Inorg. Chem. **2002**, *41*, 4068–4075

Inorganic Chemistry Article

Two-Dimensional Rhombohedral Grid Coordination Polymers $[M(bbbt)_2(NCS)_2]_n$ (M = Co, Mn, or Cd; bbbt = 1,1′-(1,4-butanediyl) bis-1*H*-benzotriazole): Synthesis, Crystal Structures, and Third-Order Nonlinear Optical Properties

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Received March 11, 2002

In this paper, treatment of 1,1′-(1,4-butanediyl) bis-1*H*-benzotriazole (bbbt) and KSCN with Co(II), Mn(II), or Cd(II) afforded three two-dimensional rhombohedral grid coordination polymers $[M(bbbt)_2(NCS)_2]_n$ (M = Co, **1**; Mn, **2**; Cd, **3**). The two-dimensional rhombohedral grids are parallel to the crystallographic *ac* plane. The rhombohedral grid consists of 44-membered rings of $M_4(bbbt)_4$, and gives the dimensions of 12.913 × 10.764 Å for polymer **1**, 13.106 × 10.797 Å for polymer **2**, and 13.256 × 10.870 Å for polymer **3**. The three polymers' third-order nonlinear optical (NLO) properties were determined by Z-scan technique in DMF solution. The results show that all three polymers show very large NLO absorption and strong NLO refraction properties. The third-order NLO absorptive coefficients α_2 are 5.4×10^{-9} m W^{-1} for polymer **1**, 5.2×10^{-9} m W^{-1} for polymer **2**, and 5.0×10^{-9} m W^{-1} for polymer **3**. The α_2 values are larger than those of all the reported cluster compounds. The NLO refractive index values n_2 of the three polymers are 5.73×10^{-19}, 3.55×10^{-19}, and 3.07×10^{-19} m^2 W^{-1}, respectively. Their hyperpolarizability γ values are calculated to be 2.40×10^{-30} esu for polymer **1**, 1.52×10^{-30} esu for polymer **2**, and 1.50×10^{-30} esu for polymer **3**. The γ values are comparable to those of clusters and better than those of organometallic compounds, semiconductors, and fullerene.

Introduction

Recently the design and assembly of coordination polymers have been of great interests due to their interesting topologies[1−4] and potential applications as catalyst, superconductor, magnetic, and optical materials.[5−14] The generation of this type of molecular architecture rests on several factors, such as the metals, the solvents, the reaction conditions, the performance of the ligands, etc. The design of ligands is often a useful way of manipulating the structures. Bi- or multidentate ligands containing N- or O-donors are usually used to bind metal centers to form covalent high-dimensional arrangements. There have been numerous reports in which 4,4′-bipyridyl-based ligands have been used to construct coordination polymers showing novel features.[15−36] Metal-4,4′-bpy can form a large range of infinite frameworks, including honeycomb, diamondoid,

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10.1021/ic0255858 CCC: $22.00

rhombic networks, square grids, ladder, brick, octahedral, and T-shaped. Treatment of 1,2-bis(4-pyridylmethyl) disulfenyl (bpms) with $Co(NO_3)_2 \cdot 6H_2O$ and KSCN affords a zigzag chain coordination polymer $[Co(NCS)_2(bpms)_2]_n$.[31] The reaction of $Co(NO_3)_2 \cdot 6H_2O$ and KSCN with 1,4-(di-4-pyridylmethoxy)benzene (bpmob) can produce a polymer with a two-dimensional grid network structure.[32] Furthermore, there are also many coordination polymers involving bis-1,2,4-triazolyl- or bis-imidazolyl-based ligands, 2,2′-bipyrazine (bpyz), pyrazine[2,3-f]quinoxaline (pyq), etc.[37−53] For example, the reaction of 1,3-bis(1,2,4-triazol-l-yl)propane (btp) with Cu(II) gives an unusual double-layered polymer $\{[Cu(btp)_2(CH_3CN)_2](ClO_4)_2\}_n$;[37] 1,4-bis(imidazol-1-yl-methyl)benzene (bix) coordinates with Ag(I) to afford a polymer showing two-dimensional polyrotaxane networks.[49] As far as we are aware, researchers have been concentrating on novel structure and magnetic properties of coordination polymers, and do not give much effort toward the study of NLO properties, especially the third-order NLO properties.

Third-order NLO materials are currently of interest to a large number of research groups as they can be used for a number of photonic applications, for example, optical signal processing, optical communication, optical computing, electrooptic modulation, optical limiting effect, etc.[54,55] In principle, compared with traditional NLO material, the incorporation of metal atoms in coordination polymers introduces more sublevels into the energy hierarchy, which permits more allowed electronic transition to take place and hence a larger NLO effect.[10,11,31,56] Recently, the third-order NLO properties of a series of coordination polymers such as $[Co(NCS)_2(bpms)_2]_n$,[31] $[Mn(SO_4)(4,4'\text{-bpy})(H_2O)_2]_n$, $[Mn(N_3)_2(4,4'\text{-bpy})]_n$,[56] $[Mn(N_3)_2(bbp)_2]_n$, and $\{[Mn(NCS)_2(bbp)_2] \cdot 0.25H_2O\}_n$ (bbp = 4,4′-trimethylene-dipyridine)[57] were measured. The results show that these coordination polymers have strong third-order NLO properties. To further explore coordination polymers with novel structures and their third-order NLO properties, in this paper we prepared three coordination polymers $[M(bbbt)_2(NCS)_2]_n$ (M = Co, Mn, or Cd; bbbt = 1,1′-(1,4-butanediyl) bis-1*H*-benzotriazole). All of them have a two-dimensional rhombohedral grid network structure and exhibit a layered packing mode. Moreover the polymers have very strong third-order NLO absorptive and refractive properties in DMF solution. The third-order NLO absorptive coefficients α_2 are 5.4×10^{-9} m W^{-1} for polymer **1**, 5.2×10^{-9} m W^{-1} for polymer **2**, and 5.0×10^{-9} m W^{-1} for polymer **3**. The α_2 values are larger than those of the reported cluster compounds. The NLO refractive index values n_2 are 5.73×10^{-19}, 3.55×10^{-19}, and 3.07×10^{-19} m^2 W^{-1}, respectively. The γ values are calculated to be 2.40×10^{-30} esu for polymer **1**, 1.52×10^{-30} esu for polymer **2**, and 1.50×10^{-30} esu for polymer **3**.

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Table 1. Crystal Data and Structure Refinement for Polymers **1**−**3**

polymers	**1**	**2**	**3**
formula	$C_{34}H_{32}CoN_{14}S_2$	$C_{34}H_{32}MnN_{14}S_2$	$C_{34}H_{32}CdN_{14}S_2$
fw	759.79	755.80	813.26
temp (K)	291(2)	291(2)	293(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst size (mm)	0.30 × 0.30 × 0.20	0.30 × 0.20 × 0.20	0.30 × 0.30 × 0.30
color	red	colorless	colorless
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	10.764(2)	10. 797(2)	10. 870(2)
b (Å)	15.174(3)	15.224(3)	15.280(3)
c (Å)	11.446(2)	11.391(2)	11.384(2)
α (deg)	90	90	90
β (deg)	108.98(3)	107.65(3)	106.92(3)
γ (deg)	90	90	90
V (Å^3)	1767.9(6)	1784.2(6)	1808.9(6)
Z	2	2	2
D_c (g·cm^{-3})	1.427	1.407	1.493
abs coeff (mm^{-1})	0.652	0. 535	0. 766
F(000)	786	782	828
reflcns collected/unique	4957/3184	5351/3233	5708/3376
data/restraints/params	3184/0/249	3233/0/249	3376/0/249
goodness-of-fit on F^2	1.048	1.152	1.118
R1, wR2[a]	0.0797, 0.0989	0.0623, 0.0926	0.0502, 0.0895

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = \{\sum w(|F_o| - |F_o|)^2/\sum wF_o^2\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o^2, 0)]/3$.

Experimental Section

General Information and Materials. All chemicals were of A. R. Grade and were used without further purification. UV−vis spectra were recorded, ranging from 200 to 800 nm, on a Hitachi-220A ultraviolet−visible spectrophotometer. IR spectra were performed on a PE spectrophotometer in the region of 400−4000 cm^{-1}. Carbon, hydrogen, and nitrogen analyses were carried out on a Carlo-Erba 1106 elemental analyzer. Proton NMR spectra were recorded on a Bruker DPX-400 spectrometer. The molecular weight of the polymer was determined by Waters 515.

Synthesis of the *N,N*′-Bidentate Ligand 1,4-Bis(1*H*-benzotriazole)butane (bbbt). bbbt was prepared according to the literature.[58] Mp 150−152 °C. Anal. Calcd for $C_{16}H_{16}N_6$: C, 65.75; H, 5.48; N, 28.78. Found: C, 65.36; H, 5.44; N, 28.70. IR (KBr)/cm^{-1}: 3061 m, 2951 m, 1617 w, 1569 w, 1497 w, 1455 m, 1327 s, 737 s. ^{1}H NMR (Ace): δ 7.383−7.997 (s, 8H), 4.821−4.858 (s, 4H), 2.039−2.178 (s, 4H).

Synthesis of [Co(bbbt)$_2$(NCS)$_2$]$_n$ (1). A methanol solution (5 mL) of bbbt (55.6 mg, 0.2 mmol) was added dropwise into an aqueous solution (5 mL) of $Co(NO_3)_2 \cdot 6H_2O$ (29.1 mg, 0.1 mmol) and KSCN (19.4 mg, 0.2 mmol) to give a clear solution. Red crystals (55% yield) suitable for X-ray diffraction were obtained one week later. Anal. Calcd for $C_{34}H_{32}CoN_{14}S_2$: C, 53.75; H, 4.24; N, 25.81. Found: C, 54.01; H, 4.13; N, 25.92. IR (KBr)/cm^{-1}: 3060 m, 2938 m, 2096 s, 1612 w, 1493 w, 1457 m, 1329 m, 746 s.

Synthesis of [Mn(bbbt)$_2$(NCS)$_2$]$_n$ (2). A methanol solution (5 mL) of bbbt (55.6 mg, 0.2 mmol) was slowly added, with stirring at 60 °C, to an aqueous solution (5 mL) of $MnSO_4 \cdot H_2O$ (16.9 mg, 0.1 mmol) and KSCN (19.4 mg, 0.2 mmol). The resultant solution was cooled to room temperature after being stirred for 2 h, and crystals of X-ray quality were obtained two months later (35% yield). Anal. Calcd for $C_{34}H_{32}MnN_{14}S_2$: C, 54.03; H, 4.27; N, 25.94. Found: C, 53.92; H, 4.15; N, 26.03. IR (KBr)/cm^{-1}: 3062 m, 2938 m, 2083 s, 1612 w, 1498 w, 1457 m, 1329 m, 746 s.

Synthesis of [Cd(bbbt)$_2$(NCS)$_2$]$_n$ (3). An aqueous solution (2 mL) of KSCN (19.4 mg, 0.2 mmol) was added into an aqueous solution (1 mL) of $Cd(CH_3COO)_2 \cdot 2H_2O$ (26.6 mg, 0.1 mmol), then a methanol solution (5 mL) of bbbt (55.6 mg, 0.2 mmol) was slowly diffused into the above mixture. The resultant solution was left at room temperature. Colorless crystals suitable for X-ray diffraction were formed 4 days later (60% yield). Anal. Calcd for $C_{34}H_{32}CdN_{14}S_2$: C, 50.21; H, 3.97; N, 24.11. Found: C, 50.45; H, 3.88; N, 24.32. IR (KBr)/cm^{-1}: 3061 m, 2938 m, 2084 s, 1611 w, 1498 w, 1457 m, 1328 m, 745 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 = 0.71073 Å). The structures were solved by direct methods and expanded with 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 based on observed reflections and variable parameters. All calculations were performed with the SHELXL-97 crystallographic software package.[59] Table 1 shows crystallographic crystal data and processing parameters for polymers **1**−**3**, and Table 2 lists their selected bond lengths and bond angles.

Nonlinear Optical Measurements. A DMF solution of polymer **1** (**2** or **3**) was placed in a 1-mm quartz curette for NLO measurements, respectively. The NLO properties were measured as described in the literature.[60−62]

Results and Discussion

Description of Crystal Structures. The structural unit of polymer **1** is depicted in Figure 1. Co(II) is at a slightly distorted octahedral coordination environment. The equatorial positions are occupied by four nitrogen atoms from four bbbt ligands (the Co−N$_{\text{bbbt}}$ bond length (av) is 2.218 Å), and two nitrogen atoms from NCS$^-$ groups occupy the axial positions

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Polymers **1**−**3**[a]

	Polymer **1**		
Co(1)−N(7)#1	2.055(4)	Co(1)−N(7)	2.055(4)
Co(1)−N(1)#1	2.216(4)	Co(1)−N(1)	2.216(4)
Co(1)−N(4)#1	2.221(5)	Co(1)−N(4)	2.221(5)
N(7)#1−Co(1)−N(7)	180.0(3)	N(7)−Co(1)−N(4)	90.02(17)
N(7)#1−Co(1)−N(1)#1	88.56(17)	N(1)#1−Co(1)−N(4)	83.94(16)
N(7)−Co(1)−N(1)#1	91.44(17)	N(1)−Co(1)−N(4)	96.06(16)
N(7)#1−Co(1)−N(1)	91.44(17)	N(7)#1−Co(1)−N(4)#1	90.02(17)
N(1)#1−Co(1)−N(1)	180.0(2)	N(7)−Co(1)−N(4)#1	89.98(17)
N(7)#1−Co(1)−N(4)	89.98(17)	N(1)#1−Co(1)−N(4)#1	96.06(16)
N(1)−Co(1)−N(4)#1	83.94(16)	N(4)−Co(1)−N(4)#1	180.0(3)
N(7)−Co(1)−N(1)	88.56(17)		
	Polymer **2**		
Cd(1)−N(7)#1	2.265(4)	Cd(1)−N(7)	2.265(4)
Cd(1)−N(1)#1	2.390(3)	Cd(1)−N(1)	2.390(3)
Cd(1)−N(4)#1	2.422(3)	Cd(1)−N(4)	2.422(3)
N(7)#1−Cd(1)−N(7)	180.0(2)	N(1)#1−Cd(1)−N(4)	83.36(11)
N(7)#1−Cd(1)−N(1)#1	89.50(13)	N(1)−Cd(1)−N(4)	96.64(11)
N(7)−Cd(1)−N(1)#1	90.50(13)	N(7)#1−Cd(1)−N(4)#1	88.55(13)
N(7)#1−Cd(1)−N(1)	90.50(13)	N(7)−Cd(1)−N(4)#1	91.45(13)
N(7)−Cd(1)−N(1)	89.50(13)	N(1)#1−Cd(1)−N(4)#1	96.64(11)
N(1)#1−Cd(1)−N(1)	180.0(2)	N(1)−Cd(1)−N(4)#1	83.36(11)
N(7)#1−Cd(1)−N(4)	91.45(13)	N(4)−Cd(1)−N(4)#1	180.00(15)
N(7)−Cd(1)−N(4)	88.55(13)		
	Polymer **3**		
Mn(1)−N(7)#1	2.166(3)	Mn(1)−N(7)	2.166(3)
Mn(1)−N(1)#1	2.316(3)	Mn(1)−N(1)	2.316(3)
Mn(1)−N(4)#1	2.345(2)	Mn(1)−N(4)	2.345(2)
N(7)−Mn(1)−N(7) #1	180.00(12)	N(1)#1−Mn(1)−N(4)#1	96.26(9)
N(7)−Mn(1)−N(4)#1	90.08(9)	N(4)−Mn(1)−N(1)#1	83.74(9)
N(7)#1−Mn(1)−N(4)#1	89.92(9)	N(7)−Mn(1)−N(1)	87.93(9)
N(7)−Mn(1)−N(4)	89.92(9)	N(7)#1−Mn(1)−N(1)	92.07(9)
N(7)#1−Mn(1)−N(4)	90.08(9)	N(4)#1−Mn(1)−N(1)	83.74(9)
N(4) #1−Mn(1)−N(4)	180.0	N(4)−Mn(1)−N(1)	96.26(9)
N(7)−Mn(1)−N(1)#1	92.07(9)	N(1)#1−Mn(1)−N(1)	180.00(15)
N(7)#1−Mn(1)−N(1)#1	87.93(9)		

[a] Symmetry codes: #1 −*x*, −*y*, −*z*; #2 −*x* + 1, −*y*, −*z*; #3 −*x* − 1, −*y*, −*z* − 1 for polymers **1**−**3**.

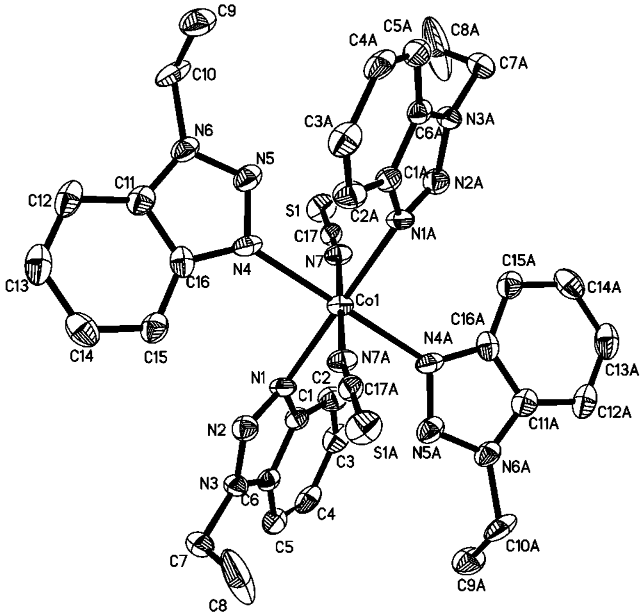

Figure 1. Structural unit of polymer **1** with atom numberings, showing 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

with bond length of 2.055(4) Å for Co−N_{NCS}. The Co−N bond lengths are similar to those of the known coordination polymer $[Co(NCS)_2(bpms)_2]_n$ (Co−N_{bpms}(av) = 2.218 Å, Co−N_{NCS} = 2.085 Å).[31] Every bbbt ligand binds with two Co atoms leading to the two-dimensional rhombohedral grid polymer **1** (Figure 2). In a grid, the distance for Co1A and Co1D is 12.913 Å, and that for Co1A and Co1C is 10.764 Å. The rhombohedral grid gives the dimensions of 12.913 × 10.764 Å and the diagonal distances of 20.838 × 11.446 Å, and the angle between the two ligands is 57.0° or 123.0°. The shortest distance between two parallel benzene rings from the parallel bbbt ligands of the rhombohedral grid is 3.324 Å, indicating a significant $\pi-\pi$ interaction between parallel edges,[63−67] and the shortest distance between the other two parallel ligands is 6.440 Å. The structural motif is similar to that of the polymer $[Co(NCS)_2(\textit{trans}\text{-bpmob})_2]_n$,[32] in which Co atoms serve as four-coordination nodes and the bpmob ligands act as edges, but different from that of the polymer $[Co(4,4'\text{-bpy})(H_2O)_4](ClO_4)_2{\cdot}2H_2O$, in which the adjacent one-dimensional polymeric chains are interconnected by double hydrogen bond bridges of the type Co−H_2O···4,4′-bpy···H_2O−Co to give a two-dimensional rhombic network.[26] Each grid of polymer **1** consists of 44-membered rings $Co_4(bbbt)_4$. $Co_4(bbbt)_4$ fragments are bridged by Co(II) ions and bbbt ligands into the two-dimensional network, which is parallel to the crystallographic *ac* plane.

The solid-state structure of polymer **1** exhibits a layered packing mode (Figure 3). The shortest distance between adjacent layers is 2.901 Å, which shows that there are $\pi-\pi$ interactions between adjacent layers. These interactions are weaker than the metal−nitrogen bonds, but they are important in supramolecular chemistry.

The crystal structure of polymer **2** is similar to that of polymer **1**. The coordination environment around the Mn(II) ion is a distorted octahedron. The bond lengths of Mn−N_{bbbt} (2.330 Å) and Mn−N_{NCS} (2.166 Å) are slightly longer than those of Co−N_{bbbt} (2.218 Å) and Co−N_{NCS} (2.055 Å) in polymer **1**, identical with those found in $[Mn(NCS)_2(bpe)_2(H_2O)_2]$ (Mn−N_{bpe} = 2.285 Å, Mn−N_{NCS} = 2.164 Å).[16] The bond angles around Mn(II) ions are 180° or close to 90° [83.74(9)−96.26(9)°]. The Mn(II) centers are linked by bbbt ligands leading to a two-dimensional rhombohedral grid plane. Those planes are parallel to the crystallographic *ac* plane and are packed through $\pi-\pi$ interactions between adjacent layers. Each grid consists of four Mn(II) ions and four bbbt ligands; the angle between two ligands is 55.9°or 124.1° with the dimensions of 13.106 × 10.797 Å and the diagonal distances of 21.140 × 11.396 Å. Parallel benzene rings from two parallel edges of the rhombohedral grid have the shortest distances of 3.340 or 6.060 Å, respectively. The data are slightly different from those of polymer **1**.

Polymer **3** also has a similar layered packing mode and two-dimensional rhombohedral grid structure as polymers **1** and **2**. Four vertexes of the rhombic grid are occupied by

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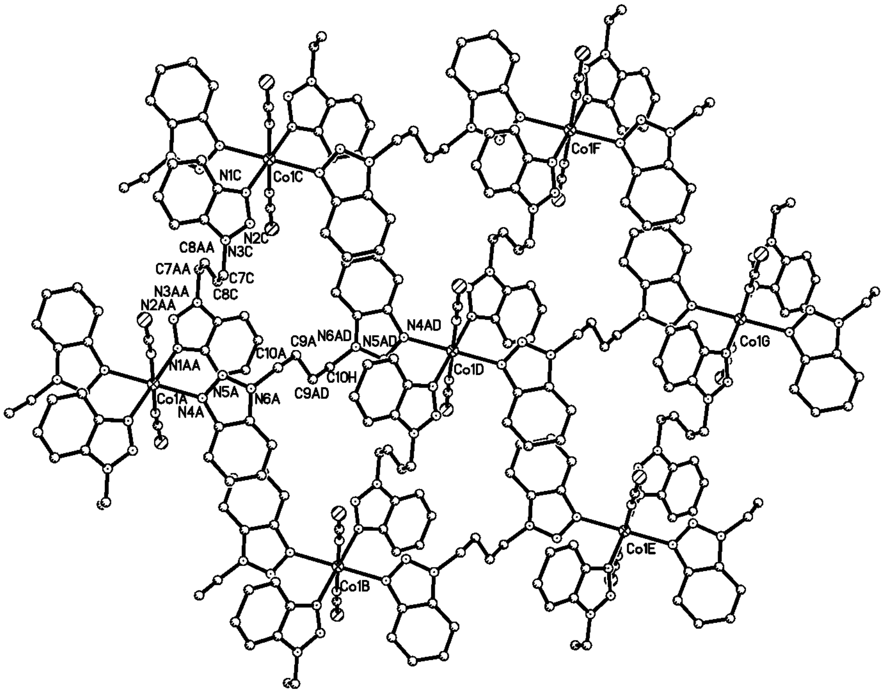

Figure 2. The two-dimensional rhombohedral grid structure of polymer **1** along the *b* direction.

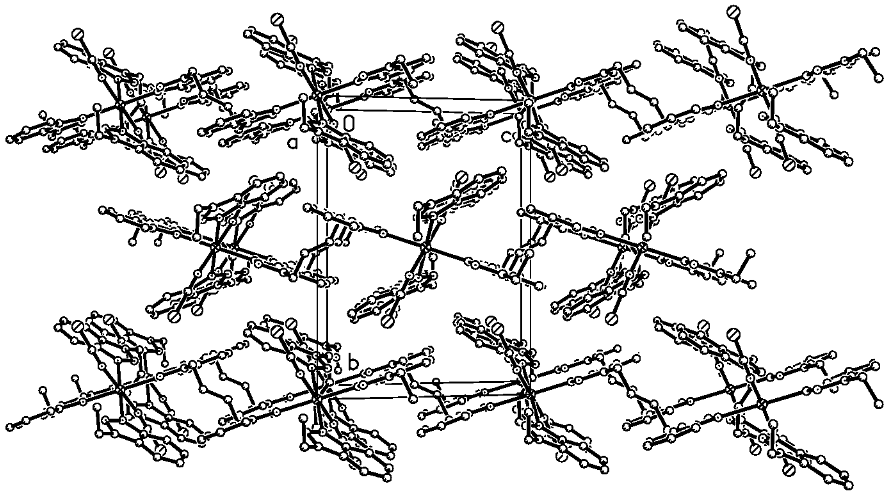

Figure 3. The solid-state structure of polymer **1** showing layered packing along the *a* direction.

Cd(II) ions and four bbbt ligands occupy the four edges. The angle between the two edges of the rhombohedral grid (55.2° or 124.8°) is different from those of polymers **1** and **2**. The dimension of the rhombohedral grid is 13.256 × 10.870 Å, which is larger than those of polymers **1** and **2**. The Cd(II) ion is in a distorted octahedral geometry too. The bond lengths of $Cd-N_{bbbt}$ (2.406 Å) and $Cd-N_{NCS}$ (2.265 Å) are longer than those of polymers **1** and **2**, but $Cd-N_{bbbt}$ bond lengths are consistent with those of the reported polymer $[Cd(NO_3)_2(py_2CH_2)_2]_n$ (the $Cd-N_{py}$ bond length is 2.369 Å).[68]

Nonlinear Optical Properties. The study about coordination polymers is greatly focused on novel structures and magnetic properties,[9,13] and a few papers reported their second-order NLO properties.[8,10,11] Our research interest is third-order NLO properties of coordination polymers. The UV−vis spectrum of polymers **1**−**3** in DMF solution shows that all three polymers have a strong peak at about 276 nm, and they give very low linear absorption ranging from 360 to 800 nm. They exhibit linear absorption similar to other coordination polymers.[31,56] We determined the molecular weight of polymers **1** and **3** in DMF solution and the results show that their molecular weights are 8458 and 8385, respectively. Because the solubility of polymer **2** is very small in DMF, we cannot obtain its molecular weight. After polymer **2** was left in DMF for one week, we found that its solubility did not increase.

The NLO properties of polymers **1**−**3** are investigated with a 532 nm laser pulse of 8 ns duration in 3.6×10^{-4} mol·dm^{-3} for polymer **1**, 3.5×10^{-4} mol·dm^{-3} for polymer **2**, and 3.3×10^{-4} mol·dm^{-3} for polymer **3** in a DMF solution. We found that all three polymers possess strong nonlinear optical

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Table 3. Optical Parameters of Selected NLO Chromophores

compds	color	α_2/m W^{-1}	n_2/m^2 W^{-1}	γ/esu	ref
organometallic compounds					
Group 10 metal alkynyl polymers				5.6×10^{-35} to 8.6×10^{-34}	71, 72
metallophalocyanines				1.0×10^{-32} to 1.0×10^{-31}	73
octopolar alkynylruthenium complexes				9.3×10^{-35} to 3.6×10^{-33}	74
ferrocene				$(1.61 \pm 0.18) \times 10^{-35}$	75
ferrocenecarboxaldehyde				$(1.69 \pm 0.08) \times 10^{-35}$	76
$FcCH{=}CHC_6H_5$				$(8.55 \pm 1.98) \times 10^{-35}$	76
$1,1'$-$Fc(CH{=}CHC_6H_5)_2$				$(2.70 \pm 0.26) \times 10^{-34}$	76
$CHO(-FcCH{=}CHC_6H_5CH{=}CH-)_n$				$(1.55 \pm 0.27) \times 10^{-33}$	76
$FcC(CH_3){=}N_2HCS_2CH_2C_6H_5$				3.11×10^{-35}	76
trans-$[Mo(CO)_4(PPh_3)_2]$				3.3×10^{-32}	77
cis-$[Mo(CO)_4(PPh_3)_2]$				1.7×10^{-31}	77
semiconductors					
InSb				1.7×10^{-33}	78
Ge				2.3×10^{-33}	78
fullerene					
C_{60}				5×10^{-34}	79
C_{70}				3×10^{-33}	79
cluster compounds					
$[MoCu_2OS_3(pph_3)_3]$	red	2.6×10^{-10}	5.0×10^{-17}	9.8×10^{-28}	62
$[WCu_2OS_3(pph_3)_4]$	yellow		8.0×10^{-18}	9.0×10^{-29}	62
$[MoOS_3Cu_3(SCN)(Py)_5]$	deep red	4.8×10^{-10}	-6.8×10^{-17}	5.8×10^{-27}	69
$[WOS_3Cu_3(SCN)(Py)_5]$	orange	6.0×10^{-11}	-1.2×10^{-17}	2.2×10^{-27}	69
$\{[Et_4N]_2[MoS_4Cu_4(CN)_4]\}_n$	black	1.5×10^{-9}	1.8×10^{-16}	1.2×10^{-29}	80
$\{[Et_4N]_2[WS_4Cu_4(CN)_4]\}_n$	red	1.6×10^{-9}	1.2×10^{-16}	1.3×10^{-29}	80
$[W_2Ag_4S_8(AsPh_3)_4]$	orange	2.8×10^{-9}	5.9×10^{-17}	8.3×10^{-28}	81
$[Et_4N]_3[WOS_3(CuBr)_3(\mu_2\text{-}Br)]\cdot 2H_2O$	deep red	6.0×10^{-10}	1.1×10^{-16}	1.6×10^{-28}	82
$[Et_4N]_3[WOS_3(CuI)_3(\mu_2\text{-}I)]$	yellow	1.0×10^{-10}	-5.0×10^{-18}	2.8×10^{-29}	83
coordination polymers					
$[Co(NCS)_2(bpms)_2]_n$	pale red		-3.0×10^{-18}	1.02×10^{-30}	31
$[\{Mn(NCS)_2(4,4'\text{-}bbp)(H_2O)_2\}(4,4'\text{-}bbp)]_n$	yellow		$<-10^{-19}$	$<5.4 \times 10^{-32}$	56
$[Mn(N_3)_2(bbp)_2]_n$	pale yellow		1.21×10^{-18}	1.18×10^{-30}	57
$\{[Mn(NCS)_2(bbp)_2]\cdot 0.25H_2O\}_n$	pale yellow		6.71×10^{-19}	2.92×10^{-30}	57
$\{[Zn(NCS)_2(bpfp)_2]\cdot 2H_2O\}_n$	colorless	7.1×10^{-9}	5.5×10^{-19}	1.8×10^{-30}	84
$[Co(bbbt)_2(NCS)_2]_n$	pale red	5.4×10^{-9}	5.7×10^{-19}	2.40×10^{-30}	this work
$[Mn(bbbt)_2(NCS)_2]_n$	colorless	5.2×10^{-9}	3.6×10^{-19}	1.52×10^{-30}	this work
$[Cd(bbbt)_2(NCS)_2]_n$	colorless	5.0×10^{-9}	3.1×10^{-19}	1.50×10^{-30}	this work
$[Mn(SO_4)(4,4'\text{-}bpy)(H_2O)_2]_n$	pale yellow		-1.4×10^{-18}	1.45×10^{-30}	56
$[Mn(N_3)_2(4,4'\text{-}bpy)]_n$	pale yellow		-3.4×10^{-18}	3.64×10^{-31}	56
$[Cd(N_3)_2(bpfp)]_n$	colorless	6.9×10^{-9}	4.1×10^{-19}	2.7×10^{-30}	84

absorption and refraction effects. The NLO absorption components were evaluated by Z-scan experiment under an open aperture configuration. The NLO absorption data can be well represented by eq 1 and 2, which describe a third-order NLO process[60] where 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, t is the time, and t_0 is the pulse width.

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

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

Panels a−c in Figure 4 depict NLO absorptive properties of polymers **1**−**3**, respectively. The panels clearly illustrate that the absorption increases as the incident light irradiance rises. It can be seen from Figure 4a that the normalized transmittance drops to about 67% at the focus, which shows polymer **1** has a strong NLO absorptive effect. The third-order NLO absorptive coefficient α_2 is calculated to be 5.4×10^{-9} m W^{-1}. The normalized transmittances drop to about 90% for cluster compounds $WOS_3Cu_3(SCN)(Py)_5$ ($\alpha_2 = 6.0 \times 10^{-11}$ m W^{-1})[69] and $[MoI(bPy)_2][MoOS_3Cu_3I_2(bPy)]$ ($\alpha_2 = 3.0 \times 10^{-10}$ m W^{-1}),[70] 80% for $MoCu_2OS_3(pph_3)_3$ ($\alpha_2 = 2.6 \times 10^{-10}$ m W^{-1})[61] and $MoOS_3Cu_3I(bMebPy)_2$ ($\alpha_2 = 3.5 \times 10^{-10}$ m W^{-1}),[70] and 60% for cluster compound $MoOS_3Cu_3(SCN)(Py)_5$ ($\alpha_2 = 4.8 \times 10^{-10}$ m W^{-1}).[69] Figure 4b shows that the normalized transmittance of polymer **2** drops to about 70% at the focus, and the corresponding α_2 value is 5.2×10^{-9} m W^{-1}. The normalized transmittance of polymer **3** drops to about 74% at the focus, as given in Figure 4c, α_2 is 5.0×10^{-9} m W^{-1}. The reported parameters of some best performing organometallic compounds, semiconductors, fullerene, cluster compounds, and related coordination polymers are listed in Table 3. It is obvious that the three polymers exhibit very strong NLO absorption, and the α_2 values are larger than those of all the reported cluster compounds.

The NLO refractive effects are assessed by dividing the normalized Z-scan data obtained under the closed aperture

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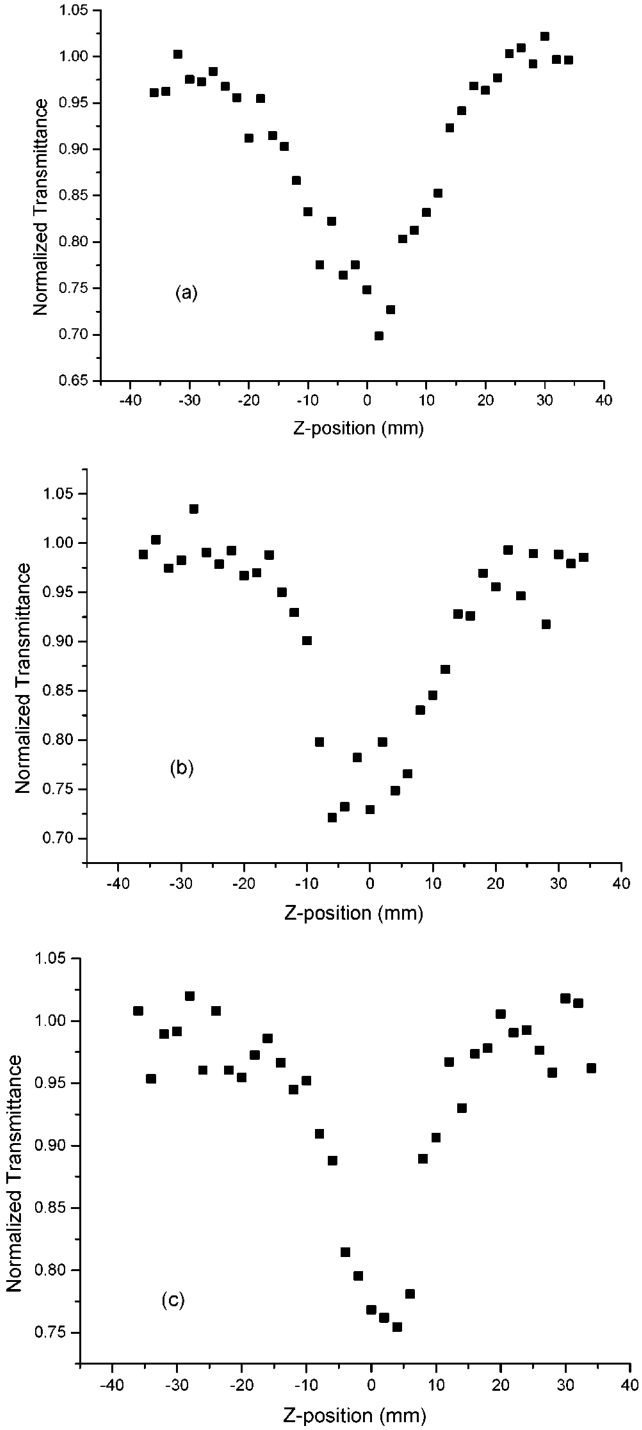

Figure 4. The data were collected under an open aperture configuration at 532 nm. (a) NLO absorptive behavior of polymer **1** in 3.6 × 10^{-4} mol·dm^{-3} DMF solution. (b) NLO absorptive behavior of polymer **2** in 3.3 × 10^{-4} mol·dm^{-3} DMF solution. (c) NLO absorptive behavior of polymer **3** in 3.5 × 10^{-4} mol·dm^{-3} DMF solution.

configuration by the normalized Z-scan data obtained under the open aperture configuration. The third-order NLO refractive index n_2 can be derived by eq 3, where ΔT_{V-P} is

$$n_2 = \frac{\lambda\alpha_0}{0.812\pi I(1 - e^{-\alpha_0 L})}\Delta T_{V-P} \qquad (3)$$

the difference between normalized transmittance values at the valley and peak portions.

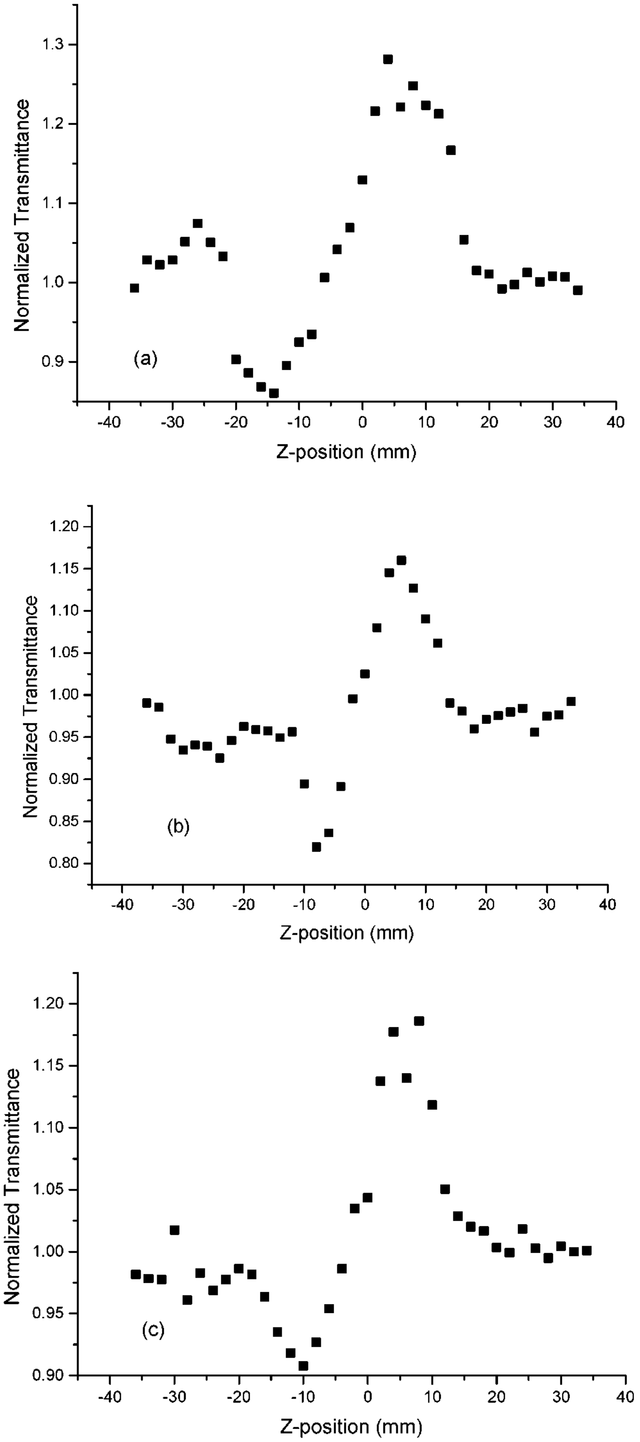

Figure 5. The data are assessed by dividing the normalized Z-scan data obtained under the closed aperture configuration by the normalized Z-scan data obtained under the open aperture configuration. (a) The self-focusing effects of polymer **1** in 3.6 × 10^{-4} mol·dm^{-3} DMF solution at 532 nm. (b) The self-focusing effects of polymer **2** in 3.3 × 10^{-4} mol·dm^{-3} DMF solution at 532 nm. (c) The self-focusing effects of polymer **3** in 3.5 × 10^{-4} mol·dm^{-3} DMF solution at 532 nm.

Figure 5a−c gives the NLO refractive effects of polymers **1**−**3**, respectively. The data show that the three polymers have a similar positive sign for the refractive nonlinearity, which gives rise to self-focusing behavior. It can be seen from Figure 5a that the difference of valley−peak positions, ΔZ_{V-P}, is 17 mm; the difference between normalized transmittance values at valley and peak portions, ΔT_{V-P}, is 0.42. The refractive index n_2 of polymer **1** can be calculated to be 5.73×10^{-19} m^2 W^{-1} by eq 3. The data are close to those of the reported clusters $WCu_2OS_3(pph_3)_4$ ($\Delta Z_{V-P} =$ 12 mm, $\Delta T_{V-P} = 0.04$)[62] and $MoCu_2OS_3(pph_3)_3$ ($\Delta Z_{V-P} =$ 12 mm, $\Delta T_{V-P} = 0.49$).[62] In accordance with Figure 5b, ΔZ_{V-P} and ΔT_{V-P} are 14 mm and 0.34, respectively; an n_2 value of 3.55×10^{-19} m^2 W^{-1} is obtained from eq 3. This shows polymer **2** has strong self-focusing behavior too. In Figure 5c, $\Delta Z_{V-P} = 18$ mm, $\Delta T_{V-P} = 0.28$, and the n_2 value of polymer **3** is 3.07×10^{-19} m^2 W^{-1}.

The third-order NLO susceptibility $\chi^{(3)}$ values of polymers **1**−**3** are calculated by eq 4, where ϵ_0 and c are the

$$|\chi^3| = \sqrt{\left|\frac{(9 \times 10^8)\epsilon_0 {n_0}^2 c^2}{2\nu}\alpha_2\right|^2 + \left|\frac{c{n_0}^2}{80\pi}n_2\right|^2} \qquad (5)$$

permittivity and speed of light in a vacuum, ν is the frequency of the laser light, n_0 is the linear refractive index of the sample, and α_2 and n_2 are third-order nonlinear absorptive and refractive indexes, respectively. Thus, the larger the α_2 and n_2 values of a polymer, the larger is $\chi^{(3)}$. The $\chi^{(3)}$ values of polymers **1**−**3** are calculated to be 2.05×10^{-12}, 1.27×10^{-12}, and 1.10×10^{-12} esu, respectively. The corresponding modulus of the hyperpolarizability γ was obtained from $|\gamma| = \chi^{(3)}/NF$,[4] where N is the number density of a compound (concentration) and $F^4 = 3$ is the local field correction factor. The γ values of polymers **1**, **2**, and **3** are calculated to be 1.52×10^{-30}, 1.50×10^{-30}, and 1.45×10^{-30} esu, respectively. One can see from Table 3 that the γ values of coordination polymers ranging from 10^{-32} to 10^{-30} esu are comparable to those of clusters and better than those observed in organometallic compounds, semiconductors, and fullerene. The γ values of clusters are in the range of 10^{-29}–10^{-27} esu, such as 2.2×10^{-27} and 1.3×10^{-29} esu for clusters $[WOS_3Cu_3(SCN)(Py)_5]$ and $\{[Et_4N]_2[WS_4Cu_4(CN)_4]\}_n$; the γ values of organometallic compounds range from 10^{-35} to 10^{-31} esu; and the γ values of semiconductors InSb, Ge, C_{60}, and C_{70} are 1.7×10^{-33}, 2.3×10^{-33}, 7.5×10^{-34}, and 1.3×10^{-33} esu, respectively. Thus coordination polymers will become promising candidates for NLO materials.

We have investigated the reported literature concerning the third-order NLO properties of coordination polymers. One-dimensional coordination polymers $[Co(NCS)_2(bpms)_2]_n$[31] and $[\{Mn(NCS)_2(4,4'\text{-bbp})(H_2O)_2\}(4,4'\text{-bbp})]_n$[56] show self-defocusing behavior. All two-dimensional rhombohedral grid coordination polymers, such as $[Mn(N_3)_2(bbp)_2]_n$, $\{[Mn(NCS)_2(bbp)_2]\cdot 0.25H_2O\}_n$,[57] $\{[Zn(NCS)_2(bpfp)_2]\cdot 2H_2O\}_n$,[84] $[Co(bbbt)_2(NCS)_2]_n$, $[Mn(bbbt)_2(NCS)_2]_n$, and $[Cd(bbbt)_2(NCS)_2]_n$, show strong self-focusing effects. Three-dimensional polymers $[Mn(SO_4)(4,4'\text{-bpy})(H_2O)_2]_n$ and $[Mn(N_3)_2(4,4'\text{-bpy})]_n$[56] exhibit self-defocusing behavior, but $[Cd(N_3)_2(bpfp)]_n$[84] shows self-focusing effects. We can conclude that all two-dimensional rhombohedral grid polymers possess strong self-focusing properties; one-dimensional chain polymers have self-defocusing behavior; and three-dimensional polymers have either self-focusing or self-defocusing effects depending on their structures. In addition, the valence shell structure of central ions may has some influence on the strength of NLO properties. The valence shell structures of Co(II), Mn(II), and Cd(II) ions are 3d^7, 3d^5, and 4d^{10}, respectively. The decreased π back-donation capacity from Co(II) to Cd(II) reduces the extension of the electronic π-system.[85] Inspection of γ values (polymers **1**, **2**, and **3**) reveals a slight decrease in this parameter though the difference among **1**, **2**, and **3** is negligible considering the experimental errors in the data.

Acknowledgment. We are grateful for financial support from the National Natural Science Foundation of China (No. 20001006), Innovation Engineering Foundation of Henan Province, and Outstanding Young Teacher Foundation of Ministry of Education.

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