Supporting Information

# Alkyl decorated metal-organic frameworks for selective trapping of ethane from ethylene

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# S1 Synthesis

All precursors and solvents were bought from commercial suppliers and used without any further purification.

#### **MOF Synthesis**

1 mmol H<sub>2</sub>X-bdc (for weights see table below),  $Zn(NO_3)_2 \cdot 6H_2O$  (1mmol, 298 mg) and dabco (0.7 mmol, 112 mg) were put in a scintillation vial and 20 mL of DMF were added. The mixture was sonicated for 10 minutes and afterwards placed in an isothermal oven at 120 °C for 24h. Afterwards, the reaction mixture was cooled to room temperature and the mixture was transferred into centrifugation tubes. After centrifugation (8700 rpm, 3 min) the DMF was removed and replaced with fresh DMF. The DMF was replaced twice with fresh DMF and three times with dichloromethane. Afterwards the samples were dried in vacuo at 120 °C and transferred into a glovebox until further manipulation. In order to achieve higher yields of material for co-adsorption measurements, several batches of the same material were combined.

Zn<sub>2</sub>(bdc)<sub>2</sub>(dabco) – Yield: 28.4% (162.5 mg, 0.284 mmol)

Zn<sub>2</sub>(DM-bdc)<sub>2</sub>(dabco) - Yield: 25.3% (158.9 mg, 0.253 mmol)

Zn<sub>2</sub>(TM-bdc)<sub>2</sub>(dabco) - Yield: 28.5% (195.0 mg, 0.285 mmol)

Table S1: Summary of the used amount of dicarboxylate linkers (H<sub>2</sub>R-bdc)

MOF	m H <sub>2</sub> X-bdc
Zn <sub>2</sub> (bdc) <sub>2</sub> (dabco)	166.13 mg
Zn <sub>2</sub> (DM-bdc) <sub>2</sub> (dabco)	194.18 mg
Zn <sub>2</sub> (TM-bdc) <sub>2</sub> (dabco)	222.24 mg

# S2 Powder X-ray Diffraction Patterns



**Figure S1:** Powder X-ray diffraction patterns of activated  $Zn_2(bdc)_2(dabco)$  (**DMOF**, black),  $Zn_2(DM-bdc)_2(dabco)$  (**DMOF-DM**, red) and  $Zn_2(TM-bdc)_2(dabco)$  (**DMOF-TM**, blue) compared to simulated patterns.

### S3 IR Spectroscopy



Figure S2: IR spectra of activated  $Zn_2(bdc)_2(dabco)$  (DMOF, black),  $Zn_2(DM-bdc)_2(dabco)$  (DMOF-DM, red) and  $Zn_2(TM-bdc)_2(dabco)$  (DMOF-TM, blue).

The IR spectra feature all the expected signals of the  $Zn_2(R-bdc)_2(dabco)$  MOFs. In the range from ~2940 - 2880 cm<sup>-1</sup> the sp3-CH<sub>3</sub> and -CH<sub>2</sub>- stretching vibration can be observed which originates from the dabco building block and from the CH<sub>3</sub> groups located on the DM-bdc<sup>2-</sup> and TM-bdc<sup>2-</sup> linkers. The prominent feature at ~1600 cm<sup>-1</sup> is attributed to the CO stretching vibrations of the carboxylate anion and the features in the range of 1600 cm<sup>-1</sup> - 1500 are commonly associated with the stretching vibrations of aromatic compounds.



**Figure S3:** Nitrogen adsorption isotherms of  $Zn_2(bdc)_2(dabco)$  (**DMOF**) (black squares),  $Zn_2(DM-bdc)_2(dabco)$  (**DMOF-DM**) (red circles) and  $Zn_2(TM-bdc)_2(dabco)$  (**DMOF-TM**) (blue triangles) measured at 77 K. Filled and open symbols represent adsorption and desorption respectively. Lines are a guide to the eye only.

The initial synthesis for DMOF was reported in 2004 by the group of Kimoon Kim and a BET surface area below the value in this study was reported (1450 m<sup>2</sup>g<sup>-1</sup> vs 1779.9 m<sup>2</sup>g<sup>-1</sup> in this study).<sup>1</sup> In a follow up study by the Kim lab a variety of differently substituted DMOF analogues was presented, among them also DMOF-TM, which featured a BET surface area of 920 m<sup>2</sup>g<sup>-1</sup>, which is in a similar range as the materials surface area in this study.<sup>2</sup> DMOF-DM was reported first by the group of Krista Walton in 2013 and a BET surface area of 1115 m<sup>2</sup>g<sup>-1</sup> was reported, which is in good agreement with the BET surface area for this material reported in here (1133 m<sup>2</sup>g<sup>-1</sup>).<sup>3</sup>



Figure S4: TGA curves of DMOF (black), DMOF-DM (red) and DMOF-TM (black) measured under  $N_2$  atmosphere with a heating ramp of 10 K min<sup>-1</sup>.

# S5 Thermogravimetric Analysis

### S6 Scanning Electron Microscopy



Figure S5: Scanning Electron Micrographs of  $Zn_2(bdc)_2(dabco)$  (DMOF, (a)),  $Zn_2(DM-bdc)_2(dabco)$  (DMOF-DM, (b)) and  $Zn_2(TM-bdc)_2(dabco)$  (DMOF-TM (c)).

For all three samples we observe a polydisperse size distribution. For DMOF (a) we observed crystallites in the range from 5-25  $\mu$ m after activation. In the case of DMOF-DM (b) there are some larger crystallites in the range of 50  $\mu$ m, but mostly smaller crystallites in the few micron to submicron regime are observed. In comparison to DMOF the edges are less sharp and pronounced in this sample. In the case of DMOF-TM a very wide range of crystallite sizes is observed with larger crystals in the range of 25  $\mu$ m, which are decorated with submicron crystals.

### S7 Calculation of Isosteric Heats of Adsorption

The binding energy of  $C_2H_6$  and  $C_2H_4$  to the adsorption sites (isosteric heat of adsorption,  $Q_{st}$ ) within the MOFs are determined via the Clausius Clapeyron expression, as follows:

$$Qst = RT^2 \left(\frac{\partial lnp}{\partial T^q}\right)$$

Calculations of  $Q_{st}$  were accomplished using the pure component dual site Langmuir Freundlich isotherm fits:

$$V_{ads} = \frac{V_{max,1} \cdot k_1 \cdot p^{\nu_1}}{1 + k_1 \cdot p^{\nu_1}} + \frac{V_{max,2} \cdot k_2 \cdot p^{\nu_2}}{1 + k_2 \cdot p^{\nu_2}}$$

with  $V_{max}$  = adsorption capacity at saturation, k = Langmuir-Freundlich constant, p = pressure of the adsorbate and v = dimensionless exponent. The fit parameters and the C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>8</sub> isotherms measured at 288, 298 and 308 K are shown in Figures S6-S13. In the case of **DMOF-DM**, due to the slight stepped shape of the adsorption isotherm, it was not possible to obtain a reasonable fit with a dual site Langmuir Freundlich isotherm over the whole pressure range, hence we conducted a single site Langmuir Freundlich fit for the low pressure region and a dual site Langmuir Freundlich fit for the high pressure region of the isotherm.



**Figure S6:** Dual site Langmuir Freundlich fits for ethane adsorption isotherms on **DMOF** measured at 288 K (blue squares), 298 K (black circles) and 308 K (red triangles) displayed in linear form (top left) and with a logarithmic x-axis(top right). Parameters of the dual site Langmuir Freundlich fit can be found at the bottom.



**Figure S7:** Dual site Langmuir Freundlich fits for ethylene adsorption isotherms on DMOF measured at 288 K (blue squares), 298 K (black circles) and 308 K (red triangles) displayed in linear form (top left) and with a logarithmic x-axis(top right). Parameters of the dual site Langmuir Freundlich fit can be found at the bottom.



**Figure S8:** Dual site Langmuir Freundlich fits for ethane adsorption isotherms on **DMOF-DM** measured at 288 K (blue squares), 298 K (black circles) and 308 K (red triangles) displayed in linear form (top left) and with a logarithmic x-axis(top right). Parameters of the dual site Langmuir Freundlich fit can be found at the bottom.



**Figure S9:** Single site Langmuir Freundlich fits for ethane adsorption isotherms on DMOF measured at 288 K (blue squares), 298 K (black circles) and 308 K (red triangles) displayed in linear form (top left) and with a logarithmic x-axis(top right). Parameters of the dual site Langmuir Freundlich fit can be found at the bottom.



**Figure S10:** Dual site Langmuir Freundlich fits for ethane adsorption isotherms on DMOF-DM measured at 288 K (blue squares), 298 K (black circles) and 308 K (red triangles) displayed in linear form (top left) and with a logarithmic x-axis(top right). Parameters of the dual site Langmuir Freundlich Fit can be found at the bottom.



**Figure S11:** Single site Langmuir Freundlich fits for the low pressure region of the ethylene adsorption isotherms on **DMOF-DM** measured at 288 K (blue squares), 298 K (black circles) and 308 K (red triangles) displayed in linear form (top left) and with a logarithmic x-axis(top right). Parameters of the single site Langmuir Freundlich fit can be found at the bottom.



**Figure S12:** Dual site Langmuir Freundlich fits for ethane adsorption isotherms on DMOF-TM measured at 288 K (blue squares), 298 K (black circles) and 308 K (red triangles) displayed in linear form (top left) and with a logarithmic x-axis(top right). Parameters of the dual site Langmuir Freundlich fit can be found at the bottom.



High P	288K		298K		308K	
V <sub>max.1</sub>	123.48313	0.75423	100.73721	24.30101	127.711	0.83691
k <sub>1</sub>	0.07826	5.33E-04	0.03379	0.00542	0.03284	2.78E-04
v <sub>1</sub>	1.01517	0.0018	1.10036	0.02912	1.01314	0.0016
V <sub>max.2</sub>	5.30451	0.70322	27.36276	24.2849	1.69909	0.61751
k <sub>2</sub>	0.00231	8.22E-04	0.11101	0.05062	6.15E-05	1.15E-04
ν <sub>2</sub>	2.18688	0.12782	0.9457	0.02035	2.78943	0.56047

**Figure S13:** Dual site Langmuir Freundlich fits for ethylene adsorption isotherms on **DMOF-TM** measured at 288 K (blue squares), 298 K (black circles) and 308 K (red triangles) displayed in linear form (top left) and with a logarithmic x-axis(top right). Parameters of the dual site Langmuir Freundlich fit can be found at the bottom.

# S8 Calculation of Ideal Adsorbed Solution Theory Selectivities

The ideal adsorbed solution theory (IAST), invented by Myer and Prausnitz in 1965,<sup>4</sup> is a widely used method to assess the sorption selectivity in a binary mixture based on their single-component isotherms. For its calculation, the fits of the single site Langmuir isotherms at 298 were used (see previous section). The adsorption selectivity  $S_{ads}$  is defined by the following equation:

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2}$$

with qi = molar loadings of species *i* in the adsorbed phase and pi = bulk gas pressure of species *i*.

### S9 Transformation of High Pressure Isotherms

The high pressure isotherms were converted from excess absorption to absolute absorption according to the following equation:

$$n_{absolute} = n_{excess} + V_g \cdot \rho_g$$

with

 $V_g = Pore Volume of the adsorbent$ 

 $\rho_a = Bulk$  molar density of adsorbate

The pressure dependent molar densities of the adsorbates were obtained from optimized equations of state, which can be found on the homepage of the National Institute of Standards and technology (<u>https://webbook.nist.gov/chemistry/fluid/</u>). The equation of state used to describe the pressure dependent density for ethane was developed by Friend and coworkers<sup>5</sup> and the equation of state used to describe the behavior of ethane was developed by Smukala and coworkers.<sup>6</sup>



**Figure S14:** Isothermal properties of ethane and ethylene determined through optimized equations of state from the National Institute of Standards and Technology.

The Curves obtained through the equations of state were fit with a 5<sup>th</sup> order polynomial equation. The fits were used to calculate densities for all measurement pressures:

	Ethane	Ethene
Coefficient	Value	Value
A <sub>0</sub>	-1.808·10 <sup>-4</sup>	-1.21·10 <sup>-5</sup>
A <sub>1</sub>	4.060·10 <sup>-4</sup>	4.04·10 <sup>-4</sup>
A <sub>2</sub>	2.285·10 <sup>-8</sup>	2.23·10 <sup>-8</sup>
A <sub>3</sub>	1.261·10 <sup>-11</sup>	2.72·10 <sup>-12</sup>
A <sub>4</sub>	-3.888·10 <sup>-15</sup>	-1.10·10 <sup>-16</sup>
A <sub>5</sub>	9.928·10 <sup>-19</sup>	1.03·10 <sup>-19</sup>

$$\rho = A_0 + A_1 \cdot p + A_2 \cdot p^2 + A_3 \cdot p^3 + A_4 \cdot p^4 + A_5 \cdot p^5$$

The pore volumes of the materials were determined from optimized 0 K crystal structures using the iRASPA package.<sup>7</sup>

Table S2: Pore volumes of DMOF, DMOF-DM and DMOF-TM.

Material	Pore Volume
Zn <sub>2</sub> (bdc) <sub>2</sub> (dabco) (DMOF)	0.79220 cm <sup>3</sup> g <sup>-1</sup>
$Zn_2(DM\text{-bdc})_2(dabco)$ ( <b>DMOF-DM</b> )	0.62357 cm <sup>3</sup> g <sup>-1</sup>
Zn <sub>2</sub> (TM-bdc) <sub>2</sub> (dabco) (DMOF-TM)	0.43965 cm <sup>3</sup> g <sup>-1</sup>

Below a comparison between the excess and absolute adsorption can be found



**Figure S15:** Comparison of the excess (empty symbols) and the absolute (filled symbols) adsorption isotherms for **DMOF** ( $Zn_2(bdc)_2(dabco)$ ), **DMOF-DM** ( $Zn_2(DM-bdc)_2(dabco)$ ) and **DMOF-TM** ( $Zn_2(TM-bdc)_2(dabco)$ ) measured at 298 K. Data from ethane and ethylene adsorption experiments are shown as blue circles and green triangles, respectively. Lines connecting the measurement points are a guide to the eye only.

S10 Dual Site Langmuir Freundlich Fits of High Pressure Isotherms



**Figure S16:** Dual Site Langmuir Freundlich Fits of the ethane (blue circles) and ethylene (green triangles) high pressure adsorption isotherms of DMOF.



**Figure S17:** Dual Site Langmuir Freundlich Fits of the ethane (blue circles) and ethylene (green triangles) high pressure adsorption isotherms of DMOF-DM.



**Figure S18:** Dual Site Langmuir Freundlich Fits of the ethane (blue circles) and ethylene (green triangles) high pressure adsorption isotherms of DMOF-TM.

# S11 Additional Computational Data



Figure S19: Interaction energies of ethane (blue) and ethylene (orange) with DMOF, DMOF-DM and DMOF-TM derived through molecular simulations.

# S12 Tabulated Co-adsorption Data

Below the tabulated results from the coadsorption measurements are displayed. Herein,  $p_e$  is the equilibration pressure,  $q_n$  and  $p_n$  are the molar fractions of the respective gases in the gas phase and in the adsorbed phase, and S is the adsorption selectivity.

**Table S3:** Tabulated measurement data of coadsorption measurements conducted at 298 K on **DMOF** with a  $C_2H_6:C_2H_4$  ratio of 10:90.

#	p <sub>e</sub> / kPa	q(C <sub>2</sub> H <sub>6</sub> )	q(C <sub>2</sub> H <sub>4</sub> )	p(C₂H₀)	p(C <sub>2</sub> H <sub>4</sub> )	V <sub>ads, total</sub> / cm <sup>3</sup> g <sup>-1</sup>	S(C <sub>2</sub> H <sub>6</sub> /C <sub>2</sub> H <sub>4</sub> )
1	77.06	8.74%	91.26%	10.81%	89.19%	21.90	0.79
2	151.73	13.07%	86.93%	10.52%	89.48%	37.71	1.28
3	232.91	13.86%	86.14%	10.21%	89.79%	47.77	1.42
4	348.18	13.09%	86.91%	9.40%	90.60%	55.87	1.45
5	442.17	13.23%	86.77%	9.77%	90.23%	60.22	1.41
6	534.29	12.71%	87.29%	9.38%	90.62%	63.33	1.41
7	630.87	14.30%	85.70%	9.80%	90.20%	65.94	1.54
8	725.16	14.16%	85.84%	9.80%	90.20%	68.07	1.52
9	820.13	14.50%	85.50%	9.81%	90.19%	69.80	1.56
10	915.75	14.16%	85.84%	9.85%	90.15%	71.41	1.51

DMOF 10:90

**Table S4:** Tabulated measurement data of coadsorption measurements conducted at 298 K on **DMOF** with a  $C_2H_6:C_2H_4$  ratio of 50:50.

#	p <sub>e</sub> / kPa	q(C₂H₀)	q(C <sub>2</sub> H <sub>4</sub> )	p(C <sub>2</sub> H <sub>6</sub> )	p(C <sub>2</sub> H <sub>4</sub> )	V <sub>ads, total</sub> / cm <sup>3</sup> g <sup>-1</sup>	S(C <sub>2</sub> H <sub>6</sub> /C <sub>2</sub> H <sub>4</sub> )
1	157.03	59.10%	40.90%	50.90%	49.10%	42.58	1.39
2	331.23	60.93%	39.07%	51.36%	48.64%	56.79	1.48
3	536.14	57.94%	42.06%	49.30%	50.70%	64.04	1.42
4	725.76	58.68%	41.32%	49.40%	50.60%	68.09	1.45
5	915.70	59.32%	40.68%	49.54%	50.46%	71.08	1.49
6	1107.76	60.22%	39.78%	49.55%	50.45%	73.44	1.54
7	1299.19	58.74%	41.26%	49.68%	50.32%	75.41	1.44
8	1491.96	60.57%	39.43%	49.69%	50.31%	76.73	1.56
9	1684.58	60.26%	39.74%	49.74%	50.26%	78.23	1.53

#### DMOF 50:50

**Table S5:** Tabulated measurement data of coadsorption measurements conducted at 298 K on **DMOF-DM** with a  $C_2H_6$ : $C_2H_4$  ratio of 10:90.

#	p <sub>e</sub> / kPa	q(C₂H₀)	q(C <sub>2</sub> H <sub>4</sub> )	p(C <sub>2</sub> H <sub>6</sub> )	p(C <sub>2</sub> H <sub>4</sub> )	V <sub>ads, total</sub> / cm <sup>3</sup> g <sup>-1</sup>	S(C <sub>2</sub> H <sub>6</sub> /C <sub>2</sub> H <sub>4</sub> )
1	56.76	9.25%	90.75%	11.34%	88.66%	43.16	0.79
2	128.01	12.63%	87.37%	10.04%	89.96%	62.63	1.30
3	229.03	13.12%	86.88%	8.89%	91.11%	74.77	1.55
4	321.99	13.93%	86.07%	9.27%	90.73%	81.04	1.59
5	413.52	13.66%	86.34%	9.06%	90.94%	84.93	1.59
6	508.12	14.09%	85.91%	9.50%	90.50%	87.81	1.56
7	603.58	14.70%	85.30%	9.51%	90.49%	90.01	1.64
8	698.14	15.01%	84.99%	9.56%	90.44%	91.71	1.67
9	793.41	14.95%	85.05%	9.59%	90.41%	93.08	1.66
10	888.78	15.23%	84.77%	9.64%	90.36%	94.33	1.68

DMOF-DM 10:90

DMOF-TM 10:90

**Table S6:** Tabulated measurement data of coadsorption measurements conducted at 298 K on **DMOF-DM** with a  $C_2H_6$ : $C_2H_4$  ratio of 50:50.

DN	DMOF-DM 50:50										
#	p <sub>e</sub> / kPa	q(C₂H₀)	q(C <sub>2</sub> H <sub>4</sub> )	p(C₂H₀)	p(C <sub>2</sub> H <sub>4</sub> )	V <sub>ads, total</sub> / cm <sup>3</sup> g <sup>-1</sup>	S(C <sub>2</sub> H <sub>6</sub> /C <sub>2</sub> H <sub>4</sub> )				
1	129.40	59.71%	40.29%	49.13%	50.87%	69.05	1.53				
2	301.39	63.00%	37.00%	50.15%	49.85%	83.33	1.69				
3	508.01	61.13%	38.87%	48.40%	51.60%	89.14	1.68				
4	699.37	62.04%	37.96%	48.67%	51.33%	92.20	1.72				
5	889.53	62.44%	37.56%	49.01%	50.99%	94.22	1.73				
6	1082.06	62.55%	37.45%	49.18%	50.82%	95.69	1.73				
7	1275.17	63.12%	36.88%	49.27%	50.73%	96.85	1.76				
8	1469.65	62.78%	37.22%	49.37%	50.63%	97.70	1.73				
9	1664.06	63.23%	36.77%	49.42%	50.58%	98.47	1.76				

**Table S7:** Tabulated measurement data of coadsorption measurements conducted at 298 K on **DMOF** with a  $C_2H_6:C_2H_4$  ratio of 10:90.

#	p <sub>e</sub> / kPa	q(C₂H₀)	q(C <sub>2</sub> H <sub>4</sub> )	p(C₂H₀)	p(C <sub>2</sub> H <sub>4</sub> )	V <sub>ads, total</sub> / cm <sup>3</sup> g <sup>-1</sup>	S(C <sub>2</sub> H <sub>6</sub> /C <sub>2</sub> H <sub>4</sub> )
1	25.30	11.03%	88.97%	9.74%	90.26%	72.21	1.15
2	83.09	13.40%	86.60%	8.13%	91.87%	107.13	1.75
3	185.58	13.46%	86.54%	7.57%	92.43%	119.18	1.90
4	279.40	14.24%	85.76%	7.98%	92.02%	122.65	1.92
5	373.39	14.66%	85.34%	8.26%	91.74%	124.56	1.91
6	470.60	15.51%	84.49%	8.82%	91.18%	125.97	1.90
7	566.69	16.01%	83.99%	8.91%	91.09%	127.86	1.95
8	662.48	16.38%	83.62%	9.00%	91.00%	128.56	1.98
9	758.48	16.75%	83.25%	9.10%	90.90%	129.08	2.01
10	853.50	16.74%	83.26%	9.22%	90.78%	129.54	1.98

**Table S8:** Tabulated measurement data of coadsorption measurements conducted at 298 K on **DMOF** with a  $C_2H_6$ : $C_2H_4$  ratio of 10:90.

#	p <sub>e</sub>	q(C₂H₀)	q(C <sub>2</sub> H <sub>4</sub> )	p(C <sub>2</sub> H <sub>6</sub> )	p(C <sub>2</sub> H <sub>4</sub> )	V <sub>ads, total</sub> / cm <sup>3</sup> g <sup>-1</sup>	S(C <sub>2</sub> H <sub>6</sub> /C <sub>2</sub> H <sub>4</sub> )
1	91.42	57.57%	42.43%	41.77%	58.23%	116.13	1.89E+00
2	267.19	63.32%	36.68%	46.65%	53.35%	124.63	1.97E+00
3	445.79	65.07%	34.93%	49.05%	50.95%	126.80	1.94E+00
4	632.63	65.85%	34.15%	49.75%	50.25%	127.86	1.95E+00
5	814.71	66.69%	33.31%	50.49%	49.51%	128.47	1.96E+00
6	1000.60	66.99%	33.01%	50.86%	49.14%	128.87	1.96E+00
7	1243.97	65.29%	34.71%	48.77%	51.23%	129.36	1.98E+00
8	1440.03	65.42%	34.58%	48.91%	51.09%	129.59	1.98E+00
9	1637.93	65.38%	34.62%	48.99%	51.01%	129.86	1.97E+00

Zn<sub>2</sub>(TM-bdc)<sub>2</sub>(dabco) 50:50

## S13 Comparison with Literature Values

The table underneath summarizes some key data of other ethane selective materials

MOF	T∕°C	Q <sub>st,</sub> (C <sub>2</sub> H <sub>6</sub> ) / kJ mol <sup>-1</sup>	Q <sub>st,</sub> (C <sub>2</sub> H <sub>4</sub> ) / kJ mol <sup>-1</sup>	n <sub>ads</sub> (C <sub>2</sub> H <sub>6</sub> ) 100 kPa / cm <sup>3</sup> g <sup>-1</sup>	n <sub>ads</sub> (C <sub>2</sub> H <sub>6</sub> ) 100 kPa/ mmol g <sup>-1</sup>	q <sub>C2H6, mixed</sub> / mmol g <sup>-1</sup>	Q C2H4, mixed / mmol g <sup>-1</sup>	Selectivity / C <sub>2</sub> H <sub>6</sub> /C <sub>2</sub> H <sub>4</sub>	Ref
IRMOF-8	25	52.5	50	92	4.2	2.16	1.25	1.7	8
MAF-49	43	61	48	38.8	1.71	1.21	0.44	2.7	8
MIL-142A	25	27.2	26.2	85.1	3.84	2.1	1.39	1.51	9
Ni <sub>2</sub> (bdc) <sub>2</sub> (dabco)	25	21.5	18.3	112	5.13	2.48	1.38	1.8	10
PCN-245	25	22.8	21	73.2	3.31	1.8	1	1.8	11
ZIF-4	20	NA	NA	51.5	2.3	1.56	0.73	2.15	12
PCN-250	25	23.2	21.1	116.7	5.21	2.96	1.6	1.85	13
ZIF-7	25	NA	NA	41.1	2	1.2	0.8	1.5	14
ZIF-8	22	17.2	16.1	45.4	2.54	1.26	0.7	1.8	15
Cu(Qc)2	25	30	25.4	41.5	1.85	1.65	0.48	3.45	16
Fe2O2dobdc	25	66.8	36.5	74.3	3.29	2.53	0.57	4.4	17
MUF-15	20	29.2	28.2	105.1	4.67	3.13	1.6	1.96	18
Ni₂(TM- bdc)₂(dabco)	25	39	NA	121.8	5.44	NA	NA	1.98ª	19
CPM-733	25	23.4	22.5	159.6	7.13	4.01	NA	1.75	20
ZJU-120	23	27.6	NA	110.0	4.91	3.51	NA	2.74	21
LIFM-63	25	25.8	NA	67.2	3.0	NA	NA	1.56	22
Zn(atz)(ipa)	25	45.8	40.0	40.5	1.81	NA	NA	1.7	23
TJT-100	25	29	25	82	3.66	2.05	NA	1.2 <sup>b</sup>	24
Azole-Th-1	25	28.6	26.1	100.8	4.5	2.3 <sup>c</sup>	1.4 <sup>c</sup>	1.46	25
NPU-3	25	18.7	17.8	74.59	3.33	NA	NA	3.25	26
UiO-66-2CF₃	25	14.5	NA	19.712	0.88	NA	NA	2.54	27
DMOF-TM	25	31.5	30.2	118.94	5.31	2.98 <sup>d</sup>	2.2 <sup>d</sup>	1.88	This Work

**Table S9:** Summary of relevant data for a range of different ethane selective MOFs

<sup>a</sup> – 1:15  $C_2H_6/C_2H_4$ ; <sup>b</sup> – 1:99  $C_2H_6/C_2H_4$ ; c – estimated from a Figure in ref<sup>21</sup>; d – from coadsorption experiments a 91 kPa.





**Figure S20:** Comparison of the heats of adsorption of  $Ni_2(TM-bdc)_2(dabco)$  published by Ma and coworker in ref<sup>16</sup> and heats of adsorption calculated from the fitting parameters published by Ma and coworkers.

# S15 Adsorbate Properties

Table S10: Summary of the kinetic diameter, polarizability and quadrupole moment of CH<sub>4</sub>,  $C_2H_6$ ,  $C_2H_4$  and  $C_2H_2$ .<sup>28</sup>

Adsorbates	Sum Formula	Kinetic Diameter	Polarizability	Quadrupole Moment
Ethane	$C_2H_6$	4.443 Å	44.3-44.7 × 10 <sup>25</sup> /cm <sup>3</sup>	0.65 × 10 <sup>26</sup> /esu cm <sup>2</sup>
Ethylene	$C_2H_4$	4.163 Å	42.52 × 10 <sup>25</sup> /cm <sup>3</sup>	1.5 × 10 <sup>26</sup> /esu cm <sup>2</sup>

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