RSC Advances

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Solvent-controlled Cd(II) metal–organic frameworks constructed from a tetrapodal silicon-based linker†

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Two solvent-modulated Cd(II) metal–organic frameworks (MOFs), [Cd₄(TCS)₂(DMF)₂(EtOH)(H₂O)₇·4DMF]ₙ (1) and [Cd₂(TCS)(DMF)₂·4H₂O]ₙ (2) (H₄TCS = tetrakis(3-carboxyphenyl)silicon, DMF = *N,N*-dimethylformamide), were constructed from a novel tetrapodal silicon-based linker. In 1 and 2, the TCS ligands exhibit different coordination modes and link mononuclear [Cd(COO)₄] and tetranuclear [Cd₄(COO)₈(DMF)₄] SBUs (secondary building units) to give 1 and 2 2D 4⁴-sql net and (4,8)-connected 3D framework with rare fluorite (flu) topology, respectively. Dissimilarities in the geometry of both SBUs are originated from the different solvent systems which result in the formation of different networks in each case. The photoluminescence behaviours of them were also discussed.

1. Introduction

The design and synthesis of metal–organic frameworks (MOFs) aiming at exploration of fascinating topology and potential applications have been a subject of intensive research.[1] MOFs are commonly constructed from diverse organic ligands which act as connecting units between metal-based nodes or clusters (often defined as secondary building units or SBUs)[2] to give a multi-dimensional structure. Contrary to the well-known behaviors of metal centers, organic ligands, such as 3-connected bte (4,4′,4″-[benzene-1,3,5-triyl-tris(ethyne-2,1-diyl)]tribenzoate),[3] 6-connected btei (5,5′,5″-[benzene-1,3,5-triyl-tris(ethyne-2,1-diyl)]triisophthalate),[4] even 8-connected bttcd (9,9′,9″,9‴-([1,1′-biphenyl]-3,3′,5,5′-tetrayl)tetrakis(9*H*-carbazole-3,6-dicarboxylate),[5] are a relatively underdeveloped field needing to be explored, which has stimulated recent investigations into the systematic design and synthesis of novel connecting ligands with specifically tailored geometries or pendant functional groups. Compared with the simple and commercial 1,3-benzene dicarboxylic acid, 1,3,5-benzenetricarboxylic acid, 1,2,3-benzenetricarboxylic acid, and

1,2,4,5-benzenetetracarboxylic acid,[6] tetrahedral silicon-based carboxylic acid has distinguishing features such as decreased conformational rigidity, increased bond angle flexibility, and longer bond lengths to silicon, when compared to its carbon counterpart.[7] In addition, the tetrahedral silicon center is more synthetically accessible than its carbon counterpart and is a promising candidate for novel connecting units. Recently, Davies and coworkers constructed an IMP (where IMP is short for Imperial College London) series of MOFs based on tetrakis(4-carboxyphenyl)silicon, among them, IMP-8Cd contains metal carboxylate infinite chains (often named rod SBUs), which are cross-linked into a 3D microporous MOF by tetrahedral tetrakis(4-carboxyphenyl)silicon.[8c] In spite of some examples, the tetrakis(4-carboxyphenyl)silicon linker shows its ability to construct 3D microporous networks,[8] to the best of our knowledge, the coordination chemistry of its isomer tetrakis(3-carboxyphenyl)silicon (H₄TCS)[9] has been almost unexplored to date. We have been interested in the synthesis of a novel silicon-based N-donor connecting unit (bis(4-(imidazol-1-yl)phenyl)dimethylsilane) using the Ullmann condensation reaction, which is further used to construct a 3D-braided porous silver(I) MOF by both braid and interpenetration of two series of 1D polymer chains.[10] Recently, as an extension of our work, a silicon-based O-donor connecting unit has attracted our intense attention.

Meanwhile, solvent is very significant in modulating the framework topology and the dimensionality of the structures.[11] To some extent the kinetic and/or thermodynamical conformers could be controlled by changing the solvent.[12] To the best of our knowledge, solvent molecules with different sizes, polarities, and coordination abilities present in the coordination spheres of the metal ions usually exert their impact on the formation of MOFs through (i) solvents control structures, without being entrapped by the host networks; (ii) intercalation of solvent guests in the host adjusts the supramolecular arrays.[13]

Sparked by the above points and our recent studies on silicon-based ligands as well as their usage for construction of MOFs, we developed the synthesis of the H₄TCS which greatly facilitates the access to two Cd(II) silicon-based tetracarboxylate MOFs [Cd₄(TCS)₄(DMF)₂(EtOH)(H₂O)₇·4DMF]ₙ (1) and [Cd₂(TCS)(DMF)₂·4H₂O]ₙ (2) (H₄TCS = tetrakis(3-carboxyphenyl)silicon, DMF = *N,N*-dimethylformamide), through changing the solvent system. They show 2D 4⁴-sql net and (4,8)-connected 3D framework with fluorite (flu) topology, respectively (Scheme 1).

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† Electronic Supplementary Information (ESI) available: IR, additional figures and X-ray crystallographic data. CCDC 836455 (**1**) and 836456 (**2**). See DOI:10.1039/c2ra20384g/
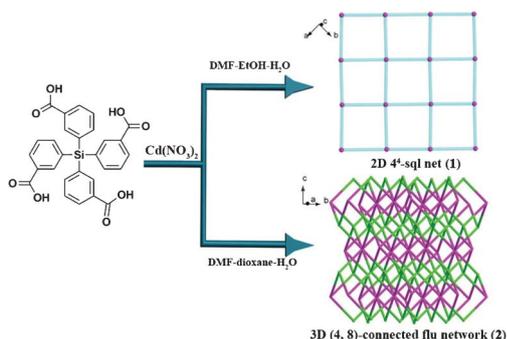
Scheme 1 Synthetic procedures of the title compounds **1** and **2**.

2. Experimental

2.1. Materials and methods

All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. IR spectra were measured on a Nicolet 330 FTIR Spectrometer at the range of 4000–400 cm^{-1}. Elemental analyses (C, H, N) were obtained on a Perkin-Elmer 240 elemental analyzer. NMR spectra were recorded on a Bruker AV-400 spectrometer. Photoluminescence spectra were performed on a Perkin Elmer LS 50B luminescence spectrometer. X-ray powder diffractions were measured on a Panalytical X-Pert pro diffractometer with Cu-Kα radiation. Thermal gravimetric analysis (TGA) was performed under N$_2$ on a Perkin Elmer TGA 7 instrument.

2.2. Syntheses

2.2.1. Synthesis of tetrakis(3-carboxyphenyl)silicon (H$_4$TCS).
A solution of n-BuLi (20 mL, 50 mmol, 2.5 M in hexane) in 100 mL Et$_2$O was added to a solution of 1,3-dibromobenzene (**I**, 11.8 g, 50 mmol) in 100 mL Et$_2$O at -78 °C and stirred for 3 h under N$_2$. Silicon tetrachloride (2.47 g, 12.5 mmol) was then added dropwise and the reaction mixture heated at reflux for 2 h. After being quenched with 50 mL H$_2$O, the organic layer was separated, washed with brine, and dried over anhydrous MgSO$_4$. Removal of the solvents under a vacuum yielded a yellow oil, to which was recrystallized from hot CHCl$_3$: EtOH (v/v = 1 : 3) to obtain white solids Si(3-C$_6$H$_4$Br)$_4$ (**II** 5.13 g). ^{1}H NMR (CDCl$_3$) δ (ppm): 7.7 (dd, 4H) 7.9 (t, 4H), 8.2 (dd, 4H), 8.3 (s, 4H).

A solution of Si(3-C$_6$H$_4$Br)$_4$ (5.13 g, 7.9 mmol) in 20 mL of THF was added dropwise to a solution of n-BuLi (2.5 M, 14 mL, 35 mmol) in 100 mL of THF at -78 °C and was stirred at this temperature for a further 2 h under N$_2$. CO$_2$ was then bubbled through the cooled solution for 2 h, before warming to room temperature and stirring for an additional 18 h. The reaction was quenched by the addition of 50 mL 1 M HCl. The organic layer was separated and washed with brine and dried over anhydrous MgSO$_4$. Removal of the solvents under a vacuum gave the crude product, which was recrystallized from hot EtOAc (30 mL) to obtain pure Si(3-C$_6$H$_4$CO$_2$H)$_4$ (**III**, 3.5 g). ^{1}H NMR (CDCl$_3$) δ (ppm): 7.7 (dd, 4H) 7.9 (t, 4H), 8.2 (dd, 4H), 8.3 (s, 4H), 11.3 (s, 4H).

2.2.2. [Cd$_4$(TCS)$_2$(DMF)$_2$(EtOH)(H$_2$O)$_7$·4DMF]$_n$ (1).
Cd(NO$_3$)$_2$·4H$_2$O (554.4 mg, 1.8 mmol) and H$_4$TCS (36.8 mg, 0.072 mmol) were dissolved in DMF–EtOH–H$_2$O (40 mL v/v/v

1 : 1 : 1). We divided this solution equally into 40 parts. So 1 mL of solution was sealed in a glass tube, and heated to 75 °C in 5 h, kept 75 °C for 48 h then slowly cooled to 30 °C in 10 h. The colourless crystals were collected, washed with EtOH and dried in the air (yield: 80%). Elemental analysis calcd (%) for **1** (C$_{76}$H$_{94}$Cd$_4$N$_6$O$_{30}$Si$_2$): C 43.94, H 4.56, N 4.05; found: C 42.47, H 4.44, N 3.27. Selected IR peaks (cm^{-1}): 3565 (s), 1663 (s), 1598 (s), 1550 (s), 1414 (s), 1377 (s), 1257 (w),1164 (w), 1104 (m), 883 (m), 763 (m), 662 (w).

2.2.3. [Cd$_2$(TCS)(DMF)$_2$·4H$_2$O] (2).
The procedure was similar to the preparation of **1**, except that the DMF–EtOH–H$_2$O (1 mL v/v 1 : 1 : 1) was replaced by DMF–dioxane–H$_2$O (1 mL v/v/v 5 : 2 : 1) as the solvent (yield: 45%). Elemental analysis calcd (%) for **2** (C$_{34}$H$_{38}$Cd$_2$N$_2$O$_{14}$Si): C 42.91, H 4.03, N 2.94; found: C 42.58, H 4.02, N 3.55%. Selected IR peaks (cm^{-1}): 3466 (w), 3078 (m), 2938 (m), 1661 (s), 1595 (s), 1551 (s), 1416 (s), 1384 (s), 1256 (w),1161 (w), 1107 (m), 884 (m), 761 (m), 666 (w), 527 (w).

2.3. X-ray crystallography

Single crystals of the complexes **1–2** with appropriate dimensions were chosen under an optical microscope and mounted on a glass fiber for data collection. X-ray crystallography: single-crystal X-ray diffraction was performed using a Bruker Apex II CCD diffract-ometer equipped with a fine-focus sealed-tube X-ray source (Mo-Kα radiation, graphite monochromated). In both cases, the highest possible space group was chosen. Both structures were solved by direct methods using SHELXS-97[14] and refined on F^2 by full-matrix least-squares procedures with SHELXL-97.[15] Atoms were located from iterative examination of difference F-maps following least squares refinements of the earlier models. All the non-hydrogen atoms were treated anisotropically, with the exception of atoms N1, C9, C10 belonging to a DMF molecule in complex **2**, which were refined with isotropic thermal parameters. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2–1.5 times U_{eq} of the attached C atoms. Both structures were examined using the Addsym subroutine of PLATON[16] to assure that no additional symmetry could be applied to the models. There are large solvent accessible void volumes in the both crystals of **1** and **2** which are occupied by highly disordered DMF for **1** and H$_2$O molecules for **2**. No satisfactory disorder model could be achieved, and therefore the SQUEEZE program implemented in PLATON was used to remove these electron densities. A refinement using reflections modified by the SQUEEZE procedure behaved well. Pertinent crystallographic data collection and refinement parameters are collated in Table 1. Selected bond lengths and angles for **1** and **2** are collated in Table 2.

3. Result and discussion

3.1. Synthesis and general characterization

The tetrakis(3-carboxyphenyl)silicon was prepared from its tetra-bromo derivative according to literature procedures[17] (Scheme 2). Powder X-ray diffraction (Fig. S1, see ESI†) has been used to check the phase purity of the bulk samples in the solid state. For complexes **1** and **2**, the portions of the samples that are crystalline appears to be the same as the single crystalline diffraction experiments, which may be due to the quick loss of lattice solvents at room temperature. In the IR spectra of **1** and **2**, the characteristic vibrations of

Table 1 Crystal data for **1** and **2**[a]

Complex	1	2
Crystal system	tetragonal	tetragonal
Space group	$P4_1$	$I4/m$
a/Å	15.6484(1)	12.9879(15)
c/Å	36.3862(5)	25.025(6)
V/Å^3	8909.98(15)	4221.4(12)
T/K	173(2)	173(2)
Z, D_c/Mg m^{-3}	4, 1.320	4, 1.384
$F(000)$	3512	1752
μ/mm^{-1}	1.032	1.084
Ref. collected/unique	32774/12795	10549/1922
R_{int}	0.0377	0.0300
Parameters	883	116
Flack parameter	0.02(2)	N/A
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0435$	$R_1 = 0.0413$
	$wR_2 = 0.1042$	$wR_2 = 0.1190$
R indices (all data)	$R_1 = 0.0523$	$R_1 = 0.0460$
	$wR_2 = 0.1082$	$wR_2 = 0.1221$
GOF	0.987	1.103
Max./min., $\Delta\rho$/e Å^{-3}	0.928/−0.589	1.025/−0.494

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$

$\nu_{asym}(COO^-)$ are at ~1550 cm^{-1}, whereas the $\nu_{sym}(COO^-)$ absorption is at ~1415 cm^{-1} (Fig. S2, see ESI†). The separations (Δ) between $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ indicate the presence of chelating coordination modes in both **1** and **2**.[18] The absence of the characteristic bands at around 1700 cm^{-1} in both **1** and **2** attributed to the protonated carboxyl group indicates that the complete deprotonation of TCS ligand upon reaction with Cd ions, which is consistent with the result of the X-ray diffraction analysis.

3.2. Structure descriptions.
$[Cd_4(TCS)_2(DMF)_2(EtOH)(H_2O)_7\cdot4DMF]_n$ (1)

X-ray structure analysis of crystalline **1** reveals that it crystallizes in chiral space group $P4_1$ with Flack parameter[19] of 0.02(2), showing a 2D (4,4) net. Although the space group of complex **1** is chiral, the CD spectrum of the bulk sample collected from one glass tube is silent which reveals that **1** crystallizes as a racemic conglomerate, which is a mechanical mixture of enantiomerically pure crystals of one enantiomeric form and its opposite. So the solid sample of complex **1** is achiral. There are four crystallographically independent Cd(II) ions, four TCS ligands, two coordinated DMF molecules, one coordinated EtOH, seven coordinated water molecules and four lattice DMF molecules in an asymmetric unit. As shown in Fig. 1a, both Cd1 and Cd2 are located in an eight-coordinated [CdO$_8$] environment completed by eight O atoms from four different carboxyl groups, resulting in an unusual tetragonal antiprismatic geometry (only 11 similar examples indicated by a Cambridge Structure Database survey),[20] which may be due to the crowded environment around the Cd(II) ion. Different from Cd1 and Cd2, Cd3 is octahedrally coordinated by four water molecules, one DMF and one carboxyl group and Cd4 is also in the usual [CdO$_6$] octahedral coordination environment with three water molecules, one DMF, one EtOH and one carboxyl group. The distances between Cd and the coordination atoms are in the range 2.181(8)–2.600(5) Å, which are well-matched to those observed in similar complexes.[21]

In **1**, tetrahedral TCS adopts a μ_5-η^1:η^1:η^1:η^1:η^1:η^1:η^1:η^2 coordination mode to link Cd1 and Cd2 forming a 2D sheet which does not involve Cd3 and Cd4 due to their terminal coordinated

Table 2 Selected bond lengths (Å) and angles (°) for **1** and **2**

Complex 1[a]

Cd1–O11^i	2.312 (5)	Cd2–O15^i	2.570 (5)
Cd1–O8^i	2.337 (5)	Cd3–O4W	2.271 (6)
Cd1–O14^{ii}	2.340 (4)	Cd3–O22	2.278 (5)
Cd1–O3	2.365 (5)	Cd3–O3W	2.279 (5)
Cd1–O4	2.422 (6)	Cd3–O2W	2.280 (5)
Cd1–O13^{ii}	2.472 (5)	Cd3–O15	2.287 (5)
Cd1–O7^i	2.482 (5)	Cd3–O1W	2.301 (6)
Cd1–O12^i	2.600 (5)	Cd4–O5W	2.181 (8)
Cd2–O2^{iii}	2.315 (4)	Cd4–O18	2.271 (6)
Cd2–O16^i	2.328 (4)	Cd4–O6W	2.284 (7)
Cd2–O10	2.332 (5)	Cd4–O1	2.298 (5)
Cd2–O5	2.352 (5)	Cd4–O7W	2.306 (6)
Cd2–O6	2.419 (5)	Cd4–O17	2.312 (6)
Cd2–O9	2.462 (5)		
O11^i–Cd1–O8^i	107.57 (19)	O10–Cd2–O9	54.39 (19)
O11^i–Cd1–O14^{ii}	136.98 (19)	O5–Cd2–O9	91.61 (17)
O8^i–Cd1–O14^{ii}	98.60 (18)	O6–Cd2–O9	96.47 (18)
O11^i–Cd1–O3	89.6 (2)	O2^{iii}–Cd2–O15^i	88.48 (17)
O8^i–Cd1–O3	141.0 (2)	O16^i–Cd2–O15^i	53.04 (17)
O14^{ii}–Cd1–O3	90.94 (17)	O10–Cd2–O15^i	81.99 (18)
O11^i–Cd1–O4	129.43 (19)	O5–Cd2–O15^i	119.85 (16)
O8^i–Cd1–O4	88.83 (18)	O6–Cd2–O15^i	81.27 (17)
O14^{ii}–Cd1–O4	83.52 (18)	O9–Cd2–O15^i	136.35 (18)
O3–Cd1–O4	54.6 (2)	O4W–Cd3–O22	90.1 (2)
O11^i–Cd1–O13^{ii}	84.34 (17)	O4W–Cd3–O3W	83.3 (2)
O8^i–Cd1–O13^{ii}	135.00 (17)	O22–Cd3–O3W	92.8 (2)
O14^{ii}–Cd1–O13^{ii}	53.51 (18)	O4W–Cd3–O2W	89.9 (2)
O3–Cd1–O13^{ii}	80.11 (19)	O22–Cd3–O2W	179.4 (3)
O4–Cd1–O13^{ii}	117.28 (16)	O3W–Cd3–O2W	86.6 (2)
O11^i–Cd1–O7^i	80.0 (2)	O4W–Cd3–O15	174.9 (2)
O8^i–Cd1–O7i	53.68 (19)	O22–Cd3–O15	91.84 (19)
O14^{ii}–Cd1–O7^i	89.31 (19)	O3W–Cd3–O15	91.99 (19)
O3–Cd1–O7^i	164.9 (2)	O2W–Cd3–O15	88.0 (2)
O4–Cd1–O7^i	140.32 (19)	O4W–Cd3–O1W	86.9 (2)
O13^{ii}–Cd1–O7^i	87.97 (19)	O22–Cd3–O1W	91.9 (2)
O11^i–Cd1–O12^i	52.89 (19)	O3W–Cd3–O1W	169.1 (2)
O8^i–Cd1–O12^i	78.53 (18)	O2W–Cd3–O1W	88.7 (3)
O14^{ii}–Cd1–O12^i	169.6 (2)	O15–Cd3–O1W	97.6 (2)
O3–Cd1–O12^i	85.32 (18)	O5W–Cd4–O18	85.9 (5)
O4–Cd1–O12^i	86.37 (18)	O5W–Cd4–O6W	98.6 (5)
O13^{ii}–Cd1–O12^i	134.86 (18)	O18–Cd4–O6W	164.4 (3)
O7^i–Cd1–O12^i	96.84 (19)	O5W–Cd4–O1	84.1 (2)
O2^{iii}–Cd2–O16^i	89.24 (16)	O18–Cd4–O1	111.0 (3)
O2^{iii}–Cd2–O10	84.4 (2)	O6W–Cd4–O1	84.5 (2)
O16^i–Cd2–O10	134.76 (19)	O5W–Cd4–O7W	95.8 (3)
O2^{iii}–Cd2–O5	135.06 (18)	O18–Cd4–O7W	83.6 (3)
O16^i–Cd2–O5	83.26 (16)	O6W–Cd4–O7W	81.0 (3)
O10–Cd2–O5	130.24 (18)	O1–Cd4–O7W	165.4 (2)
O2^{iii}–Cd2–O6	169.18 (19)	O5W–Cd4–O17	166.8 (3)
O16^i–Cd2–O6	87.33 (17)	O18–Cd4–O17	89.1 (4)
O10–Cd2–O6	90.73 (18)	O6W–Cd4–O17	89.5 (4)
O5–Cd2–O6	54.60 (18)	O1–Cd4–O17	86.29 (18)
O2^{iii}–Cd2–O9	88.57 (17)	O7W–Cd4–O17	95.8 (2)
O16^i–Cd2–O9	170.26 (19)		

Complex 2[b]

Cd1–O3	2.278 (6)	Cd1–O2^{ii}	2.314 (3)
Cd1–O1	2.293 (3)	Cd1–O2	2.558 (4)
O1–Cd1–O2	53.68 (11)		
O3–Cd1–O1^i	91.50 (16)	O1^i–Cd1–O2	104.81 (12)
O1–Cd1–O1^i	96.67 (16)	O2^{ii}–Cd1–O2	124.36 (15)
O3–Cd1–O2^{ii}	87.42 (19)	O2^{iii}–Cd1–O2	81.50 (16)
O1–Cd1–O2^{ii}	170.49 (12)	O3–Cd1–O2	142.45 (10)
O1^i–Cd1–O2^{ii}	92.80 (12)	O1–Cd1–O2^i	104.81 (12)
O2^{ii}–Cd1–O2^{iii}	77.72 (18)	O2–Cd1–O2^i	69.16 (14)

[a] Symmetry codes: (i) x, $y + 1$, z; (ii) $x + 1$, $y + 1$, z; (iii) $x − 1$, y, z.
[b] Symmetry codes: (i) x, y, $-z + 1$; (ii) $y − 1$, $−x + 1$, $−z + 1$; (iii) $y − 1$, $−x + 1$, z; (iv) $−0.5 + y$, $1.5 − x$, $1.5 − z$; (v) $1.5 − y$, $0.5 + x$, $1.5 − z$; (vi) $1 − x$, $2 − y$, z
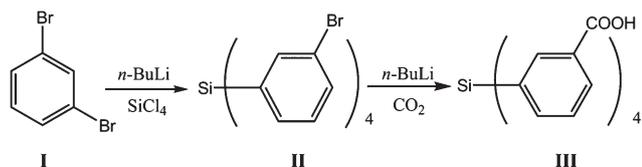
Scheme 2 Synthesis path of the new organosilicon linker tetrakis(3-carboxyphenyl)silicon.

water, DMF and EtOH molecules. Different from tetrakis(4-carboxyphenyl)silicon, H_4TCS can show diverse coordination conformations based on the different orientations of four carboxyl groups due to the free-rotation of Si–C σ-bond. In **1**, TCS can be described as a udud (upper-down-upper-down) conformation. To better understand the structure of **1**, the topological analysis approach is employed. If all nodes in one net have the identical connectivity, then according to Wells it is a platonic uniform net and can be represented by the symbol (n, p), where n is the size of the shortest circuit and p is the connectivity of the nodes.[22] In the sheet of **1**, all $[Cd(COO)_4]$ SBUs (Fig. S3, see ESI†) are 4-connecting and the shortest circuit is a four-membered ring. So this 2D sheet can be simplified to a 4^4-sql net (Fig. 1b) with the window size of 11.04 × 11.32 × 11.10 × 10.82 Å based on non-bonded Cd⋯Cd contacts. The adjacent sheets adopts ABCD stacking to give rise to a 3D chiral supramolecular architecture, which is reinforced by the inter-sheet hydrogen bonds. The TCS ligands in different sheets are connected
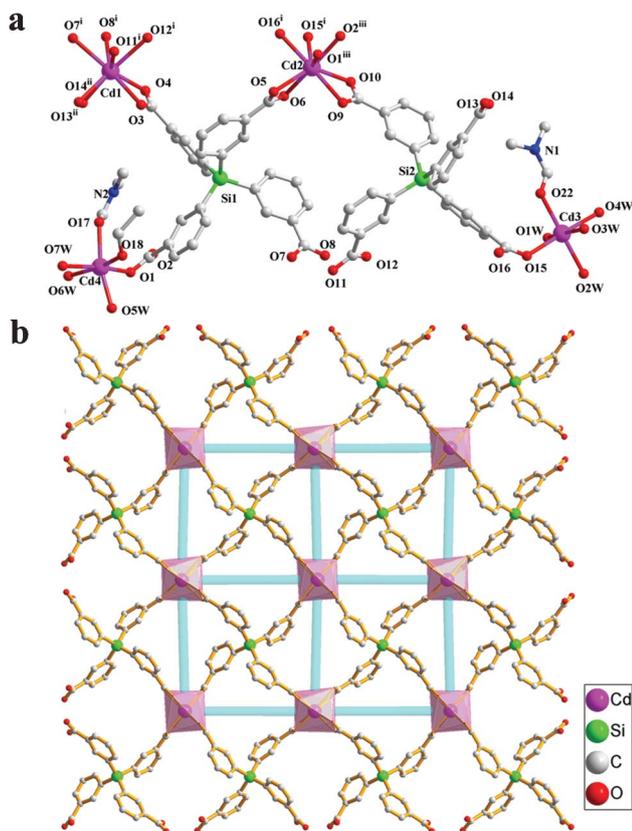
by the hydrogen bonds to form a 1D 4_1 helical chain (Fig. S4 see ESI†). Because of the rigidity of the 2D sheet and the directionality of hydrogen bonds, the same chirality of the helical chains is preserved. Thus, the whole structure is chiral.[23] PLATON calculation suggested that the resulting effective free volume, after removal of guest DMF molecules, was 30.3% of the crystal volume (2703.8 Å³ out of the 8910.0 Å³ unit cell volume).

3.3. Structure description of $[Cd_2(TCS)(DMF)_2 \cdot 4H_2O]$ (2)

Complex **2** was synthesized in a similar procedure as complex **1**, but here DMF–dioxane–H_2O (1 mL v/v 1 : 1 : 1) is used as solvent system instead of DMF–EtOH–H_2O (1 mL v/v 1 : 1 : 1). Complex **2** crystallizes in a tetragonal crystal system of the $I4/m$ space group. The asymmetric unit of **2** consists of half a Cd(II) ion, a quarter of a TCS ligand, half a coordinated DMF molecule and one lattice water molecule. Analysis of the local symmetry shows that the Cd(II) ion was bisected by a crystallographic mirror and the TCS locates on the crystallographic inversion center, and one four-fold axis also passes through the Si atom of TCS. As shown in Fig. 2, the coordination geometry of Cd1 is best described as a monocapped trigonal prism with two carboxyl oxygen atoms $O1^i$ and $O2^{iii}$ at the apical positions and the other five oxygen atoms composing the equatorial planes. Each Cd(II) ion is related to its neighbor by a crystallographic four-fold axis, giving a rare square-planar $[Cd_4(COO)_8(DMF)_4]$ unit (Fig. S5, see ESI†) through the bridging carboxyl groups, which behave as secondary building units (SBUs). The distance between adjacent Cd1 ions is 3.8548(7) Å. Although a number of tetranuclear SBUs have been reported, the geometry in these cases consistently approximates to a tetrahedron,[24] and far fewer examples containing planar tetranuclear SBUs have been documented.[25] Notably, a total of eight TCS ligands are, on average, divided into two groups by mirror plane symmetry, bridging the Cd(II) ions from above and below the Cd_4 plane. Each square-planar $[Cd_4(COO)_8(DMF)_4]$ SBU in **2** is extended by eight TCS ligands with a μ_8-$\eta^1:\eta^2:\eta^1:\eta^2:\eta^1:\eta^2:\eta^1:\eta^2$ coordination mode and pseudo-uddu conformation to form the resulting 3D framework.

To understand the framework topology, it is necessary to simplify the 3D MOF. The $[Cd_4(COO)_8(DMF)_4]$ SBUs can be regarded as 8-connected nodes (Fig. 3a) and TCS act as 4-connected tetrahedral linkers (Fig. 3b). Therefore, the whole 3D framework can thus be represented as a (4,8)-connected 2-nodal net with a fluorite (flu)
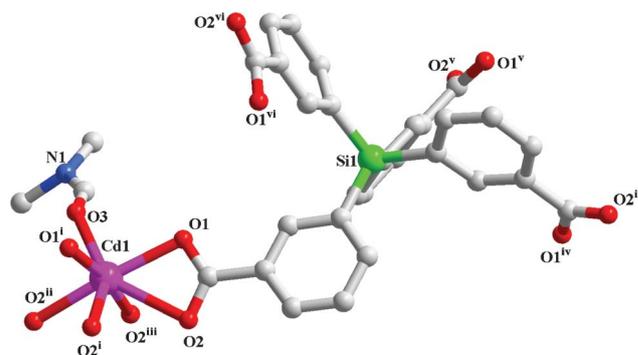

Fig. 1 (a) Perspective drawing of **1** showing the local coordination environment around Cd(II) centers. Hydrogen atoms have been omitted for clarity (symmetry codes: (i) $x, y + 1, z$; (ii) $x + 1, y + 1, z$; (iii) $x - 1, y, z$). (b) View of the 2D (4,4) net of **1** viewed along the ab plane.

Fig. 2 Perspective drawing of **2** showing the local coordination environment around the Cd(II) center. Hydrogen atoms have been omitted for clarity (symmetry codes: (i) $x, y, -z + 1$; (ii) $y - 1, -x + 1, -z + 1$; (iii) $y - 1, -x + 1, z$; (iv) $y - 0.5, -x + 1.5, -z + 1.5$; (v) $-y + 1.5, x + 0.5, -z + 1.5$; (vi) $-x + 1, -y + 2, z$).
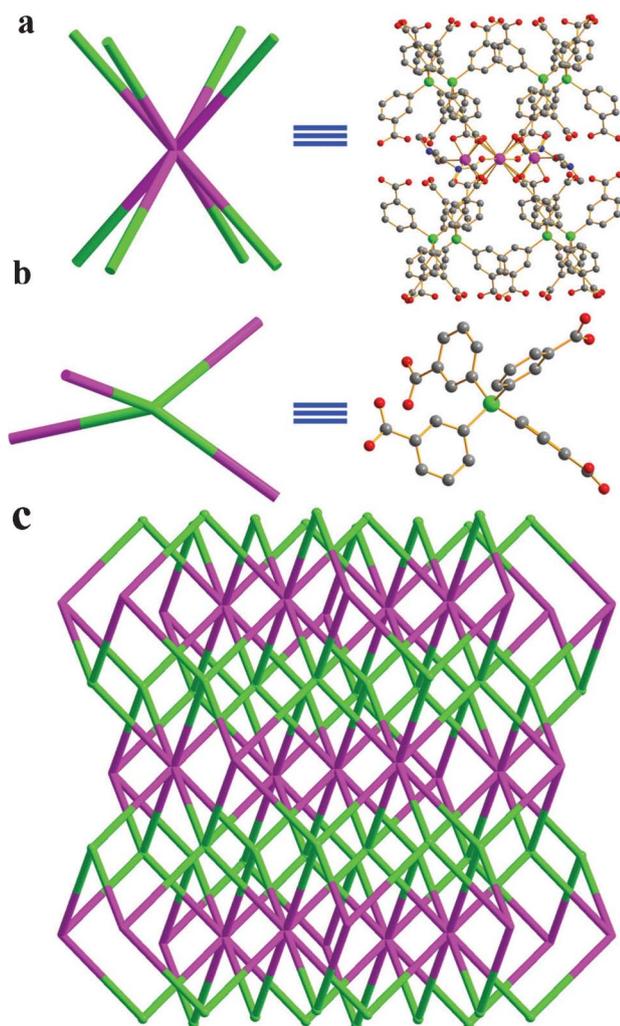
Fig. 3 (a) Ball-and-stick and schematic representations of 8-connected, and (b) 4-connected nodes, respectively. (c) A schematic diagram showing the (4, 8)-connected flu network.

topology (Fig. 3c). The Schläfli symbol for **2** is $\{4^{12} \cdot 6^{12} \cdot 8^4\}\{4^6\}_2$ indicated by TOPOS software.[26] To our knowledge, the exploration of MOFs with inorganic mineral topologies is a challenging topics in crystal engineering.[27] Although many uninodal and binodal 3D MOFs with mineral topologies including boracite (3,4-connected),[28] CdSO₄ (4-connected),[29] diamond (4-connected),[30] NbO (4-connected),[31] Pt₃O₄ (3,4-connected),[32] PtS (4,4-conneted),[33] quartz (4-connected),[34] rutile (3,6-connected),[35] sodalite (4-connected)[36] and SrSi₂/ThSi₂ (3-connected)[37] have been reported, binodal (4,8)-connected CaF₂-type frameworks based on polynuclear metal cluster nodes are very rare, owing to its 8-connected node.[38] In the simplified structure of **2**, the ratio of 8- and 4-connected nodes is 1 : 2. With the face centered cubic CaF₂ in mind, the tetranuclear $[Cd_4(COO)_8(DMF)_4]$ SBUs substitute Ca^{2+} ions as 8-connected nodes, and the tetrahedral TCS substitute F^- ions as 4-connected nodes.

3.4. Influence of solvents in structural assembly

Based on the above results, the role of solvent in determining the network structures of such Cd-tetracarboxylate MOFs has been

clearly exhibited. Two different MOFs **1** and **2** were synthesized on the basis of selection of reaction solvent systems, while the other synthetic parameters were intentionally held constant. Complexes **1** and **2** were obtained using DMF–EtOH–H₂O (1 mL v/v 1 : 1 : 1) and DMF–dioxane–H₂O (1 mL v/v 1 : 1 : 1) as reaction media, respectively. Due to the flexible nature of the ligand as well as the metal center, it is possible to modulate the reaction products by a slight variation of the synthetic conditions such as the solvent. It is immediately apparent that DMF molecules are incorporated into the both crystal lattices of complexes **1** and **2**. However, ethanol also coordinates to the Cd(II) centers in **1**, and dioxane is not observed in **2** which are essentially consistent with the coordination ability in the order of EtOH > dioxane. It is known that solvents acting as terminal ligands will normally destroy the connectivity and dimensionality of the resulting MOFs.[39] In complex **1**, both DMF and ethanol serve as terminal monodentate ligands, which hinder the formation of higher dimensionality network, giving the resulting 2D 4^4-sql sheet, whereas in complex **2**, only DMF as a terminal monodentate ligand facilitating the formation of a 3D network. As stated above, more terminal solvent molecules severely hold back the introduction of more bridging ligands in the flexible coordination sphere of the Cd(II) center and then reduce the dimensionality of the resultant MOFs. Due to the participation of the solvent molecules in the host of the MOFs, both the coordination environments of the Cd(II) center and the coordination modes of the TCS ligand (Scheme 3) are modulated *via* the choice of solvent system, as a consequence, distinctive structures are constructed.

3.5. Thermal analysis

The thermogravimetric (TG) analysis was performed in a N₂ atmosphere on polycrystalline samples of **1** and **2** and the TG curves are shown in Fig. S6 (ESI†). The TG curves reveal that a weight-loss of 27.88% (calcd: 29.40%) and 21.05% (calcd: 22.94%) at 50–370 and 50–337 °C, respectively, corresponds to the complete release of the free guest molecules as well as the coordinated solvent molecules. Further heating results in the decomposition of the frameworks, accompanying the loss of the coordinated TCS ligand.

3.6. Photoluminescence properties

The solid state excitation and emission spectra of complexes **1** and **2** at room temperature are shown in Fig. S9† and Fig. 4, respectively. The emission band is observed at 395 nm (λ_{ex} = 300 nm) for H₄TCS, which can be assigned to the ligand-centered electronic transitions, that is, the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ electronic transitions. The emission characters of complexes **1** and **2** are similar to that of the free H₄TCS
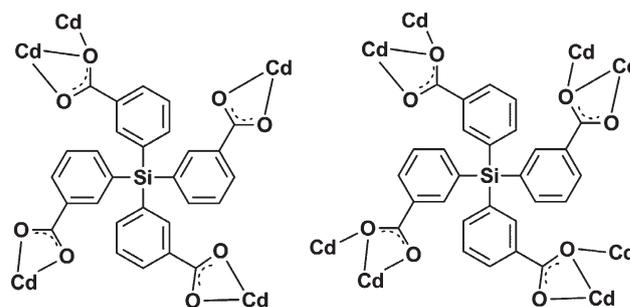
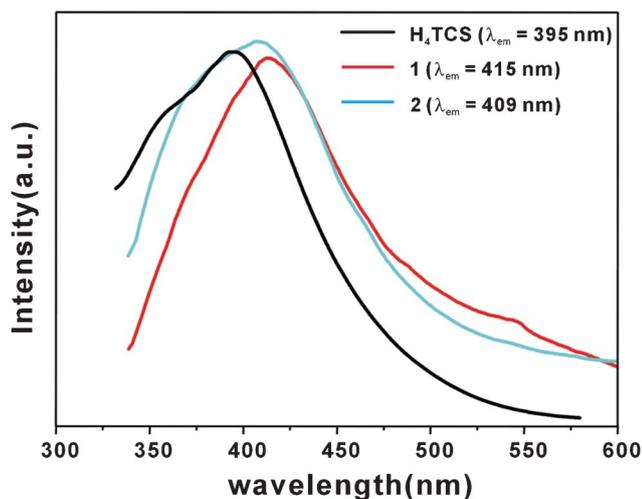**Scheme 3** Coordination modes of TCS in **1** (left) and **2** (right).

Fig. 4 Photoluminescence of free ligand and complexes **1–2**.

ligand. It was observed that the emissions occurred at 415 and 409 nm upon excitation at 320 nm for **1** and **2**, respectively. Since the Cd(II) ion is difficult to oxidize or to reduce due to its d^{10} electronic configuration, the emission bands of both complexes are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature.[40] The emissions of them can probably be assigned to the intraligand $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions because the resemblance of the emission spectra in comparison with free ligand.[41] The dissimilarity of the emission peaks is probably attributable to the differences of the coordination environment around the central metal ions and the rigidity of solid-state crystal packing.

4. Conclusions

In summary, we have successfully synthesized and characterized two Cd(II)-tetrakis(3-carboxyphenyl)silicon coordination polymers based on [Cd(COO)$_4$] and [Cd$_4$(COO)$_8$(DMF)$_4$] SBUs. They show 2D (4,4) net and (4,8)-connected 3D frameworks with fluorite (flu) topology, respectively. The solvent system plays an important role in modulating the structures. Moreover, the thermal stabilities and photoluminescent behaviours of **1** and **2** were also discussed.

Acknowledgements

References

1 (a) X. J. Kong, L. S. Long, Z. Zheng, R. B. Huang and L. S. Zheng, *Acc. Chem. Res.*, 2010, **43**, 201; (b) B. Chen, S. Xiang and G. Qian, *Acc. Chem. Res.*, 2010, **43**, 1115; (c) M. Yoshizawa, J. K. Klosterman and M. Fujita, *Angew. Chem., Int. Ed.*, 2009, **48**, 3418; (d) C. L. D. Gibb and B. C. Gibb, *J. Am. Chem. Soc.*, 2004, **126**, 11408; (e) L. Chen, F. Jiang, Z. Lin, Y. Zhou, C. Yue and M. Hong, *J. Am. Chem. Soc.*, 2005, **127**, 8588; (f) G. Peng, Y. C. Qiu, Z. H. Liu, B. Liu and H. Deng, *Cryst. Growth Des.*, 2010, **10**, 114; (g) J. J. Perry, J. A. Perman and M. J. Zaworotko, *Chem. Soc.*

Rev., 2009, **38**, 1400; (h) K. V. Domasevitch, P. V. Solntsev, I. A. Gural'skiy, H. Krautscheid, E. B. Rusanov, A. N. Chernega and J. A. K. Howard, *Dalton Trans.*, 2007, 3893; (i) C. M. Jin, Z. Zhu, Z. F. Chen, Y. J. Hu and X. G. Meng, *Cryst. Growth Des.*, 2010, **10**, 2054; (j) K. K. Tanabe, C. A. Allen and S. M. Cohen, *Angew. Chem., Int. Ed.*, 2010, **49**, 9730; (k) C. Y. Su, Y. P. Cai, C. L. Chen, M. D. Smith, W. Kaim and H. C. Zur Loye, *J. Am. Chem. Soc.*, 2003, **125**, 8595; (l) C. Janiak and J. K. Vieth, *New J. Chem.*, 2010, **34**, 2366; (m) C. Seward, W.-L. Jia, R.-Y. Wang, G. D. Enright and S. Wang, *Angew. Chem., Int. Ed.*, 2004, **43**, 2933.

2 O. M. Yaghi, D. J. Tranchemontagne, J. L. Mendoza-Cortes and M. O'Keeffe, *Chem. Soc. Rev.*, 2009, **38**, 1257.

3 D. Q. Yuan, D. Zhao, D. F. Sun and H. C. Zhou, *Angew. Chem., Int. Ed.*, 2010, **49**, 5357.

4 D. Zhao, D. Q. Yuan, D. F. Sun and H. C. Zhou, *J. Am. Chem. Soc.*, 2009, **131**, 9186.

5 W. Lu, D. Q. Yuan, T. A. Makal, J. R. Li and H. C. Zhou, *Angew. Chem., Int. Ed.*, 2012, **51**, 1580.

6 (a) H. Y. He, D. Q. Yuan, H. Q. Ma, D. F. Sun, G. Q. Zhang and H. C. Zhou, *Inorg. Chem.*, 2010, **49**, 7605; (b) D. Sun, Q. J. Xu, C. Y. Ma, N. Zhang, R. B. Huang and L. S. Zheng, *CrystEngComm*, 2010, **12**, 4161; (c) J. R. Li, R. J. Kuppler and H. C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477; (d) Q. Fang, G. Zhu, M. Xue, Z. Wang, J. Sun and S. Qiu, *Cryst. Growth Des.*, 2008, **8**, 319.

7 R. P. Davies, R. Less, P. D. Lickiss, K. Robertson and A. J. P. White, *Inorg. Chem.*, 2008, **47**, 9958.

8 (a) S. E. Wenzel, M. Fischer, F. Hoffmann and M. Fröba, *Inorg. Chem.*, 2009, **48**, 6559; (b) J. B. Lambert, Z. Liu and C. Liu, *Organometallics*, 2008, **27**, 1464; (c) R. P. Davies, R. Less, P. D. Lickiss, K. Robertson and A. J. P. White, *Cryst. Growth Des.*, 2010, **10**, 4571; (d) R. P. Davies, P. D. Lickiss, K. Robertson and A. J. P. White, *Aust. J. Chem.*, 2011, **64**, 1239.

9 H. Hopff, J. M. Deuber, P. Gallegra and A. Said, *Helv. Chim. Acta*, 1971, **54**, 117.

10 D. X. Wang, H. Y. He, X. H. Chen, S. Y. Feng, Y. Z. Niu and D. F. Sun, *CrystEngComm*, 2010, **12**, 1041.

11 (a) X. D. Chen, M. Du and T. C. W. Mak, *Chem. Commun.*, 2005, 4417; (b) M. Du, X. J. Zhao, J. H. Guo and S. R. Batten, *Chem. Commun.*, 2005, 4836; (c) H. He, J. Dou, D. Li, H. Ma and D. Sun, *CrystEngComm*, 2011, **13**, 1509; (d) S. K. Ghosha and S. Kitagawa, *CrystEngComm*, 2008, **10**, 1739; (e) L. L. Qu, Y. L. Zhu, Y. Z. Li, H. B. Du and X. Z. You, *Cryst. Growth Des.*, 2011, **11**, 2444; (f) J. Fan, M. H. Shu, T. Okamura, Y. Z. Li, W. Y. Sun, W. X. Tang and N. Ueyama, *New J. Chem.*, 2003, **27**, 1307.

12 (a) H. Y. He, D. Collins, F. N. Dai, X. L. Zhao, G. Zhang, H. Ma and D. Sun, *Cryst. Growth Des.*, 2010, **10**, 895; (b) D. Sun, Y. H. Li, H. J. Hao, F. J. Liu, Y. M. Wen, R. B. Huang and L. S. Zheng, *Cryst. Growth Des.*, 2011, **11**, 3323; (c) D. Sun, Z. H. Wei, D. F. Wang, N. Zhang, R. B. Huang and L. S. Zheng, *Cryst. Growth Des.*, 2011, **11**, 1427.

13 (a) L. L. Qu, Y. L. Zhu, Y. Z. Li, H. B. Du and X. Z. You, *Cryst. Growth Des.*, 2011, **11**, 2444; (b) B. X. Dong, X. J. Gu and Q. Xu, *Dalton Trans.*, 2010, **39**, 5683; (c) X. Y. Wang, L. Wang, Z. M. Wang and S. Gao, *J. Am. Chem. Soc.*, 2006, **128**, 674; (d) E. Y. Choi and Y. U. Kwon, *Inorg. Chem.*, 2005, **44**, 538; (e) C. P. Li and M. Du, *Chem. Commun.*, 2011, **47**, 5958.

14 G. M. Sheldrick, *SHELXS-97, Program for X-ray Crystal Structure Determination*, University of Gottingen, Germany, 1997.

15 G. M. Sheldrick, *SHELXL-97, Program for X-ray Crystal Structure Refinement*, University of Gottingen, Germany, 1997.

16 A. L. Spek, *Implemented as the PLATON Procedure, a Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1998.

17 J. H. Fournier, X. Wang and J. D. Wuest, *Can. J. Chem.*, 2003, **81**, 376.

18 L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1958.

19 (a) H. D. Flack, M. Sadki, A. L. Thompson and D. J. Watkin, *Acta Crystallogr., Sect. A*, 2011, **67**, 21; (b) H. D. Flack and G. Bernardinelli, *Chirality*, 2008, **20**, 681; (c) H. D. Flack and G. Bernardinelli, *Acta Crystallogr., Sect. A*, 1999, **55**, 908.

20 (a) F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 380; (b) Cambridge Structure Database search, CSD Version 5.28 (November 2006) with 15 updates (January 2007–Nov 2011).

21 (a) B. F. Abrahams, A. Hawley, M. G. Haywood, T. A. Hudson, R. Robson and D. A. Slizys, *J. Am. Chem. Soc.*, 2004, **126**, 2894; (b) Z. F. Chen, R. G. Xiong, B. F. Abrahams, X. Z. You and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 2001, 2453; (c) K. O. Ashiry, Y. H. Zhao, K. Z. Shao, Z. M. Su, Y. M. Fu and X. R. Hao, *Inorg. Chem. Commun.*, 2008, **11**, 1181; (d) X. Wang, L. Li, H. Hou, J. Wu and Y. Fan, *Eur. J. Inorg. Chem.*, 2007, 5234.

22 A. F. Wells, *Three-dimensional nets and polyhedra*, Wiley-Interscience, New York, 1977.

23 (a) C. Janiak, A.-C. Chamayou, A. K. M. Royhan Uddin, M. Uddin, K. S. Hagen and M. Enamullah, *Dalton Trans.*, 2009, 3698; (b) M. Enamullah, A. Sharmin, M. Hasegawa, T. Hoshi, A. C. Chamayou and C. Janiak, *Eur. J. Inorg. Chem.*, 2006, 2146.

24 H. Oshio, Y. Saito and T. Ito, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2673.

25 (a) S. Das, H. Kim and K. Kim, *J. Am. Chem. Soc.*, 2009, **131**, 3814; (b) P. Knuuttila, *Inorg. Chim. Acta*, 1982, **58**, 201; (c) S. H. Gou, M. Qian, Z. Yu, C. Y. Duan, X. F. Sun and W. Huang, *J. Chem. Soc., Dalton Trans.*, 2001, 3232.

26 V. A. Blatov, *IUCr CompComm Newsletter*, 2006, **7**, 4, see also http://www.topos.ssu.samara.ru..

27 (a) B. Chen, F. R. Fronczek and A. W. Maverick, *Chem. Commun.*, 2003, 2166; (b) C. A. Bremner, M. Simpson and W. T. A. Harrison, *J. Am. Chem. Soc.*, 2002, **124**, 10960; (c) V. Niel, A. L. Thompson, M. C. Muñoz, A. Galet, A. E. Goeta and J. A. Real, *Angew. Chem., Int. Ed.*, 2003, **42**, 3760; (d) B. F. Abrahams, M. G. Haywood, R. Robson and D. A. Slizys, *Angew. Chem., Int. Ed.*, 2003, **42**, 1111; (e) S. R. Batten, B. F. Hoskins, B. Moubaraki, K. S. Murray and R. Robson, *J. Chem. Soc., Dalton Trans.*, 1999, 2977.

28 S. S. Y. Chu, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.

29 (a) M. Eddaoudi, J. Kim, D. Vodak, A. Sudik, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4900; (b) T. Hu, H. He, F. Dai, X. Zhao and D. Sun, *CrystEngComm*, 2010, **12**, 2018.

30 (a) M. J. Zaworotko, *Chem. Soc. Rev.*, 1994, **23**, 283; (b) O. R. Evans and W. Lin, *Acc. Chem. Res.*, 2002, **35**, 511; (c) O. R. Evans and W. Lin, *Chem. Mater.*, 2001, **13**, 2705; (d) R. Robson, *J. Chem. Soc., Dalton Trans.*, 2000, 3735; (e) S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276.

31 (a) M. Eddaoudi, J. Kim, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2002, **124**, 376; (b) B. Chen, F. R. Fronczek and A.W. Maverick, *Chem. Commun.*, 2003, 2166; (c) F. Dai, P. Cui, F. Ye and D. Sun, *Cryst. Growth Des.*, 2010, **10**, 1474.

32 (a) B. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe and O. M. Yaghi, *Science*, 2001, **291**, 1021; (b) R. P. Farrell, T. W. Hambley and P. A. Lay, *Inorg. Chem.*, 1995, **34**, 757.

33 (a) B. F. Abrahams, B. F. Hoskins, D. M. Michael and R. Robson, *Nature*, 1994, **369**, 727; (b) R. W. Gable, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1990, 762; (c) B. Chen, M. Eddaoudi, T. M. Reineke, J. W. ampf, M. 'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 11559.

34 (a) J. Sun, L. Weng, Y. Zhou, J. Chen, Z. Chen, Z. Liu and D. Zhao, *Angew. Chem., Int. Ed.*, 2002, **41**, 4471; (b) B. F. Hoskins, R. Robson and N. V. Y. Scarlett, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1203.

35 (a) S. R. Batten, B. F. Hoskins, B. Moubaraki, K. S. Murray and R. Robson, *J. Chem. Soc., Dalton Trans.*, 1999, 2977; (b) S. R. Batten, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1991, 445.

36 B. F. Abrahams, M. G. Haywood, R. Robson and A. Slizys, *Angew. Chem., Int. Ed.*, 2003, **42**, 1111.

37 (a) O. M. Yaghi, C. E. Davis, G. Li and H. Li, *J. Am. Chem. Soc.*, 1997, **119**, 2861; (b) C. J. Kepert, T. J. Prior and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2000, **122**, 5158; (c) K. Biradha and M. Fujita, *Angew. Chem., Int. Ed.*, 2002, **41**, 3392.

38 (a) H. Chun, D. Kim, D. N. Dybtsev and K. Kim, *Angew. Chem., Int. Ed.*, 2004, **43**, 971; (b) R. Q. Zou, R. Q. Zhong, M. Du, T. Kiyobayashi and Q. Xu, *Chem. Commun.*, 2007, 2467; (c) H. Park, G. Krigsfeld, S. J. Teat and J. B. Parise, *Cryst. Growth Des.*, 2007, **7**, 1343; (d) Y. E. Cheon and M. P. Suh, *Chem. Commun.*, 2009, 2296; (e) Q. G. Zhai, C. Z. Lu, X. Y. Wu and S. R. Batten, *Cryst. Growth Des.*, 2007, **7**, 2332; (f) S. L. Li, Y. Q. Lan, J. S. Qin, J. F. Ma and Z. M. Su, *Cryst. Growth Des.*, 2008, **8**, 2055; (g) L. Zhang, Z. J. Li, Q. P. Lin, Y. Y. Qin, J. Zhang, P. X. Yin, J. K. Cheng and Y. J. Yao, *Inorg. Chem.*, 2009, **48**, 6517; (h) C. H. Zhan, M. X. Jiang, Y. L. Feng and J. W. Cheng, *CrystEngComm*, 2010, **12**, 420; (i) L. L. Liang, S. B. Ren, J. Wang, J. Zhang, Y. Z. Li, H. B. Du and X. Z. You, *CrystEngComm*, 2010, **12**, 2669; (j) S. Wu, L. Ma, L. S. Long, L. S. Zheng and W. B. Lin, *Inorg. Chem.*, 2009, **48**, 2436.

39 S. C. Chen, Z. H. Zhang, K. L. Huang, Q. Chen, M. Y. He, A. J. Cui, C. Li, Q. Liu and M. Du, *Cryst. Growth Des.*, 2008, **8**, 3437.

40 (a) L. Wen, Z. Lu, J. Lin, Z. Tian, H. Zhu and Q. Meng, *Cryst. Growth Des.*, 2007, **7**, 93; (b) J. G. Lin, S. Q. Zang, Z. F. Tian, Y. Z. Li, Y. Y. Xu, H. Z. Zhu and Q. J. Meng, *CrystEngComm*, 2007, **9**, 915; (c) L. Wen, Y. Li, Z. Lu, J. Lin, C. Duan and Q. Meng, *Cryst. Growth Des.*, 2006, **6**, 530.

41 (a) N. W. Alcock, P. R. Barker, J. M. Haider, M. J. Hannon, C. L. Painting, Z. Pikramenon, E. A. Plummer, K. Rissanen and P. Saarenketo, *J. Chem. Soc., Dalton Trans.*, 2000, 1447; (b) J. P. Collin, I. M. Dixon, J. P. Sauvage, J. A. G. Williams, F. Barigelletti and L. Flamigni, *J. Am. Chem. Soc.*, 1999, **121**, 5009; (c) H. A. Habib, A. Hoffmann, H. A. Höppe, G. Steinfeld and C. Janiak, *Inorg. Chem.*, 2009, **48**, 2166; (d) H. A. Habib, A. Hoffmann, H. A. Höppe and C. Janiak, *Dalton Trans.*, 2009, 1742; (e) H. A. Habib, J. Sanchiz and C. Janiak, *Dalton Trans.*, 2008, 1734; (f) S. Q. Zang, Y. Su, Y. Z. Li, J. G. Lin, X. Y. Duan, Q. J. Meng and S. Gao, *CrystEngComm*, 2009, **11**, 122; (g) P. Ren, M. L. Liu, J. Zhang, W. Shi, P. Cheng, D. Z. Liao and S. P. Yan, *Dalton Trans.*, 2008, 4711; (h) W. L. Liu, L. H. Ye, X. F. Liu, L. M. Yuan, J. X. Jiang and C. G. Yan, *CrystEngComm*, 2008, **10**, 1395; (i) S. L. Zheng and X. M. Chen, *Aust. J. Chem.*, 2004, **57**, 703.