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Synthetic, spectral, structural and catalytic activity of 3-D metal formats/acetates framework materials for CO_2 conversion

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Supplementary Information

Table 1. Crystallographic data for **1**, and **2**.

Empirical Formula	$C_2H_6O_6Cu$	$C_{12}H_{19}O_{12}NaNi_2$
FW	189.61	495.64
crystal system	Monoclinic	Monoclinic
space group	$P2_1$/c	*C* 12/c 1
a, Å	8.4955(15)	14.641(2)
b, Å	7.0739(14)	17.787(3)
c, Å	9.4178(18)	8.0993(12)
α, deg	90	90
β, deg	97.021(5)	114.446(5)
γ, deg	90	90
V, $Å^3$	561.73(18)	1920.1(5)
Z	4	4
d_{calc}, g cm^{-3}	2.242	1.715
μ, mm^{-1}	3.846	2.041
T, K	100(2)	100(2)
R_1 all	0.0271	0.0864
R_1 [I > 2σ(I)]	0.0218	0.0686
wR_2	0.0592	0.1952
wR_2 [I > 2σ(I)]	0.0565	0.1740
GOF on F^2	1.070	1.349

Table 2. Selected bond lengths (Å), and bond angles (°) for **1**, and **2**.

Complex-1		**Complex-2**	
Cu(1)-O(5)$^{\#1}$	1.9659(10)	Ni(1)-Ni(1)	2.5885(11)
Cu(1)-O(5)	1.9659(10)	Ni(1)-Na(1)	3.3712(14)
Cu(1)-O(1)	2.0079(9)	Ni(1)-O(1)	1.953(3)
Cu(1)-O(1)$^{\#1}$	2.0079(9)	Ni(1)-O(2)	1.977(4)
Cu(1)-O(6)$^{\#2}$	2.3314(10)	Ni(1)-O(3)	2.159(3)
Cu(1)-O(6)$^{\#3}$	2.3314(10)	Ni(1)-O(5)	1.956(3)
Cu(2)-O(4)$^{\#4}$	1.9499(10)	Ni(1)-O(6)	1.958(3)
Cu(2)-O(4)	1.9499(10)	Na(1)-O(2)	2.364(4)
Cu(2)-O(3)$^{\#4}$	2.0074(11)	Na(1)-O(3)	2.406(3)
Cu(2)-O(3)	2.0074(11)	Na(1)-O(4)	2.402(4)
Cu(2)-O(2)	2.3900(11)	O(1)-C(1)	1.262(6)
Cu(2)-O(2)$^{\#4}$	2.3900(11)	O(2)-C(1)	1.264(6)
O(1)-C(1)	1.2732(15)	O(3)-C(3)	1.247(6)
O(2)-C(1)	1.2482(16)	O(4)-C(3)	1.306(6)
O(5)-C(2)	1.2773(15)	O(5)-C(5)	1.270(6)
O(6)-C(2)	1.2424(16)	O(6)-C(5)	1.260(6)
O(6)-Cu(1)$^{\#5}$	2.3314(10)	Ni(1)-Ni(1)-Na(1)	124.31(4)
O(5)$^{\#1}$-Cu(1)-O(5)	180.0	O(1)-Ni(1)-Ni(1)	86.49(10)
O(5)#1-Cu(1)-O(1)	87.54(4)	O(1)-Ni(1)-Na(1)	145.97(10)

O(5)-Cu(1)-O(1)	92.46(4)	O(1)-Ni(1)-O(2)	169.48(14)
O(5)#1-Cu(1)-O(1)$^{\#1}$	92.46(4)	O(1)-Ni(1)-O(3)	103.89(13)
O(5)-Cu(1)-O(1)$^{\#1}$	87.54(4)	O(1)-Ni(1)-O(5)	90.35(15)
O(1)-Cu(1)-O(1)$^{\#1}$	180.0	O(1)-Ni(1)-O(6)	88.65(16)
O(5)$^{\#1}$-Cu(1)-O(6)$^{\#2}$	89.41(4)	O(2)-Ni(1)-Ni(1)	83.07(10)
O(5)-Cu(1)-O(6)$^{\#2}$	90.59(4)	O(2)-Ni(1)-Na(1)	43.41(10)
O(1)-Cu(1)-O(6)$^{\#2}$	92.42(4)	O(2)-Ni(1)-O(3)	86.52(13)
O(1)#1-Cu(1)-O(6)$^{\#2}$	87.58(4)	O(3)-Ni(1)-Ni(1)	169.52(9)
O(5)#1-Cu(1)-O(6)#3	90.59(4)	O(3)-Ni(1)-Na(1)	45.31(9)
O(5)-Cu(1)-O(6)#3	89.41(4)	O(5)-Ni(1)-Ni(1)	85.23(11)
O(1)-Cu(1)-O(6)#3	87.58(4)	O(5)-Ni(1)-Na(1)	105.01(11)
O(1)#1-Cu(1)-O(6)#3	92.42(4)	O(5)-Ni(1)-O(2)	90.03(16)
O(4)-Cu(2)-O(3)	90.79(4)	O(5)-Ni(1)-O(3)	96.04(13)
O(4)-Cu(2)-O(2)	90.40(4)	O(5)-Ni(1)-O(6)	169.59(14)
O(3)-Cu(2)-O(2)	86.64(4)	O(6)-Ni(1)-Ni(1)	84.37(11)
C(1)-O(1)-Cu(1)	126.05(9)	O(6)-Ni(1)-Na(1)	81.29(11)
C(1)-O(2)-Cu(2)	129.33(9)	O(6)-Ni(1)-O(2)	89.07(16)
O(2)-C(1)-O(1)	123.92(13)	O(6)-Ni(1)-O(3)	94.25(14)
O(6)-C(2)-O(5)	123.51(11)	Ni(1)-Na(1)-Ni(1)	124.29(8)
		O(2)-Na(1)-Ni(1)	35.06(9)
		O(2)-Na(1)-Ni(1)	106.14(12)

	O(2)-Na(1)-O(3)	110.00(13)
	O(2)-Na(1)-O(4)	150.75(12)
	O(3)-Na(1)-Ni(1)	144.10(11)
	O(4)-Na(1)-Ni(1)	118.65(9)
	C(1)-O(1)-Ni(1)	121.8(3)
	Ni(1)-O(2)-Na(1)	101.53(15)

Table 3. Hydrogen bond parameters for **1**, and **2**.

D-H···A-X	*d* H···A Å	*D* D···A Å	*θ* D-H···A°
Complex-1			
C(1)-H(1)...O(5)	2.427(17)	3.0163(17)	119.4(13)
C(2)-H(2)...O(6)#2	2.390(18)	2.9408(18)	115.9(12)
O(4)-H(4A)...O(2)#6	1.80(2)	2.6652(14)	174(2)
O(4)-H(4B)...O(6)#7	1.86(2)	2.7105(14)	169(2)
O(3)-H(3A)...O(1)	1.92(2)	2.7301(15)	168(2)
O(3)-H(3A)...O(2)	2.60(2)	3.0299(15)	113.6(17)
O(3)-H(3B)...O(5)#7	1.94(2)	2.7549(14)	175(2)
Symmetry transformations used to generate equivalent atoms: #2 -x+2,y+1/2,-z+3/2; #6 -x+1,y+1/2,-z+3/2; #7 x,y+1,z.			
Complex-2			
O(4)-H(4)...O(4)#4	1.18(2)	2.3529(14)	180(2)
C(2)-H(2C)...O(6)#5	2.41(2)	3.3007(15)	150(2)
C(4)-H(4B)...O(5)#6	2.57(2)	3.5105(15)	162(2)
Symmetry transformations used to generate equivalent atoms: #4 1-x,-y,-2-z; #5 1/2+x,1/2-y,-1/2+z; #6 x,-y,-1/2+z.			

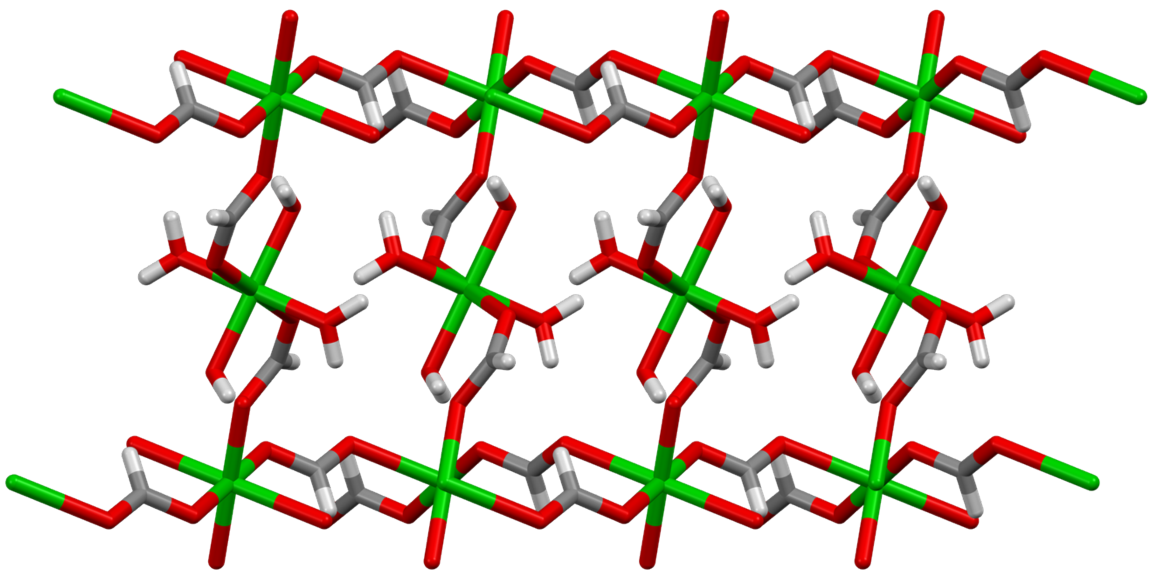

Figure S1. Packing diagram down *b*- axis in compound **1**.

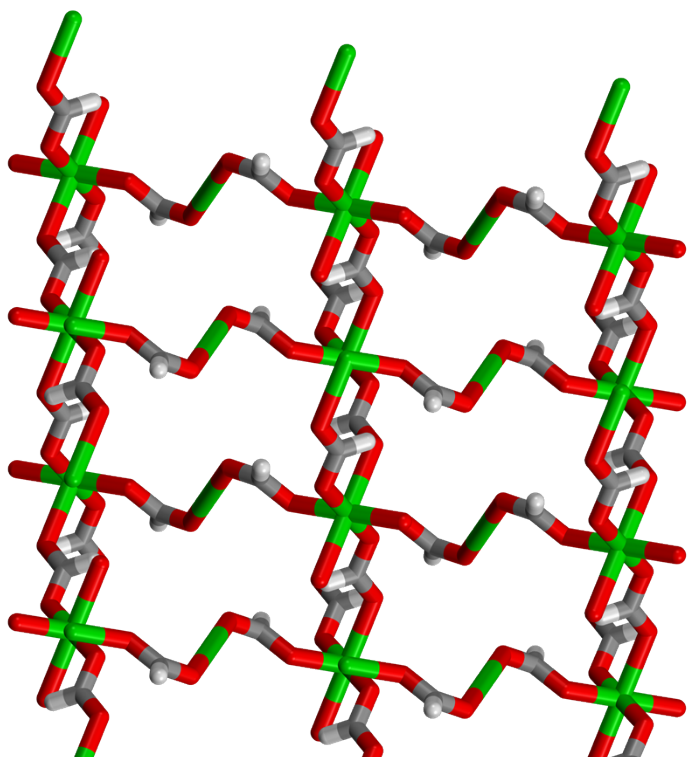

Figure S2. Packing diagram down *b*-axis without water in compound **1**.

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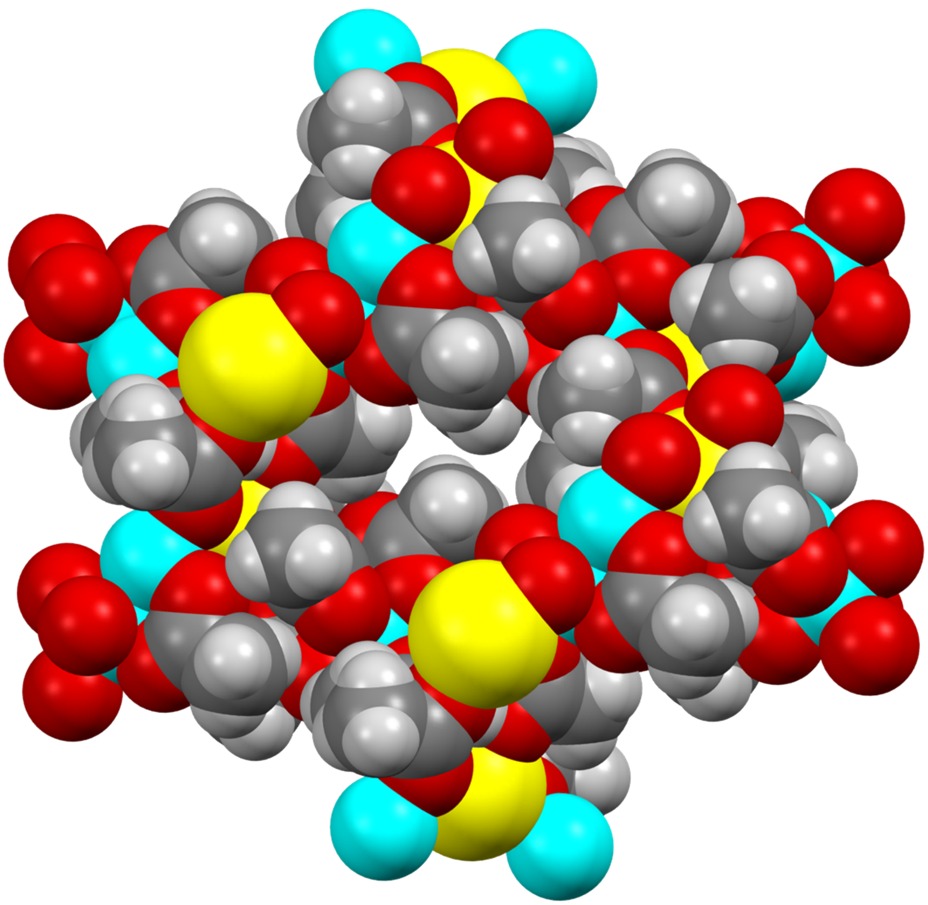
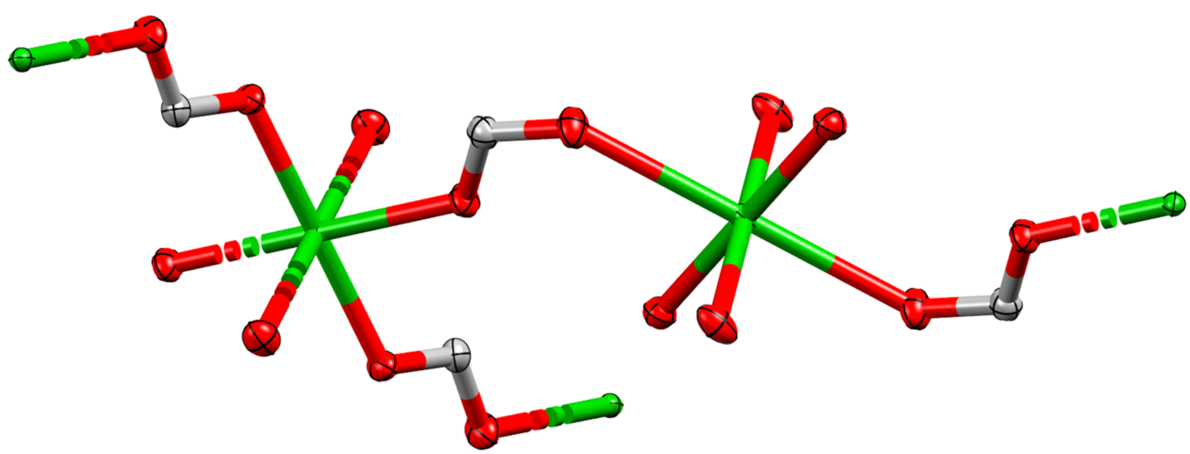
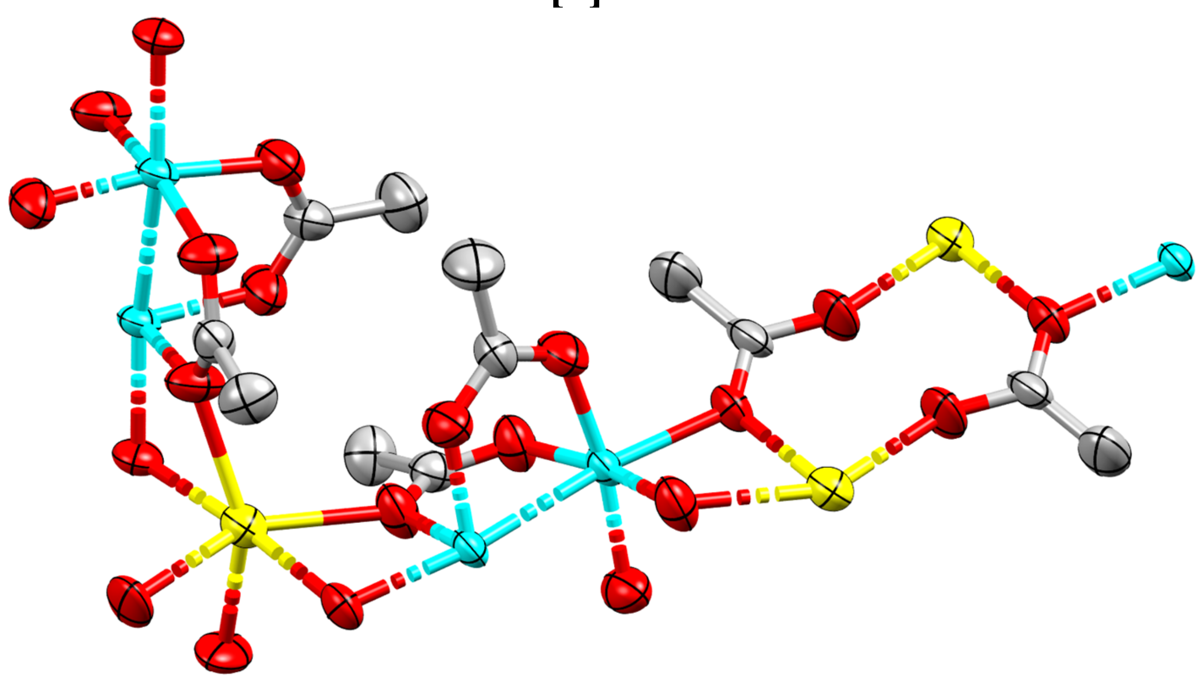


Figure S3. Channels formed down the *c*-axis in **2**.



[1]



[2]

Figure S4. Elipsoidal (adp) molecular view of $[Cu_2(HCO_2)_2(H_2O)_2]_n$ (**1**), and $[Na\{Ni(CH_3CO_2)_2(CH_3CO_2H)\}]_n$ (**2**). Colour code: Cu (green), Ni (cyan), Na (yellow), C (grey) and O (red). H-atoms are omitted for the clarity of the picture.

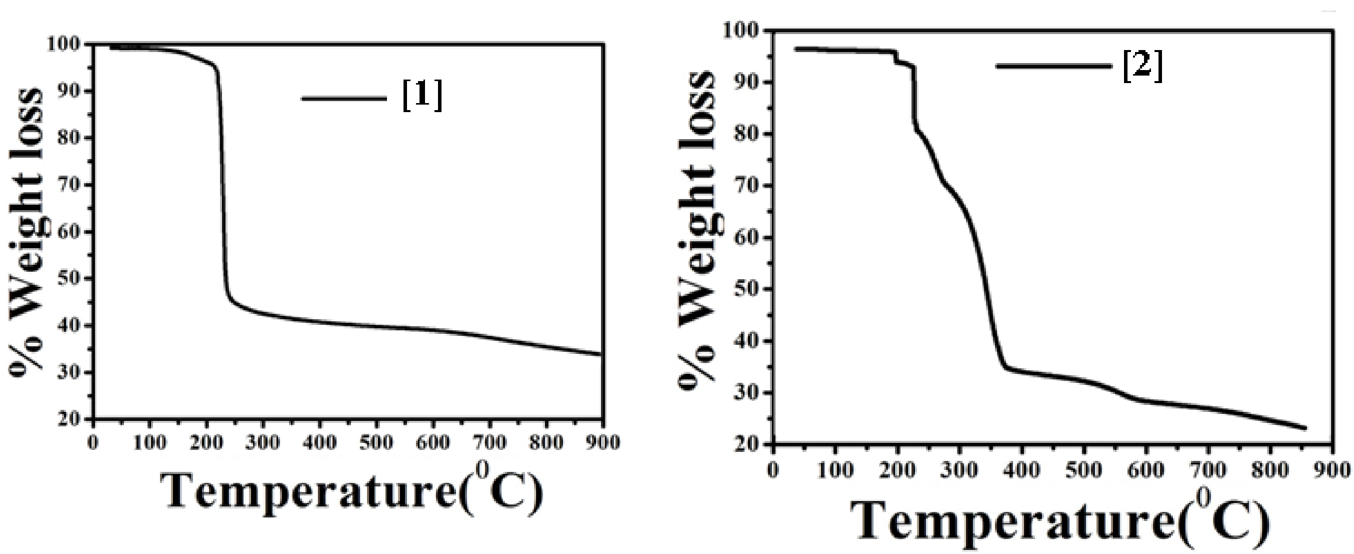


Figure S5. TGA profiles of $[Cu_2(HCO_2)_2(H_2O)_2]_n$ (**1**), and $[Na\{Ni(CH_3CO_2)_2(CH_3CO_2H)\}]_n$ (**2**) recorded under nitrogen flow.

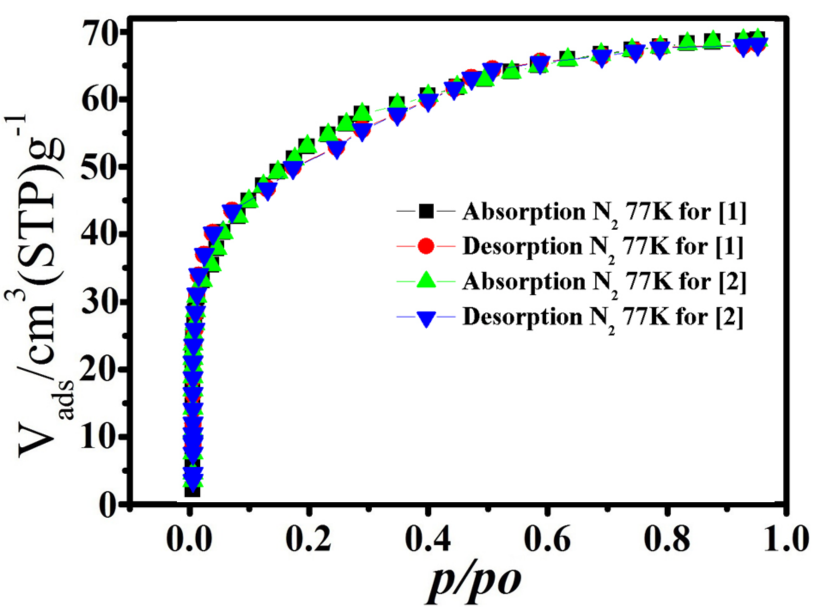


Figure S6. N_2 adsorption and desorption isotherm at 77K of **1** and **2**.

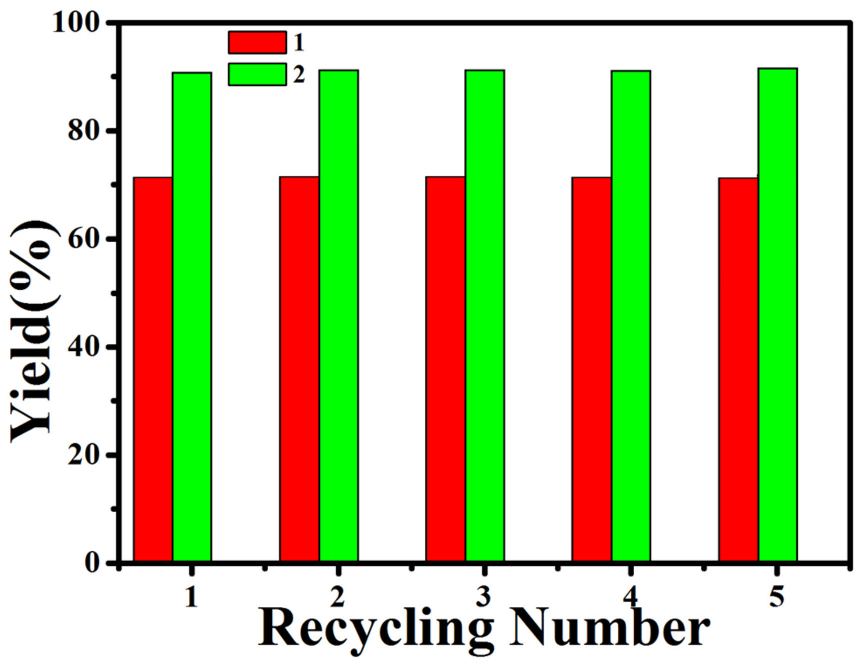


Figure S7. Histogram of recyclability study (five cycles) for catalytic activities of **1** and **2** in coupling of glycidol with CO_2.

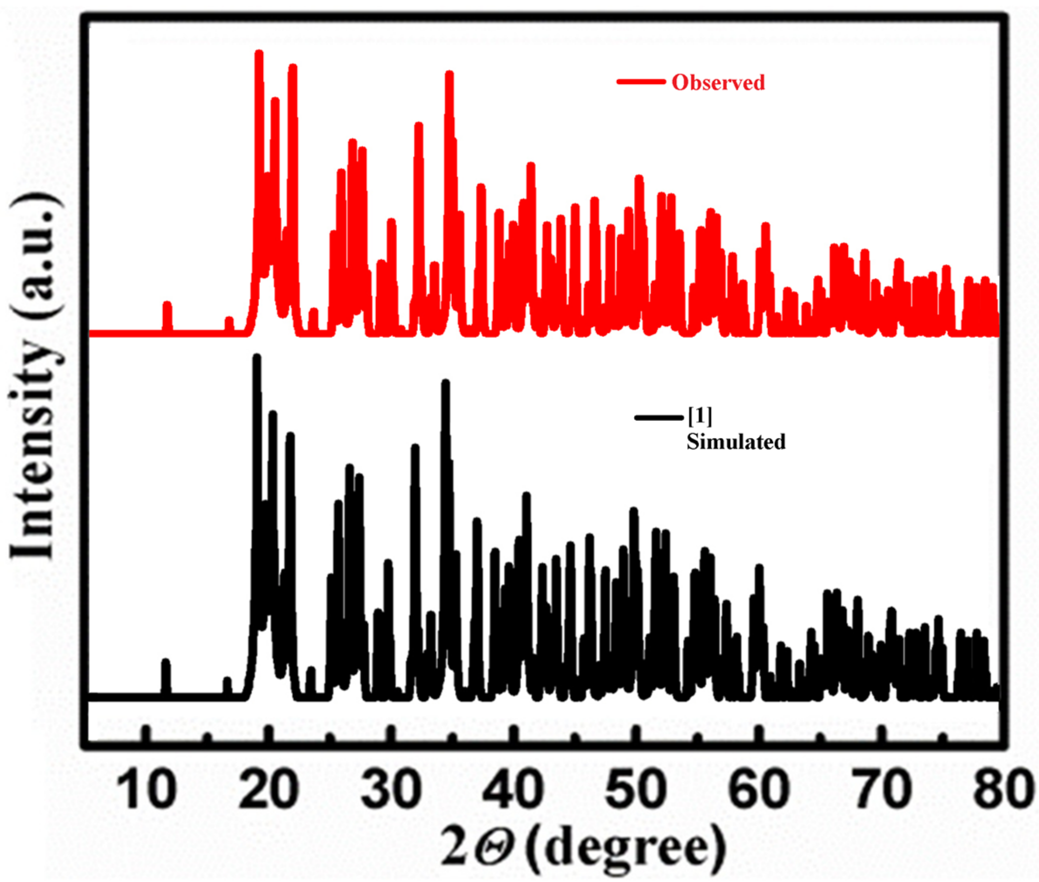


Figure S8. Powder XRD pattern of **1** after the catalytic reaction for coupling of glycidol with CO_2. (Simulated = theoretical profile based on the structures determined by single-crystal XRD; Observed= experimental data).

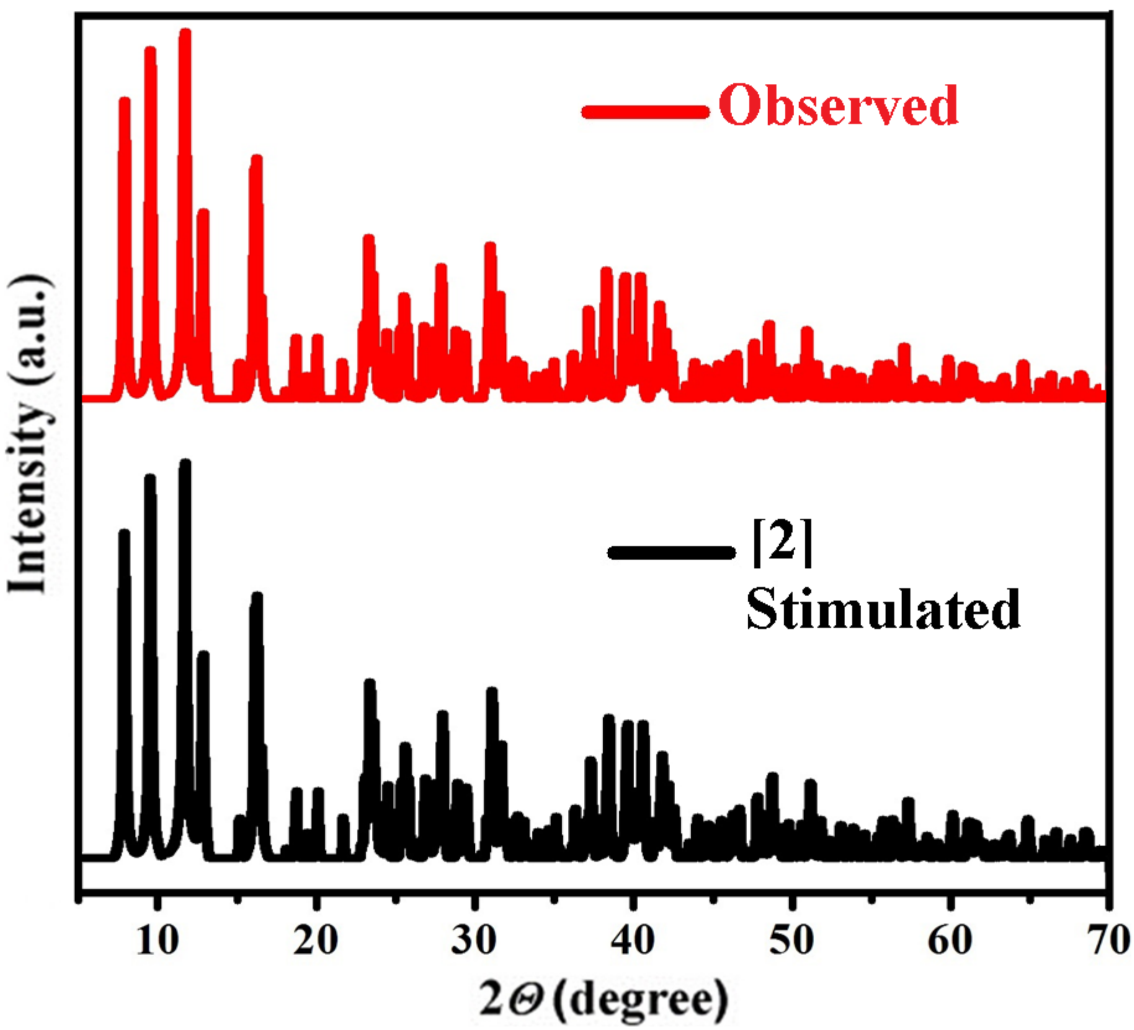

Observed
[2]
Stimulated
Intensity (a.u.)
10
20
30
40
50
60
70
2Θ (degree)

Figure S9. Powder XRD pattern of **2** after the catalytic reaction for coupling of glycidol with CO_2. (Simulated = theoretical profile based on the structures determined by single-crystal XRD; Observed= experimental data).

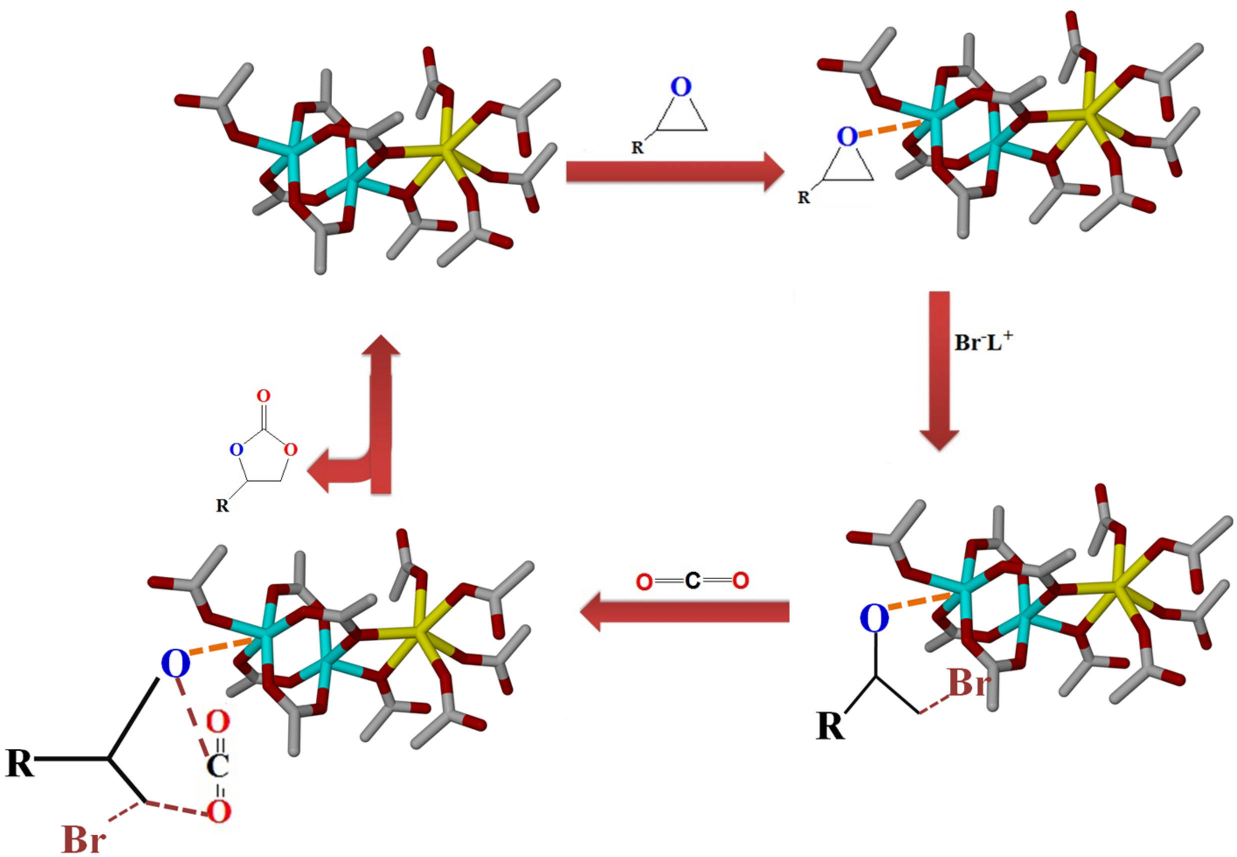


Figure S10. The proposed mechanism for the cycloaddition reaction of epoxide and CO_2 to form cyclic carbonates catalyzed by **2**.

Entry	MOFs	Co-catalyst	Reaction conditions T[K]/P[atm]/Time[h]	% yield	Ref.
1.	$[Cu_3(BTC)_2]$ or HKUST-1	$n\text{-}Bu_4NBr$	273/1 atm./48h	49	1
2.	$[Cu_2(BPTC)(H_2O)_2]$or MOF-505	$n\text{-}Bu_4NBr$	273/1 atm./48h	48	1
3.	[CuL1] or BIT-C	$n\text{-}Bu_4NBr$	333/1 atm./6h	95-99	2
4.	$[Cu(HIP)_2(BPY)]$	-	393/12 atm./6h	10-73	3
5.	$Cu_2(Cu\text{-}TACTMB)(H_2O)_3(NO_3)_2$ or MMCF-2	$n\text{-}Bu_4NBr$	273/1 atm/48h	42-95	1
6.	$Cu_6(Cu\text{-}TDPBPP)(HCO_2)_4(H_2O)_6$ or MMPF-9	$n\text{-}Bu_4NBr$	273/1 atm/48h	30-87	4
7.	Cu_4MTTP	$n\text{-}Bu_4NBr$	273/1 atm/48h	83-96	5
8.	$[Cu_7(H_1L)_2(TPT)_3(H_2O)_6]$	$n\text{-}Bu_4NBr$	373/9.86 atm/3-12h	>99	6
9.	$[Cu_2(C_{20}H_{12}N_2O_2)(COO)_4]_n$	$n\text{-}Bu_4NBr$	273/1 atm/48h	88-96	7
10.	[Cu-ABF@ASMNPs]	DBU	353/1atm/12h	89-92	8
11.	$[Cu_{24}(BDPO)_{12}(H_2O)_{12}]\cdot 30DMF\cdot 14H_2O$ or (JUC1000)	TBABr	298/1 atm/48	29-96	9
12.	$[Cu_2(BDC)_2(DABCO)]$	-	373/8 atm./12h	13	10
14.	FJI-H14	$n\text{-}Bu_4NBr$	353/0.15 atm/24h	27-95	11
15.	$\{[Cu_6(L)_3(H_2O)_6].(14DMF)(9H_2O)\}_n$	$n\text{-}Bu_4NBr$	298/1 bar/8-24h	30-95	12
16.	$[Cu_5(TPTC)_3(BPDC\text{-}NH_2)_{0.5}(H_2O)_5]$ (1-NH_2)	$n\text{-}Bu_4NBr$	298/1 atm/36h	50	13
17.	$[Cu_5(TPTC)_3(BPDC\text{-}Urea)_{0.5}(H_2O)_5]$ (1-Urea)	$n\text{-}Bu_4NBr$	298/1 atm/36h	19-98	13
18.	$[Cu_2(OAc)_4(\mu_4\text{-}hmt)_{0.5}]_n$	$n\text{-}Bu_4NBr$	273/1 atm./18h	87-96	14
19.	$[Cu\{C_6H_4(COO\text{-})_2\}_2]_n.2C_9H_{14}N_3$	$n\text{-}Bu_4NBr$	273/1 atm./18h	60-80	14
20.	$[Cd_2(Ni(salen))(DMF)_3]\cdot 4DMF\cdot 7H_2O$	$n\text{-}Bu_4NBr$	353/1MPa/12h	54-99	15
21.	$M_2(EDOB)$ [$EDOB_4^-$ = 4,4′-(ethyne-1,2-diyl)bis(2-oxidobenzoate), M = Mg, Ni, Co, Zn, Cu, Fe]	$n\text{-}Bu_4NBr$	353/1 atm/12h	35-86	16
22.	$[Cu_2(HCO_2)_2(H_2O)_2]_n$	$n\text{-}Bu_4NBr$	273/1 atm./12h	66-87	Present work
23.	$[Na\{Ni(CH_3CO_2)_2(CH_3CO_2H)\}]_n$	$n\text{-}Bu_4NBr$	273/1 atm./12h	86-98	Present work

Table 4. Comparative catalytic performance of the **1** and **2** with others previously reported MOFs catalysts for cycloaddition of epoxides with CO_2.

4-methyl-1, 3-dioxolan-2-one:

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.49 (d, J=6.8 Hz, 3H), 4.06 (t, J=4.5 Hz, 1H), 4.73 (t, J=8.4 Hz, 1H), 4.86-4.93 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): 19.15, 70.53, 73.48, 154.95; GC-MS (EI) m/z (%):102 (M^+, 100).

4-ethyl-1, 3-dioxolan-2-one:

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (t, J=1.5Hz, 3H), 1.73-1.86 (m, 2H), 4.09 (t, J=8Hz, 1H), 4.53 (t, J=4.4Hz, 1H), 4.61 (q, J=3.6Hz, 1H) ; ^{13}C NMR (400 MHz, $CDCl_3$): 155.08, 76.40, 68.04, 26.67, 8.36; GC-MS (EI) m/z (%):116 (M^+, 100).

4-(chloromethyl)-1, 3-dioxolan-2-one:

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.67-3.80 (m, 2H), 4.01 (dd, J = 3.6, 3.2 Hz, 1H), 4.58 (t, J = 1.0 Hz, 1H), 4.89-4.98 (m, 1H); ; ^{13}C NMR (400 MHz, $CDCl_3$): 43.83, 66.84, 75.48, 154.28; GC-MS (EI) m/z (%):137 (M^+, 100).

4-(bromomethyl)-1, 3-dioxolan-2-one:

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.45-3.52 (m, 2H), 4.27-4.35 (dd, J = 13.7, 7.3 Hz, 1H), 4.58 (t, J = 1.0 Hz, 1H), 4.86-4.88 (m, 1H); ; ^{13}C NMR (400 MHz, $CDCl_3$): 31.32, 68.05, 73.92, 154.09; GC-MS (EI) m/z (%):181 (M^+, 100).

4-(hydroxymethyl)-1,3-dioxolan-2-one:

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.80-4.82 (m, 1H), 4.14-4.21 (m, 2H), 4.01-4.02 (m, 1H), 3.30-3.58 (m, 1H), 2.45-2.50 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): 38.87, 39.08, 39.29, 39.50, 39.91, 40.41 , 60.61, 65.88, 155.20; GC-MS (EI) m/z (%):118 (M^+, 100).

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