Polyhedron 152 (2018) 55-60

Contents lists available at ScienceDirect

# Polyhedron

journal homepage: www.elsevier.com/locate/poly

# NH<sub>4</sub>MSO<sub>4</sub>F (M = Mn, Fe, Co, Ni): A series of thermally stable transition metal fluorosulfates with KTP-type structure



POLYHEDRON

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# ARTICLE INFO

Article history: Received 23 March 2018 Accepted 5 June 2018 Available online 14 June 2018

Keywords: Metal fluorosufates Solvothermal synthesis Crystal structures Thermal stability Magnetic property

# ABSTRACT

Four new transition metal fluorosulfates NH<sub>4</sub>MSO<sub>4</sub>F (M = Mn, **1**; Fe, **2**; Co, **3**; Ni, **4**) were solvothermally synthesized in the solvent of N,N-dimethylacetamide (DMA) with HF as the mineralization agent. The X-ray single crystal diffraction analyses revealed that **1–4** are isomorphous, and possess a three-dimensional framework with the same structural topology as the known nonlinear optical material KTiOPO<sub>4</sub> (KTP). The four compounds were constructed from MO<sub>4</sub>F<sub>2</sub> octahedra and SO<sub>4</sub> tetrahedra to form two kinds of intersecting 6-membered ring channels along the *a* and *c* axes, respectively. Within the channels locate the NH<sub>4</sub><sup>+</sup> cations from the decomposition of DMA molecules. All the compounds are thermally stable up to 330 °C. The magnetic studies of **1–4** revealed the antiferromagnetic interaction behaviors in the range of 1.8–300 K.

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# 1. Introduction

Porous solid materials based on TO<sub>4</sub> (T = Si, Al, P, etc.) tetrahedra have been extensively studied due to their potential applications in the fields of catalysis, separation and ion-exchange [1]. The similarities of coordination chemistry and geometry between SO<sub>4</sub> and PO<sub>4</sub> tetrahedra suggest the possibility to prepare a large family of openframework metal sulfates with diverse structures. Compared to the abundance and diversity of metal phosphates reported in the literature [2], however, the metal sulfates constructed from SO<sub>4</sub> tetrahedra have not been paid much attention until a few transition metal sulfates and rare earth sulfates with interesting framework structures and properties were reported in the past decades [3]. Recently, alkali ion containing metal fluorosulfates LiMSO<sub>4</sub>F (M = Mn, Fe, Co, Ni, Zn, etc.) with olivine, tavorite and sillimanite structures have been of particular interests because these materials exhibit excellent electrochemical properties with promising applications in lithium-ion based batteries [4]. By using the methods of preparation of zeolites and aluminophosphates, i.e., hydrothermal synthesis with the presence of structure-directing agents and/or mineralizer  $F^{-}$  ion, a number of metal sulfates have been reported [5], which exhibit rich structural chemistry. The incorporation of fluoride into the transition metal sulfate frameworks results in linkage of MO<sub>4</sub>F<sub>2</sub>

\* Corresponding authors. E-mail addresses: gegenwu@163.com (G.-w. Ge), liangjyt@163.com (L.-l. Liang). or  $MO_2F_4$  units through vertex, edge, or face sharing to form additional M–F–M linkages, this allows the control of the structural dimensionality and linking fashion of the polyhedra [6], while most known 3D framework sulfates are formed by strict alternation of  $MO_6$  or  $MO_4$  and  $SO_4$  units without any direct connection between two  $MO_6$  octahedra or  $MO_4$  tetrahedra.

On the other hand, it is known that  $KTiOPO_4$  (KTP) is an outstanding nonlinear optical material for second harmonic generation (SHG) due to its high power conversion efficiencies [7]. The Ti and P atoms in the KTP framework can be replaced by other transition or main-group metals, and other group V elements, respectively, while the K<sup>+</sup> ions can also be substituted with other alkali, ammonium ions, and organic amines etc. [8]. There have been a number of metal phosphates [9] and arsenates [10] with KTP-type structure reported in the literature. However, the metal sulfates with KTP-type structure have not been reported so far. We herein report the synthesis and characterization of four new transition metal fluorosulfates NH<sub>4</sub>MSO<sub>4</sub>F (M = Mn, **1**; Fe, **2**; Co, **3**; Ni, **4**) possessing KTP-type structure.

# 2. Experimental

# 2.1. Synthesis

All reagents were of analytical grade and used as received without any further purification. The four compounds were



solvothermally prepared by using nearly identical methods from a mixture of metal nitrate, concentrated H<sub>2</sub>SO<sub>4</sub> and aqueous HF. A typical procedure is as follows: 0.5 mmol of metal nitrates (0.375 g of 50% Mn(NO<sub>3</sub>)<sub>2</sub> solution for **1**, 0.202 g of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O for **2**, 0.146 g of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O for **3** and 0.375 g of 33% Ni(NO<sub>3</sub>)<sub>2</sub> solution for 4) were first dissolved in 6 ml of N,N-dimethylacetamide (DMA), followed by dropwise addition of 2 mmol of concentrated H<sub>2</sub>SO<sub>4</sub> (98%, 0.11 ml) under stirring. To the above solution was added 2 mmol of 40% HF solution (be cautious!) with a syringe. The clear solution after stirring for 30 min was transferred into a 15 ml Teflon-lined stainless steel autoclave, and heated at 180 °C for 5 days. After cooling to room temperature naturally, colourless diamond crystals (1 and 2), red (3) or light green (4) bipvramid crystals were obtained by filtration, and washed with ethanol and acetone, then dried in air.

# 2.2. Characterization

Powder X-ray diffraction (PXRD) data were obtained using Bruker D8 Advance diffractometer with Cu K $\alpha$  radiation  $(\lambda = 1.54056 \text{ Å})$ , with a step speed of 0.2° per second. FT-IR spectra were recorded on a Nicolet Impact 410 spectrometer between 400 and 4000 cm<sup>-1</sup> using the KBr pellet method. Thermogravimetric analyses (TGA) were conducted on a Perkin-Elmer Pyris I thermogravimetric analyzer with a heating rate of 20 °C min<sup>-1</sup> in an N<sub>2</sub> atmosphere. The temperature-dependent magnetic susceptibility measurements of compounds 1-4 were performed on the powdered samples in the temperature range of 1.8-300 K at a 2000 Oe external field with a Quantum Design MPMS-XL7 SQUID magnetometer.

#### 2.3. Crystal structure determinations

Suitable single crystals of 1-4 were selected for single-crystal X-ray diffraction analyses. The measurements were carried out on a Bruker SMART APEX CCD diffractometer operating at room temperature. Intensities were collected with graphite monochromatized Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) operating at 50 kV and 30 mA. Data reductions and absorption corrections were performed using the saint and sadabs programs [11], respectively. The structures were solved by direct methods using the SHELXS-97 program and refined with full-matrix least squares on  $F^2$  using the

#### Table 1

	Crystallographic	and	structural	data	for	1-4
--	------------------	-----	------------	------	-----	-----

1	2	3	4
843552	843553	843554	843555
NH <sub>4</sub> MnSO <sub>4</sub> F	NH <sub>4</sub> FeSO <sub>4</sub> F	NH <sub>4</sub> CoSO <sub>4</sub> F	NH <sub>4</sub> NiSO <sub>4</sub> F
188.04	188.95	192.03	191.81
orthorhombic	orthorhombic	orthorhombic	orthorhombic
13.4004(12)	13.2721(9)	13.1861(7)	13.0229(16)
11.0933(10)	10.8809(7)	10.6969(5)	10.6215(13)
6.7101(6)	6.6449(4)	6.6201(3)	6.5487(8)
997.49(15)	959.61(11)	933.77(8)	905.83(19)
291(2)	291(2)	291(2)	291(2)
Pnna	Pnna	Pnna	Pnna
8	8	8	8
4918	4766	4561	4529
986	947	921	893
0.0689	0.0606	0.0607	0.0602
0.0542	0.0567	0.0505	0.0515
0.0974	0.1249	0.1079	0.0927
0.0809	0.0724	0.0700	0.0763
0.1032	0.1291	0.1131	0.0969
1.014	1.066	1.089	1.022
	1           843552           NH₄MnSO₄F           188.04           orthorhombic           13.4004(12)           11.0933(10)           6.7101(6)           997.49(15)           291(2)           Pnna           8           4918           986           0.0689           0.0542           0.0974           0.0809           0.1032           1.014	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

<sup>a</sup>  $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_o|$ ,  $wR = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$ .

SHELXL-97 program [12]. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Details of the crystal parameters, data collection and refinement results are summarized in the Table 1. Selected interatomic bond lengths and angles with their estimated standard deviations and further details can also be obtained from the Supplementary information.

# 3. Results and discussion

#### 3.1. Synthesis

The four title compounds were solvothermally synthesized from the DMA solution of metal nitrates, concentrated H<sub>2</sub>SO<sub>4</sub> and aqueous HF. Even though the DMA molecules were not incorporated into the final products, part of the DMA molecules may decompose to  $NH_4^+$  ion in the acidic solution under high temperature and press. It is noted that although Fe(III) nitrate was used during the synthesis, the valence of iron in the final product turned to be divalent while ammonia decomposed from the solvent of DMA may act as the reducing agent in the reduction procedure



Fig. 1. PXRD patterns of 1: (a) calculated, (b) as-synthesized.



Fig. 2. Plots of the unit-cell volume vs. ionic radius for the KTP-type compounds.



Fig. 3.  $_{\mbox{\scriptsize ORTEP}}$  drawing of the asymmetric unit of 1 with ellipsoids drawn at the 50% probability.

of Fe(III) to Fe(II). The use of Fe(II) chloride also resulted in the formation of the title compound NH<sub>4</sub>FeSO<sub>4</sub>F. The ion exchange of NH<sub>4</sub><sup>+</sup> have been carried out by mixing and boiling the title compound with lithium salts (LiI, LiBr, LiCl) in the solvent of anhydrous  $C_2H_5OH$  or CH<sub>3</sub>CN for several hours. However, the results showed to be unsuccessful that almost no Li<sup>+</sup> ions can penetrate into the structures.

The PXRD patterns for all the products are identical. As exemplified in Fig. 1 (see Fig. S2 for the PXRD patterns of **4** in Supplementary information), the PXRD peaks of **1** are consistent with those calculated on the basis of the single-crystal structures, indicating the pure phase of the as-synthesized samples. Slight differences in reflection intensities between the calculated and experimental patterns may be attributed to the variation in crystal orientation

for the powder samples. Elemental analysis for **1**, H, 2.3%; N, 7.3% (calculated as H, 2.2%; N, 7.5%), for **2**, H, 2.2%; N, 7.1% (calculated as H, 2.1%; N, 7.4%); for **3**, H, 2.2%; N, 7.1% (calculated as H, 2.1%; N, 7.3%); for **4**, H, 2.1%; N, 7.0% (calculated as H, 2.1%; N, 7.3%).

### 3.2. Descriptions of crystal structures

All the four title compounds crystallize in the orthorhombic system with Pnna space group. In comparison, most of other known KTP-type structures crystallize in the space group of  $Pna2_1$ , with the exception of NH<sub>4</sub>VPO<sub>4</sub>F [9c], which preclude the possibility of nonlinear optics at room temperature like other KTP-type materials. In fact, the space group of  $Pna2_1$  was initially considered in solving these structures, however, the structural model cannot be refined properly in this acentric space group, while it can only be well solved in the centric space group of Pnna. It can be seen from Table 1 that the cell volume of 1 to 4 decreases from 997.49(15) to 905.83(19) Å<sup>3</sup>, which was correlated with the reduced ionic radii of Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup> ions and consistent with the Vegard's law [13]. Similar observations have been obtained in the KTP-type metal fluorophosphates  $NH_4MPO_4F$  (M = Ga, V, Fe) [9], as shown in Fig. 2. Compared to the metal phosphates or arsenates with KTP-typed structures, the metal sulfates show slightly larger changes in cell volumes.

Since four compounds are isomorphous, compound **1** is chosen as an example for structural description. As shown in Fig. 3, the asymmetric unit of compound 1 consists of ten crystallographically unique non-hydrogen atoms, including two Mn, two S, four O and one F framework atoms, and one N atom from extra-framework ammonium ion. Both Mn sites are six-coordinated by four O and two F atoms in MnO<sub>4</sub>F<sub>2</sub> octahedron geometry. However, the Mn1 adopt a cis-configuration with the F-Mn1-F angles of 87.37°, while the Mn2 is in a trans-configuration with the F-Mn2-F angles of 180°. The two Mn atoms are linked by an F bridge with the Mn1–F–Mn2 angle of 122.52°. The Mn–O bond distances are in the range of 2.145(4) to 2.211(4) Å, while the Mn-F lengths is 2.083(3) Å. Both sulfur atoms are in a tetrahedral coordination geometry with the S–O lengths in the range of 1.465(4)–1.479(4) Å and O-S-O angles in the range of 106.5(4)-111.1(2)°, which are consistent with those of the other transition metal sulfates in the literature [6]. The calculated bond valence sums [14] for the metal sites in 1-4 are within the expected values, as listed in the Table 2.

The 3-dimensional framework of compound **1** is constructed by linkages of  $MnO_4F_2$  octahedra and  $SO_4$  tetrahedra. As shown in Fig. 4, the alternative connections of *cis*- and *trans*- $MnO_4F_2$ octahedra via F atoms form two identical sets of infinite zig-zag Mn-F-Mn chains, running along the [011] and [01-1] directions, respectively. The adjacent parallel chains within each set are linked by  $S1O_4$  tetrahedra to form a pair of two-dimensional sheets with 3- and 6-membered rings along the *a* axis. The sheets are then stacked alternatively along the *c* axis and further linked by  $S2O_4$ tetradedra to form a three-dimensional framework of **1** (Fig. 5).

Average bond lengths	(Å) of M-O and M-F.	and bond valences (	BV) for M <sup>2+</sup>	ions in 1-4.
	· · · · · · ·			

1		2		3		4	
Mn1–O Mn1–F BV <sub>Mn1</sub> = 2.06	2.1909 2.0833	Fe1–O Fe1–F BV <sub>Fe1</sub> = 1.98	2.1535 2.0444	Co1-O Co1-F BV <sub>Co1</sub> = 1.98	2.1309 2.0043	Ni1–O Ni1–F BV <sub>Ni1</sub> = 1.98	2.1033 1.9673
Mn2–0 Mn2–F BV <sub>Mn2</sub> = 2.12	2.1764 2.0833	Fe2-O Fe2-F BV <sub>Fe2</sub> = 2.12	2.1424 1.9974	Co2–O Co2–F BV <sub>Co2</sub> = 2.05	2.1124 2.0013	Ni2-O Ni2-F BV <sub>Ni2</sub> = 2.08	2.0719 1.9714



Fig. 4. Polyhedral view of the zig-zag chain made by alternation of cis- and trans- $MnO_4F_2$  octahedra in 1 along the [011] direction.

The open channels of six-membered rings constructed from four  $MnO_4F_2$  octahedra and two  $SO_4$  tetrahedra along the *a* and *c* axis are formed, where the ammonium cations locate (Fig. 6). The  $NH_4^+$  cations, formed by the decomposition of DMA molecules during the synthesis under high temperature and high pressure, play important roles not only to balance the anionic charges of the inorganic skeleton, but also to stabilize the framework by forming hydrogen bonds with the framework O atoms. This may be the reason why the ammonium cation can't be replaced by the Li<sup>+</sup> ion in the ion-exchange experiments.

In order to further understand the structure of **1**, the framework can be simplified into a topological net by considering the  $MnO_4F_2$ octahedra and  $SO_4$  tetrahedra as a 6- and 4-connected node, respectively. Therefore, **1** can be reduced into a (4,4,6,6)-connected net (Fig. 5). The point (Schlafli) symbol for the net is ( $3^2 \cdot 6^2 \cdot 7^2$ ) ( $3^2 \cdot 6^3 \cdot 7$ )( $3^4 \cdot 4^2 \cdot 6^3 \cdot 7^6$ )( $3^4 \cdot 4^2 \cdot 6^4 \cdot 7^4 \cdot 8$ ) as calculated by using TOPOS software [15]. This net is the same as that of known nonlinear optical material KTiOPO<sub>4</sub>. As one of the most important structure types in minerals, a number of metal phosphates [9] and arsenates [10]



**Fig. 6.** Polyhedral presentation of the 3D framework of **1** along the *a* axis, showing the ammonium cations located in the channels.

with KTP-type structure have been prepared so far. However, the metal sulfates with KTP-type structure have not been reported in the literature. Compounds **1–4** are new members to this class of materials.



**Fig. 5.** Polyhedral and simplified presentation of **1**, (a) the 3D framework constructed from the 2D sheets connecting by S2O<sub>4</sub> tetrahedra, and (b) the different orientation 1D zig-zag chain was connected by S1O<sub>4</sub> to form the 2D layer along the *bc*-plane. The teal and yellow balls represent the MnO<sub>4</sub>F<sub>2</sub> octahedra and SO<sub>4</sub> tetrahedra, respectively.

#### 3.3. FT-IR spectrum and TG analyses

The FT-IR spectra of four title compounds are almost identical. As shown in Fig. S1 (see Supplementary information), FT-IR spectrum of 1 exhibits the bands corresponding to the vibrations of ammonium cation and the  $SO_4^{2-}$  sulfate. The strong and broad band at 3235  $\text{cm}^{-1}$  with shoulders at *ca*. 3000  $\text{cm}^{-1}$  can be attributed to the stretching modes of the  $NH_4^+$  group. The band near 1419 cm<sup>-1</sup> can be assigned to the bending vibration of the  $NH_4^+$  cation. The stretching  $(v_3)$  and bending  $(v_4)$  vibrational bands of the  $SO_4^{2-}$  group appears as doublets at 1153–1105 cm<sup>-1</sup> and 617–603 cm<sup>-1</sup>, respectively. The presence of two sets of bands is related to the different local symmetry of the sulfate groups, which is consistent with the crystal structure analysis results.

The TG analyses of 1-4 are shown in Fig. 7. All the compounds are thermally stable up to at least 330 °C. The weight losses of



23.8% from 330 to 480 °C for 1 (calculated: 19.7%), 20.0% from 330 to 435 °C for 2 (calculated: 19.6%), 19.5% from 335 to 430 °C for 3 (calculated: 19.3%) and 20.7% from 405 to 515 °C for 4 (calculated: 19.3%) can be attributed to the loss of NH<sub>4</sub>F. The weight losses above 550 °C in all the four compounds could be attributed to the loss of SO<sub>3</sub> as results of thermal decomposition. It is noted that although compounds 1-4 are isomorphous, they exhibited slightly different thermal decomposition behaviors. For example, compound **2** turned to be FeSO<sub>4</sub> after the loss of  $NH_4F$ , which start to decompose almost immediately from ca. 450 °C to loss SO<sub>2</sub> or SO<sub>3</sub> [16], unlike the others with a relatively long thermally stable region. Since compound 4 possess the highest thermal stability, which was chose as an example to examine the thermal stability by PXRD studies. The as-synthesized samples were calcined in atmosphere at different temperatures in the range of 200–800 °C. As shown in Fig. S2, the framework of **4** was sustainably stable up to *ca.* 400 °C, consistent with TG results. Upon losing NH<sub>4</sub>F above 400 °C, 4 was converted to an orthorhombic phase NiSO<sub>4</sub> (JCPDS no. 13-0435). As the temperature increased to more than 650 °C, it began to transform into the cubic oxide phase NiO (JCPDS no. 75-197). The residue after calcination at 800 °C under atmosphere for the other three compounds turned to be metal oxides hausmannite  $Mn_3O_4$  (JCPDS no. 89-4837) for 1,  $\alpha$ -hematite Fe<sub>2</sub>O<sub>3</sub> (ICPDS no. 87-1165) for 2, and cobalt oxide Co<sub>3</sub>O<sub>4</sub> (JCPDS no. 78-1969) for 3, respectively.

## 3.4. Magnetic studies of 1-4

The plots of  $\chi_M T$  versus T and  $1/\chi_M$  versus T for **1–4** are shown in Fig. 8(a-d). All compounds show similar magnetic behaviors. The  $\gamma_M T$  value at room temperature is 3.68 cm<sup>3</sup> K mol<sup>-1</sup> (for 1), which is slightly lower than spin-only value of 4.375 cm<sup>3</sup> K mol<sup>-1</sup> of one magnetically isolated  $Mn^{2+}$  ions (for S = 5/2 and g = 2), while 3.21 (for **2**), 5.43 (for **3**) and 2.47 (for **4**) cm<sup>3</sup> K mol<sup>-1</sup>, respectively, which is much higher than the spin-only value of 3.0 cm<sup>3</sup> K mol<sup>-1</sup> for one magnetically isolated  $Fe^{2+}$  ions (for S = 2 and g = 2),

4.0

3.5

2.5

lom

Y 2.0

cm 1.5

1.0 L - 0.5

- 0.0 -0.5

3.0

2.5

2.0 K mol

1.0

0.5

0.0

300

ŝ

300

250

100

100

150

T/K

200

250

150 T / K

200



 $3.75 \text{ cm}^3 \text{ K} \text{ mol}^{-1}$  for one Co<sup>2+</sup> ions (for S = 3/2 and g = 2), and  $2 \text{ cm}^3 \text{ K mol}^{-1}$  for one Ni<sup>2+</sup> ions (for S = 1 and g = 2), indicating the involvement of orbital contributions of the octahedral Fe<sup>2+</sup>,  $Co^{2+}$  and Ni<sup>2+</sup> ions [17]. Upon cooling down to 1.8 K, the  $\gamma_M T$  values gradually decrease, suggesting the presence of antiferromagnetic interactions and also the involvements of the spin-orbital coupling. On the other hand, the molar magnetic susceptibilities  $1/\chi_{\rm M}$ decrease with decreasing temperature and reach a minimum around 12 K (for 1), 28 K (for 2) 10 K (for 3) and 28 K (for 4), respectively. Upon further cooling, the  $1/\chi_M$  values increase and reach a maximum around 8 K (for 1), 5 K (for 2), and 6 K for both **3** and **4**. The anomalies seen around 12 K (for **1**), 28 K (for **2**), 10 K (for **3**) and 28 K (for **4**) of  $1/\chi_{\rm M}$  versus *T* data sets in all the four compounds indicate the presence of short-range magnetic ordering [18], while the decreases of  $1/\chi_M$  under 6 K may involve the paramagnetic impurities. We have failed so far to fit the molar magnetic susceptibilities of 1-4 by using the models such as 3D simple cubic network or 1D chain [19], so we simply fitted the data of **1–4**, in the range of 50–300 K, by using the Curie–Weiss law  $\chi_{\rm m}$ =  $C/(T - \theta)$ . The best fitted Weiss constants ( $\theta$ ) are -44.44 (1), -62.59 (2), -51.34 (3) and -72.49 K (4) with the Curie constants of 4.25 (1), 3.94 (2), 6.396 (3) and 3.072 (4) cm<sup>3</sup> K mol<sup>-1</sup>, respectively. The negative Curie-Weiss temperatures again indicate a strong antiferromagnetic coupling associated with the fluoride and sulfate bridges in these compounds.

## 4. Conclusions

Four new thermally stable transition metal fluorosulfates NH<sub>4</sub>MSO<sub>4</sub>F (M = Mn, 1; Fe, 2; Co, 3; Ni, 4) were solvothermally synthesized in DMA with the presence of HF. The four compounds are isomorphous and adopt a KTP-type structure. Each compound is constructed from MO<sub>4</sub>F<sub>2</sub> octahedra and SO<sub>4</sub> tetrahedra to form two kinds of intersecting 6-membered ring channels along the a and *c* axes, in which the ammonium cations from the decomposition of the DMA molecules locate to balance the framework charges. The syntheses of 1-4 further show the rich structural chemistry of metal sulfates. More new metal sulfates with interesting structure and properties are expected by using similar synthetic methods.

# Acknowledgements

We gratefully appreciate financial support by Program for Innovative Research Team (in Science and Technology) in University of Henan Province (14IRTSTHN009), Henan Province Higher Educational Science and Technology Program (15A150086), and Scientific Funds of Zhoukou Normal University (ZKNU2014103).

#### Appendix A. Supplementary data

CCDC 843552-843555 contains the supplementary crystallographic data for 1–4. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.poly.2018.06.017.

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