

Supporting Information for the manuscript

A Rod Packing Microporous Metal-Organic Framework with Open Metal Sites for Selective Guest Sorption and Sensing of Nitrobenzene

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Experimental Section

Materials and Measurements. All reagents and solvents were used as received from commercial suppliers without further purification. TGA (thermal gravimetric analysis) was performed under a nitrogen atmosphere with a heating rate of 3 °C/min using a Shimadzu TGA-50 thermogravimetric analyzer. Powder X-ray diffraction (XRD) data were collected on a RIGAMU D/MAX 2550/PC X diffractometer with CuK α radiation. Analyses for C, H and N were carried out on a Flash EA1112 analyzer. N₂, H₂, C₂H₂, CH₄ and CO₂ adsorption isotherms were measured on ASAP 2020. A Coulter Omnisorp 100cx analyzer was used to measure methanol, ethanol, propanol, isopropanol sorption isotherm for activated **1a** formed by heating of the as-synthesized MOF **1a** at the temperature of 150 °C under high vacuum overnight. Fourier-transform (FT-IR) spectra (4000-650 cm⁻¹) were measured with a Bruker Equinox 55 FTIR spectrometer on KBr disks.

Fluorescence Measurements. The fluorescence properties of MOF **1** and solvent included MOF **1a** were investigated in the solid state at room temperature. A fresh sample (30mg) of MOF **1** was activated and then immersed into methanol solvent (20 mL) with different organic solvent (0.2

mL) to form solvent included MOF **1a** which was collected by filtration and drying for 24 hrs at 20 °C. The sample was pressed on a glass slide for the photoluminescence studies. The photoluminescence (PL) spectra were recorded by a Hitachi F4500 fluorescence spectrometer. The photomultiplier tube voltage was 700 V and the scan speed was 240 nm/min, and the slit widths were 1.0 and 2.5 nm, respectively, for excitation and emission spectra.

Derivation of the Isothermic Heats of Adsorption: A virial type expression of the following form was used to fit the combined isotherm data for a given material at 295.0 and 273.2 K.¹

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

Here, P is the pressure expressed in Torr, N is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_i are virial coefficients, and m , n represents the number of coefficients required to adequately describe the isotherms. The equation was fit using the statistical software package **SPSS** 16.0. 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, as determined using the average value of the squared deviations from the experimental values was minimized. In all cases, $m \leq 6$ and $n \leq 3$. The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using the following expression.

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

Here, Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant of 8.3147 J K⁻¹mol⁻¹.

From these results, the Henry's constant (K_H) is calculated from where T is temperature.²

$$K_H = \exp(-b_0) \cdot \exp(-a_0/T)$$

The Henry's Law selectivity for gas component i over j at 295 K is calculated based on equation:

$$S_{ij} = K_{Hi} / K_{Hj}$$

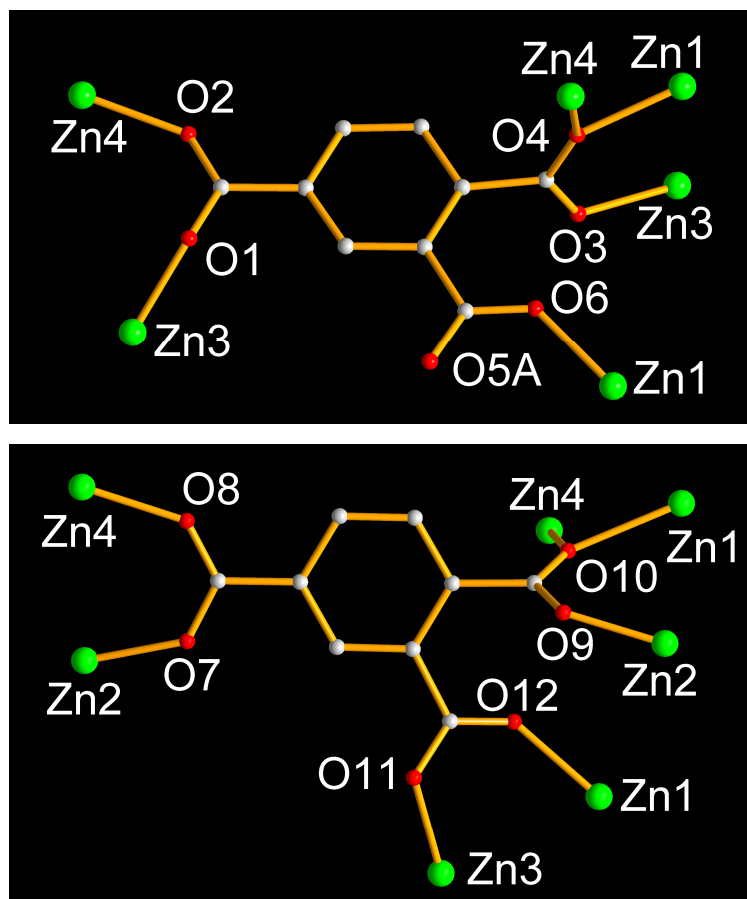


Figure S1. Coordination mode of two BTC ligands.

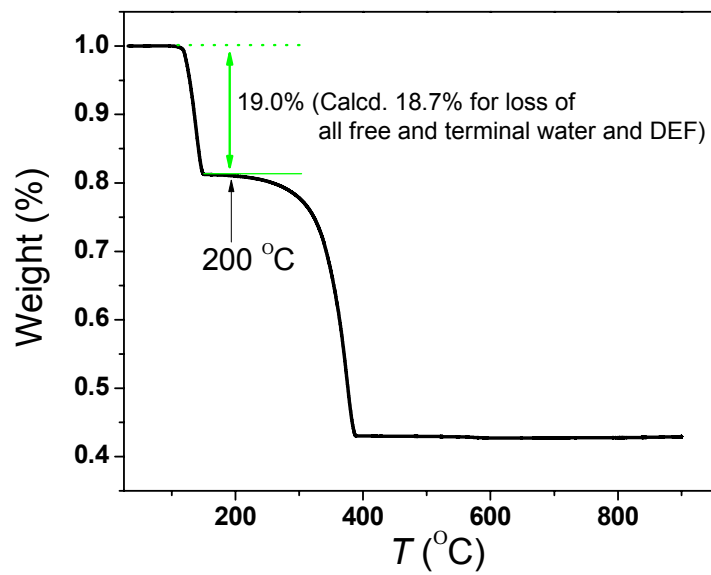


Figure S2. TGA traces of **1** ranging from room temperature to 900 °C.

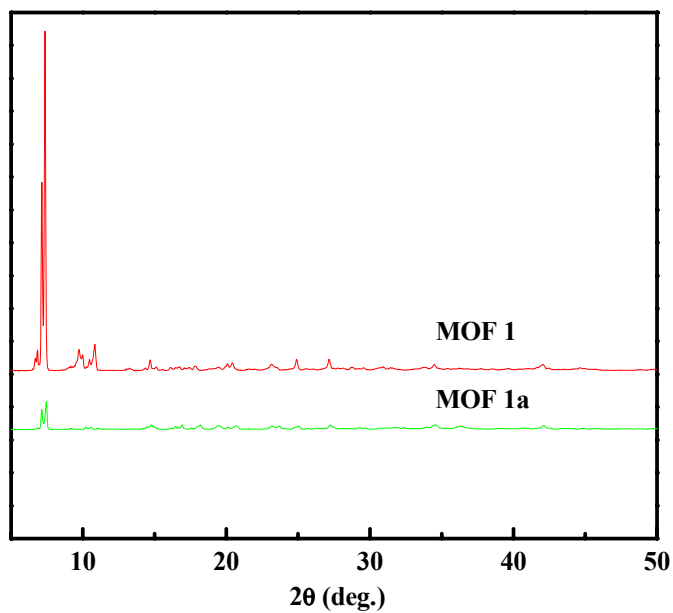


Figure S3. PXRD patterns of the as-synthesized **1** and the activated **1a**.

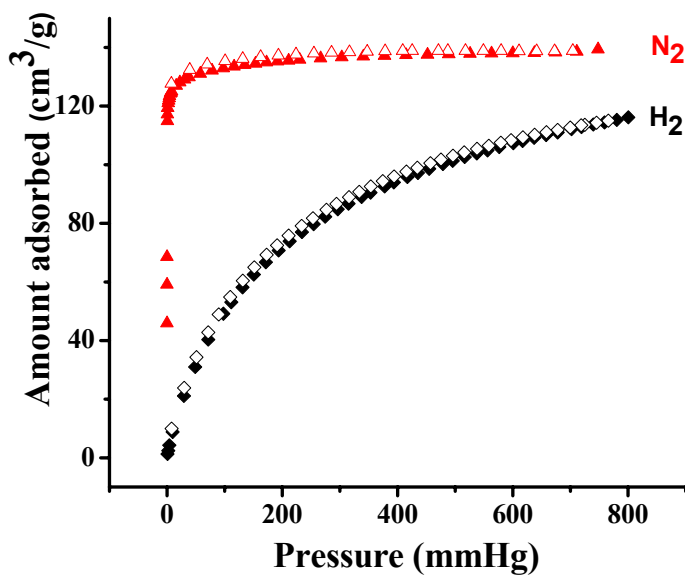


Figure S4. Gas sorption isotherms of MOF **1a** for N₂ and H₂ at 77 K.

Table S1. Virial coefficients employed to fit the 273.2 K and 295.0 K adsorption isotherm data of C₂H₂, CO₂ and CH₄ for MOF **1a**.

	C ₂ H ₂	CO ₂	CH ₄
<i>a</i> 0	-3397.9±163.1	-1383.4±247.2	-1774.2±43.8
<i>a</i> 1	118.0±6.7	-1304.9±125.1	-689.3±150.0
<i>a</i> 2	0±0	60.1±3.5	0±0
<i>a</i> 3	0±0	0±0	0±0
<i>a</i> 4	0±0	0±0	0±0
<i>a</i> 5	0±0	0±0	0±0
<i>a</i> 6	0±0	0±0	0±0
<i>b</i> 0	16.2±0.6	9.6±0.8	13.4±0.2
<i>b</i> 1	0±0	4.3±0.4	2.5±0.5

b_2	0±0	0±0	0.2±0.1
b_3	0±0	0±0	0±0
R	0.964	1.000	0.998
K_H	0.009337	0.002856	0.000636
S_{i/CH_4}	14.7	4.5	

R is the correlation coefficient.

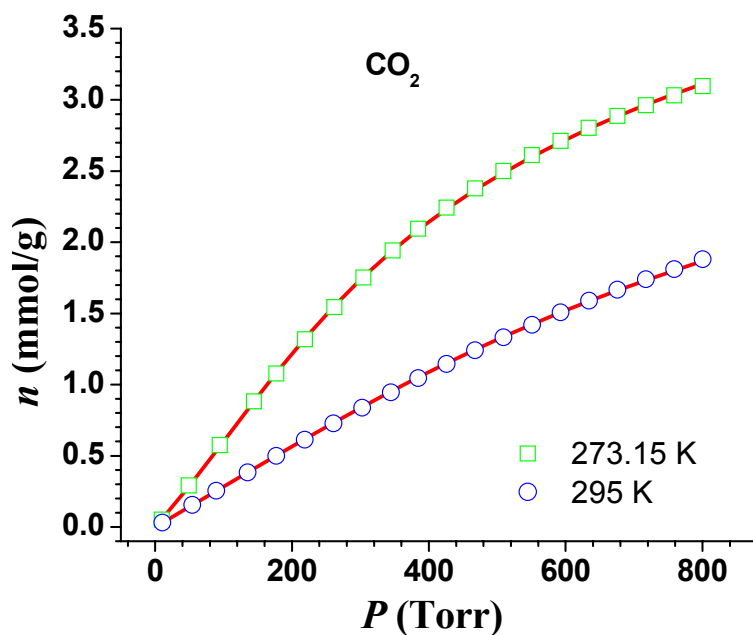


Figure S5. Adsorption isotherms for the uptake of CO₂ within the **1a** at 273.2 K (square) and 295.0 K (circle). The red solid lines represent the fitting by using the virial expression.

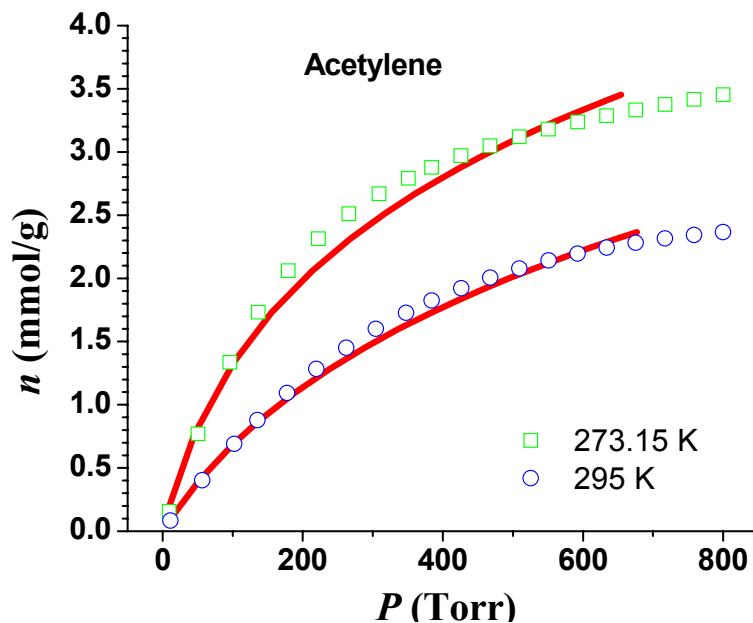


Figure S6. Adsorption isotherms for the uptake of acetylene within the **1a** at 273.2 K (square) and 295.0 K (circle). The red solid lines represent the fitting by using the virial expression.

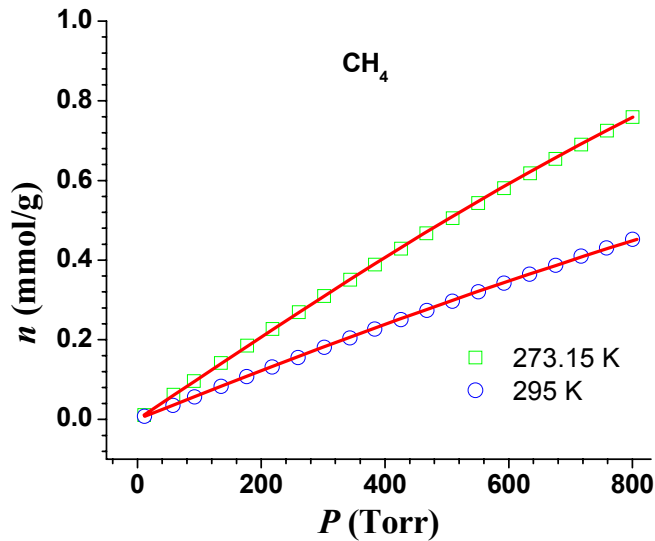


Figure S7. Adsorption isotherms for the uptake of methane within the **1a** at 273.2 K (square) and 295.0 K (circle). The red solid lines represent the fitting by using the virial expression.

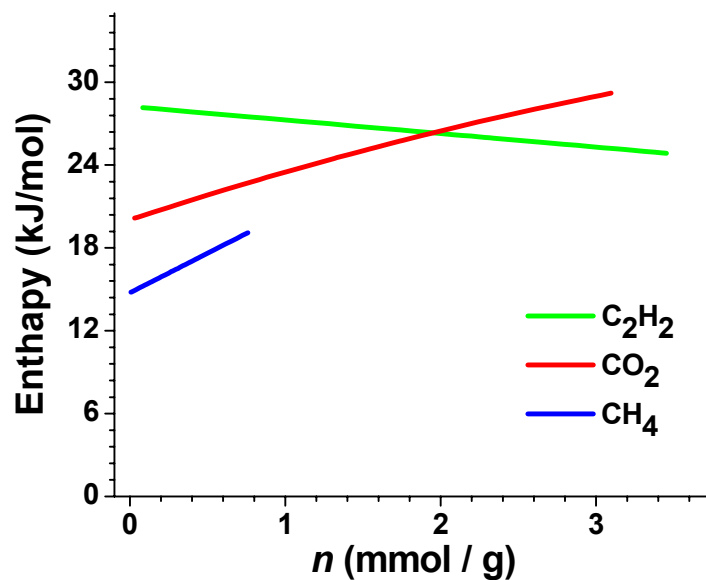


Figure S8. Coverage dependencies of the isosteric heats of adsorption for C_2H_2 (green), CO_2 (red) and CH_4 (blue) in the **1a** calculated from fits of their 273.2 and 295.0 K isotherms using the virial method.

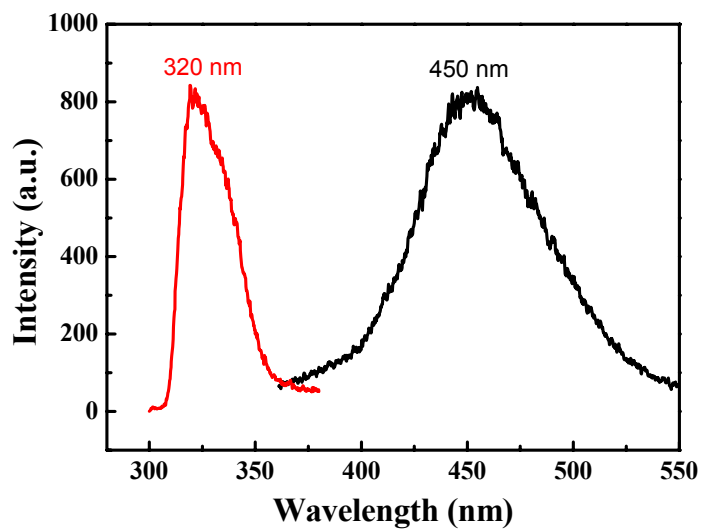


Figure S9. Excitation (red) and emission (black) spectra of BTC ligand.

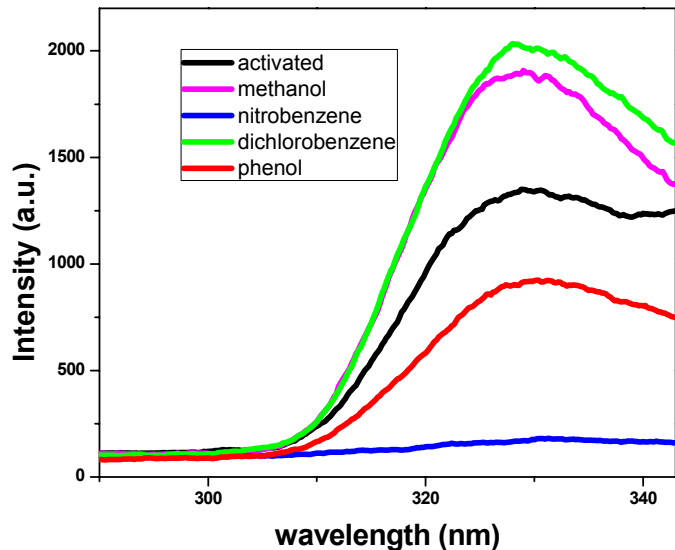


Figure S10. Excitation spectra of **1a** in different solvent.

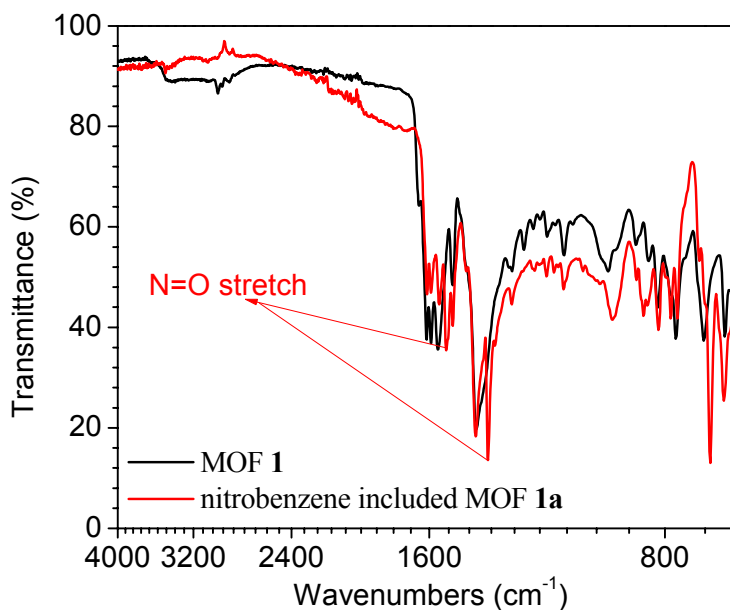


Figure S11. IR spectra (4000-650 cm^{-1}) of MOF **1** (black) (2979 (w), 1612 (m), 1592 (m), 1559 (m), 1493 (m), 1393 (s), 1254 (w), 1211 (w), 1132 (m), 1077 (w), 945 (m), 871 (m), 839 (m), 817 (m), 774 (m), 713 (m), 670 (m)) and nitrobenzene included MOF **1a** (red) (1611 (w), 1592 (w), 1554 (w), 1522 (m), 1494 (m), 1396 (s), 1347 (s), 1255 (w), 1173 (w), 1133 (w), 1078 (m), 934 (m), 871 (s), 852 (m), 816 (m), 786 (m), 772 (m), 723 (m), 700 (s), 673 (s)).

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- 1 J. Roswell, O. M. Yaghi, *J. Am. Chem. Soc.* **2006**, *128*, 1304.
 - 2 (a) Czepirski, L. & Jagiełło, J., *Chem. Eng. Sci.* **1989**, *44*, 797. (b) Jagiello, J., Bandosz, T. J., Putyera, K. & Schwarz, J. A., *J. Chem. Eng. Data* **40**, 1288 (1995). (c) Furukawa, H., Miller, M. A. & Yaghi, O. M., *J. Mater. Chem.* **17**, 3197 (2007). (d) Rahul Banerjee, Hiroyasu Furukawa, David Britt, Carolyn Knobler, Michael O’Keeffe and Omar M. Yaghi, *J. Am. Chem. Soc.*, **2009**, *131* (11), pp 3875.