

## **Supplementary Information for**

### **Post-Synthetic Modification of Alkyne-tagged Zirconium Metal-Organic Framework *via* “Click” Reaction**

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## 1. Materials and Methods

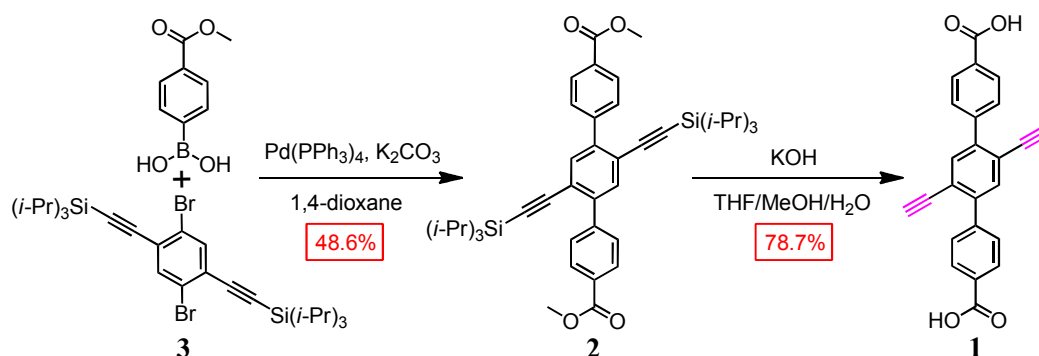
4-Methoxyl carbonylphenylboronic acid (97%) was purchased from AK Scientific, Inc.. Pd(PPh<sub>3</sub>)<sub>4</sub> was bought from Aladdin. Zirconium (IV) chloride (99.5%) was purchased from Alfa Aesar. Triisopropylsilane and copper(I) iodide were purchased from admas. Compound **3**,<sup>S1</sup> azidoethane,<sup>S2</sup> Ethyl azidoacetate,<sup>S3</sup> azidomethy benzene<sup>S4</sup> were synthesized according to the literature procedure.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker Fourier 300M and 400 M spectrometer. High resolution mass spectra was collected on Bruker Daltonics Inc. APEXII FT-ICR mass spectrometer, which was equipped with EI, ESI and MALDI as ionization source. Powder X-ray diffraction (PXRD) data was collected on Rigaku miniflex600 with CuKα<sub>1</sub> (λ = 1.54056 Å) radiation operated at 40 kV and 15 mA, from 2θ = 2° up to 50° with 0.02° increment. Thermogravimetric analysis from 50-800 °C was carried out on a DTA-60 Simultaneous DTG-TG Apparatus (Shimadzu) in air atmosphere using a 5 °C/min ramp without equilibration delay. For supercritical CO<sub>2</sub> activation, the solvent-exchanged MOFs were immersed in liquid CO<sub>2</sub>, kept under supercritical CO<sub>2</sub> atmosphere, and then bled using a Tousimis Samdri PVT-3D critical point dryer. The nitrogen adsorption and desorption isotherms were measured at 77 K using a Quantachrome Nova 4200e surface area & pore size analyzer. Before measurement, the samples were degassed in vacuum at room temperature for 12 h. The BET surface areas were determined by multi-point BET method using the adsorption data in the relative pressure (P/P<sub>0</sub>) range of 0.05 to 0.30. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker TENSOR-27 infrared spectrometer using KBr pellets. Elemental analyses (C, H and N) are performed on a Thermo Flash EA 1112 elemental analyzer. Single crystal X-ray data were collected at 100 K at the Beijing Synchrotron Radiation Facility, beam line station 3W1A equipped with a MarCCD-165 detector. CCDC 1042778 contains crystallographic data for this paper.

**MOFs Digestion:** In a typical procedure, approximately 10 mg activated MOF samples were digested with sonication in 1 mL DMSO and 10 µl 30% HF aqueous

solution. After that, water was added to the resulting solution until no further precipitate was detected. The precipitate was collected by filtration, washed with and dried in vacuum.

## 2. Chemical Synthesis

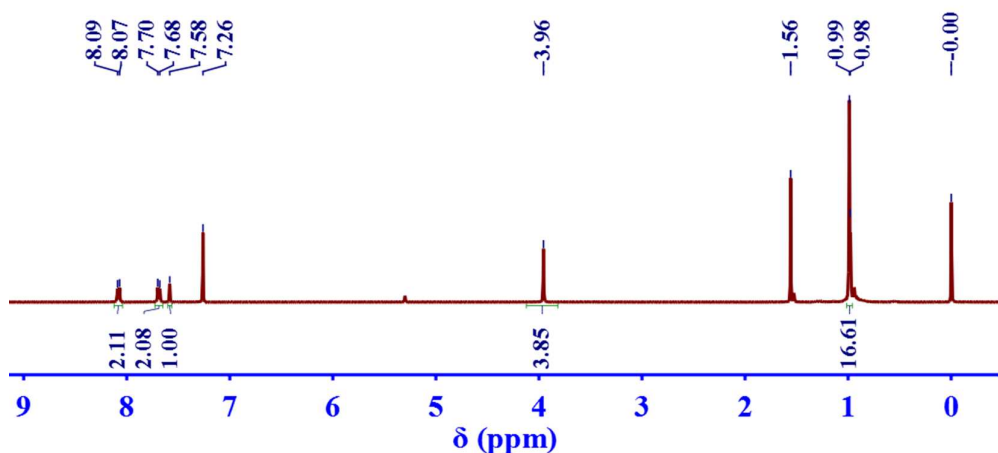


**Scheme S1** Synthesis of ligand **1**

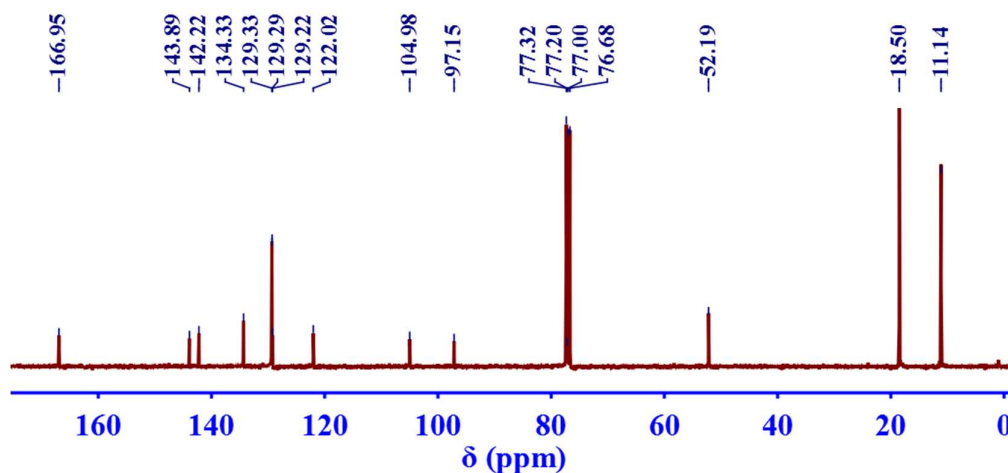
**Synthesis of compound 2:** 4-Methoxyl carbonylphenyl boronic acid (0.8 g, 4.45 mmol), compound **3** (0.92 g, 1.54 mmol),  $K_2CO_3$  (2 M aqueous solution, 25 mL) and  $Pd(PPh_3)_4$  (0.4 g, 0.347 mmol) were added to flask containing 1,4-dioxane (60 mL). The reaction mixture was bubbled for around 1 h and then was allowed to reflux for 12 h under  $N_2$ . After the reaction was cooled down,  $CH_2Cl_2$  (100 mL) was added. The organic layer was washed with brine and dried over  $Na_2SO_4$ . After that, the solvents were evaporated under reduced pressure and the resulting residue was subjected to column chromatography [ $SiO_2$  :  $CH_2Cl_2$  / petroleum ether (1 : 3)]. Compound **2** was isolated as a white solid (0.562 g, 48.6%, yield).  $^1H$  NMR (400 MHz,  $CDCl_3$ , ppm):  $\delta$  = 8.08 (d,  $J$  = 8.4 Hz, 4H), 7.69 (d,  $J$  = 8.4 Hz, 4H), 7.58 (s, 2H), 3.96 (s, 6H), 0.98 (m, 42H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , ppm):  $\delta$  = 167.0, 143.9, 142.2, 134.3, 129.33, 129.29, 129.20, 122.0, 105.0, 97.2, 52.2, 18.5, 11.1. HR-MS (EI): calcd for  $C_{44}H_{58}O_4Si_2$ :  $m/z$  = 729.3771  $[M+Na]^+$ ; found,  $m/z$  = 729.3770  $[M+Na]^+$ .

**Synthesis of ligand 1:** In a mixture of 10% KOH aqueous solution (60 mL), MeOH (100 mL) and THF (100 mL), compound **2** (900 mg, 1.27 mmol) were added. The reaction mixture was refluxed for 6 h under  $N_2$ . After cooling to room temperature,

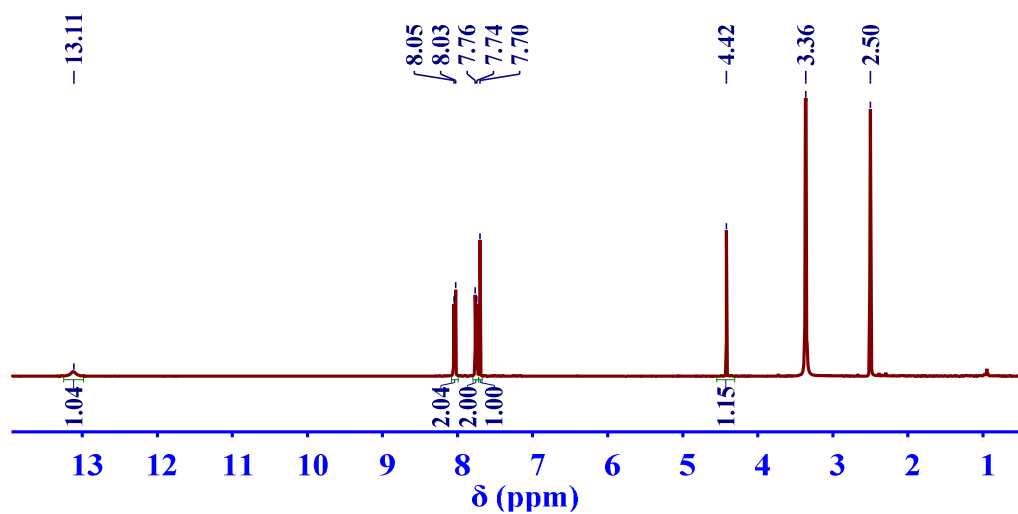
MeOH and THF were evaporated under reduced pressure. Additional water (40 mL) was added to the resulting solution and the mixture was heated until the solid was fully dissolved, then the homogeneous solution was acidified with diluted HCl until no further precipitate was detected ( $\text{pH} \approx 2$ ). The precipitate was collected by filtration, washing with water and drying in vacuum. Ligand **1** was isolated as light yellow solid (360 mg, 78.7% yield)  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , ppm):  $\delta = 13.11$  (s, 2H), 8.04 (d,  $J = 8.4$  Hz, 4H), 7.75 (d,  $J = 8.4$  Hz, 4H), 7.70 (s, 2H), 4.42 (s, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ , ppm):  $\delta = 167.1, 142.4, 142.0, 134.4, 130.4, 129.3, 129.2, 120.9, 86.3, 81.7$ . HR-MS (ESI): calcd for  $\text{C}_{24}\text{H}_{13}\text{O}_4$ : 365.0814  $[\text{M-H}]^-$  found, 365.0819  $[\text{M-H}]^-$ .



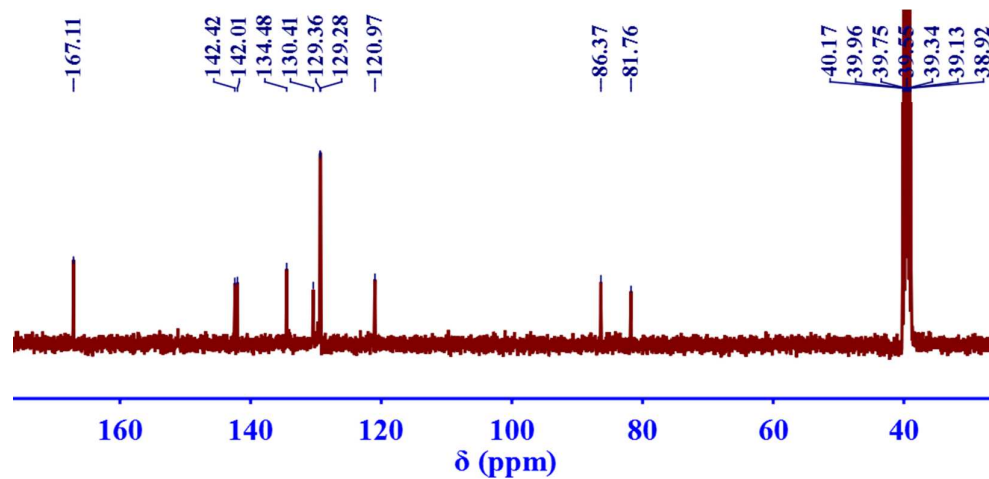
**Figure S1**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound **2**.



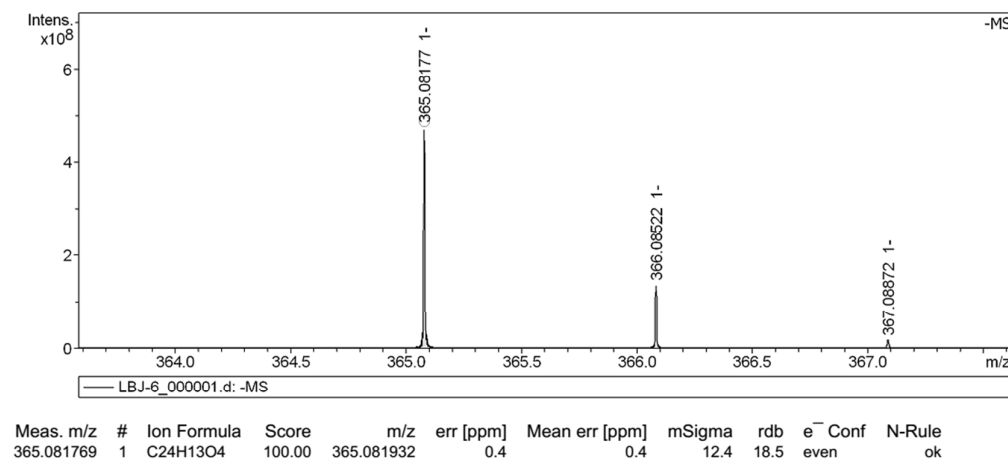
**Figure S2**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **2**.



**Figure S3**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ) spectrum of ligand **1**



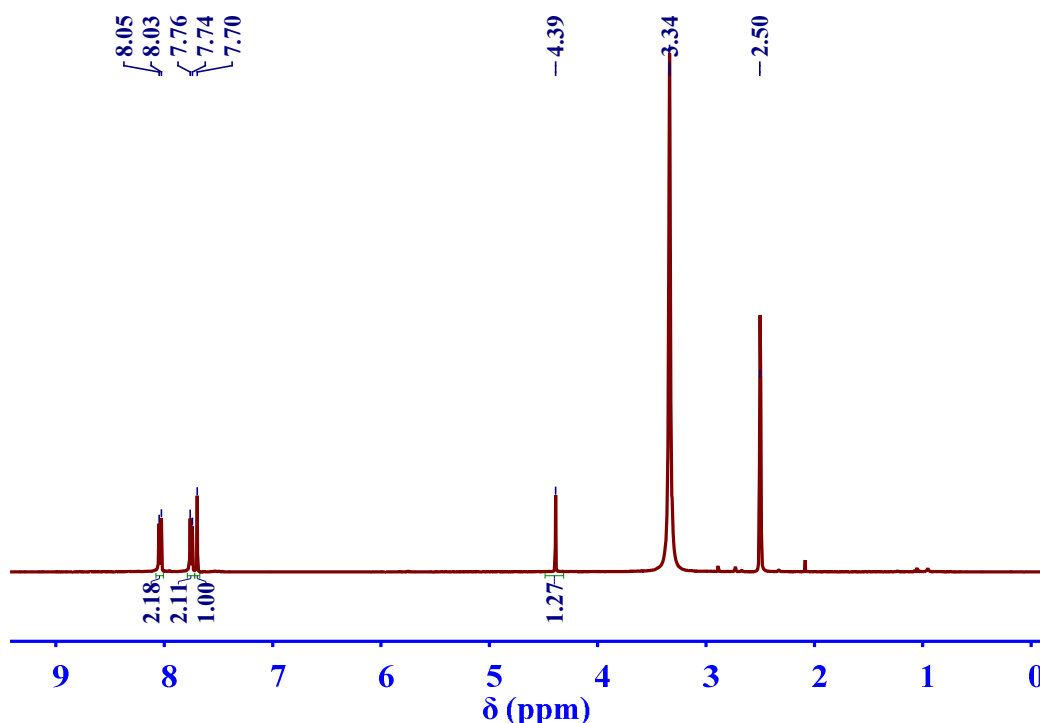
**Figure S4**  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ) spectrum of ligand **1**



**Figure S5** High resolution mass spectrum of the ligand **1**

### 3. MOF Synthesis

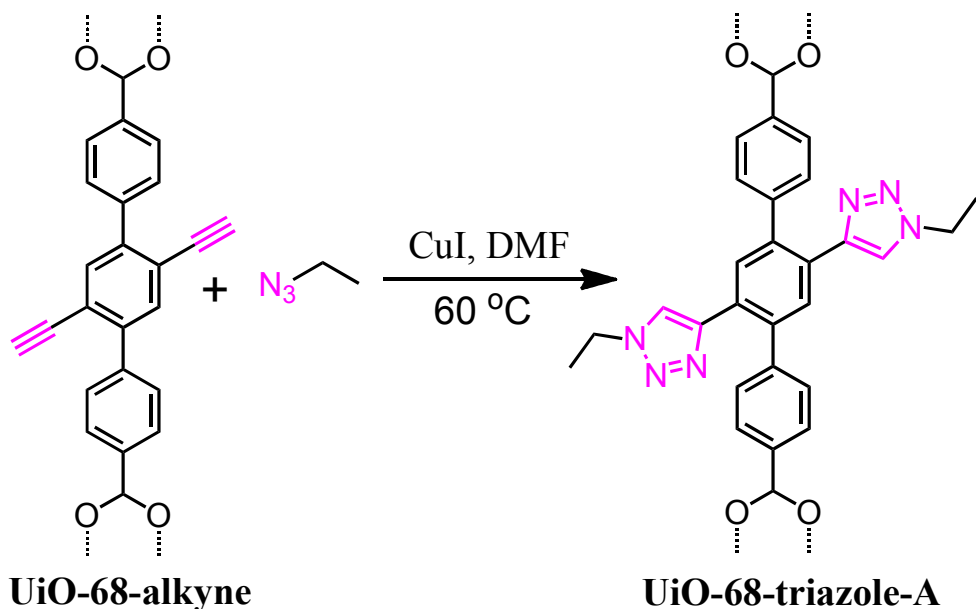
**Synthesis of UiO-68-alkyne:**  $\text{ZrCl}_4$  (9.0 mg), ligand **1** (14.0 mg) and acetic acid (370  $\mu\text{L}$ ) were ultrasonically dissolved in DMF (1.6 mL) and then placed in a preheated 100  $^\circ\text{C}$  oven for 48 h. Single crystals with octahedral shape suitable for single crystal diffraction were harvested with a yield of  $\sim 8.5$  mg. The as-synthesized UiO-68-alkyne was rinsed with DMF overnight to remove unreacted starting materials and trapped acetic acid. The crystal were kept in DMF for further modification. In addition, samples not undergoing subsequent modification was allowed to immerse in anhydrous ethanol for 3 days to exchange and remove DMF. During this period, ethanol was freshly exchanged three times per day. Ethanol exchanged crystal samples was activated with a supercritical  $\text{CO}_2$  activation protocol. Elemental analyses on the activated sample found [C (55.18%), H (3.50%), N (0.47%)]; This would roughly correspond to a formula of  $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{C}_{24}\text{H}_{12}\text{O}_4)_6(\text{C}_3\text{H}_7\text{NO})(\text{H}_2\text{O})_{14}$  (mw 3181), which gives a calculated profile as [C (55.33%), H (3.51%), N (0.44%)].



**Figure S6**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ) spectrum of digested UiO-68-alkyne

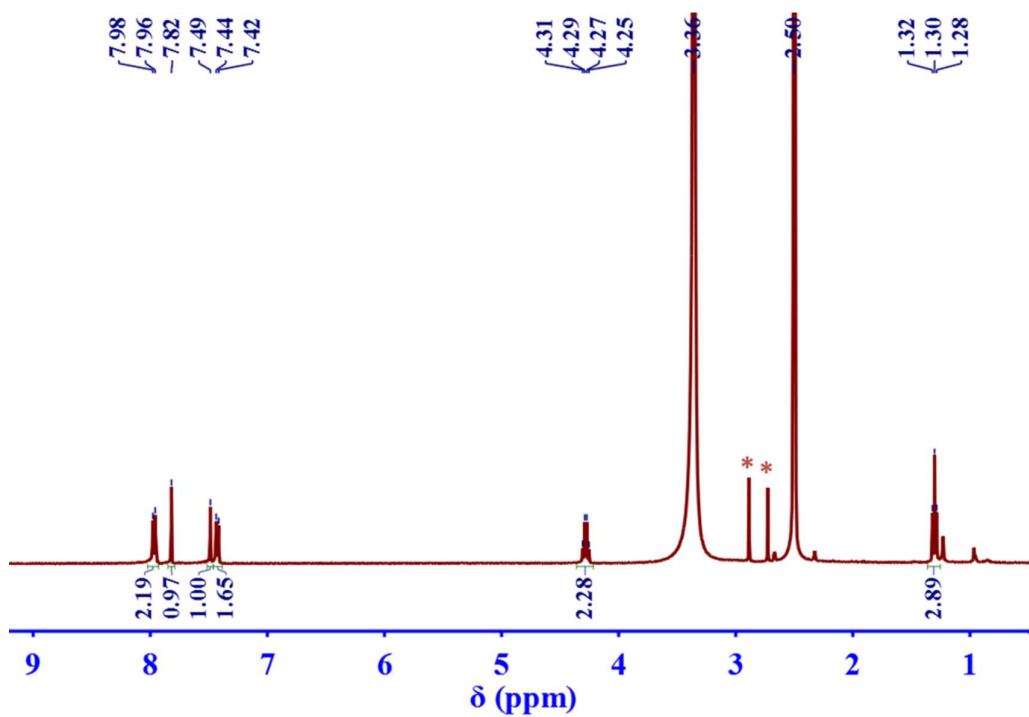
## 4. Post-Synthetic Modification of UiO-68-alkyne

### a) Click with azidoethane



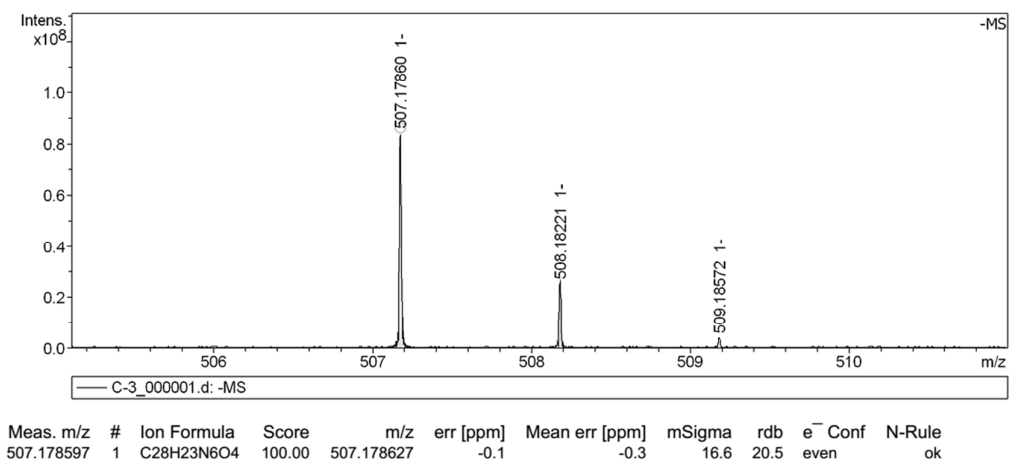
**Scheme S2** Synthesis of UiO-68-traizole-A

Azidoethane (0.238 mL) were added to a mixture of UiO-68-alkyne (20 mg) and CuI (3.0 mg) in DMF (3.0 mL). The reaction mixtures were kept at 60 °C under N<sub>2</sub> atmosphere for 24 h without stirring. The resultant octahedral crystals were collected by centrifugation, and then rinsed with DMF overnight. After that, crystals was allowed to immerse in anhydrous ethanol for 3 days to exchange and remove DMF. During this period, ethanol was freshly exchanged three times per day. Ethanol exchanged crystal samples was activated with a supercritical CO<sub>2</sub> activation protocol. UiO-68-traizole-A was obtained as yellow solid in quantitative yield. Elemental analyses on the activated sample found [C (51.13%), H (4.39%), N (12.78%)]; This would roughly correspond to a formula of  $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{C}_{28}\text{H}_{24}\text{N}_6\text{O}_4)_6(\text{C}_3\text{H}_7\text{NO})(\text{H}_2\text{O})_8$  (mw 3938), which gives a calculated profile as [C (52.03%), H (4.37%), N (13.13%)].



**Figure S7**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) spectrum of digested UiO-68-triazole-A.

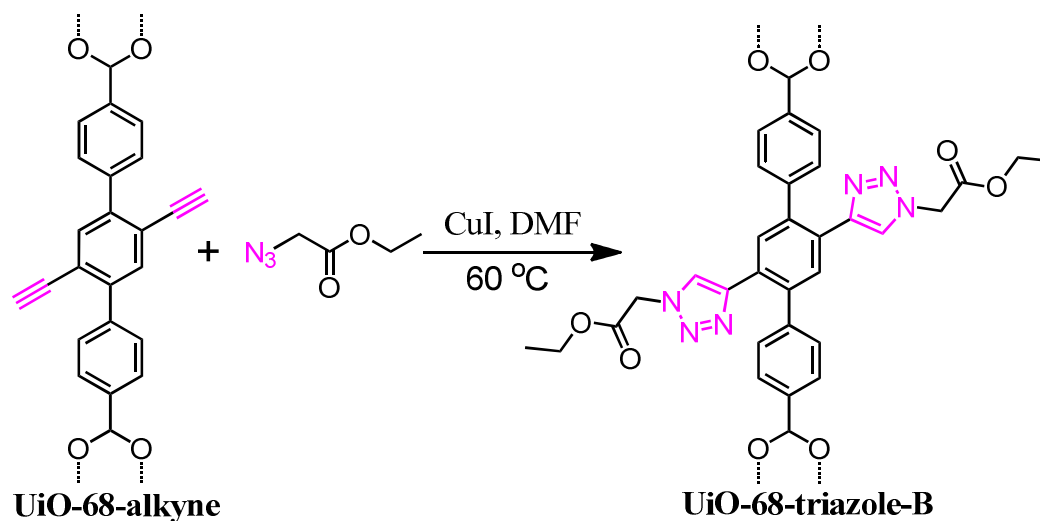
The stars mark DMF



**Figure S8** High resolution mass spectrum of digested UiO-68-triazole-A

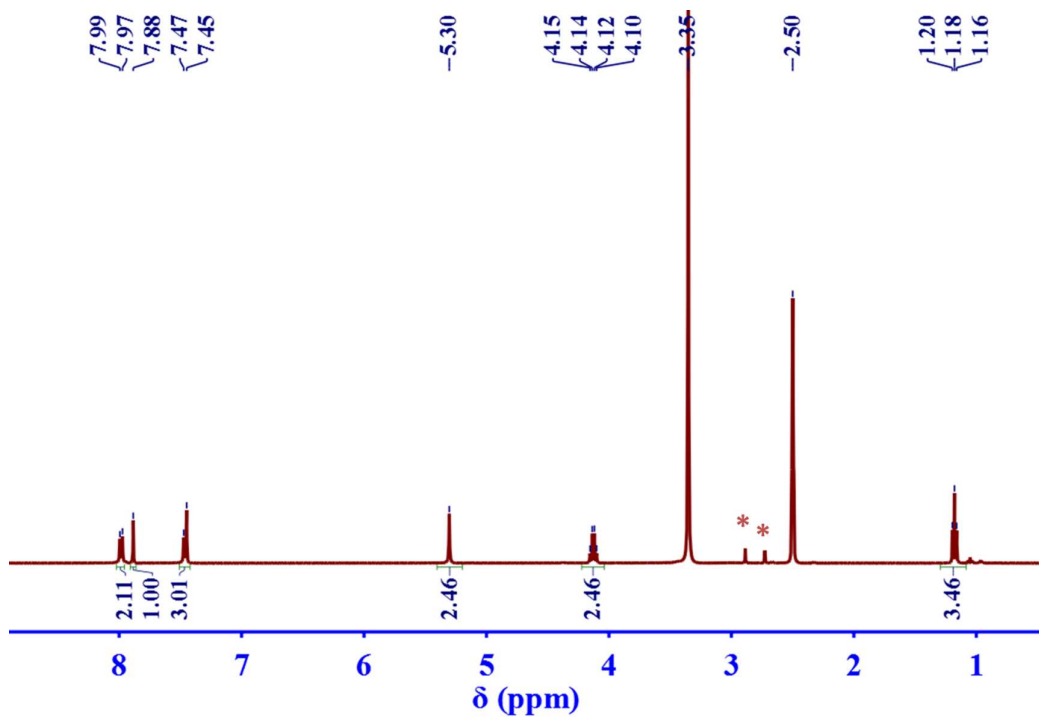


**b) Click with ethyl azidoacetate**

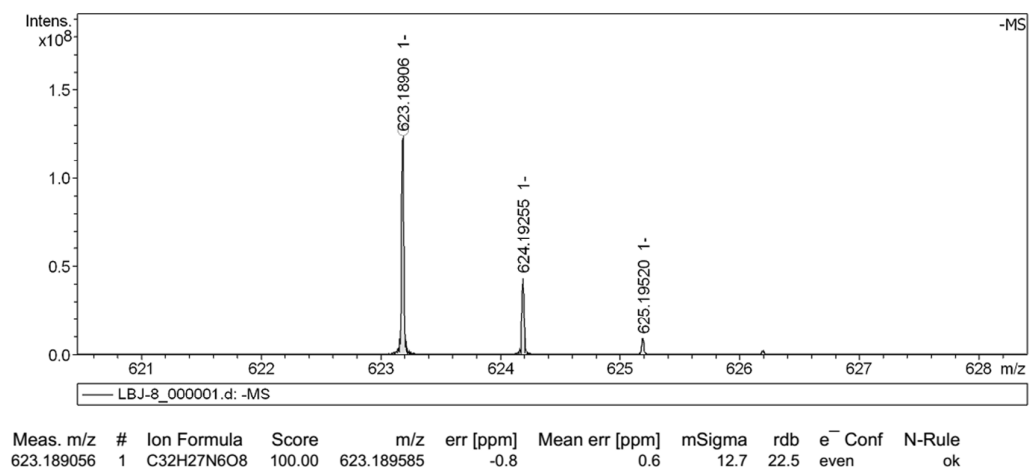


**Scheme S3** Synthesis of UiO-68-traizole-B

Ethyl azidoacetate (0.1 mL, 0.775mmol) were added to a mixture of UiO-68-alkyne (20 mg) and CuI (3.0 mg) in DMF (2.0 mL). The reaction mixtures were kept at 60 °C under N<sub>2</sub> atmosphere for 24 h without stirring. The resultant octahedral crystals were collected by centrifugation, and then rinsed with DMF overnight. After that, crystals was allowed to immerse in anhydrous ethanol for 3 days to exchange and remove DMF. During this period, ethanol was freshly exchanged three times per day. Ethanol exchanged crystal samples was activated with a supercritical CO<sub>2</sub> activation protocol. UiO-68-traizole-B was obtained as light yellow solid in quantitative yield. Elemental analyses on the activated sample found [C (50.89%), H (4.45%), N (9.03%)]; This would roughly correspond to a formula of Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(C<sub>32</sub>H<sub>28</sub>N<sub>6</sub>O<sub>8</sub>)<sub>6</sub>(C<sub>3</sub>H<sub>7</sub>NO)(H<sub>2</sub>O)<sub>8</sub> (mw 4634), which gives a calculated profile as [C (50.43%), H (4.23%), N (11.16%)].

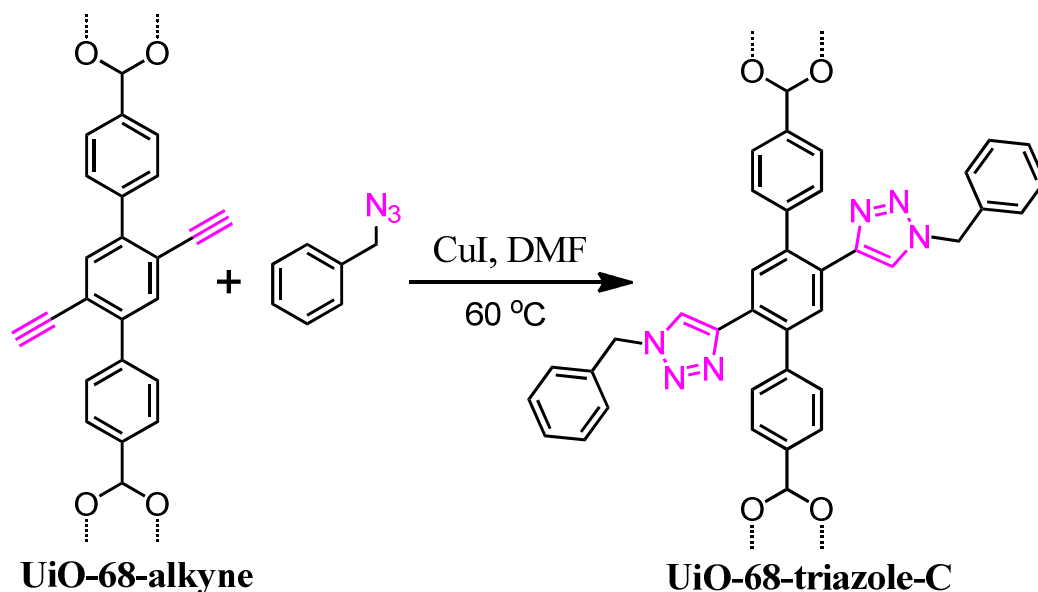


**Figure S9**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) spectrum of digested UiO-68-triazole-B. The stars mark DMF



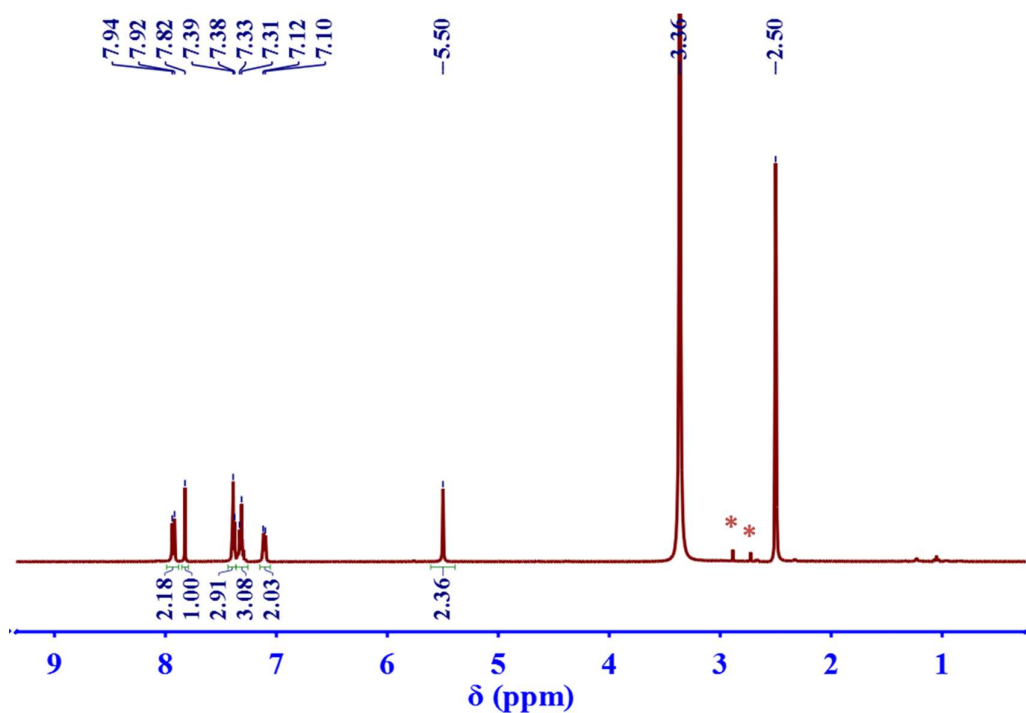
**Figure S10** High resolution mass spectrum of digested UiO-68-triazole-B

c) Click with azidomethyl benzene

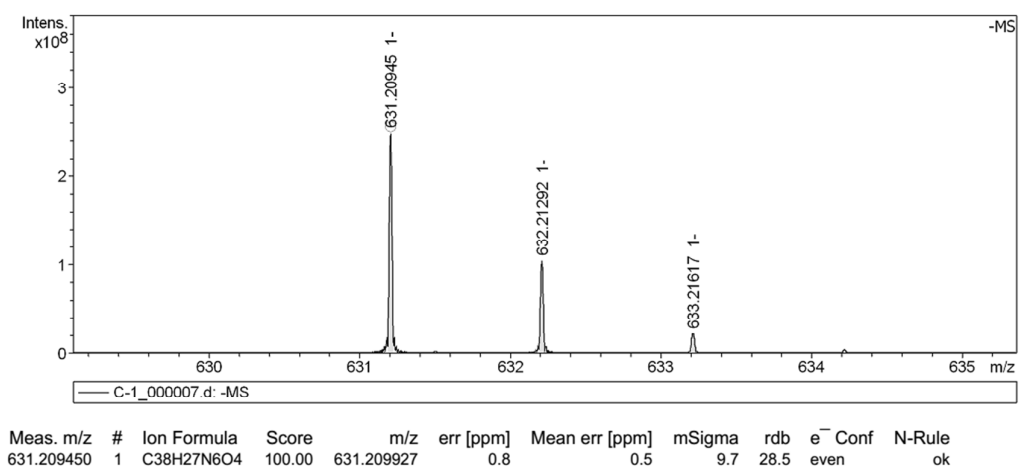


**Scheme S4** Synthesis of UiO-68-traizole-C

Azidomethyl benzene (0.1 mL, 0.714mmol) was added to a mixture of UiO-68-alkyne (20 mg) and CuI (3.0 mg) in DMF (2.0 ml). The reaction mixtures were kept at 60 °C under N<sub>2</sub> atmosphere for 24 h without stirring. The resultant octahedral crystals were collected by centrifugation, and then rinsed with DMF overnight. After that, crystals was allowed to immerse in anhydrous ethanol for 3 days to exchange and remove DMF. During this period, ethanol was freshly exchanged three times per day. Ethanol exchanged crystal samples was activated with a supercritical CO<sub>2</sub> activation protocol. UiO-68-traizole-A was obtained as pale brown solid in quantitative yield. Elemental analyses on the activated sample found [C (58.19%), H (4.67%), N (8.35%)]; This would roughly correspond to a formula of Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(C<sub>38</sub>H<sub>28</sub>N<sub>6</sub>O<sub>4</sub>)<sub>6</sub>(C<sub>3</sub>H<sub>7</sub>NO)(H<sub>2</sub>O)<sub>8</sub> (mw 4754), which gives a calculated profile as [C (58.23%), H (4.29%), N (10.88%)].

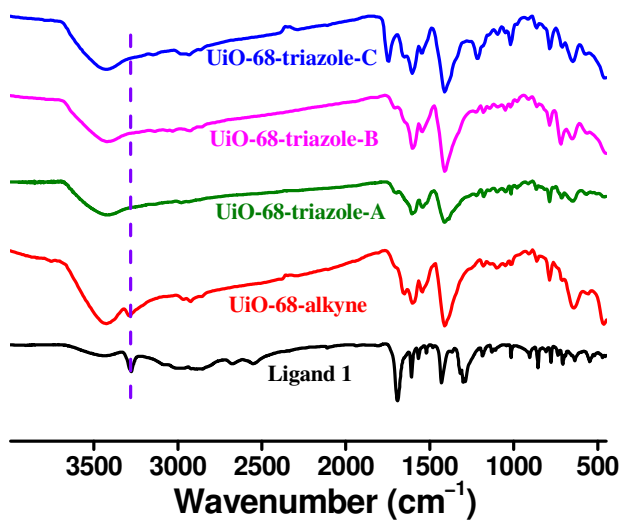


**Figure S11**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) spectrum of digested UiO-68-triazole-C. The stars mark DMF



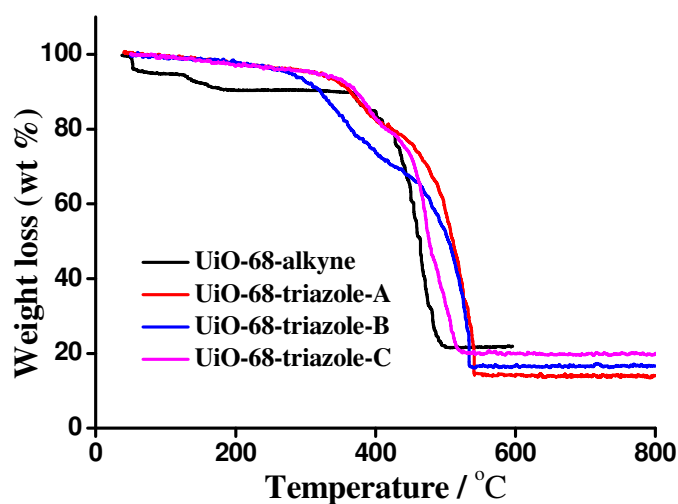
**Figure S12** High resolution mass spectrum of digested UiO-68-triazole-C

## 5. FT-IR Spectra of MOFs



**Figure S13** FT-IR spectra of ligand **1** (black), UiO-68-alkyne (red), UiO-68-triazole-A (green), UiO-68-triazole-B (pink), UiO-68-triazole-C (blue). The disappearance of characteristic peak at  $\sim 3286\text{ cm}^{-1}$  for alkyne group indicates the complete click reaction.

## 6. Thermo Gravimetric Analyzer (TGA)



**Figure S14** TGA plots of UiO-68-alkyne, UiO-68-triazole-A, UiO-68-triazole-B and UiO-68-triazole-C.

## 7. X-ray Crystallography

**Data Collection for UiO-68-alkyne:** A colorless prism crystal, having the approximate dimensions of  $0.08 \times 0.06 \times 0.05$  mm, was mounted using oil on a glass fiber. All measurements were made at the Beijing Synchrotron Radiation Facility, beam line station 3W1A equipped with a MarCCD-165 detector (the monochrome X-ray source is produced by an accelerator and selected by a double crystal monochromator,  $\lambda = 0.8000 \text{ \AA}$ ). Scattering factors for the wavelength of  $0.800 \text{ \AA}$  for use in Shelxl-2014 were calculated for all elements using the program XDISP<sup>S5</sup> and were implemented in Shelxl-2014 using DISP commands. Structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  using Shelxl-2014<sup>S6</sup>. In the initial model for both structures, only the Zr clusters and the carboxylate groups had been resolved. Due to the very low and diffuse residual electron densities, it was very difficult to identify the center benzene ring and alkynyl group of the ligand. C atoms were approximately located and restrained by AFIX instructions to maintain their expected geometries. The alkynyl groups were statistically disordered over two sites. The center benzene rings are very flexible, but are clearly resolved in the final single crystal structure, with the benzene rings turned by about 90 degrees with respect to the rings of the adjacent benzoate units to avoid interaction between alkynyl groups and benzene C-H units. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final refinement cycles. An enhanced rigid bond restraint was applied for all ligand atoms (RIGU 0.001). The C atom in the center benzene ring and alkynyl group was restrained to be approximately isotropic. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to  $1.2 \times U_{eq}$  of the attached atom. The content of the voids is partially recognizable as highly disordered solvent molecules. Attempts to include solvent molecules in the structural model yielded less than satisfactory results. The data were thus instead corrected for the contribution of the solvate molecules to the electron density using back Fourier transform methods as implemented in the Squeeze

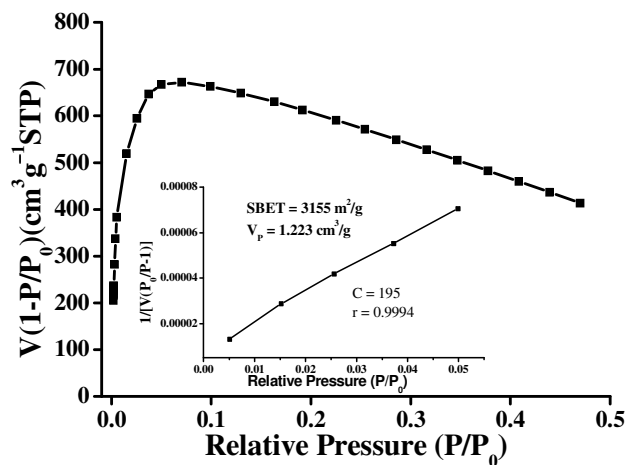
algorithm of the Platon program package. Crystal data and a structure determination summary for UiO-68-alkyne are listed in Table S1.

**Table S1** Crystal data and structure refinement for UiO-68-alkyne

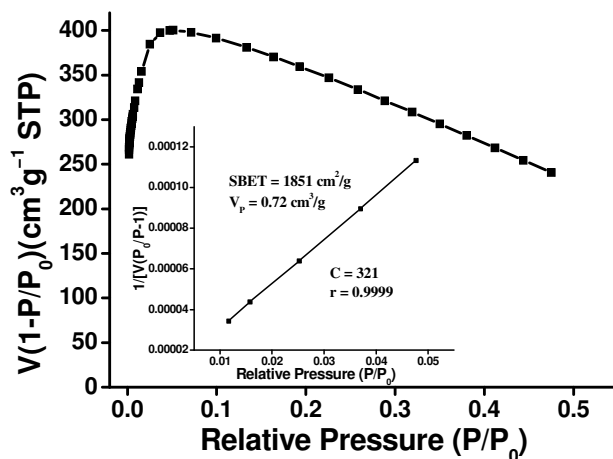
Identification code	UiO-68-alkyne
CCDC No.	1042778
Empirical formula	C <sub>72</sub> H <sub>38</sub> O <sub>16</sub> Zr <sub>3</sub>
Formula weight	1432.68
Temperature	100(2) K
Wavelength	0.800 Å
Crystal system	Cubic
Space group	F m -3 m
Unit cell dimensions	a = 32.7304(6) Å
Volume	35063.4(19) Å <sup>3</sup>
Z	8
Density (calculated)	0.543 Mg/m <sup>3</sup>
Absorption coefficient	0.257 mm <sup>-1</sup>
F(000)	5744
Crystal size	0.080 × 0.060 × 0.050 mm <sup>3</sup>
Theta range for data collection	3.054 to 29.535°.
Index ranges	-28 ≤ h ≤ 40, -35 ≤ k ≤ 36, -40 ≤ l ≤ 27
Reflections collected	29238
Independent reflections	1720 [R(int) = 0.0334]
Completeness to theta = 28.685°	99.3 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	1720 / 116 / 60
Goodness-of-fit on F <sup>2</sup>	1.549
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0979, wR <sub>2</sub> = 0.3164
R indices (all data)	R <sub>1</sub> = 0.1021, wR <sub>2</sub> = 0.3256
Extinction coefficient	0.0009(3)
Largest diff. peak and hole	1.776 and -1.079 e.Å <sup>-3</sup>

## 8. Gas Absorption

Approximately 100 mg of activated sample was used for all measurements. Total pore volumes were calculated from the uptake at a relative pressure ( $P/P_0$ ) of 0.99. The isotherm points chosen to calculate the BET surface area were subject to the three consistency criteria detailed by Walton and Snurr.

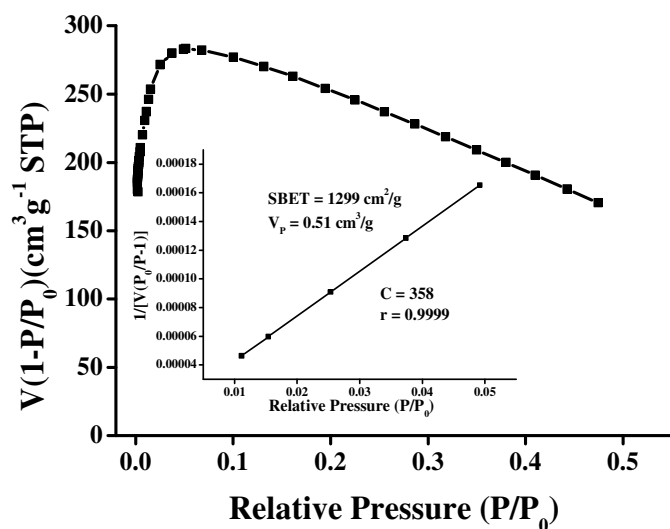


**Figure S15**  $V(P_0-P)$  vs.  $P/P_0$  for UiO-68-alkyne. Only the range below  $P/P_0 = 0.071$  satisfies the first consistency criterion for applying the BET theory. Inset: Plot of the linear region for the BET equation.

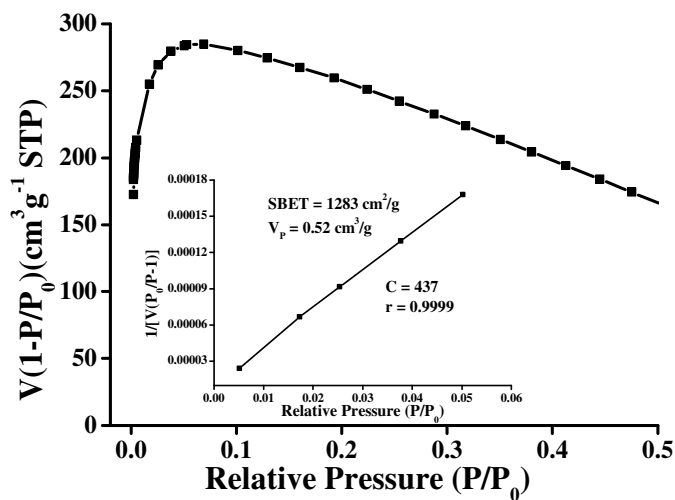


**Figure S16**  $V(P_0-P)$  vs.  $P/P_0$  for UiO-68-triazole-A. Only the range below  $P/P_0 = 0.051$  satisfies the first consistency criterion for applying the BET theory. Inset: Plot of the linear region for the BET equation.

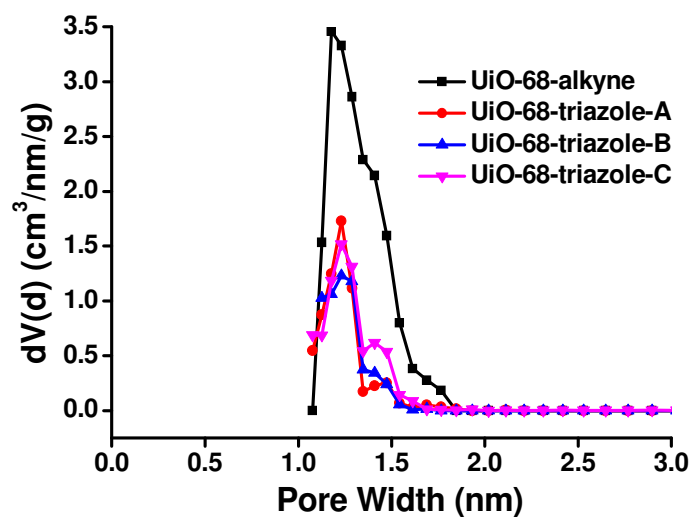




**Figure S17**  $V(P_0-P)$  vs.  $P/P_0$  for UiO-68-triazole-B. Only the range below  $P/P_0 = 0.051$  satisfies the first consistency criterion for applying the BET theory. Inset: Plot of the linear region for the BET equation.



**Figure S18**  $V(P_0-P)$  vs.  $P/P_0$  for UiO-68-triazole-C. Only the range below  $P/P_0 = 0.052$  satisfies the first consistency criterion for applying the BET theory. Inset: Plot of the linear region for the BET equation.



**Figure S19** The pore size distribution of UiO-68-alkyne before and after ‘click’ reaction

## 9. References

- S1 Tovar, J. D.; Swager, T. M., *J. Organomet. Chem.* **2002**, 653, 215–222.
- S2 Bhattacharya, S.; Biswas, J., *Langmuir* **2011**, 27, 1581–1591.
- S3 Zhang, F.; Zhao, Y.; Sun, L.; Ding, L.; Gu, Y.; Gong, P., *Eur. J. Med. Chem.* **2011**, 46, 3149–3157.
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- S6 Sheldrick, G. M., *Acta Cryst. A* **2008**, 64, 112–122.