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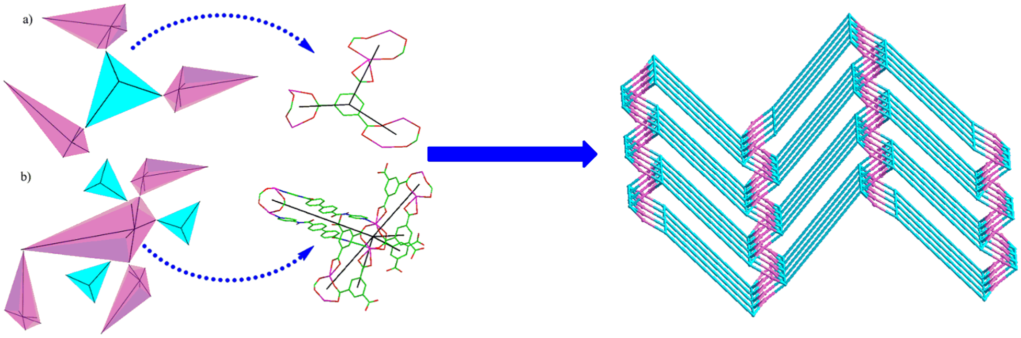

We present here an unprecedented **tcj-3,6-P2_1/c** (3, 6)-connected net based on both metal nodes and organic ligand nodes, featuring $(3\cdot5^2)(3^2\cdot4^2\cdot5^5\cdot6^5\cdot7)$ topology symbol.

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ARTICLE TYPE

An unprecedented (3, 6)-connected net featuring tcj-3,6-P2_1/c topology

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A new Cd(II) coordination polymer, namely [$(CH_3)_2NH_2$][Cd_2(BTC)(HBTC)(L)]·(DMF)(H_2O)$_3$ (1), was obtained by solvo(hydro)thermal self-assembly of Cd$(NO_3)_2$, N^4,N$^{4'}$-di(pyridin-4-yl)biphenyl-4,4'-dicarboxamide(L) and 1,3,5-benzenetricarboxylic acid (H_3BTC). The skeleton of it can be described as a (3, 6)-connected net, classified by an unprecedented ($3\cdot5^2$)($3^2\cdot4^2\cdot5^5\cdot6^5\cdot7$) tcj-3,6-P$2_1$/c topology.

Nowadays, metal-organic frameworks (MOFs) have drawn more and more attentions, not only because of their potential application in molecular selection, ion exchange, adsorption, fluorescence, and magnetism, but also duo to their fascinating architectures, intriguing topologies.[1-5] Topology analysis was wildly used to define the structure prototype of generated MOFs, since it was firstly employed in crystal engineering.[6-8] Until now, a large number of MOFs with mimic topology prototype have been deliberately designed and obtained.[9-11] From the viewpoint of topology, many factors involving the connectivity and geometry of nodes, the connecting mode among nodes, will make generation of desired topology prototype more difficult and consequentially make the resulted topology prototype more complicated and productive. For example, recent advances have disclosed many (3, 6)-connected MOFs belonging to **flu-3,6-C2/c**,[12-14] **pyr**,[15] **kgd**,[16-18] **anh**,[19] **ant**,[20] **rtl**,[19] **loh1**,[21] and ($4\cdot5^2$)($4^2\cdot5^2\cdot6^7\cdot7^3\cdot8$) topology prototype,[22] where the topological diversity is mainly derived from the various geometries of six-connecting nodes (such as octahedral node, trigonal-prism node) and the connecting mode between three- and six-connecting nodes. Herein, we report a novel (3, 6)-connected MOF with an unprecedented **tcj-3,6-P2_1/c** topology prototype.

Polymer **1** was obtained by solvo(hydro)thermal method (115□). The acylamide ligand of L was synthesized according to the literature method.[23] The crystal of **1** was characterized by single crystal X-ray diffraction, giving the monoclinic, *P2(1)/n* space group. Based on the consideration of charge balance, the existence of one [$(CH_3)_2NH_2$]$^+$ cation is suggested, which can be confirmed by elemental analysis. It is well known that [$(CH_3)_2NH_2$]$^+$ cation would be produced from DMF molecule under higher temperature condition.[24] Thus, in the present case the generation of [$(CH_3)_2NH_2$]$^+$ cation from the decomposition of DMF molecule under solvo(hydro)thermal condition is reasonable. But, the bad disorder of [$(CH_3)_2NH_2$]$^+$ cation prevents us to solve the structure of it, and is further removed by using the SQUEEZE program. The asymmetric unit contains two crystallography-independent Cd(II) ions: Cd1 and Cd2. As shown in Figure 1, Cd1 and Cd2 are bridged by three carboxylate groups from three H_3BTC ligands, constructing a binuclear Cd_2 unit. Both Cd1 and Cd2 are six-coordinated. Cd1 site connects to five oxygen atoms from two (BTC)$^{3-}$ ligands and two (HBTC)$^{2-}$ ligands (Cd1-O=2.253(5)-2.411(5)Å), one nitrogen atom from L ligand (Cd1-N=2.309(5)Å), while Cd2 site coordinates to five oxygen atoms from three (BTC)$^{3-}$ ligands and one (HBTC)$^{2-}$ ligand (Cd2-O=2.249(5)-2.490(5)Å), one nitrogen atom from L ligand (Cd2-N=2.299(6)Å). The Cd-O/N bond lengths are in the normal range.[25] The H_3BTC ligands perform two kinds of coordination mode, *viz.* complete deprotonation and part deprotonation. Corresponding to this, the coordination fashion is described as $\mu_5:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1$ and $\mu_3:\eta^1:\eta^1:\eta^1:\eta^1:\eta^0:\eta^0$, respectively (see Figure 2). The L ligand connects to two Cd(II) ions, affording *trans* conformation, where *trans* means that the two C=O groups orientate in the opposite direction. And a slight distortion is observed for L ligand, as evidenced by the dihedral angel of ca. 19.7° and 32.02° between the terminal pyridyl ring and the middle phenyl ring.

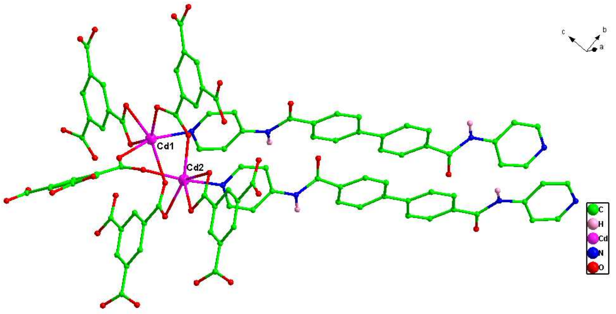

Figure 1. The coordination surrounding around Cd(II) ions.The hydrogen atoms except on the acylamide group are omitted for clarity. [Cd/purple, C/green, N/blue, O/red, H/pink]

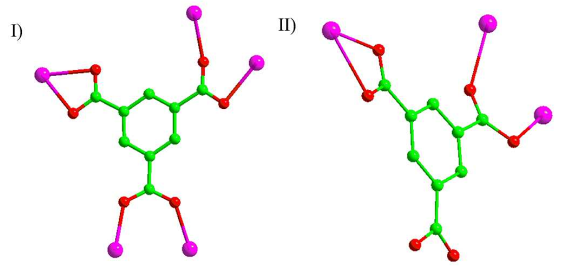

Figure 2. The coordination mode of BTC^{3-} and $HBTC^{2-}$ ligand.

As shown in Figure 3, the combination of binuclear Cd(II) fragments and $(HBTC)^{2-}$ ligands forms a 1D chain, and further connected by $(BTC)^{3-}$ ligands to create a 2D wave-shaped layer. Furthermore, the 2D layers are supported by L ligands, resulted in an overall 3D layer-pillared framework (Figure 4), where extensive hydrogen bonds of N2-H2A…O1 (2.906(3)Å, 161.46(3)°) and N4-H4A…O9 (2.931(3)Å, 161.25(3)°) between acylamide group and $(BTC)^{3-}$ ligand, and π-π contacts among two parallel L phenyl rings (centroid-to-centroid distance of ca. 3.867(3)Å) are observed.

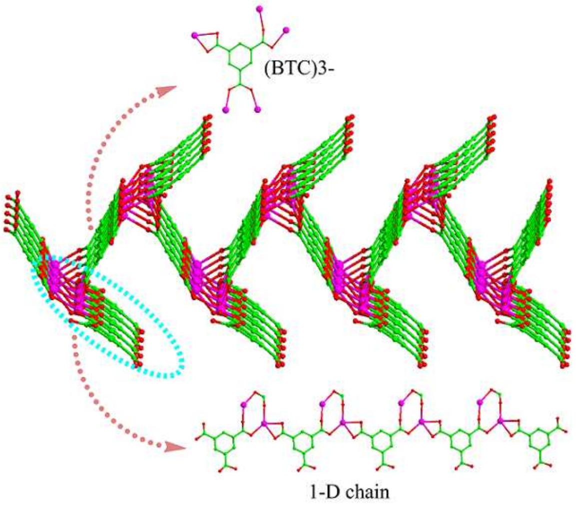

Figure 3. View of the wave-shaped 2D layer constructed by Cd(II), $HBTC^{2-}$, and BTC^{3-} ligands.

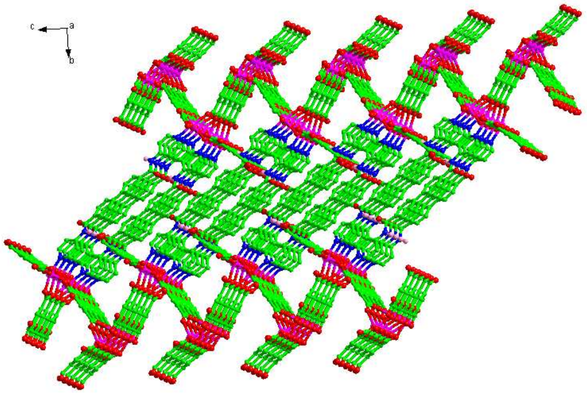

Figure 4. View of the layer-pillared 3D framework.

A further insight into the structure of **1** is carried out by topology analysis. If binuclear Cd(II) unit (Cd1, Cd2) is viewed to be a node, then $(BTC)^{3-}$ ligand acts as a three-connecting node which links to three binuclear Cd(II) units, performing three connectivity with triangle geometry. Binuclear Cd(II) unit, besides, connects to three other identical binuclear Cd(II) units through two $(HBTC)^{2-}$ ligands plus two L ligands, but also links to three $(BTC)^{3-}$ nodes, giving six connectivity with highly irregular octahedron geometry (Figure 5), ultimately resulted in the overall (3, 6)-connected net, see Figure 6. Further topological analysis by Topos40 program gives a (3, 6)-connecting **tcj-3,6-P2$_1$/c** net with $(3 \cdot 5^2)(3^2 \cdot 4^2 \cdot 5^5 \cdot 6^5 \cdot 7)$ symbol.[26]

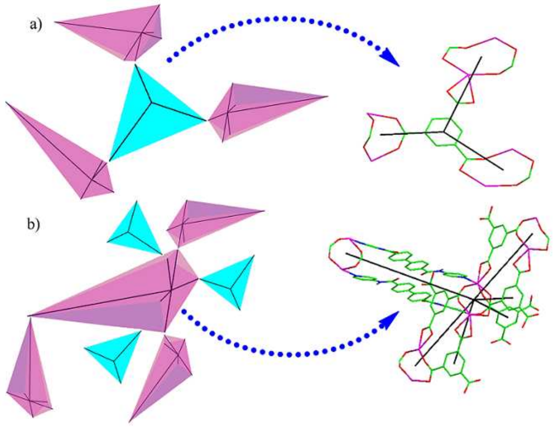

Figure 5. a) View of the three-connecting $(BTC)^{3-}$ node, geometry, and connecting mode; b) the six-connecting Cd_2 node, geometry, and connecting mode.

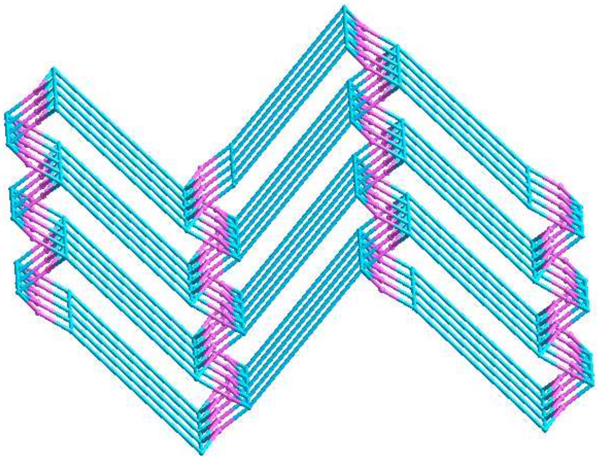

Figure 6. View of the (3, 6)-connected net (color code: blue/ Cd_2 unit, pink/ $(BTC)^{3-}$ node).

In literature, there are a handful of (3, 6)-connected net characterized by **flu-(3**, **6)-C2/c**, **pyr**, **kgd**, **anh**, **ant**, **rtl**, as well as $(4 \cdot 5^2)(4^2 \cdot 5^2 \cdot 6^7 \cdot 7^3 \cdot 8)$ topology. A simple summarization involving topological type, vertex geometry, symbol, the type of node, and the connecting mode between three- and six-connecting node is listed in Table 1. It is clear that the triangle/octahedron, triangle/trigonal-prism ratio is 2:1 for most of the previous (3, 6)-connected nets, 2:3 for **loh1**, 1:1 for the $(4 \cdot 5^2)(4^2 \cdot 5^2 \cdot 6^7 \cdot 7^3 \cdot 8)$ net and our case. Notably, the significant difference between the $(4 \cdot 5^2)(4^2 \cdot 5^2 \cdot 6^7 \cdot 7^3 \cdot 8)$ net and our case is the connecting mode between nodes. In the $(4\cdot5^2)(4^2\cdot5^2\cdot6^7\cdot7^3\cdot8)$ net, there only exists trangle-to-octahedron connecting mode, whereas in our case both trangle-to-octahedron and octahedron-to-octahedron connecting modes are observed, which is rare in the (3, 6)-connected net. In addition, it is clear that the present case is very rare in which it contains the unique three-membered ring. Furthermore, the symbol of 6-connected node contains three kinds of odd rings, involving three-, five- and seven-membered ring, which is unique and distinctively different from the previous 6-connected nodes.

Thermogravimetry analyses have been studied for **1**, as shown in Figure 7. Polymer **1** has a first 10.6% weight loss in the temperature range of 30-350°C, which corresponds to the loss of three water molecules and one DMF molecule (calc. 10.5%). The second sharp loss above 350°C indicates the decomposition of polymer **1**.

In conclusion, we report here the synthesis, structure, and topology analysis of a new acylamide MOF by solvo(hydro)thermal condition of $Cd(NO_3)_2$, N^4,$N^{4'}$-di(pyridin-4-yl)biphenyl-4,4'-dicarboxamide and 1,3,5-benzenetricarboxylic acid. Notably, this case presents a novel (3, 6)-connected net with an unprecedented **tcj-3,6-P2$_1$/c** topology built on an uncommon six-connecting highly distorted node. Moreover, a summarization for (3, 6)-connected nets in detail is provided for further design and preparation of (3, 6)-connected net.

Table 1. A summarization of (3, 6)-connected nets.

Type	Vertex geometry	Symbol	Three-connected node	Six-connected node	Connecting mode	References
flu-3,6-C2/c	triangle, octahedron	$(4^26)_2(4^46^28^710^2)$	$dccptp^{2-}$	Cu_2 unit	triangle-to-octahedron	12
			$(CPEIP)^{3-}$	Tb_2 unit	triangle -to-octahedron	13
			PDC^{2-}	Gd_2 unit	triangle -to-octahedron	14
pyr	triangle, octahedron	$(6^3)_2(6^{12}8^3)$	4,4′,4′′-Tricarboxytriphenylamine	$[Zn_4O(CO_2)_6]$	triangle -to-octahedron	15
kgd	distorted trigonal planar, distorted octahedron	$(4^3)_2(4^66^68^3)$	Ag(I)	Cu(II)	distorted trigonal planar-to-distorted octahedron	16
			HPO_3^{2-}	In(III)	distorted trigonal planar-to-distorted octahedron	17
			$Hbcpb^-$	Cu(II)	distorted trigonal planar-to-distorted octahedron	18
anh	triangle, distorted trigonal-prism	$(46^2)_2(4^46^28^810)$	$cpna^{2-}$	Co_2 unit	triangle-to-distorted trigonal-prism	19
ant	triangle, octahedron	$(4^26)_2(4^46^28^810)$	Co(II)	Co_4 unit	triangle-to-octahedron	20
			Cu(II)	Cu(II)	triangle-to-octahedron	16
rtl	triangle, octahedron	$(46^2)_2(4^26^{10}8^3)$	$cpna^{2-}$	Co_2 unit	triangle-to-octahedron	19
loh1	triangle, octahedral cage	$(4^3)_2(4^66^68^3)_3$	4′-(4-pyridyl)-4,2′:6′,4″-terpyridine	Mn_2 unit	triangle-to-octahedron , octahedron -to-octahedron	21
	triangle, octahedron	$(45^2)(4^25^26^77^38)$	L^{2-}	Pb(II)	triangle-to-octahedron	22
tcj-3,6-P2$_1$/c	triangle, highly irregular octahedron	$(3\cdot5^2)(3^2\cdot4^2\cdot5^5\cdot6^5\cdot7)$	BTC^{3-}	Cd_2 unit	triangle-to-irregular octahedron, irregular octahedron-to-irregular octahedron	This work

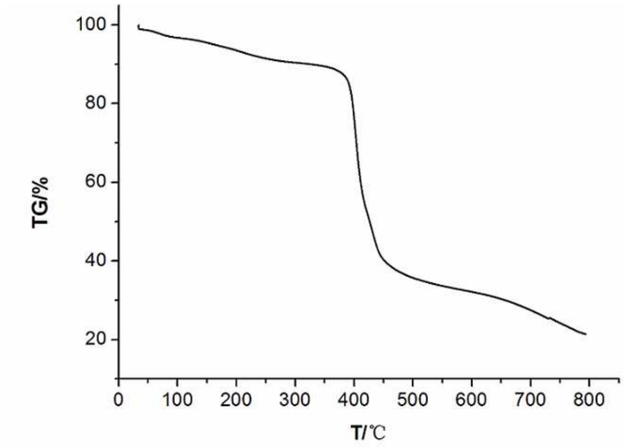

Figure 7. The TG study of polymer **1**.

Notes and references

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The synthesis of 1. A mixture of $Cd(NO_3)_2$ (0.2mmol), N^4,$N^{4'}$-di(pyridin-4-yl)biphenyl-4,4'-dicarboxamide (0.2mmol), 1,3,5-benzenetricarboxylic acid (0.15mmol) in 4mL DMF and 1ml water, was sealed in a Teflon reactor, and heated at 115˚C for 3000 mins, then gradually cooled to ambient temperature at 3˚C/h. Subsequently, colorless crystals were obtained in 72% yield based on Cd. Element analysis (%) for **1**: calc: C 46.74, H 3.84, N 6.96; exp: C 46.72, H 3.85, N 6.97.

Crystal data. Single-crystal diffraction intensity data were preformed by phi and omega scans measurement method with MoKα radiation (0.71073Å) on Bruker Smart Breeze CCD at 298K, and corrected with SADABS program. The structures were solved by direct methods with the SHELXTL program and all non-hydrogen atoms were refined with anisotropic refinement by full matrix least-squares on F^2. The details of crystal data for polymer **1** were summerized in here: monoclinic, *P2(1)/n* space group, *a*=10.2076(6)Å, *b*= 48.035(3)Å, *c*= 11.1580(8)Å, *β*= 103.722(3)˚, *V*=5314.9(6)$Å^3$, Z=4, *GOF*=0.968, all data final *R1*=0.0936, *ωR2*=0.1449.The CCDC number is 1001047.

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