## CrystEngComm

### PAPER

Cite this: CrystEngComm, 2013, 15, 365

Received 11th August 2012, Accepted 26th October 2012

DOI: 10.1039/c2ce26720a

www.rsc.org/crystengcomm

#### Introduction

Over the past decades, there has been a dramatic increase in the synthesis of tetrazole compounds, not only owing to their novel structural architectures and topologies, but also to their potential applications in speciality explosives, adsorption, sensors, magnetic and optical materials.<sup>1</sup> Since the first tetrazole compound was found by Bladin,<sup>2</sup> the synthesis of 5-substituted 1H-tetrazole derivatives has been an active field of study in the development supramolecular chemistry and crystal engineering.<sup>3</sup> It is a landmark breakthrough that Demko and Sharpless pioneered a safe, convenient and environmentally friendly synthetic method for the synthesis of 5-substituted 1*H*-tetrazoles derivatives via a  $\begin{bmatrix} 2 + 3 \end{bmatrix}$ cycloaddition reaction of azide anions and nitriles in water with the aid of Lewis acid as a catalyst.<sup>4</sup> Xiong et al. improved this method using Zn(II) as a catalyst for *in situ* cycloaddition and the formation of zinc tetrazole coordination compounds

# *In situ* hydrothermal syntheses of five new cadmium(II) coordination polymers based on 3-(1*H*-tetrazol-5-yl)benzoate ligand<sup>†</sup>

Li Liang, Chengfeng Yang, Yingzhao Ma and Hong Deng\*

Five new cadmium(II) tetrazole-based compounds, { $[Cd_4(3-tzba)_4(H_2O)_2]\cdot 2H_2O(1), [Cd(3-tzba)(2,2'-bipy)_2]$ (2), [Cd(3-tzba)(1,10-phen)] (3), [Cd<sub>3</sub>(3-tzba)<sub>2</sub>(NA)<sub>2</sub>(H<sub>2</sub>O)] (4) and [Cd(3-tzba)(BIO)] (5), where 3-tzba = 3-(1H-tetrazol-5-yl)benzoate, 2,2'-bipy = 2,2'-bipyridine, 1,10-phen = 1,10-phenanthroline, NA = nicotinic acid, BIO = benzo-biimidazolediones}, were successfully synthesized involving the in situ generation of ligand under hydrothermal conditions. The compounds were thoroughly characterized by elemental analyses, Fourier transform infrared spectroscopy, thermal studies, and single crystal and powder X-ray diffraction. Compound 1 represents a three-dimensional (3D) coordination framework built up by the assembly of two-dimensional (2D) Cd-3-tzba wheel layers and 3-tzba linkers, exhibiting a pcu ( $4^{12} \cdot 6^3$ ) topological net. Compound 2 displays a one-dimensional (1D) zigzag chain formed by the linkage of Cd(II) centers and 3-tzba ligands. Compound 3 shows a 1D pearl-necklace-like chain built by the interconnection of Cd(II) centers and 3-tzba ligands. Compound 4 is a 3D coordination framework which is constructed by 1D [Cd<sub>3</sub>] chains with 3-tzba and NA ligands linkers displaying a hxl (3<sup>6</sup>) type net. Compound **5** exhibits a 3D sql (4<sup>4</sup>) topological network, with 1D Cd chains linking the adjacent 3-tzba and BIO ligands. It is noted that the 3-tzba and BIO ligands are generated in situ from the precursor 3-cyanobenzoic acid and 1,2,4,5benzenetetracarboxylic acid ( $H_4$ bta), respectively. In addition, the luminescent properties of these compounds were investigated.

> via hydrothermal synthesis.<sup>5</sup> With the development of this method, a variety of tetrazole-based coordination frameworks which present various novel coordination networks with diverse topologies and interesting functional properties have been reported via in situ solvo-hydrothermal synthesis.<sup>6</sup> For example, Long et al. systematically synthesized a series of highly porous 3,8-connected frameworks by linking cubic  $M_4Cl(BTT)_8(H_2O)_4$  (H<sub>3</sub>BTT = 1,3,5-benzenetristetrazolate; M =  $Mn^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{2+}$ ) clusters with different triangular polytetrazolate ligands, while Zubieta et al. reported a microporous material  $[Co_2(H_{0.67}bdt)_3] \cdot 20H_2O$ [H<sub>2</sub>bdt = 5,5'-(1,4phenylene)bis(1H-tetrazole)] exhibiting single chain magnetism and reversible changes in magnetism upon desolvation and resolvation.7,8 Bu et al. obtained a microporous compound, [Zn(tdp)] (H<sub>2</sub>tdp = 2,3-di-1*H*-tetrazol-5-ylpyrazine), in which each Zn(II) ion is chelated by three  $tdp^{2-}$  ligands and each ligand bridges three Zn(II) ions, giving a chiral 3-connected etd network.9 We also constructed a luminescent microporous cadmium-organic compound  $[Cd(\mu_2-Cl)(\mu_4-$ 5MT]<sub>n</sub> (5MT = 5-methyl-1*H*-tetrazole) that exhibits high sensitivity to nitrite in both DMF and water.<sup>10</sup>

> Recently, bridging ligands, for example, multidentate aromatic ligands containing multiple coordination sites such as the *N*-heterocyclic group<sup>6</sup> and carboxylate group<sup>11</sup> have

View Article Online

School of Chemistry & Environment, South China Normal University, Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, Guangzhou 510006, P. R. China. E-mail: dh@scnu.edu.cn

<sup>†</sup> Electronic supplementary information (ESI) available. CCDC 854939–854943. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce26720a

been extensively studied and proved to be a rational choice to synthesize coordination compounds possessing unique structures and potential applications. The tetrazolate-benzoate ligand containing tetrazolate and carboxyl groups with four nitrogen and two oxygen potential coordination sites has excellent coordination ability and displays diverse coordination modes.<sup>12,13</sup> However, the investigation of bifunctional tetrazolate-benzoate ligand as building blocks for constructing coordination frameworks has been less developed so far.<sup>14</sup> On the other hand, the introduction of auxiliary ligands has an important influence on structural and functional diversity as well. Generally, the chelating auxiliary ligands (such as 2,2'-bipy, 1,10-phen) manipulate the structures in terminal mode forming lower dimension frameworks,<sup>13e,14a,15</sup> while some other bridging ligands (such as 4,4'-bipy, nicotinic acid, isonicotinic acid) control the structures in bridging mode, forming higher dimension frameworks.<sup>13b,16</sup> Therefore, to a certain extent, the crystal structures with different dimensions can be obtained by the introduction of suitable ancillary ligands.

Based on the above considerations and in our continuing research on the assembly of tetrazole-based coordination compounds,<sup>17</sup> we used 3-cyanobenzoic acid, sodium azide and different auxiliary ligands (2,2'-bipyridine, 1,10-phenanthroline, nicotinic acid and 1,2,4,5-benzenetetracarboxylic acid) with different Cd(II) salts to synthesize novel tetrazole-based metal– organic frameworks (MOFs), since 3-cyanobenzoic acid can form 3-(1H-tetrazol-5-yl)benzoic acid ( $3-H_2$ tzba) ligand through the [2 + 3] cycloaddition reaction of azide anions and nitriles in water with the aid of Lewis acid Cd(II) salts as the catalysts. The  $3-H_2$ tzba ligand containing tetrazole and carboxylate functional groups permits a range of versatile bridging modes. Meanwhile, the addition of different auxiliary ligands can make the structures of the targeted products more versatile, due to the chelating ligands (2,2'-bipyridine and 1,10-phenanthroline) and the bridging ligands (nicotinic acid and 1,2,4,5-benzenetetracarboxylic acid) having different coordination modes. Furthermore, the cadmium metal ions not only can adopt various coordination numbers and geometries, but also exhibit luminescent properties when bound to functional ligands.<sup>18</sup>

In this paper, by the *in situ* ligand reaction and by the presence/absence of secondary ligands, five cadmium(II) tetrazole-based coordination compounds: [Cd<sub>4</sub>(3 $tzba)_4(H_2O)_2] \cdot 2H_2O$  (1);  $[Cd(3-tzba)(2,2'-bipy)_2]$  (2);  $[Cd(3-tzba)(2,2'-bipy)_2]$ (1,10-phen) (3);  $[Cd_3(3-tzba)_2(NA)_2(H_2O)]$  (4) and  $[Cd(3-tzba)_2(NA)_2(H_2O)]$  (4) tzba)(BIO)] (5) were obtained through hydrothermal synthesis. In these compounds, the tetrazole and carboxylate groups of the tetrazolate-benzoate adopt different coordination modes generating different coordination motifs, including 1D chains (2, 3) and 3D frameworks (1, 4, 5), respectively. It is interesting that 3-tzba and BIO ligands were generated in situ. In particular, in the case of the BIO, an unexpected ligand was generated via the Schmidt reaction of H4bta and NaN3 in the in situ formation of compound 5. To the best our knowledge, the BIO ligand was first prepared by hydrothermal technique and used for constructing coordination compounds. The thermal stabilities and the solid-state photoluminescence properties of these cadmium(II) compounds were also investigated.

#### **Experimental section**

#### Materials and physical measurements

All the materials and reagents were obtained commercially and used without further purification. Elemental (C, H, N)

Table 1 Crystallographic data and structure refinement summary for compounds 1-5

Compound	1	2	3	4	5
Formula	C <sub>32</sub> H <sub>24</sub> Cd <sub>4</sub> N <sub>16</sub> O <sub>12</sub>	C <sub>28</sub> H <sub>20</sub> CdN <sub>8</sub> O <sub>2</sub>	C <sub>20</sub> H <sub>12</sub> CdN <sub>6</sub> O <sub>2</sub>	C <sub>28</sub> H <sub>18</sub> Cd <sub>3</sub> N <sub>10</sub> O <sub>9</sub>	C <sub>16</sub> H <sub>10</sub> CdN <sub>8</sub> O <sub>4</sub>
M <sub>r</sub>	1274.31	612.93	480.77	975.75	490.73
T/K	296	296	296	296	296
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	Pbca	C2/c	$P2_1/c$	$Pna2_1$
a (Å)	12.380(3)	10.984(10)	25.919(4)	13.6219(13)	18.220(3)
b (Å)	16.488(3)	17.667(16)	9.9766(16)	16.5119(16)	13.269(2)
c (Å)	21.246(4)	26.08(2)	17.701(3)	13.4293(13)	6.8783(11)
αÌ	90	90	90	90	90
β(°)	90	90	128.489(2)	93.153(1)	90
γÕ	90	90	90	90	90
$V(Å^3)$	4336.8(15)	5061(8)	3582.7(10)	3016.0(5)	1662.9(5)
Z	4	8	8	4	4
$\rho_{\rm calcd} ({\rm g}  {\rm cm}^{-3})$	1.952	1.609	1.783	2.149	1.960
$M (\mathrm{mm}^{-1})$	2.011	0.907	1.250	2.170	1.361
F(000)	2464.0	2464.0	1904.0	1888.0	968.0
Reflns collected	21 808	24 237	8754	15 162	8231
Unique reflns	7791	4541	3216	5400	2958
GOF	1.077	1.031	1.067	1.191	1.020
R <sub>int</sub>	0.0596	0.0418	0.0236	0.0229	0.0392
$R_1 \left[ I > 2\sigma(I) \right]^a$	0.0682	0.0307	0.0289	0.0273	0.0278
$wR_2$ (all data) <sup>b</sup>	0.2049	0.0732	0.0685	0.0615	0.0603

<sup>a</sup>  $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$ . <sup>b</sup>  $wR_2 = \{\sum [w(F_0^2 - F_c^2)^2] / \sum (w(F_0^2)^2)^{1/2}$ .

analyses were performed on a Perkin-Elmer 2400 element analyzer. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 4000–400 cm<sup>-1</sup> range using a Nicolet Avatar 360 FT-IR spectrophotometer. Thermogravimetric analysis (TGA) experiments were carried out on a Perkin-Elmer TGA 7 thermogravimetric analyzer with the heating rate of 10 °C min<sup>-1</sup> from 35 to 900 °C under dry air atmosphere. Powder XRD investigations were carried out on a Philips PW-1830 X-ray diffractometer with Cu K $\alpha$  radiation. Fluorescence spectra were recorded with an Edinburgh FLS920 spectrophotometer analyzer.

#### Syntheses

**CAUTION!** Azido and tetrazolate compounds are potentially explosive under the hydrothermal reaction conditions. Only a small amount of compound should be prepared and they should be handled with extreme care.

#### Synthesis of $[Cd_4(3-tzba)_4(H_2O)_2] \cdot 2H_2O$ (1)

A mixture of CdCl<sub>2</sub> (0.092 g, 0.5 mmol), 3-cyanobenzoic acid (0.074 g, 0.5 mmol), NaN<sub>3</sub> (0.033 g, 0.5 mmol) and H<sub>2</sub>O (10 mL) was stirred for 30 min at room temperature and kept in a 23 mL Teflon-lined autoclave at 150 °C for 3 days. The mixtures were cooled to room temperature at 5 °C h<sup>-1</sup>. Colorless block single crystals of **1** were obtained (yield: 45% based on Cd). Elemental Anal. Calcd (%) for **1**,  $C_{32}H_{24}Cd_4N_{16}O_{12}$ : C, 30.16; H, 1.90; N, 17.59. Found: C, 30.10; H, 1.98; N, 17.50. IR data (KBr, cm<sup>-1</sup>): 3412 (br), 1609 (s), 1585 (s), 1508 (s), 1475 (s), 1457(s), 1408 (s), 1168 (m), 1082 (m), 885 (w), 745 (w), 683 (w).

#### Synthesis of [Cd(3-tzba)(2,2'-bipy)<sub>2</sub>] (2)

A mixture of CdCl<sub>2</sub> (0.092 g, 0.5 mmol), 3-cyanobenzoic acid (0.074 g, 0.5 mmol), 2,2'-bipy (0.078 g, 0.5 mmol), NaN<sub>3</sub> (0.033 g, 0.5 mmol) and H<sub>2</sub>O (10 mL) was stirred for 30 min at room temperature and kept in a 23 mL Teflon-lined autoclave at 150 °C for 3 days. The mixtures were cooled to room temperature at 5 °C h<sup>-1</sup>. Colorless block single crystals of 2 were obtained (yield: 35% based on Cd). Elemental Anal. Calcd (%) for 2,  $C_{28}H_{20}CdN_8O_2$ : C, 54.87; H, 3.29; N, 18.28. Found: C, 54.35; H, 3.34; N, 18.25. IR data (KBr, cm<sup>-1</sup>): 3099 (br), 1623 (s), 1591 (s), 1503 (s), 1467 (s), 1447 (s), 1383 (s), 1155 (m), 1011 (m), 877 (w), 748 (w), 667 (w).

#### Synthesis of [Cd(3-tzba)(1,10-phen)] (3)

A mixture of CdSO<sub>4</sub> (0.128 g, 0.5 mmol), 3-cyanobenzoic acid (0.074 g, 0.5 mmol), 1,10-phen (0.099 g, 0.5 mmol), NaN<sub>3</sub> (0.033 g, 0.5 mmol) and H<sub>2</sub>O (10 mL) was stirred for 30 min at room temperature and kept in a 23 mL Teflon-lined autoclave at 150 °C for 3 days. The mixtures were cooled to room temperature at 5 °C h<sup>-1</sup>. Colorless block single crystals of 3 were obtained (yield: 32% based on Cd). Elemental Anal. Calcd (%) for 3,  $C_{20}H_{12}CdN_6O_2$ : C, 49.97; H, 2.52; N, 17.48. Found: C, 49.60; H, 2.40; N, 17.50. IR data (KBr, cm<sup>-1</sup>): 3068 (br), 1611 (s), 1594 (s), 1504 (s), 1473 (s), 1445 (s), 1396 (s), 1145 (m), 943 (m), 881 (w), 745 (w), 694 (w).

#### Synthesis of [Cd<sub>3</sub>(3-tzba)<sub>2</sub>(NA)<sub>2</sub>(H<sub>2</sub>O)] (4)

A mixture of  $CdCl_2$  (0.092 g, 0.5 mmol), 3-cyanobenzoic acid (0.074 g, 0.5 mmol), nicotinic acid (0.062 g, 0.5 mmol),  $NaN_3$ 

(0.033 g, 0.5 mmol) and  $H_2O$  (10 mL) was stirred for 30 min at room temperature and kept in a 23 mL Teflon-lined autoclave at 150 °C for 3 days. The mixtures were cooled to room temperature at 5 °C h<sup>-1</sup>. Colorless block single crystals of 4 were obtained (yield: 42% based on Cd). Elemental Anal. Calcd (%) for 4,  $C_{28}H_{18}Cd_3N_{10}O_9$ : C, 34.47; H, 1.86; N, 14.36. Found: C, 34.50; H, 1.92; N, 14.30. IR data (KBr, cm<sup>-1</sup>): 3424 (br), 1614

<b>ubic 2</b> Sciected bolid distances (A) for compounds <b>1 3</b>	Гable	2	Selected	bond	distances	(Å)	for	compounds	1–5	
---	-------	---	----------	------	-----------	-----	-----	-----------	-----	--

Compound <b>1</b> <sup><i>a</i></sup>			
$\begin{array}{c} Cd(1)-N(13)\\ Cd(1)-N(2)\#1\\ Cd(1)-O(7)\\ Cd(2)-N(9)\\ Cd(2)-N(3)\#1\\ Cd(2)-N(14)\\ Cd(3)-N(14)\\ Cd(3)-N(11)\#3\\ Cd(3)-N(1)\#1\\ Cd(3)-O(12)\#1\\ Cd(3)-O(12)\#1\\ Cd(4)-N(6)\#5\\ Cd(4)-O(9)\\ Cd(4)-O(4W)\\ Cd(4)-O(5)\\ \end{array}$	$\begin{array}{c} 2.282(8)\\ 2.412(9)\\ 2.444(8)\\ 2.274(9)\\ 2.304(9)\\ 2.332(8)\\ 2.332(8)\\ 2.377(8)\\ 2.377(9)\\ 2.246(10)\\ 2.342(8)\\ 2.431(10)\\ 2.627(8)\end{array}$	$\begin{array}{c} Cd(1)-O(5)\\ Cd(1)-O(8)\\ Cd(2)-O(3W)\\ Cd(2)-O(3W)\\ Cd(2)-O(10)\#2\\ Cd(3)-O(6)\\ Cd(3)-O(6)\\ Cd(3)-N(7)\#4\\ Cd(3)-O(11)\#1\\ Cd(4)-O(11)\\ Cd(4)-O(10)\\ Cd(4)-N(10)\#6\\ \end{array}$	$\begin{array}{c} 2.316(7)\\ 2.412(7)\\ 2.447(8)\\ 2.279(11)\\ 2.330(7)\\ 2.350(8)\\ 2.297(7)\\ 2.356(9)\\ 2.447(8)\\ 2.297(8)\\ 2.394(8)\\ 2.553(9) \end{array}$
Compound 2 <sup>b</sup>			
Cd(1)-N(6)#1 Cd(1)-N(2) Cd(1)-N(4) Cd(1)-O(2)	$\begin{array}{c} 2.272(3) \\ 2.385(3) \\ 2.412(3) \\ 2.574(3) \end{array}$	Cd(1)-O(1) Cd(1)-N(1) Cd(1)-N(3)	2.325(3) 2.407(3) 2.522(3)
Compound 3 <sup>c</sup>			
Cd(1)-O(1) Cd(1)-N(2) Cd(1)-N(1)	2.242(3) 2.341(3) 2.371(3)	Cd(1)-N(4)#1 Cd(1)-N(5)#2 Cd(1)-O(2)	2.297(3) 2.366(3) 2.440(3)
Compound 4 <sup>d</sup>			
$\begin{array}{c} Cd(1)-O(8)\#1\\ Cd(1)-N(4)\#2\\ Cd(1)-O(2)\#3\\ Cd(2)-N(5)\\ Cd(2)-N(1)\\ Cd(2)-O(7)\#4\\ Cd(2)-O(7)\#4\\ Cd(2)-O(5)\#3\\ Cd(3)-O(9)\#1\\ Cd(3)-O(3)\#3\\ Cd(3)-N(2) \end{array}$	$\begin{array}{c} 2.223(3)\\ 2.332(3)\\ 2.365(3)\\ 2.293(3)\\ 2.380(3)\\ 2.558(3)\\ 2.640(3)\\ 2.240(3)\\ 2.311(2)\\ 2.348(3) \end{array}$	$\begin{array}{c} Cd(1)-N(10)\\ Cd(1)-N(6)\\ Cd(1)-O(3)\#3\\ Cd(2)-O(6)\#4\\ Cd(2)-O(4)\#3\\ Cd(2)-N(9)\#5\\ Cd(3)-O(5)\#3\\ Cd(3)-O(5)\#3\\ Cd(3)-O(1)\\ Cd(3)-N(7) \end{array}$	$\begin{array}{c} 2.286(3)\\ 2.356(3)\\ 2.401(3)\\ 2.273(3)\\ 2.295(3)\\ 2.439(3)\\ 2.274(3)\\ 2.331(4)\\ 2.383(3) \end{array}$
Compound 5 <sup>e</sup>			
Cd(1)-O(3) Cd(1)-N(6)#2 Cd(1)-O(2) Cd(1)-O(1)	$2.287(3) \\ 2.327(4) \\ 2.358(2) \\ 2.554(3)$	Cd(1)-N(7)#1 Cd(1)-O(4)#3 Cd(1)-O(4)#4	2.297(4) 2.354(3) 2.538(3)

<sup>a</sup> Symmetry codes: #1: -x + 5/2, y + 1/2, -z + 1/2; #2: -x + 3/2, y + 1/2, -z + 1/2; #3: x + 1, y, z; #4: x + 1/2, -y + 3/2, z - 1/2; #5: -x + 2, -y + 1, -z + 1; #6: -x + 3/2, y - 1/2, -z + 1/2. <sup>b</sup> Symmetry codes: #1: x - 1/2, -y + 1/2, z - 1/2; #2: -x + 1/2, -y + 1/2, -z + 1. <sup>d</sup> Symmetry codes: #1: x - y + 1/2, z - 1/2; #2: -x + 1/2, -y + 1/2, -z + 1; #3: x, -y + 3/2, z - 1/2; #2: -x + 1/2, -y + 1/2, -z + 1; #3: x, -y + 3/2, z + 1/2; #4: x, y, z - 1; #5: -x + 1, -y + 2, -z + 1; #3: x, -y + 3/2, z + 1/2; #4: x, -y + 1/2, z; #2: -x + 3/2, y + 1/2, z + 1/2; #3: x + 1/2, -y + 1/2, z - 1; #4: -x + 1/2, y + 1/2, z - 1/2.

(s), 1593 (s), 1500 (s), 1481 (s), 1448 (s), 1403 (s), 1165 (m), 1030 (m), 878 (w), 752 (s), 694 (w).

#### Synthesis of [Cd(3-tzba)(BIO)] (5)

A mixture of CdCl<sub>2</sub> (0.092 g, 0.5 mmol), 3-cyanobenzoic acid (0.074 g, 0.5 mmol), H<sub>4</sub>bta (1.27 g, 0.5 mmol), NaN<sub>3</sub> (0.033 g, 0.5 mmol) and H<sub>2</sub>O (10 mL) was stirred for 30 min at room temperature and kept in a 23 mL Teflon-lined autoclave at 150 °C for 3 days. The mixtures were cooled to room temperature at 5 °C h<sup>-1</sup>. Red prismatic single crystals of 5 were obtained (yield: 45% based on Cd). Elemental Anal. Calcd (%) for 5, C<sub>16</sub>H<sub>10</sub>CdN<sub>8</sub>O<sub>4</sub>: C, 39.16; H, 2.05; N, 22.83. Found: C, 39.10; H, 2.10; N, 22.90. IR data (KBr, cm<sup>-1</sup>): 3082 (br), 1693 (s), 1639 (s), 1581 (s), 1510 (s), 1483 (s), 1451 (s), 1410 (s), 1167 (m), 926 (m), 895 (w), 743 (w), 687 (w).

#### Crystal structure determination

Single crystal X-ray diffraction data collections of 1-5 were performed on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data collection and reduction were performed using the APEX II software.<sup>19</sup> Multiscan absorption corrections were applied for all the data sets using the APEX II program.<sup>19</sup> The structures were solved by direct methods and refined by fullmatrix least-squares on  $F^2$  using the SHELXL program package.<sup>19</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. Hydrogen atoms on water molecules were located from difference Fourier maps and were also refined using a riding model. Crystallographic data for compounds 1-5 are listed in Table 1. Selected bond lengths and angles are given in Table 2 and Table S1 (ESI<sup>†</sup>) for compounds 1-5.

#### **Results and discussion**

#### Synthesis

Compounds 1–5 were obtained through the hydrothermal reaction of 3-cyanobenzoic acid, sodium azide and different auxiliary ligands with the aid of cadmium salts. The synthetic route to the five compounds is shown in Scheme 1. With the aid of cadmium salts, the *in situ* [2 + 3] cycloaddition reactions of 3-cyanobenzoic acid and sodium azide took place. As a

bifunctional bridging main ligand, the 3-H<sub>2</sub>tzba ligands possessing the four nitrogen atoms of tetrazole and the two oxygen atoms of carboxylate serve as either bridging building blocks or as multidentate ligands, which can lead the formation of a variety of coordination frameworks. In compounds 1–5, the 3-tzba ligand presents eight kinds of coordination modes (Scheme 2). In particular, it is the first time that the coordination modes a–d and f–h are observed in tetrazole-5-carboxylate ligands.

In the absence of a secondary ligand, a 3D molecular configuration of compound **1** exhibiting a pcu (4<sup>12</sup>·6<sup>3</sup>) topological net was obtained. As we know, the addition of small auxiliary ligands can lead to the formation of different coordination frameworks, so the influence of secondary ligands on the architecture of coordination compounds was investigated. By the addition of bidentate chelating ligand, 2,2'-bipyridine for **2** and 1,10-phenanthroline for **3**, into the reaction system, the 1D frameworks were obtained. As NA and BIO secondary ligands as building units can build a bridge to connect metal ions at both ends, thus compounds **4** and **5** all display a 3D network. These results indicate that the choice of different auxiliary ligands has significant effect on structural diversity.

The solvo/hydrothermal method has been widely used in the preparation of high quality stable single crystals.<sup>20</sup> Many coordination compounds, which are difficult to obtain by routine synthetic methods, can be formed in situ via a facile solvo/hydrothermal strategy. In particular, these reactions are not always simple coordination between metal ion and ligands, some unique reaction may occur that involves in situ hydrolysis, oxidation, and ligand synthesis.<sup>20</sup> For example, Xu et al. reported a new route for preparing a 2D coordination compounds  $[Co(\mu_3-Hbcbh)(bpy)]_n (H_3bcbh = benzene-4-carbox$ ylate-1,2-bihydrazide). The H<sub>3</sub>bcbh is derived from the in situ acylation reaction of H4bta with N2H4·H2O.21 In our experiment, reaction of 3-cyanobenzoic acid, H<sub>4</sub>bta, NaN<sub>3</sub> with cadmium salt under hydrothermal conditions results in the formation of compound 5 exhibiting a 3D network based on 3-tzba and BIO and Cd(II) center. It is interesting that both 3-tzba and BIO were generated via in situ ligand synthesis. Undoubtedly, as discussed earlier, 3-tzba was formed via the [2 + 3] cycloaddition reaction of an azide with nitriles in water with the aid of a Lewis acid.<sup>4</sup> But how was the BIO ligand generated?



Scheme 1 In situ hydrothermal synthesis of compounds 1-5.



 $\label{eq:scheme-sche$ 

According to the synthetic systems we adopted, the Schmidt reaction mechanism for the formation of BIO ligand can be proposed.<sup>22</sup> The carboxylic acid Schmidt reaction starts with

acylium ion I obtained from protonation and loss of water. Reaction with hydrazoic acid gets the protonated azido ketone II, which goes through a rearrangement reaction with the alkyl group R, migrating over the C-N bond with expulsion of nitrogen. The protonated III is attacked by water forming carbamate IV, which after deprotonation loses CO<sub>2</sub> to obtain the amine V (Scheme S1, ESI<sup>†</sup>). According to our reaction, H<sub>4</sub>bta goes through a rearrangement reaction with expulsion of nitrogen and CO<sub>2</sub> obtaining (a) and loses the water forming (b), which automatically change to (c) through tautomerism (Scheme 3). Due to the complexities involved in the *in situ* ligand syntheses and supramolecular assemblies, it is difficult to explain the exact reaction mechanism in the one-pot, blackbox-like hydrothermal metal–ligand reactions.<sup>20</sup>

#### Description of crystal structures

[CD<sub>4</sub>(3-TZBA)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (1). Compound 1 represents a 3D coordination framework constructed by the assembly of 2D Cd-3-tzba wheel layers and 3-tzba linkers, exhibiting the orthorhombic space group  $P2_1/n$ . The asymmetric unit contains four crystallographically independent Cd(II) ions, four types of 3-tzba ligands, two coordinated water molecules and two free water molecules (Fig. 1a). As shown in Fig. S1, ESI,<sup>†</sup> among the four unique Cd(II) metal ions, the Cd1, Cd2 and Cd3 ions adopt slightly distorted octahedral coordination environments: Cd1 ion is coordinated by four oxygen atoms from two different 3-tzba ligands, and two nitrogen atoms from two different 3-tzba ligands; Cd2 ion is surrounded by three nitrogen donors of three different 3-tzba ligands, and three oxygen donors of two different 3-tzba ligands and one coordinated water; Cd3 ion is bound to three nitrogen atoms of three different 3-tzba ligands, and three oxygen atoms of two different 3-tzba ligands. Meanwhile the Cd4 center has a slightly distorted monocapped trigonal prism coordination geometry that is defined by five oxygen atoms of three different 3-tzba ligands and one coordinated water, and two nitrogen atoms of two different 3-tzba ligands. This kind coordination mode of Cd(II) ion has been found in many metal-organic frameworks,<sup>23</sup> but it is the first time that the Cd(II) ion has been observed in a tetrazolate compound so far. The Cd-N/O bond lengths range from 2.274(9) to 2.627(8) Å and the N-Cd-N/O bond angles fall between 53.4(3) and 179.2(3)°. The bridging 3-tzba ligands adopt four different coordination modes: μ<sub>5</sub>-κN1:κN2:κN3:κO5:κO6;  $\mu_4$ кN6:кN7:кO7:кO8; μ<sub>6</sub>-κN9:κN10:κN11:κO9:κO10;  $\mu_4$ кN13:кN14:кO11:кO12 (Scheme 2, a-d), all of which are observed in tetrazole-5-carboxylate compounds at the first time.

On the basis of the connectivity of the multifunctional 3-tzba ligands, a 10-membered ring is generated containing three Cd1 ions, two Cd2 ions, two Cd3 ions and three Cd4 ions, where each Cd(II) ion is linked by 3-tzba ligands. Each 10-membered ring is further connected to the adjacent rings by sharing three Cd(II) ions, resulting in a highly ordered layered wheel network along the *c*-axis (Fig. 1b). The adjacent wheel layers are interconnected through 3-tzba ligands to form a 3D coordination framework (Fig. 1c and d). To better understand the nature of the intricate framework, a topological approach to simplify the 3D frameworks can be accomplished. Thus, if



Scheme 3 The probable reaction mechanism of 1,2,4,5-benzenetetracarboxylic acid (H<sub>4</sub>bta) in compound 5.

the 10-membered rings are considered as the six-connected nodes (Fig. S2, ESI<sup>†</sup>), the whole framework of **1** can be described as a *pcu* net with Schläfli symbol  $(4^{12} \cdot 6^3)$  (Fig. 1e).

[CD(3-TZBA)(2,2'-BIPY)<sub>2</sub>] (2). Compound 2 represents a 1D zigzag chain constructed by the linkage of the Cd(II) centers and 3-tzba ligands and crystallizes in the orthorhombic space group Pbca. As shown in Fig. 2a, in the asymmetric unit of 2 there are one crystallographically independent Cd(II) ion, one 3-tzba ligand and two 2,2'-bipy ligands. Each Cd(II) ion is coordinated to five nitrogen atoms from two different 2,2'-bipy ligands and one 3-tzba ligand, and two oxygen atoms from the carboxyl group of 3-tzba ligand exhibiting a slightly distorted monocapped trigonal prism coordination geometries, which has been found in a tetrazole compound for the first time so far as well. The Cd-N bond lengths range from 2.272(3) to 2.522(3) Å and the N-Cd-N bond angles fall between 66.99(10) and 165.52(9)°. The Cd-O bond lengths are 2.325(3) and 2.574(3) Å and the N-Cd-O bond angles range from 52.64(8) to 146.50(9)°. The Cd(II) centers are spanned by a 3-tzba ligand with a distance of 11.83 Å between the metal ions. All 3-tzba ligands coordinated to the two Cd(II) ions are involved in  $\mu_2$ кN6:кO1:кO2 bridging (Scheme 2e), while the 2,2'-bipy ligand displays a chelating coordination mode, the nitrogen atoms of pyridine rings connecting one Cd(II) ion.

It is very interesting that the 3-tzba ligands ligate Cd(II) ions, forming an infinite zigzag cadmium chain running along the *c*-axis (Fig. 2b). In addition, hydrogen bonding interactions play an important role in forming this structure. The adjacent chains are assembled by two kinds of hydrogen bonding interactions  $[C(4)-H(4)\cdots O(2): 3.140(6) \text{ Å}; C(13)-H(13)\cdots O(2): 3.401(6) \text{ Å}]$  forming a 3D supramolecular framework along the *c* direction (Table 3, Fig. 2c, Fig. S2, ESI<sup>†</sup>).

[CD(3-TZBA)(1,10-PHEN)] (3). Compared with the structure of 2, compound 3 crystallizes in the monoclinic system space group C2/c and displays a 1D pearl-necklace-like chain constructed by the interconnection of the Cd(II) centers and 3-tzba ligands. As depicted in Fig. 3a, the asymmetric unit consists of one

Cd(II) ion, one 3-tzba ligand and one 1,10-phen ligand. Each Cd(II) ion is coordinated by four nitrogen atoms from two different 3-tzba ligands and one 1,10-phen ligand, and two oxygen atoms from carboxyl group of the 3-tzba ligand in a slightly distorted octahedral coordination environment. The Cd–N and Cd–O bond lengths range from 2.242(3)–2.440(3) Å, and the N–Cd–N/O bond angles fall between 53.87(9)–142.06(9)°. The 3-tzba ligands acting in  $\mu_3$ - $\kappa$ N4: $\kappa$ N5: $\kappa$ O1: $\kappa$ O2 coordination mode are connected to three Cd(II) ions (Scheme 2f), and it is the first time observed in tetrazolate-5-carboxylate compounds as well. Whereas the 1,10-phen ligand is involved in chelating coordination mode with nitrogen atoms of pyridine rings linking one Cd(II) ion.

It is noted that the tetrazole groups of 3-tzba ligands connect two neighboring Cd(II) ions forming a dimeric unit  $[Cd_2N_4]$ with the Cd···Cd distance of 4.05 Å, far different to that in compound 2. The dimeric unit  $[Cd_2N_4]$  is doubly bridged by two 3-tzba ligands generated an 18-membered ring. Finally, each 18-membered ring is further linked to the adjacent rings by sharing two Cd(II) octahedrons, resulting in a 1D pearlnecklace-like chain running in the *ab*-plane (Fig. 3b). These chains are in turn interconnected by C–H···N hydrogen bonds [C6–H6···N3: 3.501(18) Å] and extend to form a 2D supramolecular network (Table 3, Fig. 3c).

Compared with 2 and 3, two similar frameworks have been recently reported:<sup>13e</sup> [Zn(3-tzba)(2,2-bipy)(H<sub>2</sub>O)]·3H<sub>2</sub>O (2') and  $[Zn_2(3-tzba)_2(1,10-phen)_2]·3H_2O$  (3'), in which the central metal ions differ from those in 2 and 3. In compounds 2 and 3, the central metal ions are Cd(II) ions, while in 2' and 3' the central metal ions are Zn(II) ions. So the coordination geometries are different: monocapped trigonal prism  $[CdN_5O_2]$  in 2; octahedron  $[CdN_4O_2]$  in 3; octahedron  $[ZnN_3O_3]$  in 2'; square-pyramidal  $[ZnN_3O_2]$  in 3'. The coordination modes of 3-tzba and 2,2'-bipy ligands in 2 and 2' are the same, while in 3 and 3', the 3-tzba ligand has different modes:  $\mu_3$ - $\kappa$ N4: $\kappa$ N5: $\kappa$ O1: $\kappa$ O2 in 3;  $\mu_3$ - $\kappa$ N3: $\kappa$ O1: $\kappa$ O2 in 3'.



**Fig. 1** (a) Ball and stick plot showing the asymmetric unit of compound **1**. All H atoms and free water molecules are omitted for clarity. (b) A polyhedral view of the 2D Cd-3-tzba wheel layer of compound **1** in the *c*-axis direction. All 3-tzba ligands are omitted for clarity. (c) A polyhedral view of 3D coordination frameworks constructed by the assembly of 2D Cd-3-tzba wheel layers and 3-tzba linkers in the *ac*-plane and (d) in the *ab*-plane. (e) View of the *pcu* net when each 10-membered ring is considered as a node.

[CD<sub>3</sub>(3-TZBA)<sub>2</sub>(NA)<sub>2</sub>(H<sub>2</sub>O)] (4). Single crystal X-ray diffraction structure analysis reveals that compound 4 crystallizes in the monoclinic space group  $P2_1/c$  and features a 3D coordination framework constructed by 1D [Cd<sub>3</sub>] chains, 3-tzba and NA linkers. As shown in Fig. 4a, the asymmetric unit of 4 contains three crystallographically independent Cd(II) ions, two types of 3-tzba ligands, two NA ligands and one coordinated water. The two unique Cd(II) ions, Cd1 and Cd3, both have a distorted octahedral coordination geometry: Cd1 is coordinated by three nitrogen atoms from two different 3-tzba ligands and one NA ligand, and three oxygen atoms from one 3-tzba ligand and one NA ligand; Cd3 is surrounded by two nitrogen donors of two different 3-tzba ligands, and four oxygen atoms from two different NA ligands, one 3-tzba ligand and one coordinated water. Cd2 has a slightly distorted monocapped trigonal prism coordination geometry which is bound to three nitrogen donors of two different 3-tzba ligands and one NA ligand, and four oxygen atoms from one 3-tzba ligand and one NA ligand. The Cd–N/O bond lengths fall between 2.223(3)–2.640(3) Å and the N-Cd-N/O bond angles range from 52.32(9) to 175.82(12)°.



**Fig. 2** (a) Ball and stick plot showing the asymmetric unit of compound **2**. All H atoms are omitted for clarity. Symmetry code: a: 0.5 - x, 0.5 + y, z. (b) View of the 1D zigzag chain constructed by the linkage of the Cd(II) centers and 3-tzba ligands along the *c*-axis. (c) View of the 3D supramolecular framework of compound **2** formed by hydrogen bonding.

The bridging 3-tzba ligands adopt two different coordination modes:  $\mu_5$ - $\kappa$ N6: $\kappa$ N7: $\kappa$ N9: $\kappa$ O6: $\kappa$ O7;  $\mu_4$ - $\kappa$ N1: $\kappa$ N2: $\kappa$ N4: $\kappa$ O2: $\kappa$ O3 (Scheme 2, g and h), both of which are also found for the first time in tetrazolate-5-carboxylate compounds. And NA ligands are also involved in two different bridging coordination modes:  $\mu_3$ - $\kappa$ N5: $\kappa$ O4: $\kappa$ O5;  $\mu_3$ - $\kappa$ N10: $\kappa$ O8: $\kappa$ O9 (Scheme 2, i and j).

It is noted that the structure of **4** contains a  $[Cd_3]$  chain which is built by the interconnection Cd(II) ions and 3-tzba ligands (Fig. 4b). When viewed along the *b/c* axis, it is noted that these parallel 1D chains are alternately connected through  $\mu_4/\mu_5$ -3-tzba ligands and  $\mu_3$ -NA ligands. Therefore, an inter-

D-H···A	Distance (D····A)	Angle (D–H···A)
Compound <b>2</b> <sup><i>a</i></sup> C(4)–H(4)···O(2)#1	3.140(6)	165
$C(13)-H(13)\cdots O(2)#2$ Compound 3 <sup>b</sup>	3.401(6)	148
C(6)-H(6)N(3)#1	3.501(8)	160

<sup>*a*</sup> Symmetry codes: #1: 1/2 + x, y, 1/2 - z; #2: 3/2 - x, 1/2 + y, z. <sup>*b*</sup> Symmetry codes: #1: -1/2 + x, 3/2 - y, -1/2 + z.



**Fig. 3** (a) Ball and stick plot showing the asymmetric unit of compound **3**. All H atoms are omitted for clarity. Symmetry code: a: -0.5 + x, 0.5 - y, -0.5 + z; b: 0.5 + x, 0.5 - y, 1 - z. (b) View of the 1D pearl-necklace-like chain constructed from the interconnection of the Cd(II) centers and 3-tzba ligands in the *ab*-plane. (c) View of the 2D supramolecular framework of compound **3** formed by hydrogen bonding.

locked 3D network is produced (Fig. 4c and d). It is difficult to assign a topological network to this structure. Since a series of metal carboxylate coordination frameworks in terms of the packing and interconnection of 1D rods are proposed by Yaghi and O'Keeffe,<sup>24</sup> 4 has a *hxl* type net with Schläfli symbol (3<sup>6</sup>) when the [Cd<sub>3</sub>] chains are regarded as finite "nodes" (Fig. 4e and f).

[CD(3-TZBA)(BIO)] (5). Compound 5 crystallizes in an orthorhombic space group *Pna2*<sub>1</sub>. X-ray crystallographic analysis shows that it is a 3D coordination framework with 1D Cd chains linking the adjacent 3-tzba and BIO ligands. As shown in Fig. 5a, the asymmetric unit of 5 contains one crystallographically independent Cd(II) ions, one 3-tzba ligand and one BIO ligand. The seven-coordinated Cd(II) ion has a slightly distorted monocapped trigonal prism coordination geometries with two nitrogen atoms from two different 3-tzba ligands, and five oxygen atoms from one 3-tzba ligand and three BIO ligands. The bond lengths of Cd-O/N fall between 2.287(3)-2.554(3) Å and the O-Cd-N/O bond angles range from 53.22(10) to  $162.91(11)^{\circ}$ . All bridging 3-tzba ligands involved in μ<sub>3</sub>-κN6:κN7:κO1:κO2 mode (Scheme 2f) and the BIO ligands also show the bridging coordination mode in  $\mu_3$ - $\kappa$ O3: $\kappa$ O4 (Scheme 2k).

It is noted that the adjacent Cd(II) ions are interconnected through the tetrazole group of 3-tzba ligands and the oxygen



**Fig. 4** (a) Ball and stick plot showing the asymmetric unit of compound **4**. All H atoms are omitted for clarity. Symmetry code: a: x, 2.5 - y, -0.5 + z; b: 2 - x, 2 - y, 1 - z; c: x, 1.5 - y, 0.5 + z; d: x, y, -1 + z; e: 1 - x, 2 - y, 1 - z. (b) View of the infinite [Cd<sub>3</sub>] chain for compound **4** constructed from each set of three Cd(II) ions linked by the tetrazole group of 3-tzba ligands in *ac*-plane. (c) View of the 3D coordination framework constructed from 1D [Cd<sub>3</sub>] chains and 3-tzba and NA linkers along the *c*-axis, *b*-axis (d) and *a*-axis (e). The ligands were simplified as lines for clarity. (f) A *hxl* type net when the [Cd<sub>3</sub>] chains are regarded as finite "node".

atom of BIO ligands with Cd<sup>...</sup>Cd separation of around 4.088 Å forming a 1D Cd chain along the *c*-axis. The chains are alternately connected by 3-tzba and BIO ligands generating a 3D framework (Fig. 5b). If the chains are considered as finite four-connected nodes, the whole structure of 5 can also be described as an *sql* net with Schläfli symbol (4<sup>4</sup>) (Fig. 5c).

## Thermal analyses and powder X-ray diffraction (PXRD) measurements

To examine the thermal stabilities of compounds 1–5, the thermogravimetric analyses of these compounds were carried out from 35 to 900 °C at a heating rate of 10 °C min<sup>-1</sup> in dry air atmosphere. As shown in Fig. S4, ESI,<sup>†</sup> compounds 2–5 are stable up to approximately 300 °C, while beyond that, their frameworks start the decomposition of the host network. The first weight loss for compound 1 occurs below 300 °C, corresponding to the loss of free or coordinated water molecules.

Simulated and experimental powder X-ray diffraction (PXRD) patterns of 1–5 are shown in Fig. S5–S9, ESI.† They are in fairly good agreement with the experimental patterns,



**Fig. 5** (a) Ball and stick plot showing the asymmetric unit of compound **5**. All H atoms are omitted for clarity. Symmetry code: a: 0.5 - x, 0.5 + y, -0.5 + z; b: 0.5 + x, 0.5 - y, -1 + z; c: 1.5 - x, 0.5 + y, 0.5 + z; d: -0.5 + x, 0.5 - y, z. (b) View of the 3D coordination framework built from 1D Cd chains linked by the 3-tzba ligands and BIO ligands. (c) An *sql* type net when 1D Cd chains are regarded as finite "node".

which clearly confirms the phase purity of the as-prepared products.

#### Infrared spectroscopy

The FT-IR spectra of compounds 1–5 are similar, the broad absorption bands around 3400 cm<sup>-1</sup> in 1 and 4 are ascribed to the stretching vibrations of O–H, suggesting the presence of free and/or coordinated water molecules. The emergence of peaks 1400–1500 cm<sup>-1</sup> clearly confirms the formation of tetrazole groups.<sup>18</sup> The strong peaks of carboxyl groups in 1–5 appear in the region of 1581–1639 cm<sup>-1</sup> (antisymmetric stretching vibrations) and 1383–1457 cm<sup>-1</sup> (symmetric stretching vibrations). The strong band in 5 at 1693 cm<sup>-1</sup> corresponds to the C=O stretching vibration. No peaks around 1700 cm<sup>-1</sup> are found, illustrating complete deprotonation of the carboxylic acid groups in all compounds.<sup>25</sup>

#### Photoluminescence properties

It is universally acknowledged that many Cd(II) compounds show excellent luminescence properties.<sup>18</sup> Herein, the photoluminescence measurement of all compounds were carried out in the solid state at room temperature. The emission spectra of compounds 1–5 have main peaks at 434, 439, 539, 436 and 451 nm, with the excitation at 372, 376, 382, 346 and 374 nm, respectively (Fig. S10, ESI $\dagger$ ).

There are typical two types of electronic excited state transition: ligand-to-ligand charge transfer (LLCT) and ligand-to-metal charge transfer (LMCT) in Zn<sup>II</sup>/Cd<sup>II</sup> complexes.<sup>26</sup> In order to better understand the room-temperature fluorescent mechanism, Zheng et al. demonstrated the origin of the spectral emissions observed in the spectra of the complexes can be attributed to ligand-centered charge transitions based on the 3-tzba and mixed-ligand base on the theoretical calculated results by evaluation of the density of states (DOS).<sup>13e</sup> From the reported literature, the free 3-H<sub>2</sub>tzba ligands present the photoluminescence emission centered at 407 nm with the excitation at 362 nm at room temperature.<sup>13e</sup> In our case, it is noted that the emission spectra of compound 3 shows a main peak at 539 nm with a shoulder peak at 457 nm excited at 382 nm. The twin peaks appeared in the emission spectra may originate from the mixed-ligand system (3-tzba and 1,10-phen ligands) and supramolecular interactions such as  $\pi$ - $\pi$  stacking and hydrogen bonds interaction, leading to multiple electronic transitions with close transition energies. Compared with the free 3-H2tzba ligands emitted at 407 nm, the fluorescence emission spectra of compounds 1-5 show the fluorescence intensity increased and exhibits a significant red-shift in the emission maximum, which may be ascribed to the cooperative effects of intraligand emission.<sup>27</sup> The variation of photoluminescence may be attributed to the difference of the auxiliary ligands to cadmium metal ions and/ or their local coordination environment.

#### Conclusion

In summary, we have synthesized five new cadmium(II) tetrazole-based coordination polymers using one-pot hydrothermal methods involving the in situ generation of 3-tzba and BIO ligands. The 3-tzba ligand was prepared via the [2 + 3]cycloaddition reaction of 3-cyanobenzonic acid and azide with the aid of Cd(II) salts, while the BIO ligand was obtained via the Schmidt reaction of H<sub>4</sub>bta and azide. These experimental results demonstrate in situ ligand synthesis under solvo/ hydrothermal conditions can generate new ligands and unexpected structures, which cannot be obtained by the direct reaction of metal salts and ligands under normal conditions. Undoubtedly, in situ metal-ligand reactions open a new avenue for the construction of new metal-organic compounds under a solvo/hydrothermal condition. In addition, by the absence of an auxiliary ligand, compound 1 produces a 3D molecular configuration exhibiting a *pcu*  $(4^{12} \cdot 6^3)$  topology. With the introduction of bidentate 2,2'-bipyridine and 1,10phenanthroline, both compounds 2 and 3 exhibit 1D frameworks, while by the addition of bridging NA and H<sub>4</sub>bta ligands compounds 4 and 5 show 3D structures featuring the hxl (3<sup>6</sup>) and sql (4<sup>4</sup>) topologies, respectively. These results indicated that the introduction of appropriate secondary ligands cannot only control synthesis of the different dimension crystal structures but also generate versatile tetrazole-based MOFs.

This work was supported by the National Natural Science Foundation of China (21171060).

#### References

Paper

- (a) M. Dincă, W. S. Han, Y. Liu, A. Dailly, C. M. Brown and J. R. Long, Angew. Chem., Int. Ed., 2007, 46, 1419; (b) F. Nouar, J. F. Eubank, T. Bousquet, L. Wojtas, M. J. Zaworotko and M. Eddaoudi, J. Am. Chem. Soc., 2008, 130, 1833; (c) T. M. Klapotke and J. Stierstorfer, J. Am. Chem. Soc., 2009, 131, 1122; (d) W. Quellette, A. V. Prosvirin, K. Whitenake, K. R. Dunbar and J. Zubieta, Angew. Chem., Int. Ed., 2009, 48, 2140; (e) X. M. Zhang, J. Lv, F. Ji, H. S. Wu, H. Jiao and P. R. Schleyer, J. Am. Chem. Soc., 2011, 133, 4788.
- 2 J. A. Bladin and B. Dtsch, Chem. Geol., 1885, 18, 1544.
- 3 (a) V. A. Ostrovskii and A. O. Koren, *Heterocycles*, 2000, 53, 1421; (b) M. M. Harding and G. Mokdsi, *Curr. Med. Chem.*, 2000, 7, 1289; (c) T. Y. Luo, H. L. Tsai, S. L. Yang, Y. H. Liu, R. D. Yadav, C. C. Su, C. H. Ueng, L. G. Lin and K. L. Lu, *Angew. Chem., Int. Ed.*, 2005, 44, 6063; (d) M. Dincă and J. R. Long, *J. Am. Chem. Soc.*, 2007, 129, 11172.
- 4 (a) Z. P. Demko and K. B. Sharpless, J. Org. Chem., 2001, 66, 7945; (b) Z. P. Demko and K. B. Sharpless, Org. Lett., 2001, 3, 4091; (c) Z. P. Demko and K. B. Sharpless, Angew. Chem., Int. Ed., 2002, 12, 2110; (d) F. Himo, Z. P. Demko, L. Noodleman and K. B. Sharpless, J. Am. Chem. Soc., 2002, 124, 12210; (e) F. Himo, Z. P. Demko, L. Noodleman and K. B. Sharpless, J. Am. Chem. Soc., 2003, 125, 9983.
- 5 (a) H. Zhao, Z. R. Qu, H. Y. Ye and R. G. Xiong, Chem. Soc. Rev., 2008, 37, 84; (b) R. G. Xiong, X. Xue, H. Zhao, X. Z. You, B. F. Abrahams and Z. L. Xue, Angew. Chem., Int. Ed., 2002, 41, 3800; (c) X. Xue, X. S. Wang, L. Z. Wang, R. G. Xiong, B. F. Abrahams, X. Z. You, Z. L. Xue and C. H. Che, Inorg. Chem., 2002, 41, 6544; (d) X. S. Wang, Y. Z. Tang, X. F. Huang, Z. R. Qu, C. M. Che, W. H. Chan and R. G. Xiong, Inorg. Chem., 2005, 44, 5278; (e) L. Z. Wang, Z. R. Qu, Z. R. Zhao, H. Zhao, X. S. Wang, R. G. Xiong and Z. Xue, Inorg. Chem., 2003, 42, 3969.
- 6 (a) W. Ouellette and J. Zubieta, Chem. Commun., 2009, 4533; (b) Y. L. Yao, L. Xue, Y. X. Che and J. M. Zheng, Cryst. Growth Des., 2009, 9, 606; (c) M. Li, Z. Li and D. Li, Chem. Commun., 2008, 3390; (d) X. M. Zhang, T. Jiang, H. S. Wu and M. H. Zeng, Inorg. Chem., 2009, 48, 4536; (e) J. Y. Zheng, A. L. Cheng, Q. Sun, Q. Yue and E. Q. Gao, Cryst. Growth Des., 2010, 10, 2908; (f) P. Cui, Z. Chen, D. L. Gao, B. Zhao, W. Shi and P. Cheng, Cryst. Growth Des., 2010, 10, 4370; (g) W. C. Song, Q. H. Pan, P. C. Song, Q. Zhao, Y. F. Zeng, T. L. Hu and X. H. Bu, Chem. Commun., 2010, 46; (h) Y. H. Lu, Coord. Chem. Rev., 2003, 327.
- 7 (a) M. Dincă, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann and J. R. Long, *J. Am. Chem. Soc.*, 2006, **128**, 16876; (b) M. Dincă, W. S. Han, Y. Liu, A. Dailly, C. M. Brown and J. R. Long, *Angew. Chem., Int. Ed.*, 2007, **46**, 1419; (c) S. Horike, M. Dincă, K. Tamaki and J. R. Long, *J. Am. Chem. Soc.*, 2008, **130**, 5854.
- 8 W. Ouellette, A. V. Prosvirin, K. Whitenack, K. R. Dunbar and J. Zubieta, *Angew. Chem., Int. Ed.*, 2009, **48**, 2140.

- 9 J. R. Li, Y. Tao, Q. Yu, X. H. Bu, H. Sakamoto and S. Kitagawa, *Chem.-Eur. J.*, 2008, **14**, 2771.
- 10 Y. C. Qiu, H. Deng, J. X. Mou, S. H. Yang, M. Zeller, S. R. Batten, H. H. Wu and J. Li, *Chem. Commun.*, 2009, 5415.
- 11 (a) S. Takamizawa, E. Nakata, T. Akatsuka, R. Miyake, Y. Kakizaki, H. Takeuchi, G. Maruta and S. Takeda, J. Am. Chem. Soc., 2010, 132, 3783; (b) Q. Li, C. H. Sue, S. Basu, A. K. Shveyd, W. Zhang, G. Barin, L. Fang, A. A. Sarjeant, J. F. Stoddart and O. M. Yaghi, Angew. Chem., Int. Ed., 2010, 49, 6751; (c) S. T. Zheng, T. Wu, J. Zhang, M. Chow, R. A. Nieto, P. Y. Feng and X. H. Bu, Angew. Chem., Int. Ed., 2010, 49, 5362; (d) P. K. Allan, B. Xiao, S. J. Teat, J. W. Knight and R. E. Morris, J. Am. Chem. Soc., 2010, 132, 3605; (e) S. Bureekaew, W. Sato, R. Matsuda, Y. Kubota, R. Hirose, J. Kim, K. Kato, M. Takata and S. Kitagawa, Angew. Chem., Int. Ed., 2010, 49, 7660; (f) J. Rinck, G. Novitchi, W. V. D. Heuvel, L. Ungur, Y. Lan, W. Wernsdorter, C. E. Anson, L. F. Chibotaru and A. K. Powell, Angew. Chem., Int. Ed., 2010, 49, 7583; (g) D. Yuan, D. Zhao, D. Sun and H. C. Zhou, Angew. Chem., Int. Ed., 2010, 49, 5357.
- 12 (a) D. C. Zhong, W. X. Zhang, F. L. Cao, L. Jiang and T. B. Lu, Chem. Commun., 2011, 47, 1204; (b) D. C. Zhong, M. Meng, J. Zhou, G. Y. Yang and T. B. Lu, Chem. Commun., 2010, 46, 4354; (c) F. He, M. L. Tong, X. L. Yu and X. M. Chen, Inorg. Chem., 2005, 44, 559; (d) Q. Yu, X. Q. Zhang, H. D. Bian, H. Liang, B. Zhao, S. P. Yan and D. Z. Liao, Cryst. Growth Des., 2008, 8, 1140; (e) J. Tao, Y. F. Zhao and X. M. Zhang, Inorg. Chem. Commun., 2007, 10, 1194; (f) Z. P. Yu, Y. Xie, S. J. Wang, G. P. Yong and Z. Y. Wang, Inorg. Chem. Commun., 2008, 11, 372; (g) G. W. Yang, Q. Y. Li, Y. Zhou, P. Sha, Y. S. Ma and R. X. Yuan, Inorg. Chem. Commun., 2008, 11, 723.
- 13 (a) M. F. Wu, M. S. Wang, S. P. Guo, F. K. Zheng, H. F. Chen, X. M. Jiang, G. N. Liu, G. C. Guo and J. S. Huang, Cryst. Growth Des., 2011, 11, 372; (b) M. F. Wu, F. K. Zheng, A. Q. Wu, Y. Li, M. S. Wang, W. W. Zhou, F. Chen, G. C. Guo and J. S. Huang, CrystEngComm, 2010, 12, 260; (c) Q. Y. Chen, Y. Li, F. K. Zheng, W. Q. Zou, M. F. Wu, G. C. Guo, A. Q. Wu and J. S. Huang, Inorg. Chem. Commun., 2008, 11, 969; (d) Y. Li, G. Xu, W. Q. Zou, M. S. Wang, F. K. Zheng, M. F. Wu, H. Y. Zeng, G. C. Guo and J. S. Huang, Inorg. Chem., 2008, 47, 7945; (e) F. Chen, W. F. Wu, G. N. Liu, M. S. Wang, F. K. Zheng, C. Yang, Z. N. Xu, Z. F. Liu, G. C. Guo and J. S. Huang, Eur. J. Inorg. Chem., 2010, 4982; (f) M. F. Wu, F. K. Zheng, G. Xu, A. Q. Wu, Y. Li, H. F. Chen, S. P. Guo, F. Chen, Z. F. Liu, G. C. Guo and J. S. Huang, Inorg. Chem. Commun., 2010, 13, 250.
- 14 (a) Q. X. Jia, H. Tian, L. Yan, Y. Ma and E. Q. Gao, *Inorg. Chim. Acta*, 2010, 363, 3750; (b) Q. X. Jia, Y. Q. Wang, Q. Yue, Q. L. Wang and E. Q. Gao, *Chem. Commun.*, 2008, 4894; (c) Q. X. Jia, W. W. Sun, C. F. Yao, H. H. Wu, E. Q. Gao and C. M. Liu, *Dalton Trans.*, 2009, 2721; (d) Q. X. Jia, X. B. Qian, H. H. Wu, Q. L. Wang and E. Q. Gao, *Inorg. Chim. Acta*, 2009, 362, 2213.
- 15 (a) Y. W. Li, W. L. Chen, Y. H. Wang, Y. G. Li and E. B. Wang, *J. Solid State Chem.*, 2009, 182, 736; (b) H. Zhao, Q. Ye, Q. Wu, Y. J. Liu and R. G. Xiong, *Z. Anorg. Allg. Chem.*, 2004, 630, 1367.
- 16 (a) D. S. Liu, X. H. Huang, C. C. Huang, G. S. Huang and J.
   Z. Chen, J. Solid State Chem., 2009, 182, 1899; (b) E.

C. Yang, Y. Feng, Z. Y. Liu, T. Y. Liu and X. J. Zhao, *CrystEngComm*, 2011, 13, 230; (c) D. S. Liu, Y. Sui, C. C. Huang, T. H. Pan, X. H. Huang, J. Z. Chen and X. Z. You, *Inorg. Chem. Commun.*, 2010, 13, 762; (d) L. Ma, Y. C. Qiu, G. Peng, J. B. Cai and H. Deng, *Eur. J. Inorg. Chem.*, 2011, 3446.

- 17 (a) H. Deng, Y. C. Qiu, Y. H. Li, Z. H. Liu, R. H. Zeng, M. Zeller and S. R. Batten, *Chem. Commun.*, 2008, 2239; (b)
  Y. C. Qiu, Y. H. Li, G. Peng, J. B. Cai, L. M. Jin, L. Ma, H. Deng, M. Zeller and S. R. Batten, *Cryst. Growth Des.*, 2010, 10, 1332; (c) B. Liu, Y. C. Qiu, G. Peng and H. Deng, *CrystEngComm*, 2010, 12, 270; (d) L. Sun, L. Ma, J. B. Cai, L. Liang and H. Deng, *CrystEngComm*, 2012, 14, 890; (e)
  L. Ma, Y. C. Qiu, G. Peng, J. B. Cai and H. Deng, *Eur. J. Inorg. Chem.*, 2011, 3446; (f) L. Liang, G. Peng, L. Ma, L. Sun, H. Deng, H. Li and W. S. Li, *Cryst. Growth Des.*, 2012, 12, 1151.
- 18 (a) L. Yi, B. Ding, P. Cheng, D. Z. Liao, S. P. Yan and Z. H. Jiang, *Inorg. Chem.*, 2004, 43, 33; (b) Y. L. Yao, L. Xue, Y. X. Che and J. M. Zheng, *Cryst. Growth Des.*, 2009, 9, 606; (c) B. Liu, Y. C. Qiu, G. Peng, L. Ma, L. M. Jin, J. B. Cai and H. Deng, *Inorg. Chem. Commun.*, 2009, 12, 1e.
- 19 (a) Bruker, APEXII software, Version 6.12, Bruker AXS Inc, Madison, Wisconsin, USA, 2004; (b) G. M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997; (c) G. M. Sheldrick, Acta Crystallogr., 2008, A64, 112.
- 20 (a) X. M. Chen and M. L. Tong, Acc. Chem. Res., 2007, 40, 162; (b) X. M. Zhang, Coord. Chem. Rev., 2005, 249, 1201.

- 21 X. X. Hu, J. Q. Xu, P. Cheng, X. Y. Chen, X. B. Cui, J. F. Song, G. D. Yang and T. G. Wang, *Inorg. Chem.*, 2004, 43, 2261.
- 22 (a) K. F. Schmidt, Angew. Chem., 1923, 36, 511; (b) J. H. Boyer and J. Hamer, J. Am. Chem. Soc., 1955, 77, 951; (c) J. Aube and G. L. Milligan, J. Am. Chem. Soc., 1991, 113, 8965; (d) P. A. S. Smith, J. Am. Chem. Soc., 1950, 72, 3718; (e) W.H. Pearson, R. Walavalkar, J. M. Schkeryantz, W. K. Fang and J. D. Blickensdorf, J. Am. Chem. Soc., 1993, 115, 10183; (f) S. K. Datta, C. Grundmann and N. K. Bhattachaerra, J. Chem. Soc., 1970, 2058.
- 23 (a) S. L. Li, K. Tan, Y. Q. Lan, J. S. Qin, M. N. Li, D. Y. Du, H. Y. Zang and Z. M. Su, *Cryst. Growth Des.*, 2010, 10, 1699; (b)
  L. L. Liang, S. B. Ren, J. Zhang, Y. Z. Li, H. B. Du and X. Z. You, *Cryst. Growth Des.*, 2010, 10, 1307; (c) Z. Su, M. S. Chen, J. Fan, M. Chen, S. S. Chen, L. Luo and W. Y. Sun, *CrystEngComm*, 2010, 12, 2040; (d) S. T. Zheng, T. Wu, J. Zhang, M. Chow, R. A. Nieto, P. Y. Feng and X. H. Bu, *Angew. Chem., Int. Ed.*, 2010, 49, 5362; (e) P. D. Frischmann, G. A. Facey, P. Y. Ghi, A. J. Gallant, D. L. Bryce, F. Lelj and M. J. Maclachlan, *J. Am. Chem. Soc.*, 2010, 132, 3893; (f) Q. L. Zhu, T. L. Sheng, R. B. Fu, C. H. Tan, S. M. Hu and X. T. Wu, *Chem. Commun.*, 2010, 46, 9001.
- 24 N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe and O. M. Yaghi, J. Am. Chem. Soc., 2005, 127, 1504.
- 25 L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1958.
- 26 S. L. Zheng and X. M. Chen, Aust. J. Chem., 2004, 57, 703.
- 27 X. W. Wang, J. Z. Chen and J. H. Liu, *Cryst. Growth Des.*, 2007, 7, 1227.