

Supporting Information

One-of-A-Kind: A Microporous Metal-Organic Framework Capable of Adsorptive Separation of Linear, Mono- and Di-branched Alkane Isomers via Temperature- and Adsorbate-Dependent Molecular Sieving

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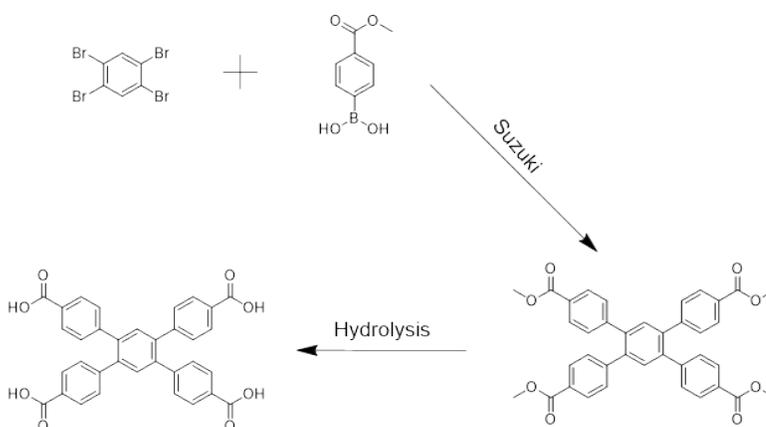
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Experimental Details

Materials and characterizations. All reagents were obtained from commercial sources and used without further purification. ^1H NMR data were collected on a 300 MHz Oxford NMR unit. Powder X-ray diffraction patterns were recorded on a Ultima IV with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Data were collected at room temperature at $2\theta = 3\text{-}40^\circ$ with a scan speed of 2° min^{-1} and operating power of 40 kV and 44 mA. Thermogravimetric analysis was carried out on a Q5000 (TA Instruments) analyzer. For each run 3-4 mg of sample was heated from room temperature to 600°C at a ramp rate of $10^\circ \text{C min}^{-1}$.

Synthesis of H_4tcpb . H_4tcpb was synthesized through Suzuki coupling reactions and subsequent hydrolysis: 1,2,4,5-tetrabromobenzene (1.97 g, 5 mmol), 4-Methoxycarbonylphenylboronic acid (5.4 g, 30 mmol), K_3PO_4 (6.36 g, 30 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.578 g, 0.5 mmol) were mixed in degassed 1,4-dioxane (200 mL). The mixture was heated at 90°C under nitrogen atmosphere for 3 days. After the reaction was complete, organic solvent was removed by rotovap and 100 mL of water was added to the solid residual which was extracted by dichloromethane ($3 \times 50 \text{ mL}$). The organic phase was combined and dried over MgSO_4 overnight. The organic solvent was removed by rotovap to give the crude product which was purified by column chromatography (eluent: Hexane/ethyl acetate= 4:1 and then dichloromethane). The obtained ester was hydrolyzed in a mixture of KOH aqueous solution (3M, 50 mL), 1,4-dioxane (50 mL), and methanol (50 mL) by reflux overnight to give pure form of H_4tcpb (2.1 g, Yield: 75%). ^1H NMR (300 MHz, $\text{DMSO-}d_6$, δ): 7.35 (d, 8H, Ar H), 7.56 (s, 2H, Ar H), 7.84 (d, 8H, Ar H), 12.97 (s, 4H, COOH).

Scheme S1. Synthesis of H_4tcpb .



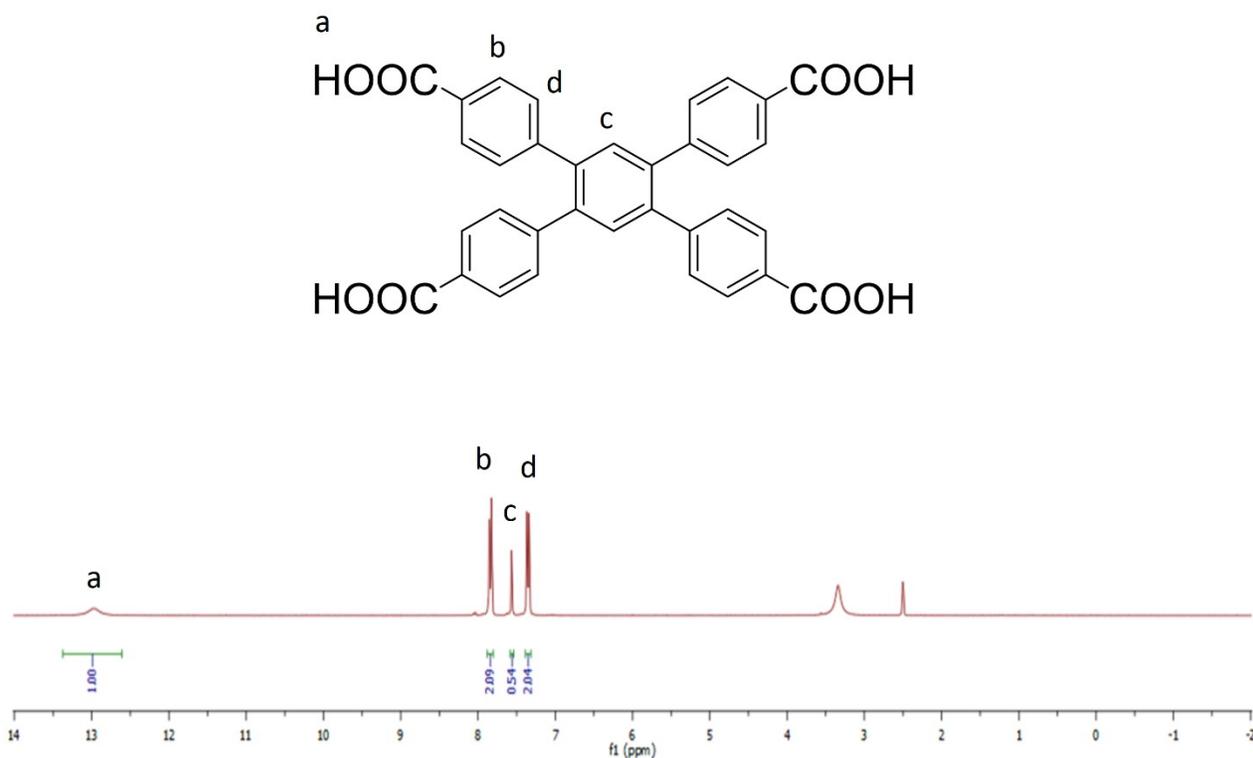


Fig. S1. ^1H NMR spectrum of H_4tcpb .

Synthesis of $\text{Ca}(\text{H}_2\text{tcpb})$. $\text{CaCl}_2 \cdot x\text{H}_2\text{O}$ (90 mg) and H_4tcpb (90 mg) was added to ethanol (10 mL) and the mixture was stirred at room temperature for 2 hours before being transferred to a 20 mL Teflon bomb. The bomb was placed at an oven preset at $100\text{ }^\circ\text{C}$ for 3 days. Colorless crystals were obtained after the reaction was cooled to room temperature (Yield: 25% based on the organic ligand).

Hydrocarbon adsorption measurements. Single component hydrocarbon adsorption experiments were performed on a gravimetric adsorption unit modified from a Q50 thermogravimetric analyzer (TA Instruments). For each measurement, ~ 20 mg of MOF sample was heated at $200\text{ }^\circ\text{C}$ under nitrogen flow for 2 hours to remove any residual solvent in the pore. After cooling down to the adsorption temperature ($30, 60, 90, 120,$ or $150\text{ }^\circ\text{C}$) another nitrogen flow passing through a hydrocarbon bubbler connected to a condenser maintained at $18\text{ }^\circ\text{C}$ was mixed with the pure nitrogen stream and then introduced to the adsorption chamber. A certain hydrocarbon partial pressure was achieved by adjusting the relative flow rates of the two gas streams. Sample weight was recorded throughout the process which dictates the adsorbed amount of the adsorbate.

Multicomponent breakthrough measurements. The two-column breakthrough experiment was conducted using two lab-scale fix-bed reactors at 120 and 60 °C, respectively. Similarly, the one-column breakthrough measurement was performed with a lab-scale fix-bed reactor at 120 or 60 °C. In a typical experiment, 0.25 g of MOF material was packed into a quartz column (5.8 mm I.D. ×150 mm) with silane treated glass wool filling the void space. A nitrogen flow (1 mL min⁻¹) was used to purge the adsorbent. The MOF powder was activated at 200 °C overnight and the flow of Nitrogen was then turned off while another dry nitrogen flow at a rate of 1 mL/min was bubbled through a mixture of hexane isomers according to the following volumes (the volumes were determined through trial and error and calculated by GC: the experiment was run without any sample and the vapor phase ratios were optimized to an equimolar mixture): 5.84 mL of nHEX, 4.12 mL of 3MP, and 2.57 mL of 22DMB for nHEX/3MP/22DMB ternary mixture (partial pressure of each component is 49 torr), 7.56 mL of nHEX and 4.22 mL of 3MP for nHEX/3MP binary mixture (partial pressure of each component is 72 torr), 4.22 mL of 3MP, and 2.47 mL of 22DMB for 3MP/22DMB binary mixture (partial pressure of each component is 78 torr). For humid conditions, another nitrogen flow bubbling through a water bubbler was mixed with the 3MP/22DMP binary mixture (partial pressure of each alkane component is 39 torr). The effluent from the column was monitored using an online GC equipped with HP-PONA column and FID. The absolute adsorbed amount of gas *i* (*q_i*) is calculated from the breakthrough curve by the equation:

$$q_i = \frac{F_i \times t_0 - V_{dead} - \int_0^{t_0} F_e \Delta t}{m}$$

Where *F_i* is the influent flow rate of the specific gas (cm³ min⁻¹); *t₀* is the adsorption time (min); *V_{dead}* is the dead volume of the system (cm³); *F_e* is the effluent flow rate of the specific gas (cm³/min); and *m* is the mass of the sorbent (g).

The breakthrough experiment of pure hydrocarbon feeds was conducted using a lab-scale fix-bed reactor at 60 °C. In a typical experiment, 0.25 g of MOF material was packed into a quartz column (5.8 mm I.D. ×150 mm) with silane treated glass wool filling the void space. A nitrogen flow (1 cm³/ min) was used to purge the adsorbent. The MOF powder was activated at 200 °C overnight and the flow of nitrogen was then turned off while the liquid hydrocarbon mixture (22DMB:3MP = 1:1) was pumped into the reactor using a KDS LEGATO® 200 syringe pump with a flow rate of 120 μL/hr (The flow rate of the liquid hydrocarbon mixture is small and the gas phase flow is not quite stable). The syringe pump was connected to the reactor using stainless steel capillary. The effluent from the column was carried into the GC using 5 cm³/ min of nitrogen and was monitored using an online GC equipped with HP-PONA column and FID. All the tubes and stainless steel capillary were heated to keep the temperature at 60 °C to prevent condensation.

PXRD measurement on the alkane loaded Ca(H₂tcpb). ~20 mg of as synthesized MOF was activated at 150 °C on a TGA for 30 minutes. The activated sample was immersed in 5 mL of alkane (nHEX, 3MP, or 22DMB) overnight. The solid was pipetted out for PXRD measurement.

Adsorption simulation. Simulation of helium adsorption was performed using Cerius2 software (Accelrys, Inc.). GCMC method and Burchard Universal Force Field were employed in the modeling system. The simulation was carried out with a unit of ~ 40 × 40 × 40 Å of the MOF framework which contains several unit cells. The simulation was done at 10 K and 1 bar.

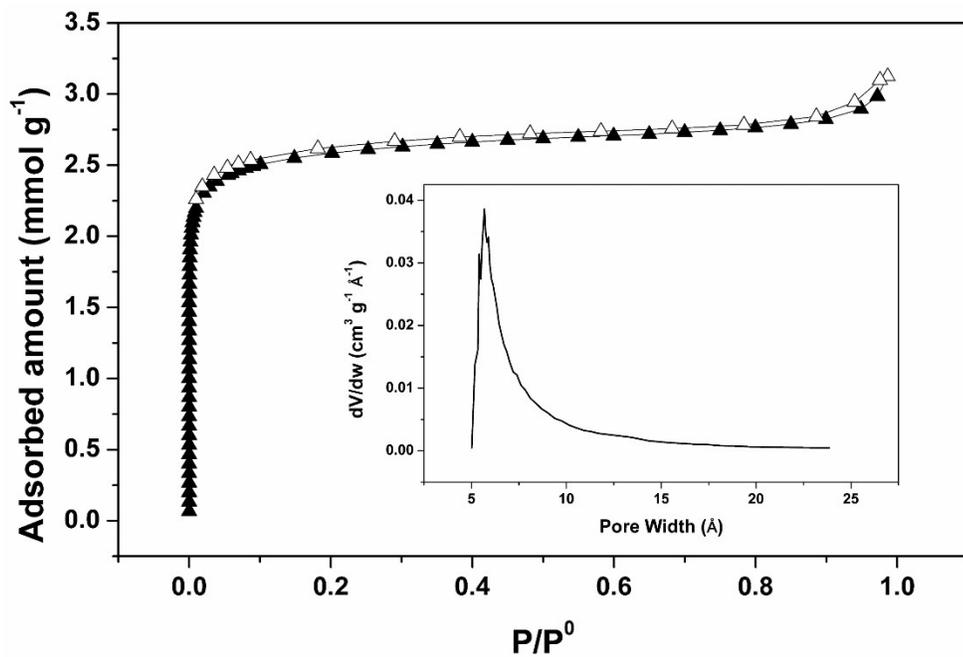


Fig. S2. N₂ adsorption-desorption isotherm at 77 K (open and closed symbols represent adsorption and desorption branches, respectively). Insert: H-K pore size distribution.

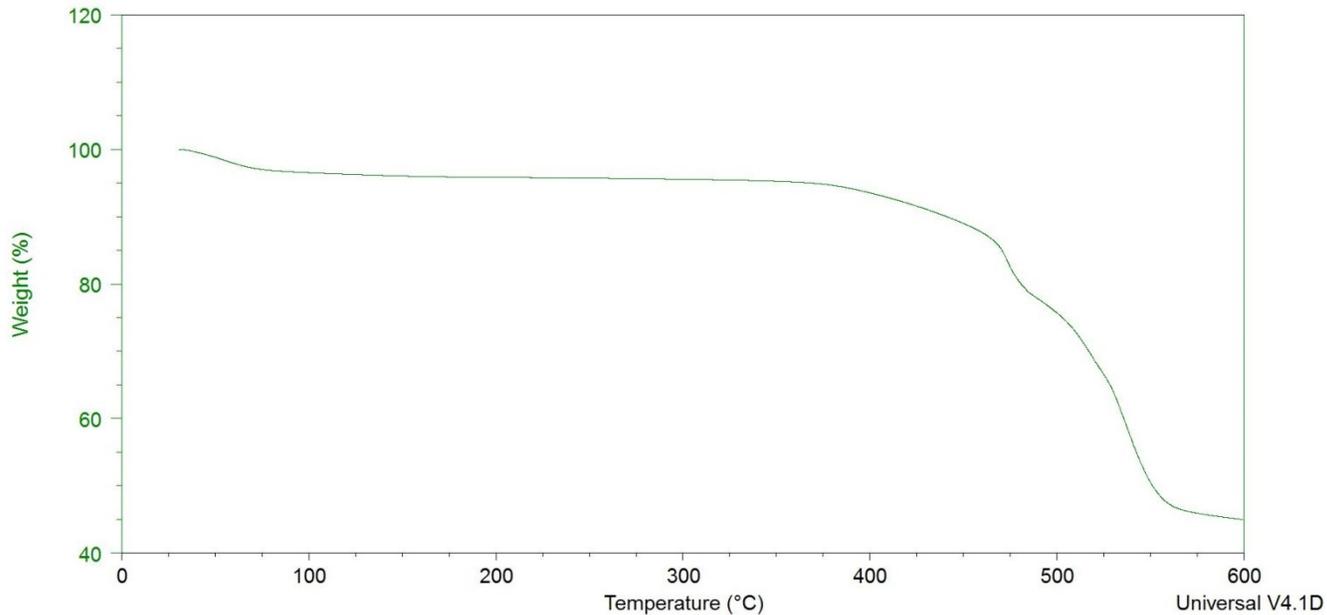


Fig. S3. TGA of as synthesized Ca(H₂tcpb)·xH₂O.

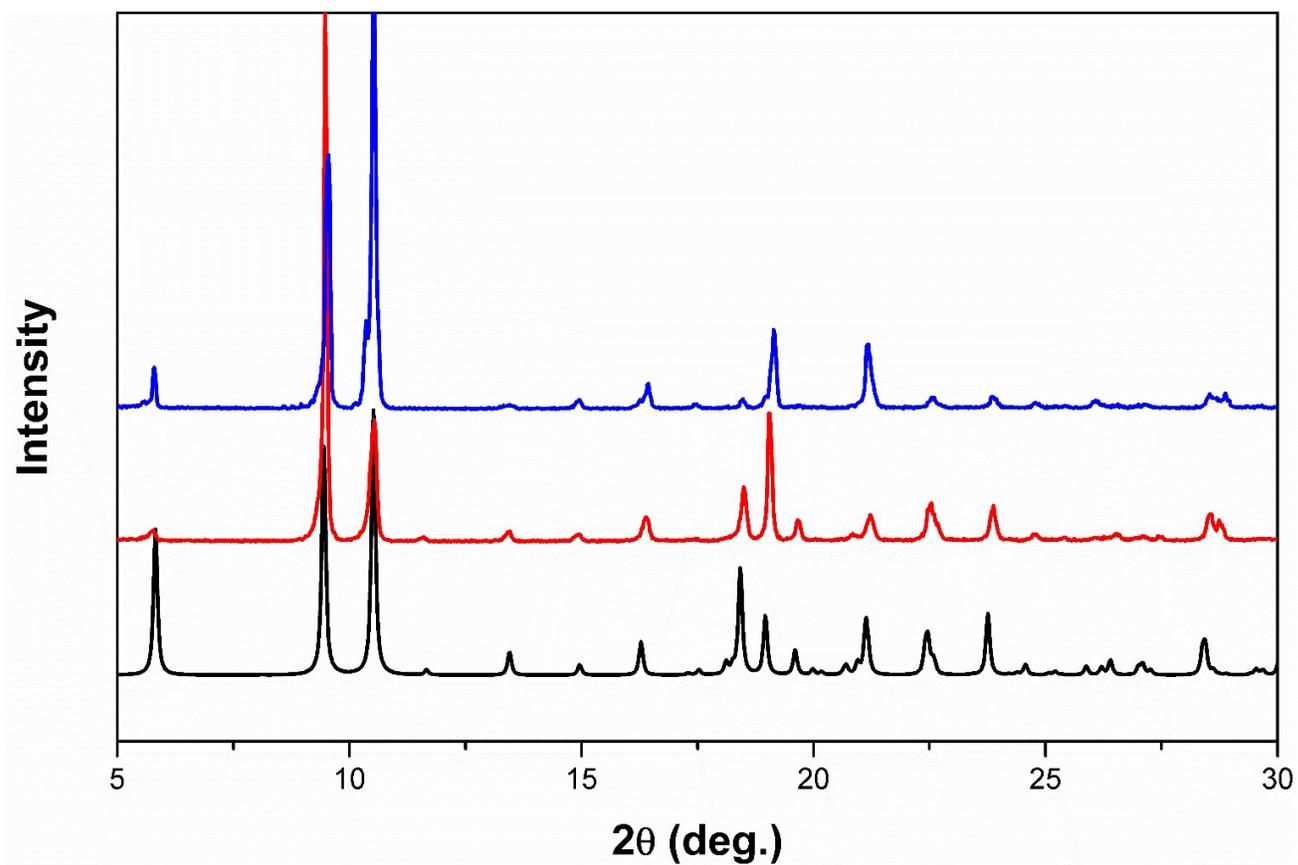


Fig. S4. PXRD of as-synthesized $\text{Ca}(\text{H}_2\text{tcpb})$. From bottom to top: Simulated (black), fresh (red), and on shelf for 3 years (blue).

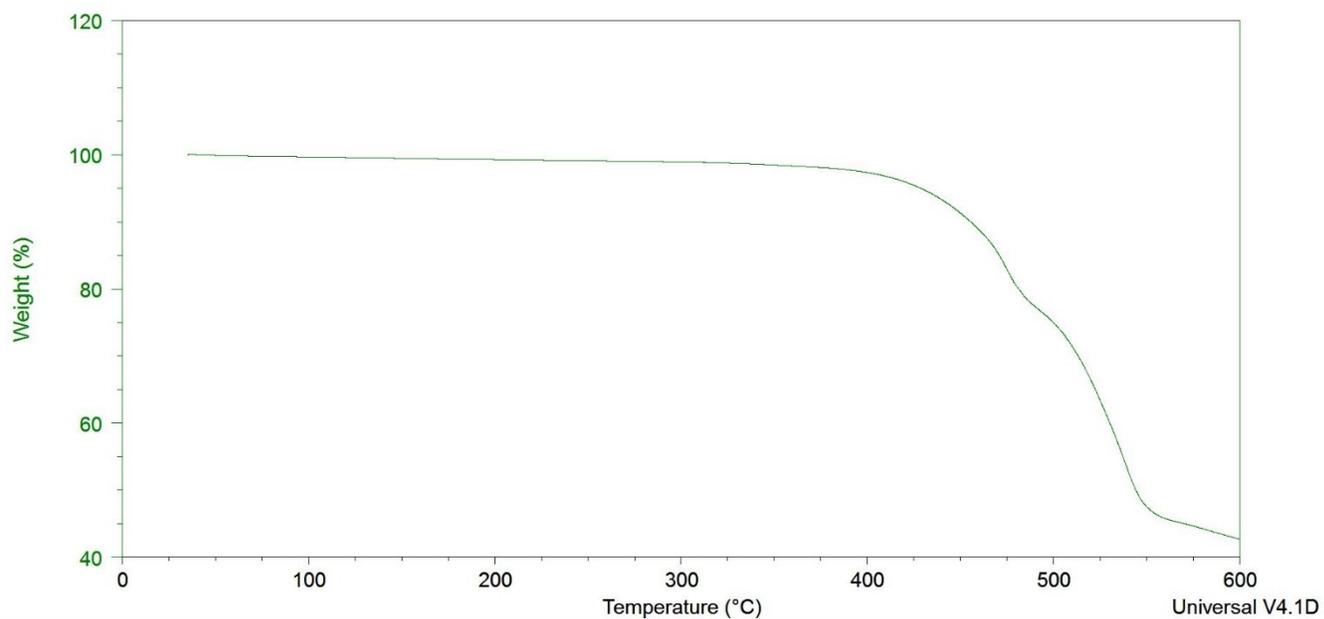


Fig. S5. TGA of activated $\text{Ca}(\text{H}_2\text{tcpb})$ after being exposed in open air for 5 days.

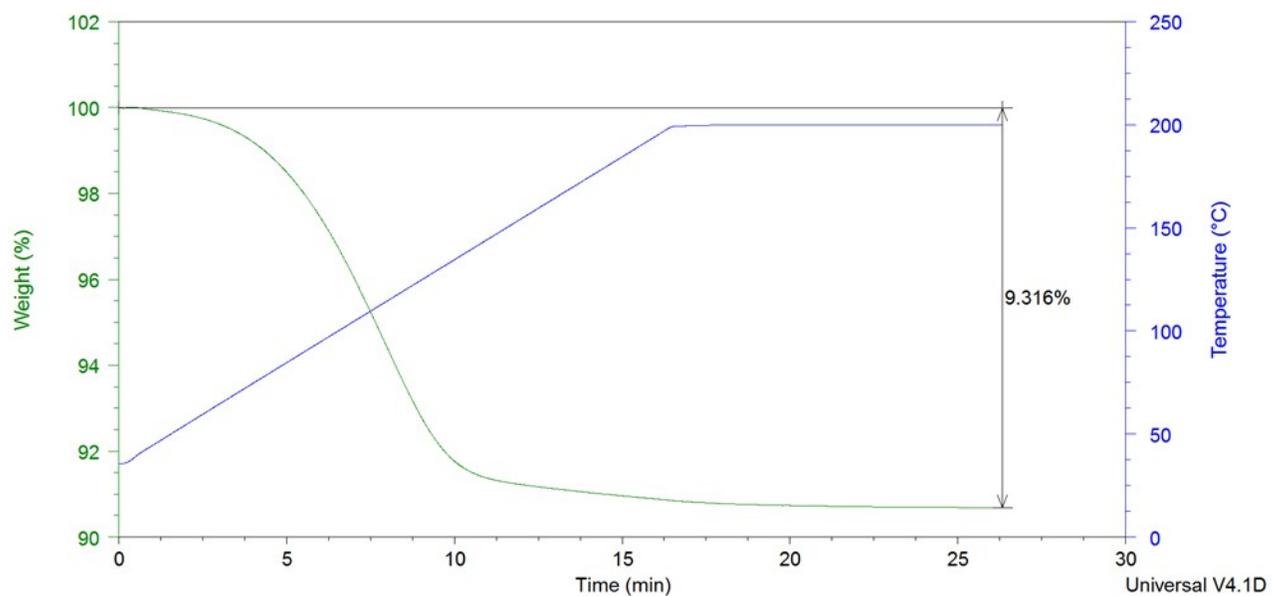


Fig. S6. TGA curve of nHEX loaded $\text{Ca}(\text{H}_2\text{tcpb})$.

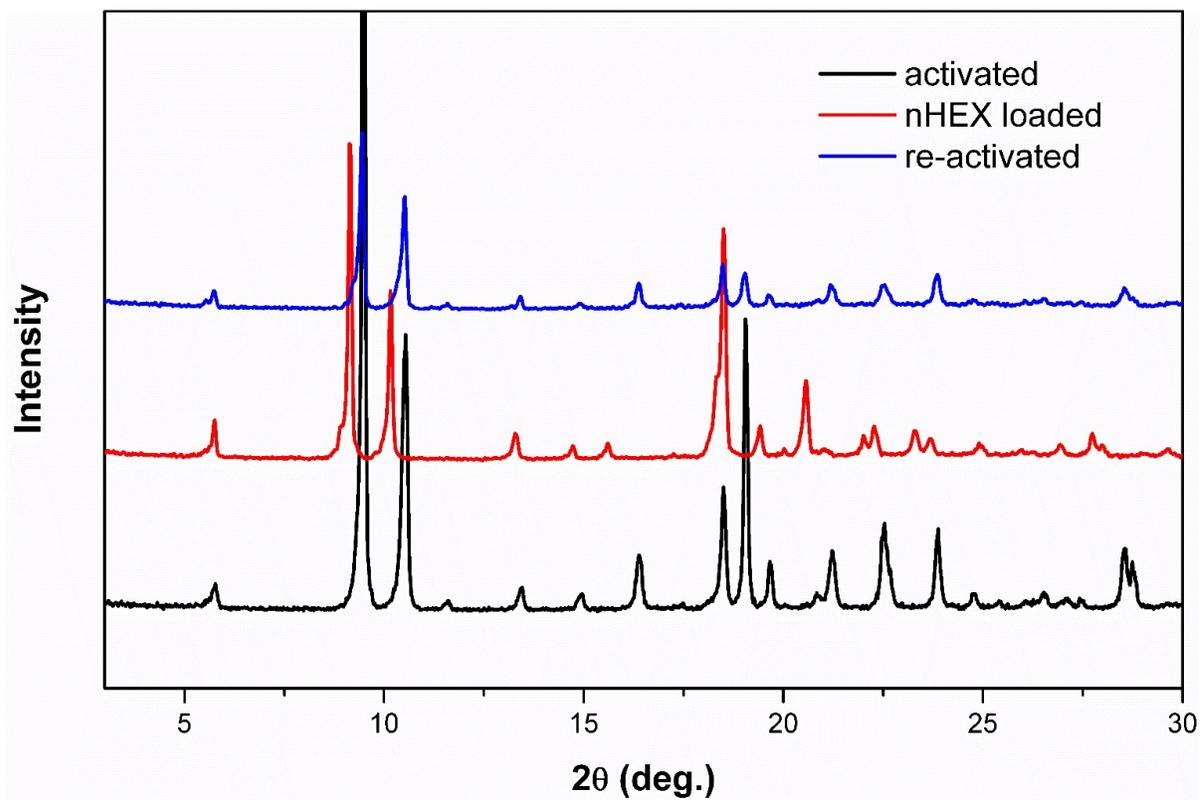


Fig. S7. PXRD patterns $\text{Ca}(\text{H}_2\text{tcpb})$: Activated (black), nHEX loaded (red), and reactivated (blue).

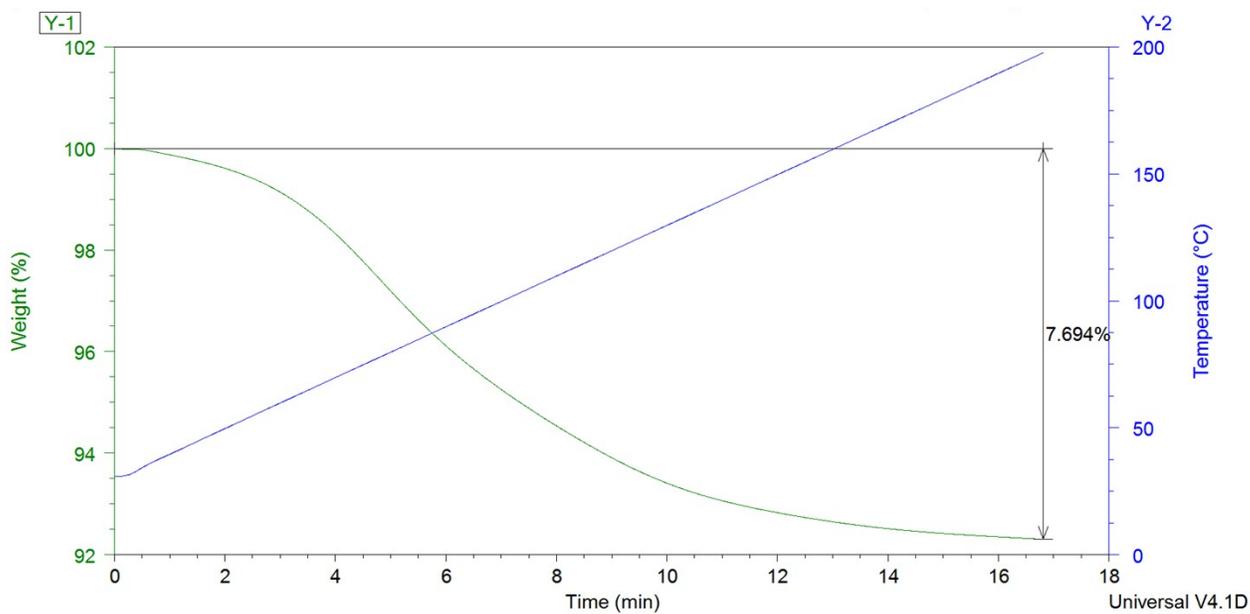


Fig. S8. TGA curve of 3MP loaded Ca(H₂tcpb).

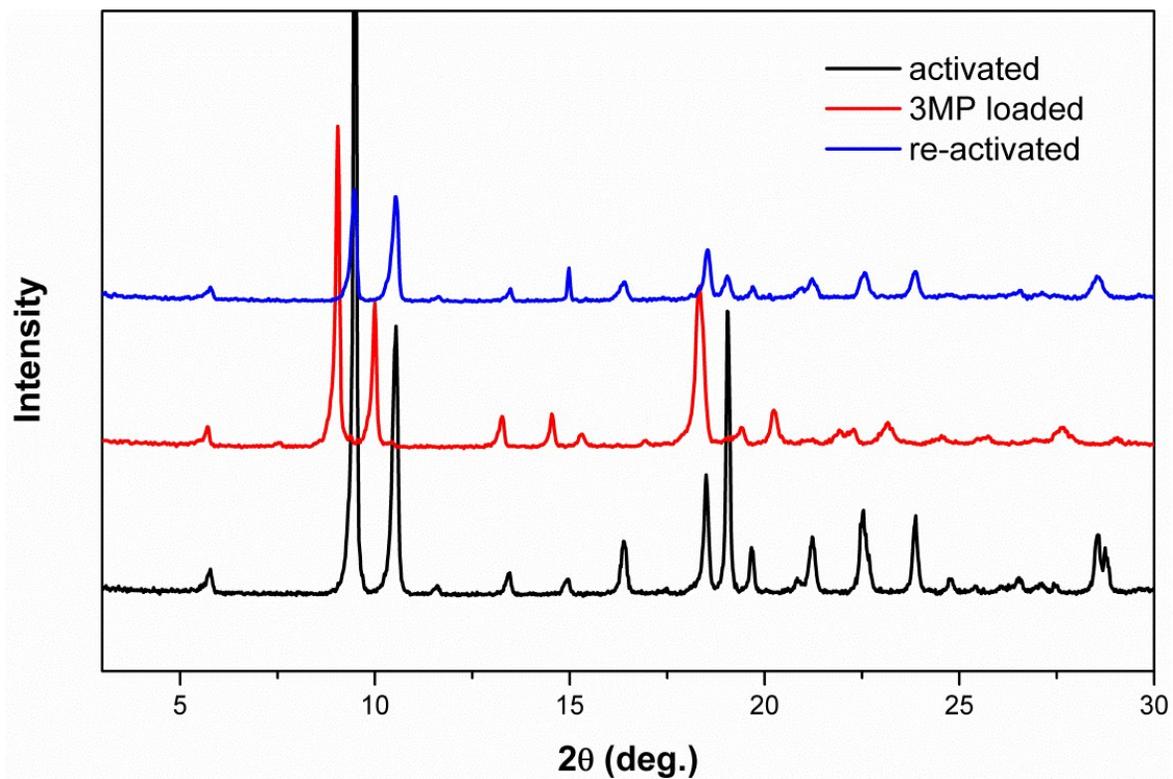


Fig. S9. PXRD patterns Ca(H₂tcpb): Activated (black), 3MP loaded (red), and reactivated (blue).

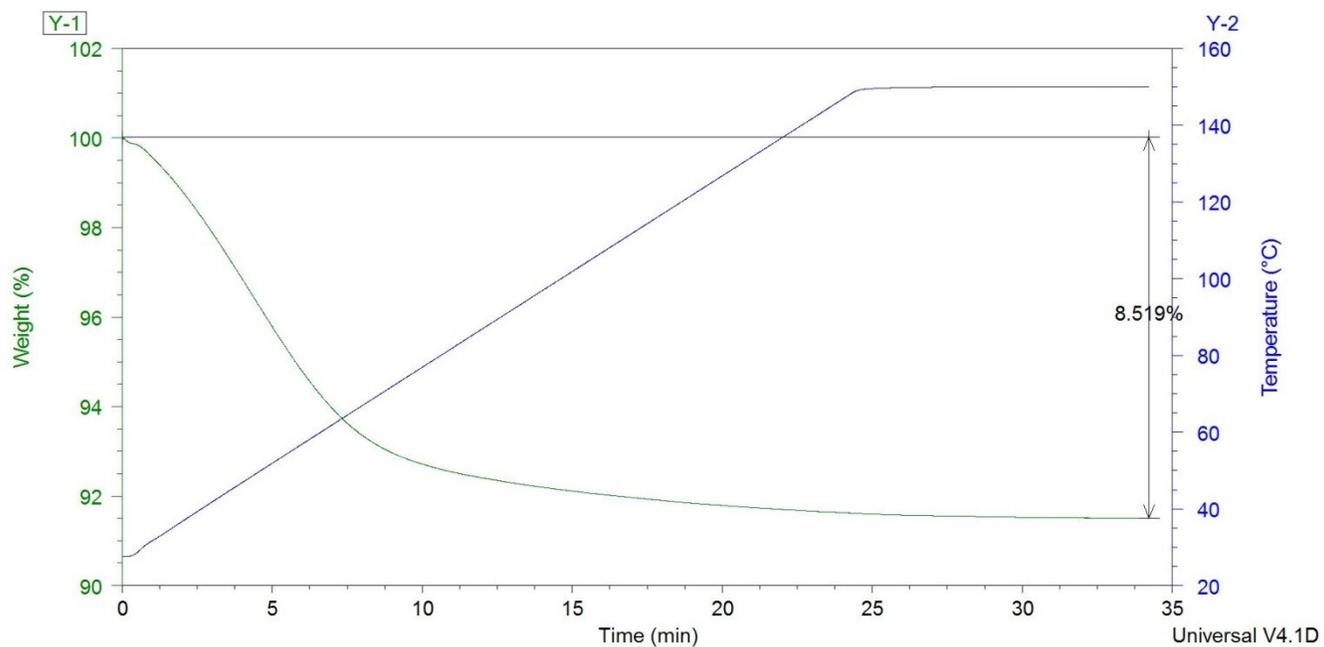


Fig. S10. TGA curve of 22DMB loaded Ca(H₂tcpb).

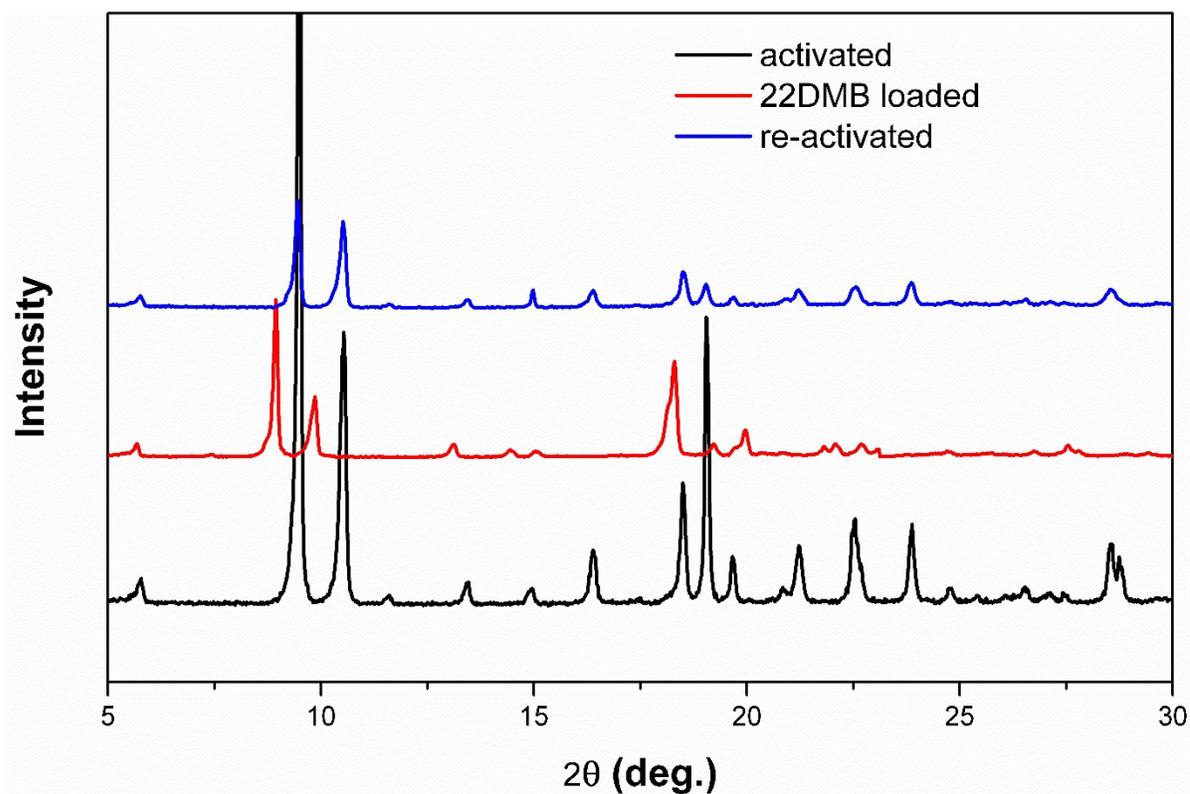


Fig. S11. PXRD patterns Ca(H₂tcpb): Activated (black), 22DMB loaded (red), and reactivated (blue).

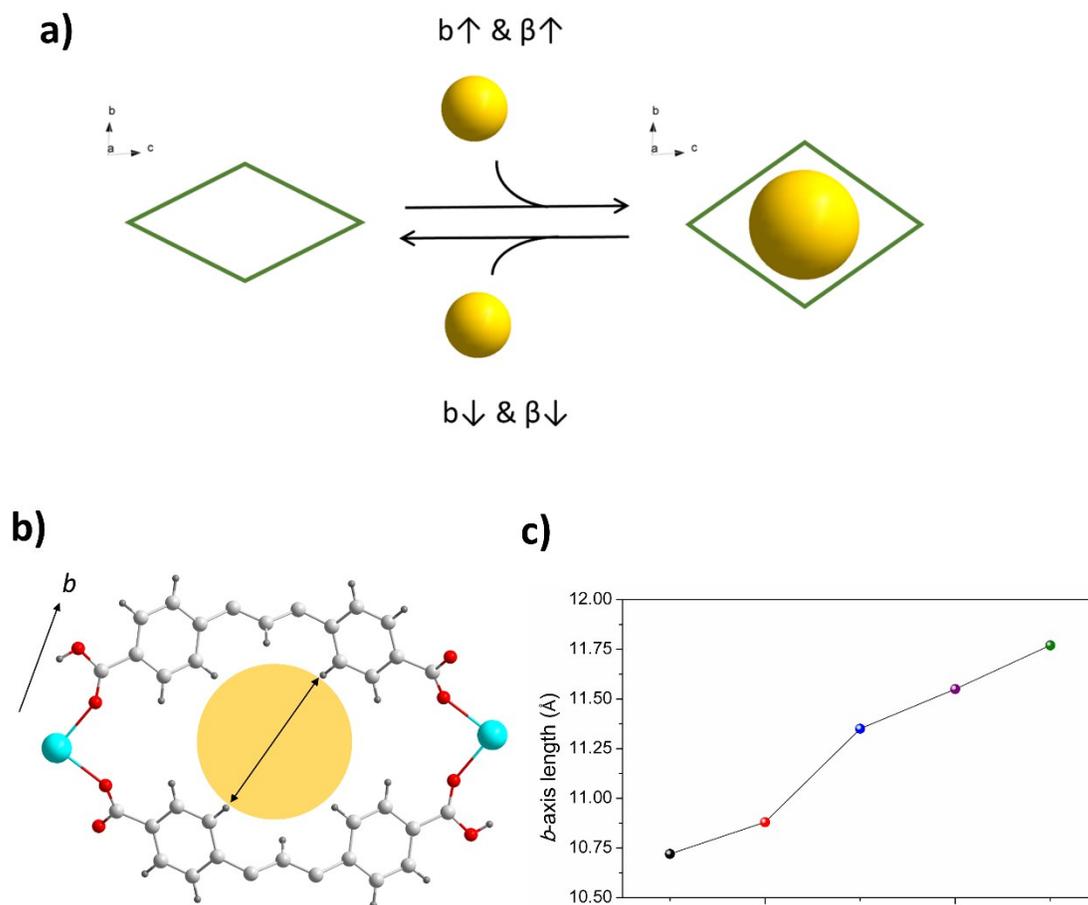


Fig. S12. (a) Schematic representation of the pore enlargement of $\text{Ca}(\text{H}_2\text{tcpb})$ upon guest inclusion. (b) Structure drawing showing the direct correlation between the changes in the b -axis and pore window size. (c) Plotted length of b -axis of activated (black), as synthesized (red), nHEX loaded (blue), 3MP loaded (purple), and 22DMB loaded (green) $\text{Ca}(\text{H}_2\text{tcpb})$.

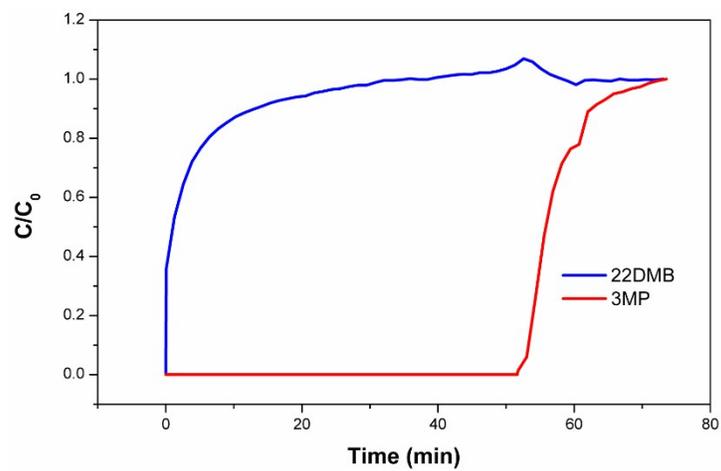


Fig. S13. Column breakthrough results for an equimolar binary mixture of 3MP and 22DMB under humid (50%RH) conditions.

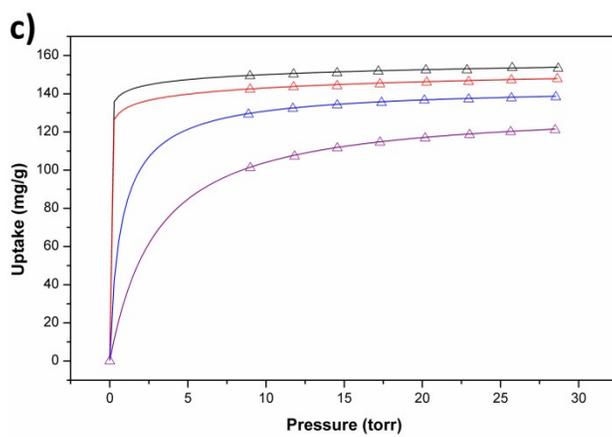
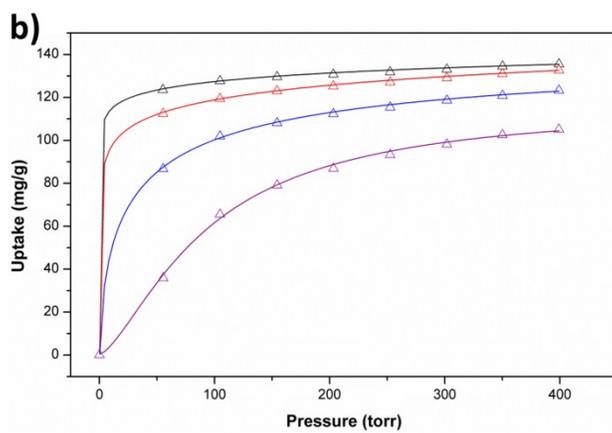
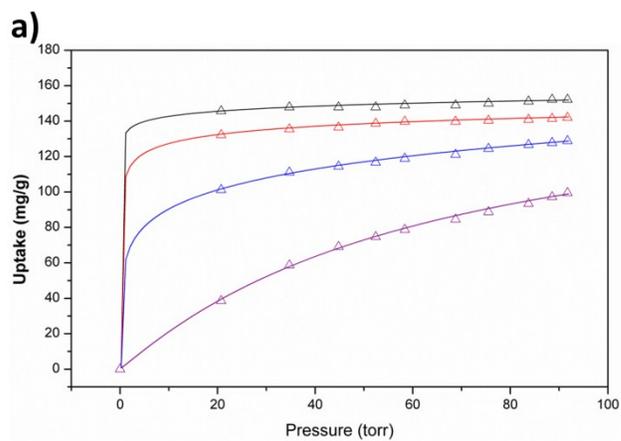


Fig. S14. Adsorption isotherms of (a) nHEX, (b) nPEN, and (c) nHEP on Ca(H₂tcpb). Color scheme: 30 °C (black), 60 °C (red), 90 °C (blue), and 120 °C (purple).

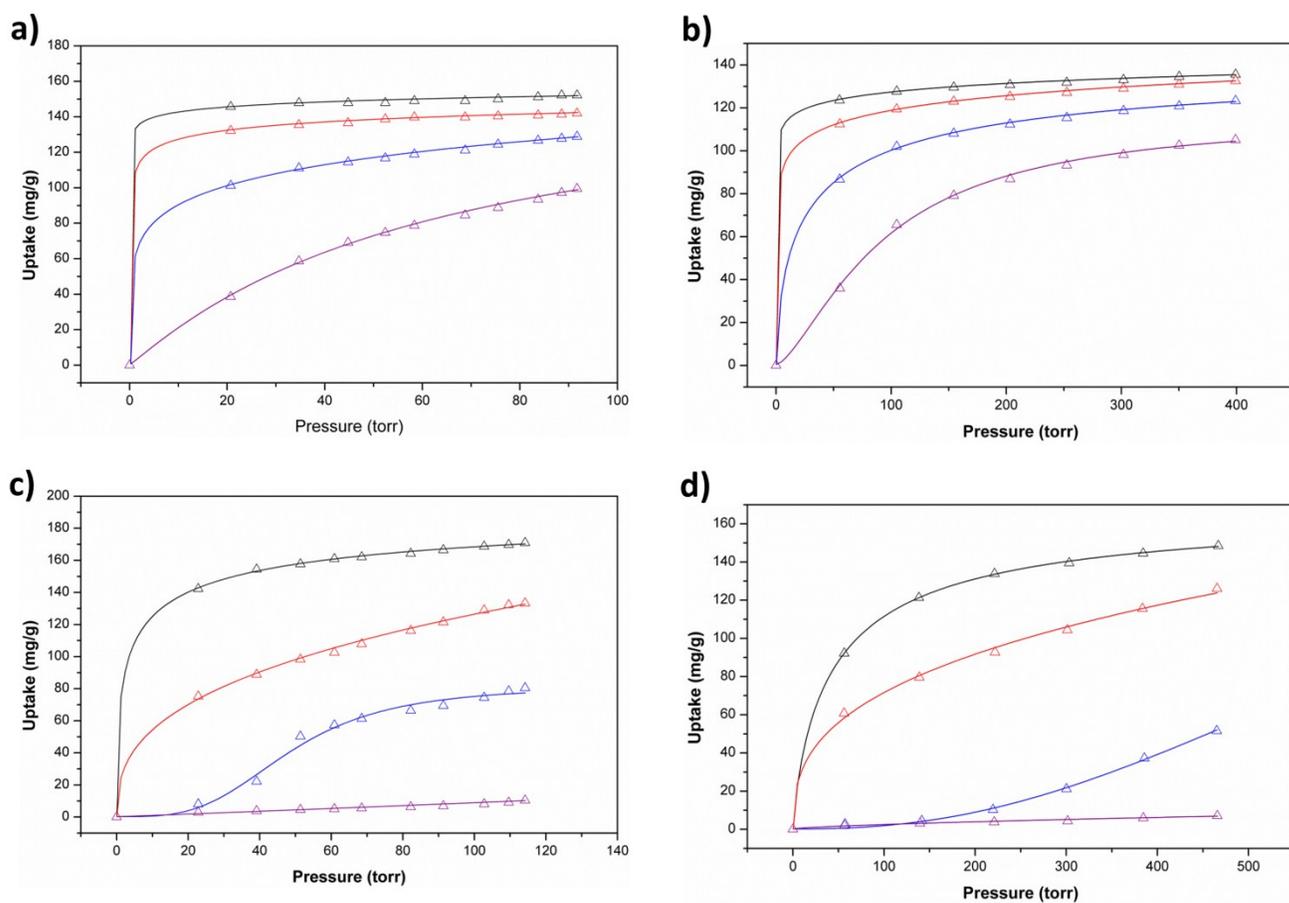


Fig. S15. Adsorption isotherms of C5 and C6 alkane isomers on Ca(H₂tcpb). (a) nHEX, (b) nPEN, (c) 3MP, (d) 2MB. Color scheme: 30 °C (black), 60 °C (red), 90 °C (blue), and 120 °C (purple).

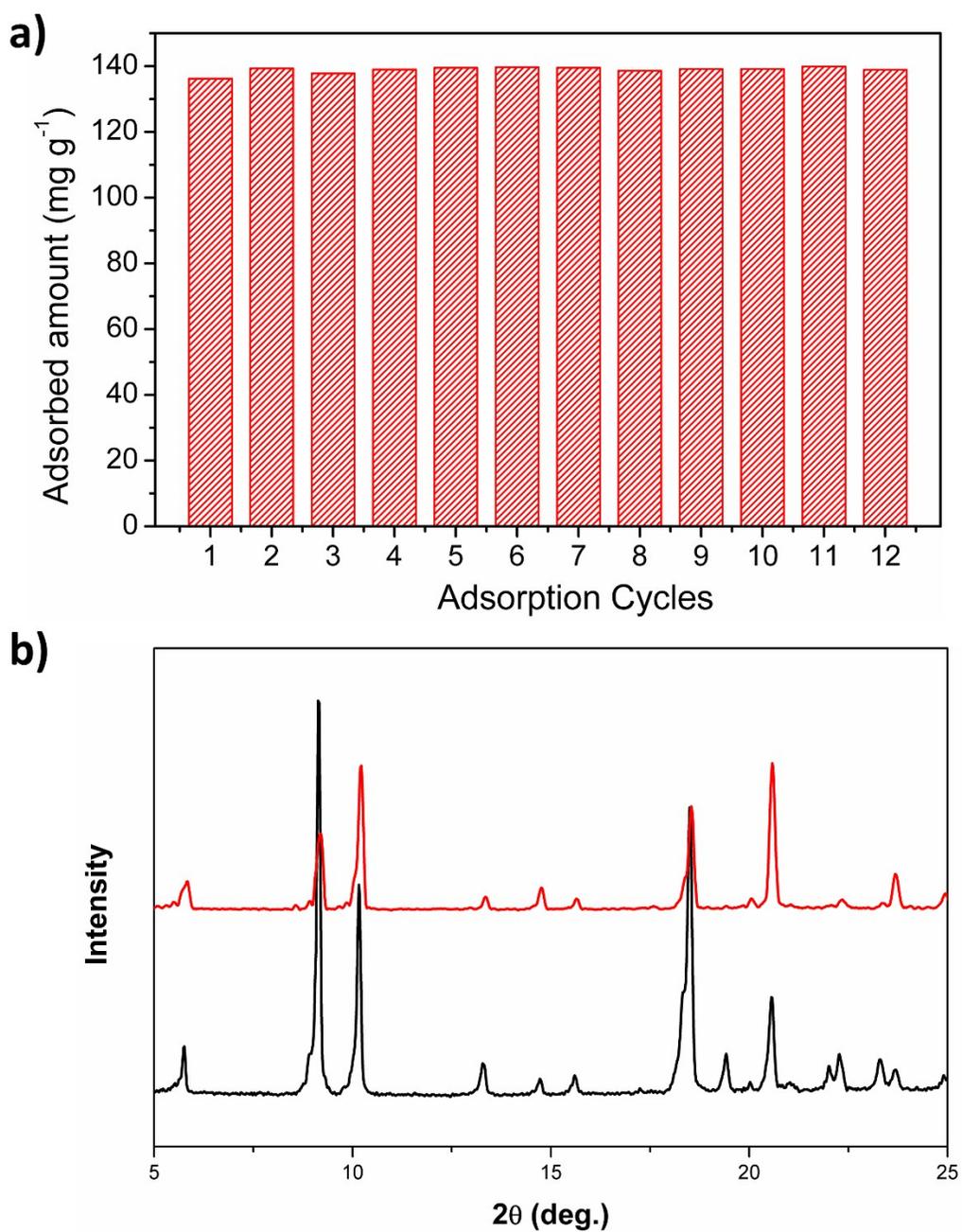


Fig. S16. (a) Adsorbed amount of nHEX for the 12 consecutive adsorption cycles of Ca(H₂tcpb) (Adsorption condition: 60 °C, nHEX vapor pressure 100 torr; Regeneration condition: 150 °C, nitrogen flow). (b) PXRD patterns of Ca(H₂tcpb) before (black) and after (red) the 12 adsorption-desorption cycles.

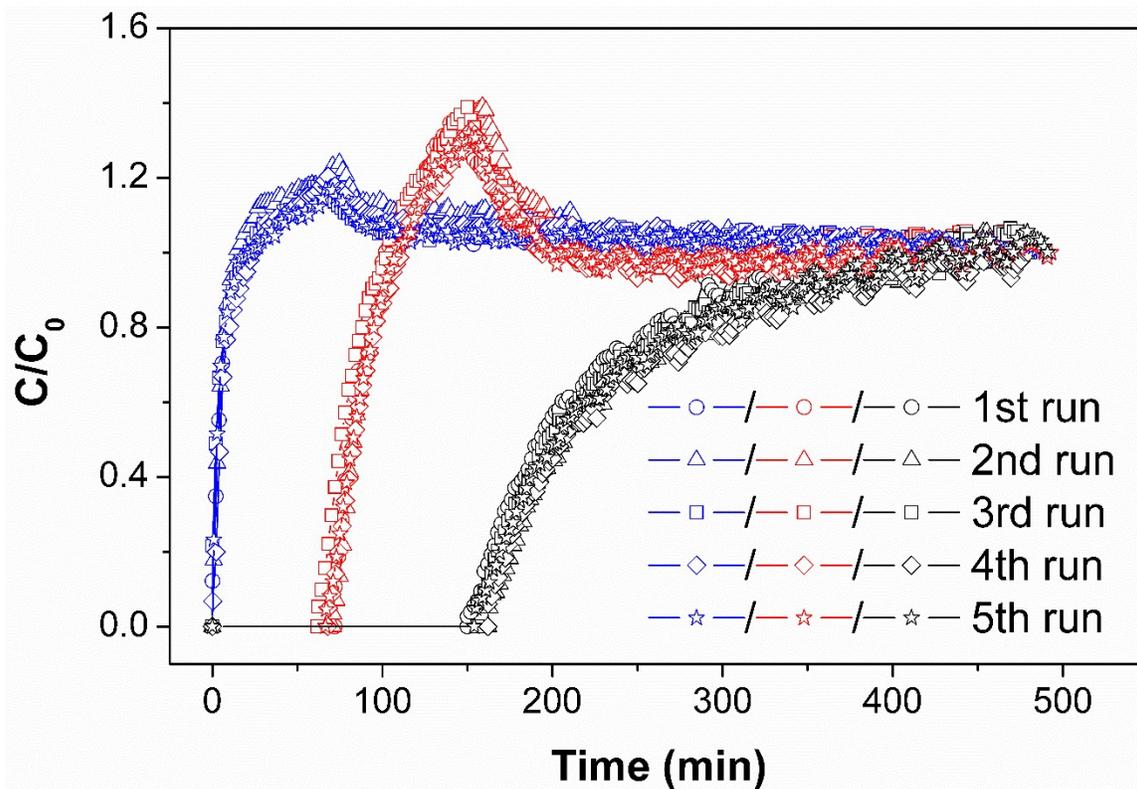


Fig. S17. Breakthrough curves of the 5 consecutive cycles of a ternary mixture of nHEX, 3MP, and 22DMB, using the same setup depicted in Figure 3a. Black, red, and blue curves represent nHEX, 3MP, and 22DMB, respectively.

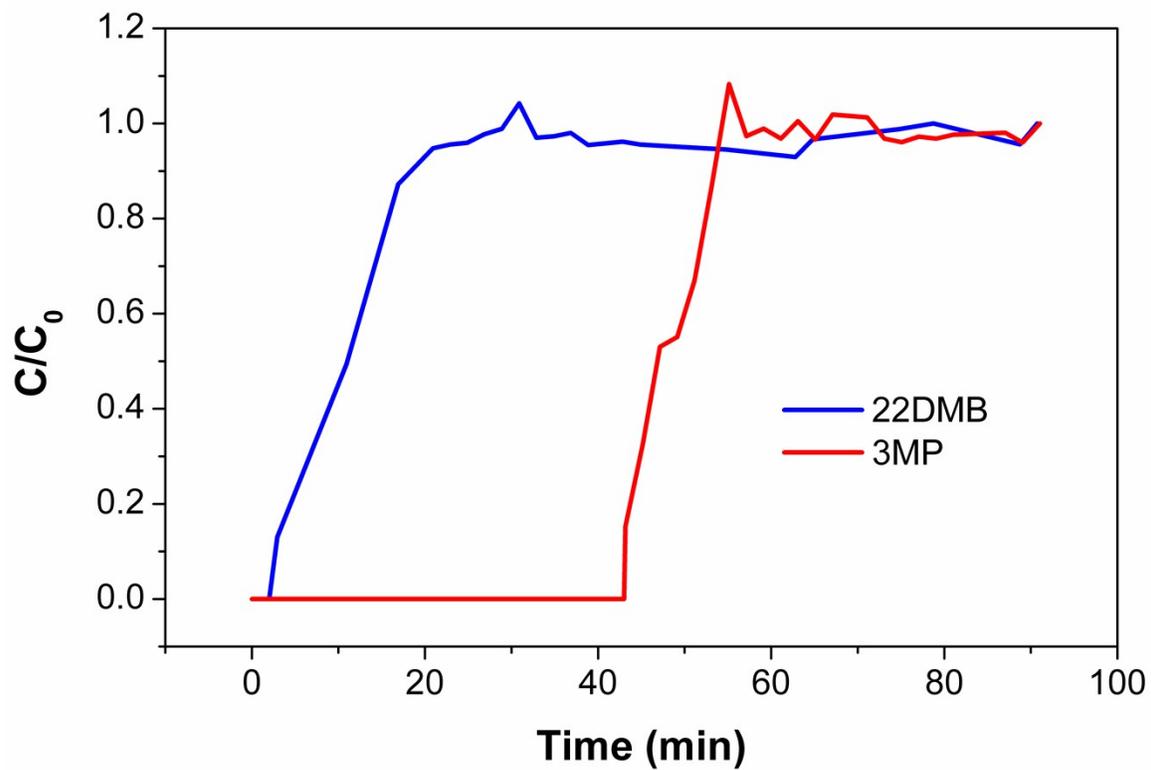


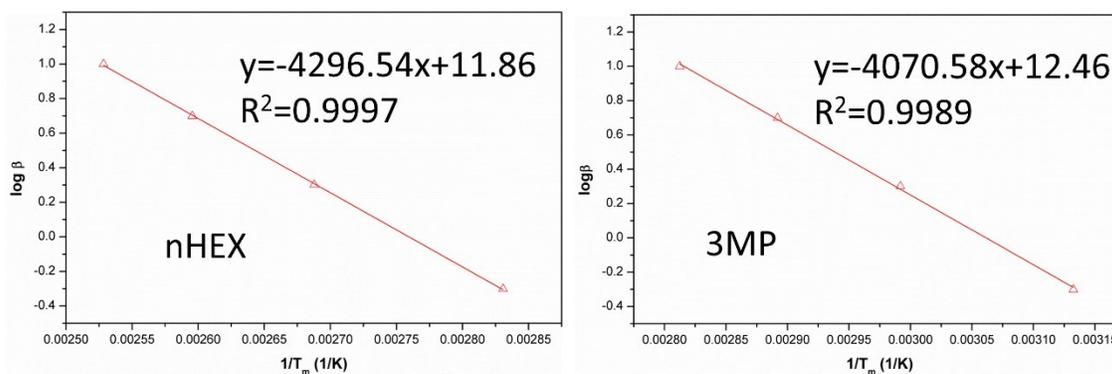
Fig. S18. Column breakthrough results for an equimolar binary liquid mixture of 3MP and 22DMB (60 °C, without carrier gas).

Desorption energy fitting

$$-\log \beta = \alpha + (\Delta H / 2.21R)(1/T_m)$$

β is the ramp rate K/min, α is a constant, T_m is the temperature corresponding to peak maximum.

β (K/min)		0.5	2	5	10
nHEX	T_m ($^{\circ}\text{C}$)	80.13	98.90	112.72	122.36
	T_m (K)	353.28	372.05	385.27	395.51
3MP	T_m ($^{\circ}\text{C}$)	46.08	61.10	72.65	82.42
	T_m (K)	319.23	334.25	345.8	355.57



$$\Delta H(\text{nHEX}) = 2.21 \times 8.314 \times 4296.54 = 78944 \text{ J/mol} = 78.9 \text{ kJ/mol}$$

$$\Delta H(\text{3MP}) = 2.21 \times 8.314 \times 4070.58 = 74.793 \text{ J/mol} = 74.8 \text{ kJ/mol}$$

Fig. S19. Calculation of desorption energy of nHEX and 3MP by temperature-programmed desorption from adsorption at 30 $^{\circ}\text{C}$ and 100 torr. Desorption of 22DMB occurred too fast so calculation cannot be done, but this is an indication of its low adsorption affinity.

Table S1. Selected crystallographic data of Ca(H₂tcpb) and Ca(H₂tcpb)·xH₂O

	Ca(H ₂ tcpb) (activated)	Ca(H ₂ tcpb)·xH ₂ O (as synthesized)
a (Å)	5.1011(3)	5.1594(2)
b (Å)	10.8715(9)	11.0274(6)
c (Å)	15.2363(8)	15.2740(8)
α (°)	83.132(5)	83.310(4)
β (°)	85.982(4)	87.657(4)
γ (°)	83.032(5)	83.128(4)
Volume (Å ³)	831.37(10)	856.57(7)