Three Novel Lanthanide Metal-Organic Frameworks (Ln-MOFs) Constructed by Unsymmetrical Aromatic Dicarboxylic Tectonics: Synthesis, Crystal Structures and Luminescent Properties

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Abstract: Three novel Ln(III)-based coordination polymers, [{[Ln2 (2,4-bpda)3 (H2O)]yH2O}n (Ln = La (III) (1), x = 2, y = 0, Ce (III) (2), Pr (III) (3), x = 4, y = 1) (2,4-H2bpda = benzophenone-2,4-dicarboxylic acid) have been prepared via a solvothermal method and characterized by elemental analysis, IR, and single-crystal X-ray diffraction techniques. Complex 1 exhibits a 3D complicated framework with a new 2-nodal (3,7)-connected (4^2·5) (4^4·5^1·6^6·8) topology. Complexes 2 and 3 are isomorphous, and feature a 3D 4-connected (6^3·8)-CdSO4 network. Moreover, solid-state properties such as thermal stabilities and luminescent properties of 1 and 2 were also investigated. Complex 1 crystallized in a monoclinic space group P21/c with a = 14.800 (3), b = 14.500 (3), c = 18.800 (4) Å, β = 91.00 (3), V = 4033.9 (14) Å³ and Z = 4. Complex 2 crystallized in a monoclinic space group Cc with a = 13.5432 (4), b = 12.9981 (4), c = 25.7567 (11) Å, β = 104.028 (4), V = 1374.16 (7) Å³ and Z = 4.

Keywords: Ln (III) coordination polymers; crystal structure; topology; luminescent properties
1. Introduction

Lanthanide metal-organic frameworks (Ln-MOFs) have attracted ever-increasing interest not only because of their intriguing structural diversity, but also due to special photophysical properties [1–4]. However, due to their high coordination numbers and mutable coordination geometries, the assembly of lanthanide coordination polymers with specific geometry and properties might be uncontrollable [5], so designing and controlling lanthanide metal-organic frameworks (Ln-MOFs) with presupposed topological networks and functions remains a difficult and challenging task. According to the latest CCDC research (version 5.35), a number of aromatic multicarboxylate ligands such as benzene-dicarboxylate, benzenetricarboxylate, benzenetetracarboxylate, etc. have been extensively used to assemble fascinating structures with luminescent and atypical magnetic properties [6–8].

Among the various aromatic carboxylate ligands, rigid phenyl-, biphenyl- or polyphenyl-carboxylates with π-conjugated systems have been more extensively employed to provide a great variety of topological architectures with desired properties due to their remarkable versatile coordination modes [9,10]. By contrast, organic carboxylates with specific geometric configurations are poorly studied. More recently, we have focused on unsymmetrical semirigid aromatic dicarboxylatic ligand benzophenone-2,4-dicarboxylic acid (2,4-H₂bpda) to construct new coordination polymers with different structures and properties. The ligand benzophenone-2,4-dicarboxylic acid (2,4-H₂bpda) could freely bend and rotate to meet the requirements of coordination geometries of metal ions in the assembly process [11]. To our knowledge, so far no more than twenty examples of transition metal coordination polymers based on the 2,4-H₂bpda ligand have been reported [11–16], and no Ln (III)-bpda coordination polymers have been synthesized and researched. However, the lanthanide cations exhibit different characteristic photoluminescent emissions in the ultraviolet or visible region. Herein, we report the synthesis, crystal structure of three new Ln (III)-based coordination polymers, \([\text{Ln}_2 (2,4-\text{bpda})_3 (\text{H}_2\text{O})_2] \cdot \text{yH}_2\text{O}\) \(\text{n} (\text{Ln}=\text{La (III) (1)}, x = 2, \text{y} = 0, \text{Ce (III) (2)}, \text{Pr (III) (3)}, x = 4, \text{y} = 1, ) (2,4-\text{H}^2\text{bpda} = \text{benzophenone-2,4-dicarboxylic acid}).\) Moreover, the thermogravimetric analysis and luminescent properties of 1 and 2 were also discussed.

2. Results and Discussion

2.1. Crystal Structure Descriptions

2.1.1. Structure of \([\text{La}_2 (2,4-\text{bpda})_3 (\text{H}_2\text{O})_2] \cdot \text{yH}_2\text{O}\) \(\text{n} (\text{1})\)

X-ray diffraction analysis reveals that 1 is a new 3D 2-nodal (3,7)-connected topological network based on infinite \([\text{La}_2(\text{COO})_4(\text{H}_2\text{O})_2]\) chain SBUs. The asymmetric unit of 1 contains two crystallographically independent La (III) ion, three fully deprotonated 2,4-bpda\(^{2-}\) ligands and two coordinated water molecules. As shown in Figure 1, the La1 (III) is nine-coordinated by eight O atoms from six 2,4-bpda\(^{2-}\) carboxylate groups and one O atom from a coordinated water molecule, forming a distorted monocapped squareantiprism geometry. The La2 (III) is of a distorted bicapped triangle prism geometry surrounding by seven O atoms of six 2,4-bpda ligands and one O atom of one coordinated water molecule. The La-O bond distances range from 2.401 (3) to 2.689 (2) Å and the
O-La-O bond angle varies from 48.81 (7) to 153.75 (8). These bond lengths and angles all are comparable with those reported in the La$^{3+}$-carboxylate compounds [17].

**Figure 1.** The coordination environment of La (III) center of 1. Symmetry codes, A: $-x$, $-y + 2$, $-z$; B: $-x$, $-y + 1$, $-z$; C: $-x$, $y + 1/2$, $-z + 1/2$; D: $-x + 1$, $-y + 1$, $-z$; E: $-x + 1$, $y + 1/2$, $-z + 1/2$. All H atoms are omitted for clarity.

It is noted that three crystallographically independent 2,4-bpda ligands display three different coordination modes: $\mu_4$-$\eta^1$-$\eta^1$-$\eta^1$ (Type A, Figure 2A) and $\mu_5$-$\eta^1$-$\eta^2$-$\eta^1$ (Type B, Figure 2B) and $\mu_6$-$\eta^1$-$\eta^2$-$\eta^1$-$\eta^1$ (Type C, Figure 2C), respectively. In 1, the interlinkage between La (III) ions and carboxylate groups of bpda$^{2-}$ generates an infinite La-carboxylate chain along the c axis (Figure 3a). Finally, these chains are extended by different oriented 2,4-bpda ligands to generate a complicated 3D frameworks (Figure 3b). Topologically, if binuclear [La$_2$ (COO)$_4$ (H$_2$O)$_2$] unit is considered as a 7-connected node, the type B and type C 2,4-bpda ligands are viewed as a linker and the type A 2,4-bpda ligands are viewed as 3-connected nodes. Hence, the structure of 1 can be best regarded as a new 2-nodal (3,7)-connected topology with a point symbol of (4$^2$·5) (4$^4$·5$^1$·6$^6$·8) (Figure 3c).

**Figure 2.** The coordination modes of 2,4-H$_2$bpda ligand in complexes 1–3. A $\mu_4$-$\eta^1$-$\eta^1$-$\eta^1$ mode; B $\mu_5$-$\eta^1$-$\eta^2$-$\eta^1$ mode; C $\mu_6$-$\eta^1$-$\eta^2$-$\eta^1$-$\eta^1$ mode; D $\mu_2$-$\eta^2$-$\eta^2$ mode.
Figure 3. (a) View of the 1D \([\text{La}_2\text{(COO)}_4\text{(H}_2\text{O})_2]\) chain SBUs along the \(c\) axis; (b) View of the complicated 3D framework of 1 along the \(b\) axis. All H atoms are omitted for clarity; (c) Schematic description of a new 2-nodal (3,7)-connected topology with a point symbol of \((4^2\cdot 5)\ (4^4\cdot 5^1\cdot 6^1\cdot 8)\), constructed from the 3-connected 2,4-H\_2bpda\(^2^-\) and 7-connected binuclear La\(_2\) nodes (green: 2,4-H\_2bpda\(^2^-\) pink: La\(_2\) nodes).

2.1.2. Structure of \([\text{Ce}_2\text{(2,4-bpda)}_3\text{(H}_2\text{O})_4]\)·\(\text{H}_2\text{O}\)_\(n\) (2)

The complex 2 and 3 are isostructural and feature similar 3D framework; herein, only the structure of 2 will be discussed in detailed as a representation. X-ray crystallography reveals that complex 2 is of the monoclinic \(Cc\) space group. The asymmetric unit of 2 contains two Ce (III) ions, three 2,4-bpda ligand, two coordinated water molecules and one free water molecule. Similar to complex 1, the central Ce (III) ions have analogous coordination numbers. As shown in Figure 4, the eight-coordinated Ce1 (III) ion is distorted bicapped triangle prism geometry, which is completed by five carboxylic O atoms (O1, O2, O7, O9, O12, O14) from five 2,4-bpda\(^2^-\) liands, two water oxygen atoms (O16 and O17) of coordinated water molecule. The La2 (III) shows is of a distorted bicapped triangle prism geometry \([\text{CeO}_9]\), which is ligated by seven oxygen atoms from five 2,4-bpda\(^2^-\) liands and two water oxygen atoms of coordinated water molecule. The coordination Ce-O bonds, varying from 2.344 (3) to 2.608 (3) Å, are within the reported results [18].
Figure 4. The coordination environment of Ce (III) center of 2. Symmetry codes, A: x + 1/2, −y + 1/2, z + 1/2; B: x + 1/2, y + 1/2, z; C: x − 1/2, y − 1/2, z. All H atoms are omitted for clarity.

Although there are three different coordination modes in complex 2, different from complex 1, one new coordination mode $\mu_2$-$\eta^2$-$\eta^2$ (Type D, Figure 2D) was found. The two carboxylates of independent 2,4-bpda ligands adopt $\mu_2$-$\eta^2$-$\eta^2$ and $\mu_2$-$\eta^2$-$\eta^2$ coordination modes and link two Ce$^{3+}$ centers to form a 1D [Ce$_2$ (COO)$_2$] binuclear chain SBUs with the Ce-Ce separation of 4.217 Å (Figure 5a). Each binuclear SBU is coordinated by six 2,4-bpda ligands through the bidentate bridging, bidentate chelating, and monodentate coordination modes. Moreover, the 1D [Ce$_2$ (COO)$_2$] binuclear chain were extended in a 2D wave-like layer structure in the $bc$ plane (Figure 5b). Finally, three kinds of 2,4-bpda ligands (type A, type B and type D) bridge adjacent four binuclear SBUs, which resulted in the complicated 3D networks (Figure 5c). From the view of topology, the [Ce$_2$ (COO)$_2$] binuclear SBUs can be simplified as 4-connected nodes and the 2,4-bpda ligands are viewed as a linker. And the whole framework forms a uninodal 4-connected CdSO$_4$ net with the point symbol (6$^5$·8) (Figure 5d).

Figure 5. (a) View of the 1D [Ce$_2$ (COO)$_2$] binuclear chain SBUs in the $ab$ plane; (b) The 2D wave-like layer structure in the $bc$ plane; (c) View of the complicated 3D framework of 2 along the $b$ axis. All H atoms are omitted for clarity; (d) Schematic description of the uninodal 4-connected (6$^5$·8) CdSO$_4$ topology, constructed from the 4-connected Ce$_2$ node (pink: Ce$_2$ nodes).
2.2. Luminescent Properties

The solid-state fluorescent properties of complexes 1 and 2 at room temperature are shown in Figure 6. Complexes 1 and 2 display a fluorescent emission at around 471 nm ($\lambda_{ex} = 421$ nm) and 439 nm ($\lambda_{ex} = 344$ nm), respectively. As for the free organic ligands, a weak emission is observed at 394 nm ($\lambda_{ex} = 280$ nm) [14]. The crystal-field splitting of the 5d orbital was not observed in the two complexes because of the high coordination number of Ln (III) ions [17]. The emission spectra of complexes 1 and 2 are similar to that of the free 2,4-H$_2$bpda ligand, indicating that the fluorescence of these two complexes is a ligand-based emission [19]. Compared with the free 2,4-H$_2$bpda, the emission peaks of 1 and 2 have a visible red shift and their intensity is also increased, which could be due to intraligand $\pi$-$\pi^*$ or n-n* electron transitions [20]. The obvious enhanced intensities of complexes 1 and 2 could be attributed to the increased rigidity of the ligand after coordination to the Ln (III) center, which effectively reduced the loss of energy [21].
**Figure 6.** Fluorescence excitation and emission spectra of 1 (a) and 2 (b) in the solid state at room temperature. \( \lambda_{\text{ex}} = 421 \text{ nm}, \lambda_{\text{em}} = 471 \text{ nm} \) for 1; \( \lambda_{\text{ex}} = 344 \text{ nm}, \lambda_{\text{em}} = 439 \text{ nm} \) for 2.

**2.3. Thermogravimetric Analysis**

Thermogravimetric analyses (TGA) were monitored to observe the thermal behavior of complexes 1 and 2 (Figure 7). Complexes 1 and 2 showed similar thermal decomposition processes. Therefore, only the patterns of 1 will be discussed as an example. The first weight loss of 3.25% in the range of 50–150 °C is related to the loss of two coordinated water molecules (Calc. 3.22%). The residue is stable up to about 200 °C. After 300 °C, the network of 1 gradually collapses corresponding to the decomposition of organic components and the remaining residue is lanthanum oxide.

**Figure 7. (a,b)** Thermogravimetric curve of complexes 1 and 2.
3. Experimental

3.1. Materials and Physical Measurements

The inorganic salts and organic regents were commercially available and used as supplied without further purification. The ligand benzophenone-2,4-dicarboxylic acid (2,4-H₂bpda) was obtained from Alfa Aesar China Co. Ltd. (Beijing, China) and used as received. Elemental analysis for C and H were performed on a GmbH VarioEL V3.00 automatic elemental analyzer. The FT-IR spectra were recorded as KBr pellets with a Thermo Electron NEXUS FT-IR spectrometer in the 4000–400 cm⁻¹ region. Thermogravimetric analysis was recorded with a NETZSCH STA 449C microanalyzer in air at a heating rate of 10 °C·min⁻¹. Luminescence spectra for the solid samples were recorded with a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

3.2. Synthesis of Complexes 1–3

Single-crystal samples of complexes 1–3 suitable for X-ray analysis were obtained by a similar method to that described for complex 1.

\[\text{[La}_2(2,4\text{-bpda})_3(\text{H}_2\text{O})_2]\_n \ (1).\] A mixture of La (NO₃)₂·6H₂O (0.0866 g, 0.2 mmol), 2,4-H₂bpda (0.0268 g, 0.1 mmol), oxalic acid (0.0090 g, 0.1 mmol), NaOH (0.5 mL, 0.1 mol/L) and H₂O (8 mL) was stirred under air atmosphere for 15 min and then sealed in a 25 mL Teflon-lined stainless steel vessel. After heating for 96 h at 160 °C, then the reaction system was cooled to room temperature and yellow block crystals of 1 were collected by filtration, washed with water and dried in air. Yield: 55%. Anal. Calc. for C₄₅H₂₈O₁₇La₂: C, 48.32; H, 2.52%; Found: C, 48.35; H, 2.50%. IR (KBr, cm⁻¹) 3415 m, 3020 m, 1715 s, 1583 s, 1525 s, 1420 s, 1229 s, 1135 s, 847 m, 783 m, 725 m, 635 m.

\[\text{[Ce}_2(2,4\text{-Bpda})_3(\text{H}_2\text{O})_4]\_n\text{·H}_2\text{O} \ (2).\] This complex was prepared in a similar method to that of 1 except for the fact La (NO₃)₂·6H₂O was replaced by an equivalent molar quantity of Ce (NO₃)₂·6H₂O. Yield: 52%. Anal. Calc. for C₄₅H₃₄O₂₀Ce₂: C, 46.00; H, 2.92%; Found: C, 45.85; H, 2.90%. IR (KBr, cm⁻¹) 3425 m, 3012 m, 1735 s, 1573 s, 1521 s, 1415 s, 1218 s, 1145 s, 830 m, 775 m, 710 m, 621 m.

\[\text{[Pr}_2(2,4\text{-bpda})_3(\text{H}_2\text{O})_4]\_n\text{·H}_2\text{O} \ (3).\] This complex was prepared in a similar method to that of 1 except for the fact the La (NO₃)₂·6H₂O was replaced by an equivalent molar quantity of Pr (NO₃)₂·6H₂O. Yield: 48%. Anal. Calc. for C₄₅H₃₂O₂₀Pr₂: C, 46.02; H, 2.75%; Found: C, 46.05; H, 2.78%. IR (KBr, cm⁻¹) 3410 m, 1725 s, 3018 m, 1580 s, 1519 w, 1425 s, 1225 s, 1120 s, 845 m, 785 m, 730 m, 627 m.

3.3. X-ray Crystallography

Single crystal X-ray diffraction analysis of 1–3 were collected on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated MoKR radiation (λ = 0.71073 Å) by using φ/ω scan technique at 296 (2) K. The structures were solved by direct methods with SHELXS-97 [22]. A full-matrix least-squares refinement on F² was carried out using SHELXL-97 [22]. Absorption corrections were applied by using multi-scan program SADABS [23]. The hydrogen atoms were
assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. Generally, the positions of C/N-bound H atoms were generated by a riding model on idealized geometries. The H atoms of coordinated water molecules of 1 and 2 were first located in difference Fourier maps, and then fixed in the calculated sites as riding. For 3, the lattice water molecule was located at the special position and the affiliated H atoms were not determined. The crystallographic data and selected bond lengths and angles for 1 and 2 are listed in Tables 1 and 2.

Table 1. Crystal data and structure refinement parameters for complexes 1–3.

|                | 1                   | 2                   | 3                   |
|----------------|---------------------|---------------------|---------------------|
| Empirical formula | C_{45}H_{28}O_{17}La_{2} | C_{45}H_{34}O_{20}Ce_{2} | C_{45}H_{32}O_{20}Pr_{2} |
| Formula weight  | 1118.49             | 1174.96             | 1174.53             |
| Temperature     | 293 (2) K           | 293 (2) K           | 293 (2) K           |
| Wavelength      | 0.71073             | 0.71073             | 0.71073             |
| Crystal system  | Monoclinic P21/c    | Monoclinic Cc       | Monoclinic Cc       |
| a (Å)           | 14.800 (3)          | 13.5432 (4)        | 13.533 (3)          |
| b (Å)           | 14.500 (3)          | 12.9981 (4)        | 12.990 (3)          |
| c (Å)           | 18.800 (4)          | 25.7567 (11)       | 25.768 (5)          |
| α (°)           | 90                  | 90                  | 90                  |
| β (°)           | 91.00 (3)           | 104.028 (4)        | 104.22 (3)          |
| γ (°)           | 90                  | 90                  | 90                  |
| Volume (Å³)     | 4033.9 (14)         | 4398.9 (3)         | 4391.3 (15)         |
| Calculated density (Mg·m⁻³) | 4.1,842          | 4.1,774            | 4.1,777             |
| Absorption coeff. (mm⁻¹) | 2.170           | 2.127              | 2.276               |
| F (000)         | 2192                | 2320                | 2320                |
| Crystal size (mm) | 0.20 × 0.17 × 0.14 | 0.32 × 0.27 × 0.23 | 0.50 × 0.35 × 0.30 |
| θ range for data collection (°) | 3.01–25.43         | 3.00–25.50          | 3.11–25.05          |
| Limiting indices |                    |                     |                     |
| reflections collected/unique | 37806/7406     | 9876/6116           | 19982/7245          |
| [R (int) = 0.0341] |                     |                     |                     |
| Max. and min. transmission | 0.7509 and 0.6707 | 0.6405 and 0.5493  | 0.505 and 0.400     |
| Refinement method | Full-matrix least-squares on F² | Full-matrix least-squares on F² | Full-matrix least-squares on F² |
| data/restraints/parameters | 7406/0/577       | 6116/11/605         | 7245/11/617         |
| Goodness-of-fit on F² | 1.079            | 1.196               | 1.010               |
| R1, wR2 [I > 2sigma (I)] | 0.0280, 0.0616   | 0.0552, 0.1341     | 0.0245, 0.0578      |
| R indices (all data) | 0.0316, 0.0635   | 0.0568, 0.1350     | 0.0255, 0.0589      |
| Largest diff. peak and hole e.Å⁻³ | 0.963, −0.658    | 1.971, −2.656      | 0.837, −0.539       |

a R₁ = Σ(|Fₐ| − |Fₓ|)/Σ|Fₐ|; b wR₂ = [Σw(F_o² − F_c²)²]/Σw(F_o²).
Table 2. Selected bond lengths (Å) and bond angles (°) for complexes 1–3.

|       | 1         | 2         | 3         |
|-------|-----------|-----------|-----------|
| La1-O8B | 2.404 (2) | Ce1-O14C  | 2.417 (13) Pr1-O1 | 2.454 (3) |
| La1-O13D | 2.480 (2) | Ce1-O7    | 2.457 (12) Pr1-O3A | 2.441 (4) |
| La1-O7 | 2.487 (2) | Ce1-O16   | 2.504 (11) Pr1-O6 | 2.417 (3) |
| La1-O3A | 2.498 (2) | Ce1-O1    | 2.572 (12) Pr1-O9B | 2.408 (3) |
| La1-O1  | 2.582 (2) | Ce2-O8B   | 2.416 (10) Pr1-O14C | 2.479 (4) |
| La1-O12 | 2.577 (3) | Ce2-O11   | 2.506 (11) Pr1-O13C | 2.551 (4) |
| La1-O16 | 2.630 (3) | Ce2-O4A   | 2.526 (12) Pr1-O16 | 2.505 (3) |
| La1-O2  | 2.689 (2) | Ce2-O19   | 2.561 (11) Pr1-O17 | 2.557 (4) |
| La1-O11 | 2.688 (2) | Ce2-O12   | 2.866 (10) Pr2-O2 | 2.429 (3) |
| La2-O9C | 2.402 (3) | O4-Ce2    | 2.526 (12) Pr2-O4A | 2.414 (3) |
| La2-O4A | 2.410 (2) | O9-Ce1C   | 2.501 (12) Pr2-O6 | 2.822 (4) |
| La2-O14E | 2.434 (2) | O14-Ce1B  | 2.417 (13) Pr2-O7 | 2.478 (3) |
| La2-O6 | 2.454 (2) | Ce1-O12   | 2.427 (10) Pr2-O8B | 2.514 (4) |
| La2-O17 | 2.560 (3) | Ce1-O9B   | 2.501 (12) Pr2-O11 | 2.529 (3) |
| La2-O2 | 2.560 (2) | Ce1-O2    | 2.516 (12) Pr2-O12 | 2.529 (3) |
| La2-O15 | 2.586 (2) | Ce1-O17   | 2.595 (13) Pr2-O18 | 2.548 (3) |
| La2-O11 | 2.605 (2) | Ce2-O6    | 2.455 (12) Pr2-O19 | 2.566 (4) |
| O3-La1A | 2.498 (2) | Ce2-O13C  | 2.506 (13) O3-Pr1B | 2.441 (4) |
| O4-La2A | 2.410 (2) | Ce2-O3A   | 2.531 (12) O4-Pr2B | 2.413 (4) |
| O8-La1B | 2.404 (2) | Ce2-O18   | 2.592 (12) O8-Pr2A | 2.514 (4) |
| O9-La2 | 2.401 (3) | O3-Ce2    | 2.531 (12) O9-Pr1A | 2.408 (3) |
| O13-La1D | 2.480 (2) | O8-Ce2C   | 2.416 (10) O13-Pr1 | 2.551 (4) |
| O14-La2 | 2.434 (2) | O13-Ce2B  | 2.506 (13) O14-Pr1 | 2.479 (4) |
| O8B-La1-O13D | 74.76 (8) | O14C-Ce1-O12 | 73.3 (4) | O9B-Pr1-O6 | 72.48 (12) |
| O8B-La1-O7 | 146.86 (8) | O12-Ce1-O7 | 122.2 (3) | O9B-Pr1-O3A | 129.47 (11) |
| O13D-La1-O7 | 78.79 (8) | O12-Ce1-O9B | 79.9 (4) | O6-Pr1-O3A | 79.60 (12) |
| O8B-La1-O3A | 81.85 (8) | O14C-Ce1-O16 | 141.7 (4) | O9B-Pr1-O1 | 79.78 (13) |
| O13D-La1-O3A | 134.34 (9) | O7-Ce1-O16 | 74.4 (4) | O6-Pr1-O1 | 120.74 (11) |
| O7-La1-O3A | 131.28 (8) | O14C-Ce1-O2 | 86.7 (4) | O3A-Pr1-O1 | 79.62 (12) |
| O8B-La1-O1 | 79.13 (8) | O7-Ce1-O2 | 127.0 (4) | O9B-Pr1-O14C | 85.92 (14) |
| O13D-La1-O1 | 136.64 (9) | O16-Ce1-O2 | 86.8 (4) | O6-Pr1-O14C | 101.32 (12) |
| O7-La1-O1 | 108.27 (8) | O12-Ce1-O1 | 143.8 (4) | O3A-Pr1-O14C | 141.37 (13) |
| O3A-La1-O1 | 73.37 (8) | O9B-Ce1-O1 | 136.3 (4) | O1-Pr1-O14C | 127.98 (12) |
| O8B-La1-O12 | 96.35 (8) | O2-Ce1-O1 | 51.6 (4) | O9B-Pr1-O16 | 142.41 (12) |
| O13D-La1-O12 | 70.19 (9) | O12-Ce1-O17 | 76.7 (4) | O6-Pr1-O16 | 144.93 (12) |
| O7-La1-O12 | 93.10 (9) | O9B-Ce1-O17 | 74.7 (4) | O3A-Pr1-O16 | 72.64 (12) |
| O3A-La1-O12 | 74.20 (9) | O2-Ce1-O17 | 67.7 (4) | O1-Pr1-O16 | 75.11 (13) |
| O1-La1-O12 | 147.57 (9) | O8B-Ce2-O6 | 72.7 (4) | O14C-Pr1-O16 | 87.92 (14) |
| O8B-La1-O16 | 81.94 (9) | O6-Ce2-O11 | 124.3 (4) | O9B-Pr1-O13C | 80.67 (13) |
| O13D-La1-O16 | 75.75 (10) | O6-Ce2-O13C | 76.3 (4) | O6-Pr1-O13C | 143.48 (13) |
| O7-La1-O16 | 72.39 (9) | O8B-Ce2-O4A | 124.4 (4) | O3A-Pr1-O13C | 136.89 (12) |
| O3A-La1-O16 | 139.01 (9) | O11-Ce2-O4A | 144.2 (4) | O1-Pr1-O13C | 76.74 (12) |
| O1-La1-O16 | 66.71 (9) | O8B-Ce2-O3A | 73.5 (4) | O14C-Pr1-O13C | 51.56 (12) |
| O12-La1-O16 | 145.04 (10) | O11-Ce2-O3A | 129.3 (4) | O16-Pr1-O13C | 66.72 (13) |
| 1          | 2                | 3     |
|------------|------------------|-------|
| O8B-La1-O2 | 126.76 (8)       | O9B-Pr1-O17 134.60 (12) |
| O13D-La1-O2| 151.47 (7)       | O6-Pr1-O17 77.37 (13)   |
| O7-La1-O2  | 73.89 (7)        | O3A-Pr1-O17 75.22 (12)  |
| O3A-La1-O2 | 72.31 (8)        | O1-Pr1-O17 145.56 (13)  |
| O1-La1-O2  | 49.39 (7)        | O14C-Pr1-O17 67.54 (13) |
| O12-La1-O2 | 118.90 (7)       | O16-Pr1-O17 75.18 (13)  |
| O16-La1-O2 | 88.15 (9)        | O13C-Pr1-O17 106.65 (13)|
| O8B-La1-O11| 139.67 (8)       | O3A-Pr2-O2 73.30 (12)   |
| O13D-La1-O11| 104.25 (9)     | O4A-Pr2-O7 76.62 (13)   |
| O7-La1-O11 | 66.45 (8)        | O2-Pr2-O7 124.40 (11)   |
| O3A-La1-O11| 70.41 (8)        | O19-Pr2-O8B 131.44 (11) |
| O1-La1-O11 | 117.95 (7)       | O14C-Pr2-O8B 76.60 (12) |
| O12-La1-O11| 48.81 (7)        | O4A-Pr2-O8B 90.55 (13)  |
| O16-La1-O11| 137.79 (9)       | O7-Pr2-O12 124.23 (12)  |
| O2-La1-O11 | 72.19 (7)        | O12-Pr2-O12 91.50 (12)  |
| O9C-La2-O4A| 80.18 (10)       | O2-Pr2-O12 143.72 (12)  |
| O9C-La2-O14E| 76.44 (9)       | O12-Pr2-O12 93.42 (11)  |
| O4A-La2-O14E| 87.56 (9)       | O4A-Pr2-O11 73.29 (11)  |
| O9C-La2-O6 | 121.04 (8)       | O2-Pr2-O11 82.69 (12)   |
| O4A-La2-O6 | 132.95 (8)       | O7-Pr2-O11 130.43 (13)  |
| O14E-La2-O6| 135.64 (8)       | O8B-Pr2-O11 138.60 (12) |
| O9C-La2-O17| 80.18 (10)       | O12-Pr2-O11 51.38 (11)  |
| O4A-La2-O17| 158.67 (9)       | O12-Pr2-O17 142.50 (12) |
| O14E-La2-O17| 76.06 (9)       | O16-Pr2-O17 141.79 (12) |
| O6-La2-O17 | 67.47 (8)        | O16-Pr2-O17 76.60 (11)  |
| O9C-La2-O2 | 80.49 (8)        | O11-Pr2-O17 143.72 (12) |
| O4A-La2-O2 | 76.23 (9)        | O2-Pr2-O17 91.50 (12)   |
| O14E-La2-O2| 153.75 (8)       | O2-Pr2-O17 141.79 (12)  |
| O6-La2-O2 | 68.07 (7)        | O2-Pr2-O17 141.79 (12)  |
| O17-La2-O2 | 113.38 (9)       | O2-Pr2-O17 141.79 (12)  |
| O9C-La2-O15| 145.33 (8)       | O2-Pr2-O17 69.81 (12)   |
| O4A-La2-O15| 108.74 (10)      | O2-Pr2-O17 137.33 (13)  |
| O14E-La2-O15| 70.72 (8)       | O8B-Pr2-O17 67.90 (11)  |
| O6-La2-O15 | 78.08 (8)        | O12-Pr2-O17 67.90 (11)  |
| O17-La2-O15| 78.93 (10)       | O12-Pr2-O17 67.90 (11)  |
| O2-La2-O15 | 133.91 (7)       | O8B-Pr2-O17 71.46 (11)  |
| O9C-La2-O11| 70.99 (9)        | O4A-Pr2-O6 48.17 (10)   |
| O14E-La2-O11| 146.07 (8)     | O2-Pr2-O6 78.07 (11)    |
| O4A-La2-O11| 70.99 (9)        | O2-Pr2-O6 78.07 (11)    |
| O14E-La2-O11| 118.66 (8)     | O8B-Pr2-O6 65.60 (11)   |
| O6-La2-O11 | 71.23 (8)        | O12-Pr2-O6 158.11 (11)  |

Symmetry codes: 1: A: −x, −y + 2, −z; B: −x, −y + 1, −z; C: −x, y + 1/2, −z + 1/2; D: −x + 1, −y + 1, −z; E: −x + 1, y + 1/2, −z + 1/2; 2: A: x + 1/2, −y + 1/2, z + 1/2; B: x + 1/2, y + 1/2, z; C: x − 1/2, y − 1/2, z; 3: A: x + 1/2, y − 1/2, z; B: x − 1/2, y + 1/2, z; C: x − 1/2, −y + 1/2, −z + 1/2.
CCDC 1008351, 1008352 and 1008366 contain the supplementary crystallographic data of complexes 1, 2 and 3 for this paper. These data could be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

4. Conclusions

In summary, three novel Ln (III)-based coordination polymers, \{[Ln2 (2,4-bpda)3 (H2O)x]yH2O\}_n (Ln = La (III) (1), x = 2, y = 0, Ce (III) (2), Pr (III) (3), x = 4, y = 1,) have been prepared via a solvothermal method and characterized. The structural analysis indicates complexes 1, 2 and 3 show a novel 3D 2-nodal (3,7)-connected (4^2·5) (4^4·5^1·6^6·8) topological network and a 3D 4-connected (6^5·8)-CdSO4 net. Complexes 1 and 2 exhibit intense fluorescent emission in the solid state at room temperature upon photoexcitation. To the best of our knowledge, these three complexes represent the first Ln (III)-based coordination polymers constructed using the unsymmetrical semi-rigid 2,4-bpda ligand. The results will enrich current rare earth coordination chemistry and provide new insights into its application in engineering such Ln-MOFs with different structures and properties.

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Author Contributions

Guo S.S. and Dong W.W. acquired and analyzed elemental analysis, IR and thermogravimetric analysis. Xia W. performed the fluorescence spectroscopy measurements. All authors participated in the data interpretation. Wu Y.P. designed the experiments and wrote the manuscript, which was revised and accepted by all the co-authors.

Conflicts of Interest

The authors declare no conflict of interest.

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*Sample Availability*: Samples of the compounds \{[Ln \_2 (2,4-bpda)\_3 (H\_2O)\_x] \_yH\_2O\}_n (Ln = La (III) (1), x = 2, y = 0, Ce (III) (2), Pr (III) (3), x = 4, y = 1) are available from the authors.

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