Synthesis, crystal structures and properties of four topological structures based on 2,3,5,6-tetramethyl-1,4-benzenedicarboxylate acid and bipyridine ligands†

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Five coordination polymers with four different typological structures have been obtained based on 2,3,5,6-tetramethyl-1,4-benzenedicarboxylate acid (H_2TBDC) and bipyridine ligands: 1D zigzag chain Cd(2,2′-bpy)(TBDC)(H_2O)·H_2O (1), 2D grid with (4,4)-net Co(H_2O)$_2$(4,4′-bpy)(TBDC)·2H_2O (2), 3D interpenetrating frameworks with diamond topology Ni(4,4′-bpy)(TBDC) (3) and Cu(4,4′-bpy)(TBDC) (4), 3D porous framework with *pcu* network Co$_2$(4,4′-bpy)(TBDC)$_2$·2H_2O·5DMF (5). Especially, complexes **2** and **5** with different topologies were obtained by use of the same reactant but change of the solvents. The gas sorption of complex **5** has also been studied.

Introduction

The construction of coordination polymers are currently of great interests due to their fascinating structures and potential applications in fields of molecular recognition, non-linear optics, magnetism, selected catalysis and gas adsorption *etc.*[1–3]

By application of organic ligands, particularly the rigid neutral donor ligands, anionic ligands, or their combination, to link the metal ions or clusters, coordination polymers with diverse structures can be constructed.[4] The construction of supramolecular arrays relies on the combination of several factors, such as solvents, auxiliary ligands and so on. Thus, it is a tremendous challenge to understand and control how these considerations influence the crystal packing and hence build the exactly predictable coordination supramolecular architectures. In the past decades, much effort has focused on the rational design and controllable synthesis of such materials and a large number of compounds with interesting topological structures and excellent properties according to some basic principles and feasible experiences have been successfully synthesized and reported.

As an important kind of O-donor ligands, 1,4-benzenedi-carboxylate (BDC) anions is of special interests and widely used in the assembly of metal–organic frameworks due to its various coordination modes and bridging abilities.[5] The benzenedi-carboxylic acids were selected to play such a role, on the basis that they may link metal ions into different dimensional structures *via* various coordination modes. Many coordination polymers base on BDC ligand with one-dimensional zigzag chains, two-dimensional square networks and three-dimensional open frameworks have been designed and synthesized in the past

decades.[6] As known, the ligand conformation and coordination geometries of the metal ion have significant influence on the final structures of coordination polymer. A little change of the ligand may result in new topological complexes. Thus, a kind of derivative benzenedicarboxylate acid, 2,3,5,6-tetramethyl-1,4-benzenedicarboxylate acid (H_2TBDC) was chosen as the main bridging ligands in this work, whose carboxylate groups are non-planar with the central benzene ring owing to the steric hindrance between the carboxylate and methyl groups (Scheme 1).[7]

As mentioned above, metal–organic frameworks with novel structures and/or characteristic properties can be influenced by adding auxiliary ligands.[8] In the realm of reported MOFs based on mixed ligands containing bipyridine, 4,4′-bipyridine usually acts as a ditopic bridging ligand to link metal centers to form single structural motif, such as 1D chain, ladder or 2D layer, or further link these low dimension to generate high dimensional motifs; while 2,2′-bipyridine appears chelating ability to block the further connection and keep motifs in low dimension. In this work, we describe the preparation and characterization of five MOFs with 1D zigzag chain of Cd(2,2′-bpy)(TBDC)(H_2O)·H_2O (1), 2D grid of Co(H_2O)$_2$(4,4′-bpy)(TBDC)·2H_2O (2), 3D three-fold interpenetrating framework of Ni(4,4′-bpy)(TBDC) (3) and Cu(4,4′-bpy)(TBDC) (4), 3D porous framework of Co$_2$-(4,4′-bpy)(TBDC)$_2$·H_2O·5DMF (5) based on mixed ligands of 2,3,5,6-tetramethyl-1,4-benzenedicarboxylate acid and bipyridine ligands. In particular, complexes **2** and **5** possess totally different configurations due to the solvent effect. All the products
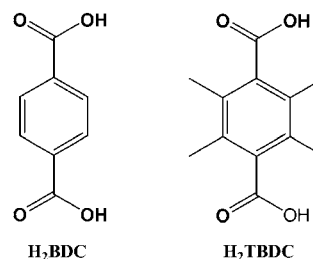
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Scheme 1

were characterized by single-crystal X-ray diffraction, thermo-gravimetric analysis, and element analysis.

Results and discussion

Crystal structure of Cd(2,2′-bpy)(TBDC)(H₂O)·H₂O (1)

Single-crystal X-ray diffraction reveals that complex **1** is a one-dimensional zigzag chain. The asymmetric unit consists of one cadmium ion, one TBDC ligand, one 2,2′-bpy ligands, one coordinated and one uncoordinated water molecules. The cadmium atom in **1** exhibits a distorted octahedral geometry (Fig. 1) with two nitrogen atoms from 2,2′-bpy and two oxygen atoms from two carboxylate groups of different TBDC ligands comprising the equatorial plane, while one coordinated water
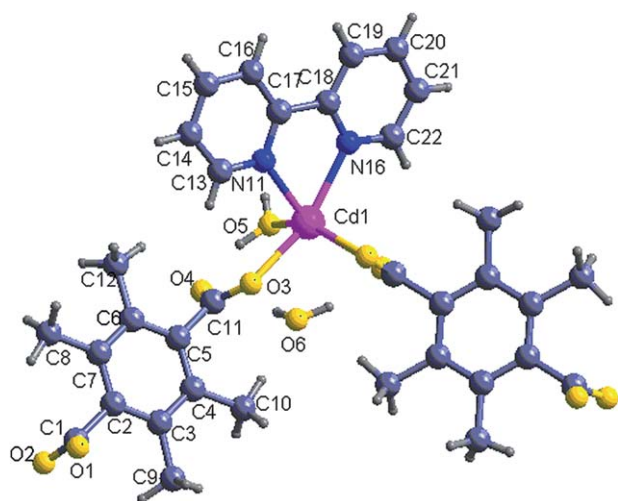

Fig. 1 The coordination environment of complex **1**.

molecule and one oxygen atom from the bidentate carboxylate group of TBDC ligand occupying the axial positions. The Cd–N and Cd–O distances are 2.306/2.349 and 2.333/2.343 Å, in agreement with other cadmium complexes.[9] As expected, the two carboxylate groups of TBDC do not locate in a plane with the central benzene ring with the dihedral angles between the carboxylate groups and the benzene ring of 90.0 and 101.3°, which is much larger than those found in MOFs constructed by benzene-1,4-bicarboxylic acid (normally 0–30°).[10]

Both carboxylate groups of H₂TBDC are deprotonated during the reaction and possess different coordination modes: one adopts bidentate chelating mode to coordinate one cadmium atom, the other adopts a unidentate coordination mode with one cadmium atom. Thus, the cadmium atoms are infinitely linked by TBDC ligands to generate a one-dimensional zigzag chain, as shown in the Fig. 2a. The nearest Cd⋯Cd distance in the 1D zigzag chain is 11.432 Å.

There are five types of supramolecular interactions in complex **1**: (i) the intramolecular hydrogen bonding interaction between the uncoordinated oxygen atom of carboxylate group and the coordinated water molecule (O⋯O: 2.638 Å); (ii) the hydrogen bonding interaction between the coordinated water molecules and the uncoordinated water (O⋯O: 2.746 Å); (iii) the weak hydrogen bonding interaction between the uncoordinated water molecules and coordinated O3 of carboxylate group (O⋯O: 2.779 Å); (iv) the weak hydrogen bonding interaction between the uncoordinated water molecules and coordinated O2 of carboxylate group (O⋯O: 2.873 Å); (v) the weak π⋯π stacking between the coordinated 2,2′-bpy in different crossed chains (4.186 Å). If the hydrogen bonding interactions (ii) and (iii) serve as linkage, then adjacent polymeric chains could be connected to a hydrogen-bonded 2D sheet (Fig. 2b). Then, the π⋯π stacking interaction further connect the one-dimensional chains to generate a three-dimensional supramolecular architecture (as
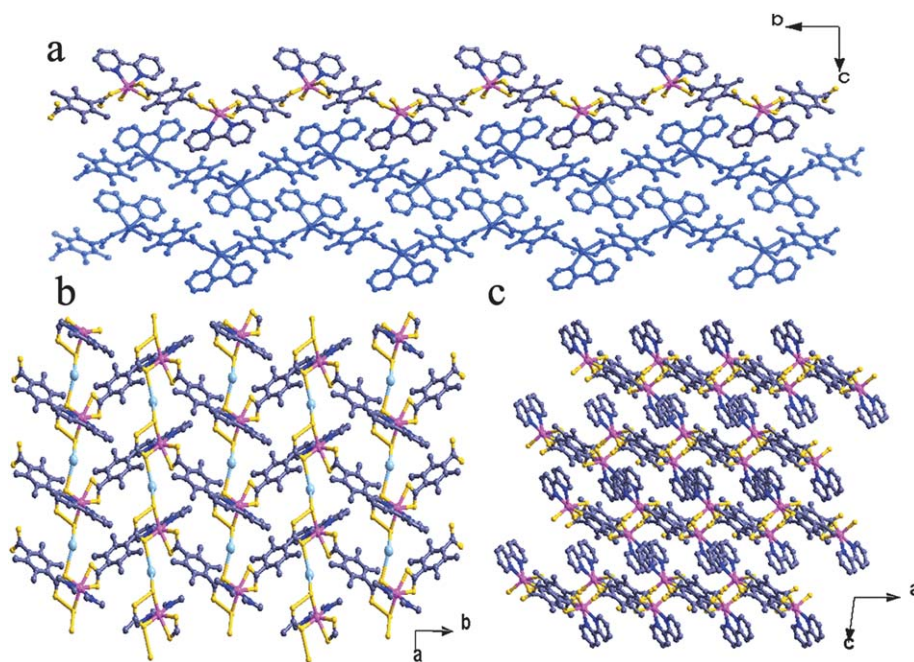

Fig. 2 (a) The zigzag chains array; (b) hydrogen-bonded 2D sheet with hydrogen bonding interaction from *c* axis (oxygen atoms of free water molecules are in light blue and other oxygen atoms are in yellow); (c) the 3D packing structure from the *b* axis.
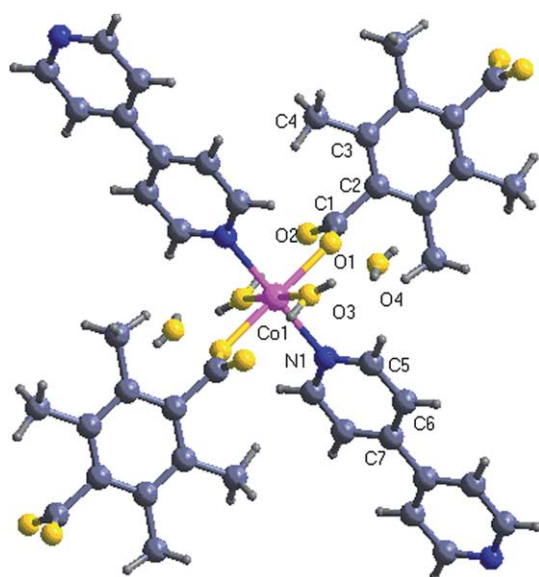
Fig. 3 The coordination environment of complex **2**.

shown in Fig. 2c) with the nearest Cd···Cd distance in adjacent chains of 8.897 Å.

Crystal structure of $Co(H_2O)_2(TBDC)(4,4'\text{-bpy})\cdot 2H_2O$ (2)

Complex **2** is a two-dimensional grid network. The asymmetric unit consists of one quarter cobalt ion, one half TBDC ligand, one half 4,4'-bpy ligands, one half coordinated and one half uncoordinated water molecules. The central metal ion exhibits a normal octahedral geometry, which is coordinated by two carboxyl oxygen atoms from different TBDC ligands, two nitrogen atoms from two 4,4'-bpy ligands and two coordinated water molecules. The two carboxyl oxygen atoms and two nitrogen atoms comprise the equatorial plane, while two coordinated water molecules occupy the axial positions (Fig. 3). The Co–N and Co–O_w/Co–O_L distances are 2.170 and 2.118/2.134 Å, respectively. As the central metal in a normal octahedral geometry, the angles of O1–Co–N and O3–Co–N are all 90°.

The two carboxylate groups are deprotonated during the reaction and each adopts unidentate coordination mode with one metal ion. The ligand is also non-planar with the average
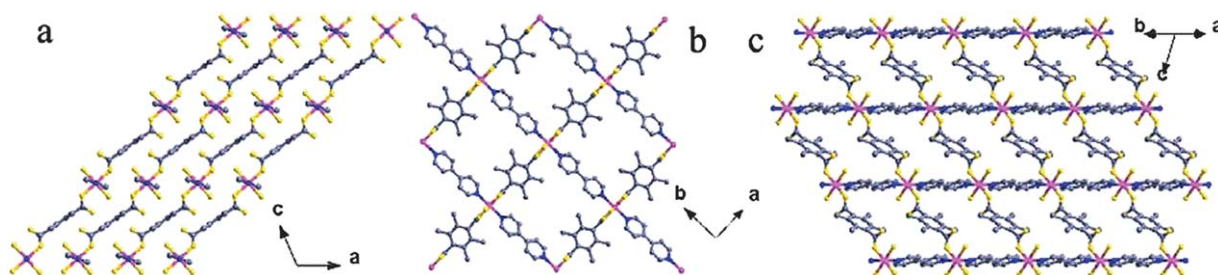

Fig. 4 (a) The linear chain along the *b* axis; (b) one single layer along the *c* axis; (c) 3D supramolecular architecture.
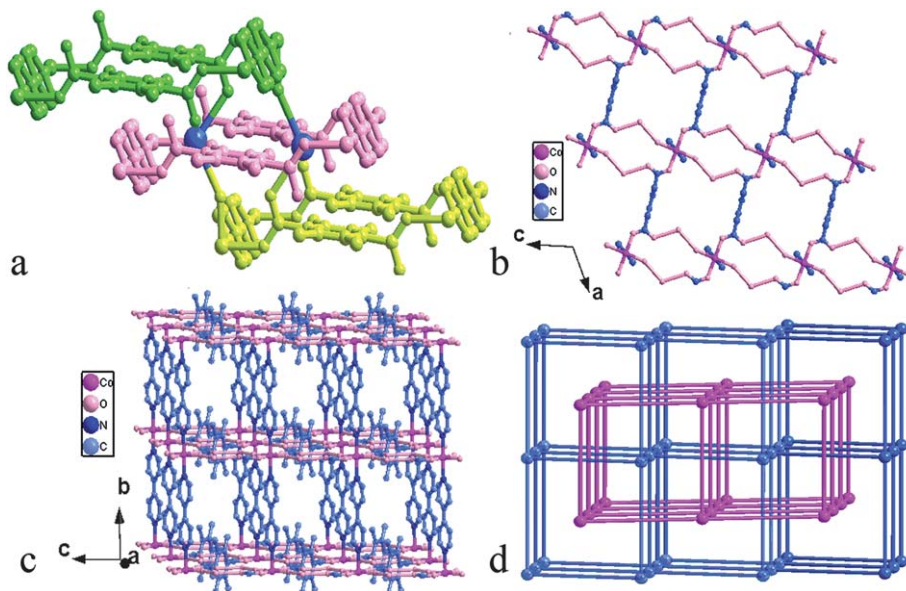

Fig. 5 (a) Two water molecules (blue balls) residing in one grid connect with two adjacent layers by hydrogen bonding interaction, (b) the 2D layer constructed from hydrogen bonding interactions showing the 12-membered metallamacrocycle, (c) the 3D structure along the *a* axis, (d) the interpenetrating *pcu* topological network of complex **2**.
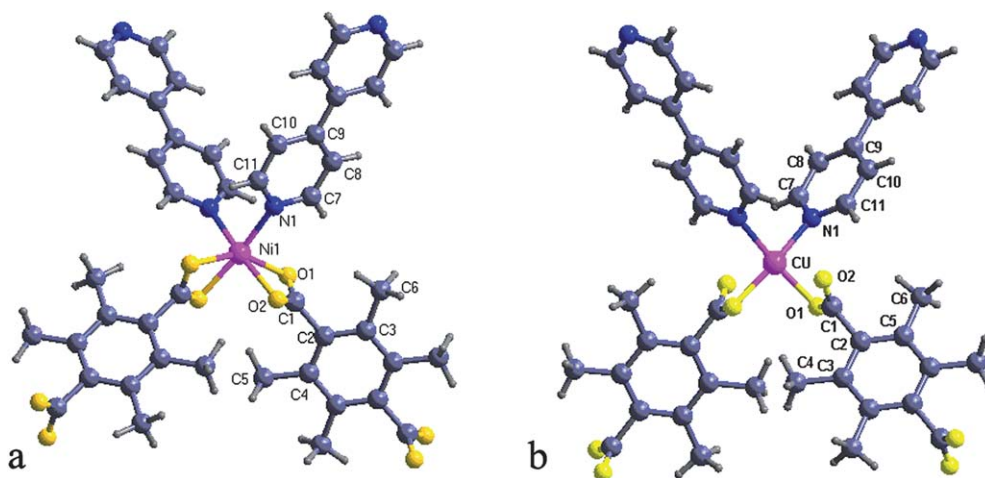
Fig. 6 The similar coordination environment of central metal in complex **3** (a) and **4** (b).

dihedral angle between the central benzene ring and the carboxylate groups of 88.9°. The whole ligand acts as a bridging linker to connect two cobalt ions to result in the formation of a one-dimensional linear chain (Fig. 4a), which is further connected by 4,4′-bpy ligands to give rise to a 2D layer with approximate rhombus grid (distance from atom to atom: 11.63 × 11.49 Å) (Fig. 4b). The coordinated water molecules in the axial position of cobalt ion prevent the further connection to build a 3D framework. As seen from the [110] direction, there are parallelo-gram channels with free water molecules residing in it, as shown in Fig. 4c. If the cobalt atom can be considered as a single node and the TBDC and the 4,4′-bpy as the linear linkers, then complex **2** displays a normal (4,4) net.[11]

It is worthy to be noted that, there are three kinds of O–H···O hydrogen bonding interactions in complex **2**: (i) the distance between the uncoordinated oxygen atom of carboxylate and coordination water is 2.581 Å (slightly shorter than that in complex **1**), showing strong intramolecular hydrogen bonding interaction; (ii) the hydrogen bonding interaction between the uncoordinated oxygen atom of carboxylate group and uncoordinated water (2.696 Å);[12] (iii) the distance between the uncoordinated and coordinated water is 2.741 Å, it shows the weakest hydrogen bonding interactions. Each rhombus grid of the layer contains two uncoordinated water molecules and every uncoordinated water molecule connects two adjacent (4,4) sheets through hydrogen bonding interactions (Fig. 5a).

Especially, if latter two kinds of hydrogen bonds could be seen as coordinative bonds in this structure, it could be found that the uncoordinated and coordinated water molecules and carboxylate groups connect two cobalt ions to form a 12-membered metallamacrocycle, which is connected to form a 1D chain by sharing the cobalt ions. The connection of these chains by TBDC linkers gave rise to a grid layer (Fig. 5b). Further, each grid layer is pillared by 4,4′-bpy ligands to generate a three-dimensional porous framework with large channels (atom to atom: 9.34 × 7.39 Å) along the *b* axis. If we still view the cobalt atoms as the nodes, but the metallamacrocycle and 4,4′-bpy as the linear linkers, thus, the 3D architecture shows a typical *pcu* topology (Fig. 5c). Ultimately, two such networks

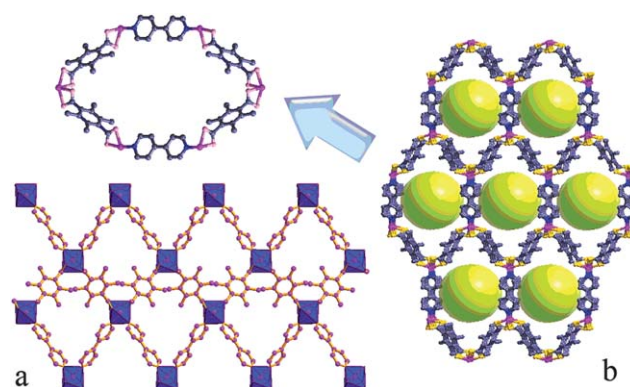interpenetrate each other to generate a nonporous framework (Fig. 5d).

Fig. 7 (a) The zigzag chains formed by bpy and TBDC ligands, respectively; (b) the single net with a 56-membered hexagonal ring of complex **3**.
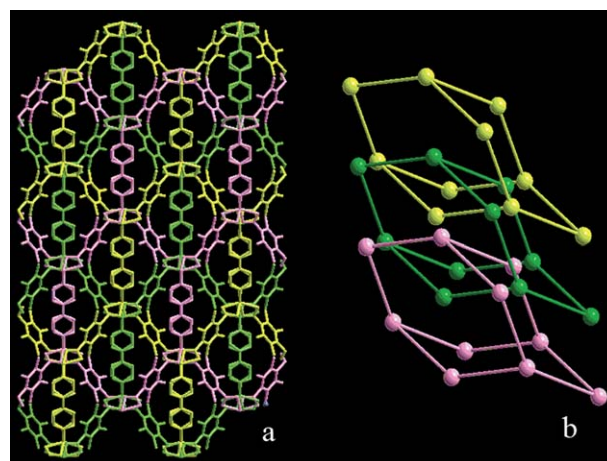

Fig. 8 (a) The three-fold interpenetrating 3D framework and (b) the diamond topology of complex **3** with each fold in different colours.

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Crystal structures of Ni(4,4′-bpy)(TBDC) (3) and Cu(4,4′-bpy)(TBDC) (4)

Single-crystal X-ray diffraction reveals that complexes **3** and **4** are isomorphous and both crystallize in monoclinic *C*2/*c* space group. The following discussions on structural aspects will mainly be focused on complex **3**.

Complex **3** is a three-fold interpenetrating three-dimensional metal–organic framework. The asymmetric unit of **3** consists of one half nickel ion, half TBDC and half 4,4′-bpy ligand as shown in Fig. 6. The central nickel ion is six-coordinated by two nitrogen atoms from two different 4,4′-bpy ligands, four oxygen atoms from two different TBDC ligands. The coordination geometry of the central nickel ion can be best described as a center of distorted octahedral, with the angles of N1–Ni–N2, O1–Ni–N1, O2–Ni–N1 and O1–Ni–O2 of 86.35, 94.63, 94.21 and 62.53°, respectively. While complex **4** shows slight difference about central metal: copper ion is four-coordinated in a square planar geometry with weak axial interactions (distance from atom to atom: 2.498 Å), which exhibits a distorted octahedron with a Jahn–Teller elongation (Fig. 6b).

In complex **3**, both of carboxylate groups of TBDC ligand are deprotonated during the reaction, and each adopts bidentate chelating mode. Thus, every TBDC links two nickel ions to form a one-dimensional zigzag chain along [101] direction (Fig. 7a) and each nickel ion also attaches to two 4,4′-bpy ligands to build a similar zigzag chain along [001] direction, which is further connected by sharing nickel ions to spread in four directions. Then, all these kinds of linkage generate a three-dimensional porous metal–organic framework with rhombic channels (distance from atom to atom: 23.80 × 15.93 Å) along the *c* axis. The framework can also be viewed as formation by infinitely sharing 56-membered hexagon ring, in which the axial positions are occupied by nickel ions and the edges are formed by four TBDC ligands and two 4,4′-bpy ligands (Fig. 7b).

In the three-dimensional framework, if each nickel ion can be considered as a single node and the TBDC ligands and 4,4′-bpy as linear bridging linkers, and then the structure possesses a typical diamond-type topology,[13] as shown in Fig. 8b. Meanwhile, the other two similar networks repeat in the structure and the 4,4′-bpy ligands fill in the large ring of the basic one to engender three-fold interpenetrating frameworks without any pores (Fig. 8a and ESI, Fig. SI2b).†

Crystal structure of Co₂(4,4′-bpy)(TBDC)₂·2H₂O·5DMF (5)

As shown in Fig. 9, Complex **5** crystallizes in *I*4/*mcm* space group, forming binuclear SBU achieved through four bridging carboxyl groups, which is isostructural with $Zn_2(TBDC)_2(bpy)$ reported by Kim and co-workers.[14a] The Co···Co distance in the SBU is 2.675 Å, indicating a weak metal–metal interaction.

In the structure, the 4,4-bipy ligands are disordered, as found in other reported results. The dimensions of the channels are 10.90 × 11.14 Å (from atom to atom), in which uncoordinated solvates reside. The solvent–accessible volume in the structure calculated after removal of uncoordinated solvates is 61.1%. In the three-dimensional framework, each binuclear cobalt ions SBUs can be considered as a six-connected node and the TBDC ligands and 4,4′-bpy as linear bridging linkers, and then the
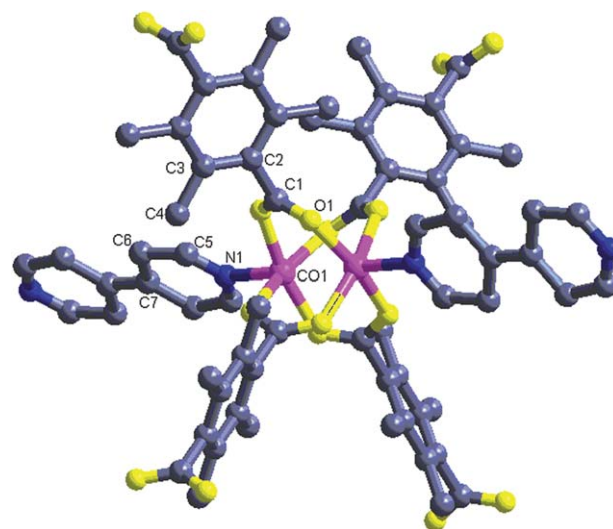

Fig. 9 The coordination environment of complex **5**.

structure possesses a typical *pcu* (or α-Po) topology, as shown in Fig. 10b.[14]

Gas–adsorption property of complex 5

In order to check the permanent porosity of complex **5**, various gas–adsorption studies have been performed, as shown in Fig. 11. The activated complex **5**, which had been vacuum-dried at 120 °C after soaking in methanol, have been studied for N₂, O₂ and H₂ at 77 K, and CO₂, CH₄ at 196 K.

The activated complex **5** can adsorb moderate amount of O₂ (188.85 cm³ g⁻¹), N₂ (144.28 cm³ g⁻¹) at 77 K and CO₂ (141.32 cm³ g⁻¹) at 196 K, with type-I behaviours. The CH₄ and H₂ sorption isotherm are reversible without a significant hysteresis between sorption and desorption curves. The final amount of adsorption for CH₄ at 196 K is 50.25 cm³ g⁻¹, whereas H₂ isotherms display the ultimate value of 77.1 cm³ g⁻¹ (0.69 wt%) at 77 K. The amount of H₂ adsorption at 87 K is 55.68 cm³ g⁻¹ (0.5 wt%). Derived from the H₂ adsorption data, complex **5** has the heat of adsorption of 6.7527 kJ mol⁻¹ (Fig. 12), which is smaller than other reported results.[15] Owing to the lack of the cages or polyhedra in complex **5**, the gas sorption study does not show obvious advantage than other MOFs structures.[16]
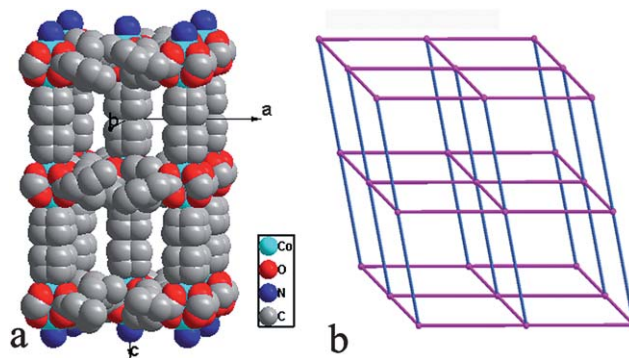

Fig. 10 (a) TBDC linkers and all the possible conformations of disordered bpy pillars are shown; (b) the *pcu* network of complex **5**.
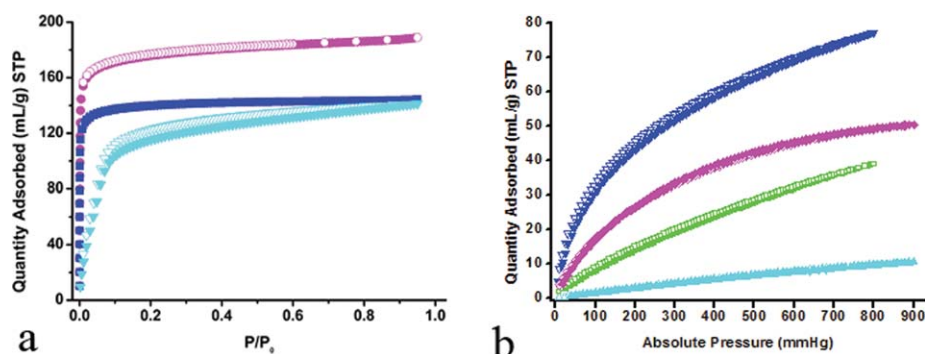
Fig. 11 Gas sorption isotherm of complex **5**. (a) blue, N_2 at 77 K; magenta, O_2 at 77 K; cyan, CO_2 at 196 K; (b) blue, H_2 at 77 K; magenta, CH_4 at 196 K, green, CO_2 at 273 K; cyan, CH_4 at 273 K.

Compared with the similar structure of $Zn_2(TBDC)_2(bpy)$, the Langmuir surface area (BET) of complex **5** is 626.86 (465.02) m^2 g^{-1}, which is much lower than that of $Zn_2(TBDC)_2(bpy)$ (1740 (1120) m^2 g^{-1}. The N_2 and H_2 sorption seems that complex **5** could adsorb less amount of gas. However, **5** possesses higher solvent occupation of crystal volume than that of $Zn_2(TBDC)_2(bpy)$ (61.1% *vs.* 48%). The lower gas adsorption amounts of complex **5** may derive from zinc ions with the favour of gas molecules than cobalt atom, or the partly collapse of the framework when the sample was activated.

Thermal stabilities for 1–5

Thermogravimetric analysis has measured for complexes **1–5**. A TGA study on an as–isolated crystalline sample of **1** shows a 4.7% weight loss from 50 to 210 °C, corresponding to the loss of one uncoordinated and one coordinated water molecule (calcd 6.8%). The second gradually weight loss of 8.1% from 210 to 330 °C corresponds to the framework partly collapse, and after 330 °C, **1** starts to fully decompose. For complex **2**, the weight loss of 13.5% from 50 to 120 °C corresponds to the loss of four water molecules including two coordinated water molecules (calcd 14.2%). There is no further weight loss from 120 to 370 °C, and after that temperature, **2** starts to decompose. For complex **3** and **4**, both are very stable. After 405 °C for **3** and 270 °C for **4**, the decompositions happen. For complex **5**, from 50 to 205 °C, there is a weight loss of 34.9%, which corresponds to the loss of two water molecules and five uncoordinated DMF molecules (calcd 35.9%). After 370 °C, **5** starts to decompose.
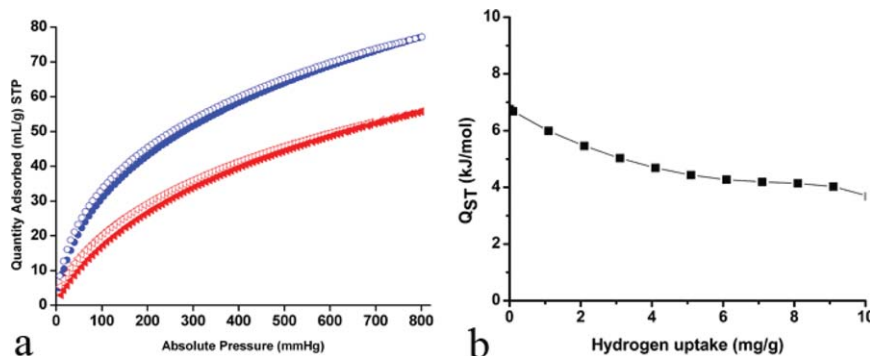
Effect of auxiliary ligands on the structures of complexes 1–5

(i) Ligand effect. Both 2,2′-bpy and 4,4′-bpy ligands are rigid diamine ligands, while they show distinct coordination modes due to the different position of nitrogen atom. The former one exhibits excellent chelation ability, which might occupy the limit coordination positions to block the structure of final product to further extend. Thus, when 2,2′-bpy acts as a coordination ligands, the structure inclines to form chains or layers only if the central metal possesses high coordination ability such as rare metal elements. On the other hand, 4,4′-bpy displays strong connective ability as a linker, which could joint each two chains or ladders to form two dimension layer or connect each two layers to give rise to high dimension framework as pillar.[14a,d,17] Besides the effect of metal ion in complexes **1–5**, we believe the formation of 1D chain (**1**), 2D grid (**2**) and 3D frameworks (**3–5**) is mainly derived from the effect of auxiliary ligands (chelating 2,2′-bpy and bridging 4,4′-bpy).

(ii) Solvent effect. It is well known that the solvent has a significant effect on the formation of the MOFs with different structures.[18] The same ratio of starting materials in different solvents may induce various complexes with different structural topologies. The ability as O-donor of reagents exhibit great differences. As mentioned above, complexes **2** and **5** have quite different structures: complex **2** is a 2D grid based on single cobalt node with (4,4) net or 3D supramolecular structure with *pcu* net based on hydrogen bonding interaction, while complex **5** is a 3D porous framework with *pcu* net based on binuclear cobalt ions.

Fig. 12 (a) The H_2 sorption isotherm of complex **5**: blue, at 77 K; red, at 87 K; (b) Heat of H_2 adsorption.

The structural difference between complexes **2** and **5** mainly results from the different solvents used in the synthesis. Complex **5** was synthesized by use of DMF and EtOH (v/v = 2 : 1) as the solvents, while complex **2** was obtained just with water in the reaction system. Therefore, the synthesis of complex **2** indicates the water solvent plays an important role in the formation of the final structure: coordinating to central cobalt ion to prevent its further extension and acting hydrogen bonding donor and acceptor to form supramolecular architecture. Although, the hydrogen bonding interaction in **2** contributes a lot to build the final *pcu* net, the single cobalt node and metallamacrocycle/TBDC/4,4′-bpy as linker indicate obviously distinct *pcu* net with complex **5**.

Conclusion

We have successfully synthesized and fully characterized five coordination polymers with four different topological structures: 1D zigzag chain **1**, 2D grid with (4,4)-net or two-fold inter-penetrating *pcu* net **2**, 3D interpenetrating frameworks with diamond topology **3** and **4**, 3D porous framework with *pcu* network **5**, based on 2,3,5,6-tetramethyl-1,4-benzenedicarboxy-late acid and bipyridine ligands. In particular, the porous framework of **5** shows moderate adsorption for CO_2, N_2, CH_4 and H_2, although it is much lower than its isostructural complex, $Zn_2(TBDC)_2(bpy)$. The metal–bicarboxylate–diamine system in our work produces omnifarious architectures due to its change-able coordination modes and auxiliary ligands with diversified functions, which further indicate that the ligand geometry and solvent have highly effect on the structure of the product and should always be considered in design and synthesis of MOF with desired topology.

Experimental

Materials and physical measurements

Unless otherwise noted, all reagents were obtained from commercial suppliers for analytical grade and used without further purification. Elemental analyses (C, H, N) were obtained on a PerkinElmer 240 elemental analyzer. Thermogravimetric experiments were performed using a TGA/SDTA851 instrument (heating rate of 10 °C min^{-1}, nitrogen stream).

Preparation

Synthesis of Cd(2,2′-bpy)(TBDC)(H$_2$O)·H$_2$O (1). A mixture of $Cd(NO_3)_2$·4H$_2$O (20 mg, 0.06 mmol), H$_2$TBDC (10 mg, 0.05 mmol) and 2,2′-bpy (10 mg, 0.06 mmol) was suspended in 15 mL mixed solvents of H$_2$O and EtOH (v/v = 1 : 1), and heated in a Teflon-lined steel bomb at 140 °C for 3 d. The colourless prism-like crystals (16 mg) formed were collected, washed with water and dried in the air. Yield: 61% (based on H$_2$TBDC). Calcd for $C_{22}N_2H_{24}O_6Cd$: C 50.36, N 5.34, H 4.61%. Found: C 50.93, N 5.21, H 4.50%.

Synthesis of Co(H$_2$O)$_2$(4,4′-bpy)(TBDC)·2H$_2$O (2). A mixture of $Co(NO_3)_2$·6H$_2$O (30 mg, 0.10 mmol), H$_2$TBDC (20 mg, 0.09 mmol) and 4,4′-bpy (10 mg, 0.06 mmol) was suspended in 15 mL water and heated in a Teflon-lined steel bomb at 140 °C for 3 d.

The purple block crystals (14 mg) were collected, washed with water and dried in the air. Yield: 46% (based on 4,4′-bpy). Calcd for $C_{22}H_{28}N_2O_8Co$: C 52.08, N 5.52, H 5.56%. Found: C 53.23, N 5.31, H 5.04%.

Synthesis of Ni(4,4′-bpy)(TBDC) (3). A mixture of $Ni(NO_3)_2$·6H$_2$O (20 mg, 0.07 mmol), 4,4′-bpy (10 mg, 0.06 mmol) and H$_2$TBDC (10 mg, 0.05 mmol) was suspended in 15 mL mixed solvent of H$_2$O and EtOH (v/v = 1 : 1), and heated in a Teflon-lined steel bomb at 140 °C for 3 d. The green block crystals (16 mg) formed were collected, washed with water and dried in the air. Yield: 74% (based on H$_2$TBDC). Calcd for $C_{22}H_{20}N_2NiO_4$: C 60.73, N 6.44, H 4.63%; Found: C 59.65, N 6.14, H 4.60%.

Synthesis of Cu(4,4′-bpy)(TBDC) (4). A mixture of $Cu(NO_3)_2$·3H$_2$O (20 mg, 0.08 mmol), 4,4′-bpy (10 mg, 0.06 mmol) and H$_2$TBDC (10 mg, 0.05 mmol) was suspended in the solution of H$_2$O (15 mL), and heated in a Teflon-lined steel bomb at 140 °C for 3 d. The green block crystals (14 mg) formed were collected, washed with water and dried in the air. Yield: 64% (based on H$_2$TBDC). Calcd for $C_{22}H_{20}CuN_2O_4$: C 60.06, N 6.37, H 4.58%. Found: C 59.92, N 6.08, H 4.46%.

Synthesis of Co$_2$(4,4′-bpy)(TMBDC)$_2$·2H$_2$O·5DMF (5). A mixture of $Co(NO_3)_2$·6H$_2$O (30 mg, 0.10 mmol), H$_2$TBDC (20 mg, 0.09 mmol) and 4,4′-bpy (10 mg, 0.06 mmol) was suspended in 15 mL mixed solvents of DMF and EtOH (v/v = 2 : 1) and heated in a Teflon-lined steel bomb at 100 °C for 3 d. The black-purple block crystals (12 mg) were collected, washed with EtOH and dried in the air. Yield: 64% (based on H$_2$TBDC). Calcd for $C_{21}H_{24}CoNO_5$: C 52.74, N 8.79, H 6.41%. Found: C 52.64, N 9.04, H 6.56%.

Crystal structure determinations

Crystallographic data for **1**–**5** were collected on a Bruker Smart APEXII CCD diffractometer with Mo-Kα (λ = 0.71073 Å) at room temperature. All structures were solved by the direct method using the SHELXS program of the SHELXTL package and refined by the full–matrix least–squares method with SHELXL.[19] The metal atoms in each complex were located from the *E*-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with aniso-tropic thermal parameters on F^2. The organic hydrogen atoms were generated geometrically (C–H 0.96 Å).

Crystal data for 1. $C_{22}H_{24}CdN_2O_6$, monoclinic, space group $P2_1/n$, a = 7.7773(6), b = 17.6806(13), c = 16.5160(13) Å, β = 97.3930(10)°, U = 2252.2(3) Å^3, T = 273 K, Z = 4, D_c = 1.548 g cm^{-3}, λ = 0.71073 Å, refinement of 5007 reflection (292 parameters) with $I > 2\sigma(I)$ converged at final R_1 = 0.0772, wR_2 = 0.1018, GOF = 0.979. Crystal data for **2**: $C_{22}H_{28}CoN_2O_8$, monoclinic, space group $C2/m$, a = 11.578(4), b = 11.488(4), c = 9.342(3) Å, β = 113.459(6)°, U = 1139.9(7) Å^3, T = 173(2) K, Z = 2, D_c = 1.478 g cm^{-3}, λ = 0.71073 Å, refinement of 1331 reflection (100 parameters) with $I > 2\sigma(I)$ converged at final R_1 = 0.0375, wR_2 = 0.0750, GOF = 1.051. Crystal data for **3**: $C_{22}H_{20}NiN_2O_4$, monoclinic, space group $C2/c$, a = 14.1443(10), b = 10.5695(7),

$c = 13.5488(9)$ Å, $\beta = 109.791(10)°$, $U = 1905.9(2)$ Å^3, $T = 173(2)$ K, $Z = 4$, $D_c = 1.516$ g cm^{-3}, $\lambda = 0.71073$ Å, refinement of 2148 reflection (134 parameters) with $I > 2\sigma(I)$ converged at final $R_1 = 0.0356$, w$R_2 = 0.0798$, GOF = 1.061. Crystal data for **4**: C$_{22}$H$_{20}$CuN$_2$O$_4$, monoclinic, space group $C2/c$, $a = 14.2254(8)$, $b = 10.6516(6)$, $c = 13.6134(8)$ Å, $\beta = 110.370(10)°$, $U = 1933.75(19)$ Å^3, $T = 293$ K, $Z = 4$, $D_c = 1.511$ g cm^{-3}, $\lambda = 0.71073$ Å, refinement of 1988 reflection (132 parameters) with $I > 2\sigma(I)$ converged at final $R_1 = 0.0314$, w$R_2 = 0.0834$, GOF = 1.066. Crystal data for **5**: C$_{42}$H$_{24}$Co$_2$N$_2$O$_{10}$, tetragonal, space group $I4/mcm$, $a = 15.4168(7)$, $b = 15.4168(7)$, $c = 27.623(2)$ Å, $\alpha = \beta = \gamma = 90°$, $U = 6565.4(6)$ Å^3, $T = 293$ K, $Z = 4$, $D_c = 0.844$ g cm^{-3}, $\lambda = 0.71073$ Å, refinement of 2042 reflection (71 parameters) with $I > 2\sigma(I)$ converged at final $R_1 = 0.0866$, w$R_2 = 0.2135$, GOF = 1.030.

Acknowledgements

References

1 (a) R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keffe and O. M. Yaghi, *Science*, 2008, **319**, 939; (b) L. Carlucci, G. Ciani, D. M. Proserpio and A. Soroni, *J. Am. Chem. Soc.*, 1995, **117**, 4562; (c) O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1996, **118**, 295; (d) M. Dinca and J. R. Long, *J. Am. Chem. Soc.*, 2005, **127**, 9376; (e) G. Sundarababu, M. Leibovitch, D. R. Corbin, J. R. Scheffer and V. Ramamurthy, *Chem. Commun.*, 1996, 2159; (f) B. Kesanli and W. Lin, *Coord. Chem. Rev.*, 2003, **246**, 305; (g) P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638; (h) R. Q. Zou, H. Sakurai and Q. Xu, *Angew. Chem., Int. Ed.*, 2006, **45**, 2542; (i) S. R. Batten, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1991, 445; (j) B. Moulton and M. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (k) S. Kitagawa and M. Kondo, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1739.

2 (a) S. Kitagawa, R. Kitaura and S. I. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (b) R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 3875; (c) Y.-Z. Tang, X.-F. Huang, Y.-M. Song, P. W. H. Chan and R. G. Xiong, *Inorg. Chem.*, 2006, **45**, 4868; (d) T. Y. Shvareva, S. Skanthakumar, L. Soderholm, A. Clearfield and T. E. Albrecht-Schmitt, *Chem. Mater.*, 2007, **19**, 132; (e) C. Janiak, *Dalton Trans.*, 2003, 2781; (f) A. Y. Robin and K. M. Fromm, *Coord. Chem. Rev.*, 2006, **250**, 2127; (g) M. Dinca and J. R. Long, *Angew. Chem., Int. Ed.*, 2008, **47**, 6766.

3 (a) C. N. R. Rao, S. Natarajan and R. Vaidhyanathan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1466; (b) C. R. Perez, M. H. Molina, P. L. Luis, F. Lloret, J. Cano and M. Julve, *Inorg. Chem.*, 2000, **39**, 3845; (c) B. Wang, A. P. Cote, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Nature*, 2008, **453**, 207; (d) D. N. Dybtsev, A. L. Nuzhdin, H. Chun, K. P. Bryliakov, E. P. Talsi, V. P. Fedin and K. Kim, *Angew. Chem., Int. Ed.*, 2006, **45**, 916; (e) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; (f) B. L. Chen, M. Eddoudi, S. T. Hyde, M. O'Keeffe and O. M. Yaghi, *Science*, 2001, **34**, 319.

4 (a) D.-L. Long, A. J. Blake, N. R. Chempness, C. Wilson and M. Schroder, *Chem.–Eur. J.*, 2002, **8**, 2026; (b) L. R. MacGillivray, J. L. Reid and J. A. Ripmeester, *Chem. Commun.*, 2001, 1034; (c) X.-M. Zhang, *Coord. Chem. Rev.*, 2005, **249**, 1201.

5 (a) P. S. Mukherjee, N. Das, Y. K. Kryschenko, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2004, **126**, 2464; (b) O. R. Evan and W. B. Lin, *Acc. Chem. Res.*, 2002, **35**, 511; (c) K. Barthelet, J. Marrot, G. Ferey and D. Riou, *Chem. Commun.*, 2004, 520.

6 (a) C. Daiguebonne, N. Kerbellec, K. Bernot, Y. Gerault, A. Deluzet and O. Guillou, *Inorg. Chem.*, 2006, **45**, 5399; (b) C.-G. Wang,

Y.-H. Xing, Z.-P. Li, J. Li, X.-Q. Zeng, M.-F. Ge and S.-Y. Niu, *J. Mol. Struct.*, 2009, **921**, 126; (c) R. G. Lawrence, T. A. Hamor, C. J. Jones, K. Paxton and N. M. Rowley, *J. Chem. Soc., Dalton Trans.*, 2001, 2121.

7 (a) S. V. Kolotuchin, P. A. Thiessen, E. E. Fenlon, S. R. Wilson, C. J. Loweth and S. C. Zimmerman, *Chem.–Eur. J.*, 1999, **5**, 2537; (b) M. Braun, C. Steffek, J. Kim, P. Rasmussen and O. M. Yaghi, *Chem. Commun.*, 2001, 2532; (c) H. He, F. Dai and D. Sun, *Dalton Trans.*, 2009, 763; (d) H. He, F. Dai, A. Xie, X. Tong and D. Sun, *CrystEngComm*, 2008, **10**, 1429.

8 (a) M. E. Chapman, P. Ayyappan, B. M. Foxman, G. T. Yee and W. B. Lin, *Cryst. Growth Des.*, 2001, **1**, 159; (b) A. J. Blake, N. R. Brooks, N. R. Champness, P. A. Cooke, A. M. Deveson, D. Fenske, P. Hubberstey, W. S. Li and M. Schroder, *J. Chem. Soc., Dalton Trans.*, 1999, 2103; (c) G. Liu, K. Zhu, H. Xu, S. Nishihara, R. Huang and X. Ren, *CrystEngComm*, 2009, **11**, 2784; (d) A. de Sousa, S. Reisinger, M. Fernandes, C. Perry, P. R. Varadwaj and H. Marques, *Dalton Trans.*, 2009, 10208; (e) M. Janjua, W. Guan, C. Liu, S. Muhammand, L. Yan and Z. Su, *Eur. J. Inorg. Chem.*, 2009, 5181; (f) X. Wang, C. Qin and E. Wang, *Chem.–Eur. J.*, 2006, **12**, 2680; (g) H. Jin, Y. F. Qi, E. B. Wang, Y. G. Li, X. L. Wang, C. Qin and S. Chang, *Inorg. Chem.*, 2007, **46**, 9213; (h) L. Liu, Z.-G. Sun, N. Zhang, Y.-Y. Zhu, Y. Zhao, X. Lu, F. Tong, W.-N. Wang and C.-Y. Huang, *Cryst. Growth Des.*, 2010, **10**, 406.

9 (a) B.-H. Ye, B.-B. Ding, Y.-Q. Weng and X.-M. Chen, *Cryst. Growth Des.*, 2005, **5**, 801; (b) Y.-Q. Lan, S.-L. Li, J.-S. Qin, D.-Y. Du, X.-L. Wang, Z.-M. Su and Q. Fu, *Inorg. Chem.*, 2008, **47**, 10600; (c) X. Shi, G.-S. Zhu, Q.-R. Fang, G. Wu, G. Tian, R.-W. Wang, D.-L. Zhang, M. Xue and S.-L. Qiu, *Eur. J. Inorg. Chem.*, 2004, 185.

10 (a) P. S. Mukherjee, N. Das, Y. K. Kryschenko, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2004, **126**, 2464; (b) S. Kuang, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 2002, **41**, 405; (c) Y.-C. Liao, Y.-C. Jiang and S.-L. Wang, *J. Am. Chem. Soc.*, 2005, **127**, 12794; (d) G. Guilera and J. W. Steed, *Chem. Commun.*, 1999, 1563.

11 (a) E. Yang, J. Zhang, Z.-J. Li, S. Gao, Y. Kang, Y.-B. Chen, Y.-H. Wen and Y.-G. Yao, *Inorg. Chem.*, 2004, **43**, 6525; (b) D. K. Kumar, D. A. Jose, A. Das and P. Dastidar, *Inorg. Chem.*, 2005, **44**, 6933; (c) Y.-M. Xie, J.-H. Liu, X.-Y. Wu, Z.-G. Zhao, Q.-S. Zhang, F. Wang, S.-C. Chen and C.-Z. Lu, *Cryst. Growth Des.*, 2008, **8**, 3914.

12 (a) D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375; (b) T. Steiner, *Angew. Chem., Int. Ed.*, 2002, **41**, 48; (c) M. Nishio, *CrystEngComm*, 2004, **6**, 130; (d) B.-H. Ye, M.-L. Tong and X.-M. Chen, *Coord. Chem. Rev.*, 2005, **249**, 545.

13 (a) Z. M. Wang, B. Zhang, M. Kurmoo, M. A. Green, H. Fujiwara, T. Otsuka and H. Kobayashi, *Inorg. Chem.*, 2005, **44**, 1230; (b) D. Sun, S. Ma, Y. Ke, T. Petersen and H.-C. Zhou, *Chem. Commun.*, 2005, 2663; (c) M. O'Keeffe, M. Eddaoudi, H. L. Li, T. Reineke and O. M.Yaghi, *J. Solid State Chem.*, 2000, **152**, 3; (d) H. S. Lin and P. A. Maggard, *Inorg. Chem.*, 2009, **48**, 8940.

14 (a) H. Chun, D. N. Dybtsev, H. Kim and K. Kim, *Chem.–Eur. J.*, 2005, **11**, 3521; (b) F. Luo, Y.-X. Che and J.-M. Zheng, *Microporous Mesoporous Mater.*, 2009, **117**, 486; (c) L. Yan, Q. Yue, Q. X. Jia, G. Lemercier and E.-Q. Gao, *Cryst. Growth Des.*, 2009, **9**, 2984; (d) R. Kitaura, F. Iwahori, R. Matsuda, S. Kitagawa, Y. Kubota, M. Takata and T. Kbayashi, *Inorg. Chem.*, 2004, **43**, 6522.

15 (a) M. Dinca, A. Dailly, Y. Liu, C. W. Brown, D. A. Neumann and J. R. Long, *J. Am. Chem. Soc.*, 2006, **128**, 16876; (b) H. Frost, T. Duren and R. Q. Snurr, *J. Phys. Chem. B*, 2006, **110**, 9565; (c) Z. Yang, Y. Xia and R. Mokaya, *J. Am. Chem. Soc.*, 2007, **129**, 1673; (d) S. Mohapatra, K. P. S. S. Hembram, U. Waghmare and T. K. Maji, *Chem. Mater.*, 2009, **21**, 5406; (e) Y. Xia, G. Walker, D. Grant and R. Mokaya, *J. Am. Chem. Soc.*, 2009, **131**, 16493.

16 (a) X. Lin, J. Jia, X. Zhao, K. M. Thomas, A. Blake, G. Walker, N. R. Champness, P. Hubberstey and M. Schroder, *Angew. Chem., Int. Ed.*, 2006, **45**, 7358; (b) D. Sun, D. Collins, Y. Ke, J. Zuo and H.-C. Zhou, *Chem.–Eur. J.*, 2006, **12**, 3768; (c) D. Sun, S. Ma, Y. Ke, D. Collins and H.-C. Zhou, *J. Am. Chem. Soc.*, 2006, **128**, 3896; (d) J. L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 1304.

17 (a) J. Tao, X.-M. Zhang, M.-L. Tong and X.-M. Chen, *J. Chem. Soc., Dalton Trans.*, 2001, 770; (b) J. Sun, Y. Zhou, Q. Fang, Z. Chen, L. Weng, G. Zhu, S. Qiu and D. Zhao, *Inorg. Chem.*, 2006, **45**, 8677.

18 (a) L. Delhaye, A. Ceccato, P. Jacobs, C. Kottgen and A. Merschaert, *Org. Process Res. Dev.*, 2007, **11**, 160; (b) K. M. Kadish, L. L. Wang, A. Thuriere, L. Giribabu, R. Garcia, E. V. Caemelbecke and J. L. Bear, *Inorg. Chem.*, 2003, **42**, 8309; (c) H. He, D. Collins, F. Dai, X. Zhao, G. Zhang, H. Ma and D. Sun, *Cryst. Growth Des.*, 2010, **10**, 895; (d) S. Xu, C. Wang and Y. Cui, *J. Mol. Struct.*, 2009, **938**, 133.

19 (a) G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, Göttingen University, Germany, 1997; (b) G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, Göttingen University, Germany, 1997.