Polymeric Complexes with "Piperazine–Pyridine" Building Blocks: Synthesis, Network Structures, and Third-Order Nonlinear Optical Properties

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ABSTRACT: A new bidentate "building block", N,N-bis(3-pyridylformyl)piperazine (bpfp), was synthesized. X-ray diffraction studies reveal that the piperazine ring in bpfp forms a chairlike structure conformation. bpfp self-assembled into two-dimensional layered rhombohedral grid polymers $\{[Mn(H_2O)_2 (SO_4)(bpfp)](H_2O_3(CH_3OH))_n$ (1) and $\{[Zn(NCS)_2(bpfp)_2]\cdot 2H_2O\}_n$ (2) with Mn(II) and Zn(II), a threedimensional polymer $[Cd(N_3)_2(bpfp)]_n$ (3) with Cd(II), and a one-dimensional zigzag polymer $[HgI_2(bpfp)]_n$ (4) with Hg(II). Each rhombohedral grid in polymer 1 is composed of four Mn, two bpfp, and two $SO_4^{2^2}$ the dimensions of the grid are 6.537×12.843 Å. In polymer 2, each rhombohedral grid consists of 60membered rings $Zn_4(bpfp)_4$ showing the dimensions of 14.231×15.586 Å. $Zn_4(bpfp)_4$ grids are bridged by Zn ions and all pyridyl-N atoms of bpfp ligands into the 2-D network structure along a and c directions. Polymer **3** exhibits a 3-D layered structure with tetragonal prism channel viewing from *a* direction. The bpfp ligands occupy the four edges of tetragonal prism channel, which is cut off by layers consisting of rhombohedral grids $Cd_4(N_3)_4$. Polymer **4** is quite different from polymers **1**-**3**; it exhibits a 1-D zigzag framework extending along the c axis. Polymers 1-3 possess a very strong NLO absorption and selffocusing effect. Their third-order NLO absorptive coefficients α_2 are 9.2×10^{-9} , 6.9×10^{-9} , and 7.1×10^{-9} m W⁻¹. The third-order NLO hyperpolarizabilities γ are 1.79×10^{-28} , 9.10×10^{-29} , and 9.66×10^{-29} esu, respectively. The γ values are comparable to those of the best NLO materials and coordination polymers. We found that the valence shell structures of central metal ions can influence the NLO properties of coordination polymers.

Introduction

Crystal engineering of supramolecular architectures is the most efficient approach toward novel organic/ inorganic composite materials, catalysis, auxetic, and optical, electronic, and magnetic materials.^{1–5} We are interested in developing both novel structures and nonlinear optical (NLO) materials of coordination polymers.^{6–10}

The existing coordination polymers can be classified into three categories. The first is "bipyridyl-based" or O(S)-containing polymers, which have generated a wide range of infinite frameworks, including diamondoid, honeycomb, square grid, ladder, brick, octahedral, and T-shaped.^{11–20} The second is the polymers with macrocyclic structure, such as one-dimensional molecular ladder with macrocyclic platforms, two-dimensional layered polymers, and three-dimensional PtS-like net structure.^{21–23} The third is polyoxomolybdate or vanadate cluster anion-containing polymers, such as one-dimensional chain Ni₂(2,2'-bpy)₄Mo₈O₂₆, layered structure [Ni(H₂O)₂(4,4'-bpy)₂]₂Mo₈O₂₆, and threedimensional network compound (N₂H₅)₂[Zn₃V₁₈O₄₂ (SO₄)(H₂O)₁₂]·24H₂O.^{24–26}

In addition, coordination polymers are of great current interest because of the formation of fascinating structures with potentials in applications. Among all the networks, the polymers with large pores and chiral or helical structures are of particular importance.^{27–30}

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Fujita synthesized a big square-grid polymer with dimensions of about 20 \times 20 Å.²⁸ Zaworotko reported several helical coordination polymers with large chiral cavities.³⁰ A square-grid polymer $\{[Cd(bpy)_2](NO_3)_2\}_n$ shows catalytic activity, and it accelerates cyanosilylation reactions.³¹ A honeycomb-like polymer Ag-tris(pcyanobenzene)ethynylbenzene exhibits auxetic properties, such as a negative coefficient of thermal expansion.³² Polymer { $[Cd_3(\mu_3-OH)L_3(py)_6](ClO_4)_2$ }_n (L = 4-[2-(4pyridyl)ethenyl]benzoate) has a powder SHG efficiency approximately 10 times higher than that of technologically useful potassium dihydrogen phosphate (KDP).² $[NdM(bpym)(H_2O)_4(CN)_6] \cdot 3H_2O$ (M = Fe, Co) exhibits unusual magnetic behavior.³³ 3-D porous structural [Ag-(4,4'-bpy)(NO₃)] shows ion-exchange properties.³⁴ NLO properties, especially third-order NLO properties, have received little attention. In principle, compared with traditional NLO material, such as organic molecules, the incorporation of metal atoms introduce more sublevels into the energy hierarchy, which permits a more allowed electronic transition to take place and hence a larger NLO effect.^{35–39} In this paper, we synthesized a new bidentate ligand, N,N-bis(3-pyridyl formyl)piperazine (bpfp), and solved its crystal structures. The bpfp self-assembled into 2-D polymers $\{[Mn(H_2O)_2(SO_4) (bpfp)](H_2O)_3(CH_3OH)_n$ (1) and $\{[Zn(NCS)_2(bpfp)_2]$. $2H_2O_{n}$ (2) with Mn(II) and Zn(II), a 3-D layered polymer $[Cd(N_3)_2(bpfp)]_n$ (3) with Cd(II), and a 1-D zigzag polymer [HgI₂(bpfp)]_n (4) with Hg(II). Polymers 1-3 exhibit a very strong NLO absorption and selffocusing effect. Their third-order NLO absorptive coefficients α_2 are 9.2 \times 10⁻⁹, 6.9 \times 10⁻⁹, and 7.1 \times 10⁻⁹ m

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Table 1. Crysta	llographic Data	for bpfp, {	$[Mn(H_2O)_2(SO_4)]$	ı)(bpfp)](H ₂ O) ₃ (CH ₃ OH)} _n	(1), { [Zn(NCS)2(bpfp)2]·2H2O}n (2)),
		[Cd()	$N_{3}_{2}(bpfp)_{2}]_{n}$ (3)), and [HgI ₂ (bpfp)] _n (4)			

	bpfp	1	2	3	4
formula	$C_{16}H_{16}N_4O_2$	C17H30MnN4O12S	$C_{34}H_{36}N_{10}O_6S_2Zn$	$C_{16}H_{16}CdN_{10}O_2$	$C_{16}H_{16}HgI_2N_4O_2$
fw	296.33	569.45	405.11	492.79	750.72
crystal system	monoclinic	triclinic	triclinic	monoclinic	orthorhombic
space group	p2(1)/c	<i>p</i> -1	<i>p</i> -1	p2(1)/c	pca2(1)
<i>T</i> /K	293(2)	291(2)	293(2)	291(2)	291(2)
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
a/Å	7.8217(16)	8.5560(17)	8.5726(17)	12.582(3)	23.079(5)
b/Å	8.0253(16)	12.543(3)	8.6870(17)	7.4652(15)	6.3628(13)
c/Å	11.648(2)	12.843(3)	12.487(3)	9.903(2)	14.063(3)
α/deg	90	90	93.05(3)	90	90
β/deg	96.94(3)	96.44(3)	97.21(3)	101.33(3)	90
γ/deg	90	90	91.58(3)	90	90
V/Å ^{3*}	725.8(3)	1213.9(4)	920.7(3)	912.0(3)	2065.2(7)
Ζ	2	2	2	2	4
$ ho_{ m calcd}/ m mg~ m cm^{-3}$	1.356	1.558	1.461	1.795	2.415
absorption coeff/mm 0.093	0.698	0.839	1.236	10.459	
F(000)	312	594	420	492	1368
reflections collected	1672	4598	3292	3220	6874
unique reflections (<i>R</i> (int))	1277 (0.0549)	4598 (0.0000)	3292 (0.0000)	1865 (0.0304)	23051 (0.06031)
data/restraints/parameters	1277/0/117	4598/0/394	3292/0/250	1865/0/150	2305/1/227
goodness-of-fit on F^z	1.104	1.111	1.047	1.180	1.097
$R1[I > 2\sigma(I)]$	0.0561	0.0540	0.0451	0.0354	0.0452
$WR2[I > 2\sigma(I)]$	0.1317	0.1536	0.0947	0.0849	0.1043

W⁻¹. The α_2 values are larger than those of all the reported NLO materials. The third-order NLO hyperpolarizabilities γ are 1.79×10^{-28} , 9.10×10^{-29} , and 9.66×10^{-29} esu, respectively. The γ values are comparable to those of the best NLO materials and coordination polymers.

Experimental Section

Both $SOCl_2$ and py were freshly distilled prior to use. Piperazine was obtained by drying piperazine hexahydrate with Na_2SO_4 .

IR spectra were recorded on a Fourier Nicolet FT-170SX spectrophotometer with pressed KBr pellets. Carbon, hydrogen, and nitrogen analyses were performed by a PE 240C elemental analyzer. Thermoanalysis were recorded on a TG-DTA-DSC instrument. UV-vis spectra were recorded, ranging from 250 to 800 nm, on a Hitachi-220A UV-vis spectrophotometer. NMR spectra were recorded on a Bruker DPX-400 spectrometer.

Synthesis of N,N-Bis(3-pyridylformyl)piperazine (bpfp). SOCl₂ (17.5 g, 0.147 mol) was dropwise added into nicotinic acid (4.45 g, 0.0362 mol) in a three-necked roundbottom flask (100 mL) with constant stirring. The resultant pale-yellow solution was refluxed for 2 h. Yellow powder could be obtained after distilling off solvent in a vacuum at room temperature. Then we dissolved the yellow powder in 10 mL of py. A solution of 1.55 g (0.018 mol) of piperazine in 15 mL of py was added to the above py solution. The mixture was refluxed for 10 h. The color of the solution changed to brownred, and a pale brown powder precipitated. After filtering, the precipitate was recrystallized from 20 mL of H_2O at pH = 8to yield bpfp as pale yellow crystals. Yield: 2.1 g (40%); mp 197-198 °C. Anal. Calcd for C₁₆H₁₆N₄O₂: C, 57.83; H, 4.82; N, 16.87. Found: C, 58.01; H, 4.98; N, 16.94. ¹H NMR (CDCl₃) δ : 8.694 (s, 8H, piperazine), 7.284–7.427 (s, 4H, py), 7.783–7.802 (s, 4H, py). $^{13}\mathrm{C}$ NMR (CDCl_3) δ : 168.088 (m, –CO–), 151.298 (m, py), 147.932 (m, py), 135.188 (m, py), 130.808 (m, py), 123.675 (m, py), 47.580 (w, piperazine), 42.416 (w, piperazine).

Synthesis of {**[Mn(H₂O)₂(SO₄)(bpfp)](H₂O)₃(CH₃OH)**}_n (1). A 5 mL methanol solution of bpfp (59.2 mg, 0.2 mmol) was slowly added into a 5 mL water solution of MnSO₄·H₂O (16.9 mg, 0.1 mmol) to give a clear solution. The colorless crystals (yield 57%) suitable for X-ray single-crystal analysis were obtained after standing for 1 week at room temperature. Crystals of 1 are stable in the air. IR (KBr): 3386 (s), 1616 (s), 1598 cm⁻¹ (s). Anal. Calcd for C₁₇H₃₀MnN₄O₁₂S (%): C, 35.82; H, 5.27; N, 9.83. Found: C, 35.73; H, 5.35; N, 9. 92. **Synthesis of** {**[Zn(NCS)₂(bpfp)₂]·2H₂O**}_{*n*} (2). A solution of KNCS (19.4 mg, 0.2 mmol) in 1 mL of H₂O was added into a solution of Zn(NO₃)₂·6H₂O (29.7 mg, 0.1 mmol) in 1 mL of CH₃OH, and then bpfp (59.2 mg, 0.2 mmol) in 3 mL of CH₃OH was dropwise added into above mixture. Colorless crystals (62%) were yielded at room temperature 1 week later. IR (KBr): 2100 cm⁻¹ (s, NCS⁻). Anal. Calcd for C₃₄H₃₆N₁₀O₆S₂-Zn: C, 50.37; H, 4.44; N, 17.28. Found: C, 50.82; H, 4.57; N, 17.48.

Synthesis of $[Cd(N_3)_2(bpfp)]_n$ (3). NaN₃ (13.0 mg, 0.2 mmol) in 1 mL of H₂O was slowly added to an aqueous solution of Cd(NO₃)₂·6H₂O (34.5 mg, 0.1 mmol, 2 mL), and then bpfp (29.6 mg, 0.1 mmol) in 2 mL of CH₃OH was dropwise added into the above mixture. Pale yellow crystals (45%) were obtained at room temperature 2 weeks later. IR (KBr): 2100 cm⁻¹ (s, N₃⁻). Anal. Calcd for C₁₆H₁₆CdN₁₀O₂: C, 38.95; H, 3.25; N, 28.40. Found: C, 39.23; H, 3.35; N, 28.87.

Synthesis of [HgI₂(bpfp)]_n (4). A 5 mL methanol solution of bpfp (59.2 mg, 0.2 mmol) was dropwise added into a 5 mL THF solution of HgI₂ (46 mg, 0.1 mmol). After slow evaporation of the solvent, colorless crystals (yield 48%) suitable for X-ray single-crystal analysis were obtained after 2 days at room temperature. Crystals of 4 are air-stable. IR (KBr): 1627 (s), 1482 (s), 1463 (s), 730 cm⁻¹ (s). Anal. Calcd for C₁₆H₁₆HgI₂N₄O₂ (yield 56%): C, 25.58; H, 2.13; N, 7.46. Found: C, 25.77; H, 2.08; N, 7.51.

Crystallographic Data Collection and Refinement of the Structures. All the data were collected on a Rigaku RAXIS-IV imaging plate area detector diffractometer using graphite monochromatic Mo–K α radiation ($\lambda = 0.710$ 73 Å). A prismatic single crystal was mounted on a glass fiber. The data were collected at a temperature of 18 ± 1 °C and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied. The structures were solved by direct methods and expanded using Fourier techniques. The nonhydrogen 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 using the SHELXL-97 program.⁴⁰ Table 1 shows crystal data and structure refinement of the three polymers. Selected bond lengths and bond angles are listed in Table 2.

Molecular Weight Measurements. The molecular weight and molecular weight distribution of the polymers were determined at 40 °C with gel permeation chromatography (Waters Associates model HPLC/GPC 515 liquid chromatograph, equipped with a refractive index detector, μ -Styragel columns and calibrated with standard polystyrene), using DMF as eluent and a flow rate of 1.0 mL min⁻¹.



Figure 1. Layered structure formed by hydrogen bonds in bpfp.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of bpfp, $\{[Mn(H_2O)_2(SO_4)(bpfp)](H_2O)_3 (CH_3OH)\}_n$ (1), $\{[Zn(NCS)_2(bpfp)_2]\cdot 2H_2O\}_n$ (2), $[Cd(N_3)_2(bpfp)_2]_n$ (3), and $[HgI_2(bpfp)]_n$ (4)

			bpfp				
C(6) - O(1) N(2) - C(8)	1.228(3) 1.465(3)	C(6)-N(2) N(1)-C(1)	1.351(3) 1 341(3)	C(6)-C(4)	1.509(3)	N(2)-C(7)	1.462(3)
O(1) - C(6) - N(2)	122 6(2)	O(1) - C(6) - C(4)	119 0(2)	N(2) - C(6) - C(4)	118 3(2)		
C(6) - N(2) - C(7)	125.5(2)	C(6) - N(2) - C(8)	119.8(2)	C(7) - N(2) - C(8)	113.9(2)		
C(2) - C(3) - C(4)	119.1(2)		110.0(2)		110.0(2)		
	11011(2)			(CII OII)) (4)			
$\mathbf{M}_{\mathrm{res}}(1) = O(2)$	0.004(0)	$\{[Mn(H_2O)_2($	SO_4)(bpfp)](H ₂ ($J_{3}(CH_{3}OH)_{n}(\mathbf{I})$	0.010(0)		
Mn(1) = O(3)	2.204(2)	Mn(1) = O(2)	2.218(2)	Mn(1) = N(3) Mn(2) = N(2)	2.313(2)		
Mn(2) = O(6)	2.175(2)	Mn(z) = O(7)	2.181(2)	Mn(z) = N(3)	2.291(2)		
N(1) = C(5)	1.336(3)	N(2) = C(8)	1.403(3)	S(1) = O(3) $S(1) = O(2)$ $M_{12}(1)$	1.504(2)		
N(3) - Mn(1) - O(2)	84.63(7)	O(6) = Min(2) = N(3)	88.91(7)	S(1) = O(3) = Min(1)	138.41(9)		
N(1) = MII(1) = N(3)	89.08(0)	C(9) = N(3) = MII(2)	120.9(2)	C(3) = N(1) = C(1)	117.3(2)		
O(3) - S(1) - O(4)	110.6(1)						
		{[Zn(NCS)2(bpfp)2]·2	$H_2O_{n}(2)$			
Zn(1) - N(5)	2.101(2)	Zn(1)–N(3) 2.241(2)	Zn(1) - N(1)	2.247(2)	C(14) - O(2)	1.232(3)	
S(1)-C(17)	1.626(2)	N(1)-C(1)	1.347(2)	N(2) - C(6)	1.349(3)	N(3)-C(9)	1.347(2)
N(4)-C(14)	1.349(3)	N(4)-C(15) 1.467(3)	N(5)-C(17)	1.166(3)			
$N(5)-Zn(1)-N(3)\#^{1}$	92.20(7)	$N(5)-Zn(1)-N(1)\#^{1}$	88.98(7)	N(3) - Zn(1) - N(1)	94.29(6)		
N(5) - Zn(1) - N(3)	87.80(7)	C(17) - N(5) - Zn(1)	142.1(2)	C(1) - N(1) - Zn(1)	117.8(1)		
C(5) - N(1) - Zn(1)	123.8(1)	N(5)-C(17)-S(1)	178.2(2)	C(7) - N(2) - C(8)	114.1(2)		
			[Cd(N ₃) ₂ (hnfn) ₂]	" (3)			
Cd(1) - N(1)	2.326(3)	Cd(1) - N(2)	2.330(3)	Cd(1) - N(4)	2.362(2)	O(1) - C(6)	1.230(3)
N(2) - N(3)	1.160(4)	N(4) - C(1)	1.346(4)	N(5) - C(7)	1.469(3)	C(3) - C(2)	1.401(4)
N(1) - Cd(1) - N(2)	92.4(1)	N(1) - Cd(1) - N(4)	91.71(9)	N(2) - Cd(1) - N(4)	92.5(1)	., .,	
N(3) - N(2) - Cd(1)	152.5(3)	C(1) - N(4) - Cd(1)	122.7(2)	N(5) - C(6) - C(4)	119.2(2)		
N(4) - C(1) - C(2)	123.6(2)	$N(2) - N(3) - N(1)^{\#}$	175.3(3)	O(1) - C(6) - N(5)	123.1(2)		
O(1) - C(6) - C(4)	117.7(2)	C(6) - N(5) - C(7)	119.8(2)	C(6) - N(5) - C(8)	126.8(2)		
			[Hol_(hnfn)]	(4)			
$I(1) - H\sigma(1)$	2 656(2)	$H_{\sigma}(1) - N(1)$	$2 10^{12}(0^{12})^{10}$	$I(2) - H_{\sigma}(1)$	2 659(2)	$H_{\sigma}(1) - N(4)$	2 45(1)
$N(1) - H\sigma(1) - N(4)$	90.4(5)	$N(1) - H_{\sigma}(1) - I(1)$	103 1(3)	$I(1) - H\sigma(1) - I(2)$	14073(5)	118(1) 11(1)	w. 10(1)
$C(12) - N(4) - H_{\sigma}(1)$	123(1)	$C(16) - N(4) - H_{\sigma}(1)$	116(1)	·(·, ··································	110.70(0)		
	-~~(1)						

Nonlinear Optical Measurements. A DMF solution for polymer **1** (or **2**, **3**, **4**) was placed in a 1 mm quartz cuvette for NLO measurements. Their NLO properties were measured as described in the literature.⁴¹

Results and Discussion

Crystal Structures of *N*,*N*-**Bis(3-pyridyl formyl)piperazine (bpfp).** X-ray diffraction studies reveal that bpfp depicts a linear structure with a p2/c crystallographic symmetry center. The piperazine ring forms a chairlike conformation. The two NC₂ trigonal planes in piperazine unit are parallel and recline at an angle of 130.9° with the four C atoms plane. Two pyridine rings are in the *trans*-position and away from the center of symmetry center. They are also parallel; the dihedral angle with the four C atoms plane of the piperazine unit is 74.7°, and the dihedral angle with the NC₂ trigonal plane is 65.0°. The solid-state structure exhibits layered packing along *b* and *c* directions. Each layer consists of two types of bpfp, which are cross-linked together through O····H−C hydrogen bonds (Figure 1). In the same type of bpfp, the distance of N2C−N2A is 8.025 Å, and that of N2C−N2D is 11.648 Å.



Crystal Structures of { $[Mn(H_2O)_2(SO_4)(bpfp)]$ -(H₂O)₃(CH₃OH) $_n$ (1). Polymer 1 shows a 2-D layered structure with corrugated rhombohedral grids (Figure



Figure 2. Two-dimensional rhombohedral grid structure of $\{[Mn(H_2O)_2(SO_4)(bpfp)](H_2O)_3(CH_3OH)\}_{n}$.



Figure 3. Stacking mode of $\{[Mn(H_2O)_2(SO_4)(bpfp)](H_2O)_3(CH_3OH)\}_n$ along the *a* axis.

2). All Mn atoms are at a slightly distorted octahedron, in which the equatorial positions are occupied by four oxygen atoms from two H_2O and two SO_4^{2-} and the axial sites are occupied by two nitrogen atoms from bpfp groups. But these Mn atoms are not in the same coordination environment. The bond lengths of Mn1–O2 (2.218(2) Å), Mn1–O3 (2.204(2) Å), and Mn1–N1 (2.313(2) Å) are little longer than corresponding lengths of Mn2–O6 (2.175(2) Å), Mn2–O7 (2.181(2) Å), and Mn2–N3 (2.291(2) Å). The corresponding bond angles around Mn1 and Mn2 are also slightly different.

The bpfp ligands act as a μ_2 -bridge connecting Mn atoms into two types of chains along the *c* direction: -Mn1-bpfp-Mn1-bpfp- and -Mn2-bpfp-Mn2- bpfp-. The two types of -Mn-bpfp- chains are parallel and arranged alternatively along the *b* direction, which

are separated by 6.537 Å. At the same time, sulfate anions link two adjacent chains to result in an infinite 2-D corrugated rhombohedral grid structure. Each rhombohedral grid is composed of four Mn, two bpfp, and two SO₄²⁻. The dimensions of the grid are 6.537 × 12.843 Å, and the two neighboring angles in the grid are 113.4° and 66.6°. The diagonal-to-diagonal distances are 11.876 and 16.562 Å, respectively. Each 2-D layer is packed along the *a*-axis to lead a three-dimensional structure (Figure 3); the distance between two adjacent layers is 8.556 Å.

Several SO_4^2 -containing coordination polymers have been reported. In $[Mn(SO_4)(4,4'-bpy)(H_2O)_2]_{n}$ ⁷ two coordination SO_4^{2-} anions are in *cis*-positions; -Mn-bpy-Mn-bpy- chains between adjacent layers have an angle of 45° and are joined by zigzag $-Mn-SO_4^{2-}-Mn-SO_4^{2-}$



Figure 4. Two-dimensional rhombohedral grid structure of {[Zn(NCS)2(bpfp)2]·2H2O}n.

chains leading to the 3-D framework. The structure of $[Cu(bpe)(H_2O) (SO_4)]$ is constructed from one-dimensional $[Cu(bpe)(H_2O)]^{2+}$ chains linked through bridging sulfate groups into a 3-D framwork.⁴²

Crystal Structures of {**[Zn(NCS)**₂(**bpfp**)₂]·2H₂O}_{*n*} (2). Polymer 2 shows a two-dimensional rhombohedral grid network structure (Figure 4). Each grid consists of 60-membered rings Zn₄(bpfp)₄, in which Zn ions are linked by coordinatively bonded bridging bpfp. The distance of Zn1A–Zn1B is 15.586 Å, and those of Zn1A– Zn1D and Zn1B–Zn1D are 12.835 and 14.231 Å, respectively. The rhombohedral grid shows the dimensions of 14.231 × 15.586 Å. Zn₄(bpfp)₄ grids are bridged by Zn ions and all pyridyl-N atoms of bpfp ligands into the 2-D network structure along *a*- and *c*-directions. All Zn atoms are equivalent and serve as four-coordinated nodes. Zn ions adopt a distorted octahedral geometry with four equatorial pyridyl-N atoms and two axial NCS anions. The Zn–N_{py} bond lengths of 2.240 and 2.247 Å are longer than the Zn–N_{NCS} bond lengths of 2.10 Å.

There are two slightly different kinds of bpfp ligands, bpfp1 and bpfp2, in polymer **2**. Concerning bpfp1, the two pyridine rings are parallel and recline at an angle of 74.7° with NC₂ trigonal planes in the piperazine unit, and the dihedral angle with the four C atoms plane of piperazine unit is 112.9°. In bpfp2, the corresponding dihedral angles are 127.9° and 90.5°, respectively. The dihedral angle between a py ring of bpfp1 and one of bpfp2 is 71.1°.

Bpfp is a flexible dipyridyl ligand; treatment of the flexible ligands, py−X−py (X = (CH₂)_{1−6}, CH=CH, C≡ C, N=N, CH₂OC₆H₄OCH₂), with metal atoms gives rhombohedral grid rather than square-grid polymers.^{9,18−20,43−45} The reaction of rodlike rigid ligands with metal atoms forms square-grid polymers, such as $[Zn(bpy)_2(PF_6)_2]_n$, $\{[Cd(bpy)_2(H_2O)_2](NO_3)_2\}_n$, and $\{[Ni-(ptmdb)_2(NO_3)_2]\cdot 4(o-xylene)\}_n$ (ptmdb = 2-(4-pyridyl)-4,4,5,5-tetramethyl-1,3-dioxaboralone).^{27,28,46} The longer a ligand, the bigger the dimensions of rhombohedral (or square) grid. ptmdb is 8.5 Å longer than bpy; $\{[Ni-(ptmdb)_2(NO_3)_2]\cdot 4(o-xylene)\}_n$ has great pore with dimensions of about 20×20 Å. bpfp is about 6 Å longer than bpy; the rhombohedral grid in polymer **2** shows the dimensions of 14.231×15.586 Å. However, pyCH₂-CH₂py, pyCH=CHpy, or pyC=Cpy is longer than bpy by only 2 Å; the corresponding polymers give smaller dimensions of rhombohedral grid.

Crystal Structures $[Cd(N_3)_2(bpfp)]_n$ (3). Polymer 3 exhibits three-dimensional layered structure with tetragonal prism channels viewing from *a* direction (Figure 5). Each layer is formed by the extension of rhombohedral grid $Cd_4(N_3)_4$. Layers are connected by bpfp coordinating with Cd atoms leading to the 3-D channel polymer. bpfp ligands occupy the four edges of the tetragonal prism channel.

Figure 6 gives the polymeric sheet with rhombohedral grid Cd₄(N₃)₄ along *b* and *c* directions. Each grid is composed of 16-membered rings (Cd–N–N–N)₄. The edge length of the grid, Cd1–Cd1A, is 6.281 Å, and the distances of two diagonals (Cd1A–Cd1C and Cd1–Cd1I) are 7.465 and 9.903 Å, respectively, giving smaller rhombohedral grids with the dimensions of 6.281 × 6.281 Å. Each Cd atom exhibits an octahedral coordinate environment; four μ -1,3-N₃⁻ units are in the equatorial position, and two N atoms from different bpfp are in the axial position. Six Cd–N bond lengths are close, in the range 2.326–2.362 Å, and bond angles are about 90°.

Each bpfp adopts a *trans*-mode to coordinate with two Cd atoms from different layers. Two py rings are parallel; the dihedral angle with the NC₂ trigonal plane from the piperazine unit is 54.4°, and the dihedral angle with the C₄ plane of the piperazine unit is 37.0°. The NC₂ plane reclines at an angle of 52.6° with the C₄ plane. The several dihedral angles have a large difference corresponding to those of free bpfp and polymer **2**.

Coordination polymers containing azide units have been largely reported.^{47–51} [Mn(N₃)₂(pyrazine)]_n consists of linear chains of [Mn(N₃)₂]_n comprised of μ -1,1-N₃ bridges together with μ -pyrazine to afford 2-D planar layers.⁴⁸ The sheet of 2-D polymer [Cu(pyza)(N₃)]_n (pyza = pyrazinecarboxamide) is formed by the extension of



Figure 5. Three-dimensional tetragonal prism channel structure of [Cd(N₃)₂(bpfp)₂]_n.



Figure 6. Rhombohedral grid layer in $[Cd(N_3)_2(bpfp)_2]_n$ along the *b*- and *c*-axis.

the 10-membered Cu–NNN–Cu–N–Cu–NNN ring; within the $[Cu(N_3)]_n$ sheet azido groups behave as μ -1,1,3 bridges.⁴⁹ In the 3-D network structure $[Mn(N_3)_2-(bpy)]_n$, it does not have Mn–NNN–Mn rings, but –Mn–bpy–Mn–bpy– chains are cross-linked by μ -1,3-N₃ units to form the network.⁵⁰ In polymer **3** each bpfp coordinates to two Cd centers from adjacent layers which are composed of 16-membered rhombohedral grids Cd–NNN–Cd–NNN–Cd–NNN–Cd–NNN leading to the 3-D layered structure with the tetragonal prism channel.

Crystal Structure of [HgI₂(bpfp)]_{*n*} (4). The crystal structure of polymer **4** exhibits a one-dimensional zigzag framework extending along the *c* axis (Figure 7), and it is quite different from polymers **1**–**3**. Each Hg atom lies in a severely distorted tetrahedral environment coordinating to two nitrogen atoms from different bpfp

ligands and two iodide atoms. Its crystal structure is very similar to the known coordination polymer [HgI2- $(bpmp)]_n$ (bpmp = N,N-bis(4-pyridylmethyl)piperazine),⁵² but bond lengths and bond angles around Hg atoms in the two polymers are different. The Hg-I bond lengths of polymer 4 (2.656(2) and 2.659(2) Å) are shorter than those of $[HgI_2(bpmp)]_n$ (2.6628(8) and 2.6683(2) Å), and the Hg-N bond lengths (2.40(1) and 2.45(1) Å) are slightly longer than those of $[HgI_2(bpmp)]_n$ (2.3626(6) and 2.4331(6) Å); the N-Hg-N bond angle of $[HgI_2 (bpfp)]_n$ is 90.4(5)°, and that of $[HgI_2(bpmp)]_n$ is 83°. From the comparisons, we consider that the electron-withdrawing effect of the carbonyl group in bpfp ligands has a great influence on N-Hg bond lengths and the N-Hg-N bond angle. In the solid-state structure of polymer 4, 1-D zigzag chains are parallel to each other. The adjacent chains are connected by



Figure 7. 1-D zigzag chain structure of [HgI₂(bpfp)]_n.



Figure 8. UV-vis absorption spectra of $\{[Mn(H_2O)_2(SO_4)(bpfp)](H_2O)_3(CH_3OH)\}_{n}, \{[Zn(NCS)_2(bpfp)_2]\cdot 2H_2O\}_n, [Cd(N_3)_2(bpfp)_2]_n, and [HgI_2(bpfp)]_n, [HgI_2(bpfp)]_n, [Cd(N_3)_2(bpfp)_2]_n, [Cd(N_3)_2(bpfp)_2]_n,$

CHO hydrogen bonds, where the hydrogen bond distance is 3.481 Å and the bond angle is 134.0°.

Thermoanalysis. The TG-DTA of polymers **1**–**4** was determined in the range 20-900 °C in air. On the DTA curve of 1 there are two endothermic peaks from 80 to 376 °C corresponding to the removal of lattice water, coordinate methanol, and water molecules in the TG curve, and then a plateau region is observed until 720 °C; from 720 to 900 °C a strong exothermic peak demonstrates the decomposition of 1. There is an endothermic peak from 76 to 130 °C on the DTA curve of **2** corresponding to the removal of lattice water in the TG curve; three moderate exothermic peaks at 380, 500, and 600 °C on the DTA curve and weight loss between 360 and 600 °C in the TG curve show 2 undergoes decomposition. In the DTA curve of **3**, there are one very strong exothermic peak at 294 °C and one moderate exothermic peak at 440 °C; polymer 3 keeps losing weight from 290 to 490 °C, and then a plateau region is observed from 490 to 900 °C. Polymer 4 undergoes a one-step decomposition process from 212 to 530 °C; this great mass loss is due to the losses of bpfp ligands, iodide atoms, and Hg.

Molecular Weight. We determined the molecular weights of polymers **1**, **2**, and **4** in a DMF solution. The results show that the number-average molecular weights (M_n) are 3232 for polymer **1**, 11 089 for polymer **2**, and 3139 for polymer **4**. The weight-average molecular weights (M_w) are 4181, 13 226, and 4017 for polymers **1**, **2**, and **4**, respectively. The solubility of polymer **3** in

DMF is so small that we cannot determine its molecular weight. After polymer **3** was put into DMF for 1 week, we found that its solubility did not increase. We confirm that these polymers are polymeric in DMF solution.

Nonlinear Optical Properties. Recently coordination polymers have been concerned for nonlinear optical (NLO) applications.^{2,6-10} Here we report third-order NLO properties of polymers **1**–**4**. Their UV–vis spectrum in a DMF solution show there is only one absorption peak at 273 nm for **1**, 269 nm for **2**, 268 nm for **3**, and 268 nm for **4** (Figure 8). These polymers have a very low linear absorption ranging from 400 to 800 nm, promising low-intensity loss and little temperature change caused by photon absorption when light propagates in the materials. A broad transparent range is important for NLO applications especially in waveguide forms. They show linear absorption similar to other 1-D, 2-D, and 3-D coordination polymers.^{6–10}

The NLO properties of polymers 1-4 were investigated with 532 nm laser pulses of 8 ns duration in 1.8 $\times 10^{-4}$ M for polymer 1, or 2.5×10^{-4} M for polymer 2, or 2.0×10^{-4} M for polymer 3, or 1.3×10^{-4} M for polymer 4 in a DMF solution. We found that polymers 1-3 possess very strong NLO absorption and selffocusing effects, but polymer 4 gives weak NLO absorption components were evaluated by *Z*-scan experiment under an open-aperture configuration. The NLO refractive effects are assessed by dividing the normalized *Z*-scan data obtained under the closed aperture configuration



Figure 9. Z-scan data of 1.8×10^{-4} M DMF solution of {-[Mn(H₂O)₂(SO₄)(bpfp)](H₂O)₃(CH₃OH)}_n at 532 nm. (a) The data were evaluated under an open-aperture configuration. (b) 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.

by the normalized Z-scan data obtained under the open aperture configuration.

Figures 9a, 10a, and 11a depict NLO absorptive properties of polymers **1**–**3**, respectively. They clearly illustrate that the absorption increases as the incident light irradiance rises. The normalized transmittance drops to about 31% for Figure 9a, or 56% for Figure 10a, or 51% (T_d) for Figure 11a at the focus. It is obvious that the three polymers exhibit very strong NLO absorption. The third-order NLO absorption data can be well represented by eqs 1 and 2, which describe a third-order NLO process.⁴¹

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

q(Z) =

$$\int_{0}^{\infty} \int_{0}^{\infty} \alpha_{2} \frac{I_{0}}{1 + (Z/Z_{0})^{2}} e^{[-2(\gamma/\omega_{0})^{2} - (t/t_{0})^{2}]} \frac{1 - e^{-\alpha_{0}}L}{\alpha_{0}} r \, dr \, dt$$
(2)

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



Figure 10. Z-scan data of 2.5×10^{-4} M DMF solution of {-[Zn(NCS)₂(bpfp)₂]·2H₂O}_n at 532 nm. (a) The data were evaluated under an open-aperture configuration. (b) 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.

is the peak irradiation intensity at focus; $Z_0 = \pi \omega_0^{2/\lambda}$ with ω_0 is the spot radius of the laser beam at focus and λ is the wavelength of the laser; r is the radial coordinate; t is the time; and t_0 is the pulse width. The three polymers' third-order NLO absorptive coefficients α_2 are listed in Table 3. In accordance with the known NLO properties of coordination polymers, we find that most coordination polymers possess very strong NLO absorptive properties; their α_2 values are in the range $10^{-8}-10^{-9}$ m W⁻¹. Their α_2 values are larger than those of all the reported NLO materials.

Polymers 1-3' NLO refractive effects are given in Figures 9b, 10b, and 11b, respectively. The data show that the polymers have a similar positive sign for the refractive nonlinearity, which gives rise to self-focusing behavior. Polymer **4** shows a weaker self-focusing effect. The difference between normalized transmittance values at valley and peak portions, ΔT_{V-P} , can be obtained from Figures 9b, 10b, and 11b and are listed in Table 3. The effective third-order NLO refractive index n_2 can be derived by eq 3, and these values are given in Table 3.

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



					-		
polymer	$C/mol \ dm^{-3}$	<i>T</i> _d (%)	$\Delta T_{ m V-P}$	α_2/mW^{-1}	$n_2/{ m m}^2{ m W}^{-1}$	χ ⁽³⁾ /esu	γ/esu
1	$1.8 imes 10^{-4}$	31	0.55	$9.2 imes10^{-9}$	$2.73 imes10^{-17}$	6.39×10^{-11}	1.79×10^{-28}
2	$2.5 imes10^{-4}$	56	0.39	$6.9 imes10^{-9}$	$1.93 imes10^{-17}$	$4.52 imes10^{-11}$	$9.1 imes10^{-29}$
3	$2.0 imes10^{-4}$	51	0.33	$7.1 imes10^{-9}$	$1.64 imes10^{-17}$	$3.84 imes 10^{-11}$	$9.66 imes10^{-29}$



Figure 11. *Z*-scan data of 2.0×10^{-4} M DMF solution of [Cd-(N₃)₂(bpfp)₂]_n at 532 nm. (a) The data were evaluated under an open-aperture configuration. (b) 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.

Most of the one-dimensional coordination polymers give self-focusing behaviors except polymers [Co(bpms)2- $[NCS]_2]_n$ and $[{Mn(NCS)_2(4,4'-bbp)(H_2O)_2}(4,4'-bbp)].$ We found that the valence shell structures of central metal ions can influence the NLO properties of onedimensional coordination polymers. Coordination polymers with d^{<10} valence shell structures exhibit selfdefocusing behavior, such as [{Mn(NCS)₂(4,4'-bpy)- $(H_2O)_2$ $(4,4'-bpy)]_n$ and $[Co(bpms)_2(NCS)_2]_n$. But coordination polymers with d¹⁰ valence shell structures show self-focusing behaviors, such as [HgI₂(4,4'-azopyridine)]_n, [HgI₂(bpea)]_n, [Pb(NCS)₂(bpea)]_n (bpea = 1,2-bis-(4-pyridyl)ethane), $[Cd(en)(NO_3)_2(4,4'-bpy)]_m^{53-56}$ and polymer 4. Three-dimensional coordination polymers exhibit the same character as one-dimensional coordination polymers. 3-D polymers [Mn(SO₄)(4,4'-bpy)- $(H_2O)_2]_n$ and $[Mn(N_3)_2(4,4'-bpy)]_n$ possess d⁵ valence shell structures; they show strong self-defocusing effects. Polymer **3** has d¹⁰ valence shell structures; it gives self-focusing behavior.

Table 4. γ Values of Some Reported NLO Materials

	- I	
compound	γ/esu	ref
${[Et_4N]_2[WS_4Cu_4(CN)_4]}_n$	$1.26 imes10^{-29}$	57
MoOS ₃ Cu ₃ (SCN)(Py) ₅	5.8×10^{-27}	36
C ₆₀	$7.5 imes10^{-34}$	58
C ₇₀	$1.3 imes10^{-33}$	58
InSb	$1.7 imes10^{-33}$	59
Ge	$2.3 imes10^{-33}$	59
ferrocene	$(1.61 \pm 0.18) imes 10^{-35}$	60
$CHO(-FcCH=CHC_6H_5CH=CH-)_n$	$(1.55 \pm 0.27) imes 10^{-33}$	60
group 10 metal alkynyl polymers	5.6×10^{-35} to	61, 62
metallophalocyanines	$1.0 imes 10^{-32}$ to $1.0 imes 10^{-31}$	63
octopolar alkynylruthenium complexes	$\begin{array}{c} 9.3\times 10^{-35}to\\ 3.6\times 10^{-33} \end{array}$	64
2-ethenylthiophene	$1.04 imes10^{-36}$	65
α, ω -diphenylhexatriene	${\sim}10^{-32}$	65, 66
C ₆₀ H ₆₂ polyene	8×10^{-32}	65, 67
$\{[Mn(NCS)_2(bbp)_2] \cdot 0.25H_2O\}_n$	$2.92 imes10^{-30}$	9
$[Co(bbbt)_2(NCS)_2]_n$	2.40×10^{-30}	10

All of two-dimensional coordination polymers possess large NLO absorption and strong self-focusing effects regardless of the central ions, such as 2-D rhombohedral grid structural polymers $[Mn(X)_2(bbp)_2]$ ($X = N_3^-$ or NCS; bbp = 4,4'-trimethylenedipyridine) and $[M(bbtb)_2(NCS)_2]_n$ (M = Co, Mn, or Cd; bbtb = 1,4-bis(1H-benzotriazole)butane).^{9,10} Polymers **1** and **2** exhibit 2-D rhombohedral grid structure and also give strong self-focusing effects.

The third-order NLO susceptibility $\chi^{(3)}$ is characterized by NLO refractive effects based on the equation $\chi^{(3)} = cn_0^2 n_2/80\pi$. The corresponding modulus of the hyperpolarizability γ are obtained from $\gamma = \chi^{(3)}/NF^4$, where *N* is the number density (concentration) of the polymers in the sample; $F^4 = 3.3$ is the local field correction factor. These $\chi^{(3)}$ and γ values are shown in Table 3. The results show that polymers **1**–**3** possess strong third-order optical nonlinearities. Their γ values are comparable to those of best NLO materials and coordination polymers.

To put the optical nonlinearity of polymers 1-3 in a proper perspective with reference to other known thirdorder NLO materials, γ values are listed in Tables 3 and 4 along with the reported γ values of related coordination polymers and a few best performing known NLO materials. Most of the well-performing NLO materials reported in the literature are clusters, organic polymers, fullerene, semiconductors, and organometallic compounds. The γ values of polymers **1**-**3** can be comparable to those of the known cluster compounds (γ values are in the range of 10^{-29} – 10^{-27} esu), such as 1.26 \times 10⁻²⁹ and 5.8 \times 10⁻²⁷ esu for clusters {- $[Et_4N]_2[WS_4Cu_4(CN)_4]_n$ and $MoOS_3Cu_3(SCN)(Py)_5$, and are better than those of other compounds, such as C₆₀- $(7.5 \times 10^{-34} \text{ esu})$ and C_{70} $(1.3 \times 10^{-33} \text{ esu})$, semiconductors InSb (1.7 \times 10⁻³³ esu) and Ge (2.3 \times 10⁻³³ esu), ferrocene derivatives (γ values are ranging from 10^{-35} to 10^{-33} esu), group 10 metal alkynyl polymers (γ values are in the range $8.6 \times 10^{-35} - 5.6 \times 10^{-34}$ esu), metallophalocyanines (γ values are ranging from 10^{-32} to 10^{-31} esu), octopolar alkynylruthenium complexes (γ values are from 9.3×10^{-35} to 3.6×10^{-33} esu), organic compounds 2-ethenylthiophene(1.04×10^{-36} esu), α, ω - diphenylhexatriene ($\sim 10^{-32}$ esu), and C₆₀H₆₂ polyene (8 $\times 10^{-32}$ esu).

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Supporting Information Available: X-ray crystallographic files in CIF format for the crystal structures of bpfp and 1-4. This material is available free of charge via the Internet at http://pubs.acs.org.

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