Th-MOF showing six-fold imide-eealed pockets for middle-size-separation of propane from nature gas

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**Experimmental section**

**Reagents and materials**

***Caution!*** *Th(NO3)4 used in this study is radioactive and chemically toxic reactant, so standard precautions*

*and protection for handling such substances have been followed.* All chemicals are directly purchased

from innochem without further purification.

**Synthesis of N,N’-bis-(4-benzoic acid)-1,4,5,8- naphthalenediimide (H2L):** N,N’-bis-(4-benzoic acid)-1,4,5,8-naphthalenediimide (H2L) was synthesized according to the procedures in reference[1]. 10 mmol (2.68 g) 1,4,5,8-Naphthalenete-tracarboxylicdianhydride (NTCDA) was weighted in 250 ml round-bottom flask. 50 mL dried acetic acid was added and stirred for 10 min. Then 20 mmol (2.74 g) 4-aminobenzoic acid was added in the solution and allowed reflux at 119℃. After 12h, the reaction was cooled to room. The product was washed by distilled water and ethanol through filtration and dried in vacuum.

**Synthesis of ECUT-Th-10:** 15 mg H2L and 8 mg Th(NO3)4 were mixed together in N,N-Dimethylformamide (DMF). Then 100 μL perchloric acid was added in the mixture. The mixture was placed into screw-capped glass vial and sealed. The vial was heated at 110ºC for 72 h. After that, the system was cooled down to room temperature. The light orange crystals (**ECUT-Th-10**) were obtained after washing by DMF.

**Synthesis of ECUT-Th-10a:** The as-synthesized **ECUT-Th-10** was exchanged with methanol three times every day. After 3-day exchange, the products were evacuated at 100 ºC under dynamic vacuum to obtain **ECUT-Th-10a** for confirming the porosity.

**Synthesis of UiO-66:** ZrCl4 (0.227 mmol, 0.053 g) and 4-Aminobenzoic acid (0.227 mmol, 0.034 g) were dissolved in N,N’- dimethylformamide (DMF, 3 mL) at room temperature. Then the mixture was placed into autoclave and transferred to muffle furnace. The autoclave was heated at 120ºC for 24 h. After that, the system was cooled down to room temperature. The obtained UiO-66 were washed by DMF and dried for further use.

**Synthesis of activated UiO-66:** The as-synthesized UiO-66was exchanged with methanol three times every day. After 3-day exchange, the products were evacuated at 60ºC under dynamic vacuum to obtain activated UiO-66.

**Physical measurements**

The powder X-ray diffraction (PXRD) patterns were recorded on Bruker AXSD8 Discover powder diffractometer at 40 kV, 40 mA for Cu Kα, (λ= 1.5406 Å) at room temperature. Thermal gravimetric analysis (TGA) was performed using a TGA Q500 thermal analysis system from 30 to 800 °C under N2 atmosphere at a constant rate of 10 °C/min.

**X-ray Crystallography**

X-ray diffraction data of **ECUT-Th-10** was collected at 298 K on a Bruker-Appex (II) diffractometer using graphite monochromated MoKα radiation (λ=0.71073 Å). The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS). The crystal structure was solved and refined using the SHELXTL program suite. Direct methods yielded all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were riding on their respective atoms. CCDC 2103477 contains the supplementary crystallographic data of **ECUT-Th-10**. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/](http://www.ccdc.cam.ac.uk/)data\_ request/cif.

**Gas adsorption experiments.**

The gas sorption isotherms were collected on a Belsorp-max. Roughly 100 mg of **ECUT-Th-10** were taken for the nitrogen adsorption experiments at 77 K. The adsorption isotherms for CH4, C2H6, C3H8, and n-C4H10 were obtained at temperature of 273 K and 298 K, respectively. Liquid nitrogen and water bath were used to maintain the experimental temperatures of 77 K, 273 K, and 298 K. Roughly 100 mg of activated UiO-66 were also taken for the single-component adsorption isotherms. The adsorption isotherms for different alkane were measured at 298 K.

**Calculation of Isosteric Heat of Adsorption**

The unary isotherm data for CH4, C2H6, C3H8, and n-C4H10 in **ECUT-Th-10a** at 273 K and 298 K were fitted with with the dual-site Langmuir-Freundlich model

|  |  |
| --- | --- |
|  | (1) |

The isosteric heats of adsorption were calculated from the dual-site Langmuir-Freundlich isotherms for **ECUT-Th-10a** using

|  |  |
| --- | --- |
|  | (2) |

Where *p* is the pressure, *T* is the temperature, *R* is the gas constant (8.314 J mol-1 K-1). By drawing the ln*P* vs 1/T plot of gas at various loading, *Qst* = -slope×R.

|  |  |
| --- | --- |
| **Calculation of selectivity via ideal adsorption solution theory (IAST)** |  |

The adsorption selectivity of C3H8/CH4 (50/50), C3H8/C2H6 (50/50), and C3H8/C4H10 (50/50) in **ECUT-Th-10a** and UiO-66 was established by the Ideal Adsorbed Solution Theory (IAST). The adsorption selectivity was calculated from

|  |  |
| --- | --- |
|  | (2) |

where the *q*A, and *q*B represent the molar loadings in **ECUT-Th-10a** or UiO-66 that is in equilibrium with a bulk fluid mixture with mole fractions *y*A, and *y*B = 1 - *y*A. The molar loadings, also called *gravimetric* *uptake capacities*,are expressed in mol kg-1.

**Breakthrough experiments.**

The breakthrough experiments were performed at 298 K. Bulk **ECUT-Th-10a** (around 500 mg) were filled into stainless steel column. First, the helium gas (100 mL/min) was introduced into the column for 30 min. Then the different gas mixture C2H6/C3H8 (50/50, v/v), CH4/C2H6/C3H8 (33/33/33, v/v/v), C2H6/C3H8/C4H10 (33/33/33, v/v/v), and CH4/C2H6/C3H8/C4H10 (25/25/25/25, v/v/v/v) passed through the column with 2 mL/min. The eluted gas stream from the column is monitored by a gas chromatography (TCD-Thermal Conductivity Detector, detection limit 0.1%). Prior to each cycling experiment, the adsorption bed was regenerated by He flow for 3h at 333 K to ensure complete removal of adsorbed gas.

**Density Functional Theory Calculations**

The density functional theory (DFT) calculations were performed by using the Vienna Ab initio Simulation Package (VASP) code with the projector augmented wave (PAW) method.[2-3] The exchange-functional was treated using the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional.[4] Wave functions were expanded using a plane-wave basis set with kinetic energy cutoff of 400 eV and the geometries were fully relaxed until the residual force convergence value on each atom being less 0.05 eV/Å. The Brillouin zone integration was performed using 2×2×2 Monkhorst-Pack k-point sampling for a primitive cell.[5] The self-consistent calculations applied a convergence energy threshold of 10-4 eV. Spin-polarization was considered in all calculations.[6]

The average adsorption energy of those alkanes were calculated with following equation[7]:

where the *L* means alkane molecules, such as methane, ethane, propane or butane; *n* is the number molecules were adsorbed in a unit.

**Supplementary Table 1.** crystal data and structure refinements for **ECUT-Th-10**

|  |  |
| --- | --- |
| Compound | **ECUT-Th-10** |
| Formula | C84H36N6O5Th3 |
| Formula weight | 2273.31 |
| Color | Light orange |
| Crystal system | cubic |
| Space group | *Fd-3m* |
| a(Å) | 39.5857(7) |
| b(Å) | 39.5857(7) |
| c (Å) | 39.5857(7) |
| α | 90.00 |
| β | 90.00 |
| γ | 90.00 |
| Volume (Å3) | 62032(3) |
| Z | 16 |
| Temperature for data collection (K) | 296 |
| Range for data collection θ(º) | 2 to 25 |
| No. of measured reflections | 14178 |
| No. of unique reflections | 2591 |
| No. of parameters | 116 |
| No. of restraints | 251 |
| Goodness-of-fit on F2 | 1.014 |
| Final R indexes[I≥2σ(I)] | R1=0.0882, wR2=0.2513 |
| Final R indexes [all data] | R1=0.1159, wR2=0.2771 |

a*R*1 = Σ||*F*o|−|*F*c||/Σ|*F*o|. b*wR*2 = [Σ*w* (*F*o2−*F*c2)2/Σ*w* (*F*o2)2]1/2.



**Supplementary Figure 1.** Powder X-ray diffraction pattern of **ECUT-Th-10** and simulated pattern from single crystal data.



**Supplementary Figure 2.** Thermal analysis of **ECUT-Th-10** from room temperature to 800℃ under air condition.



**Supplementary Figure 3.** The adsorption isotherms of **ECUT-Th-10** for CH4, C2H6, C3H8 and C4H10 at 273 K, respectively.



**Supplementary Figure 4.** Experimental breakthrough curves at 298 K on **ECUT-Th-10** with C2H6/C3H8 (50/50, v/v) binary mixture for three cycles.



**Supplementary Figure 5.** Powder X-ray diffraction pattern of synthesized UiO-66 in this work and simulated UiO-66.



**Supplementary Figure 6.** The C-H∙∙∙O interaction between CH4 and imide units in **ECUT-Th-10**.



**Supplementary Figure 7.** The C-H∙∙∙O interaction between C2H6 and imides units in **ECUT-Th-10**.

**Supplementary References**

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