Electronic Supplementary Information (ESI)

Highly Robust Heterometallic Tb^{III}/Ni^{II} Organic Framework for C$_2$ Hydrocarbons Separation and Capture

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Experiment details

All the starting reagent and solvent expect the H_6TDP ligand ordered commercially without further purification. IR spectra were measured on a Nicolet 740 FTIR Spectrometer at the range of 500−4000 cm^{-1}. Elemental analyses (C, H and N) were carried out on a CE instruments EA 1110 elemental analyzer. X-ray powder diffractions were measured on a Panalytical X-Pert pro diffractometer with Cu Kα radiation. Thermogravimetric analyses were performed under air condition from room temperature to 800 °C with a heating rate of 10 °C min^{-1} on Perkin-Elmer TGA-7 thermogravimetric analyzer. Single component low pressure gas sorption measurements were performed with an ASAP 2020 Plus instrument.

X-ray data collection and structure refinement

The diffraction intensity data for **NUC-2** was obtained at 296(2) K using a Bruker Smart-APEX II CCD area detector (Mo Kα radiation, λ = 0.071073 nm) with graphite-monochromated radiation. The reflection data were also corrected for empirical absorption corrections and Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELXL package.[1,2] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms except those on water molecules were generated geometrically with fixed isotropic thermal parameters, and included in the structure factor calculations. The block of SQUEEZE in PLATON was employed to eliminate the highly disordered solvent molecular. The solvent section in formula of **NUC-2** was determined by the thermogravimetric analysis and elemental analysis. Crystallographic data for **NUC-2** is given in Table S1. Selected bond lengths and angles for **NUC-2** are listed in Table S2. Further details on the crystal structure investigations may be obtained from the Cambridge Crystallographic Data Centre, with the depository number CCDC-1967303 for **NUC-2**.

Preparation of NUC-2

A mixture of H_6TDP (0.12 mmol, 31.9 mg), $Ni(NO_3)_2\cdot6H_2O$ (0.20 mmol, 58.2 mg), and $Tb(NO_3)_2\cdot6H_2O$ (0.10 mmol, 45.3 mg) was dissolved in 10 mL mixed solution of N,N-dimethyl formamide (DMF) and deionized water (v:v = 8:2) followed by adding 0.3 mL HNO_3 solution. After stirring for 30 minutes to make a homogeneous solution, the reaction mixture was sealed and heated in a 25 mL Teflon-lined stainless steel vessel at 110 °C for 4 and then cooled to room temperature at a rate of 10 °C/h. Blue block crystals of **NUC-2** were collected by filtration and washed by DMF/H_2O (3:1) with a yield of calcd. 62 % (based on H_6TDP). Anal. Calcd. for $C_{44}H_{55}NiN_6O_{21}Tb$: C, 43.26; H, 4.54; N, 6.88 (%). Found: C, 42.97; H, 4.75; N, 6.36 (%). IR (KBr pellet, cm^{-1}): 3406 (vs), 1597 (vs), 1387 (vs), 1105 (w), 1020 (w), 787 (s), 700 (w), 515 (w).

Synthesis of H_6TDP

The chemicals of dimethyl 4-bromoisophthalate, 2,4,6-tribromopyridine, bis(pinacolato)diborane and $Pd(PPh_3)_4$ were purchased from Jinan Henghua Sci. & Tec. Co. Ltd. without further purification.

Synthesis of 4,4,5,5-tetramethyl-2-(diethyl 2,4-dicarboxylatephenyl)-1,3-dioxolane (II)

The mixture of I (0.1 mol, 27.2 g), bis(pinacolato)diborane (11.8 mmol, 3.0 g), potassium acetate (0.29 mmol, 28.0 g), $Pd(dppf)_2Cl_2$ (7.0 mmol, 5.0 g), and dried 1,4-dioxane (500 mL) at 100 ˚C overnight and afterward extracted with ethyl acetate (200 mL × 3). The organic layer was decolored with activated carbon, and dried by anhydrous Na_2SO_4. The crude product was obtained from concentration under a vacuum and purified by column chromatography (silica gel, ethylacetate/petroleum ether, 6 v %). Yield 65 %. Anal. (%) calcd. for $C_{16}H_{21}BO_6$: C, 60.03; H, 6.61. Found: C, 59.78; H, 6.46.

Synthesis of 2,4,6-tri(dimethyl 2,4-dicarboxyphenyl)pyridine (III)

The mixture of II (0.15 mol, 48.0 g), 2,4,6-tribromopyridine (0.05 mol, 15.6 g), and K_3PO_4 (0.3 mol, 63.6 g) were mixed in 1,4-dioxane (2000 mL), and the mixture was deaerated using N_2 for 10 min. $Pd(PPh_3)_4$ (0.9 mmol, 1.0 g) was added to the stirred reaction mixture and the mixture was heated to reflux for ca. one week under N_2. The crude product of III was obtained after 1,4-dioxane was removed under a vacuum. Recrystallization from methanol offered the pure product. Anal. (%) calcd. for $C_{35}H_{29}NO_{12}$: C, 64.12; H, 4.46; N, 2.14. Found: C, 63.69; H, 4.32; N, 2.01.

Synthesis of 2,4,6-tri(2,4-dicarboxyphenyl)pyridine (IV)

The mixture of III (0.05 mol, 32.8g) and 40 g NaOH in 2000 mL H_2O and 1600 mL MeOH was refluxed for 2 hours, and then cooled to room temperature. The solution was neutralized with concentrated HCl. White powder was obtained with the yield of 90 %. ESI-MS: m/z $[M-H]^-$, 570.08 (calcd for $C_{22}H_{14}O_8$, 571.08). Anal. (%) calcd. for $C_{35}H_{29}NO_{12}$: C, 60.95; H, 3.00; N, 2.45. Found: C, 60.27; H, 2.80; N, 2.79.

Scheme S1: Synthetic procedure of H_6TDP.

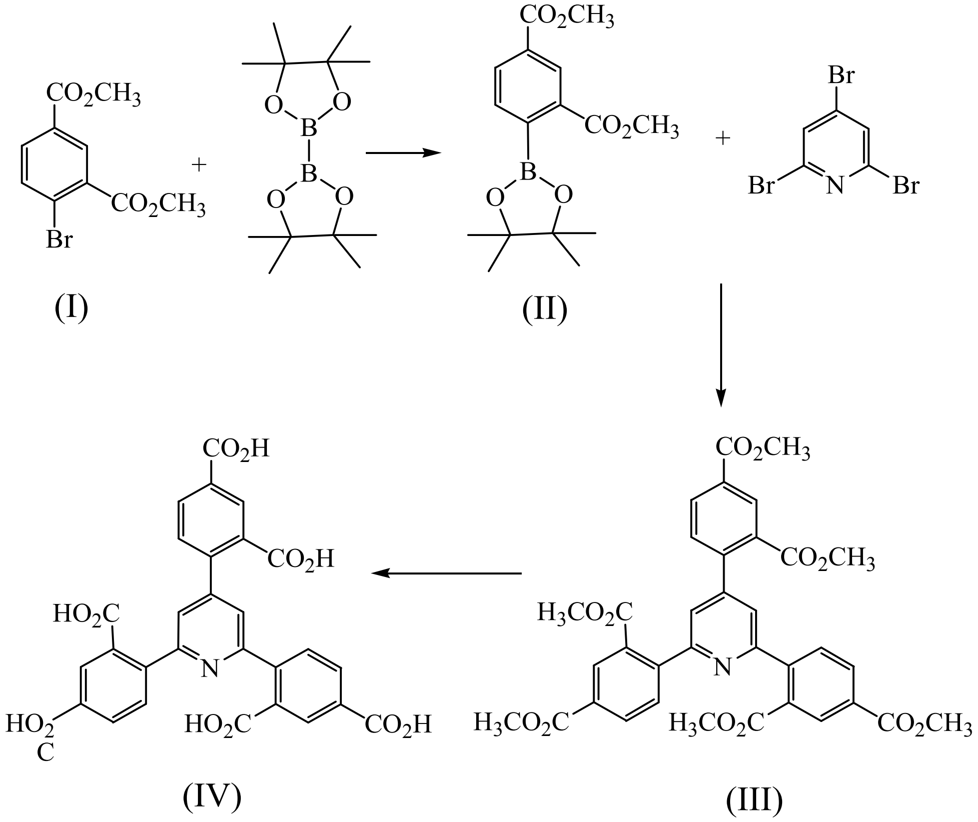


Figure S1: Mass spectrum of H_6TDP.

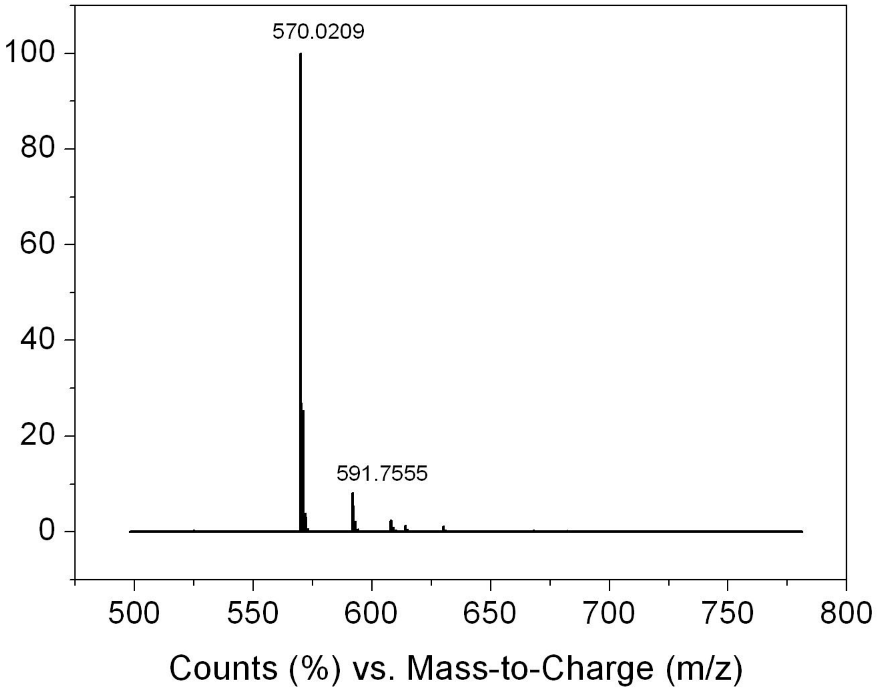


Figure S2: 1H NMR spectra of H_6TDP

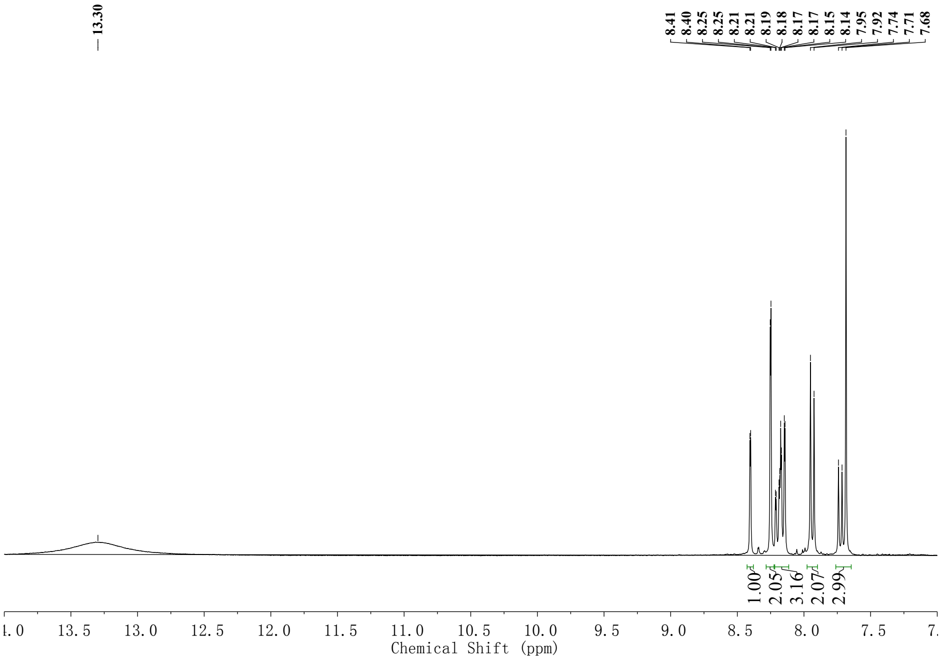


Figure S3: the Tb-Ni bimetallic cluster nodes in NUC-2 (a), the porous 3D framework of NUC-2 view along *c* axis (b), the 3D 5,5-connected fng net with the point symbol of $\{4^6.6^4\}$ (c). The coordination mode of HTDP ligand (d).

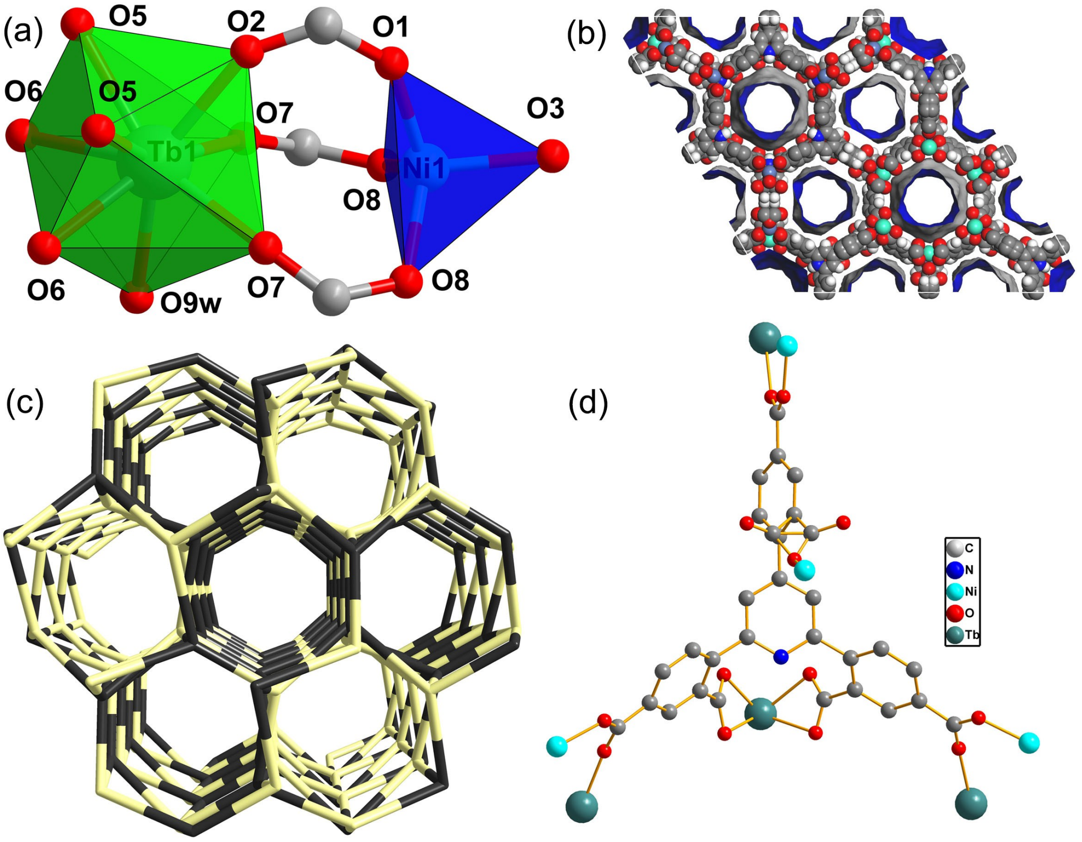


Figure S4: The TGA curves of as-synthesized (black) and activated (red) sample of NUC-2.

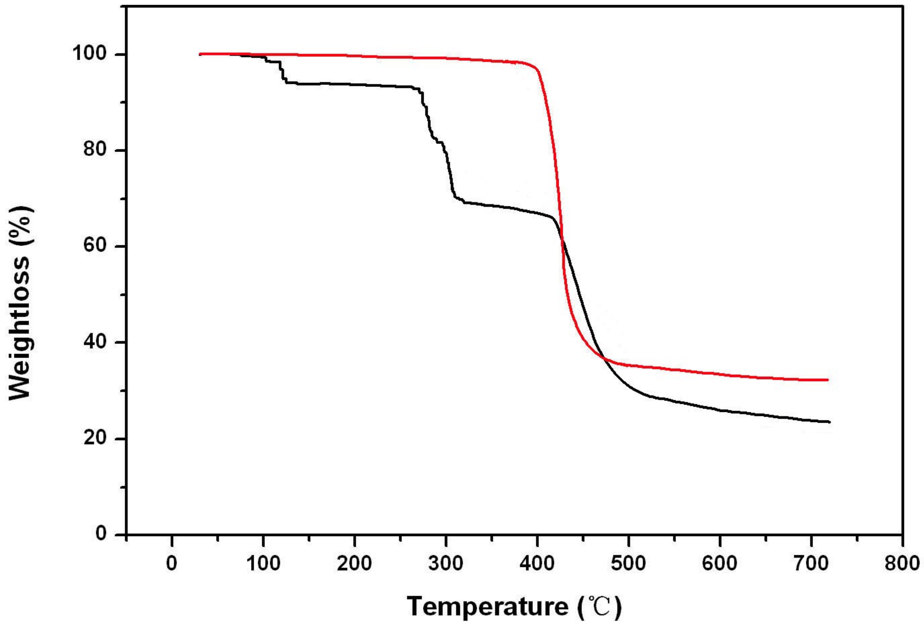


Figure S5: the PXRD patterns of NUC-2.

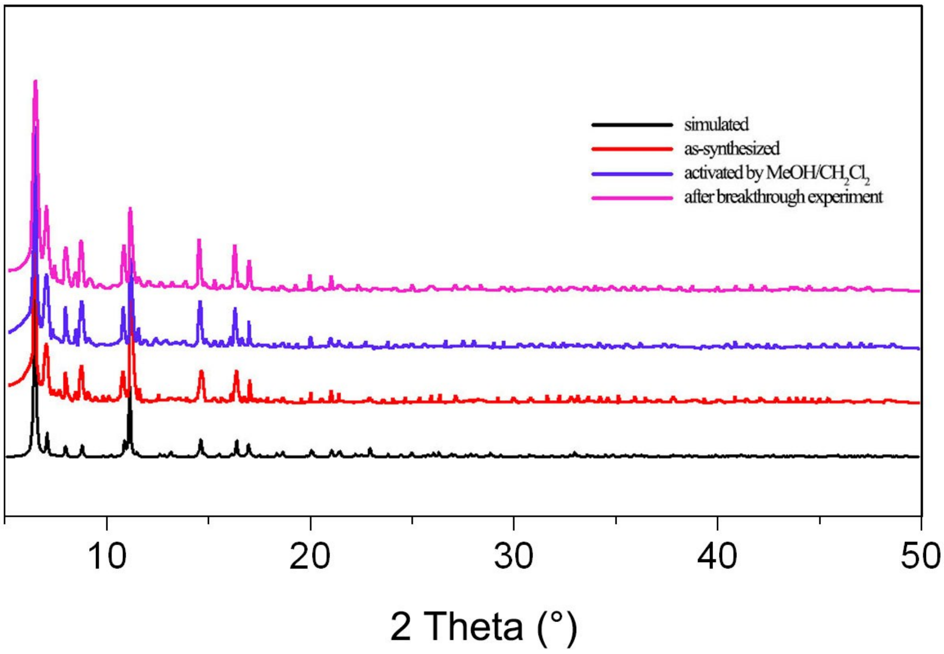
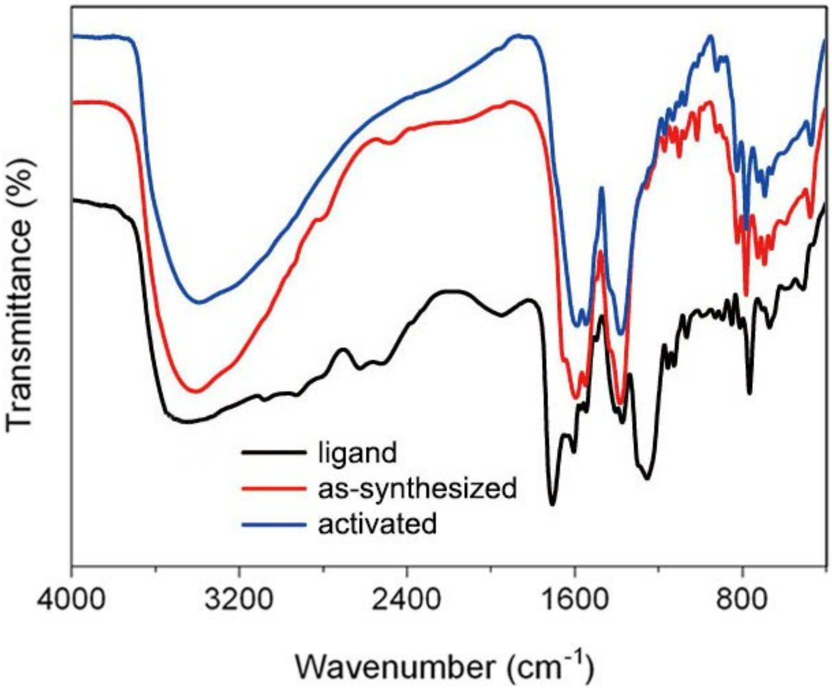


Figure S6: IR spectra.



Gas adsorption and selectivity measurements

The adsorption heats (Q_{st}) of light hydrocarbons (C_2H_2 and C_2H_4) for **NUC-2** were estimated from the sorption data measured at 273 and 298 K by Clausius-Clapeyron equation:

$$-Q_{st} = \frac{\partial(\ln P)}{\partial(1/T)}$$

In ideal adsorbed solution theories (IAST), the adsorption isotherm of pure gas is fitted by the single-site Langmuir-Freundlich equation:

$$Y = \frac{A1 * b1 * x^{c1}}{1 + b1 * x^{c1}}$$

Y: molar loading of species i, mmol/g
$A1$: saturation capacity of species i, mmol/g
$b1$: constant, Pa^{-1}
$c1$: constant
The adsorption selectivity is defined as:

$$S_{i/j} = \frac{q1/q2}{p1/p2}$$

$S_{i/j}$: adsorption selectivity
qi: the amount of i adsorbed
pi: the partial pressure of i in the mixture

Figure S7: N_2 absorption/desorption isotherms of NUC-2 at 77 K.

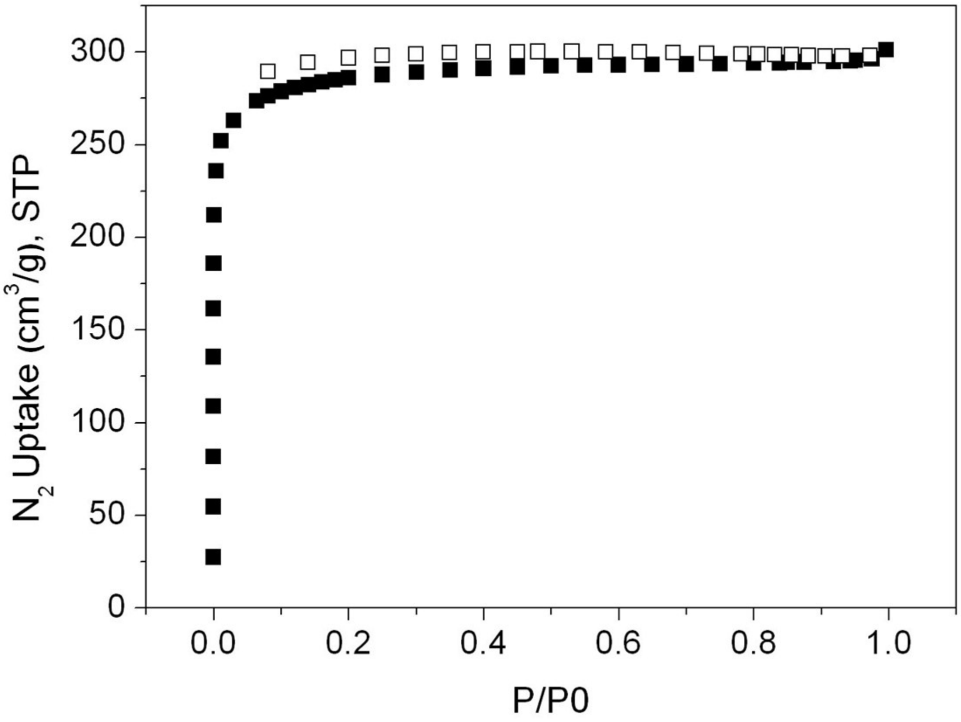
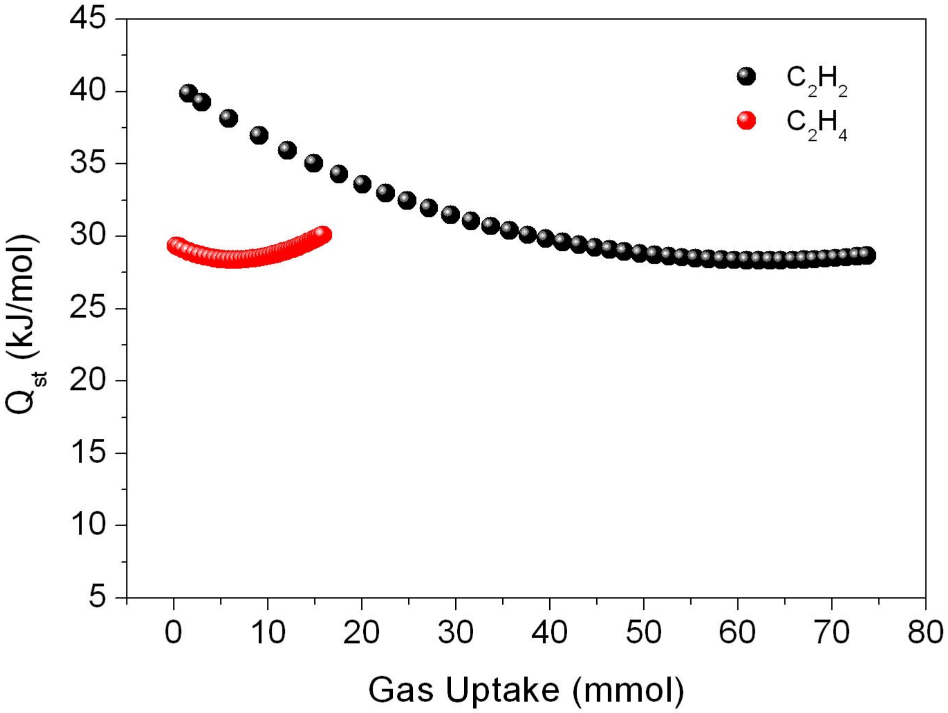


Figure S8: The adsorption heats of NUC-2 for C_2H_2 and C_2H_4.



Breakthrough separation experiments

The mixed-gas breakthrough separation experiment was conducted at 298 K using a lab scale fix-bed reactor. In a typical experiment, 0.48 g activated **NUC-2** sample was packed into a stainless steel column (the steel column was 20 cm in length with a 5.8 mm inner (6.0 mm outer) diameter) with silica wool filling the void space. The sorbent was activated in situ in the column with a vacuum pump at 298 K for 12 h. An Ar flow (2.0 $mL\cdot min^{-1}$) was used after the activation process to purge the adsorbent for 1h. Then a gas mixture of C_2H_2/C_2H_4 (1:99, v/v) at 2 $mL\cdot min^{-1}$ was allowed to flow into the column. The outlet gases of the breakthrough column were kept in the sample sacks which were further detected by using a gas chromatograph. After the breakthrough experiment, the sample was regenerated with Ar flow (7 to 15 ml min^{-1}) at 323 K for 4 hours. The complete breakthrough of C_2H_2 and other species was indicated by the downstream gas composition reaching that of the feed gas.

DFT calculation

All density functional theory (DFT) calculation were performed using the Vienna ab initio simulation package (VASP).[3-5] The Perdew-Burke-Ernzerhof (PBE) functional with the generalized gradient approximation (GGA),[6] accounting for inhomogeneous charge-density distributions, was used to describe the exchange-correlation effect in Kohn-shame equation. Projector-augmented wave (PAW)[4] method, featuring the accuracy of all-electron method as well as the efficiency of pseudopotential method, was used to treated inner core and valent electrons. The cutoff energy of 450 eV is set to expansion of plane wave function basic set. Following Monkhorst-Pack method, The K-point of the Brillouin zone was sampled under the 2× 2× 2 grid with Γ-pointer center,[7] having enough accuracy for energy calculation. The tolerance for SCF and ionic optimization were set to 1×10^{-5} and 0.01 eV/Å, respectively. In order to get accurate weak interaction between adsorption species and MOF, the Van der Waals correction method (DFT-D3BJ)[8] was adopted for all self-consistent field calculations. The adsorption energies (E_{ads}) of different adsorbates were calculated by following formula:

$$E_{\mathrm{ads}} = E_{\mathrm{total}} - E_{\mathrm{sub}} - E_{\mathrm{mol}} \qquad \text{Eq(1)}$$

where E_{total}, E_{sub}, E_{mol} are the total energy after adsorption, bare MOF, and the adsorbate molecules including the C_2H_2 and C_2H_4, respectively. The dissociation energy of aqua ligand was obtained by following fomula:

$$E_{\mathrm{d}} = E(\mathrm{H_2O}) + \mathrm{E(MOF\ with\ open\ metal\ site\ )} - \mathrm{E(Pristine\ MOF)} \qquad \text{Eq(2)}$$

Figure S9: adsorption structures of C_2H_2 (a) and C_2H_4 (b) on the open-metal site of NUC-2.

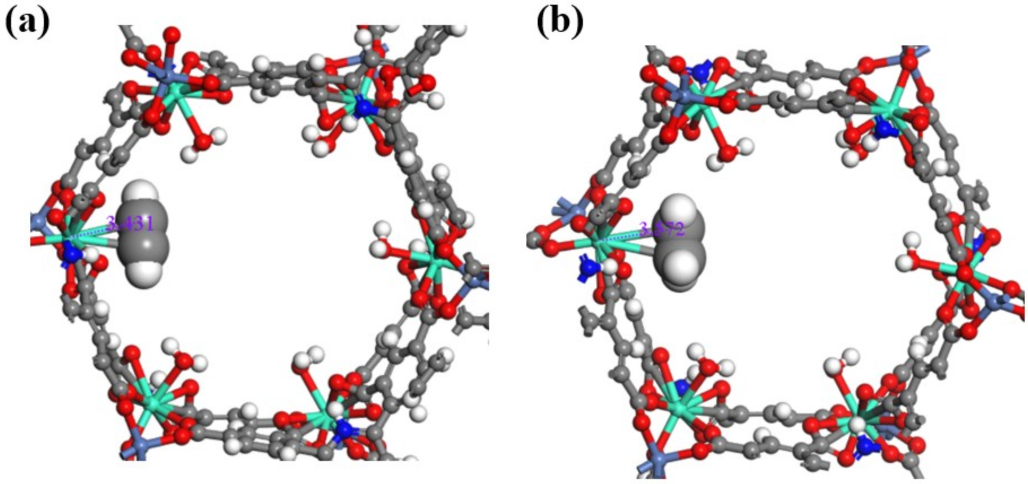


Table S1: Crystal data collection and structure refinement for NUC-2.

Complex	**NUC-2**
Formula	$C_{87}H_{39}N_3Ni_3O_{39}Tb_3$
Mr	2403.05
Crystal system	Trigonal
Space group	*R*-3m
a (Å)	47.989(10)
b (Å)	47.989(10)
c (Å)	13.297(3)
α (°)	90
β (°)	90
γ (°)	120
V(Å^3)	26520(10)
Z	6
Dcalcd(g·cm^{-3})	0.903
μ(mm^{-1})	1.544
GOF	1.002
R_1 [I＞2σ(I)]a	0.0781
wR_2 [I＞2σ(I)]b	0.2292
R_1^a (all data)	0.1359
wR_2^b (all data)	0.2856
R_{int}	0.1049

$^a R_1 = \sum \left| |F_o| - |F_c| \right| / \sum |F_o|$. $^b wR_2 = |\sum w(|F_o|^2 - |F_c|^2)| / \sum |w(F_o{}^2)^2|^{1/2}$

Table S2: Selected bond distances (Å) and angles (°) for NUC-2.

NUC-2					
Ni(1)-O(3)	1.913(12)	Ni(1)-O(1)#3	1.929(11)	Ni(1)-O(8)#4	1.971(9)
Ni(1)-O(8)#5	1.971(9)	O(1)-Ni(1)#3	1.929(11)	O(2)-Tb(1)#6	2.32(1)
O(5)-Tb(1)#2	2.391(9)	O(6)-Tb(1)#2	2.459(8)	O(7)-Tb(1)	2.266(8)
O(8)-Ni(1)#7	1.971(9)	O(9)-Tb(1)	2.361(13)	Tb(1)-O(7)#8	2.266(8)
Tb(1)-O(2)#9	2.319(11)	Tb(1)-O(5)#10	2.391(9)	Tb(1)-O(5)#11	2.391(9)
Tb(1)-O(6)#10	2.459(8)	Tb(1)-O(6)#11	2.459(8)		
O(3)-Ni(1)-O(1)#3	102.2(5)	O(3)-Ni(1)-O(8)#4	104.5(3)	O(1)#3-Ni(1)-O(8)#4	113.9(3)
O(3)-Ni(1)-O(8)#5	104.6(3)	O(1)#3-Ni(1)-O(8)#5	113.9(3)	O(8)#4-Ni(1)-O(8)#5	115.7(6)
O(7)-Tb(1)-O(7)#8	87.5(4)	O(7)-Tb(1)-O(2)#9	79.9(3)	O(7)#8-Tb(1)-O(2)#9	79.9(3)
O(7)-Tb(1)-O(9)	78.2(3)	O(7)#8-Tb(1)-O(9)	78.2(3)	O(2)#9-Tb(1)-O(9)	149.5(4)
O(7)-Tb(1)-O(5)#10	154.2(3)	O(7)#8-Tb(1)-O(5)#10	91.0(3)	O(2)#9-Tb(1)-O(5)#10	74.5(3)
O(9)-Tb(1)-O(5)#10	126.7(3)	O(7)-Tb(1)-O(5)#11	91.0(3)	O(7)#8-Tb(1)-O(5)#11	154.2(3)
O(2)#9-Tb(1)-O(5)#11	74.5(3)	O(9)-Tb(1)-O(5)#11	126.7(3)	O(5)#10-Tb(1)-O(5)#11	79.4(5)
O(7)-Tb(1)-O(6)#10	153.8(3)	O(7)#8-Tb(1)-O(6)#10	89.5(4)	O(2)#9-Tb(1)-O(6)#10	125.0(3)
O(9)-Tb(1)-O(6)#10	75.8(3)	O(5)#10-Tb(1)-O(6)#10	51.8(3)	O(5)#11-Tb(1)-O(6)#10	102.6(3)
O(7)-Tb(1)-O(6)#11	89.5(4)	O(7)#8-Tb(1)-O(6)#11	153.8(3)	O(2)#9-Tb(1)-O(6)#11	125.1(3)
O(9)-Tb(1)-O(6)#11	75.8(3)	O(5)#10-Tb(1)-O(6)#11	102.6(3)	O(5)#11-Tb(1)-O(6)#11	51.8(3)
O(6)#10-Tb(1)-O(6)#11	81.9(6)				

Symmetry transformations used to generate equivalent atoms: #1 x, x-y+1, z; #2 x-y+2/3, x+1/3, -z+1/3; #3 -x+4/3, -y+5/3, -z+5/3; #4 x-y+2/3, -y+4/3, -z+4/3; #5 x-y+2/3, x+1/3, -z+4/3; #6 -x+y+2/3, -x+4/3, z+1/3; #7 y-1/3, -x+y+1/3, -z+4/3; #8 -y+1, -x+1, z; #9 -y+4/3, x-y+2/3, z-1/3; #10 y-1/3, -x+y+1/3, -z+1/3; #11 x-y+2/3, -y+4/3, -z+1/3.

Table S3: Comparison of some microporous MOFs for C_2H_2/C_2H_4 separation.

	Surface area (m^2/g)[a]	Pore volume (cm^2/g)	C_2H_2 uptake (mmol/g)	C_2H_4 uptake (mmol/g)	C_2H_2/C_2H_4 uptake ratio	Selectivity[c]	Ref.
UTSA-67a	1137	0.47	5.37	2.81	1.84	5-6	19
M'MOF-3a	110	0.165	1.90	0.40	4.75	24.03	7
FeMOF-74	1350	0.626	6.80	6.10	1.11	2.08	7
NOTT-300	1370	0.433	6.34[b]	4.28[b]	1.48	2.17	31
UTSA-100a	970	0.399	4.27	1.66	2.57	5–10.7	12
Ni-DCPTP	857	0.428	6.53	4.48	1.46	5.5	33
Cu^I -MOF			1.74	1.30	1.22	1.4	21
NUC-2	1072	0.47	2.99	0.60	4.98	8.1	This work

[a] BET. [b] At a temperature of 293 K. [c] IAST analysis for C_2H_2/C_2H_4 (v/v = 1/99) mixtures at 100 kPa and room temperature.

Reference:

1. (a) G. M. Sheldrick, *SHELXTL*, version 5.1; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1998. (b) G. M. Sheldrick, *SHELX-97*, PC Version; University of Gottingen: Gottingen, Germany, 1997; (c) SMART, Saint and SADABS; Bruker AXS Inc.: Madison, Wisconsin, USA, 1998.

2. (a) V. A. Blatov, A. P. Shevchenko and V. N. Serezhkin, *J. Appl. Crystallogr.*, 2000, **33**, 1193; (b) H. W. Kuai, T. A. Okamura, W. Y. Sun. *Polyhedron*, 2014, **72**, 8–18.

3. P. E. Blochl, *Phys. Rev. B*, 1994, **50**, 17953-17979.

4. G. Kresse and J. Furthmuller, *Comput. Mater. Sci.*, 1996, **6**, 15-50.

5. G. Kresse and D. Joubert, *Phys. Rev. B.*, 1999, **59**, 1758-1775.

6. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.

7. R. A. Evarestov and V. P. Smirnov, *Phys. Rev. B.*, 2004, **70**, 233101.

8. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.