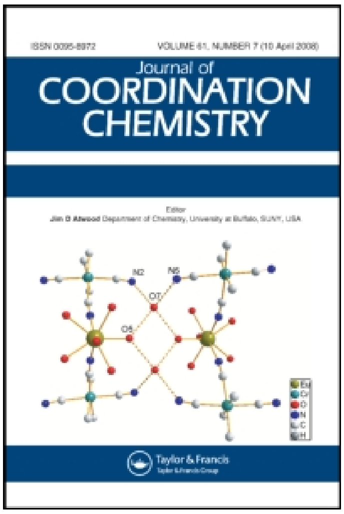

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Employing Cd-O-C rod-shaped secondary building units to construct 2D metal-organic frameworks (MOFs): hydrothermal synthesis, structures, and luminescent properties

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Employing Cd–O–C rod-shaped secondary building units to construct 2D metal-organic frameworks (MOFs): hydrothermal synthesis, structures, and luminescent properties

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Under hydrothermal conditions, in the presence of H_2BDC, the self-assembly of $CdCl_2$, H_2ip or H_2NDC at pH = 7 generated two Cd(II)-containing coordination polymers, $Cd_6(ip)_6(\mu\text{-}H_2O)_4 \cdot H_2O$ (**1**) and $Cd_2(NDC)_2(\mu\text{-}H_2O)_2$ (**2**) ($H_2BDC/H_2ip/H_2NDC = 1,4/1,3/1,2$-benzenedicarboxylic acid). The structures are 2D metal-organic frameworks constructed from Cd-O-C rod-shaped SBUs (Secondary Building Units). Crystal samples in the solid state display strong fluorescence at 335 and 343 nm.

Keywords: Hydrothermal synthesis; MOFs; SBUs; Inorganic–organic rod structure

1. Introduction

Synthesis of coordination polymers has developed rapidly in recent years [1], motivated by their interesting molecular topologies [2] and crystal packing motifs, along with potential applications as functional materials [3]. In interpretation of MOF structures, SBUs are considered as the ‘‘joints’’ and the organic links as the ‘‘struts’’ of the underlying net. MOFs based on discrete shapes (triangles, squares, tetrahedra, etc.) have been prepared and studied [4]. The large majority of studies have been done on MOFs built on discrete SBUs, yet analogous chemistry involving infinite rod-shaped SBUs remains largely unexplored. Recent research suggests that rod-shaped metal-carboxylate SBUs allow access to MOFs that do not interpenetrate due to the intrinsic packing arrangement of such rods in the crystal structure [5]. Herein, we report two 2D metal-organic frameworks that are built on infinite Cd–O–C rod-shaped SBUs.

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Table 1. Crystallographic data for **1** and **2**.

Compound	**1**	**2**
Chemical formula	$C_{48}H_{30}Cd_6O_{29}$	$C_{16}H_{12}Cd_2O_{10}$
M	1745.10	589.06
Crystal system	Monoclinic	Orthorhombic
Space group	$P2/n$	$Pbca$
a (Å)	13.942(3)	9.2921(19)
b (Å)	9.877(2)	7.7304(15)
c (Å)	22.784(7)	23.473(5)
β (°)	119.34(2)	90
V (Å^3)	2735.0(12)	1686.1(6)
Z	2	4
Density (mg m^{-3})	2.117	2.320
S	1.136	1.088
R_1, wR_2 (all data)	0.0342, 0.0830	0.0199, 0.0457

2. Experimental

2.1. *Materials and methods*

All reagents were bought from commercial sources and used without further purification. Fluorescence spectroscopic data were recorded on a LS55 luminescence spectrometer. Elemental analyses were carried out on a Perkin-Elmer 240C elemental analyzer.

2.2. *Synthesis*

A mixture (10 ml, $C_2H_5OH:H_2O = 3:2$) of $CdCl_2$, H_2BDC, H_2ip or H_2NDC in the ratio of 1 : 0.8 : 1 with pH = 7 adjusted by 1 mol L^{-1} NaOH solution was placed in a Teflon reactor (23 mL) and heated at 170°C for 3 days, and then it was cooled to room temperature at 5°C h^{-1}. Colorless crystals were obtained in 65% yield for **1** and 71% for **2** based on Cd. In the resultant products, H_2BDC is not coordinated, but plays an important role in providing a suitable environment for formation of **1** and **2**, as without it, no product is obtained. Elemental analysis (%) Calcd for **1**: C, 33.03; H, 1.73; found: C, 33.04; H, 1.74; for **2**: C, 32.62; H, 2.05; found: C, 32.63; H, 2.07.

2.3. *Crystallographic measurements on 1 and 2*

A colorless single crystal was selected for the diffraction analysis. Data collection was performed on a Rigaku r-axis rapid IP area detector using Mo-Kα radiation. Data were integrated and corrected for absorption using the RAXIS-RAPID Auto program. The structures were solved by Direct Methods and refined by SHELXL-97 [8]. All non-hydrogen atoms (cadmium, oxygen, carbon) were located first in difference Fourier maps; the organic hydrogen atoms are calculated and other hydrogen atoms were found and refined with the O–H/0.85 ± 0.01, H–H/1.25 ± 0.01 restriction. Some crystallographic details are listed in table 1, and selected bond lengths and bond angles are listed in table 2.

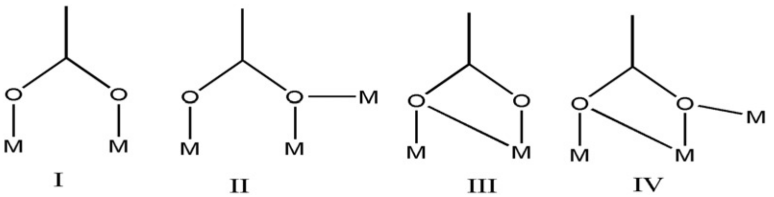
Table 2. Selected bond lengths (Å) and angles (°).

1		**2**	
Cd(1)–O(2)	2.210(3)	Cd(1)–O(1)	2.2574(15)
Cd(1)–O(7)	2.276(3)	Cd(1)–O(3)#1	2.3198(18)
Cd(1)–O(9)	2.292(3)	Cd(1)–O(5)	2.3252(16)
Cd(1)–O(6)	2.367(3)	Cd(1)–O(2)#1	2.3337(15)
Cd(1)–O(5)	2.415(3)	Cd(1)–O(3)#2	2.3619(15)
Cd(1)–O(13)#1	2.466(4)	Cd(1)–O(4)#2	2.4389(17)
Cd(1)–O(14)#1	2.555(3)	Cd(1)–O(2)#3	2.4670(15)
Cd(2)–O(4)#2	2.192(3)	O(1)–Cd(1)–O(3)#1	81.79(6)
Cd(2)–O(12)	2.258(4)	O(1)–Cd(1)–O(5)	157.46(6)
Cd(2)–O(14)	2.357(3)	O(3)#1–Cd(1)–O(5)	116.28(6)
Cd(2)–O(8)#3	2.369(3)	O(1)–Cd(1)–O(2)#1	93.43(6)
Cd(2)–O(10)	2.372(3)	O(3)#1–Cd(1)–O(2)#1	75.97(5)
Cd(2)–O(11)	2.426(3)	O(5)–Cd(1)–O(2)#1	79.18(6)
Cd(2)–O(9)#3	2.535(3)	O(1)–Cd(1)–O(3)#2	95.77(6)
Cd(3)–O(3)#4	2.163(3)	O(3)#1–Cd(1)–O(3)#2	128.68(4)
Cd(3)–O(3)#2	2.163(3)	O(5)–Cd(1)–O(3)#2	83.39(6)
Cd(3)–O(11)#5	2.317(3)	O(2)#1–Cd(1)–O(3)#2	154.70(5)
Cd(3)–O(11)	2.317(3)	O(1)–Cd(1)–O(4)#2	113.14(6)
Cd(3)–O(8)#3	2.365(3)	O(3)#1–Cd(1)–O(4)#2	79.67(5)
Cd(3)–O(8)#6	2.365(3)	O(5)–Cd(1)–O(4)#2	84.66(6)
Cd(4)–O(1)#7	2.172(3)	O(2)#1–Cd(1)–O(4)#2	140.70(5)
Cd(4)–O(1)	2.172(3)	O(3)#2–Cd(1)–O(4)#2	54.11(5)
Cd(4)–O(5)	2.299(3)	O(1)–Cd(1)–O(2)#3	76.30(5)
Cd(4)–O(5)#7	2.299(3)	O(3)#1–Cd(1)–O(2)#3	144.42(5)
Cd(4)–O(13)#8	2.344(3)	O(5)–Cd(1)–O(2)#3	81.31(6)
Cd(4)–O(13)#1	2.344(3)	O(2)#1–Cd(1)–O(2)#3	77.73(6)
Cd(3)#1–O(8)–Cd(2)#1	97.90(11)	O(3)#2–Cd(1)–O(2)#3	81.64(5)
Cd(1)–O(9)–Cd(2)#1	104.79(10)	O(4)#2–Cd(1)–O(2)#3	134.82(5)
Cd(4)#3–O(13)–Cd(1)#3	96.25(11)		
Cd(2)–O(14)–Cd(1)#3	102.27(10)		

Symmetry code: **1**: 1 $x, y-1, z$; #2 $x-1, y+1, z$; #3 $x, y+1, z$; #4 $-x+2, y+1, -z+3/2$; #5 $-x+1, y, -z+3/2$; #6 $-x+1, y+1, -z+3/2$; #7 $-x+2, y, -z+3/2$; #8 $-x+2, y-1, -z+3/2$.
2: 1 $x+1/2, -y+1/2, -z$; #2 $-x+1, -y+1, -z$; #3 $-x+3/2, y+1/2, z$; #5 $-x+3/2, y-1/2, z$.

3. Results and discussion

Coordination modes of the carboxyl groups involved in this research are listed in scheme 1.



Scheme 1. The coordinated mode of the carboxyl groups involved in this research.

3.1. *Crystal structure of 1*

Polymer **1** crystallizes in the $P2/n$, monoclinic space group. In an asymmetry unit, there are four independent Cd(II) ions: Cd1 and Cd2 are seven-coordinate by six ip^{2-} oxygen

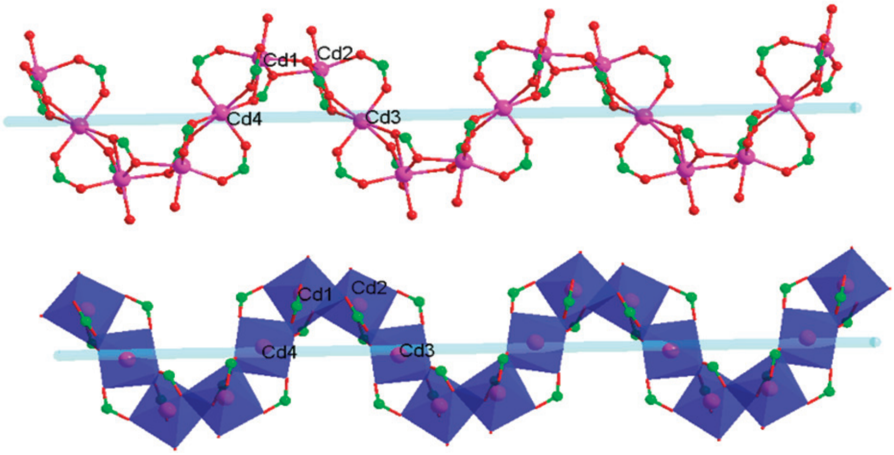


Figure 1. Ball-and-stick description of the helical Cd–O–C rod around one 2-fold axis (top); polyhedral description (bottom).

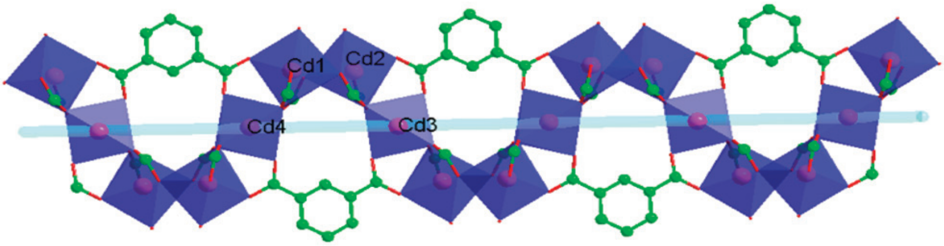


Figure 2. View of the 1D tape structure along *a* assembled from ip^{2-} and Cd–O–C rod.

atoms and one terminal water in a pentagonal bipyramid; Cd3 and Cd4 located on an inversion center have six-coordinate octahedral geometry completed by six ip^{2-} oxygen atoms. The Cd–O bond lengths are in the range 2.172–2.555 Å, comparable with those observed in other Cd-containing complexes [6].

Along *a*, these Cd(II) ions are connected in the –Cd4–Cd1–Cd2–Cd3–Cd2–Cd1–Cd4– arrangement by μ_2-$O_{carboxylate}$ and carboxyl groups, with Cd–O–C rod of edge-sharing polyhedra. The Cd–Cd distance is 3.583 Å for Cd4–Cd1, 3.827 Å for Cd1–Cd2, 3.570 Å for Cd2–Cd3, 3.827 Å for Cd2–Cd1. These Cd–O–C rods are somewhat helical around one 2-fold axis, as illustrated in figure 1. These Cd–O–C rods are interlinked by ip^{2-} ligands to generate the 1D tape structure of edge-sharing Cd_6 SBU (figure 2). Furthermore, these defined 1D tapes are linked by ip^{2-} ligands into 2D frameworks (figure 3), which are further extended to the 3D supramolecular framework by $O_{water} \cdots O_{MOFs}$/3.033 Å, $O_{water} \cdots C_{MOFs}$/3.481 Å hydrogen bonds between water and 2D MOFs.

3.2. *Crystal structure of 2*

Polymer **2** crystallizes in *Pbca*, with an orthorhombic space group, and the asymmetric unit is comprised of one Cd(II), one ip^{2-}, and one coordinated water. Cd(II) is

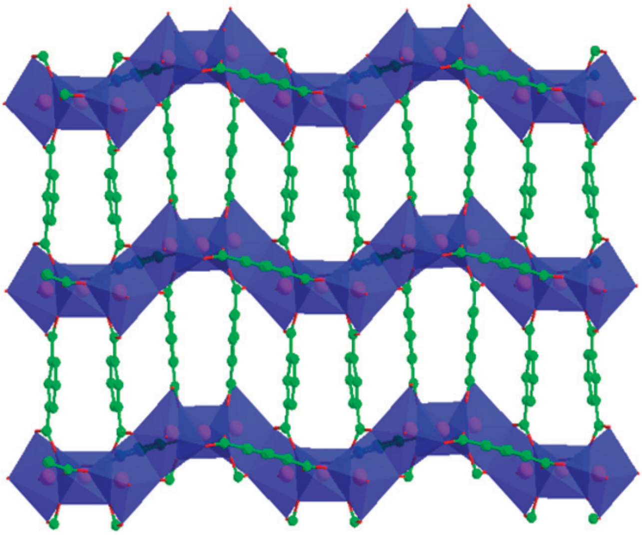


Figure 3. View of the 2D MOFs built from Cd–O–C rods.

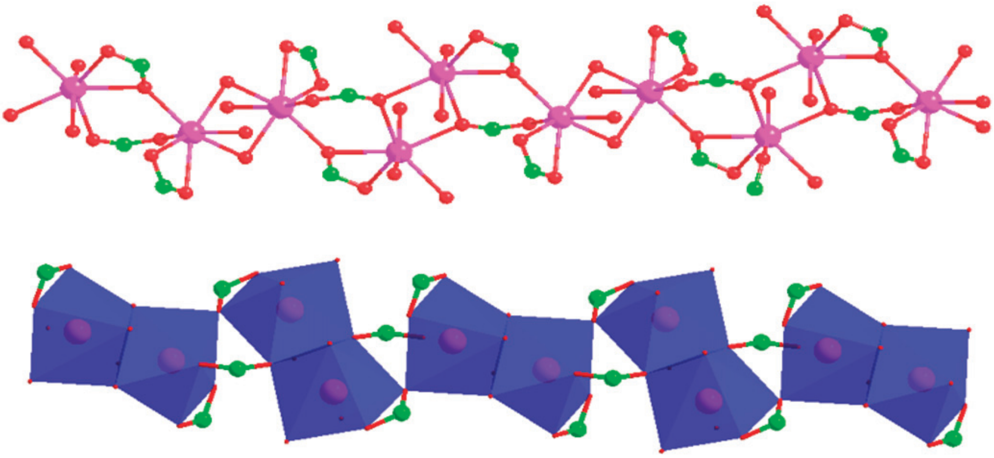


Figure 4. Ball-and-stick description of the Cd–O–C rod (top); polyhedral description (bottom).

pentagonal bipyramidal, similar to **1**, with six NDC^{2-} O atoms and one water. The Cd–O bond lengths are in the normal range from 2.257 to 2.467 Å [6].

Along *a* or *b* direction, the Cd–O–C rod of alternately edge- and vertex-sharing polyhedra can be observed, where Cd1 and related Cd1A are linked by double μ_2-$O_{carboxylate}$ atoms to generated Cd_2 fragments; these Cd_2 fragments are connected by one μ_2-$O_{carboxylate}$ and one carboxyl group (figure 4). As shown in figure 5, these Cd–O–C rods are cross-linked to construct the irregular honeycomb-like MOFs of dimensions 3.739 × 4.228 Å. In this honeycomb-like MOF, rare inorganic Cd_6 SBU are observed (figure 6). Additionally, no significant supramolecular interaction exists between these honeycomb-like layers.

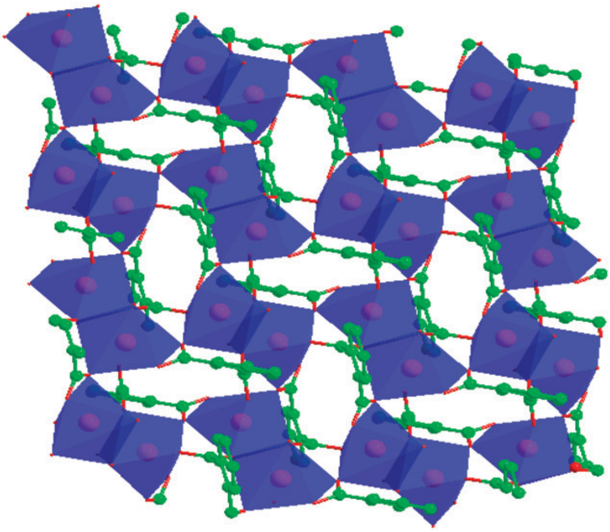


Figure 5. View of the honeycomb-like MOFs.

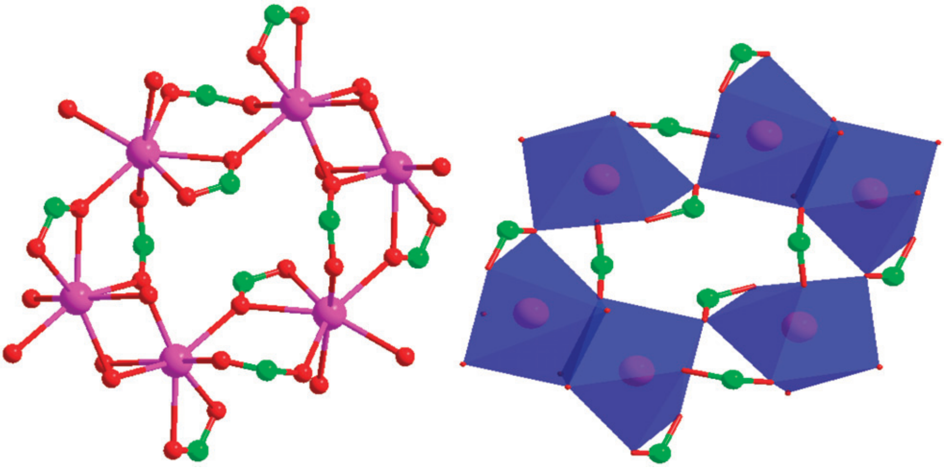


Figure 6. Ball-and-stick description of inorganic Cd_6 SBU (left); polyhedral description (right).

Self-assembly of Cd(II) ions and multi-carboxylates is good for construction of MOFs based on rod-shaped SBUs. Comparing with MOF-79 [9], we also found that the structure matrix is influenced by the angle for the carboxyl groups of ligands. In **1** and **2**, the Cd–O–C rods bridged by ip^{2-} (120° angle for the two carboxyl groups) or NDC^{2-} (60°) are two-dimensional, whereas for MOF-79, the linear multi-carboxylate (180°) connects the Cd–O–C rods, leading to the 3D structure.

3.3. *Fluorescent properties*

Metal-organic complexes with a d^{10} electronic configuration exhibit fluorescence. The fluorescent properties of **1** and **2** in the solid state at room temperature (figure 7)

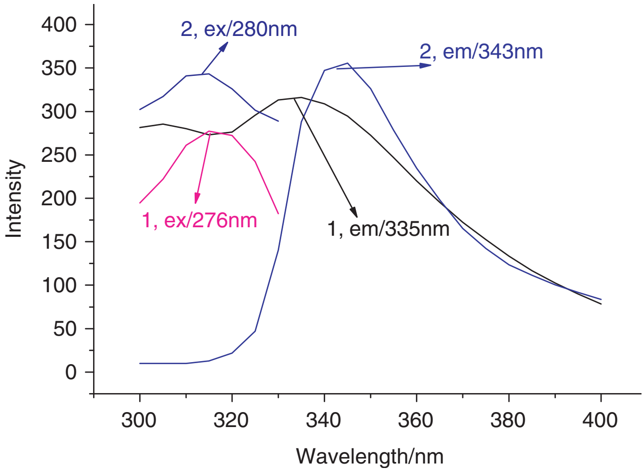


Figure 7. Fluorescence plots of **1** and **2**.

show intense emission maximum at 335 nm for **1** and 343 nm for **2** upon excitation at 276 nm and 280 nm, respectively. H_2ip and H_2NDC display intense fluorescent properties in the solid state at room temperature with the emission about 362.5 nm and 346.5 nm, respectively. This blue-shift may be assigned to the ligand-to-metal charge transfer (LMCT) and/or metal-metal interactions [7].

4. Conclusion

We isolated two Cd-containing coordination polymers with 2D MOFs built from Cd–O–C rods. Polymer **1** contains the rare 1D tape configuration of edge-sharing Cd_6 SBU; meantime, polymer **2** displays the inorganic Cd_6 SBU. Both in the solid state display strong fluorescence, showing fluorescence material.

Acknowledgements

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