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Two d^{10} metal–organic frameworks based on a novel semi-rigid aromatic biscarboxylate ligand: Syntheses, structures and luminescent properties

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Two new d^{10} metal–organic frameworks based on a novel semi-rigid aromatic biscarboxylate ligand, namely, [Zn (**RGAA**)(**BPY**)$_{1/2}$] (**1**) and [Cd$_5$(μ_3-OH)$_2$(**RGAA**)$_4$] (**2**) [H$_2$**RGAA** = 4-(carboxymethyl)-2-ethoxybenzoic acid, **BPY** = 4,4′-bipyridine], have been synthesized by the hydrothermal reaction, and characterized by Fourier transform-infrared, elemental analyses, X-ray single-crystal diffraction, powder X-ray diffraction and thermogravimetric analyses. Complex **1** displays a three-dimensional (3D) network with a (2,3,4)-connected (6^3.8^2.10)$_2$(6^3)$_2$(8) topology, while complex **2** exhibits a 3D framework with a (3,10)-connected (3.4.5)$_2$(3^4.4^6.5^18.6^14.7^2.8) topology. The luminescent properties of compounds **1** and **2** have been investigated in detail, where the emission maxima are 464 and 349 nm, respectively.

KEYWORDS

4-(carboxymethyl)-2-ethoxybenzoic acid, d^{10} metal ions, luminescence, metal–organic frameworks, semi-rigid ligand

1 | INTRODUCTION

Metal–organic frameworks (MOFs) are crystalline solids constructed via self-assemblies of single metal cations and organic ligands having multiple binding sites, to form three-dimensional (3D) extended coordination networks, which are a kind of fascinating materials due to their charming structures and the potential applications in the field of photoluminescence,[1–28] ion exchange,[29–32] separation and storage,[33–40] catalysis,[41–53] and magnetism.[54–63] Typically, luminescent materials have been extensively explored for their diverse functionalities and application in sensing and optical devices.[64–66] The syntheses and preparation of MOFs are mainly dependent on several factors, such as center metal ions,[67–69] organic ligands,[70,71] inorganic/organic anions,[72–74] the ratios of metals and organic ligands,[75] pH values,[76,77] reaction temperature,[78,79] and reaction time.[80] Among these, the organic ligands and center metals play vital roles in the synthesis of MOFs.[81,82] So far, a large number of MOFs containing the rigid organic linkers or the soft ones have been documented, which display interesting physical properties.[83–88] However, the development and investigation of MOFs based on the semi-rigid organic connectors remain still sparse. Thus, one novel semi-rigid aromatic biscarboxylate organic linker, 4-(carboxymethyl)-2-ethoxybenzoic acid, was designed and investigated to construct novel MOFs in our research group (Scheme 1). Therefore, the design and preparation of MOFs based on this novel semi-rigid aromatic dicarboxylate ligand is unprecedented.

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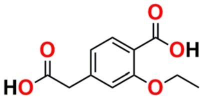


SCHEME 1 The structure of H2RGAA

Additionally, MOFs based on 4,4′-bipyridine ligand have been explored and progress has been made, and they display interesting structures and physical properties.[89–93] For example, Zn-based metal coordination polymers with this bipyridine ligand exhibit exciplex fluorescence as a diagnostic probe.[94] Metal coordination polymers with bipyridine ligands display interesting luminescent behaviors.[91]

Metal–organic frameworks containing d^{10} metal ions are of great interest in view of their appealing structures and photoluminescent properties, which should lead to new functional materials.[95–104] Much effort has been devoted to the design of d^{10} MOFs owing to the ability to form bonds with different donors simultaneously, various coordination modes, and the special physical properties of d^{10} metal ions. To date, a number of metal coordination polymers with d^{10} metal ions have been designed and investigated, which display charming structures and interesting physical properties.[12,13,105–114] Thus, the development and investigation of novel MOFs with d^{10} metal ions that exhibit interesting fluorescent behaviors is still a big challenge.

With the background above, we would like to report the syntheses, crystal structures and topological features of two MOFs based on a semi-rigid aromatic bis-carboxylate ligand, namely [Zn (**RGAA**)(**BPY**)$_{1/2}$] (**1**) and [$Cd_5(\mu_3\text{-}OH)_2$(**RGAA**)$_4$] (**2**) [H$_2$**RGAA** = 4-(carboxymethyl)-2-ethoxybenzoic acid; **BPY** = 4,4′-bispyridine] (Scheme 1). To the best of our knowledge, MOFs with these novel semi-rigid aromatic bis-carboxylate linkers were first investigated and developed. Both MOFs based on this ligand were characterized by single-crystal X-ray diffraction (XRD, Supporting Information), elemental analysis, infrared (IR), XRD and thermogravimetric analyses (TGA, Supporting Information). Moreover, the fluorescence properties of complexes **1** and **2** were studied in detail.

2 | EXPERIMENTAL

2.1 | Materials and measurements

Reagents and solvents employed were commercially available and not purified further. The reagents and solvents employed were used as received without further purification. The Fourier transform (FT)-IR spectra were recorded from KBr pellets in the range 400–4000 cm^{-1} on a Bruker spectrometer. Elemental analyses microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. Powder X-ray diffraction (PXRD) was recorded on a Bruker D8 Advance diffractometer at 40 kV, 40 mA with a Cu-target tube and a graphite monochromator. 2θ falls in the range of 5–60°. The experimental PXRD patterns are in good agreement with the corresponding simulated ones, except for the relative intensity variation because of the preferred orientations of the crystals. Therefore, the phase purity of the as-synthesized products is substantiated. At room temperature, solid-state fluorescent studies were conducted on a HITACHI F-4500 system. TGA data were collected with a TA SDT Q600 analyzer in N_2 at a heating rate of 10°C/min.

2.2 | Synthesis of 4-(carboxymethyl)-2-ethoxybenzoic acid (H$_2$RGAA)

To a solution of distilled water (10 ml) and NaOH (25 mmol, 1.000 g), 2-(3-ethoxy-4-(methoxycarbonyl) phenyl) acetic acid (10 mmol, 2.380 g) was added. The reaction mixture was refluxed on a steam bath for 4 hr. After cooling to room temperature, the pH value of the solution was adjusted to 1 by adding the concentrated HCl solution. The solid formed was collected and dried. The samples were recrystallized. Yield (77%, 1.724 g); m.p. 139–141°C. Elemental analysis calcd (%) for $C_{11}H_{12}O_5$ (224.21): C, 58.93; H, 5.39; found: C, 58.81; H, 5.38. IR (KBr, cm^{-1}): 3424 (br), 3288 (w), 3215 (w), 1728 (s), 1614 (m), 1576 (m), 1443 (m), 1408 (m), 1302 (m), 1225 (m), 1179 (m), 1036 (m), 914 (w), 945 (m), 772 (m), 692 (m), 613 (w), 459 (w).

2.3 | Synthesis of [Zn (RGAA)(BPY)$_{1/2}$] (1)

A solution of H$_2$**RGAA** (0.0448 g, 0.2 mmol), NaOH (0.016 g, 0.4 mmol), Zn $(NO_3)_2 \cdot 6H_2O$ (0.1190 g, 0.4 mmol), **BPY** (0.156 g, 0.1 mmol) and distilled water (8 ml) was transferred into a 15-ml Teflon reactor under autogenous pressure at 120°C for 3 days. The reaction mixture was cooled to room temperature at a rate of 5°C/hr. Colorless flake crystals of complex **1** suitable for XRD analysis were obtained (0.0562 g; yield: 38.4% based on Zn). Elemental analysis calcd (%) for $C_{16}H_{14}NO_5Zn$ (365.65): C, 52.55; N, 3.83; H, 3.86; found: C, 52.69; H, 3.82; N, 3.87. IR (KBr, cm^{-1}): 3433 (br), 3090 (w), 3059 (w), 2981 (w), 2916 (w), 2872(w), 1587 (s), 1498 (m), 1385 (s), 1298 (m), 1254 (m), 1176 (m), 1109 (m), 1043 (m), 995 (w), 842 (m), 765 (m), 736 (m), 677(w), 642 (m), 611 (m), 580 (w), 478 (m).

2.4 | Synthesis of $[Cd_5(\mu_3\text{-}OH)_2(RGAA)_4]$ (2)

A solution of H_2**RGAA** (0.0448 g, 0.2 mmol), NaOH (0.016 g, 0.4 mmol), Cd $(NO_3)_2{\cdot}4H_2O$ (0.0925 g, 0.3 mmol), distilled water (6 ml) and 95% ethanol (6 ml) was transferred to a 15-ml Teflon reactor under autogenous pressure at 160°C for 3 days. The reaction mixture was cooled to room temperature at a rate of 5°C/hr. Colorless bulk crystals of complex **2** suitable for XRD analysis were obtained (0.0210 g, yield: 23.6% based on Cd). Elemental analysis calcd (%) for $C_{44}H_{42}Cd_5O_{22}$ (1484.77): C, 35.59; H, 2.85; found: C, 35.71; H, 2.86. IR (KBr, cm^{-1}): 3388 (br), 2978 (w), 1581 (s), 1519 (m), 1431 (m), 1375 (s), 1286 (w), 1242 (s), 1178 (m), 1107 (m), 1035 (m), 991 (w), 867 (m), 795 (m), 761 (m), 719 (m), 667 (m), 603 (w), 484 (w).

2.5 | Single-crystal structure determination

Single-crystal structure determinations of two complexes **1** and **2** were measured by Bruker SMART CCD diffractometer equipped with a graphite crystal monochromator. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package[115,116] and refined by full-matrix least-squares methods with SHELXL,[117] and the semiempirical absorption corrections were applied using SADABS program.[118] All non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. The hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. A summary of the crystallographic data and structure refinements is presented in Table 1. Selected bond lengths and angles are given in Table 2. The topological analyses were generated using the TOPOS4.0 program.[119]

3 | RESULTS AND DISCUSSION

3.1 | Description of the crystal structures

3.1.1 | Structure description of complex 1

The results of the X-ray crystallographic analysis showed that complex **1** is a 3D framework and it crystallizes in the monoclinic system with space group $P2_1/c$. As depicted in Figure 1(a), the asymmetric unit of complex **1** is made of one zinc ion, half of one **RGAA** ligand, half of one **BPY** ligand. The central Zn (II) ion takes a distorted tetrahedral geometry via coordinating to one nitrogen atom (N1) of one **BPY** ligand and three carboxylic oxygen atoms (O1, O3A, O4B) of three **RGAA** ligands. The Zn-O bond lengths range from 1.954(2) to 2.017(2) Å, and the Zn-N bond distance is 2.051(3) Å (Table 2). The average Zn-O distance is 1.995 Å, and the bond angles of O-Zn-O and O-Zn-N vary from 99.24(10) to 129.32(10)° and 92.38(10) to 119.75(11)°, respectively, which is in agreement with those found in the literature published previously.[120–122] To generate a 3D framework, a pair of **RGAA** ligands link three Zn (II) atoms, which adopts μ_3-η^1:η^1:η^1:η^0 coordination mode (Scheme 2a). On the other

TABLE 1 Crystal data and structure refinement parameters for complexes **1** and **2**

Compound reference	1	2
Chemical formula	$C_{16}H_{14}NO_5Zn$	$C_{44}H_{42}Cd_5O_{22}$
Formula mass	365.65	1484.77
Crystal system	Monoclinic	Monoclinic
a/Å	10.007(2)	8.7206(2)
b/Å	19.600(4)	19.3343(4)
c/Å	7.6670(15)	14.3120(3)
α/°	90	90
β/°	92.77(3)	90.5653(8)
γ/°	90	90
Unit cell volume/Å^3	1502.1(5)	2412.98(9)
Temperature/K	293(2)	293(2)
Space group	$P2_1/c$	$P2_1/c$
No. of formula units per unit cell, Z	4	2
Radiation type	Mo Kα	Mo Kα
Absorption coefficient, μ/mm	1.660	2.250
No. of reflections measured	14724	14686
No. of independent reflections	3679	5484
R_{int}	0.0640	0.0300
Final R_1 values $[I > 2\sigma(I)]^a$	0.0423	0.0347
Final $wR(F^2)$ values $[I > 2\sigma(I)]^b$	0.0979	0.0793
Final R_1 values (all data)^a	0.0886	0.0445
Final $wR(F^2)$ values (all data)^b	0.1172	0.0837
Goodness of fit on F^2	1.014	1.096
CCDC number	15000825	15000826

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
$^bwR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

TABLE 2 Selected bond lengths (Å) and bond angles (°) for **1** and **2**, respectively

1			
Zn1–O1	1.954(2)	Zn1–N1	2.051(3)
Zn1–O3^{a}	1.972(2)	Zn1–O4^{b}	2.017(2)
O1–Zn1–N1	119.75(11)	N1–Zn1–O4^{b}	92.38(10)
O1–Zn1–O3^{a}	129.32(10)	O1–Zn1–O4^{b}	99.24(10)
O3^{a}–Zn1–O4^{b}	107.33(9)	N1–Zn1–O3^{a}	101.68(11)
2			
Cd1–O2	2.323(3)	Cd1–O11	2.196(3)
Cd1–O4^{c}	2.293(3)	Cd1–O2^{d}	2.323(3)
Cd1–O11^{d}	2.196(3)	Cd1–O4^{f}	2.293(3)
Cd2–O11	2.222(3)	Cd2–O5^{c}	2.188(3)
Cd2–O1^{d}	2.352(4)	Cd2–O7^{e}	2.239(3)
Cd2–O9^{g}	2.326(3)	Cd3–O2	2.236(3)
Cd3–O6	2.268(3)	Cd3–O11	2.236(3)
Cd3–O10^{g}	2.175(3)		
O2–Cd1–O11	81.43(11)	O2–Cd1–O4^{c}	84.84(12)
O2–Cd1–O2^{d}	180.00	O2–Cd1–O11^{d}	98.57(11)
O2–Cd1–O4^{f}	95.16(12)	O2^{d}–Cd1–O11^{d}	81.43(11)
O11–Cd1–O2^{d}	98.57(11)	O11–Cd1–O11^{d}	180.00
O11–Cd1–O4^{f}	94.23(13)	O4^{c}–Cd1–O2^{d}	95.16(12)
O4^{c}–Cd1–O11^{d}	94.23(13)	O2^{d}–Cd1–O4^{f}	84.84(12)
O11^{d}–Cd1–O4^{f}	85.77(13)	O4^{c}–Cd1–O4^{f}	180.0(2)
O11–Cd1–O4^{c}	85.77(13)	O1–Cd2–O5^{c}	102.14(12)
O11–Cd2–O1^{d}	92.06(11)	O11–Cd2–O7^{e}	116.58(10)
O11–Cd2–O9^{g}	89.20(10)	O5^{c}–Cd2–O1^{d}	91.87(13)
O5^{c}–Cd2–O7^{e}	140.43(12)	O5^{c}–Cd2–O9^{g}	110.80(11)
O1^{d}–Cd2–O7^{e}	79.44(11)	O1^{d}–Cd2–O9^{g}	156.50(12)
O7^{e}–Cd2–O9^{g}	79.03(10)	O2–Cd3–O6	98.11(11)
O6–Cd3–O10^{g}	110.79(13)	O2–Cd3–O11	82.53(10)
O2–Cd3–O10^{g}	142.70(12)	O6–Cd3–O11	133.34(10)
O11–Cd3–O10^{g}	93.51(12)		

Symmetry codes:
$^{a}-1+x, y, z$.
$^{b}-1+x, ½-y, ½+z$.
$^{c}1-x, 1/2+y, 3/2-z$.
$^{d}1-x, 1-y, 1-z$.
$^{e}2-x, 1-y, 1-z$.
$^{f}x, ½-y, -½+z$.
$^{g}x, ½-y, ½+z$.

hand, each **BPY** ligand links two Zn (II) atoms, which makes use of μ_2-η^1:η^1:η^0:η^0 coordination mode by Zn-N coordinated bonds (Figure 1b).

To further get an insight into the structure of **1**, topological analysis was carried out. Each **BPY** and **RGAA** ligand can be considered as a 2-connected node and 3-connected one, respectively. The Zn center can be regarded as a 4-connected node. Thus, it can be described as a 3-nodal net, which displays an unreported topology. The network of **1** is simplified to a (2,3,4)-connected (6^3.8^2.10)$_2$(6^3)$_2$(8) topology analyzed by TOPOS 4.0 program (Figure 1c).[119]

3.1.2 | Structure description of complex 2

X-ray crystallographic analysis revealed that complex **2** displays a 3D framework with monoclinic $P2_1/c$ space group. As shown in Figure 2(a), the fundamental unit contains three Cd (II) ions, two deprotonated H$_2$**RGAA** ligands and one μ_3-OH (O11) group. The metal centers of Cd1, Cd2 and Cd3 exhibit the difference coordination environment in asymmetric unit for **2**. The Cd1 center coordinated by four oxygen atoms (O2C, O2, O4G, O4B) from four **RGAA** ligands and two (O11, O11E) from μ_3-OH adopts a distorted octahedral coordination geometry. The bond lengths of Cd1-O are in the range of 2.196(3)–2.323(3) Å (Table 2). The bond angles around Cd1 vary from 81.43(11) to 180.00°. The Cd2 center is coordinated by five oxygen atoms (O1C, O9A, O7A, O5B and O11) of **RGAA** ligands and μ_3-OH, which adopts a distorted trigonal bipyramidal coordination geometry. The bond distances of Cd2-O change from 2.188(3) to 2.352(4) Å. The bond angles of O-Cd2-O are in the range of 79.03(10)–140.43(12)°. The Cd3 center is coordinated by three oxygen atoms (O2, O6, O10A) from three **RGAA** ligands and one μ_3-OH (O11), which adopts a distorted tetrahedron coordination geometry. The bond lengths of Cd3-O fall in the range of 2.175 (3) –2.268(3) Å (Table 2). The bond angles around Cd3 center range from 82.53(10) to 142.70° (Table 2), which is in agreement with those found in the literature published previously.[123–125] As shown in Figure 2b, it is important to note that five Cd atoms locate the coplanar state. Each **RGAA** ligand is completely deprotonated. Two deprotonated **RGAA** ligands adopt μ_4-η^1:η^1:η^1:η^1 and μ_5-η^1:η^2:η^1:η^1 coordination modes, respectively (Scheme 2b and 2c). With these kinds of connection modes, the 3D framework is generated (Figure 2c). For the sake of topological classification, this framework was simplified. If five cadmium atoms are viewed as a sub-unit, the sub-unit can be considered as 10-connected nodes. The **RGAA** ligand can be considered as 3-connected nodes. Thus, the 3D framework could be described as a 2-nodal net feature with 3,10 T4 topology style. The network of **2** features a (3,10)-connected (3.4.5)$_2$(3^4.4^6.5^18.6^14.7^2.8) topology analyzed by TOPOS4.0 program (Figure 2d).[119]

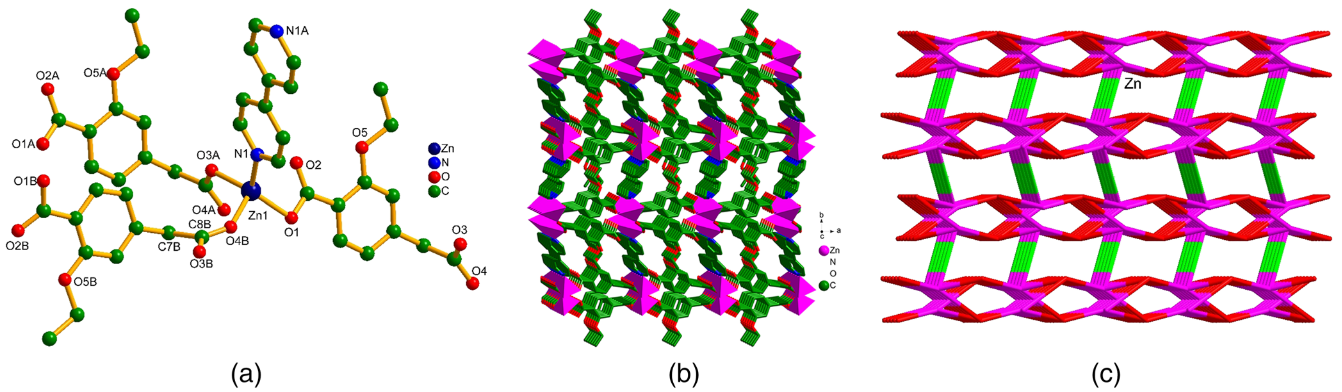
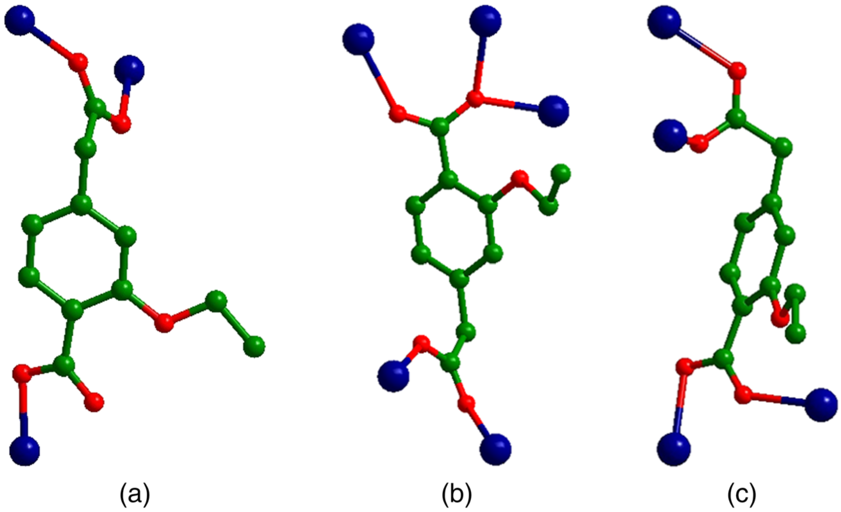


FIGURE 1 (a) The coordination environments of the Zn (II) ion in **1**. Hydrogen atoms are omitted for clarity. A: $-1 + x, y, z$; B: $-1 + x, \frac{1}{2} - y, \frac{1}{2} + z$. (b) View of the 3D coordination framework. (c) The topology structure of (2,3,4)-connect 3D framework (pink, red and bright nodes stand for 4- connected Zn, 3-connected RGAA and 2-connected BPY, respectively)

SCHEME 2 Various coordination modes of RGAA (a for **1**, b and c for **2**)



So far, there exist several examples of MOFs with Cd_5O cluster,[126–130] which are constituted by different components and display interesting structures. To compare their components and the features, compounds with Cd_5O clusters are listed in Table 3. As shown in Table 3, all MOFs with Cd_5O cluster contain the bridged –OH/O. Interestingly, in the reported MOFs structures, these 3D frameworks consist of three kinds of ligands. Notably, the present architecture is made of two types of ligands (**RGAA** and the bridged hydroxyl group).

3.1.3 | Coordination modes of RGAA in complexes 1 and 2

According to the structure descriptions mentioned above, we found that the H_2**RGAA** ligand displays a variety of coordination modes when binding to specific metal ions, which plays a key role in determining the solid structures of MOFs. Two carboxylate groups of **RGAA** ligand can exhibit two kinds of coordination modes (Scheme 2). In complexes **1** and **2**, all of the **RGAA** ligands are completely deprotonated. Each **RGAA** ligand links three Zn (II) atoms adopted μ_3-η^1:η^1:η^1:η^0 (Scheme 2a) coordination mode for **1**. However, in complex **2**, two carboxyl groups in **RGAA** ligands adopt the completely different coordination modes, that is, μ_4-η^1:η^1:η^1:η^1 (Scheme 2b) and μ_5-η^1:η^2:η^1:η^1 (Scheme 2c), to connect the Cd metal ions to construct a 3D framework. The present results obviously reveal that the coordination modes of carboxylate groups can affect the structural motifs of the final product.

To further compare the coordination modes of aromatic carboxylic groups, several Cd-based MOFs containing aromatic dicarboxylic acid were selected and investigated.[131–134] For example, these complexes $[Cd_3(bdc)_3(H_2O)_2]\cdot(\text{tm-urea})_x$ (H_2bdc and tm-urea = represent *p*-benzene dicarboxylic acid and tetramethyl urea, respectively), $[Cd_4(btec)_2(H_2O)_5]$ (H_4btec = 1,2,3,5-benzenetetracarboxylic acid), $[Cd_3(bdc)_3(DMF)_2]$

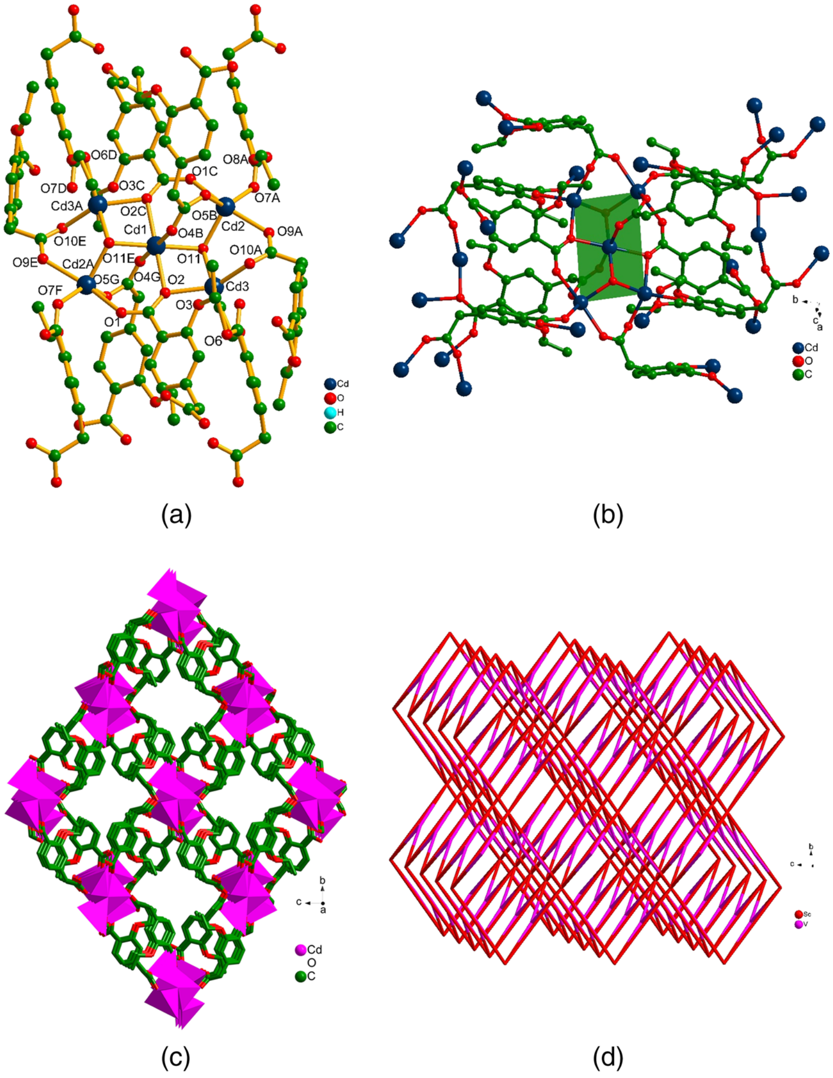


FIGURE 2 (a) Coordination environments of the Cd (II) ion in **2**. Hydrogen atoms are omitted for clarity. A: 1 − *x*, ½ + *y*, 3/2 − *z*; B: 1 − *x*, 1 − *y*, 1 − *z*; C: 2 − *x*, 1 − *y*, 1 − *z*; D: *x*, ½ − *y*, −1/2 + *z*; E: *x*, ½ − *y*, ½ + *z*. (b) Five Cd atoms coplanar in **2**. (c). View of the 3D coordination framework. (d) The topology structure of (3,10)-connect 3D framework (pink nodes and red ones represent 10- connected Cd and 3-connected RGAA, respectively)

(DMF = *N*,*N*′-dimethylformamide) and [Cd (NDC)(DMF)]$_n$ (H_2NDC = 1,4-naphthalenedicarboxylic acid) have been obtained. In these MOFs, the biscarboxylic groups can play a role in high connectivity, which displays five-coordinated mode (Scheme 2b).

3.2 | IR spectra

The FT-IR spectra were recorded from KBr pellets in the range 400–4000 cm^{-1} on a Bruker spectrometer. The IR spectra of **1** and **2** are shown in Figure 3. The carboxylic groups of H_2**RGAA** are completely deprotonated because of an absence of the vibration band at 1728 cm^{-1} assigned to the -COOH functional group for **1** and **2**, which has been confirmed by the single-crystal X-ray crystallographic analyses. The IR data can provide us with valuable information about the coordination mode of dicarboxylate ligands in **1** and **2**. As is well known, asymmetric and symmetric stretching vibration bands of carboxylic groups are expected to be at 1500–1630 cm^{-1} and 1350–1460 cm^{-1}, respectively. As a result, the strong bands at 1587 and 1581 cm^{-1} for **1** and **2** can be assigned to the asymmetric stretching vibration of carboxylic groups ν_{as} (CO_2^-), respectively, while the strong peaks at 1385 and 1375 cm^{-1} for **1** and **2** can be assigned to the symmetric stretching vibration of carboxylic groups ν_s (CO_2^-), respectively. Generally, the separation ($\Delta\nu$) between ν_{as} (CO_2^-) and ν_s (CO_2^-) in the IR spectrum has been often used to diagnose the coordination modes of carboxylate groups. The separation for mono-dentate carboxylate groups is > 200 cm^{-1}, whereas the separation for didentate carboxylate groups is < 200 cm^{-1}.[135] In the present cases, the $\Delta\nu$ values of 202 and 206 cm^{-1} for **1** and **2** can be observed, respectively. According to the results of IR spectra for compounds **1** and **2**, the mono-dentate coordination mode of the carboxylic groups can be observed. The characteristic stretching vibration of the -OH groups can be found at 3388 cm^{-1} in complex **2**. Actually, the carboxylate IR adsorption is very

TABLE 3 Comparison of MOFs with Cd_5O cluster

Compounds	Ligands	Refs
$[Cd_5(\mu_3\text{-}O)_2(L)_3(H_2L)(CH_3OH)(DMF)]$	H_2L = *N*, *N*′-bis(5-ethyl-1,3,4-thiadiazol-2-yl)-2,6-pyridinedicarboxamide DMF = *N*,*N*′-dimethylformamide	[126]
$[Cd_5(\mu_3\text{-}OH)_2(sdba)_4(2,2'\text{-}bpy)_2(H_2O)_2]\cdot 2H_2O$	sdba = 4,4′-sulfonyldibenzoato bpy = bipyridine	[127]
$[Cd_5(atz)_4(\mu_5\text{-}SO_4)_2(\mu_3\text{-}OH)_2]_n$	atz = 5-amino-tetrazolate	[128, 129]
$[Cd_5(L1)_2(OH)_2(trz)_4(L3)]\cdot 2H_2O$	H_2L1 = 4-(1-carboxy-ethoxy)-benzoic acid L3 = 1,2-bis(1,2,4-triazole-1-yl)ethane Htrz = 1,2,4-triazole	[130]
$[Cd_5(\mu_3\text{-}OH)_2($**RGAA**$)_4]$	H_2**RGAA** = 4-(carboxymethyl)-2-ethoxybenzoic acid	This work

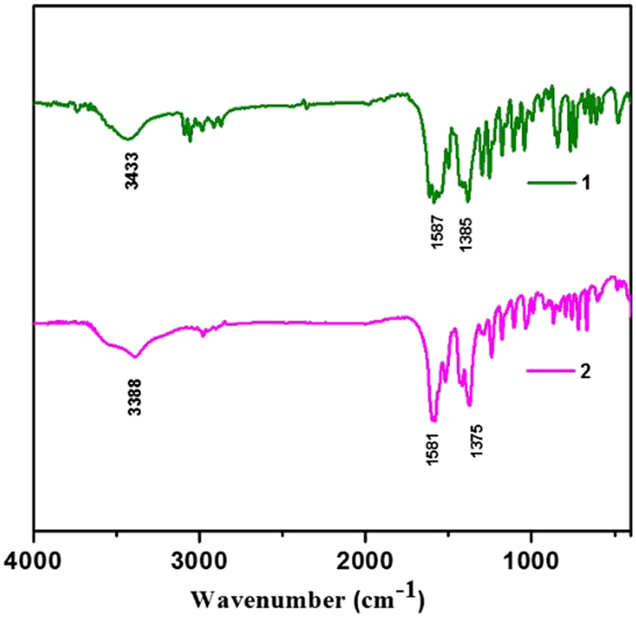


FIGURE 3 IR spectra of complexes **1** and **2**

complicated due to its coordination diversity with metal ions. These IR spectral results are in good agreement with the crystallographic structural analyses mentioned above.

3.3 | PXRD patterns and TGA

In order to characterize the phase purities of compounds **1** and **2**, PXRD patterns have been checked at ambient temperature (Figures S1 and S2). For **1** and **2**, the peak positions of the simulated and experimental PXRD patterns are in agreement with each other, which confirms their phase purity. By contrast, the difference in intensity of some diffraction peaks may be attributed to the preferred orientation of the crystalline powder samples.[136]

In order to estimate the stabilities of the coordination architectures of **1** and **2**, TGA were carried out. The experiments were performed on samples consisting of numerous single crystals of **1** and **2** under a N_2 atmosphere with a heating rate of 10°C/min, as illustrated in Figures S3 and S4. The TGA curve shows that the decomposition of the organic ligands occurs from a temperature of 311–924°C for **1** (obsd 76.1%, calcd 77.8%). The remaining weight loss is in accordance with the formation of ZnO (obsd 23.9%, calcd 22.3%) for **1**. For complex **2**, the TG curve shows that the initial weight loss is observed above 305°C, which indicates the decomposition of the organic ligands. The residue corresponds to the formation of CdO (obsd 44.7%, calcd 43.2%).

3.4 | Luminescent properties

Metal–organic frameworks containing d^{10} metal ions with aromatic ligands are well known for their excellent luminescence behavior.[137–140] The luminescent properties of d^{10}-based metal coordination polymers with carboxylate ligands have been investigated.[141,142] Thus, the solid-state photoluminescence spectra of complexes **1** and **2** were investigated at ambient temperature. As

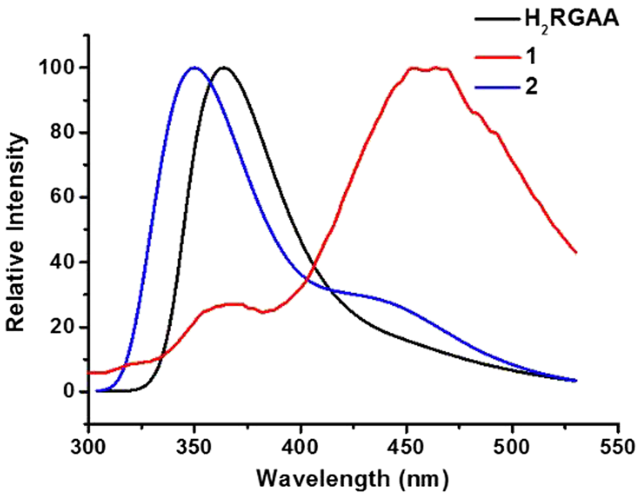


FIGURE 4 Fluorescent emission spectra of H2RGAA and its complexes **1** and **2** in the solid state at room temperature

illustrated in Figure 4, complexes **1** and **2** display emission peaks at 464 and 349 nm upon excitation at 273 and 284 nm, respectively. The difference in their emissions and excitations is probably due to the differences in metal ions and the coordination environment around them; the photoluminescence behavior is closely associated with the local environments around metal ions. To further study the nature of emission of the complexes, the emission spectrum of free H$_2$**RGAA** ligand was also performed. The results show that the maximum emission exists at 364 nm (λ_{ex} = 284 nm), which can be tentatively attributed to $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions. Compared with the emission maxima of free H$_2$**RGAA** ligand, that of complex **1** and **2** is red-shifted about 100 nm and blue-shifted about 15 nm, respectively. The observed red or blue shifts of the emission peak may be attributed to the following factors: (a) the ligands reduced energy levels between the highest occupied molecular orbital and the lowest unoccupied molecular orbital when binding to the metal ions; (b) there may exist metal-to-ligand charge transfer or ligand-to-metal charge transfer in complexes **1** and **2**.[2,143,144] These observations suggest that these compounds can serve as candidates for potential photoactive materials.

4 | CONCLUSIONS

In summary, two new d^{10} MOFs based on a semi-rigid aromatic biscarboxylate ligand have been synthesized under solvothermal conditions, which display interesting photoluminscent behaviors. The versatile semi-rigid aromatic biscarboxylate ligand and transition metal ions play important roles in governing the final structures. The present results demonstrate that the semi-rigid aromatic biscarboxylate ligand can be a potential building block to construct novel MOFs. Further exploration and investigation of novel MOFs with other semi-rigid aromatic biscarboxylate ligands is underway in our laboratory.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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APPENDIX A: Supplementary Material

CCDC 15000825 and 15000826 contain the supplementary crystallographic data of the ligand and its complex for this article. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Telephone: +44 01223 762910; Facsimile: +44 01223 336033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1002/aoc.5654.