Supporting Information

Effective CO_2 and CO Separation Using [M_2(DOBDC)](M=Mg, Co, Ni) with Unsaturated Metal Sites and Excavation of Their Adsorption Sites

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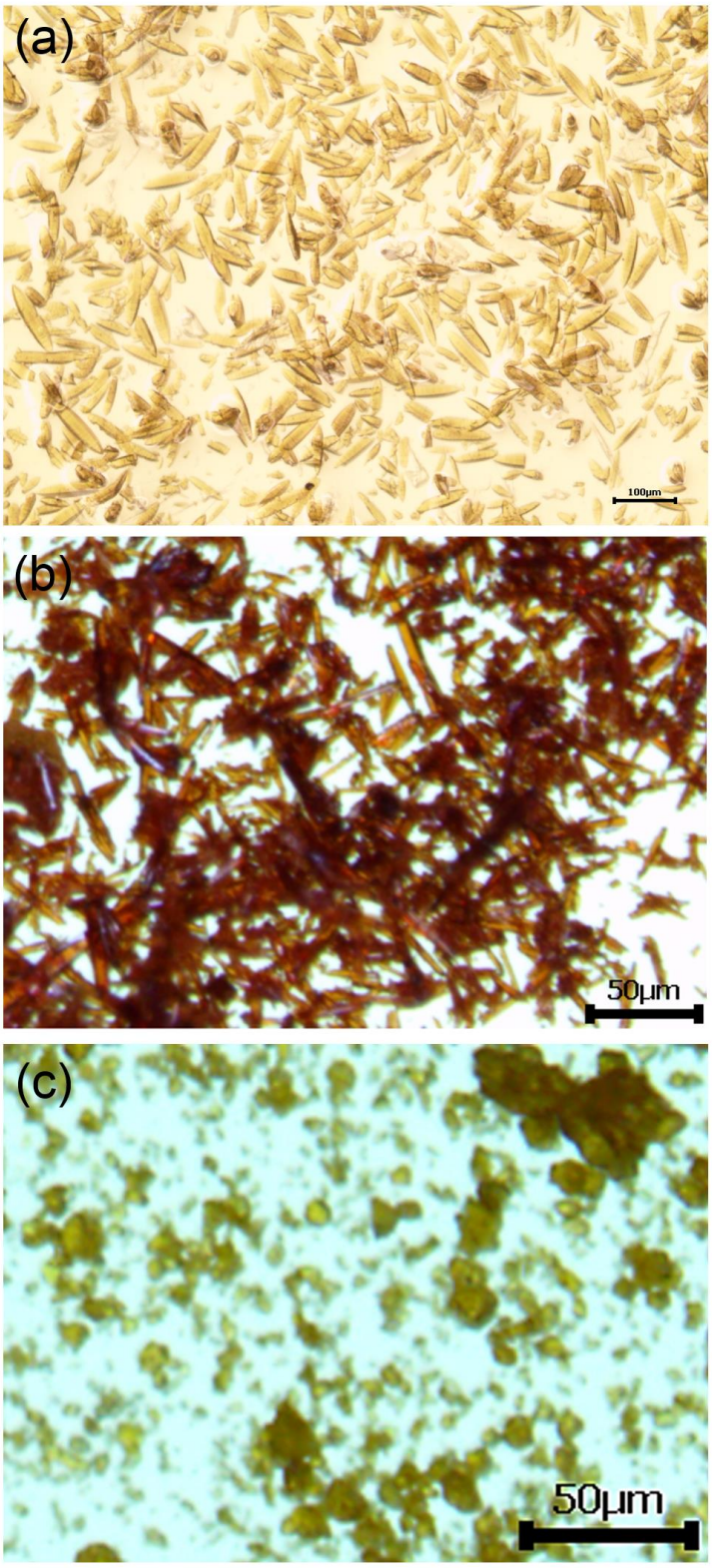

Figure S1. Single-crystal images of (a) **1_EG**, (b) **2_EG** and (c) **3_EG**

Table S1. Crystal data and structure refinement for **1_EG** (CCDC 1859138).

Empirical formula	C14 H20.33 Mg2 O12.33	
Formula weight	434.59	
Temperature	100(2) K	
Wavelength	0.70000 Å	
Crystal system	Trigonal	
Space group	*R*-3	
Unit cell dimensions	a = 25.951(4) Å	α = 90°
	b = 25.951(4) Å	β = 90°
	c = 13.632(3) Å	γ = 120°
Volume	7951(2) Å^3	
Z	18	
Density (calculated)	1.634 g/cm^3	
Absorption coefficient	0.194 mm^{-1}	
F(000)	4086	
Crystal size	0.150 × 0.080 × 0.020 mm^3	
Theta range for data collection	2.313 to 29.993 °	
Index ranges	-37≤h≤36, -37≤k≤37, -18≤l≤19	
Reflections collected	5385	
Completeness to theta = 29.99°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	1.897 and 0.662	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5385 / 62 / 294	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R1 = 0.0838, wR2 = 0.2288	
R indices (all data)	R1 = 0.0910, wR2 = 0.2386	
Largest diff. peak and hole	2.723 and -0.974 e.Å^{-3}	

Table S2. Crystal data and structure refinement for **2_EG** (CCDC 1859144).

Empirical formula	C14 H20.33 Co2 O12.33	
Formula weight	503.83	
Temperature	100(2) K	
Wavelength	0.70000 Å	
Crystal system	Trigonal	
Space group	*R*-3	
Unit cell dimensions	a = 26.070(4) Å	α = 90°
	b = 26.070(4) Å	β = 90°
	c = 13.521(3) Å	γ = 120°
Volume	7958(2) Å^3	
Z	18	
Density (calculated)	1.892 g/cm^3	
Absorption coefficient	1.854 mm^{-1}	
F(000)	4626	
Crystal size	0.20 × 0.02 × 0.02 mm^3	
Theta range for data collection	2.315 to 25.985°	
Index ranges	-32≤h≤31, -32≤k≤32, -15≤l≤16	
Reflections collected	3629	
Completeness to theta = 25.99°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	1.365 and 0.760	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3629 / 166 / 312	
Goodness-of-fit on F^2	1.108	
Final R indices [I>2sigma(I)]	R1 = 0.0581, wR2 = 0.1566	
R indices (all data)	R1 = 0.0634, wR2 = 0.1637	
Largest diff. peak and hole	3.182 and -1.282 e.Å^{-3}	

Table S3. Crystal data and structure refinement for **3_EG** (CCDC 1859140).

Empirical formula	C14 H20.33 Ni2 O12.17	
Formula weight	500.72	
Temperature	100(2) K	
Wavelength	0.70000 Å	
Crystal system	Trigonal	
Space group	*R*-3	
Unit cell dimensions	a = 25.871(4) Å	α = 90°
	b = 25.871(4) Å	β = 90°
	c = 13.500(3) Å	γ = 120°
Volume	7825(3) Å^3	
Z	18	
Density (calculated)	1.913 g/cm^3	
Absorption coefficient	2.136 mm^{-1}	
F(000)	4638	
Crystal size	0.080 × 0.080 × 0.040 mm^3	
Theta range for data collection	1.735 to 29.997°.	
Index ranges	-36≤h≤36, -36≤k≤36, -18≤l≤19	
Reflections collected	5309	
Completeness to theta = 30.00°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	75.683 and 0.0128	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5309 / 77 / 257	
Goodness-of-fit on F^2	1.247	
Final R indices [I>2sigma(I)]	R1 = 0.0973, wR2 = 0.2932	
R indices (all data)	R1 = 0.1094, wR2 = 0.3197	
Largest diff. peak and hole	5.246 and -1.930 e.Å^{-3}	

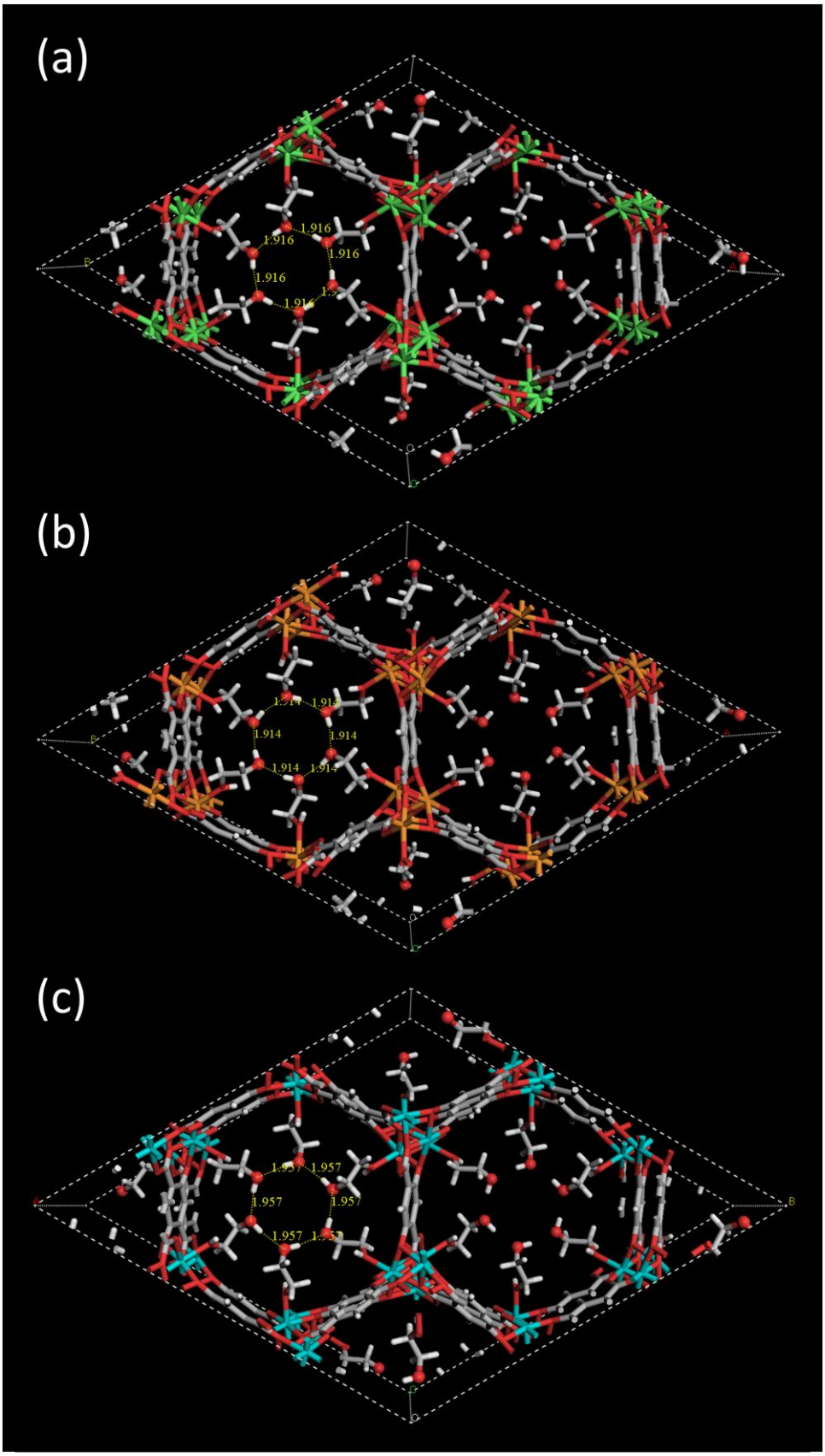

Figure S2. OH hexagonal clusters of 6 ethylene glycol molecules in channels of $[M_2(DOBDC)(EG)_2]$ (M=Mg(**1_EG**), Co(**2_EG**), Ni(**3_EG**)) through hydrogen bonds with a distance of 1.916 Å for **1**, 1.914 Å for **2** and 1.957 Å for **3**

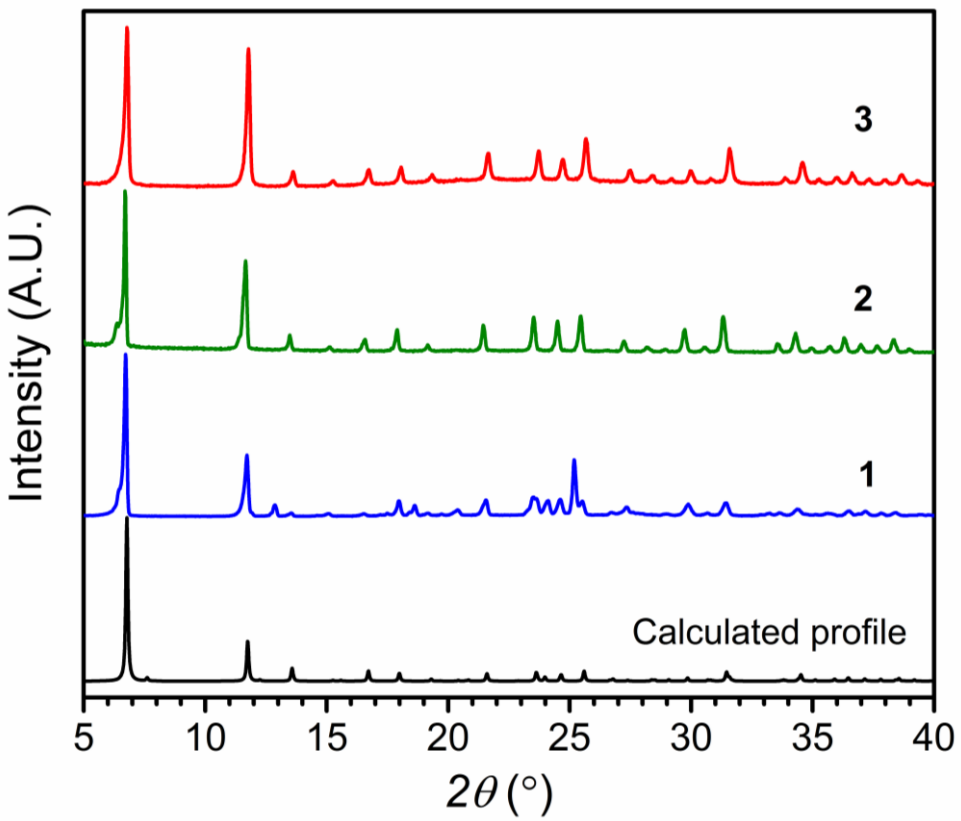

Figure S3. Powder X-ray diffraction profiles of **1_EG**, **2_EG** and **3_EG**

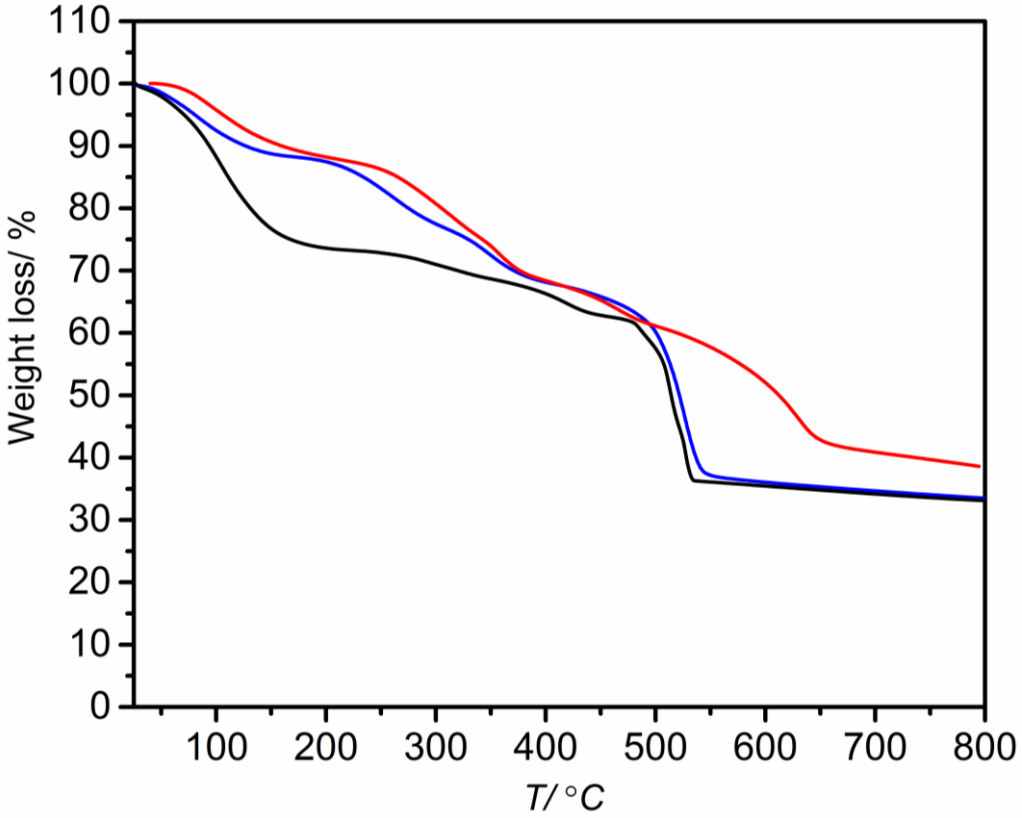

Figure S4. TGA data of **1_EG** (red line), **2_EG** (blue line) and **3_EG** (black line)

Table S4. Crystal data and structure refinement for **1_MeOH** (CCDC 1859134).

Empirical formula	C6 H9 Mg O5	
Formula weight	185.44	
Temperature	100(2) K	
Wavelength	0.700 Å	
Crystal system	Trigonal	
Space group	*R*-3	
Unit cell dimensions	a = 26.023(4) Å	α = 90°
	b = 26.023(4) Å	β = 90°
	c = 6.6525(13) Å	γ = 120°
Volume	3901.5(13) Å^3	
Z	18	
Density (calculated)	1.421 g/cm^3	
Absorption coefficient	0.176 mm^{-1}	
F(000)	1746	
Crystal size	0.250 × 0.100 × 0.020 mm^3	
Theta range for data collection	3.084 to 29.577°	
Index ranges	-36≤h≤34, -36≤k≤36, -6≤l≤8	
Reflections collected	2381	
Completeness to theta = 24.835°	93.3 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2381 / 0 / 119	
Goodness-of-fit on F^2	1.103	
Final R indices [I>2sigma(I)]	R1 = 0.0598, wR2 = 0.1639	
R indices (all data)	R1 = 0.0617, wR2 = 0.1654	
Extinction coefficient	0.082(9)	
Largest diff. peak and hole	0.724 and -0.909 e.Å^{-3}	

Table S5. Crystal data and structure refinement for **2_MeOH** (CCDC 1859143).

Empirical formula	C6 H9 Co O5	
Formula weight	220.06	
Temperature	100(2) K	
Wavelength	0.700 Å	
Crystal system	Trigonal	
Space group	*R*-3	
Unit cell dimensions	a = 26.133(4) Å	α = 90°
	b = 26.133(4) Å	β = 90°
	c = 6.6390(13) Å	γ = 120°
Volume	3926.6(14) Å^3	
Z	18	
Density (calculated)	1.675 g/cm^3	
Absorption coefficient	1.857 mm^{-1}	
F(000)	2016	
Crystal size	0.400 x 0.020 x 0.020 mm^3	
Theta range for data collection	3.071 to 30.978°.	
Index ranges	-38≤h≤36, -37≤k≤37, -9≤l≤9	
Reflections collected	2864	
Completeness to theta = 24.835°	99.0 %	
Absorption correction	Empirical	
Max. and min. transmission	2.113 and 0.194	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2863 / 0 / 123	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0268, wR2 = 0.0747	
R indices (all data)	R1 = 0.0276, wR2 = 0.0752	
Largest diff. peak and hole	0.593 and -0.985 e.Å^{-3}	

Table S6. Crystal data and structure refinement for **3_MeOH** (CCDC 1859139).

Empirical formula	C6 H9 Ni O5	
Formula weight	219.84	
Temperature	100(2) K	
Wavelength	0.700 Å	
Crystal system	Trigonal	
Space group	*R*-3	
Unit cell dimensions	a = 25.899(4) Å	α = 90°
	b = 25.899(4) Å	β = 90°
	c = 6.6350(13) Å	γ = 120°
Volume	3854.2(13) Å^3	
Z	18	
Density (calculated)	1.705 g/cm^3	
Absorption coefficient	2.147 mm^{-1}	
F(000)	2034	
Crystal size	0.050 × 0.050 × 0.050 mm^3	
Theta range for data collection	3.099 to 29.502°	
Index ranges	-36≤h≤34, -36≤k≤36, -9≤l≤9	
Reflections collected	2499	
Completeness to theta = 24.835°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	1.489 and 0.739	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2499 / 1 / 117	
Goodness-of-fit on F^2	1.130	
Final R indices [I>2sigma(I)]	R1 = 0.0564, wR2 = 0.1775	
R indices (all data)	R1 = 0.0586, wR2 = 0.1812	
Extinction coefficient	0.0148(16)	
Largest diff. peak and hole	1.889 and -1.341 e.Å^{-3}	

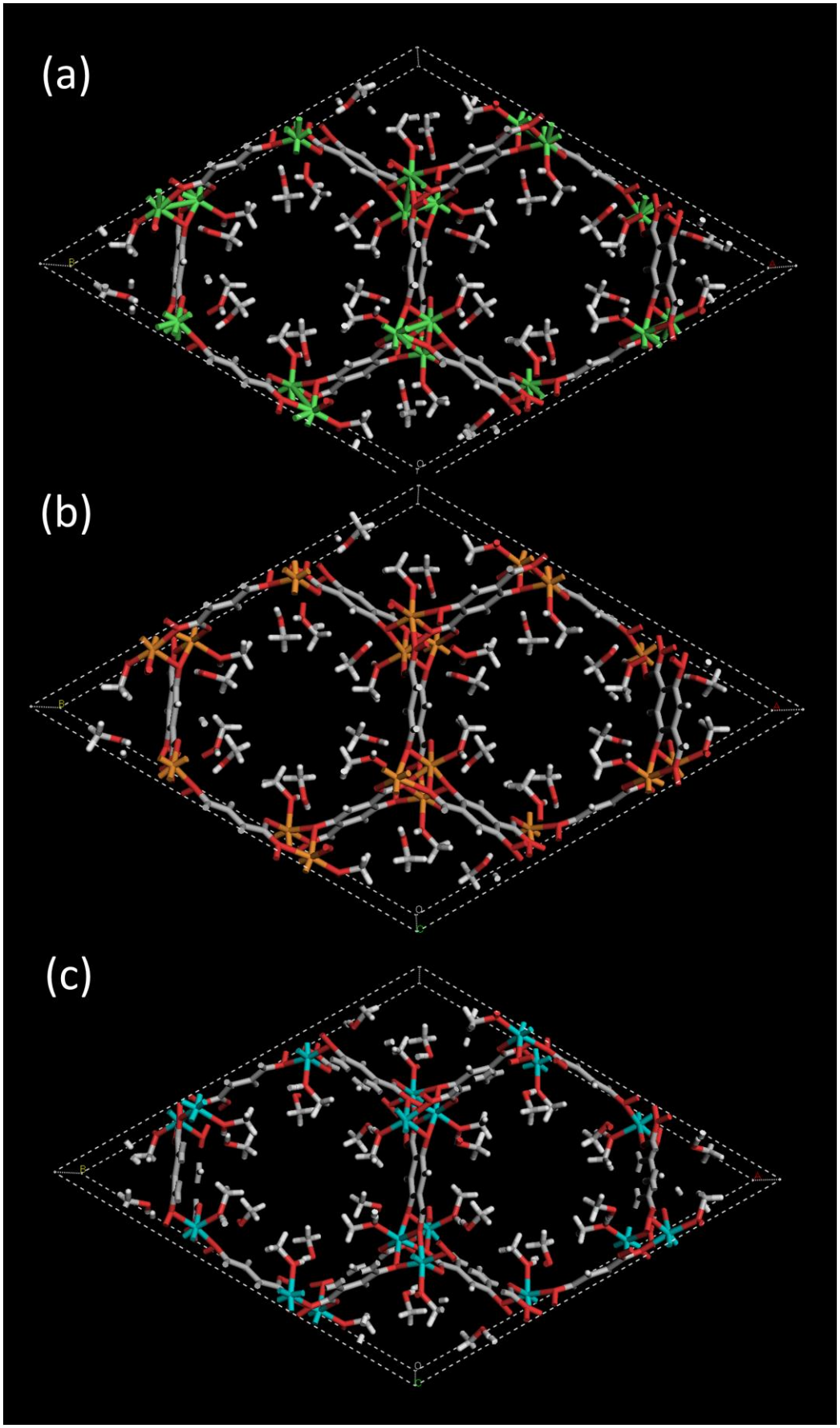

Figure S5. MeOH-exchanged materials, (a) $[Mg_2(DOBDC)(MeOH)_2]$,MeOH (**1_MeOH**), (b) $[Co_2(DOBDC)(MeOH)_2]$,MeOH (**2_MeOH**), (c) $[Ni_2(DOBDC)(MeOH)_2]$,MeOH (**3_MeOH**)

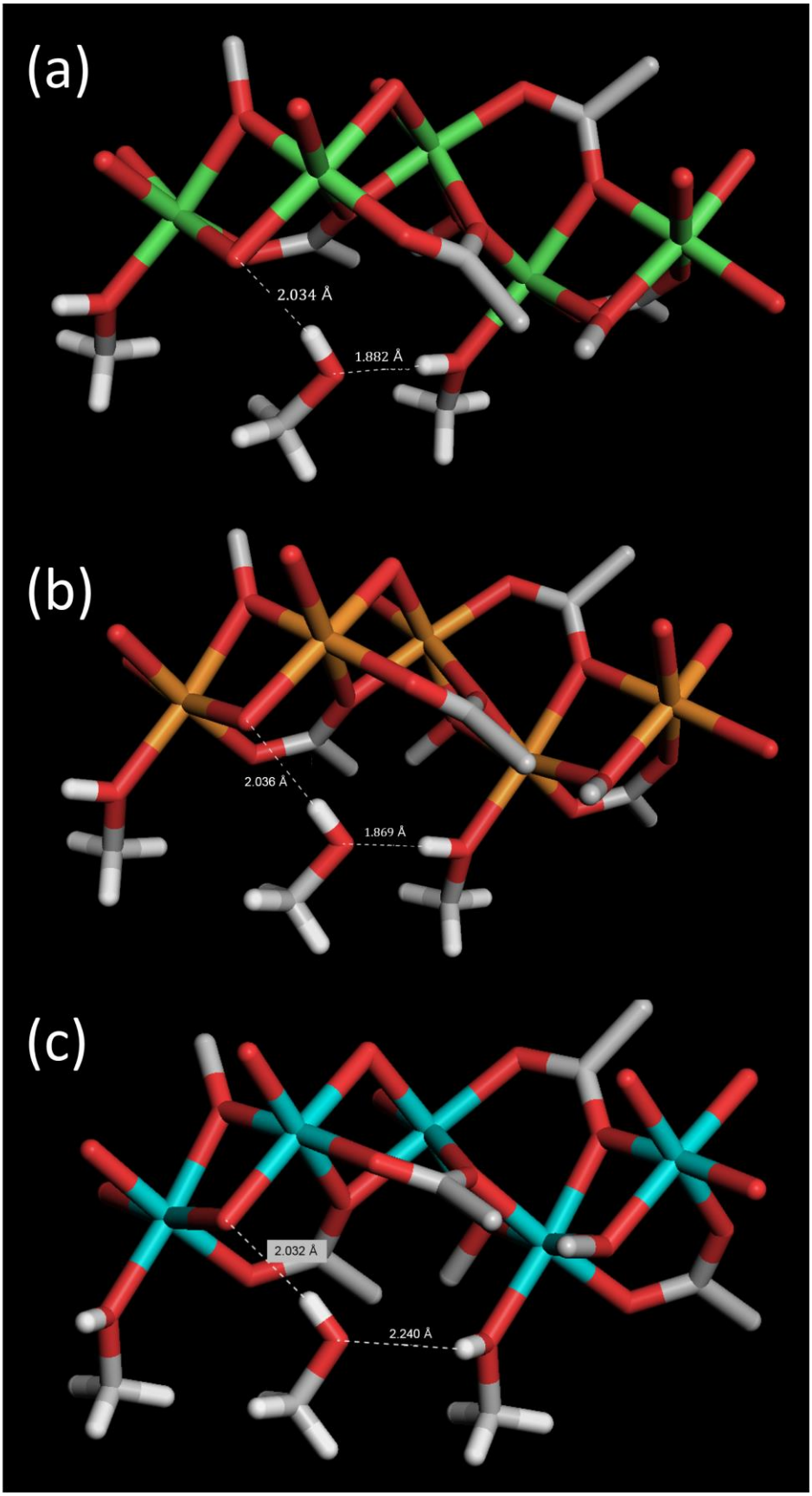

Figure S6. (a) **1_MeOH**, (b) **2_MeOH**, (c) **3_MeOH** indicating hydrogen bonding interactions between free methanol and coordinated methanol, and between free methanol and deprotonated OH group of DOBDC.

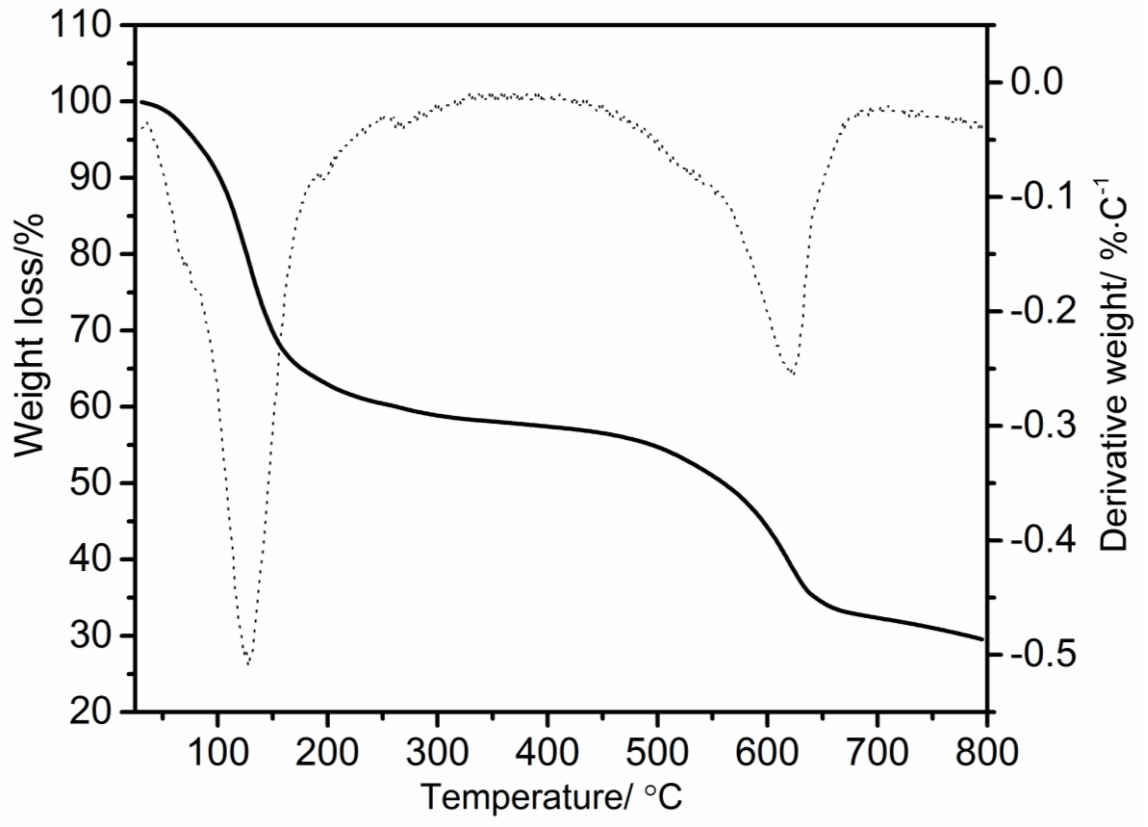

Figure S7. TGA data of **1**_MeOH

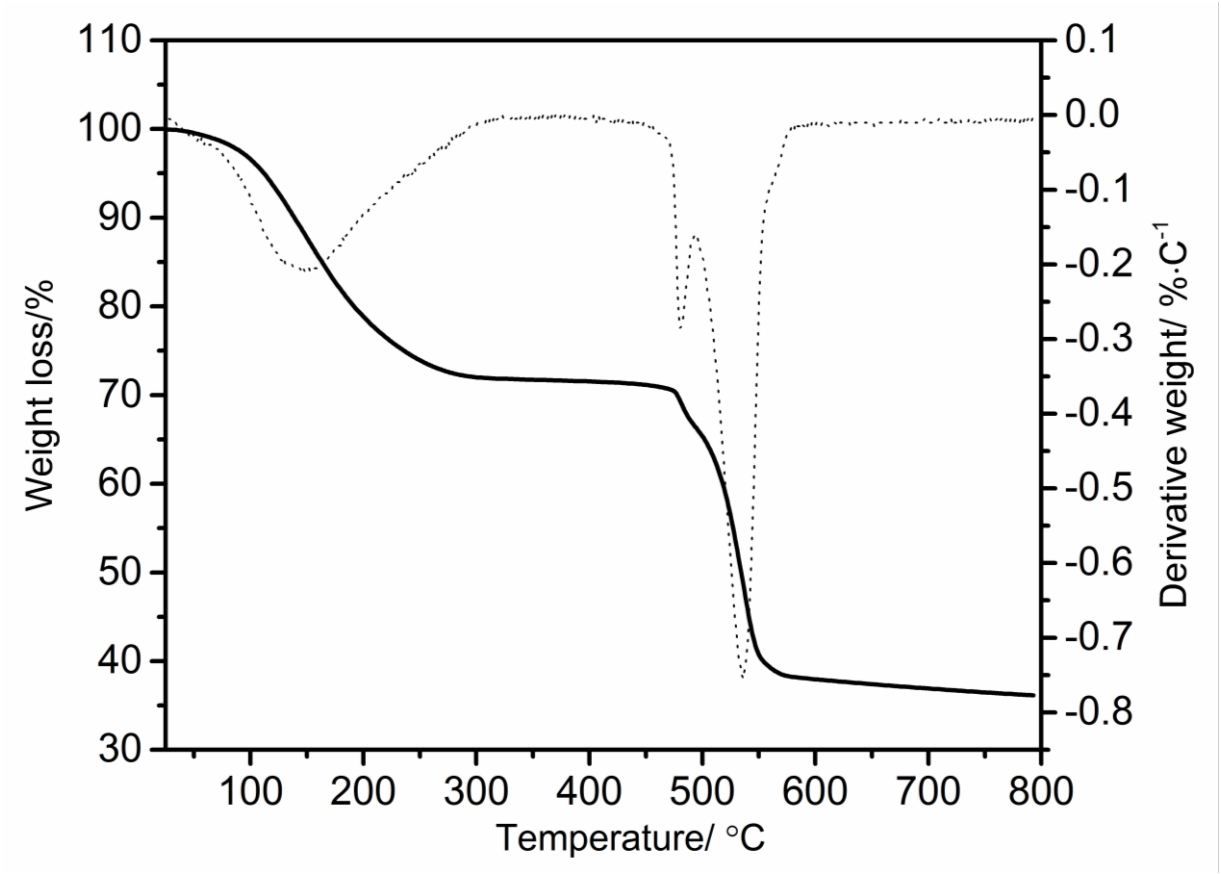

Figure S8. TGA data of **2**_MeOH

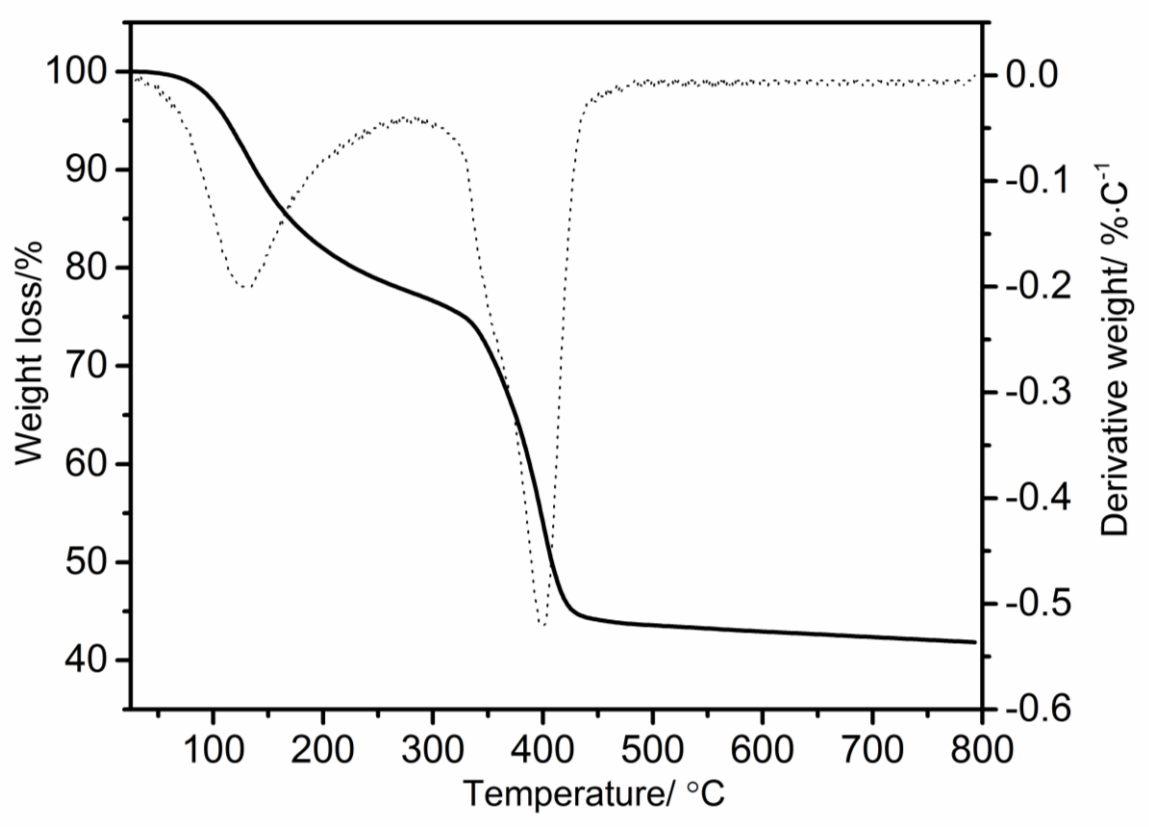

Figure S9. TGA data of **3**_MeOH

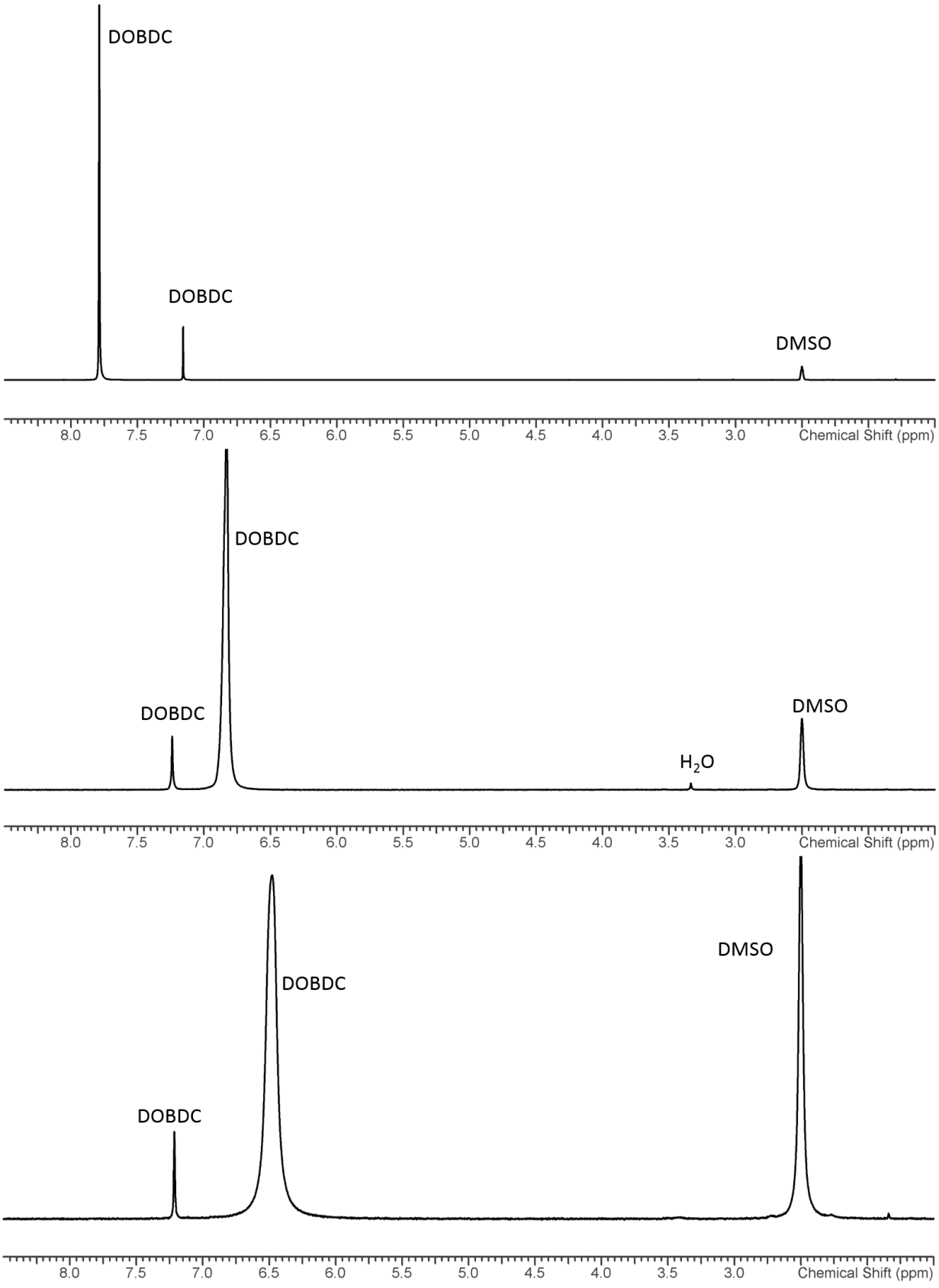

Figure S10. ^{1}H-NMR spectra of activated **1**, **2** and **3** dissolved in DCl/D_2O/DMSO

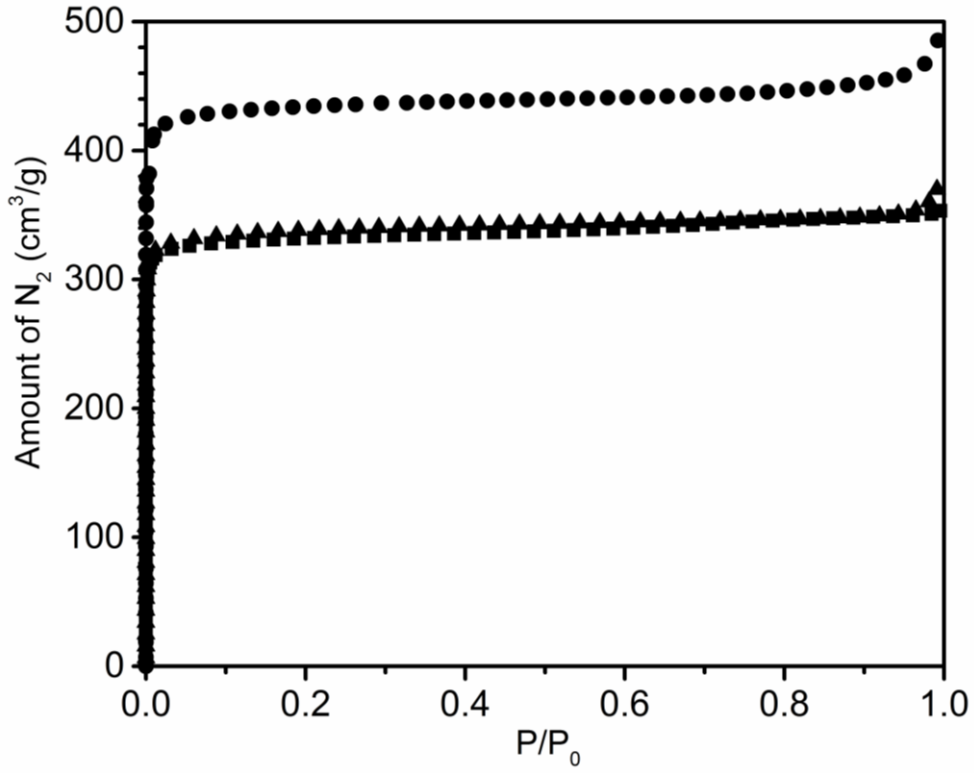

Figure S11. Nitrogen adsorption isotherms of activated **1** (circles), **2** (squares) and **3** (triangles)

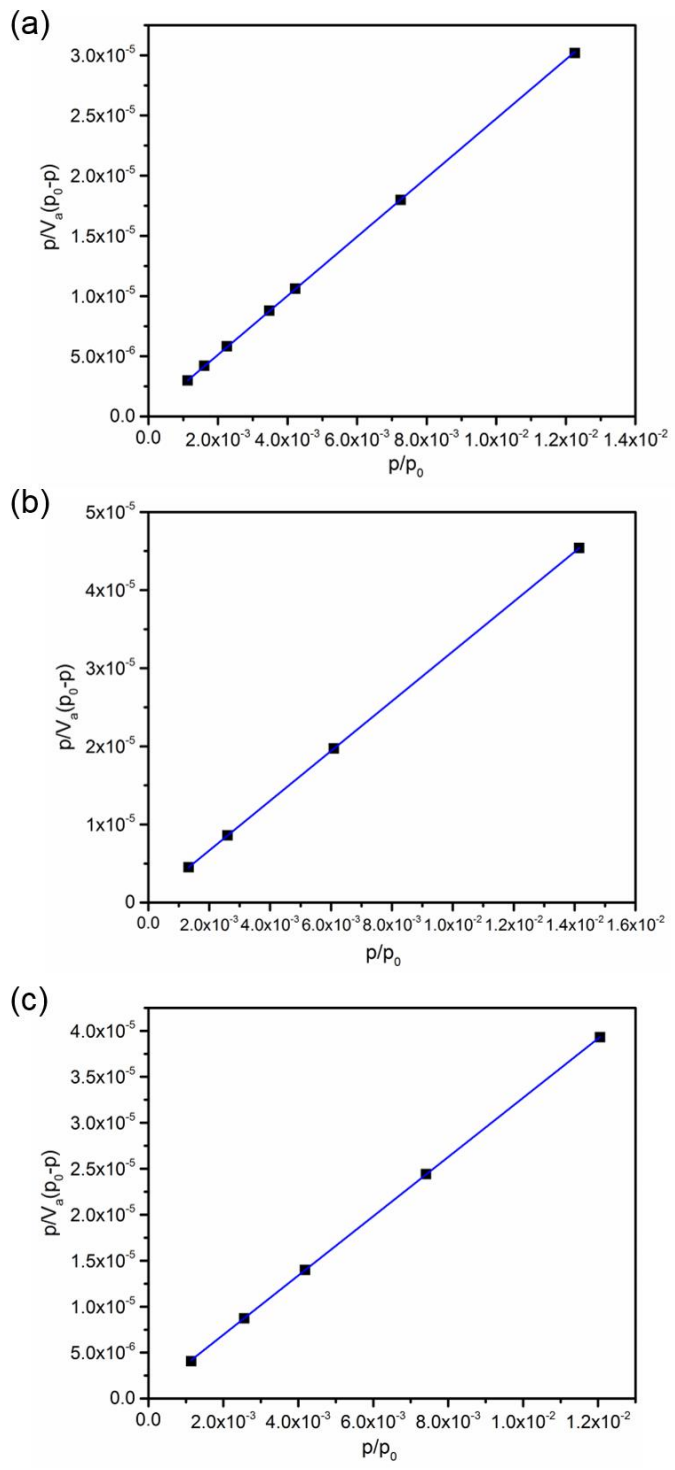

Figure S12. BET plots of (a) **1** (slope: 0.0024518, intercept: 2.1585×10^{-7}, correlation coefficient: 1), (b) **2** (slope: 0.0031485, intercept: 3.336×10^{-7}, correlation coefficient: 1) and (c) **3** (slope: 0.0032219, intercept: 4.9303×10^{-7}, correlation coefficient: 1).

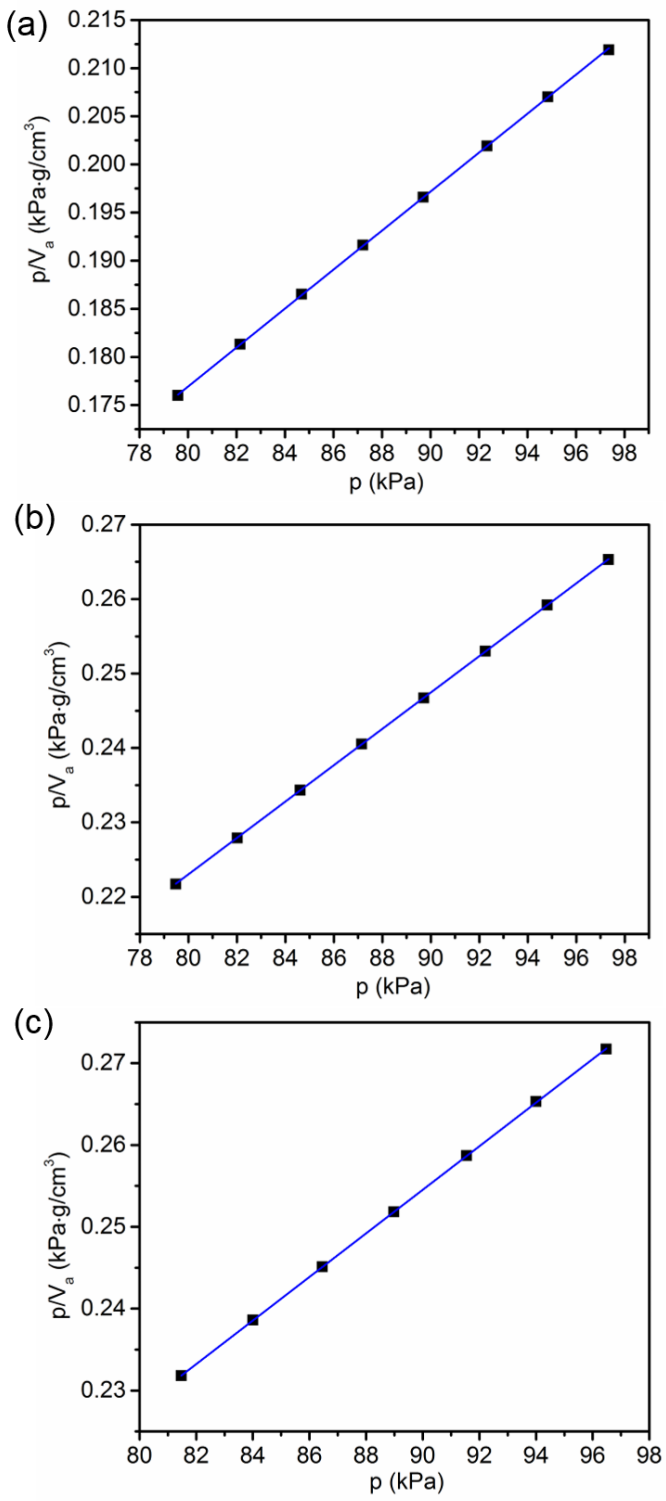

Figure S13. Langmuir plots of (a) **1** (slope: 0.0020251, intercept: 0.014905, correlation coefficient: 1), (b) **2** (slope: 0.0024428, intercept: 0.027593, correlation coefficient: 1) and (c) **3** (slope: 0.0026634, intercept: 0.014812, correlation coefficient: 1).

Table S7. Surface area, total pore volume and micropore volume of [M_2(DOBDC)] (M=Mg, Co, Ni)

[M_2(DOBDC)]	BET surface area, m^2/g	Langmuir surface area, m^2/g	Total pore volume,[a] cm^3/g	Micropore volume,[b] cm^3/g
Mg(II)	1775	2149	0.7159	0.6988
Co(II)	1382	1782	0.5445	0.5347
Ni(II)	1350	1634	0.5604	0.5451

[a]calculated at P/P_0=0.990, [b]calculated by t-plot analysis

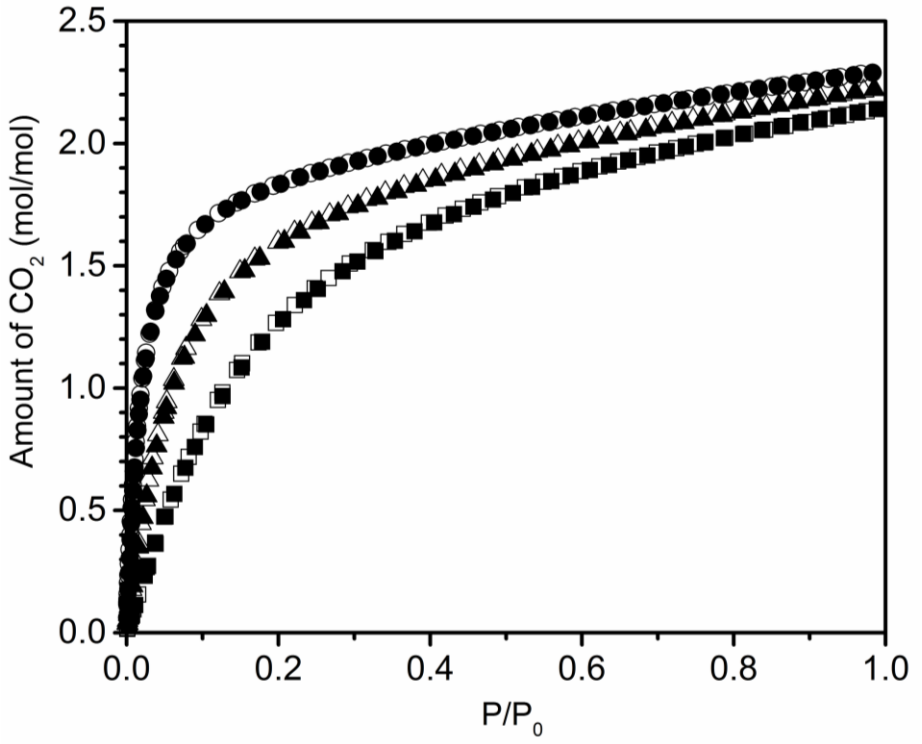

Figure S14. CO_2 adsorption (open symbols) and desorption (closed symbols) isotherms of activated **1** (circles), **2** (squares) and **3** (triangles)

Heat of CO_2 adsorption

The CO_2 adsorption data measured at 288 K, 298 K and 303 K were fitted by the virial equation (**1**) to estimate the enthalpy of adsorption.

$$\ln(p) = \ln(n) + (1/T)\sum_{i=0}^{m} a_i n^i + \sum_{i=0}^{m} b_i n^i \qquad (1)$$

where p is the pressure, n is the amount adsorbed, T is the temperature, and a_i and b_i are temperature independent empirical parameters. The isosteric heat of adsorption was estimated from the following equation (**2**) as a function of the CO_2 uptake.

$$Q_{st} = -R\sum_{i=0}^{m} a_i n^i \qquad (2)$$

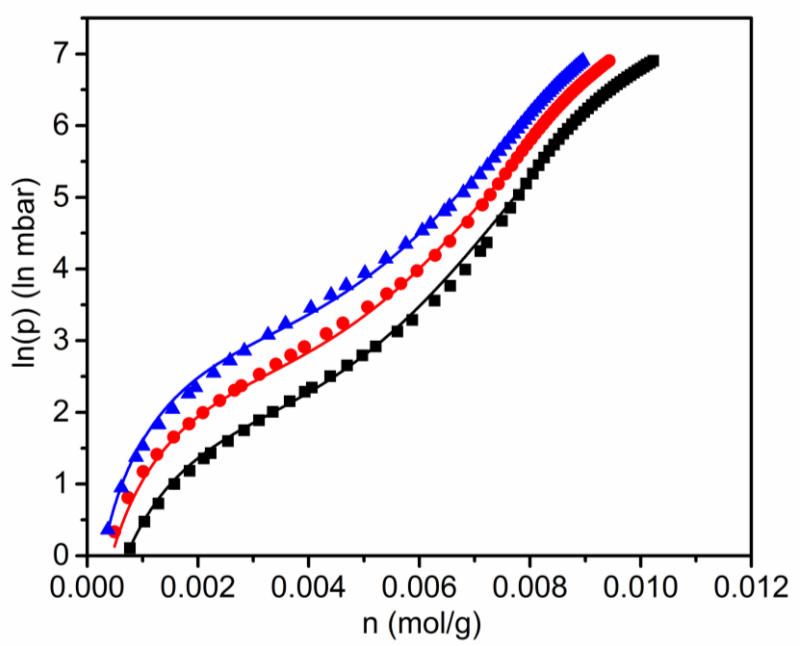

Figure S15. Virial analysis of the CO_2 adsorption data for activated **1**. a_0= -5290.50415, a_1= 284938.60286, a_2= -9.30635×10^7, a_3= 1.56717×10^{10}, a_4= -7.44157×10^{11}, b_1= 25.16618, b_2=-51.72501 (blue triangles; 308 K data, red circles; 298 K data, black squares; 288 K data).

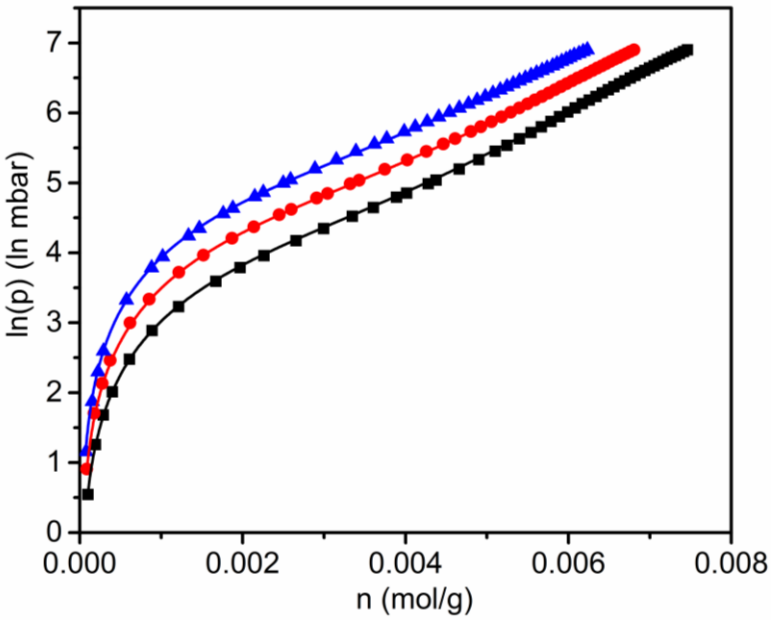

Figure S16. Virial analysis of the CO_2 adsorption data for activated **2**. a_0= -4136.8429, a_1= 113188.49321, a_2= -2.79416×10^7, a_3= 6.92975×10^9, a_4= -4.11772×10^{11}, b_1= 24.11216, b_2=-138.23897. (blue triangles; 308 K data, red circles; 298 K data, black squares; 288 K data)

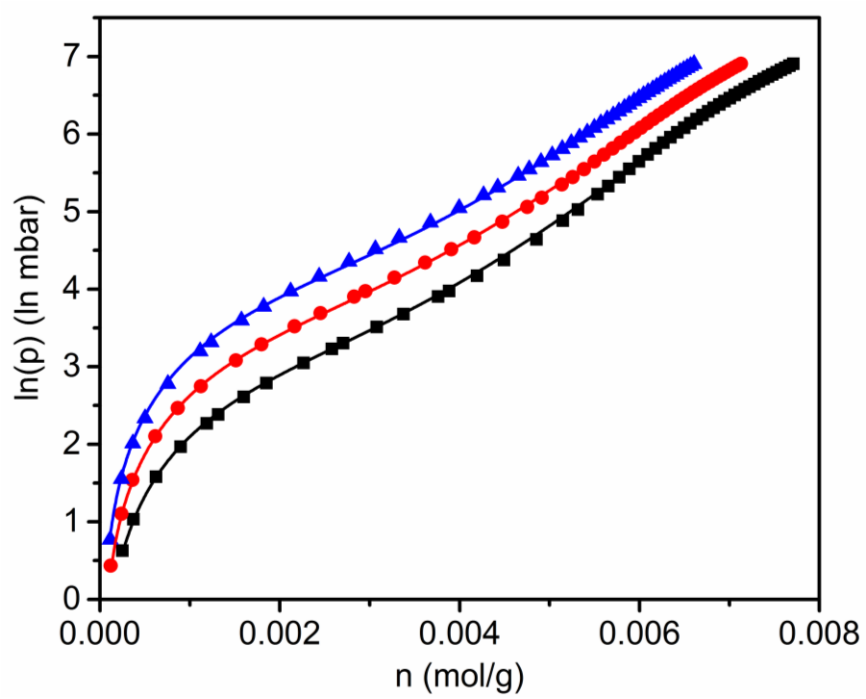

Figure S17. Virial analysis of the CO_2 adsorption data for activated **3**. a_0 = -4670.59331, a_1= 164466.71598, a_2= -4.55722×10^7, a_3= 1.27108×10^{10}, a_4= -8.3587×10^{11}, b_1= 25.02768, b_2=-259.56093. (blue triangles; 308 K data, red circles; 298 K data, black squares; 288 K data)

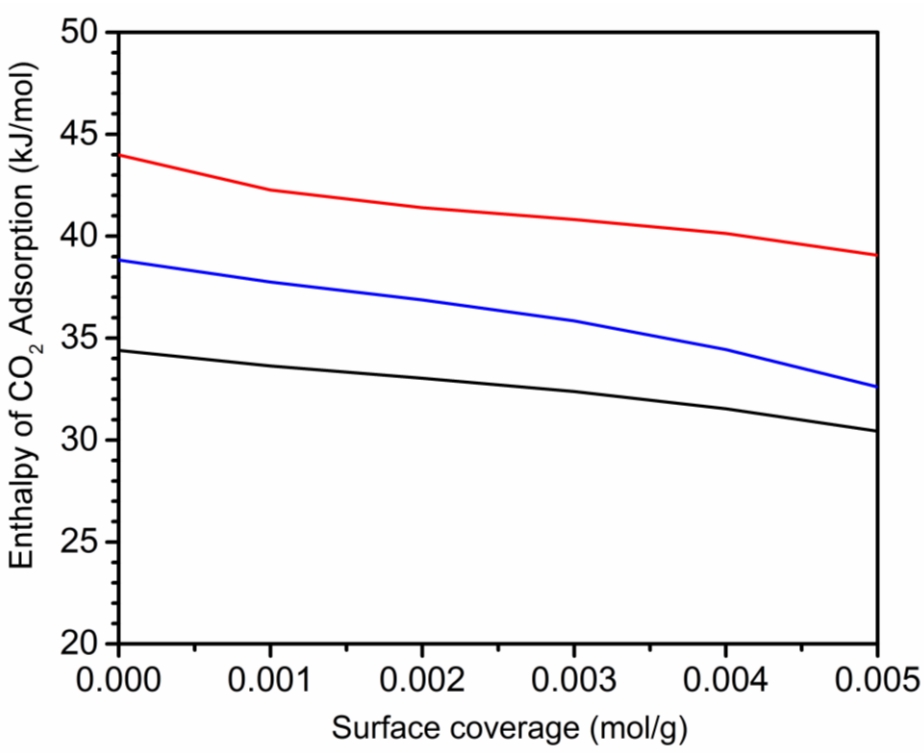

Figure S18. Heat of CO_2 adsorption for activated **1** (red line), **2** (black line) and **3** (blue line)

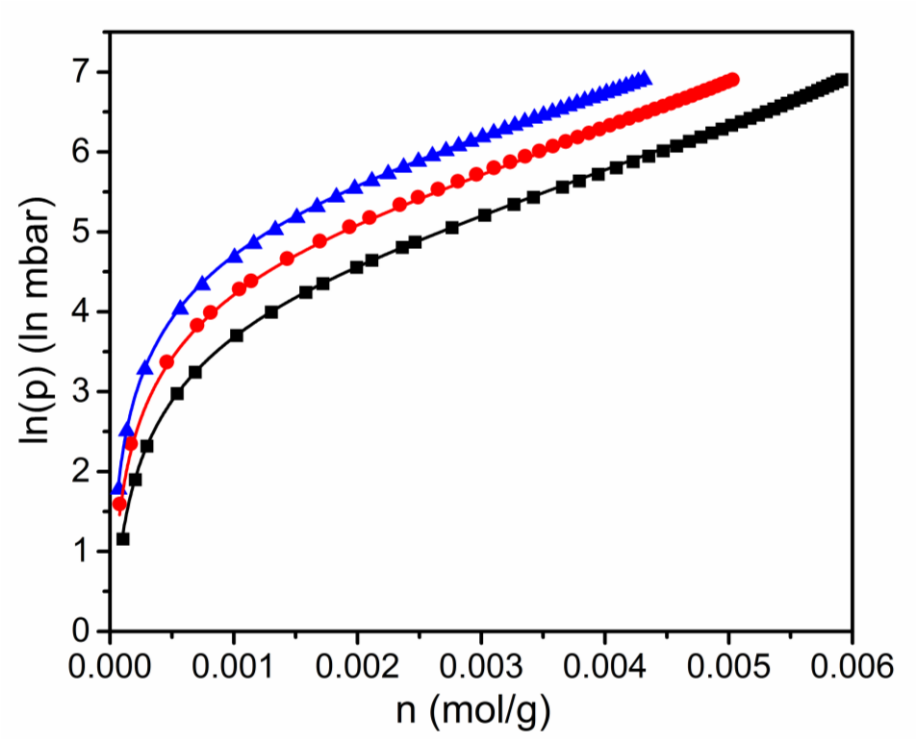

Figure S19. Virial analysis of the CO adsorption data for activated **1**. a_0= -4608.05349, a_1= 90802.1616, a_2= -3.4287×10^7, a_3= 1.31912×10^{10}, a_4= -1.95739×10^{12}, a_5= 1.11832×10^{14}, b_1= 26.35132, (blue triangles; 308 K data, red circles; 298 K data, black squares; 288 K data)

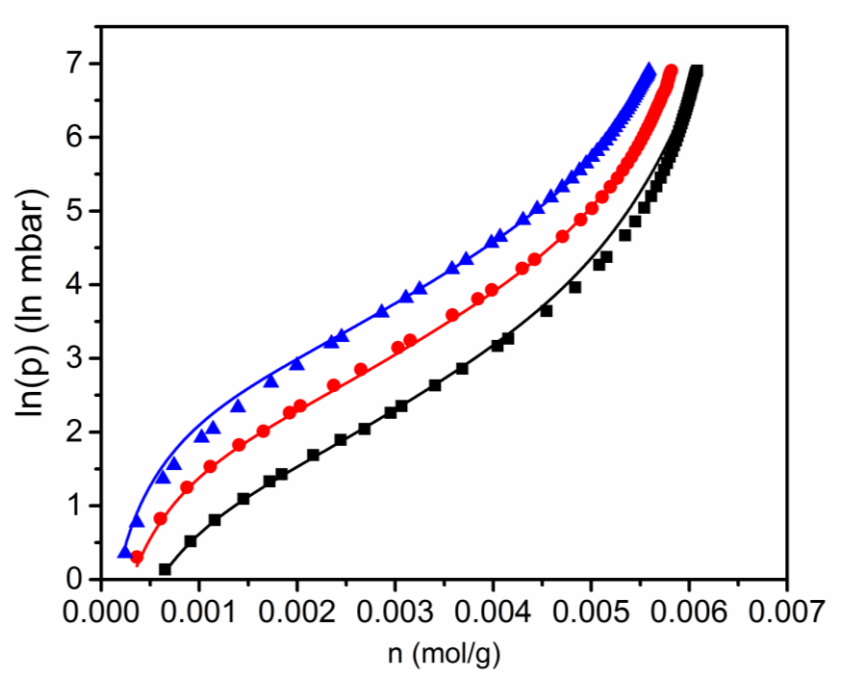

Figure S20. Virial analysis of the CO adsorption data for activated **2**. a_0= -6669.49773, a_1= 228157.25352, a_2= -1.68526×10^8, a_3= 7.31195×10^{10}, a_4= -1.34675×10^{13}, a_5= 9.86863×10^{14}, b_1= 30.26494. (blue triangles; 308 K data, red circles; 298 K data, black squares; 288 K data)

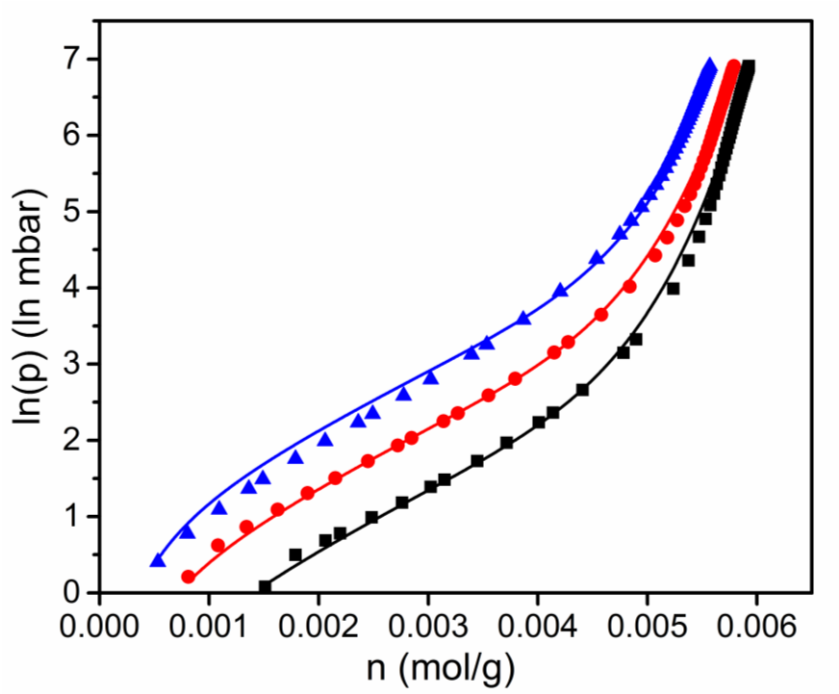

Figure S21. Virial analysis of the CO adsorption data for activated **3**. a_0= -7185.17074, a_1= 111398.62646, a_2= -7.63061×10^7, a_3= 5.02845×10^{10}, a_4= -1.27334×10^{13}, a_5= 1.22164×10^{15}, b_1= 31.16352. (blue triangles; 308 K data, red circles; 298 K data, black squares; 288 K data)

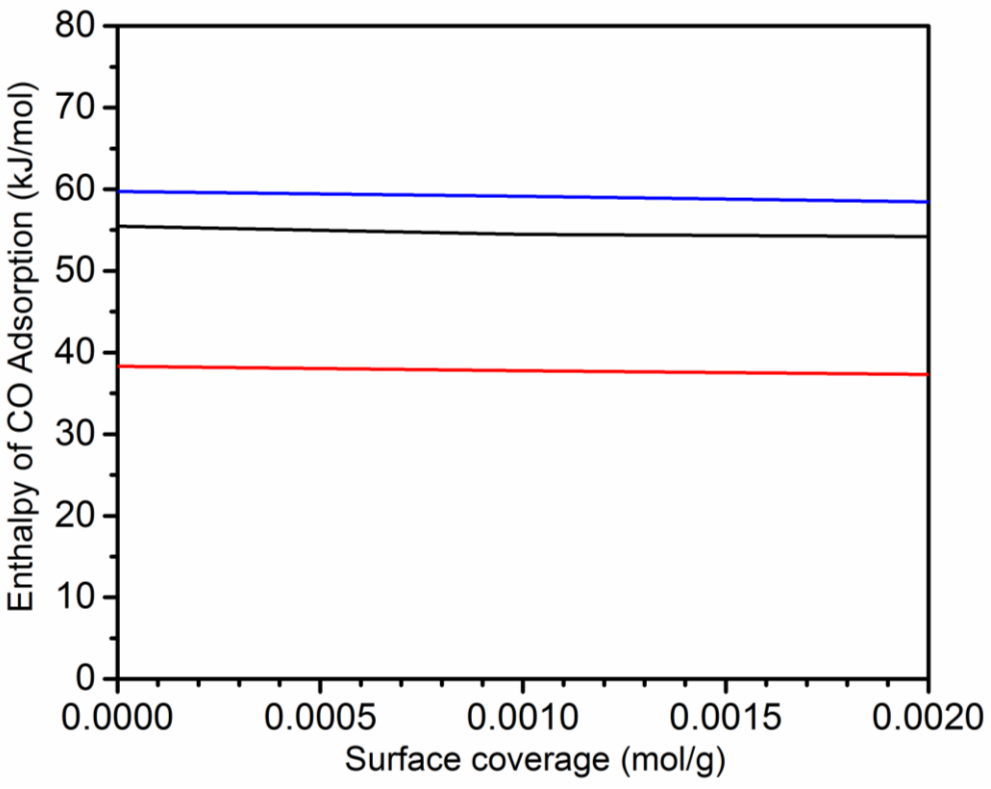

Figure S22. Heat of CO adsorption for activated **1** (red line), **2** (black line) and **3** (blue line)

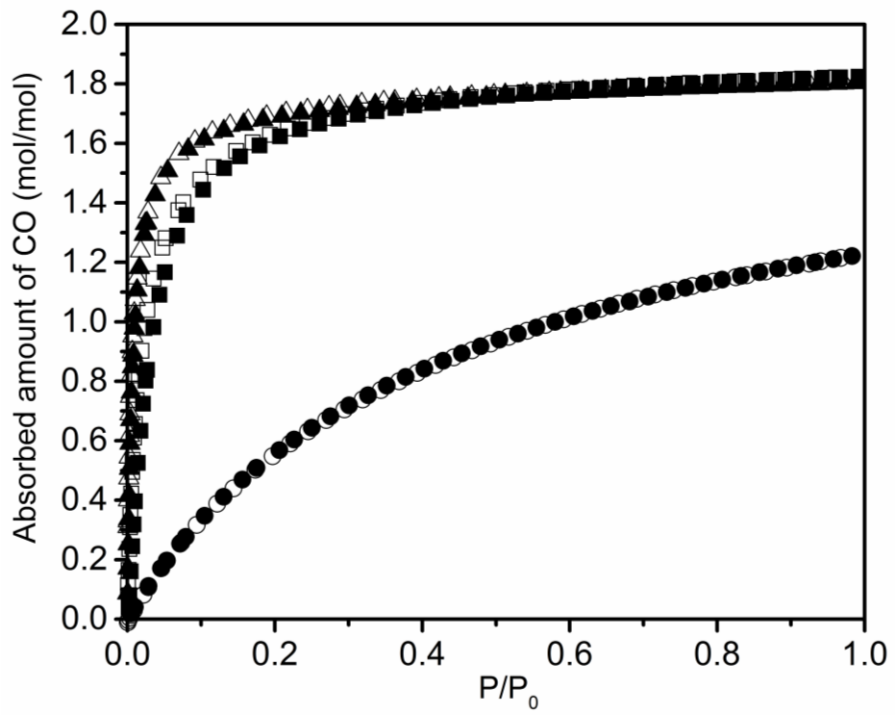

Figure S23. CO adsorption (open symbols) and desorption (closed symbols) isotherms of activated **1** (circles), **2** (squares) and **3** (triangles)

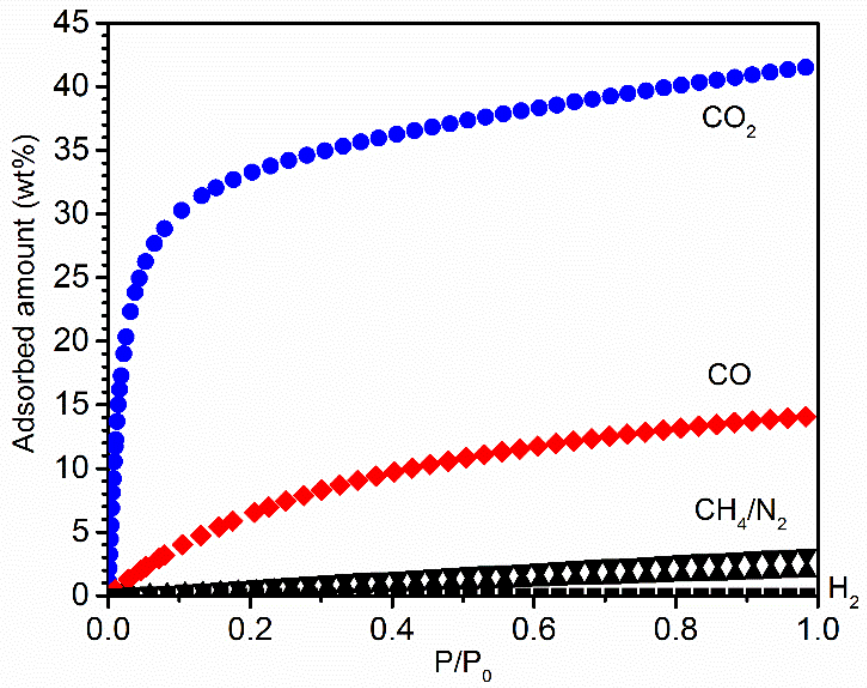

Figure S24. CO_2 (circles), CO (rhombohedral), CH_4 (reverse triangles), N_2 (triangles) and H_2 (squares) adsorption isotherms of activated **1** at 298 K

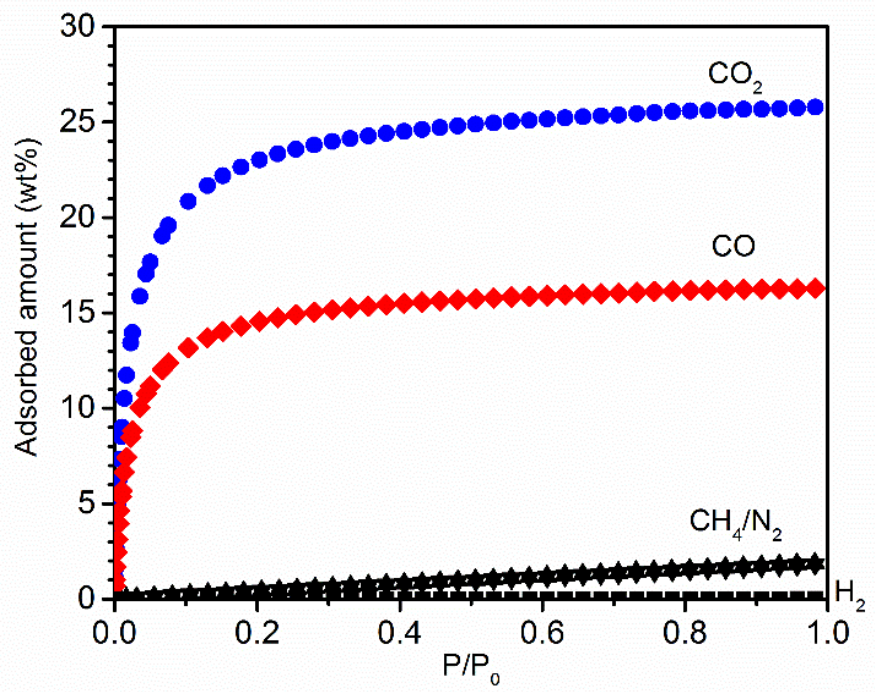

Figure S25. CO_2 (circles), CO (rhombohedral), CH_4 (reverse triangles), N_2 (triangles) and H_2 (squares) adsorption isotherms of activated **2** at 298 K

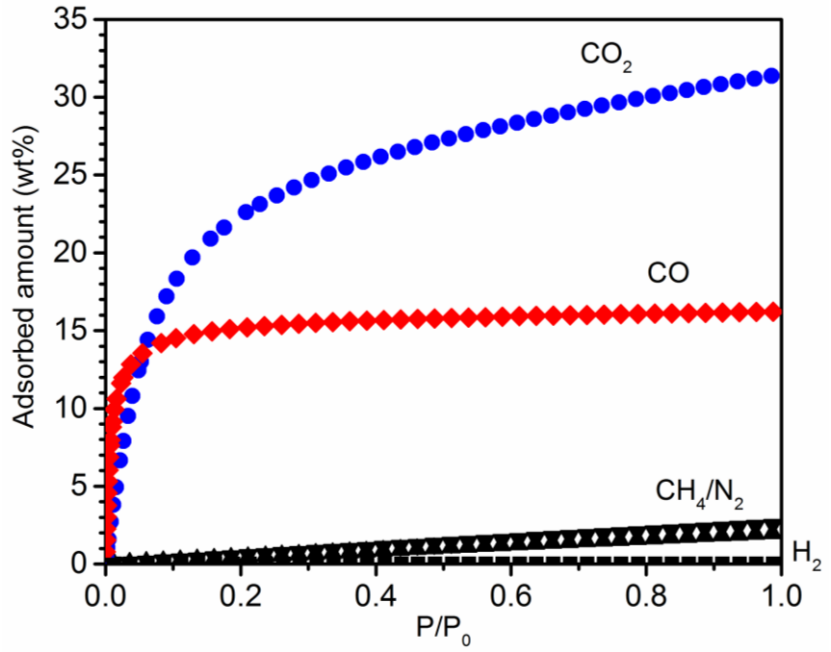

Figure S26. CO_2 (circles), CO (rhombohedral), CH_4 (reverse triangles), N_2 (triangles) and H_2 (squares) adsorption isotherms of activated **3** at 298 K

Table S8. Crystal data and structure refinement for CO_2-adsorbed **1** (CCDC 1859135).

Empirical formula	C5.60 H Mg O6.20	
Formula weight	191.77	
Temperature	100(2) K	
Wavelength	0.700 Å	
Crystal system	Trigonal	
Space group	*R*-3	
Unit cell dimensions	a = 25.839(4) Å	α = 90°
	b = 25.839(4) Å	β = 90°
	c = 6.8930(14) Å	γ = 120°
Volume	3985.6(14) $Å^3$	
Z	18	
Density (calculated)	1.438 g/cm^3	
Absorption coefficient	0.185 mm^{-1}	
F(000)	1732	
Crystal size	0.350 × 0.050 × 0.050 mm^3	
Theta range for data collection	3.046 to 37.669°	
Index ranges	-44≤h≤43, -44≤k≤44, -9≤l≤11	
Reflections collected	4302	
Completeness to theta = 24.835°	96.6 %	
Absorption correction	Empirical	
Max. and min. transmission	1.3213 and 0.7499	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4302 / 17 / 132	
Goodness-of-fit on F^2	1.193	
Final R indices [I>2sigma(I)]	R1 = 0.1063, wR2 = 0.2581	
R indices (all data)	R1 = 0.1166, wR2 = 0.2752	
Largest diff. peak and hole	2.114 and -1.067 $e.Å^{-3}$	

Table S9. Crystal data and structure refinement for CO_2-adsorbed **2** (CCDC 1859137).

Empirical formula	C5.67 H Co O6.34	
Formula weight	229.47	
Temperature	100(2) K	
Wavelength	0.700 Å	
Crystal system	Trigonal	
Space group	*R*-3	
Unit cell dimensions	a = 25.897(4) Å	α = 90°
	b = 25.897(4) Å	β = 90°
	c = 6.8390(14) Å	γ = 120°
Volume	3972.2(14) $Å^3$	
Z	18	
Density (calculated)	1.727 g/cm^3	
Absorption coefficient	1.851 mm^{-1}	
F(000)	2029	
Crystal size	0.500 × 0.050 × 0.050 mm^3	
Theta range for data collection	3.067 to 37.696°.	
Index ranges	-41≤h≤40, -42≤k≤42, -9≤l≤10	
Reflections collected	4359	
Completeness to theta = 24.835°	99.1 %	
Absorption correction	Empirical	
Max. and min. transmission	1.626 and 0.392	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4359 / 12 / 133	
Goodness-of-fit on F^2	1.089	
Final R indices [I>2sigma(I)]	R1 = 0.0452, wR2 = 0.1386	
R indices (all data)	R1 = 0.0466, wR2 = 0.1403	
Extinction coefficient	0.0118(12)	
Largest diff. peak and hole	1.534 and -1.064 e.$Å^{-3}$	

Table S10. Crystal data and structure refinement for CO_2-adsorbed **3** (CCDC 1859141).

Empirical formula	C5.84 H Ni O6.68	
Formula weight	236.74	
Temperature	293(2) K	
Wavelength	0.70000 Å	
Crystal system	Trigonal	
Space group	*R*-3	
Unit cell dimensions	a = 25.880(4) Å	α = 90°
	b = 25.880(4) Å	β = 90°
	c = 6.6950(13) Å	γ = 120°
Volume	3883.4(13) $Å^3$	
Z	18	
Density (calculated)	1.822 g/cm^3	
Absorption coefficient	2.152 mm^{-1}	
F(000)	2115	
Crystal size	0.100 × 0.020 × 0.020 mm^3	
Theta range for data collection	3.128 to 31.887°.	
Index ranges	-35≤h≤33, -14≤k≤36, -9≤l≤9	
Reflections collected	2299	
Completeness to theta = 24.835°	98.3 %	
Absorption correction	Empirical	
Max. and min. transmission	1.274 and 0.859	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2299 / 33 / 131	
Goodness-of-fit on F^2	1.165	
Final R indices [I>2sigma(I)]	R1 = 0.1007, wR2 = 0.2583	
R indices (all data)	R1 = 0.1233, wR2 = 0.2797	
Largest diff. peak and hole	3.584 and -1.373 e.$Å^{-3}$	

Table S11. Crystal data and structure refinement for CO-adsorbed **1** (CCDC 1859133).

Empirical formula	$C_{5.56}$ H Mg $O_{4.56}$	
Formula weight	165.10	
Temperature	100(2) K	
Wavelength	0.700 Å	
Crystal system	Trigonal	
Space group	*R*-3	
Unit cell dimensions	*a* = 25.822(4) Å	α = 90°
	b = 25.822(4) Å	β = 90°
	c = 6.9350(14) Å	γ = 120°
Volume	4004.6(14) $Å^3$	
Z	18	
Density (calculated)	1.232 g/cm^3	
Absorption coefficient	0.161 mm^{-1}	
F(000)	1492	
Crystal size	0.170 × 0.140 × 0.040 mm^3	
Theta range for data collection	3.029 to 29.561°.	
Index ranges	-36≤h≤34, -36≤k≤36, -9≤l≤9	
Reflections collected	2507	
Completeness to theta = 24.835°	96.5 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.8750	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2507 / 0 / 114	
Goodness-of-fit on F^2	0.838	
Final R indices [I>2sigma(I)]	R1 = 0.0482, wR2 = 0.1431	
R indices (all data)	R1 = 0.0499, wR2 = 0.1472	
Extinction coefficient	0.046(5)	
Largest diff. peak and hole	0.569 and -0.431 $e.Å^{-3}$	

Table S12. Crystal data and structure refinement for CO-adsorbed **2** (CCDC 1859136).

Empirical formula	C5.56 H Co O4.56	
Formula weight	199.67	
Temperature	100(2) K	
Wavelength	0.70000 Å	
Crystal system	Trigonal	
Space group	*R*-3	
Unit cell dimensions	a = 25.844(4) Å	α = 90°
	b = 25.844(4) Å	β = 90°
	c = 6.8710(14) Å	γ = 120°
Volume	3974.5(14) Å^3	
Z	18	
Density (calculated)	1.502 g/cm^3	
Absorption coefficient	1.824 mm^{-1}	
F(000)	1761	
Crystal size	0.110 × 0.040 × 0.020 mm^3	
Theta range for data collection	3.054 to 37.625°.	
Index ranges	-44≤h≤43, -44≤k≤44, -9≤l≤10	
Reflections collected	4344	
Completeness to theta = 24.835°	99.6 %	
Absorption correction	Empirical	
Max. and min. transmission	1.294 and 0.764	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4344 / 8 / 115	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0604, wR2 = 0.1629	
R indices (all data)	R1 = 0.0636, wR2 = 0.1676	
Extinction coefficient	0.045(3)	
Largest diff. peak and hole	3.020 and -1.644 e.Å^{-3}	

Table S13. Crystal data and structure refinement for CO-adsorbed **3** (CCDC 1859142).

Empirical formula	C5.98 H Ni O4.98	
Formula weight	211.22	
Temperature	100(2) K	
Wavelength	0.7000 Å	
Crystal system	Trigonal	
Space group	*R*-3	
Unit cell dimensions	a = 26.150(4) Å	α = 90°
	b = 26.150(4) Å	β = 90°
	c = 6.7210(13) Å	γ = 120°
Volume	3980.1(14) Å^3	
Z	18	
Density (calculated)	1.586 g/cm^3	
Absorption coefficient	2.076 mm^{-1}	
F(000)	1885	
Crystal size	0.040 × 0.040 × 0.020 mm^3	
Theta range for data collection	3.069 to 33.385°.	
Index ranges	-38≤h≤37, -38≤k≤38, -9≤l≤9	
Reflections collected	3117	
Completeness to theta = 24.835°	97.9 %	
Absorption correction	Empirical	
Max. and min. transmission	1.603 and 0.375	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3117 / 28 / 115	
Goodness-of-fit on F^2	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.0656, wR2 = 0.1969	
R indices (all data)	R1 = 0.0701, wR2 = 0.2081	
Extinction coefficient	0.019(2)	
Largest diff. peak and hole	2.317 and -1.524 e.Å^{-3}	

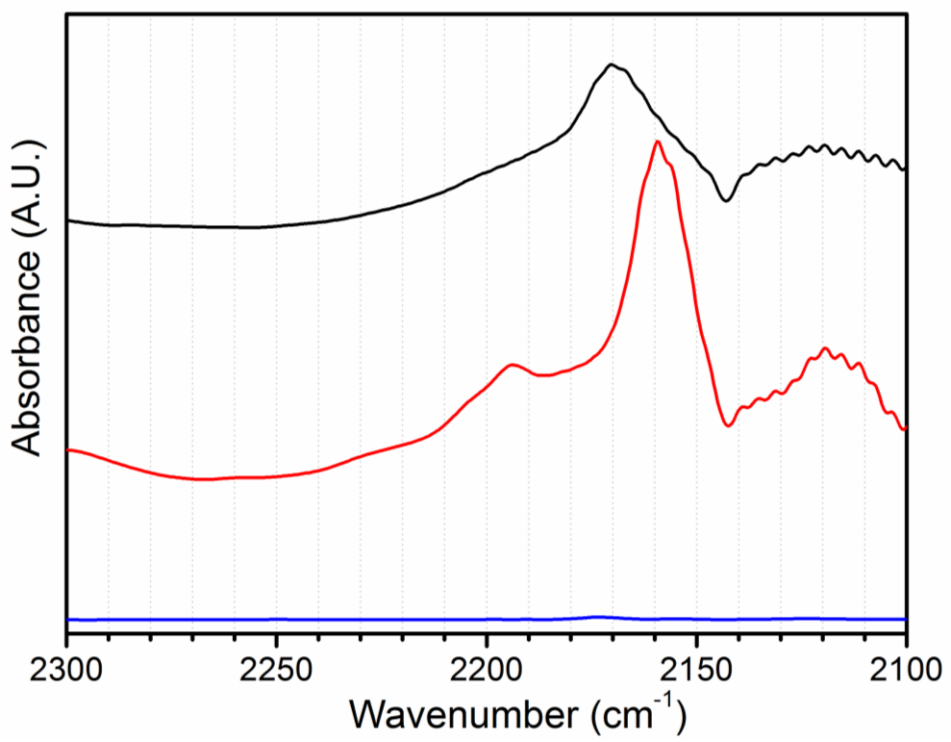

Figure S27. *In situ* FT-IR spectra of CO-adsorbed **1** (blue line), **2** (red line) and **3** (black line)

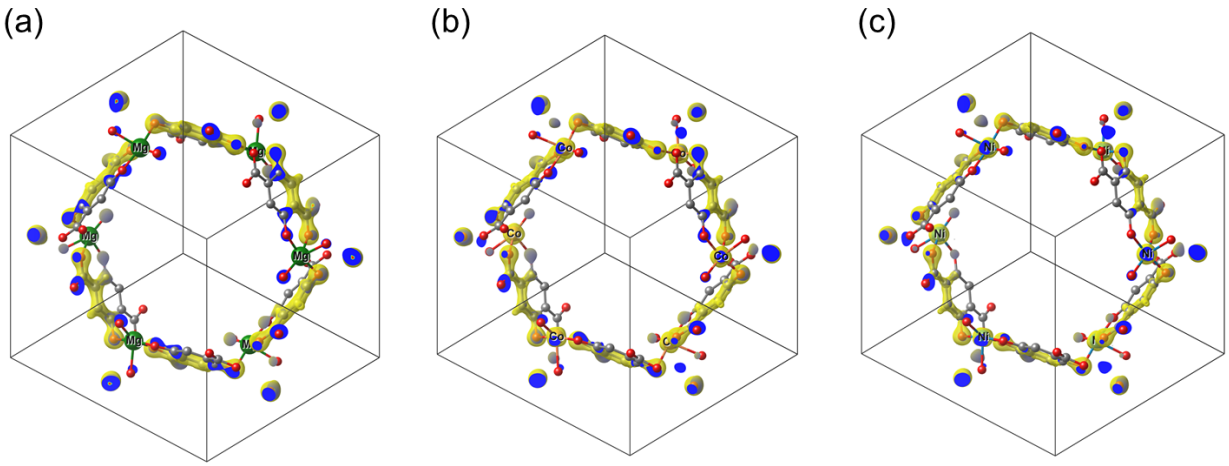

Figure S28. Total charge density of guest-free (a) **1**, (b) **2** and (c) **3**

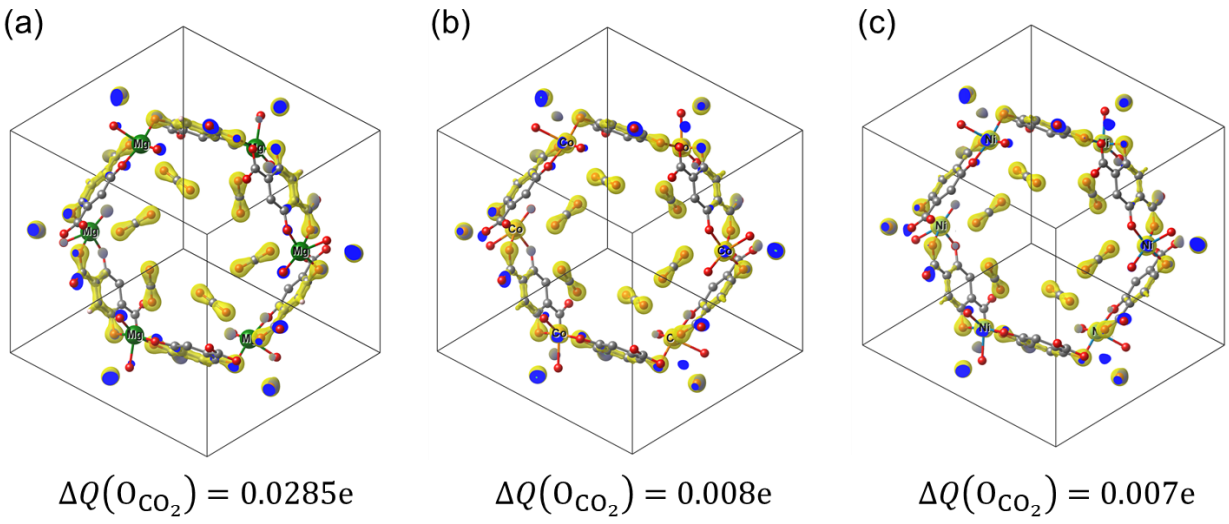

Figure S29. Total charge density of CO_2-adsorbed (a) **1**, (b) **2** and (c) **3**. The differences of the Bader charges (ΔQ) of oxygen atoms in CO_2 molecules after adsorption are shown below each image.

Since electronic hybridizations between M (M = Mg, Co, Ni) and CO_2 are harldy observed, the change of bader charge in oxygen atoms adjacent to M-site are compared based on Bader charge analysis. ΔQ values shown in Figure S29 indicate the charge gain of the oxygen atoms in CO_2 which are adjacent to the M-sites. Mg(II) site shows the largest charge gain for the adjacent oxygen while Co(II) and Ni(II) sites show a slight differences. This implies that Mg(II) site makes bigger interaction with CO_2 molecule.