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Journal of Solid State Chemistry 177 (2004) 1060–1066

JOURNAL OF
SOLID STATE
CHEMISTRY

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Synthesis, structure and fluorescence of a novel three-dimensional inorganic–organic hybrid polymer constructed from trimetallic clusters and mixed carboxylate ligands

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Received 2 July 2003; received in revised form 9 October 2003; accepted 14 October 2003

Abstract

A new inorganic–organic hybrid framework coordination polymer, $Cd_3(BDC)_{0.5}(BTC)_2(DMF)(H_2O)\cdot 3DMF\cdot H_3O\cdot H_2O$ **1**, in which two carboxylate ligands, 1,4-benzenedicarboxylic acid (H_2BDC) and 1,3,5-benzenetricarboxylic acid (H_3BTC), coordinate with cadmium ions, has been synthesized under mild conditions and its structure solved by single-crystal X-ray diffraction (XRD) analysis. Polymer **1** crystallizes in the monoclinic system, space group $P2_1/c$ (No. 14) with $a = 15.750(3)$ Å, $b = 14.501(3)$ Å, $c = 19.363(4)$ Å, $\beta = 113.67(3)^\circ$, $V = 4050.4(14)$ Å^3, $Z = 4$, $R1 = 0.0374$ and $wR2 = 0.1148$. Its structure revealed that the nine vertices of the secondary building units are linked by benzene rings from both H_3BTC and H_2BDC ligands to form a 3D network with 10×10 Å channels along [001] direction. Complex **1** is characterized by inductively coupled plasma analysis, powder XRD, infrared spectroscopy and thermogravimetric analysis. Polymer **1** exhibits intense fluorescence at 358 and 377 nm with $\lambda_{excitation} = 208$ nm in the solid state at room temperature.

Keywords: Inorganic–organic hybrid polymer; Trimetallic clusters; Mixed carboxylate ligands; Fluorescence

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1. Introduction

Inorganic–organic hybrid polymers are currently of considerable interest and importance for their novel coordination configurations and a wide range of properties, which make them useful in host–guest recognition, molecular sieves, separation and catalysis [1–2]. Some examples of inorganic–organic hybrid polymers are composed of metal ions and ligands containing N-donors such as pyridine, imidazole, 4,4′-bipyridine, 4,4′-trimethyllenedipyridine, 1,2-bis(4-pyridyl)ethane, as well as O-donors such as polycarboxylates [3–22]. 1,4-benzenedicarboxylic acid (H_2BDC) and 1,3,5-benzenetricarboxylic acid (H_3BTC) are two common O-donor ligands in inorganic–organic hybrid complexes. H_3BTC and H_2BDC, the building blocks, exhibit a variety of coordination forms [23–25] (Scheme 1). Although there have been a lot of reports on the infinite 1D, 2D and 3D inorganic–organic hybrid compounds assembled from the single one of above two ligands [26–34], there has been little study on the complexes containing both H_3BTC and H_2BDC coordinated with metal ions [35]. To address this issue, we attempted the preparation of novel coordination polymers using mixed H_2BDC and H_3BTC ligands. Here, we report the synthesis and structure of a new compound with strong fluorescent emission, constructed from H_2BDC, H_3BTC and cadmium(II).

2. Experimental

2.1. Synthesis and characterization

Complex **1** was prepared under mild conditions from a mixture of $H_2BDC(C_8H_6O_4$, 99%), $H_3BTC(C_9H_6O_6$,

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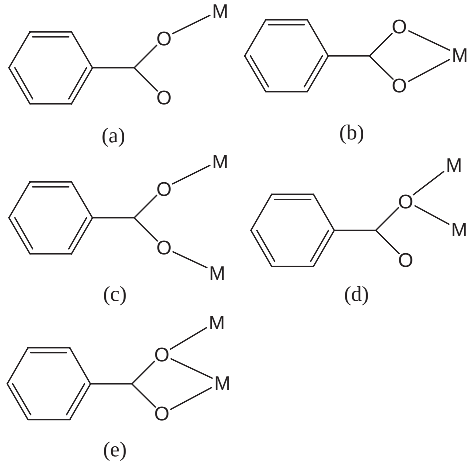
doi:10.1016/j.jssc.2003.10.013



Scheme 1. The coordination fashions of the carboxylic groups: (a) unidentate, (b) chelating bidentate, (c) bidentate, (d) bridging unidentate, and (e) chelating/bridging bidentate.

98%), cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$, 99%), N,N-dimethylformamide (DMF)($HCON(CH_3)_2$, 99.5%), ethanol (CH_3CH_2OH, 99.7%), distilled water and triethylamine (TEA) ($N(CH_2CH_3)_3$, 99%) at the molar ratio 0.005 H_2BDC:0.005 H_3BTC:0.005 $Cd(NO_3)_2 \cdot 4H_2O$:0.5 DMF:0.08 ethanol:0.7 H_2O:0.001 TEA. The above-mentioned mixture was placed in a small vial and dissolved under vigorous stirring, then sealed and left undisturbed for 2 days at 65°C. The resulting colorless block-shaped crystals (about 25% yield based on the Cd source) were collected by filtration, washed thoroughly with ethanol, and dried at room temperature.

The elemental analyses were carried out on a Perkin-Elmer 240C element analyzer. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV ICP instrument. Powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffratometer with Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). The image of the crystal was taken by Leica DMR optical microscope. The infrared (IR) spectra were recorded (400–4000 cm^{-1} region) on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. A Perkin-Elmer TGA 7 thermogravimetric analyzer was used to obtain thermogravimetric analysis (TGA) curve in N_2 with a heating rate of 20°C/min. Fluorescence spectroscopy data were collected on a LS55 luminescence spectrometer.

2.2. *Determination of crystal structure*

Table 1
Crystal data and structure refinement for polymer **1**

Empirical formula	$C_{34}H_{43}N_4O_{21}Cd_3$
Formula weight	1180.93
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 15.750(3)$ Å, $\alpha = 90°$ $b = 14.501(3)$ Å, $\beta = 113.67(3)°$ $c = 19.363(4)$ Å, $\gamma = 90°$
Volume	4050.4(14) Å^3
Z	4
Density (calculated)	6.671 mg/m^3
Absorption coefficient	5.396 mm^{-1}
$F(0\,0\,0)$	7904
Crystal size	$0.323 \times 0.233 \times 0.127$
θ range for data collection	1.41°–27.43°
Limiting indices	$-18 \leqslant h \leqslant 20$, $0 \leqslant k \leqslant 18$, $-17 \leqslant l \leqslant 25$
Reflections collected/unique	8801/8801 [R(int) = 0.0333]
Completeness to $\theta = 27.43$	95.1%
Absorption correction	Empirical
Max. and min. transmission	0.611 and 0.382
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8801/0/559
Goodness-of-fit on F^2	0.686
Final R indices [$I > 2\sigma(I)$]	$R1^a = 0.0374$, w$R2^b = 0.1148$
R indices (all data)	$R1 = 0.0489$, w$R2 = 0.1271$
Largest diff. peak and hole	1.322 and -1.340 e Å^{-3}

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.

[b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; weighting: $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

A single crystal with dimensions $0.323 \times 0.233 \times 0.127$ mm^3 was selected for single-crystal XRD analysis. Structural analysis was carried out on a Bruker SMART CCD diffractometer using graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). The data were collected at 293 K. A total of 8801 reflections were collected with 8801 unique reflections ($R_{int} = 0.0333$), of which 7061 were considered to be observed with $I > 2\sigma(I)$. The structures were solved by direct methods using SHELXS-97 [36] and were refined by full matrix least-square methods using SHELXL-97 [37]. All non-hydrogen atoms were found from the final difference Fourier map, and refined anisotropically. The detailed crystallographic data are listed in Table 1.

3. Results and discussion

3.1. *Characterization*

The elemental analyses and the ICP analysis for **1** are in good agreement with the theoretical values: C, 33.97 wt%; H, 3.20 wt%; N, 4.64 wt%; Cd, 29.63 wt% (calculated: C, 34.61 wt%; H, 3.59 wt%; N, 4.75 wt%; Cd, 28.58 wt%).

The microscopy image of **1** shows that the crystal is uniform and has good morphology (Fig. 1). The powder XRD pattern agrees well with that simulated (Fig. 2). The diffraction peaks on both patterns match well in position, indicating the phase purity of complex **1**.

The IR spectrum of compound **1** shows the presence of vibrational bands at 1620–1550 cm^{-1}, which are

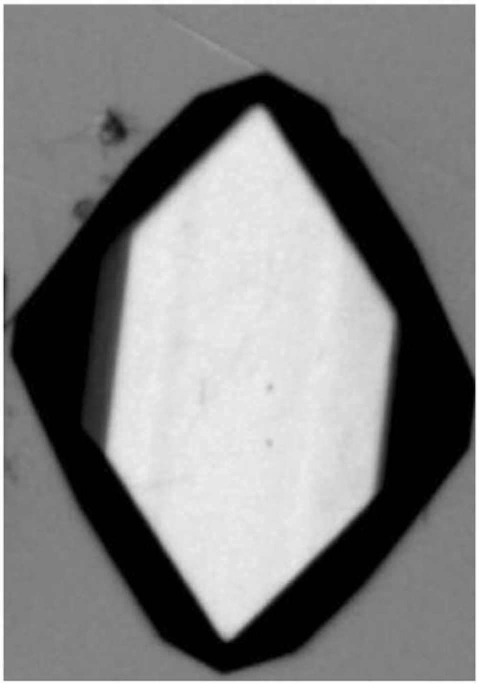


Fig. 1. The image of polymer **1** under Leica.

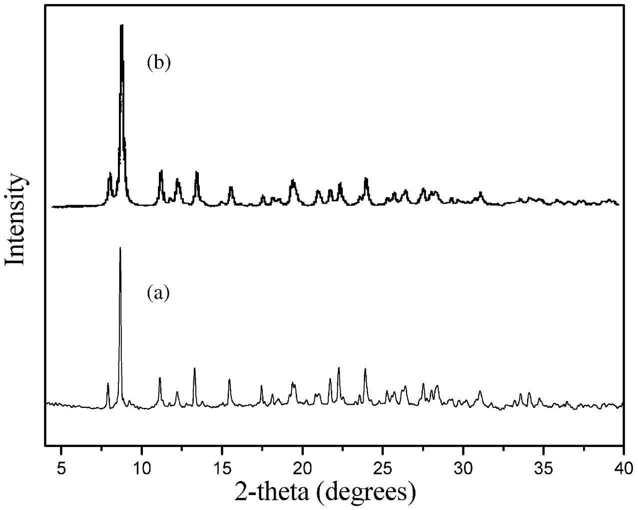


Fig. 2. Experimental (a), and simulated (b) powder XRD patterns of polymer **1**.

characteristic of the asymmetric stretching of the carboxylic groups of BTC and BDC. The absorptions at 1432–1363 cm^{-1} are due to the symmetric vibrations of the carboxylic groups of BTC and BDC. The broad bands at 3220–3443 cm^{-1} are attributed to the vibrations of the water ligand. The lack of the characteristic bands of the carboxylic groups of any protonated forms of BDC (1715–1680 cm^{-1}) [38,39] and BTC (1730–1690 cm^{-1}) [40] indicates the complete deprotonation of H_2BDC and H_3BTC after the reaction.

The TGA shows that the weight loss of complex **1** can be divided into three steps in the 80–575°C range (Fig. 3). The weight loss of 9.26 wt% during the first step from 80°C to 150°C corresponds to the decomposition of two water guests and one DMF molecule (calculated: 9.25 wt%). The weight loss of 20.21 wt% during the second step from 150°C to 398°C is attributed to the removal of one water ligand and three DMF molecules (calculated: 20.11 wt%). The weight loss of 42.08 wt% during the third step from 398°C to 575°C is in accordance with the removal of two BTC and half BDC (calculated: 42.06 wt%). However, after calcining the polymer at 150°C for 1 h, the intensity of diffraction peaks of the polymer become very weak and many reflections cannot be observed in the XRD pattern, implying the partial decomposition of the structure for the complex at 150°C. After calcination at 200°C for 1 h, any peak cannot be observed in the XRD pattern, indicating the collapse of the framework.

3.2. *Description of structure*

The atomic coordinates, selected bond lengths and bond angles for the single crystal are presented in Tables 2 and 3, respectively.

The single-crystal structure analysis revealed that the polymer, $Cd_3(BDC)_{0.5}(BTC)_2(DMF)(H_2O) \cdot 3DMF \cdot H_3O \cdot H_2O$ **1**, is a 3D extended framework. The fundamental building units of **1** include three crystallographically distinct Cd atoms, six BTC units, two BDC units, a DMF ligand and a water ligand (Fig. 4(a)). Among the three different Cd(II) centers, Cd(1) is coordinated with six oxygen atoms, three [O(1), O(4) and O(6)] come from the bidentate carboxylate groups of three separated BTC ligands, and the other three [O(2), O(3) and O(5)] come from two different chelating/bridging bidentate carboxylate groups of two distinct BTC ligands. Cd(2) is also coordinated with six

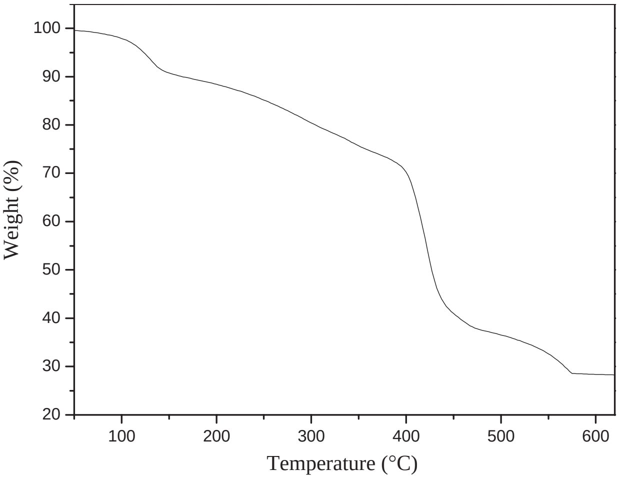


Fig. 3. TGA curve of polymer **1**.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å \times 10^3$) for polymer **1**[a]

	X	*Y*	*Z*	*U*(eq)
Cd(1)	(1)	(1)	4633(1)	16(1)
Cd(2)	3449(1)	6995(1)	6518(1)	18(1)
Cd(3)	2330(1)	9198(1)	2848(1)	18(1)
N(1)	5676(4)	5015(4)	7124(4)	56(2)
N(2)	1429(5)	2766(5)	3249(4)	68(2)
N(3)	6656(11)	5415(12)	5209(8)	157(5)
N(4)	1515(16)	2903(16)	580(12)	285(9)
O(1)	910(2)	9532(3)	3853(2)	30(1)
O(2)	1166(2)	7265(2)	3937(2)	26(1)
O(3)	2100(2)	7983(2)	3518(2)	19(1)
O(4)	3047(2)	9730(2)	5018(2)	26(1)
O(5)	3326(2)	7535(2)	5231(2)	21(1)
O(6)	1315(3)	8726(3)	5391(2)	30(1)
O(7)	2630(2)	8333(3)	6357(2)	30(1)
O(8)	2222(3)	6171(3)	5852(2)	37(1)
O(9)	3500(2)	6716(2)	7717(2)	22(1)
O(10)	4921(3)	6931(3)	7797(2)	34(1)
O(11)	4584(2)	7737(3)	6273(2)	27(1)
O(12)	4221(3)	5587(3)	6533(3)	48(1)
O(13W)	2915(4)	10303(3)	2280(2)	50(1)
O(14)	1527(2)	8715(2)	1651(2)	26(1)
O(15)	1039(2)	9909(3)	2773(2)	29(1)
O(16)	3148(2)	9961(3)	3909(2)	30(1)
O(17)	1137(11)	3463(10)	2162(9)	187(6)
O(18)	7160(11)	6491(15)	4585(10)	272(7)
O(19)	601(6)	3371(7)	640(6)	129(3)
O(1W)	3570(4)	2026(4)	2715(4)	91(2)
O(2W)	3209(7)	2714(11)	1476(8)	190(7)
C(1)	682(3)	9965(3)	3249(3)	21(1)
C(2)	−126(3)	10624(3)	3056(3)	21(1)
C(3)	1490(3)	7358(3)	3453(2)	19(1)
C(4)	1185(3)	6750(3)	2770(2)	19(1)
C(5)	435(3)	6149(3)	2603(3)	21(1)
C(6)	4149(3)	7820(3)	5568(3)	19(1)
C(7)	4637(3)	8238(3)	5121(2)	17(1)
C(8)	4292(3)	8075(3)	4345(3)	20(1)
C(9)	4749(3)	8451(3)	3925(2)	19(1)
C(10)	3380(3)	10113(3)	4602(2)	20(1)
C(11)	5844(3)	9197(3)	5040(2)	18(1)
C(12)	5414(3)	8798(3)	5466(2)	19(1)
C(13)	1792(3)	8568(3)	6087(3)	23(1)
C(14)	1317(3)	8697(3)	6617(3)	21(1)
C(15)	553(3)	9272(3)	6442(2)	21(1)
C(16)	1654(3)	8199(3)	7295(2)	20(1)
C(17)	1559(3)	6027(3)	6048(3)	24(1)
C(18)	748(3)	5496(3)	5500(3)	22(1)
C(19)	142(3)	5055(4)	5758(3)	26(1)
C(20)	−607(3)	4569(4)	5260(3)	28(1)
C(21)	4380(3)	6744(3)	8095(2)	21(1)
C(22)	5086(4)	5671(5)	6776(4)	45(2)
C(23)	5365(7)	4118(8)	7277(10)	133(6)
C(24)	6677(5)	5200(7)	7439(7)	87(3)
C(25)	1612(18)	2779(14)	2600(11)	203(9)
C(26)	775(9)	3234(11)	3494(8)	117(4)
C(27)	1985(7)	2101(7)	3739(9)	126(5)
C(28)	5527(3)	9007(3)	4270(2)	19(1)
C(29)	7072(14)	5703(12)	4815(11)	147(6)
C(30)	6111(14)	6232(14)	5279(14)	227(9)
C(31)	6998(14)	4598(12)	5534(11)	177(7)
C(32)	577(8)	2411(8)	497(10)	125(5)
C(33)	1362(9)	3919(7)	445(6)	86(3)
C(34)	2050(30)	1880(20)	910(20)	415(16)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond lengths (Å) and angles (°) for polymer **1**[a]

Cd(1)–O(4)	2.206(3)	Cd(2)–O(9)	2.327(3)
Cd(1)–O(6)	2.232(3)	Cd(2)–O(12)	2.371(4)
Cd(1)–O(1)	2.308(3)	Cd(2)–O(5)	2.544(3)
Cd(1)–O(3)	2.342(3)	Cd(3)–O(16)	2.232(3)
Cd(1)–O(5)	2.387(3)	Cd(3)–O(15)	2.232(3)
Cd(1)–O(2)	2.420(3)	Cd(3)–O(14)	2.260(3)
Cd(2)–O(8)	2.196(4)	Cd(3)–O(3)	2.301(3)
Cd(2)–O(7)	2.281(4)	Cd(3)–O(13W)	2.332(4)
Cd(2)–O(11)	2.293(3)	Cd(3)–O(9A)	2.364(3)
O(4)–Cd(1)–O(6)	100.60(14)	O(6)–Cd(1)–O(2)	95.88(13)
O(4)–Cd(1)–O(1)	91.21(14)	O(1)–Cd(1)–O(2)	88.80(14)
O(6)–Cd(1)–O(1)	83.40(13)	O(3)–Cd(1)–O(2)	55.15(11)
O(4)–Cd(1)–O(3)	108.31(12)	O(5)–Cd(1)–O(2)	88.04(12)
O(6)–Cd(1)–O(3)	149.17(13)	O(8)–Cd(2)–O(7)	93.78(16)
O(1)–Cd(1)–O(3)	85.49(12)	O(8)–Cd(2)–O(11)	135.17(13)
O(4)–Cd(1)–O(5)	88.79(12)	O(7)–Cd(2)–O(11)	91.02(13)
O(6)–Cd(1)–O(5)	107.55(12)	O(8)–Cd(2)–O(9)	99.25(13)
O(1)–Cd(1)–O(5)	168.86(11)	O(7)–Cd(2)–O(9)	94.33(12)
O(3)–Cd(1)–O(5)	83.94(11)	O(11)–Cd(2)–O(9)	124.80(12)
O(4)–Cd(1)–O(2)	163.41(12)	O(8)–Cd(2)–O(12)	82.25(16)
O(7)–Cd(2)–O(12)	173.45(15)	O(16)–Cd(3)–O(14)	167.51(13)
O(11)–Cd(2)–O(12)	88.19(16)	O(15)–Cd(3)–O(14)	87.51(13)
O(9)–Cd(2)–O(12)	91.46(15)	O(16)–Cd(3)–O(3)	91.36(12)
O(8)–Cd(2)–O(5)	83.65(13)	O(15)–Cd(3)–O(3)	92.59(12)
O(7)–Cd(2)–O(5)	77.75(11)	O(14)–Cd(3)–O(3)	101.01(12)
O(11)–Cd(2)–O(5)	54.00(11)	O(16)-Cd(3)–O(13W)	84.39(14)
O(9)–Cd(2)–O(5)	171.78(11)	O(15)–Cd(3)–O(13W)	100.03(17)
O(12)–Cd(2)–O(5)	96.57(15)	O(14)–Cd(3)–O(13W)	83.91(14)
O(8)–Cd(2)–O(10)	140.29(14)	O(3)–Cd(3)-O(13W)	166.68(16)
O(7)–Cd(2)–O(10)	113.29(14)	O(16)–Cd(3)–O(9A)	100.93(13)
O(11)–Cd(2)–O(10)	75.28(11)	O(15)–Cd(3)–O(9A)	168.77(12)
O(9)–Cd(2)–O(10)	52.34(11)	O(14)–Cd(3)–O(9A)	81.72(12)
O(12)–Cd(2)–O(10)	72.78(14)	O(3)–Cd(3)–O(9A)	86.41(12)
O(5)–Cd(2)–O(10)	128.74(10)	O(13W)–Cd(3)–O(9A)	82.04(16)
O(16)–Cd(3)–O(15)	90.27(14)		

[a] Symmetry code: (A) x, $-y+3/2$, $z-1/2$.

oxygen atoms, which come from a bridging unidentate [O(9)], a bidentate [O(7)], a chelating/bridging bidentate [O(5) and O(11)] carboxylate groups of three separated BTC ligands as well as a DMF molecule [O(12)] and a bidentate [O(8)] carboxylate group from a BDC ligand. Similar to Cd(1) and Cd(2), the six oxygen atoms bonded to Cd(3) include O(15) and O(16) of two bidentate carboxylate groups from two different BTC ligands, O(9A) of a bridging unidentate carboxylate group from a BTC ligand and O(3) of a chelating/bridging bidentate carboxylate group from a BTC ligand as well as O(14) of a bidentate carboxylate group from a BDC ligand and O(13W) from the terminal aqua molecule. In this structure, the distances (2.196(4)–2.544(3) Å) of Cd–O are quite similar to those of normal Cd–OCO structures (2.251–2.879 Å) [41]; and the bond angles of O–Cd–O range from 54.00(11)° to 173.45(15)°. Therefore, the structure of CdO_6 is a distorted octahedral coordination geometry. In complex **1**, three cadmium centers and the carboxylate groups of BTC

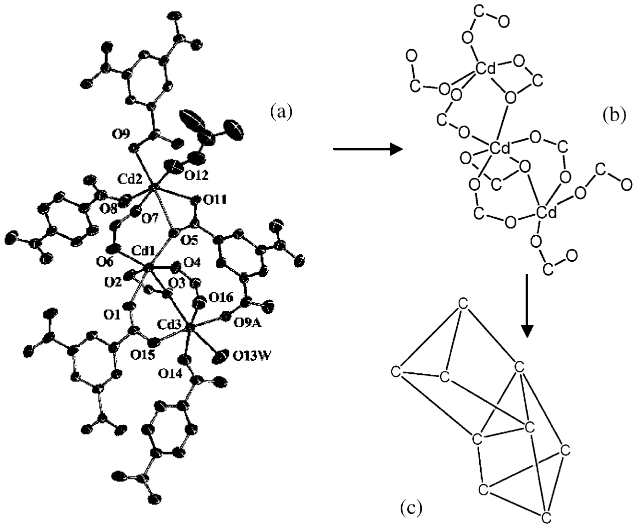


Fig. 4. In the fundamental building unit (a) of **1**, three cadmium centers and the carboxylate groups of BTC and BDC construct a trimetallic cluster $Cd_3(CO_2)_9$ (b) which can be seen as an SBU (c) with two conjoint trigonal prisms. (The H atoms and three BTC molecules except for their carboxylate groups are not shown for clarity).

and BDC construct a trimetallic cluster $Cd_3(CO_2)_9$ (Fig. 4(b)). The cluster can be seen as a secondary building unit (SBU) with two conjoint trigonal prisms (Fig. 4(c)). The nine vertices of the SBUs are linked by benzene rings of BTC and BDC to form a 3D network (Fig. 5(a)). Two types of rings are evident in the structure of **1**: (1) the small rings formed by two Cd(II) and two BTC ligands, and filled by two coordinated DMF; (2) the large rings created by four Cd(II) and four BTC or BDC ligands, and the vacancies are filled with guest DMF and H_2O molecules connected to the framework via hydrogen bonds $\{O1W\cdots O11 = 2.803\,Å, O2W\cdots O10 = 2.772\,Å, O19_{DMF}\cdots O6 = 2.908\,Å\}$. There also exist $10 \times 10\,Å$ channels along [001] direction (Fig. 5(b)). When van der Waals radii of the atoms are taken into account, these channels are $7 \times 7\,Å$. Because of the presence of the channels, complex **1** can be potentially applied in molecular sieve, ion exchanger, and catalyst.

3.3. Fluorescent properties

Fig. 6(a) and (b) shows solid-state excitation–emission spectrum of the free BDC and BTC ligands, respectively. The strongest emission peak for BDC is at 393 nm and that for BTC is 370 nm with the distinct excitation peak (347 and 334 nm) at room temperature. The emission bands of two free ligands are attributed to the $\pi^* \rightarrow n$ transitions. Compared to the free ligands, the strongest excitation peak for polymer **1** is at 208 nm, a higher energy than those for the BDC and BTC excitation peaks, and its emission spectrum shows two strong main peaks at 358 and 377 nm (Fig. 6(c)). Moreover, the emission wavelength of polymer **1** is also different from those of cadmium coordinated polymers containing single ligand of BTC or BDC [42–43]. A similar emission band at 358 nm has been observed previously for other cadmium-organic polymer compound, $Cd_3(tma)_2 \cdot 13H_2O$ [42]. This emission can be assigned to the ligand-to-metal charge-transfer band. However, the emission peak at 377 nm may be due to the $\pi^* \rightarrow n$ transition because an approximate emission peak also appears for the BTC ligand. The strong fluorescent emission of **1** makes it a potentially useful photoactive material.

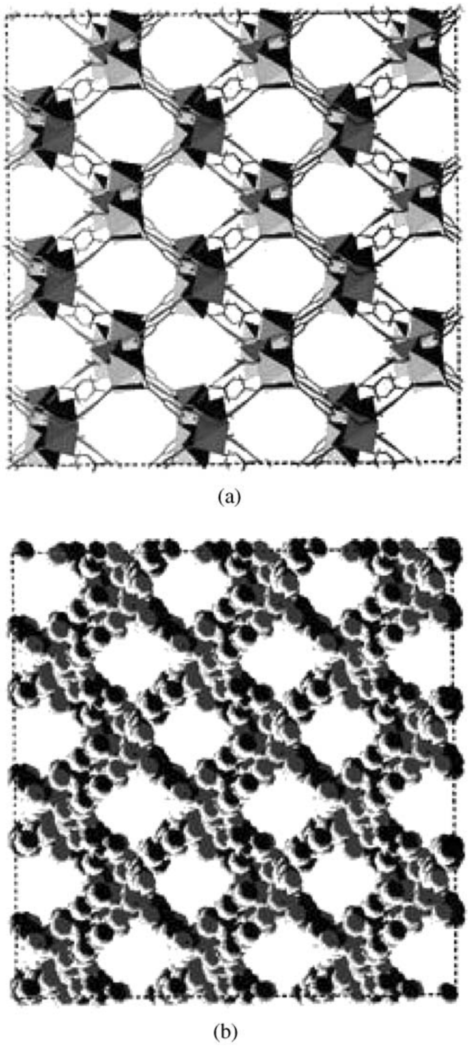


Fig. 5. (a) Inorganic SBUs are linked by benzene rings of BTC and BDC to form two types of rings, and (b) there exist $10 \times 10\,Å$ channels along [001] direction.

4. Conclusions

A novel inorganic–organic hybrid polymer, $Cd_3(BDC)_{0.5}(BTC)_2(DMF)(H_2O) \cdot 3DMF \cdot H_3O \cdot H_2O$ **1**,

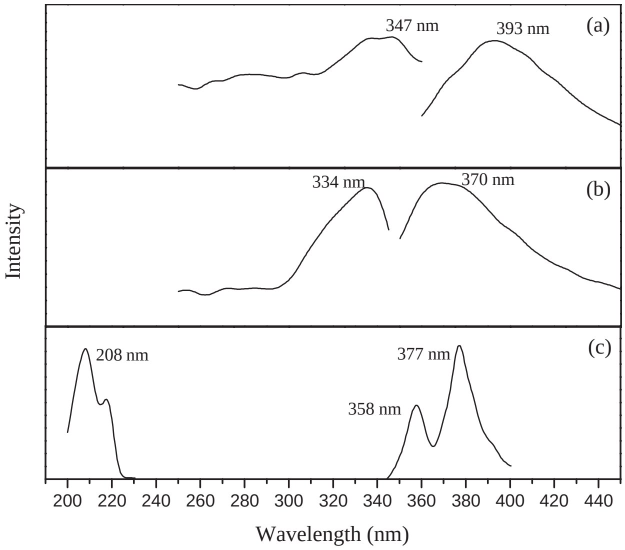


Fig. 6. Solid-state excitation–emission spectrum for the H_2BDC (a), H_3BTC (b), and polymer **1** (c).

in which mixed carboxylate ligands coordinate with cadmium ions simultaneously, was obtained under mild conditions. In the structure of the crystal, the nine vertices of the SBUs are linked by benzene rings of BTC and BDC to form a 3D network with 10 × 10 Å channels. Moreover, polymer **1** exhibits intense fluorescence at 358 and 377 nm with the excitation peak at 208 nm in the solid state at room temperature. Because of the presence of the channels and the good fluorescent property, complex **1** has the potential to be used in molecular sieve, ion exchanger, catalyst and photoactive material. It is believed that new inorganic–organic hybrid polymers with mixed carboxylate ligands and novel coordination architectures will be continuously synthesized under suitable conditions.

Acknowledgments

We are grateful to the financial support of the State Basic Research Project (G2000077507), and the National Nature Science Foundation of China (Grant nos. 29873017, 20273026 and 20101004).

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