



Syntheses, structures and third-order nonlinear optical properties of three coordination polymers based on bis(imidazol-1-yl-methyl)benzene and aromatic dicarboxylic ligands



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ABSTRACT

Three novel Zn(II) and Ni(II) coordination polymers, $\{Zn(BDA)(1,4-bib)\}_n$ (**1**), $\{Ni(BDA)(1,4-bib)\}_n$ (**2**) and $\{[Ni(H_2O)_2(1,2-bib)](HBDA)_2\}_n$ (**3**) ($H_2BDA = 1,2$ -benzenedicarboxylate; $1,4$ -bib = $1,4$ -bis(imidazol-1-yl-methyl)benzene; $1,2$ -bib = $1,2$ -bis(imidazol-1-yl-methyl)benzene), have been synthesized and characterized by X-ray diffraction. Compound **1** exhibits a 4-connected 3D framework with a 6^6 topology, which is comprised of Zn(II) ions, $1,4$ -bib and BDA ligands. Compound **2** possesses a 2D framework with a 6^3 topology, which contains 26-membered metallocyclic rings. In **3**, each Ni(II) ion is coordinated by four $1,2$ -bib ligands, resulting in 2D grid sheets. Two symmetry-related $HBDA^-$ ions are located in the grids in a head-to-head fashion. Their third-order nonlinear optical (NLO) properties were determined by the Z-scan technique in DMSO solution. Compounds **1**, **2** and **3** show NLO absorption with absorptive coefficients, β (MKS), of 3.55×10^{-11} , 9.38×10^{-11} and $1.14 \times 10^{-10} \text{ m W}^{-1}$. Compound **1** exhibits a strong self-focusing effect with a refractive index, γ (MKS), of $6.54 \times 10^{-18} \text{ m}^2 \text{ W}^{-1}$. The third-order NLO susceptibility $\chi^{(3)}$ of the three compounds were calculated to be 0.95×10^{-11} , 2.06×10^{-11} and 2.51×10^{-11} esu, respectively. The hyperpolarizability γ' is 1.43×10^{-29} for **1**, 2.63×10^{-29} for **2** and 7.58×10^{-29} esu for **3**.

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1. Introduction

The design and synthesis of third-order nonlinear optical (NLO) materials is a challenge for chemists. In the past decade, considerable efforts have been focused on inorganic semi-conductors, conjugated polymers and organometallic compounds [1–5]. Hou et al. and other authors have reported a few Mo(W)/M/S ($M = \text{Ag, Cu}$) clusters with strong NLO properties [6–11]. The hyperpolarizability values of these clusters compounds are about 10^{-28} esu, which are larger than those of C_{60} , C_{70} and semi-conductors. These compounds are expected to be developed as very promising candidates for third-order NLO materials. Currently, metal–organic coordination polymers (CPs) are of great interest, not only because of their intriguing variety of architectures, but also because of their potential applications in luminescence, catalysis, molecular adsorption, magnetism, and molecular sensing [12–17]. However, study of the third-order NLO properties of CPs is limited [18–20]. Although Lin and coworkers have reported a large number of CPs with NLO prop-

erties, their works concern secondary NLO properties [21]. It will be very interesting to explore the third-order NLO properties of CPs. An effective and facile approach for the synthesis of CPs is still the appropriate choice of well-designed organic ligands and metal ions. Carboxylate-based ligands, especially aromatic polycarboxylates, including $1,n$ -benzenedicarboxylate ($n = 2, 3$ or 4), $1,3,5$ - or $1,2,4$ -benzenetricarboxylate and $1,2,4,5$ -benzenetetracarboxylate, constitute an important family of multidentate O-donor ligands and have been extensively employed in the preparation of CPs [22,23]. As well, the combination of carboxylate linkers along with semi-flexible N-donor ligands, such as $1,4$ -bis(imidazol-1-yl-methyl)benzene, is a good choice for the construction of novel CPs. A few CPs based on these ligands and aromatic polycarboxylate ligands are observed in the literature [24–29]. The semi-flexible ligand can form different configurations by changing the C–C part to conform to the coordination geometries of central metal atoms by adopting *trans* and *cis* conformations. Herein, we selected $1,4$ -bib or $1,2$ -bib ($1,4$ -bib = $1,4$ -bis(imidazol-1-yl-methyl)benzene; $1,2$ -bib = $1,2$ -bis(imidazol-1-yl-methyl)benzene) and H_2BDA ($1,2$ -benzenedicarboxylate) ligands as spacers, with Zn(II) and Ni(II) ions as nodes, to explore the coordination chemistry of this system,

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and diverse structural frameworks were expected. Three compounds (**1**, **2** and **3**) were obtained and their third-order NLO properties were determined by the Z-scan technique in DMSO solution. The three compounds exhibit strong NLO properties. The corresponding third-order NLO absorptive coefficients, β (MKS), are 3.55×10^{-11} for **1**, 9.38×10^{-11} for **2** and $1.14 \times 10^{-10} \text{ m W}^{-1}$ for **3**. The refractive index γ (MKS) is $6.54 \times 10^{-18} \text{ m}^{28} \text{ W}^{-1}$ for **1**. The third-order NLO susceptibility $\chi^{(3)}$ is calculated to be 0.95×10^{-11} for **1**, 2.06×10^{-11} for **2** and 2.51×10^{-11} esu for **3**. The hyperpolarizability γ' is 1.43×10^{-29} for **1**, 2.63×10^{-29} for **2** and 7.58×10^{-29} esu for **3**.

2. Experimental

2.1. Materials and measurements

All chemical materials were A.R. Grade, and used as received. The ligand 1,4-bib and 1,2-bib were prepared by methods reported previously [26]. Elemental analyses were carried out with a German Elementary Vario MICRO elemental analyzer. The FT-IR spectra were recorded within the 400–4000 cm^{-1} region on a Perkin-Elmer spectrum-2000 with KBr pellets.

2.2. Preparation of the compounds

2.2.1. Synthesis of $\{\text{Zn}(\text{BDA})(1,4\text{-bib})\}_n$ (**1**)

A mixture of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.2 mmol, 0.044 g), H_2BDA (0.2 mmol, 0.033 g) and 1,4-bib (0.2 mmol, 0.047 g) in distilled water (15 mL), with the pH value adjusted to 4.0 by the addition of 0.2 M NaOH, was transferred into a Parr Teflon-lined stainless steel vessel, sealed and then heated to 393 K for 3 days, followed by cooling to ambient temperature. Colorless block-like crystals were collected by hand, washed with distilled water and dried in air at ambient temperature. $\{\text{Zn}(\text{BDA})(1,4\text{-bib})\}_n$ (**1**), yield: 90% based on Zn. Elemental Anal. Calc. for: C, 56.48; N, 11.98; H, 3.88. Found: C, 56.46; N, 11.96; H, 3.86%. IR (KBr, cm^{-1}): 3112(s), 2970(w), 1621(s), 1521(m), 1440(m), 1369(s), 1288(m), 1240(m), 1141(m), 1105(m), 991(w), 952(m), 860(w), 833(s), 754(m), 738(m), 701(m), 653(m), 584(m).

2.2.2. Synthesis of $\{\text{Ni}(\text{BDA})(1,4\text{-bib})\}_n$ (**2**)

The synthesis of compound **2** was similar to the above description for compound **1** except that nickel acetate (0.2 mmol, 0.052 g) was used instead of zinc acetate. $\{\text{Ni}(\text{BDA})(1,4\text{-bib})\}_n$ (**2**), yield: 83% based on Ni. Elemental Anal. Calc. for **2**: C, 57.31; N, 12.15; H, 3.93. Found: C, 57.33; N, 12.12; H, 3.91%. IR (KBr, cm^{-1}): 3126(m), 2960(w), 1619(s), 1544(s), 1494(s), 1446(s), 1413(s), 1355(m), 1274(m), 1249(m), 1230(m), 1112(m), 1083(m), 1025(m), 987(w), 943(m), 850(m), 808(m), 746(m), 723(m), 705(m), 659(m), 617(m).

2.2.3. Synthesis of $\{[\text{Ni}(\text{H}_2\text{O})_2(1,2\text{-bib})_2](\text{HBDA})_2\}_n$ (**3**)

The synthesis of compound **3** was similar to the above description for compound **2** except that 1,2-bib (0.2 mmol, 0.048 g) was used instead of 1,4-bib. $\{[\text{Ni}(\text{H}_2\text{O})_2(1,2\text{-bib})_2](\text{HBDA})_2\}_n$ (**3**), yield: 67% based on Ni. Elemental Anal. Calc. for **3**: C, 58.62; N, 12.43; H, 4.70. Found: C, 58.63; N, 12.41; H, 4.68%. IR (KBr, cm^{-1}): 3446(s), 3120(m), 1637(s), 1604(s), 1535(s), 1494(m), 1448(m), 1411(s), 1284(w), 1249(m), 1214(w), 1108(m), 1079(m), 1029(w), 995(m), 946(m), 869(m), 850(m), 771(m), 740(m), 705(m), 651(m), 539(w).

2.3. Crystal structure determination

The X-ray intensity data for the three compounds were recorded on a Bruker Smart CCD using Mo $K\alpha$ radiation and a graphite

monochromator at room temperature. Data integration and reduction were processed with the SADABS program. All heavy atoms were solved by direct methods with SHELX-97 [30]; other non-hydrogen atoms were solved by difference Fourier synthesis. All non-hydrogen atoms were refined with anisotropic displacement parameters and full-matrix least-squares refinement. Hydrogen atoms bound to C atoms were placed geometrically and held in the rigid mode. Further details of the structure analysis are given in Table 1. Selected bond lengths and angles are presented in Tables 2.

2.4. Nonlinear optical measurements

DMSO solutions of **1**, **2** and **3** were placed in a 1 mm quartz cell for NLO measurements. The nonlinear optical refraction and absorption were obtained with a linearly polarized laser light (7 ns, 10 Hz, 532 nm) generated from a mode-locked Q-switched Nd:YAG laser. The spatial profiles of the optical pulses are nearly Gaussian after passing through a filter. The focal length of the positive lens is 30 cm. Incident and transmitted pulsed energies are measured simultaneously by two energy detectors (RJP-765 energy probes, laser precision, Laserprobe Corp), which are linked to a computer through an RS232 interface. The sample was mounted on a translation stage that was controlled by the computer to move along the z-axis with respect to the focal point. An aperture 0.5 mm radius was placed in front of the transmission detector, and the transmittance was recorded as function of the sample position on the z-axis (closed aperture Z-scan). For measuring the NLO absorption, the Z-dependent sample transmittance was taken without the aperture (open aperture Z-scan). In our experiments, we performed a Z-scan on the solvent (DMSO) at the pulse energy focused on our samples, and no obvious nonlinear optical phenomenon was observed.

3. Results and discussion

3.1. The structure of compound **1**

Selected bond distances and angles for compounds **1**, **2** and **3** are listed in Table 2. Single-crystal X-ray diffraction studies reveal that **1** crystallizes in the space group *Cc* and is composed of a 3D coordination network. There are one crystallographically independent Zn(II) ion, one BDA^{2-} anion and one 1,4-bib ligand in the asymmetric unit. Each Zn(II) ion is coordinated by two oxygen atoms from two BDA^{2-} anions and two nitrogen atoms from two 1,4-bib ligands in a tetrahedral geometry, as shown in Fig. 1a. The Zn–N and Zn–O bond lengths are comparable to those reported in other Zn(II) compounds [31,32]. The distance between Zn1 and O1 is 2.7188 Å, which suggests a weak non-covalent interaction. The BDA^{2-} ligand is bidentate. Each carboxylate group of BDA is monodentately coordinated to one Zn(II) center. The whole BDA ligand adopts the $\mu_2:\eta^1,\eta^1$ mode. The 1,4-bib ligand adopts a *trans* conformation and coordinates to two Zn(II) centers.

In **1**, the Zn(II) centers are linked by BDA ligands to form an infinite chain structure along the *c* axis. The Zn...Zn separation within the chains is 6.85 Å. Adjacent chains are cross-linked by the 1,4-bib ligands, leading to a 3D network. A better insight into the nature of this intricate framework can be achieved by the application of a topological approach. As depicted in Fig. 1b, each Zn(II) center is surrounded by two BDA^{2-} and two 1,4-bib ligands. Thus the Zn(II) center can be viewed as a four-connected node. The BDA^{2-} and 1,4-bib ligands serve as shorter and longer two-connected spacers, respectively, to bridge two Zn(II) centers. The resulting structure can be viewed as having a 6^6 topology.

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