Unprecedented trinodal four-connected FRL MOF based on mixed ligands†

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The hydrothermal reaction of Zn(OAc)2·2H2O, H3btc, and 4-bpo affords a novel trinodal four-connected frl topology coordination polymer, [Zn4(btc)2(4-bph)(H2O)4]·2n(H2O) (4-bphH2, in situ synthesized) (1), which exhibits reversible two-step dehydration–dehydration.

Metal–organic frameworks (MOFs) with mineral topologies have been widely explored in the past decade.1,2 However, as the natural choice for porous materials, the topologies of zeolites are still very difficult to realize in MOFs. In order to recreate MOFs with more extensive zeolitic topologies, understanding the key factors that influence the formation of extensive zeolitic structures is crucial. Among all kinds of topologies, MOFs with four-connected topologies are the one type mostly investigated.3–6 Generally, square planar nodes prefer to assemble into a 2D (4, 4) square net rather than the less common 3D NbO (6482-a), CdSO4 (658), quartz (6482-b), and zeolite related nets. In addition, there are a number of nets containing more than one type of node, such as the PIS (48°) net which contains equal numbers of tetrahedral and square-planar nodes.7,8 Trinodal four-connected nodal nets have been reported less, most of which are self-penetrating networks.9,10 frl is one of the tetrahedral topology not occurring in zeolites, which contains two different kinds of nodes. Previous work from Yaghi et al. have enumerated the possible frl net based on rod-shaped secondary building units.11 Only a few examples of frl topology have been reported in the ZIFs (zeolitic imidazolate frameworks) structures according to the known literature.12

On the other hand, derived from the known literature,13,14 it may be expected to generate a multidentate ligand N,N'-bis(4-picolinoyl) hydrazine (4-bphH2) utilizing an hydrolysis reaction of 2,5-bis(4-pyridyl)-1,3,4-oxadiazole) (4-bpo) with the aid of acid under hydrothermal conditions. As a versatile ligand, 4-bphH2 may function as a four-connect ligand through pyridyl and acylamide groups.

Herein, we report the first successful isolation and characterization of a MOF, containing the mixed carboxylate ligands btcH+: H3btc = 1,3,5-benzenetricarboxylic acid) and an in situ synthesized 4-bphH2 ligand, [Zn4(btc)2(4-bph)(H2O)4]·2n(H2O) (1), which displays non-interpenetrated trinodal four-connected frl topology (4·6*), (6·6*). It is noticeable that 1 can undergo reversible dehydration–dehydration of both guest water molecules and coordinated water molecules, respectively, in two steps, which can be relevant for sensing devices.15–17

Hydrothermal reaction of Zn(OAc)2·2H2O with 4-bpo and H3btc in the molar ratio of 4:2:1 at 160 °C (72h) gives colorless block crystals I in an approximate 65% yield. The 4-bphH2 ligands, which can exist either in the keto form, enol form I or enol form II, were in situ generated from the starting materials 4-bpo via a hydrolysis reaction along with the ring-opening of the oxadiazole ring (Scheme 1). The bulk purities of the product were confirmed from elemental analyses and powder X-ray diffraction (PXRD) measurements.

![Scheme 1](image-url)

Scheme 1 In situ hydrothermal synthesis of 4-bphH2 and its three different isomers.

Single crystal X-ray analysis has revealed that compound 1 crystallizes in the triclinic space group P-1. As shown in Fig. 1, there are two independent Zn(II) atoms: Zn1 is coordinated by three oxygen atoms from different bdc2- ligands and one pyridyl nitrogen atom to give the distorted tetrahedral geometry, and Zn2 is five-coordinated by one hydrazide nitrogen atom N2a from 4-bph2- ligand and four oxygen atoms to show a trigonal bipyramidal geometry, of the four oxygen atoms, O2 from btc2-, O8, O9 from two water molecules, and O7d from a carbonyl oxygen atom of 4-bph2- ligand.

In compound 1, the btc2- anion is completely deprotonated and coordinates to four Zn centers (three Zn1 centers, one Zn2 center). The deprotonated ligand 4-bph2- displays a μ2 coordination mode (Fig. S1, See ESI†). The two Zn2 cations are chelated by the
acylamino groups of the 4-bph ligand to form a binuclear unit of \([\text{Zn}_2\text{(4-bph)}]\) (Fig. 2a) with a Zn–Zn distance 4.907(2) Å. Each binuclear Zn2 unit is regarded as planar 4-connected to two btc\(^{-}\) anions and two Zn1 centers through Zn2 centers and pyridyl nitrogen atoms separately. The C15–O7 bond distance is 1.287(4) Å, which is shorter than 1.43 Å for a C–O single bond and longer than 1.22 Å for a C=O double bond. The C15–N2 (1.300 (4) Å) bond length is close to a C=N double bond (C=N, 1.28 Å). It indicates the bph\(^{2-}\) adopts the enol form I with a certain degree of delocalization of the negative charge of the enolate atoms O7 and O7a along the hydrazone skeleton \([\text{C15} = \text{N2} – \text{N2a} = \text{C15a}]\) and then participates in bonding. The enol form I of bph\(^{2-}\) is also confirmed by the absence of a band in the range of 1640–1680 cm\(^{-1}\) of the IR spectra. As shown in Fig. 2, the binuclear unit \([\text{(Zn2)}_2\text{(4-bph)}]\) has a square planar geometry, while the Zn1 and btc\(^{-}\) anions have a distorted tetrahedral geometry. The overall 3D network can be simplified to a trinodal 4-connected \((4^2\cdot 6^3\cdot 8^3)\) frl topology (Fig. 3). Two kinds of 1D channels are observed along the c axis in the 3D framework of I. The diameter of the largest sphere that will pass through the pore \(d_h\) is 3.8 Å, which is slightly larger than that of the ZIFs reported by Yaghi et al. with frl topology \(d_h = 1\) Å for ZIF 73, \(d_h = 2.9\) Å for ZIF 77. Moreover, the guest water molecules (O10) are clathrated in one channel. The other channel is occupied by coordinated water molecules (O11), leaving no space for accommodation of guest water (Fig. S2†).

Fig. 1 View of coordination environment of Zn ions in I. Hydrogen atoms are omitted for clarity. Symmetry code: a, \(-1 + x, y, z\); b, \(-1 - y, 1 - y, 1 - z\); c, \(2 - x, -y, 1 - z\); d, \(-2 + x, 1 - y, 2 - z\).

Fig. 2 The three different types of 4-connected nodes in I [(a) red node for binuclear Zn2 units, (b) cyan node for bte\(^{-}\) anions, (c) blue node for Zn1 atom].

Fig. 3 Topological view of the 3D \((4^2\cdot 6^3\cdot 8^3)\) FRL network. The red pellets for binuclear Zn2 units, cyan for bte\(^{-}\) anions, and blue for Zn1 atoms.

To study the thermal stability of I, thermogravimetric analyses (TGA) were performed on crystalline samples under an air atmosphere between 30–600 °C (Fig. S3, See ESI†). The TGA curve of I reveals that the first step weight loss of 3.68% from 90 to 140 °C, which can be assigned to the weight loss of the guest water molecules (calcd 3.52%), yielded a composition of \([\text{Zn}_4\text{(btc)}_2\text{(4-bph)(H}_2\text{O})_4]\) for I. In the second step there was a gradual weight loss to 89.1% (calcd 89.5%) during 190 to 300 °C, indicating the release of four coordinated water molecules, resulting in a totally dehydrated composition of \([\text{Zn}_4\text{(btc)}_2\text{(4-bph)}]\) for 3. Further heating of 3 reveals that it is stable up to 450 °C, from which the decomposition of the framework starts.

One interesting feature of I is that it undergoes a two-step reversible dehydration–rehydration transformation between I and 2 and between 2 and 3 respectively. In-situ high-temperature powder X-ray diffraction (PXRD) patterns for compound I under an air atmosphere were recorded between 30 °C to 300 °C (Fig. 4). Remarkably, PXRD analysis of 1 heated to 100 °C revealed that the thermally induced dehydration of guest water resulted in crystal phase transformation to 2. Further heating of 2 at 200 °C yielded totally dehydrated 3 as confirmed by another phase transformation. Interestingly, the rehydration of 3 to 2 was observed when cooling down to R.T. When 2 were immersed in water for one day the original composition of 1 was recovered, demonstrating a two-step reversible dehydration and rehydration.

The luminescence properties of compound I and free ligand 4-bph have been studied at room temperature (Fig. S4, See ESI†). Compound I shows an intensive and broad band emission maximum at 470 nm \(\left(\lambda_{em} = 386\right.\) nm), and 4-H\(_2\)bph displays a very weak emission peak at maximum emission at 466 nm with three shoulder peaks at 453, 480 and 488 nm, respectively.
remarkable enhancement of the intensities for compound 1: triclinic $P-1$, with $a = 8.623 (4) \, \AA$, $b = 9.466 (4) \, \AA$, $c = 11.371 (5) \, \AA$, $\alpha = 80.005 (6)^{\circ}$, $\beta = 79.760 (6)^{\circ}$, $\gamma = 69.169 (5)^{\circ}$, $V = 947.5 (6) \, \AA^3$, $Z = 1$, $\mu = 2.894 \, \text{mm}^{-1}$, $\rho = 2.006 \, \text{g} \, \text{cm}^{-3}$, $T = 293(2) \, \text{K}$, $\text{GOF} = 1.056$, $F(000) = 514$, $R1 (wR2) = 0.0355$ (0.0995) [2588 observed ($I > 2\sigma(I)$)] for 2939 ($R_{int} = 0.0252$) independent reflections with 281 parameters. Data collection was performed on a Bruker SMART Apex CCD diffractometer with graphite-monochromated Mo-$K_{\alpha}$ radiation. The structure was solved by direct methods using the SHELXTL program and extended using Fourier techniques.