Supporting Information

A highly porous NbO type metal-organic framework constructed from an expanded tetracarboxylate

Jianfeng Cai,[a] Xingtang Rao,[a] Yabing He,[c] Jiancan Yu,[a] Chuande Wu,[d] Wei Zhou,[e,f] Taner Yildirim,[f,g] Banglin Chen,[a,b]* and Guodong Qian[a]*

[a] *State Key Laboratory of Silicon Materials, Cyrus Tang Center for Sensor Materials and Applications, Department of Materials Science & Engineering, Zhejiang University, Hangzhou 310027, China. E-mail: gdqian@zju.edu.cn.*

[b] *Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249-0698, USA. E-mail: banglin.chen@utsa.edu; Fax: (+1) 210-458-7428.*

[c] *College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, China*

[d] *Department of Chemistry, Zhejiang University, Hangzhou 310027, China.*

[e] *NIST Center for Neutron Research, Gaithersburg, Maryland 20899-6102, USA.*

[f] *Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742, USA.*

1.1 Materials and Measurements

All the chemicals were commercially available and used without further purification. Dimethyl 5'-bromo-[1,1':3',1"-terphenyl]-4,4"-dicarboxylate (**1**) and dimethyl 5-ethynylisophthalate (**2**) were synthesized according to Ref. [1] and Ref. [2]. ^{1}H NMR spectra were recorded on a Bruker Advance DMX 500 spectrometer using tetramethylsilane (TMS) as an internal standard. Thermogravimetric analyses (TGA) were carried out on a Netzsch TG209F3 with a heating rate of 10 ^{o}C/min in N_2 atmosphere. Infrared spectrum (IR) was recorded on Thermo Fisher Nicolet iS10 spectrometer using KBr pallets. Elemental analyses for C, H, and N were performed on an EA1112 microelemental analyzer. Powder X-ray diffraction (PXRD) patterns were collected in the 2θ = 3-40 ° range on an X'Pert PRO diffractometer with Cu Kα (λ = 1.542Å) radiation at room temperature.

1.2 Gas Sorption Measurements

A Micromeritics ASAP 2020 surface area analyzer was used to perform the gas sorption measurements. In order to remove guest solvent molecules in the framework, a freshly prepared sample of **ZJU-32** was exchanged with dry acetone 10 times and then activated at 373 K under high vacuum for 12 h until the outgas rate was 5 μmHg min^{-1} prior to measurements to get the activated **ZJU-32a** for gas sorption studies.. High-pressure CH_4 and CO_2 sorption isotherms were measured using a computer controlled Sieverts-type apparatus, details of which have been published elsewhere.[3]

Isotherm data were analysed using the virial equation[4]:

$$\ln(n/p) = A_0 + A_1 n + A_2 n^2 + \ldots\ldots$$

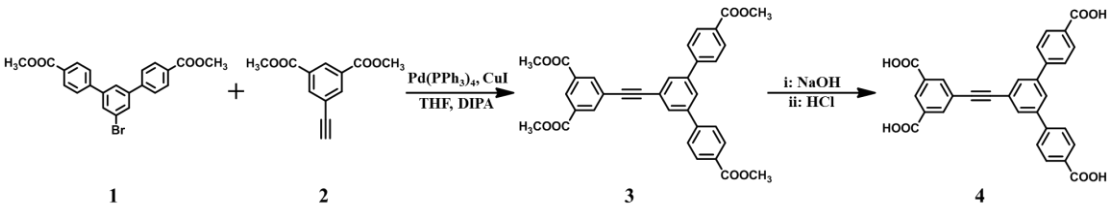
where the p is pressure, n is the amount adsorbed, and A_0, A_1, etc., are virial coefficients.

1.3 X-ray Collection and Structure Determination

Crystallographic measurements for **ZJU-32** were taken on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector using graphite-monochromatic Mo K$_\alpha$ radiation (λ = 0.71073Å) at 293 K. The determination of the unit cell and data collection for the crystal of **ZJU-32** were performed with CrysAlisPro. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.[5] The structure of **ZJU-32** was determined by direct methods and refined by the full-matrix

least-squares method with the SHELX-97 program package.[6] All non-hydrogen atoms were located successfully from Fourier maps and were refined anisotropically. The disordered lattice DEF and water molecules could not be located successfully from Fourier maps in the refinement cycles. The scattering from the highly disordered lattice guest molecules were removed using the SQUEEZE procedure implemented in the PLATON package.[7] The composition of the as-synthesized **ZJU-32** was figured out based on the elemental analysis, TGA and single crystal structure. Crystallographic data are summarized in Table S1.

1.4 Synthesis of the organic linker H_4L



Scheme S1. Synthetic route to the organic linker H_4L used to construct **ZJU-32**.

Synthesis of Dimethyl 5'-((3,5-bis(methoxycarbonyl)phenyl)ethynyl)- [1,1':3',1''-terphenyl]-4,4''-dicarboxylate (3): compound **1** (4.25g, 10mmol), compound **2** (3.27 g, 15 mmol), THF (100ml), and diisopropylamine (DIPA, 50ml) were added to a 250 mL Schlenk flask equipped with a magnetic stir bar and a rubber stopper., and the mixture was purged with argon and stirred for half an hour at room temperature. Then $Pd(PPh_3)_4$ (500mg, 0.43mmol) and CuI (166mg, 0.87 mmol) was added and the mixture heated at 65 ℃ for 24 h under argon. The resultant mixture was extracted with water and $CHCl_3$, and the water phase was then removed. Organic solvent was removed under reduced pressure, and the crude product was purified with toluene recrystallization to obtain pure compound **3** (3.58g, Yield: 64.6%). ^{1}H NMR (500 MHz, $CDCl_3$), δ = 3.99 (s, 6 H), 3.97 (s, 6 H), 8.67 (d, 1H), 8.42 (d, 2H), 8.17 (d, 4H), 7.85 (s, 3H), 7.75 (d, 4H). Anal. Calcd for $C_{34}H_{26}O_8$: C, 72.59; H, 4.66. Found: C, 72.26; H, 4.93.

Synthesis of 5'-((3,5-dicarboxyphenyl)ethynyl)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid (H_4L, 4): **3** (2.81 g, 5 mmol) was then suspended in a mixture of THF (20 mL) and H_2O (50 mL), to which 100 mL of 10 M NaOH aqueous solution was added. The mixture was stirred under reflux overnight and the THF was removed under a vacuum. Dilute HCl was added to the remaining aqueous solution until the solution was at pH = 3. The solid was collected by filtration,

washed with water, and dried to give H_4L (2.50 g, 98.8% yield). ^1H NMR (500 MHz, DMSO-D_6): δ= 8.48 (d, 1H), 8.34 (d, 2H), 8.14 (s, 1H), 8.07 (d, 6H), 8.01 (d, 4H). Anal. Calcd for $C_{30}H_{18}O_8$: C, 71.15; H, 3.58. Found: C, 71.11; H, 3.79.

1.5 Synthesis of ZJU-32:

A mixture of H_4L (5 mg, 0.010 mmol) and $CuCl_2$•$2H_2O$ (10.00mg, 0.0587mmol) was dissolved in DEF/H_2O (2.4 mL, 5:1, *v*/*v*) in a screw-capped vial. After HNO_3 (25 μL) (65%, aq.) were added to the mixture, the vial was capped and placed in an oven at 70 ^oC for 15 days. The resulting blue cubic shaped crystals were washed with DEF several times to give **ZJU-32** Elemental analysis: Calcd. For $[Cu_2(C_{30}H_{14}O_8)(H_2O)_2](DEF)_8(H_2O)_2$ ($C_{70}H_{106}Cu_2N_8O_{12}$, %): C, 55.65; H, 7.35; N, 7.42; Found: C, 55.53; H, 7.29; N, 7.88.

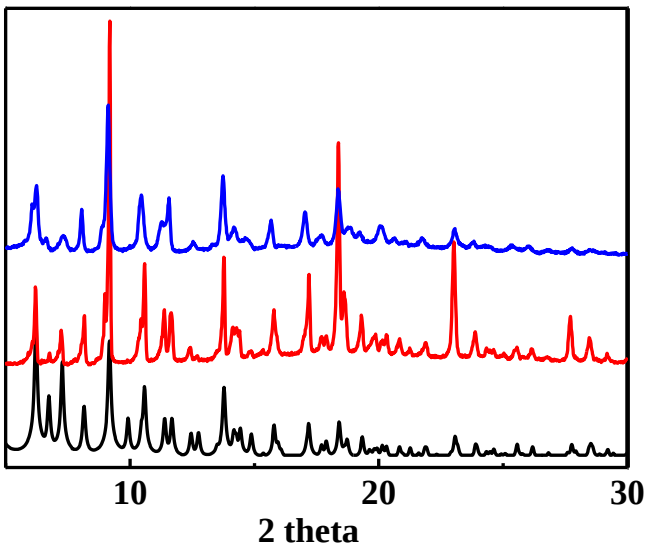
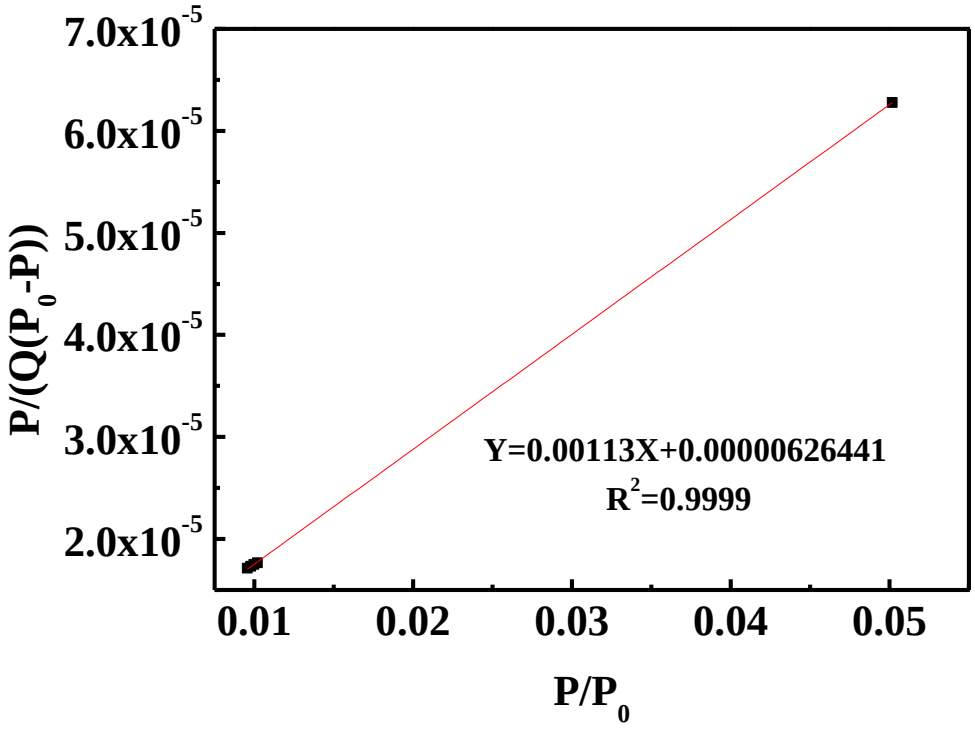


Figure S1. PXRD patterns of activated sample (blue), as-synthesized **ZJU-32** (red) and the simulated XRD pattern from the single-crystal X-ray structure (black).



S_{BET}= 1/(0.00113+0.00000626441)/22414×6.023×10^{23}×0.162×10^{-18}=3831 m^2/g

Figure S2. The BET surface area of **ZJU-32a** obtained from N2 adsorption isotherm at 77 K

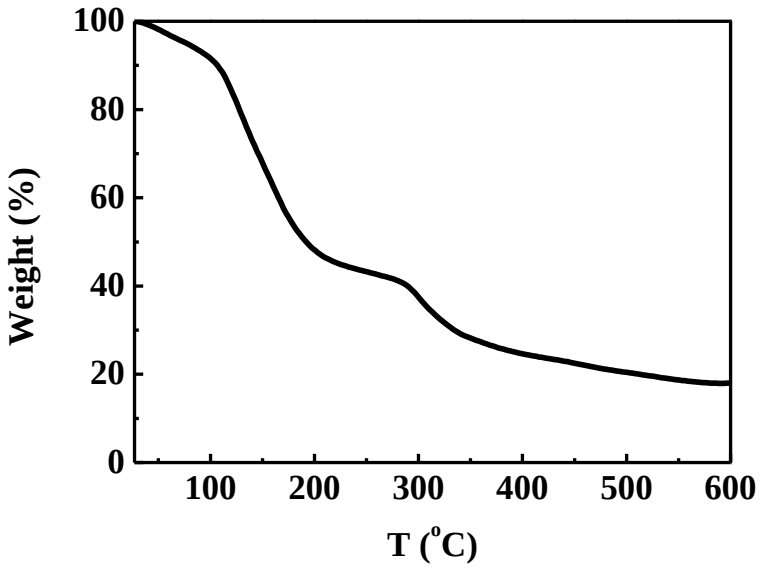


Figure S3. TGA curves of as-synthesized **ZJU-32** under a nitrogen atmosphere at a heating rate of 10 K min^{-1}.

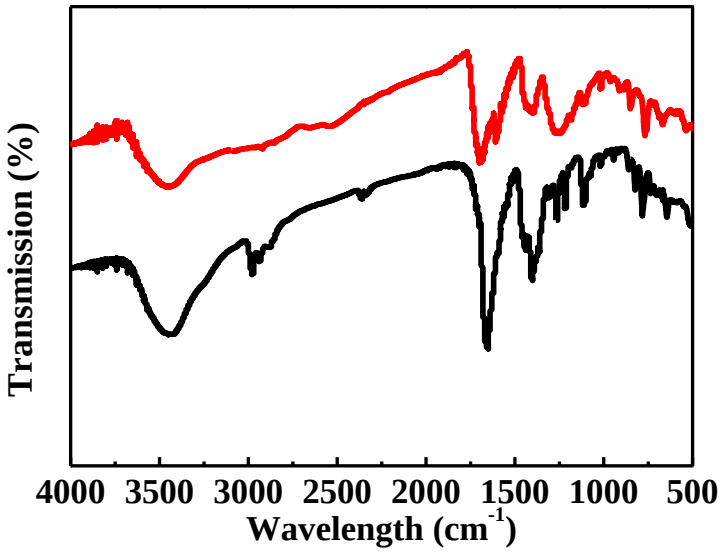
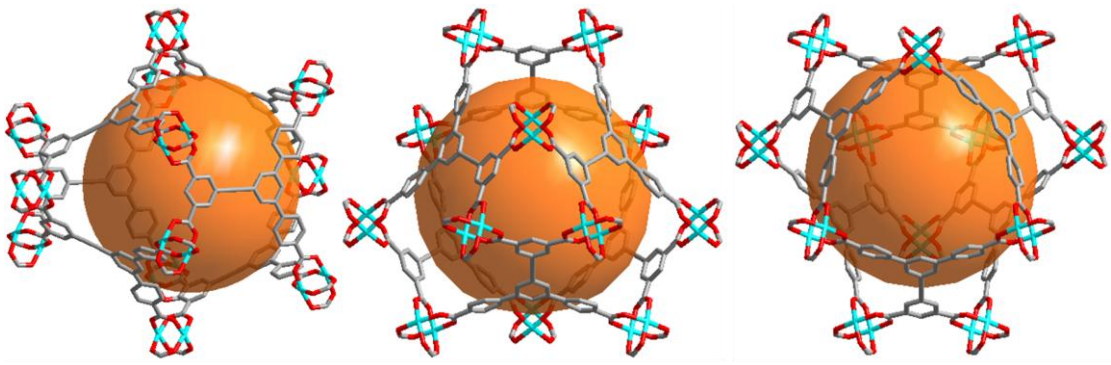


Figure S4 IR spectrum of ligand H_4L(black) and **ZJU-32** fresh sample (red)

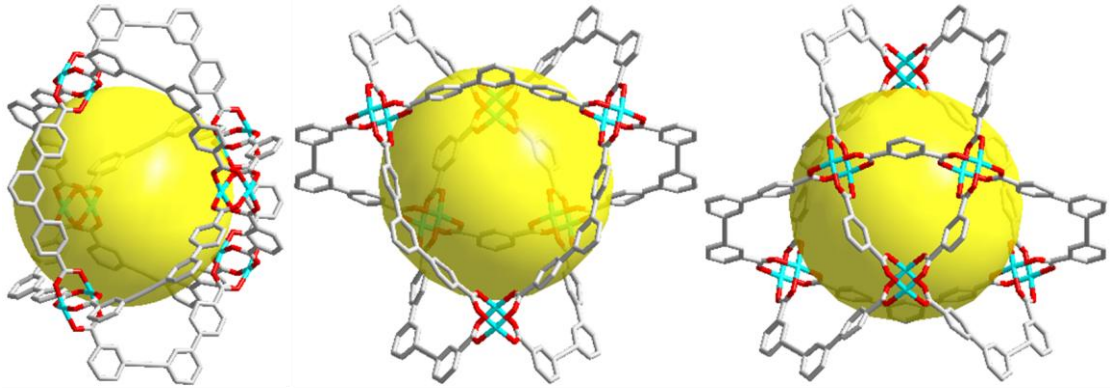
The **ZJU-32** structure has a noncatenated lattice, in which the framework nodes consist of Cu-paddle wheels coordinated by the carboxylates of the linkers. The overall structure can be viewed as the packing of two cages as shown below.

Cage 1



Side view 1 Side view 2 Side view 3

Cage 2



Side view 1 **Side view 2** **Side view 3**

Table S1 Crystallographic Data collection and Refinement result for **ZJU-32**.

	ZJU-32
chemical formula	C_{30} H_{18} Cu_2 O_{10}
formula weight	330.76
temperature (K)	293(2)
wavelength (Å)	0.71073
crystal system	Trigonal
space group	R-3m
a (Å)	26.2119(14)
b (Å)	26.2119(14)
c (Å)	36.423(3)
α (°)	90
β (°)	90
γ (°)	120
V (Å^3)	21672(2)
Z	18
density (calculated g/cm^{-3})	0.456
absorbance coefficient (mm^{-1})	0.459
F(000)	3023
crystal size (mm^3)	0.45 ×0.39 ×0.28
goodness of fit on F_2	0.944
R1, wR2 (I>2σ(I))[a]	0.0665, 0.1266
R1, wR2 (all data)[a]	0.1321, 0.1397
largest difference peak and hole (e/Å^3)	0.997, -0.348

[a] $R1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$; $wR2 = [\Sigma w(|F_o|-|F_c|^2) / \Sigma wF_o^2]^{1/2}$.

Table S2. Comparison of some highly porous NbO or Pts type MOFs in terms of their surface areas, pore volumes and cage/pore sizes

Material	S_{BET} [m^2g^{-1}]	$V_p{}^a$ [cm^3g^{-1}]	Pore dimensions [Å]	Ref.
ZJU-32	3831	1.482	17.0, 18.8	This work
ZJU-5	2823	1.074	9.5×22.5, 10.5	8
PCN-10	1407	0.67	-	9
PCN-11	1931	0.91	-	9
PCN-14	1753	0.87	9.23×18.45	10
PCN-16	2273	1.06	-	11
PCN-16’	1760	0.84	-	11
PCN-46	2500	1.01	-	12
NOTT-100	1661	0.677	13, 11	13
NOTT-101	2805	1.080	13×24, 14	13
NOTT-102	3342	1.268	13×34, 18	13
NOTT-103	2958	1.157	13×30, 16	13
NOTT-107	1770	0.767	-	14
NOTT-109	2110	0.85	9×12, 17	13
NOTT-110	2960	1.228	-	15
NOTT-111	2930	1.194	-	15
NJU-Bai12-ac	3038	1.135	-	16
UTSA-40	1630	0.65	6×11, 11×12	17

References

1 J. Jia, F. Sun, Q. Fang, X. Liang, K. Cai, Z. Bian, H. Zhao, L. Gao and G. Zhu, *Chem. Commun.*, 2011, **47**, 9167-9169.

2 M. Lamberto, C. Pagba, P. Piotrowiak and E. Galoppini, *Tetrahedron Letters*, 2005, **46**, 4895-4899.

3 W. Zhou, H. Wu, M. R. Hartman and T. Yildirim, *J. Phys. Chem. C*, 2007, **111**, 16131-16137.

4 X. Lin, I. Telepeni, A. J. Blake, A. Dailly, C. M. Brown, J. M. Simmons, M. Zoppi, G. S. Walker, K. M. Thomas, T. J. Mays, P. Hubberstey, N. R. Champness and M. Schröder, *J. Am. Chem. Soc.*, 2009, **131**, 2159-2171.

5 L. D. Oxford, CrysAlisPro, Version 1.171.33.56. UK, 2010.

6. G. M. Sheldrick, Program for Structure Refinement. Germany, 1997.

7 L. Spek, PLATON: The University of Utrecht: Utrecht, The Netherlands, 1999.

8 X. Rao, J. Cai, J. Yu, Y. He, C. Wu, W. Zhou, T. Yildirim, B. Chen and G. Qian, *Chem. Commun.*, 2013, **49**,

6719-6721.

9. X. S. Wang, S. Ma, K. Rauch, J. M. Simmons, D. Yuan, X. Wang, T. Yildirim, W. C. Cole, J. J. López, A. d. Meijere and H. C. Zhou, *Chem. Mater.*, 2008, **20**, 3145-3152.

10. S. Ma, D. Sun, J. M. Simmons, C. D. Collier, D. Yuan and H. C. Zhou, *J. Am. Chem. Soc.*, 2008, **130**, 1012-1016.

11 D. Sun, S. Ma, J. M. Simmons, J.-R. Li, D. Yuan and H.-C. Zhou, *Chem. Commun.*, 2010, **46**, 1329-1331.

12 D. Zhao, D. Yuan, A. Yakovenko and H.-C. Zhou, *Chem. Commun.*, 2010, **46**, 4196-4198.

13 Y. He, W. Zhou, T. Yildirim and B. Chen, *Energy Environ. Sci.*, 2013, **6**, 2735-2744.

14. C. E. Wilmer, M. Leaf, C. Y. Lee, O. K. Farha, B. G. Hauser, J. T. Hupp and R. Q. Snurr, *Nature Chem.*, 2012, **4**, 83-89.

15 S. Yang, X. Lin, A. Dailly, A. J. Blake, P. Hubberstey, N. R. Champness and M. Schröder, *Chem. Eur. J.*, 2009, **15**, 4829-4835.

16. B. Zheng, R. Yun, J. Bai, Z. Lu, L. Du and Y. Li, *Inorg. Chem.*, 2013, **52**, 2823-2829.

17 Y. He, S. Xiang, Z. Zhang, S. Xiong, C. Wu, W. Zhou, T. Yildirim, R. Krishna and B. Chen, *J. Mater. Chem.A*, 2013, **1**, 2543-2551.