

Electronic Supplementary Information (ESI)

Rational Synthesis of a novel 3,3,5-c polyhedral Metal-Organic Framework with highly thermal stability and hydrogen storage capability

Jianqiang Liu,^{a*} Guoliang Liu,^{bc} Chuying Gu,^a Weicong Liu,^a Jingwen Xu^a, Baohong Li^a and Wenjing Wang^{bc*}

*Email: jianqiangliu2010@126.com, wjwang@fjirsm.ac.cn

Materials and Methods

All chemicals were purchased from Jinan Henghua Sci. & Tec. Co. Ltd. without further purification. Powder X-ray diffraction (PXRD) data was collected on a Rigaku D/max-2550 diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Elemental analyses (C, H, and N) were achieved by vario MICRO (Elementar, Germany). The thermal gravimetric analyses (TGA) were performed on TGA Q500 thermogravimetric analyzer used in air with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$.

Synthesis of GDMU-2

Single crystal of compound **GDMU-2** was obtained by solvothermal reaction of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (25 mg 0.1 mmol) and H_6PHB (15 mg, 0.005 mmol) in N, N'-dimethylformamide (DMF) (2 mL) with HNO_3 (0.45 mL) (2.2 mL HNO_3 in 10 mL DMF) at $105 \text{ }^\circ\text{C}$ for 72 hours. The mixture was then cooled to room temperature. Bright-blue block crystals were obtained and air-dried (yield 55%, based on Cu). Elemental analysis (%): calcd: C, 40.61; H, 4.35; N, 4.98. Found: C, 40.69; H, 4.60; N, 5.15. The experimental PXRD pattern is in good agreement with the simulated one based on the single crystal X-ray data, indicating the purity of the as-synthesized product (Fig. S3).

Single Crystal X-ray Structure Determination

Crystallographic data for **GDMU-2** was collected on a Bruker Apex II CCD diffractometer using graphite-monochromated Mo- $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation at 123 K. All non-hydrogen atoms were easily found from the difference Fourier map. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using version 5.1. All non-hydrogen atoms were refined anisotropically. Since the highly disordered guest molecules were trapped in the channels of **GDMU-2** and could not be modeled properly, there are “Alert level A” about “Check Reported Molecular Weight” and “VERY LARGE Solvent Accessible VOID(S) in Structure” in the “check CIF/PLATON report” files for **GDMU-2**. The final formula of **GDMU-2** was derived from crystallographic data combined with elemental and thermogravimetric analysis data. The detailed crystallographic data and selected bond lengths and angles for compound are listed in Table S1-S2, respectively.

Crystallographic data for **GDMU-2** (CCDC:1437348) have been deposited with Cambridge Crystallographic Data Centre. Data can be obtained free of charge upon request at www.ccdc.cam.ac.uk/data_request/cif. We also very thanks Prof S. R. Batten for discussion the topology.

Stability Analysis

The stability analyses of **GDMU-2** are shown in Fig. S3-S4, it indicates that **GDMU-2** exhibits good thermal stability. The powder XRD pattern for **GDMU-2** after adsorption-desorption tests is also in good agreement with the simulated one, indicating the stability of the material (Fig. S4). And the powder XRD patterns of different solvent exchanged samples are similar to the one simulated from the single-crystal structure, which proved the stability of the structure.

Gas Sorption

The nitrogen adsorption-desorption measurements were carried out at liquid nitrogen temperature (77 K) by using an automatic volumetric adsorption equipment (Micromeritics, ASAP2020). Low pressure (< 800 torr) gas sorption isotherms were performed using a Micromeritics ASAP 2020 surface area and pore size analyzer. Pore

size distribution data were obtained from the N₂ sorption isotherms based on the DFT model in the Micromeritics ASAP 2020 software package (assuming slit pore geometry). An ultra-high purity (UHP, 99.999% purity) grade of N₂, H₂, CH₄, and CO₂ gases was used throughout the adsorption experiments. Prior to the measurements, all the samples were degassed at 80 °C for 10 h to remove the adsorbed impurities. The hydrogen isosteric heat of sorption was calculated as a function of the hydrogen uptake by comparing the adsorption isotherms at 77 K and 87 K. The data were modeled with a virial-type expression composed of parameters a_i and b_i (Equation 1), and the heat of adsorption (Q_{st}) was then calculated from the fitting parameters using Equation 2, where p is the pressure, N is the amount adsorbed, T is the temperature, R is the universal gas constant, and m and n determine the number of terms required to adequately describe the isotherm. In order to compare the efficacy of **GDMU-2** for CO₂/CH₄ and CO₂/N₂ separation, we used the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz¹ along with the pure component isotherm fits to determine the molar loadings in the mixture for specified partial pressures in the bulk gas phase.

$$\ln p = \ln N + \frac{1}{T} \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i \quad (\text{Equation 1})$$

$$Q_{st} = -R \sum_{i=0}^m a_i N^i \quad (\text{Equation 2})$$

$$N = a \times \frac{bp^c}{1+bp^c} \quad (\text{Equation 3})$$

Thermogravimetric analysis

Thermogravimetric analysis (TGA) for **GDMU-2** shows a weight loss of 29.6 % between 35 and 270 °C, which corresponding to the loss of DMF, free water and coordinated H₂O molecules (calcd: 31.3 %). Upon further heating, a weight loss of 33.6 % should correspond to the release of the organic HPB ligands, and then the collapse of the framework (calcd 34.8 %) (Fig.S5).

Supplementary Figures

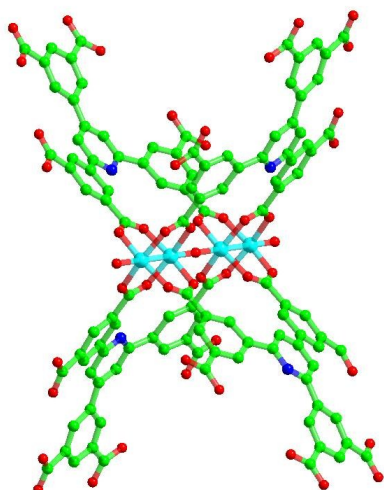


Fig. S1 View of coordination environment of metal ions and ligands

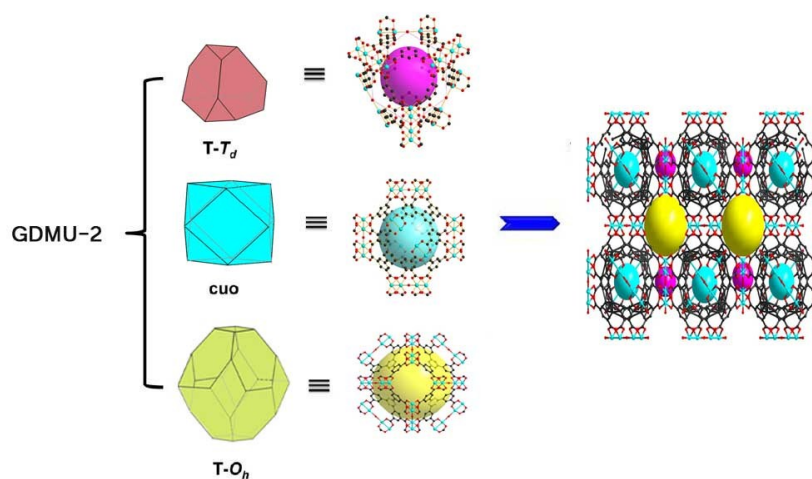


Fig. S2 Description of the structure of **GDMU-2** for its three types of cages with different sizes.

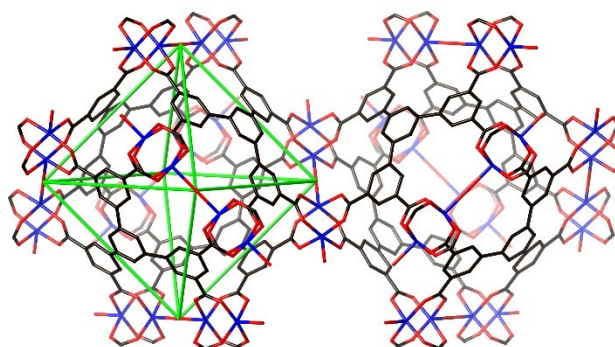


Fig. S3 two linked cages in the 3D network of **GDMU-2**. The octahedral arrangement of the $\text{Cu}_4\text{O}(\text{O}_2\text{CR})_8$ nodes of one cage is highlighted by the green lines.

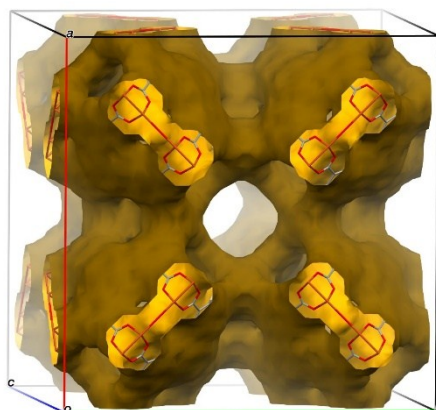


Fig. S3 View of the pores in the structure of **GDMU-2** (with water ligands removed).

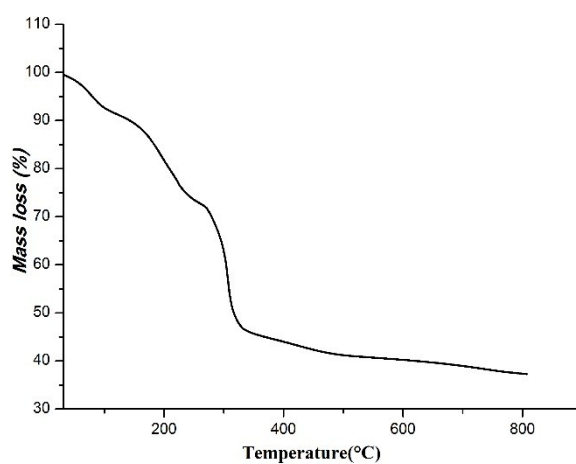


Fig. S5 Thermogravimetric analysis curves for the as-synthesized of **GDMU-2**.

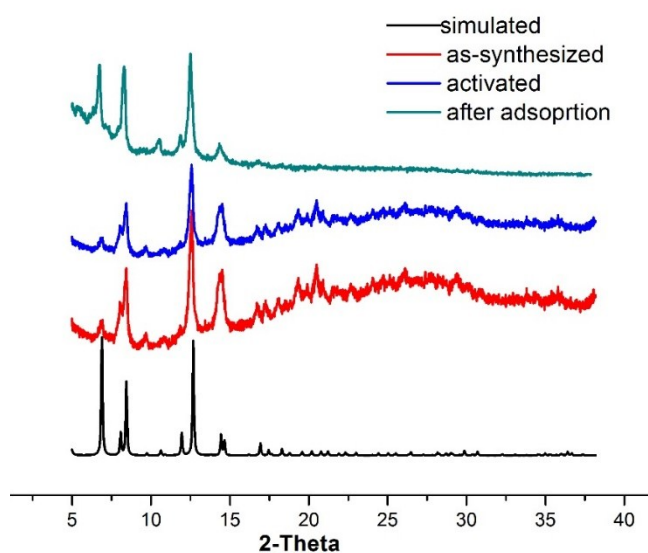


Fig. S6 Simulated, as-synthesized and activated powder X-ray diffraction (PXRD) patterns for **GDMU-2** samples.

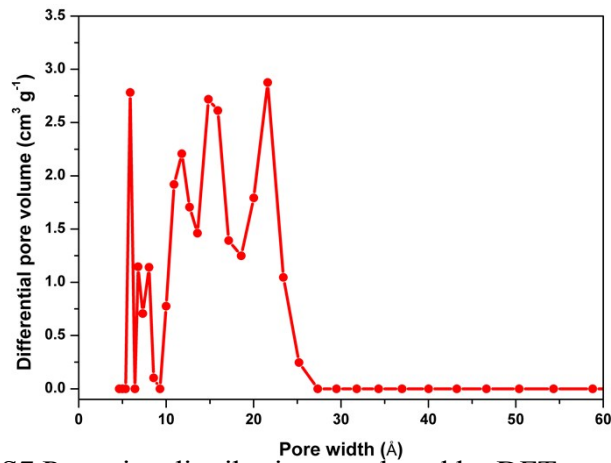


Fig. S7 Pore size distributions analyzed by DFT methods.

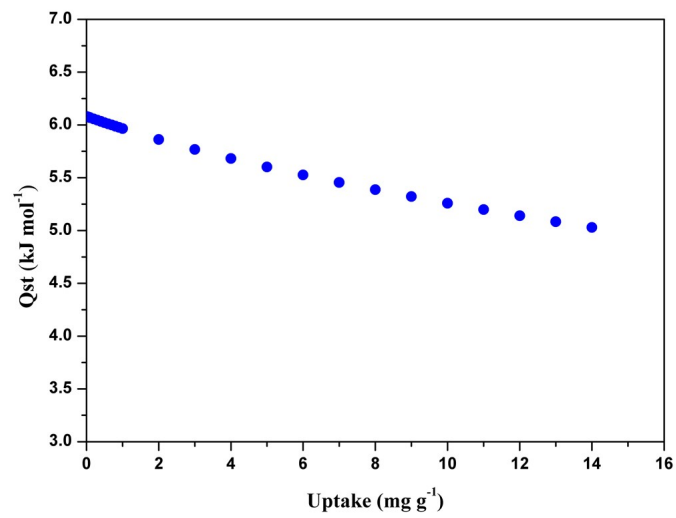


Fig. S8 The adsorption heat (Q_{st}) of hydrogen for GDMU-2

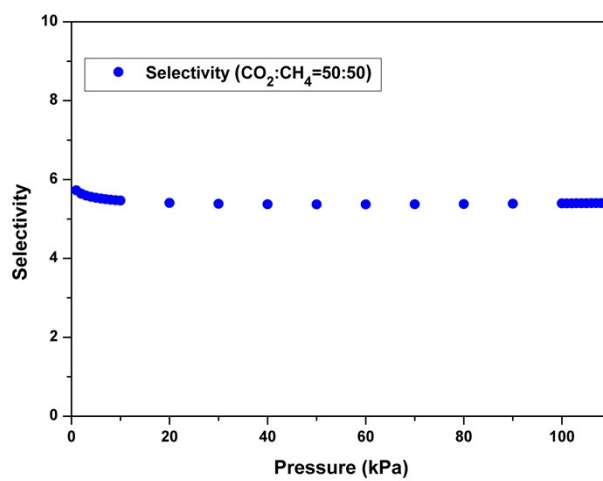
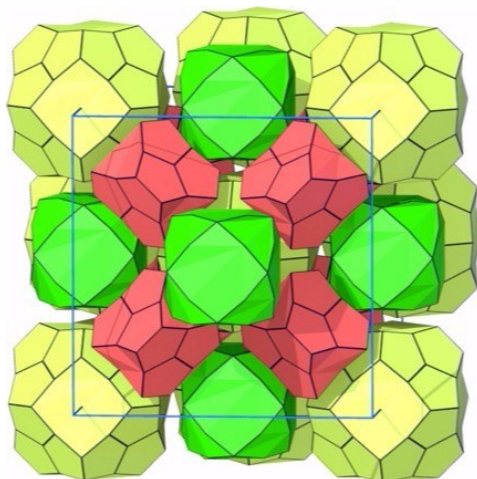


Fig. S9 Adsorption selectivity of CO₂ over CH₄ at 293 K.

Topology analysis

From the viewpoints of topology, the topology type for the compound of **GDMU-2** can be classified as different types, which were calculated by TOPOS 4.0.

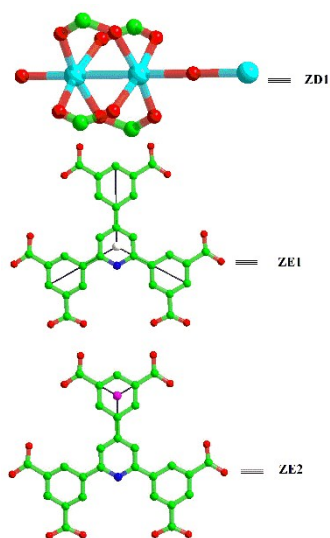
(1) **gdm** topology



Structure consists of molecules (ZD1). The composition of molecule is C₄₀O₈Cu₂

Structure consists of molecules (ZE1). The composition of molecule is C₆

Structure consists of molecules (ZE2). The composition of molecule is C₆



Vertex symbols for selected sublattice

ZD1 Point symbol: {5⁴.6².8⁴}

Extended point symbol: [5.5.5.5.6.6.8.8.8(2).8(2)]

ZE1 Point symbol: {5².6}

Extended point symbol: [5.5.6]

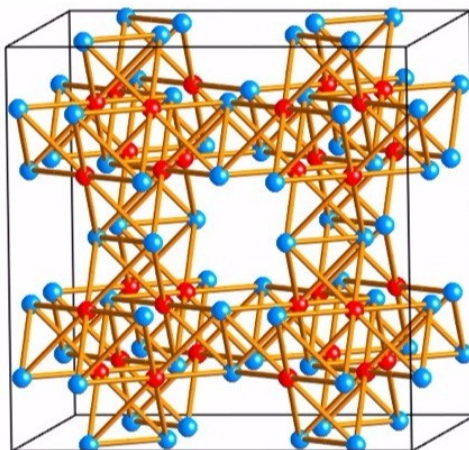
ZE2 Point symbol: {5³}

Extended point symbol: [5.5.5]

Point symbol for net: {5².6}6{5³}2{5⁴.6².8⁴}3

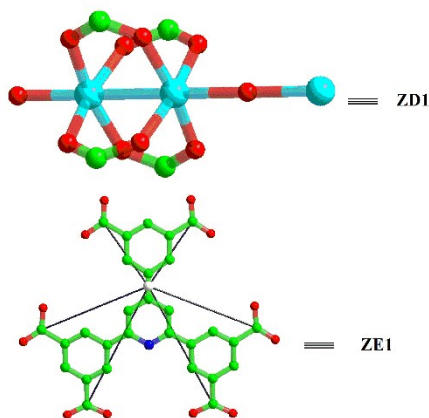
3,3,5-c net with stoichiometry (3-c)6(3-c)2(5-c)3; 3-nodal net

(2) **gdl topology**



Structure consists of molecules (ZD1). The composition of molecule is C₄O₈Cu₂

Structure consists of molecules (ZE1). The composition of molecule is C₂₄



Vertex symbols for selected sublattice

ZD1 Point symbol: {3⁴.4⁶}

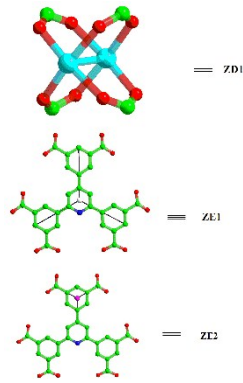
Extended point symbol: [3.3.3.3.4.4.4.4.4]

ZE1 Point symbol: {3³.6¹²}

Extended point symbol: [3.3.3.6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2)]

Point symbol for net: {3³.6¹²}2{3⁴.4⁶}3

5,6-c net with stoichiometry (5-c)3(6-c)2; 2-nodal net



Vertex symbols for selected sublattice

 ZD1 Point symbol: {6².8⁴}

Extended point symbol:[6.6.8.8.8(2).8(2)]

 ZE1 Point symbol: {6.8²}

Extended point symbol:[6.8(3).8(3)]

 ZE2 Point symbol: {8³}

Extended point symbol:[8(3).8(3).8(3)]

 Point symbol for net: {6.8²}6{6².8⁴}3{8³}2

3,3,4-c net with stoichiometry (3-c)6(3-c)2(4-c)3; 3-nodal net

Topological type: ntt (topos&RCSR.ttd) {6.8²}6{6².8⁴}3{8³}2 - VS [6.8(3).8(3)]
 [8(3).8(3).8(3)] [6.6.8.8.8(2).8(2)] (16813 types in 3 databases)

Table S1. Crystal data and structure refinement information for compound **GDMU-2**

Crystal system	Cubic
Space group	<i>Fm-3m</i>
Crystal color	blue
<i>a</i> , Å	36.240(4)
<i>b</i> , Å	36.240(4)
<i>c</i> , Å	36.240(4)
β , °	90
<i>V</i> , Å ³	47595(5)
<i>Z</i>	1
ρ_{calcd} , g/cm ³	1.100
μ , mm ⁻¹	0.888
<i>F</i> (000)	12672
θ Range, deg	2.51-21.94
Reflection collected	30331
Independent reflections (<i>R</i> _{int})	0.0776
Reflections with <i>I</i> > 2 σ (<i>I</i>)	12672
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))*	0.0914, 0.0934
<i>R</i> ₁ , <i>wR</i> ₂ (all data)**	0.1142, 0.2824

* $R = \sum(F_o - F_c) / \sum(F_o)$, ** $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum(F_o^2)\}^{1/2}$.

Table S2. Selected bond distances (Å) and angles (deg) of structure **GDMU-2**

Cu1- O1#1	1.965(4)	Cu1-O3	2.2408(13)
Cu1- Cu2	2.6254(18)	Cu2- O2#2	1.942(4)
Cu2- O4	2.189(10)		
O1- Cu1-O1	169.9(3)#1	O1- Cu1-O3	95.07(13)
O2- Cu2-O2#2	167.3(3)	O2- Cu2- O4	96.33(14)

#1: x, y, z; #2: -x, -y, z.

References:

1. A. L. Myers, and J. M. Prausnitz, *AIChE J.*, 1965, **11**, 121.
2. V. A. Blatov, A. P. Shevchenko, D. M. Proserpio, *Cryst. Growth Des.*, 2014, **14**, 3576
3. <http://rcsr.anu.edu.au/nets>