



Studies on two coordination polymers $[M(\mu_4\text{-pz25dc})]_n$ ($M = \text{Cd}$ or Zn , pz25dc = pyrazine-2,5-dicarboxylato) with three-dimensional pillared-layer three-nodal framework: Synthesis, structural characterization, strong optical non-linearities and optical limiting properties

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ARTICLE INFO

Article history:

Received 15 May 2009

Received in revised form 2 July 2009

Accepted 6 July 2009

Available online 9 July 2009

Keywords:

Coordination polymers

Third-order NLO properties

Pyrazine-2,5-dicarboxylato

Optical limiting

ABSTRACT

Two isomorphous new candidates $[M(\mu_4\text{-pz25dc})]_n$ ($M = \text{Cd}$, **1**; Zn , **2**; pz25dc = pyrazine-2,5-dicarboxylato) for nonlinear optical (NLO) materials have been synthesized hydrothermally and characterized crystallographically as pillared-layer three-nodal frameworks with one four-connected metal nodes and two crystallographically different four-connected ligand nodes. Their optical non-linearities are measured by the z-Scan technique with an 8 ns pulsed laser at 532 nm. These two coordination polymers both exhibit strong NLO absorptive abilities [$\alpha_2 = (63 \pm 6) \times 10^{-12} \text{ m W}^{-1}$ **1**, $(46 \pm 6) \times 10^{-11} \text{ m W}^{-1}$ **2**] and effective self-focusing performance [$n_2 = (67 \pm 5) \times 10^{-18}$ **1**, $(13 \pm 3) \times 10^{-18} \text{ m}^2 \text{ W}^{-1}$ **2**] in 1.02×10^{-4} **1** and $1.05 \times 10^{-4} \text{ mol dm}^{-3}$ **2** DMF solution separately. The values of the limiting threshold are also measured from the optical limiting experimental data. The heavy atom effect plays important role in the enhancement of optical non-linearities and optical limiting properties.

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1. Introduction

Research into nonlinear optical (NLO) materials has become increasingly intensive because of their potential applications in data storage, optical fibers, optical computing, image transmission, optical switching, and optical limiting [1–8]. Thus, the design and synthesis of new materials with large third-order nonlinear optical properties and strong optical limiting (OL) effects is currently the focus of intense research [9–17]. Coordination polymers have proven to be one of the promising candidates for third-order NLO materials since the incorporation of transition metal ions in organic-metal polymers introduces more sublevels into the energy hierarchy, which permits more allowed electronic transition to take place and hence larger NLO effects [5,18–42]. These compounds have a large variety of structures and a diversity of electronic properties tunable by virtue of the coordination metal centers and ligands. Moreover, coordination polymers can also extend the π -conjugation length of molecule which is one of many strategies to increase molecular NLO hyperpolarizability γ values, because the origin of NLO properties is delocalization of the π -electron cloud [5,8,10,16]. In contrast, only a few 3D metal-organic coordination polymers with strong NLO properties have been prepared

thus far [16,35] for the incorporation of terminal ligands which block further polymerization, as a result of the fragmentary data, correlations between structure and NLO function for these polymers are yet to be established, and more systematic experiments should be performed to better understand the physical mechanisms. In fact, 3D NLO materials represent the next step in complexity when their performance is compared to that of the mostly investigated 1D or 2D compounds, and the correlation between structures and NLO response is much richer for 3D and offers more variables for optimization [5].

With this in mind, we have selected the π -conjugated N and O-donor ligand pyrazine-2,5-dicarboxylato (pz25dc) as bridging blocks, because it is a rigid ligand with multifunctional groups and possesses central symmetry (C_i) to favor the construction of high-dimension frameworks. Till now, people's research interest on pz25dc focuses on the design and synthesis of novel coordination polymers with optimal magnetic properties, and do not give efforts toward the study of their third-order NLO properties [43–46]. On the other hand, d¹⁰-metal ions possess favorable optical transparency and similar electronic configuration [47,48]. As a result, in order further to develop the study in this active field and also to search for better NLO materials, the present investigation details the synthesis, characterization, NLO properties and OL effects of two interesting isomorphous three-dimensional coordination polymers, **1** and **2**, which were prepared hydrothermally.

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2. Results and discussion

2.1. Crystal structures of $[Cd(\mu_4\text{-pz25dc})_n]$ (**1**)

Single crystal X-ray diffraction analysis shows that the asymmetric unit of **1** presents an extended 3D framework formed by a crystallographic independent Cd(II) atom and two centrosymmetric hexadentate μ_4 -pz25dc bridging ligands (**L-1** for O1–C1–O2 pyrazine and **L-2** for O3–C4–O4 pyrazine).

As shown in Fig. 1, the four-connected Cd1 node exhibits a distorted octahedral surrounding which is formed by two pyrazine N atoms (Cd1–N1 2.328(2) Å, Cd1–N2 2.290(2) Å) from two two crystallographically different ligands and four O atoms (Cd1–O1 2.193(2) Å, Cd1–O2C 2.257(2) Å, Cd1–O3 2.274(2) Å, Cd1–O4D 2.186(2) Å) belonging to the carboxylate groups of four pz25dc ligands. The **L-1** ligand is non-planar, the dihedral angle between the pyrazine ring and O1/C1/O2 carboxylate group is 23.22(8)°, while the 12 atoms containing pyrazine ring and two O3/C4/O4 carboxylate groups in **L-2** are coplanar and the maximum deviation from the Least-Squares Plane is only 0.030(2) Å for C6. Both **L-1** and **L-2** ligands act as four-connected linkers and have similar hexadentate coordination mode. The nitrogen atoms of pyrazine and neighboring oxygen atoms of carboxyl groups chelate two metal Cd²⁺ ions via five-member ring to form alternate (–Cd²⁺–**L-1**–Cd²⁺–**L-2**–Cd²⁺–) chains along the [1 1 1] direction. The Cd–Cd distances in these chains are 7.3459(4) Å for **L-1** ligand and 7.2743(4) Å for **L-2** ligand, respectively. These chains are bridged by the non-planar **L-1** ligand through the O1/C1/O2 carboxylate groups form puckered sheets parallel to the (20 $\bar{1}$) plane (Fig. 2a). These sheets are further crosslinked by the planar **L-2** ligands through the O3/C4/O4 carboxylate groups to build up a pillared-layer three-nodal framework with one four-connected Cd nodes and two crystallographically different four-connected **L-1** and **L-2** nodes, (Fig. 2b and c). The Cd–Cd distances across the **L-2** ligands are 11.1594(5) Å. As a result, the one-dimensional rectangular channels were formed along the [0 1 0] direction (Fig. 2c).

2.2. Third-order NLO properties for **1** and **2**

The UV–Vis absorption spectra of the polymers **1** and **2** in DMF solution demonstrates that both polymers have the same absorption peak at about 277 nm, and they give very low linear absorption ranging from 300 to 1000 nm, promising low intensity loss and little temperature change caused by photon absorption when light propagates in the materials, which are similar to other re-

ported coordination polymers [18–21]. This absorptive band could be attributed to the π – π^* transitions of the ligand. Furthermore, in order to confirm that the skeleton of polymers **1** and **2** is intact in DMF solution, we determined their molecular weights in DMF solution. The results show that the number average molecular weights (M_n) are 12056 for polymer **1** and 13268 for polymer **2**. The weight average molecular weights (M_w) are 14784 and 15951 for polymers **1** and **2**, respectively. The results indicate that the dissolved polymers exist in the form of oligomers (the solid structures of the polymers are insoluble in DMF and must be broken into soluble pieces). Given the polydispersity indexes very close to 1, the dissolved polymers are broken into small pieces of the same size, which do not further dissociate into smaller species, and stable oligomers with a constant polymerization degree (43 and 57, respectively, for polymers **1** and **2**) are thus formed. This fact is that solution processing is known to have some unique advantages including better molecular weight control [41,64]. Coordination polymers with very narrow molecular weight distributions and strong optical non-linearities are also observed in some reported metal-organic polymers, such as $[\text{NiCl}_2(\text{bfpf})_2(\text{H}_2\text{O})_3]_n$ (bfpf = *N,N'*-bis(3-pyridylformyl) piperazine), $[\text{Co}(\text{bipy})_3\text{Co}_2(\mu_2\text{-ox})_3]_n$, $[\text{NiCl}_2(\text{bfpf})_2(\text{H}_2\text{O})_3]_n$, $[\text{Pb}(\text{bbbm})_2(\text{NO}_3)_2]_n$ (bbbm = 1,1-(1,4-butadienyl) bis(1*H*-benzimidazole)), $[\text{Zn}(\text{pbbt})(\text{NCS})_2]_n$ (pbbt = 1,1-(1,3-propylene) bis(1*H*-benzo triazole)) ($M_w/M_n < 1.3$) [31,41].

The NLO absorption components of the two coordination polymers were evaluated under the open-aperture configuration. Figs. 3a and 4a display their NLO absorptive behavior and clearly illustrate that the absorption increases with increasing intensity of the incident laser, the light transmittance (*T*) dropping to 46% and 59% at the focal point for polymers **1** and **2**, respectively. A reasonably good fit between the experimental data and the theoretical curves was obtained, which suggests that the experimentally detected NLO effects have an effective third-order characterization. It is clear that the theoretical curves qualitatively reproduce the general pattern of the observed experimental data [49]. The nonlinear absorptive coefficients α_2 were calculated to be $(46 \pm 6) \times 10^{-11}$ for **1** and $(63 \pm 6) \times 10^{-12} \text{ m W}^{-1}$ for **2**. The nonlinear refractive components were assessed by dividing the normalized *z*-Scan data obtained from the close-aperture configuration by the normalized *z*-Scan data obtained from the open-aperture configuration, as depicted in Figs. 3b and 4b separately for **1** and **2**. The valleys and peaks occur at equal distances from the focus. These results are consistent with the notion that the observed optical nonlinearity has an effective third order dependence on the incident electromagnetic field [49]. A reasonably good fit between the experimental data (black squares) and the theoretical curves (solid curves) was obtained [50,51]. The effective third-order refractive index n_2 of **1** and **2** were calculated to be $(67 \pm 5) \times 10^{-18}$ for **1** and $(13 \pm 3) \times 10^{-18} \text{ m}^2 \text{ W}^{-1}$ for **2**. Based on the above NLO absorptive and refractive values of **1** and **2**, the $\chi^{(3)}$ values were calculated to be $(22 \pm 3) \times 10^{-11}$ and $(82 \pm 5) \times 10^{-12} \text{ esu}$ for **1** and **2**, respectively. The corresponding modulus of the hyperpolarizability γ , which reflects the integrated third-order NLO property, was deduced to be $(12 \pm 3) \times 10^{-28}$ and $(45 \pm 5) \times 10^{-29}$ for polymers **1** and **2**, respectively.

From the above discussions, we can reasonably state that polymers **1** and **2** exhibit similar NLO properties. All exhibit strong RSA and effective self-focusing performances, as depicted in Figs. 3 and 4. In the light of the aforementioned nonlinear absorptive and refractive experimental data, a significant improvement in the NLO absorptive and refractive effects was observed on going from Zn-containing polymer **2** to Cd-containing polymer **1**, may be derived from the heavy atom effect: the strength of the NLO properties can be altered by the π -back-donation capacity of the metal ions to the ligands, and the increased π -back-donation capacity

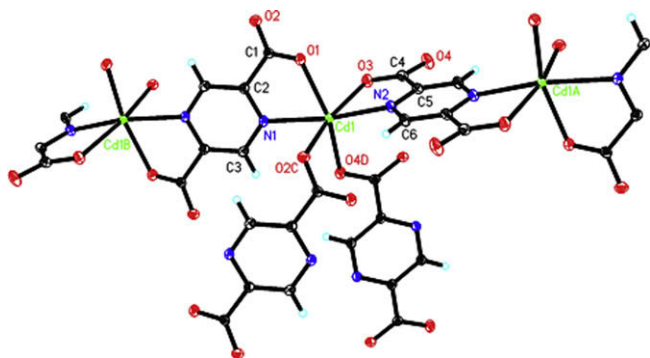


Fig. 1. Perspective drawing of a fragment of the coordination environment of Cd(II) for compound **1**, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability. Symmetry codes: (A) 2 –*X*, 1/2 +*Y*, 3/2 –*Z*; (B) 1 –*X*, 3/2 +*Y*, 1/2 –*Z*; (C) *X*, *Y* – 1, *Z*; and (D) 2 –*X*, –*Y* – 1, –*Z*. Selected bond lengths (Å) and angles (°): Cd1–O1 2.193(2), Cd1–O2C 2.257(2), Cd1–O3 2.274(2), Cd1–O4D 2.186(2), Cd1–N1 2.328(2), Cd1–N2 2.290(2), O1–Cd1–N1 72.11(7), O3–Cd1–N2 70.48(8).

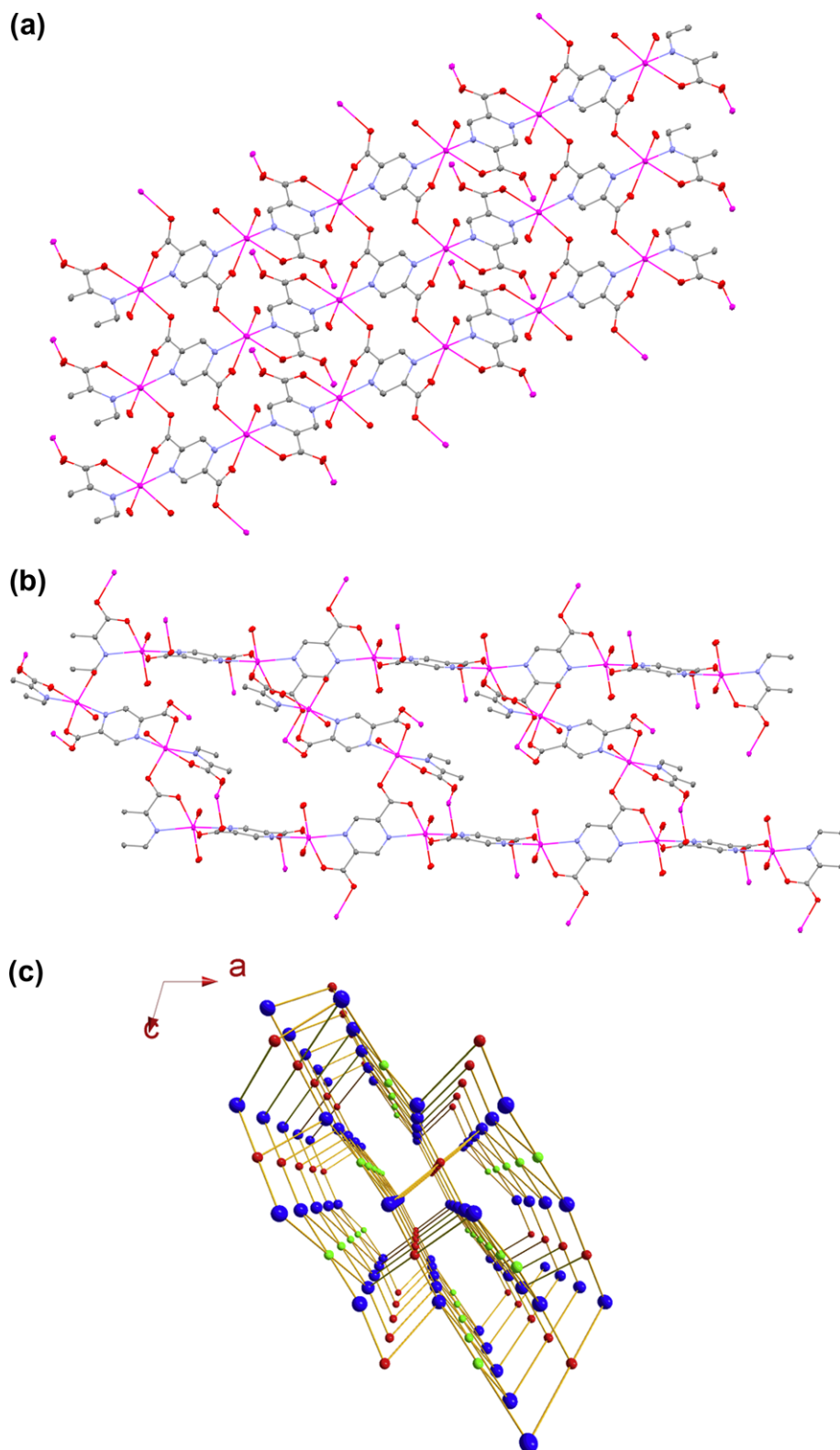


Fig. 2. (a) Layered architecture formed by Cd(II) ions and L-1 ligands parallel to $(20\bar{1})$ plane. (b) Crystal structure along the c -axis showing the pillared-layer framework linked by L-2 ligands along the c -axis. (c) Schematic presentations of 3D topology of **1**: (4,4,4)-connected three-nodal net. Blue spheres, Cd; green spheres, L-1; red spheres, L-2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the metal ions to the ligands may enhance the extension of the electronic π system and improve the NLO properties [10,18].

To put the optical nonlinearity of polymers **1** and **2** in a proper perspective with reference to other known third-order NLO mate-

rials, the α_2 , n_2 and γ values of related coordination polymers and a few neat semiconductors, fullerene and some best performing clusters at 532 nm are listed in Table 1. It can be seen from Table 1 that the hyperpolarizability γ values of coordination polymers

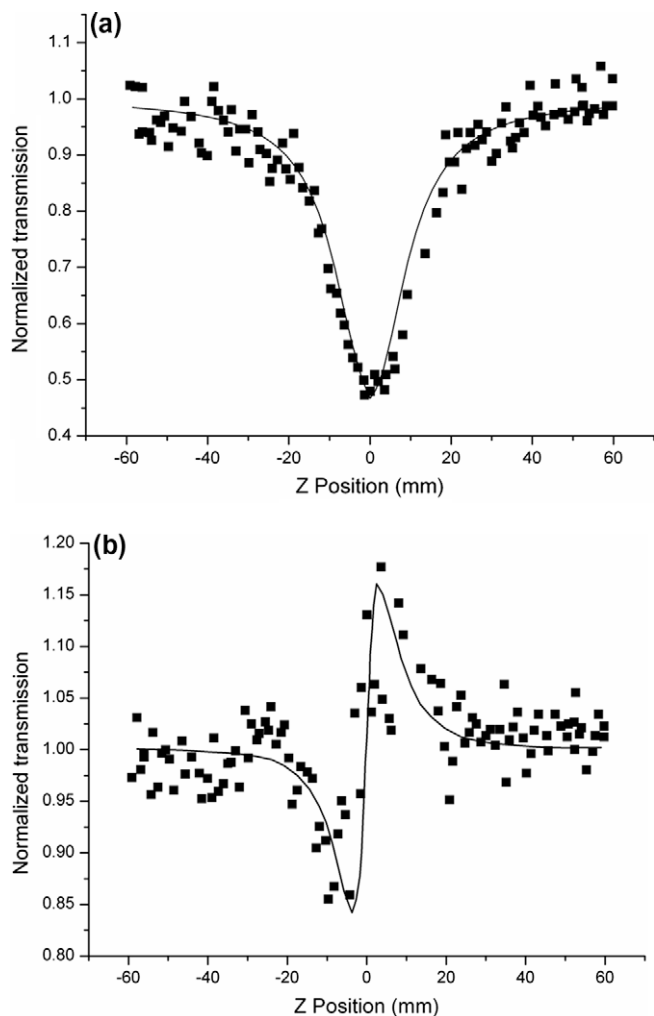


Fig. 3. z-Scan measurement of **1** in 1.02×10^{-4} mol dm $^{-3}$ DMF at 532 nm, 8 ns laser pulses, with a linear transmittance of 90%. The black squares represent the z-Scan experimental data and the solid lines are the theoretical fitting curves. (a) Data collected under the open-aperture configuration. (b) Data obtained by dividing the normalized z-Scan data obtained under the closed-aperture configuration by the normalized z-Scan data in (a).

1 and **2** are comparable to those of best performing clusters and better than those observed in neat semiconductors, fullerene and coordination polymers reported before. The γ values of clusters are in the range of 10^{-29} – 10^{-27} esu, such as 2.38×10^{-27} and 6.78×10^{-29} esu for clusters $[\text{Mo}_2\text{S}_8\text{Ag}_4(\text{PPh}_3)_4]$ and $\{[\text{Et}_4\text{N}]_2\text{-}[\text{MoOS}_3\text{Cu}_2(\mu\text{-CN})_2\text{-}2\text{aniline}]_n\}$; the γ values of coordination polymers reported range from 10^{-30} to 10^{-28} esu; and the γ values of semiconductors InSb, Ge, C60, and C70 are 1.7×10^{-33} , 2.3×10^{-33} , 7.5×10^{-34} , and 1.3×10^{-33} esu, respectively. Thus coordination polymers **1** and **2** will become promising candidates for NLO materials and among the best NLO materials known to date.

The large γ values may be attributed to the high electrontransport capability of the coordination polymers **1** and **2**. As we know, the third-order optical nonlinearity can be enhanced by increasing the carrier transport [56]. On the other hand, the ligand molecule with two nitrogen atoms and four oxygen atoms is conjugated and rich in electrons and the central Zn and Cd atom can act as electron acceptor, therefore the polarization of π -electron conjugation will be highly enhanced [57]. Besides, the 3D structure of the two coordination polymers helps to enhance the rigidity of conjugated ligands, which adds to the enhancement of third-order sus-

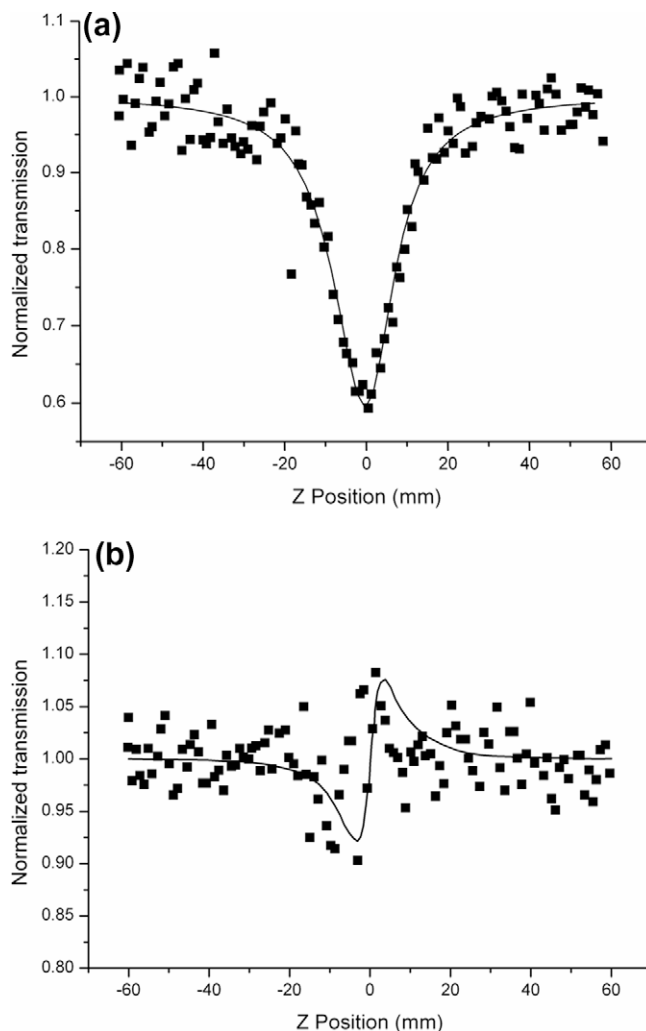


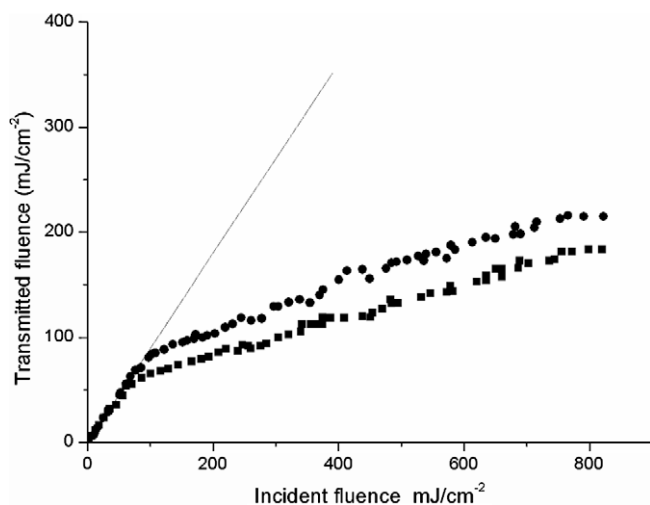
Fig. 4. z-Scan measurement of **2** in 1.05×10^{-4} mol dm $^{-3}$ DMF at 532 nm, 8 ns laser pulses, with a linear transmittance of 90%. The black squares represent the z-Scan experimental data and the solid lines are the theoretical fitting curves. (a) Data collected under the open-aperture configuration. (b) Data obtained by dividing the normalized z-Scan data obtained under the closed-aperture configuration by the normalized z-Scan data in (a).

ceptibilities as it promotes the overlap of π orbitals and the electron delocalization. All of the above factors would lead to the large third-order NLO susceptibility.

The presence of the combined effects of strong RSA and self-focusing in polymers **1** and **2** may significantly enhance the overall optical limiting (OL) performance. The OL experimental results of **1** and **2** and with an identical linear transmittance of 90% are shown in Fig. 5. The linear and nonlinear transmission data (filled squares for **1** and filled circles for **2**) were measured with 532 nm laser pulses of 8-ns duration at polymer concentrations of 1.02×10^{-4} (**1**) and 1.05×10^{-4} mol dm $^{-3}$ (**2**) in DMF solution. At low incident laser energy, polymer **1** and **2** exhibit a linear response of transmitted energy obeying Beer's law, but the transmission decreases obviously as the incident energy increases. Experiment with DMF solvent alone affords no detectable OL effect indicating the solvent contribution is negligible. Moreover, the optical limiting threshold, defined as input fluence at which the transmission decreases to be half of the linear transmission, is found to be 0.21 and 0.29 J cm $^{-2}$ for polymers **1** and **2**, respectively. These values are comparable to those of many heterothiometalate clusters [39,54]. It is expected that higher threshold value could be attained if higher concentrations are attained and if the polymers could be deposited as thin

Table 1
Optical parameters of selected NLO chromophores.

Compound	α_2 (m W ⁻¹)	n_2 (m ² W ⁻¹)	γ (esu)	Reference
1	$(46 \pm 6) \times 10^{-11}$	$(67 \pm 5) \times 10^{-18}$	$(12 \pm 3) \times 10^{-28}$	This work
2	$(63 \pm 6) \times 10^{-12}$	$(13 \pm 3) \times 10^{-18}$	$(45 \pm 5) \times 10^{-29}$	This work
<i>Fullerene</i>				
C ₆₀			5×10^{-34}	[52]
C ₇₀			3×10^{-33}	[52]
<i>Semiconductors</i>				
InSb			1.7×10^{-33}	[53]
Ge			2.3×10^{-33}	[53]
<i>Cluster compounds</i>				
{[Et ₄ N] ₂ [MoOS ₃ Cu ₂ (μ-CN)] ₂ · 2aniline} _n	5.10×10^{-11}		6.78×10^{-29}	[39]
{[Et ₄ N] ₄ [MoOS ₃ Cu ₃ CN(μ'-CN)] ₂ (μ-CN) ₂] _n	1.58×10^{-10}		2.47×10^{-28}	[39]
[Mo ₂ S ₈ Ag ₄ (PPh ₃) ₄]	1.8×10^{-9}	2.2×10^{-16}	2.38×10^{-27}	[54]
<i>Coordination polymers</i>				
[Co(bbbt) ₂ (NCS) ₂] _n	5.4×10^{-9}	5.73×10^{-19}	1.52×10^{-30}	[18]
[Mn(bbbt) ₂ (NCS) ₂] _n	5.2×10^{-9}	3.55×10^{-19}	1.50×10^{-30}	[18]
[Cd(bbbt) ₂ (NCS) ₂] _n	5.0×10^{-9}	3.07×10^{-19}	1.45×10^{-30}	[18]
[AgI(inh)] ₆ (KI) _n	1.044×10^{-9}	2.827×10^{-11}	$\sim 2.29 \times 10^{-28}$	[20]
{[Cd(fc ₂) ₂ Cl ₂] · CH ₃ OH · 2H ₂ O} _n		3.59×10^{-18}	1.18×10^{-30}	[21]
{[Co(fc ₂) ₂ Cl ₂] · 2CH ₃ OH} _n	/	4.15×10^{-18}	1.47×10^{-30}	[21]
{[Zn(fc ₂) ₂ Cl ₂] · CH ₃ OH} _n	1.2×10^{-9}	7.08×10^{-18}	1.09×10^{-29}	[21]
{[HgI ₂ (bpba)] · 1.5CH ₃ OH} _n	/	9.14×10^{-18}	2.10×10^{-29}	[22]
{[Ni(pbbt) ₂ (NCS) ₂](H ₂ O) _n	/	3.02×10^{-18}	1.68×10^{-29}	[26]
{[Co(pbbt) ₂ (NCS) ₂](H ₂ O) _n	1.4×10^{-9}	8.23×10^{-18}	4.58×10^{-29}	[26]
[Cd(en)(NO ₃) ₂ (4,4'-bpy)] _n	/	6×10^{-18}	1.7×10^{-29}	[30]
[Fe ₂ (μ ₁₀ -btc)0.5(μ ₂ -ox)0.5(μ ₂ -O) _{1.5}] _n	5.03×10^{-11}	-7.32×10^{-18}	5.98×10^{-30}	[35]
{[Co(bipy) ₃][Co ₂ (μ ₂ -ox) ₃]} _n	4.25×10^{-11}	-6.40×10^{-18}	5.75×10^{-30}	[36]
{[NiCl ₂ (bfpf) ₂](H ₂ O) ₃] _n	/	1.47×10^{-11}	1.59×10^{-30}	[38]
[ZnCl ₂ (bfpf)] _n	/	1.73×10^{-11}	1.06×10^{-30}	[38]
[CoCl ₂ (bfpf)] _n	3.31×10^{-11}	1.65×10^{-11}	2.70×10^{-30}	[38]
[Co ₂ (μ ₂ -4,4'-bipy) ₂ (μ ₂ -be) ₂ (be) ₂] _n	6.27×10^{-11}	-7.10×10^{-18}	8.30×10^{-30}	[42]
[Co(NCS) ₂ (bpms) ₂] _n	/	-3.0×10^{-18}	1.0×10^{-30}	[55]

**Fig. 5.** Optical limiting responses of polymers **1** (■) in 1.02×10^{-4} mol dm⁻³ DMF solution and **2** (●) in 1.05×10^{-4} mol dm⁻³ DMF solution.

films via CVD techniques. The Cd-containing polymer **1** outperforms its corresponding Zn-containing counterparts **2** in OL performance at a given wavelength and with similar linear transmittance. This is consistent with the fact that the OL effects of Ag-containing clusters are better than those of their Cu-containing homologues, which may be due to the heavy atom effect. The importance of the heavy atom effect with regard to the efficiency of nonlinear absorption and the OL capabilities has already been noted in the case of the metallophthalocyanine system [58,59]. The obvious optical limiting enhancement may result from the fact that the Cd- or Ag-containing polymers have much lower pump energies than their Zn- or Cu-containing counterparts and,

hence, plasmas of the Cd- and Ag-containing polymers may be more easily generated, resulting in better optical limiting effects, even though both compounds have the same structure [65].

3. Experimental

3.1. General

All chemicals were of reagent grade and were used as commercially obtained. Elemental analyses for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 1400C analyzer. Infrared spectra were recorded with a Nicolet FT-170SX Fourier transform spectrometer (KBr pellets). Electronic spectra were measured on a Shimadzu UV-3100 spectrophotometer. The molecular weights of the polymers were determined with Gel Permeation Chromatography (Agilent 1100 liquid chromatography, 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.

3.2. Synthesis

3.2.1. Synthesis of [Cd(μ₄-pz25dc)]_n (**1**)

A mixture of 2,5-pyrazinedicarboxylic acid (0.042 g), KOH (0.014 g) and distilled water (15 ml) is heated till boiling. When cooling, the solution is put into a 20 ml Teflon-lined stainless steel autoclave where Cd(NO₃)₂ · 4H₂O (0.077 g) is. The autoclave is sealed and heated at 180 °C for 72 h, then slowly cools to room temperature. Colorless rhombohedral crystals suitable for X-ray diffraction were collected and air-dried. Yield: ~46% (based on Cd). Anal. Calc. for C₆H₂N₂O₄: Cd, 25.88; H, 0.72; N, 10.06. Found: C, 25.82; H, 0.74; N, 10.03%. Main IR features (cm⁻¹, KBr pellet): 1648 vs, 1627 vs, for ν_{as}(O-C-O); 1488 w, 1476 w,

1435 w, for $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N}) + \nu(\text{pyrazine ring})$; 1402 vs, 1333 s, 1325 s, for $\nu_{\text{as}}(\text{O}-\text{C}-\text{O})$; 1182 m, 1052 m, for $\delta_{\text{ip}}(\text{C}-\text{H})$; 951 w, 942 w, 836 s, 779 m, 770 m, for $\delta(\text{C}=\text{C}-\text{H})$; 551 m, for $\pi(\text{CO}_2)$; 511 m, 481 m, 445 m, for $\nu(\text{Cd}-\text{O} + \text{Cd}-\text{N})$.

3.2.2. Synthesis of $[\text{Zn}(\mu_4\text{-pz25dc})_n(\mathbf{2})]$

The same procedure as used for the synthesis of polymer **1** was applied to synthesize polymer **2**, except using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.074 g,) instead of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Colorless crystals were obtained. Yield: ~49% (based on Zn). Anal. Calc. for $\text{C}_6\text{H}_2\text{N}_2\text{O}_4\text{Zn}$: C, 31.13; H, 0.87; N, 12.10. Found: C, 31.11; H, 0.83; N, 12.06%. Main IR features (cm^{-1} , KBr pellet): 1643 vs, 1626 vs, for $\nu_{\text{as}}(\text{O}-\text{C}-\text{O})$; 1487 w, 1472 w, 1425 w, for $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N}) + \nu(\text{pyrazine ring})$; 1400 vs, 1327 s, 1322 s, for $\nu_{\text{s}}(\text{O}-\text{C}-\text{O})$; 1171 m, 1042 m, for $\delta_{\text{ip}}(\text{C}-\text{H})$; 950 w, 931 w, 834 s, 776 m, 760 m, for $\delta(\text{C}=\text{C}-\text{H})$; 550 m, for $\pi(\text{CO}_2)$; 510 m, 479 m, 436 m, for $\nu(\text{Zn}-\text{O} + \text{Zn}-\text{N})$.

3.3. X-ray diffraction studies of poly $[(\mu_4\text{-pyrazine-2, 5-dicarboxylato})\text{cadmium(II)}] (\mathbf{1})$

$\text{C}_6\text{H}_2\text{N}_2\text{O}_4\text{Cd}$, monoclinic, $P2_1/c$, $a = 10.4643(5)$, $b = 5.1867(3)$, $c = 12.0396(6)$, $\beta = 106.110(3)^\circ$, $V = 627.796(3)$, $Z = 4$. The experimental data were collected using Colorless rhombohedral crystal, dimensions of $0.20 \times 0.20 \times 0.10$ mm, with a SMART Apex II diffractometer (Bruker SMART 4 K CCD area detector, graphite monochromator, Mo $K\alpha$ radiation, $\lambda = 0.71073\text{\AA}$, θ and ω scans, $2\theta \leq 56^\circ$); 8306 reflections were obtained at 293 K, 1508 unique. The experimental completeness is 98.5% in $2\theta \leq 56^\circ$ limits. Absorption corrections ($\mu_{\text{Mo}} = 3.453 \text{ mm}^{-1}$) have been applied using multiscan procedure [60], $R_{\text{int}} = 0.0156$. The structure was solved by direct methods and refined by full-matrix least squares on F^2 , using SHELXTL program [61]. Hydrogen atoms have been placed in calculated positions and taken into account in the final stages of refinement in the "riding model" approximation. Refinement converged at a final $R_1 = 0.0196$ for 1267 reflections with $I > 2\sigma(I)$ and 0.0283 for all 1508 data; $wR_2 = 0.0457$, $\text{GoF} = 1.006$, 118 refined parameters.

The supplementary crystallographic data for compound **1** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 719333. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk> or e-mail: deposit@ccdc.cam.ac.uk.

3.4. Nonlinear optical measurements

The nonlinear properties were measured with a linearly polarized laser light ($\lambda = 532 \text{ nm}$; pulse width = 8 ns) generated from a Q-switched and frequency-doubled Nd-YAG laser. The spatial profiles of the optical pulses were nearly Gaussian. DMF solutions of polymers **1** and **2** were placed in the 2 mm quartz cuvette, respectively, for NLO measurements. The crystal sample of each polymer is stable toward oxygen, moisture and laser light. The laser beam was focused with a 25-cm focal-length focusing mirror. The radius of the beam waist was measured to be $35 \pm 5 \mu\text{m}$ (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 [62,63]. 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. An aperture of 0.5 mm in radius was placed in front of the detector to assist the measurement of the refractive effects.

Acknowledgements

This work was supported by the NSF of China (Nos. 20601015, 20871072), the NSF of Shandong Province (No. Y2006B12), the

Doctoral Science Foundation of Shandong Province (No. 2007BS04023), the Doctoral Science Foundation of QUST.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.07.005.

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