CrystEngComm

Cite this: CrystEngComm, 2012, 14, 1681

www.rsc.org/crystengcomm

Three unprecedented open frameworks based on a pyridyl-carboxylate: synthesis, structures and properties[†]

Shengqun Su,^{ab} Wan Chen,^{ab} Xuezhi Song,^{ab} Min Zhu,^a Chao Qin,^a Shuyan Song,^a Zhiyong Guo,^d Song Wang,^{ab} Zhaoming Hao,^{ab} Guanghua Li^c and Hongjie Zhang^{*a}

Received 26th July 2011, Accepted 7th December 2011 DOI: 10.1039/c2ce05948g

Three open frameworks, $[Ni(pnta)_2] \cdot 1.3DMF$ (1), $[Zn_2(pnta)_3(OH)] \cdot 2DMF$ (2), and $[Cd(pnta)_2] \cdot 3.8DMF$ (3), were obtained by solvothermal reactions between 6-(pyridin-4-yl)nicotinic acid (Hpnta) and nickel(II), zinc(II) and cadmium(II) nitrate, respectively. Compound 1 is a chiral framework with a fourfold interpenetrated diamondoid network structure and two types of chiral channels. Compound 2 also possesses the fourfold interpenetrated adamantanoid architecture with helical rhombic nanotube-like channels, each of which has two sides of double-layer walls and two other sides of single-layer walls. Compound 3 is a rarely reported double-walled framework with bcu topology. The luminescent properties of compounds 2 and 3 have been studied in the solid state at room temperature.

Introduction

The rational design and construction of coordination polymers based upon assembly of metal ions and multifunctional organic ligands has drawn widespread attention because of their potential applications as functional materials and intriguing varieties of architectures and topologies. However, targeted synthesis of coordination polymers with the predesigned structure and desired property is still a formidable challenge.^{1,2} The structures of coordination polymers are usually influenced by a multitude of factors such as geometrical and electronic properties of the metal ions employed, coordination abilities of the ligands, the ligand-to-metal ratio, and the use of different solvents.³ Amid them, the careful selection of organic ligands and metal ions plays a decisive role in the preparation of coordination polymers.

The bulk of research endeavors in this arena have so far been revolving around coordination polymers with either neutral donor ligands or strictly anionic groups.⁴ However, multifunctional ligands combining neutral groups with anionic groups have attracted a great deal of interest currently.⁵ Lin *et al.*, for

example, have probed into the preparation of novel optical and magnetic materials by utilizing unsymmetrical pyridyl-carboxylate and analogous bridging moieties.⁶ The presence of varying functionalities in these ligands confers interesting properties on the resultant compounds, and the asymmetry of such ligands renders it possible to construct helical motifs.⁷ Additionally, both neutral and anionic donor groups in the ligands can coordinate to metal ions potentially to form neutral frameworks. The absence of counterions in such neutral networks increases the odds of resulting in porous solids.

With this in mind, we synthesized a bifunctional ligand Hpnta (6-(pyridin-4-yl)nicotinic acid) as the organic linker (Scheme 1) and successfully obtained three novel compounds, $[Ni(pnta)_2]$ · 1.3DMF (1), $[Zn_2(pnta)_3(OH)]$ ·2DMF (2), and $[Cd(pnta)_2]$ · 3.8DMF (3). The crystal structures of these compounds and topological analyses, along with the investigation of the modulated effect of various metal ions and coordination modes of pnta⁻ anions on the ultimate structures, will be represented and discussed below in detail.



Scheme 1 Synthesis route for ligand.

^aState Key Laboratory of Rare Earth Resource Utilizations, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China. E-mail: hongjie@ciac.jl.cn; Fax: +86 431 85698041; Tel: +86 431 85262127

^bGraduate School of the Chinese Academy of Sciences, Beijing, 100039, P. R. China

^cState Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun, 130012, P. R. China ^dDepartment of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas, 78249-0698, USA

[†] Electronic supplementary information (ESI) available. CCDC reference numbers 836983–836985. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce05948g

Experimental section

Materials and methods

Hpnta (6-(pyridin-4-yl)nicotinic acid) was synthesized as reported in the literature with some modification,8 and other reagents were purchased from commercial sources and used as received. IR spectra were obtained from KBr pellets on a Perkin-Elmer 580B IR spectrometer in the 400-4000 cm⁻¹ region (ESI[†]). Elemental analyses (C, H, N) were performed with a VarioEL analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer heated from 40 to 700 °C under nitrogen. The luminescent properties of compounds were measured on a HITACHI F-7000 spectrometer. Powder X-ray diffraction data were collected on a Bruker D8-ADVANCE diffractometer equipped with Cu K α at a scan speed of 2° min⁻¹. Nitrogen sorption experiments were carried out on a Quantachrome Autosorb Automated Gas Sorption System. Prior to the N₂ isotherm measurements at 77 K, the samples were outgassed under vacuum at 120 °C overnight.

Synthesis

[Ni(pnta)₂] · 1.3DMF (1). A mixture of Ni(NO₃)₂ · 6H₂O (0.0174 g, 0.06 mmol), Hpnta (0.0201 g, 0.1 mmol), triethylamine (TEA) (0.045 ml), DMF (2 ml) and ethanol (1 ml) was stirred for 10 min and transferred to a Teflon reactor (20 ml) and heated at 105 °C for 2 d. After the sample was gradually cooled to room temperature at a rate of 5 °C h⁻¹, green crystals of 1 were obtained with 38% yield based on Hpnta. Anal. calcd for C_{25.90}H_{23.10}N_{5.30}NiO_{5.30} ($M_r = 552.11$): C, 56.34; H, 4.22; N, 13.44%. Found: C, 56.58; H, 3.84; N, 13.39%. IR (cm⁻¹): 3240 (m), 2921(m), 1610(s), 1584(s), 1560(s), 1381(m), 1161(w), 1055 (w), 1014(w), 834(w), 779(m), 753(m), 534(w), 468(w).

[Zn₂(pnta)₃(OH)]·2DMF (2). A mixture of Zn(NO₃)₂·6H₂O (0.0208 g, 0.07 mmol), Hpnta (0.0201 g, 0.1 mmol), TEA (0.045 ml), DMF (2 ml) and ethanol (1 ml) was stirred for 10 min and transferred to a Teflon reactor (20 ml) and heated at 90 °C for 3 d. After cooling to room temperature, colorless crystals of **2** were obtained with 43% yield based on Hpnta. Anal. calcd for C₃₉H₃₆Zn₂N₈O₉ ($M_r = 891.50$): C, 52.54; H, 4.07; N, 12.57%. Found: C, 52.65; H, 4.15; N, 12.52%. IR (cm⁻¹): 3256(m), 2930 (m), 1617(s), 1601(s), 1577(s), 1397(m), 1169(w), 1071(w), 1022 (w), 843(w), 794(m), 770(m), 541(w), 476(w).

[Cd(pnta)₂]·3.8DMF (3). A mixture of Cd(NO₃)₂·4H₂O (0.0185 g, 0.06 mmol), Hpnta (0.0201 g, 0.1 mmol), TEA (0.030 ml), DMF (1 ml) and ethanol (0.5 ml) was stirred for 10 min and transferred to a Teflon reactor (20 ml) and heated at 90 °C for 3d. After cooling to room temperature, colorless crystals of **3** were obtained with 51% yield based on Hpnta. Anal. calcd for C_{33.40}H_{40.60}CdN_{7.80}O_{7.80} ($M_r = 788.54$): C, 50.87; H, 5.19; N, 13.85%. Found: C, 50.85; H, 4.97; N, 13.51%. IR (cm⁻¹): 3231 (m), 1593(s), 1569(s), 1390(m), 1063(w), 1014(w), 835(w), 786(m), 762(m), 631(w), 566(w), 541(w), 468(w).

X-Ray crystallography

The X-ray intensity data for the three compounds were collected on a Bruker SMART APEX CCD diffractometer with graphite-

monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). The crystal structure was solved by means of Direct Methods and refined employing full-matrix least squares on F^2 (SHELXTL-97).⁹ All the hydrogen atoms except for the disordered guest DMF molecules were generated geometrically and refined isotropically using the riding model. C3 and C4 atoms in 1 and C35, C37, C41, C42 and O10 atoms in 2 were refined with isotropic temperature parameters and other non-hydrogen atoms were refined anisotropically. The restrains of DFIX were applied to keep the disordered DMF molecules reasonable in compound 2. For compounds 1 and 3, during the structure refinement, the atoms of the (DMF) solvent molecule were observed but could not be modeled satisfactorily. Therefore, the contributions of the disordered solvent molecules (DMF) were removed from the diffraction data using the SQUEEZE routine of PLATON software and then final refinements were carried out.¹⁰ Additionally, the numbers of disordered guest molecules were determined according to elemental analyses and thermogravimetric analyses. Crystal data and details of the structure determination for complexes 1-3 are listed in Table 1.

Results and discussion

Structural description of 1

Compound 1 crystallizes in the chiral tetragonal space group P42 (1)2. Note that Flack's parameter for the crystal is 0.52(2), which means that the chiral framework forms a twinned racemate crystal. The asymmetric unit of 1 contains one independent Ni center and two organic ligands. The Nil center adopts a distorted octahedral geometry by coordinating to four oxygen atoms from two different pnta- ligands (O1, O2, O3A and O4A) and two nitrogen atoms (N4 and N2B) from two pnta⁻ ligands. The Ni-O and Ni–N bond lengths are all within the normal ranges.^{6b} The six-coordinated Ni^{II} center acts as a pseudo-tetrahedral fourconnected node, which connects to four other Ni^{II} centers through four pnta- ligands, resulting in the formation of a diamondoid network (Fig. 1a). The separations of the adjacent Ni... Ni atoms in the adamantanoid cage unit are 12.82 A and 12.87 A. The long spacers between coordination sites result in large cavities within the adamantanoid cages. In order to minimize the big void cavities and stabilize the framework by nature, the potential voids are effectively filled via mutual interpenetration in the aligned normal type with four independent equivalent frameworks along the c-axis, generating a fourfold interpenetrated adamantanoid architecture (Fig. 1b).

Despite the fourfold interpenetration, the structure generates 1D square channels of window size *ca.* 10.99 \times 10.99 Å² with DMF molecules located in channels (measured between opposite atoms). Interestingly, when viewed along the [001] direction, the structure presents two kinds of square nanotubelike channels (Type I and Type II) assembled from two types of helices (Fig. 2a).¹¹ The Type I chiral channel contains fourfold right-handed helical chains, while II contains fourfold left-handed helical chains (Fig. 2b). The effective free volume calculated with PLATON for the inclusion is 3010 Å³ per unit cell (after free molecules have been hypothetically removed) corresponding to 47.51% of the cell volume.

Table 1 Crystal data and structure refinements for complexes 1-3

	1	2	3
Formula	C _{25 90} H _{23 10} N _{5 30} NiO _{5 30}	$C_{39}H_{36}Zn_2N_8O_9$	$C_{3340}H_{4060}CdN_{780}O_{780}$
Formula weight	552.11	891.50	788.54
Crystal system	Tetragonal	Monoclinic	Monoclinic
Space group	P42(1)2	P21/c	P21/c
T/K	185(2)	185(2)	185(2)
a/Å	22.3163(5)	6.1802(4)	8.1191(5)
b/Å	22.3163(5)	29.4218(18)	18.8297(11)
c/Å	12.7222(6)	23.3127(14)	18.7331(12)
β/deg	90.00	95.6630(10)	100.5740(10)
$V/Å^3$	6335.9(4)	4218.3(5)	2815.3(3)
Z	8	4	4
$D_{\rm calcd}/{\rm g}~{\rm cm}^{-3}$	1.112	1.404	1.722
F(000)	2192	1832	1496
Data collected	35 274	23 187	15 363
Unique data	6259	8320	5550
R(int)	0.0598	0.0644	0.0417
GOF on F^2	1 015	1.062	1 030
$R_1^a [I > 2\sigma(I)]$	0.0470	0.0630	0.0373
ωR_2^{b} (all data)	0.1225	0.2100	0.1048
Flack (y)	0.52(2)		

Structural description of 2

X-Ray crystallography reveals that 2 crystallizes in space group $P2_1/c$ and exhibits a 3D open framework with 1D rhombic channels along the x-axis. The asymmetric unit consists of two Zn atoms, three pnta⁻ ligands and one μ_2 -OH. The Zn1 center is coordinated by two oxygen atoms, one pnta- ligand (O1) and one μ_2 -OH (O7), two nitrogen atoms (N4A and N6B) from two different pnta- ligands. The Zn2 center adopts distorted tetrahedral coordination geometry, surrounded by three oxygen atoms (O4, O5 and O7) from two pnta- anions and one hydroxyl group, one nitrogen atom (N2C) from a pnta- ligand. The Zn1 and Zn2 centers are linked by one μ_2 -OH to form Zn₂ units. Each unit is connected to four others through six pnta- ligands in a tetrahedral fashion, which gives rise to a diamondoid network composed of large adamantanoid cages. In consequence of mother nature's horror vacui, such a structure with extra-large pores is unstable.¹² In this case, four identical diamondoid networks are filled via mutual interpenetration forming a fourfold interpenetrated framework. It is noteworthy that there are still sizable voids in spite of interpenetration. As shown in Fig. 3b, two types of helical nanotubelike channels (Type I and Type II) are also visible along the [100] direction (Fig. 3b). Each of the two channels has two sides of double-layer walls and two other sides of single-layer walls, which is different from the channels in complex 1.13 The two channels contain 4-fold righthanded and left-handed helical chains respectively and hold the same channel size. PLATON analysis showed that the effective free volume of 2 is 36.22% of the crystal volume.

Structural description of 3

X-Ray crystallographic analysis indicates that, in the asymmetric unit of **3**, there are one Cd(Π) atom and two pnta⁻ ligands. The central Cd(Π) ion adopts a distorted octahedral geometry surrounded by four oxygen atoms from two different pnta⁻ ligands in the equatorial plane and two nitrogen atoms from another two

pnta⁻ ligands at the axial position (Cd-O 2.195(5)-2.466(4) Å). Neighboring Cd(II) ions are doubly bridged by two -COO⁻ from pnta⁻ ligands to give a centrosymmetric dinuclear Cd₂(COO)₂ moiety (Fig. 4a), with the distance of Cd…Cd being 3.837 Å. Each dinuclear unit is further connected to neighboring counterparts through eight pnta⁻ ions to generate a 3D open framework with the rectangular channels along the a-axis (Fig. 4b). Because the eight pnta- linkers link the dinuclear units just along four directions, the channels are double-walled. To the best of our knowledge, only one example of such double-walled frameworks has been reported to date.14 The DMF molecules are trapped in channels. Without guest molecules, the effective free volume is calculated by PLATON analysis to be 37.72% of the crystal volume. If the dinuclear units are considered as eightconnected nodes, the resulting network is of the bcu topology with the Schläfli symbol of $(4^{24} \cdot 6^4)$ (Fig. 4c).

Compounds 1–3 are synthesized under similar conditions using the same organic ligands with different metal ions. They have different structures, that is, the chiral fourfold interpenetrated adamantanoid architecture, fourfold interpenetrated diamondoid net and double-walled framework, respectively. It can be discerned that the central metal ions may play a dominant role in the construction of the resulting complexes because different metal ions have varied coordination configurations, metal radii and coordination spheres. In addition, the coordination modes of the pyridyl-carboxylate ligand pnta⁻ for complexes 1–3 are also diverse. The carboxylates of the ligands in compounds 1–3 adopt chelating-mono (I), mono (II) and bischelating (III)/mono coordination modes, respectively (Fig. 5). So different coordination modes of the ligand also exert some influence on the structures of the compounds.

Thermal analysis

In order to characterize the thermal stabilities of compounds 1–3, their thermal behaviors were investigated by TGA under



Fig. 1 (a) A single diamondoid network structure and coordination environments of the Ni(II) ions in 1. Hydrogen atoms are omitted for clarity. Symmetry codes: (A) -x + 1/2, y + 1/2, -z + 1; (B) x - 1/2, -y + 3/2, -z. (b) Interpenetration of four independent diamondoid nets in 1.



Fig. 2 (a) Perspective view along the [001] axis showing Type I and Type II helical 1D square channels. (b) Type I and II channels containing fourfold right- and left-hand helical chains, respectively.



Fig. 3 (a) Coordination environments of the Zn(II) ions (left) and a single adamantanoid cage (right) in **2**. Hydrogen atoms are omitted for clarity. Symmetry codes: (A) -x, -y, -z + 1; (B) -x, -y, -z; (C) -x + 2, y - 1/2, -z + 1/2. (b) Perspective view along the [100] axis showing two types of helical channels with fourfold left- and right-hand helical chains, respectively.

a nitrogen atmosphere with a heating rate of 10 °C min⁻¹ (Fig. S1†). The TGA curve of **1** shows that the weight loss in the temperature range of 40–220 °C corresponds to the loss of one free DMF molecule (obsd 13.22%, calcd 13.79%). The decomposition of the compound occurs at *ca.* 325 °C. The remaining weight is assigned to the formation of NiO (obsd 13.21%, calcd 13.53%). Compound **2** lost its DMF molecules between 40 and 370 °C (obsd 16.10%, calcd 16.40%). Likewise, the formation of ZnO (obsd 18.26%, calcd 18.76%) is responsible for the residual weight of the final solids. For compound **3**, the weight loss attributed to the release of one and a half guest DMF molecule is observed from 40 to 350 °C (obsd 14.82%, calcd 13.89%). The framework begins to decompose at 370 °C.

Photoluminescence properties

Luminescent properties of compounds with d^{10} metal centers have been attracting mounting interest owing to their potential applications in chemical sensors, photochemistry, and electroluminescent displays. The luminescence properties of compounds 2 and 3 as well as free Hpnta ligand were studied in the solid state at room temperature (Fig. 6). Upon excitation at 370 nm, compound 2 exhibits strong fluorescent emission bands at 422 and 441 nm. Compound 3 shows a main peak at 451 nm with two shoulders at 422 and 518 nm upon excitation at 380 nm. These



Fig. 4 (a) Coordination environments of the Cd(II) ions in 3. (b) Perspective views of the double-walled framework with nanotube-like channels in 3. (c) The bcu topological network with Cd_2 clusters as nodes.

emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT) in nature since the Zn²⁺ or Cd²⁺ ions with d¹⁰ configuration are difficult to oxidize or reduce. Rather, they can probably be assigned to intraligand (n– π *) fluorescent emission because almost similar emissions are observed for the free Hpnta at 421 nm and 453 nm.¹⁵



Fig. 5 The coordination modes of ptna⁻ ligands in compounds 1–3.



Fig. 6 Emission spectra of ligand and compounds 2 and 3 in the solid state at room temperature.

Gas sorption property

To examine permanent porosity, methanol-exchanged compound **2** was activated at a temperature of 120 °C under vacuum overnight for gas sorption studies. As revealed in its PXRD (Fig. S5†), the activated compound **2** still has a crystalline form. The nitrogen sorption isotherm at 77 K (Fig. 7) shows type I sorption behavior with a limited adsorption capacity, which is



Fig. 7 N_2 adsorption isotherm (77 K) of compound 2 activated at 120 °C (red and blue curves represent adsorption and desorption, respectively).

significantly low for such a highly porous crystal structure. Obviously, the pores in activated compound **2** have not been fully expanded in 1 atm of nitrogen, and the nitrogen adsorption is not saturated. The nitrogen sorption displays hysteretic sorption behavior owing to the dynamic feature of the interpenetrating frameworks.¹⁶

Conclusions

Three unprecedented open frameworks have been successfully synthesized under solvothermal conditions by reacting Hnpta with Ni(II), Zn(II) and Cd(II) ions. They exhibit intriguing structures with the chiral fourfold interpenetrated adamantanoid architecture, fourfold interpenetrated diamondoid net and double-walled framework, respectively. The structural diversification of compounds illustrates that the different coordination environments around central metal ions and the diverse coordination modes of the organic ligands play an important role in the construction of frameworks. It is believed that the preliminary results about the effects of different metal ions on structures are instrumental in the rational design and synthesis of frameworks with specific structural motifs.

Acknowledgements

The authors are grateful for financial aid from the National Natural Science Foundation of China (grant no. 20631040 and 20771099) and the MOST of China (grant no. 2006CB601103 and 2006DFA42610).

References

- (a) S. R. Batten and R. Robson, Angew. Chem., Int. Ed., 1998, 37, 1460;
 (b) P. J. Hagrman, D. Hagrman and J. Zubieta, Angew. Chem., Int. Ed., 1999, 38, 2638;
 (c) J. J. Perry, IV, J. A. Perman and M. J. Zaworotko, Chem. Soc. Rev., 2009, 38, 1400;
 (d) L. Carlucci, G. Ciani and D. M. Proserpio, Coord. Chem. Rev., 2003, 246, 247;
 (e) A. Erxleben, Coord. Chem. Rev., 2003, 246, 203;
 (f) D. J. Tranchemontagon, J. L. Mendoza-Cortés, M. O'Keeffe and O. M. Yaghi, Chem. Soc. Rev., 2009, 38, 1257;
 (g) O. K. Farha and J. T. Hupp, Acc. Chem. Res., 2010, 43, 1166.
- (a) M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, J. Am. Chem. Soc., 1994, 116, 1151; (b) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, Nature, 2000, 404, 982; (c) C. J. Kepert, T. J. Prior and M. J. Rosseinsky, J. Am. Chem. Soc., 2001, 123, 10001; (d) O. R. Evans and W. Lin, Acc. Chem. Res., 2002, 35, 511; (e) S. Kitagawa, R. Kitaura and S. I. Noro, Angew. Chem., Int. Ed., 2004, 43, 2334; (f) X. M. Zhang, Z. M. Hao, W. X. Zhang and X. M. Chen, Angew. Chem., Int. Ed., 2007, 46, 1; (g) B. L. Chen, S. Q. Ma, E. J. Hurtado, E. B. Lobkovsky and H. C. Zhou, Inorg. Chem., 2007, 46, 8490; (h) T. Uemura, N. Yanai and S. Kitagawa, Chem. Soc. Rev., 2009, 38, 1380; (j) Z. Y. Guo, G. H. Li, L. Zhou, S. Q. Su, Y. Q. Lei, S. Dang and H. J. Zhang, Inorg. Chem., 2009, 48, 8069.
- 3 (a) X. D. Chen, H. F. Wu, X. H. Zhao and M. Du, Cryst. Growth Des., 2007, 7, 124; (b) Q. R. Fang, G. S. Zhu, Z. Jin, M. Xue,

X. Wei, D. J. Wang and S. L. Qiu, Cryst. Growth Des., 2007, 7, 1035; (c) J. L. Du, T. L. Hu, J. R. Li, S. M. Zhang and X. H. Bu, Eur. J. Inorg. Chem., 2008, 1059; (d) H. D. Guo, X. Min, S. R. GuoBatten, J. F. Song, S. Y. Song, S. Dang, G. L. Zheng, J. K. Tang and H. J. Zhang, Cryst. Growth Des., 2009, 9, 1394; (e) J. Q. Liu, Y. Y. Wang, Y. N. Zhang, P. Liu, Q. Z. Shi and S. R. Batten, Eur. J. Inorg. Chem., 2009, 147; (f) M. Hirotsu, N. Kuwamura, I. Kinoshita, M. Kojima, Y. Yoshikama and K. Ueno, Dalton Trans., 2009, 7678; (g) B. Li, G. Li, D. Liu, Y. Peng, X. Zhou, J. Hua, Z. Shi and S. Feng, CrystEngComm, 2011, 13, 2457.

- 4 (a) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, Acc. Chem. Res., 2001, 34, 319; (b)
 S. A. Barnett and N. R. Champness, Coord. Chem. Rev., 2003, 246, 145; (c) J. Xu, Z. S. Bai, M. S. Chen, Z. Su, S. S. Chen and W. Y. Sun, CrystEngComm, 2009, 11, 2728; (d) L. L. Li, H. X. Li, Z. G. Ren, D. Liu, Y. Chen, Y. Zhang and J. P. Lang, Dalton Trans., 2009, 8567.
- P. Zhang, B. Li, Y. Zhao, X. Meng and T. Zhang, *Chem. Commun.*, 2007, 2293; (b) M. Chen, M. S. Chen, T. A. Okamura, M. F. Lv, W. Y. Sun and N. Ueyama, *CrystEngComm*, 2011, 13, 3801; (c) H. D. Guo, X. M. Guo, X. Wang, G. H. Li, Z. Y. Guo, S. Q. Su and H. J. Zhang, *CrystEngComm*, 2009, 11, 1509; (d) S. L. Xiang, J. Huang, L. Li, J. Y. Zhang, L. Jiang, X. J. Kuang and C. Y. Su, *Inorg. Chem.*, 2011, 50, 1743; (e) L. Hou, W. X. Zhang, J. P. Zhang, W. Xue, Y. B. Zhang and X. M. Chen, *Chem. Commun.*, 2010, 46, 6311.
- 6 (a) P. Ayyappan, O. R. Evans, Y. Cui, K. A. Wheeler and W. Lin, Inorg. Chem., 2002, 41, 4978; (b) P. Ayyappan, O. R. Evans and W. Lin, Inorg. Chem., 2001, 40, 4627; (c) O. R. Evans and W. Lin, Chem. Mater., 2001, 13, 2705; (d) M. E. Chapman, P. Ayyappan, B. M. Foxman, G. T. Yee and W. Lin, Cryst. Growth Des., 2001, 1, 159; (e) W. B. Lin, O. R. Evans, R. G. Xiong and Z. Y. Wang, J. Am. Chem. Soc., 1998, 120, 13272.
- 7 (a) S. L. Li, Y. Q. Lan, J. S. Qin, J. F. Ma and Z. M. Su, Cryst. Growth Des., 2008, 8, 2055; (b) J. Luo, Y. Zhao, H. Xu, T. L. Kinnibrugh, D. Yang, T. V. Timofeeva, L. L. Daemen, J. Zhang, W. Bao, J. D. Thompson and R. P. Currier, Inorg. Chem., 2007, 46, 9021.
- 8 (a) J. F. Marcoux, F. A. Marcotte, J. Wu, P. G. Dormer, I. W. Davies, D. Hughes and P. J. Reider, J. Org. Chem., 2001, 66, 4194.
- 9 G. M. Sheldrick, SHELXL-97, Program for Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
- 10 P. van der Sluis and A. L. Spek, Acta Crystallogr., Sect. A: Found. Crystallogr., 1990, 46, 194.
- 11 (a) H. L. Jiang, B. Liu and Q. Xu, Cryst. Growth Des., 2010, 10, 806; (b) H. Y. Liu, Z. J. Zhang, W. Shi, B. Zhao, P. Cheng, D. Z. Liao and S. P. Yan, Dalton Trans., 2009, 4416.
- 12 (a) H. Kim and M. P. Suh, *Inorg. Chem.*, 2002, **41**, 4978; (b) J. P. Ma, Y. B. Dong, R. Q. Huang, M. D. Smith and C. Y. Su, *Inorg. Chem.*, 2005, **44**, 6143; (c) L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *Chem.–Eur. J.*, 2002, **8**, 1519.
- 13 (a) S. N. Wang, H. Xing, Y. Z. Li, J. F. Bai, M. Scheer, Y. Pan and X. Z. You, *Chem. Commun.*, 2007, 2293; (b) X. R. Hao, X. L. Wang, Z. M. Su, K. Z. Shao, Y. H. Zhao, Y. Q. Lan and Y. M. Fu, *Dalton Trans.*, 2009, 8562.
- 14 M. H. Zeng, Q. X. Wang, Y. X. Tan, S. Hu, H. X. Zhao, L. S. Long and M. Kurmoo, J. Am. Chem. Soc., 2010, 132, 2561.
- 15 J. Wang, Z. J. Lin, Y. C. Ou, N. L. Yang, Y. H. Zhang and M. L. Tong, *Inorg. Chem.*, 2008, 47, 190.
- 16 (a) B. Chen, S. Ma, F. Zapata, E. B. Lobkovsky and J. Yang, *Inorg. Chem.*, 2006, **45**, 5718; (b) B. Chen, S. Ma, E. J. Hurtado, E. B. Lobkovsky and H. C. Zhou, *Inorg. Chem.*, 2007, **46**, 8490.