PAPER

Two novel high-dimensional iron(II) coordination polymers modeled by semi-rigid tetrapyridines[†]

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Two new iron(II) coordination polymers with the formula [Fe(TPOM)(SCN)₂]·2(HN(CH₃)₂)·4(H₂O) (**1**, TPOM = tetrakis(4-pyridyloxymethylene)methane) and [Fe(TPOM2)(SCN)₂]·2(CH₃OH) (**2**, TPOM2 = tetrakis(3-pyridyloxymethylene)methane), have been synthesized and characterized by elemental analysis, IR spectroscopy, TGA, magnetic measurements and X-ray single-crystal diffraction. Compound **1** crystallizes in the orthorhombic space group *C*ccm, and exhibits a 3D porous *pts* framework in which the Fe^{II}(NCS)₂ units are linked by the tetra-topic TPOM ligands. In contrast, compound **2** crystallizes in the monoclinic space group *C*2/*c*, whose crystal structure consists of a 2D sheet formed by the connection of Fe^{II}(NCS)₂ units and tetra-topic TPOM2 ligands. Interestingly, every 2D sheet interleavingly stacks over each other to totally construct a [4] tiling structure with a plane net signature of $[122]_4[4\cdot4\cdot4\cdot4]$. Temperature-dependent SQUID under variable external pressure and X-ray diffraction measurements indicate that the iron(II) ions in **1** and **2** remain in the high spin state over the temperature range of 2–300 K.

Introduction

Coordination polymers (CPs) have attracted great interest in the fields of supramolecular chemistry and crystal engineering, not only for their intriguing variety of molecular topologies and architectures,¹ but for their potential applications as functional materials in diverse areas such as magnetism, heterogeneous catalysis, gas storage, non-linear optics and chirality.² In this regard, many synthetic efforts have been devoted to the design and synthesis of 2D or 3D iron(II) coordination compounds with the typically octahedral FeN_6 ,³ motivated by their potential properties of spin crossover (SCO) behaviours and proposition that direct covalent linking of the active coordination sites through chemical bridges may improve cooperative communication between SCO centers in extended systems compared to mononuclear ones.⁴ Therefore, it is of great interest and essentiality to investigate every new 2D or 3D iron(II) CPs with the typically octahedral FeN_6 .

Generally, the construction of high dimensional iron(II) CPs with charming structural topologies greatly depends on organic ligands with appropriate functional groups and metal ions acting

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as connecting nodes.⁵ However, the predicted and controlled synthesis of the final products is still a great challenge at this stage because the self-assembly of coordination polymeric frameworks with unique structures and functions are frequently influenced by many factors, such as the nature of organic ligands, the coordination geometry of metal ions, and the pH value of the solution, etc.⁶⁻⁹ Therefore, the proper design and selection of organic linkers with modifiable backbone and high connectivity assembled with iron(II) ions would be a facile route to modulate novel iron(II) network topologies with anticipated properties.¹⁰ Among the reported studies, the bidentate and tridentate N-ligands are commonly utilized to connect isolated iron(II) ions to promote the formation of high dimensional coordination frameworks with fascinating SCO properties.¹¹ In contrast, high dimensional iron(II) CPs constructed from the more extended N-ligands that possess four or more coordination arms and resulting conformation have received little attention, which might be ascribed to the rare selection of multi-dentate ligands and the difficulty of crystallization of iron(II) networks.

Among these N-containing ligands, TPOM, an important flexible tetra-dentate ligand, is a good candidate for the construction of CPs with diverse structures. Several structural topologies including *pts*, *pcu*, *bbf* and *qtz*, *etc.*, built from the connection of TPOM and variable metal ions have been reported, ^{12,13} which are commonly seen for CPs based on 4-connected organic linkers. However, rare CPs constructed of TPOM and iron(II) ions have been reported, ^{variable} while no CPs with FeN₆ octahedral have been presented. ¹⁴ Herein, as an effort to explore the potential of such a versatile ligand, we tried our best to synthesize high dimensional iron(II) CPs with typical FeN₆

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octahedra assembled with TPOM and SCN-. In addition, the simplest structural type of *pts* network is known to be constructed of 4-connected tetrahedral and square-planar shapes, and it is very interesting for us to question the possibility whether the appearance of a pts network would be achieved by the combination of tetrahedral TPOM ligands and neutral Fe(NCS)₂ units. In accordance with our hypothesis, the simplified pts topological structure of [Fe(TPOM)(SCN)₂]·2(HN(CH₃)₂)·4(H₂O) (1) is truly presented. Furthermore, with the consideration of the key role of the organic linkers in directing the self-assembly of final structure of CPs, a similar tetra-topic ligand TPOM2 was generated. Compared to the flexibility of TPOM, TPOM2 would adopt much more variable conformations because of the additional rotation of the pyridinate rings, illustrated in Scheme 1, leading to much more unpredictable CPs. A new iron(II) CP, [Fe(TPOM2)(SCN)₂]·2(CH₃OH) (2), with [4] tiling structure was concomitantly obtained. These two new compounds are characterized by X-ray crystallography, topological analysis, elemental analysis, IR spectra, TGA and magnetic susceptibility, and discussed in detail.

Experimental sections

Materials and general methods

All starting materials were obtained commercially and were used without further purification. Elemental analysis for C, H, N were performed on a Perkin-Elmer 240Q elemental analyzer. The IR spectra were recorded in range of 400–4000 cm^{-1} on a Nicolet 5DX spectrometer (KBr pellets). Magnetic susceptibility measurements were carried out in the temperature range of 2-300 K with a magnetic field of 5000 Oe on a Quantum Design MPMS XL-7 magnetometer. The ligand TPOM was synthesized by a literature method.¹⁵ The magnetic measurements under pressure were performed by using an EasyLab Mcell 10 hydrostatic pressure cell, which is specially designed for the MPMS setup and made of hardened beryllium bronze with silicon oil as the pressure transmitting medium. The applied pressure was measured by using the pressure dependence of the superconducting transition temperature of a built-in pressure sensor made of high-purity tin. Magnetic data were calibrated with the sample holder and the diamagnetic contributions. Three tripodal ligands were synthesized by a literature method.

Synthesis of [Fe(TPOM)(SCN)₂]·2(HN(CH₃)₂)·4(H₂O) (1)

FeSO₄·7H₂O (0.2 mmol) and KSCN (0.4 mmol), with a small amount of ascorbic acid (5 mg) were stirred in 8 mL methanol for 5 min, then the solution was filtered and 1 mL water was added to the filtrate. The resulting solution was placed in a test tube, above which was layered 1 mL methanol, and 10 mL methanol containing 0.05 mmol TPOM was layered on the top. After one week, glittering yellow crystals were obtained (30% based on TPOM). Anal. Calcd for dehydrated C₂₇H₂₄FeN₆O₄S₂: C, 52.6%, H, 3.92%, N, 13.63%; found C, 53.1%, H, 3.66%, N, 13.98%. IR (KBr, cm-1): 3437, 2071, 1607, 1571, 1482, 1434, 1301, 1158, 1101, 1011, 754.

Synthesis of [Fe(TPOM2)(SCN)₂]·2(CH₃OH) (2)

The synthetic route was similar to 1, excepted for TPOM2. Anal. Calcd for C₂₉H₃₂FeN₆O₆S₂: C, 51.18%, H, 4.74%, N, 12.35%; found C, 50.45%, H, 5.15%, N, 13.11%. IR (KBr, cm⁻¹): 3441, 2066, 1600, 1570, 1485, 1432, 1301, 1154, 1102 1011, 757.

X-Ray structural determination

Diffraction data for 1 (0.5 \times 0.3 \times 0.15 mm) and 2 (0.5 \times 0.3 \times 0.2 mm) were collected using an Oxford Gemini S Ultra diffractometer using Mo-K α ($\lambda = 0.71073$ Å) radiation at 123 K. The structures of complexes were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix leastsquares procedure based on F^2 values.¹⁶ The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. Structure refinement after modification of the data for the noncoordinate lattice solvent molecules with the SQUEEZE routine of PLATON led to better refinement and data convergence. CCDC-875827 (1), and CCDC-875828 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/ datarequest/cif.

Table 1 Crystal data of 1-2

	1	2
Chemical formula	C31H48FeN8O8S2	C ₂₉ H ₃₂ FeN ₆ O ₆ S ₂
Formula mass	778.71	680.56
Crystal system	Orthorhombic	Monoclinic
Space group	Cccm	C2/c
aĺÅ	8.9846(5)	16.5531(9)
b/Å	22.9562(11)	11.7181(7)
c/Å	24.0229(12)	17.4935(8)
β (°)	90.00	103.372(5)
Unit cell volume/Å ³	4954.8(4)	3301.2(3)
T/K	123(2)	123(2)
Space group	Cccm	C2/c
Z	4	4
No. of reflections measured	2503	3233
$R_{\rm int}$	0.0000	0.0223
Final R_1 values $(I > 2\sigma(I))$	0.0541	0.0312
Final R_1 values (all data)	0.0787	0.0396



Scheme 1 The flexibility of the tetra-pyridinate ligands TPOM and TPOM2.

	1		2
Fe(1)–N(1)	2.219(2)	Fe(1)–N(1)	2.239(2)
Fe(1) - N(2)	2.120(3)	Fe(1)-N(2)	2.218(2)
		Fe(1)-N(3)	2.109(2)
$\langle d_{\text{Fe-N}} \rangle$ [Å]	2.169(2)	$\langle d_{\rm Fe-N} \rangle$ [Å]	2.189(2)
ΣFe [°]	11.3	ΣFe [°]	12.1
Fe…Fe distance [Å]	8.528(2)	Fe…Fe distance [Å]	8.511(2)

Results and discussion

Synthesis of CPs 1 and 2

Yellow crystalline samples of 1 and 2 were synthesized by the diffusion method at room temperature with different layers containing $Fe(NCS)_2$ and TPOM or TPOM2. Both of the two samples are very unstable when removed from the mother liquid. X-Ray single crystal analyses at 123 K show that CPs 1 and 2 are constituted of metal isothiocyanate and tetrapyridinate ligand. The presence of the SCN groups is also supported by the strong vibration peak around 2050 cm⁻¹ in the FT-IR spectrum of each compound. The crystal data and structural parameters of 1 and 2 are summarized in Table 1 and 2.

Crystal structure of 1

The X-ray crystallographic analyses reveal that compound **1** crystallizes in the orthorhombic crystal system *C*ccm. The asymmetric unit contains an independent SCN group, a quarter iron atom and a quarter TPOM ligand (Fig. 1). The central iron atom is coordinated by 6 N atoms. The Fe–N_{pyridine} and Fe–



Fig. 1 The asymmetric unit of 1(a) and the octahedral coordination environment of Fe atom (b).

N_{SCN} bond lengths are 2.219 and 2.120 Å¹⁷ respectively, in accordance with the typical values of a high-spin iron(II) state. The connections between iron ions and NCS⁻ groups are bent with a C–N–Fe angle of 166.1(2)°. Due to centrosymmetry, the angles of N–Fe–N are almost around 90 and 180°, indicating a regular octahedral geometry of the coordinated iron ion. The axial positions are occupied by two *trans*-disposed NCS⁻ groups, while the equatorial positions are occupied by four pyridyl rings that are *cis*-disposed to the opposite ring. The octahedral distortion parameter, Σ , which is used to quantify the angular deviation from the ideal octahedral geometry,¹⁸ is 11.3°, indicating a more regular octahedron shape compared to other 3D iron(II) SCO compounds possessing similar FeN₆ connectivity.

Each central iron(II) ion connects four distinct TPOM ligands, while the tetradentate ligand TPOM connects four independent iron(II) ions. The N···Ccentral···N angles of the flexible TPOM ligand range from 93.09(2)° to 152.90(2)°, and the torsion angles of C_{central}-O-CH₂-C_{pyridyl} equal to 179.05(2)°, indicating that the ligand deviates slightly from tetrahedral geometry and adopts a fully extended configuration. In this way, the ligands in such conformations serve as quaternary bridges to link four iron(II) ions into an infinite 3D crystal structure with three directional channels, as shown in Fig. 2. The shortest Fe…Fe distance is about 8.985(4) Å. The isolated agua molecules and (CH₃)₂NH in situ generated from DMF molecules during the synthesis process of organic ligand¹⁹ are housed inside these pores. Calculated using the PLATON routine, the solvent accessible volume in the dehydrated structure of 1 is about 54.2%. Considering the central iron atoms and TPOM ligands as four-connecting nodes, the overall structure of 1 topologically possesses a 4,4-connected 2-nodal pts net²⁰ with the point (Schläfli) symbol $\{4^2 \cdot 8^4\}$ calculated with TOPOS software (Fig. 3).²¹

Crystal structure of 2

In contrast to the crystal structure of **1**, the X-ray crystallographic analyses reveals that compound **2** crystallizes in the monoclinic crystal system C2/c. The asymmetric unit contains half an iron atom, an independent SCN group, and a half TPOM2 ligand containing N1 and N2 atoms (Fig. 4). The central iron atom is also coordinated by 6 N atoms. The average Fe–N_{pyridine} and Fe–N_{SCN} bond lengths are 2.229 and 2.109 Å, respectively, also indicating the high-spin iron(II) state in **2**. The similar regular octahedron of the iron(II) ions of **2** could be also confirmed by the Σ value of 12.1°. The axial positions are



Fig. 2 The 3D crystal packing mode of 1 along a, b, and c axis, respectively, which show the three directional channels in the whole crystal structure.



Fig. 3 View of the *pts* network of **1** in a simplified ball-and-stick model (the purple and gray balls represent the centers of iron atoms and 4-connected TPOM, respectively).



Fig. 4 The asymmetric unit of 2(a) and the octahedral coordination environment of Fe atom (b).

occupied by two nearly linear NCS⁻ groups, while the equatorial positions are occupied by four pyridyl rings that are also *cis*disposed to the opposite ring. The connections between the iron ions and NCS⁻ groups are bent with an C–N–Fe angle of 175.0(2)°.

Each tetradentate TPOM2 ligand adopts the highly-distorted tetrahedral geometry to connect four independent iron(II) ions with the range of $N \cdots C_{central} \cdots N$ angles from 58.46(2)° to



Fig. 5 (a) The 2D sheet crystal packing mode of 2 in the *bc* plane; (b) the cavities left between the adjacent layers.

156.25(2)°. While the torsion angles of $C_{central}$ –O–CH₂– $C_{pyridyl}$ are 2 × 137.90(2)° and 2 × 167.41(2)°, indicating the not fully extended conformation. The infinite 2D sheet structure in the *bc* plane (Fig. 5(a)) is constructed by the connection of such distorted quaternary bridges and four-connected iron(II) ions. Tiny channels are found between adjacent 2D sheets (Fig. 5(b)), which are occupied by the isolated methanol molecules. Within a sheet, the shortest Fe···Fe distance is about 8.767(2) Å. The adjacent sheets stack over each other to block the voids and form the 3D strucutre (Fig. 5(b)). Calculated using the PLATON routine, the solvent accessible volume in the dehydrated structure of **2** is about 20.4%.

Considering the central iron atoms as four-connecting nodes and TPOM2 ligands as another four-connecting nodes, the 2D sheet of **2** topologically possesses a 4-connected uninodal *sqll Shubnikov* tetragonal plane²² net with the point (Schläfli) symbol $\{4^4 \cdot 6^2\}$ calculated with *TOPOS* software (Fig. 6(a)).²¹ Thus interleaved *sqllShubnikov* tetragonal planes net stack over each other along the *a* axis direction. Interestingly, a [4] tiling structure with plane net signature of $[122]_4[4 \cdot 4 \cdot 4 \cdot 4]$ is further presented, which not only tends to decrease the pore volume, but stabilize the whole crystal structure (Fig. 6(b)) through weak interactions.

Thermal stability

The thermogravimetric (TG) analysis was performed in N_2 atmosphere on fresh polycrystalline samples of 1 and 2 and the TG curves are shown in Fig. 7. The TG curve of 1 shows the first weight loss of 11% in the temperature range of 25–90 °C, which indicates the loss of lattice molecules per formula unit. The



Fig. 6 (a) View of the *sql/Shubnikov* tetragonal plane net of **2** in a simplified ball-and-stick model; (b) the [4] tiling of *sql/Shubnikov* plane net (the red/purple octahedrons and blue/green balls represent the centers of iron atoms and 4-connected TPOM2, respectively).



Fig. 7 TGA analysis of 1 and 2.

deviation between the observed and calculated values was mostly caused by the quick loss of guest molecules of a fresh sample in the air. The metal–organic framework retains until 300 °C, and then starts to decompose accompanying the loss of organic ligands. For **2**, the weight loss attributed to the gradual release of two methanol molecules per formula unit is observed in the range of 25–150 °C (obsd: 8.53% and calcd: 8.83%), then the framework retains in the temperature range of 150–350 °C, and then decomposes. The higher thermostability of **2** over **1** is in



Fig. 8 $\chi_{M}T$ versus T plots of **1**(a) and **2**(b) in the temperature range of 2–300 K under 5 kOe and variable external pressures.

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accordance with the tiling structure of **2** compared to the porous structure of **1**.

Magnetic properties of 1 and 2

The variable-temperature magnetic susceptibilities of 1 and 2 were measured on crystalline samples under 5 KOe in the range of 2–300 K and shown as $\chi_{\rm M}T$ versus T plots in Fig. 8. For 1, at T = 300 K and P = 1 bar, the $\chi_M T$ value is 3.54 cm³ mol⁻¹ K featuring the high spin state of Fe(II) atoms. As the temperature is lowered, $\chi_{\rm M}T$ values practically remain constant, the dropping of $\gamma_{\rm M}T$ values at temperatures below 25 K might be caused by the occurrence of zero-field splitting of the high spin iron(II) ions. The magnetic data was fitted with the Curie–Weiss expression (C = 3.267(2) cm³ mol⁻¹ K and θ = -1.47(3) K). With the consideration of the Fe...Fe distance and the low values of the Weiss constant, the decrease below 50 K might be also attributed to very weak antiferromagnetic interactions or the presence of zero-field splitting or both. The presence of guest molecules in the crystal lattice of porous iron(II) CPs is known to play an important role in affecting or triggering SCO behavior. However, for 1, no thermal-driven SCO behavior could be observed for the desolvated sample or samples immersed in different solvents such as ethanol, acetonitrile, and benzene, etc. In addition, to further track the possibility of pressure-induced SCO behavior, magnetic properties of 1 were also investigated under external hydrostatic pressures up to 8.88 Kbar in the temperature range of 2-300 K, but no obvious spin transition was observed from the $\chi_{M}T$ values. Similar magnetic properties of 2 under different external pressures and guest molecules could be observed, also indicating the absence of SCO behavior.

Compared to the distorted octahedron of FeN₆ in other SCO compounds,⁵ for **1** and **2**, the regular octahedron of high-spin iron(II) state was exhibited, mostly caused by the centrosymmetry and expanded low density structure.³ In particular, the octahedron of the low spin state is more regular than the high spin state. Therefore, in **1** and **2**, the high spin iron(II) ions could not be switched either by hydrostatic pressure or thermally in the temperature region of 2–300 K. Future efforts might be focused on increasing the steric hindrance of the pyridyl rings around central iron ions, which might be helpful to form irregular octahedra at high temperature ranges, and subsequently trigger the occurrence of spin transition.

Conclusions

In summary, two new iron(II) coordination polymers modeled by the distinct tetra-pyridine ligands have been synthesized and structurally characterized. The structural results show that utilizing the flexible tetra-pyridinate ligands is a good approach to achieve high dimensional iron(II) CPs structures with FeN₆ octahedra. **1** has a 3D crystal structure with typical *pts* topology, while **2** has a 2D crystal structure with a [4] tiling structure. The variable coordination position of the pyridyl rings must be responsible for assembling of the distinct structure, as well as the regular octahedron shape, might play a crucial role in the absence of the spin transition. More similar and systematic attention are needed to build upon on the successful construction of high dimensional iron(II) CPs modeled by the other new multi-pyridine ligands.

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References

- (a) M. D. Allendorf, C. A. Bauer, R. K. Bhaktaa and R. J. T. Houka, Chem. Soc. Rev., 2009, 38, 1330; (b) X. L. Zheng, Y. Liu, M. Pan, X. Q. Liu, J. Y. Zhang, C. Y. Zhao, Y. X. Tong and C. Y. Su, Angew. Chem., Int. Ed., 2007, 46, 7399; (c) S. Kitagawa, R. Kitaura and S. I. Noro, Angew. Chem., Int. Ed., 2004, 43, 2334; (d) R. Cao, Q. Shi, D. F. Sun, M. C. Hong, W. H. Bi and Y. J. Zhao, Inorg. Chem., 2002, 41, 6161; (e) K. S. Gavrilenko, S. V. Punin, O. Cador, S. Golhen, L. Ouahab and V. V. Pavlishchuk, J. Am. Chem. Soc., 2005, 127, 12246; (f) Z. R. Pan, H. G. Zheng, T. W. Wang, Y. Song, Y. Z. Li, Z. J. Guo and S. R. Batten, Inorg. Chem., 2008, 47, 9528; (g) Y. F. Bi, X. T. Wang, B. W. Wang, W. P. Liao, X. F. Wang, H. J. Zhang, S. Gao and D. Q. Lia, Dalton Trans., 2009, 2250.
- 2 (a) C. D. Wu, A. G. Hu, L. Zhang and W. B. Lin, J. Am. Chem. Soc., 2005, **127**, 8940; (b) S. H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp and A-T. E. Schmitt, Chem. Commun., 2006, 2563; (c) L. Alaerts, E. Seguin, H. Poelman, F. T. Starzyk, P. A. Jacobs and D. E. D. Vos, Chem.-Eur. J., 2006, **12**, 7353; (d) Z. L. Liao, G. D. Li, M. H. Bi and J. S. Chen, Inorg. Chem., 2008, **47**, 4844; (e) R. Matsuda, T. Tsujino, H. Sato, Y. Kubota, K. Morishige, M. Takata and S. Kitagawa, Chem. Sci., 2010, **1**, 315; (f) G. Seeber, G. J. T. Cooper, G. N. Newton, M. H. Rosnes, D.-L. Long, B. M. Kariuki, P. Kögerler and L. Cronin, Chem. Sci., 2010, **1**, 62.
- 3 (a) Y. Garcia, G. Bravic, C. Gieck, D. Chasseau, W. Tremel and P. Gütlich, *Inorg. Chem.*, 2005, 44, 9723; (b) G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray and J. D. Cashion, *Science*, 2002, 298, 1762; (c) S. M. Neville, B. Moubaraki, K. S. Murray and C. J. Kepert, *Angew. Chem., Int. Ed.*, 2007, 46, 2059.
- 4 (a) C. Genre, E. Jeanneau, A. Bousseksou, D. Luneau, S. A. Borshch and G. S. Matouzenko, *Chem.-Eur. J.*, 2008, **14**, 697; (b) A. Białonńska, R. Bronisz, M. F. Rudolf and M. Weselski, *Inorg. Chem.*, 2012, **51**, 237; (c) S. M. Neville, G. J. Halder, K.W. Chapman, M. B. Duriska, B. Moubaraki, K. S. Murray and C. J. Kepert, *J. Am. Chem. Soc.*, 2009, **131**, 12106; (d) G. J. Halder, K. W. Chapman, S. M. Neville, B. Moubaraki, K. S. Murray, J. F. Létard and C. J. Kepert, *J. Am. Chem. Soc.*, 2008, **130**, 17552; (e) B. Li, R. J. Wei, J. Tao, R. B. Huang, L.-S. Zheng and Z.-P. Zheng, *J. Am. Chem. Soc.*, 2010, **132**, 1558.
- 5 (a) V. Niel, A. L. Thompson, M. C. Muñoz, A. Galet, A. E. Goeta and J. A. Real, Angew. Chem., Int. Ed., 2003, 42, 3760; (b) S. Bonhommeau, G. Molnár, A. Galet, A. Zwick, J. A. Real, J. J. McGarvey and A. Bousseksou, Angew. Chem., Int. Ed., 2005, 44, 4069; (c) M. Ohba, K. Yoneda, G. Agustí, M. C. Muñoz, A. B. Gaspar, J. A. Real, M. Yamasaki, H. Ando, Y. Nakao, S. Sakaki and S. Kitagawa, Angew. Chem., Int. Ed., 2009, 48, 4767; (d) Y.-L. Bai, J. Tao, R.-B. Huang, L.-S. Zheng, S.-L. Zheng, K. Oshida and Y. Einaga, Chem. Commun., 2008, 1753.
- 6 (a) D. N. Dybtsev, H. Chun and K. Kim, *Chem. Commun.*, 2004, 1594; (b) Y. B. Dong, H. X. Xu, J. P. Ma and R. Q. Huang, *Inorg. Chem.*, 2006, 45, 3325; (c) Y. Q. Tian, Y. M. Zhao, Z. X. Chen, G. N. Zhang, L. H.Weng and D. Y. Zhao, *Chem.-Eur. J.*, 2007, 13, 4146; (d) R. Sarma, D. Kalita and J. B. Baruah, *Dalton Trans.*, 2009, 7428.

- 7 (a) Y. T. Wang, H. H. Fan, H. Z. Wang and X. M. Chen, *Inorg. Chem.*, 2005, 44, 4148; (b) L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *New J. Chem.*, 2003, 27, 483; (c) G. H. Cui, J. R. Li, J. L. Tian, X. H. Bu and S. R. Batten, *Cryst. Growth Des.*, 2005, 5, 1775; (d) I. S. Lee, D. MokShin and Y. K. Chung, *Chem.–Eur. J.*, 2004, 10, 3158.
- M. L. Tong, S. Kitagawa, H. C. Chang and M. Ohba, *Chem. Commun.*, 2004, 418; (b) P. M. Forster, A. R. Burbank, C. Livage, G. Férey and A. K. Cheetham, *Chem. Commun.*, 2004, 368; (c) Y. B. Go, X. Q. Wang, E. V. Anokhina and A. J. Jacobson, *Inorg. Chem.*, 2005, 44, 8265; (d) Y. B. Dong, Y. Y. Jiang, J. Li, J. P. Ma, F. L. Liu, B. Tang, R. Q. Huang and S. R. Batten, *J. Am. Chem. Soc.*, 2007, 129, 4520.
- 9 (a) S. T. Wu, L. S. Long, R. B. Huang and L. S. Zheng, Cryst. Growth Des., 2007, 7, 1746; (b) X. Q. Lu, J. J. Jiang, C. L. Chen, B. S. Kang and C. Y. Su, Inorg. Chem., 2005, 44, 4515; (c) D. M. Shin, I. S. Lee, D. Cho and Y. K. Chung, Inorg. Chem., 2003, 42, 7722; (d) B. Zheng, H. Dong, J. F. Bai, Y. Li, Sh. Li and M. Scheer, J. Am. Chem. Soc., 2008, 130, 7778.
- (a) E. D. Bloch, D. Britt, C. Lee, C. J. Doonan, F. J. Uribe-Romo, H. Furukawa, J. R. Long and O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, 132, 14382; (b) 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; (c) P. Zhang, B. Li, Y. Zhao, X. Meng and T. L. Zhang, *Chem. Commun.*, 2011, 47, 7722.
- (a) S. M. Neville, G. J. Halder, K. W. Chapman, M. B. Duriska, P. D. Southon, J. D. Cashion, J. F. Létard, B. Moubaraki, K. S. Murray and C. J. Kepert, J. Am. Chem. Soc., 2008, 130, 2869; (b)
 P. D. Southon, L. Liu, E. A. Fellows, D. J. Price, G. J. Halder, K. W. Chapman, B. Moubaraki, K. S. Murray, J. F. Létard and C. J. Kepert, J. Am. Chem. Soc., 2009, 131, 10998; (c) A. Galet, V. Niel, M. C. Muñoz and J. A. Real, J. Am. Chem. Soc., 2003, 125, 14224; (d)
 F.-L. Yang, B. Li, T. Hanajima, Y. Einaga, R.-B. Huang, L.-S. Zheng and J. Tao, Dalton Trans., 2010, 39, 2288.
- 12 (a) L. L. Liang, S.-B. Ren, J. Zhang, Y. Z. Li, H. B. Du and X. Z. You, Cryst. Growth Des., 2010, 10, 1307; (b) J. S. Hu, Y. J. Shang, X. Q. Yao, L. Qin, Y. Z. Li, Z. J. Guo, H. G. Zheng and Z. L. Xue, Cryst. Growth Des., 2010, 10, 2676; (c) S.-B. Ren, L. Zhou, J. Zhang, Y.-Z. Li, H.-B. Du and X.-Z. You, CrystEngComm, 2009, 11, 1834; (d) S.-B. Ren, L. Zhou, J. Zhang, Y.-L. Zhu, Y.-Z. Li, H.-B. Du and X.-Z. You, CrystEngComm, 2010, 21, 1635; (c) Q. Zhang, X. Bu, Z. Lin, T. Wu and P. Feng, Inorg. Chem., 2008, 47, 9724.
- 13 (a) J. Guo, J.-F. Ma, B. Liu, W.-Q. Kan and J. Yang, Cryst. Growth Des., 2011, 11, 3609; (b) F. Yu and B. Li, CrystEngComm, 2011, 13, 7025; (c) B. Li, L. Q. Chen, R. J. Wei, J. Tao, R. B. Huang, L. S. Zheng and Z. Zheng, Inorg. Chem., 2011, 50, 424.
- 14 J. Zhang, Y.-S. Xue, L.-L. Liang, S.-B. Ren, Y.-Zh. Li, H.-B. Du and X.-Z. You, *Inorg. Chem.*, 2010, 49, 7685.
- 15 P. E. Ryan, C. Lescop, D. Laliberté, T. Hamilton, T. Maris and J. D. Wuest, *Inorg. Chem.*, 2009, 48, 2793.
- 16 (a) A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, J. Appl. Crystallogr., 1999, 32, b115; (b) G. M. Sheldrick, SHELXL-97; Program for refinement of crystal structures. University of Göttingen, Göttingen, Germany, 1997.
- (a) K. S. Murray and C. J. Kepert, *Top. Curr. Chem.*, 2004, 233, 195;
 (b) J. F. Létard and P. L. Guionneau, *Top. Curr. Chem.*, 2004, 235, 221.
- 18 (a) G. S. Matouzenko, A. Bousseksou, S. Lecocq, P. J. Van Koningsbruggen, M. Perrin, O. Kahn and A. Collet, *Inorg. Chem.*, 1997, **36**, 5869; (b) B. Li, R.-J. Wei, J. Tao, R.-B. Huang and L.-S. Zheng, *Inorg. Chem.*, 2010, **49**, 745.
- 19 (a) K. Xiong, F. Jiang, Y. Gai, Y. Zhou, D. Yuan, K. Su, X. Wang and M. Hong, *Inorg. Chem.*, 2012, **51**, 3283; (b) X. Y. Wang, L. Gan, S. W. Zhang and S. Gao, *Inorg. Chem.*, 2004, **43**, 4615.
- 20 K. I. Nalttinen and K. Rissanen, Inorg. Chem., 2003, 42, 5126.
- 21 V. A. Blatov, *IUCr CompComm Newsletter*, 2006, 7, 4; see also http:// www.topos.ssu.samara.ru..
- 22 J. F. Eubank, L. Wojtas, M. R. Hight, T. Bousquet, V. C. Kravtsov and M. Eddaoudi, J. Am. Chem. Soc., 2011, 133, 17532.