

# Two novel two-dimensional double-sheet layered manganese(II) coordination polymers: synthesis, crystal structures and third-order nonlinear optical properties

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Two novel Mn(II) coordination polymers  $[\text{Mn}(\text{N}_3)_2(\text{bbp})_2]_n$  **1** and  $\{[\text{Mn}(\text{NCS})_2(\text{bbp})_2] \cdot 0.25\text{H}_2\text{O}\}_n$  **2** (bbp = 4,4'-trimethylenedipyridine) with 2D double-sheet layered structures were obtained by a normal synthesis method at room temperature. Interestingly, each layer contains two sheets; the double-sheet layer is formed around an octahedral coordination center, Mn(II), with bbp ligands knitted into each other. The structures both contain channels with dimensions of about  $6.5 \times 6.5 \text{ \AA}$  for **1** and  $6.7 \times 6.0 \text{ \AA}$  for **2**. Both compounds have a similar construction, giving the same third-order nonlinear optical (NLO) behavior and weak antiferromagnetic properties. Their third-order NLO refractive indexes  $n_2$  are  $1.21 \times 10^{-18} \text{ m}^2 \text{ W}^{-1}$  for **1** and  $6.71 \times 10^{-19} \text{ m}^2 \text{ W}^{-1}$  for **2**. The NLO susceptibilities  $\chi^{(3)}$  were calculated to be  $4.78 \times 10^{-12} \text{ esu}$  and  $2.40 \times 10^{-12} \text{ esu}$ , respectively.

## Introduction

The crystal engineering of supramolecular arrays has always been considered by researchers for their wide implications in the rational design of functional materials,<sup>1-3</sup> e.g. non-linear optical (NLO) properties, catalysis, magnetism, electronics and chemical separation.<sup>4,5</sup> In particular, coordination networks containing large pores or tunnels with controlled sizes, shapes and chemical environments are of great interest,<sup>6-8</sup> in that the diversity of structures is attractive, and they have enormous potential applications in molecular absorption, ion exchange and heterogeneous catalysis.<sup>6,9-12</sup> Moreover, the host frameworks of coordination polymers with porous or tunnels structure can withstand the removal/addition of guest molecules, compared with unstable organic hydrogen-bonded motifs,<sup>13,14</sup> or they exhibit high shape specificity in clathration.<sup>12</sup> In addition, the design and synthesis of molecular-based magnets containing transition metal ions is driving many researchers' attention.<sup>15-18</sup> It is well known that coordination polymers play an important role in the family of NLO materials.<sup>19-21</sup>

A variety of coordination polymers have been extensively investigated in supramolecular architectures. 4,4'-Bipyridine (bpy) has been used to construct coordination polymers showing novel structural features, such as zigzag, railroad or ladder 1D structures,<sup>22-24</sup> 2D square-grid networks,<sup>22,25,26</sup> and 3D diamondoid frameworks.<sup>22,27</sup> The bpe-based (bpe = 1,2-*trans*-bis(4-pyridyl)ethene) coordination polymers are not scarce either, such as  $[\text{Co}(\text{bpe})_{1.5}(\text{NO}_3)_2]$ ,<sup>22,28</sup>  $[\text{Cu}(\text{bpe})_2] \cdot [\text{Cu}(\text{bpe})(\text{H}_2\text{O})(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$ ,<sup>22,29</sup>  $[\text{Cu}(\text{bpe})(\text{H}_2\text{O})(\text{SO}_4)]$ ,<sup>22,29</sup>  $[\text{Cu}(\text{bpe})(\text{MoO}_4)]$ .<sup>22,30</sup> Moreover, bpbd- (bpbd = 1,4-bis(4-pyridyl)butadiene) or bbp-based (bbp = 4,4'-trimethylenedipyridine) structures also have been reported, such as the ladder structure of  $[\text{Cu}_2(\text{bpbd})_3(\text{MeCN})_2](\text{PF}_6)_2$ ,<sup>22,31</sup> 3D rhombohedral structure of  $[\text{Mn}(\text{bbi})_3](\text{BF}_4)_2$  (bbi = *N,N'*-butylenebisimidazole),<sup>22,32</sup> the sinusoidal chain of  $[\text{Ag}(\text{bbp})] \cdot (\text{CF}_3\text{SO}_4) \cdot \text{EtOH}$ , the helical chains of  $[\text{Ag}(\text{bbp})](\text{CF}_3\text{SO}_4)$ , and tubular channel structure of  $[\text{Ag}_2(\text{bbp})_4](\text{CF}_3\text{SO}_4)_2 \cdot \text{bbp}$ .<sup>22,33</sup>

Meanwhile, some other coordination polymers containing manganese ions also can exhibit as weak bimetallic magnet. And many magnetic properties of Mn(II)-bpy based polymers have been reported.<sup>34,35</sup> Most of them exhibited moderate antiferromagnetic properties.

In this contribution, we report the crystal structures, third-order NLO and magnetic properties of the coordination polymer  $[\text{Mn}(\text{N}_3)_2(\text{bbp})_2]_n$  **1** and the polymer  $\{[\text{Mn}(\text{NCS})_2(\text{bbp})_2] \cdot 0.25\text{H}_2\text{O}\}_n$  **2**. The two polymers have a similar 2D double-sheet layered structure, which contain channels with dimensions of about  $6.5 \times 6.5 \text{ \AA}$  for **1** and  $6.7 \times 6.0 \text{ \AA}$  for **2**. We determined the third-order NLO properties by Z-scan technique, their NLO refractive indexes  $n_2$  are  $1.21 \times 10^{-18} \text{ m}^2 \text{ W}^{-1}$  for **1** and  $6.71 \times 10^{-19} \text{ m}^2 \text{ W}^{-1}$  for **2**. The susceptibilities  $\chi^{(3)}$  were calculated to be  $4.78 \times 10^{-12} \text{ esu}$  and  $2.40 \times 10^{-12} \text{ esu}$ , respectively. The two compounds also exhibit weak antiferromagnetic properties.

## Experimental

### General

Bbp was purchased from Aldrich. Other chemicals were of AR grade and were used without further purification. IR spectra were recorded on a Shimadzu Model 435 instrument. Elemental analysis was carried out on a Carl-Erba Model 1106 instrument. Molecular weight in DMF solution was determined on a Waters 515 instrument.

### Preparation of polymer $[\text{Mn}(\text{N}_3)_2(\text{bbp})_2]_n$ **1**

A mixture of bbp (79.01 mg, 0.4 mmol) with  $\text{NaN}_3$  (26.00 mg, 0.4 mmol) in 5 ml methanol solution was added dropwise into 3 ml aqueous solution of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (33.80 mg, 0.2 mmol). Pale-yellow crystals (65 mg, yield 30%) suitable for X-ray single crystal analysis were obtained after standing for 1 week at room temperature. IR (KBr):  $2100 \text{ cm}^{-1}$  (s,  $\text{N}_3^-$ ). Anal. calc. for  $\text{C}_{26}\text{H}_{28}\text{MnN}_{10}$  (%): C, 58.26; H, 5.23; N, 26.14. Found: C, 59.03; H, 5.80; N, 25.88.

## Preparation of polymer $\{[\text{Mn}(\text{NCS})_2(\text{bbp})_2] \cdot 0.25\text{H}_2\text{O}\}_n$ **2**

An aqueous solution of KNCS (19.4 mg, 0.2 mmol) was added into a solution of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (16.9 mg, 0.1 mmol), then bbp (26.9 mg, 0.1 mmol) in 3 ml ethanol was added dropwise into the above solution with mixing. Pale-yellow crystals (30 mg, yield 38%) were obtained at room temperature after 2 days. IR (KBr):  $2100 \text{ cm}^{-1}$  (s,  $\text{NCS}^-$ ). Anal. calc. for  $\text{C}_{56}\text{H}_{56}\text{Mn}_2\text{N}_{12}\text{O}_{0.5}\text{S}_4$  (%): C, 58.79; H, 4.90; N, 14.70. Found: C, 59.12; H, 4.95; N, 14.98.

## 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  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Both light-yellow prismatic single crystals having dimensions of  $0.2 \times 0.2 \times 0.2 \text{ mm}$  for **1** and  $0.3 \times 0.2 \times 0.2 \text{ mm}$  for **2** were mounted on a glass fiber. The data were collected at a temperature of  $18 \pm 1^\circ \text{C}$  and corrected for Lorentz-polarization effects, and absorption was corrected for by using empirical scan data. A correction for secondary absorption was applied.

The structures were resolved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2413 observed reflections and 186 variable parameters for polymer **1** and 10021 observed reflections and 672 variable parameters for polymer **2**. All calculations were performed using the SHELXL-97 Program.<sup>36</sup> Table 1 shows the crystal data and structure refinements of the two polymers. Selected bond lengths and bond angles are listed in Table 2.

CCDC reference numbers 163569 and 163570. See <http://www.rsc.org/suppdata/jm/b1/b107375n/> for crystallographic data in CIF or other electronic format.

## NLO measurements

A DMF solution of polymer **1** (or **2**) was placed in a 1 mm quartz cuvette for NLO measurements. The NLO properties were measured as described in the literature.<sup>37</sup>

## Magnetic measurement

Magnetic measurement was carried out on a Quantum Design MPMS-5 SQUID ac/dc magnetometer in the temperature range 5.0–300 K with an applied field of 1 T. Diamagnetic

**Table 1** Crystallographic data for  $[\text{Mn}(\text{N}_3)_2(\text{bbp})_2]_n$  **1** and  $\{[\text{Mn}(\text{NCS})_2(\text{bbp})_2] \cdot 0.25\text{H}_2\text{O}\}_n$  **2**

	Polymer <b>1</b>	Polymer <b>2</b>
Formula	$\text{C}_{26}\text{H}_{28}\text{MnN}_{10}$	$\text{C}_{56}\text{H}_{56}\text{Mn}_2\text{N}_{12}\text{O}_{0.5}\text{S}_4$
MW	535.52	1143.25
Space group	$C2/c$	$P2(1)/n$
$T/\text{K}$	291(2)	291(2)
$\lambda/\text{\AA}$	0.71073	0.71073
$a/\text{\AA}$	19.439(4)	19.006(4)
$b/\text{\AA}$	7.1280(14)	16.679(3)
$c/\text{\AA}$	21.489(4)	20.788(4)
$\beta/^\circ$	112.76(3)	115.04(3)
$V/\text{\AA}^3$	2745.8(9)	5970.4(21)
$Z$	4	4
$\rho_{\text{calc}}/\text{mg cm}^{-3}$	1.295	1.272
Absorption coefficient/mm	0.515	0.610
$F(000)$	1116	2376
Reflections collected	2413	15204
Unique reflections ( $R(\text{int})$ )	2413 (0.0000)	10021 (0.0374)
Data/restraints/parameters	2413/0/186	10021/0/672
Goodness-of-fit on $F^2$	1.097	1.073
$R1[I > 2\sigma(I)]$	0.0613	0.0772
$wR2[I > 2\sigma(I)]$	0.0813	0.1412

**Table 2** Selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) of  $[\text{Mn}(\text{N}_3)_2(\text{bbp})_2]_n$  **1** and  $\{[\text{Mn}(\text{NCS})_2(\text{bbp})_2] \cdot 0.25\text{H}_2\text{O}\}_n$  **2**

Polymer <b>1</b>			
Mn(1)–N(1)	2.1811(17)	N(1)–Mn(1)–N(1A)	180.00(14)
Mn(1)–N(4)	2.3414(15)	N(5)–Mn(1)–N(5A)	180.00(6)
Mn(1)–N(5)	2.2969(17)	N(4)–Mn(1)–N(4A)	180.00(4)
N(1)–N(2)	1.177(2)	N(1)–Mn(1)–N(5)	89.08(6)
N(4)–C(5)	1.327(3)	N(1)–Mn(1)–N(4)	92.47(6)
N(4)–C(1)	1.329(2)	N(4)–Mn(1)–N(5)	87.89(6)
Polymer <b>2</b>			
Mn(1)–N(1)	2.293(3)	N(6)–Mn(1)–N(5)	178.76(12)
Mn(1)–N(4)	2.303(4)	N(6)–Mn(1)–N(3)	90.49(13)
Mn(1)–N(5)	2.192(3)	N(5)–Mn(1)–N(3)	90.67(12)
N(1)–C(5)	1.311(5)	N(1)–Mn(1)–N(3)	176.83(13)
N(4)–C(16)	1.325(5)	N(2)–Mn(1)–N(4)	179.34(11)
N(5)–C(28)	1.163(5)	N(4)–Mn(1)–N(5)	90.31(13)
Mn(2)–N(12)	2.186(3)	N(12)–Mn(2)–N(11)	176.82(11)
Mn(2)–N(7)	2.300(3)	N(10)–Mn(2)–N(8)	177.53(11)
Mn(2)–N(10)	2.279(3)	N(7)–Mn(2)–N(9)	173.96(10)
N(10)–C(44)	1.346(5)	N(12)–Mn(2)–N(10)	90.11(11)
N(11)–C(55)	1.144(4)	N(12)–Mn(2)–N(7)	90.32(11)
N(9)–C(43)	1.324(4)	N(10)–Mn(2)–N(9)	89.56(10)

corrections were estimated from the Pascal tables ( $-268.58 \times 10^{-6} \text{ emu mol}^{-1}$  for **1** and  $-347.98 \times 10^{-6} \text{ emu mol}^{-1}$  for **2**)

## Results and discussion

### Description of crystal structures

The general features of polymers  $[\text{Mn}(\text{N}_3)_2(\text{bbp})_2]_n$  **1** and  $\{[\text{Mn}(\text{NCS})_2(\text{bbp})_2] \cdot 0.25\text{H}_2\text{O}\}_n$  **2** are similar. In both polymers, the manganese atoms are coordinated to four nitrogen atoms from four bbp ligands, and the other two remaining coordination sites are occupied by different small groups  $\text{N}_3^-$  or  $\text{NCS}^-$ , among which bbp units act as the bridging ligands. This set of bridges, extended as an infinite structure, lead to the 2D double-sheet layered structure.

With regard to polymer **1**, the central metal ion Mn(II) is six-coordinated with octahedral geometry (Fig. 1). The four N atoms from different bbp ligands are on the equatorial plane, and are at an angle of about  $90^\circ$  to each other. Two  $\text{N}_3^-$  anions, as terminal ligands, coordinate to the Mn(II) in the axial direction. Many Mn(II) centers adjoined by bbp ligands form a 2D network of rhombohedral grid structure. The four vertex of the rhombohedral grid are occupied by four Mn atoms, the four edges are four bbp ligands. The distance between Mn1O and Mn1R is 21.489  $\text{\AA}$ , and the distance between Mn1E and Mn1P is 14.256  $\text{\AA}$ . The edge length of the rhombohedral grid is 12.894  $\text{\AA}$ . It is interesting that the layered feature is a double-sheet consisting of two 2D sheets. The two sheets are interpenetrating, and the Mn atoms in one sheet occupy the exact centers of the rhombohedral grid in the other sheet.

Fig. 2 shows the stacking mode of the structure along the  $b$  axis. A 2D double-sheet layered structure with parallel channels can be seen from the figure. The dimensions of the channels are about  $6.5 \times 6.5 \text{ \AA}$ , which is quarter of the rhombohedral grid. Moreover, the formation of  $\text{N}\cdots\text{H}-\text{C}(\text{CH})$  hydrogen bonds makes a quasi-3D-structure by connecting the different layers, the shortest interplane distance between Mn and Mn is about 9.8  $\text{\AA}$ . The hydrogen bond length is 3.425  $\text{\AA}$ , among which the distance between the N atom and the H atom is 2.612  $\text{\AA}$ , the bond angle is  $146.4^\circ$ . In this structure,  $\text{N}_3^-$  units do not coordinate as bridging ligands but act as terminal ones, which leads to a weak superexchange between the metal centers; this is different from that of the reported structures, in which  $\text{N}_3^-$  act either as end or as end-to-end bridging ligands.<sup>34,35</sup>

Polymer **2** has a similar structure to polymer **1**. The Mn(II) centers are also in an octahedral coordination environment. But it is different in that all the Mn(II) atoms are not planar,

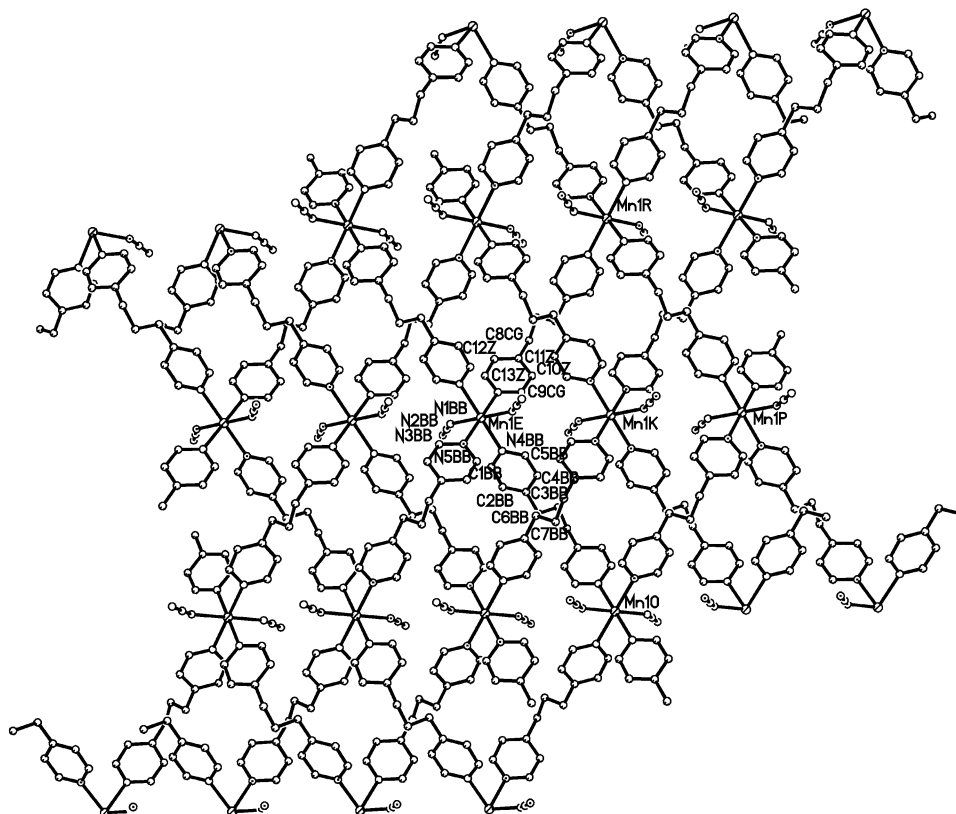


Fig. 1 2D rhombohedral grid structure of  $[\text{Mn}(\text{N}_3)_2(\text{bbp})_2]_n$ .

they are divided into two types: Mn1 and Mn2 (Fig. 3). Mn1, bridged by bbp ligands, constitute one sheet, and Mn2 make the other. The two 2D sheets also inter-knitted into a double-sheet layer. The coordination octahedron of the Mn(II) atom is quite regular with all the bonds lengths comprised in the range 2.192(3)–2.303(4) Å for Mn1, and 2.186(3)–2.300(3) Å for Mn2. Four N atoms from four pyridine rings occupy an

equatorial position. The two pyridine rings at the *p*-position are vertical, which is different from polymer 1. Polymer 2 has smaller channels with dimensions of about  $6.7 \times 6.0$  Å, in contrast to that of polymer 1. Some  $\text{H}_2\text{O}$  molecules can be found between the different layers, and link the two layers together by hydrogen bonds. There are also hydrogen bonds formed between the S atoms, from  $\text{NCS}^-$ , and the C atoms

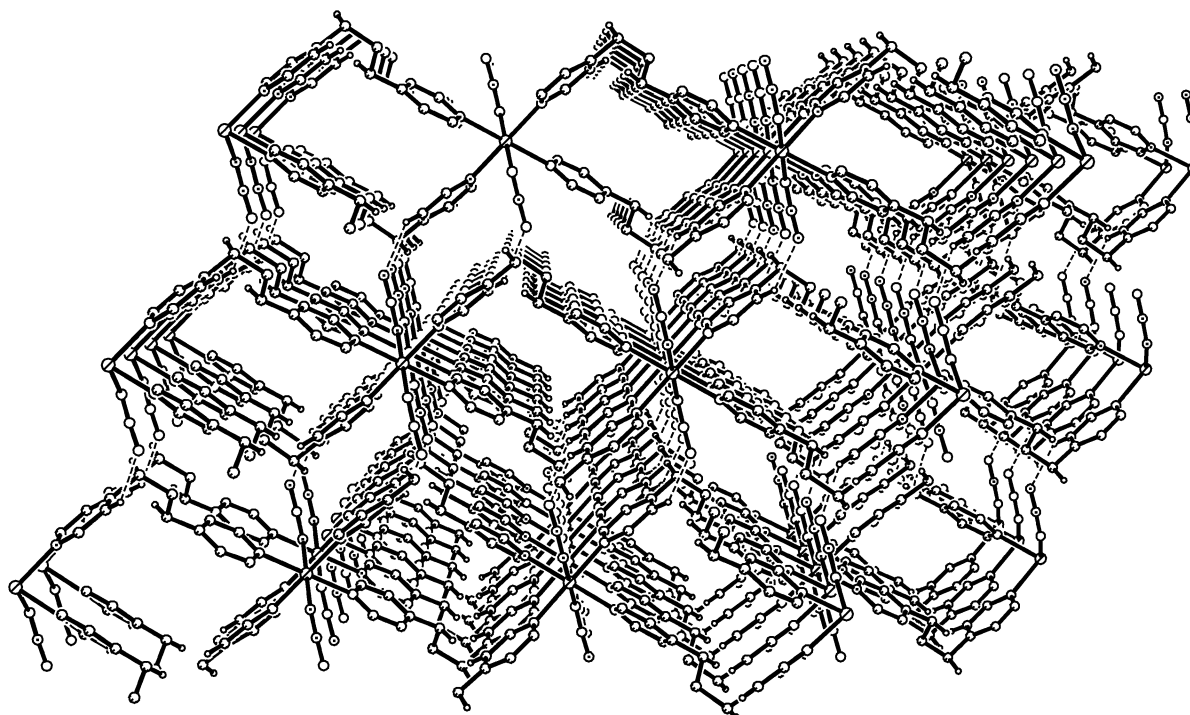


Fig. 2 The stacking mode of  $[\text{Mn}(\text{N}_3)_2(\text{bbp})_2]_n$  along *b* axis.

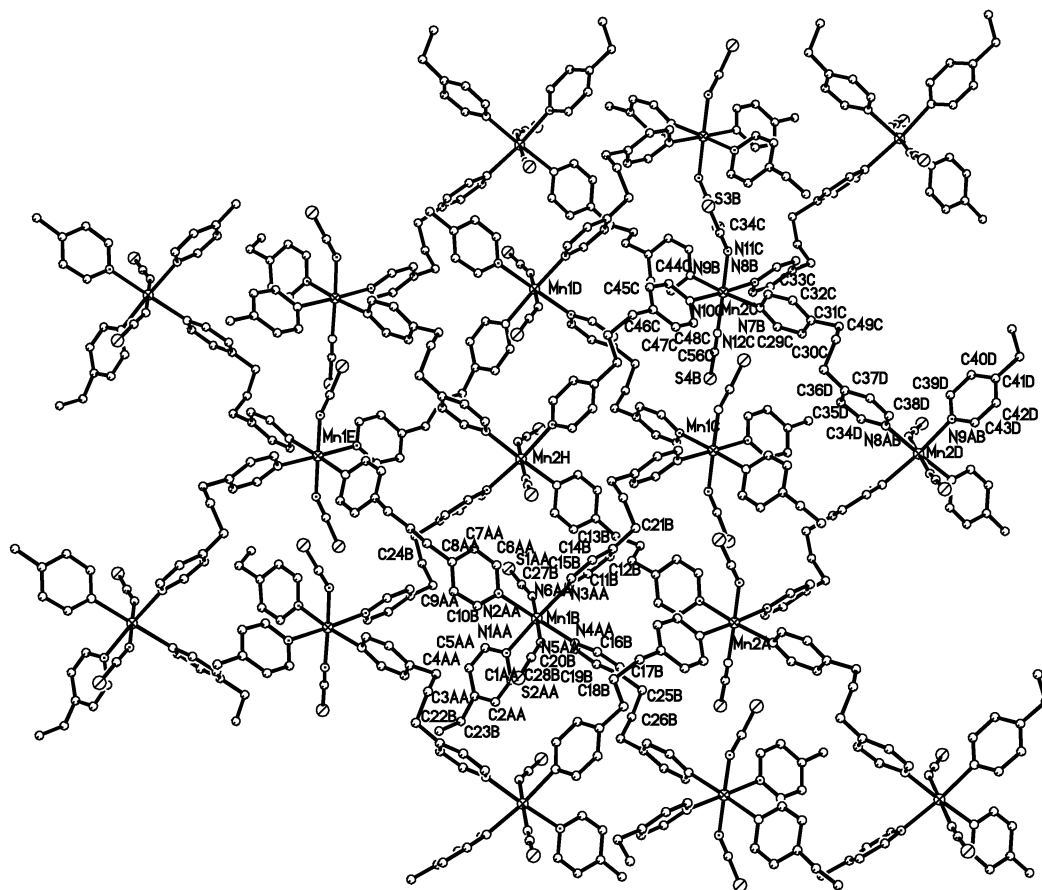


Fig. 3 2D double-sheet structure of  $\{[\text{Mn}(\text{NCS})_2(\text{bbp})_2] \cdot 0.25\text{H}_2\text{O}\}_n$ .

from the pyridine rings. The  $\text{S} \cdots \text{H}-\text{C}(\text{CH})$  hydrogen bond length is 3.642 Å, the  $\text{S} \cdots \text{H}-\text{C}$  bond angle is 145.8°.

There have been structures based on bbp reported before, they are the sinusoidal chain of  $[\text{Ag}(\text{bbp})](\text{CF}_3\text{SO}_4) \cdot \text{EtOH}$ , the helical chains of  $[\text{Ag}(\text{bbp})](\text{CF}_3\text{SO}_4)$ , and the interpenetration of the tubular channels of  $[\text{Ag}_2(\text{bbp})_4](\text{CF}_3\text{SO}_4)_2 \cdot \text{bbp}$ .<sup>22,33</sup> All these structures have a coordination center involving Ag, and the modes of coordination are different from  $[\text{Mn}(\text{N}_3)_2(\text{bbp})_2]$  and  $\{[\text{Mn}(\text{NCS})_2(\text{bbp})_2] \cdot 0.25\text{H}_2\text{O}\}_n$ . The double-sheet motif of  $[\text{Co}_2(4,4'\text{-bpy})_3(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$ <sup>22,38</sup> is constructed from  $\{\text{Co}_2(4,4'\text{-bpy})(\text{NO}_3)_2\}$  linear chains linked by 4,4'-bpy bridges. One set of chains lies parallel to the plane of the page while the second set is normal to the page. The 2D motif of  $[\text{Zn}(\text{bix})_2](\text{NO}_3)_2 \cdot 4.5\text{H}_2\text{O}$  ( $\text{bix} = 1,4\text{-bis}(\text{imidazol-1-ylmethyl})\text{benzene}$ ) exhibits the interpenetration of two independent sheets, the structure is constructed of  $\{\text{Zn}_2(\text{bix})_2\}$  rings linked by bix bridges into a 2D rotaxane structure,<sup>22,39</sup> which is similar to the structures of polymers **1** and **2**. It is noteworthy that the structures of polymers **1** and **2** also exhibit the interpenetration of two independent sheets, and the stacking modes lead to the existence of channels.

### NLO properties

Coordination polymers are considered as very promising candidates for NLO applications.<sup>1,19–21</sup> Here we report third-order NLO properties of polymers **1** and **2**. Their UV–Vis spectrum in DMF solution shows that both of them have a very low linear absorption, ranging from 350 to 1000 nm. The molecular weight of polymer **1** is 3473. We can observe two peaks on the molecular weight measurements of polymer **2**, which show that the molecular weight of polymer **2** is 24101 or 3439.

The NLO properties of polymers **1** and **2** were measured as described in the literature<sup>19–21,37</sup> except that the concentration

was  $1.2 \times 10^{-3} \text{ mol dm}^{-3}$  for polymer **1** or  $2.6 \times 10^{-4} \text{ mol dm}^{-3}$  for polymer **2** in a DMF solution. We found that polymers **1** and **2** possess strong NLO refractive effects. Figs. 4 and 5 depict their NLO refractive properties, respectively. 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. The data show that the two polymers have a similar positive sign for the refractive nonlinearity, which gives rise to self-focusing behavior. The effective third-order NLO refractive index  $n_2$  is based on:

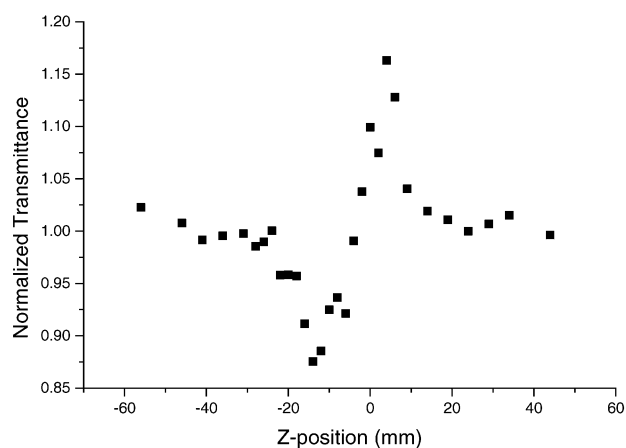
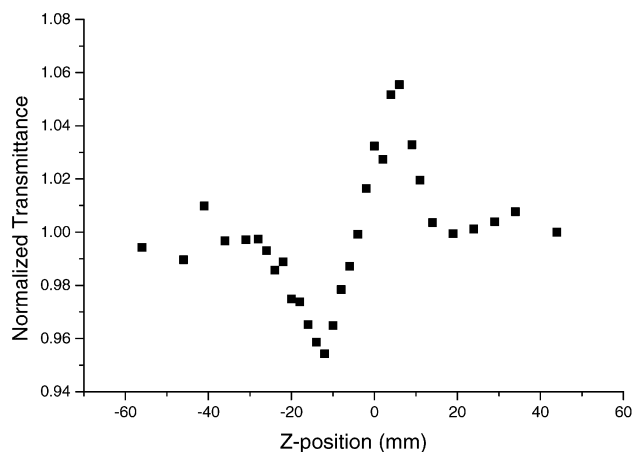


Fig. 4 Z-scan data of  $1.2 \times 10^{-3} \text{ mol dm}^{-3}$  DMF solution of  $[\text{Mn}(\text{N}_3)_2(\text{bbp})_2]_n$  at 532 nm with incident energy of 150  $\mu\text{J}$ . The data were manifested by moving the sample along the axis of the incident beam (Z-direction) with respect to the focal point. An aperture of 1 mm radius was placed in front of the detector measuring the self-focusing effect.



**Fig. 5** Z-scan data of  $2.6 \times 10^{-4}$  mol  $\text{dm}^{-3}$  DMF solution of  $\{[\text{Mn}(\text{NCS})_2(\text{bbp})_2] \cdot 0.25\text{H}_2\text{O}\}_n$  at 532 nm with incident energy of 150  $\mu\text{J}$ . The data were manifested by moving the sample along the axis of the incident beam (Z-direction) with respect to the focal point. An aperture of 1 mm radius was placed in front of the detector measuring the self-focusing effect.

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

where  $\Delta T_{V-P}$  is the difference between the normalized transmittance values at the valley and peak portions,  $\alpha_0$  is the linear coefficient,  $L$  is the sample thickness,  $I$  is the peak irradiation intensity at focus, and  $\lambda$  is the wavelength of the laser.

It can be seen from Fig. 4 that the difference of valley – peak positions,  $\Delta Z_{V-P}$ , is 29 mm, the difference between normalized transmittance values at valley and peak portions,  $\Delta T_{V-P}$ , is 0.18. In accordance with Fig. 5,  $\Delta Z_{V-P}$  and  $\Delta T_{V-P}$  are 18 mm and 0.10, respectively. The refractive index  $n_2$  of the two polymers can be calculated to be  $1.21 \times 10^{-18} \text{ m}^2 \text{ W}^{-1}$  for **1** and  $6.71 \times 10^{-19} \text{ m}^2 \text{ W}^{-1}$  for **2**. The third-order NLO susceptibility based on  $\chi^{(3)} = cn_0^2 n_2 / 80\pi$  are  $4.78 \times 10^{-12}$  esu and  $2.40 \times 10^{-12}$  esu, respectively. The data are comparable to those of the 1D coordination polymers  $[\text{Co}(\text{NCS})_2(\text{bpms})_2]_n$  (bpms = 1,2-bis(4-pyridylmethyl)disulfenyl) and  $\{[\text{Mn}(\text{NCS})_2(\text{bpy})(\text{H}_2\text{O})_2] (\text{bpy})\}_n$ , and the 3D coordination polymers  $[\text{Mn}(\text{SO}_4)(\text{bpy})(\text{H}_2\text{O})_2]_n$  and  $[\text{Mn}(\text{N}_3)_2(\text{bpy})]_n$ .<sup>20,21</sup>

Polymers **1** and **2** have a 2D structure and both of them exhibit self-focusing behavior. The behavior differs from those of the 1D polymers  $[\text{Co}(\text{NCS})_2(\text{bpms})_2]_n$  and

$\{[\text{Mn}(\text{NCS})_2(\text{bpy})(\text{H}_2\text{O})_2] (\text{bpy})\}_n$ , and the 3D polymers  $[\text{Mn}(\text{SO}_4)(\text{bpy})(\text{H}_2\text{O})_2]_n$  and  $[\text{Mn}(\text{N}_3)_2(\text{bpy})]_n$ , which gives rise to self-defocusing effects. These polymers have the same metal atom and are similar “bpy-based” ligands, but they show different structures, so they give different NLO properties, which illustrates that the NLO properties of coordination polymers are altered through structural manipulation.

Coordination polymers are different to organic polymers, semiconductors and cluster polymers. When some coordination polymers are dissolved in an organic solution, the solvent may substitute some weak ligands (such as  $\text{H}_2\text{O}$ ) to form new complexes; the NLO data obtained may be from these new complexes. Coordination polymers **1** and **2** possess a 2D network structure, they are very stable in general organic solution because bbp ( $\text{NCS}^-$  or  $\text{N}_3^-$ ) has a stronger coordination ability than DMF. To put the optical nonlinearity of polymers **1** and **2** in a proper perspective with reference to other known third-order NLO materials, the  $n_2$  and  $\chi^{(3)}$  values are listed in Table 3 along with the reported  $n_2$  and  $\chi^{(3)}$  values of related coordination polymers and a few best performing inorganic oxide glasses, semiconductors, organic polymers and cluster polymers. Most of the best performing third-order NLO materials reported in the literature are neat materials, such as inorganic oxide glasses, semiconductors and organic polymers; the NLO properties of coordination polymers were determined in a  $10^{-4}$  M solution. It can be seen from Table 3 that the  $n_2$  and  $\chi^{(3)}$  values for polymers **1** and **2** are close to those of inorganic oxide glasses, semiconductors and organic polymers. A much larger  $n_2$  or  $\chi^{(3)}$  value may be expected if a much higher concentration can be achieved. Cluster polymers show very strong NLO properties, and are considered as potential candidates for NLO applications. Coordination polymers possess the advantage of cluster polymers, and they also have strong NLO properties. It is obvious that coordination polymers will be better candidate NLO materials.

The two polymers were shown to exhibit weak antiferromagnetic coupling as expected for the long pathway through the organic ligands, with superexchange parameters  $J = -0.038 \text{ cm}^{-1}$ ,  $g = 2.04$  for **1** and  $J = -0.040 \text{ cm}^{-1}$ ,  $g = 2.06$  for **2**. The experimental value  $\mu_{\text{eff}}$ , which is  $5.85 \mu_{\text{B}}$  for **1** ( $5.97 \mu_{\text{B}}$  for **2**), suggests that the Mn(II) ions are in a high-spin state with  $S = 5/2$  (theoretically,  $\mu_{\text{eff}} = 5.92 \mu_{\text{B}}$ ). This is much smaller than that of reported complexes,<sup>34,35</sup> whose bridging ligands are  $\text{N}_3^-$ , with a very short pathway. It shows that there are weak magnetic interactions between two adjacent Mn(II) centers in polymers **1** and **2**.

**Table 3** Optical parameters of selected candidate NLO materials

Compound <sup>a</sup>	$N/\text{mol dm}^{-3}$	Color	$n_2/\text{m}^2 \text{ W}^{-1}$	$\chi^{(3)}/\text{esu}$	Ref.
$\text{SiO}_2$	Neat		$2 \times 10^{-20}$		40
RN	Neat		$1.3 \times 10^{-18}$		40
$\text{AlGaAs}$	Neat		$2 \times 10^{-17}$		40
GaAs	Neat		$-3 \times 10^{-17}$	$4.8 \times 10^{-11}$	40–42
Ge	Neat			$4 \times 10^{-10}$	41,42
PA	Neat			$5.0 \times 10^{-10}$	41,42
PDA–PTS	Neat			$8.5 \times 10^{-10}$	41,42
PDA–4BCMU	Neat			$1.8 \times 10^{-10}$	41,42
Poly-4BCMU	Neat		$8 \times 10^{-18}$		40
DANS	Neat		$8 \times 10^{-18}$		40
PTS	Neat		$-2 \times 10^{-16}$		40
$[\text{MoOS}_3\text{Cu}_3(\text{CN})(\text{py})_3]_n$	$5.3 \times 10^{-5}$	Deep red	$-8 \times 10^{-18}$		43
$[\text{MoS}_4\text{Cu}_6\text{I}_4(\text{py})_4]_n$	$6.5 \times 10^{-5}$	Black	$-2.5 \times 10^{-17}$		19
$\{[\text{Et}_4\text{N}]_2[\text{MoS}_4\text{Cu}_4(\text{CN})_4]\}_n$	$3.6 \times 10^{-5}$	Black	$1.84 \times 10^{-16}$	$4.58 \times 10^{-9}$	44
$\{[\text{Et}_4\text{N}]_2[\text{WS}_4\text{Cu}_4(\text{CN})_4]\}_n$	$2.9 \times 10^{-5}$	Red	$1.22 \times 10^{-16}$	$5.12 \times 10^{-9}$	44
$[\text{Mn}(\text{N}_3)_2(\text{bbp})_2]_n$	$1.2 \times 10^{-3}$	Pale yellow	$1.21 \times 10^{-18}$	$4.78 \times 10^{-12}$	This work
$\{[\text{Mn}(\text{NCS})_2(\text{bbp})_2] \cdot 0.25\text{H}_2\text{O}\}_n$	$2.6 \times 10^{-4}$	Pale yellow	$6.71 \times 10^{-19}$	$2.40 \times 10^{-12}$	This work

<sup>a</sup>RN = rubidium nitrate, PA = polyacetylenes, PDA = polydiacetylenes, 4BCMU = a polydiacetylenes derivative, DANS = (dimethylanilino)-nitrostilbene, PTS = *p*-toluenesulfonate.

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