

双咪唑基丁烷及邻苯二甲酸根构筑的镍多孔配位聚合物的 合成、结构及性质研究

巩 伟¹ 牛 琼¹ 牛和林^{*1} 胡 林²
毛昌杰¹ 宋吉明¹ 张胜义¹ 郑 君¹ 陈乾旺²

(¹ 安徽大学化学化工学院, 合肥 230039)

(² 中国科学技术大学, 合肥微尺度物质科学国家实验室材料科学与工程系, 合肥 230026)

摘要: 在水热反应条件下, 合成了一种新的镍配位聚合物, $[\text{Ni}(\text{Pht})(\text{bbim-4})]_n$ (Pht=邻苯二甲酸阴离子, bbim-4=1, 4-双(咪唑-1-基)丁烷), 经元素分析、粉末 X 射线衍射、热重和 X 射线单晶衍射表征了配合物。该配合物属于单斜晶系, 空间群 $C2/c$ 。结构分析表明, 该配合物是一个三维的具有三角形孔道的多孔配位聚合物。配位聚合物表现出一个整体上的铁磁行为。77 K 温度下, 气体吸附研究表明该多孔配位聚合物对 N_2 和 CO_2 气体的吸附具有选择性。

关键词: 镍配位聚合物; 1,4-双(咪唑-1-基)丁烷; 邻苯二甲酸阴离子; 水热合成; 晶体结构; 吸附

中图分类号: O614.81+3 文献标识码: A 文章编号: 1001-4861(2013)03-0642-07

DOI: 10.3969/j.issn.1001-4861.2013.00.115

Synthesis, Structure and Properties of a Porous Ni(II) Coordination Polymer Constructed from 1,1'-(1,4-Butanediyl)bis(imidazole) and *o*-Phthalate Acid

GONG Wei¹ NIU Qiong¹ NIU He-Lin^{*1} HU Lin² MAO Chang-Jie¹ SONG Ji-Ming¹
ZHANG Sheng-Yi¹ ZHENG Jun¹ CHEN Qian-Wang²

(¹ College of Chemistry & Chemical Engineering, Anhui University, Hefei 230039, China)

(² Hefei National Laboratory for Physical Sciences at Microscale and Department of Materials Science & Engineering,
University of Science and Technology of China, Hefei 230026, China)

Abstract: A coordination polymer $[\text{Ni}(\text{Pht})(\text{bbim-4})]_n$ (Pht=*o*-phthalate acid anion, bbim-4=1, 1'-(1, 4-butanediyl) bis (imidazole) was synthesized by hydrothermal reaction and characterized by elemental analysis, powder X-ray diffraction, TGA and X-ray single crystal diffraction. The crystal belongs to monoclinic system, space group $C2/c$. Coordination polymer $[\text{Ni}(\text{Pht})(\text{bbim-4})]_n$ is a three-dimensional porous coordination polymer with triangular channels. The coordination polymer shows an overall ferromagnetic behavior. Gas sorption studies suggest that the coordination polymer has selectivity in adsorption of N_2 and CO_2 gas. CCDC: 818068.

Key words: nickel coordination polymer; 1, 1'-(1,4-butanediyl)bis(imidazole); *o*-phthalate acid anion; hydrothermal synthesis; crystal structure; gas sorption

The increasingly rapid development of metal polymers (PCPs) over the past two decades has organic frameworks (MOFs) or porous coordination attracted considerable attention because of their

收稿日期: 2012-04-29。收修改稿日期: 2012-10-23。

国家自然科学基金(Nos.20905001, 21071002), 安徽省自然科学基金(Nos.KJ2010A014) 和安徽大学“211”创新团队资助项目。

*通讯联系人。E-mail: niuhelin@ahu.edu.cn

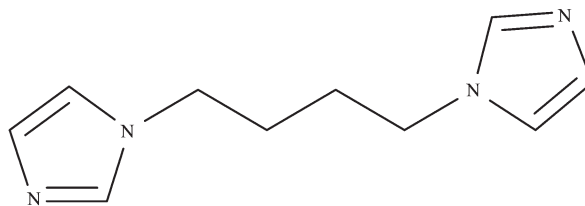
interesting molecular topologies and potential applications such as gas adsorption^[1-2], separation^[3], Storage^[4-5], et al. To date, a large number of coordination polymers with complicated architectures have been synthesized successfully^[6]. However, the controllable synthesis of coordination polymer is still a great challenge because there are many factors that play important roles in their self-assembling such as the chemical structures of the ligands^[7], the anions^[8], reaction temperature^[9], pH value^[10] and hydrogen bonds^[11]. But Among these factors, it is well-known that structures of the ligands play crucial roles in the design and construction of desirable coordination polymers^[12]. Recently, coordination polymers constructed by bent N-donor ligands of five-membered ring backbone such as 2,2'-bis(1*H*-imidazolyl)ether^[13], and bis (imidazole) ligands^[14] bearing alkyl spacers have been widely reported. Because the flexible nature of spacers allows the ligands to bend and rotate when coordinating to metal centers so as to conform to the coordination geometries of metal ions^[15]. Furthermore, flexible N-containing polydentate ligands have multiple coordination sites and adopt versatile conformations and coordination networks made from long bridging ligands can give rise to the formation of large voids according to the literature^[16]. In this work, we chosen 1,1'-(1,4-butanediyl)bis (imidazole) (bbim) as the first ligand, and *o*-phthalate are selected as the second ligand for possible increasing dimensionality.

Based on above mixed bridging ligands, a novel coordination polymer [Ni(Pht)(bbim-4)]_n have been synthesised.

1 Experimental

1.1 Reagent and apparatus

All reagents and solvents employed were commercially available and used as received without further purification. The bbim-4 ligand (Scheme 1) as N-donor ligand was synthesized by following the procedures described previously^[17]. The C, H and N microanalysis were carried out with a Vario ELIII elemental analyzer. Power XRD pattern of sample was collected on a Bruker-AXS SMART CCD area detector diffractometer with graphite monochromated Cu K α radiation ($\lambda = 0.154\ 18\ \text{nm}$) and 2θ ranging from $10^\circ \sim 60^\circ$. The FT-IR spectra was recorded from KBr pellets in the range $4\ 000 \sim 400\ \text{cm}^{-1}$ on a NEXUS-870 spectrometer. The thermogravimetric analyses were carried out on a Shimadzu-50 thermal analyzer in flowing air with a heating rate of $10\ ^\circ\text{C} \cdot \text{min}^{-1}$ in the temperature range $30 \sim 600\ ^\circ\text{C}$. The adsorption isotherm for N₂ and CO₂ gas were measured with an automatic adsorption apparatus (Micromeritics TriStar II 3020 V1.03) at 77 K. The magnetic field was approximately 100 Oe. The magnetic measurements were performed with Quantum Design SQUID MPMS -7 instruments. The diamagnetism of the sample and holder were taken into account.



Scheme 1 Structure of the bbim-4 ligand

1.2 Syntheses of [Ni(Pht)(bbim-4)]_n

A mixture of Ni (NO₃) \cdot 6H₂O (0.029 1 g, 0.10 mmol), H₂Pht(0.0116 g, 0.10 mmol), bbim-4 (0.019 0 g, 0.10 mmol), LiOH (0.006 g), and water (10 mL) was sealed in a Teflon reactor (15 mL), which was heated at $160\ ^\circ\text{C}$ for 3 d and then gradually cooled to room

temperature. Lastly, green granular crystals were collected. Calcd. for C₁₈H₁₈N₄NiO₄ (%): C, 52.34; H, 4.39; N, 13.56. Found (%): C, 49.70; H, 4.15; N, 12.80.

1.3 X-ray crystallography

A green single crystal of the coordination

polymer (0.42 mm×0.38 mm×0.32 mm) was put on a Gemini S Ultra, Oxford Diffractometer diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at 293 K using an scan mode ($3.71^\circ<\theta<26.36^\circ$). Absorption correction was applied with the multi-scan technique. All the structures were solved by the direct method of SHELXS-97 and reneved by full-matrix least-squares techniques using the SHELXL-97 program^[18]. All non-hydrogen atoms were refined anisotropically, and the

hydrogen atoms of organic ligands were generated geometrically^[19]. The detailed crystallographic data and structure refinement parameters are summarized in Table 1. Selected bond lengths(nm) and bond angles($^\circ$) for the coordination polymer are given in Table 2. Further details of the crystal structure determination have been deposited to the Cambridge Crystallographic Data Centre as supplementary publication.

CCDC: 818068.

表 1 配位聚合物的晶体学数据和主要参数

Table 1 Crystal data and structure refinement parameter for coordination polymer

Crystal system	Monoclinic	V / nm^3	1.797 84(7)
Morphology	green granular	Z	4
Formula	$\text{C}_{18}\text{H}_{18}\text{N}_4\text{NiO}_4$	$D_c / (\text{g}\cdot\text{mm}^{-3})$	1.526
Formula weight	413.05	$F(000)$	856
Temperature / K	293(2)	Index ranges	$-19\leq h\leq 17, -11\leq k\leq 11, -14\leq l\leq 15$
Wavelength / nm	0.071 073	Independent reflections	1 837 ($R_{\text{int}}=0.0166$)
Space group	$C2/c$	Data/restraints/parameters	1 837/0/124
a / nm	1.540 79(4)	Goodness-of-fit on F^2	1.046
b / nm	0.947 74(2)	Final R indexes ($I>2\sigma(I)$)	$R_1=0.024\ 5, wR_2=0.062\ 3$
c / nm	1.274 37(3)	Final R indexes (all data)	$R_1=0.0285, wR_2=0.0645$
$\beta / (^\circ)$	104.961(3)	Largest diff. peak and hole / ($\text{e}\cdot\text{nm}^{-3}$)	245 and -315

表 2 配位聚合物的部分键长和键角

Table 2 Selected bond lengths(nm) and bond angles($^\circ$) for the coordination polymer

Ni1-N1	0.20606(13)	Ni1-N1i	0.20606(13)	Ni1-O2i	0.21254(12)
Ni1-O2	0.21254(12)	Ni1-O1	0.2078(2)	Ni1-O1i	0.2078(2)
N1-Ni1-N1i	180.0	O2i-Ni1-O2	180.000(1)	N1-Ni1-O1i	88.26(5)
N1-Ni1-O2i	90.90(5)	N1-Ni1-O1	91.74(5)	N1-Ni1-O1i	91.74(5)
N1i-Ni1-O2	89.10(5)	N1i-Ni1-O1	88.26(5)	O2i-Ni1-O1i	61.50(4)
N1-Ni1-O2	89.10(5)	O2i-Ni1-O1	118.50(4)	O2-Ni1-O1i	118.50(4)
N1i-Ni1-O2	90.90(5)	O2-Ni1-O1	61.50(4)	O1-Ni1-O1i	180.0

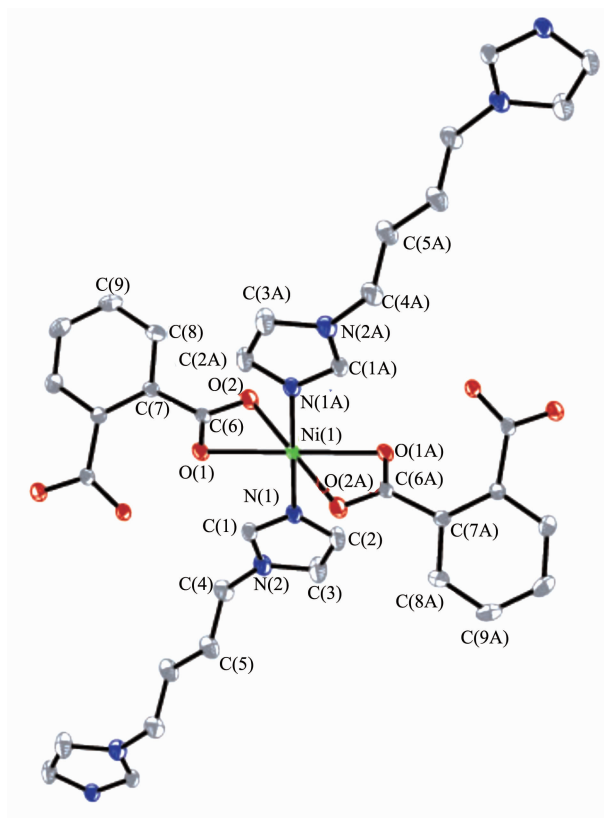
Symmetry code: $i\ 2-x, -y, 1-z$

2 Results and discussion

2.1 Crystal structures

As shown in Fig.1, the unit of coordination polymer contains one crystallographically unique Ni(II) atom, one unique *o*-phthalate anion, and one unique bbim-4 ligand. The Ni(II) ion is six-coordinated by four carboxylate O atoms from two L1 anions (Ni-O1

0.21598(14) nm, and Ni1-O2 0.21257(10) nm), two N atoms from two bbim-4 ligands (Ni-N 0.20603 (14) nm), showing a distorted octahedral coordination environment. The bbim-4 ligands connect the Ni (II) ions in a trans-comformation, generating an infinite 1D zigzag chain with the Ni...Ni distance of 1.39110 (4) nm along the b axis. These zigzag polymeric chains are arranged on parallel levels in two different



Hydrogen atoms omitted for clarity, displace ellipsoids are drawn at the 30% probability level. Symmetry codes: $1-x, -y, 1-z$

图 1 配位聚合物中二价镍原子的配位环境

Fig.1 Coordination environment of Ni(II) atom in coordination polymer

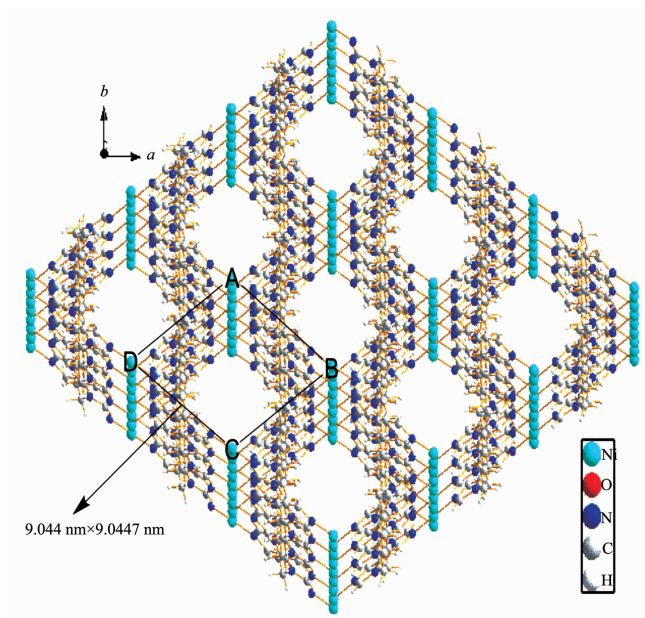


图 2 由横跨两个不同方向的一维链堆积形成的棒-包装图

Fig.2 Rod-packing diagram of the 1D chains spanning two different directions

propagating directions, rotated by 63.19° on passing from one level to the successive one, thus resulting in

an ABAB sequence and not having point of intersection (Fig.2). Then adjacent polymeric chains

are bridged by *o*-phthalate anions which adopt two bidentate chelating coordination mode, and each *o*-phthalate anion separates the metal ions by a distance of 0.63719 nm. Lastly, a 3D three-dimensional porous coordination polymer with rhombohedral channels is built up from infinite 1-D chains which had been

bridged by the *o*-phthalate anions. Because of the *o*-phthalate anions' participating, rhombohedral channels tend to form triangular channels (Fig.3). Similar packing fashions of 1D chain polymers have rarely been observed^[20].

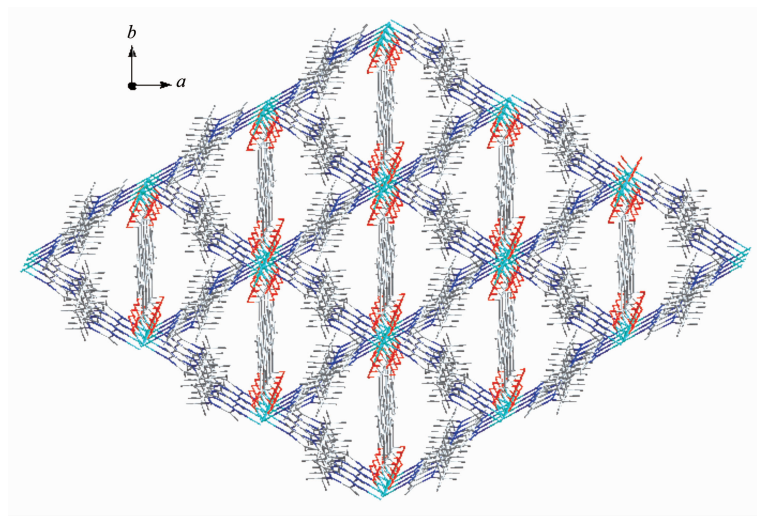


图 3 具有三角形孔道的 3D 的配位聚合物

Fig.3 3D coordination polymer with triangular channels

2.2 PXRD, IR and thermal stability analysis

The sample of the selected coordination polymer was characterized by powder X-ray diffraction at room temperature. The powder XRD experimental and computer-simulated patterns from the single crystal data using Mercury 1.4 software are shown in Fig.S1 (Supporting Information). The powder XRD experimental pattern is in good agreement with the corresponding simulated one except for the relative intensity variation as the result of preferred orientations of the crystal, so the result shows that the as-synthesized products have high degree of purity^[21].

The result of IR spectra for complex is shown in Fig.S2, Supporting Information. The strong absorption in $3\,122\text{ cm}^{-1}$ is ascribed to the characteristic vibration of $=\text{C}-\text{H}$ belonging to benzene ring. The middle strong vibrations appearing around $2\,949$ and $2\,869\text{ cm}^{-1}$ correspond to the asymmetric and symmetric stretching vibrations of the $-\text{CH}_2-$ belonging to the organic ligand L1. So we know that two organic ligands *o*-phthalate and bbim-4 are exist in

coordination polymer. The strong vibrations appearing around $1\,537$ and $1\,415\text{ cm}^{-1}$ correspond to the asymmetric and symmetric stretching vibrations of the carboxylate groups. Except that, The separation between $\nu_{\text{asym}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$ is 122 cm^{-1} and less than 200 cm^{-1} . The result imply that carboxylate groups of the complex adopt bidentate chelating coordination mode according to the literature^[22]. Obviously the result of IR analysis is in good agreement with really crystal structure.

The TGA of coordination polymer was performed in air atmosphere from 30 to $600\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. We can see that the coordination polymer undergo two steps of weight loss. The consecutive weight loss from 250 to $500\text{ }^{\circ}\text{C}$ is probably caused by the decomposition of the *o*-phthalate and bbim-4 ligands (in Fig.S3, Supporting Information). Compared with organic ligands, stability of coordination polymer has been improved obviously, which are results of coordination bond formation between organic ligand and central metal ion^[23].

Furthermore, TGA of the porous framework of coordination polymer shows no weight loss between 30 to 330 °C, suggesting no solvent guest in coordination polymer, which is consistent with the single-crystal X-ray diffraction analysis.

2.3 Sorption properties

No guest water molecules were found in the small channel according to thermogravimetric analysis. This results suggest that channels of porous coordination polymer are hydrophobic. And such porous coordination polymer has perhaps potential applications in gas separation [24]. To confirm the structure-dependent porous properties, gas sorption experiments were measured for N₂ and CO₂ at 77 K. As shown in Fig.4, the amount of N₂ sorption increases slowly with increasing absolute pressure and the value reaches 7.246 0 cm³·g⁻¹ at saturation, but saturation value of CO₂ only reaches 1.391 7 cm³·g⁻¹, the saturation value reveal that the porous coordination polymer [Ni(Pht)(bbim-4)]_n has very small adsorption capacity but has selectivity in adsorption of N₂ and CO₂.

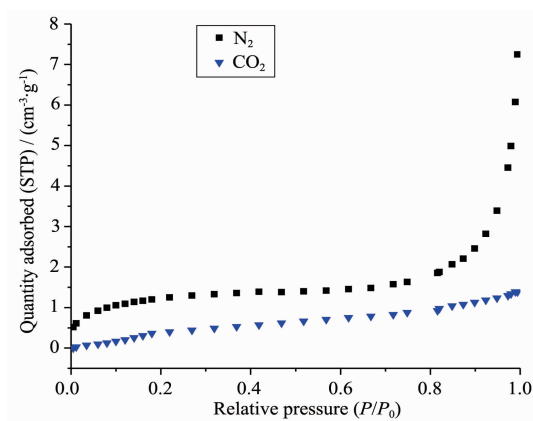


图4 配位聚合物气体吸附等温线

Fig.4 Gas adsorption isotherm at 77 K of coordination polymer

For pore-skeleton of some coordination polymer, only part of the free space is accessible [25], and accessibility of the pore would decline because of contraction of unit-cell volume at low temperature [26]. Also, there is a possibility of strong interaction of N₂ with the pore window, which effectively blocks the pores for access by other molecules [27]. All of these would be the reasons why the gas molecules could not

diffuse into the inner channels of these solids freely and the complex show a low adsorption ability to N₂ and CO₂.

2.4 Magnetic properties

The magnetic properties of the coordination polymer have also been studied, and the plot of $\chi_M T$ vs T are shown in Fig.5. When the $\chi_M T$ values reach a maximum 1.394 cm³·mol⁻¹·K from 2 K to 64.3 K rapidly. This nature of the $\chi_M T$ vs T curve is a signature of the global ferromagnetic behavior of the coordination polymer. According to the structure of coordination polymer, there are perhaps two different pathways in the polymeric chain: the first coupling between chains and/or between cations and chains, the coupling through bbim-4 ligands which will be very small antiferromagnetic because of the long-length exchange. The second through the *o*-phthalate anions, which can perhaps produce ferromagnetic interaction. While the latter one can be regarded as chains due to the distance of Ni(II)···Ni(II) 0.63719 nm bridged by *o*-phthalate anions along the chain being much shorter than that of 0.904 47 nm bridged by the bbim-4 ligand; The magnetic exchange through the bridging *o*-phthalate anions should be much stronger than that through the bbim-4 ligand. Therefore, the magnetic point of view the coordination polymer shows an overall ferromagnetic behavior.

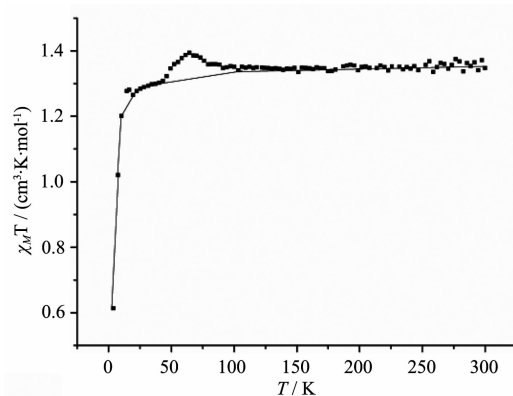


图5 配合物 $\chi_M T$ 随温度 T 的变化曲线

Fig.5 Plots of $\chi_M T$ vs T for the coordination polymer

3.0 Conclusions

In summary, using rigid *o*-phthalate and the flexible bbim-4 ligands under hydrothermal

conditions, we obtained a three-dimensional porous coordination polymer with triangular channels. The gas adsorption measurement show that the porous coordination polymer $[\text{Ni}(\text{Pht})(\text{bbim-4})_n]$ has very small adsorption capacity but has selectivity in adsorption of N_2 and CO_2 . We can conclude that adsorption capacity of coordination polymer per unit volume is not necessarily large, although it has stable framework and large cavity, since the adsorption capacity is affected by a variety of factors. Except that, the coordination polymer shows an overall ferromagnetic behavior.

References:

- [1] Xue D X, Lin Y Y, Cheng X N, et al. *Cryst. Growth Des.*, **2007**,**7**(7):1332-1336
- [2] Zhu A X, Lin J B, Zhang J P, et al. *Inorg. Chem.*, **2009**,**48**: 3882-3889
- [3] Shimomura S, Horike S, Matsuda R, et al. *J. Am. Chem. Soc.*, **2007**,**129**:10990
- [4] Millward A R, Yaghi O M. *J. Am. Chem. Soc.*, **2005**,**127**: 17998-17999
- [5] Furukawa H, Yaghi O M. *J. Am. Chem. Soc.*, **2009**,**131**:8875-8883
- [6] Noro S I, Kitagawa S, Nakamura T, et al. *Inorg. Chem.*, **2005**, **44**:3960-3971
- [7] Wen L L, Lu Z D, Ren X M, et al. *Cryst. Growth Des.*, **2009**, **1**:227-238
- [8] Notash B, Safari N, Khavasi H R. *Inorg. Chem.*, **2010**,**49**: 11415-11420
- [9] Chen J X, Ohba M, Zhao D Y, et al. *Cryst. Growth Des.*, **2006**,**6**(3):664-668
- [10] Zheng P Q, Ren Y P, Long L S, et al. *Inorg. Chem.*, **2005**,**44**:1190-1192
- [11] Zingiryan A, Zhang J, Bu X H. *Inorg. Chem.*, **2008**,**47**: 8607-8609
- [12] Kathalikkattil A C, Bisht K K, Alcalde N A, et al. *Cryst. Growth Des.*, **2011**,**11**:1631-1641
- [13] Wei G H, Yang J, Ma J F, et al. *Dalton Trans.*, **2008**:3038-3039
- [14] Zhang L P, Ma J F, Pang Y Y, et al. *CrystEngComm*, **2010**,**12**:4433-4442
- [15] Zhang L P, Ma J F, Yang J, et al. *Cryst. Growth Des.*, **2009**,**11**:4660-4673
- [16] Zhang W L, Liu Y Y, Ma J F, et al. *Polyhedron*, **2008**,**27**: 3351-3358
- [17] Ma J F, Liu Y Y, Xing Y, et al. *J. Chem. Soc., Dalton Trans.*, **2000**:2403-2407
- [18] Ma J C, Liu Y Y, Yang J, et al. *CrystEngComm*, **2011**,**13**: 3498-3505
- [19] Liu Y Y, Ma J F, Yang J, et al. *CrystEngComm*, **2008**,**10**: 565-572
- [20] Jiang H, Ma J F, Zhang W L, et al. *Eur. J. Inorg. Chem.*, **2008**:745-755
- [21] Yang J, Ma J F, Liu Y Y, et al. *CrystEngComm*, **2009**,**11**: 151-159
- [22] LIU Jia-Cheng(刘家成), CAO Jing(曹靖), DENG Wen-Ting(邓文婷). *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2010**,**26**(2):343-346
- [23] ZHANG Ju-Zhou(张居舟). *Thesis for the Doctorate of University Science and Technology of China (中国科学技术大学博士论文)*. **2009**.
- [24] Li J R, Sculley J, Zhou H C. *Chem. Rev.*, **2012**,**112**(2):869-932
- [25] CHU Chao-Xia(楚超霞). *Thesis for the Master of Jiangsu University of Science and Technology(江苏科技大学硕士论文)*. **2009**.
- [26] Swain D, Row T N G. *Inorg. Chem.*, **2007**,**46**:4411-4421
- [27] Maji T K, Matsuda R, Kitagawa S. *Nat. Mater.*, **2007**,**6**:142