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2D and 3D Cadmium(II) Coordination Polymers from a Flexible Tripodal Ligand of 1,3,5-Tris(carboxymethoxy)benzene and Bidentate Pyridyl-Containing Ligands with Three-, Eight- and Ten-Connected Topologies

Suna Wang,[a] Hang Xing,[a] Yizhi Li,[a] Junfeng Bai,*[a] Yi Pan,[a] Manfred Scheer,*[b] and Xiaozeng You[a]

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Four novel cadmium(II) coordination polymers, $[Cd_3(TCMB)_2(4,4'\text{-bipy})(H_2O)_{16}]_n$ (**1**), $[Cd_3(TCMB)_2(bpe)(H_2O)_{13}]_n$ (**2**), $[Cd_3(TCMB)_2(bpe)_2(H_2O)_4]_n$ (**3**), and $[Cd_3(TCMB)_2(dpp)_2(H_2O)_3]_n$ (**4**), [TCMB = 1,3,5-tris(carboxymethoxy)benzene, 4,4-bipy = (4,4-bipyridine), bpe = 1,2-bis(4-pyridyl)ethane, dpp = 1,3-bis(4-pyridyl)propane] have been hydrothermally synthesized by the self-assembly of the flexible tripodal acid TCMB and $Cd(OAc)_2·2H_2O$ with pyridyl-containing ligands possessing different flexibilities. Single-crystal X-ray diffraction analysis reveals that the four polymers exhibit novel frameworks due to diverse coordination modes and different conformations of the flexible TCMB as well as pyridyl-containing ligands. Complex **1** shows a unique twofold parallel interpenetrating 2D honeycomb network structure with an unusual 6^3 topology, in which two different large hexagonal rings are arranged alternately, with extraordinary dimensions of ca. 22.172(6) × 12.947(2) Å (A) and 17.233(2) × 12.947(2) Å (B) based on the distances of the atoms at the opposite positions of the rings. Complex **2** is almost isostructural to complex **1**, except that the bidentate bpe ligands bridge the cadmium centers in an *anti* conformation, rendering the network more flexible. Complex **3** features a 3D network with one of the scarce eight-connected $(4^6, 6^{14}, 8^8)(4^3)_2$ topologies based on the rare CdI_2-type layer constructed from secondary building units (SBUs) of rare $[Cd_3(CO_2)_4]^{2-}$ isosceles triangle cadmium clusters. Complex **4** possesses distorted CdI_2-type layers constructed from unprecedented ten-connected Cd_3 clusters which are linked by more flexible dpp ligands in a *trans-gauche* (TG) conformation in (4,4) networks, leading to another 3D framework of the unusual $(4^{18}, 6^{24}, 8^3)(4^3)_2$ topology. Such an arrangement represents the highest connected topology presently known for the frameworks. Among them, complex **1** displays photoluminescent properties at 460 nm due to the ligand-to-metal charge transfer (LMCT).

Introduction

In recent years, self-assembly of metal-organic frameworks (MOFs) has attracted much attention not only for the potential discovery of novel functional materials, which may have applications in the areas including gas storage, molecular sieves, ion-exchange, catalysis, magnetism, and optoelectronics, but also for their intriguing variety of architectures and topologies, such as molecular grids, bricks, herringbones, ladders, rings, boxes, diamondoids, and honeycombs.[1–4] In particular, exploring highly symmetrical multi-topic ligands and suitable metal salts in order to construct supramolecular architectures is of great interest.[5,6] On the basis of $[Cp^*Fe(\eta^5\text{-}P_5)]$, we have synthesized the inorganic fullerene-like molecules and 1D or 2D coordination polymers.[7] Generally, rigid symmetrical multi-topic ligands which have been intensively investigated can lead to more predictable supramolecular structures, but the diversity of them has been limited to some extent due to the fact that little or even no conformational changes can be observed for these kinds of ligands when treated with metal ions. By contrast, flexible ligands can adopt different conformations and coordination modes according to the geometric requirements of different metal ions and may afford unpredictable and interesting supramolecular networks. Their reactivities and coordination chemistry have been less explored and the investigation of metal-organic frameworks is still a great challenge.[6]

In order to extend our work in this field, we have turned our attention to an unexplored tripodal ligand, 1,3,5-tris(carboxymethoxy)benzene (TCMB). In comparison with the more intensively investigated rigid ligand, 1,3,5-benzenetricarboxylic acid (BTC),[8] it exhibits additional interesting characteristics, such as more flexibility because of the

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[a] The State Key Laboratory of Coordination Chemistry & School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China
E-mail: bjunfeng@nju.edu.cn
[b] Institut für Anorganische Chemie der University of Regensburg,
93040 Regensburg, Germany
E-mail: manfred.scheer@chemie.uni-regensburg.de

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presence of a –OCH_2– spacer between the benzene ring and carboxylate moiety, which may bend to enable it to coordinate metal centers, and the existence of the ether oxygen atom may function as an electron-donor forming hydrogen bonds to stabilize the entire structure. Thus, rich topologies, including coordination modes, packing fashions, and dimensionalities of supramolecular coordination solids, may result from this interesting ligand. Herein, we report four novel 2D and 3D cadmium(II) compounds with unusual topologies and different pyridyl-containing coligands, among which $[Cd_3(TCMB)_2(4,4'\text{-bipy})(H_2O)_{16}]_n$ (**1**) and $[Cd_3(TCMB)_3(bpe)(H_2O)_{13}]_n$ (**2**) exhibit a novel kind of 2D-twofold interpenetrating 6^3 network with two types of large hexagonal rings arranged alternately, whereas $[Cd_3(TCMB)_2(bpe)_2(H_2O)_4]_n$ (**3**) shows a 3D compact network composed of rare 2D CdI_2-type layers linked by the bpe ligand, with a topology of $(4^6, 6^{14}, 8^8)(4^3)_2$ where the novel isosceles triangle Cd_3 SBUs are taken as eight-connected nodes and TCMB ligands as three-connected nodes. $[Cd_3(TCMB)_2(dpp)_2(H_2O)_3]_n$ (**4**) has ten-connected nodes similar to Cd_3 SBUs connected by more flexible dpp ligands with a different topology of $(4^{18}, 6^{24}, 8^3)(4^3)_2$. Moreover, the effects of the coligand, different pyridyl-containing coligands on the structures, and luminescent properties of the metal-organic frameworks have been investigated in detail.

Results and Discussion

Syntheses of the Complexes

Because of the low solubility of the TCMB ligand, the hydrothermal method was employed in our syntheses. The crystals cannot be obtained through general hydrothermal conditions above 100 °C and only comparably low temperatures such as 80 °C are appropriate for the isolation of good-quality crystals. Additionally, the polarity of the solvent may also influence the process of assembly and it has been proven that the addition of cosolvent CH_3OH or C_2H_5OH helps with the formation of the complexes.[9] For the rigid 4,4-bipy ligand the ratio of bases/acids is in the range 1:1 to 3:1 and seems to have no effect on the product. However, increasing the ratio of bpe ligand/acids from 1:1 to 3:1 extends the two-dimensional structure to the three-dimensional network, and dpp crystals can only be formed from reactions where this coligand is in excess. Other cadmium salts such as $Cd(NO_3)_2\cdot 6H_2O$ were used instead of $Cd(OAc)_2\cdot 2H_2O$, but only precipitates were afforded, indicating that the OAc^- anion may play an important role in the formation of the crystals.

Structural Description

$[Cd_3(TCMB)_2(4,4'\text{-bipy})(H_2O)_{16}]_n$ (1)

Single-crystal X-ray studies reveal that the fundamental building unit of complex **1** consists of two repeating crystallographically independent Cd^{II} centers (Cd1 and Cd2) [Figure 1(a)]. Two chelating carboxylate groups (O4, O5, $O6^i$, $O7^i$: symmetry code i: $1+x, -1+y, z$) from different TCMB ligands as well as one nitrogen atom from the 4,4-bipy ligand occupy the equatorial positions around the Cd1 center, and two aqua molecules occur at the apical positions, leading to the heptacoordinated pentagonal-bipyramidal coordination geometry. The average Cd–O and Cd–N distances are ca. 2.376(4) Å and 2.338(5) Å, respectively. The coordinated carboxylate groups are statistically different in that for the O6 and O7 carboxylate group, the Cd–O distances are 2.350(4) Å and 2.507(4) Å, respectively, suggesting that the pentagonal bipyramid is significantly distorted. On the other hand, the Cd2 center exhibits an octahedral geometry, with two oxygen atoms from aqua molecules (O3w, $O3w^{ii}$) (symmetry code ii: $-x, -y, 2-z$) and two monodentate carboxylate groups of separated TCMB ligands (O9, $O9^{ii}$) in *trans* positions composing the equatorial plane, and two other aqua molecules (O4w, $O4w^{ii}$) in apical sites completing the coordination sphere. All the Cd–O and Cd–N distances are listed in Table 1; they are slightly larger than the results for other Cd–OFs.[10]

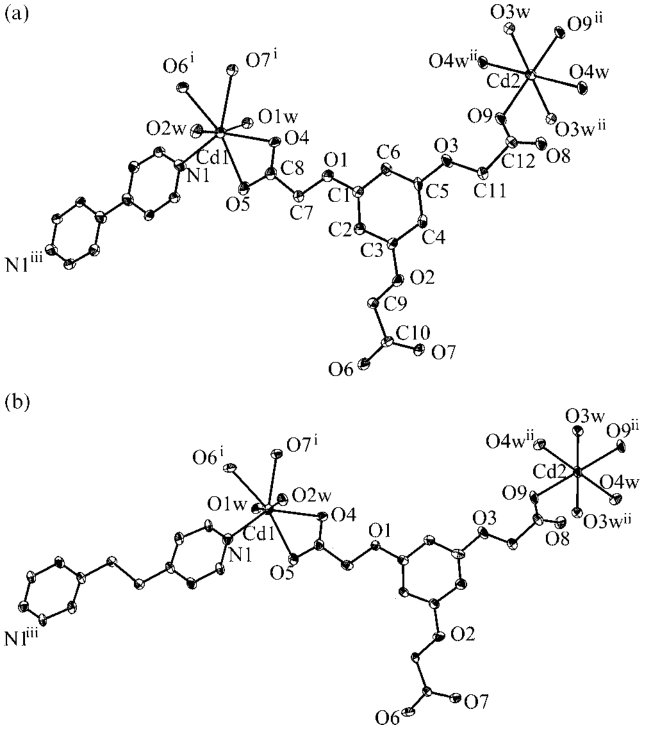


Figure 1. Coordination environments for the Cd^{2+} centers in **1** (a) and **2** (b). Hydrogen atoms and solvent molecules have been omitted for clarity, and thermal ellipsoids are drawn at the 30% probability level. Selected bond information is listed in Table 1. Symmetry codes for **1**: (i) $1+x, -1+y, z$; (ii) $-x, -y, 2-z$; (iii) $3-x, 1-y, -z$: for **2**: (i) $1+x, -1+y, z$; (ii) $2-x, 1-y, 3-z$; (iii) $1-x, 3-y, -1-z$.

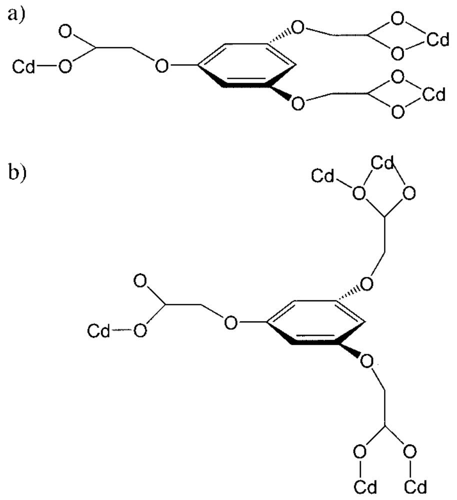
The TCMB ligand is completely deprotonated and acts as a μ^3-bridge linking three cadmium centers, and ether oxygen atoms are not involved in the coordination spheres [Scheme 1(a)]. Two kinds of coordination fashions exist for the three carboxylate groups, in which two of them adopt bidentate chelating modes to connect Cd1 centers while the third bridges one Cd2 center through one carboxylate oxy-

Table 1. Selected bond lengths [Å] and angles [°] from the four complexes.[a]

Complex **1**			
Cd(1)–O(1w)	2.300(4)	O(5)–Cd(1)–O(4)	53.97(13)
Cd(1)–O(2w)	2.295(5)	O(4)–Cd(1)–O(7)^{i}	85.23(12)
Cd(1)–O(4)	2.344(4)	O(7)^{i}–Cd(1)–O(6)^{i}	53.68(13)
Cd(1)–O(5)	2.463(4)	O(6)^{i}–Cd(1)–N(1)	85.04(16)
Cd(1)–N(1)	2.338(5)	N(1)–Cd(1)–O(5)	83.96(16)
Cd(1)–O(6)^{i}	2.350(4)	O(2w)–Cd(1)–O(1w)	167.36(14)
Cd(1)–O(7)^{i}	2.507(4)	O(2w)–Cd(1)–N(1)	99.31(18)
Cd(2)–O(9)	2.275(4)	O(2w)–Cd(1)–O(5)	83.94(16)
Cd(2)–O(3w)	2.232(4)	O(1w)–Cd(1)–O(4)	87.33(15)
Cd(2)–O(4w)	2.396(4)	O(1w)–Cd(1)–O(7)^{i}	83.16(14)
		O(3w)–Cd(2)–O(4w)^{ii}	84.78(16)
		O(9)–Cd(2)–O(9)^{ii}	180.0(2)
		O(9)–Cd(2)–O(4w)^{ii}	96.35(13)
		O(9)–Cd(2)–O(3w)	94.25(16)
Complex **2**			
Cd(1)–O(1w)	2.287(3)	O(5)–Cd(1)–O(4)	54.31(10)
Cd(1)–O(2w)	2.319(3)	O(4)–Cd(1)–O(7)^{i}	86.93(10)
Cd(1)–O(4)	2.342(3)	O(7)^{i}–Cd(1)–O(6)^{i}	52.90(10)
Cd(1)–O(5)	2.421(3)	O(6)^{i}–Cd(1)–N(1)	82.47(11)
Cd(1)–N(1)	2.308(4)	N(1)–Cd(1)–O(5)	87.26(11)
Cd(1)–O(6)^{i}	2.395(3)	O(2w)–Cd(1)–O(1w)	167.75(11)
Cd(1)–O(7)^{i}	2.399(3)	O(2w)–Cd(1)–N(1)	85.40(12)
Cd(2)–O(9)	2.317(3)	O(2w)–Cd(1)–O(5)	105.95(12)
Cd(2)–O(3w)	2.279(3)	O(1w)–Cd(1)–O(4)	90.68(12)
Cd(2)–O(4w)	2.300(3)	O(1w)–Cd(1)–O(7)^{i}	82.24(11)
		O(3w)–Cd(2)–O(4w)^{ii}	91.98(11)
		O(9)–Cd(2)–O(9)^{ii}	180.000(1)
		O(9)–Cd(2)–O(4w)^{ii}	96.43(11)
		O(9)–Cd(2)–O(3w)	95.49(11)
Complex **3**			
Cd(1)–O(4)	2.346(3)	O(5)–Cd(1)–O(4)	55.35(9)
Cd(1)–O(5)	2.368(3)	O(4)–Cd(1)–O(9)^{ii}	100.57(10)
Cd(1)–O(1w)	2.299(2)	O(9)^{ii}–Cd(1)–O(1w)	108.36(11)
Cd(1)–O(6)^{i}	2.255(3)	O(1w)–Cd(1)–O(5)	95.65(10)
Cd(1)–O(9)^{ii}	2.245(3)	N(1)–Cd(1)–O(5)	93.62(12)
Cd(1)–N(1)	2.305(3)	N(1)–Cd(1)–O(9)^{ii}	90.12(12)
Cd(2)–O(4)	2.310(2)	N(1)–Cd(1)–O(1w)	85.73(11)
Cd(2)–O(8)	2.268(3)	N(1)–Cd(1)–O(6)^{i}	168.82(12)
Cd(2)–N(2)	2.325(3)	O(6)^{i}–Cd(1)–O(9)^{ii}	84.18(11)
		O(6)^{i}–Cd(1)–O(5)	95.50(11)
		O(8)^{v}–Cd(2)–N(2)	95.28(11)
		N(2)–Cd(2)–O(8)^{ii}	89.98(11)
		O(8)^{v}–Cd(2)–O(4)^{iv}	89.17(10)
		O(4)^{iv}–Cd(2)–O(8)^{ii}	85.68(10)
		O(4)–Cd(2)–N(2)	87.97(11)
		N(2)^{iv}–Cd(2)–O(4)	178.52(11)
Complex **4**			
Cd(1)–O(5)	2.412(3)	O(5)–Cd(1)–O(4)	54.74(11)
Cd(1)–(4)	2.354(3)	O(4)–Cd(1)–O(9)^{ii}	91.93(11)
Cd(1)–O(1w)	2.311(3)	O(9)^{ii}–Cd(1)–O(1w)	88.23(11)
Cd(1)–O(6)^{i}	2.242(3)	O(1w)–Cd(1)–O(4)	147.15(12)
Cd(1)–O(9)^{ii}	2.232(3)	N(1)–Cd(1)–O(4)	95.52(13)
Cd(1)–N(1)	2.305(4)	N(1)–Cd(1)–O(9)^{ii}	172.38(12)
Cd(2)–O(4)	2.287(4)	N(1)–Cd(1)–O(1w)	84.65(13)
Cd(2)–O(7)^{i}	2.291(3)	N(1)–Cd(1)–O(6)^{i}	92.51(14)
Cd(2)–N(2)	2.307(4)	O(6)^{i}–Cd(1)–O(9)^{ii}	87.07(14)
		O(6)^{i}–Cd(1)–O(4)	104.97(12)
		O(7)^{i}–Cd(2)–N(2)	91.95(13)
		N(2)–Cd(2)–O(7)^{iv}	91.84(13)
		O(7)^{iv}–Cd(2)–O(4)^{iii}	90.18(12)
		O(4)–Cd(2)–O(7)^{iv}	86.00(12)
		O(4)–Cd(2)–N(2)	87.55(13)
		N(2)–Cd(2)–O(4)^{iii}	177.92(13)

[a] Symmetry codes for **1**: (i) $1 + x, -1 + y, z$; (ii) $-x, -y, 2 - z$; for **2**: (i) $1 + x, -1 + y, z$; (ii) $2 - x, 1 - y, 2 - z$; for **3**: (i) $x, 1 - y, -1/2 + z$; (ii) $x, 2 - y, -1/2 + z$; (iii) $3/2 - x, 5/2 - y, 2 - z$; (iv) $1 - x, y, 3/2 - z$; for **4**: (i) $x, 2 - y, -1/2 + z$; (ii) $x, 1 - y, -1/2 + z$; (iii) $2 - x, y, 1/2 - z$; (iv) $2 - x, 2 - y, 1 - z$.

gen atom. One chelating carboxylate group is approximately coplanar with the aromatic ring, while the other chelating and monodentate groups form small dihedral angles of ca. 14.4° and 30.9°, respectively.



Scheme 1. Coordination modes of the TCMB ligand in the four complexes.

Furthermore, two-dimensional frameworks containing compact triple-metallic layers are afforded by two sheets of Cd1 centers bridged through 4,4′-bipy ligands and one of the Cd2 centers connected through TCMB ligands, in which all the same kinds of metal centers are arranged in straight lines as depicted in Figure 2(a). In this way, large hexagonal rings are formed and adjacent rings have extremely different environments, i.e. ring A and ring B. Four TCMB ligands are linked together by two Cd1 centers and two Cd2 centers alternately to form a 48-membered macrocycle (ring A). The distances between two opposite pairs of Cd^{2+} centers on the macrocycle are Cd1···Cd1^{ii} with a distance of 22.172(6) Å and Cd2···Cd2^{i} with a distance of 12.947(2) Å (symmetry code i: $1+x, -1+y, z$; ii: $-x, -y, 2-z$). The second type of ring (B) is involved in Cd1 centers of adjacent layers bridged by the bidentate 4,4′-bipy ligand, which is also a macrocycle with 44 atoms, four Cd1 centers, and benzene rings of two TCMB ligands located at the vertexes of this hexagon as well as two 4,4-bipy ligands at the opposite edges. The distance between the opposite carbon atoms of the TCMB ligands at the vertexes is 17.233(2) Å, whilst the edges are separated by 12.947(2) Å based on the Cd2···Cd2^{i} distance (symmetry code i: $1+x, -1+y, z$). If only the Cd1 ions and the geometrical centers of the benzene ring of the TCMB ligands are considered as three-connected nodes, the structure can be best described as an infinite two-dimensional network with a 6^3 topology in which two types of large hexagonal rings are arranged alternately. To the best of our knowledge, in most of the reported complexes with such topologies[11] only two examples with different cavities have been found,[12] whereas the others only contain haploid cavities.

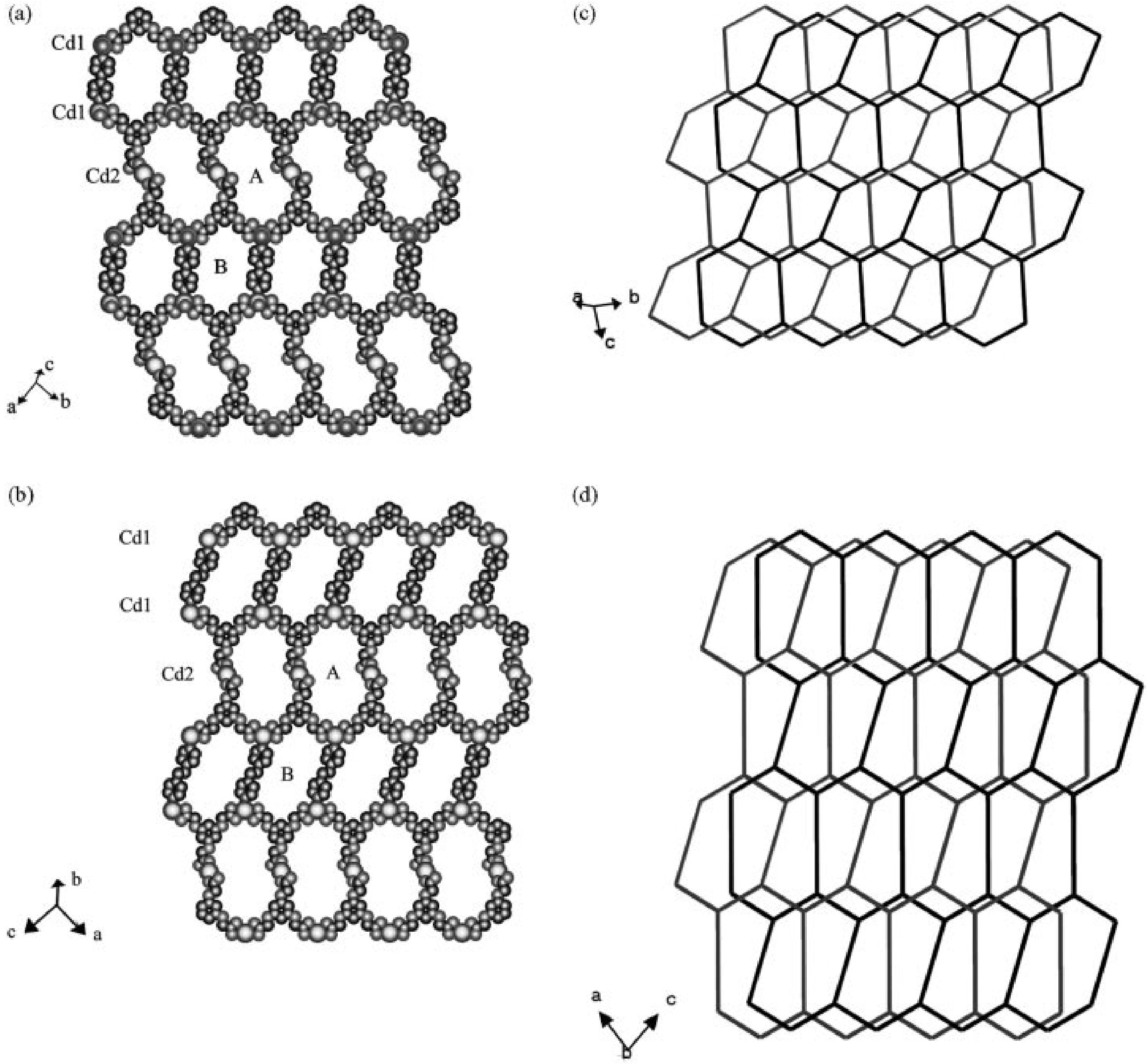


Figure 2. Space-filling representation of the 2D layer with a cross-section of the two different rings A and B for **1** (a) and **2** (b). Topological representation of the twofold interpenetration of the adjacent layers in **1** (c) and **2** (d). Cd1 centers and the geometrical centers of the benzene ring of the TCMB ligands are considered as three-connected nodes. Hydrogen atoms and the coordinated water molecules are omitted for clarity.

Because of the flexibility of the TCMB ligand, the metal atoms in one layer of the network do not lie in the same plane. All the atoms in ring B are almost coplanar while the Cd2 centers are located "above" and "below" alternately, with a dihedral angle between the monodentate carboxylate group and the plane of the aromatic ring of ca. 30.9°, leading to chair conformations for ring A. Such a bonding arrangement gives rise to a corrugated sheet topology and two undulating sheets pass through each other, forming the twofold interpenetrating 2D networks parallel to the *ac* plane with a layer thickness of ca. 3.50 Å [Figure 2(c)]. Furthermore, weak π···π interactions between the aromatic rings of adjacent layers lead to the 3D metal-organic framework, in which the composite 2D sheets are stacked in an ...ABC... fashion, with a mean distance between the double sheets of ca. 4.08 Å (Figure 3). Such an uncommon stacking mode for doubly interpenetrated sheets reduces the voids to a large extent, even though the single network contains large windows as described above. It is noteworthy that one-dimensional channels still exist along the *a* axis, and crystallographically unique uncoordinated water molecules are distributed freely in the network, which are involved in strong hydrogen bonds with the ether and carboxylate oxygen atoms between neighboring layers (see Supporting Information). Details of hydrogen bond parameters are summarized in Table 2. Interestingly, the hydrogen bonds influence the coordination environment of the Cd1 atom significantly. Because of the presence of the strong interaction between O7 and O1w with an O(1w)···O(7)^{iii} (symmetry code iii: $-x+1$, $-y+1$, $-z+1$) distance of 2.689(6) Å and an O(1w)–H1(wB)···O(7)^{iii} angle of 169.9°, which is a relatively strong hydrogen bond, the corresponding Cd1–O7^{i} (symmetry code i: $1+x$, $-1+y$, z) bond is weakened and is rather long.

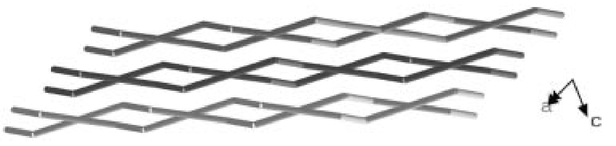


Figure 3. Topological representation of the side view of the crystal packing for **1** in the ...ABC... model.

Table 2. Hydrogen bond geometries for complex **1** [Å and °].[a]

D–H···A	d(D···A)	<(D–H···A)
O(8w)–H(8WA)···O(6)^{i}	2.725(6)	127.8
O(3w)–H(3WB)···O(5w)^{ii}	2.643(6)	145.2
O(2w)–H(2WC)···O(7w)^{iii}	2.735(6)	125.4
O(1w)–H(1WC)···O(8)^{iv}	2.732(6)	140.8
O(8w)–H(8WB)···O(4w)^{iv}	2.795(6)	131.9
O(5w)–H(5WB)···O(1w)^{v}	2.892(5)	140.2
O(2w)–H(2WA)···O(8w)^{vi}	2.753(6)	123.4
O(3w)–H(3WC)···O(7w)^{vii}	3.209(6)	151.3
O(1w)–H1(WB)···O(7)^{viii}	2.689(6)	169.9
O(6w)–H(6WB)···O(9)^{viii}	3.212(6)	156.9
O(5w)–H(5WD)···O(1)^{viii}	3.193(6)	139.2

[a] Symmetry codes for **1**: (i) x, $y - 1$, z; (ii) x, $y - 1$, $z + 1$; (iii) $x + 1$, y, z; (iv) $x + 1$, y, $z - 1$; (v) $x - 1$, $y + 1$, z; (vi) $-x + 2$, $-y$, $-z + 1$; (vii) $-x$, $-y$, $-z + 2$; (viii) $-x + 1$, $-y + 1$, $-z + 1$.

[$Cd_3(TCMB)_2(bpe)(H_2O)_{13}]_n$ (2)

Complex **2** is isostructural to complex **1**, which also consists of a 2D 6^3 network with two types of hexagonal rings as described in Figure 2(b). In general, increased flexibility of the ligand may probably lead to the corresponding change of the dimensionality, void space, degree of interpenetration, or topology.[13] However, in this case, the introduction of two CH_2 groups into the bipy molecule results in a slightly changed framework, which may be attributed to the flexible TCMB ligand with the ability to bend in order to satisfy coordination to the metal centers. The bidentate bpe ligand in an *anti* conformation bridges two Cd1 centers with a Cd1···Cd1^{iv} (symmetry code iv: $1 - x$, $3 - y$, $-1 - z$) distance of 13.624(6) Å, which is slightly shorter than that of similar bridges.[14] Apparently, the orientations of the ligands adjust themselves to the requirements of the particular networks.

Comparing these two complexes, the distances of Cd–O and Cd–N have changed after the substitution of the flexible bpe for the rigid 4,4′-bipy ligand. The carboxylate groups in the TCMB ligand coordinate to the Cd1 centers with an average Cd–O distance of 2.378(3) Å, similar to that in complex **1**. The bond lengths of Cd1–O6^{i} and Cd1–O7^{i} (symmetry code i: $1+x$, $-1+y$, z) are 2.395(3) Å and 2.399(3) Å, respectively, showing approximately symmetrical chelating conformation of the O6 and O7 carboxylate group [Figure 1(b)]. Consequently, because of the flexibility of the bpe ligands and interpenetration of the sheets, the two types of hexagonal rings become distorted with a slightly expanded ring A and a seriously compressed ring B. The dimensions corresponding to those in complex **1** are changed to 22.905(0) × 12.902(3) Å, and 18.887(4) × 12.902(3) Å, respectively. Obviously, the comparable dimensions of the two different kinds of rings enable the two adjacent layers to interpenetrate more easily than those in complex **1** [Figure 2(d)].

In addition, hydrogen bonds are involved in the neighboring layers, which may play a crucial role in constructing the whole three-dimensional network (Table 3). The ether oxygen atom (O1) can form a weak hydrogen bond with the free water molecule O6w, where the O6w···O1^{v} (symmetry code v: $1-x$, $1-y$, $1-z$) distance is 3.130(5) Å and the O6w–H6w···O1^{v} angle is 146.9°. Three water molecules O5w, O6w, and O7w are bonded to each other through hydrogen bonds (Figure 4). The O5w atom acts as a double donor, while O6w and O7w act as single acceptors, and O5w can still form hydrogen bonds with another O5w^{vi} water molecule (symmetry code vi: $-x$, $1-y$, $1-z$). Thus, hexameric water clusters are formed between the adjacent layers. Interestingly, the six O atoms of the hexameric unit assume a rather uncommon centrosymmetrical planar conformation, different from those in other reported hexameric water clusters.[15] Nonbonding Ow···Ow distances and neighboring Ow···Ow···Ow angles are listed in Table 4, and show wide variations commensurate with the MOF structure. The average Ow···Ow distance [2.883(5) Å] is slightly longer than that of liquid water with a value of 2.85 Å, determined from the X-ray diffraction radial distribution curve, and that of the gas phase value of 2.86 Å.[16]

Table 3. Hydrogen bond geometries for complex **2** [Å and °].[a]

D–H···A	d(D···A)	<(D–H···A)
O(6w)–H(6wB)···O(1)^{i}	3.130(4)	146.9
O(6w)–H(6wA)···O(2w)^{ii}	2.869(5)	130.5
O(5w)–H(5wA)···O(5w)^{iii}	2.889(8)	115.4
O(4w)–H(4wA)···O(8)^{iv}	2.833(5)	139.1
O(3w)–H(3wB)···O(7)^{v}	3.319(4)	147.5
O(2w)–H(2wA)···O(7)^{vi}	2.638(4)	173.8
O(2w)–H(2wB)···(8)^{vii}	2.777(5)	152.1
O(1w)–H(1wA)···O(5)^{viii}	2.695(4)	166.7
O(1w)–H(1wB)···O(3w)^{ix}	3.143(4)	161.5
O(5w)–H(5wB)···O(6w)	2.781(4)	112.4

[a] Symmetry codes for **2**: (i) $-x + 1$, $-y + 1$, $-z + 1$; (ii) $x - 1$, $y - 1$, $z + 1$; (iii) $-x$, $-y + 1$, $-z + 1$; (iv) $-x + 2$, $-y + 1$, $-z + 2$; (v) $-x + 1$, $-y + 1$, $-z + 2$; (vi) $-x + 1$, $-y + 2$, $-z + 1$; (vii) x, $y + 1$, $z - 1$; (viii) $-x + 1$, $-y + 2$, $-z$; (ix) $-x + 2$, $-y + 1$, $-z + 1$.

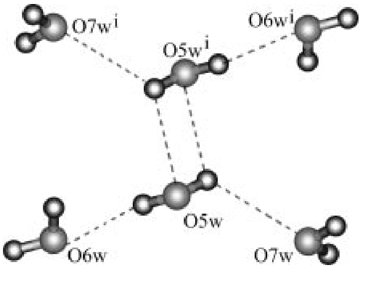


Figure 4. A perspective view of the centrosymmetrical planar hexamaric water cluster in **2**, showing the hydrogen bonds between them.

Except for the hydrogen bonds mentioned above, no classical weak hydrogen-bond C–H···O interactions between a carbon atom (C4) of the aromatic ring and the carboxylate

Table 4. Geometrical parameters of the hydrogen bonds of the hexameric water clusters in complex **2** [Å and °].[a]

O5w···O6w	2.781(5)
O5w···O7w	2.829(8)
O6w···O7w	5.237(5)
O5w···O5w^{i}	2.889(5)
O5w···O5w^{i}···O7w^{i}	103.5
O5w^{i}···O5w···O6w	118.3
O6w···O5w···O7w	138.0

[a] Symmetry code: (i) $-x$, $1-y$, $1-z$.

oxygen atom (O8) of the TCMB ligand exist in this complex. The C(4)···O(8)^{vii} interaction (symmetry code vii: $1-x$, $1-y$, $2-z$) with a distance of 3.310(6) Å and a C(4)–H(4A)···O(8)^{vii} angle of 152.8°, together with the other hydrogen bonds mentioned above, extend the 2D layers into a 3D network.

[Cd$_3$(TCMB)$_2$(bpe)$_2$(H$_2$O)$_4$]$_n$ (3)

The fundamental unit of complex **3** contains two crystallographically independent hexacoordinate Cd^{II} centers (Figure 5). The Cd1 center adopts a distorted octahedral geometry {CdO$_5$N}, and is bonded to four carboxylate oxygen atoms from three separate TCMB ligands in the basal plane, one oxygen atom from the aqua molecule, and one nitrogen atom from the bpe ligand ligating the metal atoms in the two apical positions. The average Cd–O and Cd–N distances are 2.303(3) Å and 2.305(3) Å, respectively. Comparably, the Cd2 center {CdO$_4$N$_2$} is coordinated by four different monodentate carboxylate oxygen atoms from four distinct TCMB ligands and two nitrogen atoms from different bpe ligands, displaying a slightly distorted octahedral geometry. All the values are in good agreement with the reported Cd–OFs.[9]

Unlike that in complex **1** and **2**, the TCMB ligand exhibits essentially different coordination modes and the three carboxylate groups show large deviations from the plane of the central aromatic ring [Scheme 1(b)] due to the rotation of the OCH$_2$ groups; significantly more flexible than the corresponding coordination ability of the BTC ligand.[8] Among the three arms, only one is still almost coplanar with the aromatic ring, whereas the other two are arranged "above" and "below" the plane. Meanwhile, the three carboxylate groups show different coordination fashions: in the plane, the carboxylate group functions in a monodentate fashion with one oxygen atom bonding the Cd1 center; above the plane, the carboxylate group chelates to the Cd1 center and one oxygen atom also bridges the Cd1 and Cd2 centers, exhibiting the chelating-bridging mode, and the third one below the plane behaves in a bidentate bridging fashion, linking the Cd1 and Cd2 atoms. Thus, the TCMB ligand serves as a μ_5-bridge, linking five Cd centers through its three arms in different fashions and losing the original planarity and C_3 symmetry observed in the free state.

As an effective intermetallic bridge, the bpe ligand always connects the same type of metal centers; however, in this case, it bridges two crystallographically independent centers of Cd1 and Cd2 from different [Cd$_3$(CO$_2$)$_4$]$^{2-}$ cores where the metal–metal separation for Cd1···Cd2^{viii} (symmetry code viii: $3/2-x$, $5/2-y$, $2-z$) is ca. 13.883(6) Å. The interplanar angle between the pyridyl rings in bpe is ca. 9.9° and the C–CH$_2$–CH$_2$–C torsion angle is ca. 70.5°, suggesting a deviation from the normal *anti* conformation, which can be viewed as intermediate between the *anti* and the *gauche* conformations. Notably, the dihedral angles between the planes of the 4-pyridyl rings are obviously larger than those in complex **2**, which is probably one of the main causes of the dimensions of these two complexes.

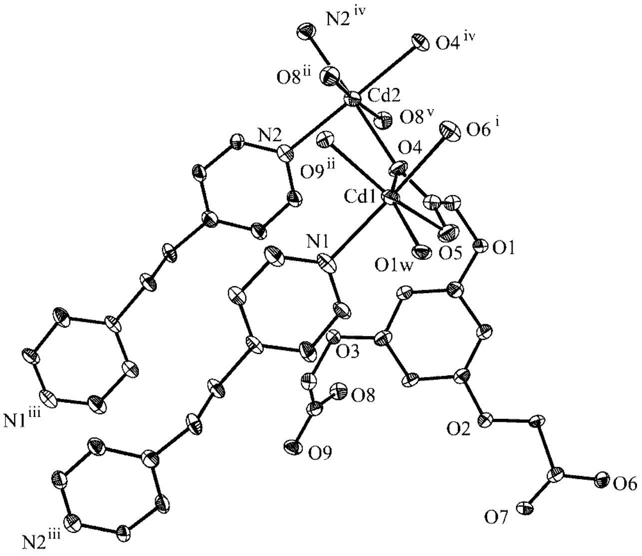


Figure 5. Schematic representation of the distorted octahedral coordination environments for the two crystallographically unique Cd^{2+} metal centers in **3**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and other solvent molecules have been omitted for clarity. For bond lengths and angles see Table 1. Symmetry codes used to generate equivalent atoms: (i) x, $1-y$, $-1/2+z$; (ii) x, $2-y$, $-1/2+z$; (iii) $3/2-x$, $5/2-y$, $2-z$; (iv) $1-x$, y, $3/2-z$; (v) $1-x$, $2-y$, $2-z$.

The most interesting feature of the complex is the presence of the unreported isosceles triangle [Cd$_3$(CO$_2$)$_4$]$^{2-}$ cores [Figure 6(a)] in which the Cd2 atom is located at the vertex and doubly bridged to adjacent Cd1 metal atoms by bidentate carboxylate groups in a *syn-syn* conformation as well as one oxygen atom from the chelating-bridging group. The metal–metal separation of Cd1···Cd2 is 4.025(6) Å, significantly longer than those in some discrete dimeric cadmium tetracarboxylate complexes (3.278–3.452 Å),[17] but slightly larger than that in a similar bridge reported recently.[18] The two symmetrical Cd1 centers are separated by the long distance of Cd1···Cd1^{ix} (symmetry code ix: $-x$, $1+y$, $3/2-z$) of ca. 6.731(1) Å. As far as we know, in the few reported Cd–OFs composed of Cd$_3$ SBUs,[19] the metal centers are mostly located in linear arrangements. The arrangement of six TCMB ligands around a [Cd$_3$(CO$_2$)$_4$]$^{2-}$ cluster is shown in Figure 6(b).

Thus, the assembly of these trinuclear SBUs leads to a 3D compact and neutral framework through the bridging of the *exo*-bidentate bpe and the TCMB ligands. On the one hand, each Cd$_3$ SBU is interlinked to other two SBUs

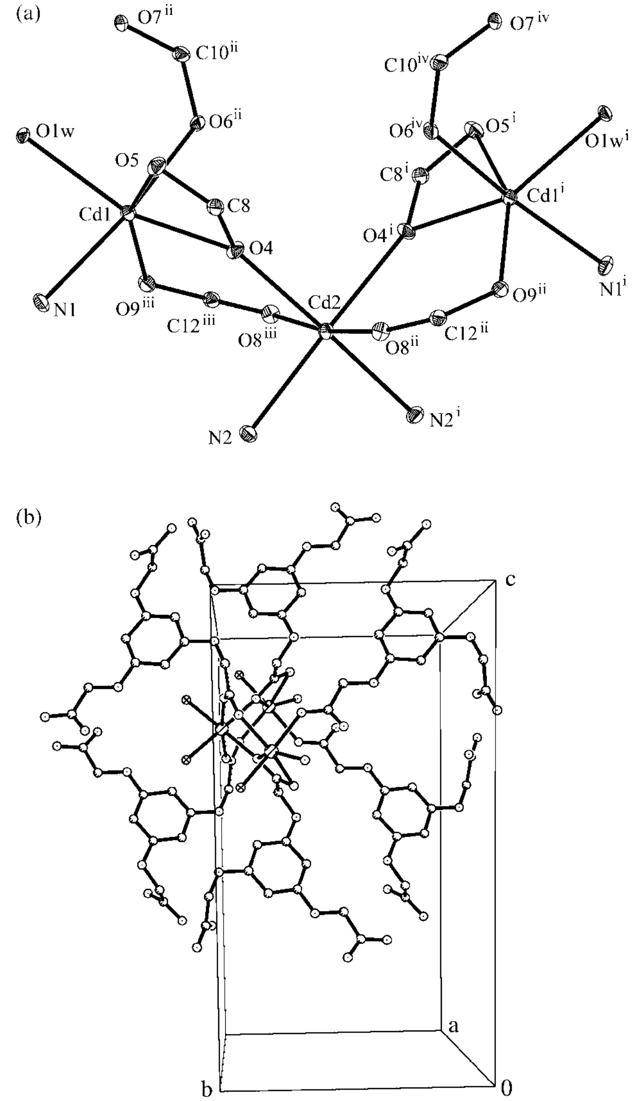


Figure 6. (a) Trinuclear secondary building unit (SBU) in **3**. All of the carboxylate groups are from different TCMB ligands and other parts of the ligand have been omitted for clarity. Nitrogen atoms are from the bpe ligand. Symmetry codes: (i) $1-x$, $+y$, $3/2-z$; (ii) x, $1-y$, $-1/2+z$; (iii) x, $2-y$, $-1/2+z$; (iv) $1-x$, $1-y$, $2-z$. (b) Perspective view showing the arrangement of six TCMB ligands around one Cd$_3$ cluster in the unit cell of **3**. Large and small open circles represent cadmium and carbon atoms, respectively. Oxygen and nitrogen atoms are shown as dotted and crossed circles, respectively. Solvent molecules, other parts of the bpe ligands and hydrogen atoms are omitted for clarity.

through four bpe ligands, resulting in the formation of one-dimensional doubly interlaced zigzag chains in the *ac* plane (Figure 7). On the other hand, two carboxylate groups "above" and "below" the plane of the aromatic ring from the TCMB ligand connect adjacent Cd$_3$ cores, which results in the helix structure along the *a* axis with a mean core distance of ca. 5 Å, and the third carboxylate groups link the neighboring helices to form the 2D networks in the *bc* plane. Accordingly, the 3D network can be interpreted as the result of inclination of 1D into 2D layers (Figure 8).

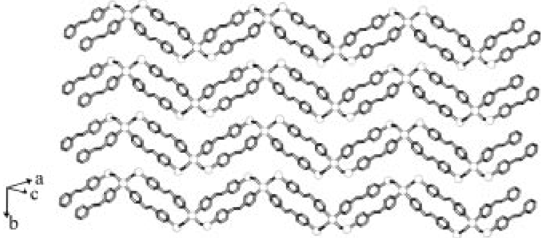


Figure 7. Doubly interlinked chains constructed from Cd$_3$ SBUs and bidentate bpe ligands in **3**.

In addition, C–H···O hydrogen bonds exist in the 3D networks. Carbon atoms with hydrogen atoms (C7–H7, C21–H21) from the OCH$_2$ groups of the TCMB ligand and aromatic rings of the bpe ligand can form C–H···O hydrogen bonds with the carboxylate oxygen atoms (O6, O7) from neighboring motifs. The C···O distance [3.280(5)–3.364(5) Å] and C–H···O angles (156.0–173.0°) of C–H···O hydrogen bonds are both within the ranges of those reported.[20] In spite of the close packing of the whole framework, small one-dimensional channels are still present and are viewed along the *c* axis (see Supporting Information).

In order to classify the network, suitable nodes should be confirmed. In this complex, every Cd$_3$ core is connected through six carboxylate groups and four bpe ligands, but two of the bpe ligands are parallel and can be considered as one linker from a topological view. Thus, the Cd$_3$ core can be viewed as an irregular eight-connected node. Additionally, taking the geometrical center of the benzene ring of the TCMB ligand as a three-connected node, the 3D framework can be represented simply by connecting these nodes according to the connectivity defined by the bpe ligand (Figure 8). When viewed along the *bc* plane, a 2D layer composed of tetragons sharing edges or vertexes can be formed, corresponding to the well-known CdI$_2$-type layer structure, which is quite common for inorganic compounds. To the best of our knowledge, except for several examples of metal alkoxides and hydroxides, few organic-inorganic hybrid materials have been reported with such a net topology.[21] Moreover, such 2D layers are linked by the linear bpe ligands. Thus, tetragons and hexagons as well as octagons can be identified in the projection, which represent the shortest circuit of the three essential rings that define the topology of the whole structure. Because the two kinds of nodes are arranged in a ratio of Cd$_3$/TCMB = 1:2, the short Schläfli symbol of the topology can be expressed as the unusual $(4^6, 6^{14}, 8^8)(4^3)_2$.[22] As far as we know, for the majority of 3D metal-organic framework structures, the connectivity of the building block does not exceed six and, in general, coordination networks with a local connectivity higher than six is very rare. Only some examples involving high coordination number lanthanide metal centers and polynuclear metal-cluster building blocks with eight-connected nodes have been reported.[23] Thus, the complex we report represents a scarce eight-connected topology, known for self-penetrating systems so far.

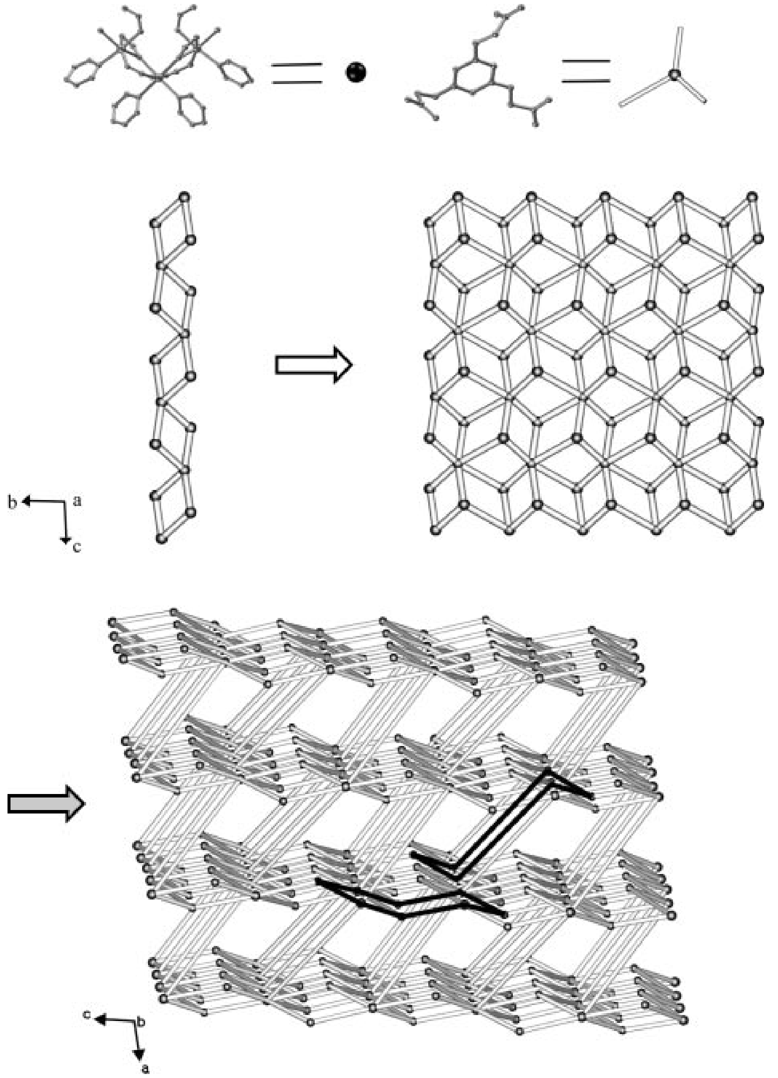


Figure 8. Topological representation of the formation of the whole structure of **3** from a 1D helical chain to a 3D network, showing the self-penetrating shortest circuits (black circles). By this notation, two parallel bpe ligands linking adjacent Cd_3 SBUs are viewed as one stick.

$[Cd_3(TCMB)_2(dpp)_2(H_2O)_3]_n$ (4)

X-ray analysis reveals that in complex **4**, similar Cd_3 SBUs are also formed with metal–metal distances for Cd1···Cd2 and Cd1···Cd1^{x} (symmetry code x: $1-x$, $+y$, $3/2-z$) of 3.967(5) Å and 6.459(8) Å, respectively, which are shorter than those in complex **3** (Figure 9). The largest difference lies in the connectivity of the more flexible dpp ligand. In general, the dpp ligand could assume a TT, TG, GG′, or GG conformation with relative orientations of the CH_2 groups.[24] In this case, the high flexibility of the dpp molecules enables them to join metal cores in different directions and one dpp ligand connects the Cd1 and Cd2 centers from adjacent cores with a metal–metal separation Cd1···Cd2^{xi} (symmetry code xi: $3/2-x$, $-1/2+y$, $1/2-z$.) of ca. 12.368(7) Å, exhibiting significant dihedral angles of 70.5° between the two phenyl rings, which can be viewed as a *trans-gauche* (TG) conformation. Additionally, the C25 atom of the methylene group is disordered in this conformation. In this way, the dpp ligands establish a physical bridge between the separated Cd_3 cores and each Cd_3 core is linked to another four adjacent clusters, resulting in the (4,4) network (Figure 10).

Similarly, in this compound, the dpp ligands and the TCMB ligands also interact with each other through C–H···O hydrogen bonds that originate from the C atoms, with hydrogen atoms, (C17–H17, C19–H19, C24–H24) of the dpp ligands and the carboxylate oxygen atoms (O5, O8^{xii}, O5^{xiii}) (symmetry code xii: x, $2-y$, $-1/2+z$; xiii: $3/2-x$, $1/2+y$, $1/2-z$), where the C···O distances are in the range 3.209(7)–3.384(7) Å and the C–H···O angles in the range 132.0–172.0°.

Figure 11 illustrates the simplified self-assembly from 1D helical chains to the 3D network of complex **4**. Similar 2D layers composed of Cd_3 SBUs bridged by carboxylate groups can be formed, with significant distortion that is closer to that for the $HgBr_2$-type layer, which is another type of inorganic structure that is very similar to the CdI_2 type.[22] Interestingly, the Cd_3 cores are bridged to one an-

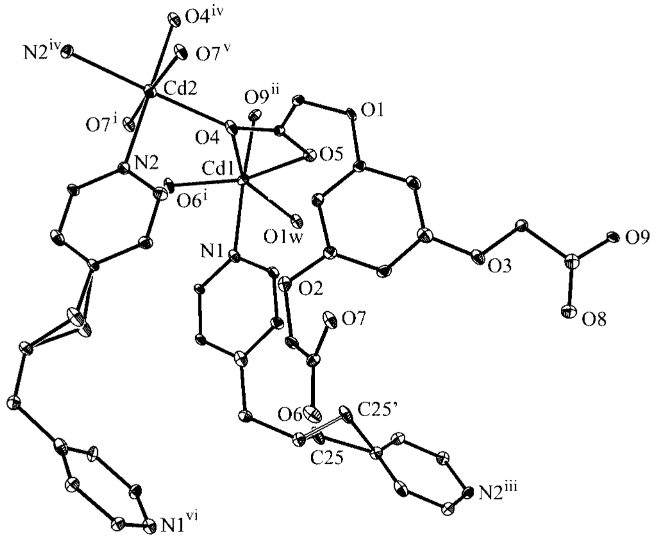


Figure 9. Schematic representation of the distorted octahedral coordination environments for the Cd metal centers in **4**. Hydrogen atoms have been omitted for clarity, and thermal ellipsoids are drawn at the 10% probability level. The disordered dpp ligand is represented in terms of C25 and C25′. For bond lengths and angles see Table 1. Symmetry codes used to generate equivalent atoms: (i) x, $2-y$, $-1/2+z$; (ii) x, $1-y$, $-1/2+z$; (iii) $-1/2+x$, $-1/2+y$, $+z$, (iv) $2-x$, y, $1/2-z$; (v) $2-x$, $2-y$, $1-z$; (vi) $3/2-x$, $1/2+y$, $1/2-z$.

other by four nonparallel dpp ligands because of the flexibility of such ligands, and thus become a more irregular ten-connected node. The final 3D network of complex **4** can be viewed as the conversion of the parallel (4,4) sheets into the 2D sheet, and the topology defined by the dpp linking of ten-connected and three-connected nodes is rare $(4^{18}, 6^{24}, 8^3)(4^3)_2$.[22] To the best of our knowledge, the complex we report represents the highest connected topology of any known entangled species.

In summary, coligands in the reactions have a great influence on the final products. Firstly, the flexibility of the pyridyl-containing ligands can induce the structures and the acids to adopt diverse coordination modes and facilitate more complicated MOFs. Secondly, different amounts of the bases in the assembly process lead to different dimensions of the final network. Though the amounts of bases in the reactions are equal, for example, complexes **3** and **4**, different frameworks of the products may result from the adjustable conformations of the ligands to enable themselves to satisfy the coordination assemblies. Furthermore, more bases can coordinate to the metal centers competing with the aqua molecules, extending the networks from low-dimensional to high-dimensional structures, such as complex **3** in comparison with complex **2**.

FT-IR Spectra and Thermogravimetric Analyses

The IR spectra show features attributable to the carboxylate stretching vibrations of the complexes. The absence of signals in the range 1760–1680 cm^{-1} indicates complete deprotonation of the TCMB ligand. The characteristic bands of the carboxylate groups appear in the range 1560–1620 cm^{-1} for the asymmetric stretching and 1370–1490 cm^{-1} for the symmetric stretching. Weak absorptions observed over the range 2900–2950 cm^{-1} can be attributed to the ν_{CH2} of the TCMB ligand. The broad bands at ca. 3300 cm^{-1} correspond to the vibration of the water ligands in the complexes. The TGA curves of complex **1** and **2** have almost the same thermal characteristics: an obvious weight loss between 40 °C and 150 °C was attributed to the loss of all the solvent water molecules (8 H_2O per unit for **1**: calcd. 10.47, found 10.49; 5 H_2O for **2**: calcd. 6.67, found 7.54) and a rapid weight loss was observed from ca. 320 °C, indicating the decomposition of the whole structure. Complexes **3** and **4** also exhibit similar curves and the gradual decrease occurs from about 100 °C, which is involved in the release of guest water molecules. The complexes begin to decompose from this temperature and the obvious weight loss was observed at ca. 330 °C (see Supporting Information).

Photoluminescent Properties

The emission spectra of all the complexes in the solid state were measured at room temperature (Figure 12). Complex **1** shows fluorescent emissions at 470 nm with a shoulder peak at about 530 nm, and no enhancement in the fluorescence intensity is realized compared with the free ligand.

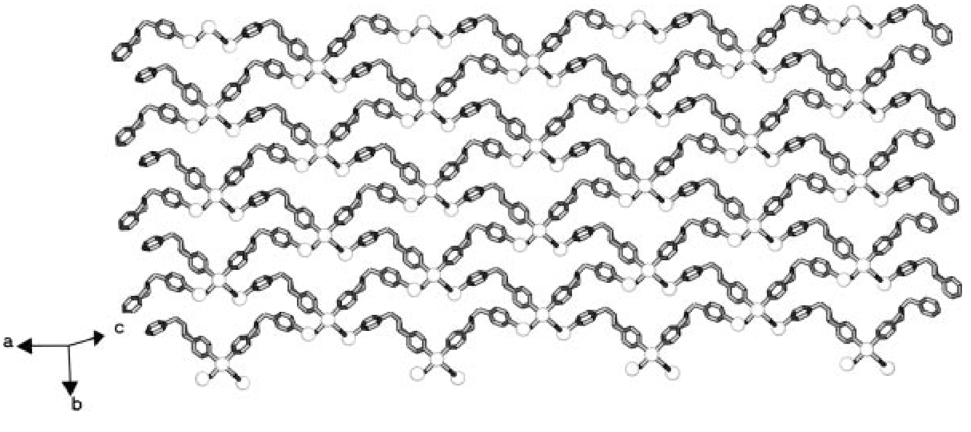


Figure 10. View of the two-dimensional (4,4) layer formed through bidentate dpp-bridging Cd$_3$ SBUs in **4**.

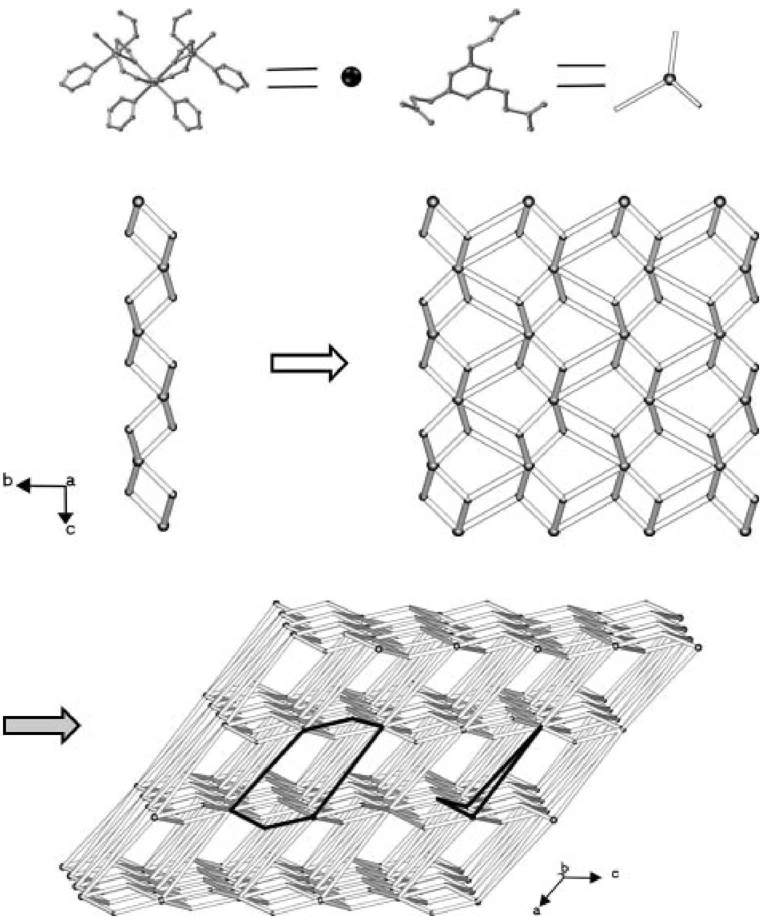


Figure 11. Topological representation of complex **4** from a 1D helical chain to a 3D network, showing the self-penetrating shortest circuits (black circles).

Since the free 4,4′-bipy ligand does not show any luminescence in the range 400–800 nm,[25] the main peak at 470 nm may be interpreted as a ligand-to-metal charge transfer (LMCT).[26] On the other hand, the shoulder peak is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature, and can probably be attributed to the intraligand fluorescent emission because of the similar emission for the free ligand with the intraligand π-π* transition at 530 nm. Thus, this complex may be an excellent candidate for blue-fluorescent materials. For complexes **2** and **3**, the fluorescence is significantly decreased, and only weak absorptions were observed at 530 nm for the intraligand transition, while complex **4** shows no photoluminescent properties at room temperature. Apparently, this phenomenon is associated with the structure of this complex. In complex **1**, strong π···π interactions exist between the adjacent 2D layers, which is favorable for the reduction of the energy of the π-π* transition to some extent, while for complexes **2**–**4**, the gradually increasing flexibility of the coligands from bpe to dpp largely weakens such interactions, which is disadvantageous to the luminescence. In complex **4**, the interactions are reduced in such a way that even the luminescence was not observed.

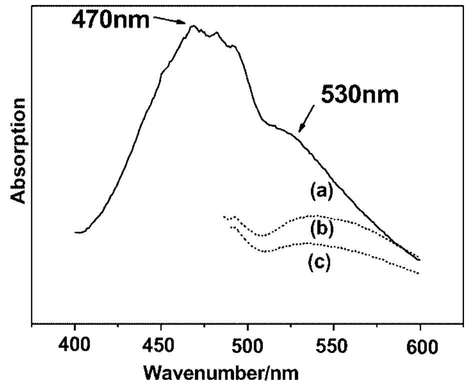


Figure 12. Photoluminescence spectra of (a) complex **1**, (b) complex **2**, and (c) complex **3** at room temperature.

Conclusions

Four novel cadmium(II) coordination polymers based on an unexplored and flexible tripodal ligand, 1,3,5-tris(carboxymethoxy)benzene (TCMB) and bipyridyl ligands (rigid 4,4-bipy, flexible bpe, dpp) have been hydrothermally synthesized and structurally characterized, and all of them show interesting topologies resulting from the different comformations and coordination modes of the flexible ligands. Complex **1** and **2** have similar unusual twofold parallel interpenetrating 2D 6^3 networks with two types of hexagonal rings of large dimensions arranged alternately. An excess of the pyridyl-containing ligands leads to the formation of 3D frameworks of complexes **3** and **4** with scarce eight- and ten-connected topologies of $(4^6, 6^{14}, 8^8)(4^3)_2$ and $(4^{18}, 6^{24}, 8^3)(4^3)_2$, respectively, both of which contain rare 2D CdI_2 layers consisting of isosceles triangle $[Cd_3(CO_2)_4]^{2-}$ SBUs. They represent one of the few eight-connected and the highest connected topologies, respectively. Complex **1** exhibits luminescent properties resulting from an LMCT and may be a potential candidate for blue luminescent materials. In summary, our research demonstrates for the first time that 1,3,5-tris(carboxymethoxy)benzene (TCMB) could be a potential building block to construct novel cadmium supramolecular architectures with unusual topologies and luminescent properties. Further investigation is ongoing.

Experimental Section

General Methods: TCMB was prepared according to the literature.[27] 4,4-Bipyridine (4,4-bipy), 1,2-bis(4-pyridyl)ethane (bpe), and 1,3-bis(4-pyridyl)propane (dpp) were purchased from Aldrich and used as received without further purification. All of the other reagents were commercially available and used as purchased. The elemental analysis was carried out with a Perkin–Elmer 240C elemental analyzer, at the Center of Materials Analysis, Nanjing University. The FT-IR spectra were recorded from KBr pellets over the range 4000–400 cm^{-1} with a Vector 22 spectrometer. Thermal analyses were performed with a TGA V5.1A Dupont 2100 instrument from room temperature to 700 °C with a heating rate of 10 °C/min under a flow of nitrogen, and the data are consistent with the structures. The emission/excitation spectra were recorded with a Hitachi 850 fluorescence spectrophotometer.

$[Cd_3(TCMB)_2(4,4'\text{-bipy})(H_2O)_{16}]_n$ (1): In a general synthesis, an equimolar mixture of TCMB (0.030 g, 0.1 mmol), 4,4′-bipy (0.016 g, 0.1 mmol), and $Cd(OAc)_2{\cdot}2H_2O$ (0.026 g, 0.1 mmol) in H_2O/C_2H_5OH (1:1, v/v) (10 mL) was placed in a Parr Teflon-lined stainless steel vessel and heated to 80 °C for 50 h. The reaction system was then slowly cooled to room temperature and colorless block crystals of **1** were obtained. After filtration, the crystals were washed with water and dried in air; yield 0.026 g [56%, based on $Cd(OAc)_2{\cdot}2H_2O$]. $C_{34}H_{58}Cd_3N_2O_{34}$ (1376.02): calcd. C 29.67, H 4.25, N 2.04; found C 29.98, H 4.36, N 1.98. IR (KBr pellet): $\tilde{\nu}$ = 3446 (s, br), 2924 (w), 1605 (s), 1418 (m), 1336 (w), 1262 (vw), 1165 (m), 1121 (w), 1075 (w), 807 (w), 726 (w), 629 (vw) cm^{-1}.

$[Cd_3(TCMB)_2(bpe)(H_2O)_{13}]_n$ (2): Similar procedures were performed to obtain colorless crystals of complex **2**, except that ligand bpe was used instead of 4,4′-bipy; yield 0.020 g [45%, based on $Cd(OAc)_2{\cdot}2H_2O$]. $C_{36}H_{56}Cd_3N_2O_{31}$ (1350.03): calcd. C 32.02, H 4.18, N 2.07; found C 32.06, H 4.38, N 2.04. IR (KBr pellet): $\tilde{\nu}$ = 3449 (s,br), 2924 (w), 1611 (s), 1509 (vw), 1422 (m), 1340 (w), 1264 (vw), 1165 (m), 1121 (w), 1075 (w), 807 (w), 726 (w), 671 (w), 629 (w) cm^{-1}.

$[Cd_3(TCMB)_2(bpe)_2(H_2O)_4]_n$ (3): A mixture of TCMB (0.030 g, 0.1 mmol), bpe (0.036 g, 0.2 mmol), and $Cd(OAc)_2{\cdot}2H_2O$ (0.026 g, 0.1 mmol) with a molar ratio of about 1:3:1 in H_2O (10 mL) with several drops of CH_3OH was placed in a Parr Teflon-lined stainless steel vessel and heated to 80 °C for 50 h. The reaction system was cooled to room temperature to give colorless block crystals of **3** that were filtered, washed with water and dried in air; yield 0.027 g [59%, based on $Cd(OAc)_2{\cdot}2H_2O$]. $C_{48}H_{50}Cd_3N_4O_{22}$ (1372.12): calcd. C 42.01, H 3.67, N 4.08; found C 41.72, H 3.92, N 3.89. IR (KBr pellet): $\tilde{\nu}$ = 3430 (m, br), 2923 (w), 1612 (s), 1474 (w), 1424 (m), 1320 (m), 1267 (vw), 1171 (s), 1157 (s), 1075 (w), 830 (w), 818 (w),712 (w) cm^{-1}.

$[Cd_3(TCMB)_2(dpp)_2(H_2O)_3]_n$ (4): Complex **4** was obtained in a similar manner to that of complex **3**, except that more flexible dpp (0.057 g, 0.3 mmol) was used instead of the bpe ligand; yield 0.033 g [72%, based on $Cd(OAc)_2{\cdot}2H_2O$]. $C_{100}H_{104}Cd_6N_8O_{42}$ (2764.31): calcd. C 43.44, H 3.79, N 4.05; found C 42.72, H 3.92, N 3.99. IR (KBr pellet): $\tilde{\nu}$ = 3447 (m), 2919 (w), 1615 (s), 1423

Table 5. Crystal data and structure refinement information for the complexes.

Complex	1	2	3	4
Emprical formula	$C_{34}H_{58}Cd_3N_2O_{34}$	$C_{36}H_{56}Cd_3N_2O_{31}$	$C_{48}H_{50}Cd_3N_4O_{22}$	$C_{100}H_{104}Cd_6N_8O_{42}$
Formula mass [g mol^{-1}]	1376.02	1350.03	1372.12	2764.31
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$C2/c$
a [Å]	9.824(3)	10.906(3)	22.408(3)	29.188(3)
b [Å]	11.936(3)	11.677(3)	11.382(3)	11.674(2)
c [Å]	12.680(3)	11.741(3)	20.863(3)	20.848(3)
α [°]	64.57 (1)	73.56(1)	90	90
β [°]	75.95(1)	69.35(2)	99.57(4)	129.62(2)
γ [°]	72.30(1)	71.18(2)	90	90
V [Å^3]	1268.1(15)	1299.9(6)	5247(2)	5471.8(17)
Z	1	1	4	2
$D_{calcd.}$ [g cm^{-3}]	1.802	1.725	1.737	1.678
μ [mm^{-1}]	1.349	1.311	1.290	1.236
θ range [°]	1.8–26.0	1.9–27.0	2.0–26.0	2.0–26.0
Index ranges	$-12 \le h \le 12$	$-13 \le h \le 13$	$-27 \le h \le 15$	$-35 \le h \le 17$
	$-14 \le k \le 12$	$-14 \le k \le 14$	$-14 \le k \le 13$	$-14 \le k \le 14$
	$-15 \le l \le 12$	$-14 \le l \le 14$	$-24 \le l \le 25$	$-23 \le l \le 24$
R_1, wR_2[a] [$I > 2\sigma(I)$]	0.0485; 0.1132	0.0514; 0.1124	0.0412; 0.0984	0.0512; 0.1257
R_1, wR_2[a] [all data]	0.0782; 0.1192	0.0660; 0.1165	0.0503; 0.1004	0.0601; 0.1284
Largest difference Fourier peak/hole [e Å^{-3}]	0.75/–0.76	0.40/–1.74	0.95/–1.58	0.42/–1.35

[a] $R_1 = \Sigma||F_o| - |F_c||/|F_o|$; $wR_2 = [\Sigma w(\Sigma F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

(m), 1317 (w), 1266 (vw), 1226 (vw), 1172 (m), 1157 (m), 1079 (w), 1020 (vw), 819 (vw), 725 (vw), 657 (vw) cm^{-1}.

X-ray Crystallographic Study: Suitable single crystals were selected for indexing and intensity data were measured with a Siemens Smart CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 293 K. The raw data frames were integrated into SHELX-format reflection files and corrected using the SAINT program. Absorption corrections based on multiscans were obtained from the SADABS program. The structures were solved with direct methods and refined with full-matrix least-squares techniques using the SHELXS-97 and SHELXL-97 programs, respectively.[28] The coordinates of the non-hydrogen atoms were refined anisotropically, and the positions of the H atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 5, and selected bond lengths and angles are listed in Table 1. The figures were obtained by using the SHELXP-97[28] and Olex program packages.[29] CCDC-294480 to -294483 for complexes **1**–**4** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Additional figures, and TGA and luminescent curves of complexes **1**–**4**.

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