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An unprecedented T4(1)4(2)5(2) water topology

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ABSTRACT

Herein, a special water cluster was observed in a metal-organic framework, namely $[Zn(\mu\text{-}(H_2O)_2)(L)(BDC)]\cdot 5H_2O$ (**1**, L = 2-(pyridine-4-yl)-1*H*-benzo[*d*]imidazole, H_2BDC = terephthalic acid). In this ice-like water cluster, tetramer water clusters are combined together by sharing one corner to give rise to the T4(1) water structure, while the pentamer water clusters are located on two sides of this T4(1) water chain by sharing two edges with two tetramer water clusters, thus resulting in the overall T4(1)4(2)5(2) water topology.

Water – a basal composition of vital system – has received explosive scientific interest during the past few years due not only to its elegant water morphologies but also to its unusual properties in many physical, chemical, and biological processes. In the past decades, isolated small water clusters such as $(H_2O)_{10}$[1], $(H_2O)_{12}$[2], and $(H_2O)_{21}$[3] have been extensively disclosed both theoretically and experimentally. Recently, more attention has been paid to the infinite 1D and 2D water morphologies, lying between small water clusters and bulk water/ice [4–7].

In the realm of water morphology, the water tetramer is popular, and we have witnessed a large number of water structures containing water tetramer such as T4(0)A2 [8], T4(1) [9,10],and T4(2)6(2) [11,12]. But recently, experimental and academic studies on the water pentamers are also becoming remarkable [13–16]. However, by contrast to the productive water morphologies based on water tetramer, the water pentamer involving water morphologies is less developed, and until now only limited cases are revealed, such as T5(0) [13], T5(1) [14],T5(2) [15],and L38(10)5(2)4(2)4(1) [16]. Thereby, exploring new 1D and 2D water morphology based on water pentamer will be very interesting but a big challenge. In this work, we presented an unprecedented water pentamer involving water morphology defined as T4(1)4(2)5(2), wherein the ratio of water tetramer and pentamer is 2:1.

Polymer **1** was synthesized by the hydrothermal reaction of Zn $(NO_3)_2$, H_2BDC, L, in the ratio of 1:1:1 and 6 ml H_2O at 160 °C for 3 days [17]. The phase purity of the bulk samples is confirmed by EA and XRD studies (see Supplementary Data, Fig. S1). The TG analysis suggests the loss of guest water molecules is about 30–210° (exp. 15.8%, calc. 16.3%), and the loss of coordination water molecules cause the chemical decomposition of this compound, see Fig. S2.

The single crystal X-ray diffraction shows that polymer **1** crystallizes in monoclinic, $P2_1/c$ space group [18]. As shown in Fig. 1, the Zn(II) ions are five-coordinated by two BDC^{2-}oxygen atoms, one L nitrogen, and two terminal water molecules, resulting in the axis-elongated triangular bipyramidal geometry, where Zn–O(water) lengths range from 2.139(3) Å to 2.121(3) Å, Zn–O(BDC^{2-}) lengths range from 1.981(2) Å to 2.007(2) Å, and Zn–N(L) length is 2.067(3) Å.

Along *a* direction, the Zn(II) ions are in-turn bridged by BDC^{2-}ligands to create the 1D chain structure. Through hydrogen bonds of O1-HA (water)···O5(BDC^{2-})/2.746 Å/170.25°, O1-HB (water)···O4(BDC^{2-})/2.761 Å/160.97°, O2-HA(water)···O5(BDC^{2-})/2.654 Å/168.46° between water molecules and BDC^{2-}oxygen atoms, these 1D chains are combined together to give rise to the 2D supramolecular net (Fig. 2). The 3D stacking architecture shows a solvent-accessible void space of 601.6 $Å^3$, equal to 24.9% of the cell volume (Fig. 3), which is filled with free water molecules.

A clear insight into this water structure is shown in Figs. 4 and 5. $H_2O(7)$, $H_2O(8)$ and two $H_2O(9)$ molecules composed of a water tetramer by H-bonds of O7-H7B···O9/2.751 Å/162.94°, O8-H8B···O9/2.752 Å/171.56°, O9-H9B···O7/2.750 Å/168.06°, O9-H9A···O8/2.754 Å/174.49°. The H-bond lengths of water tetramer are at the average value of 2.752 Å. As shown in Fig. 4, O9 displays four-fold H-bond, and adjacent tetramers share $H_2O(9)$ to create a T4(1) tape. The dihedral angle between the adjacent water tetramers is 89.64°, nearly a vertical pattern. The water pentamer consists of $H_2O(7)$, $H_2O(8)$, $H_2O(9)$, $H_2O(10)$ and $H_2O(11)$, through hydrogen bonds of O7-H7A···O11/2.730 Å/141.54°, O8-H8B···O9/2.752 Å/ 171.56°, O9-H9B···O7/2.750 Å/168.06°, O10-H10A···O8/2.782 Å/172.66°, and O10-H10B···O11/3.088 Å/ 173.12°. O10 deviates of 0.408 Å from the plane built by O7, O8, O9 and O11. The O···O···O angle in pentamers are O7···O9···O8/110.43°, O9···O8···O10/114.18°, O8···O10···O11 /96.21°, O10···O11···O7/113.39°, and O11···O7···O9/104.04°, closing to a regular polygon shape. The average H-bond lengths in this water pentamer is 2.820 Å, comparable with that such as 2.74 Å [13], 2.82 Å [14], 2.84 Å [15], and 2.81 Å [16], observed in other pentamers.

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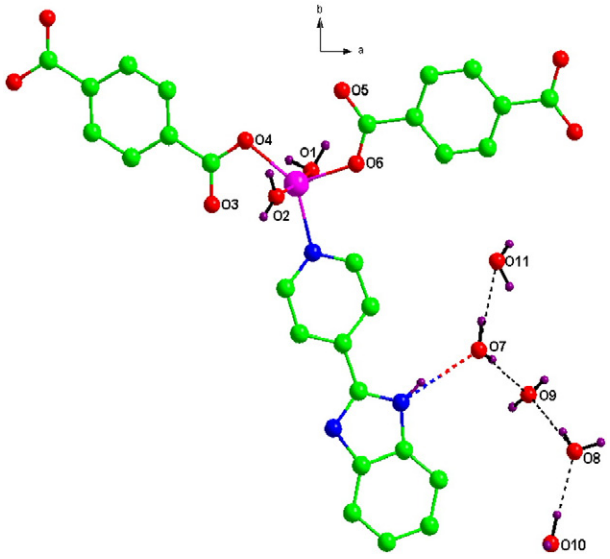

Fig. 1. The coordination surroundings of Zn(II) ions and the guest water molecules in **1**. The hydrogen atoms linked to C atoms are omitted for clarity. Atoms are colored as follows: C/green, N/blue, Zn/pink, O/red, H/ purple.

Furthermore, these water pentamers via sharing two edges with two tetramers generate the T4(2)5(2) water tape with the dihedral angle of 120.38° and 123.73°(Fig. 5). Combined with the above-defined T4(1) water structure, the overall water structure is defined as a T4(1)4(2)5(2) tape. On the whole, the average H-bond length in the T4(1)4(2)5(2) cluster is 2.801 Å, comparable to the ice II phase (2.77–2.84) Å [16]. The FTIR spectroscopic studies reveals a band centered about 3225 cm^{-1}, attributed to the O–H stretching frequency of the water cluster. Generally speaking, the O–H stretching vibration in ice appears at 3220 cm^{-1}, while in liquid it shifts to 3280 and 3490 cm^{-1}[11]. Therefore, the O–H stretching frequency of the water cluster in **1** is more like ice with a slight variation attributable to its surroundings. This result is well consistent with the analysis of average H-bond lengths.

In literatures, we find two cases composed of both water tetramers and water pentamers. In one case defined as L38(10)5(2)4(2)4(1) (Fig. S3a) [19], water tetramers connect to water pentamers through sharing one edge to give a 1D T4(2)5(2) tape, while water tetramers are isolated from each other. In the other case [20], the combination of water tetramers and water pentamers constructs a complicated 2D water layer morphology (Fig. S3b). By contrast, for the first time, a tape water structure built on water tetramers and water pentamers is observed in **1**.

Moreover, the water tape is stabilized by hydrogen bonds between water structure and host framework: N2(L)–H···O7, N3(L)–H···O8, O2–H···O10, O3–H···O11 (Fig. 6). The N(L)–O distances are 2.784 Å and 2.825 Å respectively, indicating a relatively strong interactions in this structure as the normally N···O distance

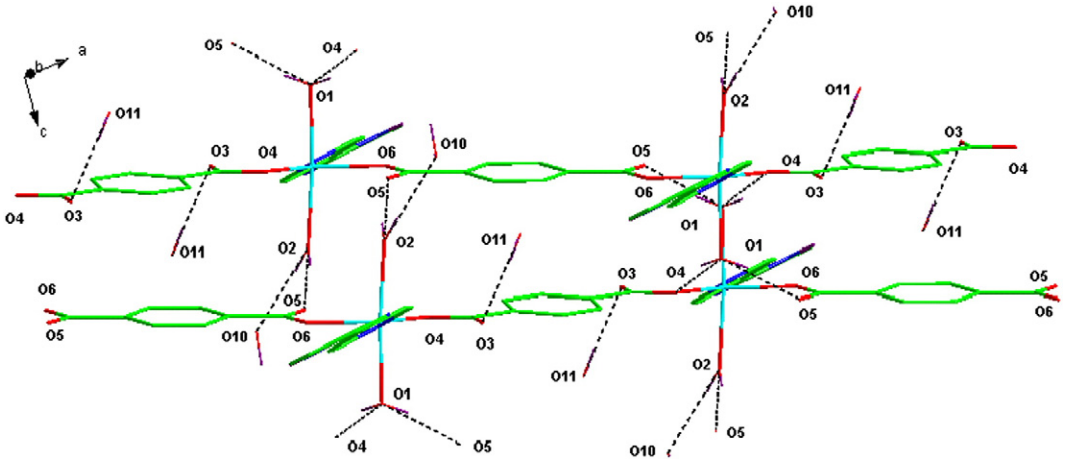

Fig. 2. H-bonded layer structure of polymer **1**.

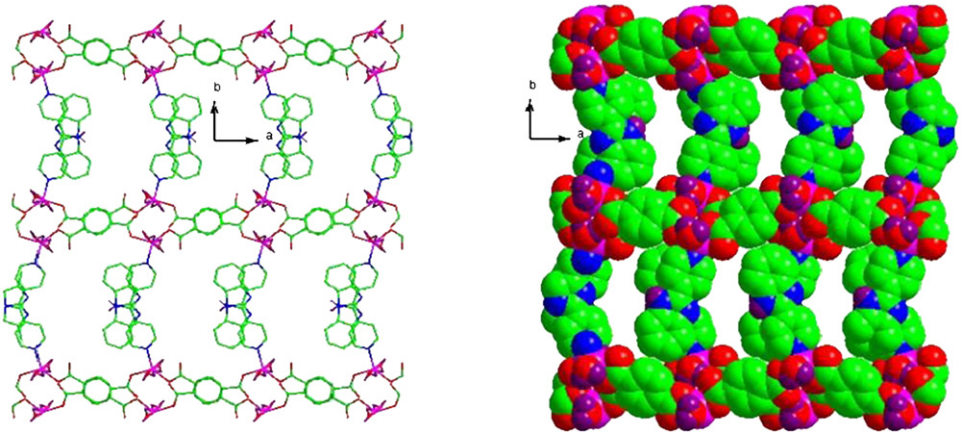

Fig. 3. Viewed down *c* axis, the 3D stacking architecture displays the channels that host water molecules.