Structure versatility of coordination polymers constructed from a semirigid ligand and polynuclear metal clusters†

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Five new coordination polymers, namely $[Cd_3(dcppa)(Hdcppa)(H_2O)]\cdot(Me_2NH_2)\cdot(DMA)_2$ (**1**), $[CdCa(dcppa)(DMA)_2]$ (**2**), $[CdCa(dcppa)(H_2O)_2(DMA)]$ (**3**), $[Ba_2(H_2dcppa)_2(\mu_2\text{-}H_2O)(H_2O)(DMA)]\cdot(H_2O)$ (**4**), and $[Ba_2(H_2dcppa)_2(\mu_2\text{-}H_2O)(H_2O)(DMF)]\cdot(H_2O)$ (**5**) ($Me_2NH_2^+$ = dimethylammonium cation; DMA = N,N-dimethylacetamide; DMF= N,N-dimethylformamide; H_4dcppa = 3-(3',5'-Dicarboxylphenoxy) phthalic acid), have been synthesized under solvothermal conditions and structurally characterized. Compound **1** presents a unique binodal (3,6)-connected {4^3}2{4^7.8^8} topology structure, which is a 2D layer anionic network with $Me_2NH_2^+$ cations occupying the voids, built upon trinuclear Cd_3 unit. Compounds **2** and **3** are all bimetallic Cd-Ca compounds consisting of tetranuclear Cd_2Ca_2 units extending to a 3D (3,6)-connected **rtl** topology structure and a 2D (3,6)-connected **kgd** topology structure, respectively. Compounds **4** and **5** are isostructural and exhibit a unprecedented 3D (4,10)-connected topology structure in which a 1D infinite barium chain is observed. From the viewpoint of crystal structure diversity and comparison, our results further demonstrate that the coordination modes of metal ions and ligands are the vital elements in forming the final crystal structure. In addition, the thermal stabilities and solid-state luminescence properties of compounds **1**-**5** have also been discussed.

Introduction

Current interest in metal-organic coordination polymers on the basis of the construction of metal ions and multifunctional organic ligands is rapidly expanding owing to their intriguing and fascinating aesthetic structures and topological features as well as their potential applications as functional materials.[1,2] With the recent development of self-assembly of coordination chemistry, it is possible to rationally design and synthesize metal-organic coordination polymers on a fundamental molecular level through elaborate choice of metal ions and organic ligands. However, it still a long-way challenge to predict the solid-state structure resulting from some unpredictable factors, including reaction temperature and pressure, solvents, auxiliary ligands, pH, templates, secondary metal ions and so on.[3-5] Metal carboxylates are particularly interesting because they present open-framework structures and their carboxylate groups act as linkers between inorganic moieties.[6] However, most of the reported work has been devoted to the use of rigid carboxylate ligands, such as benzenedicarboxylate and benzenetricarboxylate and so on, while the use of flexible carboxylate ligands has been reported infrequently.[7,8] The flexible polycarboxylate ligands can have different conformations and coordination modes when they react with metal salts, and thus can form polynuclear metal complexes with great structural diversity and unusual topologies.[9] Considering these in mind, we have introduced a versatile flexible polycarboxylate ligand, 3-(3',5'-Dicarboxylphenoxy) phthalic acid (H_4dcppa), to construct polynuclear metal complexes. It is worthy of noting that this flexible ligand have four carboxylate moieties in one ligand, therofore the intense competition among these functional groups can result in novel multidimensional metal-organic frameworks with various bridging modes. Another significant feature is that the relative flexibility around the etheric oxygen atom is assumed to generate different torsion angles for the two phenyl planes and the carboxylate groups, and further features various coordination conformations.[9] However, the related studies based on this ligand have not been reported.

In order to systematic research into this ligand, we have introduced d^{10} and alkaline-earth metal ions to prepare metal-organic coordination polymers. Compared to transition metal ions, the main group alkaline-earth metal ions have relatively larger radius, and have high affinity for oxygen donnors, which will provide unique opportunities for the formation of metal-organic coordination polymers. On the other hand, secondary building units (SBUs) (such as di-, tri-, tetranuclear cluster, rod-shaped chains and so on) will play a key role in the formation of desired framework.[10]

Herein, we report the synthesis and crystal structural studies of five homometallic or heterometallic H_4dcppa coordination polymers, $[Cd_3(\mathbf{L})(\mathbf{HL})(H_2O)]\cdot(Me_2NH_2)\cdot(DMA)_2$ (**1**), $[CdCa(\mathbf{L})(DMA)_2]$ (**2**), $[CdCa(\mathbf{L})(H_2O)_2(DMA)]$ (**3**), $[Ba_2(\mathbf{H_2L})_2(\mu_2\text{-}H_2O)(H_2O)(DMA)]\cdot(H_2O)$ (**4**), $[Ba_2(\mathbf{H_2L})_2(\mu_2\text{-}H_2O)(H_2O)(DMF)]\cdot(H_2O)$ (**5**) ($Me_2NH_2^+$ = dimethylammonium cation; DMA = N,N-dimethylacetamide; DMF = N,N-dimethylformamide). Compounds **1**-**5** were characterized by elemental analysis (EA), single-crystal X-ray crystallography, X-ray powder diffraction (XRPD), infrared spectroscopy (IR), thermogravimtric analyses (TGA) and luminescent properties.

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Experimental Section

Materials and Instrumentation

The metal salts, organic ligand and solvents for synthesis and analysis were purchased commercially and used without further purification. All compounds were synthesized under autogenous pressure with 23 mL polytetrafluoroethylene glass containers. C, H, N analyses were performed on an EA1110 CHNS-0 CE elemental analyzer. FT-IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer using KBr pellets, in the range of 400 ~ 4000 cm^{-1}. X-ray powder diffraction (XRPD) analyses were performed on a Rigaku Dmax2500 diffractometer with Cu $K\alpha$ radiation (λ = 1.54056 Å) with a scan speed of 5 °/min. The luminescence spectra for the powdered solid samples were measured at room temperature using an Edinburgh FLS920 TCSPC fluorescence spectrophotometer. TGA analyses were carried out on a NETSCHZ STA-449C thermoanalyzer with a heating rate of 10 °C/min under a nitrogen atmosphere. All the measurements were carried out under the same experimental conditions.

Syntheses of complounds 1-5

[Cd$_3$(dcppa)(Hdcppa)(H$_2$O)]·(Me$_2$NH$_2$) ·(DMA)$_2$ (1). A mixture of Cd(NO$_3$)$_2$·4H$_2$O (0.031g, 0.10mmol), Mg(NO$_3$)$_2$·3H$_2$O (0.026g, 0.1mmol) and 3-(3',5'-Dicarboxylphenoxy) phthalic acid (H$_4$dcppa) (0.035 g, 0.10 mmol) in 23 ml polytetrafluoroethylene glass container, 2mL DMA and 1mL H$_2$O were then added. The resulting mixture was stirred for 10 min at room temperature, and then the mixture was sealed in a Parr autolave and kept at 110°C for two days. After being slowly cooled to the room temperature, colorless rod crystals of **1** were obtained. Yield: 45% based on H$_4$dcppa. Anal. calc. for $C_{42}H_{41}Cd_3N_3O_{21}$(1260.98): C, 39.97; H, 3.25; N, 3.33%. Found: C, 39.94; H, 3.24; N, 3.35%. IR data (KBr pellet): 3467 (m), 2542(w), 1690 (m), 1635(m), 1511 (m), 1420 (m), 1289 (s), 1202 (m), 1140 (m), 984 (w), 928(s), 886 (s), 817 (m), 783 (w), 720 (w), 668(w).

[CdCa(dcppa)(DMA)$_2$] (2). The reaction was carried out in a procedure similar to that for **1**, using Ca(NO$_3$)$_2$·4H$_2$O (0.048g, 0.10 mmol) instead of Mg(NO$_3$)$_2$·3H$_2$O (0.026g, 0.1mmol). Colorless prism crystals of **2** were obtained in 57% yield based on H$_4$dcppa. Anal. calc. for $C_{24}H_{24}CaCdN_2O_{11}$ (668.93): C, 43.06; H, 3.59; N, 4.19% Found: C, 43.04; H, 3.58; N, 4.22%. IR data (KBr pellet): 3470 (m), 2550(w), 1697 (s), 1643(m), 1527(s), 1432 (s), 1307 (s), 1217 (m), 1160 (m), 1005 (w), 946(s), 909 (s), 835 (m), 789 (w), 722 (w), 668(w).

[CdCa(dcppa)(H$_2$O)$_2$(DMA)] (3). The reaction was carried out in a procedure similar to that for **2**, using 1ml DMA and 2ml H$_2$O instead of 2ml DMA and 1ml H$_2$O. Colorless prism crystals of **3** were obtained in 52% yield based on H$_4$dcppa. Anal. calc. for $C_{20}H_{19}CaCdNO_{12}$ (617.84): C, 38.85; H, 3.08; N, 2.27% Found: C, 38.84; H, 3.07; N, 2.29%. IR data (KBr pellet): 3473 (m), 2554(m), 1701 (m), 1650(m), 1533(s), 1441(s), 1320(s), 1226 (s), 1169 (m), 1012 (m), 955 (w), 918(s), 842 (s), 798 (m), 724 (w), 669(w).

[Ba$_2$(H$_2$dcppa)$_2$(μ_2-H$_2$O)(H$_2$O)(DMA)]·(H$_2$O) (4). The reaction was carried out in a procedure similar to that for **1**, using Ba(NO$_3$)$_2$ (0.026g, 0.10mmol) instead of Mg(NO$_3$)$_2$·3H$_2$O (0.026g, 0.1mmol). Colorless block crystals of **4** were obtained in 59% yield based on H$_4$dcppa. Anal. calc. for $C_{36}H_{30}Ba_2N_2O_{22}$ (1103.25): C, 39.16; H, 2.72; N, 2.54%. Found: C, 39.17; H, 2.73%; N, 2.56%. IR data (KBr pellet): 3532 (m), 2432(w), 1605 (s), 1497(s), 1352 (s), 1304 (s), 1213 (m), 1145 (m), 1005 (w), 928(s), 891 (s), 825 (m), 794 (w), 722 (w), 680(w).

[Ba$_2$(H$_2$dcppa)$_2$(μ_2-H$_2$O)(H$_2$O)(DMF)]·(H$_2$O) (5). The reaction was carried out in a procedure similar to that for **4**, using 2ml DMF and 1ml H$_2$O instead of 2ml DMA and 1ml H$_2$O. Colorless block crystals of **5** were obtained in 56% yield based on H$_4$dcppa. Anal. calc. for $C_{35}H_{28}Ba_2N_2O_{22}$ (1089.26): C, 38.56; H, 2.57; N, 2.57%. Found: C, 38.58; H, 2.56%; N, 2.56%. IR data (KBr pellet): 3535 (m), 2610(m), 1754(s), 1702(m), 1589 (s), 1497 (s), 1373 (m), 1261 (s), 1198(m), 1054(m), 991 (m), 942 (s), 854 (s), 811 (m), 728(w), 670(w).

X-ray Crystallography

Suitable single crystals of **1**-**5** were carefully picked under an optical microscope and then glued to thin glass fibers. Crystallographic data collections for five compounds were performed on a computer-controlled Oxford Xcalibur E diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda_{\mathrm{Mo}\ K\alpha}$ = 0.71073 Å) at T = 293.2 K. An empirical absorption corrections were made using the SADABS program.[11] The structures were solved primarily with the direct method and and then with Fourier difference techniques. They were refined by full-matrix least-squares methods on F^2 by using the SHELX-97 program package.[12] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms attached to carbon atoms were fixed at their ideal positions. All calculations were performed with SHELXL-97 package. Crystal data, as well as details of data collection and refinements of **1**-**5** are summarized in Table 1, and selected bond lengths and angles are listed in Table S1 (ESI†).

Results and discussion

Syntheses

H$_4$dcppa is an important polycarboxylic flexible ligand and is characterized by its multiple metal-bridging groups with various bridging modes, which may offer possibilities to generate novel and diversified structures and topologies. In addition, alkaline earth-metal ions can affect the construction of coordination polymers as structure-directing/templated agents. Based on these, we introuduce the family of Cd/M (Mg, Ca, Ba) to investigate the coordination chemistry of this flexible ligand. Moreover, as a consideration for the safety in the lab, the reaction temperature was kept at 110 ° C for 60-72h and then cooled to the room temperature. Compounds **1**-**5** reported here were obtained in high yield from the simple combination of H$_4$dcppa ligand, d^{10} metal and alkaline-earth metal ions with the molar ratio of 1:1:1 under solvothermal conditions. Furthermore, the use of Cd(NO$_3$)$_2$·4H$_2$O and H$_4$dcppa ligand without alkaline-earth metal ions in the reaction system gave rise to uncharacterized precipitates.

Crystal Structure of Compounds 1-5

$[Cd_3(dcppa)(Hdcppa)(H_2O)]\cdot(Me_2NH_2)\cdot(DMA)_2$ (1). X-ray crystal structure analysis reveals that compound **1** belongs to orthorhombic systerm with space group *Pbca* and features a 2D bilayer structure. As shown in Fig. 1a, the asymmetric unit of **1** contains three independent Cd(II) ions, one independent $(dcppa)^{4-}$ ligand, one $(Hdcppa)^{3-}$ ligand, one coordinated water molecule, two free DMA molecules one $NH_2(CH_3)_2^+$ cation. The $NH_2(CH_3)_2^+$ cation is generated via either hydrolysis or decarbonylation of DMA under a solvothermal condition, which is a frequently encountered phenomenon.[13] Both Cd1 and Cd2 are all seven-coordinated with a distorted monocapped octahedral geometry surrounded by senven oxygen atoms from three and four different $(dcppa)^{4-}$/$(Hdcppa)^{3-}$ ligands, respectively. Besides, there is also one water molecule connected to Cd1 center. Unlike Cd1 and Cd2, Cd3 is connected by six oxygen atoms from two $(dcppa)^{4-}$ ligands and two $(Hdcppa)^{3-}$ ligands. Cd3 nearly lies on the center between Cd1 and Cd2, and this three cadmium atoms generate a trinuclear $[Cd_3(COO)_8(H_2O)]^{2-}$ building unit (Fig. 1b). It should be noted that the trinuclear cadmium unit is an anionic cluster, which is very rare in the CPs systerm constructed by flexible polycarboxylate ligands. The non-bonding Cd1···Cd2, Cd2···Cd3 and Cd1···Cd3 separations are 6.307(6), 3.421(6), 3.528(6) Å, respectively. In addition, the Cd-O (Cd1-O, Cd2-O, Cd3-O) bond lengths are in the range of 2.155(5)-2.540(5) Å, which are in good agreement with previous studies.[14] And the O-Cd-O angles are all listed in table S1 (ESI†).

The coordination modes of $(dcppa)^{4-}$ and $(Hdcppa)^{3-}$ ligands in **1** are shown in Scheme 1a and 1b. For $(dcppa)^{4-}$ ligand, it adopts three different coordination modes: chelating, bidentate bridging, chelating and bridging; For $(Hdcppa)^{3-}$ ligand, it also exhibits three different coordination modes: monodentate bridging, chelating, bridging and chelating. In other words, there are four different connection modes in **1** totally. As a consquence, the adjacent trinuclear Cd_3 units are connected alternatively via $(dcppa)^{4-}$/$(Hdcppa)^{3-}$ ligands to propagate into a 2D anionic framework with $NH_2(CH_3)_2^+$ cation occupying the voids (Fig. 1c). From the topological point of view,[15] the intricate framework of **1** can be simplified into a unique binodal (3,6)-connected net with an unprecedented {4^3}2{4^7.8^8} topology (Fig. 1e). In this simplification, each Cd_3 unit is surrounded by six $(dcppa)^{4-}$/$(Hdcppa)^{3-}$ ligands to form six-connected node, and then each $(dcppa)^{4-}$/$(Hdcppa)^{3-}$ ligand bonds three Cd_3 units and acts as a 3-connected node. In order to have better insight into the nature of this complicated architecture, we consider removing $(dcppa)^{4-}$/$(Hdcppa)^{3-}$ ligand at a time. On removing $(dcppa)^{4-}$/$(Hdcppa)^{3-}$ ligand, the remainder is an fascinating and more simple 3-connected **fes** topology with the Schläfli symbol of {4;8^2} (Fig. 1e).

$[CdCa(dcppa)(DMA)_2]$ (2). The single X-ray diffraction analysis reveals that the asymmetric unit of **2** consists of one independent Cd(II) ion, one independent Ca(II) ion, one independent $(dcppa)^{4-}$ ligand, two coordinated DMA molecules (Fig. 2a). The Cd(II) center is hepta-coordinated and located in a distorted pentagonal bipyramid geometry. The Cd-O bond lengths are in range of 2.202(3)-2.458(3) Å, which are in good agreement with previous studies.[14] With the exception of somewhat longer Cd1-O3B and Cd1-O6A distance at 2.736(3) and 2.807(3), respectively, which should be also considered as non-negligible interaction. The Ca1 center adopts a slightly distor-ted octahedron geometry; four oxygen atoms (O2, O3D, O6A, O11) comprise the equatorial plane, and another two oxygen atoms (O9C, O10) occupy the axial positions. The Ca1-O bond lengths are in range of 2.285(3)-2.419(3) Å, which are similar to those observed in other calcium carboxylate complexes.[16,17] Moreover, the O-Cd1-O and O-Ca-O angles are also all listed in table S1 (ESI†), respectively. As shown in Scheme 1c, there are two different coordination modes of $(dcppa)^{4-}$ ligands in **2**: bidentate bridging, bridging and chelating. On the basis of these connection modes, Cd1 and Ca1 atom and their symmetry-related atoms (Cd1I, Ca1I) are integrated together by sharing eight carboxyl groups, thus forming a heterometallic tetranuclear $[Cd_2Ca_2(COO)_8(DMA)_4]$ building unit (Fig. 2b). The four atoms in the tetranuclear cluster lie in a plane with the non-bonding Cd···Ca separation of 3.620(1)-4.343(1) Å. Just like the previous one, each tetranuclear $[Cd_2Ca_2(COO)_8(DMA)_4]$ unit is associated with six $(dcppa)^{4-}$ ligands, and each $(dcppa)^{4-}$ ligand connected three tetranuclear clusters to form a 3D framework shown in Fig. 2c-2e . In order to simplify the complicated connectivity of ligands and metal centers, the network topology of **2** was analyzed by considering the tetranuclear unit as a node, generating a binodal (3,6)-connected **rtl** topology with the Schläfli symbol of {4.6^2}2{4^2.6^10.8^3} (Fig. 2f). From another point of view, we can have a better insight into the nature of this intricate architecture if we can imagine removing one of the two carboxylate groups at a time, which are located in the meta-position of the H_4dcppa ligand. In this way, we can obtain a 2D layer structure and a 1D linear structure (Fig. S1), respectively. Calculations using PLATON[18] show that the voids in compound **2** occupy 43.0% of the crystal volume after the removal of the guest molecules.

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$[CdCa(dcppa)(H_2O)_2(DMA)]$ (3). When using 1ml DMA and 2ml H_2O instead of 2ml DMA and 1ml H_2O, another different compound, **3**, was obtained, which was a 2D layer structure. The single X-ray diffraction study revealed that compound **3** crystallizes in the $P2_1/n$ space group. As depicted in Fig. 3a, the asymmetric unit of **3** has one independent Cd(II) ion, one independent Ca(II) ion, one independent $(dcppa)^{4-}$ ligand, two coordinated H_2O molecules, one coordinated DMA molecule. The coordination environment of Cd(II) center is surrounded by seven carboxylate O atoms belonging to four carboxylate groups of four different $(dcppa)^{4-}$ ligands. The Cd-O distances are in the range of 2.239(3)-2.7111(2) Å, which is comparable to the previous work.[14] The distance of 2.7111(2) Å is a little long, which is a nonnegligible interaction. Thus, the Cd(II) center can be described as a distorted monocapped octahedral geometry. Ca(II) center is six-bonded by three oxygen atoms from three different $(dcppa)^{4-}$ ligands, two oxygen atom from two coordinated water molecules and one oxygen atom from one coordinated

DMA molecule to fullfil a slightly distorted octahedral geometry. The Ca-O distances are in the range of 2.325(3)-2.420(3) Å, which are similar to those observed in **2**.

Herein, the four carboxylate groups of the $(dcppa)^{4-}$ ligand bind in three different ways: chelating, bidentate bridging, bridging and chelating (Scheme 1d). Notably, although **2** and **3** contains similar Cd(II) and Ca(II) ions, the $(dcppa)^{4-}$ ligand exhibits different bridging mode in both cases. Similar to that of **2**, **3** has a slight different heterometallic tetranuclear $[Cd_2Ca_2(COO)_8(H_2O)_4(DMA)_2]$ building unit (Fig. 3b). Interestingly, the angels of Cd1-Ca1-Cd1C and Ca1-Cd1C-Ca1C are 99.655(1) and 80.345(1) °, which indicates that four atoms are also in a same plane. Moreover, the non-bonding Cd1···Ca1 and Cd1···Ca1C distances are 4.145(1) and 4.030(2) Å, respectively. Compare to **2**, the Cd_2Ca_2 plane in **3** is getting closer to be a square. From the topoical point of view, although compound **3** has the similar nodes as **2**, it presents another distinct binodal (3,6)-connected **kgd** topology with the Schläfli symbol of {4^3}2{4^6.6^6.8^3} (Fig. 3d).

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$[Ba_2(H_2dcppa)_2(\mu_2\text{-}H_2O)(H_2O)(DMA)]\cdot(H_2O)$ (4) and $[Ba_2(H_2dcppa)_2(\mu_2\text{-}H_2O)(H_2O)(DMF)]\cdot(H_2O)$ (5). The single X-ray diffraction analysis revealed that compounds **4** and **5** are isostructural and crystallize in the triclinic space group $P\bar{1}$. As a representative example, only the crystal structure of **4** is depicted here in detail. As shown in Fig. 4a, the asymmetric unit of **2** consists of two independent Ba(II) ions, two independent $(H_2dcppa)^{2-}$ ligands, one coordinated DMA molecules, two coordinated water molecules and one free water molecule. The barium atoms are both nine-coordinated, thus, the Ba1 and Ba2 center can be described as distorted tricapped trigonal prism configurations: seven carboxylate oxygen atoms from four $(H_2dcppa)^{2-}$ ligands and one oxygen atom from one coordinated DMA molecule and one oxygen atom from one coordinated H_2O molecule. The Ba1-O distances varying in the range of 2.722(3)-2.880(3) Å are similar to those reported.[19] Besides these bonds, the Ba1-O17B, Ba2-O (O16, O17B, O20) bond distances are 3.069(3), 3.006(3), 3.046(3) and 3.038(3) Å, which are significantly longer than those observed in other alkaline earth metals complexes with oxygen donor ligands, and can be considered as nonnegligible interactions.

It should be noted that there are two different $(H_2dcppa)^{2-}$ ligands, which have four different coordination modes: monodentate bridging, bidentate bridging, bridging-chelating-bridging, bridging-anti bridging-chelating (Scheme 1e and Scheme 1f). The last one is very rare coordination mode, which is beneficial to construct novel structure and topology. As shown in Fig. 4b, the two Ba atoms and their own symmetry-related atoms are joined together by sharing four H_2O, eight $-COO^{-1}$, six -COOH and two DMA, thus forming a novel tetranuclear $[Ba_4(\mu_3\text{-}COO)_4(\mu_2\text{-}COO)_4(COOH)_6(\mu_2\text{-}H_2O)_2(H_2O)_2(DMA)_2]$ building unit. The four barium atoms (Ba1, Ba2, Ba1B, Ba2B) of tetranuclear Ba_4 unit lie in a plane, with non-bonding Ba1···Ba2 distances of 4.411-4.830 Å. These tetranuclear units via bridging carboxylates and edge-sharing to give rise to a 1D barium chain along the crystallographic b/c axis (Fig. 4g). These chains are joined into a intricate 3D coordination polymer by carboxylate groups of $(H_2dcppa)^{2-}$ ligands. The 3D structure is stabilized by O−H···O hydrogen bonds, which originate from coordinated water and carboxy late oxygen, as well as those between coordinated waters. Moreover, the free water molecules filled in apertures also have a nonnegligible impact on construction of the 3D network by forming O−H···O hydrogen bonds. The most fascinating structural feature of **4** is that it has the tetranuclear Ba_4 and 1D infinite barium chain at the same time. To our knowledge, this case is relative rare. The total potential solvent accessible void volume of **4** calculated by PLATON[18] is found to be 25.4% of the unit cell volume after removal of all guest molecules in the channels.

To have a better insight into the nature of the complicated framework, we have to simplify the 3D net of **4** by using TOPOS4.0 programme. As a result, the 3D structure of **4** can be simplified to a unique binodal (4,10)-connected network with the Schläfli symbol of {3;4^5}2{3^4;4^12;5^10;6^14;-7^3;8^2}. Up to date, although some complicated examples of binodal (4,10)-connected networks have been reported,[20] this case is unprecedented. In this simplification, each pink $(H_2dcppa)^{2-}$ ligand as a 4-connected node linking four tetranuclear Ba_4 units, and each light blue one is two-connected connecting two units, which means two light blue $(H_2dcppa)^{2-}$ ligand can be viewed as a pink one (Fig. 4c); Each tetranuclear Ba_4 unit in turn links twelve $(H_2dcppa)^{2-}$ ligands which can be divided two groups: eight pink and four light blue $(H_2dcppa)^{2-}$ ligands. Considering these four light blue $(H_2dcppa)^{2-}$ ligands are two-connected, so each Ba_4 unit can be viewed as a ten-connected node (Fig. 4d). Similar to compound **1**, further insight into the nature of the high-connected topology can be achieved if we can consider removing the pink $(H_2dcppa)^{2-}$ ligands. On removing the pink $(H_2dcppa)^{2-}$ ligands, the remainder is an intriguing and more simple 3D (4,8)-connected **flu** topology with the Schläfli symbol of {4^12.6^12.8^4}{4^6}2}. This example proves again that topological analysis is a very helpful tool to describe and compare networks in the crystal engineering, especially for those high-connected architectures.

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Effects of alkaline-earth metal ions and solvent system on the structure

Compounds **1**, **2** and **4** are synthesized under similar conditions except different metal ions were used. They have different structures consisting of trinuclear and tetranuclear metal units for these three compounds. Compound **1** is a 2D layer anionic network with an unprecedented (3,6)-connected {4^3}2{4^7.8^8} topology, where the added Mg^{2+} is not involved in the resulting structure, playing a role of alkaline-earth metal template on manipulating the structural diversities. Whereas compounds **2** and **4** present 3D structures with a binodal (3,6)-connected **rtl** topology and a unique binodal (4,10)-connected {3;4^5}2{3^4;4^12;5^10;6^14;7^3;8^2} topology, respectively. In addition, it is worth noting that the abilities of deprotonation and coordination modes of the semi-rigid ligand are also different. The reason for the results may be related to the differences of alkaline-earth metal ions radius ($Mg^{2+} < Ca^{2+} < Ba^{2+}$).

From viewpoint of solvent system, compounds **2** and **3** are synthesized under the same metal salts mixtures (Cd/Ca) with different solvent systems (DMA:H_2O, 2:1 and 1:2 for **2** and **3**, respectively). In this case, compound **3** exhibits a totally different structure, which is a 3D structure with binodal (3,6)-connected **kgd** topology, built upon another different tetranuclear Cd_2Ca_2 unit. Furthermore, the coordination modes of the $(dcppa)^{4-}$ ligand and metal ions centers are also different. It is also very interesting to note the dihedral angles between two aryl rings of $(H_ndcppa)^{4-n}$ (n=0, 1, 2) ligand: 118.1 ° and 119.3 ° for **1**; 117.0 ° for **2**; 119.5 ° for **3**; 114.8 ° and 116.3 ° for **4**. Therefore, the alkaline-earth metal ions and solvent system have significant effects on the structures of the resulting compounds.

Powder X-ray diffraction and thermal properties

To confirm the phase purity and homogeneity of the compounds **1-5,** the synthesized products of the five compounds were characterized by X-ray powder diffraction (XRPD) at room temperature. As shown in Fig. S2-S5 (ESI†), the peaker positions of the experimental patterns are in good agreement with the simulated ones, which clearly indicate the good purity and homogeneity of the compounds.

Thermal gravimetric analysis (TGA) was performed to gauge the thermal stabilities of compounds **1-5**. The TG curve of **1** shows the first weight loss of 15.11% occurs from 65 to 285 ^oC, corresponding to the loss of one coordinated H_2O molecules and two free DMA molecules per unit cell (Calcd: 15.22%). Subsequently, the weight continues to lose below the temperature of 285 ^oC. For **2**, the weight loss of 25.88% in the range of 75-290 ^oC is attributed to the exclusion of two coordinated DMA molecules (Calcd: 26.01%). And then pyrolysis of the remaining framework is observed between 290 to 550 ^oC. The thermal stability performed on **3** shows that a weight loss of 5.75% in the range of 65-185 ^oC, which can be attributed to the removal of two coordinated water molecules (Calcd: 5.82%). Beyond these temperatures, the structure skeleton of **3** begins to dramatically collapse probably due to the removal of the coordinated DMA molecule and he decomposition of organic ligand. Because **4** and **5** are isostructural,they present a similiar thermal stability and are stable to about 63 ^oC. The continuous weight losses from 63 to 310 ^oC correspond to the loss of all guest molecules (obsd: 12.21% for **4** and 11.08% for **5**; calcd: 12.23% for **4** and 11.11% for **5**). When upon heating beyond 310 ^oC, the organic ligand begins decomposing, leading to the collapse of the framework (Fig. S6 ESI†).

Photoluminescence Property

The solid-state emission spectra of compounds **1-5** have been at room temperatur, shown in Fig. 5. In order to understand these emission bands, we have also investigated the luminescent property of the free ligand (H_4dcppa). Intense blue emission bands were observed at 411 nm upon excitation of 328 nm for H_4bcppa, which can be probably assigned to π or n to π* orbital transitions. For the compounds, the blue emission bands are 424nm (λ_{ex} = 338 nm) for **1**, 405 nm (λ_{ex} = 345 nm) for **2**, 440 nm (λ_{ex} = 337 nm) for **3**, 460 nm (λ_{ex} = 352 nm) for **4**/**5**, respectively. The emissions of compounds **1** and **2** may be a mixture of characters of intraligand and ligand-to-ligand charge transition (LLCT), and the observed red (12nm) or a little blue shift (-6nm) of the emission maximum between the compounds and the ligands was considered to mainly sterm from the in fluence of the coordination modes of the ligands to metal atoms.[21] Compared to the free ligand (H_4dcppa), compounds **3** and **4**/**5** exhibit a large red shift of 29nm and 49nm, respectively. Such broad emission bands as observed in **2** and **5** may be tentatively assigned to ligand-to-metal charge transfer (LMCT).[22] Notably, although both Cd(II) compounds **2** and **3** are formed by H_4dcppa, they show different fluorescence properties. This may be result from their different formations and structure (2D coordination polymers *vs*. 3D coordination polymers). Qualitatively, emission from **2** is observed to be of comparable brightness, whereas the emission intensity is reduced for **1** and **3,** and significantly so for **4** and **5**. These differences can be assigned to the occurrence of fluorescence quenching in **1**, **3**, **4** and **5**. The reason for fluorescence quenching may be due to the coordinated water molecules which may efficiently quench the fluorescence of compounds through high-energy O-H oscillators.[23] For **1**, **3** and **4**/**5**, the number of coordinated water molecules is 1, 2 and 2, respectively. Moreover, the different locations and profiles of their emission/excitation peaks of **1-5** are probably due to different metal centers and coordination modes of ligand as well as weak interactions in the network lattice, affecting the rigidity of the whole network and promoting the energy transfer involved in the luminescence.[24] The corresponding decay lifetimes for compounds **1-5** and H_4dcppa ligand 2.87, 4.75, 2.34, 1.20, 1.15 and 1.78 ns, respectively. The luminescent lifetimes of these compounds are much shorter than the ones resulting from a triplet state ($>10^{-3}$s), so the emissions should arise from a singlet state.[25] The photoluminescence properties of these compounds indicate that they could be potentially used as luminescent materials.

<void space for Fig.5>

Conclusions

Five novel metal-organic coordination polymers based on new flexible polycarboxylate ligand were synthesized and characterized, giving from 2D to 3D architectures. Compound **1** features 2D layer structure a new binodal (3,6)-connected {4^3}2{4^7.8^8} topology. Compounds **2** and **3** are bimetallic Cd-Ca compounds containing different tetranuclear Cd_2Ca_2 units, and their structures can be simplified into a 3D (3,6)-connected **rtl** topology and a 2D (3,6)-connected **kgd** topology, respectively. Compound **4** and **5** are isostructural and feature a 3D framework with a unprecedented (4,10)-connected topology owing to their similar tetranuclear Ba_4 unit and 1D infinite barium chain. The diverse structures of the compounds are caused by different coordination modes of central metal ions and the organic ligands. Moreover, **1-5** exhibit intense ligand-centered fluorescence at room temperature, and may sever as candidates for luminescent materials.

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Notes and references

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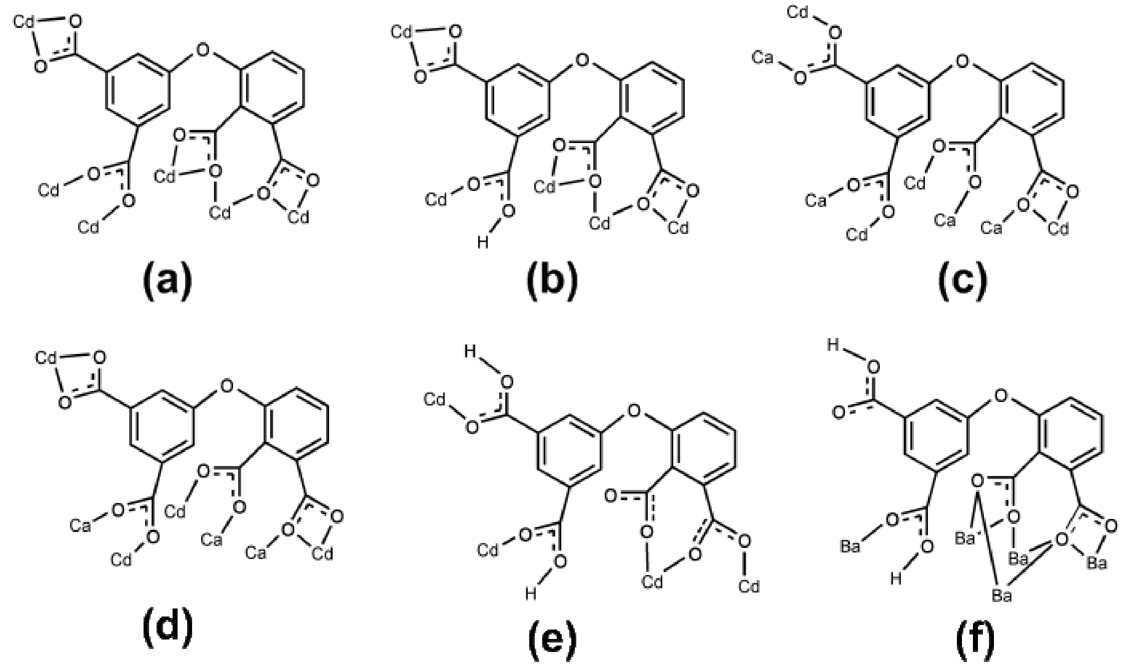
Table 1 Crystal data and structure refinements for compounds **1**-**5**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{42}H_{41}Cd_3N_3O_{21}$	$C_{24}H_{24}CaCdN_2O_{11}$	$C_{20}H_{19}CaCdNO_{12}$	$C_{36}H_{30}Ba_2NO_{22}$	$C_{35}H_{28}Ba_2NO_{22}$
temp (K)	293(2)	293(2)	293(2)	293(2)	293(2)
cryst color	Colorless	Colorless	Colorless	Colorless	Colorless
Fw	1260.98	668.93	617.84	1103.25	1089.26
cryst syst	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Triclinic
space group	*Pbca*	$P2_1$/n	$P2_1$/n	$P\bar{1}$	$P\bar{1}$
a (Å)	21.9035(6)	12.0047(7)	9.9912(3)	10.2726(4)	10.2724(6)
b (Å)	14.5496(4)	10.9563(7)	21.7677(9)	13.3346(5)	13.3126(7)
c (Å)	27.9653(6)	21.0767(15)	10.2461(4)	15.2745(6)	15.2949(10)
α (deg)	90	90	90	100.554(4)	100.307(5)
β(deg)	90	106.389(7)	91.975(3)	107.524(4)	100.414(5)
γ(deg)	90	90	90	99.341(3)	107.572(6)
V (Å^3)	8912.2(4)	2659.5(3)	2227.05(14)	1907.96(13)	1899.38(19)
Z	8	4	4	2	2
D_{calcd} (mg m^{-3})	1.880	1.671	1.843	1.917	1.905
abs coeff (mm^{-1})	1.507	1.077	1.279	2.145	2.154
F(000)	5008	1352	1240	1078	1066
Reflns. Collected	22819	6968	7986	12651	12322
Independent reflns.	7837	4683	3918	6721	6692
R_{int}	0.0585	0.0232	0.0250	0.0307	0.0419
Data/restraints/parameters	7837 / 2 / 631	4324 / 1 / 352	3918 / 7 / 328	6721 / 4 / 566	6692 / 6 / 548
GOF on F^2	0.999	1.099	1.050	1.030	1.006
$R1$, $wR2$ [I>2σ(I)][a]	0.0492, 0.1372	0.0362, 0.0804	0.0322,0.0680	0.0769,0.0328	0.0447,0.0941
$R1$,$wR2$ (all data)[b]	0.0709, 0.1608	0.0465, 0.0868	0.0407,0.0728	0.0418,0.0824	0.0672,0.1102

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$. P = $(Fo^2 + 2Fc^2)/3$.



Scheme 1. The coordination modes of carboxylate groups in compounds **1**-**5**.

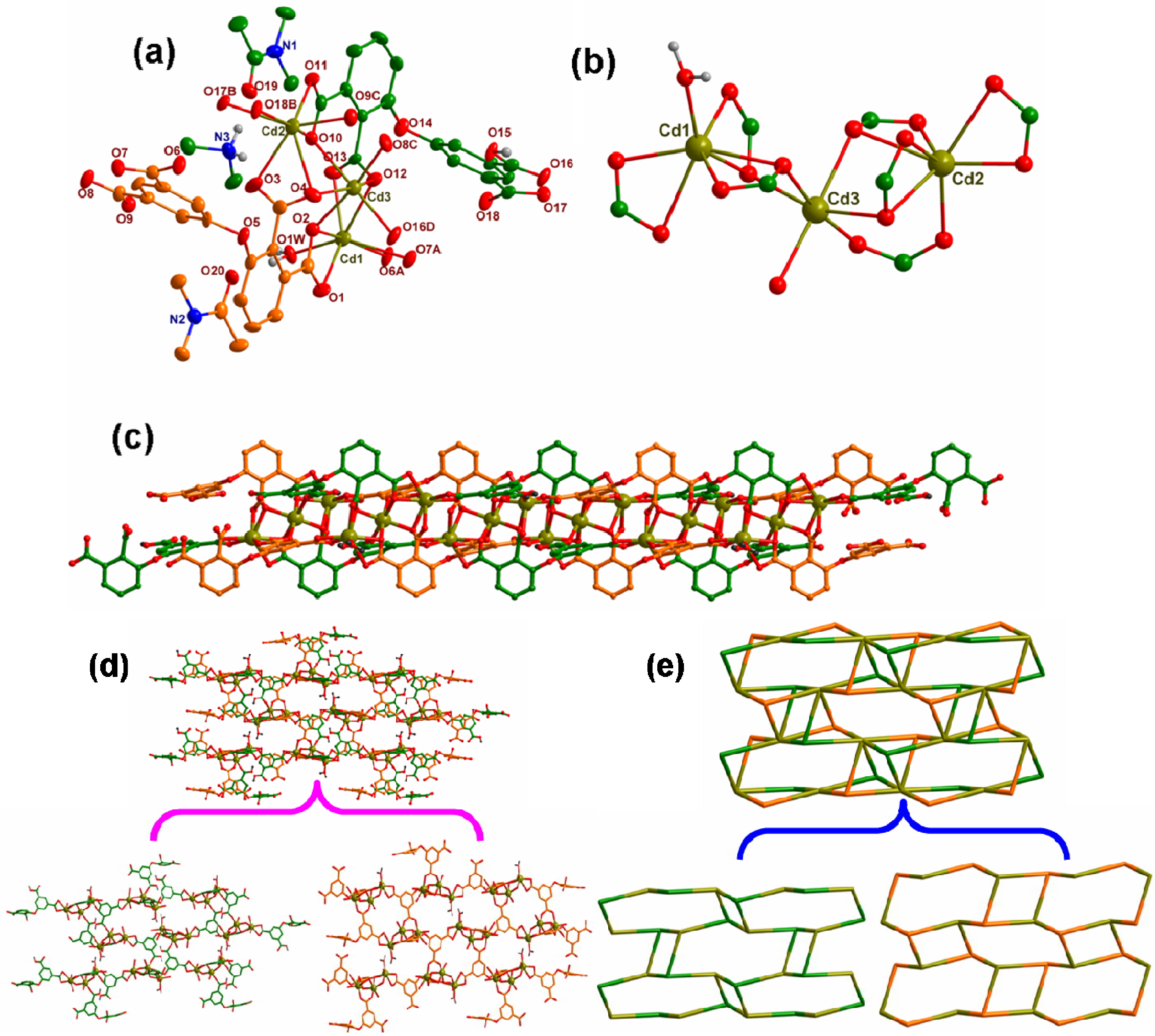


Fig. 1. View of **1**: (a) the coordination environments of Cd(II) ion with 40% thermal ellipsoids. (b) the trinuclear $[Cd_3(COO)_8(H_2O)]^{2-}$ building unit. (c) the 2D network along the crystallographic b-axis with all DMA and H atoms omitted for clarity. (d) the 2D network along the crystallographic *a*-axis and removed $(dcppa)^{4-}/(Hdcppa)^{3-}$ ligand at a time. (e) the schematic representation of the {4^3}2{4^7.8^8} topology and further simplified into two 3-connected **fes** topologies. (symmetry codes: #1: x, -y+1/2, z+1/2; #2: x, -y+1/2, z-1/2; #3:-x+2, y-1/2, -z-1/2; #4: -x+2, -y, -z; #5: -x+2, y+1/2, -z-1/2).

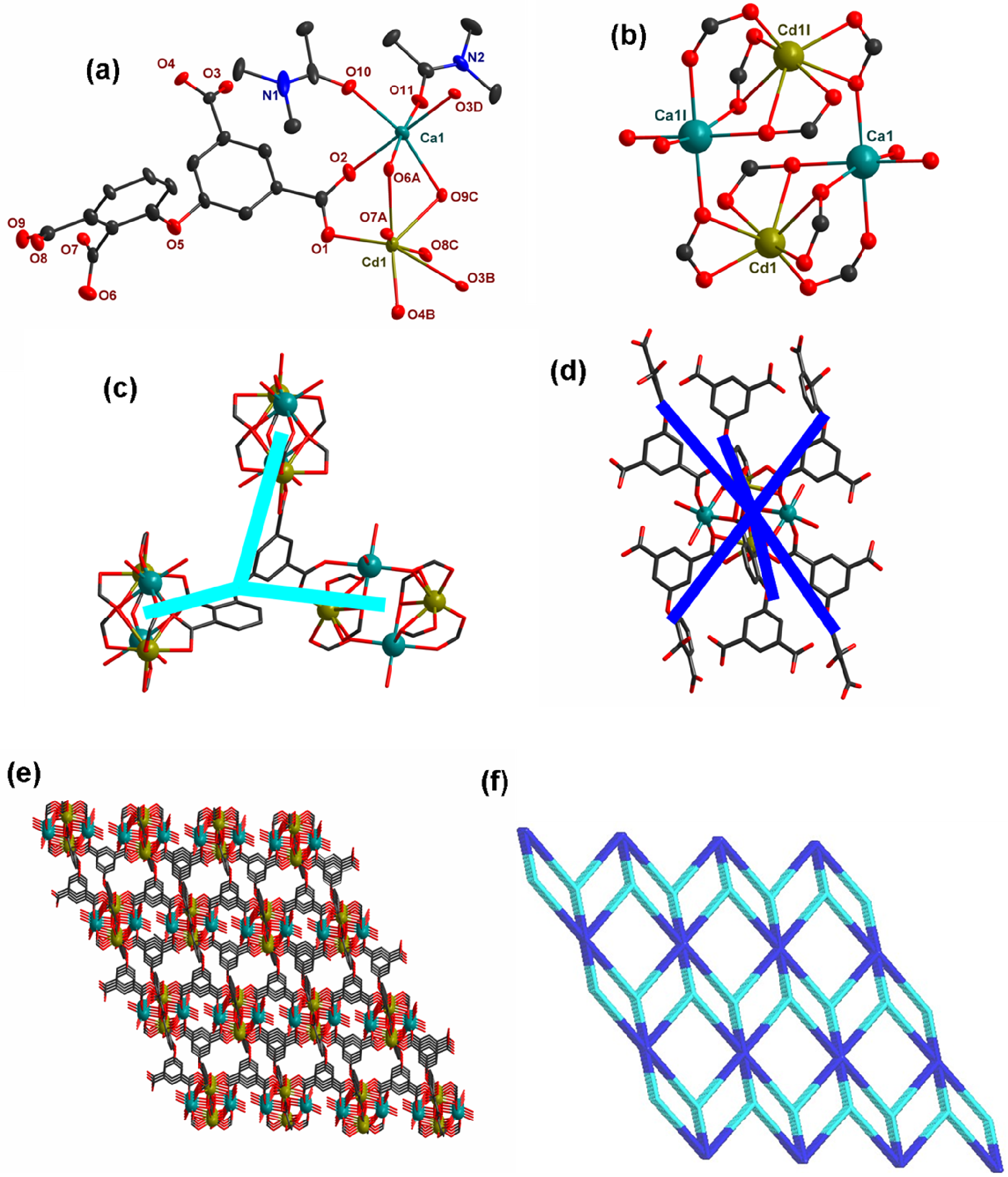


Fig. 2. View of **2**: (a) the coordination environments of Cd(II) and Ca(II) ions with 40% thermal ellipsoids. (b) the tetranuclear [$Cd_2Ca_2(COO)_8(DMA)_4$] building unit. (c) each $(dcppa)^{4-}$ ligand surrounded by three tetranuclear Cd_2Ca_2 units to form a 3-connected node. (d) each tetranuclear Cd_2Ca_2 unit surrounded by six $(dcppa)^{4-}$ ligands to form a 6-connected node. (e) the 3D network in ball-and-stick mode with all H atoms and gust molecules omitted for clarity. (f) the schematic representation of the (3,6)-connected **rtl** topology. (symmetry codes: #1: -x+3/2, y-1/2, -z-1/2; #2: x+1/2, -y+7/2, z+1/2; #3: x-1/2, -y+7/2, z+1/2; #4: -x+1/2, y-1/2, -z-1/2; #5: -x+1/2, y+1/2, -z-1/2; #6: x-1/2, -y+7/2, z-1/2; #7: -x+3/2, y+1/2, -z-1/2; #8: x+1/2, -y+7/2, z-1/2).

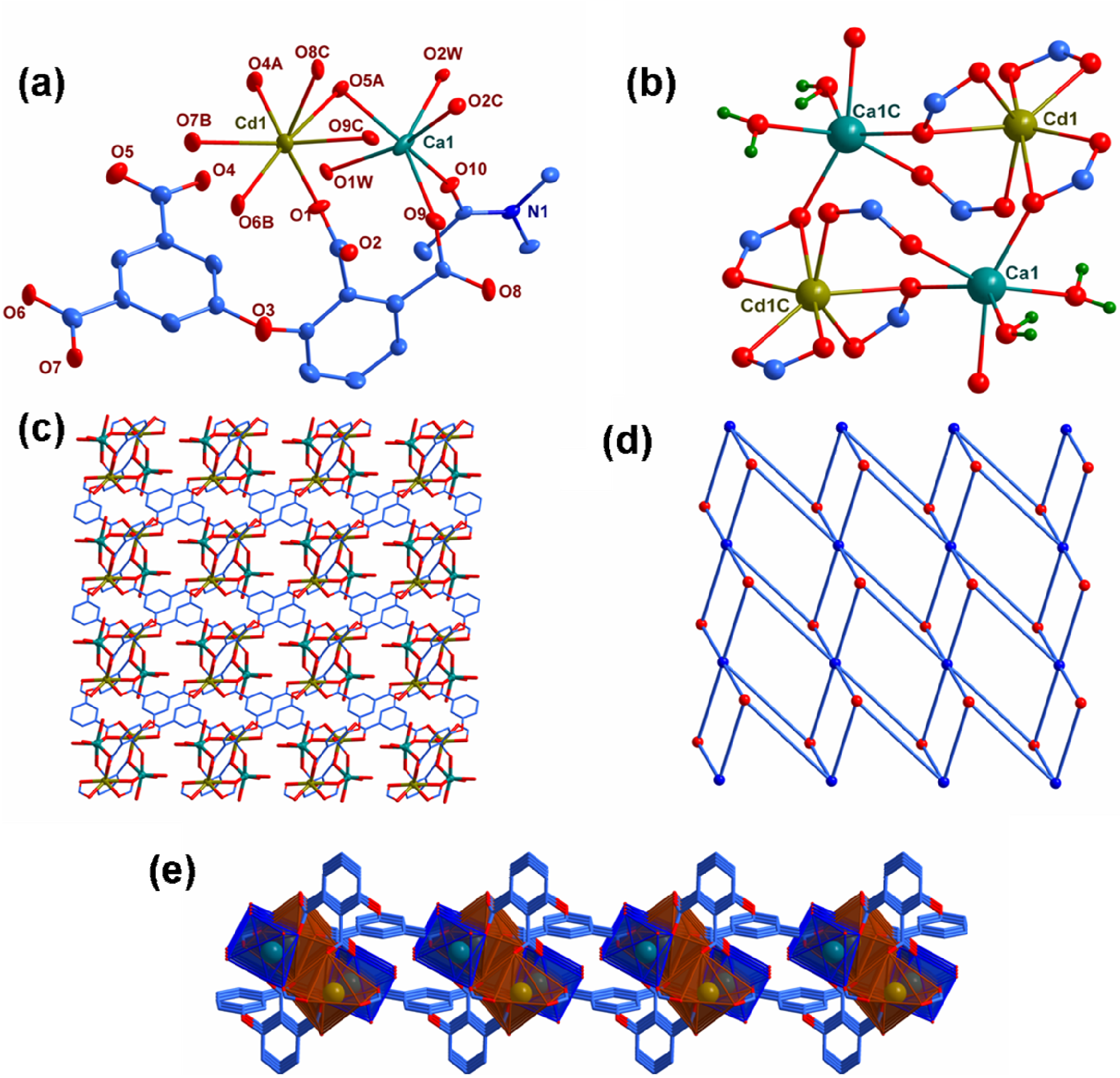
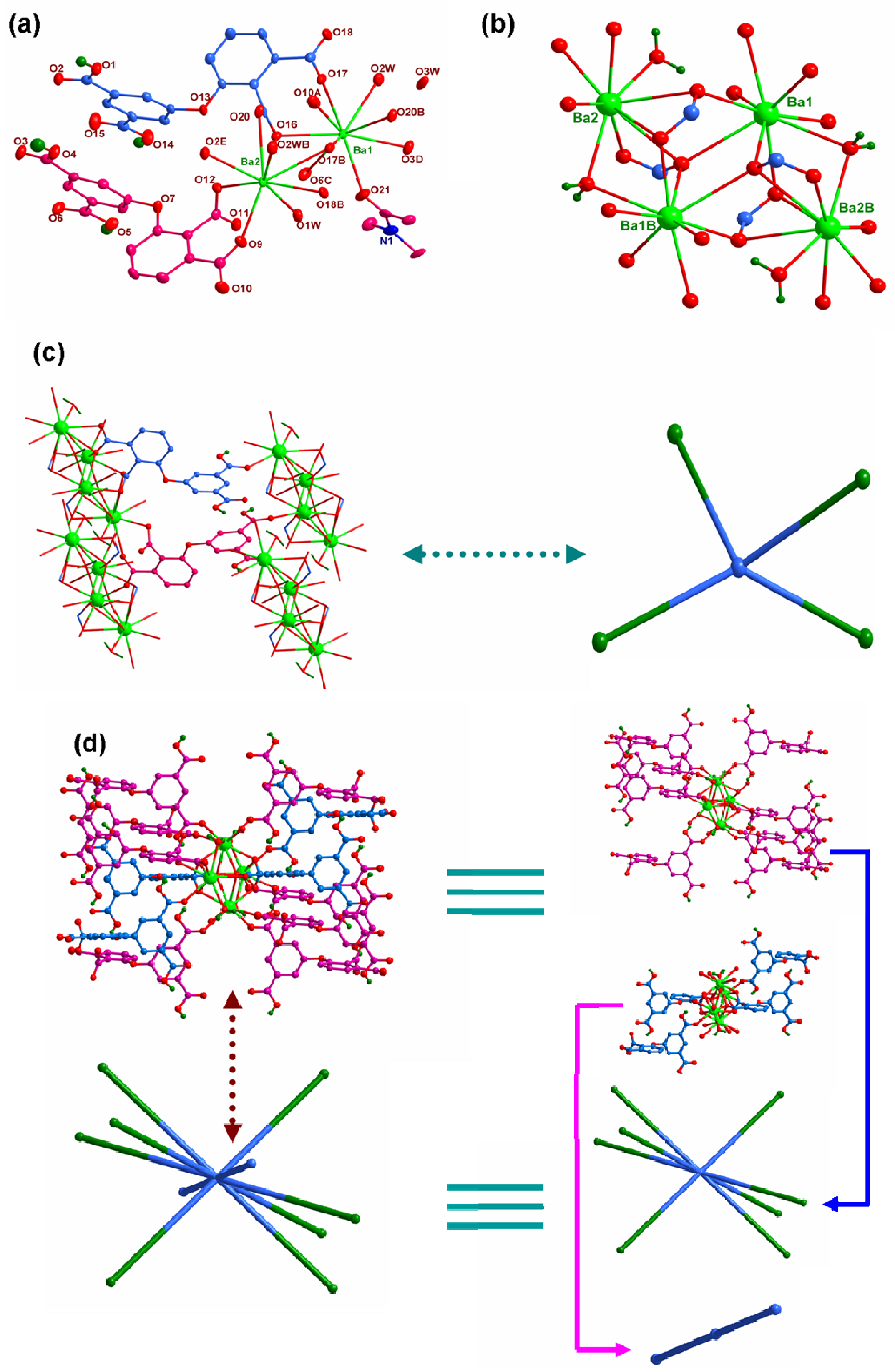


Fig. 3. View of **3**: (a) the coordination environments of Cd(II) and Ca(II) ions with 40% thermal ellipsoids. (b) the tetranuclear $[Cd_2Ca_2(COO)_8(H_2O)_4(DMA)_2]$ building unit. (c) the 2D network along the crystallographic *a*-axis with all H atoms and gust molecules omitted for clarity. (d) the schematic representation of the (3,6)-connected **rtl** topology. (e) the 2D Cd-Ca polyhedra network along the crystallographic *c*-axis. (symmetry codes: #1: -x+2, -y+1, -z+1; #2: -x+1, -y+1, -z+1; #3; -x+2, -y+1, -z+2).


(a)
O18
O2
O1
O17
O2W
O3W
O13
O10A
O20B
O20
O16
O15
O14
O2E
O2WB
O3
O4
Ba1
O3D
Ba2
O17B
O12
O6C
O18B
O21
O7
O11
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Ba1B
Ba2B
(c)
(d)

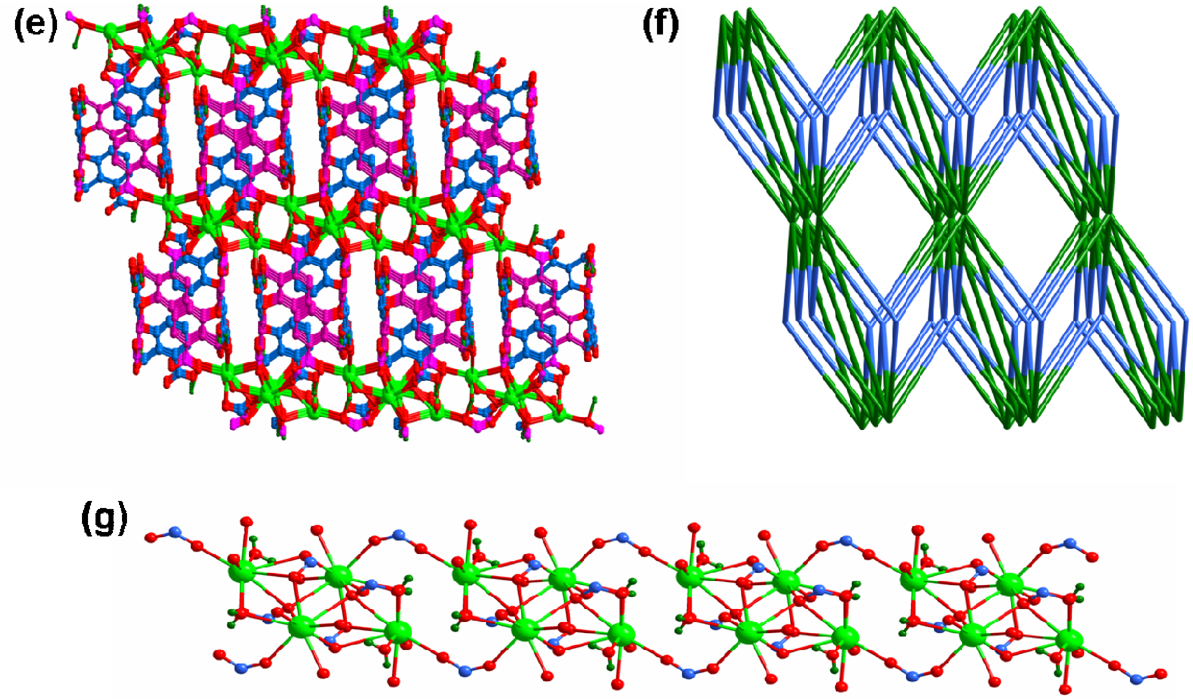

Fig. 4. View of **4**: (a) the coordination environments of Ba(II) ion with 40% thermal ellipsoids. (b) the tetranuclear [$Ba_4(\mu_3\text{-}COO)_4(\mu_2\text{-}COO)_4(COOH)_6(\mu_2\text{-}H_2O)_2(H_2O)_2(DMA)_2$] building unit. (c) and (d) ball-and-stick and schematic representations of the 4- and 10-connected nodes. (e) the 3D network in ball-and-stick mode with DMA omitted for clarity. (f) the schematic representation of the (4,10)-connected {3;4^5}2{3^4;4^12;5^10;6^14;-7^3;8^2} topology. (g) the 1D Ba-O chain view *b*-axis. (symmetry codes: #1: x+1, y, z; #2: -x+3, -y+2, -z+1 ; #3: -x+2, -y+1, -z; #4: x+1, y, z+1; #5: -x+2, -y+2, -z; #6: x-1, y, z-1; #7: x-1, y, z).

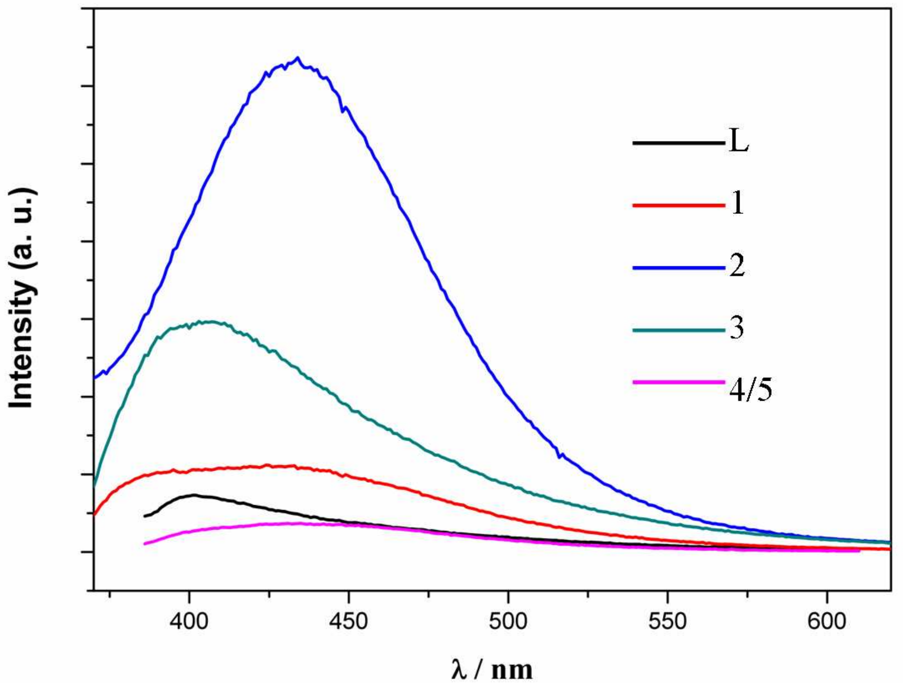

Fig. 5. The fluorescent spectra of **1-5** and **L(H_4dcppa)** in the solid-state at room temperature.