Supplementary Material (ESI) for Dalton Transactions

A pyridyl-decorated MOF-505analogue exhibiting hierarchical porosity, selective CO_2 capture and catalytic capacity

Qin-Qin Dang,[a] Yu-Fen Zhan,[a] Li-Na Duan[a]and Xian-Ming Zhang[a] *

School of Chemistry & Material Science, Shanxi Normal University Linfen 041000, P. R. China

Structure Analysis

Data collection were performed with Mo Kα radiation (λ = 0.710 73Å) on a Bruker Apex CCD diffractometer at 298(2) K for **1**. The SAINT program was used for integration of the diffraction profiles, and the SADABS program was used for X absorption correction. All the structures were solved by direct methods using the SHELXS program and refined by full-matrix least-squares methods with SHELXL. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms of organic ligands were generated theoretically onto the specific carbon and nitrogen atoms, and refined isotropically with fixed thermal factors. The Hydrogen atoms of the water molecules were calculated by Platon software. The Cand N atoms in pyridine ring are positional disordered and have been treated as two equal parts.[1,2].Thus, the disordered C atoms have occupancy of 0.375 and the disordered N atoms have occupancy of 0.125.Further details for structural analysis, selected bond lengths and bond angles are summarized in **Table S1,2**.

Table S1. Crystallographic Data and Structure Refinement for **1**.

Complex	**1**
Molecular formula	$C_{28}H_{40}Cu_2N2O_{17}$
M	803.70
Crystal system	Trigonal
Space group	R -3 m
a (Å)	18.7088(9)
b (Å)	18.7088(9)

c (Å)	38.2664(14)
α(°)	90
β (°)	90
γ(°)	120
V (Å3)	11599.5(11)
Z	9
ρcalc,(g cm-3)	0.730
μ, (mm-1)	0.850
F(000)	2556.0
Reflections collected	15695
Independent reflections	3064
R_1[a][I> 2σ(I)]	0.0330
wR_2[b] [I> 2σ(I)]	0.0977
R1 (all data)	0.0409
wR2 (all data)	0.1013

R_1[a]=∑||Fo|-|Fc||/∑|Fo|, wR_2[b]= $[\sum w(Fo^2-Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$

Table S2. Bond lengths [Å] and angles [deg] for complex **1**.

complex **1**

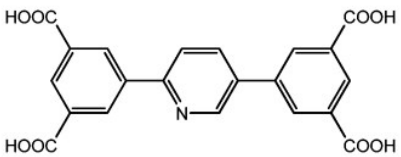
Cu1- Cu1(a)	2.6621(5)	Cu1-O1(b)	1.9568 (12)
Cu1- O1W	2.146(2)	O2- Cu1(a)	1.9649(12)
Cu1- O2(c)	1.9649(12)	C6- C7'(d)	1.352(6)
C6- N1'(d)	1.352(6)	C7'- C7'(e)	1.807(13)
C7'- N1'(e)	1.807(13)	Cu1- O2(a)	1.9648(13)
Cu1- O1	1.9569(12)	C6- C7'	1.352(6)
C7'- C7'(d)	1.967(11)		
O1- Cu1- Cu1(a)	84.37(4)	O1(b)- Cu1- Cu1(a)	84.37(4)
O1(b)- Cu1- O2(a)	89.88(6)	O1(b)- Cu1- O2(c)	167.52(5)
O1- Cu1- O2(a)	167.52(5)	O1(b)- Cu1- O1W	98.82(8)
O2(c) -Cu1- Cu1(a)	83.16(4)	O2(a)-Cu1- Cu1(a)	83.16(4)
O2(a)-Cu1- O1W	93.66(8)	O2(c)-Cu1- O1W	93.66(8)
C1-O1- Cu1	122.58(12)	C1-O2-Cu1(a)	123.67(11)
O1- Cu1-O1(b)	88.55(8)	O1- Cu1- O2(c)	89.88(6)
O1- Cu1- O1W	98.82(8)	O2(c)-Cu1- O2(a)	88.97(9)
O1W - Cu1-Cu1(a)	175.52(10)		

[a] 5/3-X, 4/3-Y, 4/3-Z; [b] 1+Y-X, +Y, +Z; [c] 2/3-Y+X, 4/3-Y, 4/3-Z; [d] 1-Y, 1-X, +Z; [e] +Y, +X, 1-Z

Table S3. The optimization of reaction condition[a].

Entry	Cat. mol %	TMSCN	Temp.(K)	Conv.(%)[b]
1	0	2 eq	293K	4
2	1	2 eq	293K	76
3	***1***	***2 eq***	***313K***	***99***
4	0.5	2 eq	313K	69

[a]Reaction conditions: Me_3SiCN (2mmol), aldehyde (1mmol),**1′**,8h, under N_2 atmosphere.[b]Determined by GC based on the carbonyl substrate.



Scheme 1s. Schematic structure of the organic linker H_4L.

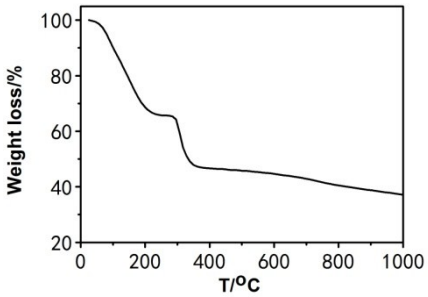


Fig.S1 The TGA plots of **1**.

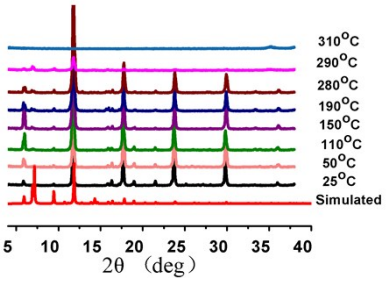


Fig.S2 Temperature-dependentpowder X-ray diffraction data under air atmosphere for**1**.

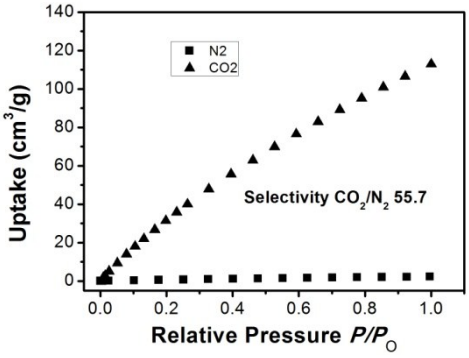


Fig. S3CO_2 andN_2adsorptionisotherm for **1**′ at 273K

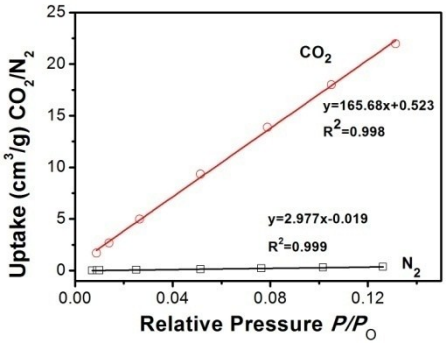


Fig. S4 The ideal selectivity of CO_2 over N_2 calculated by the Henry's Law

Analysis of carbon dioxide adsorption.

The methods are applied to dispose the sorption data according to the literature.The Langmuir-Freundlich equation is used to fit CO_2 adsorption isotherm and predict the adsorption capacity of the framework at saturation, and Clausius-Clapeyron equation is applied to the calculation of the

enthalpies of CO2 adsorption.

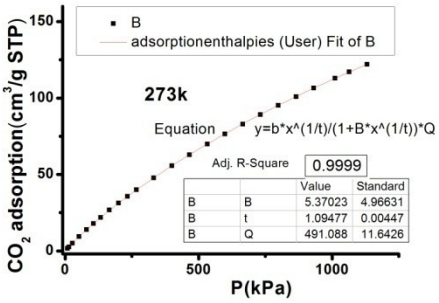


Fig. S5 Carbon dioxide isotherm at 273 K (symbols) and Langmuir-Freundlich equation fits (line) for **1**′.

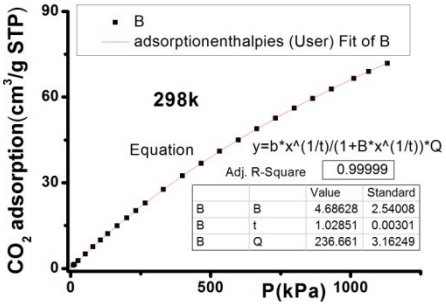


Fig. S6 Carbon dioxide isotherm at 298 K (symbols) and Langmuir-Freundlich equation fits (line) for **1**′.

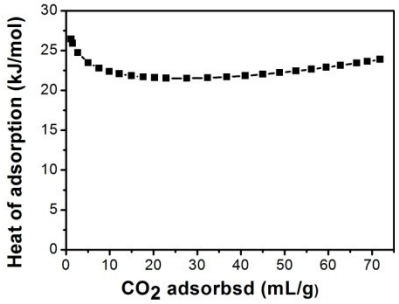


Fig.S7 The isosteric heat of adsorption of**1**′.

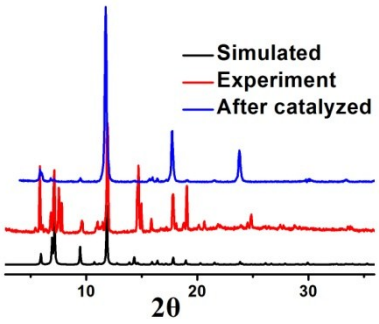


Fig. S8 The PXRD patterns of simulated, experimented and after catalyzed for **1**.

References

1.Q. Li and S. Du, *RSC Adv.*, 2015, 5, 9898-9903.
2.Q. Li and S. Du, *RSC Adv.*, 2014, 4, 30963-30967.