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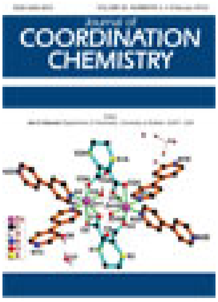

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Construction of three metal-organic frameworks based on multifunctional T-shaped tripodal ligands (4,5-dicarboxy-1H-imidazol-2-yl)pyridine-1-oxide

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Construction of three metal-organic frameworks based on multifunctional T-shaped tripodal ligands (4,5-dicarboxy-1H-imidazol-2-yl)pyridine-1-oxide

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Three metal-organic frameworks, $[Eu(C_{10}H_6N_3O_5)_3(H_2O)_2] \cdot H_2O$ (**1**), $[Tb(C_{10}H_6N_3O_5)_3(H_2O)_2] \cdot H_2O$ (**2**), and $[Cd(C_{10}H_6N_3O_5)_2Cl_2]$ (**3**) based on T-shaped tripodal ligands 3-(4,5-dicarboxy-1H-imidazol-2-yl)pyridine-1-oxide and 4-(4,5-dicarboxy-1H-imidazol-2-yl)pyridine-1-oxide (H_3DCImPyO), have been synthesized by the hydrothermal method and characterized by elemental analysis, IR, and single-crystal X-ray structure analysis. The diverse coordination modes of H_3DCImPyO ligands have afforded the three compounds. Complexes **1** and **2** are isomers and the Ln (Ln = Eu or Tb) atoms have coordination number eight with a distorted square prism geometry. The partly deprotonated $H_2DCImPyO^-$ ligands display three different coordination modes to link Ln (Ln = Tb or Eu) into 1-D double chains. In **3**, Cd(II) lies on an inversion center and displays a slightly distorted octahedral coordination. All three compounds exhibit strong fluorescent emissions in the solid state at room temperature.

Keywords: Lanthanide(III) complexes; Crystal structures; Coordination polymers; Luminescent properties; (4,5-Dicarboxy-1H-imidazol-2-yl)-pyridine-1-oxide

1. Introduction

Design of a metal-organic framework (MOF) *via* deliberate selection of metals and multifunctional ligands is an attractive topic due to their fascinating structures and potential applications as functional materials [1–12]. Luminescent lanthanide complexes have been extensively studied due to extremely narrow emission bands, large Stokes shift, long luminescence decay times, and no theoretical cap on quantum efficiency; particularly, europium, terbium, samarium, and dysprosium have interesting luminescent properties, such as red emission for Eu(III) ion and green emission for Tb(III) [13–17]. They are very attractive for applications in light-emitting diodes [18], laser materials [19], and as probes and labels in a variety of biological and chemical applications [20, 21]. Luminescent intensities of lanthanide complexes are dependent on the ligands. Considering that the lanthanide ions have high affinities for hard donors like oxygen of carboxylate, benzoic acid derivatives [22], pyridine carboxylate [23], and

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4,5-imidazoledicarboxylic acid derivatives [24] are often employed to link metal ions or metal-carboxylate clusters in lanthanide-organic frameworks which show good luminescence properties and fascinating structures. However, coordination chemistry of lanthanide and heterocyclic carboxylic acids (4,5-dicarboxy-1H-imidazol-2-yl)-pyridine-1-oxide (H_3DCImPyO) have not been carried out. (H_3DCImPyO) has seven potential donors allowing formation of interesting higher dimensional structures, and one to three hydrogen atoms can be removed forming H_nDCImPyO ($n = 0, 1, 2$) species by controlling the pH. Thus one may expect that deprotonated H_nDCImPyO ($n = 0, 1, 2$) exhibits flexible coordination. To the best of our knowledge, no frameworks constructed by H_3DCImPyO have been observed. In our continuing effort in this field [25], we chose H_nDCImPyO as an organic building block in an attempt to construct MOFs with new structural features. Herein, we report the synthesis, crystal structure, and luminescent properties of two lanthanide(III) complexes, $[Eu(C_{10}H_6N_3O_5)_3(H_2O)_2] \cdot H_2O$ (**1**), $[Tb(C_{10}H_6N_3O_5)_3(H_2O)_2] \cdot H_2O$ (**2**), and $[Cd(C_{10}H_6N_3O_5)_2Cl_2]$ (**3**).

2. Experimental

2.1. *Materials and physical measurements*

All commercially available solvents and starting materials were used as received without purification. H_3DCImPyO was prepared by the method reported in the literature [26]. Infrared (IR) spectra were taken on a Bruker Vector 22 spectrophotometer as KBr pellets from 4000 to 400 cm^{-1}. Elemental analyses were taken on a Perkin-Elmer 240C elemental analyzer. The solid-state fluorescent spectra were recorded on a SHIMADZU RF-5301PC.

2.2. *Preparation of 1*

H_3DCImPO (1 mmol, 0.25 g) and $Eu(ClO_4)_3$ (0.5 mmol, 0.225 g) were placed in a thick Pyrex tube (*ca* 20 cm in length). After addition of water (2 mL), the tube was frozen with liquid N_2, evacuated under vacuum, and sealed with a torch. The tube was heated at 150°C for 3 days and after slow cooling to room temperature, pale yellow block crystals were obtained in 31% yield. IR spectra of **1**: 3331(m), 3196(m), 3108(m), 1709(m), 1628(m), 1600(m), 1569(m), 1533(m), 1485(s), 1375(m), 1281(w), 1206(m), 1197(m), 1117(m), 1083(m), 996(m), 892(m), 849(w), 813(w), 774(w), 729(m), 668(m), 628(m), 569(w). Anal. Calcd for $C_{30}H_{24}EuN_9O_{18}$ (%): C, 37.91; H, 2.54; N, 13.26. Found: C, 37.52; H, 2.48; N, 13.19.

2.3. *Preparation of 2*

H_3DCImPyO (1 mmol, 0.25 g) and $Tb(ClO_4)_3$ (0.5 mmol, 0.227 g) were placed in a thick Pyrex tube (*ca* 20 cm in length). After addition of ethanol (0.3 mL) and water (1.7 mL), the tube was frozen with liquid N_2, evacuated under vacuum, and sealed with a torch. The tube was heated at 150°C for 3 days; after slow cooling to room temperature, colorless block crystals were obtained in 42% yield. IR spectra of **2**: 3333(m), 3198(m), 3111(m), 1707(m), 1567(m), 1529(m), 1489(m), 1458(m), 1375(m), 1309(w), 1285(w), 1219(m), 1200(m), 1170(w), 1120(w), 1002(m), 891(m), 849(w), 806(w), 774(w), 729(m), 675(w), 616(w), 569(w). Anal. Calcd for $C_{30}H_{24}N_9O_{18}Tb$ (%): C, 37.63; H, 2.53; N, 13.17. Found: C, 37.55; H, 2.51; N, 13.12.

2.4. *Preparation of 3*

$H_3DCImPyO$ (1 mmol, 0.25 g) and $CdCl_2$ (0.5 mmol, 0.09 g) were placed in a thick Pyrex tube (*ca* 20 cm in length). After addition of water (2 mL), the tube was frozen with liquid N_2, evacuated under vacuum, and sealed with a torch. The tube was heated at 150°C for 3 days; after slow cooling to room temperature, colorless block crystals were obtained in 49% yield. IR spectra of **3**: 3435(m), 3210(m), 3106(m), 1706(m), 1572(m), 1552(m), 1460(m), 1439(m), 1377(m), 1309(w), 1270(w), 1212(m), 1185(w), 1129(w), 1112(m), 858(m), 840(w), 817(w), 774(w), 737(m), 693(w), 658(w), 528(w). Anal. Calcd for $C_{20}H_{12}Cl_2N_6O_{10}Cd$ (%): C, 35.34; H, 1.78; N, 12.37. Found: C, 35.40; H, 1.81; N, 12.40.

2.5. *Single-crystal X-ray diffraction measurements*

Crystal data for **1**: $C_{30}H_{24}EuN_9O_{18}$, $M = 950.54$, triclinic, P-1, $a = 11.497(9)$ Å, $b = 11.516(8)$ Å, $c = 13.410(9)$ Å, $\alpha = 72.647(17)^\circ$, $\beta = 88.166(18)^\circ$, $\gamma = 88.029(16)^\circ$, $V = 1693(2)$ Å^3, $Z = 2$, $F(000) = 948$, goodness-of-fit = 1.056, $R_1 = 0.0583$, $wR_2 = 0.0897$ $[I > 2\sigma(I)]$.

Crystal data for **2**: $C_{30}H_{24}N_9O_{18}Tb$, $M = 957.51$, triclinic, P-1, $a = 11.4899(18)$ Å, $b = 11.503(3)$ Å, $c = 13.4310(15)$ Å, $\alpha = 88.48(3)^\circ$, $\beta = 72.706(19)^\circ$, $\gamma = 87.93(3)^\circ$, $V = 1693.6(5)$ Å^3, $Z = 2$, $F(000) = 952$, goodness-of-fit = 1.074, $R_1 = 0.0624$, $wR_2 = 0.1224$ $[I > 2\sigma(I)]$.

Crystal data for **3**: $C_{20}H_{12}N_6O_{10}Cl_2Cd$, $M = 679.66$, monoclinic, $P2_1/n$, $a = 6.414(7)$ Å, $b = 18.064(19)$ Å, $c = 9.790(11)$ Å, $\alpha = 90^\circ$, $\beta = 106.17\ (2)^\circ$, $\gamma = 90^\circ$, $V = 1090(2)$ Å^3, $Z = 2$, $F(000) = 672$, goodness-of-fit = 1.009, $R_1 = 0.0585$, $wR_2 = 0.1721$ $[I > 2\sigma(I)]$. Data collections of **1**, **2**, and **3** were performed with Mo-Kα radiation ($\lambda = 0.71073$ Å) on a Rigaku SCXmini diffractometer by the ω scan technique at room temperature. The structures were solved using direct methods and successive Fourier difference synthesis (SHELXS-97) [27], and refined using full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [28]. All non-H atoms and hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}$. Selected bond distances and angles are given in tables 1–3.

3. Results and discussion

3.1. *IR analysis*

The presence of a medium intensity band at 1710 cm^{-1} in IR spectra of **1**, **2**, and **3** indicates that the two –COOH are only partially deprotonated, in agreement with their

Table 1. Selected bond lengths (Å) and angles (°) for **1**.

Eu1–O15^{i}	2.338(3)	Eu1–O5^{ii}	2.360(3)
Eu1–O11^{ii}	2.367(3)	Eu1–O9	2.370(3)
Eu1–O16	2.396(3)	Eu1–O17	2.418(3)
Eu1–O1	2.451(4)	Eu1–N3^{ii}	2.687(4)
O15^{i}–Eu1–O5^{ii}	144.14(11)	O15^{i}–Eu1–O11	82.57(12)
O5^{ii}–Eu1–O11	104.39(12)	O15^{i}–Eu1–O9	134.30(11)
O5^{ii}–Eu1–O9	78.91(12)	O11–Eu1–O9	67.78(11)
O15^{i}–Eu1–O16	72.25(11)	O5^{ii}–Eu1–O16	141.00(11)
O11–Eu1–O16	91.38(12)	O9–Eu1–O16	74.47(11)
O15^{i}–Eu1–O17	71.93(11)	O5^{ii}–Eu1–O17	75.37(11)
O11–Eu1–O17	77.39(12)	O9–Eu1–O17	129.32(11)
O16–Eu1–O17	143.52(11)	O15^{i}–Eu1–O1	74.52(12)
O5^{ii}–Eu1–O1	85.79(11)	O11–Eu1–O1	151.84(10)
O9–Eu1–O1	140.38(11)	O16–Eu1–O1	96.90(11)
O17–Eu1–O1	80.05(11)	O15^{i}–Eu1–N3^{ii}	130.13(11)
O5^{ii}–Eu1–N3^{ii}	65.50(11)	O11–Eu1–N3^{ii}	138.70(11)
O9–Eu1–N3^{ii}	70.95(11)	O16–Eu1–N3^{ii}	79.03(11)
O17–Eu1–N3^{ii}	131.19(11)	O1–Eu1–N3^{ii}	69.45(11)

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

Table 2. Selected bond lengths (Å) and angles (°) for **2**.

Tb1–O4^{i}	2.322(4)	Tb1–O9	2.336(4)
Tb1–O5	2.345(4)	Tb1–O14	2.361(4)
Tb1–O18	2.364(4)	Tb1–O17	2.390(4)
Tb1–O10^{ii}	2.435(4)	Tb1–N4	2.673(4)
O4^{i}–Tb1–O9	143.48(15)	O4^{i}–Tb1–O5	82.47(15)
O9–Tb1–O5	104.07(15)	O4^{i}–Tb1–O14	134.87(15)
O9–Tb1–O14	78.79(15)	O5–Tb1–O14	68.14(14)
O4^{i}–Tb1–O18	72.15(14)	O9–Tb1–O18	141.84(14)
O5–Tb1–O18	91.54(15)	O14–Tb1–O18	75.12(15)
O4^{i}–Tb1–O17	72.11(14)	O9–Tb1–O17	74.48(14)
O5–Tb1–O17	77.09(14))	O14–Tb1–O17	128.78(14)
O18–Tb1–O17	143.58(14)	O4^{i}–Tb1–O10^{ii}	74.70(14)
O9–Tb1–O10^{ii}	85.52(15)	O5–Tb1–O10^{ii}	151.72(14)
O14–Tb1–O10^{ii}	140.13(13)	O18–Tb1–O10^{ii}	97.01(15)
O17–Tb1–O10^{ii}	80.13(14)	O4^{i}–Tb1–N4	130.38(14)
O9–Tb1–N4	66.07(13)	O5–Tb1–N4	138.61(14)
O14–Tb1–N4	70.49(14)	O18–Tb1–N4	79.11(14)
O17–Tb1–N4	131.25(14)	O10^{ii}–Tb1–N4	69.64(13)

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

Table 3. Selected bond lengths (Å) and angles (°) for **3**.

Cd1–O1	2.226(4)	Cd1–O1^{i}	2.226(4)
Cd1–N1	2.415(5)	Cd1–N1^{i}	2.415(5)
Cd1–Cl1	2.345(5)	Cd1–Cl1^{i}	2.345(5)
O1–Cd1–O1^{i}	180.000(1)	O1–Cd1–Cl1	90.5(2)
O1^{i}–Cd1–Cl1	89.5(2)	O1–Cd1–Cl1^{i}	89.5(2)
O1–Cd1–N1^{i}	106.05(16)	Cl1–Cd1–Cl1^{i}	180.00(17)
Cl1–Cd1–N1^{i}	87.75(17)	O1^{i}–Cd1–N1^{i}	73.95(16)
O1–Cd1–N1	73.95(16)	Cl1–Cd1–N1^{i}	92.25(17)
Cl1^{i}–Cd1–N1	87.75(17)	Cl1–Cd1–N1	92.25(17)
O1^{i}–Cd1–N1	106.05(16)	N1^{i}–Cd1–N1	180.000(1)

Symmetry code: (i) $-x+2, -y, -z+2$.

X-ray structures. The broad band at 3250 cm^{-1} indicates the presence of ν(O–H) of coordinated water; ν_{as}(COO$^-$) and ν_s(COO$^-$) were observed at 1569 and 1375 cm^{-1} for **1**, 1567 and 1375 cm^{-1} for **2**, 1572 and 1377 cm^{-1} for **3**. The difference between asymmetric stretching and symmetric stretching bands of the carboxyl groups ($\Delta\nu = \nu_{as(C=O)} - \nu_{s(C=O)}$) are 194 cm^{-1}, 192 cm^{-1}, and 195 cm^{-1}, respectively, which indicates strong coordination of carboxylate to the metal [29, 30].

3.2. *Description of the crystal structure*

In **1**, there are one Eu(III), three H$_2$DCImPyO$^-$, two coordinated water molecules and one lattice water molecule in the asymmetric unit. The Eu is eight-coordinate by five oxygen atoms from three different H$_2$DCImPyO ligands, two water molecules, and one imidazole nitrogen from H$_2$DCImPyO$^-$ as shown in figure 1. Each Eu adopts a distorted square prism geometry (figure 2). The nitrogen of imidazole and oxygen of carboxylate are a bidentate ligand forming a five-membered metallocycle. Eu–O bond distances range from 2.338(3) to 2.451(4) Å and the O–Eu–O bond angles range from

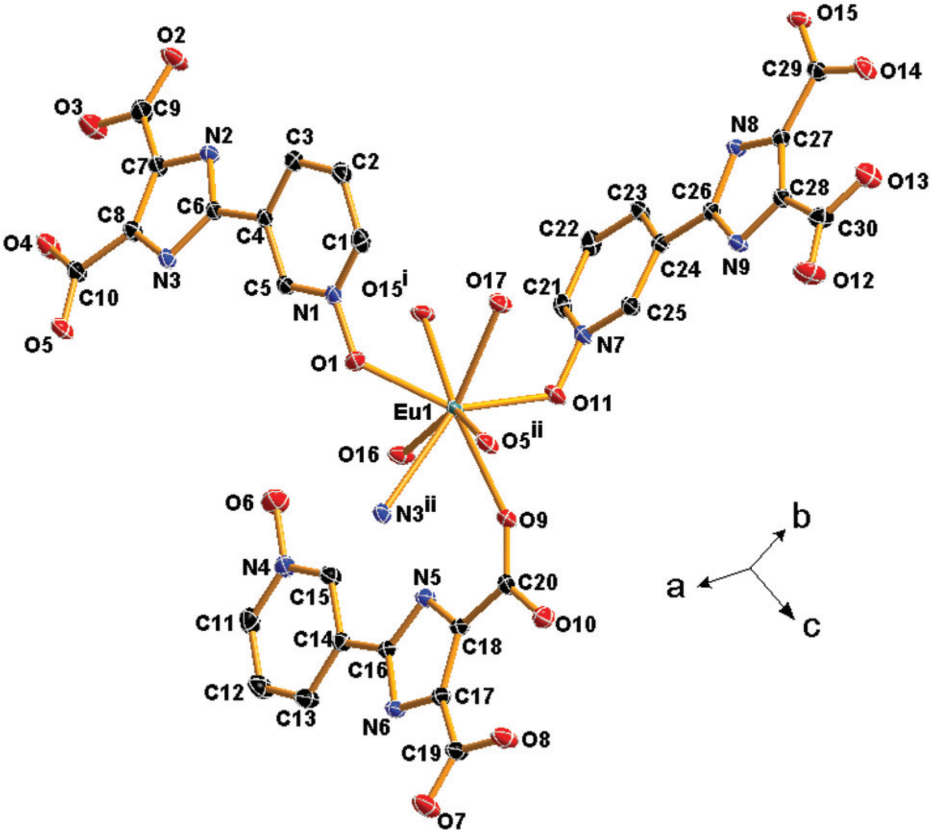


Figure 1. View of the coordination environment of Eu(III) in **1**; thermal ellipsoids drawn at the 30% probability level. Lattice water molecules and hydrogen atoms have been omitted for clarity (symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+2, -y, -z$).

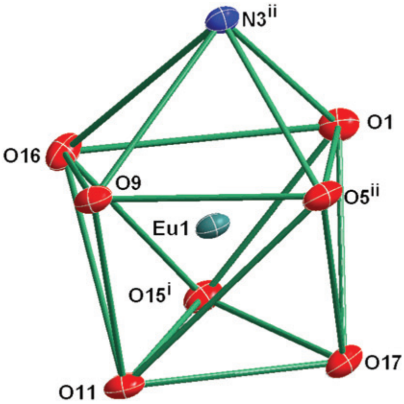
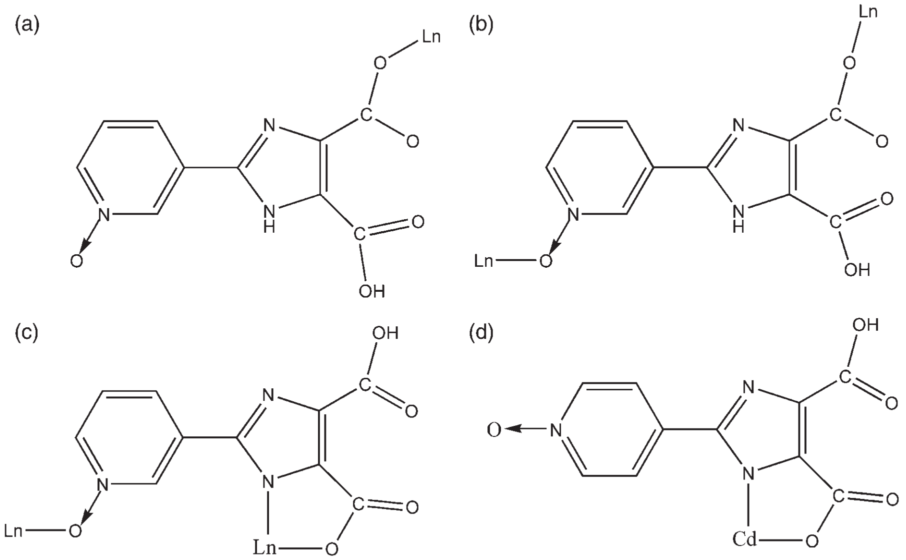


Figure 2. Coordination polyhedron of Tb(III) in **1** (Symmetry codes (i) $-x+1$, $-y+1$, $-z$ and (ii) $-x+2$, $-y$, $-z$).



Scheme 1. Coordination modes of H_2DCIPO^{-1}.

67.78(11) to 151.84(10)°, comparable to those reported for other Eu(III) carboxylate complexes, while the Eu–N bond distance is 2.687(4), longer than that reported [31–34].

All three independent $H_2DCImPyO^-$ ligands display different coordination in this structure. As shown in scheme 1: (a) monodentate with coordinated oxygen from carboxyl of $H_2DCImPyO^-$ with dihedral angles between the two carboxyl groups and the correspondingly linked imidazole ring being 8.2(3)° and 12.6(2)°; (b) bidentate, $H_2DCImPyO^-$ bridging-bidentate μ_2-O,O′ mode through oxygen from carboxyl and *N*-oxide with dihedral angles between the two carboxyl groups and the correspondingly linked imidazole ring being 12.0(3)° and 6.9(4)°; and (c) bidentate, $H_2DCImPyO^-$

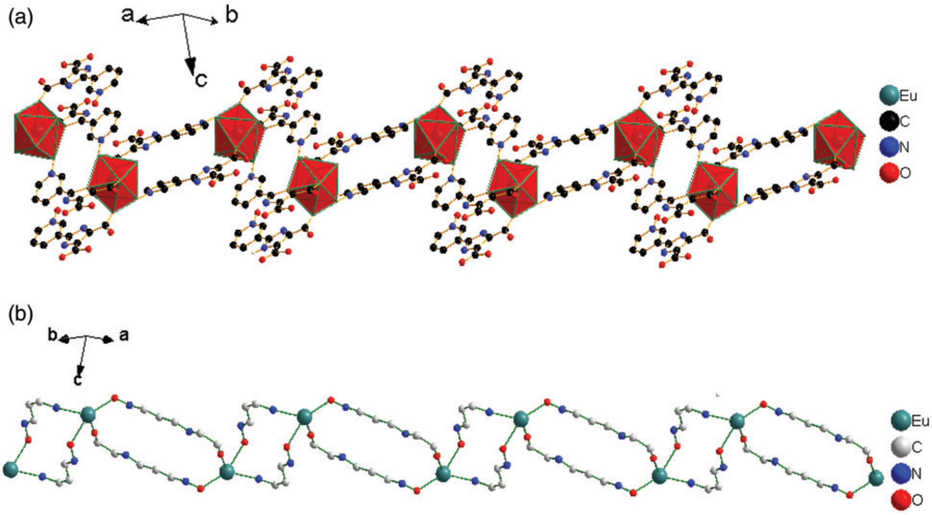


Figure 3. (a) A 1-D chain structure for **1**. (b) Simplified 1-D double chain with some atoms of ligands omitted for clarity.

bridging-bidentate μ_2-*k*N,O: *K*O′ mode through bis-N,O-chelating and the oxygen of *N*-oxide groups with dihedral angles between the two carboxyl groups and the correspondingly linked imidazole ring being 3.7(4) and 1.9(4)°; the two carboxyl groups and the imidazole ring are almost coplanar. Each Eu(III) connects to another Eu(III) by two $H_2DCImPyO^-$, resulting in two kinds of metallocycles: (i) $Eu_2(H_2DCImPyO)_2$ 20-membered metallocycle and (ii) $Eu_2(H_2DCImPyO)_2$ 14-membered metallocycle (figure 3a). The 14-membered metallocycle alternates with the 20-membered metallocycle forming a double chain structure (figure 3b). The Eu $\cdots$ Eu distances are 7.3763(39) and 11.2668(62), respectively, in 14-membered and 20-membered metallocycles.

In the crystal structure of **1**, uncoordinated water O1W is involved in two intermolecular hydrogen bonds [O1W–H1E $\cdots$ O6^{iii}, O1W–H1F $\cdots$ O1^{vii}; symmetry codes: (iii) $x-1$, y, z; (vii) $-x+1$, $-y$, $-z$]. Three intermolecular hydrogen bonds are formed between N of imidazole ring from three independent $H_2DCImPyO^-$ and oxygen atoms [N2–H2A $\cdots$ O7^{iv}, N6–H6A $\cdots$ O2^{vii}, N9–H9A $\cdots$ O6^{iii}; symmetry codes: (iii) $x-1$, y, z; (iv) x, $1+y$, $z-1$; (vii) $-x+1$, $-y$, $-z$]. Intermolecular hydrogen bonds are formed between coordinated O16 and uncoordinated carboxyl O12 [O16–H16B $\cdots$ O12^{v}; symmetry code: (v) $x+1, y, z$]. Intramolecular hydrogen-bonding interactions are found [O3–H3A $\cdots$ O4, O8–H8 $\cdots$ O10, O13–H13A $\cdots$ O14, O16–H16A $\cdots$ N5, and O17–H17A $\cdots$ N8^{i}; symmetry code: (i) $1-x$, $2-y$, $1-z$] (table 4). Hydrogen-bonding interactions generate a 3-D architecture as shown in figure 4.

The structure of **2** is similar to that of **1**, shown in figure 5. Selected bond lengths and angles are listed in table 5. The geometry of Tb is eight coordinate adopting a distorted square prism. The Tb–O distances range from 2.322(4) to 2.435(4) Å, in the range of Tb–O distances reported [35, 36]; Tb–N bond distance is 2.673(4), longer than that reported [35, 36]. In **2**, three independent H_2DCIPO^- ligands also display monodentate and bidentate coordination similar to **1** (scheme 1). Each Tb(III) connects to another

Table 4. Hydrogen-bonding geometry parameters (Å, °) for **1**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O1W–H1E···O6^{iii}	1.12	1.69	2.782(7)	166
O1W–H1F···O1^{vii}	0.91	2.310	2.984(6)	122.8
O3–H3A···O4	0.82	1.70	2.519(6)	179
O8–H8···O10	0.82	1.65	2.462(6)	173
O13–H13A···O14	0.82	1.62	2.441(6)	177
O16–H16A···N5	0.94	1.84	2.760(5)	167
O16–H16B···O12^{v}	0.82	1.99	2.780(5)	160
O17–H17A···N8^{i}	1.03	1.89	2.901(5)	166
O17–H17B···O1W	0.77	2.03	2.757(6)	157
N2–H2A···O7^{iv}	1.01	1.82	2.764(6)	155
N6–H6A···O2^{vi}	0.95	1.90	2.837(6)	167
N9–H9A···O6^{iii}	0.90	1.94	2.806(6)	161

Symmetry codes: (i) $-x+1, -y+1, -z$; (iii) $x-1, y, z$; (iv) $x, 1+y, z-1$; (v) $x+1, y, z$; (vi) $x, y-1, z+1$; (vii) $-x+1, -y, -z$.

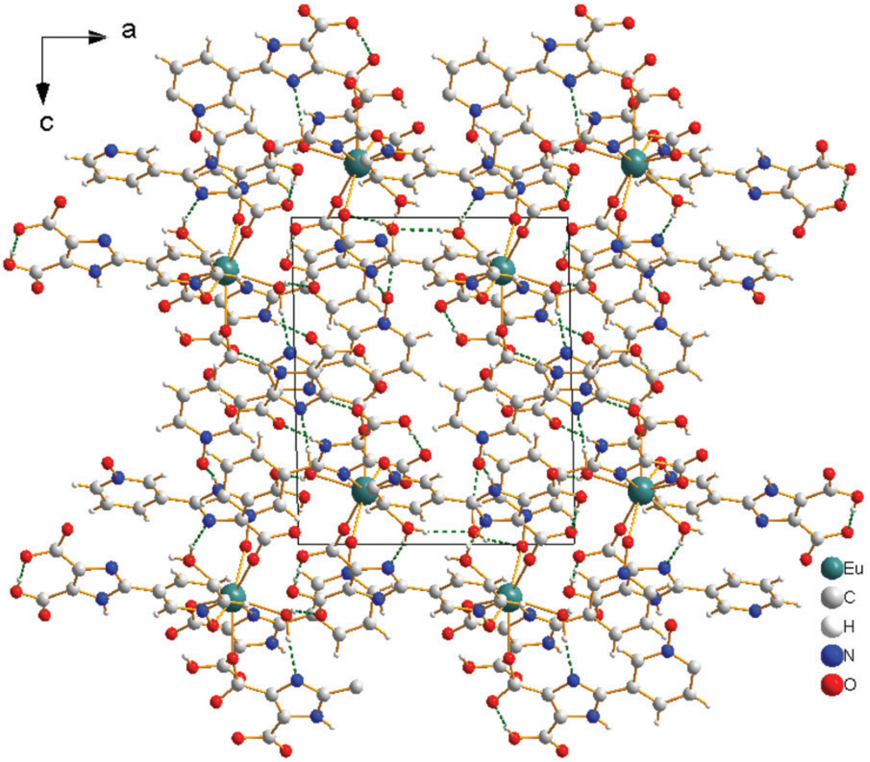


Figure 4. 3-D H-bonds packing diagrams of **1**.

Tb(III) by two $H_2DCImPyO^-$ ligands, resulting in $Tb_2(H_2DCImPyO)_2$ 20-membered metallocycle and $Tb_2(H_2DCIPO)_2$ 14-membered metallocycle. The 14-membered metallocycle alternates with the 20-membered metallocycle, held together by Tb(III), forming a double chain structure. The Tb···Tb distances are 7.3677(22) and 11.2355(36), respectively, in 14-membered and 20-membered metallocycles. In the

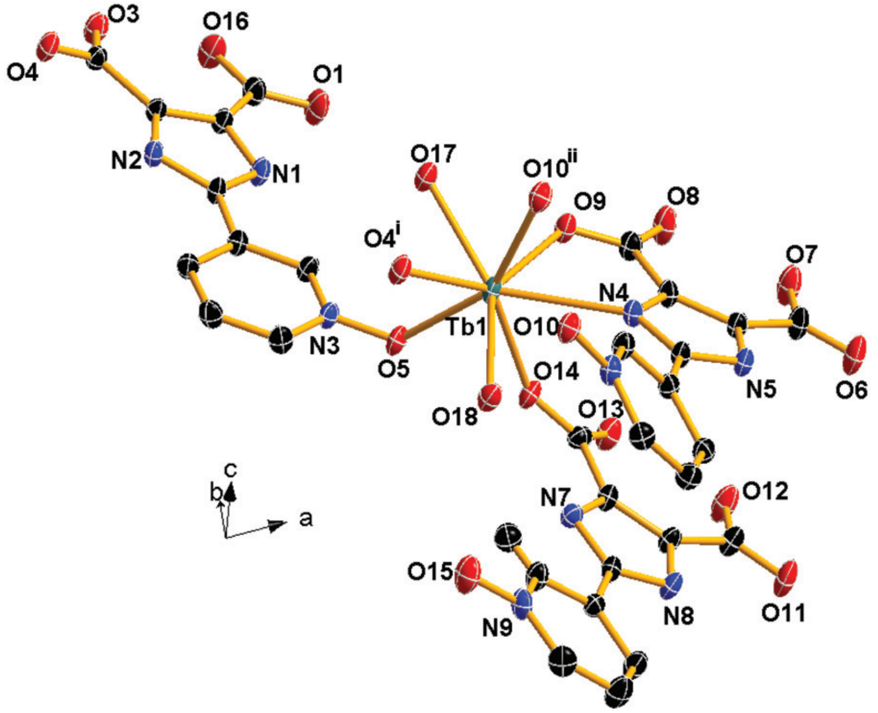


Figure 5. View of the coordination environment of Tb(III) in **2**; thermal ellipsoids drawn at the 30% probability level. Lattice water molecules and hydrogen atoms have been omitted for clarity (symmetry codes: (i) $-x+1$, $-y+2$, $-z+1$; (ii) $-x+2$, $-y+1$, $-z+1$).

Table 5. Hydrogen-bonding geometry parameters (Å, °) for **2**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O1W–H1WA···O17^{v}	0.90	2.37	2.759(7)	106
N1–H1A···O15^{iii}	0.86	1.97	2.803(7)	162
N5–H5A···O11^{iv}	0.86	1.91	2.767(7)	173
O7–H7A···O8	0.82	1.72	2.529(7)	170
N8–H8A···O6^{iv}	0.86	2.03	2.842(7)	158
O12–H12···O13	0.82	1.65	2.463(7)	169
O16–H16···O3	0.82	1.64	2.446(7)	170
O17–H17A···O1W^{iii}	0.85	2.30	2.759(7)	114
O17–H17B···N2^{i}	0.85	2.29	2.901(7)	129
O18–H18A···N7	0.85	2.32	2.771(6)	113
O18–H18B···O1^{v}	0.85	1.97	2.788(7)	163

Symmetry codes: (i) $-x+1$, $-y+2$, $-z+1$; (iii) x, $y+1$, z; (iv) $-x+3$, $-y+1$, $-z$; (v) x, $y-1$, z.

crystal structure of **2**, three intermolecular hydrogen bonds are formed between nitrogen atoms of imidazole rings from three independent H_2DCIPO^- and oxygen atoms [N1–H1A···O15^{iii}, N5–H5A···O11^{iv}, N8–H8A···O6^{iv}; symmetry codes: (iii) x, $1+y$, z; (iv) $3-x$, $1-y$, $-z$]. The uncoordinated water O1W is involved in one

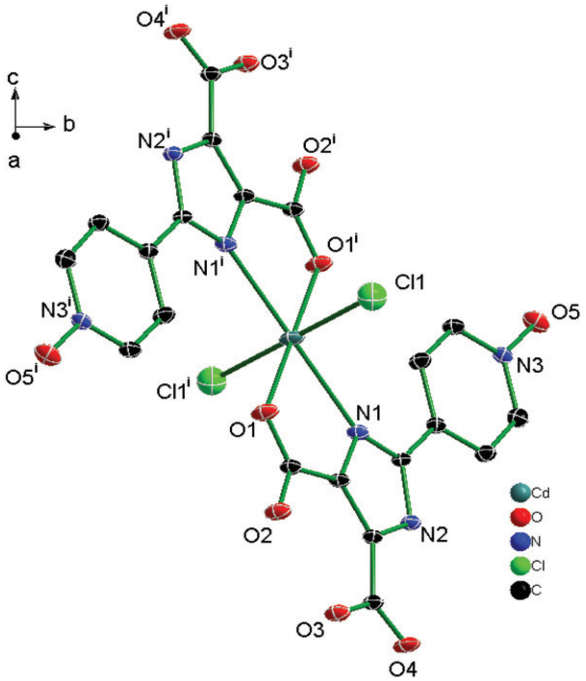


Figure 6. View of the coordination environment of Cd(II) in **3**; thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity (symmetry code: (i) $-x+2$, $-y$, $-z+2$).

intermolecular hydrogen bond [O1W–H1W$\cdots$O17^{v}; symmetry code: (v) x, $y-1$, z]. Coordinated water O17 and O18 are involved in two intermolecular hydrogen bonds [O17–H17A$\cdots$O1W^{iii}, O18–H18B$\cdots$O1^{v}; symmetry codes: (iii) x, $1+y$, z; (v) x, $y-1$, z]. Intramolecular hydrogen-bonding interactions are found [O7–H7A$\cdots$O8, O12–H12A$\cdots$O13, O16–H16$\cdots$O3, O17–H17B$\cdots$N2^{i}, and O18–H18A$\cdots$N7; symmetry code: (i) $1-x$, $2-y$, $1-z$] (table 5). All hydrogen-bonding interactions generate a 3-D architecture.

The asymmetric unit in **3** consists of one Cd(II), one partly deprotonated H_3DCImPyO, and one coordinated Cl^- as shown in figure 6. Cd(II) lies on an inversion center and displays a slightly distorted octahedral coordination geometry defined by the two imidazole nitrogen atoms and two carboxylate oxygen atoms of two chelate ligands, and two chlorides. The Cd–N distance is 2.415(5) Å, longer than reported values [33, 37]. The Cd–O bond length is 2.226(4) Å, comparable to reported values [33, 37]. In H_3DCImPyO, the imidazole and pyridyl rings are almost coplanar with a dihedral angle of 6.4(1)°. Moreover, the hydrogen bonds (table 6) at N2–H2D$\cdots$O5^{ii}, N2–H2D$\cdots$N3^{ii}, and O3–H3$\cdots$O2 (symmetry code: (ii) $x+1/2$, $-y+1/2$, $z-1/2$) give a 2-D network (figure 7).

3.3. *Fluorescence*

The luminescent properties of **1**, **2**, and **3** in the solid state were investigated at room temperature. The fluorescence spectrum of **1** was recorded upon excitation at 395 nm,

Table 6. Hydrogen-bonding geometry parameters (Å, °) for **3**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N2–H2D···O5^{ii}	0.86	1.92	2.774(7)	176.1
N2–H2D···N3^{ii}	0.86	2.62	3.416(7)	154.5
O3–H3···O2	0.82	1.66	2.482(6)	175.2

Symmetry code: (ii) $x+1/2$, $-y+1/2$, $z-1/2$.

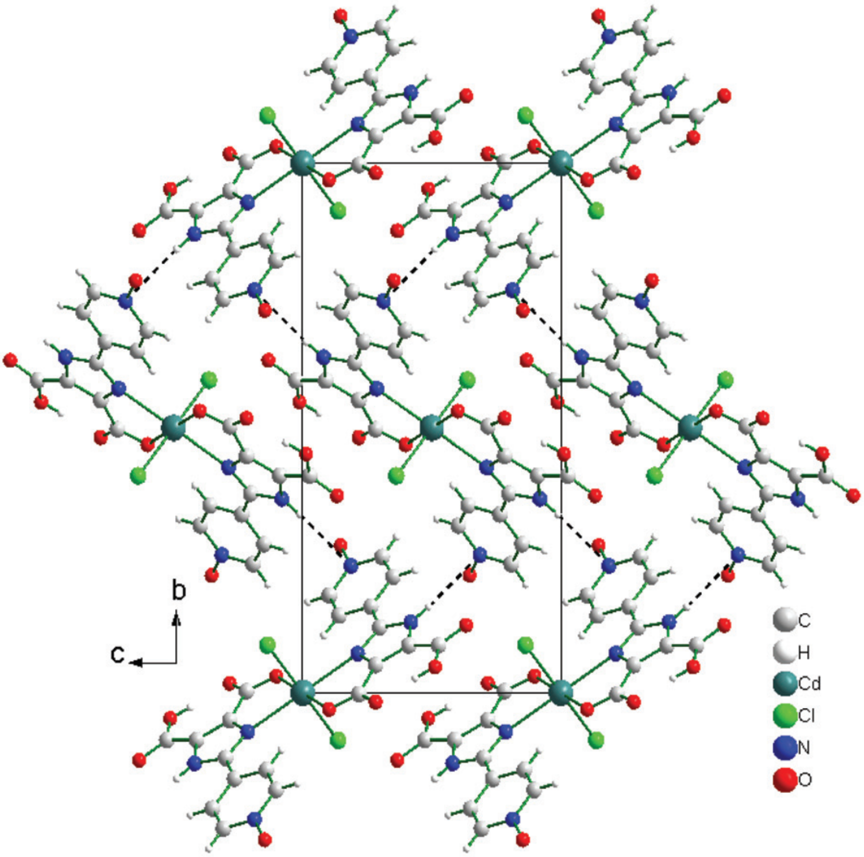


Figure 7. 2-D H-bonds packing diagrams of **3**.

showing the $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4) characteristic transitions of Eu(III). The strongest narrow-band emission at 613 nm is characteristic of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition of Eu(III), which is more intense than the $^5D_0 \rightarrow {}^7F_1$ transition at 591 nm and $^5D_0 \rightarrow {}^7F_4$ transition at 697 nm. Two weak emission bands at 578 and 649 nm correspond to $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_3$ transitions, respectively (figure 8). The emission spectrum of **2** (figure 9) upon excitation at 371 nm exhibits the characteristic transition of $^5D_4 \rightarrow {}^7F_J$ ($J = 6$, 5, 4, and 3) of Tb(III) and the highest narrow-band emission at 542 nm is characteristic of the hypersensitive $^5D_4 \rightarrow {}^7F_5$ transition of Tb(III). The emission band at 492 nm with a shoulder of 489 nm corresponds to

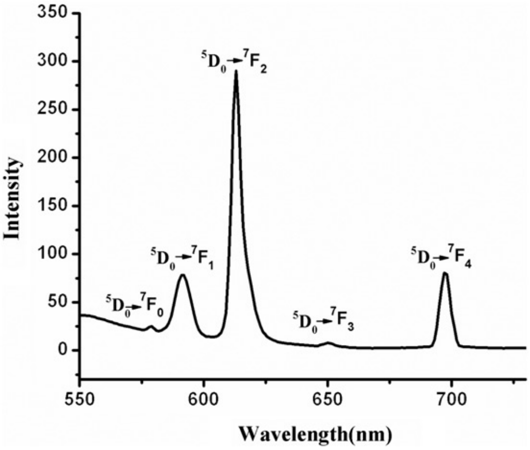


Figure 8. The solid state emission spectra of **1** (excited at 395).

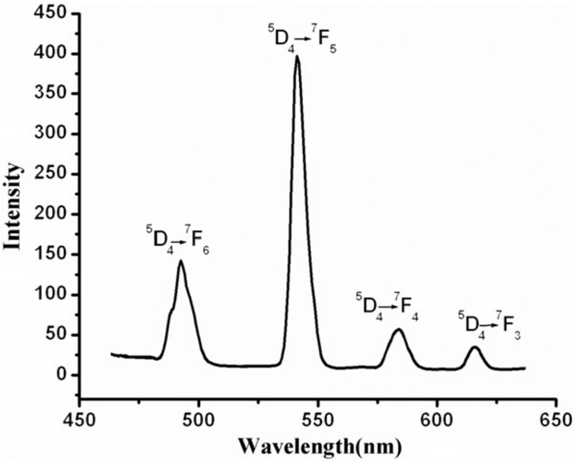


Figure 9. The solid state emission spectra of **2** (excited at 371).

$^5D_4 \to {}^7F_6$ transition. The emission bands at 582 and 620 nm correspond to $^5D_4 \to {}^7F_4$ and $^5D_4 \to {}^7F_3$ transitions, respectively.

The fluorescence of free H_3DCImPyO and **3** were evaluated in the solid state upon the excitation at 382 nm at room temperature. As shown in figure 10, **3** exhibits intensive blue luminescence (maximum at 435 nm), which undergoes a blue-shift from the free ligand around 463 nm, though much stronger and narrower. The blue-shift from the H_3DCImPyO to **3** can be assigned to an intraligand π–π* transition. The enhanced luminescence intensity can be attributed to strong interactions between deprotonated $H_2DCImPyO^-$ and Cd^{2+}, which imparts the rigidity of $H_2DCImPyO^-$ and reduces non-radiative loss. The same luminescence occurred in other H_3PyImDC based compounds [33, 38, 39].

In this work, three MOFs have been synthesized based on the T-shaped tripodal H_3DCImPyO under hydro(solvo)thermal conditions and structurally characterized.

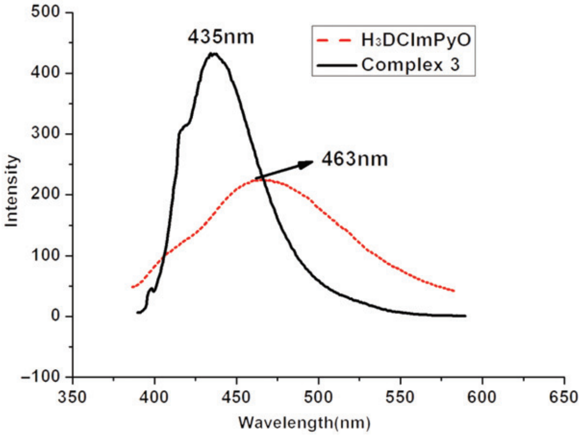


Figure 10. Solid-state photoluminescence spectra of **3** (—) and free H_3DCImPyO (----) at room temperature (excited at 382).

Intense red fluorescence for **1**, green fluorescence for **2**, and blue fluorescence for **3** are observed under UV excitation, suggesting they have potential application in photoactive materials.

Supplementary material

CCDC Nos 809388, 809389, and 847761 contain the supplementary crystallographic data of **1**, **2**, and **3** for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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