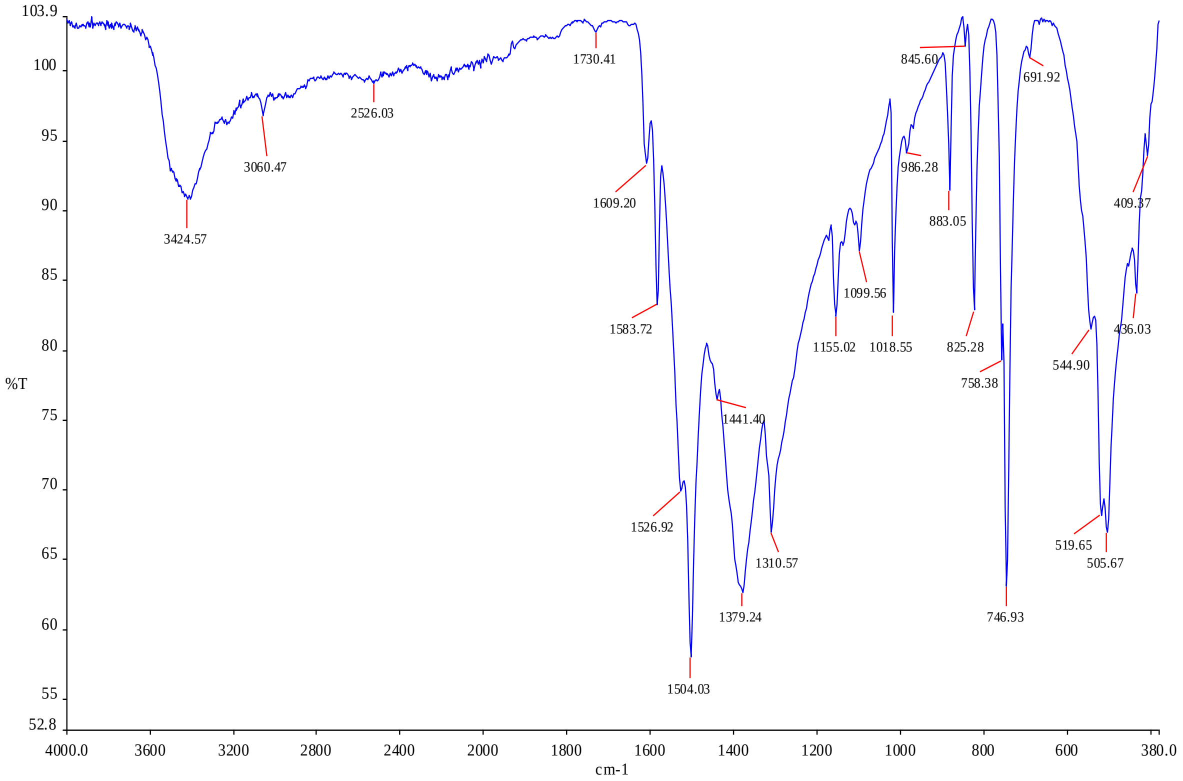


Figure A2: The IR spectrum of [La(1,4-bdc)(H_2O)]H_2O (**1**).

3.3 Thermal Analysis

To evaluate the thermal stability of compound **1**, TGA was carried out in the temperature range of 48.4-100.4^{0}C under N_2 gas flow with a heating rate of 10^{0}C/min. The thermogravimetric analysis (TGA) is conducted to assess the purity of the coordination polymer and to determine the maximum temperature at which the coordination polymer retains its thermal stability. The blue line indicates the TGA of the sample while the red line indicates the differential scanning calorimetry (DSC). DSC is a thermoanalytical technique, it measures the difference in the amount of heat required to increase the temperature of a sample and a reference material. The difference in the amount of heat is measured as a function of temperature. The thermogram show two steps of weight losses, the first one is a minor weight loss and the second one is a major weight loss. The first weight loss which is a minor loss occurred in the temperature range of 150^{0}C to 230^{0}C. The second weight loss which is a major loss occurred in the temperature range of 510^{0}C to 700^{0}C. The first weight loss occurred is approximately 8% and is due to the loss of water molecules. The second weight loss occurred is approximately 53.35% and is due to the loss of 1,4-bdc together with the lanthanum ions. This metal-organic part makes the largest weight percent of the whole coordination polymer. The TGA results reveals that the framework is thermal stable up 700^{0}C. The framework wok stability is in the temperature range of 510^{0}C to 700^{0}C. Beyond this temperature range all the water molecules were removed and the metal-organic component started to collapse.

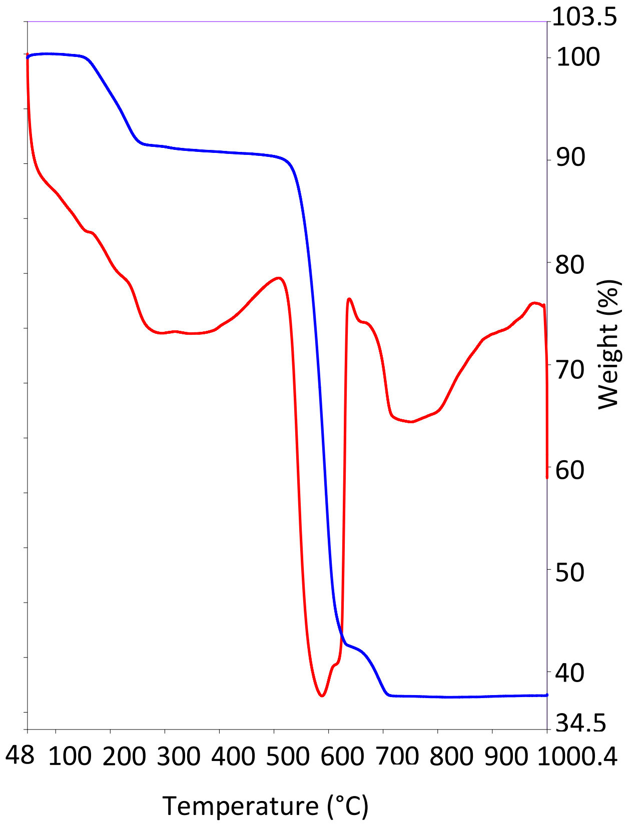
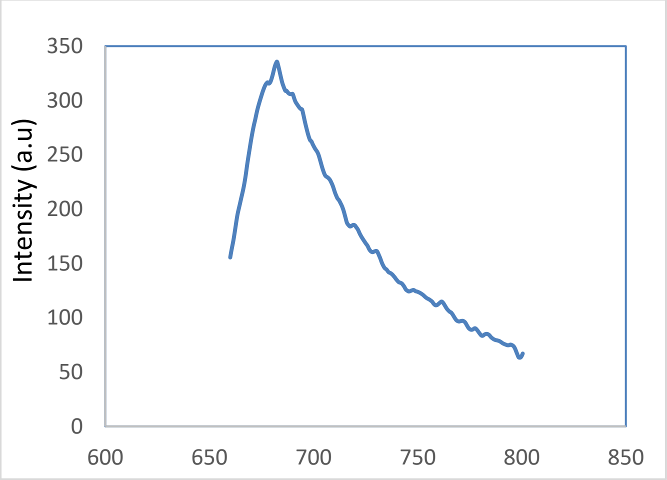


Figure A3: TGA scans of [La(1,4-bdc)(H_2O)]H_2O (**1**).

3.4 Photoluminescence Properties

The solid phase photoluminescence of the [La(1,4-bdc)(H_2O)].(H_2O) compound was conducted. The photoluminescence properties of the coordination polymers were studied at room temperature. The coordination polymer was excited at 220 nm and showed a strong emission peak at 680 nm. Upon excitation the atoms of the coordination polymers emit a red light in the visible region of the electromagnetic spectrum. Lanthanides are known for their good luminescence, Tb^{3+} and Eu^{3+} are part of the lanthanides and show intense luminescence due to them having high quantum yield. There are few studies that have been done on coordination polymers or MOFs having lanthanum as a metal center. This is due to the electron configuration $3d^{10}$ $4f^0$ of lanthanum which prevent a metal-ligand charge transfer from occurring. At this point the organic ligand terephthalic acid acted as the source of luminescence. This coordination polymer has a linker-based luminescence. This occurred because lanthanum has a filled d-orbital, which prevent any d-d transition from occurring. Unlike Tb^{3+} and Eu^{3+}, these two metal atoms have some vacant spaces in their d-orbitals. Meaning that they can absorb photons of energy, thus they have high quantum yield. These two metal atoms are more luminous. The luminescence obtained from this coordination polymer was due to the organic ligand. Since lanthanum has a filled d-orbital, it does not accept electrons into this orbital and thus it didn't take part in the absorption process. The photons of light were absorbed by terephthalic acid through its p-orbitals of the aromatic carbon atoms, thus it ended up having highest occupied valence orbitals and gave a strong emission peak.



Wavelength (nm)

Figure A4: Emission spectrum of [La(1,4-bdc)(H_2O)]H_2O (**1**) (excited at 220 nm).

4. Conclusions

The synthesis of a La(III) coordination polymer was achieved. It was done through the solvothermal method using terephthalic acid as a linker. Structural analysis reveals that compound 1 has a 3-D network with a cube topology. All the SBU units show the square antiprismatic geometry. The solid-state photoluminescence study was carried, it revealed that coordination polymer **1** has a strong luminescence peak which is characteristic of the red-light emission in the visible region of the electromagnetic spectrum.

Author Contributions: S.B. Jonnalagadda purchased the chemicals and assisted with the characterisation of the samples and S.B. Chule did the synthesis and wrote the manuscript.

Funding: This research was funded by the National Research Foundation, grant number: 104819.

Acknowledgments: S.B. Chule conveys the gratitude to the National Research Foundation for financial support.

Conflicts of Interest: The authors declare no conflict of interest.

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Sample Availability: The sample of the compound is available from the authors.