Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Influence of Co-adsorbates on CO_2 Induced Phase Transition in Functionalized Pillared-Layered Metal-organic Frameworks

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CONTENTS

S1 PXRD Patterns

Figure S1 shows the diffraction patterns of compounds **1**-**3** in the as-synthesized and dried state in a range from *2Θ* = 5-30°.

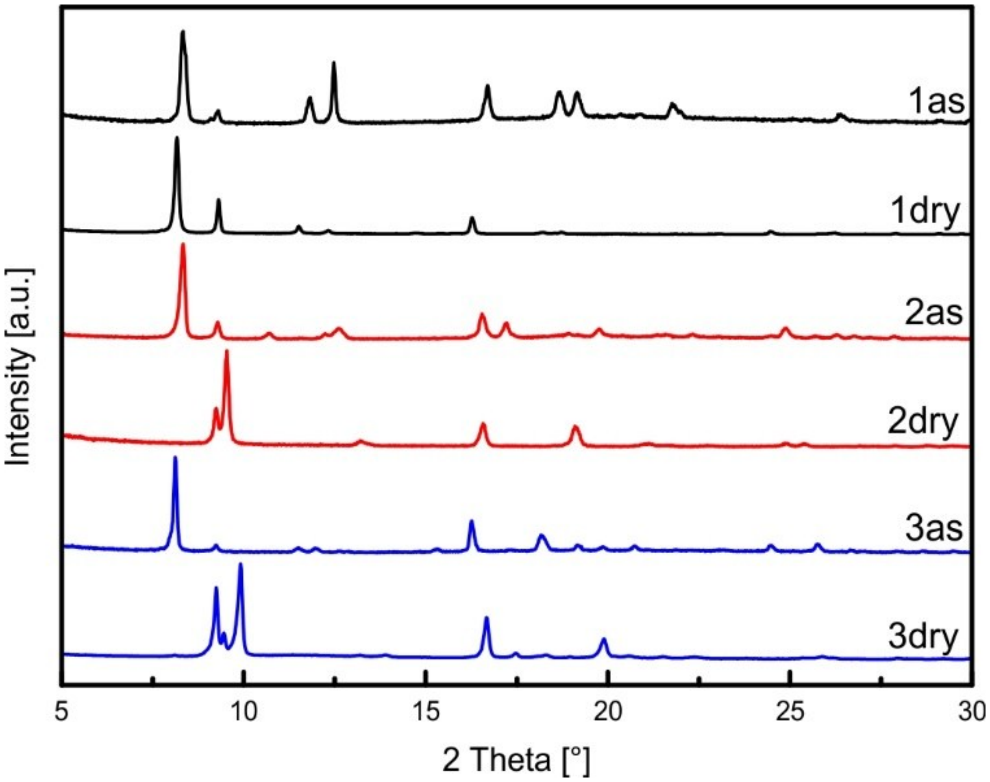

Figure S 1: PXRD patterns of compounds **1** (black), **2** (red) and **3** (blue) in the as-synthesized (as) and dried (dry) state.

S2 NMR Spectra

Liquid phase NMR spectra were performed on a Bruker Advance DPX 200 spectrometer (1H, 200 MHz) at 293 K. ^{1}H NMR spectra of the synthesized linker molecules were recorded in DMSO-d_6 and the spectra of digested MOFs were recorded in 0.5 ml DMSO-d_6 and 0.05 ml of DCl/D_2O (20%). Chemical shifts are given relative to TMS and were referenced to the solvent signals as internal standards.

Figures S2 – S4 show the ^{1}H-NMR of the MOFs **1-3** dissolved in DCl/D_2O/DMSO-d_6.

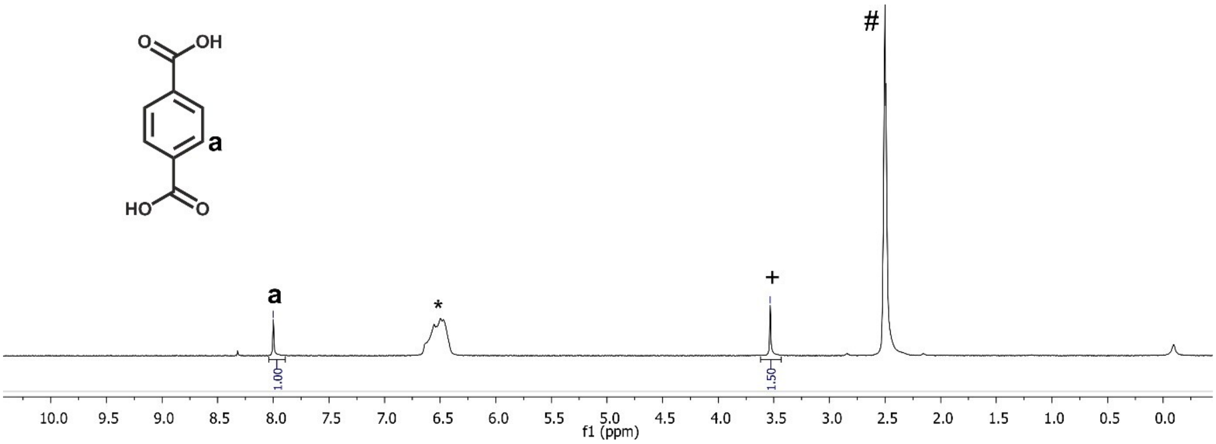

Figure S 2: NMR spectra of compound **1** ([Zn_2(bdc)$_2$(dabco)]$_n$)measured in DMSO-d_6/DCl/D_2O. Asterisk marks the DCl/D_2O peak, + the dabco peak and # the DMSO peak.

^{1}H NMR (200 MHz, DMSO) δ 8.16 – 7.81 (s, 4H), 3.81 – 3.27 (s, 6H).

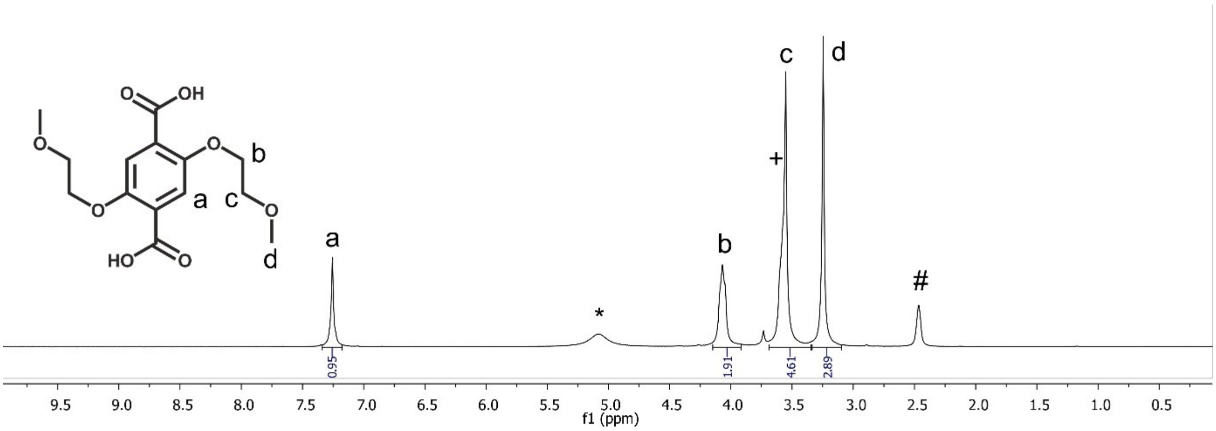

Figure S 3: NMR spectra of compound **2** ([Zn_2(BME-bdc)$_2$(dabco)]$_n$) measured in DMSO-d_6/DCl/D_2O. Asterisk marks the DCl/D_2O peak, + the dabco peak and # the DMSO peak.

^{1}H NMR (200 MHz, DMSO) δ 7.62 – 7.09 (s, 1H), 4.44 – 3.89 (s, 1H), 3.69 – 3.41 (s, 5H), 3.44 – 3.01 (s, 3H).

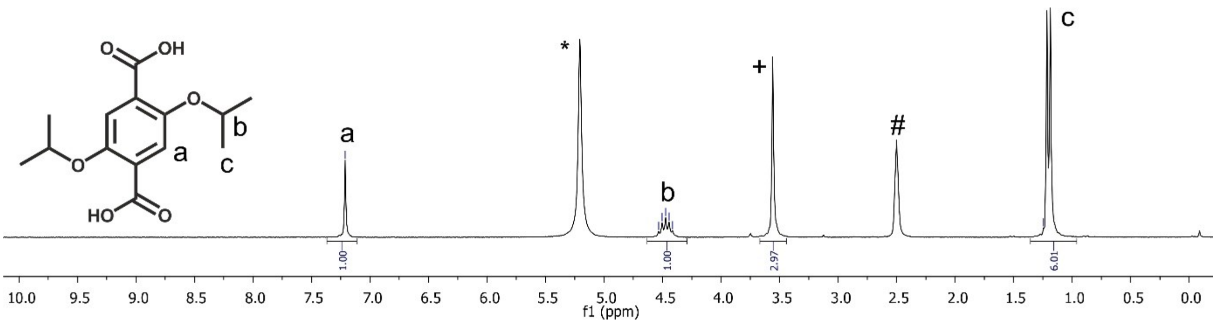

Figure S 4: NMR spectra of compound **3** ($[Zn_2(DiP\text{-}bdc)_2(dabco)]_n$) measured in DMSO-$d_6$/DCl/$D_2O$. Asterisk marks the DCl/D_2O peak, + the dabco peak and # the DMSO peak.

^{1}H NMR (200 MHz, DMSO) δ 7.21 (s, 1H), 4.47 (dt, J = 11.7, 5.9 Hz, 1H), 3.56 (s, 3H), 1.22 (t, J = 6.0 Hz, 6H).

S3 Infrared Spectroscopy

Infrared spectra were recorded on a Bruker Alpha-P FT-IR situated in a glovebox. For all measurements the ATR-Mode of the spectrometer was used and measurements with 48 scans were performed.

The IR spectra of compounds **1dry**, **2dry** and **3dry** are shown in a range from 500-4000 cm^{-1} in figure S5.

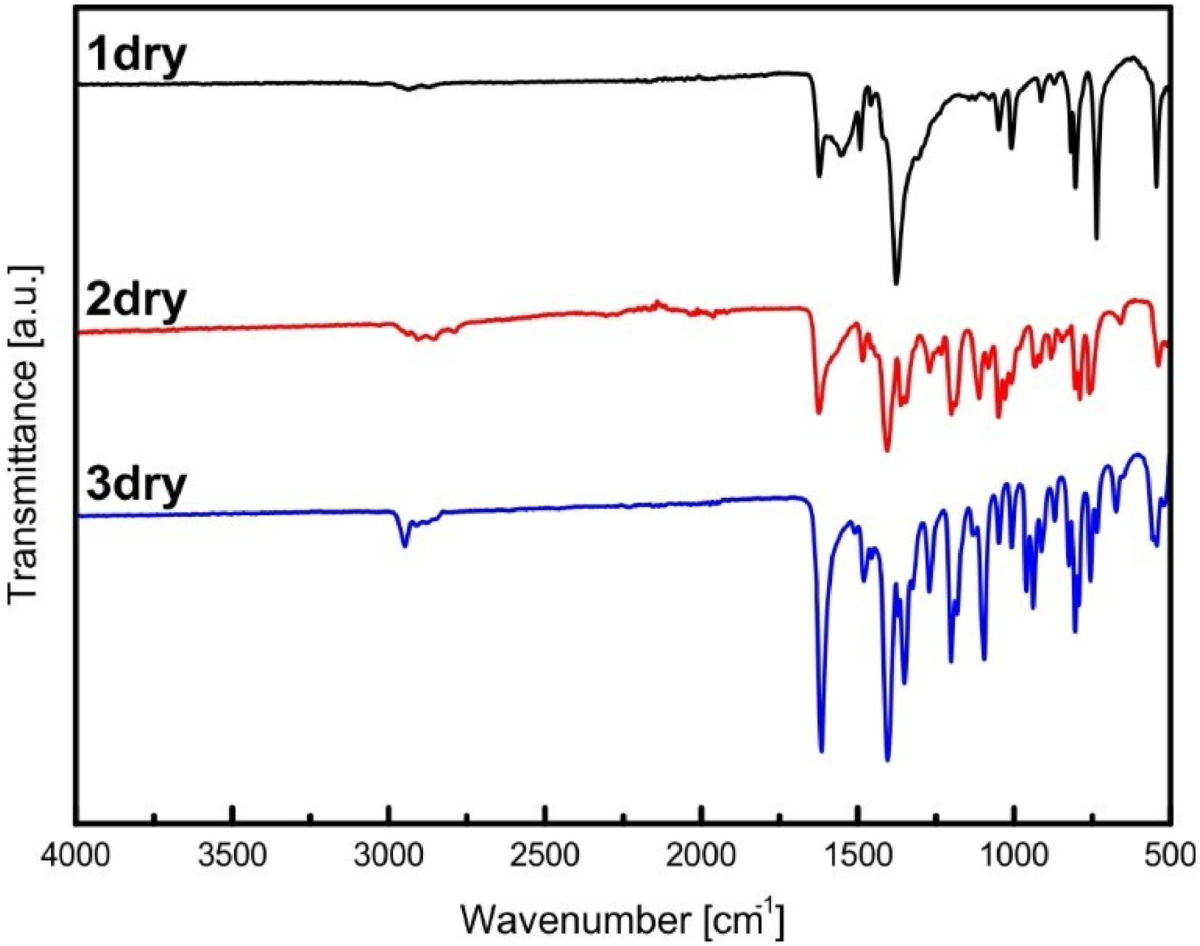

Figure S 5: Depiction of the IR Spectra of compounds **1dry** (black), **2dry** (red) and **3dry** (blue).

S4 Thermogravimetric Analysis

All Thermogravimetric Analysis (TGs) were recorded on a Netzsch STA 409 PC TG-DSC apparatus. A Heating rate of 5 K/min was applied and the samples were placed in a pre-weighted, clean aluminiumoxide crucible. All measurements were performed in a stream of N_2 gas with constant flow rates of 20ml/min.

Figure S 6 shows the TG-traces of compounds **1-3**.

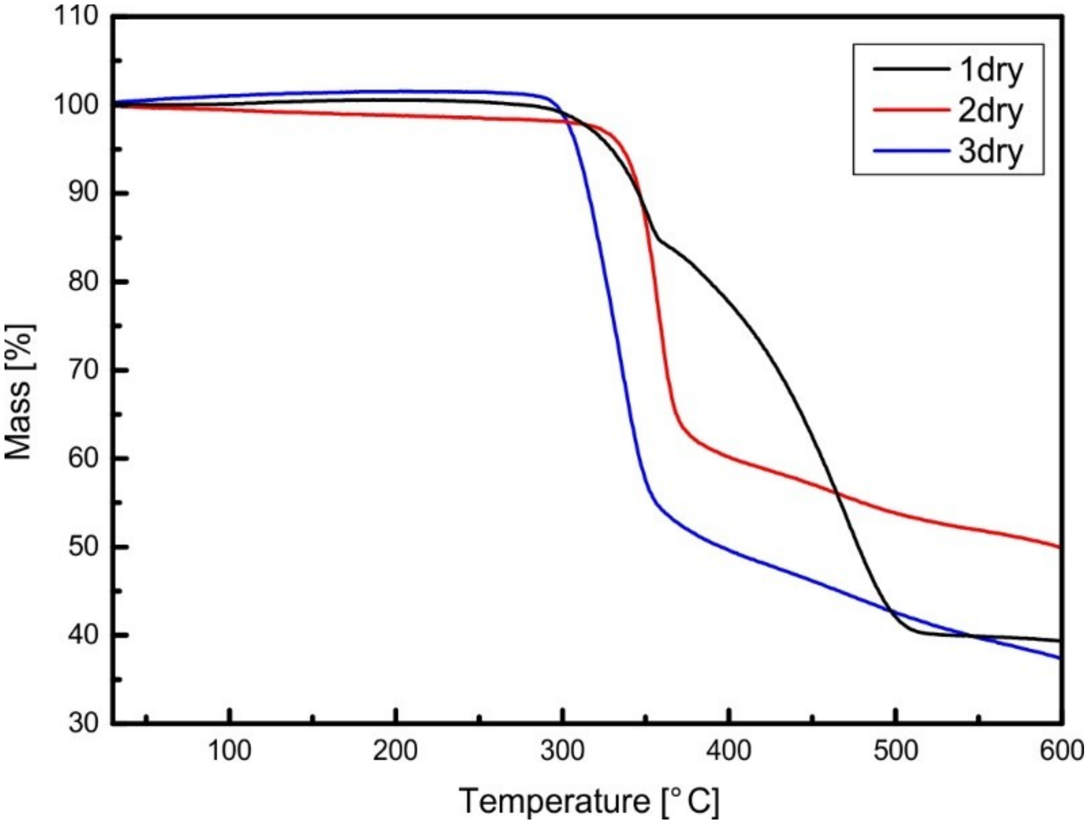

Figure S 6: TG traces of compounds **1dry** (black), **2dry** (red) and **3dry** (blue).

S5 Measurement Set Up

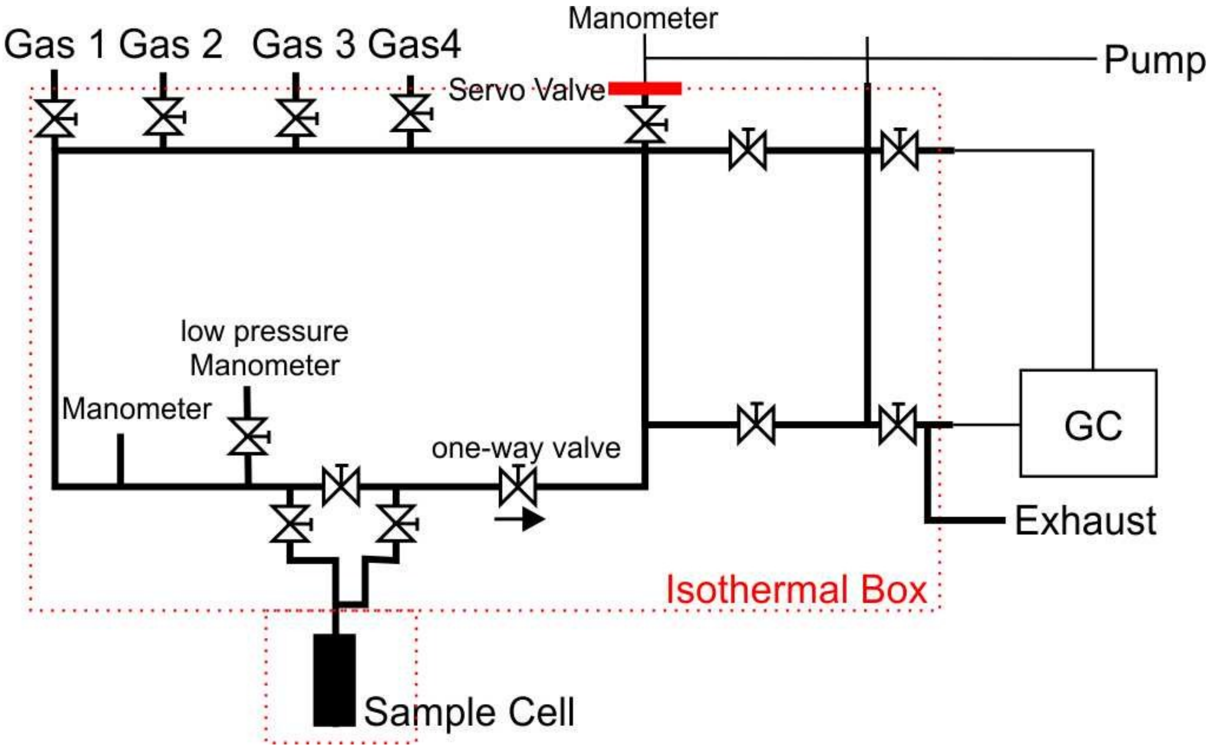

Figure S 7: Measurement set-up of the used Belsorp VC instrument

S6 Depiction of the Measurement Principle

Both gases that are used in the co-adsorption experiment are stored in separate gas bottles (a). Both components of the mixture are introduced into the manifold (b), where they are mixed (c). After both gases have been mixed sufficiently, the mixture is introduced to the MOF (d). After equilibration parts of the gas mixture are adsorbed on the framework (e). Via GC a sample is taken from the gas phase remaining over the sample (f). From the composition of the gas phase which is determined by GC, the composition of the adsorbed gas can be calculated.

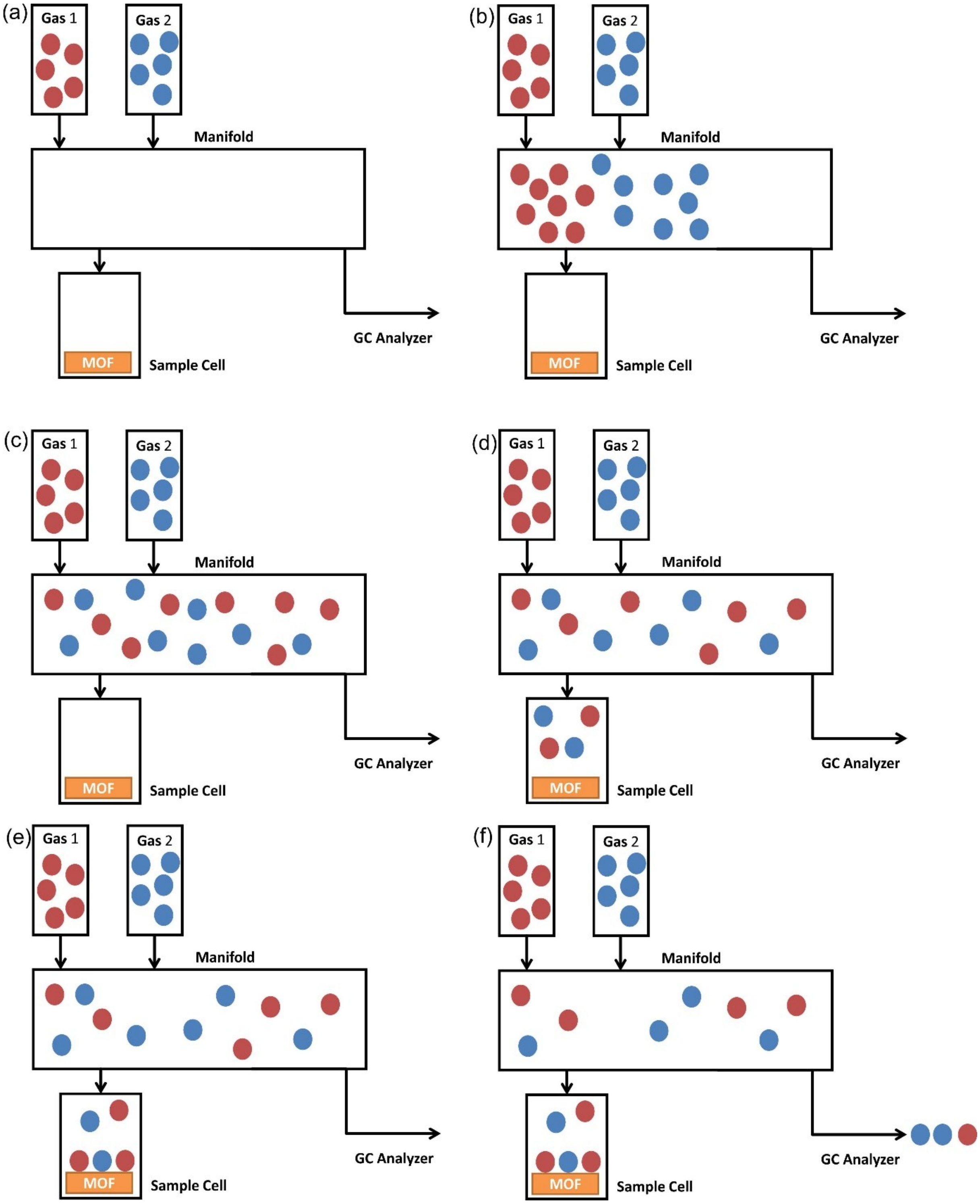

Figure S 8: Step by the depiction of the measurement principle.

S7 Calculation of Selectivities for Equilibration Points 1-5

In the following the selectivity coefficients towards CO_2 and the coadsorbate for all measurement points are given. p_e is the equilibrium pressure in kPa at which the GC was sampled.

Compound 1			**Ratio in Gas Phase**		**Ratio Adsorbed**		**Selectivity towards**	
Equilibration Point	**Gas Mixture**	p_e	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**
1	CO_2/N_2	925.80	45.71%	54.29%	101.36%	-1.36%	-	-
2	CO_2/N_2	896.08	45.68%	54.32%	101.96%	-1.96%	-	-
3	CO_2/N_2	867.39	45.71%	54.29%	102.01%	-2.01%	-	-
4	CO_2/N_2	839.72	45.75%	54.25%	102.00%	-2.00%	-	-
5	CO_2/N_2	812.90	45.79%	54.21%	101.99%	-1.99%	-	-

Compound 1			**Ratio in Gas Phase**		**Ratio Adsorbed**		**Selectivity towards**	
Equilibration Point	**Gas Mixture**	p_e	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**
1	CO_2/CH_4	1323.90	52.02%	47.98%	14.02%	85.98%	0.15	6.65
2	CO_2/CH_4	1282.02	52.00%	48.00%	14.33%	85.67%	0.15	6.48
3	CO_2/CH_4	1242.35	51.97%	48.03%	14.51%	85.49%	0.16	6.38
4	CO_2/CH_4	1202.85	51.95%	48.05%	14.94%	85.06%	0.16	6.16
5	CO_2/CH_4	1164.35	51.92%	48.08%	15.49%	84.51%	0.17	5.89

Compound 2			**Ratio in Gas Phase**		**Ratio Adsorbed**		**Selectivity towards:**	
Equilibration Point	**Gas Mixture**	p_e	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**
1	CO_2/N_2	1975.71	49.48%	50.52%	141.46%	-41.46%	-	-
2	CO_2/N_2	1912.93	49.47%	50.53%	139.00%	-39.00%	-	-
3	CO_2/N_2	1852.35	49.46%	50.54%	138.61%	-38.61%	-	-
4	CO_2/N_2	1792.91	49.45%	50.55%	134.96%	-34.96%	-	-
5	CO_2/N_2	1735.52	49.45%	50.55%	132.35%	-32.35%	-	-

Compound 2			**Ratio in Gas Phase**		**Ratio Adsorbed**		**Selectivity towards:**	
Equilibration Point	**Gas Mixture**	p_e	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**
1	CO_2/N_2	2467.88	60.33%	39.67%	142.49%	-42.49%	-	-
2	CO_2/N_2	2392.05	60.32%	39.68%	137.13%	-37.13%	-	-
3	CO_2/N_2	2318.63	60.31%	39.69%	134.40%	-34.40%	-	-
4	CO_2/N_2	2246.85	60.30%	39.70%	130.71%	-30.71%	-	-
5	CO_2/N_2	2177.51	60.29%	39.71%	129.46%	-29.46%	-	-

Compound 3			**Ratio in Gas Phase**		**Ratio Adsorbed**		**Selectivity towards:**	
Equilibration Point	**Gas Mixture**	p_e	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**
1	CO_2/N_2	1328.59	47.02%	52.98%	100.40%	-0.40%	-	-
2	CO_2/N_2	1285.32	46.95%	53.05%	101.20%	-1.20%	-	-
3	CO_2/N_2	1243.33	46.89%	53.11%	101.82%	-1.82%	-	-
4	CO_2/N_2	1202.99	46.86%	53.14%	102.19%	-2.19%	-	-
5	CO_2/N_2	1164.03	46.84%	53.16%	102.44%	-2.44%	-	-

Compound 3			**Ratio in Gas Phase**		**Ratio Adsorbed**		**Selectivity towards**	
Equilibration Point	**Gas Mixture**	p_e	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**
1	CO_2/N_2	1347.56	21.56%	78.44%	117.68%	-17.68%	-	-
2	CO_2/N_2	1302.88	21.54%	78.46%	114.20%	-14.20%	-	-
3	CO_2/N_2	1259.97	21.54%	78.46%	112.85%	-12.85%	-	-
4	CO_2/N_2	1218.12	21.54%	78.46%	108.59%	-8.59%	-	-
5	CO_2/N_2	1177.80	21.55%	78.45%	104.20%	-4.20%	-	-

Compound 3			**Ratio in Gas Phase**		**Ratio Adsorbed**		**Selectivity towards**	
Equilibration Point	**Gas Mixture**	p_e	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**
1	CO_2/CH_4	1323.98	51.95%	48.05%	15.61%	84.39%	0.17	5.85
2	CO_2/CH_4	1281.48	52.01%	47.99%	14.89%	85.11%	0.16	6.19
3	CO_2/CH_4	1240.65	52.02%	47.98%	14.72%	85.28%	0.16	6.28
4	CO_2/CH_4	1201.09	52.03%	47.97%	14.67%	85.33%	0.16	6.31
5	CO_2/CH_4	1163.00	52.03%	47.97%	14.61%	85.39%	0.16	6.34

Compound 3			**Ratio in Gas Phase**		**Ratio Adsorbed**		**Selectivity towards**	
Equilibration Point	**Gas Mixture**	p_e	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**
1	CO_2/CH_4	1167.08	23.69%	76.31%	78.51%	21.49%	11.77	0.08
2	CO_2/CH_4	1128.89	23.67%	76.33%	78.14%	21.86%	11.52	0.09
3	CO_2/CH_4	1092.21	23.65%	76.35%	78.45%	21.55%	11.75	0.09
4	CO_2/CH_4	1056.44	23.64%	76.36%	78.10%	21.90%	11.52	0.09
5	CO_2/CH_4	1022.42	23.64%	76.36%	78.14%	21.86%	11.55	0.09

Compound 3			**Ratio in Gas Phase**		**Ratio Adsorbed**		**Selectivity towards**	
Equilibration Point	**Gas Mixture**	p_e	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**
1	CO_2/C_2H_6	336.52	73.84%	26.16%	67.89%	32.11%	0.75	1.33
2	CO_2/C_2H_6	325.20	73.96%	26.04%	66.91%	33.09%	0.71	1.40
3	CO_2/C_2H_6	314.56	74.10%	25.90%	65.74%	34.26%	0.67	1.49
4	CO_2/C_2H_6	304.53	74.37%	25.63%	63.50%	36.50%	0.60	1.67
5	CO_2/C_2H_6	294.69	74.35%	25.65%	63.64%	36.36%	0.60	1.66

Compound 3			**Ratio in Gas Phase**		**Ratio Adsorbed**		**Selectivity towards:**	
Equilibration Point	**Gas Mixture**	p_e	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**
1	CO_2/C_2H_6	511.79	47.64%	52.36%	48.20%	51.80%	1.02	0.98
2	CO_2/C_2H_6	495.16	47.82%	52.18%	46.80%	53.20%	0.96	1.04
3	CO_2/C_2H_6	479.67	48.00%	52.00%	45.36%	54.64%	0.90	1.11
4	CO_2/C_2H_6	464.57	48.15%	51.85%	44.18%	55.82%	0.85	1.17
5	CO_2/C_2H_6	449.98	48.28%	51.72%	43.24%	56.76%	0.82	1.23

Compound 3			**Ratio in Gas Phase**		**Ratio Adsorbed**		**Selectivity towards:**	
Equilibration Point	**Gas Mixture**	p_e	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**
1	CO_2/C_2H_6	630.01	86.62%	14.40%	86.08%	13.92%	1.03	0.97
2	CO_2/C_2H_6	609.47	86.72%	14.26%	86.20%	13.80%	1.03	0.97
3	CO_2/C_2H_6	590.09	86.80%	14.14%	86.30%	13.70%	1.03	0.97
4	CO_2/C_2H_6	571.48	86.88%	14.02%	86.40%	13.60%	1.03	0.98
5	CO_2/C_2H_6	553.24	86.95%	13.91%	86.49%	13.51%	1.02	0.98

Compound 3			**Ratio in Gas Phase**		**Ratio Adsorbed**		**Selectivity towards**	
Equilibration Point	**Gas Mixture**	p_e	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**
1	CO_2/C_3H_8	286.63	98.01%	1.99%	87.17%	12.83%	0.14	7.25
2	CO_2/C_3H_8	276.95	98.05%	1.95%	86.89%	13.11%	0.13	7.57
3	CO_2/C_3H_8	267.63	98.09%	1.91%	86.45%	13.55%	0.12	8.06
4	CO_2/C_3H_8	258.89	98.13%	1.87%	85.95%	14.05%	0.12	8.60
5	CO_2/C_3H_8	250.49	98.17%	1.83%	85.49%	14.51%	0.11	9.10

Compound 3			**Ratio in Gas Phase**		**Ratio Adsorbed**		**Selectivity towards:**	
Equilibration Point	**Gas Mixture**	p_e	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**
1	CO_2/C_3H_8	299.25	92.45%	7.55%	77.59%	22.41%	0.28	3.54
2	CO_2/C_3H_8	289.08	92.56%	7.44%	76.75%	23.25%	0.27	3.77
3	CO_2/C_3H_8	279.20	92.76%	7.24%	75.22%	24.78%	0.24	4.22
4	CO_2/C_3H_8	270.07	92.96%	7.04%	73.58%	26.42%	0.21	4.74
5	CO_2/C_3H_8	261.36	93.18%	6.82%	71.64%	28.36%	0.18	5.41

Compound 3			**Ratio in Gas Phase**		**Ratio Adsorbed**		**Selectivity towards:**	
Equilibration Point	**Gas Mixture**	p_e	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**
1	CO_2/C_3H_8	540.17	98.76%	1.24%	98.35%	1.65%	0.75	1.33
2	CO_2/C_3H_8	522.77	98.78%	1.22%	98.23%	1.77%	0.69	1.46
3	CO_2/C_3H_8	506.03	98.80%	1.20%	98.06%	1.94%	0.61	1.63
4	CO_2/C_3H_8	489.93	98.83%	1.17%	97.85%	2.15%	0.54	1.86
5	CO_2/C_3H_8	474.36	98.86%	1.14%	97.62%	2.38%	0.47	2.11

Compound 3			**Ratio in Gas Phase**		**Ratio Adsorbed**		**Selectivity towards**	
Equilibration Point	**Gas Mixture**	p_e	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**
1	CO_2/C_3H_8	568.01	95.35%	4.65%	94.35%	5.65%	0.81	1.23
2	CO_2/C_3H_8	549.76	95.41%	4.59%	93.79%	6.21%	0.73	1.38
3	CO_2/C_3H_8	532.24	95.49%	4.51%	93.12%	6.88%	0.64	1.56
4	CO_2/C_3H_8	515.44	95.62%	4.38%	92.00%	8.00%	0.53	1.90
5	CO_2/C_3H_8	499.18	95.71%	4.29%	91.31%	8.69%	0.47	2.12

S8 CO_2/C_3H_8 Coadsorption Experiments

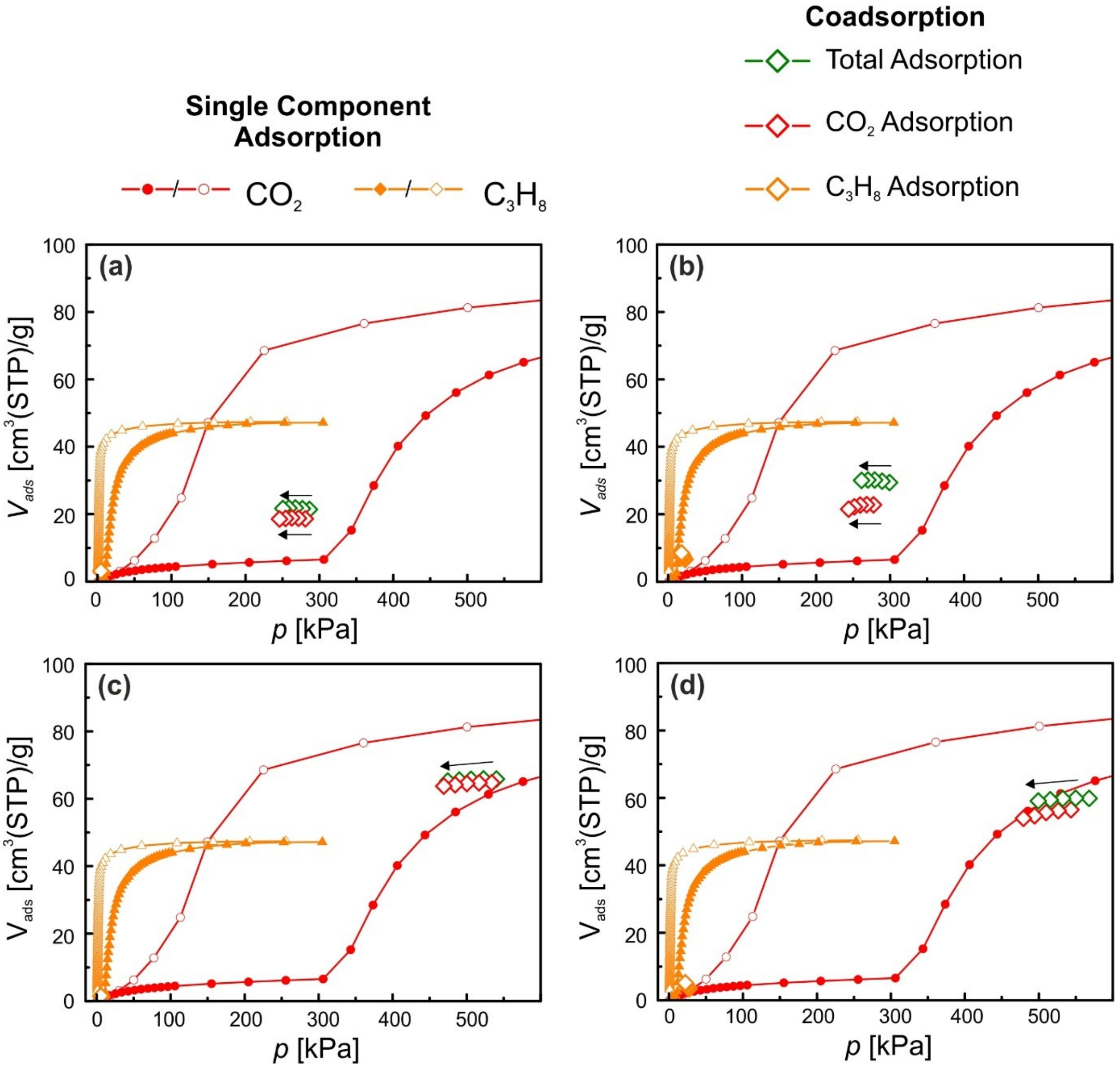

Figure S 9: Depiction of the excess single component and co-adsorption measurements of material **3**. Red circles and orange triangles represent CO_2 and C_3H_8 single component adsorption isotherms. CO_2 and C_3H_8 fractions of the co-adsorption experiments are shown in red and orange, respectively. Total adsorption is shown in green.

The last set of experiments was conducted for gas mixtures containing CO_2/C_3H_8 ratios of 281:6 kPa, 277:23 kPa, 534:6 kPa and 544: 27 kPa (Figure S9 (a-d)). The observations made are similar to the ones found for the CO_2/C_2H_6 mixtures. Due to the relatively low phase transition pressure and operating pressures of C_3H_8, the scale of the graph was decreased and the isotherms are only shown from 0 to 600 kPa. During the first measurement shown in Figure S9(a), both partial pressures are lower than the respective phase transition pressures. Again, a cooperative effect of the two gases is observed and the uptakes are increased to 18.6 and 2.74 cm^3(STP)/g for CO_2 and C_3H_8 respectively as compared to 6.5 and 1.4 cm^3(STP)/g during single component adsorption. When the partial C_3H_8 pressure is increased to exceed the threshold pressure of the **np→lp** transition (Figure S9(b)), an even more striking uptake of CO_2 is achieved amounting to 22.81 cm^3(STP)/g. In contrast, the C_3H_8 adsorption is even lower than the values determined from the single component adsorption isotherm at similar C_3H_8 pressures (6.6 cm^3(STP)/g at the first equilibration step, compared to 25.1 (STP)/g during single component adsorption at similar pressures). If the partial CO_2 pressure surpasses the threshold pressure of the phase transition (Figure S9(c)), it can be observed that the uptake of the CO_2 portion of the mixture is comaparbly high as for the single component adsorption at this pressure (64.7 cm^3(STP)/g). For the C_3H_8 molecules an uptake in line with the single component isotherms is recorded at this pressure (1.1 cm^3(STP)/g compared to 1.4 cm^3(STP)/g during single component adsorpton). In the last measurement (Figure S9(d)), both partial pressures are above the gate opening pressure, which leads to uptakes of 56.5 cm^3(STP)/g for CO_2 and 3.4 cm^3(STP)/g for C_3H_8. The value for CO_2 is close to the uptake found for single component adsorption at the respective pressure, the C_3H_8 value on the other hand, is substantially lower than for the single component adsorption (30.2 cm^3(STP)/g at similar pressures). It seems as if the cooperative effect found for this gas mixture is not as strong as in the case of CO_2/C_2H_6. C_3H_8 is barely co-adsorbed, after the phase transition is initiated by CO_2. When the C_3H_8 pressure is above the respective phase transition pressure, also much lower uptakes are found than in the single component cases. This might either be due to the sterical bulk of the adsorbate (good adsorption sites less accesible) or the much lower adsorption affinity of the framework towards C_3H_8 compared to CO_2.

A depiction of CO_2/C_3H_8 in a range from 0-100 kPa to clarify the C_3H_8 uptakes at low pressures is shown in Figure S 10.

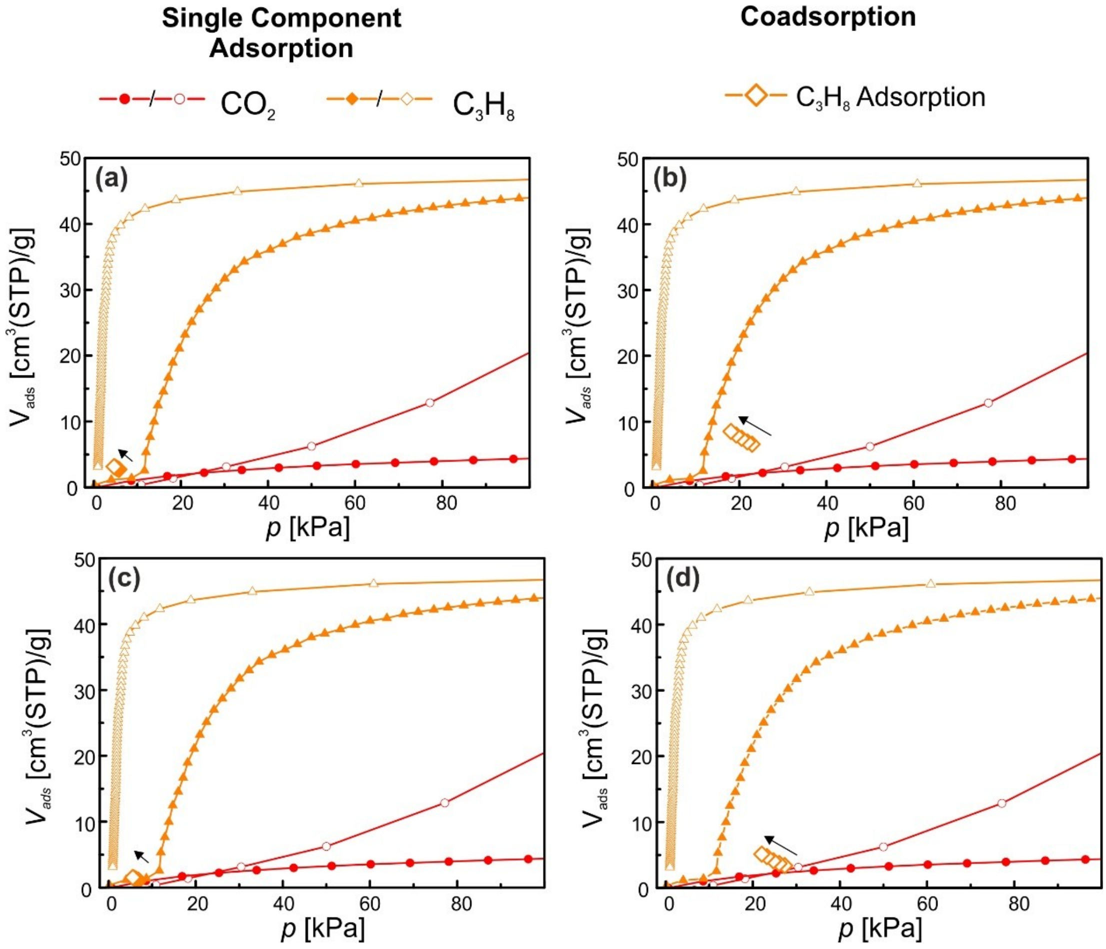

Figure S 10: Depiction of the excess single component and co-adsorption measurements of material **3**, depicted in a range from 0 - 100 kPa. Red circles and orange triangles represent CO_2 and C_3H_8 single component adsorption isotherms. CO_2 and C_3H_8 fractions of the co-adsorption experiments are shown in red and orange, respectively. Total adsorption is shown in green.

In the following the selectivity coefficients for the CO_2/C_3H_8 coadsorption measurements are listed for the first pressure point.

Table 1: Selectivity coefficients calculated from the molar fractions of the binary mixture in the gas phase and adsorbed.[a]

				Molar Fraction Gas Phase		**Molar Fraction Adsorbed**			
Figure	**Material**	**Gas Mixture**	***pe*[b] / kPa**	**CO_2**	**Coadsorbate**	**CO_2**	**Coadsorbate**	**Selectivity (CO2)**	**Selectivity (Coadsorbate)**
S 9(a)	3	CO_2/C_3H_8	286.63	0.98	0.02	0.87	0.13	0.14	7.32
S 9(b)	3	CO_2/C_3H_8	299.25	0.92	0.08	0.78	0.22	0.31	3.24
S 9(c)	3	CO_2/C_3H_8	540.17	0.99	0.01	0.98	0.02	0.49	2.02
S 9(d)	3	CO_2/C_3H_8	568.01	0.96	0.04	0.91	0.09	0.42	2.37

[a] data is from 1st equilibrium point. [b] equilibration pressure of the gas mixture.

S9 Physical Parameters of CO_2, N_2, CH_4, C_2H_6, and C_3H_8

Table S1: Summary of the kinetic diameter, polarizability and quadrupole moment of CO_2, N_2, CH_4, C_2H_6 and C_3H_8.[1]

Adsorbates	Sum Formula	Kinetic Diameter	Polarizability	Quadrupole Moment
Carbon dioxide	CO_2	3.3 Å	$29.11 \times 10^{25}/\text{cm}^3$	$4.30 \times 10^{26}/\text{esu cm}^2$
Nitrogen	N_2	3.64 Å	$17.403 \times 10^{25}/\text{cm}^3$	$1.52 \times 10^{26}/\text{esu cm}^2$
Methane	CH_4	3.758 Å	$25.93 \times 10^{25}/\text{cm}^3$	0
Ethane	C_2H_6	4.443 Å	$44.3\text{-}44.7 \times 10^{25}/\text{cm}^3$	$0.65 \times 10^{26}/\text{esu cm}^2$
Propane	C_3H_8	5.118 Å	$62.9\text{-}63.7 \times 10^{25}/\text{cm}^3$	-

S10 References

(1) Li, J.-R.; Kuppler, R. J.; Zhou, H.-C. *Chem. Soc. Rev.* **2009**, *38*, 1477.