Supporting information

Materials and Methods:

All chemicals were reagent grade and used as purchased without further purification. Elemental analysis for C, H and N was carried out on a German Elementar Vario EL III instrument. Thermogravimetric analyses was recorded on a NETZSCH STA 449C unit at a heating rate of 10 °C·min-1 under nitrogen atmosphere. The power X-ray diffractometer using Cu Kα radiation (λ = 0.154 nm).

Synthesis of compound FJI-H20

Compound **FJI-H20** $\{[Zn_4O(DPOT)](H_2O)_2(DEF)_4\}_n$ was obtained by dissolving $Zn(NO_3)_2$ (0.03mmol, 9mg) and H_6DPOT (0.015mmol, 9 mg) in DEF/H_2O (v_1:v_2 = 2:1), and heating this solution at 85°C for three days, then the colourless crystal obtained in 85% yield. Anal. calcd for $C_{47}H_{57}Zn_4N_7O_{22}$ (Mr = 1333.63): C, 42.33; H, 4.31; N, 7.35. Found: C, 42.54; H, 4.51; N, 7.53.

Gas adsorption Analysis

N_2, H_2, and CO_2 isotherms for **FJI-H20** were determined using an Accelerated Surface Area and Porosimetry 2020-M System at the Fujian Institute of Research on the Structure of Matter in a clean ultra- high vacuum system. Before measurements, about 100 mg solvent-exchanged samples were loaded into the sample basket within the adsorption instrument and then degassed under dynamic vacuum at 100 ℃ for 10 h to obtain the fully desolvated samples.

Single Crystal X-ray crystallography

Data collections were all performed on a SuperNova diffractometer with graphite mono chromated CuKa radiation (λ = 0.71073 Å). The structure was solved by direct methods, and all calculations were performed using the SHELXL package[1]. The structure of **FJI-H20** was refined by full matrix least-squares with anisotropic displacement parameters for non-hydrogen atoms. All hydrogen atoms were generated geometrically and treated as riding. The crystallographic data are summarized in Table S1-S2. CCDC 1880645-6 contains the supplementary crystallographic data for compound **FJI-H20** and its mirror. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(1) G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, **1997**.

Table S1 Crystal data and refinement results for compound **FJI-H20** and its mirror.

	FJI-H20	**FJI-H20-*mirror***
Formula	$C_{47}H_{57}Zn_4N_7O_{22}$	$C_{47}H_{57}Zn_4N_7O_{22}$
Formula weight	1333.63	1333.63
Crystal system	cubic	cubic
space group	$P2_13$	$P2_13$
a (Å)	18.1601(3)	18.1710(2)
b (Å)	18.1601(3)	18.1710(2)
c (Å)	18.1601(3)	18.1710(2)
α (°)	90	90
β (°)	90	90
γ (°)	90	90

Volume (Å^3)	5989.0(3)	5999.8(2)
T (K)	150	150
Z	4	4
F (000)	1760.0	1760.0
R1 (I>2σ(I))	0.0449	0.0376
wR2 (I>2σ(I))	0.1223	0.1053
Goodness of fit on F2	1.018	1.061

Table S2 Selected Bond Lengths (Å) and Angle (º) for compound **FJI-H20** and its mirror.

FJI-H20		**FJI-H20-*mirror***	
Bond	(Å)	Bond	(Å)
Zn2—O5^{i}	1.972 (4)	Zn2—O5^{i}	1.965 (3)
Zn2—O1	1.930 (2)	Zn2—O1	1.932 (2)
Zn2—O4^{ii}	1.979 (4)	Zn2—O4^{ii}	1.987 (4)
Zn2—O3	1.965 (5)	Zn2—O3	1.957 (4)
Zn1—O1	2.034 (7)	Zn1—O1	2.013 (5)
Zn1—O2^{iii}	1.892 (11)	Zn1—O2^{iii}	1.851 (8)
Zn1—O2^{iv}	1.892 (11)	Zn1—O2^{iv}	1.851 (8)
Zn1—O2	1.892 (11)	Zn1—O2	1.851 (8)
Angle	(º)	Angle	(º)
O5^{i}—Zn2—O3	111.7 (2)	O5^{i}—Zn2—O3	111.8 (2)
O1—Zn2—O5^{i}	111.3 (2)	O1—Zn2—O5^{i}	111.5 (2)
O1—Zn2—O4^{ii}	109.6 (2)	O1—Zn2—O4^{ii}	109.8(2)
O1—Zn2—O3	118.9 (2)	O1—Zn2—O3	118.7(2)
O4^{ii}—Zn2—O5^{i}	99.1 (2)	O4^{ii}—Zn2—O5^{i}	98.9 (2)
O4^{ii}—Zn2—O3	104.1 (2)	O4^{ii}—Zn2—O3	104.0 (2)
O2^{iv}—Zn1—O1	102.6 (4)	O2^{iv}—Zn1—O1	103.1 (3)
O2^{iii}—Zn1—O1	102.6 (4)	O2^{iii}—Zn1—O1	103.1 (3)
O2—Zn1—O1	102.6 (4)	O2—Zn1—O1	103.1 (3)
O2^{iii}—Zn1—O2^{iv}	115.4 (3)	O2^{iii}—Zn1—O2^{iv}	115.0 (2)
O2^{iv}—Zn1—O2	115.4 (3)	O2^{iv}—Zn1—O2	115.0 (2)
O2^{iii}—Zn1—O2	115.4 (3)	O2^{iii}—Zn1—O2	115.0 (2)

Symmetry codes：^{i}1/2+X,1/2-Y,-Z; ^{ii}-Z,1/2+X,1/2-Y; ^{iii}Y,Z,X; ^{iv}Z,X,Y

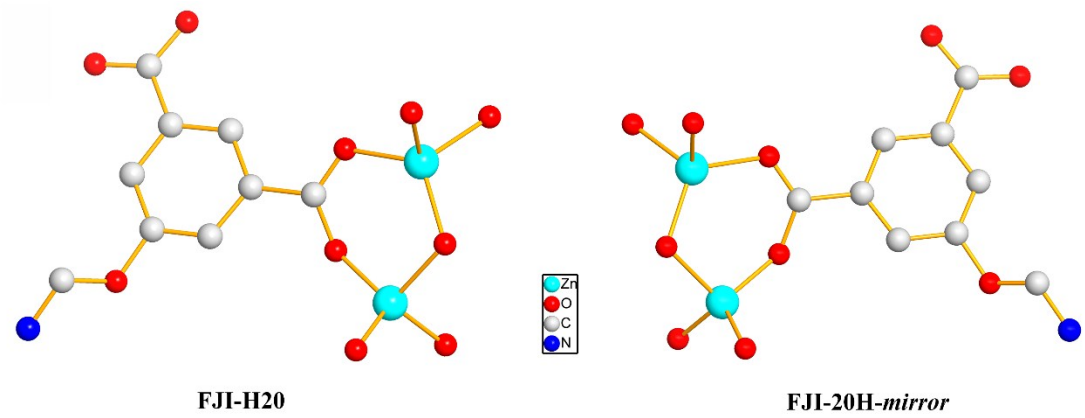

Figure S1 asymmetric unit of **FJI-H20** and **FJI-20H-*mirror***.

Table S3 Refined structure data of ten randomly selected **FJI-H20** crystals with absolute configuration and flack parameter

	a (Å)	R1	wR2	Flack parameter
Crystal-1	18.1925(6)	0.0449	0.1210	-0.02(4)
Crystal-2	18.2179(2)	0.0444	0.1274	0.08(4)
Crystal-3	18.2201(7)	0.0818	0.2369	0.95(3)
Crystal-4	18.1914(3)	0.0429	0.1087	0.94(6)
Crystal-5	18.2236(5)	0.0537	0.1335	0.04(7)
Crystal-6	18.2004(10)	0.0452	0.1072	0.05(6)
Crystal-7	18.2072(5)	0.0480	0.1336	0.08(4)
Crystal-8	18.1766(6)	0.0463	0.1124	0.04(7)
Crystal-9	18.2326(12)	0.0535	0.1416	0.01(8)
Crystal-10	18.2444(3)	0.0443	0.1255	0.06(4)

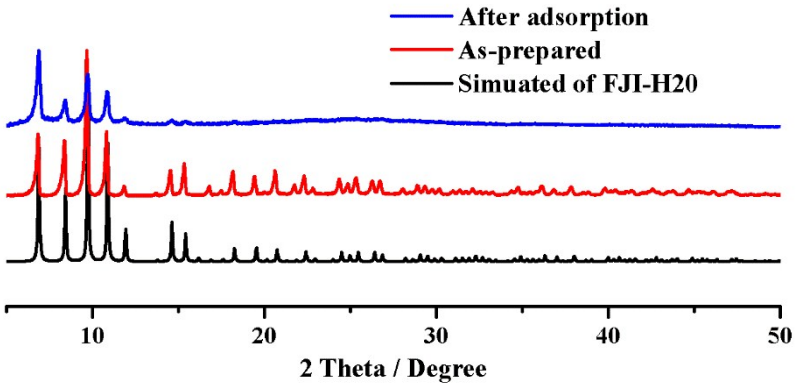

Figure S2 Powder X-ray diffraction Analyses of **FJI-H20** for adsorption.

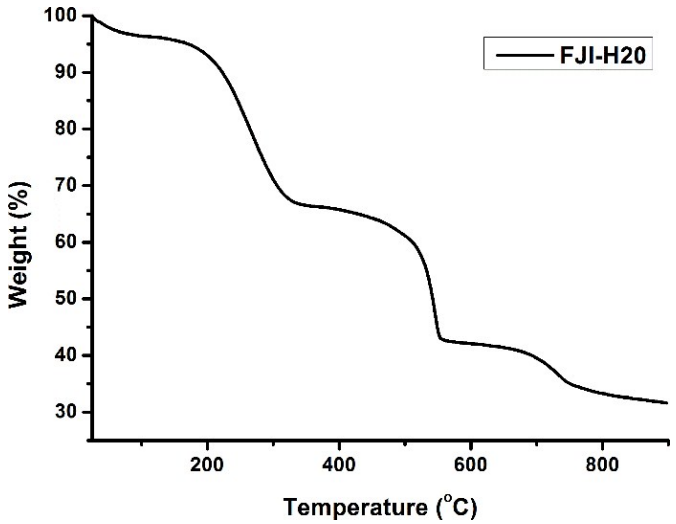

Figure S3 TGA curves of compound **FJI-H20**.

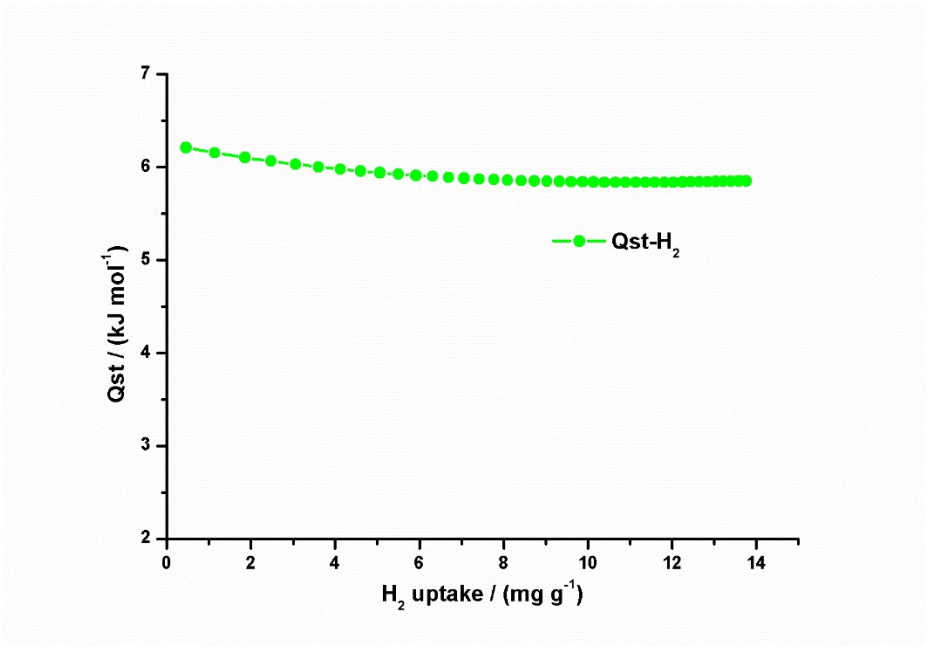

Figure S4 Adsorption heat of H_2 of **FJI-H20**.

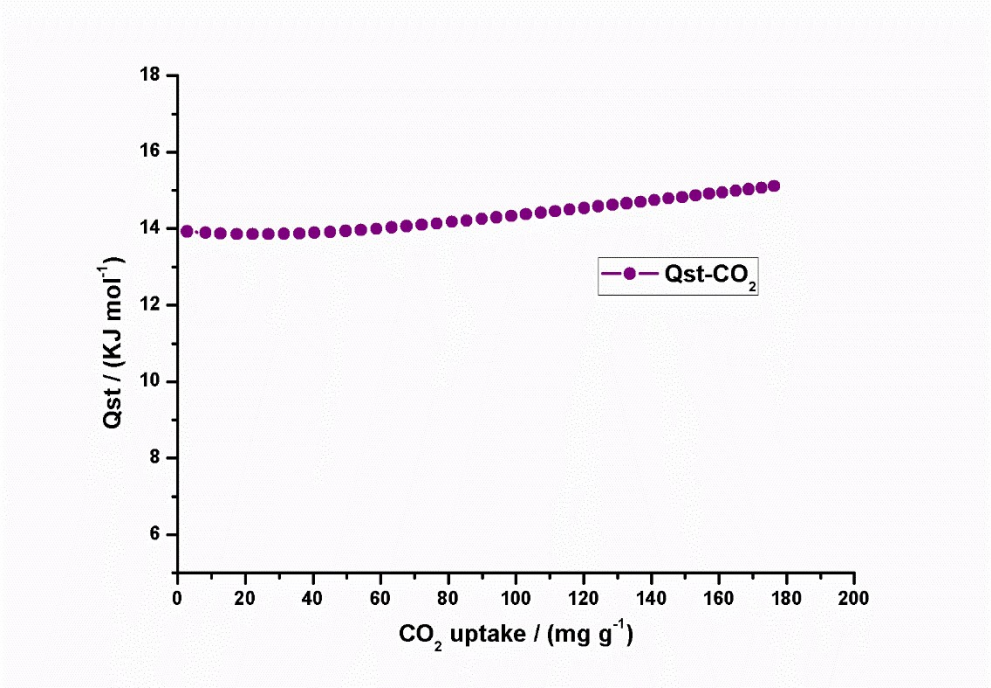

Figure S5 Adsorption heat of CO_2 of **FJI-H20**.

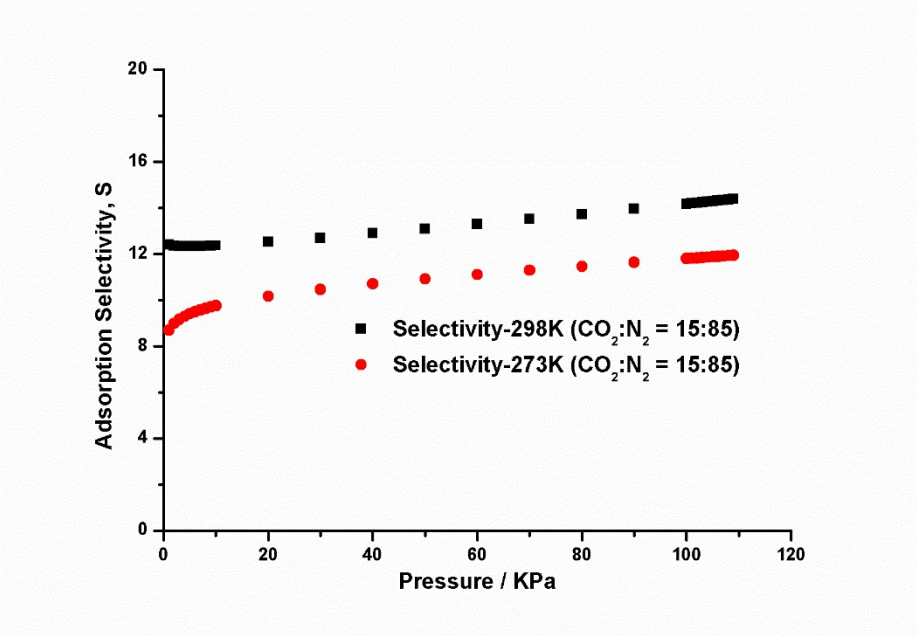

Figure S6 The CO_2/N_2 selectivity for of **FJI-H20** at 273 K and 298K, respectively.

Table S4 Hydrogen adsorption data for selected MOFs based on Zn_4O SBUs.

MOFs	H_2 uptake at 77 K[a] per 1 atm per wt%	ΔH_{ads}/Kj mol^{-1}	Reference
FJI-H16, Zn_4O(dpot)	2.04	6.0	this work
IR MOF-1(MOF-5), $Zn_4O(bdc)_3$	1.32	4.8	1a

IR MOF-2, $Zn_4O(bbdc)_3$	1.21		1b
IR MOF-3, $Zn_4O(abdc)_3$	1.42	6.1	1b
IR MOF-6, $Zn_4O(cbbdc)_3$	1.48		1b
IR MOF-8, $Zn_4O(ndc)_3$	1.5		1c
IR MOF-9, $Zn_4O(bpdc)_3$	1.17		1b
IR MOF-11, $Zn_4O(hpdc)_3$	1.62		1d
IR MOF-13, $Zn_4O(pydc)_3$	1.73	5.1-9.1	1a
IR MOF-18, $Zn_4O(tmbdc)_3$	0.89		1b
IR MOF-20, $Zn_4O(ttdc)_3$	1.35		1d
MOF-177, $Zn_4O(btb)_2$	1.25	4.4	1a
PCN-13, $Zn_4O(adc)_3$	0.41		1e
$Zn_4O(D_2\text{-tcppda})_{3/2}$	0.8		1f
$Zn_4O(ntb)_2$	1.9		1g
UMCM-2, $Zn_4O(t^2dc)(btb)_{4/3}$	1.28	6.4	1h
IRMOF-3–AM5, $Zn_4O(abdc)_{0.42}(habdc)_{2.58}$	1.21	5.7	1i
IRMOF-3–AMPh-a, $Zn_4O(abdc)_{2.04}(babdc)_{0.96}$	1.73	5.3	1i
IRMOF-3–AMPh-b, $Zn_4O(abdc)_{1.68}(babdc)_{1.32}$	1.73	5.7	1i
IRMOF-3–AMPh-c, $Zn_4O(abdc)_{0.9}(babdc)_{2.1}$	1.68	6.0	1i
IRMOF-3-URPh, $Zn_4O(abdc)_{1.77}(pubdc)_{1.23}$	1.54	5.7	1i
SNU-77H, $Zn_4O(tcbpa)_2$	1.79	7.05	1j
MOF-646, $Zn_4O(azd)_3$	1.75	7.8	1k
FJI-3, $Zn_4O(btc)_2$	1.26	4.62	1l

[a] wt% = 100×(weight of adsorbed H_2)/(weight of MOF material + weight of adsorbed H_2).

1 (a) J. L. C. Rowsell, A. R. Millward, K. S. Park and O. M. Yaghi, *J. Am. Chem. Soc.*, 2004, **126**, 5666. (b) J. L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 1304; (c) A. Dailly, J. J. Vajo and C. C. Ahn, *J. Phys. Chem. B*, 2006, **110**, 1099; (d) A. G. Wong-Foy, A. J. Matzger and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 3494; (e) S. Q. Ma, X. S. Wang, C. D. Collier, E. S. Manis and H. C. Zhou, *Inorg. Chem.*, 2007, **46**, 8499; (f) D. F. Sun, D. J. Collins, Y. X. Ke, J. L. Zuo and H. C. Zhou, *Chem.– Eur. J.*, 2006, **12**, 3768; (g) E. Y. Lee, S. Y. Jang and M. P. Suh, *J. Am. Chem. Soc.*, 2005, **127**, 6374; (h) K. Koh, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2009, **131**, 4184; (i) Z. Q. Wang, K. K. Tanabe and S. M. Cohen, *Chem.–Eur. J.*, 2010, **16**, 212; (j) H. J. Park, D.-W. Lim, W. S. Yang, T.-R. Oh, M. P. Suh, *Chem.–Eur. J.,* 2011, **17**, 7251-7260; (k) S. Barman, H. Furukawa, O. Blacque, K. Venkatesan, O. M. Yaghi, H. Berke, *Chem. Commun.,* 2010, **46**, 7981-7983; (l) J. Qian, F. Jiang, L. Zhang, K. Su, J. Pan, Q. Li, D. Yuan, M. Hong, *Chem. Commun.,* 2014, **50**, 1678-1681.