Supporting Information File

Construction of 3-fold interpenetrated 3D metal-organic frameworks (MOFs) of Ni(II) for highly efficient capture and conversion of carbon dioxide

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Figure S1. PXRD patterns of compound **1**. (a) Simulated from X-ray single crystal data; (b) bulk as-synthesized compound.



Figure S2. PXRD patterns of compound **2**. (a) Simulated from X-ray single crystal data; (b) bulk as-synthesized compound.



Figure S3. PXRD patterns of compound **3**. (a) Simulated from X-ray single crystal data; (b) bulk as-synthesized compound.

Ni1-O1	2.048(3)	O1-Ni1-N2	89.03(11)
Ni1-O1W	2.122(3)	O1W-Ni1-O2W	88.48(13)
Ni1-O2W	2.096(3)	O1W-Ni1-O3	88.28(12)
Ni1-O3	2.077(3)	O1W-Ni1-N1	92.78(12)
Ni1-N1	2.098(3)	O1W-Ni1-N2	89.67(13)
Ni1-N2	2.076(3)	O2W-Ni1-O3	92.85(12)
		O2W-Ni1-N1	87.99(13)
O1-Ni1-O1W	175.59(12)	O2W-Ni1-N2	176.94(13)
O1-Ni1-O2W	92.99(11)	O3-Ni1-N1	178.67(12)
O1-Ni1-O3	87.49(11)	O3-Ni1-N2	89.53(12)
O1-Ni1-N1	91.43(12)	N1-Ni1-N2	89.66(13)

Table S1. Selected bond lengths (Å) and angles (°) for compound 1.

Ni1-O1	2.040(4)	O1-Ni1-N2	91.80(18)
Ni1-O1W	2.117(4)	O1W-Ni1-O2W	89.02 (16)
Ni1-O2W	2.092(4)	O1W-Ni1-O3	88.16(15)
Ni1-O3	2.076(4)	O1W-Ni1-N1	89.28(17)
Ni1-N1	2.060(5)	O1W-Ni1-N2	93.34(18)
Ni1-N2	2.098(5)	O2W-Ni1-O3	91.73(15)
		O2W-Ni1-N1	178.14(16)
O1-Ni1-O1W	174.46(16)	O2W-Ni1-N2	88.30(17)
O1-Ni1-O2W	93.21(15)	O3-Ni1-N1	88.96(16)
01-Ni1-O3	86.71(16)	O3-Ni1-N2	178.51(18)
O1-Ni1-N1	88.55(16)	N1-Ni1-N2	91.06(17)

Table S2. Selected bond lengths (Å) and angles (°) for compound 2.

Ni1-O1	2.037(3)	O1-Ni1-N2	88.26(15)
Ni1-O1W	2.112(4)	O1W-Ni1-O2W	86.88(13)
Ni1-O2W	2.082(4)	O1W-Ni1-O3	87.73(13)
Ni1-O3	2.061(3)	O1W-Ni1-N1	91.93(15)
Ni1-N1	2.094(4)	O1W-Ni1-N2	91.40(15)
Ni1-N2	2.071(4)	O2W-Ni1-O3	93.23(13)
		O2W-Ni1-N1	88.90(15)
O1-Ni1-O1W	175.22(14)	O2W-Ni1-N2	177.53(14)
O1-Ni1-O2W	93.60(13)	O3-Ni1-N1	177.82(16)
01-Ni1-O3	87.50(12)	O3-Ni1-N2	88.46(14)
O1-Ni1-N1	92.84(15)	N1-Ni1-N2	89.40(16)

Table S3. Selected bond lengths (Å) and angles (°) for compound 3.

D–H···A	D…H	Н…А	D····A	D−H···A
O2WH2WA O2	0.8500	1.9200	2.665(5)	145.00
O2WH2WB O4	0.8500	1.8500	2.662(4)	149.00
O1WH1WA O3W	0.8500	1.9900	2.827(10)	166.00 ⁱ
O1WH1WB O4	0.8500	1.9200	2.725(4)	158.00 ⁱ
O3WH3WB O1W	0.8500	2.5400	2.827(10)	101.00 ⁱⁱ
O4WH4WA O2	0.8500	2.2100	2.740(14)	120.00
С3Н3 О1	0.9300	2.4400	2.772(5)	101.00
С7Н7 О1	0.9300	2.5100	3.051(6)	118.00
С8Н8 О2	0.9300	2.5800	3.428(8)	152.00 ⁱⁱⁱ
C18H18 O1	0.9300	2.5700	3.022(5)	110.00

Table S4. Selected hydrogen bonding geometry $(\text{\AA},^{\circ})$ for compound 1

Symmetry codes: (i) x,1-y,-1/2+z; (ii) x,1-y,1/2+z; (iii) x,-y,-1/2+z.

D–H····A	D…H	Н…А	D····A	D–H···A
O2W H1WA O4	0.8500	1.8600	2.627(6)	149.00
O2WH1WB O2	0.8500	1.8900	2.630(6)	144.00
O1WH2WAO5W	0.8500	2.0300	2.856(10)	165.00 ⁱ
O1WH2WAO5W	0.8500	2.5200	3.059(10)	145.00 ⁱⁱ
O4WH4WBO2W	0.8500	1.9900	2.790(10)	156.00 ⁱⁱⁱ
O5WH5WBO3W	0.8500	2.5000	3.288(18)	154.00 ^{iv}
С9 Н9 О2	0.9300	2.4200	3.192(9)	140.00 ^v
C1 H1 O1	0.9300	2.6000	3.020(7)	108.00
C8 H8 O1	0.9300	2.5100	3.050(9)	117.00
C15H15 O1	0.9300	2.4600	2.786(7)	101.00

Table S5. Selected hydrogen bonding geometry (Å,°) for compound 2

Symmetry codes: (i) -x,2-y,-z; (ii) -x,y,1/2-z; (iii)x,y,1+z; (iv) -x,2-y,1-z; (v) x,1-y,1/2+z.

D–H···A	D…H	Н…А	D····A	D−H…A
O2WH2WB O2	0.8500	1.8500	2.618(5)	150.00
O1W – H1WB O4	0.8500	1.8500	2.660(6)	158.00 ⁱ
C3 H3 O1	0.9300	2.4500	2.778(5)	101.00
C4 H4 O3	0.9300	2.5100	2.816(5)	100.00 ⁱⁱ
C7 H7 O1W	0.9300	2.4400	3.030(8)	121.00
C8 H8 O1	0.9300	2.4700	3.051(7)	121.00
С9 Н9 О2	0.9300	2.5300	3.242(9)	133.00 ⁱⁱⁱ
C13 H13 O1	0.9300	2.5700	2.998(5)	108.00

Table S6. Selected hydrogen bonding geometry $(\text{\AA}, ^{\circ})$ for compound 3

Symmetry codes: (i) x,-y,1/2+z; (ii) 1/2-x,1/2+y,-1/2-z; (iii) x,1-y,1/2+z.



Figure S4. Pore picture of 1D channel in compound 2.



Figure S5. Pore picture of 1D channel in compound 3.



Figure S6. TGA plots for the compounds **1-3.** (a) as-synthesized samples having coordinated water molecules. (b) activated samples at 120°C for 18 hrs.



Figure S7. PXRD patterns of compound **1** (a) pattern calculated from single crystal X- ray data; (b) as-synthesized sample before heating; (c) activated sample by heating at 120°C for 18 hours; (d) regenerated sample after soaking in water for 4h. (e) sample recovered after four catalytic cycles.



Figure S8. PXRD patterns of compound **2**, (a) pattern calculated from single crystal X- ray data; (b) as-synthesized sample before heating; (c) activated sample by heating at 120°C for 18 hours; (d) regenerated sample after soaking in water for 4h. (e) sample recovered after catalytic cycle.



Figure S9. PXRD patterns of compound 3, (a) pattern calculated from single crystal X- ray data;
(b) as-synthesized sample before heating; (c) activated sample by heating at 120°C for 18 hours;
(d) regenerated sample after soaking in water for 4h. (e) sample recovered after catalytic cycle.



Figure S10. Nitrogen adsorption-desorption isotherms of **1**, **2** and **3** carried out at 77K (closed circles-adsorption and open circles-desorption).

Analysis of Gas adsorption Isotherms

Clausius-Clapeyron Equation¹ was used to calculate the enthalpies of hydrogen adsorption. By using Langmuir Freundlich equation²an accurate fit was retrieved which gives a precise prediction of hydrogen adsorbed at saturation. A modification of Clausius-Clapeyron equation is used for calculations.

where, P_1 and P_2 = pressures for isotherm at 273K and 298K respectively.

 T_1 and T_2 = temperatures for isotherm at 273K and 298K respectively.

 ΔH_{ads} = Enthalpy of adsorption.

R = Universal gas constant = 8.314 J/K/mol.

Pressure is a function of amount of gas adsorbed which was determined by using the Langmuir-Freundlich fit.

$$\frac{Q}{Q_{m}} = \frac{B X P^{(1/t)}}{1 + (B X P^{(1/t)})}$$
------(ii)

where, Q = moles of gas adsorbed.

 Q_m = moles of gas adsorbed at saturation.

B and t = constants.

P = Pressure.

By rearranging equation (ii) we get equation (iii)

$$P = \left[\frac{Q/Q_{m}}{B - (B X Q/Q_{m})}\right]^{t}$$
------(iii)

Substituting equation (iii) into equation (i) we get

In equation (iv), subscript 1 and 2 are representing data corresponding to 273K and 298K in case of carbon dioxide gas.



Figure S11. Carbon dioxide adsorption isotherm for **2** at 273K. The solid line shows the best fit to the data using Langmuir- Freundlich Equation.



Figure S12. Carbon dioxide adsorption isotherm for **2** at 298K. The solid line shows the best fit to the data using Langmuir- Freundlich Equation.



Figure S13. Carbon dioxide adsorption isotherm for **3** at 273 K. The solid line shows the best fit to the data using Langmuir- Freundlich Equation.



Figure S14. Carbon dioxide adsorption isotherm for **3** at 298 K. The solid line shows the best fit to the data using Langmuir- Freundlich Equation.



Figure S15. Enthalpy of carbon dioxide adsorption for 2 using Clausius-Clapeyron Equation calculations.



Figure S16. Enthalpy of carbon dioxide adsorption for 3 using Clausius-Clapeyron Equation calculations



Figure S17. Time-dependent ¹H (CDCl₃, 400 MHz) NMR stack plot for the cycloaddition of CO_2 with styrene oxide catalyzed by compound **1**, showing gradual increase of peaks at 4.3, 4.8 and 5.6 ppm, due to product, and decrease in the intensity of peaks around 2.7, 3.1 and 3.8 ppm due to styrine oxide.



Figure S18. ¹H NMR (CDCl₃, 400 MHz) spectra for the cycloaddition reaction of CO₂ with 1,2epoxy propane catalyzed by compound **1**.



Figure S19. ¹H NMR (CDCl₃, 400 MHz) spectra for the cycloaddition reaction of CO_2 with 1,2epoxy butane catalyzed by compound **1**.



Figure S20. ¹H NMR (CDCl₃, 400 MHz) spectra for the cycloaddition reaction of CO_2 with 1,2epoxy hexane catalyzed by compound **1**.



Figure S21.¹H NMR (CDCl₃, 400 MHz) spectra for the cycloaddition reaction of CO₂ with 1,2epoxy decane catalyzed by compound **1**.



Figure S22.¹H NMR (CDCl₃, 400 MHz) spectra for the cycloaddition reaction of CO_2 with styrene oxide catalyzed by compound **1**.

S.No	Substrates	Optimized structure	Dimensions
1.	1,2-epoxy propane		~4.35 X 3.41 Å ²
2.	1,2-epoxy butane		~5.648 X 3.39 Å ²
3.	1,2-epoxy hexane		~8.198 X 3.39 Å ²
4.	1,2-epoxy decane	•	~13.321 X 3.39 Å ²
5.	Styrene oxide		~4.28 X 7.267 Å ²

Table S7. Optimized geometries of epoxides using Gaussian09³ at b3lyp/6-311g(d,p) level.

References

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