Supporting information

A ***rht*** type Metal-Organic Framework based on *Small Cubicuboctahedron* Supermolecular Building Blocks and Adsorption Properties

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S1. Ligand synthesis

The synthetic procedure of the ligand: 2,4,6-trimethylbeneze-1,3,5-tri-isophthalic acid (TMBTI) is illustrated in Fig. S1.

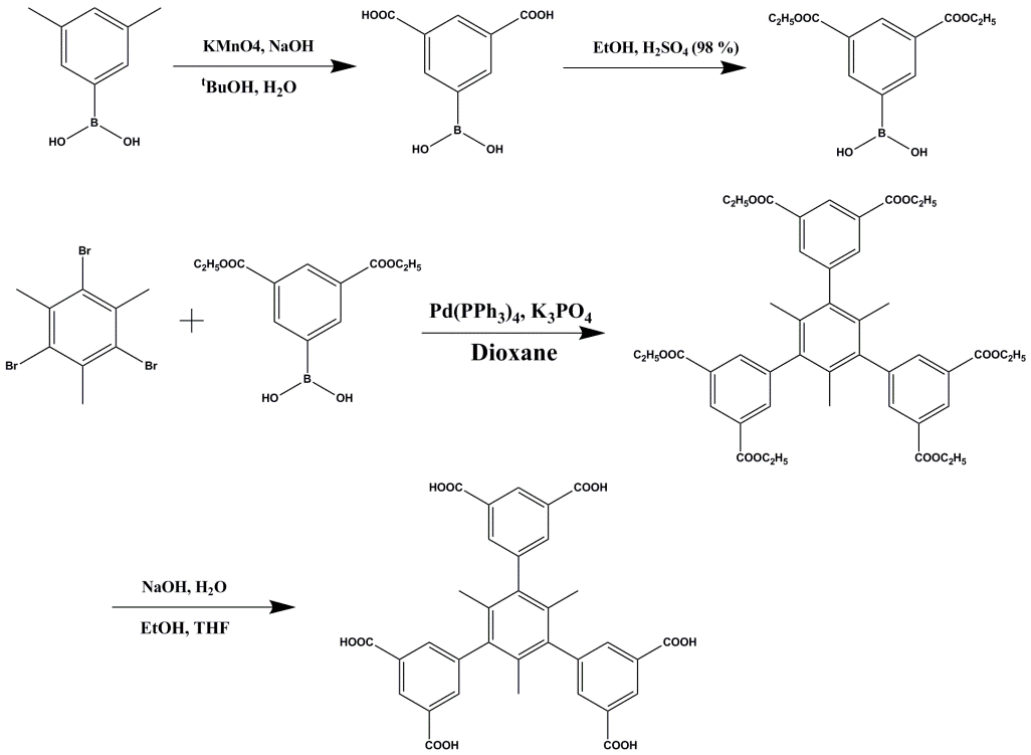
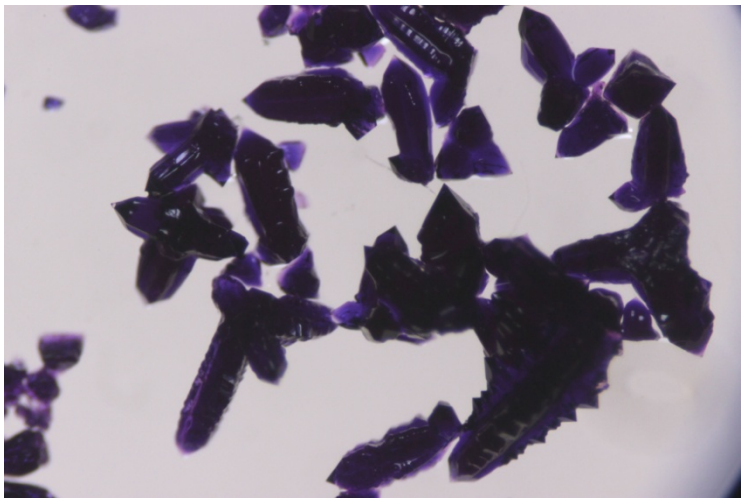


Fig. S1 Synthetic route of TMBTI

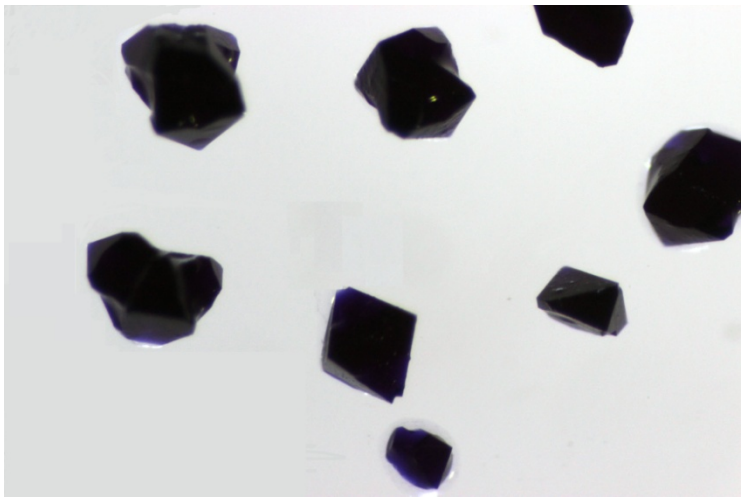
3,5-dicarboxyethylester-phenylboronic acid was prepared according to the procedure described in the literature[1]. The ligand TMBTI was synthesized by Suzuki-coupling reaction of 1,3,5-triboromo-2,4,6-trimethylbenzene and 3,5-dicarboxyethylester-phenylboronic acid. 1,3,5-triboromo-2,4,6-trimethylbenzene (3.569 g, 10 mmol), 3,5-dicarboxy0ethylester-phenylboronic acid (8.778 g , 33 mmol), K_3PO_4 (21.0 g, 100 mmol) were combined in a 500 ml round bottom flask. Then the mixture was degassed at Schlenk line and recharged with argon. The evacuate-charge procedure was repeated for at least three times to ensure the inert gas atmosphere of the reaction system. After introducing $Pd(PPh_3)_4$ (577.8 mg, 0.5 mmol), and dioxane (300 ml), the mixture of reactants and catalyst was heated to 95 °C and stirred for 72 hours under the inert gas atmosphere. When cooling to room temperature, the resulting mixture was evacuated to dryness and extracted with $CHCl_3$ (50 ml) for three times. Then, the extraction was washed with water, dried with anhydrous Na_2SO_4 and evacuated

under vacuum. The resulting yellow oil was purified by silica gel column using elute of petroleum / ethyl acetate (3/1, v/v,). The obtained white solid was hydrolyzed with the NaOH (12 g, 300 mmol) in the solution of THF/EtOH/H_2O (2/2/3, 300 ml). After acidified with concentrated HCl (adjust the pH value of the solution to 2~3), a white precipitate was separated by filtration and dried at 60 °C in vacuum. ^{1}HNMR (d^6-DMSO, 500MHz): 13.35(b, 6H), 8.48(t, 3H), 8.01(d, 6H), 1.62 (s, 9H).

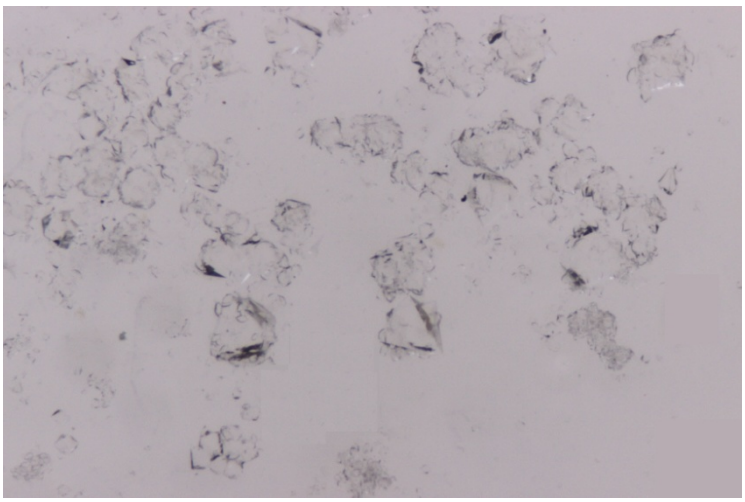
S2. Photographs



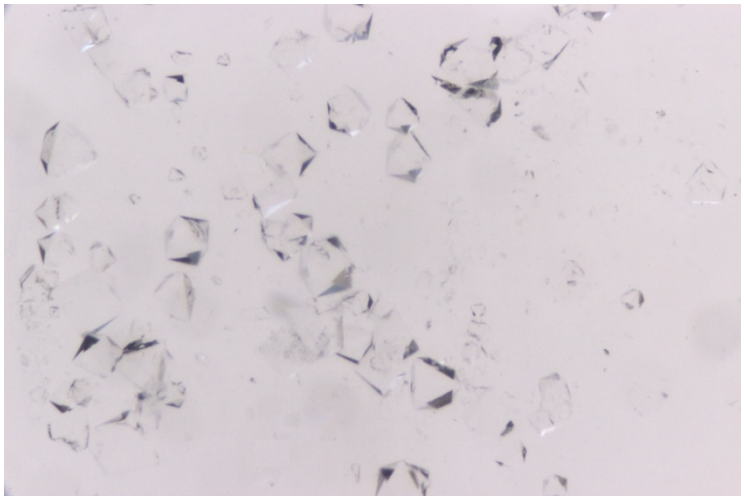
(a)



(b)



(c)



(d)

Fig. S2 Photographs of as-synthesized NPC-5 and SDU-1. (a) NPC-5 synthesized from method-1 (yield: 74%); (b) NPC-5 synthesized from method-2(yield: 81%); (c) SDU-1 synthesized from method-1(yield: 63%); (d) SDU-1 synthesized from method-2(yield: 67%).

S3. Single-crystal X-ray crystallography

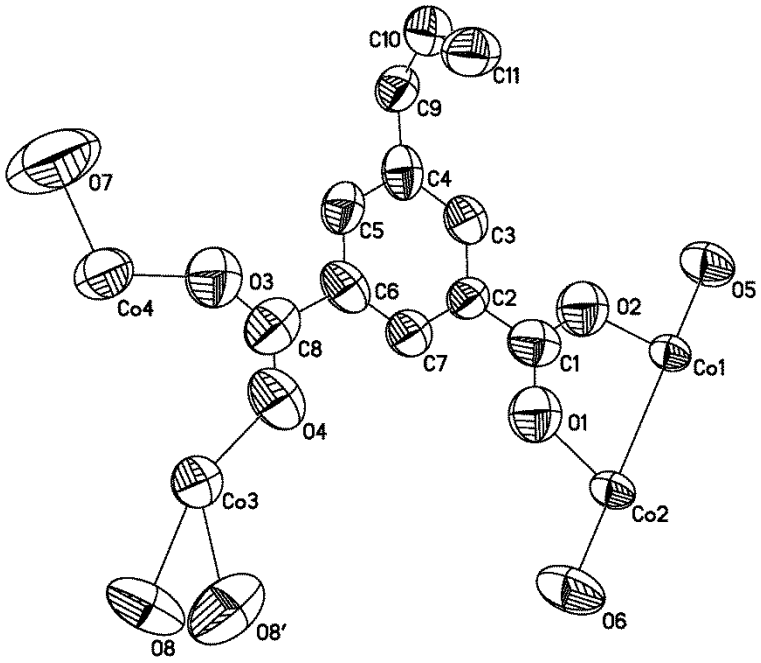


Fig. S3 Asymmetric unit of NPC-5 (Thermal ellipsoid: 40 %)

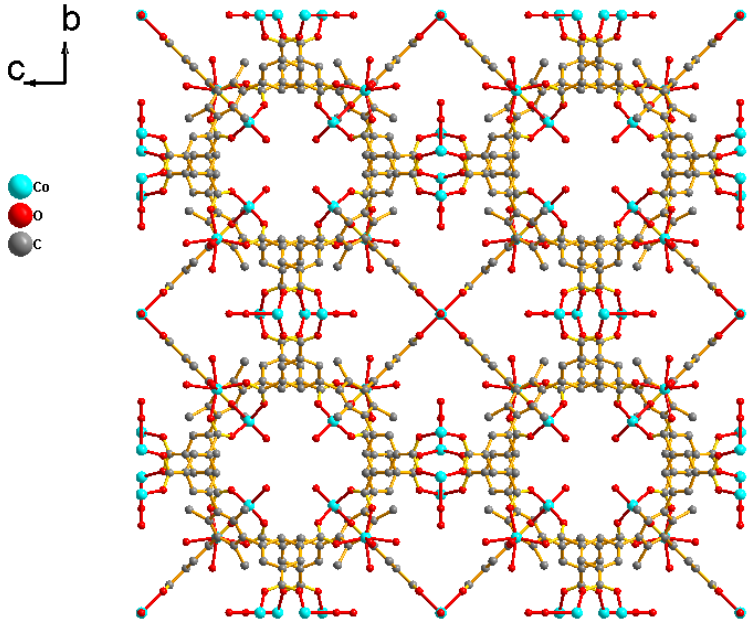


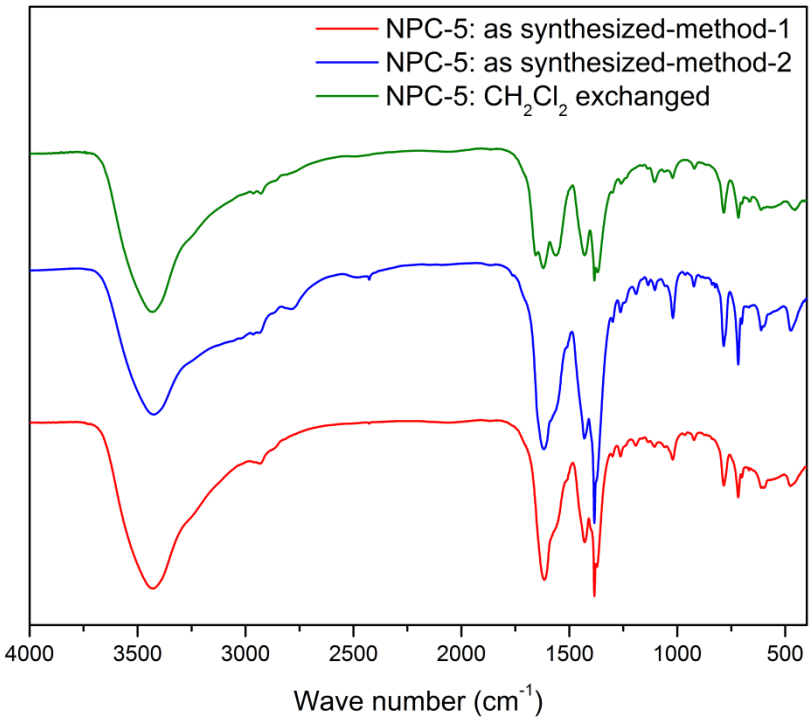
Fig.S4 Packing mode presentation of NPC-5 viewing from ***a / b / c*** direction

Table S1 Crystal data and structure refinement for SDU-1 and NPC-5

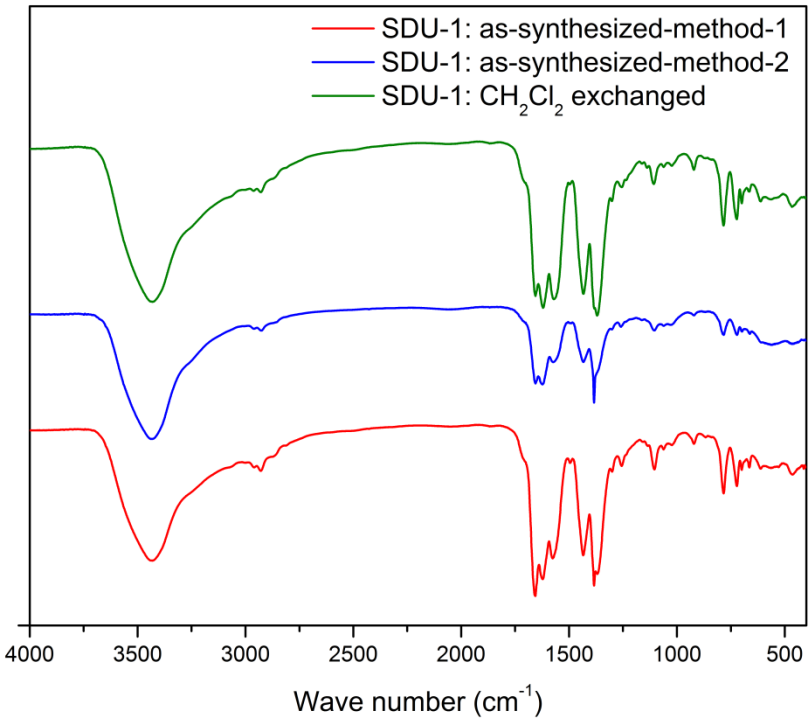
Identification code		SDU-1		NPC-5	
		Method-1	Method-2	Method-1	Method-2
Empirical formula		$C_{66}H_{36}O_{32}Zn_7$		$C_{66}H_{36}O_{32}Co_7$	
Formula weight		1798.84		1753.51	
Crystal system		Cubic	Cubic	Cubic	Cubic
Space group		Fm-3m		Fm-3m	
Unit cell parameters	a/ Å	38.623(5)	38.651	38.757(2)	38.725
	b/ Å	38.623(5)	38.651	38.757(2)	38.725
	c/ Å	38.623(5)	38.651	38.757(2)	38.725
	α/°	90	90	90	90
	β/°	90	90	90	90
	γ/°	90	90	90	90
	V/ $Å^3$	57614(12)	57740	58216(6)	58073
Z		16		16	
Calculated density, g/cm^3		0.829		0.822	
F(000)		14368		14032	
Reflections collected /unique		21913/1510		33542/2656	
Goodness-of-fit on F^2		1.037		1.057	
Final R indices [I>2sigma(I)]		R1=0.0726, wR2=0.1662		R1=0.0862 wR2=0.2838	
R indices (all data)		R1=0.1736, wR2=0.1935		R1=0.1396 wR2=0.3126	
Largest diff. Peak and hole, e $Å^3$		0.321 and -0.243		0.658 and -0.598	

*Unit cell parameters of SDU-1[2]: *cubic, Fm-3m,* $\boldsymbol{a}$ = 38.5910(8) Å, $\boldsymbol{\alpha}$ = 90 $Å^3$, *V*=57472(2),

S4. Infrared spectroscopy



(a)



(b)

Fig. S5 Infrared spectroscopy of (a) NPC-5 and (b) SDU-1

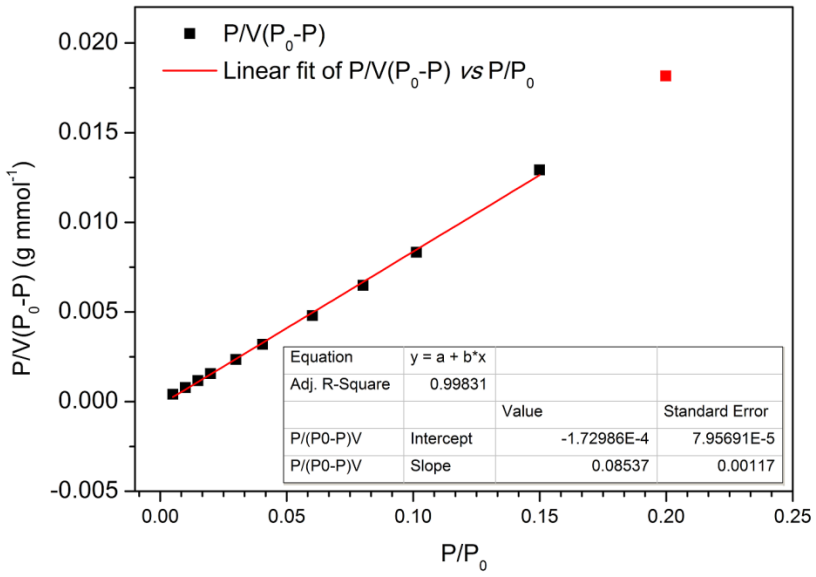
S5. Calculation of BET surface area and Langmuir surface area

1. Calculation of BET surface area.

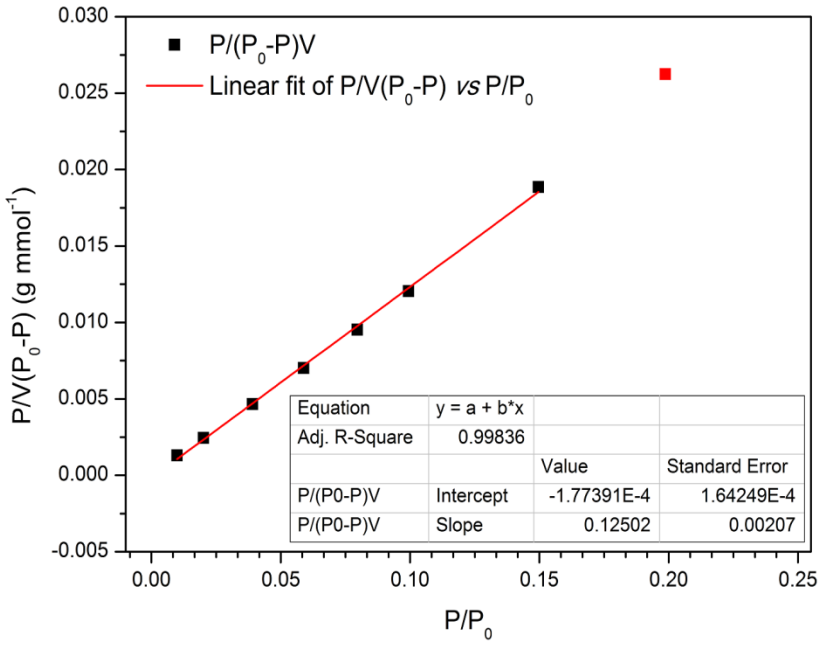
The BET surface area of NPC-5 and SDU-1 was calculated by using Brunauer-Emmett-Teller equation from N_2 adsorption isotherm at 77 K (as shown in equation 1).

$$\frac{P}{V(P_0 - P)} = \frac{1}{CV_m} + \frac{C-1}{CV_m} \cdot \frac{P}{P_0} \qquad (1)$$

Using the N_2 isotherm of NPC-5 and SDU-1 at 77 K, the term $P/V(P_0-P)$ was plotted and linear fitted with P/P_0 in the pressure range of $0.001 < P/P_0 < 0.15$, as shown in Fig. S6.



(a)



(b)

Fig. S6 (a) BET plot of NPC-5 for N_2 adsorption at 77 K in the linear region ($0.001<P/P_0<0.15$). (b) BET plot of SDU-1 for N_2 adsorption at 77 K in the linear region ($0.001<P/P_0<0.15$)

According to the Brunauer-Emmett-Teller equation, the terms (C-1) / CV_m and 1 / CV_m are equal to the slope and the intercept of the fitted line, respectively.

For NPC-5:

$$\frac{C-1}{CV_m} = 0.08537$$

$$\frac{1}{CV_m} = 1.72986\times10^{-4}$$

So, we can obtained the value of C and V_m for NPC-5 as following:

C = 494.508

V_m=11.6900 mmol g^{-1}

The BET surface area is calculated by the equation (2).

$$S_{BET} = V_m \cdot A \cdot \sigma_m \qquad (2)$$

Where A is the Avogadro constant (6.023×10^{23} mol^{-1}), σ_m is sectional area of one nitrogen molecular (1.62×10^{-19} m^2). So the BET surface area of NPC-5 is 1140 m^2 g^{-1}.

Using the same procedure as NPC-5, we can obtained the value of C and V_m for SDU-1 as following:

C = 494.508

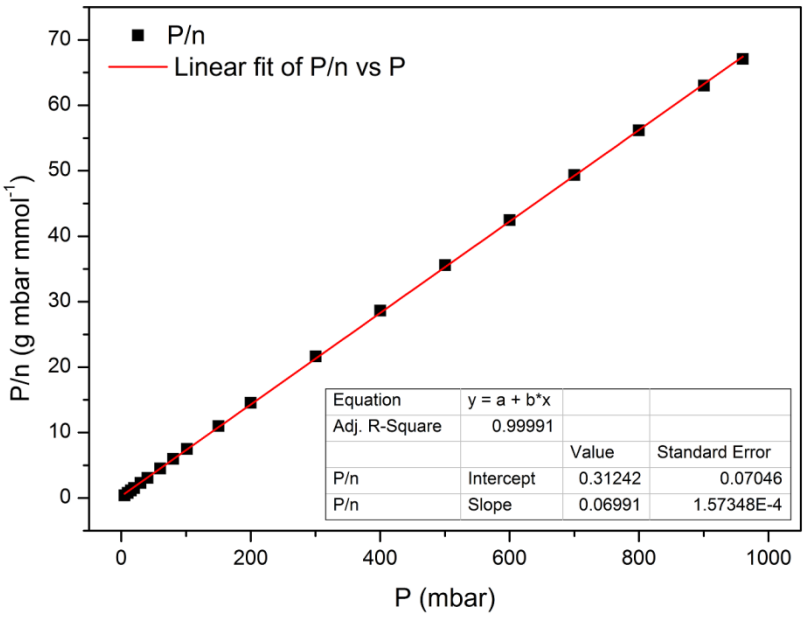
V_m=11.6900 mmol g^{-1}

And the BET surface area of SDU-1 is 779 m^2 g^{-1}.

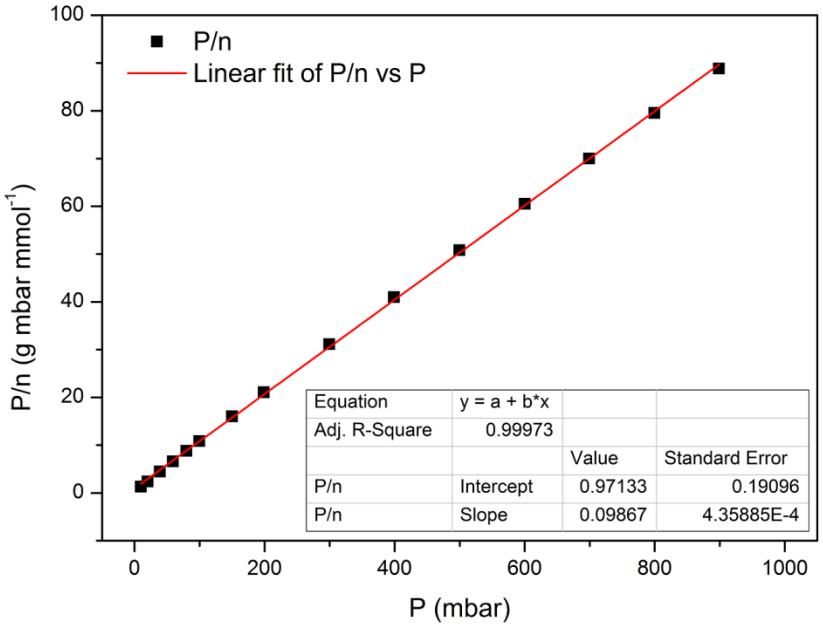
2. Calculation of Langmuir surface area.

The N_2 isotherms of NPC-5 and SDU-1 at 77 K were fitted by using Langmuir equation (as shown in equation (3). As shown in Fig. S7, the term P/n shows perfect linear relationship with the term P.

$$\frac{P}{n}=\frac{P}{n_m}+\frac{1}{bn_m} \qquad (3)$$



(a)



(b)

Fig. S7 The variation of P/n with P for N_2 adsorption at 77 K on (a) NPC-5. (b) SDU-1

For NPC-5, the slope of the fitted line is 0.0458, which is equal to $1/n_m$ in the Langmuir equation. So, we obtained the n_m as the following.

n_m= 14.30 mmol g^{-1}

The Langmuir surface area is calculated by the equation (4).

$$S_g = n_m \cdot A \cdot \sigma_m \qquad (4)$$

Where A is the Avogadro constant (6.023×10^{23} mol^{-1}) and σ_m is sectional area of one nitrogen molecular (1.62×10^{-19} m^2). So the calculated Langmuir surface area of NPC-5 is 1395 m^2 g^{-1}.

In the same way, the Langmuir surface area of SDU-1 is calculated to be 989 m^2 g^{-1}.

S6. Calculation of isosteric adsorption enthalpy

Method 1:

The gas adsorption data of NPC-5 and SDU-1 can be analyzed using Virial methods[3] based on the following equation.

$$\ln(n/P) = A_0 + A_1 \cdot n + A_2 \cdot n^2 + A_3 \cdot n^3 + \cdots \qquad (5)$$

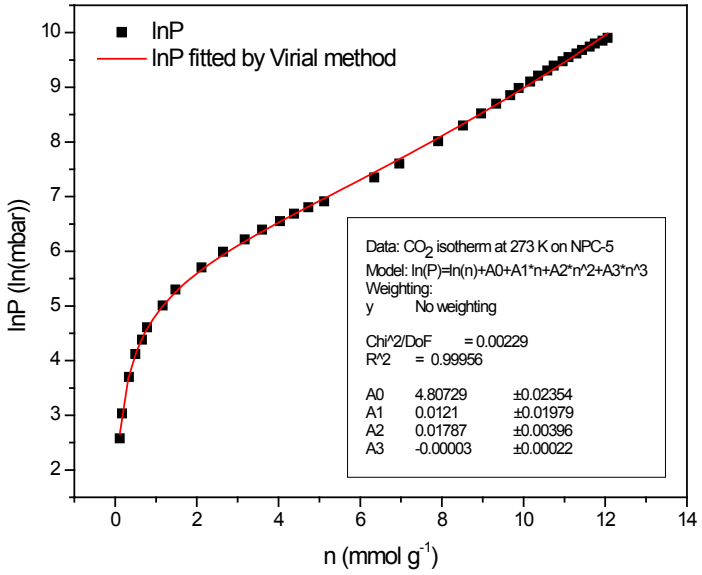
Where P is the pressure, n is the amount absorbed and A_0, A_1, A_2, A_3 are Virial coefficients.

The original Virial equation can also be transformed into another form as shown in equation (6)[3].

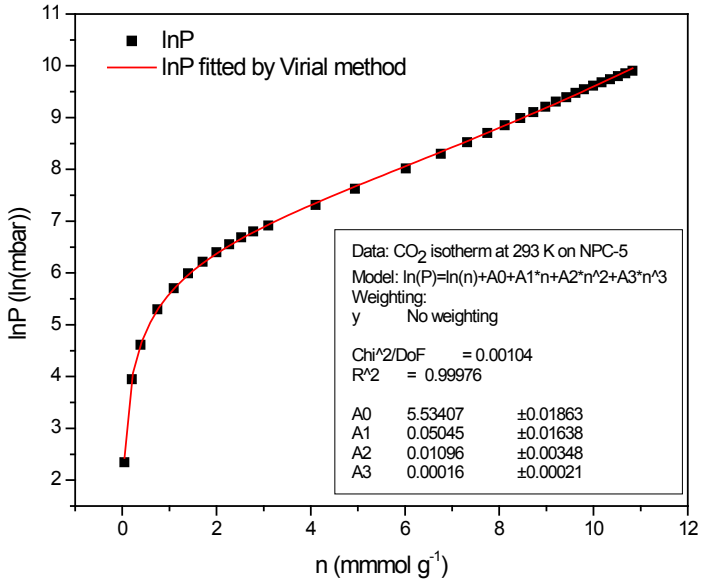
$$\ln(n) = \ln(P) + A_0 + A_1 \cdot n + A_2 \cdot n^2 + A_3 \cdot n^3 + \cdots \qquad (6)$$

Isosteric adsorption enthalpy:

The adsorption isotherms of CO_2 at two different temperatures on NPC-5 and SDU-1 were fitted using Virial equation in the pressure range of 0~20 bar (as shown in Fig. S8 and Fig. S9). Then the adsorption enthalpy was calculated by Van't Hoff isochore, and the Q_{st} of CO_2 at different uptakes were plotted in Fig. 6a. After then, the isosteric adsorption enthalpy of CH_4 on both MOFs were calculated by the same procedure as CO_2 and plotted in Fig 6a.

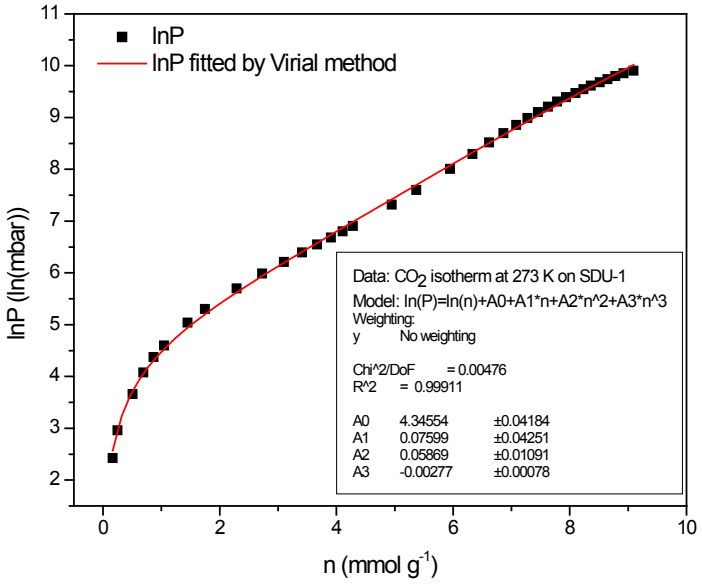


(a)

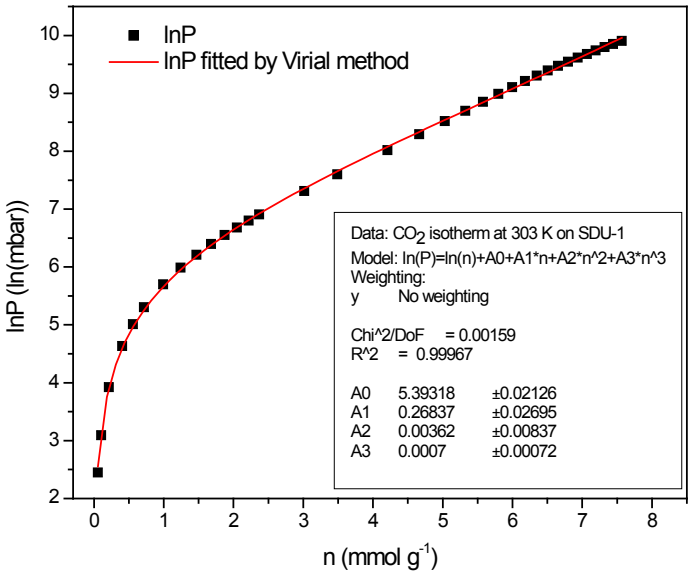


(b)

Fig. S8 CO_2 isotherms for NPC-5 fitted using Virial method (a) 273 K and (b) 293 K

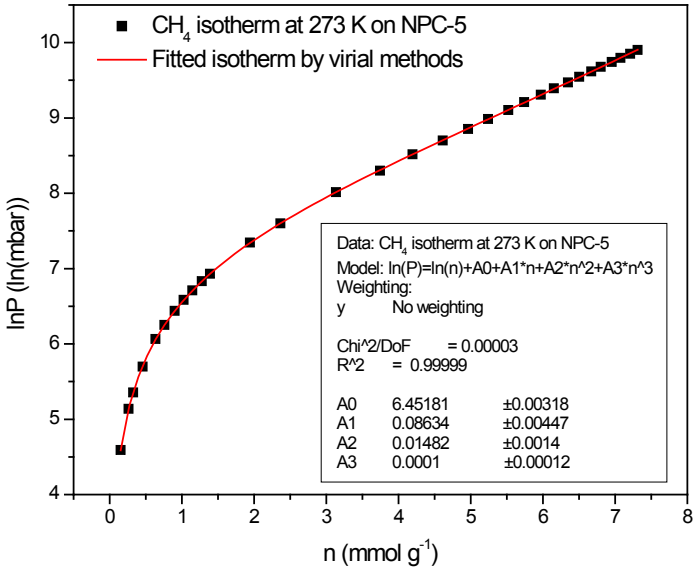


(a)

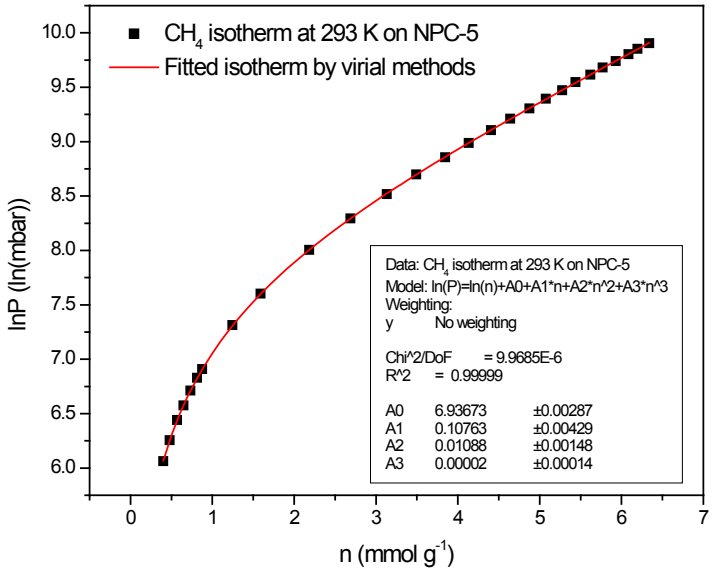


(b)

Fig. S9 CO_2 isotherms for SDU-1 fitted using Virial method (a) 273 K and (b) 303 K

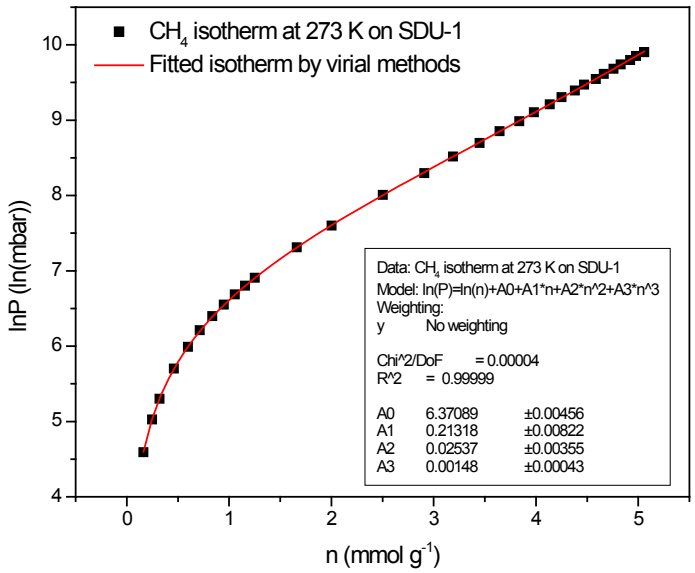


(a)

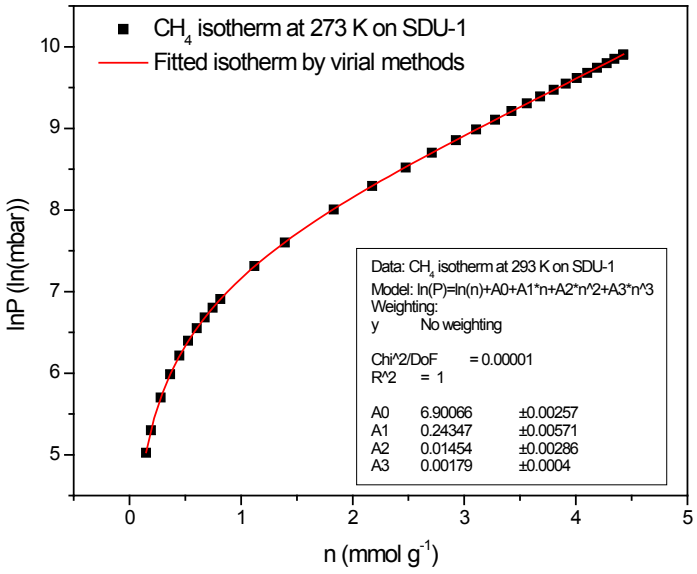


(b)

Fig. S10 CH_4 isotherms for NPC-5 fitted using Virial method (a) 273 K and (b) 293 K



(a)



(b)

Fig. S11 CH_4 isotherms for SDU-1 fitted using Virial method (a) 273 K and (b) 293 K

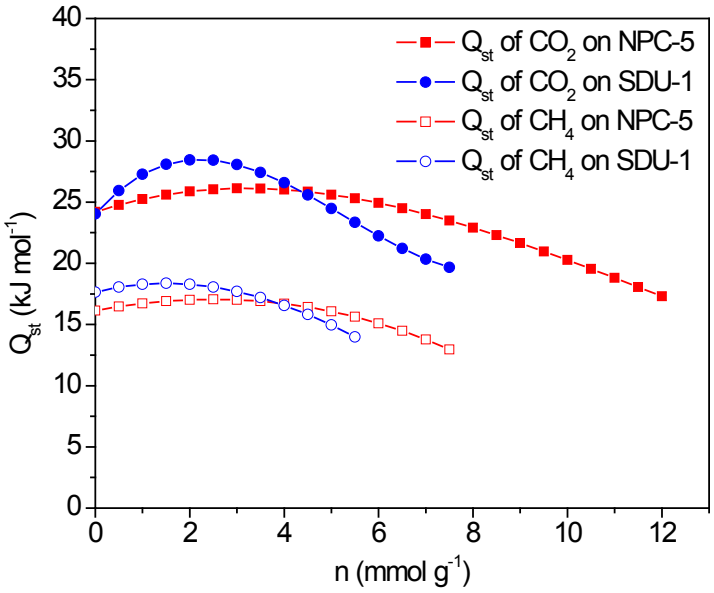


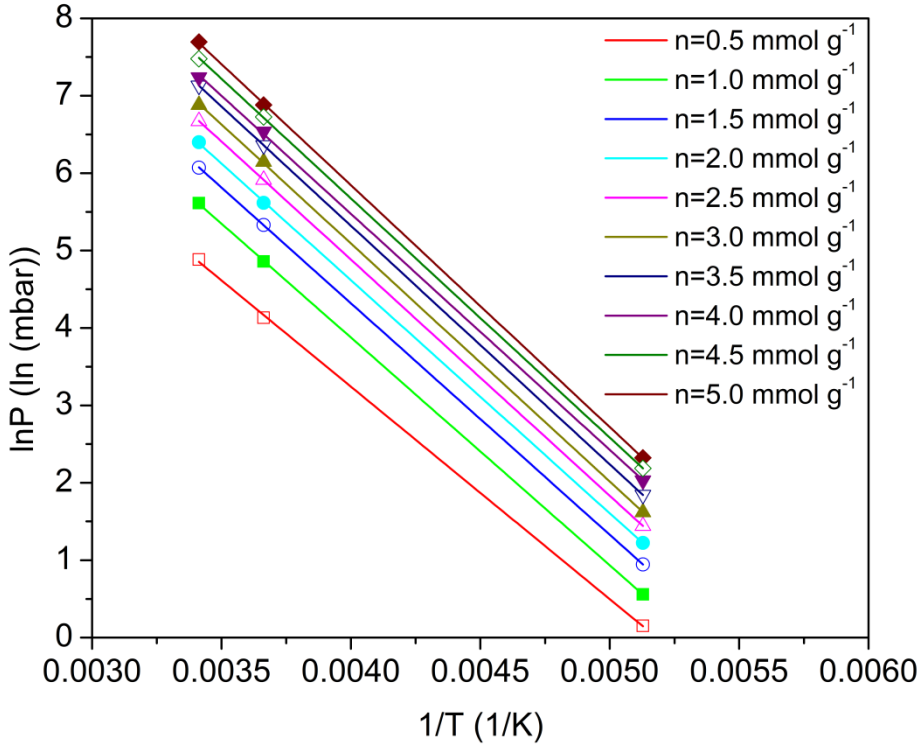
Fig. S12 Isosteric adsorption enthalpies of CO_2 and CH_4 on NPC-5 (red) and SDU-1(blue) derived from Virial analysis

Method 2:

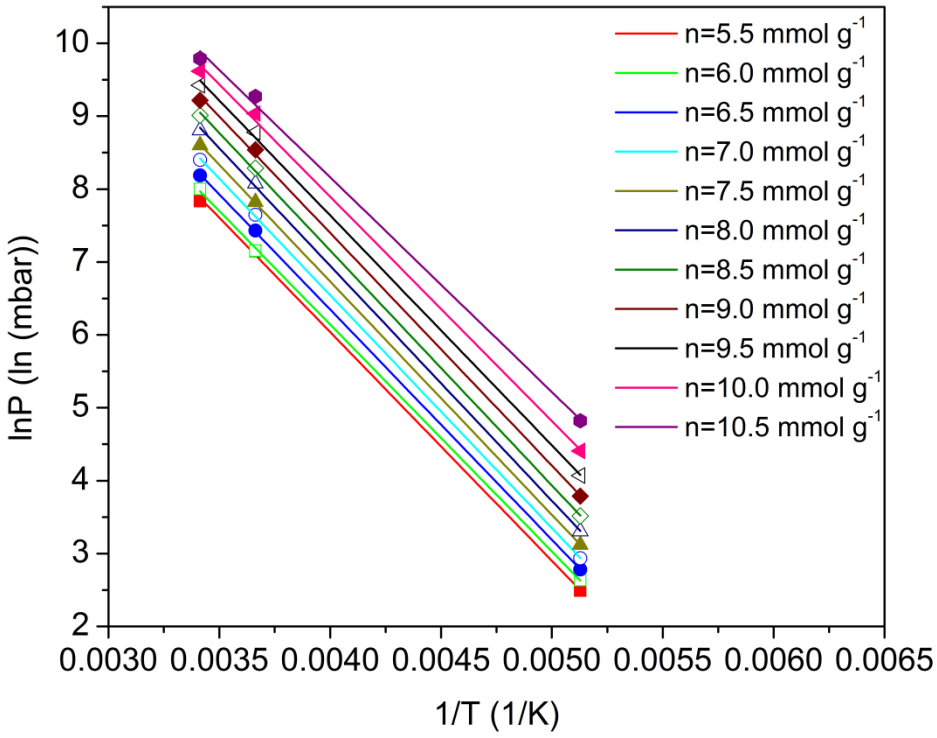
The Q_{st} were calculated by the Clausius-Clapeyron equation:

$$\frac{Q_{st}}{R} = \frac{d(\ln P)}{d(1/T)} \qquad (7)$$

lnP and 1/T were derived from isotherms at different temperatures. The relationship between lnP and 1/T were linear fitted. As shown in Figure S12 and S13, the term lnP exhibits perfect linear relationship with the term 1/T, indicating the good reliability of the adsorption data. The slope of lnP versus 1/T were derived from the fitted line, and Q_{st} was calculated from the above equation.



(a)



(b)

Figure S13 (a) Linear fitting of lnP versus 1/T for CO_2 adsorption on NPC-5 (n: 0.5~5.0 mmol g^{-1});

(b) Linear fitting of lnP versus 1/T for CO_2 adsorption on NPC-5 (n: 5.5~10.5 mmol g^{-1})

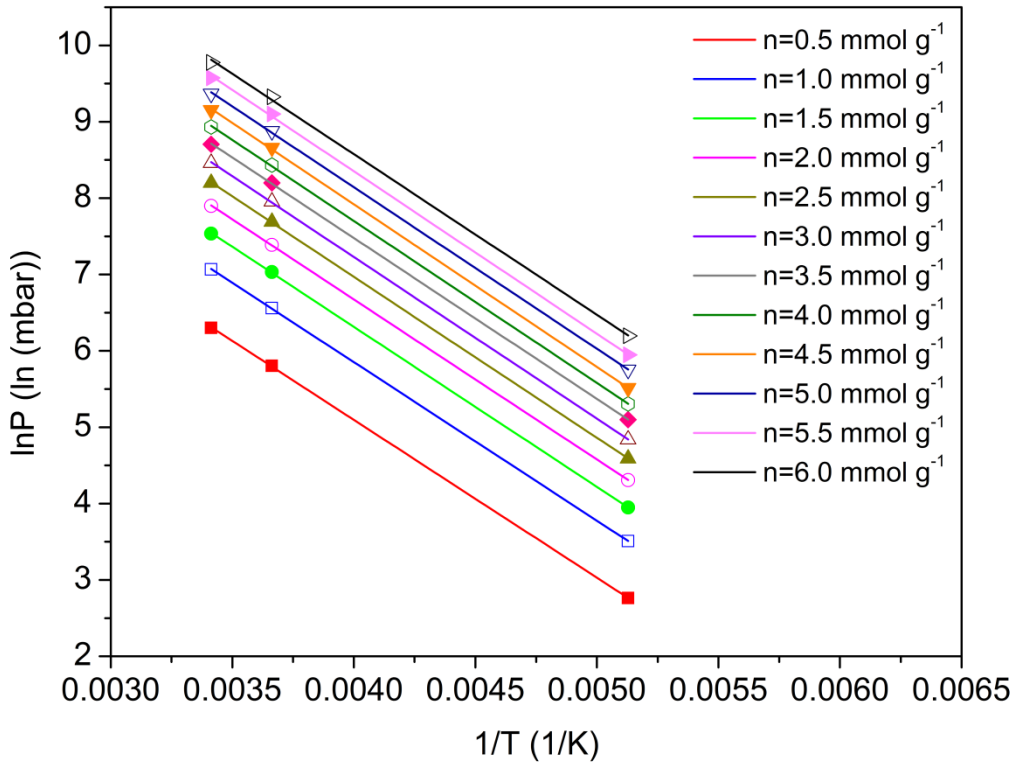


Figure S14 Linear fitting of lnP versus 1/T for CH_4 adsorption on NPC-5

S7. Langmuir equation simulation

The isotherm of CH_4 on NPC-5 at 293 K was modeled using the Langmuir equation:

$$\frac{P}{n} = \frac{P}{n_m} + \frac{1}{b \cdot n_m} \quad (8)$$

Where P is the pressure (mbar), n is adsorbed amount (mmol g^{-1}), n_m and b are constants.

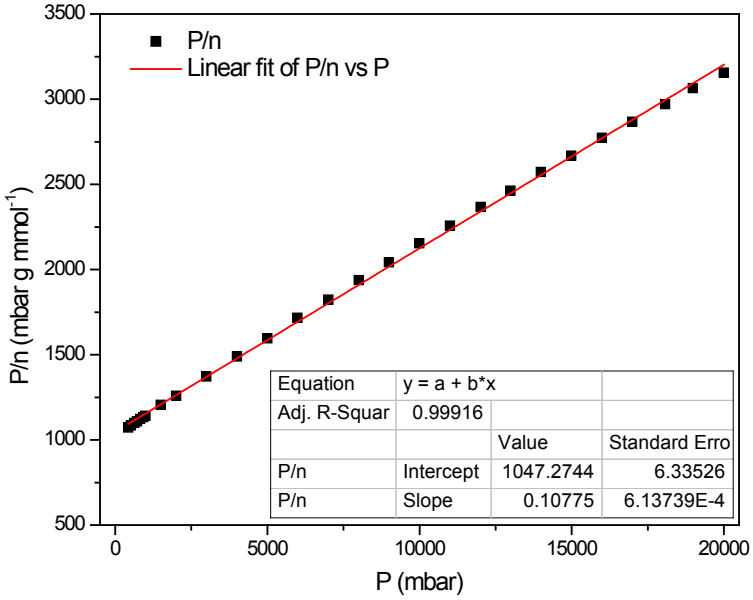


Fig. S15 Langmuir graph for CH_4 adsorption on NPC-5 at 293 K

As shown in Fig. S12, the term P/n exhibits a good linear relationship with the term P. When P/n is linearly fitted with n, the obtained fitted equation is:

$$\frac{P}{n} = 0.10775P + 1047.274$$

From the fitted equation, the relationship between n and P can be established and plotted in Fig. 6b.

S8. Comparative study of activation methods

In order to explore the right activation temperature, low-temperature activation (heating at 60 ℃ under ultrahigh vacuum) and high-temperature activation (heating at 130 ℃ under ultrahigh vacuum) on the CH_2Cl_2 exchanged sample of SDU-1 were performed, respectively. After then, CO_2 isotherms under the same conditions were conducted on two batches of samples to evaluate the porosity. The weight loss diagram of NPC-5 in the activation process before gas sorption

measurements is shown in Figure S16. The CO_2 isotherms of the NPC-5 and SDU-1 activated at different temperatures are shown in Figure S17(a) and Figure S17(b), respectively. The comparison of PXRD patterns of SDU-1 activated at two temperatures is demonstrated in Figure S18.

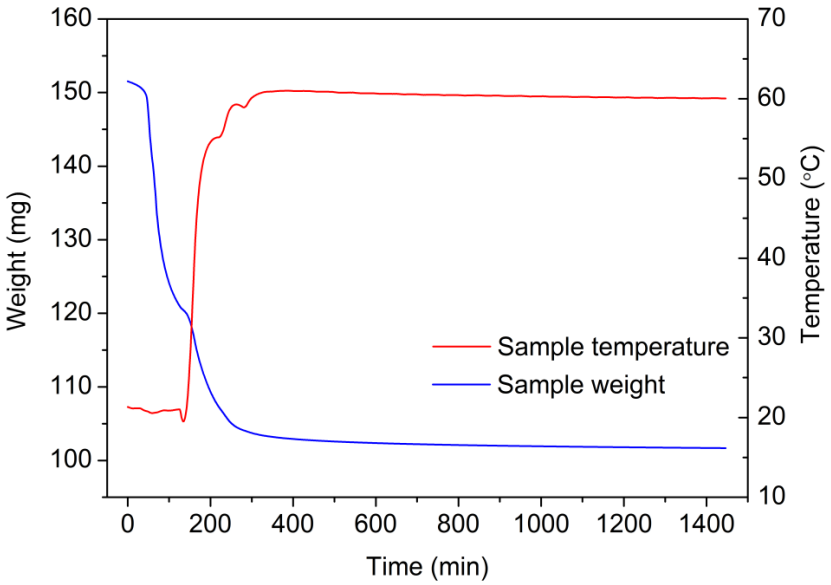
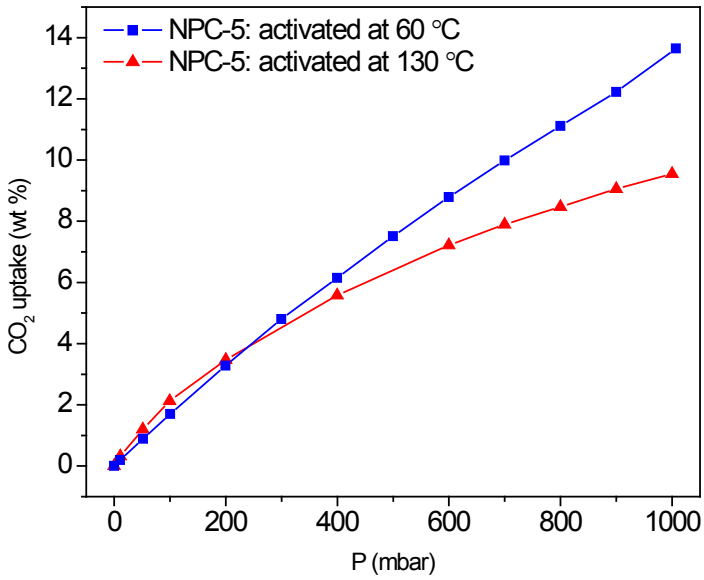
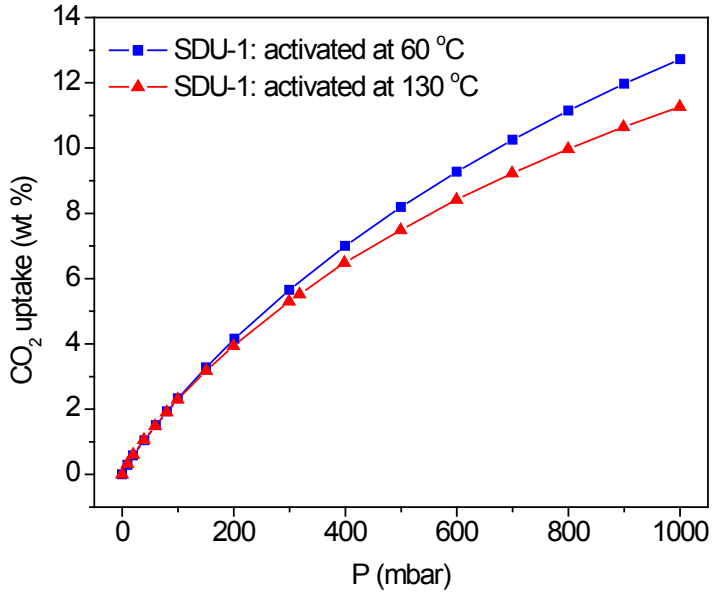


Figure S16 Weight loss diagram of NPC-5 during activation process



(a)



(b)

Figure S17 Comparison of CO_2 isotherms at 293 K on samples activated at 60 ℃ and 130 ℃.

(a) NPC-5; (b) SDU-1

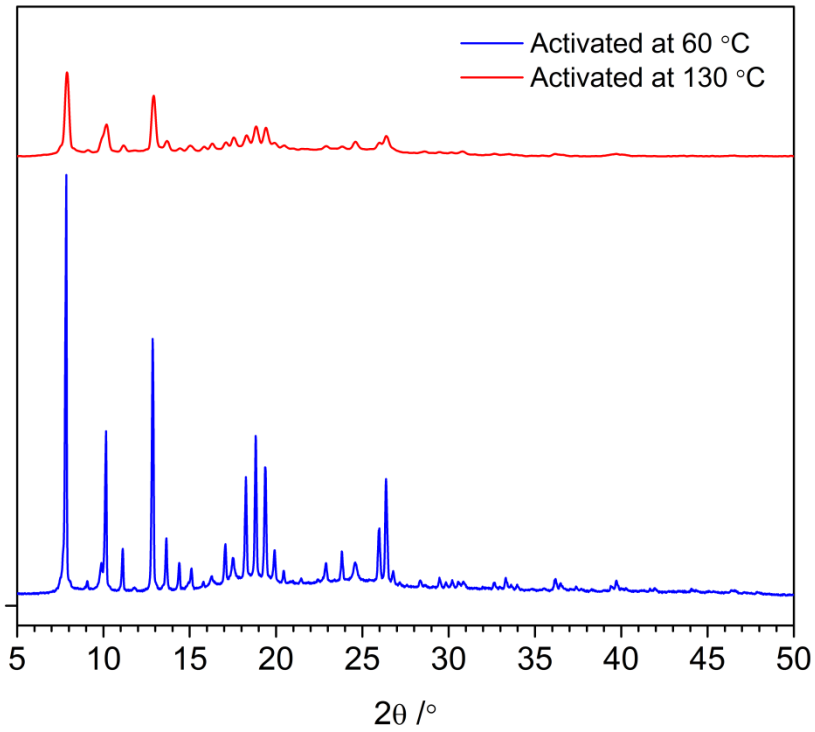


Figure S18 Comparison of PXRD patterns for SDU-1 activated at 60 ℃ and 130 ℃

Furthermore, in order to fully explore the pore space of this class of MOFs, we also have tried other activation methods. The as-synthesized SDU-1 was firstly exchanged with acetone for one month, during which the acetone was refreshed twice a day. Whereas, the color of SDU-1 turned

to yellow, and the CO_2 sorption result of the sample was not as good as that exchanged with CH_2Cl_2. In 2012.8, Zhang et al report a novel activation method[4] (which was termed as "freeze-cyclohexane drying" in the report) for the activation of a Zn-MOF. Comparative study of the activation methods showed that this method was proper to activate the MOF. In this paper, we also have tried "freeze-cyclohexane drying" method on SDU-1. The comparative results are listed as follow.

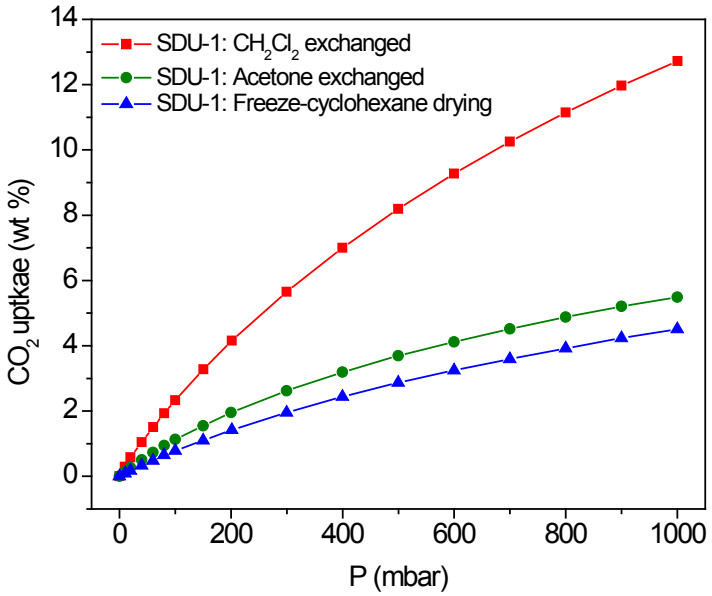


Figure S19 Comparison of CO_2 isotherms at 293 K on SDU-1 activated by different methods

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