Supporting Information

Ordered assembly of two different metal clusters with same topological connectivity in one single coordination network

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General consideration.

The metallic salts and the ligands were purchased from Energy Chemical without further purification otherwise specifically mentioned. The TPT ligand (2,4,6-tri(4-pyridinyl)-1,3,5-triazine)¹. The PXRD patterns were recorded using Rigaku D/Max-2550VB+/PC with CuKa radiation ($\lambda = 1.5418$ Å). Thermogravimetric analysis (TG) was conducted on 449C Jupiter analyzer under the flowing N₂. Elemental analyses (C, H and N) were recorded on an Elementar vario EL cube elemental analyzer. Gas adsorption measurements were tested by Micromeritics 3Flex.

Control variable experiment on the effect of acetic acid on reaction system

A mixture of Mn $(OAc)_2 \cdot 4H_2O$ (0.1 mmol), H₂BDC (0.1 mmol), TPT (0.05 mmol), DMA (6 mL), and HBF₄ (200 µL) was sealed in a 25 mL Teflon-lined stainless-steel reactor. Then, add 0, 100, 200 300, 400, 500, 600, 700, 800 µL CH₃COOH to each reactor, respectively. Stir thoroughly for half an hour until the solution is clear and transparent, and then heat in an oven at 115 °C for three days, the heating rate is 10 °C per minute, and the cooling rate is 10 °C per minute. After falling to room temperature, the mother liquor is drained and the light-yellow crystal was rinsed three times with fresh DMA.

A mixture of Mn $(NO_3)_2 \cdot 4H_2O$ (0.1 mmol), H₂BDC (0.1 mmol), TPT (0.05 mmol), DMA (6 mL), and HBF₄ (200 µL) was sealed in a 25 mL Teflon-lined stainless-steel reactor. Then, add 0, 100, 200 300, 400, 500, 600, 700, 800 µL CH₃COOH to each reactor, respectively. Stir thoroughly for half an hour until the solution is clear and transparent, and then heat in an oven at 115 °C for three days, the heating rate is 10 °C per minute, and the cooling rate is 10 °C per minute. After falling to room temperature, the mother liquor is drained and the light-yellow crystal was rinsed three times with fresh DMA.

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Synthesis of [{Mn₃(µ₃-O)}(BDC)₃(TPT)]·4DMA·4H₂O CPM-153

Into a 25 mL Teflon reactor, 0.1 mmol of Mn $(OAc)_2 \cdot 4H_2O$, 0.1 mmol of H_2BDC (benzene-1,4dicarboxylate), 0.05 mmol of TPT were dissolved in 6 mL of DMA, then 200 µL of HBF₄ were added into the solution. The mixture was ultrasonically dispersed for 15 min and transferred to a stainless-steel reactor. After heating at 115 °C for 3 days, the product was harvested as light-yellow hexagonal crystals (54% yield based on metal content). Elemental Analysis (%) for $C_{58}H_{74}N_{10}Mn_3O_{21}$ calcd: C, 49.33; H, 5.28; N, 9.92. Found: C, 49.02; H, 4.95; N, 10.17.

Synthesis of [{Mn₃(µ₃-O)}{Mn₆(µ3-O)₂(OAc)₃}(BDC)₆(TPT)₃]·12DMA·9H₂O NPU-6

Into a 25 mL Teflon reactor, 0.1 mmol of Mn $(OAc)_2 \cdot 4H_2O$, 0.1 mmol of H_2BDC (benzene-1,4dicarboxylate), 0.05 mmol of TPT were dissolved in 6 mL of DMA, then 200 µL of CH₃COOH and 200 µL of HBF₄ were added into the solution. The mixture was ultrasonically dispersed for 15 min and transferred to a stainless-steel reactor. After heating at 115 °C for 3 days, the product was harvested as light-yellow hexagonal crystals. (47% yield based on metal content). Elemental Analysis (%) for calcd: C, 48.68; H, 5.11; N, 10.92. Found: C, 48.40; H, 4.80; N, 11.06.

Synthesis of [{Mn₆(µ₃-O)₂(OAc)₃}(BDC)₆(TPT)₃]·3DMA·4H₂O NPU-1-TPT

Into a 25 mL Teflon reactor, 0.1 mmol of Mn $(OAc)_2 \cdot 4H_2O$, 0.1 mmol mg of H_2BDC (benzene-1,4dicarboxylate), 0.05 mmol of TPT were dissolved in 6 mL of DMA, then 800 µL of CH₃COOH and 200 µL of HBF₄ were added into the solution. The mixture was ultrasonically dispersed for 15 min and transferred to a stainless-steel reactor. After heating at 115 °C for 3 days, the product was harvested as light-yellow hexagonal crystals. (43% yield based on metal content). Elemental Analysis (%) for C₇₈H₈₀N₁₅Mn₆O₂₇ calcd: C, 47.10; H, 4.05; N, 10.56. Found: C, 46.82; H, 4.21; N, 10.29.

Preparation of activated samples for adsorption experiments

The activation of the sample was achieved by solvent exchange with CH_2Cl_2 for 3 days followed by degassing at 60 °C under dynamically vacuum using a degassing station.

Single-crystal X-ray diffraction.

Single-crystal data for NPU-6 and NPU-1-TPT were collected on a Bruker Apex CCD area-detector diffractometer using MoKa ($\lambda = 0.71073$ Å) and GaKa ($\lambda = 1.34139$ Å) radiation under 150 and 198 K respectively. The structures were solved by direct methods for NPU-1-TPT and NPU-6 and refined with a full-matrix least-squares technique using twin law of (-1 0 0 0 -1 0 0 0 -1 2) and (-1 -1 0 0 1 0 0 0 -1 2) by OLEX2 programpackage.² Anisotropic thermal parameters were assigned to all non-hydrogen atoms for the framework. The hydrogen atoms were generated geometrically for the framework and SQUEEZE functional was applied to eliminate the electron densities within the pore.³ CCDC- 2347593 and 2347594 contains the supplementary crystallographic data for NPU-1-TPT and NPU-6.

	NPU-1-TPT	NPU-6
Formula	$C_{66}H_{45}Mn_6N_{12}O_{20}$	$C_{110}H_{82}Mn_9N_{27}O_{36}$
Crystal system	Orthorhombic	Hexagonal
M/g mol ⁻¹	1655.78	2852.48
Space group	<i>C</i> 222 ₁	<i>P</i> -6 <i>m</i> 2
<i>a</i> , Å	17.1992(13)	17.1984(7)
b, Å	29.767(3)	17.1984(7)
c, Å	21.8387(18)	18.6767(10)
<i>V</i> , Å ³	11180.7(17)	4784.2(5)
Z	4	1
d_{cal} /g cm ⁻³	0.984	0.990
Temperature, K	150	198
Completeness	1.82/0.98	1.89/1.00
Goodness-of-fit on <i>F</i> ² [a]	1.052	0.980
R(reflections)	0.0807(11467)	0.0294 (3615)
wR2(reflections)	0.2085(11564)	0.0735 (4160)

Table S1. Crystal data and structure refinements for NPU-1-TPT and NPU-6.

[a] $GOF = [\Sigma w (F_o^2 - F_c^2)^2 / (n_{obc} - n_{param})]^{1/2}$. [b] $R_1 = ||F_o| - |F_c|| / \Sigma |F_o|$, $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (Fo^2)^2]^{1/2}$.

Single-component gas sorption experiment

The Micromeritics 3Flex instrument was used for collecting all the sorption isotherms. All the highpurity gases used in the single-gas adsorption experiments were purchased commercially: He (99.999%), C2H4 (99.995%), N2 (99.999%), C2H6 (99.9%). Before the single-gas sorption experiments, the sample was first fully exchanged with fresh CH₂Cl₂ three times daily for three days, followed by activation at 60 °C under high vacuum for 12 hours. When testing N₂ adsorption isotherms, the temperature was controlled at 77 K using a Dewar bottle containing 4 L of liquid N_2 . The precise control of 298 K was implemented by the DC-2006 of Ningbo Scientz Biotechnology, which contains a cycle control system of ethylene glycol-H₂O mixture. The sample was degassed at 25 °C under high vacuum for 6 hours to regenerate at every interval of two independent isotherms.

IAST selectivity calculation

Langmuir-Freundlich fit: The isotherm data for C_2H_4 and C_2H_6 in **CPM-153**, **NPU-1-TPT**, **NPU-6** were fitted with the single-site Langmuir-Freundlich model.

$$q = Q_{sat} \frac{(b_A p)^v}{1 + (b_A p)^v}$$

 b_A is Langmuir-Freundlich constant for species *i* at adsorption site A (Pa^{- ν}). Q_{sat} is saturation loading (mol kg⁻¹). q_i component molar loading of species *i* (mol kg⁻¹). p_i is partial pressure of species i (Pa). v is Freundlich exponent (dimensionless).

IAST selectivity calculation: Adsorption selectivity of C_2H_6/C_2H_4 mixed gases was predicted from single component adsorption isotherms using Ideal Adsorbed Solution Theory (IAST).⁴

$$S = \frac{X_A / X_B}{Y_A / Y_B}$$

Where *S* is the selectivity of component A relative to B. X_A and X_B are the molar fractions of components A and B in the adsorption phase, respectively. Y_A and Y_B are molar fractions of components A and B in the gas phase, respectively.

Grand Canonical Monte Carlo (GCMC) simulations

The host-guest interactions were calculated using Material Studio software package. Before the Grand Canonical Monte Carlo (GCMC) simulations, the guest molecules C_2H_4 and C_2H_6 were geometrically optimized using Dmol³ method⁵ and the electrostatic potential (EPS) charges were applied to the guset molecules. The Grand Canonical Monte Carlo (GCMC) simulations were performed using Sorption module. The simulation boxes were set up as supercells 2 × 2 × 2 for CPM-153, 2 × 2 × 2 for NPU-1-TPT and 2 × 2 × 2 for NPU-6, and both the framework and the guest molecules were considered as rigid bodies. The Metropolis method⁶ was applied to perform the GCMC simulations. The gas–framework interaction and the gas–gas interaction was described by the standard Universal force field.⁷ The loading steps, equilibration steps, and production steps were all set to 2.0×10^7 . The saturation/maximum uptakes were modeled at 298 K using the fixed pressure task with 1.0×10^5 equilibration steps, followed by 2.0×10^7 production steps for calculating the ensemble averages. The first favorable adsorption sites were simulated by the

locate task with one guest molecule and the fixed loading task was applied to envaluate the adsorption enthalpy at 298 K.

Dynamic gas breakthrough experiment

The breakthrough curves were recorded on a homemade apparatus. An equimolar gas mixture of C_2H_4/C_2H_6 (total gas pressure: 100 kPa; total gas flow 1 cm³ min⁻¹) and $C_2H_4/C_2H_6/C_2H_2$ (total gas pressure: 100 kPa; total gas flow 1.5 cm³ min⁻¹) passes through the packing column filled with 5.2/1.2 g NPU-6 at 298 K, and the outlet gas concentration was monitored by online mass spectrometer.

Dynamic gas breakthrough simulation

The transient breakthrough simulations were carried out by the single adsorption bed model (Figure S1), the method was set according to the reported results by Krishna.⁸⁻¹¹ All the isotherm parameters



were extracted using Langmuir-Freundlich (LF) model as described above. The bed is 0.35 m in height and 3.5 cm in diameter, the gas feeds were set as C_2H_4/C_2H_6 (1/1, v/v) with flow rate of 5 × 10⁻⁴ mol s⁻¹ at constant pressure of 1.0 bar and 298 K. During the simulation the differences of mass transfer coefficient of gases were not taken into consideration. The fixed bed was charged with He at time zero and the intra-particle diffusing is ignored.

Figure S1. diagram of a single adsorption bed model.



Figure S2. Mn 2p spectra for NPU-6. The peak of the sample at 641.4 and 653.0 eV confirming theexistence of Mn^{II}, while peak of the sample became very strong at 643.00 and 653.02 eV confirmingtheexistenceofMn^{III}.



Figure S3. FT-IR spectra for CPM-153, NPU-1-TPT and NPU-6.



Figure S4. Bridging modes of carboxylate groups in NPU-6.



Figure S5. Compared to **CPM-153** (only $[Mn_3(\mu_3-O)]$ cluster) and **NPU-1-TPT** (only $[Mn_6(\mu_3-O)_2(CH_3COO)_3]$ cluster), the two metal clusters are arranged in an ABAB layer in **NPU-6** (mixed cluster).



Figure S6. Powder X-ray diffraction pattern of obtained products in the acetic acid regulation experiments with Mn $(NO_3)_2$ ·4H₂O as manganese source.



Figure S7. Powder X-ray diffraction patterns of obtained products in the formic acid regulation experiments with Mn $(OAc)_2 \cdot 4H_2O$ as manganese source.



Figure S8. PXRD patterns of the products under different conditions. The metal salt was Mn $(OAc)_2 \cdot 4H_2O$, and the influence of HBF₄ on the reaction results was investigated by using control variable method. When no HBF₄ is added, the target product cannot be generated, and the crystal slowly grows larger as the amount of HBF₄ increases. When the amount of HBF₄ is 0.2 mL, the crystal is transparent hexagonal, continue to add HBF₄, impurities appear inside the crystal.



Figure S9. TG curves of as-synthesized and CH₂Cl₂ changed samples for CPM-153, NPU-1-TPT and NPU-6.



Figure S10. N_2 adsorption isotherms for CPM-153 at 77 K.



Figure S11. N_2 adsorption isotherms for NPU-1-TPT at 77 K.





Figure S13. H-K Pore size distribution of CPM-153, NPU-1-TPT and NPU-6 fitting from N2isothermat77K.(Poregeometry:sphere)



Figure S14. Nitrogen adsorption isotherm at 77 K of CPM-153 samples treating at different heatingtemperatures.(Holdingtime:1h)



Figure S15. Nitrogen adsorption isotherm at 77 K of NPU-1-TPT samples treating at differentheatingtemperatures.(Holdingtime:1h)



Figure S16. Nitrogen adsorption isotherm at 77 K of NPU-6 treating at different heating temperatures. (Holding time: 1 h)



Figure S17. PXRD patterns and N₂ sorption isotherm at 77 K of **CPM-153** (a, d), **NPU-6** (b, e) and **NPU-1-TPT** (c, f) after exposed to a relative humidity of 70% for a certain time.



Figure S18. C₂H₄ and C₂H₆ adsorption isotherm of CPM-153 at 298 K.



Figure S19. C₂H₄ and C₂H₆ adsorption isotherm of NPU-1-TPT at 298 K.



Figure S20. C₂H₂, C₂H₄ and C₂H₆ adsorption isotherm of NPU-6 at 298 K.



Figure S21. Langmuir-Freundlich (L-F) fitting of C_2H_4 (a), C_2H_6 (b) and fitting parameters (c) at 298 K for **CPM-153**.



Figure S22. Langmuir-Freundlich (L-F) fitting of C_2H_4 (a), C_2H_6 (b) and fitting parameters (c) at 298 K for **NPU-1-TPT**.



Figure S23. Langmuir-Freundlich (L-F) fitting of C_2H_4 (a), C_2H_6 (b) and fitting parameters (c) at 298 K for **NPU-6**.



Figure S24. Molecular modeling determined primary adsorption sites of C_2H_4 (top) and C_2H_6 (bottom) in **CPM-153** (a, d), **NPU-1-TPT** (b, e) and **NPU-6** (c, f). Adsorbed C2 molecules are presented in space-filling mode (C(network), gray; C(C2 gas), orange; H, white; O, red; N, blue; Mn, purple).



Figure S25. The $C_2H_2/C_2H_4/C_2H_6$ (total gas flow: 1.5 cc min⁻¹) breakthrough curve of NPU-6 at 298 K and 100 kPa.



Figure S26. C₂H₆ adsorption (solid) -desorption (hollow) cycling tests of NPU-6 at 298 K.

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