**Electronic Supporting Information for** 

# Robust multivariate metal-porphyrin frameworks for efficient ambient fixation of CO<sub>2</sub> to cyclic carbonates

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## Section S1: General Methods

**Chemicals:** All chemical reagents were obtained from commercial supplies without further purification. The metallated analogues of 5,10,15,20-tetrapyridylporphyrin (TPyP-M, M = Zn, Fe, Ni) and metal salt of CuNbOF<sub>5</sub> were synthesized according to the literatures.<sup>1,2</sup>



Fig. S1 Simulated and experimental PXRD patterns of CuNbOF<sub>5</sub>.

**Instrumentation:** Elemental analysis (EA) was carried out on a Vario EL-Cube. The powder X-ray diffraction (PXRD) patterns of the samples were recorded by a Rigaku Dmax 2500 X-ray diffractometer with Cu *K* $\alpha$  radiation ( $\lambda$  = 1.54056 Å). Metal contents were measured by an Ultima2 (Horbiba Jobin Yvon) inductively coupled plasma optical emission spectrometer (ICP-OES). Thermal analysis was carried out on a Netzsch STA449C thermal analyzer at a temperature range of 25~800 °C under air atmosphere with a heating rate of 10 °C min<sup>-1</sup>. The gas adsorption measurements were performed on a Micromeritics ASAP 2020 surface area and pore size analyzer. Fourier-transform infrared (FT-IR) spectra were recorded using a Nicolet iS10 spectrophotometer in 3750~450 cm<sup>-1</sup> region. Proton nuclear magnetic resonance spectra (<sup>1</sup>H NMR) were recorded on a Varian FT-NMR spectrometer (400 MHz).

## Section S2: Synthetic Procedures of FTPFs

### (1) Synthesis of Cu-Nb-Zn

A solution of 10 mg of TPyP-Zn in 8 mL of *N*-methyl-2-pyrrolidone was layered over a solution of 10 mg of CuNbOF<sub>5</sub> in 3 mL of ethylene glycol in vial. Interdiffusion of the solutions (at room temperature or heated at 60°) for a period of 5 days lead to the formation of Cu-Nb-Zn. Yield = 45% based on TPyP-Zn. EA data: C 51.36, H 4.15, N 10.20%, calculated for  $C_{40}H_{28}N_8O_3F_5CuNbZn$  C 48.75, H 2.86, N 11.37%.ICP data: Cu 4.8%, Nb 6.9%, Zn 4.3% IR: v (cm<sup>-1</sup>) = 2354 (w), 1656 (m), 1610 (s), 1535 (w), 1486 (w), 1410 (m), 1343 (w), 1297 (w), 1252 (w), 1203 (m), 1075 (m), 988 (m), 871 (m), 800 (m), 720 (s), 678 (s), 530 (s), 471 (m), 430 (w).

#### (2) Synthesis of Cu-Nb-Fe

A solution of 10 mg of TPyP-Fe in 8 mL of *N*-methyl-2-pyrrolidone was layered over a solution of 10 mg of CuNbOF<sub>5</sub> in 3 mL of ethylene glycol in vial. Interdiffusion of the solutions (at room temperature or heated at 60°) for a period of 5 days lead to the formation of Cu-Nb-Fe. Yield = 34% based on TPyP-Fe. EA data: C 48.27, H 3.24, N 10.15%, calculated for C<sub>40</sub>H<sub>28</sub>N<sub>8</sub>O<sub>3</sub>F<sub>5</sub>CuNbFe C 49.22, H 2.89, N 11.48%. ICP data: Cu 4.1%, Nb 6.6%, Fe 3.9%. IR: v (cm<sup>-1</sup>) = 3102 (w), 1698 (w), 1610 (s), 1547 (w), 1498 (w), 1422 (m), 1343 (m), 1203 (m), 1063 (m), 1003 (s), 902 (m), 803 (s), 720 (s), 686 (s), 546 (s), 471 (w), 411 (w).

#### (3) Synthesis of Cu-Nb-Ni

A solution of 10 mg of TPyP-Ni in 8 mL of *N*-methyl-2-pyrrolidone was layered over a solution of 10 mg of CuNbOF<sub>5</sub> in 3 mL of ethylene glycol in vial. Interdiffusion of the solutions (at room temperature or heated at 60°) for a period of 5 days lead to the formation of Cu-Nb-Ni. Yield = 53% based on TPyP-Ni. EA data: C 50.27, H 3.16, N 11.20%, calculated for  $C_{40}H_{28}N_8O_3F_5CuNbNi$  C 49.08, H 2.88, N 11.45%. ICP data: Cu 4.0%, Nb 5.2%, Ni 3.8%. IR: *v* (cm<sup>-1</sup>) = 2357 (w), 2173 (w), 1667 (s), 1610 (s), 1494 (m), 1419 (m), 1347 (w), 1294 (m), 1218 (m), 1146 (w), 1064 (m), 1011 (w), 973 (w), 925 (m), 856 (m), 800 (s), 728 (m), 672 (m), 558 (s), 464 (m), 430 (w).

## Section S3: Crystallographic Data and Refinement Parameters

Molecular modeling was carried out using Reflex Plus, a module implemented in Materials Studio (version 5.5.1) by Accelrys Inc. The initial structures were constructed piecewise starting with a tetragonal unit cell with space group *P4/mmm*, where *a* and *c* values were estimated according to the geometry and size of the building units, and further optimized by indexing experimental PXRD peak positions. The Pseudo-Voigt function was used for whole profile fitting and Berrar-Baldinozzi function was used for asymmetry correction during the refinement processes. The predicted structures were validated with Rietveld refinement against the observed PXRD patterns, respectively.

Atom	Х	Y	Z
Cu (1)	50000	50000	0
Nb (1)	50000	50000	50000
Ni (1)	0	0	0
C (1)	5023	30390	12
C (2)	7875	20650	81
C (3)	17714	17714	0
C (4)	25414	25414	0
C (5)	26338	31813	13509
C (6)	33608	38998	13249
N (1)	0	14656	0
N (2)	39776	39776	0
F (1)	50000	50000	24450
F (2)	50000	35461	50000
O (1)	0	0 23744	

Table S1 Atomic coordinates (×10<sup>5</sup>) parameters of Cu-Nb-Ni.

Refined composition:  $C_{40}H_{28}N_8O_3F_5CuNbNi$ ; Mass formula: 978.84; Crystal system: tetragonal; Space group: P4/mmm; a = b = 13.6484, c = 8.0870;  $R_p(\%)$ [Rietveld] = 8.35,  $R_{wp}(\%)$ [Rietveld] = 5.62.



Fig. S2 Experimentally observed and Rietveld refined PXRD patterns of Cu-Nb-Ni.

Section S4: Scanning Electron Microscopy (SEM) and X-ray Energy

Dispersive Spectroscopy (EDS)



Fig. S3 SEM image of Cu-Nb-Zn showing single-phase morphology.



Fig. S4 SEM image of Cu-Nb-Fe showing single-phase morphology.



Fig. S5 SEM image of Cu-Nb-Ni showing single-phase morphology.



Fig. S6 EDX images analyzed at different areas of sample Cu-Nb-Zn.



Fig. S7 EDX images analyzed at different areas of sample Cu-Nb-Fe.



Fig. S8 EDX images analyzed at different areas of sample Cu-Nb-Ni.

As shown in the SEM-EDX diagrams, the measured metal ratios of all the FTPFs are close to each other at three different monitoring sites, which also indicate the coexistence of the hetero-trimetallic species and their uniformity in the samples. Section S5: Fourier-transform infrared (FT-IR) and Ultraviolet-Visible

# (UV-Vis) Spectroscopy



Fig. S9 FT-IR spectra of Cu-Nb-Zn, Cu-Nb-Fe and Cu-Nb-Ni.



Fig. S10 UV-Vis diffuse-reflectance spectra of Cu-Nb-Zn, Cu-Nb-Fe and Cu-Nb-Ni.





Fig. S11 TGA curves of Cu-Nb-Zn, Cu-Nb-Fe and Cu-Nb-Ni in the air.



Fig. S12 Thermal PXRD patterns of Cu-Nb-Ni treated at different temperatures.



**Fig. S13** PXRD patterns of Cu-Nb-Ni upon immersion in different solvents (where ACN, DMF, and DMK are for acetonitrile, *N*,*N*-dimethylformamide, and acetone, respectively) for 24 h.



**Fig. S14** PXRD patterns of Cu-Nb-Ni upon immersion in water with different pH values for 24 h.



Fig. S15  $N_2$  adsorption-desorption isotherms at 77 K of Cu-Nb-Ni upon immersion in water with different pH values for 24 h.

## Section S7: Gas Absorption Measurements



All the FTPFs samples were activated by soaking in MeOH three days and MeOH was renewed two times every day before testing.

Fig. S16 N<sub>2</sub> adsorption-desorption isotherms of Cu-Nb-Zn at 77 K.



Fig. S17 N<sub>2</sub> adsorption-desorption isotherms of Cu-Nb-Fe at 77 K.



Fig. S18 N<sub>2</sub> adsorption-desorption isotherms of Cu-Nb-Ni at 77 K.



Fig. S19  $CO_2$  uptake of Cu-Nb-Zn at 273 and 298 K, respectively.



Fig. S20  $\mbox{CO}_2$  uptake of Cu-Nb-Fe at 273 and 298 K, respectively.



**Fig. S21** Fitting  $Q_{st}$  of CO<sub>2</sub> adsorption by using the data of CO<sub>2</sub> trapped at 273 and 298 K on Cu-Nb-Zn according to the virial equation.



**Fig. S22** Fitting  $Q_{st}$  of CO<sub>2</sub> adsorption by using the data of CO<sub>2</sub> trapped at 273 and 298 K on Cu-Nb-Fe according to the virial equation.



**Fig. S23** Fitting  $Q_{st}$  of CO<sub>2</sub> adsorption by using the data of CO<sub>2</sub> trapped at 273 and 298 K on Cu-Nb-Ni according to the virial equation.



**Fig. S24**  $CO_2$  isosteric heat of adsorption ( $Q_{st}$ ) for Cu-Nb-Zn, Cu-Nb-Fe and Cu-Nb-Ni, respectively.

## Section S8: Chemical Fixation of CO<sub>2</sub>

In each reaction, 20 mmol epoxide substrate, 80 mg FTPF catalyst (0.5 mol% based on metalloporphyrin), along with 0.65 g tetra-*n*-tert-butylammonium bromide (TBAB, 10 mol%) were mixed in a Schlenk tube. The Schlenk tube was solvent-free and purged with 1 atm CO<sub>2</sub> at room temperature for 12, 24, and 48 h. The reaction mixture was then filtered, and the filtrate was characterized by <sup>1</sup>H NMR to study its conversion ratio.



**Fig. S25** <sup>1</sup>H NMR spectrum of product 4-ethyl-1,3-dioxolan-2-one from coupling 2ethyloxirane and  $CO_2$  after 48 h. The unmarked peaks could be assigned to TBAB.



**Fig. S26** <sup>1</sup>H NMR spectrum of product 4-chloromethyl-1,3-dioxolane-2-one from coupling 2-(chloromethyl)oxirane and CO<sub>2</sub> after 48 h. The unmarked peaks could be

assigned to TBAB.



**Fig. S27** <sup>1</sup>H NMR spectrum of product 4,4-dimethyl-1,3-dioxolan-2-one from coupling 2,2-dimethyloxirane and CO<sub>2</sub> after 48 h. The unmarked peaks could be assigned to TBAB.

**Table S2** FTPFs-catalyzed cycloaddition of  $CO_2$  and epoxides to form cyclic carbonates.

	$\frac{0}{10}$ + $\frac{0}{10}$	Catalyst		
R		1 atm, RT	)/ R	
Entry	Catalyst	Epoxide	Yield	
	Catalyst	substrate	(%)	
1	Cu-Nb-Zn	$R = CH_3$	98	
2	Cu-Nb-Fe	$R = CH_3$	96	
3	Cu-Nb-Ni	$R = CH_3$	> 99	
4	Cu-Nb-Ni	$R = CH_2CI$	93	
5	Cu-Nb-Ni	$R = CH_2CH_3$	67	
6	Cu-Nb-Ni	$R = (CH_3)_2$	32	

Conditions: 20 mmol of epoxide, 0.5 mol% FTPFs (based on TPyP), 10 mol% TBAB,  $CO_2$  (1 atm), solvent-free, at room temperature. Yield: an average value of three runs, determined by <sup>1</sup>H NMR.

Entry	MOF	Linker	T (°C)	P (bar)	Time (h)	Yield (%)	Ref.
1	PCN-224(Co)	300 2 2 2 2 2 2	100	20	4	42	3
2	MMPF-9	toothoot	25	1	48	87,80 30,31	4
3	MMPF-10		25	1	72	63,47	5
4	MMPF-18		25	1	48	96,97	6
5	Cu-Nb-Ni	مظيمه	25	1	48	> 99	This work

**Table S3** Comparison of the epoxide- $CO_2$  cycloaddition performance on the reportedMOF catalysts based on metalloporphyrin.



**Fig. S28** PXRD patterns of Cu-Nb-Ni simulated and catalytically-tested for three-runs (> 97% conversion of each cycle).



Fig. S29 Tentatively-proposed catalytic mechanism for the cycloaddition of epoxide and  $CO_2$  into cyclic carbonate catalyzed by FTPF along with TBAB.

# Section S9: References

[1] Lin, Q.; Mao, C.; Kong, A.; Bu, X.; Zhao, X.; Feng, P., Porphyrinic coordination lattices with fluoropillars. *J. Mater. Chem. A.* **2017**, *5* (40), 21189-21195.

[2] Davidovich, R. L.; Levchishina, T. F.; Kaidalova, T. A.; Sergienko, V. I., The synthesis and properties of oxofluoroniobates and fluorotantalates of bivalent metals. *J. Less Common Met.* **1972**, *27* (1), 35-43.

[3] Feng, D.; Chung, W.-C.; Wei, Z.; Gu, Z.-Y.; Jiang, H.-L.; Chen, Y.-P.; Darensbourg, D. J.; Zhou, H.-C., Construction of Ultrastable Porphyrin Zr Metal–Organic Frameworks through Linker Elimination. *J. Am. Chem. Soc.* **2013**, *135* (45), 17105-17110.

[4] Gao, W.-Y.; Chen, Y.; Niu, Y.; Williams, K.; Cash, L.; Perez, P. J.; Wojtas, L.; Cai, J.; Chen, Y.-S.; Ma, S., Crystal Engineering of an nbo Topology Metal–Organic Framework for Chemical Fixation of  $CO_2$  under Ambient Conditions. *Angew. Chem. Int. Ed.* **2014**, *53* (10), 2615-2619.

[5] Wang, X.; Gao, W.-Y.; Niu, Z.; Wojtas, L.; Perman, J. A.; Chen, Y.-S.; Li, Z.; Aguila, B.; Ma, S., A metal-metalloporphyrin framework based on an octatopic porphyrin ligand for chemical fixation of  $CO_2$  with aziridines. *Chem. Commun.* **2018**, *54* (10), 1170-1173.

[6] Gao, W.-Y.; Tsai, C.-Y.; Wojtas, L.; Thiounn, T.; Lin, C.-C.; Ma, S., Interpenetrating Metal-Metalloporphyrin Framework for Selective CO<sub>2</sub> Uptake and Chemical Transformation of CO<sub>2</sub>. *Inorg. Chem.* **2016**, *55* (15), 7291-7294.