

## Electronic Supporting Information

### **A (3,6)-connected metal-organic framework with high CH<sub>4</sub> binding affinity and uptake capacity**

**Huiyan Liu\*, Qian Wang, Mingxing Zhang, Jingjing Jiang**

*State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering,  
Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, P. R. China*

*E-mail: liuhuiyan72@163.com. Tel: +86-25-83593384.*

## 1. Materials and Measurements

All reagents were obtained from commercial sources and, unless otherwise noted, were used as received without further purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240 analyzer.  $^1\text{H}$  NMR spectra were recorded on a Bruker DRX-500 spectrometer with tetramethylsilane as an internal reference. The IR spectra were obtained on a VECTOR TM 22 spectrometer with KBr pellets in the 4000- 400  $\text{cm}^{-1}$  region. Thermal gravimetric analyses (TGA) were performed under  $\text{N}_2$  atmosphere (100 mL/min) with a heating rate of 5  $^\circ\text{C}\cdot\text{min}^{-1}$  using a 2960 SDT thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were collected over the  $2\theta$  range 5  $\sim$  50 $^\circ$  on a Bruker D8 ADVANCE diffractometer using Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) with a routine power of 1600 W (40 kV and 40 mA) in a scan speed of 0.2  $\text{s}\cdot\text{deg}^{-1}$  at room temperature. Using a Philip X' Pert Pro system, variable temperature PXRD (VTPXRD) measurements were recorded after the sample had stayed at the respective temperature for 30 min in  $\text{N}_2$  atmosphere.

## 2. Experiment Details

**Synthesis of methyl 3,5-di(pyridin-4-yl)benzoate (HL).** Methyl 3,5-dibromobenzoate (2.0 g, 6.8 mmol), pyridin-4-ylboronic acid (2.5 g, 20.3 mmol), and  $\text{K}_3\text{PO}_4$  (15.0 g, 56.3 mmol) were added to 1,4-dioxane (120 mL). After stirring,  $\text{Pd}(\text{PPh}_3)_4$  (0.5 g, 0.4 mmol) was added, then the mixture was heated to 80  $^\circ\text{C}$  for 3 days under  $\text{N}_2$  atmosphere. The resultant was evaporated to dryness and taken up in  $\text{CH}_2\text{Cl}_2$  which later had been dried over  $\text{MgSO}_4$ . This  $\text{CH}_2\text{Cl}_2$  solution was evaporated to dryness and the residue was washed briefly with ethanol (20 mL). The crude product was hydrolyzed by refluxing in 2 M aqueous NaOH followed by acidification with 37 % HCl to afford HL. Yield = 1.5 g (78.9 %).  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ,  $\delta$  ppm): 13.51 (s, COOH), 8.79 (d, 4H,  $J = 5.0$  Hz, ArH), 8.50 (s, 1H, ArH), 8.43 (s, 2H, ArH), 8.07 (d, 4H,  $J = 5.0$  Hz, ArH). Anal. Calcd (Found) for  $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_2$ : C, 73.90 (73.85); H, 4.38 (4.18); N, 10.14 (10.34) %. Selected IR (KBr,  $\text{cm}^{-1}$ ): 3381, 3064, 1715, 1633, 1609, 1595, 1553, 1507, 1384, 1217, 1068, 817, 777, 619.

**Synthesis of NJU-Bai16,  $[\text{CuL}(\text{NO}_3)]\cdot 2\text{DMF}\cdot\text{H}_2\text{O}$ .** NJU-Bai 16 was synthesized by reaction of HL (10.0 mg, 0.04 mmol),  $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$  (20 mg, 0.08 mmol) and 4 drops of concentrated nitric acid in 2 mL *N,N'*-dimethylformamide (DMF) at 70  $^\circ\text{C}$  for 3 days. The blue octahedron-shaped crystals were collected and washed with DMF to yield 10.0 mg (yield: 70 % based on the ligand). Anal. Calcd (Found) for  $\text{C}_{23}\text{H}_{27}\text{CuN}_5\text{O}_8$ : C, 48.89 (49.86); H, 4.78 (4.54); N, 12.39 (12.07) %. Selected IR (KBr,  $\text{cm}^{-1}$ ): 3424, 3077, 1673, 1617, 1592, 1551, 1471, 1319, 1284, 1070, 834, 787, 637.

## 3. X-ray single crystal structure determination

X-ray diffraction single-crystal data were measured on a Bruker Apex II CCD diffractometer at 150 K using graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data reduction was made with the Bruker SAINT program. The structure was solved by direct methods and refined with full-matrix least squares technique using the SHELXTL package<sup>1</sup>. Displacement parameters were refined anisotropically, and the positions of the hydrogen atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. Because guest solvent molecules were highly disordered and impossible to refine using conventional discrete-atom models, the SQUEEZE subroutine of the PLATON software suite<sup>2</sup> was applied to remove them from the structure.

A summary of the crystallographic data are given in Table S1. CCDC 1049754 contains the supplementary crystallographic data for NJU-Bai16. The data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK.

#### **4. Low-Pressure gas sorption measurements**

The solvent-exchanged sample was prepared by immersing the as-synthesized samples in dry acetone for 3 days to remove the nonvolatile solvate, and the extract was decanted every 8 hours and fresh acetone was replaced. The completely activated sample was obtained by heating the solvent-exchanged sample at 90 °C under a dynamic high vacuum for 10 hours.

Low-pressure gases (H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>) sorption isotherms (up to 1 bar) were performed on a Quantachrome Autosorb-iQ volumetric gas adsorption analyzer. Ultra-high-purity grade H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub> and He (99.999% purity) gases were used throughout the gas adsorption experiments. A liquid nitrogen bath was used for the measurements at 77 K. A water circulator was used for adsorption measurements at 273 and 298 K. A part of the N<sub>2</sub> sorption isotherm at 77 K in the P/P<sub>0</sub> range 0.001–0.03 was fitted to the BET equation to estimate the BET surface area and the Langmuir surface area calculation was performed using all data points.

#### **5. High-pressure gravimetric gas sorption measurements**

High-pressure excess adsorption of CO<sub>2</sub> and CH<sub>4</sub> were measured using an IGA-003 gravimetric adsorption instrument (Hiden-Isochema, UK) over a pressure range of 0–20 bar at 273 K and 298 K after an activation procedure same to that in low-pressure volumetric gas adsorption measurement. During the gases sorption measurements, the sample mass was monitored until equilibrium was reached (within 15 minutes) at each pressure.

#### **6. Estimation of the isosteric heats of gas adsorption through the virial method**

A virial-type<sup>3</sup> expression comprising the temperature-independent parameters  $a_i$  and  $b_j$  was employed to calculate the isosteric heats of adsorption for H<sub>2</sub> (at 77 and 87 K), CO<sub>2</sub> and CH<sub>4</sub> (at 273 and 298 K) on NJU-Bai16. In each case, the data were fitted using the equation:

$$\ln P = \ln N + 1/T \sum_{i=0}^m a_i N^i + \sum_{j=0}^n b_j N^j \quad (1)$$

Here,  $P$  is the pressure expressed in Torr,  $N$  is the amount adsorbed in mmol·g<sup>-1</sup>,  $T$  is the temperature in K,  $a_i$  and  $b_j$  are virial coefficients, and  $m$ ,  $n$  represent the number of coefficients required to adequately describe the isotherms ( $m$  and  $n$  were gradually increased until the contribution of extra added  $a$  and  $b$  coefficients was deemed to be statistically insignificant towards the overall fit and the average value of the squared deviations from the experimental values was minimized). The values of the virial coefficients  $a_0$  through  $a_m$  were then used to calculate the isosteric heats of adsorption using the following expression.

$$Q_{st} = -R \sum_{i=0}^m a_i N^i \quad (2)$$

$Q_{st}$  is the coverage-dependent isosteric heat of adsorption and  $R$  is the universal gas constant. The heat of CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub> sorption for NJU-Bai16 in this manuscript is determined by using the low pressure gas sorption data measured in the pressure range from 0-1 bar.

## 7. Estimation of the isosteric heats of gas adsorption using Clausius-Clapeyron equation

The methods are applied to deal with the sorption data according to the literature 5 (*Chem. Commun.*, 2011, **47**, 3787.). The Langmuir-Freundlich equation is used to fit gas adsorption isotherms and predict the adsorption capacity of the framework at saturation, and Clausius-Clapeyron equation is employed to calculation the isosteric heats of gas adsorption.

$$\ln\left(\frac{P_1}{P_2}\right) = \Delta H_{ads} \times \frac{T_2 - T_1}{RT_1 T_2} \quad (I)$$

Where  $P_i$  = pressure for isotherm  $i$

$T_i$  = temperature for isotherm  $i$

$R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

The equation (I) can be applied to calculate the isosteric heats of adsorption of a gas as a function of the quantity of gas adsorbed. Pressure as a function of the amount of gases adsorbed was determined using the Langmuir-Freundlich fit for the isotherms.

$$\frac{Q}{Q_m} = \frac{BP^{(1/r)}}{1 + BP^{(1/r)}} \quad (II)$$

Where  $Q$  = moles adsorbed

$Q_m$  = moles adsorbed at saturation

$P = \text{pressure}$

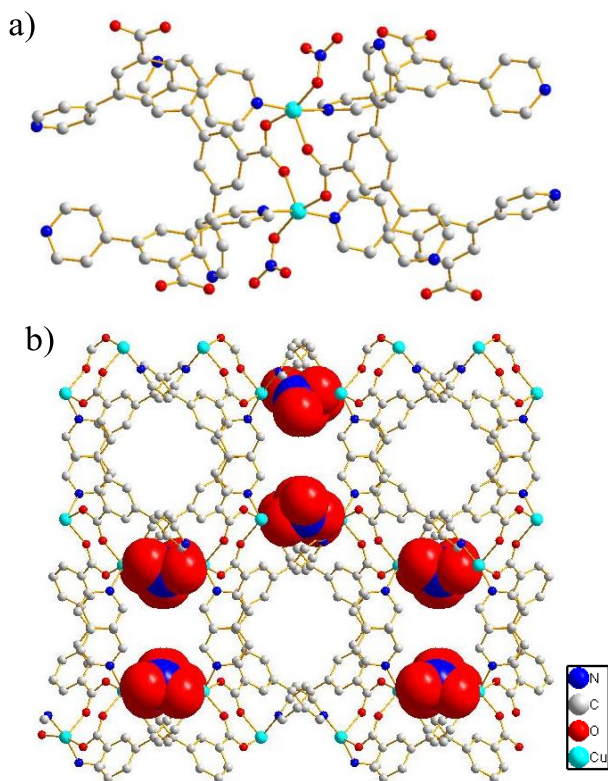
$B$  and  $t$  are constants

Rearrange (II) to get:

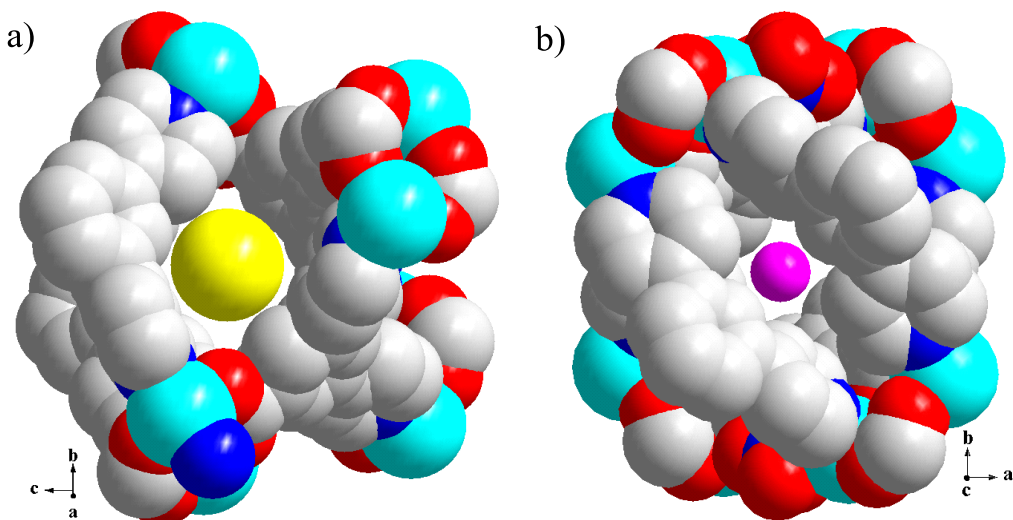
$$P = \left( \frac{Q/Q_m}{B - BQ/Q_m} \right)^t \quad (\text{III})$$

Replace P in equation (I) to obtain:

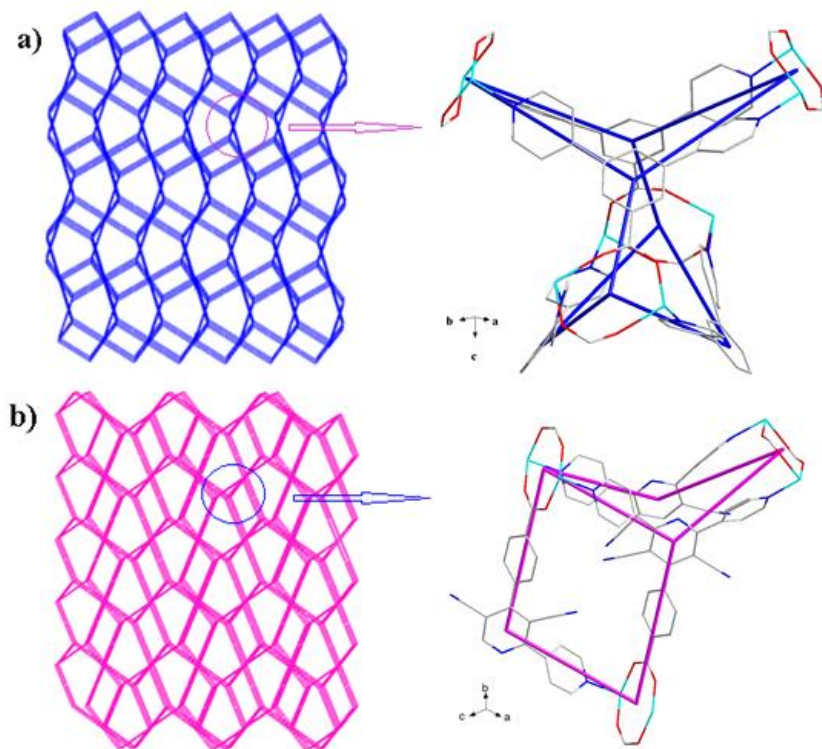
$$\Delta H_{ads} = \frac{RT_1T_2}{T_2 - T_1} \times \text{Ln} \frac{\left( \frac{Q/Q_{m1}}{B_1 - B_1Q/Q_{m1}} \right)^t}{\left( \frac{Q/Q_{m2}}{B_2 - B_2Q/Q_{m2}} \right)^t} \quad (\text{IV})$$



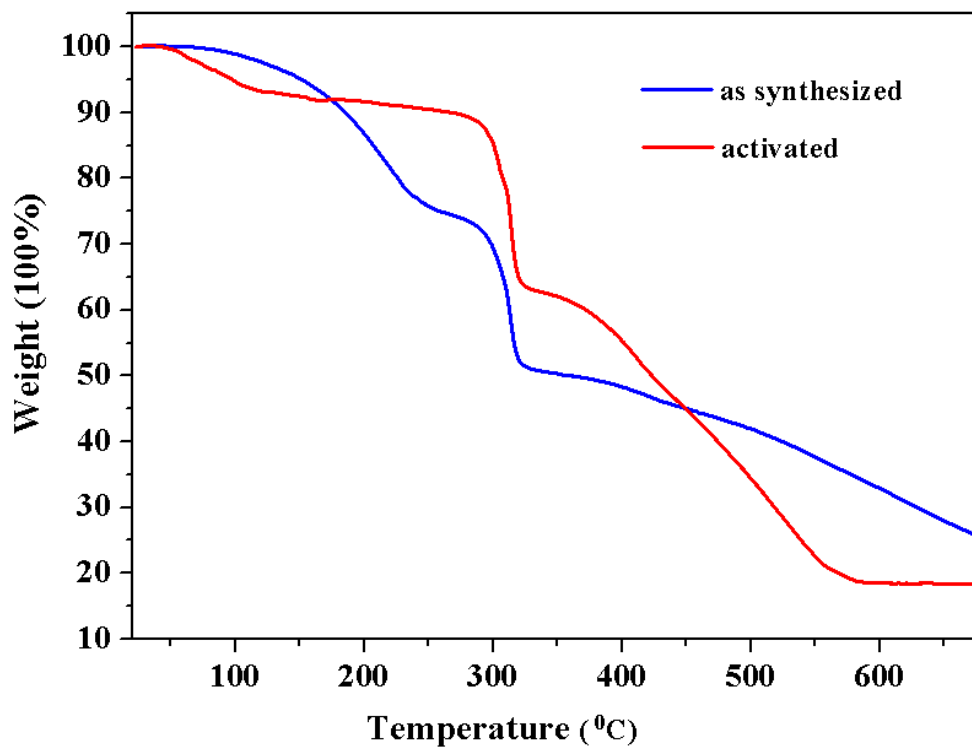
**Figure S1.** (a) Perspective view of the binuclear Cu(II) building blocks in NJU-Bai16. (b) View of the 1D channel along the [001] direction with coordinated NO<sub>3</sub><sup>-</sup> anions (space-filling mode) protruding into the pore.



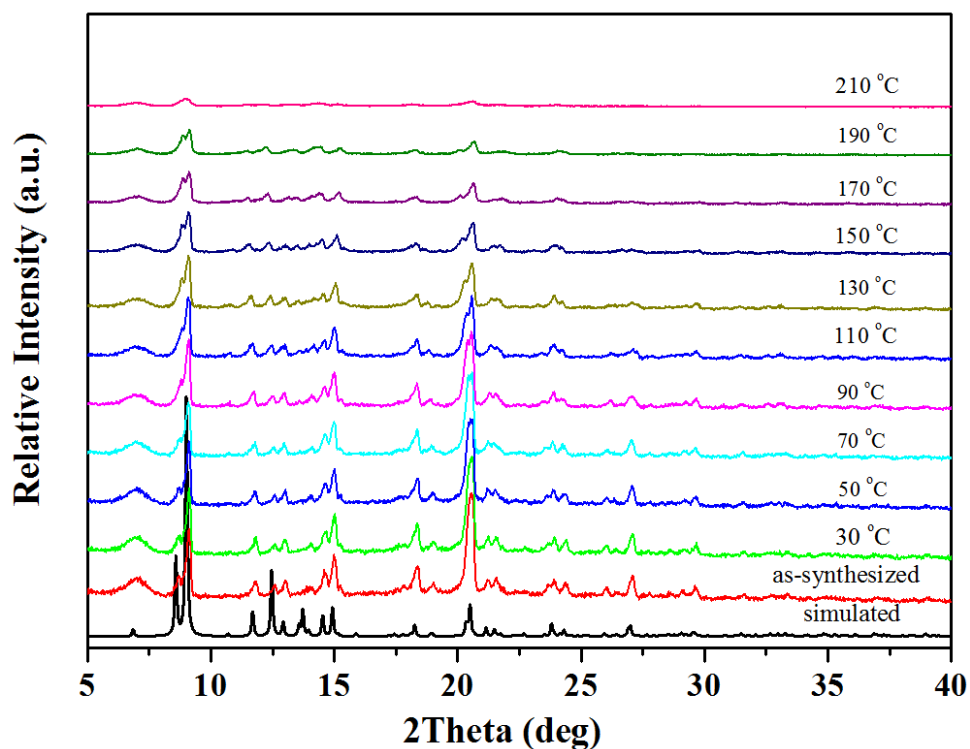
**Figure S2.** The open channel along *a* axis (a) and *c* axis in NJU-Bai16. The two kinds of spheres (in yellow and pink) represent the open spaces that can be occupied by the guest molecules without touching the framework.



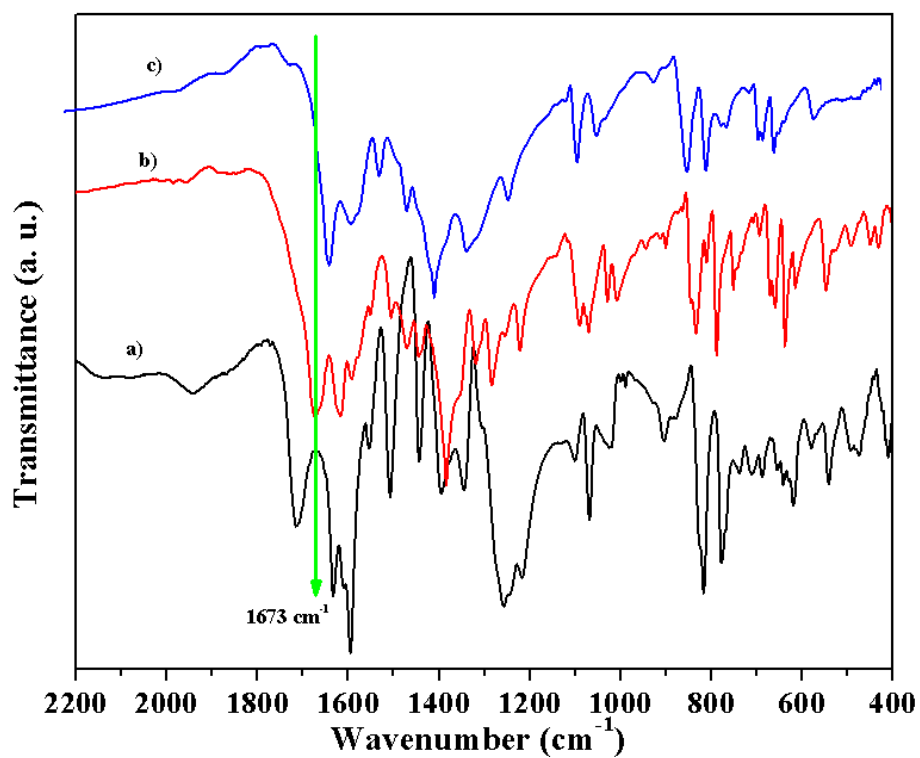
**Figure S3.** Schematic representation of the  $(4\cdot6^2)_2(4^2\cdot6^4\cdot8^7\cdot10^2)$  topological net of NJU-Bai16 (a), and the  $(4^2\cdot6)_2(4^4\cdot6^2\cdot8^7\cdot10^2)$  topological net of  $[\text{Cu}(\text{dccptp})(\text{NO}_3)]\cdot 0.5(1,4\text{-dioxane})\cdot 0.5\text{MeOH}^5$  (b).



**Figure S4.** TGA data of as-synthesized and activated sample of NJU-Bai16.

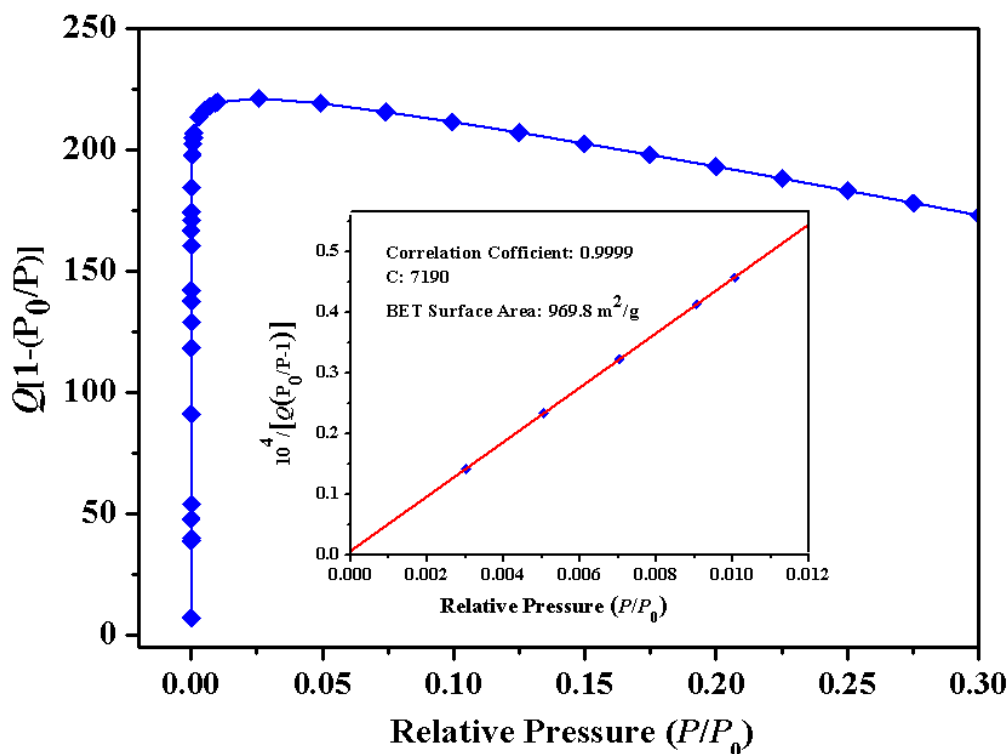


**Figure S5.** The PXRD patterns of NJU-Bai16 measured at various temperatures.

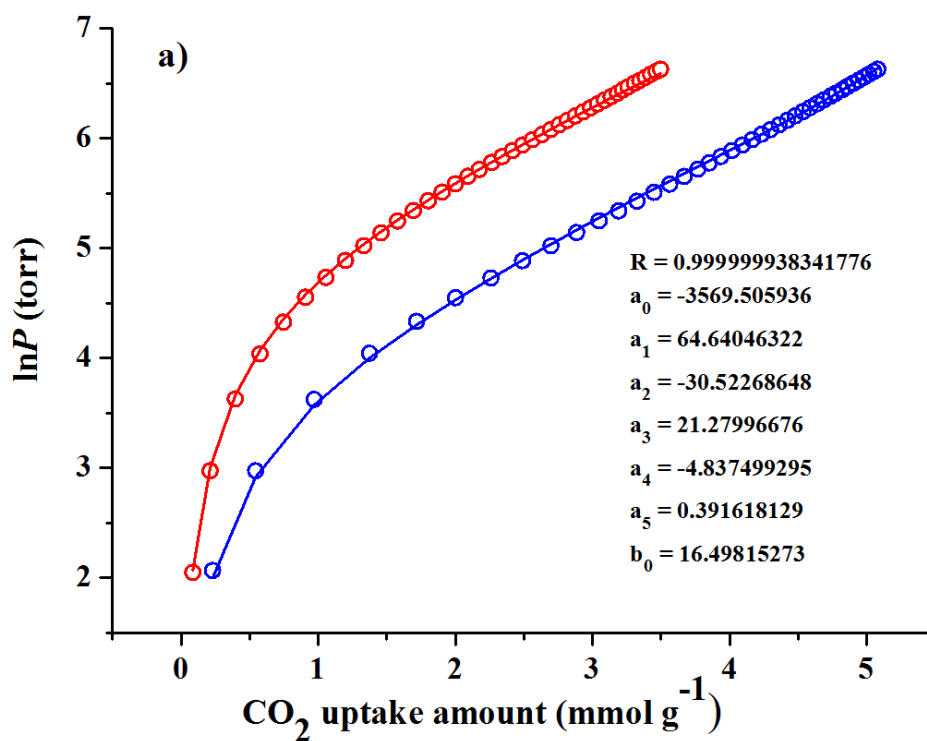


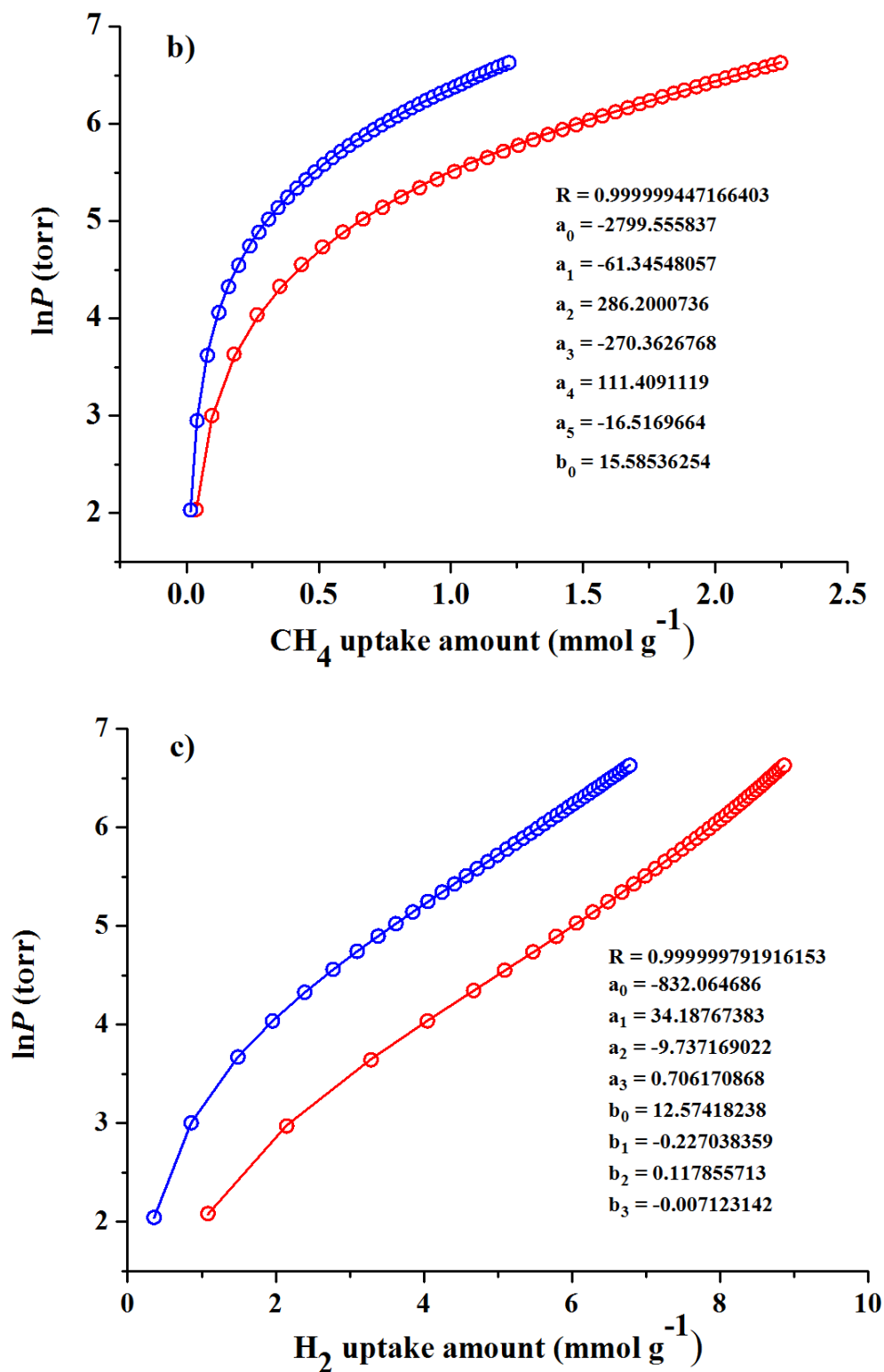
**Figure S6.** The infrared spectra for NJU-Bai16. (a) ligand, (b) as-synthesized and (c) activated MOF materials. Note the absence of the vibration frequencies of the solvent DMF molecules in activated samples. The frequencies at  $1673\text{ cm}^{-1}$  in (b) attribute to the  $\nu(\text{CO})$  vibration of the DMF.





**Figure S7.** The BET plots for NJU-Bai 16 in the chosen range ( $P/P_0 = 0.001-0.03$ ). This range was chosen according to two major criteria established in literatures<sup>6</sup>: (1) The pressure range selected should have values of  $Q(P_0-P)$  increasing with  $P/P_0$ . (2) The y intercept of the linear region must be positive to yield a meaningful value of the c parameter, which should be greater than zero.





**Figure S8.** The gases isotherms (red and blue symbols, respectively) and the corresponding virial equation fits (red and blue lines, respectively) for NJU-Bai16. (a-b):  $\text{CO}_2$  and  $\text{CH}_4$  at 273 K and 298 K; (c):  $\text{H}_2$  at 77 K and 87 K.

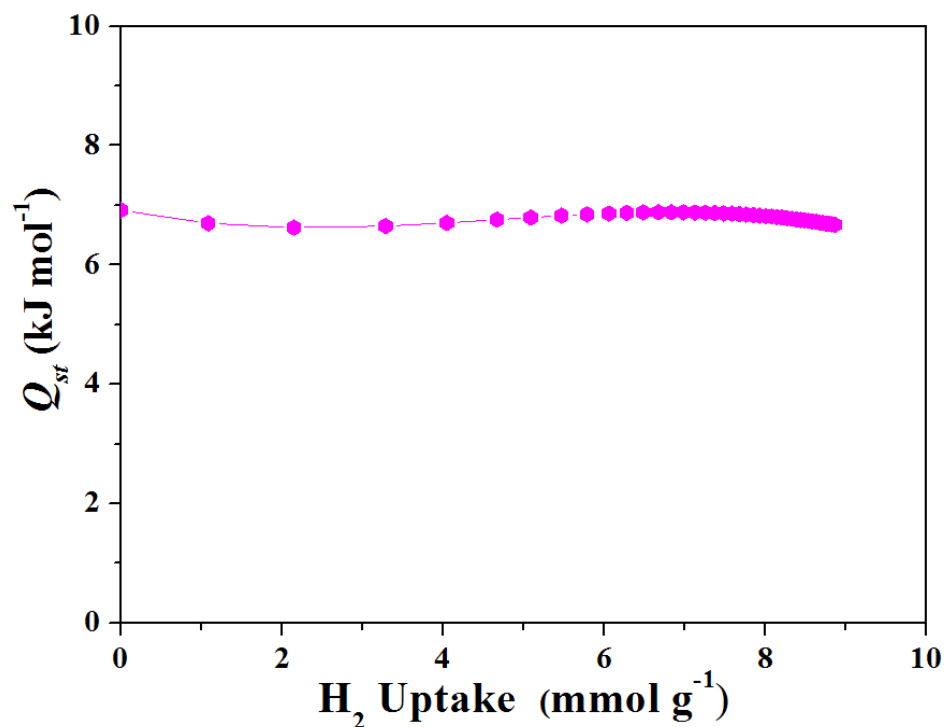
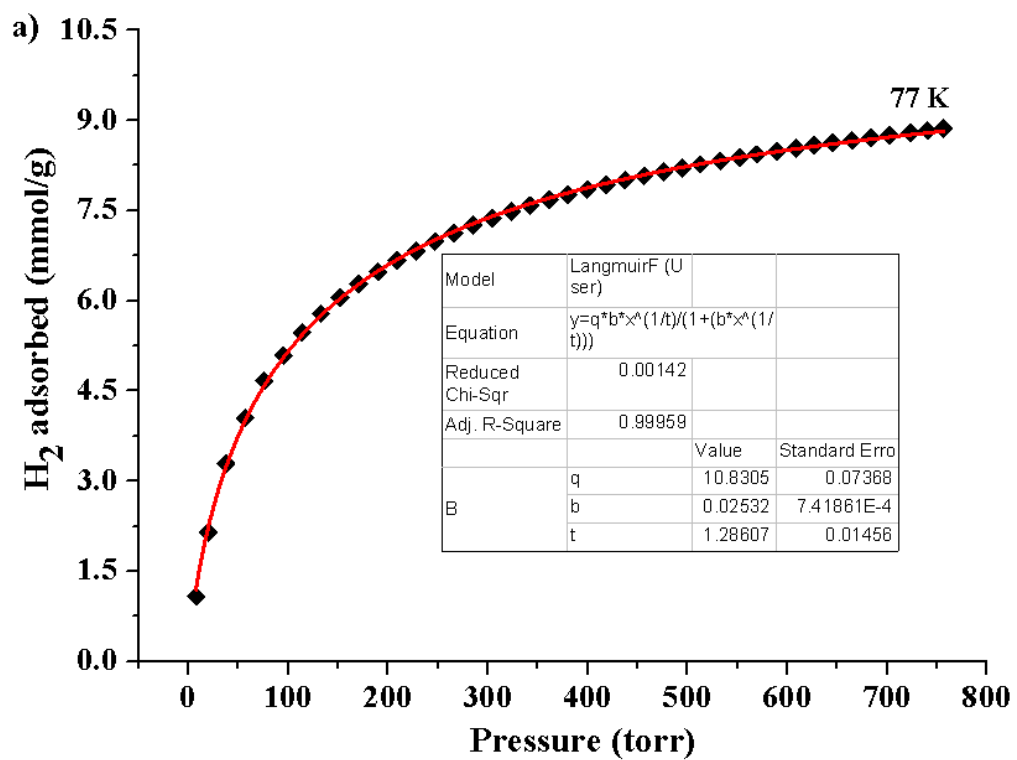
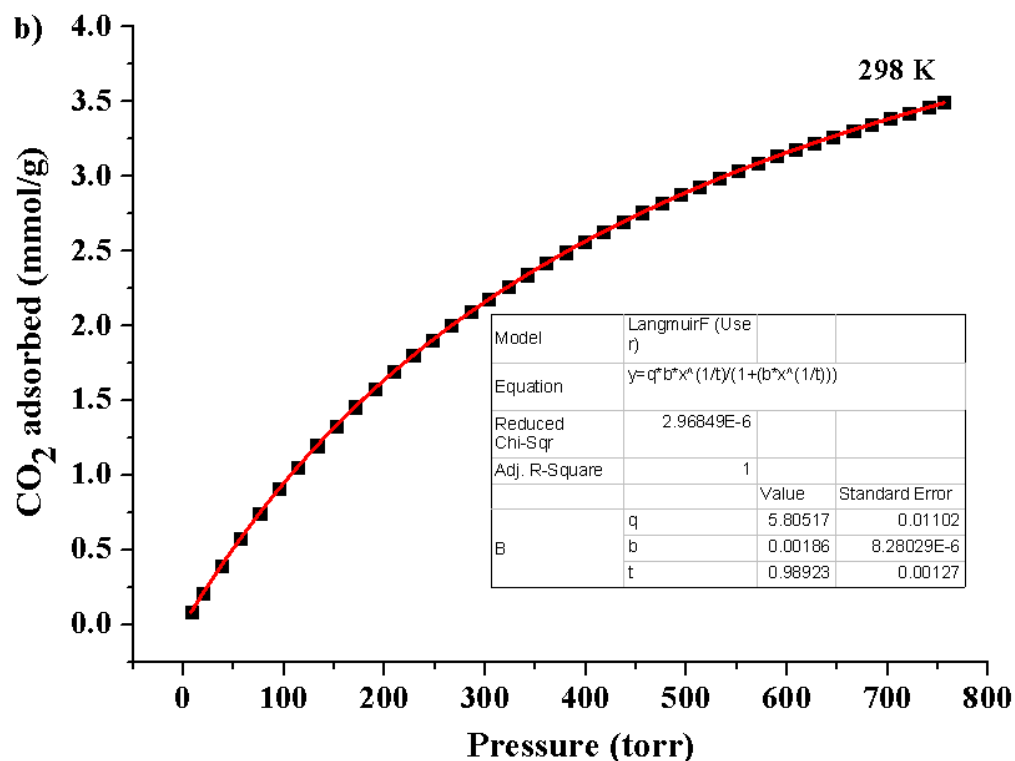


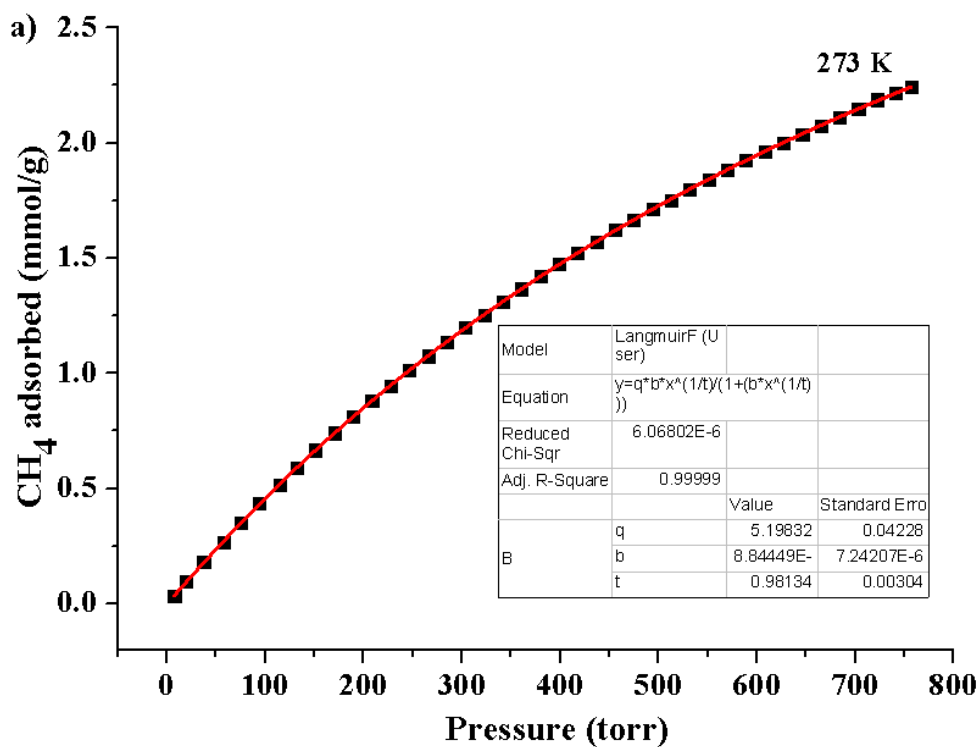
Figure S9. Isosteric heats of H<sub>2</sub> adsorption for NJU-Bai16 through the virial method.

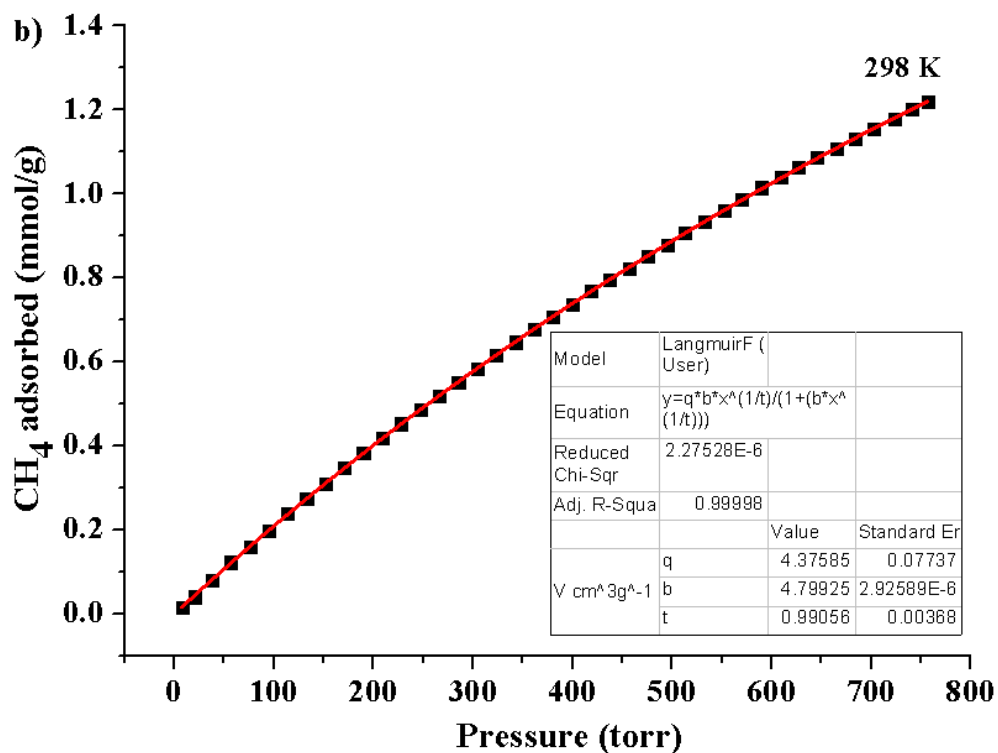




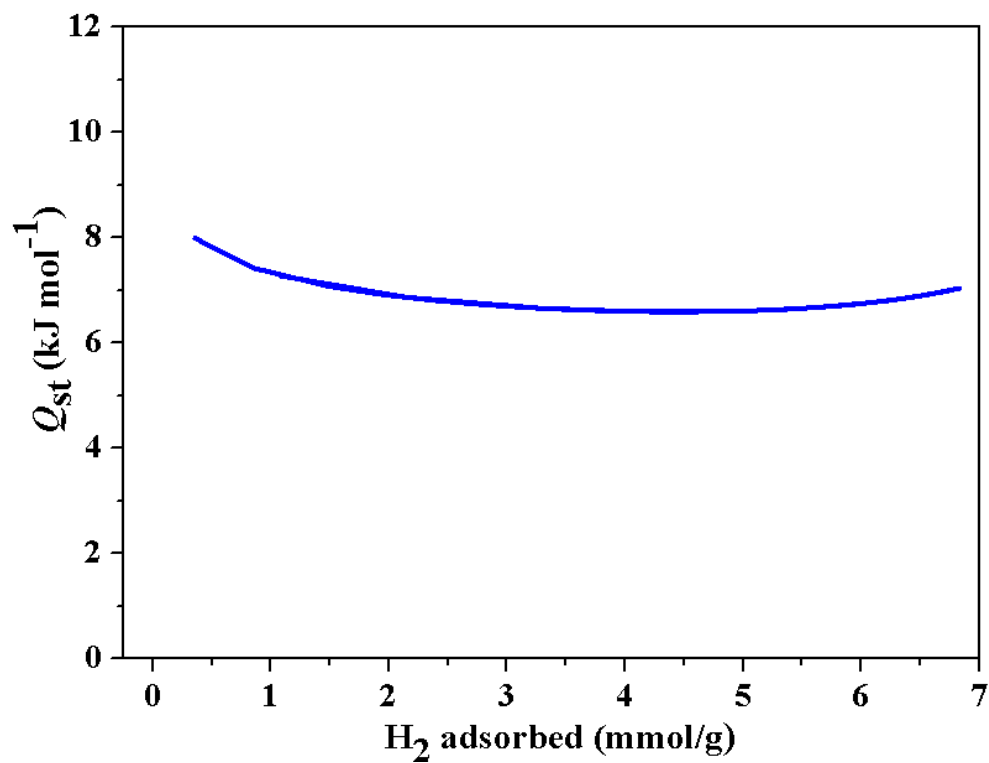


**Figure S11.** Fitting of the CO<sub>2</sub> adsorption isotherm of NJU-Bai16 recorded at 273 K (a) and 298 K (b) using Langmuir-Freundlich equation. (gases isotherm, black squares; Langmuir-Freundlich equation fits, red solid line).

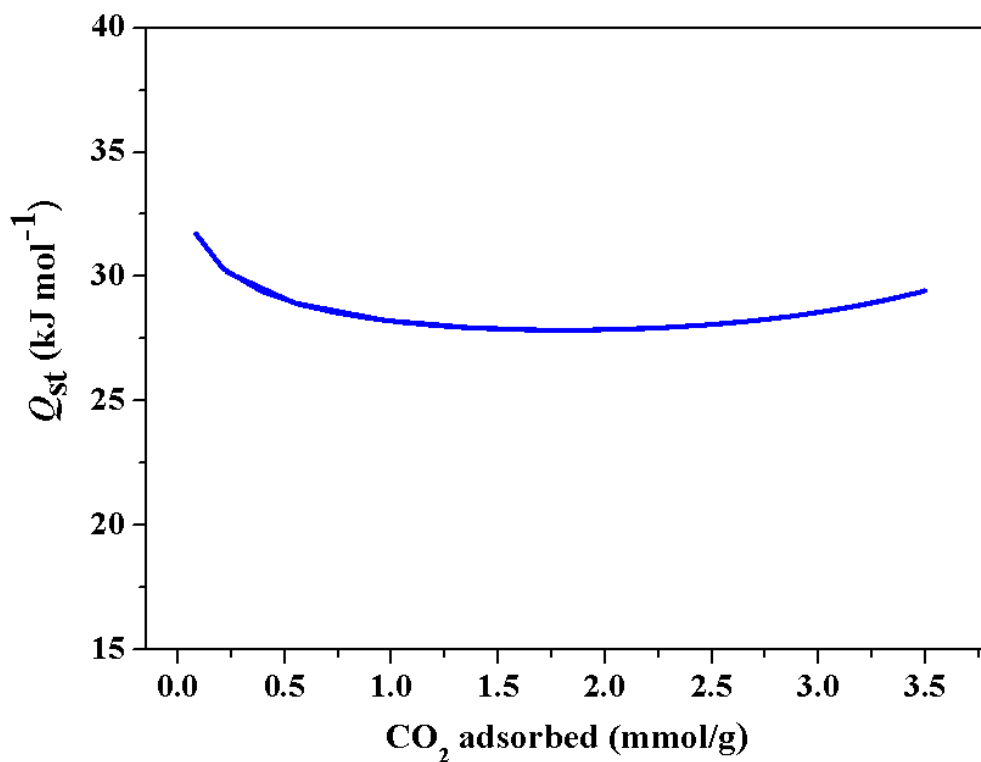




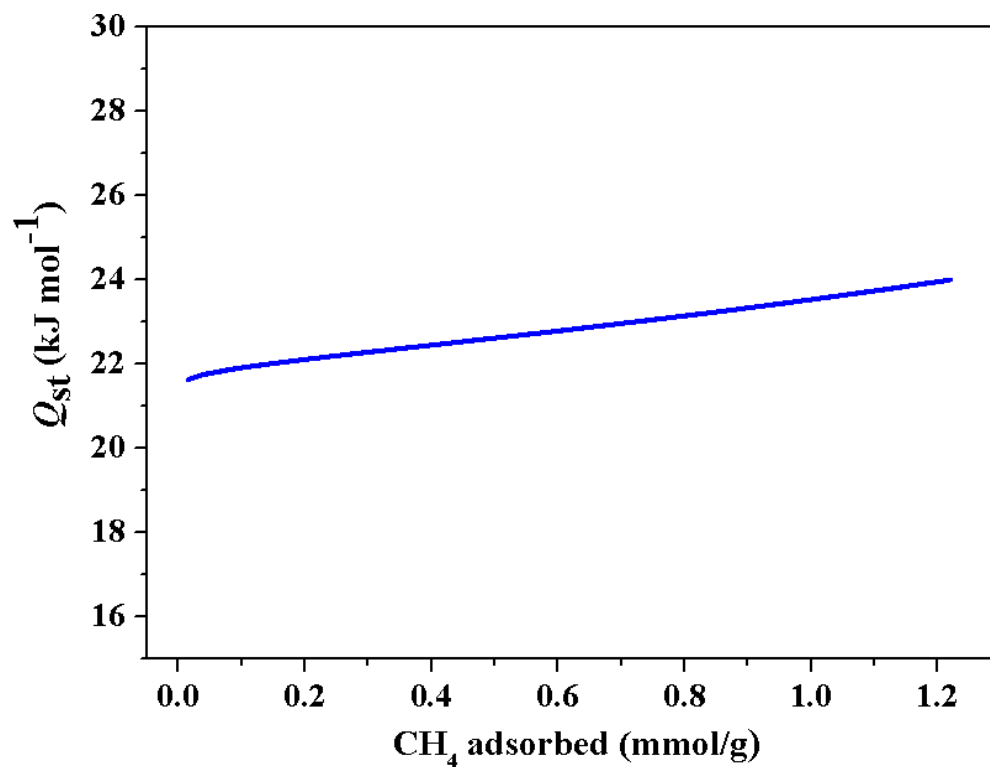
**Figure S12.** Fitting of the CH<sub>4</sub> adsorption isotherm of NJU-Bai16 recorded at 273 K (a) and 298 K (b) using Langmuir-Freundlich equation. (gases isotherm, black squares; Langmuir-Freundlich equation fits, red solid line).



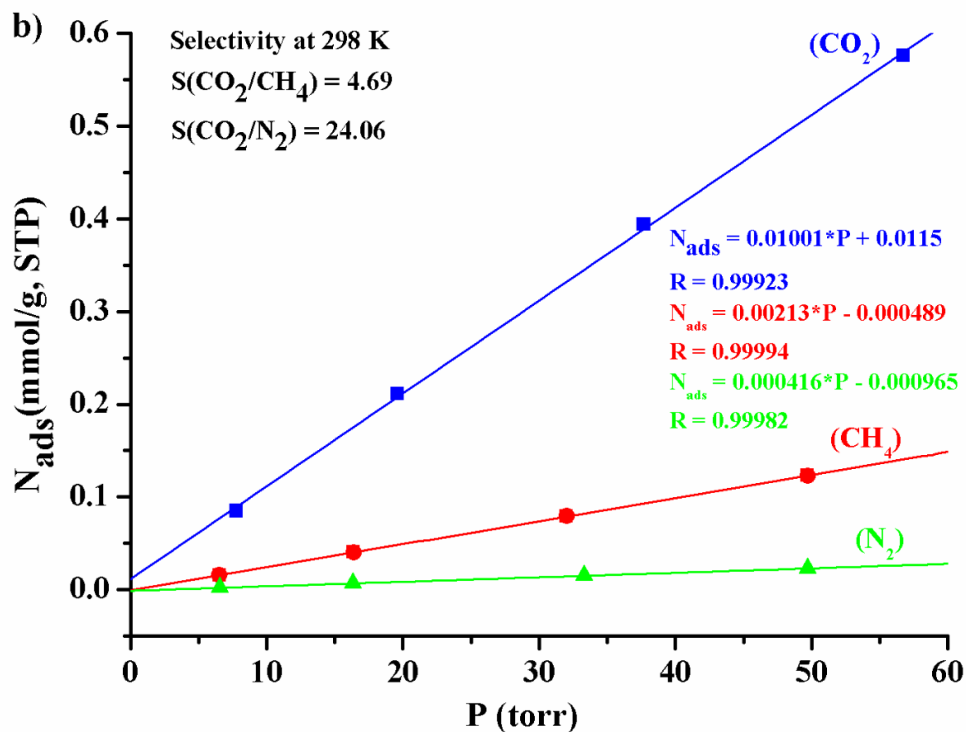
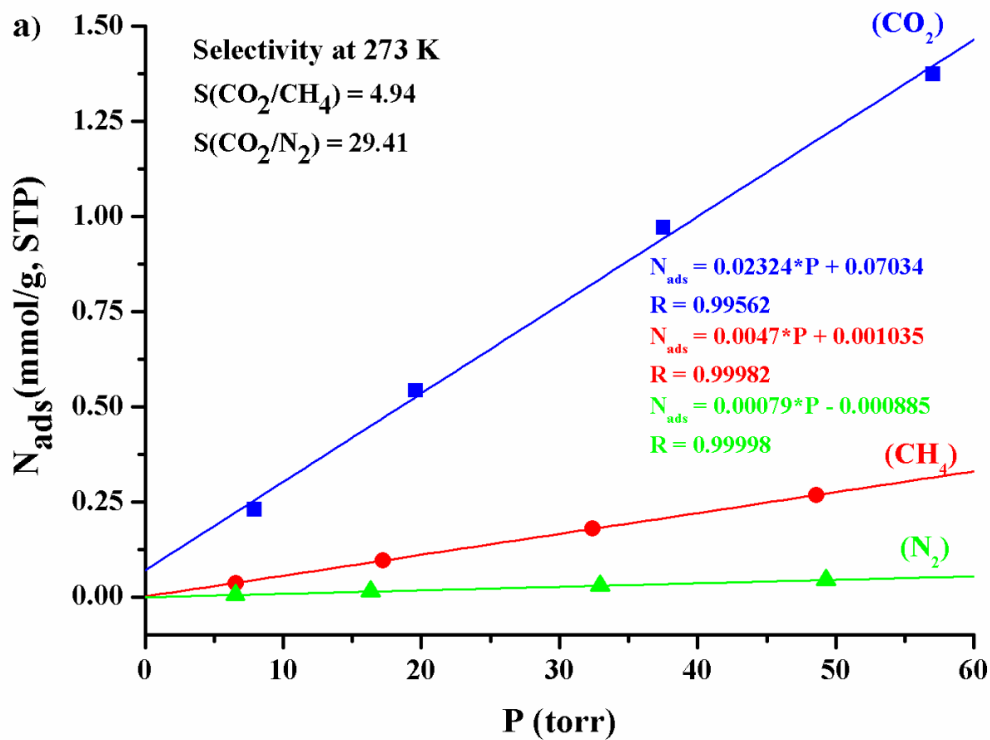
**Figure S13.** Isosteric heats of H<sub>2</sub> adsorption for NJU-Bai16 based on the Clausius-Clapeyron equation.



*Figure S14.* Isosteric heats of CO<sub>2</sub> adsorption for NJU-Bai16 based on the Clausius-Clapeyron equation.

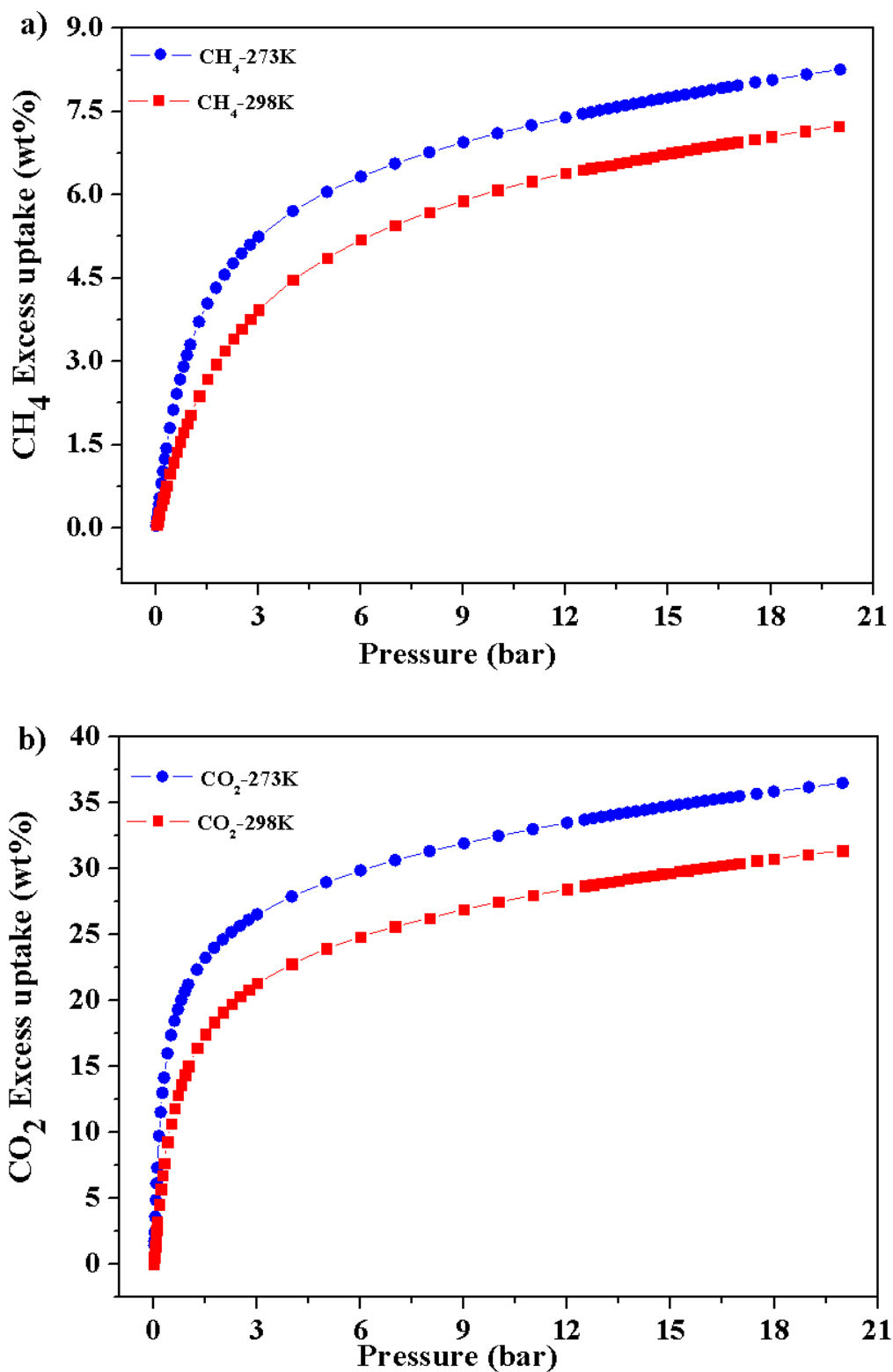


*Figure S15.* Isosteric heats of CH<sub>4</sub> adsorption for NJU-Bai16 based on the Clausius-Clapeyron equation.



**Figure S16.** The fitting initial slope for  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2$  isotherms for NJU-Bai16 collected at 273 K (a) and 298 K (b). ( $N_{\text{ads}}$  = gases uptake;  $R$  = related coefficient). The calculated selectivity of  $\text{CO}_2/\text{CH}_4$  and  $\text{CO}_2/\text{N}_2$  is 4.94, 29.41 and 4.69, 24.06 at 273 K and 298 K, respectively.





**Figure S17.** High-pressure gravimetric excess CH<sub>4</sub> (a) and CO<sub>2</sub> (b) uptake in NJU-Bai16 at 273 and 298 K, respectively.

**Table S1.** Crystal data and structure refinement for NJU-Bai16.

Identification code	NJU-Bai 16
CCDC number	1049754
Empirical formula	C17H11CuN3O5
Formula weight	400.83
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pccn
Unit cell dimensions	a = 16.269(2), b = 20.730(3), c = 14.9829(19); $\alpha = \beta = \gamma = 90^\circ$
Volume	5053.2(11) Å <sup>3</sup>
Z	8
Density (calculated)	1.054 g·cm <sup>-3</sup>
Absorption coefficient	0.887 mm <sup>-1</sup>
F(000)	1624
Crystal size	0.18 × 0.18 × 0.16
Limiting indices	-21 ≤ h ≤ 18, -26 ≤ k ≤ 22, -19 ≤ l ≤ 14
Reflections collected / unique	28595 / 5743 [R(int) = 0.0639]
Completeness	99.3 % (theta = 27.45°)
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8566 and 0.8711
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	5743 / 0 / 235
Goodness-of-fit on $F^2$	1.031
Final R indices [I > 2σ(I)]	R1 <sup>a</sup> = 0.0471, wR2 <sup>a</sup> = 0.1120
R indices (all data)	R1 <sup>a</sup> = 0.0738, wR2 <sup>a</sup> = 0.1189
Largest diff. peak and hole	-0.446 and 0.642 e·Å <sup>-3</sup>

<sup>a</sup> R1 =  $\sum ||F_o| - |F_c|| / \sum |F_o|$ ; wR2 =  $[\sum w(\sum F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ .

**Table S2.** Selected bond distances (Å) and angles (°) for NJU-Bai16.

Cu(1)-O(1)	2.2056(19)	Cu(1)-O(2) <sup>#1</sup>	1.9477(17)
Cu(1)-N(1) <sup>#2</sup>	2.003(2)	O(2)-Cu(1) <sup>#1</sup>	1.9478(17)
Cu(1)-N(2) <sup>#3</sup>	2.005(2)	N(1)-Cu(1) <sup>#4</sup>	2.003(2)
Cu(1)-O(3)	2.0270(18)	N(2)-Cu(1) <sup>#5</sup>	2.005(2)
O(2) <sup>#1</sup> -Cu(1)-N(1) <sup>#2</sup>	92.19(8)	N(2) <sup>#3</sup> -Cu(1)-O(3)	89.58(8)
O(2) <sup>#1</sup> -Cu(1)-N(2) <sup>#3</sup>	86.44(8)	O(2) <sup>#1</sup> -Cu(1)-O(1)	104.40(7)
N(1) <sup>#2</sup> -Cu(1)-N(2) <sup>#3</sup>	169.82(9)	N(1) <sup>#2</sup> -Cu(1)-O(1)	97.57(8)
O(2) <sup>#1</sup> -Cu(1)-O(3)	163.65(8)	N(2) <sup>#3</sup> -Cu(1)-O(1)	92.54(9)
N(1) <sup>#2</sup> -Cu(1)-O(3)	88.93(8)	O(3)-Cu(1)-O(1)	91.60(7)
C(8)-N(1)-Cu(1) <sup>#4</sup>	121.69(18)	C(1)-O(2)-Cu(1) <sup>#1</sup>	127.28(17)
N(3)-O(3)-Cu(1)	112.44(16)	C(13)-N(2)-Cu(1) <sup>#5</sup>	121.6(2)
C(12)-N(1)-Cu(1) <sup>#4</sup>	120.66(18)	C(17)-N(2)-Cu(1) <sup>#5</sup>	120.48(19)
C(1)-O(1)-Cu(1)	147.57(18)		

Symmetry Modes: #1 -x, -y+1, -z+1, #2 -x+1/2, y, z-1/2, -z+1/2, #3 -x, y+1/2, -z+3/2, #4 -x+1/2, y, z+1/2, #5 -x, y-1/2, -z+3/2.

**Table S3.** Summary of the isosteric heats of CH<sub>4</sub> adsorption ( $Q_{st}$ ) at low loading and pore size for selected porous materials.

Material	BET (m <sup>2</sup> g <sup>-1</sup> )	Pore size (Å)	$Q_{st}$ (kJ mol <sup>-1</sup> ) <sup>b</sup>	Ref
HKUST-1	1502	3.5, 9	17	7
MOF-5	1870	12	12.2	8, 9
PCN-11	1931	8.9	14.6	8, 10
PCN-14	1753	8	18.7	7
Mn-MOF-74	1102	13.6	19.1	11
Co-MOF-74	1056	13.6	19.6	11
Ni-MOF-74	1027	13.6	21.4	7
Zn-MOF-74	885	13.6	18.3	11
Mg-MOF-74	1332	13.6	18.5	11
UTSA-20	1156	3.4, 8.5	18.2	5

dia-4i-1	1668 <sup>a</sup>	18.2	8.7	12
dia-4i-2	1447 <sup>a</sup>	11.85	12.1 (12.0) <sup>c</sup>	12
dia-4i-3-a	758 <sup>a</sup>	8.57	20.2 (15.9) <sup>c</sup>	12
dia-7i-1-Co	833 <sup>a</sup>	5.2	26.7 (24.0) <sup>c</sup>	12
<b>NJU-Bai16</b>	<b>969.8</b>	<b>4.1</b>	<b>21.7 (23.3)<sup>c</sup></b>	<b>this work</b>

<sup>a</sup>Langmuir surface area

<sup>b</sup> $Q_{st}$  values based on Clausius-Clapeyron equation

<sup>c</sup> $Q_{st}$  values based on virial equation

## Reference

- [1] G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112.
- [2] A. L. Spek, *Acta Crystallogr. Sect. A*, 1990, **46**, C34.
- [3] J. L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 1304.
- [4] W. Yang, X. Lin, J. Jia, A. J. Blake, C. Wilson, P. Hubberstey, N. R. Champness and M. Schröder, *Chem. Commun.*, 2008, DOI: 10.1039/B712201B, 359.
- [5] M.-S. Chen, M. Chen, S. Takamizawa, T. A. Okamura, J. Fan and W.-Y. Sun, *Chem. Commun.*, 2011, **47**, 3787.
- [6] (a) K. S. Walton and R. Q. Snurr, *J. Am. Chem. Soc.*, 2007, **129**, 8552; (b) J. Rouquerol, P. Llewellyn and F. Rouquerol, *Stud. Surf. Sci. Catal.*, 2007, **160**, 49.
- [7] Y. Peng, V. Krungleviciute, I. Eryazici, J. T. Hupp, O. K. Farha and T. Yildirim, *J. Am. Chem. Soc.*, 2013, **135**, 11887.
- [8] T. A. Makal, J.-R. Li, W. Lu and H.-C. Zhou, *Chem. Soc. Rev.*, 2012, **41**, 7761.
- [9] W. Zhou, H. Wu, M. R. Hartman and T. Yildirim, *J. Phys Chem. C*, 2007, **111**, 16131.
- [10] X.-S. Wang, S. Ma, K. Rauch, J. M. Simmons, D. Yuan, X. Wang, T. Yildirim, W. C. Cole, J. J. López, A. D. Meijere and H.-C. Zhou, *Chem. Mater.*, 2008, **20**, 3145.
- [11] H. Wu, W. Zhou and T. Yildirim, *J. Am. Chem. Soc.*, 2009., **131**, 4995.
- [12] S. K. Elsaidi, M. H. Mohamed, L. Wojtas, A. Chanthapally, T. Pham, B. Space, J. J. Vittal and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2014, **136**, 5072.