Supporting information

High gas storage capacities and stepwise adsorption in a UiO type metal-organic framework with Lewis basic bipyridyl sites

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Contents

S1 General information

The starting material 2,2'-bipyridine-5,5'-dimethyl, metal salts and all the solvents were obtained from commercial lines and were used as received. Ultrapure (99.9999 %) hydrogen and nitrogen, high-purity (99.999 %) carbon dioxide, oxygen and methane were provided by Qingdao Heli gas Co., Ltd, of China and were used for gas sorption measurements without further purification. High pure (99.999 %) deuterium was purchased from Tianjin Vista Technology Co.,Ltd. Deuterium was purified from a two-step column to decontaminate the impurities before using.

Suitable crystals of UiO(bpdc) were selected for single crystal X-ray diffraction measurements. The diffraction data was collected at 195 K on a Bruker SMART APEX2 CCD area detector equipped with graphite-monochromated Mo-kα□radiation. Data reductions and adsorption corrections were carried out using SAINT[1] and SADABS[2] programs, respectively. The structure was solved by direct methods and refined by difference Fourier techniques using the SHELXTL[3] software package. Hydrogen atoms on the ligand were placed in idealized positions and were refined using a riding model. Solvent molecules in the unit cell were so highly disordered that they could not be located. To resolve these issues, the contribution of electron density of solvent molecules was removed by PLATON/SQUEEZE[4] program.

Powder X-ray diffractions (PXRD) were performed on a BRUKER D8-Focus Bragg-Brentano X-ray Powder Diffractometer equipped with a Cu-kα radiation (λ = 0.154 nm). Thermo gravimetric analyses (TGA) for as-synthesized and solvent exchanged samples were conducted on a NETZSCH STA 449F3 unit at a heating rate of 10 K/min under nitrogen atmosphere. Fourier transform infrared (FTIR) measurements were performed on a Nicolet 6700 FTIR spectrometer. Nuclear magnetic resonances (NMR) were collected on a BRUKER AVANCE-III NMR (600 MHz) spectrophotometer.

Gas sorption measurements were conducted on Intelligent Gravimetric Analyzer (IGA, Hiden). Nitrogen, hydrogen sorption isotherms were performed at 77 K using a cryogenic liquid nitrogen bath over the pressure range of 0-20 bar. Carbon dioxide sorption at 195 K was carried out using a solid carbon dioxide/ acetone bath. Carbon dioxide and methane sorption isotherms between 273K and 303 K were obtained using a circulating water/ethylene glycol bath controlled by computer using IGA software.

S2 Experimental details

Ligand 2,2'- bipyridine-5,5'-dicarboxylate acid (bpdc) was prepared from the oxidation reaction of the starting material: 2,2'-bipyridine-5,5'-dimethyl by $KMnO_4$ according the procedure in the literature[5].

Synthesis of MOF UiO(bpdc) is prepared from the modified procedure from the literature[6]: ligand bpdc (48 mg, 0.2 mmol) and $ZrCl_4$ (46.6 mg, 0.2 mmol) were mixed in DMA (12 ml), with 1.5 g benzoic acid was added as the modulate agent. After 30 minutes of stirring at ambient conditions, the mixture was transferred into a 20 ml Teflon-lined stainless steel container. Then the container was heated to 413 K for 72 hours in a programmed oven and cooled to room temperature at a rate of 0.3 K/min. A pure phase of octahedral shaped colorless crystals was obtained by filtration and washed with DMA.

For adsorption measurements, the as synthesized sample was loaded in the Soxhlet-extraction device and extracted for 72 hours, using the absolute ethanol as the extraction agent. After extraction, the treated sample was loaded into IGA apparatus and heated to 393 K under ultrahigh vacuum (10^{-7} mbar).

The solvent sorption experiments were performed using the IGA. The ethanol extracted sample was loaded in the sample cell and was activated at the conditions described above. Prior to solvent sorption measurements, the pure solvent was introduced into a screwed glass bottle attached to a branch line of IGA. Then, the bottle was fully degassed by repeated evacuation and vapor equilibration cycles in the vacuum system, ensuring the air in gaseous phase was completely removed and the gas phase was composed of pure vapor. The vapor was then served as the gas source for solvent sorption measurements. The pressure was maintained at each set point by activate computer control of inlet/outlet valves throughout the duration of the experiments.

S3 Single-crystal X-ray crystallography

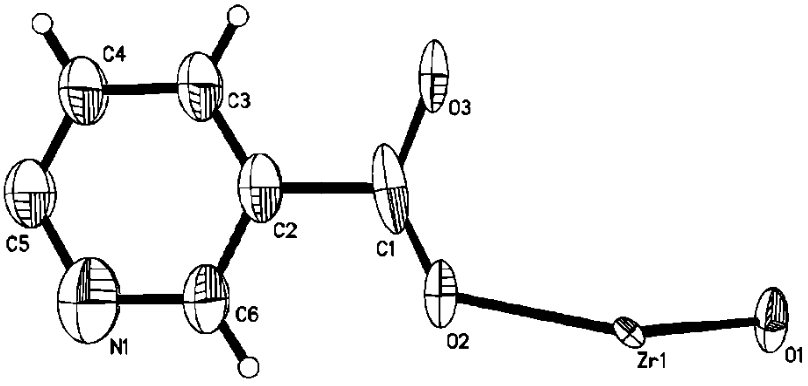


Fig. S1 Asymmetric unit MOF UiO(bpdc) (Thermal ellipsoid: 30 %)

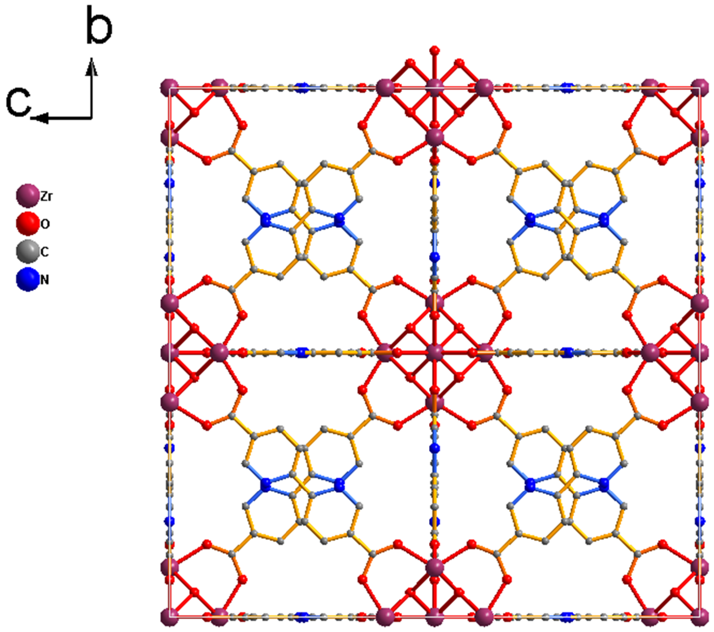


Fig. S2 Packing mode presentation of UiO(bpdc) viewing from ***a / b / c*** direction

Table S1 Crystal data and structure refinement for UiO(bpdc)

Term		UiO(bpdc)
Empirical formula		$C_{72} H_{36} N_{12} O_{32} Zr_6$
Formula weight		2128.45
Crystal system		***Cubic***
Space group		***Fm-3***
Unit cell parameters	***a=b=c*** (Å)	26.5460(19)
	α=β=γ (°)	90
	V ($Å^3$)	18707(2)
Z		4
Calculated density, g/cm^3		0.765
F(000)		4192
Reflections collected /unique		12442 / 1491
R (int)		0.0983
Goodness-of-fit on F^2		1.051
Final R indices [I>2sigma(I)]		R1 = 0.0567, wR2 = 0.1585
R indices (all data)		R1 = 0.0794, wR2 = 0.1662
Largest diff. Peak and hole,e $Å^3$		0.554 and -0.658

Table S2 Selected bond length(Å) for UiO(bpdc)

Bond	**Bond length (Å)**	**Bond**	**Bond length (Å)**
Zr(1)-O(1)#1	2.141(3)	Zr(1)-O(2)	2.193(5)
Zr(1)-O(1)#2	2.141(3)	Zr(1)-O(3)#3	2.193(5)
Zr(1)-O(1)#3	2.141(3)	Zr(1)-O(3)	2.203(5)
Zr(1)-O(1)	2.141(3)	O(1)-Zr(1)#5	2.141(3)
Zr(1)-O(2)#1	2.193(5)	O(1)-Zr(1)#7	2.141(3)

Symmetry operators for UiO(bpdc): #1 z-1/2, x+1, y-1/2; #2 -z+1/2, -x+1, -y+3/2; #3 y-1, z+1/2, x+1/2; #4 -y+1, -z+3/2, -x+1/2; #5 x, y, -z+1; #6 x, -y+2, z; #7 x, -y+2, -z+1; #8 -x+1/2, -y+3/2, -z+1.

S4 Powder XRD patterns

To evaluate the structural response to guest molecules in the adsorption process of organic solvents, the sample of this MOF was activated in the IGA system and was exposed to the solvent vapor of ethanol and cyclohexane as the procedure of solvent adsorption measurements. PXRD patterns of the samples before and after ethanol and cyclohexane adsorptions have been collected (as shown in Fig. S3).

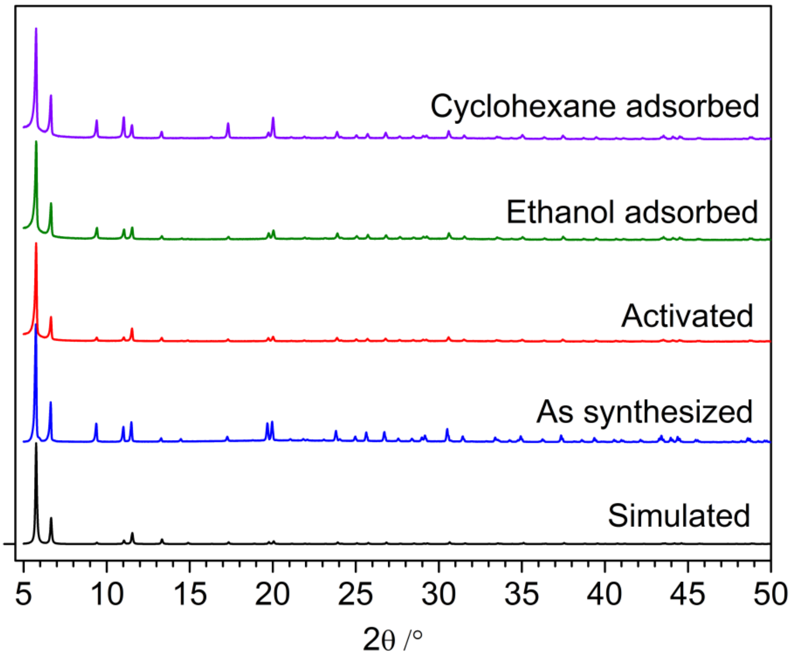


Fig. S3 PXRD patterns of as synthesized sample, the activated sample and the samples adsorbed with organic solvents

To investigate the chemical stability of this MOF, the activated sample of this MOF was treated by exposing to air, exposing to moisture, soaking in methanol, soaking in DMSO and soaking in water, respectively. After dried in air, the structural and crystalline characteristics of these samples were examined by collecting PXRD patterns (as shown in Fig. S4).

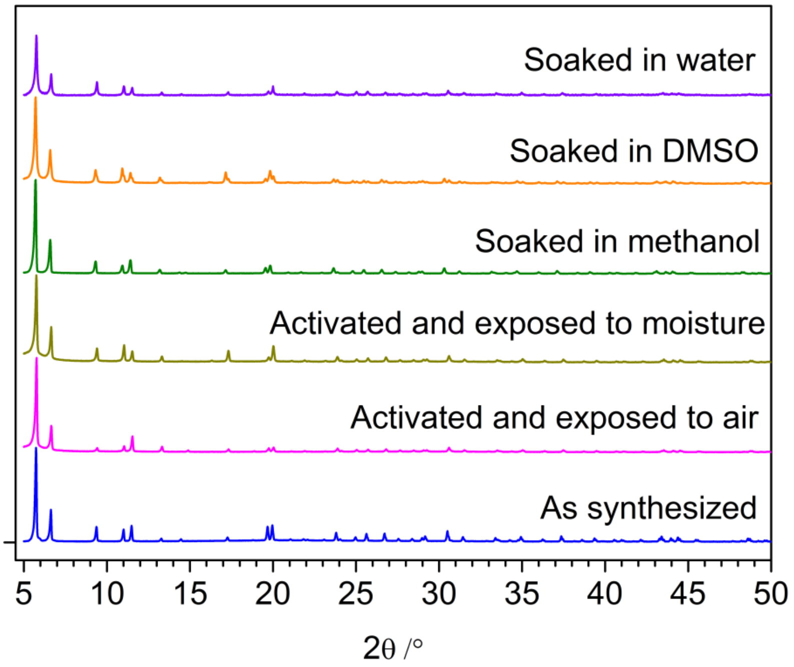


Fig. S4 PXRD pattern of samples exposed to air, exposed to moisture and treated by soaking in common solvents and water

S5 TGA plots

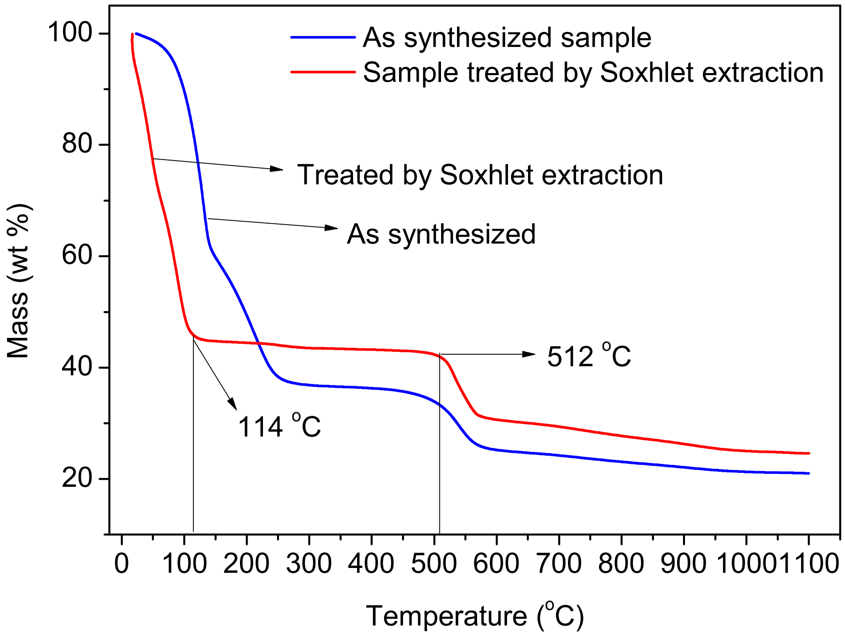


Fig. S5 TGA plots of as synthesized sample and the sample treated by Soxhlet extraction.

S6 Infrared spectroscopy

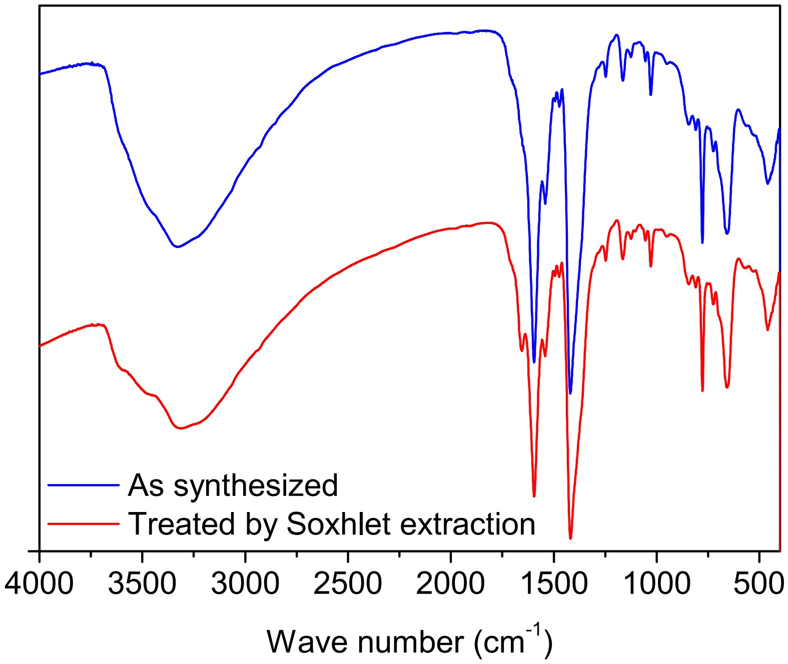


Fig. S6 Comparison of infrared spectroscopy of the as synthesized sample (blue) and the sample treated by Soxhlet-extraction (red).

S7 Calculation of BET and Langmuir surface areas

BET surface area.

The BET surface area of UiO(bpdc) was calculated by using Brunauer-Emmett-Teller equation based on N_2 adsorption isotherm at 77 K (as shown in equation 1).

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

Using the N_2 isotherm of UiO(bpdc) at 77 K, the term $P/n(P-P_0)$ was plotted with P/P_0 and linearly fitted in the pressure range of $0.001 < P/P_0 < 0.08$, as shown in Fig. S7.

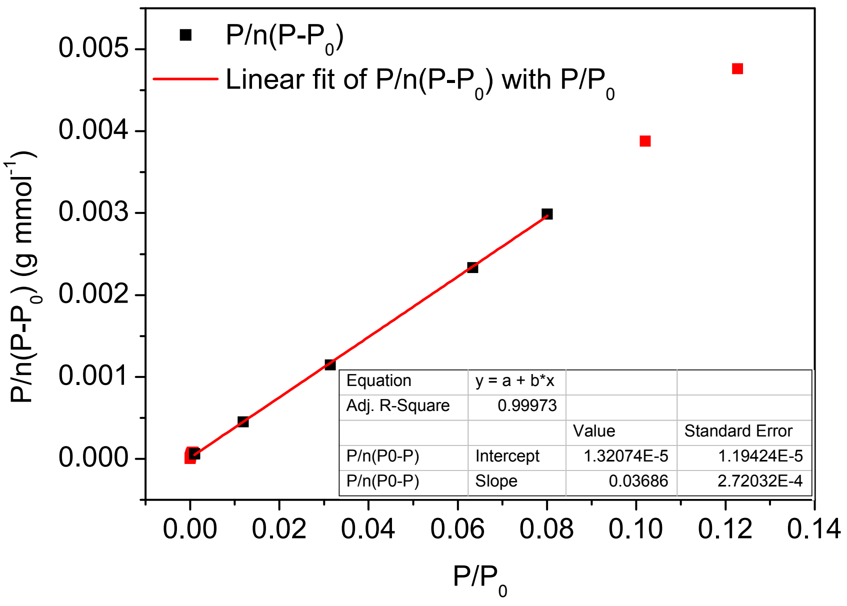


Fig. S7 BET plot of UiO(bpdc) using the N_2 isotherm at 77 K in the linear region ($0.001<P/P_0<0.08$)

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

Then,

$$\frac{C-1}{Cn_m}=0.03686$$

$$\frac{1}{Cn_m}=1.32074\times10^{-5}$$

So, the value of C and n_m can be obtained as following:

C = 2791.86

n_m=27.12 mmol g^{-1}

Then, the BET surface area of UiO(bpdc) can be calculated according to equation (2).

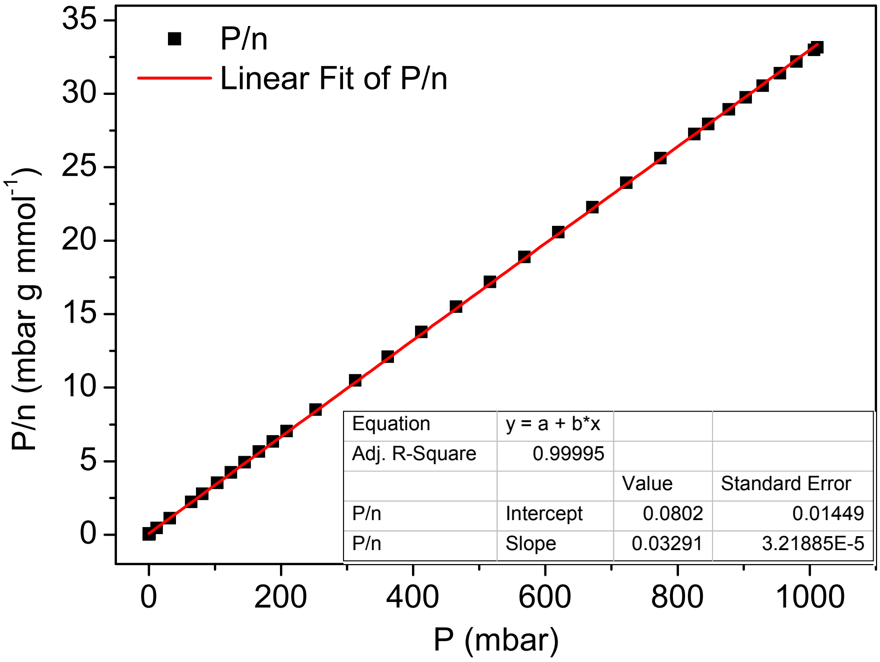
$$S_{BET}=n_m\cdot A\cdot\sigma_m \qquad (2)$$

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 UiO(bpdc) is 2646 m^2 g^{-1}.

Langmuir surface area

The N_2 isotherm of UiO(bpdc) at 77 K was fitted with P using Langmuir equation (as shown in equation (3). As shown in Fig. S8, the term P/n shows perfect linear relationship with the term P.

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



Equation	y = a + b*x		
Adj. R-Square	0.99995		
		Value	Standard Error
P/n	Intercept	0.0802	0.01449
P/n	Slope	0.03291	3.21885E-5

Fig. S8 The linear fit of P/n with P for N_2 adsorption on UiO(bpdc) at 77 K.

The slope of the fitted line is 0.03291, which is equal to $1/n_m$ in the Langmuir equation. Then, the value of n_m can be obtained as following:

n_m= 30.39 mmol g^{-1}

The Langmuir surface area of UiO(bpdc) can be calculated using 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). Then, the Langmuir surface area of UiO(bpdc) can be calculated as 2964 m^2 g^{-1}.

S8 Uptake ratio of D_2 versus H_2

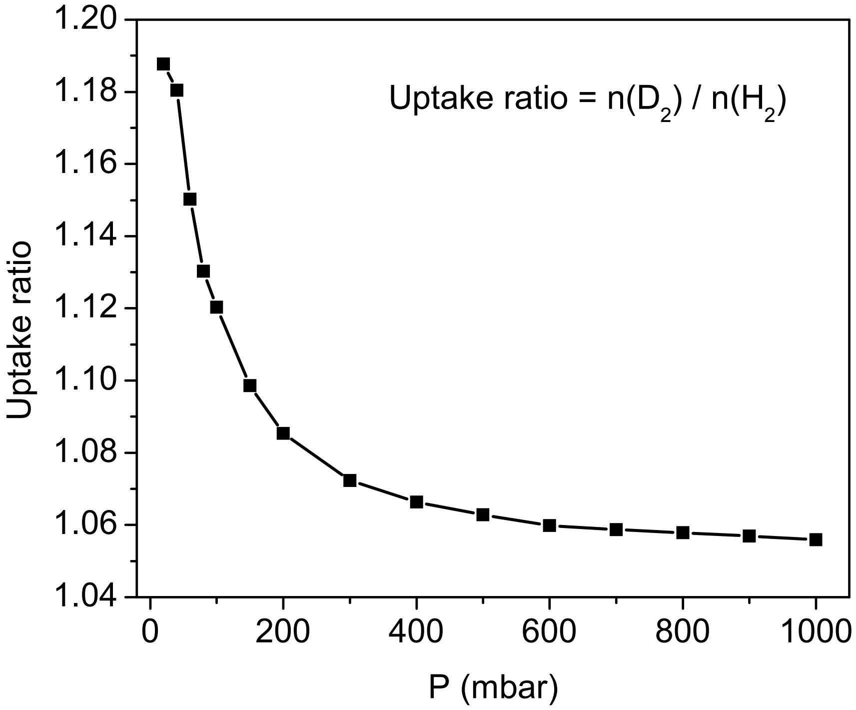


Fig. S9 The variation of uptake ratio ($n(D_2)/n(H_2)$)) with pressures at 77 K

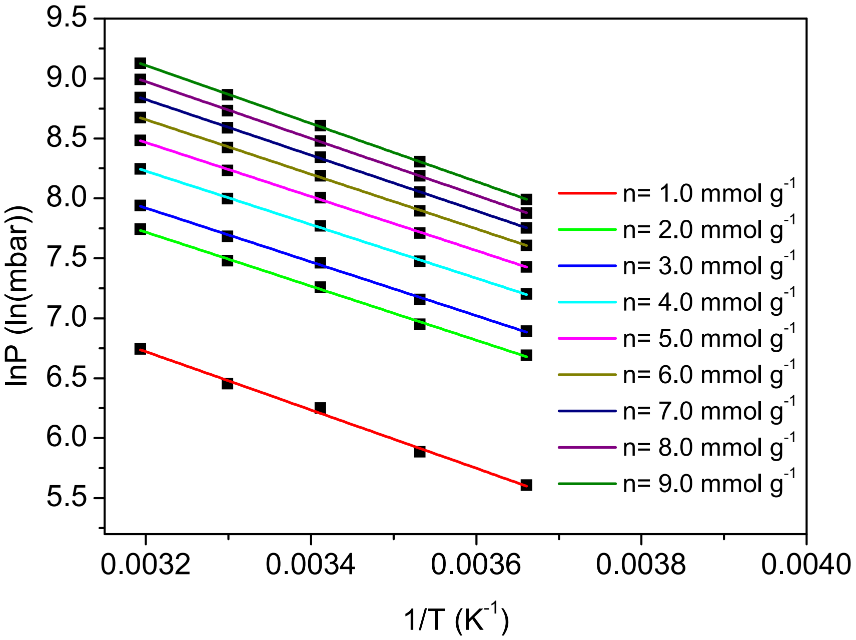
S9 Calculation procedures of isosteric adsorption enthalpy

The isosteric adsorption enthalpy (Q_{st}) of CO_2 and CH_4 were calculated by the Clausius-Clapeyron equation (equation 5)

$$\frac{Q_{st}}{R} = \frac{d(\ln P)}{d(1/T)} \qquad (5)$$

By using a linear interpolation between isotherm points, for a certain amount adsorbed, the term lnP was derived from isotherms at different temperatures. Then, the term lnP was plotted and linear fitted with 1/T. As shown in Fig. S10 and S11, the term lnP exhibits perfect linear relationship with the term 1/T, indicating the good reliability of the adsorption data. The slope of lnP ~ 1/T were derived from the fitted line, and Q_{st} was calculated from the above equation.

Calculation process of isosteric adsorption enthalpy (Q_{st})
For CO_2
(a)



(b)

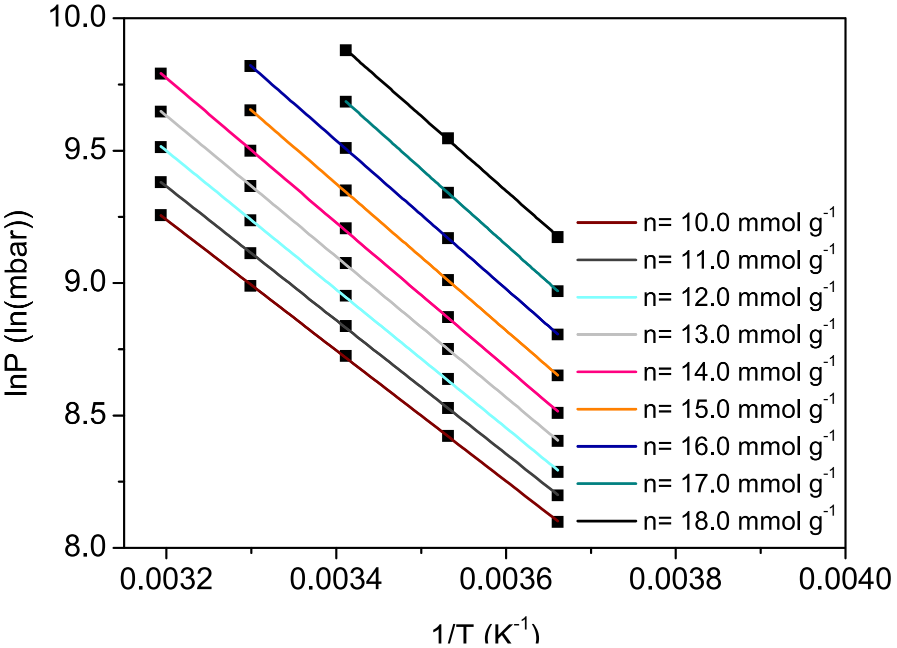


Fig. S10 Vant' Hoff isochores for CO_2 adsorption on UiO(bpdc) in the uptake range of (a) $0 \leq n \leq 9$ mmol g^{-1}, (b) $10 \leq n \leq 18$ mmol g^{-1}

For CH_4

(a)

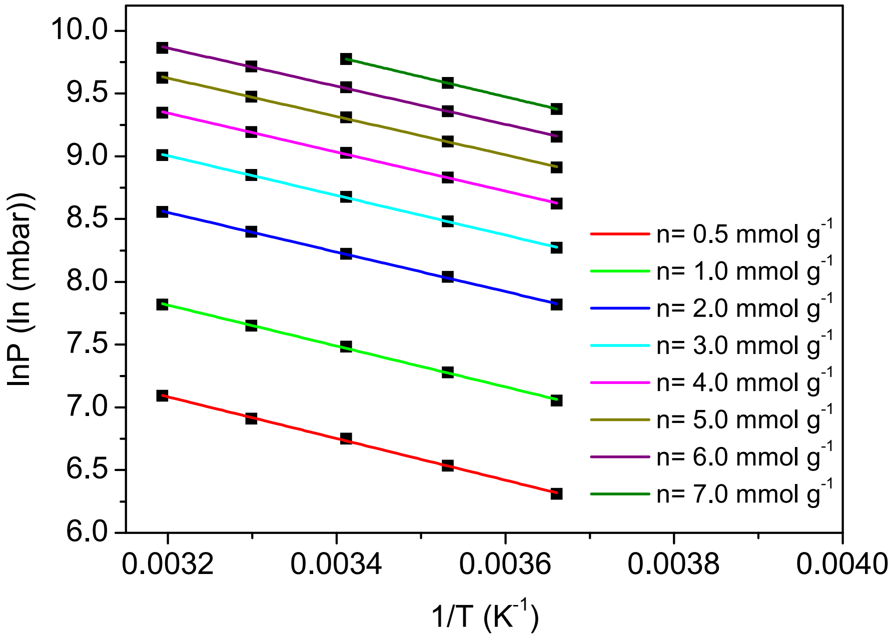


Fig. S11 Vant' Hoff isochores for CH_4 adsorption on UiO(bpdc)

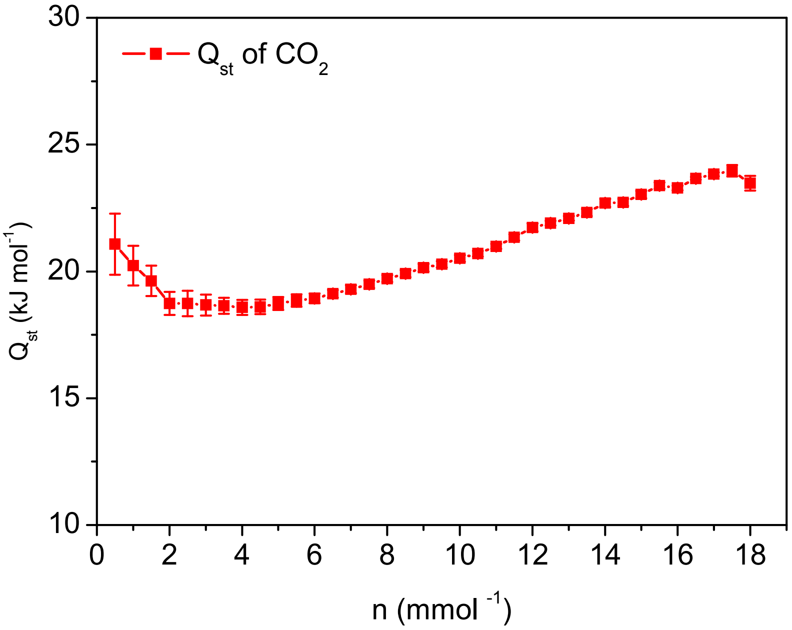


Fig. S12 The variation of Q_{st} with amount adsorbed for CO_2

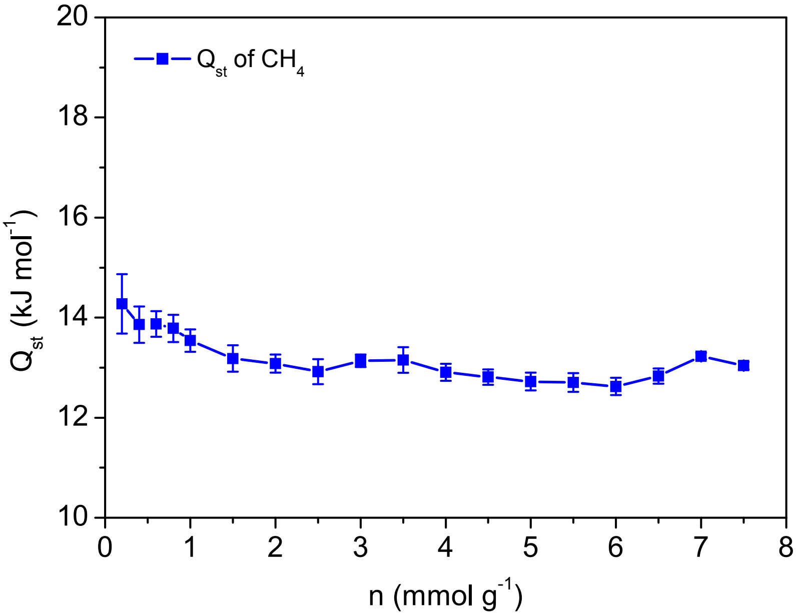
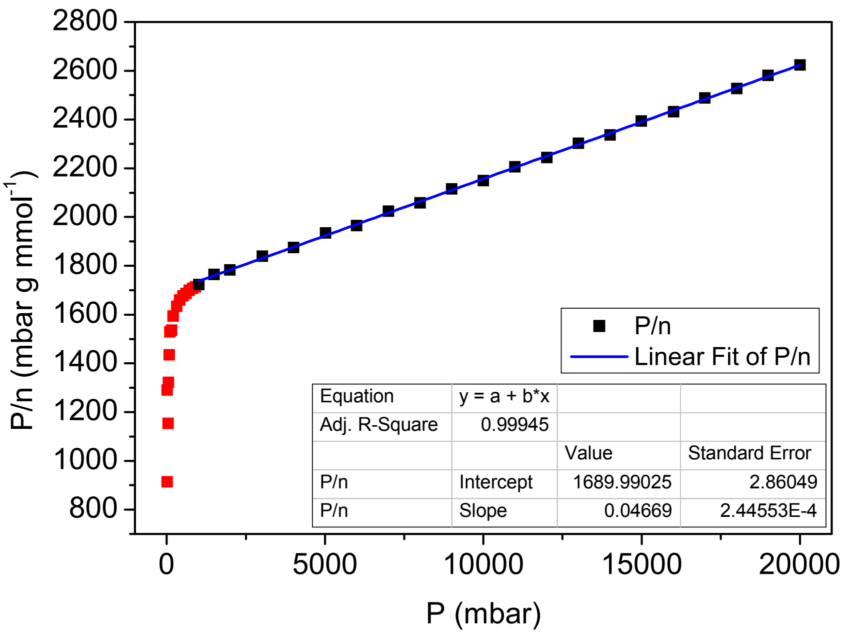


Fig. S13 The variation of Q_{st} with amount adsorbed for CH_4

S10 Simulation of methane adsorption at higher pressures

The isotherm of CH_4 on UiO(bpdc) at 293 K was modeled using the Langmuir equation (equation 3), as shown in Fig. S14. Based on the experimental isotherm of methane at 293 K in the pressure range of 1~20 bar, the relationship between P/n and P is plotted and is linearly fitted. Then the extrapolation of the isotherm was performed based on the fitted parameters shown in Fig. S15. It is clear that the simulated isotherm is consistent well with the experimental data (R^2=0.99945). Therefore, this method provided an accurate description of methane isotherms on UiO(bpdc) at higher pressures.



Equation	y = a + b*x		
Adj. R-Square	0.99945		
		Value	Standard Error
P/n	Intercept	1689.99025	2.86049
P/n	Slope	0.04669	2.44553E-4

Fig. S14 Langmuir graph for CH_4 adsorption on UiO(bpdc) at 293 K

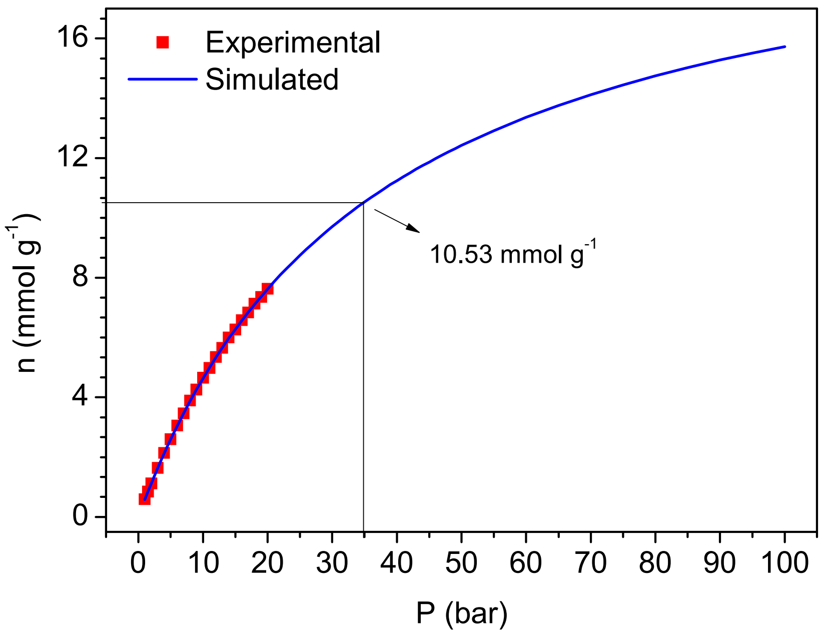


Fig. S15 Simulation of CH_4 isotherm on UiO(bpdc) at 293 K by Langmuir equation

The predicated uptake capacity of methane on UiO(bpdc) is 10.53 mmol g^{-1} at 293 K and 35 bar, corresponding to the 16.8 wt%, 180 v(STP)/v. At 273 K and 100 bar, the predicated methane uptake capacity is 15.73 mmol g^{-1} (25.2 wt%), corresponding to the volumetric uptake capacity of 270 v(STP)/v.

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