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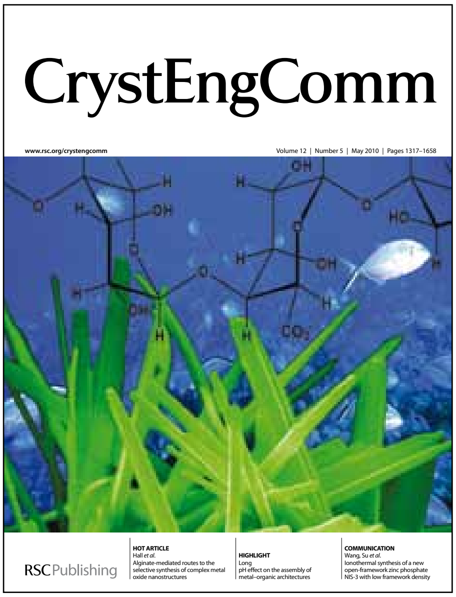

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ARTICLE TYPE

A series of metal-organic frameworks containing diverse secondary building units derived from a flexible triazine-based tetracarboxylic ligand

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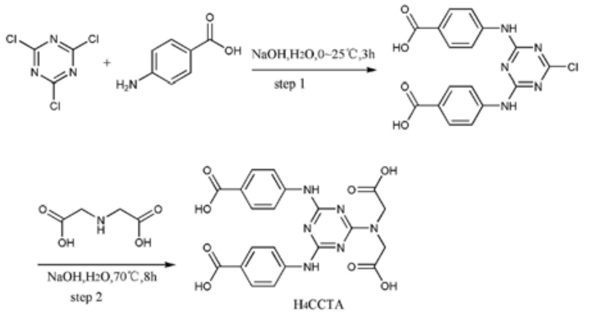
Five new coordination polymers, **$\{[Zn_2(CCTA)(DMF)_2]\cdot(DMF)\cdot(H_2O)_2\}_n$** (**1**), **$\{[Zn_{2.5}(CCTA)(OH)(H_2O)]\cdot(DMF)\cdot(H_2O)\}_n$** (**2**), **$\{[Zn_2(CCTA)(H_2O)_3]\cdot(NMP)_2\cdot(H_2O)_3\}_n$** (**3**), **$\{[Cd_4(CCTA)_2(DMF)_4(H_2O)_2]\cdot(H_2O)_6\}_n$** (**4**) and **$\{[Cd_4(CCTA)_2(H_2O)_4]\cdot(H_2O)_4\}_n$** (**5**), ($H_4$CCTA= 2,4-bis(4-carboxyphenylamino)-6-bis(carboxymethyl)amino-1,3,5-triazine, DMF=N, N'-dimethylformamide, NMP=N-methyl-2-pyrrolidone), have been solvothermally synthesized, containing diverse secondary building units (SBUs). Due to various coordination modes and different conformations of the flexible H_4CCTA ligand, the five complexes exhibit different topologies, respectively. Complex **1** has a two-dimensional (2D) structure with (4, 4)-sql topology constructed with tetranuclear zinc clusters. Complex **2** also possesses a 2D framework with an unprecedented $(4^{18}.6^{10})(4^5.6)_2$ point symbol based on pentanuclear zinc clusters. Complex **3** shows a three-dimensional (3D) framework with PtS topology, containing linear tetranuclear zinc clusters. Both complexes **4** and **5** with 3D frameworks are built with rare infinite Cd-O-Cd and Cd_2O_2 rod-shaped SBUs, respectively. Furthermore, complex **4** could be described as 4-connected uninodal umc net, instead of the pillared-layer structure of complex **5**.

1. Introduction

During the last decades, the research on the abundant self-assembled structures and topologies has attracted considerable attention, due to its potential applications, such as gas sorption, separation, catalysis, luminescence, magnetism, etc.[1] Up to now, the resulting frameworks, however, have suffered from a wide range of indeterminacy of temperature environment, solvent system, ligands and metal ions.[2] Each slight change of the above influence factors may cause quite different structures and topolgies[3]. Therefore, the rational design and prediction of MOFs is still a quite challenging task for synthetic chemists. It is acknowledged that the secondary building units (SBUs), first proposed by Yaghi' groups, have been proved helpfully to simplify complicated frameworks structures.[4] They are considered as the "joints" and significant building subunits of MOFs, playing an important role in the enhancement of topological prediction and analysis.[5] Nevertheless, only the square $Cu_2(COO)_4$ and octahedral $Zn_4O(COO)_6$ SBUs have been successful employed for directional syntheses.[6] Thereby, a long-term endeavor should be focused on the SBUs study to construct novel SBUs with metal ions and carboxylic groups. To explore different metal clusters is still necessary to afford unpredictable and intriguing supramolecular networks.[7]

As part of our longstanding interest in the triazine moieties because of their convenient synthesis and excellent luminescence properties, triazine derivatives have been widely exploited to construct MOFs in recent years, especially the flexible polycarboxylic groups connecting with aromatic triazine rings.[8] Due to their abundant coordination modes and diverse SBUs, it may be a intriguing approach to design and synthesize versatile coordination architectures. Comparing to the similar nitrogen-donor ligands, the synthesized tetracarboxylate ligand is a very promising candidates to fabricate novel and surprising SBUs. More subtly, the flexible carboxylic acid is capable of bending and rotating freely to meet the geometric requirements of different metal ions under synthetic conditions.[9]

Comparing to the half-rigid ligand 2,4-bis(4-aminobenzoic acid)-6-(dimethylamino)-1,3,5-triazine reported earlier by our group,[8e] herein, we have designed and synthesized a new more flexible triazine-based tetracarboxylic acid, 2,4-bis(4-carboxyphenylamino)-6-bis(carboxymethyl)amino-1,3,5-triazine (H_4CCTA). Under solvothermal conditions, it can be ascribed as a multi-coordinating moiety with four carboxyl functional groups, connecting with transition metal ions, as Zn(II) or Cd(II) ions, to form five metal-organic frameworks with diverse structures. The reaction leads to the formation of namely, **$\{[Zn_2(CCTA)(DMF)_2]\cdot(DMF)\cdot(H_2O)_2\}_n$ (1), $\{[Zn_{2.5}(CCTA)(OH)(H_2O)]\cdot(DMF)\cdot(H_2O)\}_n$ (2), $\{[Zn_2(CCTA)(H_2O)_3]\cdot(NMP)_2\cdot(H_2O)_3\}_n$ (3), $\{[Cd_4(CCTA)_2(DMF)_4(H_2O)_2]\cdot(H_2O)_6\}_n$ (4), $\{[Cd_4(CCTA)_2(H_2O)_4]\cdot(H_2O)_4\}_n$ (5)**. Structural analyses depict that the five aggregates have novel structures and topologies. Complexes **1**, **2** and **3** show the SBUs shapes with tetranuclear rhombus, pentanuclear double triangles and tetranuclear line, respectively, while complexes **4** and **5** illustrate the shape of infinite rod. Meanwhile, the luminescence properties of complexes **1-5** have been investigated in solid state at ambient temperature.



Scheme 1. Schematic representation of the synthesis strategy for ligand H_4CCTA

2. Experimental Section

2.1 materials and methods

The H_4CCTA ligand was prepared as illustrated in scheme 1. The other reagents and chemicals were purchased commercially and used as received without further purification. Infrared spectra were measured as KBr disks on a Spectum-One FT-IR spectrophotometer. Elemental analyses (C, H, N) were performed on a Vario EL III elemental analyzer. X-ray powder diffraction data were collected on a Miniflex2 diffractometer with Cu-Kα radiation (λ = 1.54184 Å) and scans were run for each sample over the range $5^{\circ} \leq 2\theta \leq 65^{\circ}$. Thermal gravimetric analyses were performed on a NETSCHZ STA-449C thermoanalyzer at a heating rate of 10 K min^{-1} under nitrogen atmosphere. Fluorescence spectra were measured with an Edinburgh analytical instrument FLS920. Suitable single crystals of complex **1-5** were collected on a Rigaku Mercury CCD diffractometer (Mo-Ka radiation, λ = 0.71073 Å, graphite monochromator) at 293(2) K. The structures were solved by direct methods with SHELX-97 program.[10] All of the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms attached to carbon were located at their ideal positions. Hydrogen positions of solvent water molecules were unmodelled. Crystal data for **1–5** are presented in Table 1. Selected bond lengths and angles of **1–5** are listed in Table S1 of the ESI.

Table 1 Crystallographic data and refinement details for complexes **1-5**.

complex	**1**	**2**	**3**	**4**	**5**
Empirical formula	$Zn_2C_{30}H_{39}N_9O_{13}$	$Zn_{2.5}C_{24}H_{26}N_7O_{12}$	$Zn_2C_{31}H_{44}N_8O_{16}$	$Cd_4C_{54}H_{72}N_{16}O_{28}$	$Cd_4C_{42}H_{44}N_{12}O_{24}$
M	864.44	767.94	915.54	1842.88	1550.49
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*P*-1	$P2_1$/n	*C2/c*	$P2_1$/c	$P2_1$/c
a (Å)	8.8692(7)	16.915(5)	29.542(8)	16.804(2)	27.504(3)
b (Å)	13.3176(14)	9.686(3)	7.3171(18)	16.228(2)	14.3017(15)
c (Å)	15.8973(15)	17.400(5)	35.757(10)	26.461(4)	13.3049(16)
α (°)	103.897(4)	90.00	90.00	90.00	90.00
β(°)	96.463(2)	106.905(4)	98.761(5)	103.170(2)	102.667(2)
γ(°)	98.338(4)	90.00	90.00	90.00	90.00
V/Å^3	1782.1(3)	2727.5(13)	7639(3)	7026.0(16)	5106.1(10)
Z	2	4	8	4	4
D_c/g cm^{-3}	1.611	1.870	1.589	1.742	2.017
μ/mm^{-1}	1.424	2.269	1.338	1.287	1.743
θ range (°)	2.34-27.47	2.45-25.00	3.29-27.49	2.01-27.48	2.08-27.48
F(000)	892	1560	3776	3696	3056
Nref	8079	4751	8616	16050	11695
R_1,[a] wR_2[b] [$I>2\sigma(I)$]	0.0467, 0.1317	0.0797, 0.2169	0.0479, 0.1411	0.0523, 0.1523	0.0547 , 0.1647
GOF on F^2	1.056	1.049	1.052	1.080	1.113

[a] $R = \Sigma(||Fo| - |Fc||)/\Sigma|Fo|$. [b]$Rw = \{\Sigma w[(Fo^2 - Fc^2)^2]/\Sigma w[(Fo^2)^2]\}^{1/2}$

2.2 Syntheses

2.2.1 Synthesis of H_4CCTA.

A solution of p-aminobenzoic acid (13.216 g, 96.4 mmol) and sodium hydroxide (15.424 g, 385.6 mmol) in 50ml of water was added dropwise into cyanuric chloride (8.89 g, 48.2 mmol) in 100ml of water at 0~5 °C under stirring. Half an hour later, the mixture was warmed to room temperature and reacted with stirring for 3h. Then another solution of iminodiacetic acid (12.82 g, 96.4 mmol) and sodium hydroxide (7.712 g, 192.8 mmol) in 50ml of water was added slowly to the mentioned mixture and the system was allowed to heat at 70 °C for 8 hours. After cooling, the PH value was adjusted to about 3 using diluted hydrochloride acid. The white solid was collected by filtration, washed with alcohol and water, and dried under vacuum at 70 °C, giving the product in 63% yield. ^{1}HNMR (400 MHz, DMSO-d^6): δ4.24(s, 4H, CH2), δ7.82(d, 4H, phenyl-H), δ7.92(d, 4H, phenyl-H), δ9.63(s, 2H, NH), δ12.53(s, 4H, COOH). ESI-MS: 481.0(M-1). IR(KBr,cm^{-1}): 3376(vs), 2986(vs.br), 2555(m), 1717(m), 1685(m), 1593(m), 1554(m), 1500(m), 1407(s), 1313(w), 1231(s), 1173(s), 850(s), 804(s), 770(s).

2.2.2 Synthesis of $\{[Zn_2(CCTA)(DMF)_2]\cdot DMF\cdot 2H_2O\}_n$ (1).

Complex **1** was obtained solvothermally in a 20 ml vial by heating a mixture of 0.05mmol of H_4CCTA and 0.15mmol of $Zn(NO_3)_2\cdot 6H_2O$ in DMF/H_2O (3.0ml/1.5ml) at 80 °C for 3 days and then slowly cooling to room temperature over 24 hours. Large, colorless, blocklike crystals were harvested in a yield of 43% (based on ligand). Anal.Calcd for $Zn_2C_{30}H_{39}N_9O_{13}$: C, 41.68; H, 4.55; N, 14.58. Found: C, 41.34; H, 4.67; N, 14.56. IR(KBr,cm^{-1}): 3399(vs.br), 2931(s), 1667(s), 1583(s), 1557(w), 1494(s), 1392(s.br), 1315(m), 1246(s), 1179(s), 867(s), 807(s), 783(s).

2.2.3 Synthesis of $\{[Zn_{2.5}(CCTA)(OH)(H_2O)]\cdot DMF\cdot H_2O\}_n$ (2).

Complex **2** was prepared by a similar method as described for complex **1**, except that the temperature was changed to 120 °C, instead of 80 °C. Colorless crystals were obtained by filtration in moderate yield (49%) (based on ligand). Anal.Calcd for $Zn_{2.5}C_{24}H_{26}N_7O_{12}$: C, 37.53; H, 3.41; N, 12.77. Found: C, 37.85; H, 3.54; N, 12.85. IR(KBr,cm^{-1}): 3419(w), 3284(vs.br), 2939(w), 1648(w), 1574(s.br), 1492(m), 1388(s.br), 1319(s), 1243(s), 1180(s), 861(s), 811(s), 784(s).

2.2.4 Synthesis of $\{[Zn_2(CCTA)(H_2O)_3]\cdot(NMP)_2\cdot(H_2O)_3\}_n$ (3).

Complex **3** was prepared by a similar method to that of complex **2**, except the solvent was NMP employed instead of DMF. Colorless block crystals were collected by filtration in 37% yield (based on ligand). Anal.Calcd for $Zn_2C_{31}H_{44}N_8O_{16}$: C, 40.63; H, 4.80; N, 12.23. Found: C, 40.68; H, 4.66; N, 12.40. IR(KBr,cm^{-1}): 3295(vs.br), 2930(w), 1653(w), 1579(s.br), 1497(m), 1381(s), 1316(s), 1249(s), 1176(s), 863(s), 813(s), 782(s).

2.2.5 Synthesis of $\{[Cd_4(CCTA)_2(DMF)_4(H_2O)_2]\cdot(H_2O)_6\}_n$ (4).

Complex **4** was prepared by a similar method to that of complex **1**, except that $Cd(NO_3)_2\cdot 4H_2O$ was used instead of $Zn(NO_3)_2\cdot 6H_2O$. Colorless block crystals were reaped by filtration in 23% yield (based on ligand). Anal.Calcd for $Cd_4C_{54}H_{72}N_{16}O_{28}$: C, 35.19; H, 3.94; N, 12.16; Found: C, 35.25; H, 4.10; N, 12.35. IR(KBr,cm^{-1}): 3385(br), 2951(w), 1642(w), 1564(s.br), 1490(m), 1395(s.br), 1324(s), 1241(s), 1169(s), 872(s), 819(s),787(s).

2.2.6 Synthesis of $\{[Cd_4(CCTA)_2(H_2O)_4]\cdot(H_2O)_4\}_n$ (5).

A mixture of $CdSO_4\cdot 8/3H_2O$ (0.2mmol, 52mg) and H_4CCTA (0.1mmol,48mg) in MeCN(5.0ml)/H_2O(2.0ml) was sealed in a 25ml Teflon-lined stainless steel autoclave, heated at 150 °C for three days and then cooled slowly to room temperature, affording colorless bulk crystals of **5** in 31% yield (based on ligand). Anal.Calcd for $Cd_4C_{42}H_{44}N_{12}O_{24}$: C, 32.53; H, 2.86; N, 10.84. Found : C, 32.65; H, 2.93; N,10.97. IR(KBr,cm^{-1}): 3370(vs), 2921(w), 1639(w), 1571(s.br), 1499(m), 1378(br), 1311(s), 1247(s), 1185(s), 865(s), 805(s), 769(s).

3. Results and Discussion

3.1 Crystal structure of $\{[Zn_2(CCTA)(DMF)_2]\cdot DMF\cdot 2H_2O\}_n$ (1).

X-ray single crystal structural analysis reveals that complex **1** crystallizes in triclinic space group *P*-1. As shown in Figure 1a, the asymmetric unit consists of two crystallographically independent Zn(II) ions, one CCTA^{4-} anion, two coordinated DMF molecules, one free DMF and two lattice water molecules. All atoms localize on general positions. Zn(1) is connected by five oxygen atoms from one chelating carboxyl group (O3A, O4A), two bridging carboxylate oxygen atoms (O5, O7) and one oxygen atom (O9) from the coordination DMF molecule. Zn(2) is coordinated by two carboxylate oxygen atoms (O6, O8B), a chelating carboxyl group (O1C, O2C), and one oxygen atom (O10) from a coordination DMF molecule. The coordination environment of both Zn(1) and Zn(2) can be described as a distorted trigonal bipyramid. It is noted that each H_4CCTA ligand combines five Zn(II) ions (scheme 2b), and the four carboxyl groups of H_4CCTA adopt three kinds of conformations, μ_1-η^1:η^1-OCO (scheme 2a-2), μ_2-η^1:η^1-OCO (scheme 2a-3), μ_2-η^2:η^1-OCO (scheme 2a-4), respectively.[11] In the structure, Zn(1), Zn(2), and their symmetric atoms, are linked together by four bridging carboxyl groups to form a 16-membered metallomacrocycle SBUs containing tetrameric zinc cluster with opposite Zn-Zn distance of 5.049(6) Å and 8.006(10) Å, respectively (Fig.1b).[12] As depicted in Figure 1c, a normal offset face-to-face π-π (edge to centroid, 3.5728(28) Å) interaction is presented, and also rare oxygen anion-π (oxygen to centroid, 3.1249(21) Å) interactions are observed, which can only be found in electron-deficient aromatic system. As shown in Figure 1d, compound **1** possesses 2D porous network along the crystallographic *c* axis with the pore diagonal distance of 22.6062(16)×23.0604(17) Å. In order to simplify and better understand the structure of 1, its topology is studied and presented in Figure 1e, taking a 16-membered metallomacrocycle as a 4-connected node. The adjacent layers are possessing a A~B~A~B packing model from side view (Fig.1f).

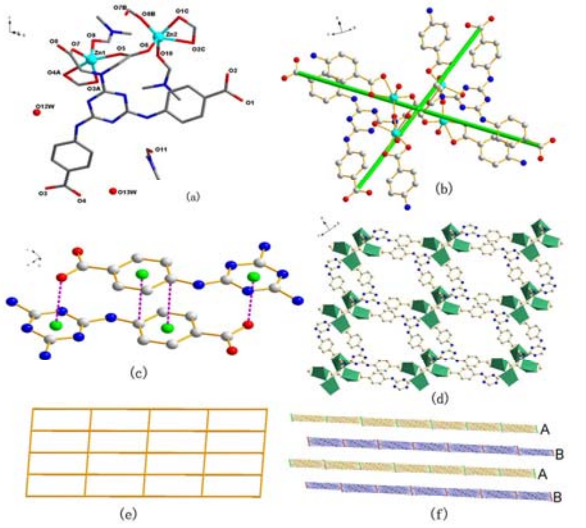
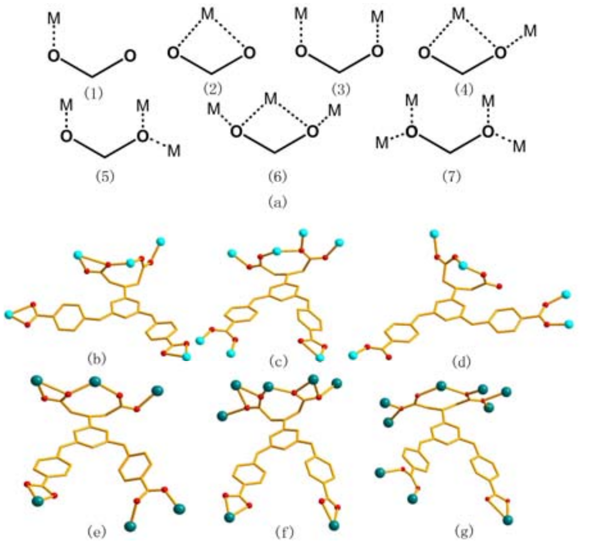


Fig.1 (a) Coordination environment of Zn atoms in **1**, hydrogen atoms are omitted for clarity. (b) Tetranuclear Zn(II) cluster. (c) π-π and anion-π interaction of the interlayer. (d) Two-dimentional network constructed from tetrameric zinc cluster SBU. (e) (4, 4)-sql net topology and (f) Interlayer A~B~A~B packing model. Symmetry codes: A -x, -y, -z; B -x+1, -y, -z+1;C -x+2, -y+1, -z+1.



Scheme 2. (a) The observed conformation of COO$^-$ and (b, c, d, e, f, g) Coordination modes of H$_4$CCTA ligands in complexes **1**, **2**, **3**, **4** and **5**, respectively.

3.2 Crystal structure of {[Zn$_{2.5}$(CCTA)(OH)(H$_2$O)]·DMF·H$_2$O}$_n$ (2).

Complex **2** crystallizes in the monoclinic space group *P*2(1)/n with the asymmetric unit consisting of three Zn(II) sites (two with whole occupancy and the third one with half occupancy), one ligand CCTA^{4-}, a μ_3-OH$^-$ anion, one coordinated water besides one H$_2$O and one DMF molecules in the lattice (Fig.2a). The Zn(1) ion shows a perfect octahedral ZnO$_6$ coordination via four carboxylate oxygen atoms (O3A, O3B, O8, O8C) from four different CCTA^{4-} ligands on the equatorial plane and two O atoms (O9, O9C) from μ_3-OH$^-$ anions in the apical position. Zn(2) ion is five coordinated with a distorted trigonal bipyramid coordination geometry from two bridging carboxyl groups (O6, O7E), one chelating carboxylate (O1A, O2A) and one μ_3-OH$^-$ anion (O9D). The Zn(3) also displays a distorted trigonal bipyramid coordination environment connected by three bridging carboxyl group (O4B, O5, O8) , one μ_3-OH$^-$ (O9)anion and one water molecule (O11). (Zn-O = 1.914(5)~2.131(5) Å).[13] Herein, each H$_4$CCTA links seven Zn(II) ions (scheme 2c), and the four carboxyl groups of H$_4$CCTA also show three kinds of coordination modes, μ_1-η^1:η^1-OCO (scheme 2a-2), μ_2-η^1:η^1-OCO (scheme 2a-3), μ_3-η^2:η^1-OCO (scheme 2a-5), respectively. The coordination of carboxylates and μ_3-OH$^-$ to the metal ions leads to a pentanuclear Zn(II) cluster secondary building unit with the five zinc ions locating at the same crystallographic plane (Zn(1)-Zn(2) = 3.3909(6); Zn(1)-Zn(3) = 2.9764(11); Zn(2)-Zn(3) = 3.4252(8)) (Fig.2b).[14] The pentanuclear zinc SBU futher propagates to a 1D infinite cluster chain via bridging carboxylates (Fig.2c). The one dimentional inorganic chains are then gripped by CCTA^{4-} with each ligand connecting to three different zinc clusters to form a novel 2D architecture (Fig.2d). Topology analysis shows that this 2-nodal net with stoichiometry of (4-c)$_2$(8-c) and a point symbol of $(4^{18}.6^{10})(4^5.6)_2$ is new (Fig.2e), no records found in the reported literature. It is clear to see that, unlike compound **1**, the interlayer of compound **2** arrange in A~A~A~A model from side look (Fig.2f).

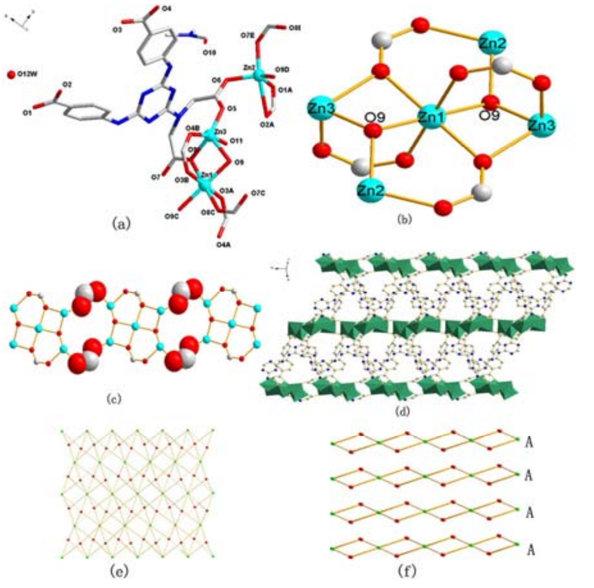


Fig.2 (a) Coordination environment of Zn atoms in **2**, hydrogen atoms are omitted for clarity. (b) View of the pentanuclear Zn(II) cluster. (c) The infinite chain constructed from zinc clusters. (d) The 2D framework with pentanuclear SBUs linked together via CCTA ligands. (e) The unprecedented $(4^{18}.6^{10})(4^5.6)_2$ topology of **2** and (f) Interlayer A~A~A~A packing model. Symmetry codes: A x-0.5, -y-1.5, z+0.5; B -x+1.5, y-0.5, -z-0.5; C -x+1, -y-2, -z; D –x+1, -y-1, -z; E x, y+1, z.

3.3 Crystal structure of {[Zn$_2$(CCTA)(H$_2$O)$_3$]·(NMP)$_2$·(H$_2$O)$_3$}$_n$ (3).

Complex **3** crystallizes in monoclinic space group *C*$_2$/c. The asymmetric unit of **3** consists of one CCTA^{4-} ligand, two crystallographically independent Zn atoms, two coordinated water molecules with full occupancy (O11, O12) and two with half occupancy (O13, O14), two free NMP molecules and three discrete water molecules. As shown in Figure 3a, Zn(1) resides in tetrahedral coordination geometry defined by three bridging carboxylate O atoms (O5, O8, O1A) from two different $CCTA^{4-}$ liands and one oxygen atom from water (O11). Zn(2) is surrounded by six oxygen atoms, three (O6, O3C, O4B) from different $CCTA^{4-}$ ligands and the rest (O12, O13, O14) from water molecules, to give a overall distorted octahedron geometry around the metal center. And each H_4CCTA ligand connects five Zn(II) ions (scheme 2d), and the four carboxyl groups of H_4CCTA have two kinds of coordination manners, μ_1-η^1:η^0-OCO (scheme 2a-1), μ_2-η^1:η^1-OCO (scheme 2a-3), respectively. Every four Zn atoms are bridged together by four carboxylates and two bridging water molecules to form a linear tetranuclear zinc cluster SBU (Fig.3b).[15] The distances between the zinc centers are Zn(1)-Zn(2) 4.7510(12), Zn(2)-Zn(2B) 3.3399(6) Å. The Zn cluster SBUs are bridged together via $CCTA^{4-}$ ligands to give a 3D non-interpenetrated framework (Fig.3d). Better insight into the framework is carried out by topological analysis, considering each two $CCTA^{4-}$ molecules combined together as a four connecting node and the metal cluster as a four linking node too, (Fig.3c), giving a classical 2-nodal PtS net with a point symbol of $(4^2.8^4)$ (Fig.3e).

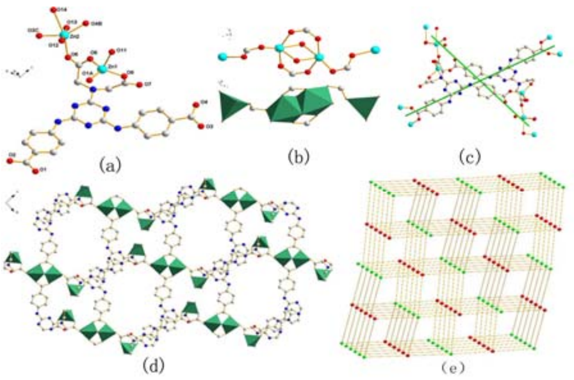


Fig.3 (a) Coordination environment of Zn atoms in **3** with hydrogen atoms, NMP and water molecules omitted for clarity. (b) The tetranuclear Zn cluster. (c) view of the combined CCTA as four linking nodes. (d) View of the 3D framework with SBUs linked together via $CCTA^{4-}$ ligands. (e) The topology of complex **3**. Symmetry codes: A –x+0.5, -y+1.5, -z; B –x+0.5, y+0.5, -z+0.5; C x+0.5, y+0.5, z.

3.4 Crystal structure of $\{[Cd_4(CCTA)_2(DMF)_4(H_2O)_2]\cdot(H_2O)_6\}_n$ (4).

Single crystal X-ray analysis reveals that complex **4** crystallizes in the monoclinic space group $P2_1/c$. As shown in Fig.4a, the asymmetric unit consists of four crystallographically independent cadmium ions, two coordinated water molecules, four coordinated DMF molecules, two $CCTA^{4-}$ anions and six free water molecules. The Cd(1) ion with slightly distorted octahedral coordination geometry is six-coordinated by two oxygen atoms (O26, O27) from two DMF molecules, one oxygen atom (O28) from coordination water molecule, three carboxylate oxygen atoms (O5, O14A, O16A) from three individual $CCTA^{4-}$ groups. The Cd(2) ion is seven coordinated forming a distorted pentagonal bipyramid by seven oxygen atoms from three chelating carboxyl groups (O1, O2, O13D, O14D, O15A, O16A) and one bridging carboxylate (O6). The coordination environment of Cd(3) forms a distorted octahedron by four oxygen atoms (O7, O8, O11B, O12B) from two chelating carboxyl groups and two oxygen atoms (O4, O10C) from two bridging carboxyl groups. The Cd(4) ion with a distorted octahedral coordination environment is connected by one oxygen atom (O25) from coordination water molecule, two oxygen atoms (O23, O24) from coordinated DMF molecules and three oxygen atoms (O3, O9B, O12B) from three different carboxylate groups. Different to the above complexes, each H_4CCTA ligand here links six metal ions (scheme 2e), and the four carboxyl groups of H_4CCTA possess three kinds of conformations, μ_1-η^1:η^1-OCO (scheme 2a-2), μ_2-η^1:η^1-OCO (scheme 2a-3), μ_2-η^2:η^1-OCO (scheme 2a-4), respectively, the same as that of complex **1**. It should be noted that the Cd ions form an infinite Cd-O-Cd zigzag chain along the *c* axis (Fig.4b).[16] The chains are connected together by the $CCTA^{4-}$ ligands to generate a 3D framework. There is a small channel formed along the c axis with crystallographic dimensions of approximately 5.7147 × 5.7147 Å^2 (Fig.4c). Thus the guest water molecule can be encapsulated in the channels. In accordance with the simplification principle, ignoring the none structure-expanding contribution of Cd(1) and Cd(4) atoms, the Cd(2) and Cd(3) can be considered as four-connected nods , and the $CCTA^{4-}$ ligands can also be simplified as four-connected nodes (Fig.4d). Therefore, the overall structure of **4** can be described as a 3D 4-connected uninodal umc net with a short point symbol of $(4^3.6^2.8)$. (Fig.4e)

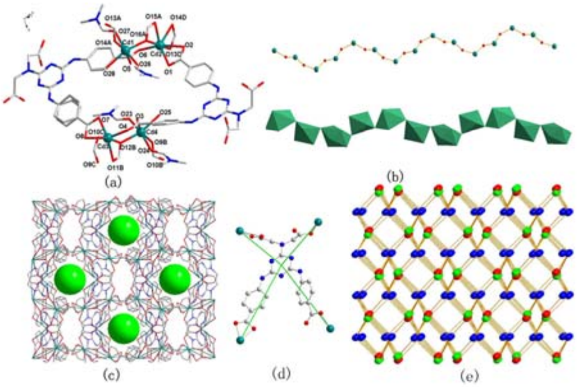


Fig.4 (a) The asymmetric unit of **4** (free H_2O molecules and hydrogen atoms are omitted for clarity). (b) The SBU of infinite rod-shaped Cd-O-Cd. (c) View of crystalline framework with channels along the *c* axis. (d) view of CCTA as four linking nodes. (e) Topology of compound **4**. Symmetry codes: A x, -y+2.5, z+0.5; B –x+1, -y+3, -z; C –x+2, -y +2, -z+1; D x, -y+2.5, z-0.5.

3.5 Crystal structure of $\{[Cd_4(CCTA)_2(H_2O)_4]\cdot(H_2O)_4\}_n$ (5).

Complex **5** crystallizes in monoclinic space group $P2_1/c$. The asymmetric unit contains four Cd atoms, two $CCTA^{4-}$ ligands, four coordination water molecules and four free water molecules. Cd(1) is coordinated by seven oxygen atoms, two chelating carboxylate O atoms (O1A, O2A, O9B, O10B) and one bridging carboxylate O atom (O5) on the equatorial plane, two bridging carboxyl group O atoms (O7, O8C) in the apical position to give overall distorted pentagonal bipyramid geometry with Cd-O distance in the range of 2.312(4)~2.570(4) Å. Coordination environments of Cd(3) and Cd(4) are similar to Cd(1), forming distorted pentagonal bipyramid geometry around the metal centers. However, the Cd(2) adopts more common distorted octahedron coordination model, four oxygen atoms (O4E, O5, O8C, O16D) from carboxyl groups and two oxygen atoms (O17, O18) from water molecules, and the bond distances of Cd-O in the range of 2.217(4)~2.398(4) Å. Herein, the two H$_4$CCTA ligands have two kinds of linking models, one combines seven Cd(II) ions (scheme 2f), and the other combines nine (scheme 2g). And the carboxyl groups of H$_4$CCTA form three kinds of conformations, μ_1-η^1:η^1-OCO (scheme 2a-2), μ_3-η^2:η^2-OCO (scheme 2a-6), μ_4-η^2:η^2-OCO (scheme 2a-7), respectively. It is interesting that a rare infinite rod-shaped Cd_2O_2 inorganic chain is formed as SBUs (Fig.5b)[17], and futher linked together via bridging carboxyl groups of $CCTA^{4-}$ ligands to generate a two dimensional net perpendicular to the *a* axis (Fig. 5c). And lastly, the $CCTA^{4-}$ ligands as pillars grip the 2D layers together to give a novel 3D non-interpenetrated crystal structure (Fig.5d).

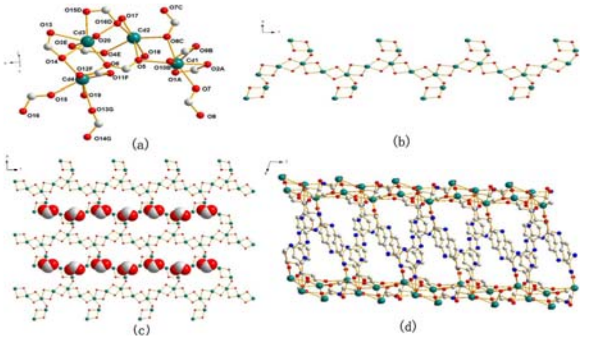
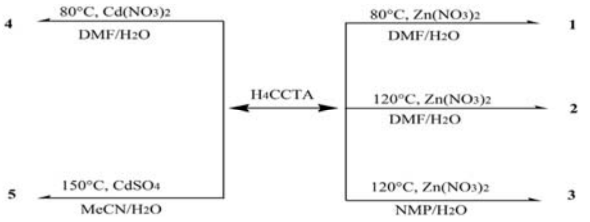


Fig.5 (a) Coordination environment of Cd atoms in **5** with solvent molecules and part of ligands omitted for clarity. (b) Infinite rod-shaped SBU of Cd-O-Cd. (c) View of 2D layer with rod-shaped SBUs linked via carboxylate groups. (d) Pillared 3D framework of compound **5**. Symmetry codes: A –x+2, y-0.5, -z+1.5; B –x+1, -y+1, -z+1; C x, -y+0.5, z+0.5; D x, -y+1.5, z+0.5; E –x+2, y+0.5, -z+1.5; F –x+1, y-0.5, -z+0.5; G x, -y+1.5, z-0.5.

3.6 Effect of temperature, solvent, metal ion and anion

The prediction of metal-organic frameworks is still challenging because the ultimate structure is often modulated by kinds of factors, such as temperature, solvent, metal ion, counter ion, and so on. As shown in scheme 3, comparing **1** with **2**, we can find that the only impacting factor is temperature. High temperature reduce the coordination possibility of organic solvent molecules to metal ions and give rise to different structure from low temperature, which can also be concluded from the overall five complexes, that is, DMF coordinating to Zn or Cd at 80 °C while DMF, NMP and MeCN not coordinating to metal ions at 120 °C or 150 °C. For **2** and **3**, they have same synthetic conditions except the solvent. Using DMF, **2** give a two dimensional framework containing pentanuclear Zn clusters while **3** generate a three dimensional structure with tetranuclear Zn cluster when NMP was employed. The difference between two Cd complexes represents the combined effect of temperature, solvent and anion. Because of the different atomic radius of Zn and Cd, their complexes often vary considerably, which can be drawn from the structural comparison of **1**, **2** and **3** with **4** and **5**. Herein, we find that Zn(II) ions prefer discrete SBUs, while the Cd(II) ions would be more likely to form infinite SBUs.



Scheme 3. Synthetic procedures of **1-5**.

3.7 PXRD , TG and photoluminescence properties

In order to confirm the phase purity of these complexes, the PXRD patterns were recorded for **1-5.** The experimental PXRD results of complexes **1-5** are in good agreement with the simulated patterns calculated from single crystal datas (Fig.S1-5, ESI†), indicating that they are in a pure phase.

To determine the stability of complex **1-5**, their thermal behaviour was investigated under N_2 by TGA. As shown in Figure S8 (ESI†), the TG curve for complex **1** shows that the free water molecules escape in the range of 30 - 88 ^oC (calcd, 4.2%; exptl, 4%), continuously losing free and coordinated DMF before 286 ^oC (calcd, 29.5%; exptl, 28%), followed by decomposition at 350 ^oC. Complex **2** loses its lattice DMF and water molecules (calcd, 12%; exptl, 12.6%) in the 30 – 337 ^oC interval and the decomposition of the framework begins at 402 ^oC. For **3**, the weight loss corresponding to the release of two free NMP and three H_2O molecules (calcd, 27.5%; exptl, 28.5%) is observed in the 30-305 ^oC range, further decomposition happens at 369 ^oC. Complex **4** loses its six lattice water molecules from 30 to 126 ^oC (calcd, 6%; exptl, 6.6%), and the decomposition occurs at 337 ^oC. For **5**, the loss of four crystallization water molecules (calcd, 4.6%; exptl, 4%) is observed when heated to 128 ^oC, and the framework decomposes at 360 ^oC.

The solid-state emission spectra of complexes **1-5** together with ligand H$_4$CCTA have been investigated at room temperature. As shown in Figure 6, the intense emission peaks appear at 371 nm (λ_{ex} = 273 nm) for **1**, 406 nm (λ_{ex} = 345 nm) for **2**, 376 nm (λ_{ex} = 269 nm) for **3**, 389 nm (λ_{ex} = 273 nm) for **4**, 362 nm (λ_{ex} = 272 nm) for **5**. And for the free H$_4$CCTA, the emission is observed at 385 nm (λ_{ex} = 272 nm). Complex **1**, **3**, **4** and **5** have nearly the same (complex **4**) or slight blue-shift of the max emission and the same max excitation (λ_{ex} = 272/273 nm) as the ligands. Therefore, they should belong to ligand-based emissions and their different emission behaviors may mainly originate from their diverse coordination interaction between ligands and metal clusters, and from different local environments within the frameworks. Presumably, the emissions for complexes **1**, **3**, **4** and **5** should be ascribed to the metal-perturbed intraligand charge transfers (ILCT).[18] As for complex **2**, its max excitation and emission red shift from 272nm to 345nm, and from 385nm to 406nm corresponding to the ligands, respectively. Herein, its luminescence may generate from metal-to-ligand charge transfer or ligand-to-metal charge transfer.[19]

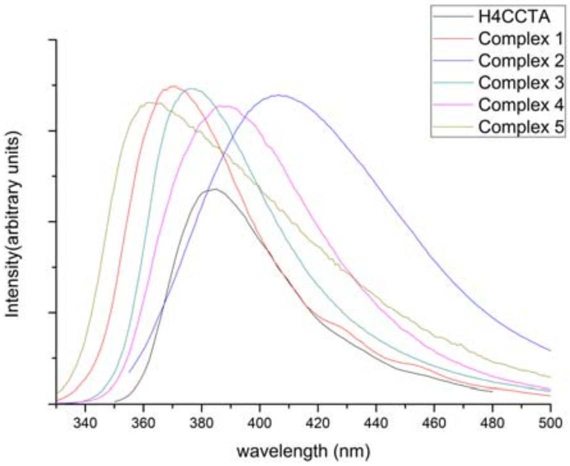


Fig.6 The emission spectra of complexes **1-5** in solid state at room temperature.

Conclusions

In summary, we have prepared five novel zinc or cadmium coordination polymers (**1-5**) built from the newly synthesized ligand (H$_4$CCTA). Complex **1** exhibits characteristic 2D layers with sql topology formed via tetranuclear zinc SBUs, while complex **2** contains pentanuclear zinc SBUs to form an unprecedented topology with the point symbol of $(4^{18}.6^{10})(4^5.6)_2$, just by changing the synthetic temperature from 80 °C to 120 °C. Interestingly, when NMP was employed, the structure of complex **3** is different from that of complexes **1** and **2**, which is built with the linear tetranuclear zinc SBUs included to form classical PtS 3D net framework. In addition, complex **4** involves rare infinite Cd-O-Cd rod-shaped SBUs and gives uninodal umc 3D topological network. Complex **5** also contains similar infinite rod-shaped SBUs, however, the building units are bridged by the adjacent two cadmiums and two carboxylate oxygen atoms to generate Cd$_2$O$_2$ infinite chains, extending to 2D layers with bridging carboxyl groups and further accumulating H$_4$CCTA backbone to produce a pillared-layer 3D framework. It is worthwhile to note that the effects of temperature, solvents, metal ions and anions have great influences on construction of these coordination polymers.

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Notes and references

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1 (a) M. D. Allendorf, C. A. Bauer, R. K. Bhakta and R. J. T. Houk, *Chem. Soc. Rev.*, 2009, **38**, 1330; (b) J. R. Li, R. J. Kuppler and H. C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477; (c) S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148; H. D. Guo, X. M. Guo, S. R. Batten, J. F. Song, S. Y. Song, S. Dang, G. L. Zheng, J. K. Tang and H. J. Zhang, *Cryst. Growth Des.*, 2009, **9**, 1394; (e) X. Y. Wang, Z. M. Wang and S. Gao, *Chem. Commun.*, 2007, 1127.

2 (a) L. Cheng, L. M. Zhang, S. H. Gou, Q. N. Cao, J. Q. Wang and L. Fang, *CrystEngComm.*, 2012, **14**, 3888; (b) M. Chen, S. S. Chen, T. Okamura, Z. Su, M. S. Chen, Y. Zhao, W. Y. Sun and N. Ueyama, *Cryst. Growth Des.*, 2011, **11**, 1901; (c) L. Dobrzanska, D. J. Kleinhans and L. J. Barbour, *New J. Chem.*, 2008, **32**, 813; (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; (e) S. L. Cai, S. R. Zheng, Z. Z. Wen, J. Fan and W. G. Zhang, *Cryst. Growth Des.*, 2012, **12**, 3575.

3 (a) J. Z. Gu, A. M. Kirillov, J. Wu, D. Y. Lv, Y. Tang and J. C. Wu, *CrystEngComm.*, 2013, **15**, 10287; (b) P. C. Cheng, M. H. Wu, M. Y. Xie, W. J. Huang, H. Y. He, T. T. Wu, Y. C. Lo, D. M. Proserpio and J. D. Chen, *CrystEngComm.*, 2013, **15**, 10346; (c) Y. F. Wang, Z. Li, Y. C. Sun, J. S. Zhao and L. Y. Wang, *CrystEngComm.*, 2013, **15**, 9980; (d) X. L. Wang, J. Luan, H. Y. Lin, C. Xu, G. C. Liu, J. W. Zhang and A. X. Tian, *CrystEngComm.*, 2013, **15**, 9995; (e) F. L. Hu, W. Wu, P. Liang, Y. Q. Gu, L. G. Zhu, H. Wei and J. P. Lang, *Cryst. Growth Des.*, 2013, **13**, 5050.

4 J. Kim, B. L. Chen, T. M. Reineke, H. L. Li, M. Eddaoudi, D. B. Moler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 8239.

5 N. L. Rosi, J. Kim, M. Eddaoudi, B. L. Chen, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 1504.

6 (a) G.J. McManus, Z. Q. Wang, D. A. Beauchamp and M. J. Zaworotko, *Chem. Commun.*, 2007, 5212; (b) B. Wisser, A. C. Chamayou, R. Miller, W. Scherer and C. Janiak, *CrystEngComm.*, 2008, **10**, 461; (c) S. Q. Ma, D. F. Sun, M. Ambrogio, J. A. Fillinger, S. Parkin and H. C. Zhou, *J. Am. Chem. Soc.*, 2007, **129**, 1858; (d) S. Henke, R. Schmid, J. D. Grunwaldt and R. A. Fischer, *Chem. Eur. J.*, 2010, **16**, 14296; (e) R. Grünker, I. Senkovska, R. Biedermann, N. Klein, M. R. Lohe, P. Müller and S. Kaskel, *Chem. Commun.*, 2011, **47**, 490; (f) T. F. Liu, J. Lü, X. Lin and R. Cao, *Chem. Commun.*, 2010, **46**, 8439.

7 (a) N. L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe and O. M. Yaghi, *Angew. Chem. Int. Ed.*, 2002, **41**,284; (b) T. Loiseaua, H. Muguerra, G. Fèrey, M. Haouas and F. Taulelle, *J. Solid. State. Chem.*, 2005, **178**, 621; (c) H. J. Li, B. Zhao, R. Ding, Y. Y. Jia, H. W. Hou and Y. T. Fan, *Cryst. Growth Des.*, 2012, **12**, 4170.

8 (a) Y. H. Huang, Q. L. Zhu, T. L. Sheng, S. M. Hu, R. B. Fu, C. J. Shen, C. H. Tan, Y. H. Wen, S. Y. Bai and X. T. Wu, *CrystEngComm.*, 2013, **15**, 3560; (b) Q. L. Zhu, T. L. Sheng, R. B. Fu, S. M. Hu, L. Chen, C. J. Shen, X. Ma and X. T. Wu, *Chem. Eur. J.*, 2011, **17**, 3358; (c) Q. L. Zhu, T. L. Sheng, R. B. Fu, C. H. Tan, S. M. Hu and X. T. Wu, *Chem. Commun.*, 2010, **46**, 9001; (d) C. J. Shen, T. L. Sheng, Q. L. Zhu, S. M. Hu and X. T. Wu, *CrystEngComm.*, 2012, **14**, 3189; (e) Q. L. Zhu, C. B. Tian, C. J. Shen, T. L. Sheng, S. M. Hu and X. T. Wu, *CrystEngComm.*, 2013, **15**, 2120.

9 (a) X. L. Hong, Y. Z. Li, H. M. Hu, Y. Pan, J. F. Bai and X. Z. You, *Cryst. Growth Des.*, 2006, **6**, 1221; (b) P. P. Cui, J. L. Wu, X. L. Zhao, D. Sun, L. L. Zhang, J. Guo and D. F. Sun, *Cryst. Growth Des.*, 2011, **11**, 5182; (c) P. Du, Y. Yang, J. Yang, Y. Y. Liu, W. Q. Kan and J. F. Ma, *CrystEngComm.*, 2013, **15**, 6986.

10 G. M. Sheldrick, *SHELXTL NT Version 5.1. program for the solution and refinement of crystal structures*, University of Göttingen, Germany, 1997.

11 X. G. Guo, W. B. Yang, X. Y. Wu, Q. K. Zhang, L. Lin, R. M. Yu and C. Z. Lu, *CrystEngComm.*, 2013, **15**, 3654.

12 (a) Q. Chu, G. X. Liu, Y. Q. Huang, X. F. Wang and W. Y. Sun, *Dalton Trans.*, 2007, 4302; (b) D. C. Wen, S. X. Liu and J. Ribas, *Ployhedron*, 2007, 26, 3849; (c) L. F. Ma, Q. L. Meng, C. P. Li, B. Li, L. Y. Wang, M. Do and F. P. Liang, *Cryst. Growth Des.*, 2010, **10**, 3036.

13 (a) E. C. Yang, Z. Y. Liu, X. G. Wang, S. R. Batten and X. J. Zhao, *CrystEngComm.*, 2008, **10**, 1140; (b) H. Ren, T. Y. Song, J. N. Xu, S.

B. Jing, Y. Yu, P. Zhang and L. R. Zhang, *Cryst. Growth Des.*, 2009, **9**, 105; (c) L. P. Zhang, J. F. Ma, J. Yang, Y. Y. Pang and J. C. Ma, *Inorg. Chem.*, 2010, **49**, 1535.

14 (a) R. Kitaura, G. Onoyama, H. Sakamoto, R. Matsuda, S. Noro and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2004, **43**,2684; (b) X. J. Li, R. Cao, D. F. Sun, D. Q. Yuan, W. H. Bi, X. Li and Y. Q. Wang, *J. Mol. Struct.*, 2004, **694**, 205; (c) E. C. Yang, H. K. Zhao, B. Ding, X. G. Wang and X. J. Zhao, *Cryst. Growth Des.*, 2007, **7**, 2009.

15 P. Nockemann, B. Thijs, K. V. Hecke, L. V. Meervelt and K. Binnemans, *Cryst. Growth Des.*, 2008, **8**, 1353.

16 (a) S. L. Zheng, J. H. Yang, X. L. Yu, X. M. Chen and W. T. Wong, *Inorg. Chem.*, 2004, **43**, 830; (b) J. C. Dai, X. T. Wu, S. M. Hu, Z. Y. Fu, J. J. Zhang, W. X. Du, H. H. Zhang and R. Q. Sun, *Eur. J. Inorg. Chem.*, 2004, 2096; (c) Z. Su, K. Cai, J. Fan, S. S. Chen, M. S. Chen and W. Y. Sun, *CrystEngComm.*, 2010, **12**, 100.

17 (a) R. P. Davies, R. Less, P. D. Lickiss, K. Robertson and A. J. P. White, *Cryst. Growth Des.*, 2010, **10**, 4571; (b) X. C. Chai, H. H. Zhang, S. Zhang, Y. N. Cao and Y. P. Chen, *J. Solid. State. Chem.*, 2009, **182**, 1889; (c) K. Bania, N. Barooah and J. B. Baruah, *Polyhedron*, 2007, **26**, 2612.

18 (a) J. Guo, J. F. Ma, B. Liu, W. Q. Kan and J. Yang, *Cryst. Growth Des.*, 2011, **11**, 3609; (b) Y. J. Cui, Y. F. Yue, G. D. Qian and B. L. Chen, *Chem. Rev.* 2012, **112**, 1126; (c) Y. B. Dong, G. X. Jin, M. D. Smith, R. Q. Huang, B. Tang and H. C. zur Loye, *Inorg. Chem.*, 2002, **41**, 4909; (d) J. Tao, M. L. Tong, J. X. Shi, X. M. Chen and S. W. Ng, *Chem. Commun.*, 2000, 2043.

19 (a) X. W. Wang, J. Z. Chen and J. H. Liu, *Cryst. Growth Des.*, 2007, **7**, 1227; (b) R. Feng, F. L. Jiang, L. Chen, C. F. Yan, M. Y. Wu and M. C. Hong, *Chem. Commun.*, 2009, 5296; (c) Y. Wei, Y. Yu and K. Wu, *Cryst. Growth Des.*, 2008, **8**, 2087; (d) M. X. Li, H. Wang, S. W. Liang, M. Shao, X. He, Z. X. Wang and S. R. Zhu, *Cryst. Growth Des.*, 2009, **9**, 4626.

Five new coordination polymers containing diverse SBUs derived from a flexible triazine-based tetracarboxylic acid have been solvothermally synthesized and characterized.