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Article

Hydrothermal Syntheses, Crystal Structures, and Characteristics of a Series of Cd–btx Coordination Polymers (btx = 1,4-Bis(triazol-1-ylmethyl)benzene)

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Four novel cadmium–btx (btx = 1,4-bis(triazol-1-ylmethyl)benzene) coordination polymers $[Cd(btx)_2(NO_3)_2]_n$ (**1**), $[Cd(btx)_2Cl_2]_n$ (**2**), $[Cd(btx)(SO_4)(H_2O)_2]_n$ (**3**), and $[Cd(btx)(S_2O_7)(H_2O)]_n$ (**4**) have been prepared by hydrothermal reaction (140 or 180 °C) and characterized. Both **1** and **2** have two-dimensional rhombohedral grid structures, **3** possesses a two-dimensional rectangular grid structure, and **4** displays a three-dimensional framework, which is formed by btx bridging parallel layers. To the author's best knowledge, polymer **4** is the first Cd(II) polymer in which the Cd(II) ion is eight-coordinated in a hexagonal bipyrimidal geometry. In addition, we studied the effects of temperature on the hydrothermal reaction system of btx and $CdSO_4$ and found that different products can be obtained at different temperatures. Furthermore, polymer **3** possesses a very strong third-order NLO absorptive effect with an α_2 value of 1.15×10^{-9} m W^{-1}. Polymers **2**–**4** display strong fluorescent emissions in the solid state at room temperature. The DTA and TGA results of the four polymers are in agreement with the crystal structures.

Introduction

Although a remarkable variety of polymeric frameworks with intriguing topologies and interesting electric, magnetic, catalytic, fluorescence, and optical properties have been syntheszed over the last 10 years,[1−11] rational control in the construction of polymeric networks remains a great challenge in crystal engineering. The generation of supramolecular frameworks rests on various factors.[12−17] Hydrothermal synthesis has been demonstrated to be an effective and powerful technique for crystal growth of many coordination polymers and hdrogen-bonded systems.[18−26] The vast major-

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ity of the reported polymeric networks with fascinating coordiantion architectures have been carried out on transition metals and polydentate organic ligands.[27−31]

On the other hand, Cd(II)-containing coordination polymers have attracted considerable recent interest owing to the ambiability to form bounds with different dornors simultaneously, the large radius, various coordination modes, and special physical properties of Cd(II) ion. To date, researchers have reported a number of 1-D, 2-D, or 3-D Cd(II) coordination polymers and explored their potential applications in catalysis, luminescent materials, NLO materials, phase transformation, and host−guest chemistry.[4−6,32−43] For instance, Fujita and co-workers have studied the catalytic activity of $\{[Cd(bpy)_2](NO_3)_2\}_n$ in the procedure of cyanosilylation reactions.[4] Several groups have investigated the fluorescent properties of $[Cd(TPT)(py)]_n$ (TPT = terephthalato),[6] $[Cd_3(tma)_2\cdot 13H_2O]_n$ (tma = trimesate, dabco = 1,4-diazabicyclo[2,2,2]octanes),[5] $\{Cd(2\text{-}PEB)_2\cdot(H_2O)\}_n$ (2-PEBN = 4-[2-(2-pyridyl)ethenyl]benzonitrile), $\{Cd(2\text{-}CEQA)(Py)\}_n$ (2-CEQH = 2-[2-(4-cyanophenyl)ethenyl]-8-quinolinol),[38] and so on. Lin et al. have reported the second-order nonlinear optical (NLO) properties of polymers $\{[Cd(4\text{-}pyridylacrylate)_2]\cdot H_2O\}_n$, $\{Cd[4\text{-}(4\text{-}pyridyl)benzoate]_2\cdot H_2O\}_n$,[39] and $\{[Cd_3(\mu_3\text{-}OH)L_3(py)_6](ClO_4)_2\}_n$ (L = 4-[2-(4-pyridyl)-ethenyl]benzoate).[40] Our group has investigated the third-order NLO properties of polymers $[Cd(bbbt)_2(NCS)_2]_n$ (bbbt = 1,1′-(1,4-butanediyl)bis(1*H*-benzotriazole))[8] and $[Cd(N_3)_2(bpfp)]_n$ (bpfp = *N*,*N*′-bis(3-pyridylformyl)piperazine)[41] and found that they exhibit very large NLO absorptive effects and strong refractive behavior. Our current research involves constructing new Cd-containing polymeric complexes by the hydrothermal reaction and further investigating their third-order NLO properties and fluorescence properties. In this paper, four novel Cd(II)−btx coordination polymers, $[Cd(btx)_2(NO_3)_2]_n$ (**1**), $[Cd(btx)_2Cl_2]_n$ (**2**), $[Cd(btx)(SO_4)(H_2O)_2]_n$ (**3**), and $[Cd(btx)(S_2O_7)(H_2O)]_n$ (**4**), are synthesized by the hydrothermal technique. To our best knowledge, **4** is the first Cd(II) polymer in which Cd(II) ion is eight-coordinated in a hexagonal bipyrimidal geometry. Furthermore, the third-order NLO properties and the fluorescence properties of polymers **1**−**4** are also investigated. The results show that polymer **3** possesses a very large third-order NLO absorptive effect and polymers **2**−**4** display strong fluorescent emissions.

Experimental Section

Materials and General Details. Commercially available solvents and chemicals were used without further purification. IR spectroscopy was performed on a PE 1710 spectrophotometer in the 400−4000 cm^{-1} regions. Carbon, hydrogen, and nitrogen analyses were performed with Carlo-Erba 1106 analyzer.

Preparation of the Ligand 1,4-Bis(triazol-1-ylmethyl)benzene (btx). Triazole (1.38 g, 20 mmol) was dissolved in acetone (30 mL), and then PEG-400 (2 g), anhydrous potassium carbonate (5 g), and potassium iodide (0.5 g) were added to the above solution. After the solution was stirring for 30 min, α,α′-dichloro-*p*-oxylene (1.75 g, 10 mmol) was dropwise added. The mixture was vigorously stirred and refluxed for 10 h. A white residue was obtained after filtering and distilling off the filtrate. The crude product was recrystallized from water to give 1.4 g (60%) of white crystalline state product, 1,4-bis(triazol-1-ylmethyl)benzene (btx). Mp: 163−164 °C. Anal. Calcd for $C_{12}H_{12}N_6$: C, 59.99; H, 5.03; N, 34.98. Found: C, 60.04; H, 5.02; N, 34.62. IR (KBr)/cm^{-1}: 3099 s, 1511 s, 1265 s, 1146 s, 1016 s, 769 s. ^1H NMR (D_2O): δ 5.300 (4H), 7.165 (4H), 7.897 (2H), 8.389 (2H).

Preparation of Polymer $[Cd(btx)_2(NO_3)_2]_n$ (1). A mixture of $Cd(NO_3)_2\cdot 6H_2O$ (30.85 mg, 0.1 mmol), btx (48.0 mg, 0.2 mmol), and H_2O (6 mL) in a mole ratio of ca. 1:2:3333 was sealed in a 25 mL stainless steel reactor with Teflon liner and directly heated to 140 °C for 3 days and then cooled to room temperature during 6 h. Colorless single crystals suitable for X-ray diffraction were obtained in 62% yield. Anal. Calcd for $C_{24}H_{24}CdN_{14}O_6$: C, 40.21; H, 3.37; N, 27.35. Found: C, 40.36; H, 3.32; N, 27.18. IR (KBr)/cm^{-1}: 3134 s, 1522 s, 1274 s, 1129 s, 1014 s, 775 s.

Preparation of Polymer $[Cd(btx)_2Cl_2]_n$ (2). The procedure was the same as that for **1**, except that $CdCl_2\cdot 2.5H_2O$ was used instead of $Cd(NO_3)_2\cdot 6H_2O$, yield ca. 55%. Anal. Calcd for $C_{24}H_{24}CdCl_2N_{12}$: C, 43.42; H, 3.64; N, 25.32. Found: C, 43.18; H, 3.67; N, 25.24. IR (KBr)/cm^{-1}: 3022 s, 1519 s, 1276 s, 1113 s, 1011 s, 767 s.

Preparation of Polymer $[Cd(btx)(SO_4)(H_2O)_2]_n$ (3). The procedure was the same as that for **1**, except that $3CdSO_4\cdot 8H_2O$ was used instead of $Cd(NO_3)_2\cdot 6H_2O$, yield ca. 58%. Anal. Calcd for $C_{12}H_{16}CdN_6O_6S$: C, 29.73; H, 3.33; N, 17.34. Found: C, 29.58; H, 3.37; N, 17.41. IR (KBr)/cm^{-1}: 3021 s, 1507 s, 1258 s, 1121 s, 1040 s, 753 s.

Preparation of Polymer $[Cd(btx)(S_2O_7)(H_2O)]_n$ (4). An aqueous mixture (6 mL) containing btx (48.0 mg, 0.2 mmol) and $3CdSO_4\cdot 8H_2O$ (25.6 mg, 0.033 mmol) was placed in a Teflon-lined stainless steel vessel (25 mL), and the vessel was sealed and heated to 180 °C for 3 days and then cooled to room temperature during 8 h. Colorless single crystals suitable for X-ray diffraction were obtained in ca. 60% yield. Anal. Calcd for $C_{12}H_{14}CdN_6O_8S_2$: C, 26.36; H, 2.58; N, 15.37. Found: C, 26.19; H, 2.61; N, 15.26. IR (KBr)/cm^{-1}: 3087 s, 1518 s, 1279 s, 1139 s, 1014 s, 772 s.

Crystal Structure Determination. A crystal suitable for X-ray determination was mounted on a glass fiber. All data were collected at room temperature on a Rigaku RAXIS-IV image plate area detector with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was

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Table 1. Crystal and Structure Refinement Data for Polymers **1**−**4**

param	**1**	**2**	**3**	**4**
formula	$C_{24}H_{24}CdN_{14}O_6$	$C_{24}H_{24}CdCl_2N_{12}$	$C_{24}H_{32}Cd_2N_{12}O_{12}S_2$	$C_{12}H_{14}CdN_6O_8S_2$
fw	716.97	663.85	969.54	546.81
temp (K)	293(2)	291(2)	291(2)	291(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73
crystal size (mm)	0.30 × 0.20 × 0.20	0.27 × 0.20 × 0.18	0.24 × 0.20 × 0.20	0.24 × 0.20 × 0.20
color	colorless	colorless	colorless	colorless
cryst system	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.3343(17)	7.6765(15)	12.407(3)	8.5563(17)
b (Å)	21.190(4)	21.895(4)	12.805(3)	12.438(3)
c (Å)	8.6625(17)	8.9479(18)	11.297(2)	8.5420(17)
α (deg)	90	90	89.90(3)	8.5420(17)
β (deg)	105.91(3)	109.23(3)	101.75(3)	97.22(3)
γ (deg)	90	90	102.37(3)	88.63(3)
V (Å^3)	1471.3(5)	1420.0(5)	1714.8(6)	860.8(3)
Z	2	2	2	2
D_c (g·cm^{-3})	1.618	1.553	1.878	2.110
abs coeff (mm^{-1})	0.808	0.995	1.440	1.573
F(000)	724	668	968	544
reflcns collcd/unique	4444/2595	956/2226	4431/4431	2282/2282
data/restraints/params	2595/0/206	2226/0/179	4431/0/476	2282/0/270
goodness-of-fit on F^2	1.105	1.077	1.153	1.375
R1, wR2	0.0604, 0.1597	0.0336, 0.0828	0.1078, 0.2777	0.0990, 0.2794

based on observed reflections and variable parameters. All calculations were performed using the SHELXL-97 crystallographic software package.[44] Table 1 shows crystallographic crystal data and processing parameters for polymers **1**−**4**. Selected bond lengths and bond angles are listed in Table 2.

Determination of TGA−DTA. TGA−DTA measurements were performed by heating the sample from 25 to 800 °C (or 1100 °C) at a rate of 10 °C min^{-1} in air on a Perkin-Elmer DTA-7 and TGA-7 differential thermal analyzer.

Nonlinear Optical Measurements. The DMF solution of polymers **1**−**4** was placed in the 1 mm quartz cuvette for NLO measurements. The nonlinear refraction was measured with a linearly polarized laser light ($\lambda = 532$ nm; pulse widths = 7 ns) generated from a Q-switched and frequency-doubled Nd:YAG laser. The spatial profiles of the optical pulses were nearly Gaussian. The laser beam was focused with a 25-cm focal-length focusing mirror. The radius of the beam waist was measured to be 35 ± 5 μm (half-width at $1/e^2$ maximum). The interval between the laser pulses was chosen to be ~5 s for operational convenience. The incident and transmitted pulse energies were measured simultaneously by two Laser Precision detectors (RjP-735 energy probes), which were linked to a computer by an IEEE interface. The NLO properties of the samples were manifested by moving the samples along the axis of the incident beam (z-direction) with respect to the focal point.[45] An aperture of 0.5 mm in radius was placed in front of the detector to assist the measurement of the self-focusing effect.

Determination of Photoluminescent Properties. The luminescent spectra were measured on powder samples at room temperature using a model F-4500 Hitachi fluorescence spectrophotometer. The excitation slit was 2.5 nm, the emission slit was 2.5 nm also, and the response time was 2 s.

Results and Discussion

Synthesis. The application of the hydrothermal technique to synthetic crystal growth has been used for some time.[46] The generation of supramolecular frameworks rests on various parameters, such as the coordination environments of metal centers, position and type of functional groups on the ligands, the ratio between metal salts and ligands, templates, solvent system, counterions, temperature, teaction time, pH value, etc.[12−17] Polymers **1**−**4** are synthesized via a self-assembly process under midtemperature hydrothermal conditions. When a mixture of $Cd(NO_3)_2{\cdot}6H_2O$ (or $CdCl_2{\cdot}2.5H_2O$ or $3CdSO_4{\cdot}8H_2O$), btx, and H_2O in a mole ratio of ca. 1:2:3333 was heated to 140 °C for 3 days and cooled to room temperature, fine colorless single crystals of polymer **1**, **2**, or **3** suitable for X-ray diffraction were obtained from the reaction mixture. To investigate the effects of temperature on the synthesis of coordination polymers, the mixtures of Cd(II) salts and btx were reacted at 180 °C. The results show that the reactions of $Cd(NO_3)_2{\cdot}6H_2O$ or $CdCl_2{\cdot}2.5H_2O$ with btx in 180 °C afford the same product as that obtained in 140 °C, but the reaction of $3CdSO_4{\cdot}8H_2O$ with btx at 180 °C generates a new product (polymer **4**) which is different from that formed at 140 °C. This may be explained as follows: when the temperature is changed from 140 to 180 °C, sulfates can polymerize to pyrosulfates and pyrosulfates have more coordination sites leading to a new coordination polymer with a novel network pattern. The formations of **1**−**4** are shown in Scheme 1.

In addition, Diez-Barra's group synthesized a series of 1,2,4-triazol ligands, such as 1,3-bis(triazol-1-ylmethyl)-benzene, and their related complexes.[47−49] In 1,3-bis(triazol-1-ylmethyl)benzene two triazol groups are in *meta* positions and nitrogen atoms are inclined to coordinate to the same metal ion; in 1,4-bis(triazol-1-ylmethyl)benzene) (btx) two

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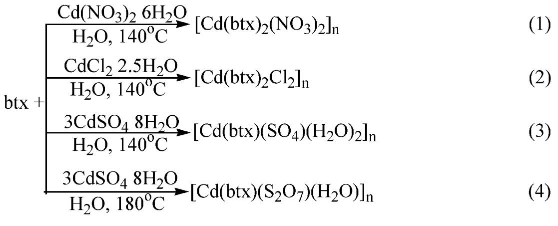
Table 2. Selected Bond Lengths (Å) and Angles (deg) for Polymers **1**−**4**

Polymer **1**[a]							
Cd(1)−N(1)$^{\#1}$	2.324(4)	Cd(1)−N(1)	2.324(4)	Cd(1)−O(1)	2.343(7)	Cd(1)−O(1)$^{\#1}$	2.343(7)
Cd(1)−N(6)$^{\#2}$	2.334(5)	Cd(1)−N(6)$^{\#3}$	2.334(5)	N(6)$^{\#2}$−Cd(1)−O(1)	96.2(3)	N(6)$^{\#3}$−Cd(1)−O(1)	83.8(3)
N(1)$^{\#1}$−Cd(1)−N(1)	180.000(1)	N(1)$^{\#1}$−Cd(1)−(6)$^{\#2}$	90.46(17)	N(1)$^{\#1}$−Cd(1)−O(1)$^{\#1}$	98.7(2)	N(1)−Cd(1)−O(1)$^{\#1}$	81.3(2)
N(1)−Cd(1)−N(6)$^{\#2}$	89.54(17)	N(1)$^{\#1}$−Cd(1)−N(6)$^{\#3}$	89.54(17)	N(6)$^{\#2}$−Cd(1)−O(1)$^{\#1}$	83.8(3)	N(6)$^{\#3}$−Cd(1)−O(1)$^{\#1}$	96.2(3)
N(1)−Cd(1)−N(6)$^{\#3}$	90.46(17)	N(6)$^{\#2}$−Cd(1)−N(6)$^{\#3}$	180.000(1)	O(1)−Cd(1)−O(1)$^{\#1}$	180.000(1)		
N(1)$^{\#1}$−Cd(1)−O(1)	81.3(2)	N(1)−Cd(1)−O(1)	98.7(2)				
Polymer **2**[b]							
Cd(1)−N(6)$^{\#1}$	2.344(3)	Cd(1)−N(6)$^{\#2}$	2.344(3)	Cd(1)−Cl(1)$^{\#3}$	2.6477(13)	Cd(1)−Cl(1)	2.6477(13)
Cd(1)−N(1)	2.354(3)	Cd(1)−N(1)$^{\#3}$	2.354(3)				
N(6)$^{\#1}$−Cd(1)−N(6)$^{\#2}$	180.00(16)	N(6)$^{\#1}$−Cd(1)−N(1)	86.93(12)	N(1)−Cd(1)−Cl(1)$^{\#3}$	90.96(9)	N(1)$^{\#3}$−Cd(1)−l(1)$^{\#3}$	89.04(9)
N(6)$^{\#2}$−Cd(1)−N(1)	93.07(12)	N(6)$^{\#1}$−Cd(1)−N(1)$^{\#3}$	93.07(12)	N(6)$^{\#1}$−Cd(1)−Cl(1)	89.19(8)	N(6)$^{\#2}$−Cd(1)−Cl(1)	90.81(8)
N(6)$^{\#2}$−Cd(1)−N(1)$^{\#3}$	86.93(12)	N(1)−Cd(1)−N(1)$^{\#3}$	180.00(18)	N(1)−Cd(1)−Cl(1)	89.04(9)	N(1)$^{\#3}$−Cd(1)−Cl(1)	90.96(9)
N(6)$^{\#1}$−Cd(1)−Cl(1)$^{\#3}$	90.81(8)	N(6)$^{\#2}$−Cd(1)−Cl(1)$^{\#3}$	89.19(8)	Cl(1)$^{\#3}$−Cd(1)−Cl(1)	180.0		
Polymer **3**[c]							
Cd(1)−O(12)$^{\#1}$	2.297(8)	Cd(1)−O(12)$^{\#2}$	2.297(8)	Cd(3)−O(6)	2.286(8)	Cd(3)−O(6)$^{\#5}$	2.286(8)
Cd(1)−O(1)	2.301(9)	Cd(1)−O(1)$^{\#3}$	2.301(9)	Cd(3)−N(7)	2.302(12)	Cd(3)−N(7)$^{\#5}$	2.302(12)
Cd(1)−N(1)	2.337(12)	Cd(1)−N(1)$^{\#3}$	2.337(12)	Cd(3)−O(7)$^{\#5}$	2.340(8)	Cd(3)−O(7)	2.340(8)
Cd(2)−O(3)	2.296(8)	Cd(2)−O(3)$^{\#4}$	2.296(8)	Cd(4)−O(9)	2.283(7)	Cd(4)−O(9)$^{\#2}$	2.283(7)
Cd(2)−N(6)$^{\#4}$	2.305(12)	Cd(2)−N(6)	2.305(12)	Cd(4)−N(12)$^{\#2}$	2.289(13)	Cd(4)−N(12)	2.289(13)
Cd(2)−O(2)$^{\#4}$	2.343(8)	Cd(2)−O(2)	2.343(8)	Cd(4)−O(8)	2.356(8)	Cd(4)−O(8)$^{\#2}$	2.356(8)
O(12)$^{\#1}$−Cd(1)−O(12)$^{\#2}$	180.0(3)	O(12)$^{\#1}$−Cd(1)−O(1)	89.9(3)	O(6)−Cd(3)−O(6)$^{\#5}$	180.00(11)	O(6)−Cd(3)−N(7)	95.6(4)
O(12)$^{\#2}$−Cd(1)−O(1)	90.1(3)	O(12)$^{\#1}$−Cd(1)−O(1)$^{\#3}$	90.1(3)	O(6)$^{\#5}$−Cd(3)−N(7)	84.4(4)	O(6)−Cd(3)−N(7)$^{\#5}$	84.4(4)
O(12)$^{\#2}$−Cd(1)−O(1)$^{\#3}$	89.9(3)	O(1)−Cd(1)−O(1)$^{\#3}$	180.000(2)	O(6)$^{\#5}$−Cd(3)−N(7)$^{\#5}$	95.6(4)	N(7)−Cd(3)−N(7)$^{\#5}$	180.0(5)
O(12)$^{\#1}$−Cd(1)−N(1)	94.7(4)	O(12)$^{\#2}$−Cd(1)−N(1)	85.3(4)	O(6)−Cd(3)−O(7)$^{\#5}$	86.9(3)	O(6)$^{\#5}$−Cd(3)−O(7)$^{\#5}$	93.1(3)
O(1)−Cd(1)−N(1)	96.4(4)	O(1)$^{\#3}$−Cd(1)−N(1)	83.6(4)	N(7)−Cd(3)−O(7)$^{\#5}$	87.1(4)	O(6)−Cd(3)−O(7)	93.1(3)
O(12)$^{\#1}$−Cd(1)−N(1)$^{\#3}$	85.3(4)	O(12)$^{\#2}$−Cd(1)−N(1)$^{\#3}$	94.7(4)	N(7)$^{\#5}$−Cd(3)−O(7)$^{\#5}$	92.9(4)	O(6)$^{\#5}$−Cd(3)−O(7)	86.9(3)
O(1)−Cd(1)−N(1)$^{\#3}$	83.6(4)	O(1)$^{\#3}$−Cd(1)−N(1)$^{\#3}$	96.4(4)	N(7)−Cd(3)−O(7)	92.9(4)	N(7)$^{\#5}$−Cd(3)−O(7)	87.1(4)
N(1)−Cd(1)−N(1)$^{\#3}$	180.000(2)	O(3)−Cd(2)−O(3)$^{\#4}$	180.000(2)	O(7)$^{\#5}$−Cd(3)−O(7)	180.000(1)	O(9)−Cd(4)−O(9)$^{\#2}$	180.0(4)
O(3)−Cd(2)−N(6)$^{\#4}$	94.1(4)	O(3)$^{\#4}$−Cd(2)−N(6)$^{\#4}$	85.9(4)	O(9)−Cd(4)−N(12)$^{\#2}$	92.8(4)	O(9)$^{\#2}$−Cd(4)−(12)$^{\#2}$	87.2(4)
O(3)−Cd(2)−N(6)	85.9(4)	O(3)$^{\#4}$−Cd(2)−N(6)	94.1(4)	O(9)−Cd(4)−N(12)	87.2(4)	O(9)$^{\#2}$−Cd(4)−N(12)	92.8(4)
N(6)$^{\#4}$−Cd(2)−N(6)	180.000(2)	O(3)−Cd(2)−O(2)$^{\#4}$	89.0(3)	N(12)$^{\#2}$−Cd(4)−N(12)	180.000(1)	O(9)−Cd(4)−O(8)	90.5(3)
O(3)$^{\#4}$−Cd(2)−O(2)$^{\#4}$	91.0(3)	N(6)$^{\#4}$−Cd(2)−O(2)$^{\#4}$	95.8(4)	O(9)$^{\#2}$−Cd(4)−O(8)	89.5(3)	N(12)$^{\#2}$−Cd(4)−O(8)	89.7(4)
N(6)−Cd(2)−O(2)$^{\#4}$	84.2(4)	O(3)−Cd(2)−O(2)	91.0(3)	N(12)−Cd(4)−O(8)	90.3(4)	O(9)−Cd(4)−O(8)$^{\#2}$	89.5(3)
O(3)$^{\#4}$−Cd(2)−O(2)	89.0(3)	N(6)$^{\#4}$−Cd(2)−O(2)	84.2(4)	O(9)$^{\#2}$−Cd(4)−O(8)$^{\#2}$	90.5(3)	N(12)$^{\#2}$−Cd(4)−O(8)$^{\#2}$	90.3(4)
N(6)−Cd(2)−O(2)	95.8(4)	O(2)$^{\#4}$−Cd(2)−O(2)	180.000(2)	N(12)−Cd(4)−O(8)$^{\#2}$	89.7(4)	O(8)−Cd(4)−O(8)$^{\#2}$	180.000(1)
Polymer **4**[d]							
Cd(1)−O(4)	2.307(8)	Cd(1)−O(4)$^{\#1}$	2.307(8)	Cd(2)−O(9)	2.313(12)	Cd(2)−O(9)$^{\#2}$	2.313(12)
Cd(1)−O(5)	2.310(9)	Cd(1)−O(5)$^{\#1}$	2.310(9)	Cd(2)−O(2)$^{\#1}$	2.435(18)	Cd(2)−O(2)$^{\#3}$	2.435(18)
Cd(1)−N(1)$^{\#1}$	2.319(10)	Cd(1)−N(1)	2.319(10)	Cd(2)−O(8)	2.61(3)	Cd(2)−O(8)$^{\#2}$	2.61(3)
Cd(2)−N(6)$^{\#2}$	2.292(11)	Cd(2)−N(6)	2.292(11)				
O(4)−Cd(1)−O(4)$^{\#1}$	180.000(2)	O(4)−Cd(1)−O(5)	88.8(4)	N(6)−Cd(2)−(2)$^{\#1}$	93.6(6)	O(9)−Cd(2)−O(2)$^{\#1}$	103.2(8)
O(4)$^{\#1}$−Cd(1)−O(5)	91.2(4)	O(4)−Cd(1)−O(5)$^{\#1}$	91.2(4)	O(9)$^{\#2}$−Cd(2)−O(2)$^{\#1}$	76.8(8)	N(6)$^{\#2}$−Cd(2)−O(2)$^{\#3}$	93.6(6)
O(4)$^{\#1}$−Cd(1)−O(5)$^{\#1}$	88.8(4)	O(5)−Cd(1)−O(5)$^{\#1}$	180.000(2)	N(6)−Cd(2)−O(2)$^{\#3}$	86.4(6)	O(9)−Cd(2)−O(2)$^{\#3}$	76.8(8)
O(4)−Cd(1)−N(1)$^{\#1}$	85.0(4)	O(4)$^{\#1}$−Cd(1)−N(1)$^{\#1}$	95.0(4)	O(9)$^{\#2}$−Cd(2)−O(2)$^{\#3}$	103.2(8)	O(2)$^{\#1}$−Cd(2)−O(2)$^{\#3}$	180.000(3)
O(5)−Cd(1)−N(1)$^{\#1}$	84.2(4)	O(5)$^{\#1}$−Cd(1)−N(1)$^{\#1}$	95.8(4)	N(6)$^{\#2}$−Cd(2)−O(8)	100.7(6)	N(6)−Cd(2)−O(8)	79.3(6)
O(4)−Cd(1)−N(1)	95.0(4)	O(4)$^{\#1}$−Cd(1)−N(1)	85.0(4)	O(9)−Cd(2)−O(8)	75.4(8)	O(9)$^{\#2}$−Cd(2)−O(8)	104.6(8)
O(5)−Cd(1)−N(1)	95.8(4)	O(5)$^{\#1}$−Cd(1)−N(1)	84.2(4)	O(2)$^{\#1}$−Cd(2)−O(8)	31.8(6)	O(2)$^{\#3}$−Cd(2)−O(8)	148.2(6)
N(1)$^{\#1}$−Cd(1)−N(1)	180.000(2)	N(6)$^{\#2}$−Cd(2)−N(6)	180.000(3)	N(6)$^{\#2}$−Cd(2)−O(8)$^{\#2}$	79.3(6)	N(6)−Cd(2)−O(8)$^{\#2}$	100.7(6)
N(6)$^{\#2}$−Cd(2)−O(9)	88.3(4)	N(6)−Cd(2)−O(9)	91.7(4)	O(9)−Cd(2)−O(8)$^{\#2}$	104.6(8)	O(9)$^{\#2}$−Cd(2)−O(8)$^{\#2}$	75.4(8)
N(6)$^{\#2}$−Cd(2)−O(9)$^{\#2}$	91.7(4)	N(6)−Cd(2)−O(9)$^{\#2}$	88.3(4)	O(2)$^{\#1}$−Cd(2)−O(8)$^{\#2}$	148.2(6)	O(2)$^{\#3}$−Cd(2)−O(8)$^{\#2}$	31.8(6)
O(9)−Cd(2)−O(9)$^{\#2}$	180.0(8)	N(6)$^{\#2}$−Cd(2)−O(2)$^{\#1}$	86.4(6)	O(8)−Cd(2)−O(8)$^{\#2}$	180.000(5)		

[a] Symmetry transformations used to generate equivalent atoms in polymer **1**: #1, $-x, -y + 1, -z + 1$; #2, $x - 1, -y + 3/2, z + 1/2$; #3, $-x + 1, y - 1/2, -z + 1/2$. [b] Symmetry transformations used to generate equivalent atoms in polymer **2**: #1, $-x + 1, y - 1/2, -z - 1/2$; #2, $x - 1, -y + 3/2, z + 1/2$; #3, $-x, -y + 1, -z$. [c] Symmetry transformations used to generate equivalent atoms in polymer **3**: #1, $x, y, z - 1$; #2, $-x + 2, -y - 2, -z$; #3, $-x + 2, -y - 2, -z - 1$; #4, $-x + 4, -y - 3, -z$; #5, $-x + 4, -y - 3, -z + 1$. [d] Symmetry transformations used to generate equivalent atoms in polymer **4**: #1, $-x, -y + 1, -z + 2$; #2, $-x + 1, -y + 1, -z + 3$; #3, $x + 1, y, z + 1$.

Scheme 1



triazol groups are in *para* positions and nitrogen atoms coordinate to different metal ions simultaneously. It is obvious that the positions of functional groups in the similar ligands affect the crystal structures of the complexes.

Crystal Structure of $[Cd(btx)_2(NO_3)_2]_n$ (1). The X-ray diffraction shows that all of the Cd(II) atoms and btx ligands in polymer **1** are equivalent. Figure 1a depicts the coordination geometry of the Cd(II) center. Each Cd(II) ion binds to four nitrogen atoms from four equatorial btx and two oxygen atoms from two axial monodentate nitrate anion leading to a slightly elongated octahedral geometry. The Cd−N bonds have the same bond length of 2.324(4) Å and are slightly shorter than the Cd−O bond length of 2.343(7) Å. N1, N1A,

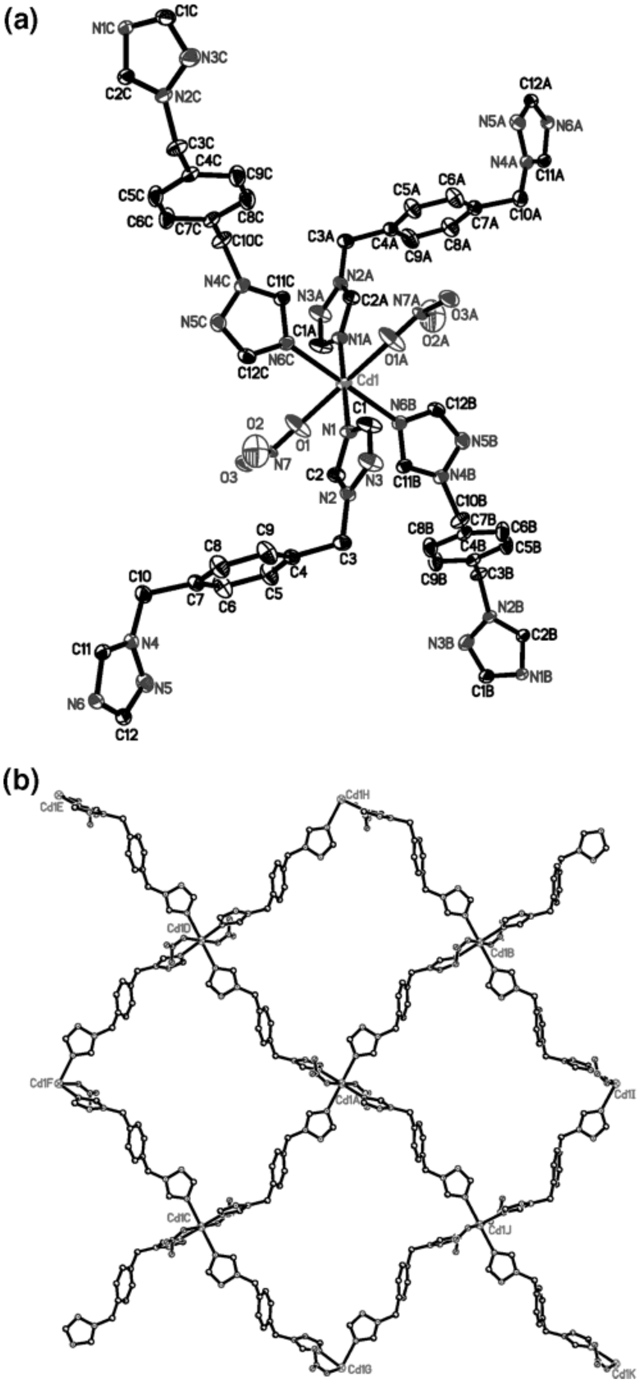


Figure 1. (a) Coordination geometry of the Cd(II) center in $[Cd(btx)_2(NO_3)_2]_n$ (**1**) with atom numbering, showing 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. (b) Two-dimensional layered structure of $[Cd(btx)_2(NO_3)_2]_n$ (**1**) with rhombohedral grid units.

N6B, and N6C atoms are completely coplanar. The mean deviations from planes N1−N2−N3−C1−C2 (1), N4−N5−N6−C11−C12 (2), C4−C5−C6−C7−C8−C9 (3), and N4C−N5C−N6C−C11C−C12C (4) are 0.0066, 0.0006, 0.0114, and 0.0006 Å, respectively. The dihedral angles between planes 1 and 2, 1 and 3, 1 and 4, and 2 and 3 are 57.1, 67.7, 89.3, and 67.5°, respectively.

Each btx ligand binds with two Cd(II) ions forming a two-dimensional layered structure with rhombohedral grid units (Figure 1b). In each layer, all Cd(II) ions are completely coplanar. Each rhombohedral grid is organized by four btx ligands acting as the four edges and four Cd(II) ions representing the four vertexes. The four edges have the same length of 14.841 Å, the diagonals are 20.786 and 21.190 Å, and the interior angles are 88.9 and 91.1°, respectively. The network resembles the rhombohedral grids in $[Cd(bbbt)_2(NCS)_2]_n$ (bbbt = 1,1′-(1,4-butanediyl)bis(1*H*-benzotriazole))[8] and other Cd(II) coordiantion polymers.[50−53]

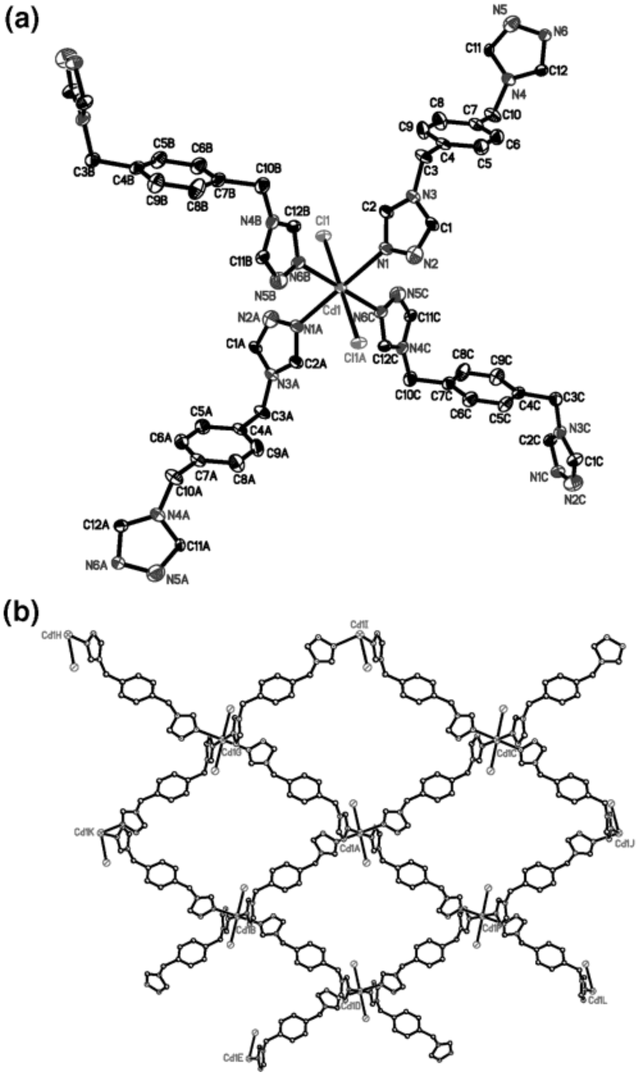


Figure 2. (a) Coordination geometry of the Cd(II) center in $[Cd(btx)_2Cl_2]_n$ (**2**) with atom numbering, showing 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. (b) Two-dimensional layered structure of $[Cd(btx)_2Cl_2]_n$ (**2**) with rhombohedral grid units.

Crystal Structure of $[Cd(btx)_2Cl_2]_n$ (2). The structure of polymer **2** is made up of two-dimensional rhombohedral grid layers, similar to that of **1**. As illustrated in Figure 2a, all of the Cd(II) ions and btx are equivalent, respectively. The N1, N1A, N6B, and N6C atoms are completely coplanar.

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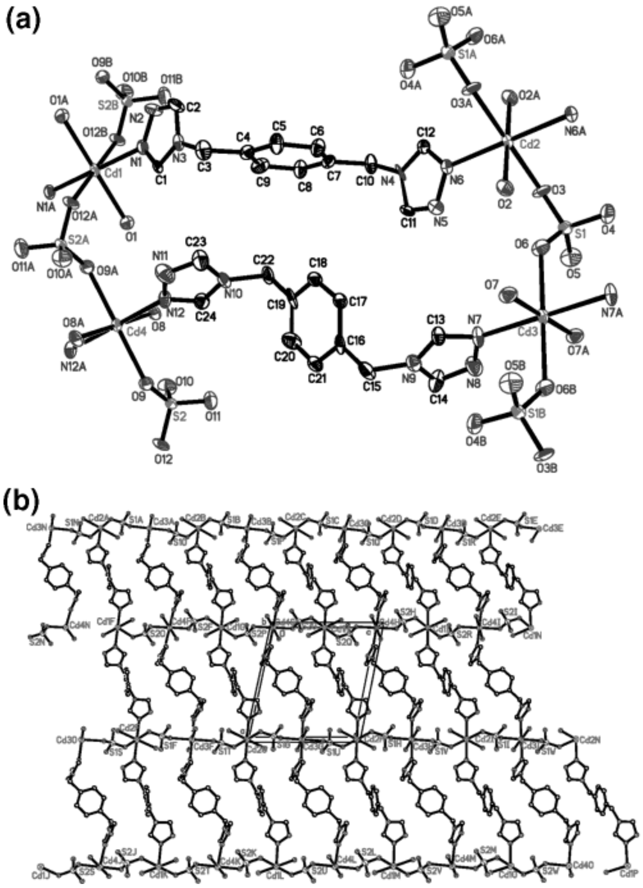

Figure 3. (a) Coordination geometry of the four Cd(II) centers in $[Cd(btx)(SO_4)(H_2O)_2]_n$ (**3**) with atom numbering, showing 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. (b) Two-dimensional layered structure of $[Cd(btx)(SO_4)(H_2O)_2]_n$ (**3**) with distorted rectangular grid units.

The Cd−N bond lengths (2.344(3) and 2.354(3) Å) are slightly longer than the Cd−N bond lengths of polymer **1**, while the Cd−Cl bond lengths (2.6477(13) Å) are obviously longer than those of Cd−N bond lengths. The Cd(II) ion is in an elongated octahedral geometry coordinated by four nitrogen atoms of four bidentate btx ligands and two chlorine atoms. The mean deviations from planes N1−N2−N3−C1−C2 (1), N4B−N5B−N6B−C11B−C12B (2), C4−C5−C6−C7−C8−C9 (3), and N4−N5−N6−C11−C12 (4) are 0.0020, 0.0016, 0.0054, and 0.0015 Å, respectively. The dihedral angles between planes 1 and 2, 1 and 3, 1 and 4, and 3 and 4 are 99.3, 72.4, 71.0, and 50.6°, respectively.

As depicted in Figure 2b, the two-dimensional layered structure is based upon the rhombohedral grid units $(Cd(btx)_4)$ which are formed by four btx ligands and four Cd(II) ions. In each grid, the edge lengths of 14.880 Å are slightly longer than those in polymer **1**, the diagonals are 20.156 and 21.156 Å, and the interior angles are 85.3 and 94.7°, respectively.

Crystal Structure of $[Cd(btx)(SO_4)(H_2O)_2]_n$ (3). Polymer **3** possesses an infinite two-dimensional layered structure with distorted rectangular grid units which are different from those of **1** and **2**. As shown in Figure 3a, there are two crystallographically independent btx ligands, two crystallographically independent bidentate sulfates, and four crystallographically independent Cd(II) ions. The coordination enviroments around the four kinds of Cd(II) ions are similar, all of which are octahedral. Each Cd(II) ion is coordinated by four oxygen atoms, of which two are from two sulfate anions and two are from two water molecules, and two nitrogen atoms from two bidentate btx. In the coordination sphere around each Cd(II) ion, there is an ideal planarity of the CdO_4 unit. Four Cd(II) ions are linked by btx and sulfate anions forming a distorted rectangular grid unit. Each grid is constructed from two btx ligands and two sulfate anion ligands acting as the four edges and four Cd(II) ions acting as the four vertexes giving a 36-membered metallocycle. The lengths of the opposite edges are equal at 15.238 and 5.648 Å, the diagonals are 15.031 and 17.299 Å, and the interior angles are 78.2 and 101.8°, respectively. In the reported two-dimensional quadrilateral grid coordination polymers, the grid is usually formed by four identical metal ions and four identical ligands, for example, polymers $[Cd(NCS)_2(L)_2]_n$ (L = 2,2′-bi-1,6-naphthyridine),[50] $[Cd(L)_2(ClO_4)_2]_n$ [L = *N*,*N*-2-pyridyl-(4-pyridylmethyl)amine],[51] $[Cd(L)_2(NO_3)_2]_n$ [L= bis(4-pyridyl)-methane],[43] $[Cd(NO_3)_2(Py_2CH_2)_2]_n$, and $[Cd_2(NO_3)_4(Py_2C_3H_6)_4(H_2O)]_n$.[53] But in polymer **3**, not only the btx ligands but also the sulfate anions act as bridging ligands, so each grid contains four Cd(II) ions, two btx ligands, and two sulfate anions. Polymer **3**'s two-dimensional layered structure is different from those of the reported Cd(II) polymers. It is a less common Cd(II) two-dimensional polymer with quadrilateral grid units.

Figure 3b gives the the two-dimensional layered structure. Along the *c*-direction, Cd2 and Cd3 are bridged by sulfate anions leading to a linear chain ···Cd2−S(1)O_4−Cd3−S(1)O_4−Cd2−S(1)O_4−Cd3···, and Cd1 and Cd4 are bridged by sulfate anions forming another linear chain ···Cd1−S(2)-O_4−Cd4−S(2)O_4−Cd1−S(2)O_4−Cd4···. Along the *a*-direction, Cd(II) ions are connected by a btx ligand generating two kinds of linear chains: one is ···Cd1−btx−Cd2−btx−Cd1−btx−Cd2···, and the other is ···Cd3−btx−Cd4−btx−Cd3−btx−Cd4···. Linear chains along the *c*-direction and *a*-direction are interconnected each other to finish the two-dimensional layered frameworks.

Crystal Structure of $[Cd(btx)(S_2O_7)(H_2O)]_n$ (4). Although the elements in **3** and **4** are completely identical, the structural determination reveals that **4** is a most remarkable and unique three-dimensional structure polymer. As depicted in Figure 4a, there are two distinct Cd(II) ions which have different coordination environments in the crystallographic asymmetric unit. Cd1 is coordinated by four oxygen atoms of pyrosulfate in a ideal square planar geometry and two nitrogen atoms from two bidentate btx. The Cd1−O distances of 2.307(8) and 2.310(9) Å and the Cd1−N distances of 2.292(11) Å are similar to those of polymers **1**−**3** and other reported Cd(II) polymers.[28,51,53] Cd2 is in a hexagonal bipyrimidal coordination environment (Figure 4b) and binds to two nitrogen atoms from two bxt ligands and six oxygen atoms from four pyrosulfate groups and two water molecules.

As shown in Figure 4c, if we neglect the interactions of Cd(II) centers with the btx ligands, the structure of **4** has a two-dimensional layered topology consisting of two kinds of independent Cd(II) ions and two kinds of independent

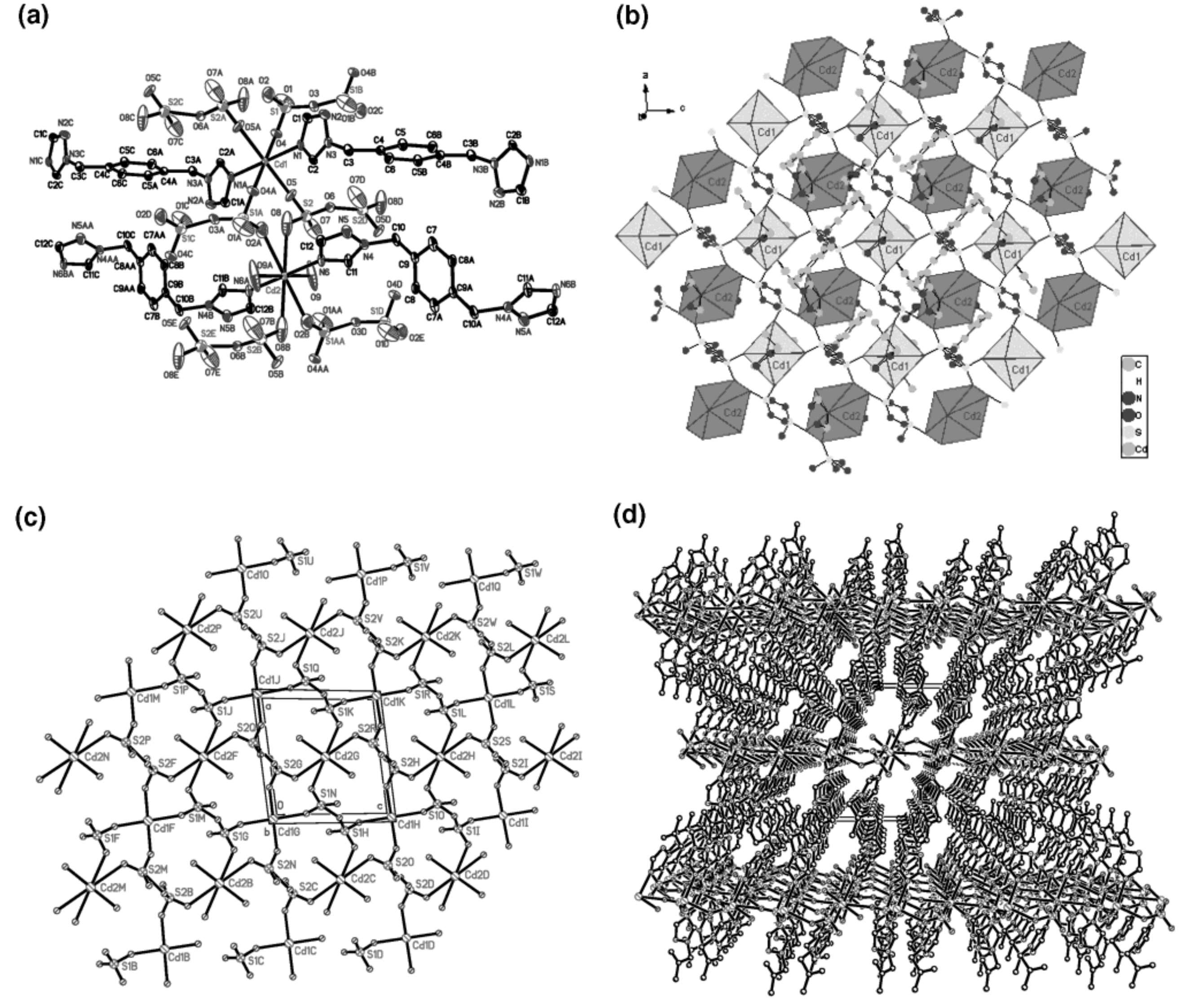

Figure 4. (a) Coordination geometry of the Cd(II) centers in $Cd_2(btx)_2(S_2O_7)_2(H_2O)_2]_n$ **(4)** with atom numbering, showing 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. (b) Polyhedral view of the octahedra of Cd1 (yellow) and dodecahedra of Cd2 (blue) in $Cd_2(btx)_2(S_2O_7)_2(H_2O)_2]_n$ **(4)**. (c) Two-dimensional layer in $Cd_2(btx)_2(S_2O_7)_2(H_2O)_2]_n$ **(4)**, neglecting the interaction of Cd(II) centers with btx ligands. (d) Three-dimensional network of $Cd_2(btx)_2(S_2O_7)_2(H_2O)_2]_n$ **(4)**. Adjacent two-dimensional layers are connected by bridging $S_2O_7^{2-}$ anions.

pyrosulfate groups. Along the *a*-direction, Cd1 atoms are bridged by $(S2)_2O_7$ groups with the Cd1···Cd1 distance of 8.556 Å and Cd2 atoms are linked by $(S1)_2O_7$ groups with the Cd2···Cd2 distance of 8.556 Å leading to two kinds of linear chains. Along the *c*-direction, Cd1 atoms are ligated by $(S1)_2O_7$ groups with the Cd1···Cd1 distance of 8.542 Å and Cd2 atoms are connected by $(S2)_2O_7$ groups with the Cd2···Cd2 distance of 8.542 Å forming other two kinds of linear chains. Linear chains along the *a*-direction intersect those along *c*-direction generating the two-dimensional frameworks only consisting of Cd(II) ions and pyrosulfate groups. These two-dimensional layers are stacked parallel and connected by btx leading to the three-dimensional framework (Figure 4d).

Due to the difference of reaction temperature, **3** and **4** exhibit completely different crystal structures; **3** shows a two-dimensional layered structure, and **4** has a three-dimensional network.

In the known Cd(II) polymers, the coordination numbers of Cd(II) ions include **4**−**7**, and the corresponding coordination geometries are quadrilateral plane, trigonal bipyramid, octahedron, and pentagonal bipyramid, respectively.[4,28,50−53,54] For example, in $[Cd(NO_3)_2(Py_2C_4H_8)(H_2O)_2]_n$ and $[Cd_2(NO_3)_4(Py_2C_3H_6)_4(H_2O)]_n$,[53] the coordination number for the Cd(II) ion is 6 and the corresponding coordination geometry is octahedal; in $[Cd_2(NO_3)_4(Py_2C_5H_{10})_3(H_2O)]_n$[53] and $[Cd(tp)(4,4'\text{-bipy})]_n$,[28] the coordination number for Cd(II) ions is 7 and the corresponding coordination geometry is pentagonal bipyramid. But in **4**, one type of Cd(II) ion is eight-coordinated and its geometry is hexagonal bipyrimid. To the authors' best knowledge this kind of coordination geometry has not previously occurred in the reported Cd(II) polymers.

Thermogravimetric Analysis (TGA). The TG−DTA of polymers **1**−**4** was determined in the range of 25−800 °C (or 1100 °C for polymer **2**) in air. TG data show that **1** is stable up to 285 °C and then loses weight from 285 to 618

°C corresponding to the release of btx and the decomposition of the nitrate anions. Finally a plateau region is observed from 618 to 800 °C. A brown residue of CdO (obsd 17.13%, calcd 17.93%) remained. There are two exothermic peaks (345 and 534 °C) in the DTA curve of **1**. The TG data of **2** show that it is also stable up to 215 °C and then keeps losing weight from 215 to 1077 °C corresponding to the losses of btx and $CdCl_2$. At 1077 °C, the weight is lost completely. One endothermic peak (291 °C) and two exothermic peaks (371, 622 °C) were observed in the DTA curve of **2**. The TG data for **3** show that it began to decompose at 103 °C. Then there are two weight loss stages in the ranges 103−151 and 293−543 °C, corresponding to the release of the crystallized water molecules and btx, respectively. Finally a plateau region is observed from 543 to 800 °C. A white residue of $CdSO_4$ (obsd 42.10%, calcd 43.02%) remained. One endothermic peak (175 °C) and two exothermic peaks (446, 514 °C) are observed in the DTA curve of **3**. In the DTA curve of **4**, there are one endothermic peak (169 °C) and three exothermic peaks (447, 509, 635 °C). The weight loss from 109 to 145 °C corresponds to the departure of the H_2O, and the weight loss from 296 to 539 °C corresponds to the loss of btx. A plateau region is observed from 539 to 800 °C. The remaining white residue is CdS_2O_7 (obsd 51.46%, calcd 52.74%).

Nonlinear Optical Properties. The third-order NLO properties of polymers **1**−**4** were investigated with 532 nm laser pulses of 7 ns duration by *Z*-scan experiment in DMF solution.[55,56] The results show that polymer **3** possesses very strong third-order NLO absorptive effect and weak refractive behavior, and polymers **1**, **2**, and **4** display both weak third-order NLO absorptive and weak refractive behaviors.

The NLO absorption components were evaluated by *Z*-scan experiment under an open aperture configuration. The NLO absorption data can be well represented by eqs 1 and 2, which describe a third-order NLO process:[55]

$$T(Z) = \frac{1}{\sqrt{\pi}q(Z)}\int_{-\infty}^{+\infty} In[1 + q(Z)]e^{\tau^2}\,d\tau \tag{1}$$

$$q(Z) = \int_0^\infty\int_0^\infty \alpha_2 \frac{I_0}{1 + (Z/Z_0)^2} e^{[-2(r/\omega_0)2-(t/t_0)^2]} \frac{1 - e^{-\alpha_0 L}}{\alpha_0} r\,dr\,dt \tag{2}$$

Here *Z* is the distance of the sample from the focal point, α_0 and α_2 are the linear and nonlinear absorption coefficients, respectively, *L* is the sample thickness, I_0 is the peak irradiation intensity at focus, $Z_0 = \pi\omega_0^2/\lambda$ with ω_0 being the spot radius of the laser beam at focus and λ being the wavelength of the laser, *r* is the radial coordinate, τ is the time, and t_0 is the pulse width. Figure 5 depicts the NLO absorptive properties of polymer **3** in a DMF solution of concentration 3.1×10^{-4} mol·dm^{-3}. In Figure 5, the filled squares are the experimental data and the solid line is the theoretical curve from eqs 1 and 2. A reasonably good fit between the experimental data and the theoretical curve suggests that the experimentally obtained NLO effects are effectively third order in nature. The figure clearly illustrate that the absorption increases as the incident light irradiance rises since light transmittance (*T*) is a function of the sample's *z* position. It can be seen from Figure 5 that the normalized transmittance drops to about 65% for polymer **3** at the focus; the corresponding third-order NLO absorptive coefficient α_2 is calculated to be 1.15×10^{-9} m W^{-1}. It is comparable to or larger than those of the well-performing coordination polymers such as $[Cd(bbbt)_2(NCS)_2]_n$ ($\alpha_2 = 5.0 \times 10^{-9}$ m W^{-1}) (bbbt = 1,1′-(1,4-butanediyl)bis(1*H*-benzotriazole)), $[HgI_2(4,4'\text{-azopyridine})]_n$ ($\alpha_2 = 1.3 \times 10^{-11}$ m W^{-1}), $[HgI_2(bpea)]_n$ ($\alpha_2 = 1.1 \times 10^{-11}$ m W^{-1}) (bpea = 1,2-bis-(4-pyridyl)ethane), and $[Pb(NCS)_2(bpea)]_n$ ($\alpha_2 = 1.1 \times 10^{-11}$ m W^{-1}).[8,57−59]

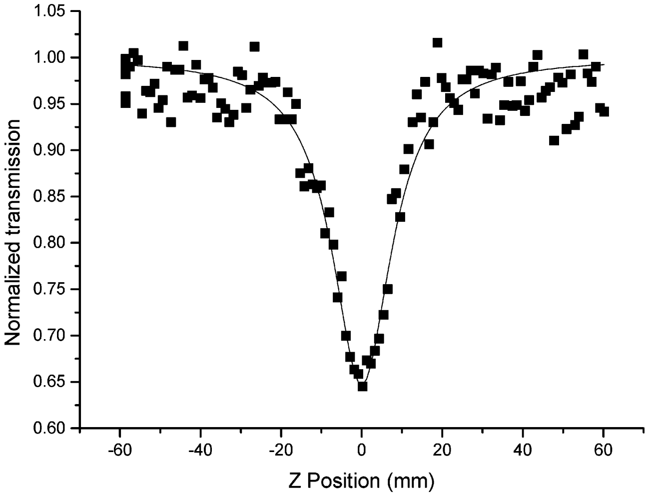

Figure 5. NLO absorption data for **3** in a 3.1×10^{-4} mol·dm^{-3} DMF solution at 532 nm with incident energy of 150 μJ. The data were collected under an open aperture configuration.

Interestingly, polymers **1**−**3** have the same btx ligand, the same metal ion, and the similar two-dimensional layered structure, but they display different NLO properties since they have different anions. Polymers **3** and **4** contain identical elements, but they exhibit different NLO effects owing to their different crystal structures. It is obvious that the third-order NLO properties of coordination polymers can be altered through anions or structural manipulation.

Photoluminescent Properties. The emission spectra of polymers **1**−**4** in the solid state at room temperature are shown in Figure 6. Excitation at 238 nm leads to violet-fluorescent emission bands at 291 nm for **1**, 287 nm for **2**, 299 nm for **3**, and 287 nm for **4** under the same conditions. The emissions observed in **1**−**4** are neither MLCT (metal-to-ligand charge transfer) nor LMCT (ligand-to-metal charge

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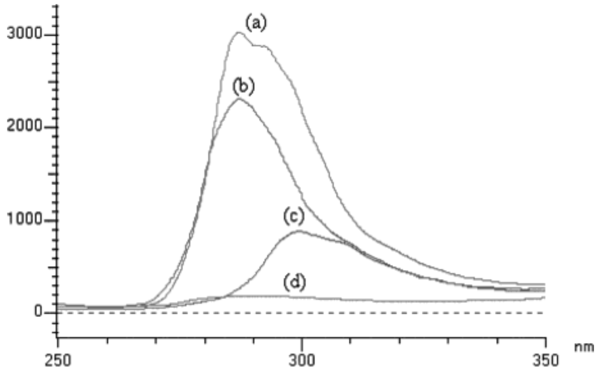

Figure 6. Solid-state emission spectra of polymers **1** (d), **2** (a), **3** (c), and **4** (b) at room temperature.

transfer) in nature and can tentatively be assigned to the intraligand fluorescent emission since a similar emission (when $\lambda_{ex} = 238$ nm, $\lambda_{em} = 289$ nm) is also observed for btx. A clearly bathochromic shift of emission occurs in **3** compared with **1**, **2**, and **4**. It is obvious that **2** possesses the strongest fluorescent intensity; **1** exhibits a quenching of the fluorescence. These observations suggest that **2** will be an excellent candidate for solvent-resistant fluorescent material because it is almost insoluble in most common solvents such as ethanol, chloroform, ethyl acetate, acetone, acetonitrile, benzene, and water.

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Supporting Information Available: Crystallographic data for polymers **1**−**4** in CIF format, TGA−DTA data, and an ^{1}H NMR spectrum of the ligand btx. This material is available free of charge via the Internet at http://pubs.acs.org.

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