Formation of a new 1D coordination polymer by *in situ* ligand reaction of 2,4,6-tris(pyrazol-1-yl)-1,3,5-s-triazine

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Solvothermal reactions of $Zn(NO_3)_2\cdot 6H_2O$, 1,4-benzenedicarboxylic acid (H_2BDC) and 2,4,6-tris(pyrazol-1-yl)-1,3,5-s-triazine, yielded a new coordination polymer $[Zn(BDC)(pz)\cdot H_2O]_n$ (pz= pyrazole). The *in situ* methanolysis reaction of 2,4,6-tris(pyrazol-1-yl)-1,3,5-s-triazine with pyrazole and 2,4,6-trismethoxy-1,3,5-triazine was confirmed by their single-crystal structures. $[Zn(BDC)(pz)\cdot H_2O]_n$ was characterised by elemental analysis, IR, powder X-ray diffraction, photoluminescence and thermogravimetric analyses.

Keywords: *in situ* ligand reaction, benzenedicarboxylic acid, crystal structure, 2,4,6-trismethoxy-1,3,5-triazine

The design and construction of metal–organic frameworks (MOFs) has attracted attention because of their applications in gas storage and separation,[1–3] catalysis,[4–6] ion exchange[7–9] and sensors.[10] Particularly, novel MOFs with *in situ* generated ligands (especially those that are inaccessible by direct preparation) have attracted considerable attention both in coordination and organic chemistry. Many metal–ligand reactions have been found and used to generate a large number of coordination polymers.[11–15] We can obtain some unexpected structures and explain some organic synthesis phenomenon directly by solving their signal crystal structures. The triazine derivative ligand can be easily substituted by the nucleopilic reagent. Other papers have focused on MOFs based on the triazine ligand.[16]

Here we report a new 1D coordination polymer $[Zn(BDC)(pz)\cdot H_2O]_n$ constructed by the reactions of 1,4-benzenedicarboxylic acid and 2,4,6-tris(pyrazol-1-yl)-1,3,5-s-triazine with $Zn(NO_3)_2\cdot 6H_2O$. Interestingly, 2,4,6-tris(pyrazol-1-yl)-1,3,5-s-triazine was found to be in the *in situ* methanolysis reaction to pyrazole ligand. Fortunately, both of the two main productions signal crystals $[Zn(BDC)(pz)\cdot H_2O]_n$ (**1**) (BDC= 1,4-benzenedicarboxylic acid, pz= pyrazole) and 2,4,6-trismethoxy-1,3,5-triazine (**2**) were collected.

Experimental

IR spectra were measured from KBr pellets on a Nicolet Avatar 370 Fourier Transform IR spectrometer; Powder X-ray diffraction(PXRD) on a Bruker AXS D8-Focus. C, H, N analyses were carried out with a Finnigan EA1112 element analyser. Thermogravimetric analyse (TGA) was carried out in a nitrogen stream using Seiko Extar 6000 TG/DTA equipment with a heating rate of 10 °C·min^{-1}. All reagents were purchased commercially and used without further purification. 2,4,6-Tris(pyrazol-1-yl)-1,3,5-s-triazine was prepared according the literature,[17] MS, *m/z*=280.10 (M^+), m.p. 240–243 °C (lit.[17] 288–289 °C).

Synthesis

A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.1 mmol, 0.020 g), 1,4-benzenedicarboxylic acid (0.1 mmol, 0.015), 2,4,6-tris(pyrazol-1-yl)-1,3,5-s-triazine (0.1 mmol, 0.047 g) and 12ml water/CH_3OH (V/V=1:1) was stirred for 20 min in air. The mixture was then transferred to a 23 mL Teflon reactor and kept at 120°C for 3 days under autogenous pressure, and then cooled to room temperature at a rate of 5 °C h^{-1}. Colourless crystals of **1** were obtained with a yield of 60% based on Zn. IR spectrum (ν, cm^{-1}): 3420 s, 3072 m, 1604 s, 1580 s, 1572 s, 1497 m, 1418 s, 1397 w, 1173 w, 1167 m, 1142s, 840 m, 779 s, 712 m. Anal. Calcd for $C_{11}H_9N_2O_5Zn$: C, 42.00; H, 2.88; N, 8.90. Found: C, 41.59; H, 2.80; N, 9.01%. Crystals of compound **2** with different shapes can be separated under a microscope, m.p. 90–93 °C, IR spectrum (ν, cm^{-1}): 1544, 1511, 1496, 1388, 1305, 1258.

Crystallography

Suitable single crystal for **1** and **2** were selected for single-crystal XRD analysis. All the single-crystal XRD data were collected on a Bruker Apex CCD area-detector diffractometer with Mo-Ka radiation at 293(2) K. The structures were resolved by a direct method and refined by full-matrix least-squares procedure on F^2 using the SHELXL-97 program.[18] All hydrogen atoms were placed geometrically and anisotropic thermal parameters were used to refine all non-hydrogen atoms of the frameworks. Crystallographic parameters are listed in Table 1.

Crystallographic data for the structural analysis of compound **1** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 866545. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union road, Cambridge, CB21EZ, UK(fax:+44 1223 336-033; E-mail: deposit@ccdc.cam.ac.ukor www: http://www.ccdc.cam.ac.uk).

Table 1 Crystallographic data and collection parameters of compounds **1** and **2**

Compound	1	2
Empirical formula	$C_{11}H_9N_2O_5Zn$	$C_6H_9N_3O_3$
Formula weight	314.57	171.16
Crystal system	Monoclinic	Orthorhombic
Space group	P2(1)/n	Pnma
a (Å)	8.2004(18)	8.4648(18)
b (Å)	9.065(2)	6.7047(14)
c (Å)	16.074(4)	14.373(3)
α (°)	90	90
β (°)	93.925(3)	90
γ (°)	90	90
Volume (Å3)	1192.1(5)	815.7(3)
Z	4	4
Density (calculated) (Mg m^{-3})	1.753	1.394
Absorption coefficient (mm^{-1})	2.078	0.113
F(000)	636	360
Crystal size (mm^3)	0.20 x 0.10 x 0.10	0.28 x 0.27 x 0.26
Theta range for data collection (°)	2.54 to 26.00	2.79 to 25.99
Index ranges	$-10\leq h\leq 9$, $-11\leq k\leq 10$, $-19\leq l\leq 17$	$-10\leq h\leq 10$, $-8\leq k\leq 7$, $-17\leq l\leq 17$
Reflections collected	7517	4314
Independent reflections	2324 [R(int) = 0.0233]	875 [R(int) = 0.0228]
Max. and min. transmission	0.8191 and 0.8191	0.9712 and 0.9690
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data/restraints/ parameters	2324/3/179	875/0/75
Goodness-of-fit on F^2	1.226	1.144
Final R indices [I>2sigma(I)]	$R^1 = 0.0297$, $wR^2 = 0.0933$	$R^1 = 0.0574$, $wR^2 = 0.1189$
R indices (all data)	$R^1 = 0.0341$, $wR^2 = 0.1043$	$R^1 = 0.0628$, $wR^2 = 0.1261$
Largest diff. peak and hole (e Å^{-3})	0.470 and –0.556	0.448 and –0.630

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Table 2 Selected bond lengths [Å] and angles [°] for compound **1**

Zn(1)–O(3)	1.9617(19)	Zn(1)–O(5)	1.981(2)
Zn(1)–N(1)	2.012(2)	Zn(1)–O(1)	2.029(2)
O(3)–Zn(1)–O(5)	112.56(9)	O(3)–Zn(1)–O(1)	93.75(8)
O(3)–Zn(1)–N(1)	98.83(10)	O(5)–Zn(1)–O(1)	114.49(9)
O(5)–Zn(1)–N(1)	109.90(9)	N(1)–Zn(1)–O(1)	124.30(9)

Results and discussion

The presence of the characteristic absorptions at 1580 and 1397 cm^{-1}; contribute to the COO$^-$ anti-stretching vibration and stretching vibration. The ORTEP view of the compound **1** with the atomic numbering scheme is presented in Fig. 1. The asymmetric unit of compound **1** consists of one independent Zn centre, a BDC ligand, one pz ligand and one coordinate

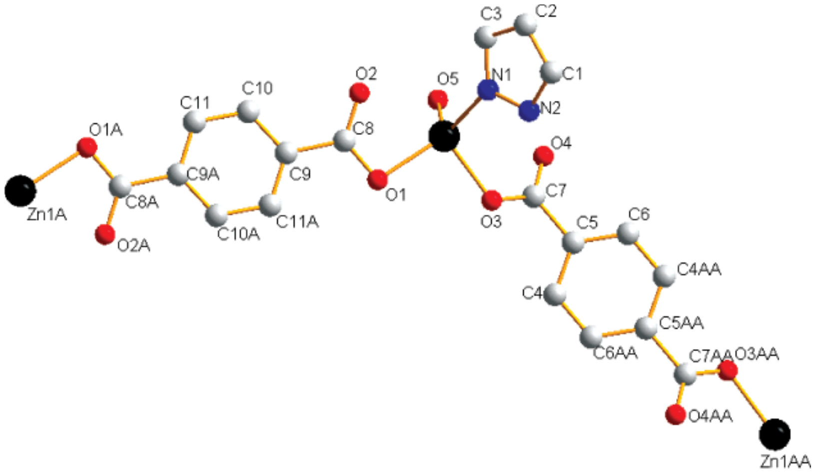


Fig. 1 ORTEP view of **1** with the atomic numbering. (A: 1–*x*, 1–y, 2–*z*; AA: 2–*x*, –1–*y*, 2–*z*).

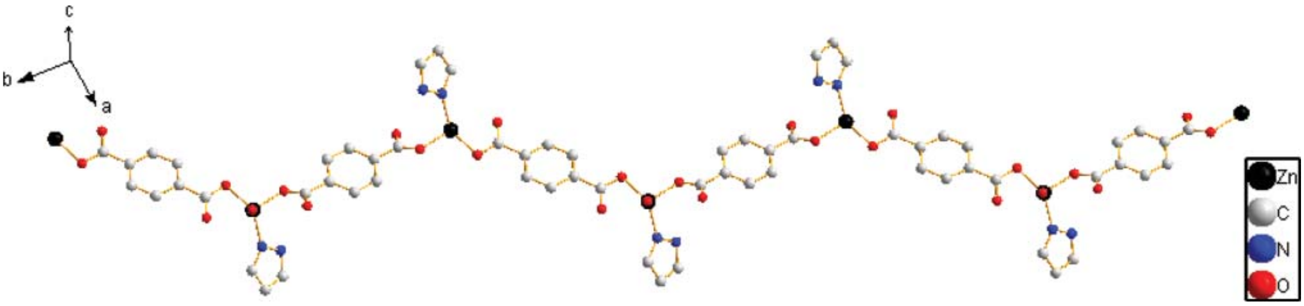


Fig. 2 1D chain structure of **1**.

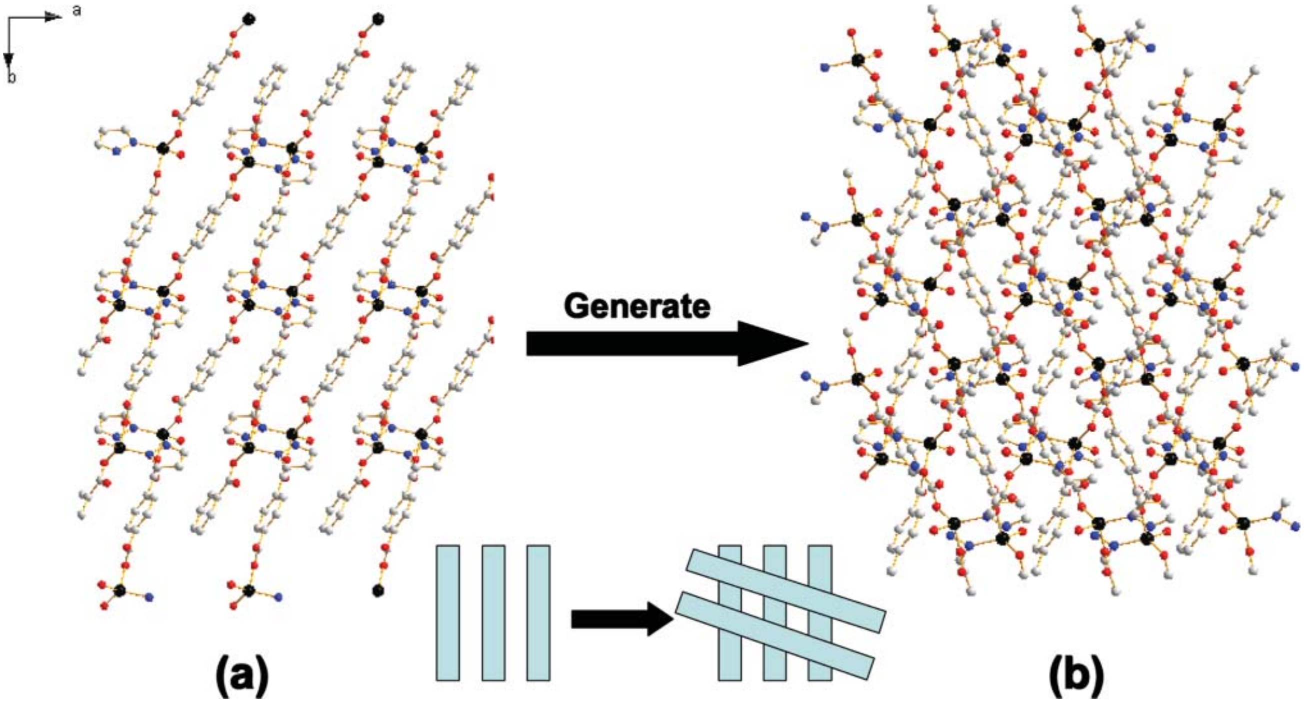


Fig. 3 Crystal packing of **1**.

water molecule. The Zn atom is four-coordinated by two carboxylate oxygen atoms from two different BDC^{2-} ligands, one water oxygen atoms and one nitrogen atom from the pz ligand with the distorted tetrahedral coordination geometry. The distances between Zn atom and coordinated oxygen atoms are in the range 1.9620–2.029 Å. Selected bond lengths and bond angles are given in Table 2. Each BDC^{2-} ligand connected to two Zn atom in monodentate coordination or fashion, formed a 1D zigzag chain (Fig. 2).

Hydrogen bonds displayed interesting interactions in the compound. The neighbouring zigzag chains connect to each other through the hydrogen bond, generated 2D layer. The 2D layers are linked by hydrogen bonds to give rise to 3D structure through an ABAB model, which further stabilises this supramolecular network (Fig. 3). PXRD is consistent with the simulated pattern based on the XRD analysis. The experimental XRD patterns match with the calculated lines from the crystal structure (Fig. 4).

Figure 5 is the ORTEP view of compound **2**. Scheme 1 shows the possible mechanism of this reaction. Compound **2** was isolated in the mixed productions. Single-crystal X-ray diffraction shows that the compound **2** is 2,4,6-trimethoxy-1,3,5-triazine, the structure has been previously reported by Krygowski[19] and Zhou[17]. Compounds **2** indicate that Zn^{2+} can act as a catalyst in certain nucleophilic substitution reactions.

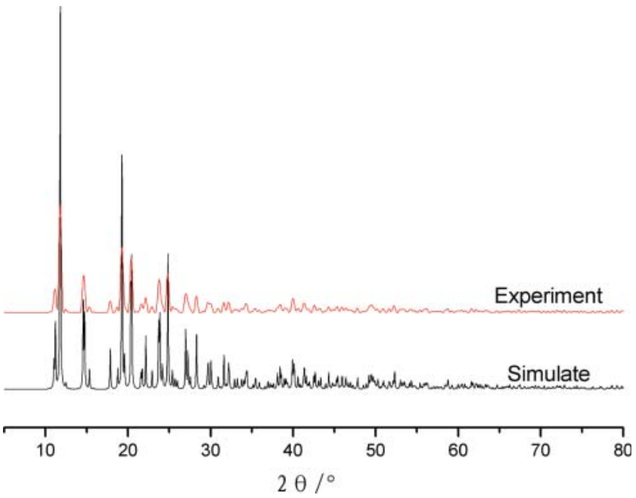


Fig. 4 PXRD of 1, black represent the simulated, red represent the experiment.

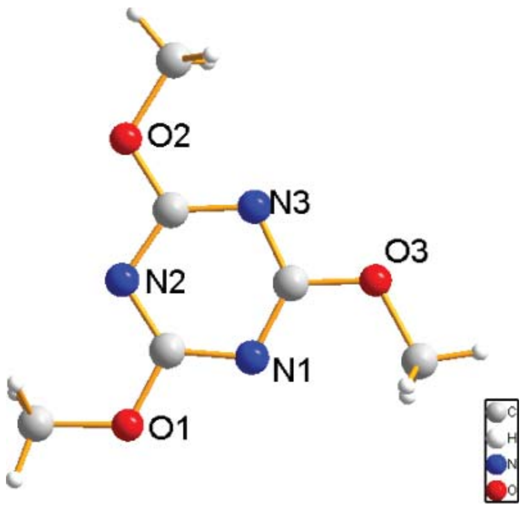
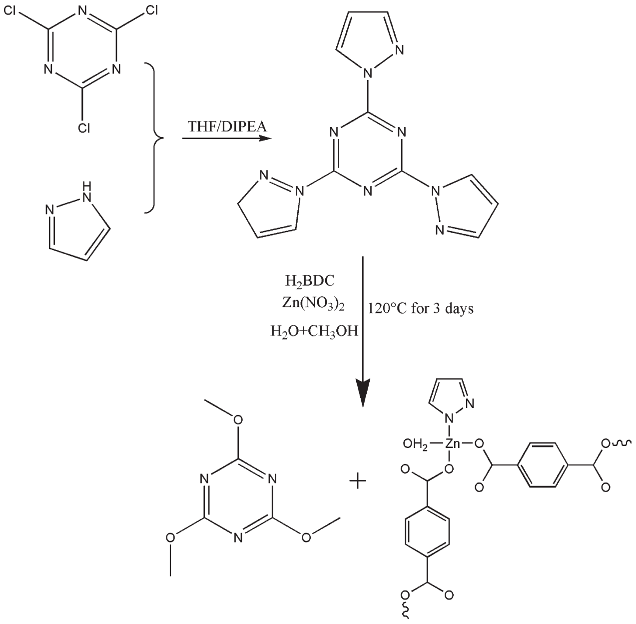


Fig. 5 ORTEP view of **2** with the atomic numbering.

Zhou suggested that we must avoid using a nucleophilic reagent (like methanol or alcohol) as the solvents. If the ligand were a "slow release formulation", small ligands could be released slowly into the MOFs. Using pz and H_2BDC with Zn^{2+}, it is not easy to obtain compound **1**. Pz ligand will coordinate to Zn^{2+} rapidly, so no other coordination site could connect with BDC^{2-}. This phenomenon demonstrates the advantage of *in situ* ligand reactions in building some MOFs.

Photoluminescence spectra and TG analysis

As compound **1** is a hybrid inorganic–organic coordination polymer with d^{10} metal centres, the photoluminescence spectra of the compound 1 in the solid state was measured at room temperature (Fig. 6), absorptions were observed at 359 nm may be tentatively assigned to a ligand-to-metal charge transfer (LMCT) process. This phenomenon suggests that compound **1** may be a new material which may have implications for the design and implementation of fluorescent sensors for studies of Zn^{2+}.



Scheme 1 The mechanism of the reaction.

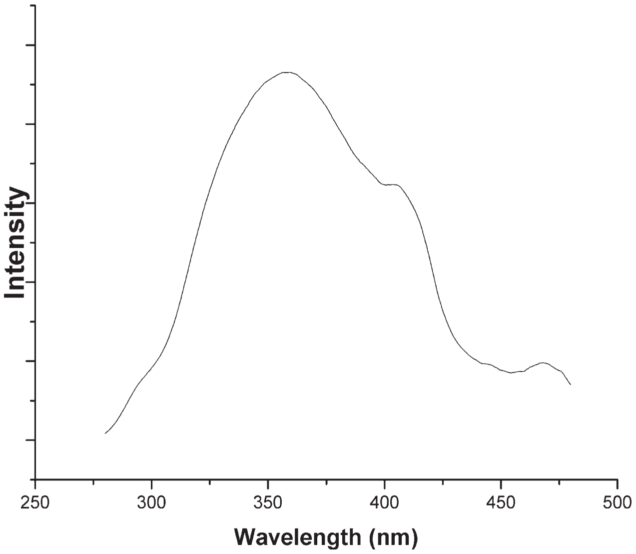


Fig. 6 Fluorescent emission spectra of compound **1**.

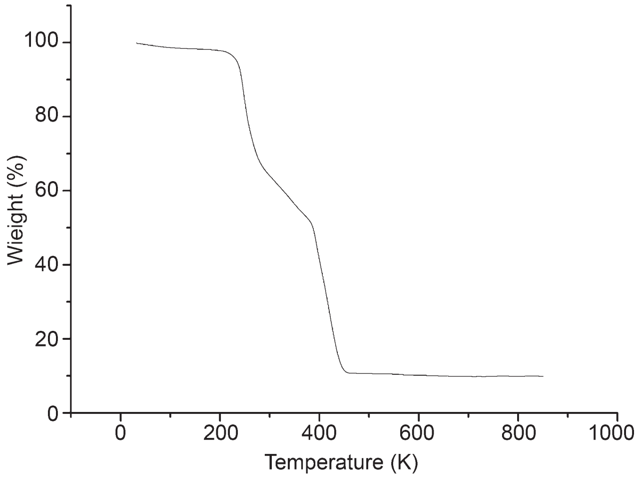


Fig. 7 The TGA curve for compound **1**.

The TGA curve for compound **1** shows that there is a weight loss of 4.2% between 29 and 230 °C, which corresponds to the water molecule (calcd 5.5%). The TGA curve exhibits the continuous weight loss stages in the temperature range 260-465 °C (Fig. 7), corresponding to the release of the coordinated ligand. The remaining weight of 11.0% corresponds to the percentage (calcd 13.7%) of Zn and O components, indicating that the final product is ZnO.

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