Direct Structural Evidence of Commensurate-to-Incommensurate Transition of Hydrocarbon Adsorption in a Microporous Metal Organic Framework

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Supporting Information

1. Crystal Data

1a. Details of Data Collection

Compound **1** was synthesized and activated as described previously.[1,2] For gaseous hydrocarbons, the activated samples were placed in a specially made glass cell under the desired gas flow for 20 hours to ensure complete diffusion of gases within the crystals. The crystals were then coated with paratone oil to avoid aerial exposure. A suitably sized crystal was selected for structure analysis. Single crystal X-ray diffraction analysis was performed at 100/150 K on a Bruker-AXS smart APEX CCD system with graphite-monochromomatized Mo Kα radiation ($\lambda = 0.71073$ Å). The crystallographic details of each gas adsorbed framework are listed in Table S1.

For liquid hydrocarbons, the activated materials were dipped in the desired hydrocarbon (approx. 10 mg in 5 mL of liquid hydrocarbon) and kept overnight at room temperature. An appropriate crystal was chosen from the solution and coated with paratone oil. Single crystal X-ray diffraction was performed using the setup described above.

The reflection data of representative crystals of HC@**1'** (except C_4H_{10}@**1'**) were collected at 100 K on a Bruker-AXS smart APEX CCD system with graphite-monochromomatized Mo Kα radiation ($\lambda = 0.71073$ Å). The reflection data of C_4H_{10}@**1'** were collected at Oxford Gemini Diffractometer at 100 K, with Mo Kα radiation ($\lambda = 0.71073$ Å). The Ca, S, C and H atoms of the guest frameworks were located first, followed by the carbon atoms of the guest from the difference Fourier maps. The hydrogen atoms on the hydrocarbon molecules were added using geometrical constraint (HFIX command). The bond distances between the carbon atoms in the adsorbate hydrocarbon atoms were fixed as 1.54 Å (1.34 Å for propene) in accordance with normal sp^3-sp^3 carbon atom distances.

1b. Summary of Crystal Data

Table S1. Crystal data and structure refinement parameters for $C_2H_6@\mathbf{1'}$

Empirical Formula	$C_{14.57}H_{9.72}CaO_6S$
Formula Weight	352.95
Crystal System	monoclinic
Space Group	$P2_1/n$
Collection Temperature (K)	100
a (Å)	11.6530(8)
b (Å)	5.5616(4)
c (Å)	22.8815(16)
α(°)	90
β (°)	100.765(1)
γ (°)	90
Volume(Å^3)	1456.84(18)
Z	4
Calculated Density(g/cm^3)	1.609
Absorption coefficient(mm-1)	0.601
F(000)	725
θ range of data collection (°)	1.81 - 31.51
Total Reflection	17825
Independent Reflection	4833 [R(int) = 0.0399]
Goodness of fit	1.008
Data/ Restraints/parameter	4833 / 1 / 207
R1(*on Fo2, I>2σ(I)*)	0.0433
wR2 (*on Fo2, I> 2 σ (I)*)	0.0996

Table S2. Crystal data and structure refinement parameters for $C_3H_6@\mathbf{1'}$

Empirical Formula	$C_{15.31} H_{11.50}CaO_6S$
Formula Weight	363.50
Crystal System	Monoclinic
Space Group	$P2_1/n$
Collection Temperature (K)	150
a (Å)	11.6426(8)
b (Å)	5.5574(4)
c (Å)	22.8446(16)
α(°)	90
β (°)	100.6810(10)
γ (°)	90
Volume(Å^3)	1452.50(18)
Z	4
Calculated Density(g/cm^3)	1.663
Absorption coefficient(mm-1)	0.612
F(000)	796
θ range of data collection (°)	1.84 - 30.42
Total Reflection	16471
Independent Reflection	4365 [R(int) = 0.0215]
Goodness of fit	1.049
Data/ Restraints/parameter	4365 / 3 / 218
R1(*on Fo2, I>2σ(I)*)	0.0324
wR2 (*on Fo2, I> 2 σ (I)*)	0.0840

Table S3. Crystal data and structure refinement parameters for $C_3H_8@\textbf{1'}$

Empirical Formula	$C_{14.50}H_{9.34}CaO_6S$
Formula Weight	351.69
Crystal System	monoclinic
Space Group	$P2_1/n$
Collection Temperature	100
a (Å)	11.7073(10)
b (Å)	5.5647(5)
c (Å)	22.830(2)
α(°)	90
β (°)	100.5860(10)
γ (°)	90
Volume($\mathring{A}^3$)	1462.0(2)
Z	4
Calculated Density(g/cm^3)	1.598
Absorption coefficient(mm-1)	0.599
F(000)	721
θ range of data collection (°)	1.81 to 30.51
Total Reflection	16777
Independent Reflection	4434 [R(int) = 0.0347]
Goodness of fit	1.054
Data/ Restraints/parameter	4434 / 3 / 218
R1(*on Fo2, I>2σ(I)*)	0.0372
wR2 (*on Fo2, I> 2 σ (I)*)	0.0904

Table S4. Crystal data and structure refinement parameters for $C_4H_{10}@\mathbf{1'}$

Empirical Formula	$C_{14.72}H_{9.79}CaO_6S$
Formula Weight	354.73
Crystal System	Monoclinic
Space Group	$P2_1/n$
Collection Temperature (K)	100
a (Å)	11.6884(5)
b (Å)	5.5643(2)
c (Å)	22.8159(10)
$\alpha(°)$	90
$\beta (°)$	100.691(4)
$\gamma (°)$	90
Volume($Å^3$)	1458.14(11)
Z	4
Calculated Density(g/cm^3)	1.616
Absorption coefficient(mm-1)	0.601
F(000)	728
θ range of data collection (°)	3.59 - 33.51
Total Reflection	26543
Independent Reflection	5563 [R(int) = 0.0325]
Goodness of fit	1.01
Data/ Restraints/parameter	5563 /55 / 236
R1(*on Fo2, I>2σ(I)*)	0.0437
wR2 (*on Fo2, I> 2 σ (I)*)	0.0858

Table S5. Crystal data and structure refinement parameters for C_5H_{12}@**1'**

Empirical Formula	$C_{15.58} H_{11.80} Ca O_6 S$
Formula Weight	367.18
Crystal System	Monoclinic
Space Group	$P2_1/n$
Collection Temperature (K)	100
a (Å)	11.8767(11)
b (Å)	5.5769(5)
c (Å)	22.486(2)
$\alpha(°)$	90
β (°)	99.8930(10)
γ (°)	90
Volume(Å^3)	1467.2(2)
Z	4
Calculated Density(g/cm^3)	1.662
Absorption coefficient(mm-1)	0.601
F(000)	757
θ range of data collection (°)	1.82 - 30.63
Total Reflection	15135
Independent Reflection	4505 [R(int) = 0.0340]
Goodness of fit	1.111
Data/ Restraints/parameter	4505 / 319 / 221
R1(*on Fo2, I>2σ(I)*)	0.0470
wR2 (*on Fo2, I> 2 σ (I)*)	0.1151

Table S6. Crystal data and structure refinement parameters for $C_6H_{14}@\mathbf{1'}$

Empirical Formula	$C_{14.63}H_{9.47}CaO_6S$
Formula Weight	353.36
Crystal System	Monoclinic
Space Group	$P2_1/n$
Collection Temperature (K)	100
a (Å)	11.7150(6)
b (Å)	5.5679(3)
c (Å)	22.8208(11)
α(°)	90
β (°)	100.5320(10)
γ (°)	90
Volume($Å^3$)	1463.48(13)
Z	4
Calculated Density(g/cm^3)	1.604
Absorption coefficient(mm-1)	0.599
F(000)	725
θ range of data collection (°)	2.96 - 32.93
Total Reflection	18014
Independent Reflection	5206 [R(int) = 0.0261]
Goodness of fit	1.005
Data/ Restraints/parameter	5206 / 11 / 219
R1(*on Fo2, I>2σ(I)*)	0.0618
wR2 (*on Fo2, I> 2 σ (I)*)	0.1292

Table S7. Crystal data and structure refinement parameters for C_7H_{16}@**1'**

Empirical Formula	$C_{14.60}H_{9.36}CaO_6S$
Formula Weight	352.86
Crystal System	monoclinic
Space Group	P2$_1$/n
Collection Temperature (K)	100
a (Å)	11.7292(13)
b (Å)	5.5685(6)
c (Å)	22.792(3)
α(°)	90
β (°)	100.493(2)
γ (°)	90
Volume(Å^3)	1463.7(3)
Z	4
Calculated Density(g/cm^3)	1.601
Absorption coefficient(mm-1)	0.599
F(000)	724
θ range of data collection (°)	1.82 -0 30.49
Total Reflection	13980
Independent Reflection	4406 [R(int) = 0.0402]
Goodness of fit	1.042
Data/ Restraints/parameter	4406 / 11 / 221
R1(*on Fo2, I>2σ(I)*)	0.0462
wR2 (*on Fo2, I> 2 σ (I)*)	0.1037
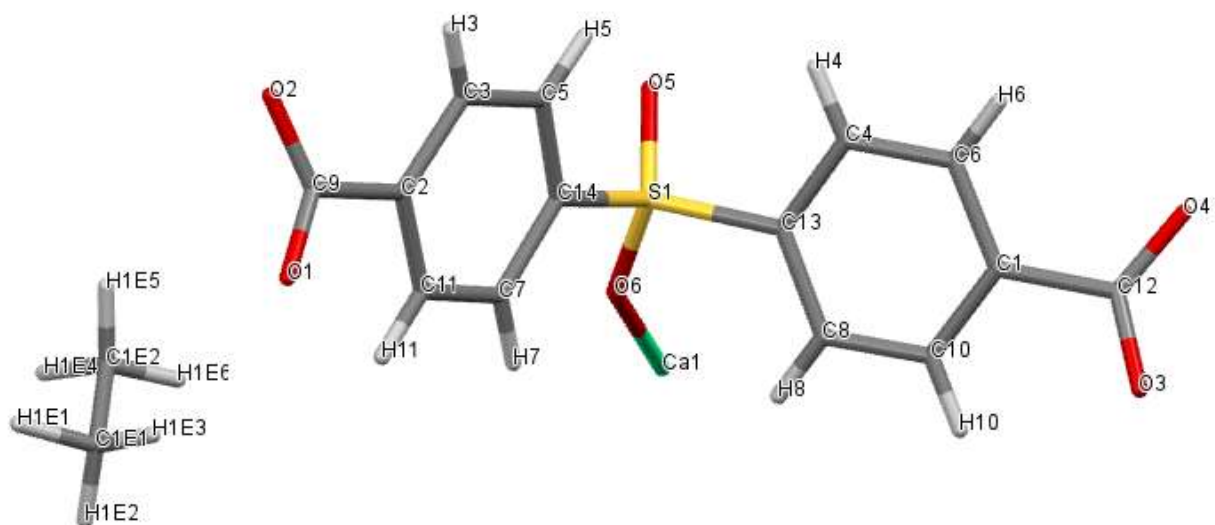
Fig. S1. Asymmetric unit of $C_2H_6@1'$ plotted using capped stick model.

(a)	(b)
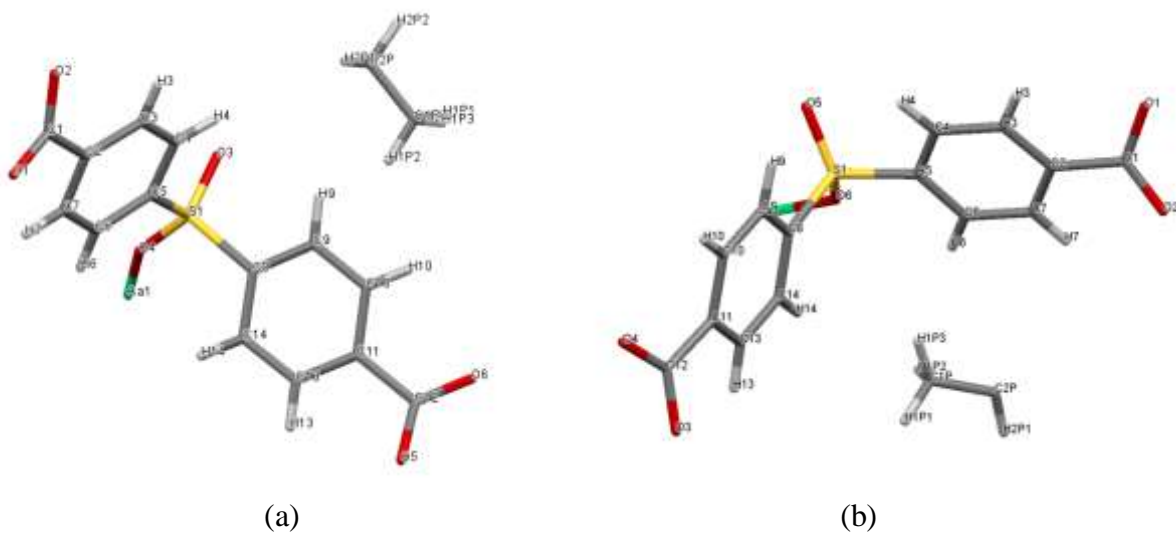
Fig. S2. The Asymmetric unit of (a) $C_3H_8@1'$ and (b) $C_3H_6@1'$ plotted using capped stick model.

(a)

(b)

(c)
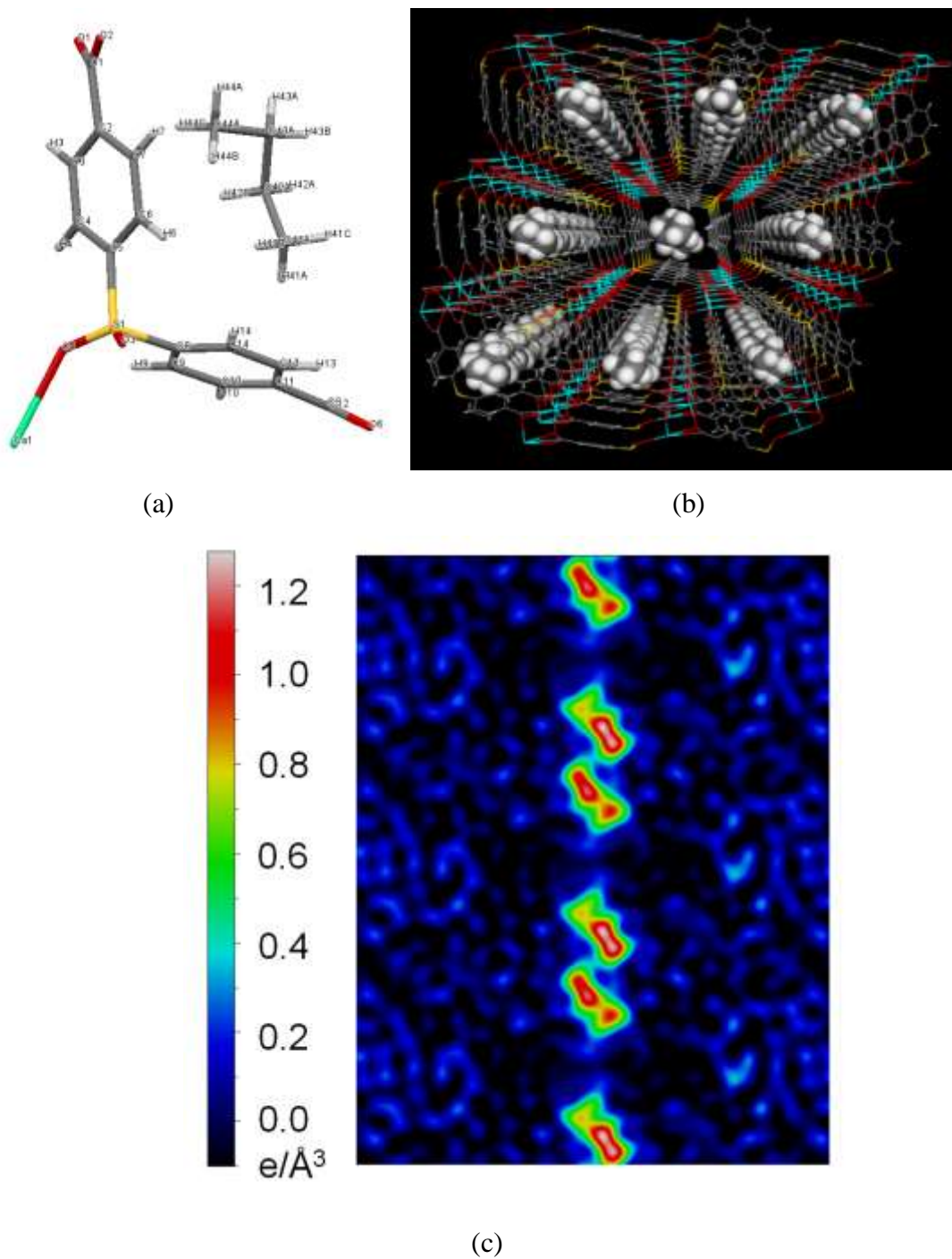
Fig. S3. (a) Asymmetric unit of C_4H_{10}@$\mathbf{1'}$ plotted using capped stick model. (b) Projected view of packing of n-C_4H_{10} along the crystallographic b direction, calcium (cyan), sulfur (yellow), oxygen (red), carbon (grey), and hydrogen (white). (c) The difference electron density map calculated before assigning the n-C_4H_{10} molecules, showing islands of electron density in the channel indicating commensurately adsorbed butane.
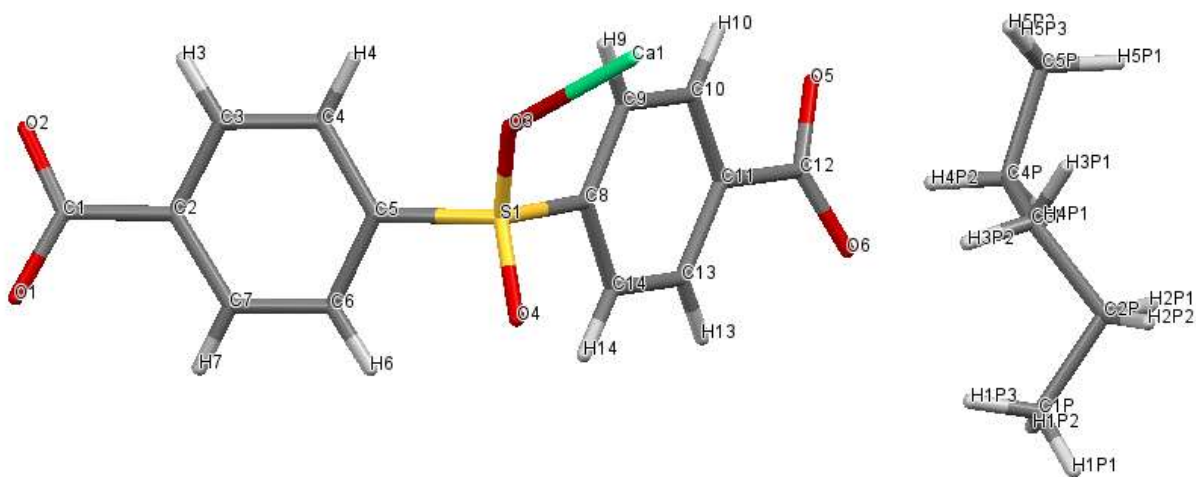
(a)
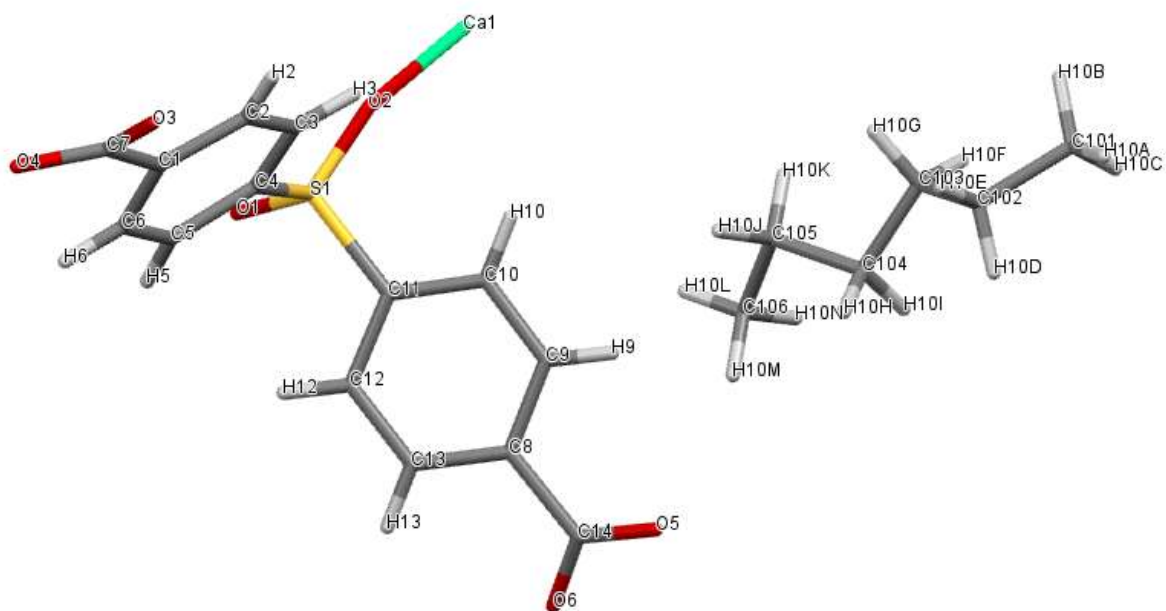
(b)

Fig. S4. Asymmetric unit of (a) n-C$_5$H$_{12}$@**1'** and (b) n-C$_6$H$_{14}$@**1'** plotted using capped stick model.

(a)   (b)
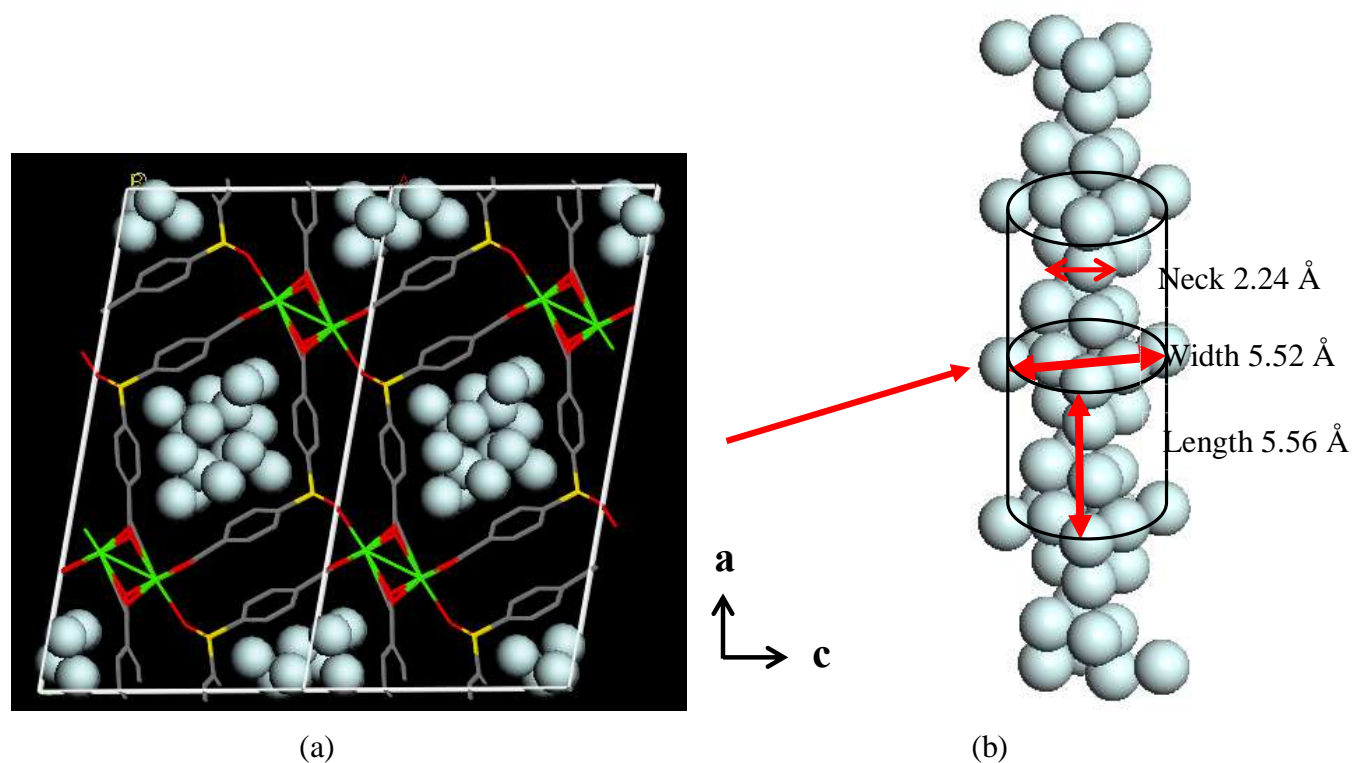
Fig. S5. Helium adsorption simulation (at 1 K and 100 kPa) of compound **1** showing (a) two independent channels along the crystallographic *b* direction, and (b) the shape of the segment and channel along the *b* direction. The unit cell length along *b* direction (5.56 Å) is represented by the cylinder, which also contains a full segment. The width of the channel at its widest section is 5.52 Å, while at the narrowest section the width is 2.24 Å.

2. Gas Adsorption Data

Adsorption isotherms of C_2-C_4 hydrocarbons were measured at various temperatures (233-298 K) using a high-resolution Micromeritics 3Flex adsorption analyzer equipped with a high-vacuum system and coupled with a cryostat (Cold Edge Technologies) maintaining cryogenic temperatures with a stability of +/- 0.001 K from the target temperature. The heats of adsorption (*Qst*) were calculated using isotherms collected at 273, 288, and 298 K using the Virial equation.[3-5] Adsorption of liquid hydrocarbons (nC_5-nC_7) was carried out on a home-made adsorption analyzer modified from a Thermogravimetric Analyzer Q-50 (TA Inst.). Nitrogen (UHP, 99.999%) was used as carrier gas. Varied partial pressure of hydrocarbons was achieved by changing the blending ratios of pure nitrogen and hydrocarbon-saturated nitrogen. The sample was outgassed using a procedure described in the gas-adsorption section. All hydrocarbons used in the study were of 99% purity or higher. The heats of adsorption for these adsorbates were calculated by fitting the adsorption data at 373, 383, and 393 K to the Virial equation.[3-5]
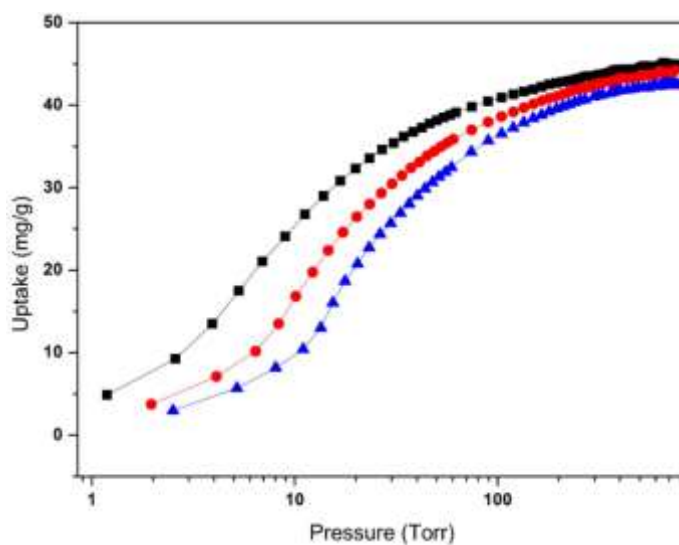

Fig. S6. The adsorption isotherms of C_2H_6 in **1'** at various temperatures (color scheme: black: 273 K, red - 288 K, blue - 298 K).
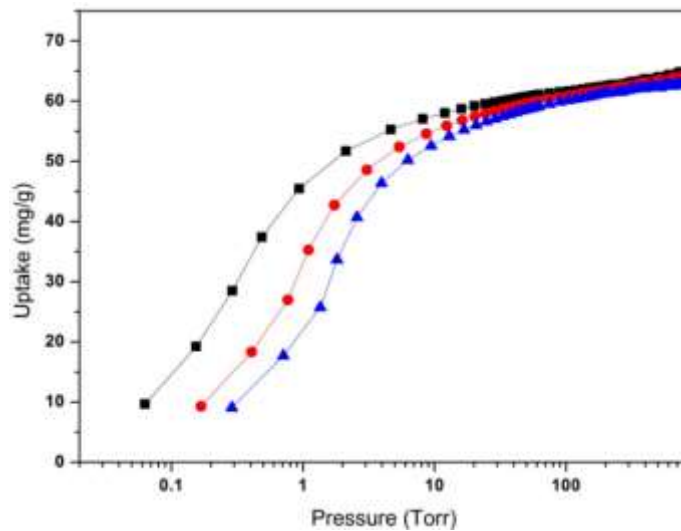
Fig. S7. The adsorption profile of $C_3^=$ (C_3H_6) in at various temperatures (color scheme: black: 273 K, red - 288 K, blue - 298 K).
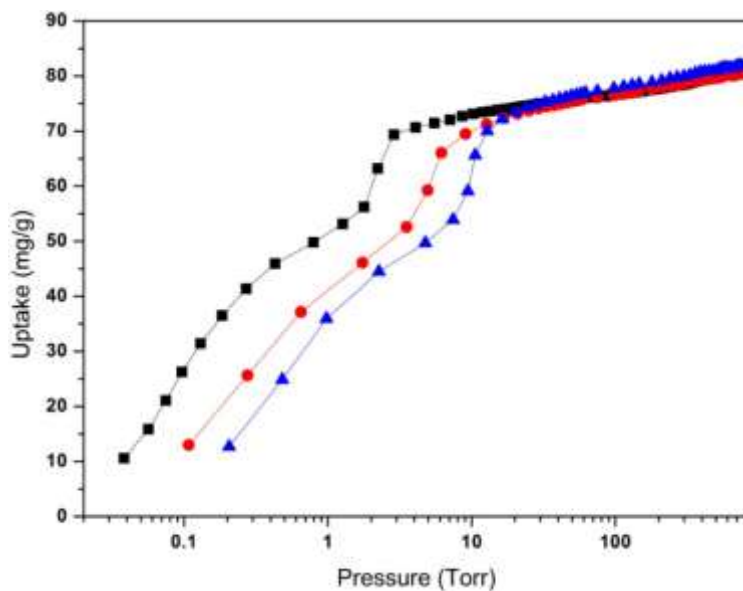

Fig. S8. The adsorption profile of nC_4 (C_4H_{10}) in activated **1'** at various temperatures (color scheme: black: 273 K, red - 288 K, blue - 298 K).
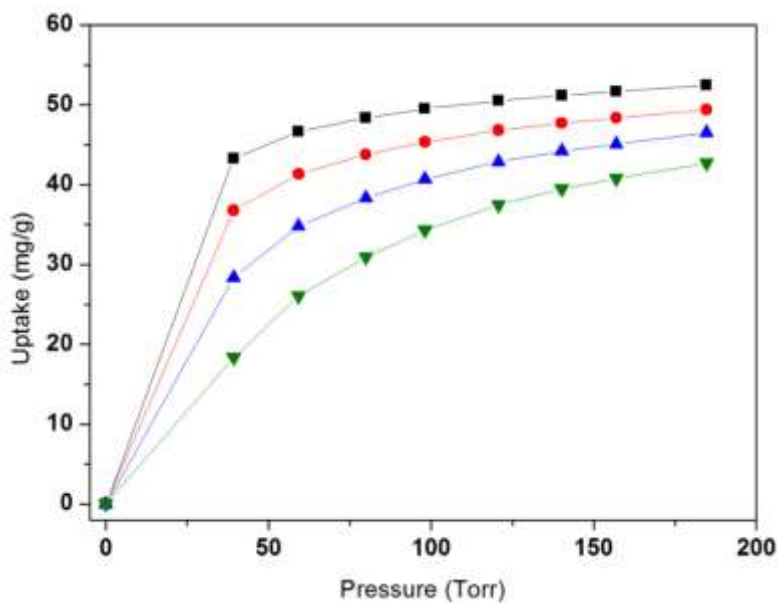
Fig. S9. The adsorption profile of nC$_5$ (C$_5$H$_{12}$) in **1'** at various temperatures (color scheme: black: 363 K, red - 373 K, blue - 383 K, green - 393 K).
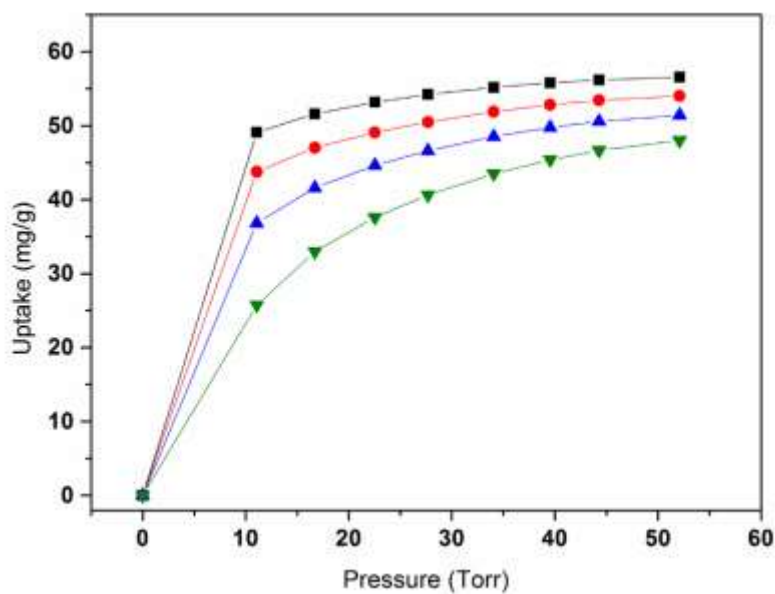

Fig. S10. The adsorption profile of nC$_6$ (C$_6$H$_{12}$) in **1'** at various temperature (color scheme: black: 363 K, red - 373 K, blue - 383 K, green - 393 K).
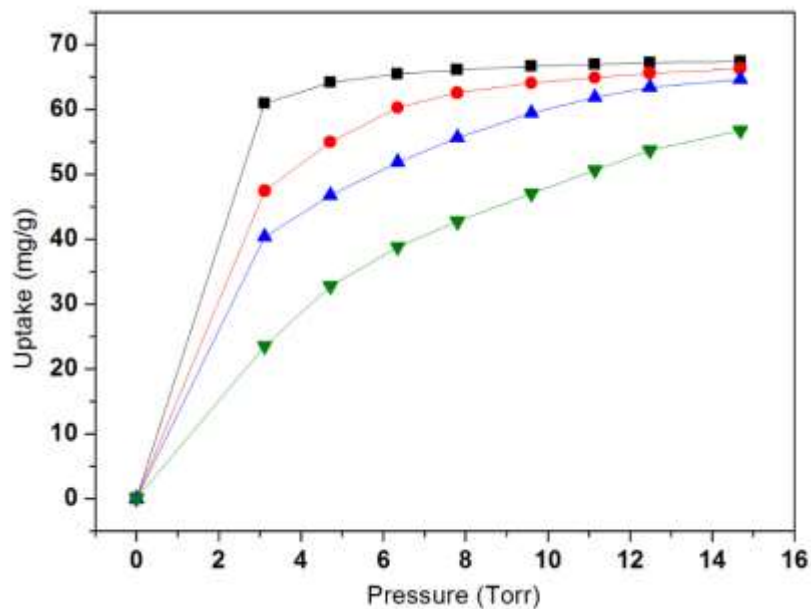
Fig. S11. The adsorption profile of nC$_7$ (C$_7$H$_{14}$) in **1'** at various temperatures (color scheme: black: 363 K, red - 373 K, blue - 383 K, green - 393 K).

Red - calculated from single crystal data (collected at 100K) of butane adsorbed CaSDB
green - experimental powder data of butane adsorbed CaSDB at 298K
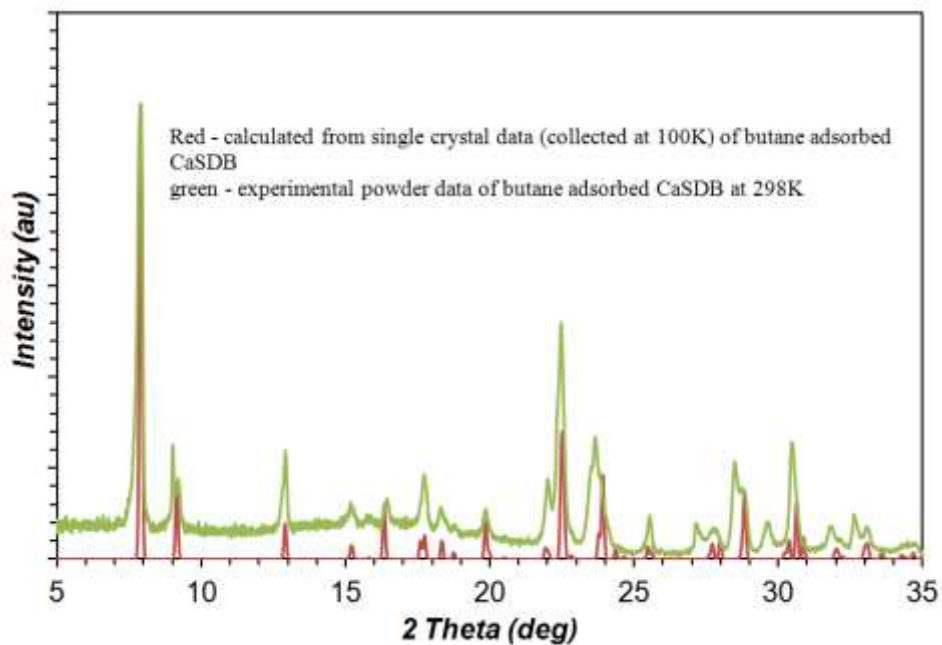
Fig. S12. Comparison of experimental PXRD patterns of butane loaded compound **1'** collected at 298 K (green) with calculated pattern (100 K, red).

Table S8. Physical properties of selected hydrocarbon molecules

Adsorbate	Size (Å) [#]			
	Length		Diameter	
	L1	L2	D1	D2
Ethane	3.2	3.9	2.1	2.8
Propane (C_3^o)	4.4	5.1	2.9	3.6
Propene ($C_3^=$)	4.2	4.9	3.3	4.0
n-Butane	5.6	6.4	2.9	3.6
n-Pentane	6.9	7.7	2.9	3.6
n-Hexane	8.2	8.9	2.9	3.6
n-Heptane	9.5	10.2	2.9	3.6

[#] The size of each molecule is measured by its molecular length and cross section as described in Ref. 9 [J. Li et. al. Commensurate Adsorption of Hydrocarbons and Alcohols in Microporous Metal Organic Frameworks. *Chemical Reviews* **112**, 836-868 (2012)].

3. Heats of Adsorption

We used Virial method to calculate the isosteric heats of adsorption, *Qst*. For gaseous hydrocarbons (C_2H_6, C_3H_6, n-C_4H_{10}), adsorption isotherms at 273, 288 and 298K were used for the calculations while for liquid ones (n-C_5H_{12}, n-C_6H_{14}, n-C_7H_{16}), adsorption isotherms at 373, 383 and 393K were used.

Virial equation:

$$\ln(p) = \ln(N) + \frac{1}{T}*(a_0 + a_1*N + a_2*N^2 + a_3*N^3 + a_4*N^4 + a_5*N^5 + a_6*N^6 + a_7*N^7 + a_8*N^8) + (b_0 + b_1*N + b_2*N^2 + b_3*N^3)$$

Where p is pressure, N is adsorbed amount, T is temperature, and a_0, a_1, a_2 … , a_8 and b_0, b_1, b_2, b_3 are temperature independent empirical parameters.

*Qst* are calculated using:

$$Q_{st} = RT^2 (\frac{\partial \ln p}{\partial T})_N$$

Fitted data (Fig. S13) and fitting parameters (Table S9) are shown below.

Table S9. Virial fitting parameters

Parameters	C_2H_6	C_3H_6	n-C_4H_{10}	n-C_5H_{12}	n-C_6H_{14}	n-C_7H_{16}
Reduced Chi-Sqr	0.0011	0.0048	0.0168	0.00037	0.0029	0.0028
Adj. R-Square	0.9989	0.9986	0.9956	0.9993	0.9961	0.9962
a_0	-4296.33	-5388.62	-6321.02	-8046.15	-9195.90	-9766.90
a_1	36.01029	-62.169	-98.2027	-726.769	-15.824	-62.33
a_2	-1.12503	5.62661	6.6135	126.76464	2.50532	1.5038
a_3	0.02503	-0.14194	-0.10819	-11.00562	-0.06707	-0.02424
a_4	2.793E-5	0.00124	6.265E-4	0.5568	6.593E-4	7.1572E-4
a_5	0	0	0.00277	-0.01695	0	0
a_6	0	0	-3.783E-5	3.057E-4	0	0
a_7	0	0	2.716E-7	-3.006E-6	0	0
a_8	0	0	-7.91E-10	1.242E-8	0	0
b_0	14.09856	16.0300	21.08846	25.4800	22.34216	22.60035
b_1	-0.06297	-0.06916	-0.18639	-0.09041	-0.03344	0.12769
b_2	0	0	0.0392	0	0	0
b_3	0	0	-3.722E-4	0	0	0

(a)

(b)

(c)

(d)

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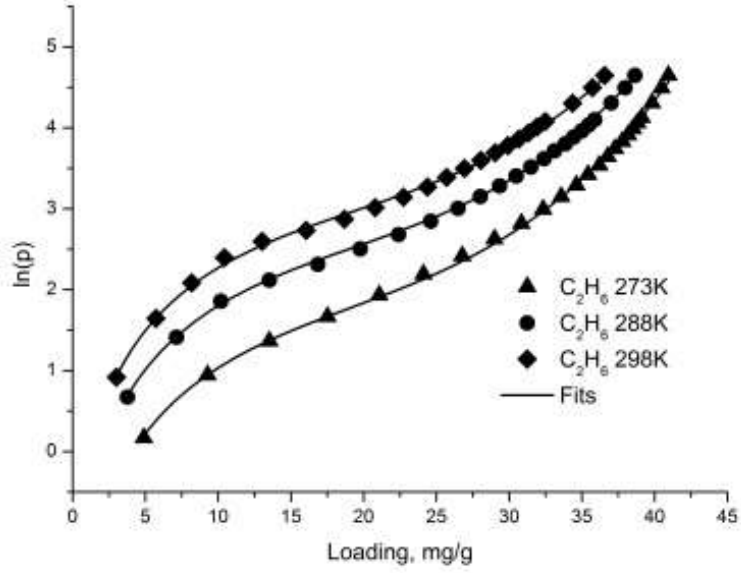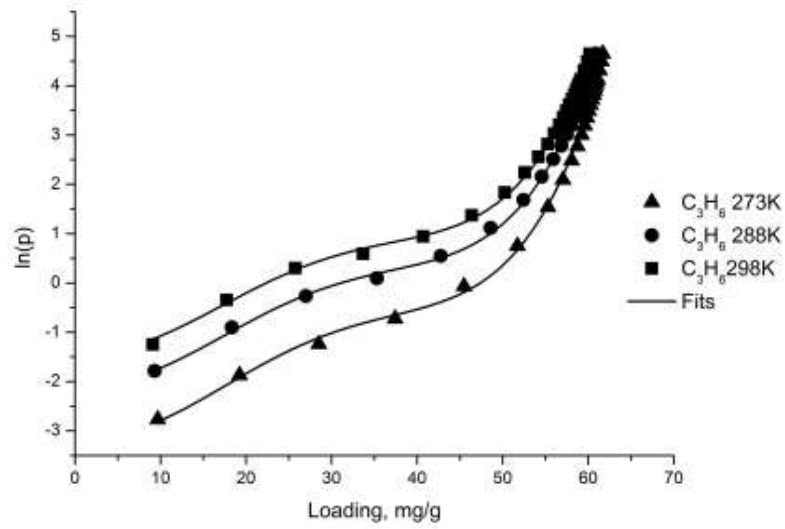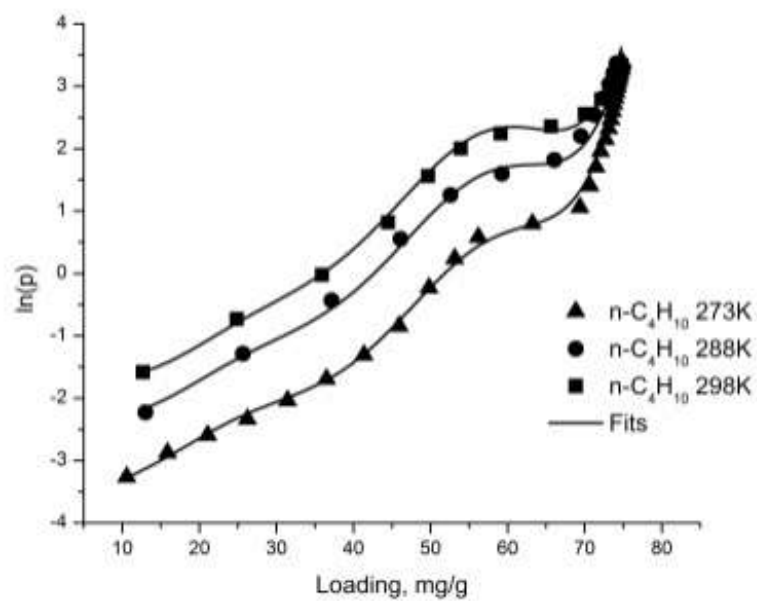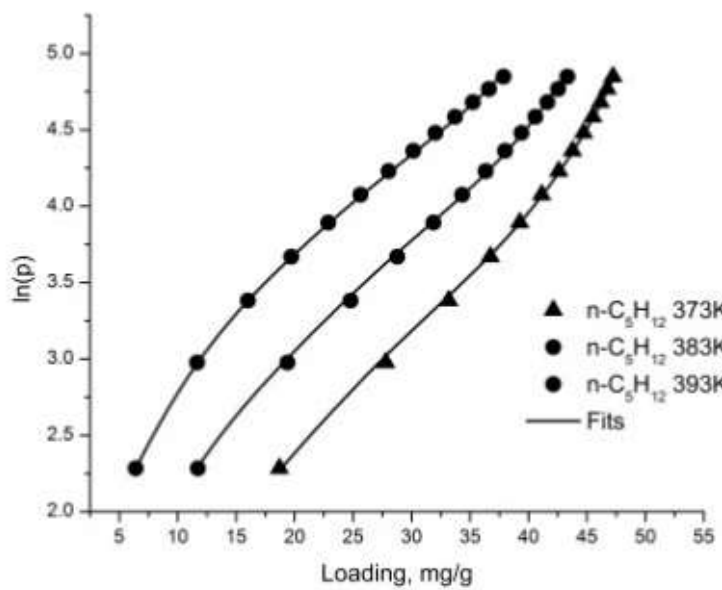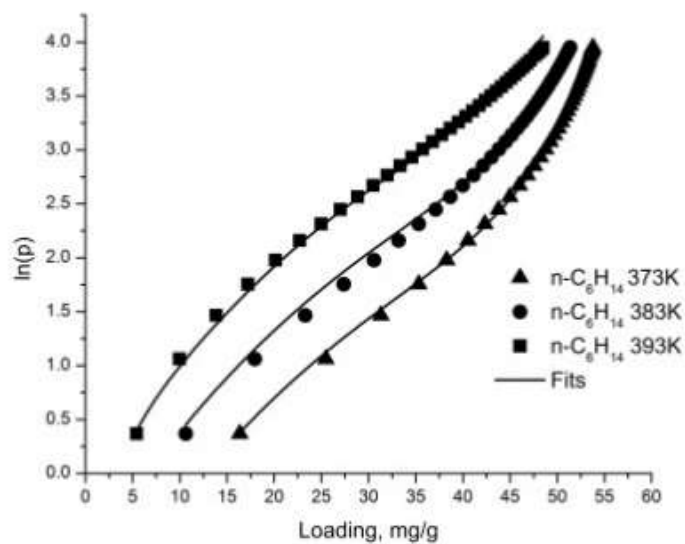
(e)
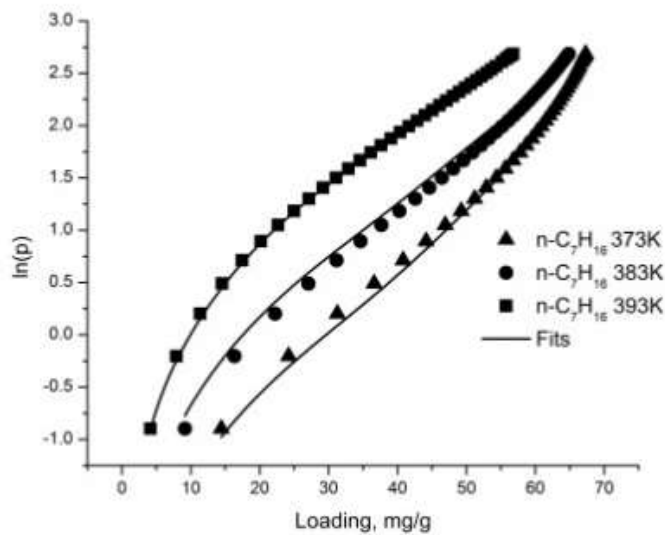
(f)

Fig. S13. Virial fits:(a) C_2H_6, (b) C_3H_6, (c) n-C_4H_{10}, (d) n-C_5H_{12}, (e) n-C_6H_{14}, and (f) n-C_7H_{16}.

4. *In situ* PXRD-DSC Measurements

PXRD-DSC measurements were obtained using a Rigaku Ultima IV diffractometer (Cu Kα) with a D/teX Ultra high speed one-dimensional position sensitive detector. The PXRD-DSC stage allows for simultaneous collection of PXRD patterns with DSC data in any controlled atmosphere (including vacuum) at any temperature between room temperature (RT) and 500 °C. The PXRD-DSC method allows for the evaluation of structural changes by measuring the gas sorption enthalpy. Experiments were conducted using 9.3 mg of as-synthesized compound **1** in an aluminum crucible with an equal amount of Al_2O_3 in the reference crucible. Each sample was activated *in situ* on the PXRD-DSC stage by pulling vacuum on the chamber and heating it to 300 °C at a rate of 2 °C/min and holding at 300 °C. The sample was then cooled to RT under vacuum, and vacuum-atmosphere swing measurements were conducted to determine the differential enthalpy between **1'** and propene/butane loaded **1'** at 298K and 1 atm. The strong interaction between the adsorbate and the framework leads to an incomplete removal under experimental vacuum conditions; as a result the enthalpies were calculated based on the averages of the exotherm of three different samples.

5. Molecular Simulation Study

The simulations were carried out by Cerius2 Sorption software (Accelrys Inc.) which employs the GCMC (grand canonical Monte Carlo) and Burchard Universal Force Field method. A box size of 35-40 Å in each crystallographic direction was chosen, containing multiple unit cells. Periodic boundary conditions were applied in all three directions. The number of configuration (~ $n \times 10^7$, n = 103), selected for a single simulation, is dependent on the energy convergence. Helium adsorption is simulated at a temperature of 1 K and pressure of 100 kPa. The simulation was carried out under experimental gas adsorption conditions.

References

1. Plonka, A.M. et al. Mechanism of Carbon Dioxide Adsorption in a Highly Selective Coordination Network Supported by Direct Structural Evidence. *Angew. Chem. Int. Ed.* **52**, 1692-1695 (2013).
2. Banerjee, D., Zhang, Z.J., Plonka, A.M., Li, J. & Parise, J.B. A Calcium Coordination Framework Having Permanent Porosity and High CO2/N-2 Selectivity. *Cryst. Growth Des.* **12**, 2162-2165 (2012).
3.Wang, H. et al. The first example of commensurate adsorption of atomic gas in a MOF and effective separation of xenon from other noble gases. *Chem. Sci.* **5**, 620-624 (2014).
40. Kim, H. et al. Highly Selective Carbon Dioxide Sorption in an Organic Molecular Porous Material. *J. Am. Chem. Soc.* **132**, 12200-12202 (2010).
41. Czepirski, L. & JagieŁŁo, J. Virial-type thermal equation of gas—solid adsorption. *Chem. Eng. Sci.* **44**, 797-801 (1989).