Electronic Supplementary Information (ESI)

Inquiry for multifunctional design of metal-organic frameworks: *in-situ* equipping additional open metal sites (OMSs) inducing high CO₂ capture/conversion abilities

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S1. Single X-Ray Diffraction Analyses

Table S1. Crystal data and structure refinements for compou	und 1 .
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compound	Compound 1
Formula	$C_{72} H_{93} Co_3 N_{20} O_{23}$
Formula weight	1783.45
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	P n m a
<i>a</i> (Å)	21.375(4)
<i>b</i> (Å)	23.679(5)
<i>c</i> (Å)	20.058(4)
α (°)	90
в (°)	90
γ (°)	90
V (Å ³)	10152(4)
$Z, D_c (Mg/m^3)$	4, 1.167
F(000)	3720
ϑ range (deg)	2.213-25.357
reflns collected/unique	53493/9522
R _{int}	0.0798
data/restraints/params	4450/105/454
GOF on <i>F</i> ²	1.066
$R_1, wR_2 (I>2\sigma(I))$	0.0725, 0.2120
R_1 , wR_2 (all data)	0.0988, 0.2278

^a R1 = Σ ||F0| - |Fc||/ Σ |F0|, ^b wR2 = [Σ w(|F0|² - |Fc|²)/ Σ |w(Fo²) ²| ^{1/2}

Note: Since the highly disordered cations and guest molecules were trapped in the channels of compound **1** and could not be modeled properly, the PLATON/SQUEEZE was applied to remove their diffraction contribution.

Compound 1						
Co1-O2	2.093(3)	O3-Co1-N5	86.47(11)			
Co1-O3	2.095(3)	O4-Co1-O2	93.00(10)			
Co1-O4	2.0071(14)	O4-Co1-O3	91.73(10)			
Co1-N3	2.188(3)	O4-Co1-N3	90.26(11)			
Co1-N4	2.167(3)	O4-Co1-N4	89.91(11)			
Co1-N5	2.178(3)	O4-Co1-N5	177.40(11)			
Co2-N6	1.944(14)	N4-Co1-N3	91.74(12)			
Co2-N7	1.951(15)	N4-Co1-N5	91.87(12)			
02-Co1-O3	91.25(12)	N5-Co1-N3	91.59(12)			
O2-Co1-N3	176.72(10)	N6-Co2-N7	92.2(6)			
O2-Co1-N4	87.90(12)	C19-O2-Co1	134.9(3)			
O2-Co1-N5	85.16(11)	C28-O3-Co1	133.1(3)			
O3-Co1-N3	89.02(11)	Co1-O4-Co1	121.10(13)			
O3-Co1-N4	178.19(11)					

 Table S2. Selected bond lengths [Å] and angles [°] for compound 1.

S2. Characterization of compound 1



Fig. S1 PXRD patterns of compound **1** for simulated, as-synthesized and activated samples. The differences in reflection intensity are probably due to preferred orientations in the powder samples.



Fig. S2 Thermogravimetric analysis curves of compound 1 for the as-synthesized and activated.



Fig. S4 The differences between the two structures and the multifunctional design routine of compound 1.



Fig. S5 The dihedral angle between the open Co site and H_2 bpydc ligand.



Fig. S6 The CPK models of compound 1 via X axis (a), Y axis (b) and Z axis (c).



Fig. S7 FT-IR spectra of the as-synthesized sample.

S3. Gas Adsorption Measurements

Calculation Procedures of Selectivity from IAST

The measured experimental data is excess loadings (q^{ex}) of the pure components CO₂, CH₄, C₂H₆ and C₃H₈ for compound **1**, which should be converted to absolute loadings (q) firstly.

$$q = q^{ex} + \frac{pV_{pore}}{ZRT}$$

Here *Z* is the compressibility factor. The Peng-Robinson equation was used to estimate the value of compressibility factor to obtain the absolute loading, while the measure pore volume is also necessary. The dual-site Langmuir-Freundlich equation is used for fitting the isotherm data at 298 K.

$$q = q_{m_1} \times \frac{b_1 \times p^{1/n_1}}{1 + b_1 \times p^{1/n_1}} + q_{m_2} \times \frac{b_2 \times p^{1/n_2}}{1 + b_2 \times p^{1/n_2}}$$

Here *p* is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), *q* is the adsorbed amount per mass of adsorbent (mol kg⁻¹), q_{m1} and q_{m2} are the saturation capacities of sites 1 and 2 (mol kg⁻¹), b_1 and b_2 are the affinity coefficients of sites 1 and 2 (1/kPa), n_1 and n_2 are the deviations from an ideal homogeneous surface. The selectivity of preferential adsorption of component 1 over component 2 in a mixture containing 1 and 2, perhaps in the presence of other components too, can be formally defined as

$$S = \frac{q_1/q_2}{p_1/p_2}$$

 q_1 and q_2 are the absolute component loadings of the adsorbed phase in the mixture. These component loadings are also termed the uptake capacities. We calculate the values of q_1 and q_2 using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.

Figures for gas adsorption performance of compound 1



Fig. S8 The CO_2 adsorption isotherms at 273 and 298 K of JLU-Liu 37 and compound 1.



Fig. S9 The calculating Q_{st} of CO₂ for compound **1**.



Fig. S10 The CH₄ adsorption isotherms for compound 1 at 273 and 298 K and the calculating Q_{st}.



Fig. S11 The C_2H_6 adsorption isotherms for compound 1 at 273 and 298 K and the calculating Q_{st} .



Fig. S12 The C_3H_8 adsorption isotherms for compound 1 at 273 and 298 K and the calculating Q_{st} .



Freundlich (DSLF) fits (a, c and e) and gas mixture adsorption selectivity predicted by IAST at 298 K for Compound **1** (b, d and f).

Compounds	SA _{BET} (m² g ⁻¹)	SA _{Langmuir} (m ² g ⁻¹)	CO₂ uptake (mmol/g)	Reference
ZJNU-40	2209	2328	7.6	1
PCN-88	3308	3845	7.1	2
Compound 1	1325	1786	4.9	This work
UTSA-16	687	904	4.2	3
ZnF(daTZ)	479	N.A.	3.9	4
USTC-253	1800	N.A.	3.7	5
CPM-5	580	733	3.6	6
JLU-Liu37	1795	N.A.	3.4	7
MAF-23	N.A.	622	3.3	8
InDCPN-Cl	997	1351	3.1	9
SNU-M10	N.A.	505	3.3	10
ZIF-78	620	N.A.	2.7	11
TMOF-1	256	N.A.	2.2	12
SNU-5	N.A.	2189	0.9	13

Table S3. CO_2 uptakes under 1 atm and 273 K of some selected MOF-based materials.

 Table S4. Gas adsorption amounts for compound 1 in 273 and 298 K.

Ads. Amount (cm ³ g ⁻¹)						
	CO ₂	CH ₄	C ₂ H ₆	C ₃ H ₈		
273 K	110.5	24.7	140.5	143.1		
298 K	54.3	14.1	95.4	126.8		

S4. Cycloaddition of CO₂ with Epoxides

Details of experiments and calculation procedures of catalytic efficiency

In a typical reaction, the catalytic reaction was conducted in a Schlenk tube using the epoxide (10 mmol) in solvent free environment at 80 °C (room temperature for PO) under a CO_2 balloon catalyzed by compound **1** (0.15 mol%) and co-catalyst of tetra-n-tertbutylammonium bromide (TBAB, 5 mol%, 322.3 mg) for 24 h. The speed of stirring was 400 rpm. After catalyst separation by centrifugation, a small aliquot of the supernatant reaction mixture was taken to be analyzed by ¹H NMR.

The conversion, selectivity and yield of SO to SC catalyzing by compound **1** were determined by calculation of the ¹H-NMR integrals of the corresponding highlighted protons in SO (Ha), SC (Ha') and the phenyl group (H_{b-f}) (from SO, SC and other by-products) according to the following equation (as SO and SC are known compounds, the characteristic peaks were pointed out according to literatures¹⁴).

Conversion (%) =
$$(1 - \frac{5I_{H_a}}{I_{H_{b-f}}}) \times 100 \%$$

Selectivity (%) =
$$\frac{5I_{H_{a'}}}{I_{H_{b-f}} - 5I_{H_{a}}} \times 100 \%$$

Yield (%) =
$$\frac{5I_{H_{a'}}}{I_{H_b} - f} \times 100 \%$$



Fig. S14 ¹H NMR spectrum of the mixture produced by cycloaddition reaction of SO to SC catalyzed by compound **1** in CDCl₃.

The yields of propylene oxide, cyclohexene oxide, benzyl phenylglycidyl ether and 4-((o-tolyloxy)methyl)-1,3dioxolan-2-one to corresponding cyclic carbonates catalyzing by compound **1** under the optimized conditions were calculated with the reported method according to the following equation. ¹ (Figure S10-13, as all of the epoxides and cyclic carbonates are known compounds, the characteristic peaks were pointed out according to literaturess¹⁴⁻¹⁶).



Fig. S15 ¹H NMR spectrum of the mixture produced by cycloaddition reaction of phenylglycidyl ether to phenylglycidyl carbonate catalyzed by compound **1** in CDCl₃.



Fig. S16 ¹H NMR spectrum of the mixture produced by cycloaddition reaction of 2-((o-tolyloxy)methyl)oxirane to 4-((o-tolyloxy)methyl)-1,3-dioxolan-2-one catalyzed by compound **1** in CDCl₃.



Fig. S17 ¹H NMR spectrum of the mixture produced by cycloaddition reaction of propylene oxide to propylene carbonate catalyzed by compound **1** in CDCl₃ with n-dodecane as internal standard.



Fig. S18 ¹H NMR spectrum of the mixture produced by cycloaddition reaction of *Cis*-Cyclohexene oxide to *Cis*-Cyclohexene carbonate catalyzed by compound **1** in CDCl₃.

The influence of the reaction time on the SO yield

To investigate the influence of the reaction time on the SO yield, the continuous sampling experiment was undertaken at 1, 6, 12, 24, 36 and 48 hours, with the optimized conditions (0.05 mol% compound **1**, 322 mg TBAB, 1 atm CO₂ and 80 °C). As shown in **Figure S19**, the curve before 12 hours was almost straight, which indicated that the reaction was within the kinetic interval. The gradual decline of the curve slope from 12 to 24 hours displayed that the inflexion existed in this interval. There was not obvious yield increase observed during 24, 36 and 48 hours, which indicated the longer reaction time was inefficient.



Fig. S19 Continuous sampling experiment of compound 1 for the cycloaddition reaction of styrene oxide with CO₂.

	t/h	Con.%	Sel.%	Yield%	TON	TOF
0.15%catalyst	1	7	86	6	40	40
5% TBAB	6	52	96	50	333	56
	12	85	98	84	560	47
	24	97	>99	97	647	27
	36			97	647	18
0.15%catalyst	1	9	67	6	40	40
1% TBAB	6	33	94	31	207	34
	12	58	98	57	380	32
	24	85	99	84	560	23
	36	95	97	92	560	17
0.15%catalyst	1	38	97	37	247	247
8% TBAB	6	91	97	88	587	98
	12	96	99	95	633	53
	24			97	647	27
	36			97	647	18
0.08%catalyst	1	8	88	7	93	93
5% TBAB	6	30	96	29	387	64
	12	53	96	51	680	57
	24	81	97	79	1053	44
	36	97	96	93	1240	34
0.3%catalyst	1	13	92	12	40	40
5% TBAB	6	50	>99	50	167	28
	12	77	98	76	253	21
	24	97	>99	97	323	13
	36			97	323	9

Table S5. Optimum conditions for cycloaddition of carbon dioxide with styrene oxide catalyzed by compound 1.



Fig. S20 Recycling experiments of compound 1 for the cycloaddition reaction of styrene oxide with CO₂.



Fig. S21 PXRD patterns of compound 1 for as-synthesized and 3th time recycled.

Table S6. ICP-OES analysis of Co^{2+} in the 3 th cycled reaction mixture filtrate
Table 50. ICI OES analysis of Co in the S cycled reaction mixture intrate

Catalyst	Compound 1		
Co ²⁺ concentration (ppm)	0.9056		

Though compound **1** was synthesized *in-situ*, it can also be obtained by post-synthetic modification.¹⁷ The samples after 3 catalysis cycles were recollected, soaked in 0.1 M $Co(NO_3)_2$ (in DMA solution) for 24 h and then activated again (Fig. S22), the two exposed pyridine-N sites of compound **1** were re-coordinated by Co^{2+} metal. The performance of the cycloaddition of carbon dioxide with styrene oxide catalyzed by the samples was investigated under optimized conditions, with conversion rate of 81 % (Fig. S23) that is much higher than it of 56 % in the third cycle. It proves that the decrease of cycle efficiency is due to the leaking of metal, and could be reversed by post-synthetical modification.



Fig. S22 PXRD patterns of compound **1** for as-synthesized, 3th time recycled and the samples soaked in Co²⁺ / DMA then activated again.



Fig. S23 ¹H NMR spectrum in CDCl₃ of the mixture produced by cycloaddition reaction of SO to SC catalyzed by the recycled samples soaked in Co²⁺ / DMA and activated again.

Table S7. Comparison of Cycloaddition of CO2 with SO by reported top performing MOF catalysts under respective optimized conditions.

Catalyst	T (°C)	P (atm)	T (h)	Yield%	TOF ^a	Ref.
Hf-NU-1000	r.t.	1	56	100	0.4	18
Compound 1	80	1	24	97	27 27 (for per Co ²⁺ unit)	This work
InDCPN-Cl	80	1	24	93	77.6 15.6 (for per In ³⁺ unit)	9
Zr-NU-1008	r.t.	1	24	99	4	19
MOF-893(Zr)	80	1	23	88	12.0 2.0 (for per Zr ⁴⁺ unit)	20
MOF-892(Zr)	80	1	16	82	16.0 2.6 (for per Zr ⁴⁺ unit)	20
MOF-894(In)	80	1	20	78	12.0 6.0 (for per In ³⁺ unit)	20
FJI-H14	80	0.15	24	86	7.5	21
PCN-700-o	50	1	10	83	21.8	14
Cu-TPTC-NH ₂	r.t.	1	8	89	55.6 27.8 (for per Cu ²⁺ unit)	22

^aTOF = Turnover frequency (product (mmol)/catalyst (mmol)/time (h)).

Catalyst	Т (°С)	P (atm)	T (h)	Yield%	Ref.
[Cu ₂ L(H ₂ O) ₂].4H ₂ O.2DMF	100	1	6	100	23
Compound 1	80	1	24	86	This work
СНВ(М)	120	1	6	71	24
CoMOF-1	60	1	12	84	25
COF-IL	80	1	48	71	26
FJI-C10	80	1	48	38	27

Table S8. Comparison with different MOFs catalysts reported in the cycloaddition reaction of CO2with phenylglycidyl ether.

References

- C. Song, Y. He, B. Li, Y. Ling, H. Wang, Y. Feng, R. Krishna and B. Chen, Enhanced CO₂ sorption and selectivity by functionalization of a NbO-type metal-organic framework with polarized benzothiadiazole moieties, *Chem. Commun.*, 2014, **50**, 12105-12108.
- J.-R. Li, J. Yu, W. Lu, L.-B. Sun, J. Sculley, P. B. Balbuena and H.-C. Zhou, Porous materials with pre-designed single-molecule traps for CO₂ selective adsorption, *Nat. Commun.*, 2013, 4, 1538.
- 3. A. Masala, J. G. Vitillo, F. Bonino, M. Manzoli, C. A. Grande and S. Bordiga, New insights into UTSA-16, *Phys. Chem. Chem. Phys.*, 2016, **18**, 220-227.
- 4. Z. Shi, Y. Tao, J. Wu, C. Zhang, H. He, L. Long, Y. Lee, T. Li and Y.-B. Zhang, Robust metal-triazolate frameworks for CO₂ capture from flue gas, *J. Am. Chem. Soc.*, 2020, **142**, 2750-2754.
- 5. Z.-R. Jiang, H. Wang, Y. Hu, J. Lu and H.-L. Jiang, Polar group and defect engineering in a metal-organic framework: synergistic promotion of carbon dioxide sorption and conversion, *ChemSusChem*, 2015, **8**, 878-885.
- S.-T. Zheng, J. T. Bu, Y. Li, T. Wu, F. Zuo, P. Feng and X. Bu, Pore space partition and charge separation in cagewithin-cage Indium-organic frameworks with high CO₂ uptake, *J. Am. Chem. Soc.*, 2010, 132, 17062-17064.
- J. Li, X. Luo, N. Zhao, L. Zhang, Q. Huo and Y. Liu, Two finite binuclear [M₂(μ₂-OH)(COO)₂] (M = Co, Ni) based highly porous metal-organic frameworks with high performance for gas sorption and separation, *Inorg. Chem.*, 2017, 56, 4141-4147.
- P.-Q. Liao, D.-D. Zhou, A.-X. Zhu, L. Jiang, R.-B. Lin, J.-P. Zhang and X.-M. Chen, Strong and dynamic CO₂ sorption in a flexible porous framework possessing guest chelating claws, *J. Am. Chem. Soc.*, 2012, **134**, 17380-17383.
- Y. Yuan, J. Li, X. Sun, G. Li, Y. Liu, G. Verma and S. Ma, Indium-organic frameworks based on dual secondary building units featuring halogen-decorated channels for highly effective CO₂ fixation, *Chem. Mater.*, 2019, **31**, 1084-1091.
- 10. H.-S. Choi and M. P. Suh, Highly selective CO₂ capture in flexible 3D coordination polymer networks, *Angew. Chem. Int. Ed.*, 2009, **48**, 6865-6869.
- R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe and O. M. Yaghi, Control of pore size and functionality in isoreticular zeolitic imidazolate frameworks and their carbon dioxide selective capture properties, *J. Am. Chem. Soc.*, 2009, **131**, 3875-3877.
- 12. G. Zhang, G. Wei, Z. Liu, S. R. J. Oliver and H. Fei, A robust sulfonate-based metal-organic framework with permanent porosity for efficient CO₂ capture and conversion, *Chem. Mater.*, 2016, **28**, 6276-6281.
- Y.-G. Lee, H. R. Moon, Y. E. Cheon and M. P. Suh, A comparison of the H₂ sorption capacities of isostructural metal-organic frameworks with and without accessible metal sites: [{Zn₂(abtc)(dmf)₂}] and [{Cu₂(abtc)(dmf)₂}] versus [{Cu₂(abtc)}], *Angew. Chem. Int. Ed.*, 2008, 47, 7741-7745.
- S. Yuan, L. Zou, H. Li, Y.-P. Chen, J. Qin, Q. Zhang, W. Lu, M. B. Hall and H.-C. Zhou, Flexible zirconium metalorganic frameworks as bioinspired switchable catalysts, *Angew. Chem. Int. Ed.*, 2016, 55, 10776-10780.
- H. He, Q. Sun, W. Gao, J. A. Perman, F. Sun, G. Zhu, B. Aguila, K. Forrest, B. Space and S. Ma, A stable metalorganic framework featuring a local buffer environment for carbon dioxide fixation, *Angew. Chem. Int. Ed.*, 2018, 57, 4657-4662.
- X. Zheng, S. Luo, L. Zhang and J.-P. Cheng, Magnetic nanoparticle supported ionic liquid catalysts for CO₂ cycloaddition reactions, *Green Chem.*, 2009, 11, 455-458.
- T. Zhang, K. Manna and W. B. Lin, Metal-organic frameworks stabilize solution-inaccessible cobalt catalysts for highly efficient broad-scope organic transformations, J. Am. Chem. Soc., 2016, 138, 3241-3249.
- 18. M. H. Beyzavi, R. C. Klet, S. Tussupbayev, J. Borycz, N. A. Vermeulen, C. J. Cramer, J. F. Stoddart, J. T. Hupp and O. K. Farha, A hafnium-based metal-organic framework as an efficient and multifunctional catalyst for facile

CO₂ fixation and regioselective and enantioretentive epoxide activation, J. Am. Chem. Soc., 2014, **136**, 15861-15864.

- J. Lyu, X. Zhang, K.-i. Otake, X. Wang, P. Li, Z. Li, Z. Chen, Y. Zhang, M. C. Wasson, Y. Yang, P. Bai, X. Guo, T. Islamoglu and O. K. Farha, Topology and porosity control of metal-organic frameworks through linker functionalization, *Chem. Sci.* 2019, **10**, 1186-1192.
- P. T. K. Nguyen, H. T. D. Nguyen, H. N. Nguyen, C. A. Trickett, Q. T. Ton, E. Gutiérrez-Puebla, M. A. Monge, K. E. Cordova and F. Gándara, New metal-organic frameworks for chemical fixation of CO₂, ACS Appl. Mater. Interface, 2017, 10, 733-744.
- L. Liang, C. Liu, F. Jiang, Q. Chen, L. Zhang, H. Xue, H.-L. Jiang, J. Qian, D. Yuan and M. Hong, Carbon dioxide capture and conversion by an acid-base resistant metal-organic framework, *Nat. Commun.*, 2017, 8, 1233.
- 22. V. Sharma, D. De, R. Saha, R. Das, P. K. Chattaraj and P. K. Bharadwaj, A Cu(ii)-MOF capable of fixing CO₂ from air and showing high capacity H₂ and CO₂ adsorption, *Chem. Commun.*, 2017, **53**, 13371-13374.
- C.-Y. Gao, H.-R. Tian, J. Ai, L.-J. Li, S. Dang, Y.-Q. Lan and Z.-M. Sun, A microporous Cu-MOF with optimized open metal sites and pore spaces for high gas storage and active chemical fixation of CO₂, *Chem. Commun.*, 2016, 52, 11147-11150.
- A. C. Kathalikkattil, D.-W. Kim, J. Tharun, H.-G. Soek, R. Roshan and D.-W. Park, Aqueous-microwave synthesized carboxyl functional molecular ribbon coordination framework catalyst for the synthesis of cyclic carbonates from epoxides and CO₂, *Green Chem.*, 2014, 16, 1607-1616.
- B. Parmar, P. Patel, R. S. Pillai, R. I. Kureshy, N.-u. H. Khan and E. Suresh, Efficient catalytic conversion of terminal/internal epoxides to cyclic carbonates by porous Co(ii) MOF under ambient conditions: structure-property correlation and computational studies, *J. Mater. Chem. A*, 2019, 7, 2884-2894.
- L.-G. Ding, B.-J. Yao, F. Li, S.-C. Shi, N. Huang, H.-B. Yin, Q. Guan and Y.-B. Dong, Ionic liquid-decorated COF and its covalent composite aerogel for selective CO₂ adsorption and catalytic conversion, *J. Mater. Chem. A*, 2019, 7, 4689-4698.
- J. Liang, Y.-Q. Xie, X.-S. Wang, Q. Wang, T.-T. Liu, Y.-B. Huang and R. Cao, An imidazolium-functionalized mesoporous cationic metal-organic framework for cooperative CO₂ fixation into cyclic carbonate, *Chem. Commun.*, 2018, 54, 342-345.