Electronic Supplementary Information

Pore Environment Engineering in Metal-Organic Frameworks for Efficient Ethane/Ethylene Separation

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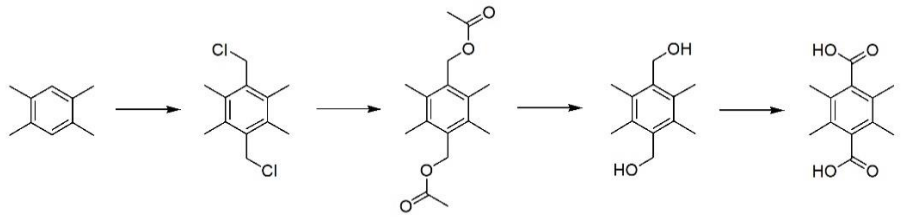
S1. Ligand synthesis

S1.1 Synthesis of 2,3,5,6-Tetramethylterephthalic acid (TMBDC)[1]



(1) (2) (3) (4)

Synthesis of 1,4-bis(chloromethyl)-2,3,5,6-tetramethylbenzene (1). 1,2,4,5-tetramethylbenzene (20.4 g , 152 mmol), NaCl (4.5 g, 77 mmol), solid paraformaldehyde (20 g, 666 mmol), were mixed in 80 mL concentrated hydrochloric acid and then heated to 120 °C for 5 h. After cooling down to room temperature, most of aqueous part was poured out. Then another part of NaCl (4.5 g, 77 mmol), solid paraformaldehyde (30 g, 999 mmol), anhydrous zinc chloride (21 g, 152 mmol), 80 mL concentrated hydrochloric acid were added and heated to 120 °C under vigorous stirring for 24 h. After cooling down to room temperature, the white solid was collected by filtration, ground finely and washed with water thoroughly. The resulting white powder was dried in air. Yield: 32 g (91%)

Synthesis of (2,3,5,6-tetramethyl-1,4-phenylene)bis(methylene)-diacetate (2). The crude product **1** (31 g, 135 mmol) and potassium acetate (83 g, 850 mmol) were suspended in 120 mL acetic acid and then heated up to 120 °C for 24 h. The resulting mixture was then poured into 200 g crushed ice and stirred for 1 h. The white solid was collected by filtration and washed with water until neutral pH of filtrate was achieved. The resulting white powder was dried in air. Yield: 35 g (92%)

Synthesis of 2,3,5,6-Tetramethylbenzene-1,4-dimethanol (3). The crude product **2** (34 g, 122 mmol), potassium hydroxide (23 g, 0.5 mmol) and 120 mL THF/EtOH/H_2O (1/1/1, v/v/v) were charged into a 250 mL round bottom flask and then stirred at 90 °C for 24 h. The turbid mixture was poured into 200 g crushed ice. The precipitate was filtered over a Buchner funnel and washed with water abundantly until neutral pH of filtrate was achieved. Additional 50 mL cold methanol was used to wash the product. The obtained white powder was dried in air. Yield: 22 g (89%)

Synthesis of 2,3,5,6-Tetramethylterephthalic acid (4). Firstly, an oxidizing reagent was prepared: chromium trioxide (7.1 g, 71 mmol) was dissolved in 25 mL water, to which 7.5 mL concentrated sulfuric acid (95% ~ 98%) was added dropwise over 20 minutes at 0 °C. The crude product **3** (2.5 g, 12.9 mmol) was dispersed in 125 mL acetone and the prepared chromic oxidizing reagent was added dropwise at 0 °C. The resulting suspension was kept stirring overnight while allowed to reach room temperature. A brown-green mixture was obtained and 70 mL isopropanol was added to destroy the excess oxidant. After the mixture had been stirred for 30 minutes, the organic solvent was removed under vacuum and then 150 mL 2M HCl was added into the residue. The mixture was stirred at 0 °C for 1 h. The obtained solid was collected by filtration and washed with water

thoroughly to remove the chromium salts to afford the product as light-yellow powder. Yield: 2.4 g (84%)

S2. Determination of exact TMBDC/BDC ratio in $Ni(BDC)_{1-x}(TMBDC)_x(DABCO)_{0.5}$

The exact ratio of TMBDC/BDC in each $Ni(BDC)_{1-x}(TMBDC)_x(DABCO)_{0.5}$ was confirmed by ^1H NMR after dissolving the MOF. Typically, about 10 mg $Ni(BDC)_{1-x}(TMBDC)_x(DABCO)_{0.5}$ crystal was dissolved in 0.5 mL 2 M HCl solution and some solid was obtained. The residual solid powder was collected through filtration and washed with 0.01 M HCl solution for three times. The obtained solid powder was dried under vacuum at 50 °C overnight and the composition of the solid powder was monitored by ^1H NMR. (Fig. S5 - S9)

S3. Fitting of ethylene and ethane adsorption isotherms

The ethylene and ethane adsorption isotherms of $Ni(BDC)_{1-x}(TMBDC)_x(DABCO)_{0.5}$ (x = 0, 0.2, 0.45, 0.71, 1), were fitted with dual-site Langmuir-Freundlich (DSLF) model. [2]

$$q = q_1 \frac{k_1 p^c}{1 + k_1 p^c} + q_2 \frac{k_2 p^t}{1 + k_2 p^t}$$

Where q is the equilibrium adsorbed amount of an adsorbent (mmol/g); q_1 and q_2 are the saturation uptakes of site 1 and site 2 (mmol/g); k_1 and k_2 are the affinity coefficients of site 1 and site 2 (1/kPa); c and t are equal to $1/n_1$ and$1/n_2$, respectively, where n_1 and n_2 are the corresponding deviations from an ideal homogeneous surface.

S4. IAST calculation of ethane/ethylene adsorption selectivity

The adsorption selectivity for C_2H_6/C_2H_4 separations is defined by

$$S = \frac{q_a/q_b}{p_a/p_b}$$

Where q_a and q_b are the molar loadings in the adsorbed phase in equilibrium with the bulk gas phase at partial pressures p_a and p_b.

S5. Isosteric heat of adsorption

The strength of the interaction between adsorbate and adsorbent is reflected on isosteric heat of adsorption (Q_{st}), which can be estimated by using the Clausius-Clapeyron equation,

$$\frac{\Delta H_s}{RT^2} = -\left(\frac{\partial \ln p}{\partial T}\right)_q$$

Integration the equation above can give

$$\ln p = -\frac{\Delta H_s}{RT} + C$$

where ΔH_s is the isosteric heat of adsorption at a given specific surface loading (kJ/mol), R is the ideal gas constant [J/(mol·K)], T is the temperature (K), *p* is the pressure (kPa), and C is an integral constant.

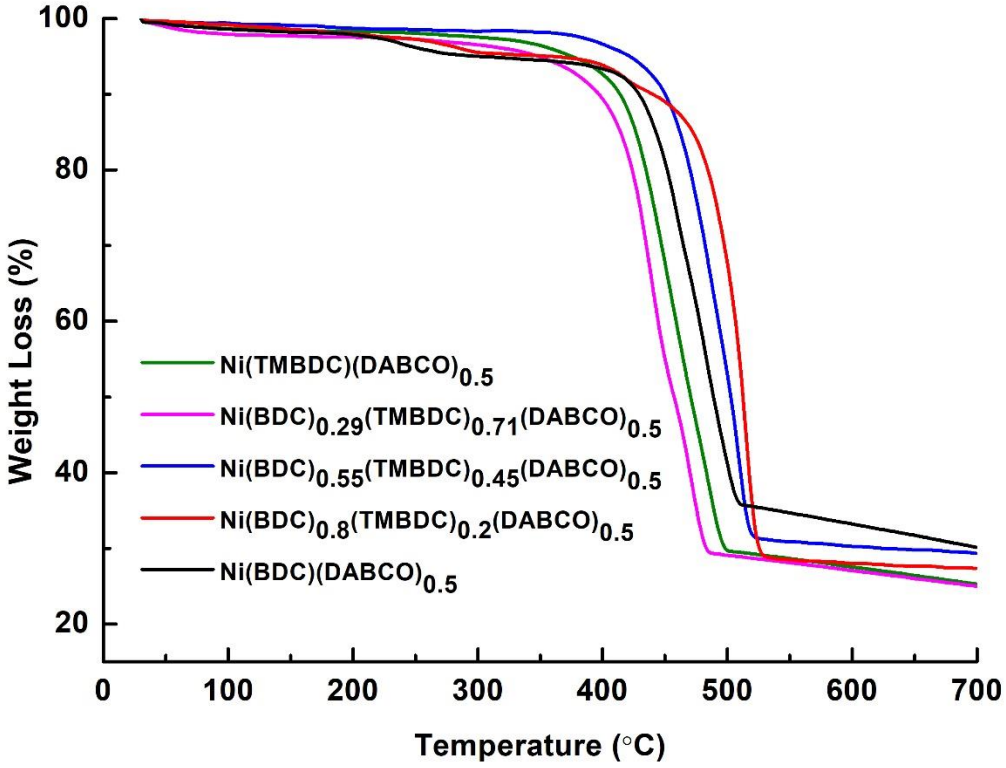


Fig. S1 TGA curves of $Ni(BDC)_{1-x}(TMBDC)_x(DABCO)_{0.5}$ (x = 0, 0.2, 0.45, 0.71, 1)

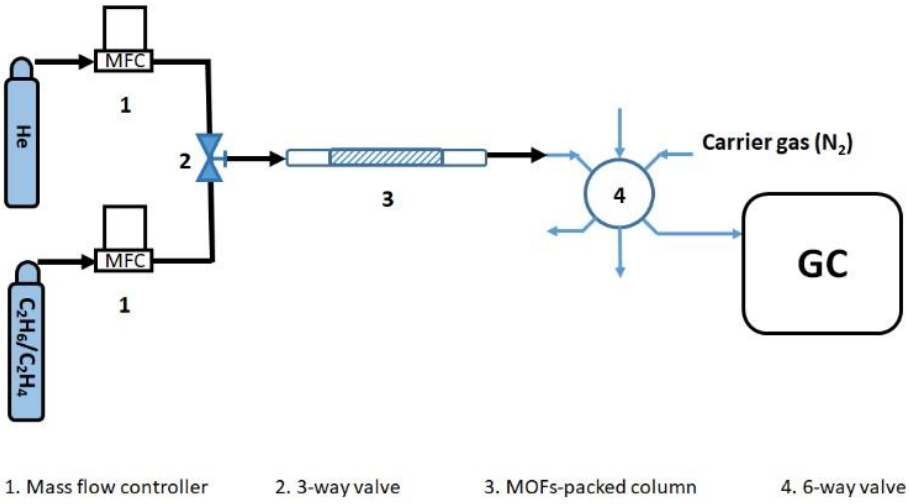
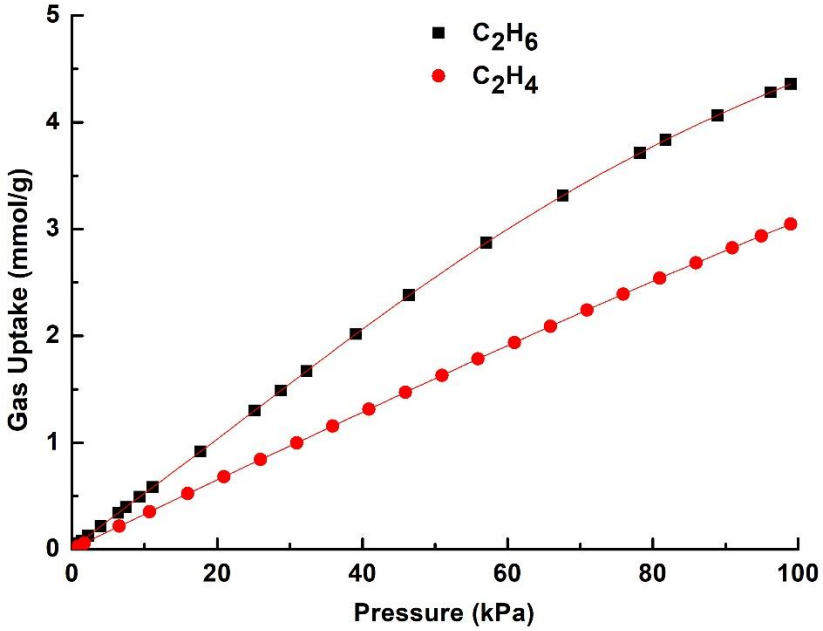
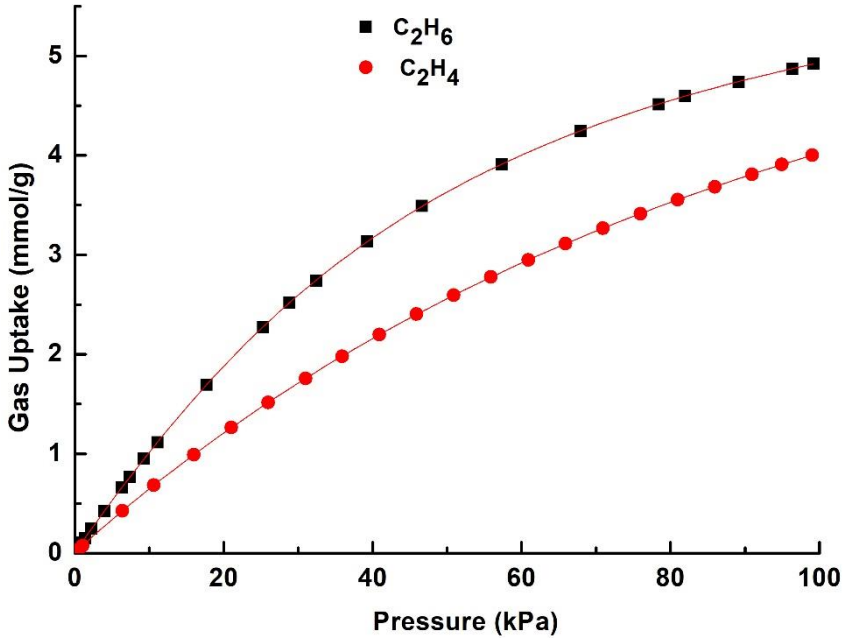


Fig. S2 Schematic illustration of the self-assembly apparatus for the breakthrough experiments



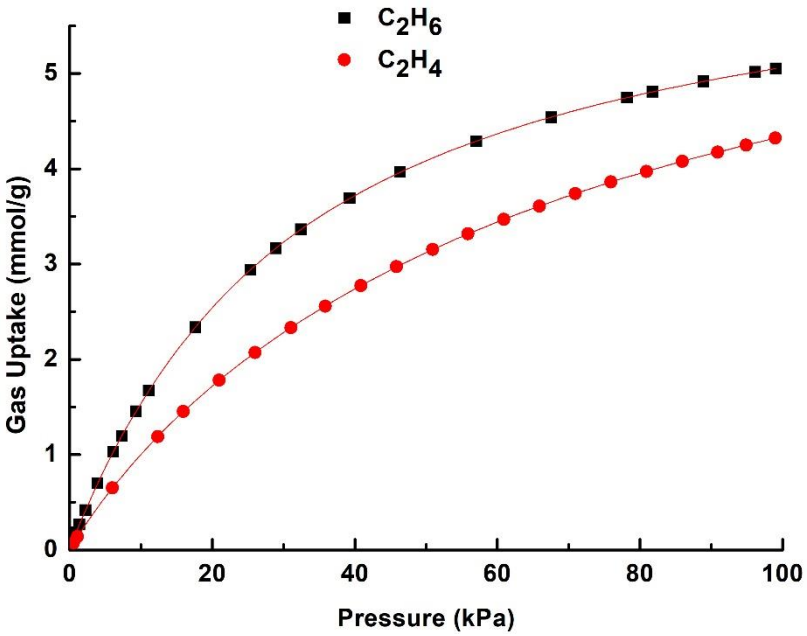
Parameters	C_2H_6	C_2H_4
q_1	6.10834	7.26075
b_1	5.34834E^{-4}	2.44498E^{-4}
c	1.69428	1.60482
q_2	1.11569	1.54413
b_2	0.05047	0.02147
t	0.99044	0.97558
R^2	0.9999	0.9999

Fig. S3 DSLF fitting curves and parameters for C_2H_6 and C_2H_4 isotherms of Ni(BDC)(DABCO)$_{0.5}$ at 298 K



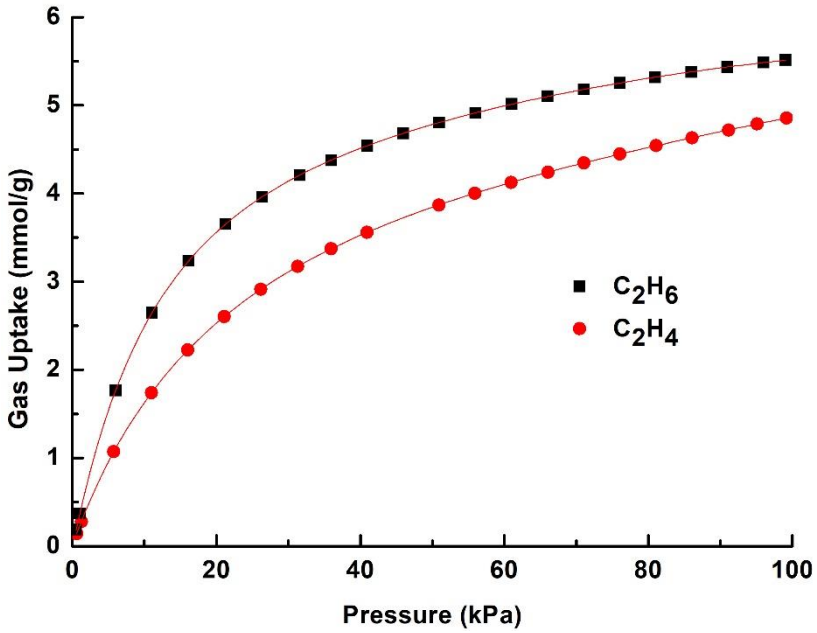
Parameters	C_2H_6	C_2H_4
q_1	5.8915	7.92323
b_1	0.00555	0.00516
c	1.35062	1.12543
q_2	0.64272	0.25122
b_2	0.13783	0.14218
t	0.97069	0.92245
R^2	0.9999	0.9999

Fig. S4 DSLF fitting curves and parameters for C_2H_6 and C_2H_4 isotherms of $Ni(BDC)_{0.8}(TMBDC)_{0.2}(DABCO)_{0.5}$ at 298 K



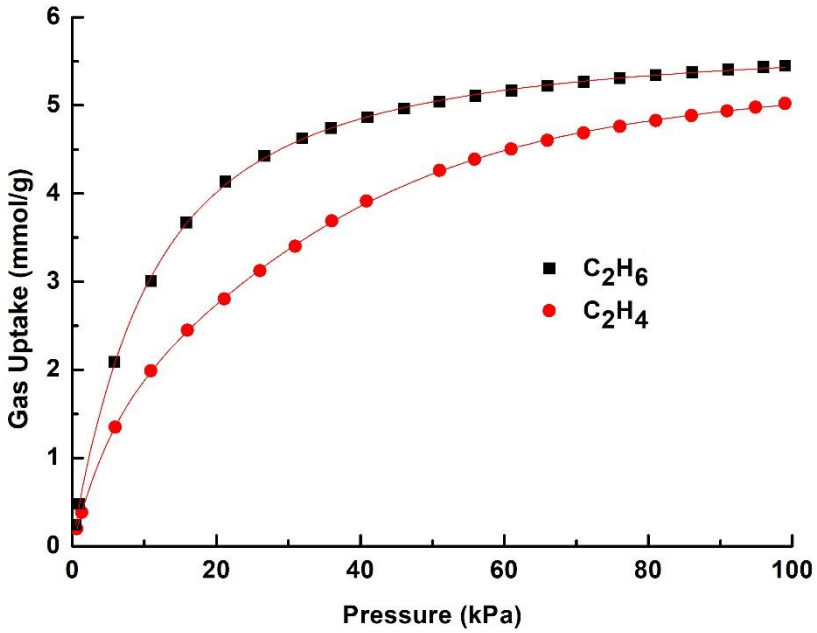
Parameters	C_2H_6	C_2H_4
q_1	6.4134	4.1501
b_1	0.03118	0.00436
c	0.99373	1.24068
q_2	0.24763	2.55945
b_2	$6.14116E^{-4}$	0.04337
t	2.37177	0.94707
R^2	0.9999	0.9999

Fig. S5 DSLF fitting curves and parameters for C_2H_6 and C_2H_4 isotherms of $Ni(BDC)_{0.55}(TMBDC)_{0.45}(DABCO)_{0.5}$ at 298 K



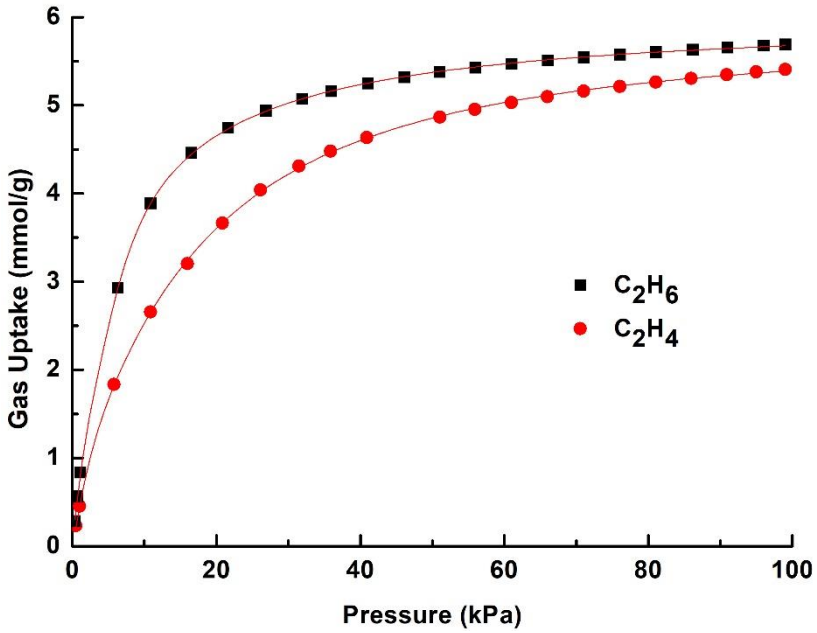
Parameters	C_2H_6	C_2H_4
q_1	5.89093	5.75613
b_1	0.06454	0.0407
c	1.05544	0.98622
q_2	0.38703	1.83384
b_2	$5.4252E^{-7}$	$7.38634E^{-7}$
t	3.29138	2.71822
R^2	0.9999	0.9999

Fig. S6 DSLF fitting curves and parameters for C_2H_6 and C_2H_4 isotherms of $Ni(BDC)_{0.29}(TMBDC)_{0.71}(DABCO)_{0.5}$ at 298 K



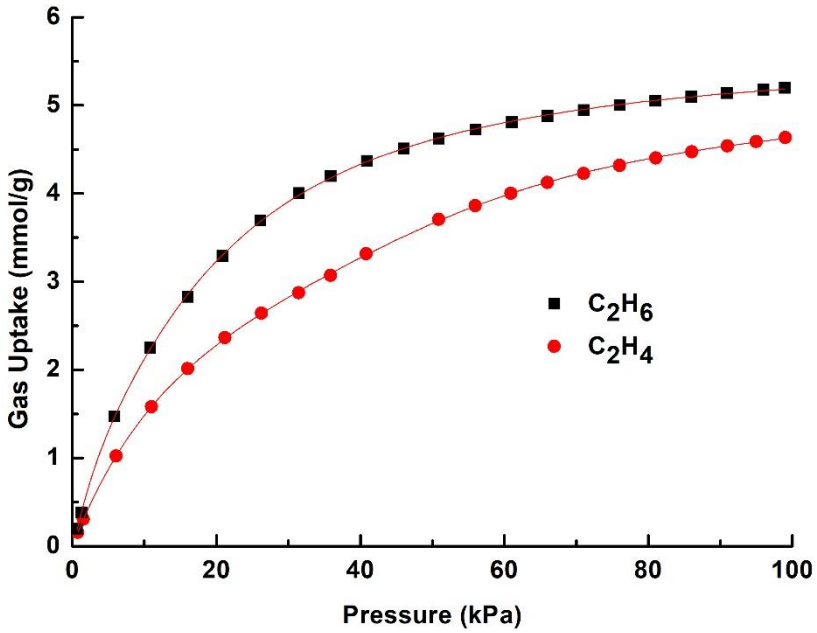
Parameters	C_2H_6	C_2H_4
q_1	5.30401	3.79184
b_1	0.05184	0.08556
c	1.22384	1.0372
q_2	0.47416	1.73657
b_2	0.8913	$1.06298E^{-4}$
t	1.22178	2.45754
R^2	0.9998	0.9999

Fig. S7 DSLF fitting curves and parameters for C_2H_6 and C_2H_4 isotherms of $Ni(TMBDC)(DABCO)_{0.5}$ at 298 K



Parameters	C_2H_6	C_2H_4
q_1	5.33585	4.24302
b_1	0.16071	0.01713
c	0.96134	1.36297
q_2	0.71271	1.5893
b_2	0.00114	0.31056
t	3.58909	1.21259
R^2	0.9999	0.9999

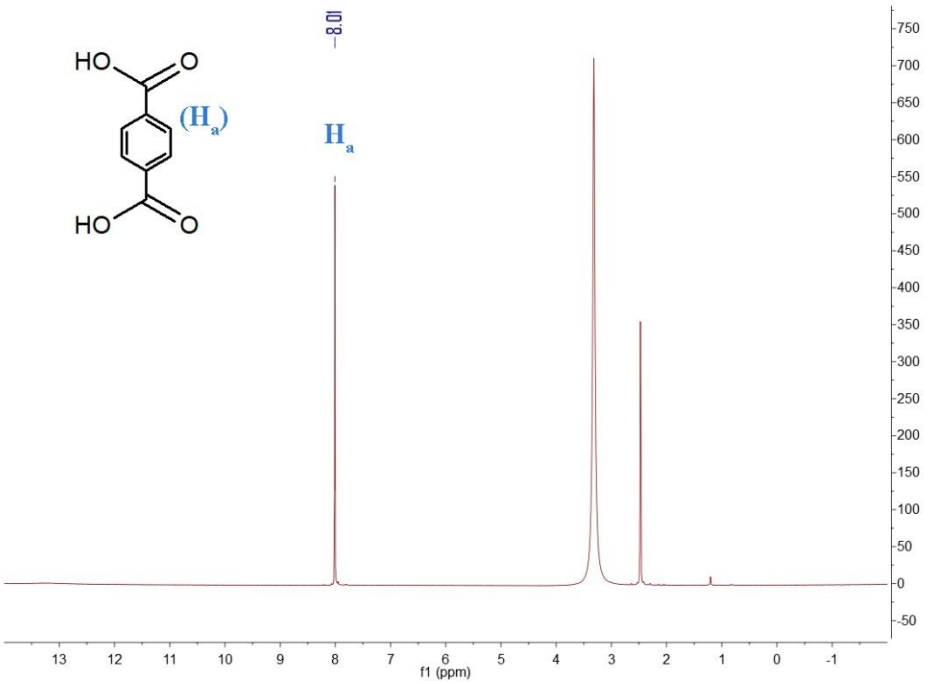
Fig. S8 DSLF fitting curves and parameters for C_2H_6 and C_2H_4 isotherms of Ni(TMBDC)(DABCO)$_{0.5}$ at 288 K



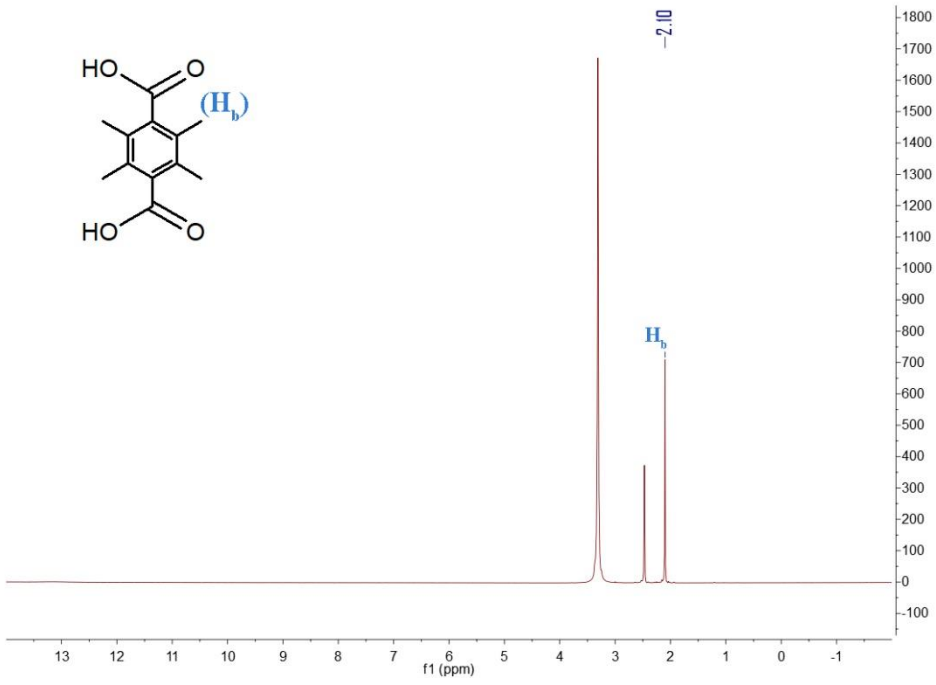
Parameters	C_2H_6	C_2H_4
q_1	4.13119	4.73061
b_1	0.00968	0.04465
c	1.49903	1.00854
q_2	1.46882	0.80285
b_2	0.21843	$2.1526E^{-7}$
t	1.22892	3.86929
R^2	0.9999	0.9999

Fig. S9 DSLF fitting curves and parameters for C_2H_6 and C_2H_4 isotherms of Ni(TMBDC)$(DABCO)_{0.5}$ at 308 K

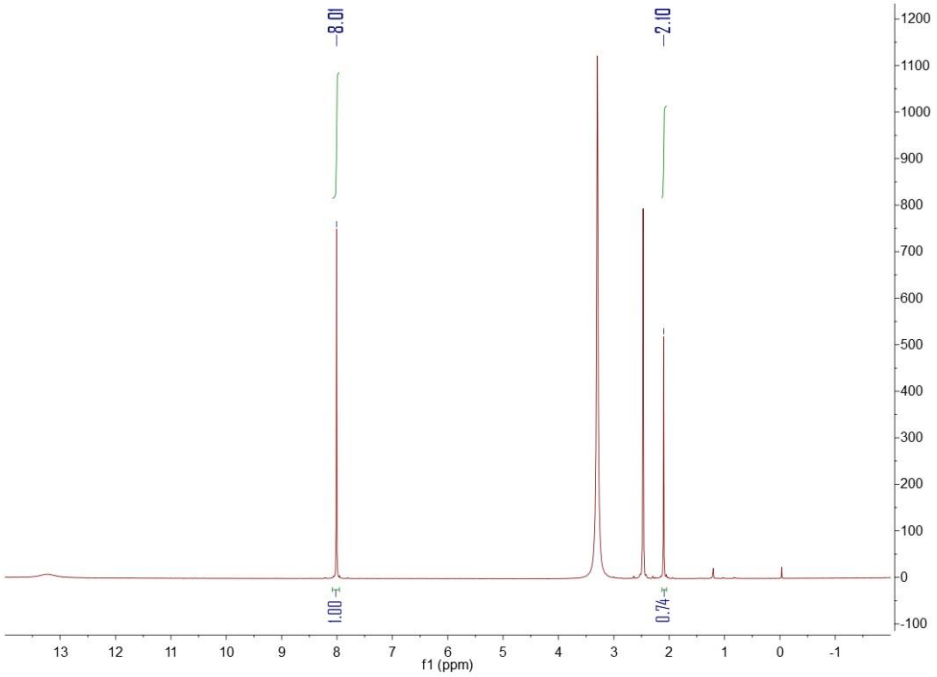
Fig. S10 ^{1}H NMR data of various compounds



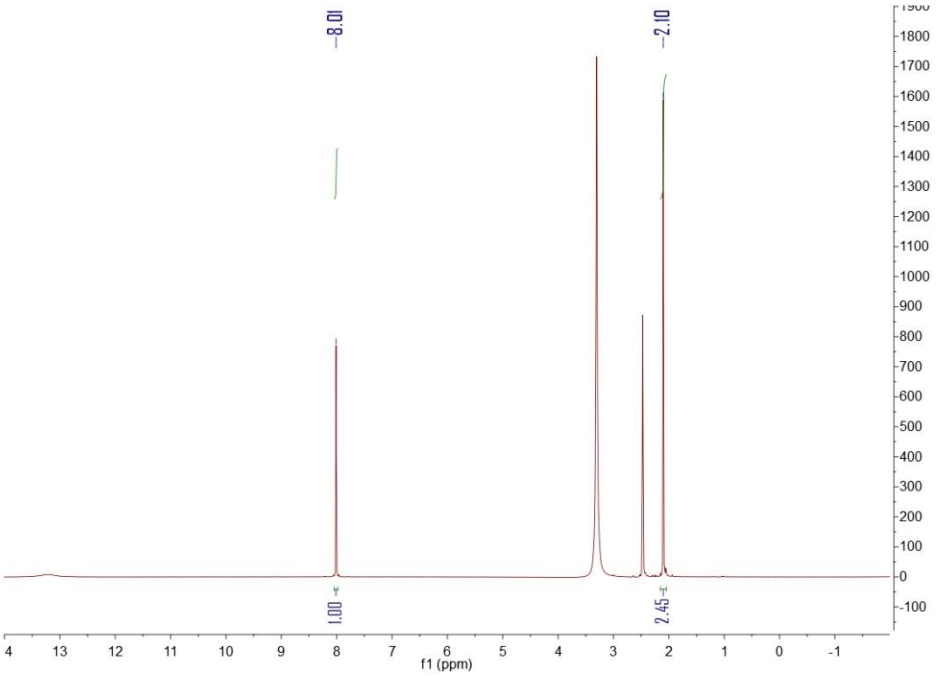
^{1}H NMR data of the dissolved Ni(BDC)(DABCO)$_{0.5}$



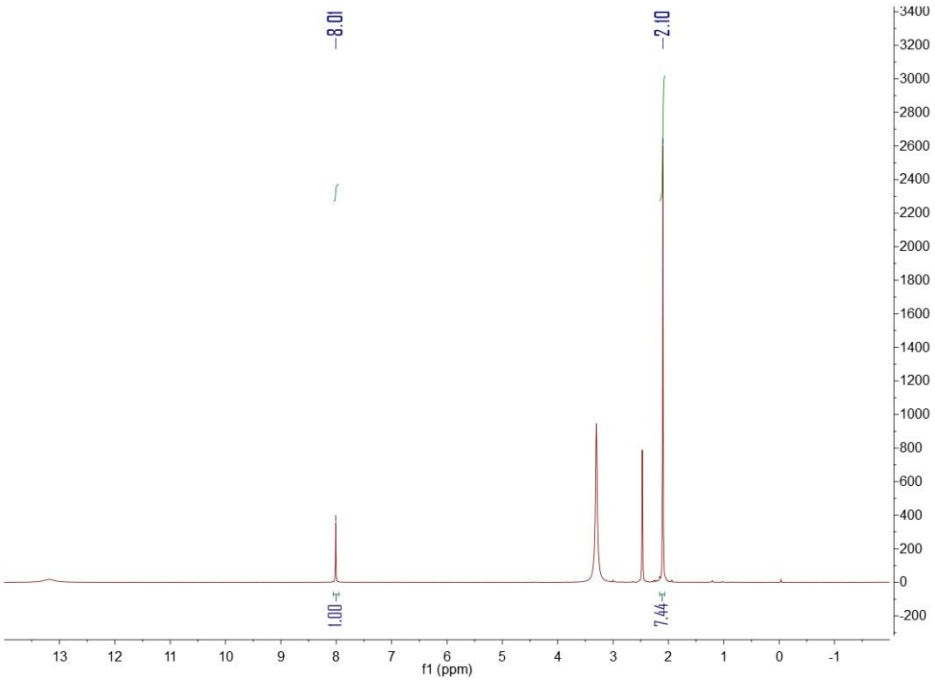
^{1}H NMR data of the dissolved Ni(TMBDC)(DABCO)$_{0.5}$



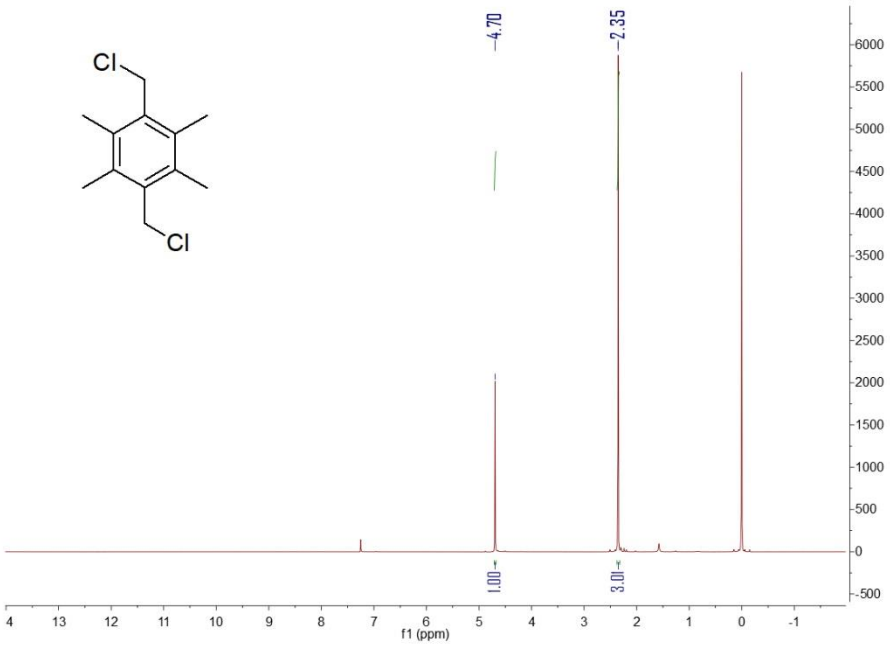
^{1}H NMR data of the dissolved $Ni(BDC)_{0.8}(TMBDC)_{0.2}$($DABCO)_{0.5}$



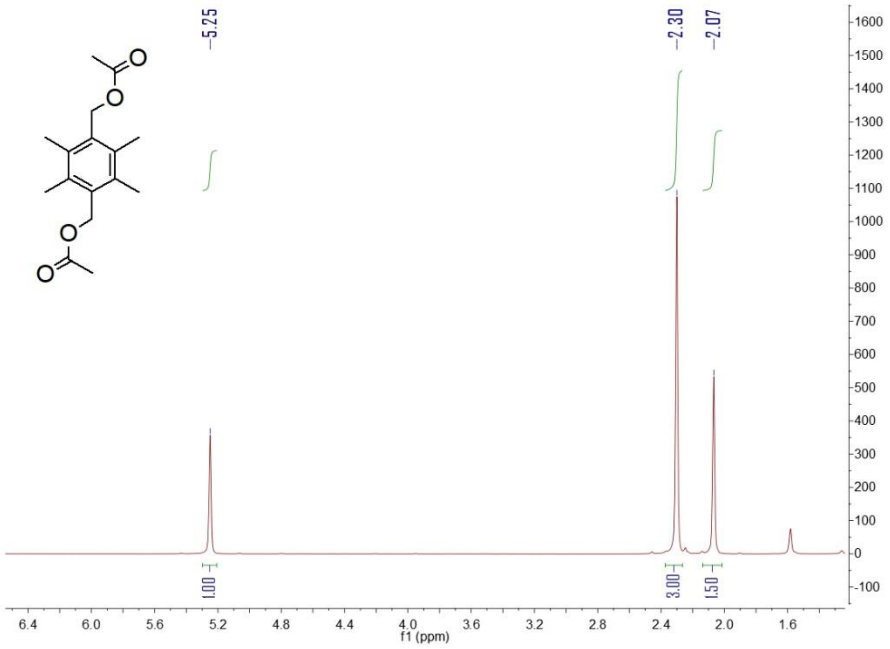
^{1}H NMR data of the dissolved $Ni(BDC)_{0.55}(TNBDC)_{0.45}(DABCO)_{0.5}$



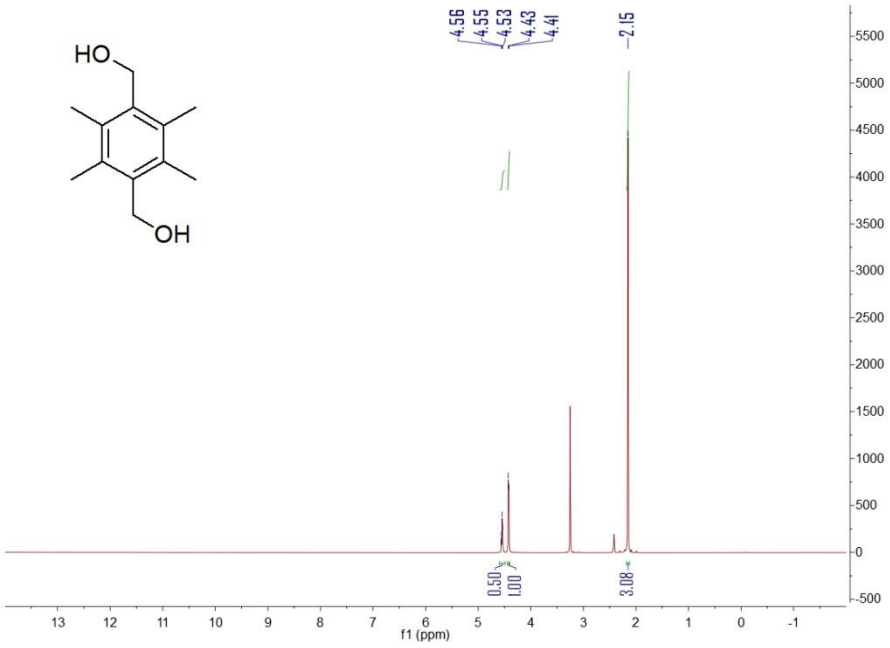
^{1}H NMR data of the dissolved $Ni(BDC)_{0.29}(TMBDC)_{0.71}(DABCO)_{0.5}$



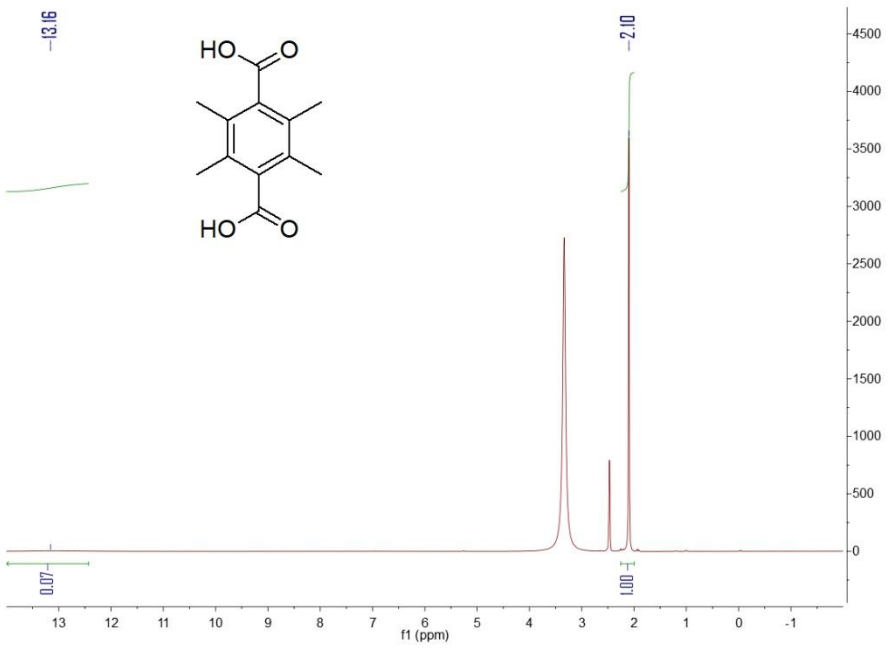
^{1}H NMR data of 1,4-bis(chloromethyl)-2,3,5,6-tetramethylbenzene (**1**)



^{1}H NMR data of (2,3,5,6-tetramethyl-1,4-phenylene)bis(methylene)-diacetate (**2**)



^{1}H NMR data of 2,3,5,6-Tetramethylbenzene-1,4-dimethanol (**3**)



[1]H NMR data of 2,3,5,6-Tetramethylterephthalic acid (**4**)

Single-Crystal X-ray Diffraction for Ni(TMBDC)(DABCO)$_{0.5}$

The X-ray diffraction data were collected using synchrotron radiation (λ = 0.41328 Å) at Advanced Photon Source, Beamline 15-ID-B of ChemMatCARS in Argonne National Lab, Argonne, IL. Indexing was performed using *APEX3*.[3] Data integration and reduction were performed using SaintPlus.[4] Absorption correction was performed by multi-scan method implemented in SADABS [5]. Space group was determined using XPREP implemented in APEX3.[3] Structure was solved using SHELXT[6] and refined using SHELXL-2018[7, 8] (full-matrix least-squares on F^2) through OLEX2 interface program.[9] Part of carboxylate ligand is disordered over two positions and DABCO was modeled as disordered over eight positions. The contribution of disordered content in structural voids (Fig. S11) was treated as diffuse using Squeeze procedure implemented in Platon program.[10-11] Crystal data and refinement conditions are shown in Table S1.

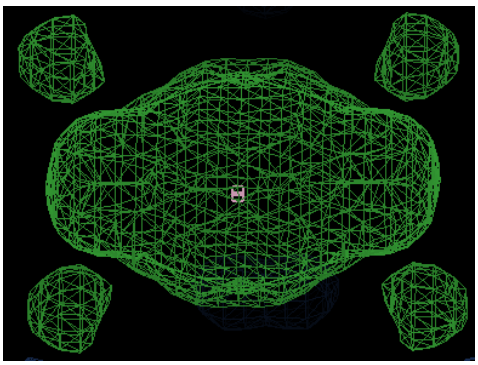


Fig. S11. Contour electron density difference map (0.59el/A^3 level, WinCOOT [12])

Crystal data and structure refinement for $Ni(TMBDC)(DABCO)_{0.5}$	
Identification code	$Ni(TMBDC)(DABCO)_{0.5}$
Empirical formula	$C_{30}H_{36}N_2Ni_2O_8$
Formula weight	670.03
Temperature/K	100.15
Crystal system	tetragonal
Space group	*P*4/*mmm*
a/Å	10.8500(7)
b/Å	10.8500(7)
c/Å	9.2239(6)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	1085.86(16)
Z	1
$\rho_{calc}g/cm^3$	1.025
μ/mm^{-1}	0.185
F(000)	350.0
Radiation	λ = 0.41328
2Θ range for data collection/°	2.568 to 40.278
Index ranges	$-18 \le h \le 18$, $-17 \le k \le 17$, $-15 \le l \le 15$
Reflections collected	49091
Independent reflections	1574 [R_{int} = 0.0722, R_{sigma} = 0.0204]
Data/restraints/parameters	1574/9/55
Goodness-of-fit on F^2	1.143
Final R indexes [I>=2σ (I)]	R_1 = 0.0388, wR_2 = 0.1203
Final R indexes [all data]	R_1 = 0.0465, wR_2 = 0.1230
Largest diff. peak/hole / e $Å^{-3}$	0.67/-0.88

Refernces

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