Supporting Information

A $[Th_8Co_8]$ Nanocage-based MOF with Extremely Narrow Window but Flexible Nature Enabling Dual-Sieving Effect for both Isotope and Isomer Separation

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Experimental Section

Materials and physical measurements. All chemicals were directly purchased from innochem with no further purification. The optical images were accepted from Optec SZ810 microscope. Thermogravimetric analysis (TG) was performed by a TGA Q500 under a N_2 atmosphere from room temperature to 800 °C at a rate of 10 °C/min. The data of X-ray powder diffraction was collected on a Bruker AXSD8 Discover powder diffractometer at 40 kV/40 mA for Cu Kα (λ = 1.5406 Å) at room temperature in the range of 5-50 °(2θ) with a scan speed of 0.1 °per step. The gas adsorption isotherms were collected on a Belsorp-max. The N_2, D_2, H_2, C_2H_4, C_3H_6, n-C_4H_{10}, and *iso*-C_4H_{10} gases used in this adsorption experiment were ultrahigh-purity-grade (>99.999%). The vapour adsorption was carried out on Belsorp-max for the pure hexane isomer.

Gas adsorption and vapour adsorption measurements. Before carrying out the adsorption experiment, the samples of **ECUT-8** were firstly treated by immerging in CH_3OH for three days to make solvent exchange. Then the samples about 100 mg were degased at 150 °C under vacuum for 24 h in Belsorp-max. The BET was investigated by nitrogen adsorption at 77 K. The single-component isotherms of CO_2, C_3H_4, C_2H_6, C_3H_6, D_2, H_2, C_2H_4, C_3H_6, n-C_4H_{10}, *iso*-C_4H_{10}, and 1,3-butadiene were collected on the Belsorp-max. To maintain the experimental temperatures liquid nitrogen (77 K) and temperature-programmed water bath (273K, 298K) were used respectively. Similarly, the pure hexane isomers were used to carry out vapour adsorption test. The time-dependent adsorption profiles of CO_2 were measured on Intelligent Gravimetric Analyzer (IGA-100, HIDEN).

Adsorption kinetics. This was carried out by a batch experiments. In a typical experiment, approximate 10 mg activated adsorbent was placed a dried little glass bottle, then it was placed into a big glass bottle with 0.2 mL pure nHEX, or 3MP, or 2MP, or 22DMB, or 23 DMB solution. Then the big glass bottle was sealed and placed at certain temperature higher than the corresponding boiling temperature about 5°C for each hexane isomer. Then the samples were taken out every five seconds. The difference in weight between the activated samples and the samples after loading C_6 vapour was obtained through a 1/10000 scales.

Hexane isomer separation. Batch experiments was carried out to test the adsorption of hexane isomers in the liquid phase. In a typical experiment, 10 mg adsorbent was accurately measured and immersed in 0.25 mL equal volume mixtures such as nHEX/3MP, nHEX/2MP, nHEX/22DMB, 2MP/3MP, 2MP/22DMB, 3MP/22DMB, nHEX/3MP/2MP, nHEX/3MP/22DMB, and

nHEX/2MP/3MP/ 22DMB for 24 h at room temperature. Then, the samples were dried on filter paper for 12 hours to remove liquid from the surface of the crystals. The guest molecules were extracted with butyl acetate (1mL) overnight. Extracted liquid (0.5 mL) was analyzed by GC, and the content and purity of hexane isomers was obtained. Because GC shows few effect on the separation of 23DMB and 22DMB, thus, in this work, we just researched 22DMB.

The intracrystalline diffusivity of gas molecules in porous media.

The intracrystalline diffusivity of gas molecules in porous media is D_c,

$$\frac{m_t}{m_\infty} \approx \frac{6}{Rc}\sqrt{\frac{Dct}{\pi}} (m_t / m_\infty < 0.3) \quad (1)$$

In Eq. 1, m_t is the gas uptake at time t; m_∞ is the gas uptake at equilibrium; D_c is the intracrystalline diffusivity of gas molecules in porous media; and R_c is the radius of the equivalent spherical particle. From the slope k ($\frac{m_t}{m_\infty}$ plotted against $\sqrt{t}$), D_c can be further derived as

$$Dc = \frac{k^2 R_c^2 \pi}{36} \quad (2)$$

Breakthrough experiment for gas separation. In a typical experiment, 0.8 g activated adsorbent was added into the packed column (Ø 46 mm×150 mm). Before starting each experiment, helium reference gas is flushed through the column and then the gas flow was switched to the desired gas mixture at the setted flow rate. The gas mixture downstream the column was monitored using a Hiden mass-spectrometer.

Breakthrough experiment for liquid separation. In a typical experiment, 0.8 g activated adsorbent was added into the packed column (Ø 46 mm×150 mm). Then, 5 ml equal volume of nHEX/2MP/3MP/22DMB mixed solution was added into this column. The breaked solution was obtained every 5 second, which was futher analyzed by GC, giving the content of hexane isomers. A multicomponent breakthrough curves were obtained by plotting the change of content of each hexane isomers with time. Because GC shows few effect on the separation of 23DMB and 22DMB, thus, in this work, we just researched 22DMB.

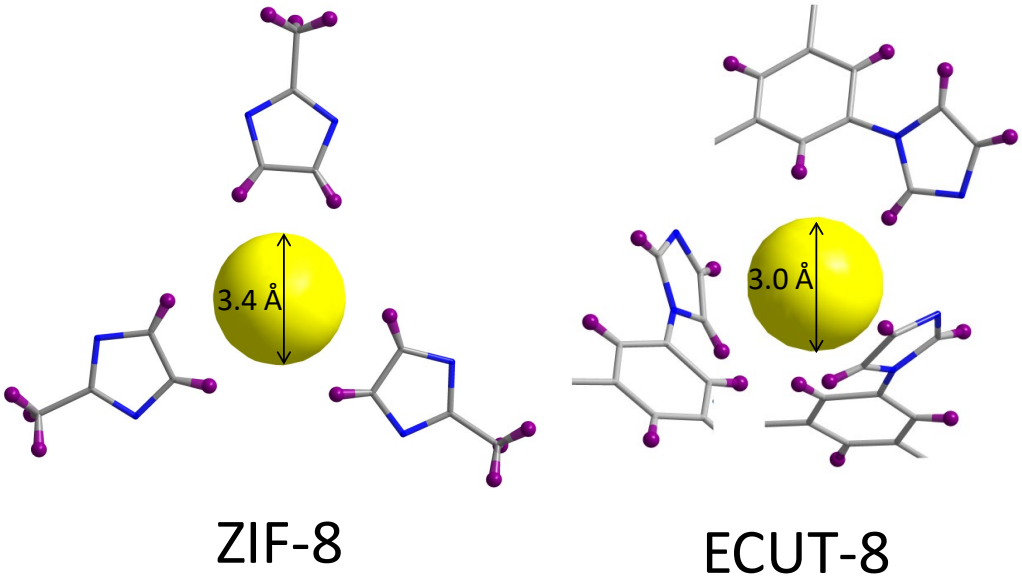

Figure S1. A comparison of the six-ring narrow window in ZIF-8 and **ECUT-8**.

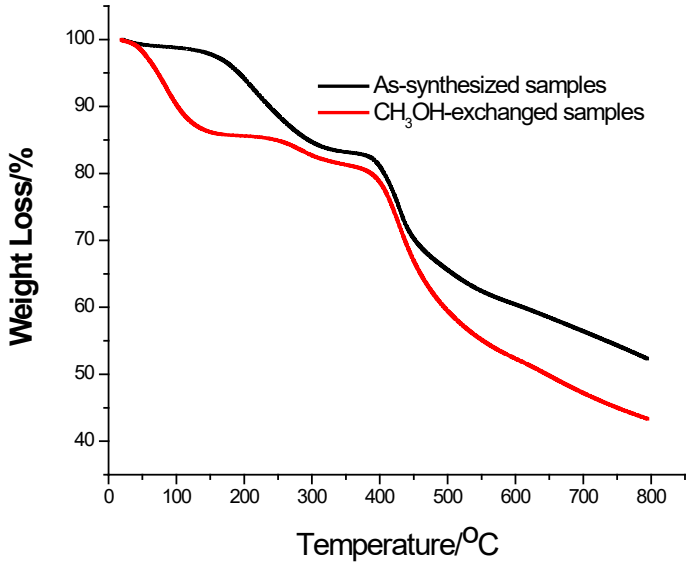

Figure S2. The TG plots of as-synthesized **ECUT-8** and the CH_3OH-exchanged samples.

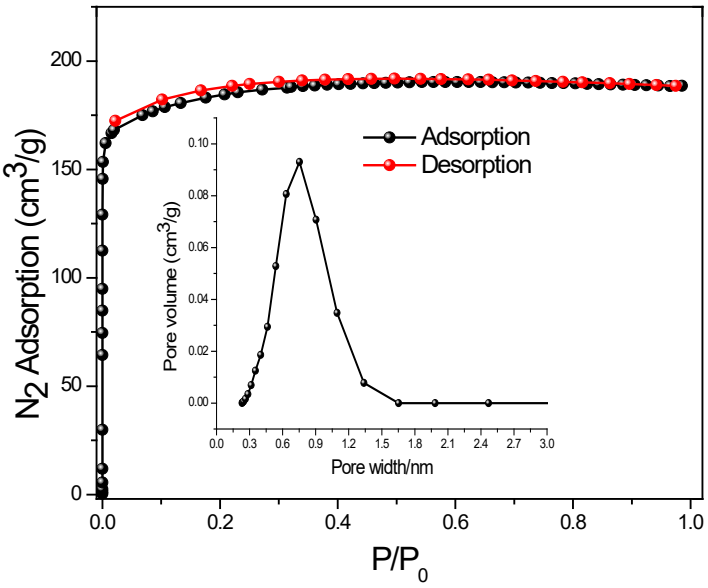

Figure S3. The N_2 adsorption at 77 K with the insert of the distribution of pore size.

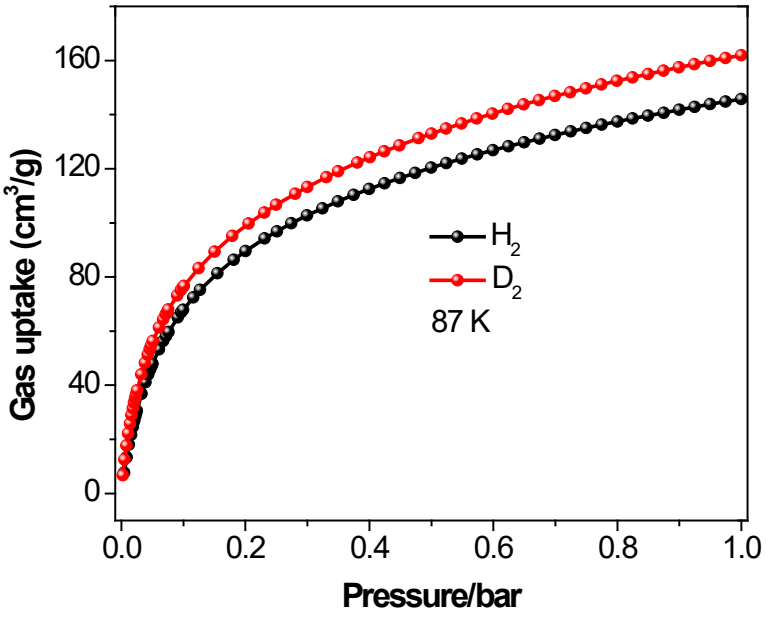

Figure S4. The H_2, D_2 adsorption isotherms at 87 K.

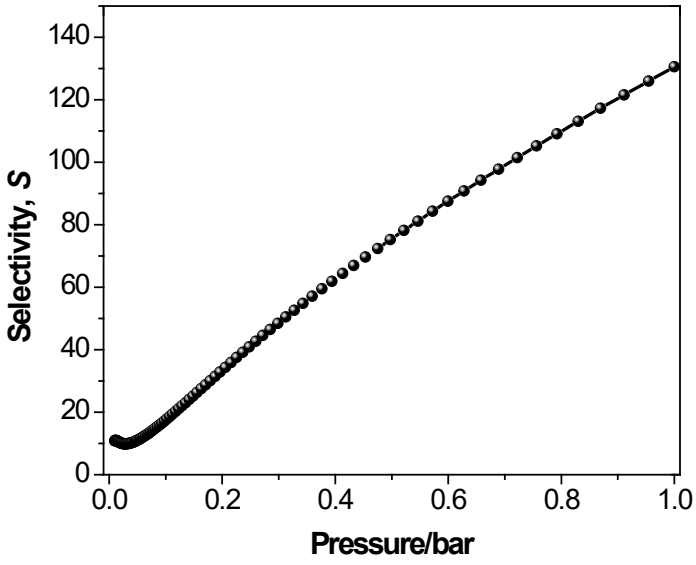

Figure S5. The n-butane/*iso*-butane selectivity at 298 K.

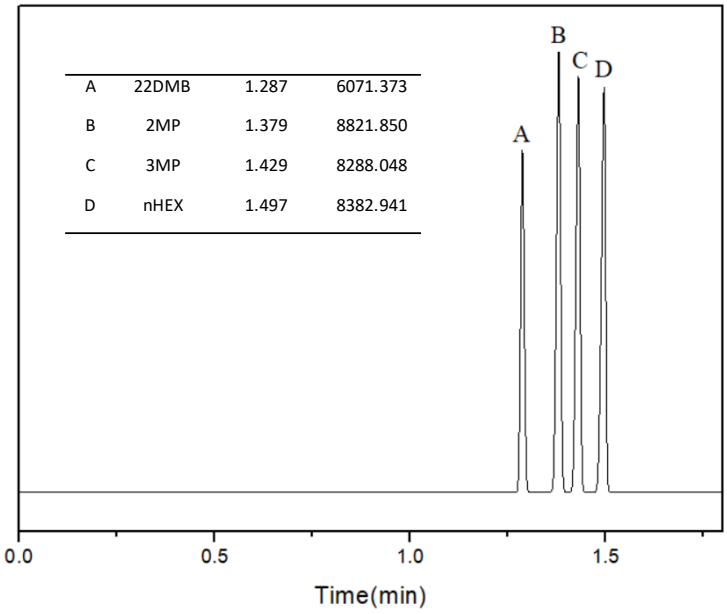

Figure S6. The GC standard peaks for the solution of nHEX, 2MP, 3MP, and 22DMB.

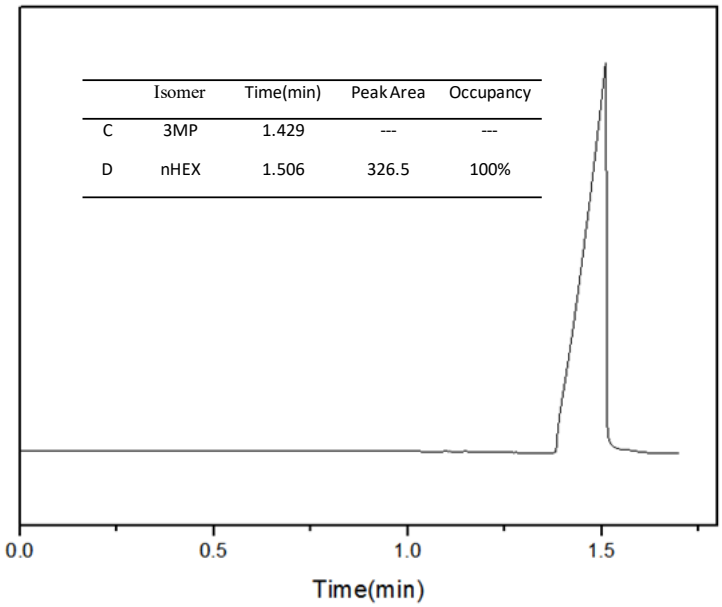

Figure S7. The GC results of the solution for nHEX/3MP separation upon activated **ECUT-8** samples.

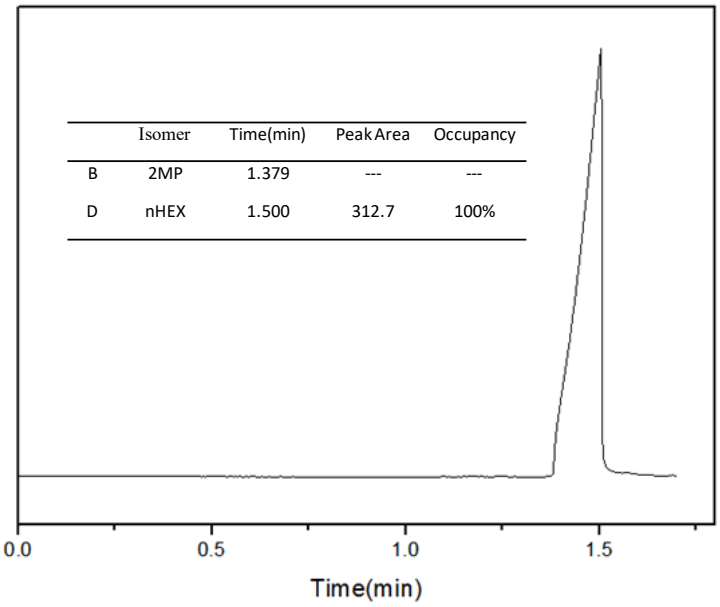

Figure S8. The GC results of the solution for nHEX/2MP separation upon activated **ECUT-8** samples.

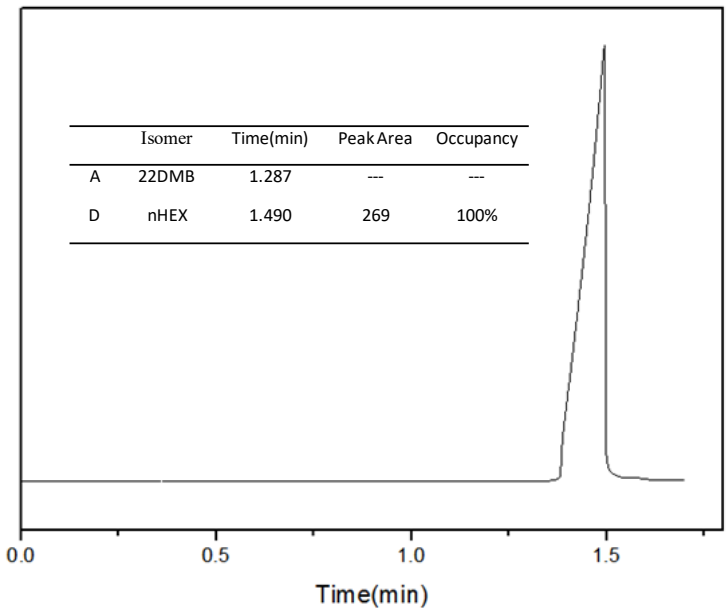

Figure S9. The GC results of the solution for nHEX/22DMB separation upon activated **ECUT-8** samples.

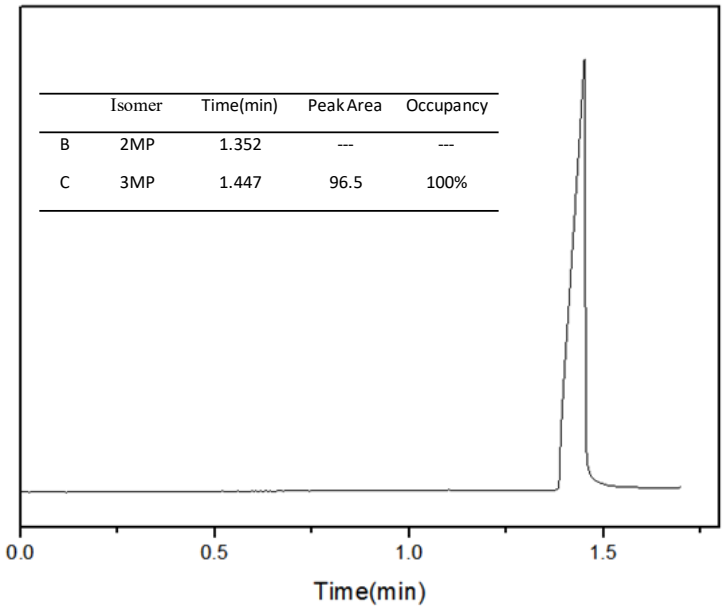

Figure S10. The GC results of the solution for 3MP/2MP separation upon activated **ECUT-8** samples.

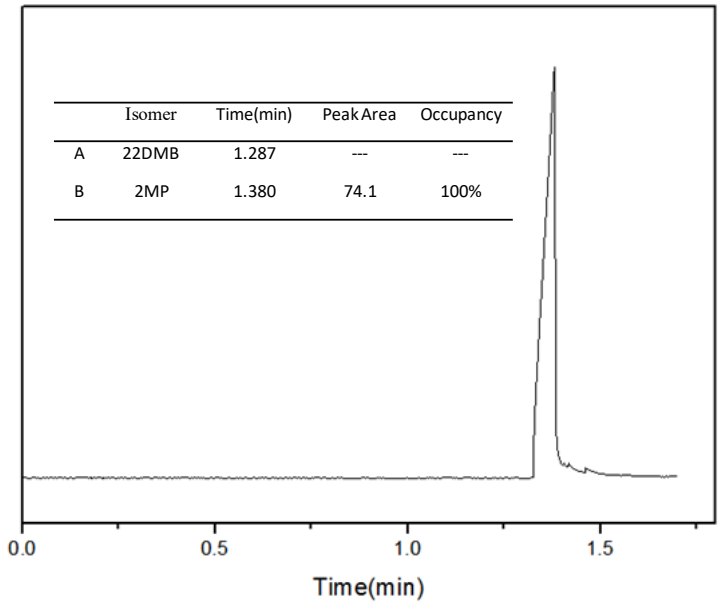

Figure S11. The GC results of the solution for 22DMB/2MP separation upon activated **ECUT-8** samples.

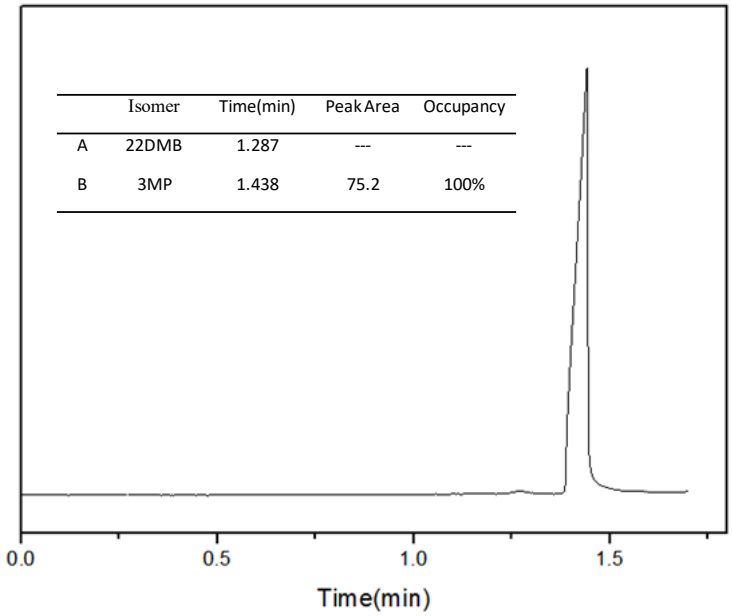

Figure S12. The GC results of the solution for 22DMB/3MP separation upon activated **ECUT-8** samples.

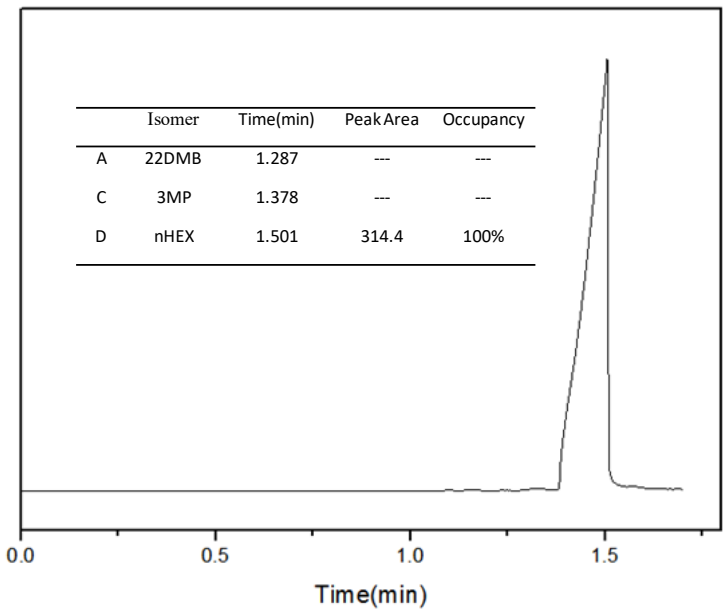

Figure S13. The GC results of the solution for nHEX/3MP/22DMB separation upon activated **ECUT-8** samples.

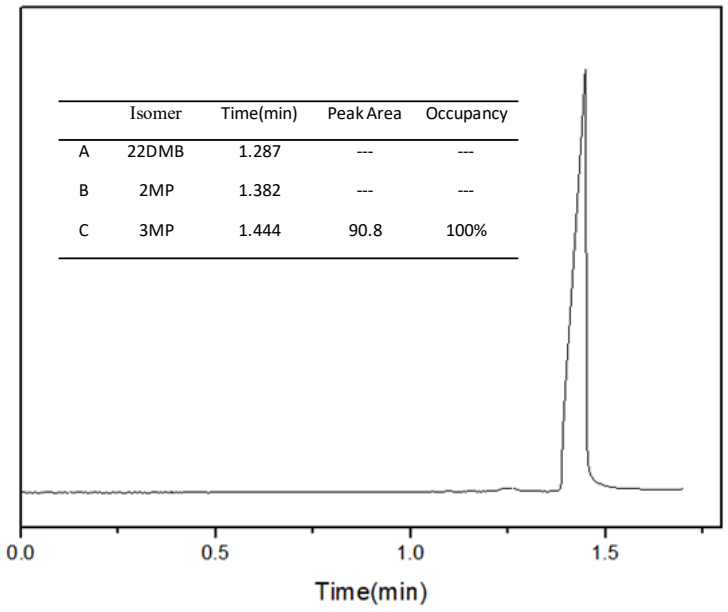

Figure S14. The GC results of the solution for 2MP/3MP/22DMB separation upon activated **ECUT-8** samples.

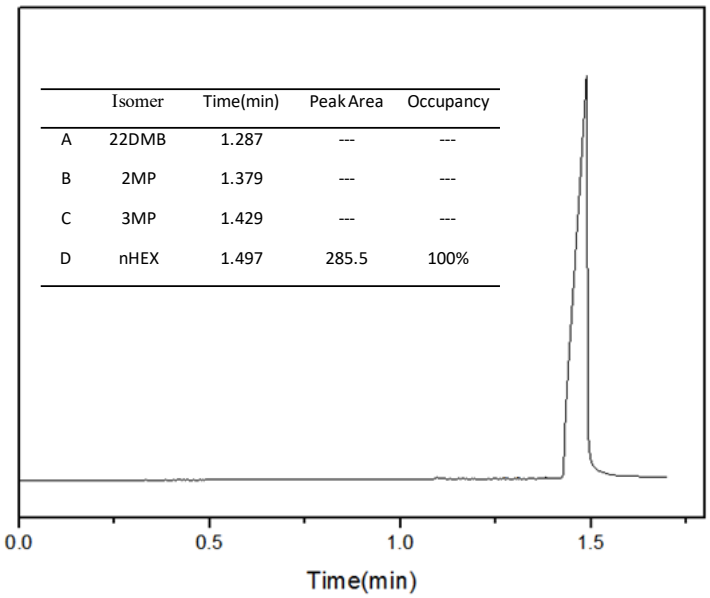

Figure S15. The GC results of the solution for nHEX/2MP/3MP/22DMB separation upon activated **ECUT-8** samples.

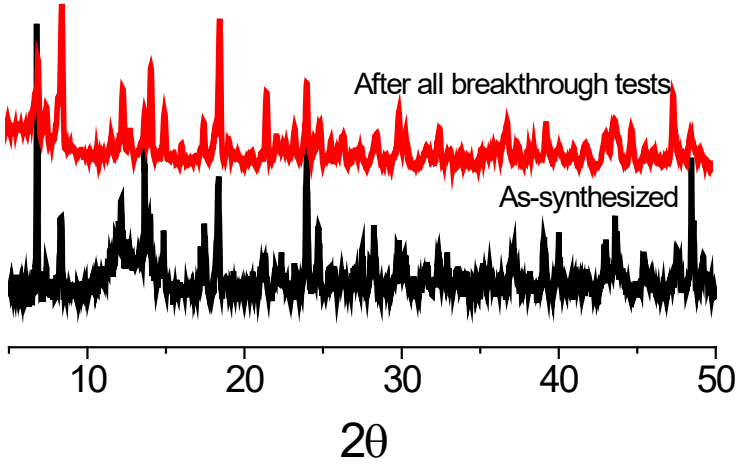

Figure S16. A comparison of PXRD patterns for the as-synthesized samples and the **ECUT-8** samples after finishing all breakthrough experiments.

Table S1. A crystallographic summarization of **ECUT-8**.

Compound	**ECUT-8**
Molecular formula	$ThCoL_3 \cdot 3$ DMF
Temperature	296 K
Crystal system	Rhombohedral
Space group	*R-3*$_2$
Unit cell, a,b,c	a=b= 14.5772(2) Å c= 38.3401(10) Å
Volume	7055.6(3) m^3
Z	6
Cell measurement reflns used	9379
F(000)	2826
Flack factor	0.5
GOF	1.127
Completion	99.9%
wR_1	0.0373
wR_2	0.1006
CCDC number	2055060