Electronic Supplementary Information for

A urea decorated (3,24)-connected *rht*-type metal-organic framework exhibiting high gas uptake capability and catalytic activity

Xiao-Jun Wang,*[a] Jian Li,[a] Qiu-Yan Li,[a] Pei-Zhou Li,[b] Han Lu,[a] Qianying Lao,[a] Rui Ni,[a] Yanhui Shi,[a] and Yanli Zhao*[b]

[a]*Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, School of Chemistry and Chemical Engineering, Jiangsu Normal University, Xuzhou 221116, P. R. China.*

E-mail: xjwang@jsnu.edu.cn

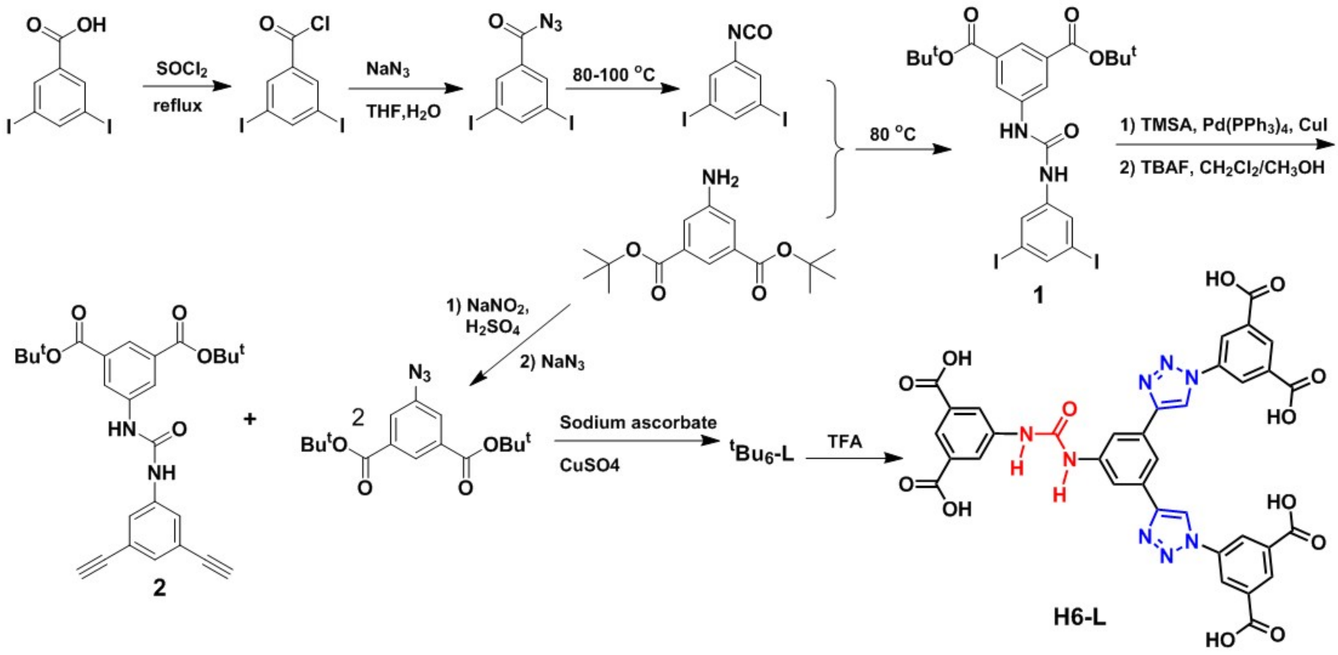
[b]*Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore.*

E-mail: zhaoyanli@ntu.edu.sg

General method and materials

Unless specifically mentioned, all chemicals are commercially available and were used as received. IR-spectra were recorded as KBr-pellet on a Perkin-Elmer 1760X FT-IR spectrometer. NMR spectra were taken on a Bruker AV 300 or Bruker AV400 and AV 500 at room temperature. EI mass spectra were obtained in a positive ion mode on a Waters GCT Premier. MALDI-TOF-MS were taken on Bruker Daltonics Microflex spectrometer. High Resolution Mass Spectra experiments were carried out on a Waters Q-tof Premier MS. Elemental analyses (C, H, and N) were obtained from EuroVector Euro EA Elemental Analyzer. Thermogravimetric analysis (TGA) was carried out on a TGA-Q500 thermoanalyzer with a heating rate of 10 °C/min under nitrogen atmosphere. The powder X-ray diffraction (PXRD) measurements were taken on a Bruker D8 diffractometer using Cu-K_α radiation (λ = 1.5418 Å) at room temperature. The metal ion concentrations were analyzed by using Thermo Fischer iCAP 6000 inductively coupled plasma optical emission (ICP-OES) spectrometer.

Synthesis and Characterization



Scheme S1. The synthetic route for organic linker **H6-L**.

3,5-Diiodophenyl isocyanate. The compound 3,5-diiodobenzoic acid (1.0 g, 2.67 mmol) was dissolved into $SOCl_2$ (10 mL), which was refluxed for 5 h at 100 °C. Then, the solution was evaporated to dryness to get 3,5-diiodobenzoyl chloride, which was added into dry THF (20 mL). The solution was added dropwise into a solution of NaN_3 (0.52 g, 8.0 mmol) in water (40 mL) while cooling with an ice bath. The white precipitates appeared in a while, which was stirred in suspension for 2 h. Then, the reaction mixture was extracted twice with toluene (40 mL x 2). The combined organic layers were washed by saturated $NaHCO_3$ (80 mL x 1) and NaCl (80 mL x 1) solution and dried with anhydrous Na_2SO_4. After filtration the solution of 3,5-diiodobenzoyl azide in toluene was concentrated by evaporating until a volume of around 20 mL was reached. Next, the concentrated solution of 3,5-diiodobenzoyl azide in toluene was gradually heated from 80 to 120 °C and stirred for 2 h, at which point no N_2 evolved anymore, indicating the formation of 3,5-diiodophenyl isocyanate. Subsequently, the solution of 3,5-diiodophenyl isocyanate in toluene was cooled to 80 °C and used as such for next reaction without purification and characterizations. Also, the intermediate compounds including 3,5-diiodobenzoyl chloride and 3,5-diiodobenzoyl azide were not purified and characterized.

Di-*tert*-butyl 5-(3-(3,5-diiodophenyl)ureido)isophthalate (1). Di-*tert*-butyl 5-aminoisophthalate[S1] (0.78 g, 2.65 mmol) in dry THF (30 mL) was added into the above solution of 3,5-diiodophenyl isocyanate in toluene at 80 °C, and stirred overnight. Then, the reaction mixture was cooled at room temperature and evaporated in vacuo to dryness. The crude product was purified by silica gel flash column chromatography (CH_2Cl_2/EtOAc, 100/3) to give **1** as a white solid (1.38 g, 2.08 mmol, yield: 78%). ^1H NMR (400 MHz, $CDCl_3$): ^1H NMR (400 MHz, DMSO) δ 9.31 (s, 1H), 8.93 (s, 1H), 8.22 (d, J = 1.4 Hz, 2H), 8.02 (s, 1H), 7.88 (d, J = 1.3 Hz, 2H), 7.68 (s, 1H), 1.56 (s, 18H). ^{13}C NMR (101 MHz, DMSO) δ 164.02, 152.13, 141.94, 140.02, 137.53, 132.11, 125.99, 123.02, 122.77, 95.76, 81.33, 27.69. MALDI-TOF-MS: *m/z* calcd for $C_{23}H_{26}I_2N_2O_5$: 664.3; found: 686.7 $[M+Na]^+$.

Di-*tert*-butyl 5-(3-(3,5-diethynylphenyl)ureido)isophthalate (2). Compound **1** (1.22 g, 1.84 mmol), CuI (20 mg) and $Pd(PPh_3)_4$ (50 mg) were added into the solution of newly-distilled THF (50 mL) and TEA (20 mL) under Argon. Then, trimethylsilylethyne (7.27 g, 7.40 mmol) was injected into the above mixture through a syringe. The reaction mixture was heated to 50 °C and stirred for 2 days under Ar. Upon the completion of the reaction monitored by TLC, the solution was evaporated in vacuo to dryness. The crude product was purified by silica gel flash column chromatography

(CH_2Cl_2/EtOAc, 100/2) to give the compound di-*tert*-butyl 5-(3-(3,5-bis((trimethylsilyl)ethynyl)phenyl)ureido)isophthalate, which was uncharacterized and used as such. Then, the obtained compound was dissolved into the mixture of CH_2Cl_2 (20 mL) and CH_3OH (20 mL) at room temperature. The excess *tetra*-n-butylammonium fluoride (2.40 g, 9.20 mmol) was added into the above solution, which was stirred at room temperature for 6 h. Then, the reaction mixture was poured into water (100 mL) and extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layer was washed by brine (100 mL x 3), dried over anhydrous Na_2SO_4 for 1 h and evaporated in vacuo to dryness. The crude product was purified by silica gel flash column chromatography (CH_2Cl_2/EtOAc, 100/2) to give the compound **2** as white solid (0.70 g, 1.52 mmol, over-all yield: 83%). ^{1}H NMR (400 MHz, DMSO) δ 9.32 (s, 1H), 8.95 (s, 1H), 8.23 (d, *J* = 1.5 Hz, 2H), 8.02 (t, *J* = 1.5 Hz, 1H), 7.62 (d, *J* = 1.3 Hz, 2H), 7.18 (t, *J* = 1.3 Hz, 1H), 4.27 (s, 2H), 1.56 (s, 18H). ^{13}C NMR (101 MHz, DMSO) δ 164.05, 152.37, 140.12, 140.05, 132.13, 128.11, 122.97, 122.66, 121.82, 82.40, 81.29, 81.24, 27.69. EI-MS: *m/z* calcd for $C_{27}H_{28}N_2O_5$: 460.5; found: 460.2 $[M]^+$.

tetra-*tert*-butyl 5,5'-(4,4'-(5-(3-(3,5-bis(tert-butoxycarbonyl)phenyl)ureido)-1,3-phenylene)bis(1*H*-1,2,3-triazole-4,1-diyl))diisophthalate (^{t}Bu$_6$-L). To a solution of THF/H_2O (80 mL / 20 mL) was added compound **2** (0.56 g, 1.22 mmol) and di-*tert*-butyl 5-azidoisophthalate[S2] (1.02 g, 3.20 mmol) at room temperature. Then, the mixture solution was degassed by Ar for 2 h. Subsequently, $CuSO_4$ (57 mg, 0.36 mmol) and sodium ascorbate (71 mg, 0.36 mmol) were added into the mixture, which was stirred at 60 °C under Ar for 3 days. Then, the reaction mixture was poured into ice water and extracted by CH_2Cl_2 (80 mL x 2). The combined organic layer was washed by brine (100 mL x 2), dried over Na_2SO_4, and evaporated in vacuo to dryness. The crude product was purified by silica gel flash column chromatography (CH_2Cl_2/EtOAc, 100/5) to give **^{t}Bu$_6$-L** as a white solid (0.98 g, 0.89 mmol, yield: 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (t, *J* = 1.5 Hz, 2H), 8.52 (d, *J* = 1.5 Hz, 4H), 8.45 (s, 2H), 8.23 (t, *J* = 1.5 Hz, 1H), 8.19 – 8.16 (m, 3H), 8.14 (d, *J* = 1.2 Hz, 2H), 7.97 (s, 1H), 7.85 (s, 1H), 1.62 (s, 36H), 1.56 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.92, 163.72, 153.06, 148.19, 140.37, 139.28, 136.93, 134.19, 132.83, 131.17, 130.38, 124.82, 124.62, 124.03, 118.91, 117.94, 117.03, 82.61, 81.57, 28.20. ESI-TOF-HRMS: *m/z* calcd for $C_{59}H_{71}N_8{}^{16}O_{12}{}^{17}O_1$: 1100.5183, found: 1100.5178 $[M+H]^+$.

5,5'-(4,4'-(5-(3-(3,5-dicarboxyphenyl)ureido)-1,3-phenylene)bis(1*H*-1,2,3-triazole-4,1-diyl))diisophthalic acid (H6-L). To a CH_2Cl_2 solution (10 mL) of the ester **^{t}Bu$_6$-L** (0.86 g, 0.78 mmol) was added trifluoroacetic acid (TFA, 10 mL). The mixture was stirred at room temperature over 6 h, obtaining a precipitate. The suspension was filtered, washed with CH_2Cl_2 to remove excess TFA, and then dried under vacuum giving **H6-L** (0.48 g, 0.63 mmol, yield: 81%) as white solid. ^{1}H NMR (400 MHz, DMSO) δ 9.73 (s, 2H), 9.27 (s, 1H), 9.11 (s, 1H), 8.80 (d, J = 1.3 Hz, 4H), 8.55 (s, 2H), 8.37 (d, J = 1.3 Hz, 2H), 8.29 (s, 1H), 8.18 (d, J = 1.1 Hz, 2H), 8.12 (t, J = 1.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 166.65, 165.74, 152.46, 147.48, 140.66, 140.42, 137.12, 133.14, 131.73, 131.25, 129.35, 123.84, 123.38, 122.68, 120.08, 116.77, 115.25. ESI-TOF-HRMS: *m/z* calcd for $C_{35}H_{23}{}^{14}N_6{}^{15}N_2O_{13}$: 765.1325, found: 765.1421 $[M+H]^+$.

MOF **Cu-UBTA**. Ligand **H6-L** (25 mg, 0.033 mmol) and $Cu(NO_3)_2{\cdot}3H_2O$ (24 mg, 0.10 mmol) were dissolved in *N,N*-dimethylformamide (DMF, 12 mL). Then, 12 drops of HNO_3 were added into the mixture. The solution was placed in a tightly capped 20 mL vial and heated in an oven at 75°C for 3 days. The blue-green block crystals were collected after cooling to room temperature. Then, these crystals were washed by fresh DMF for several times, and dried in the air (14 mg, yield: 56%). Elemental analysis calcd (%) for $Cu_3(\mathbf{L})(H_2O)_3{\cdot}10DMF{\cdot}9H_2O$: C 41.61, H 4.94, N 13.44; found: C 39.66, H 5.23, N 12.95. Selected IR (KBr) (cm^{-1}): 1660 (*s*), 1572 (*m*), 1433 (*m*), 1385 (*s*), 1106 (*m*), 1062 (*m*), 776 (*m*), 732 (*m*).

Gas sorption measurements

Low-pressure gas sorption measurements were performed by using Quantachrome Instruments Autosorb-iQ (Boynton Beach, Florida USA) with the extra-high pure gases. The as-synthesized MOF **Cu-UBTA** crystals were immersed in CH_2Cl_2 for 12 h, during which time CH_2Cl_2 was replaced three times. The samples were then moved into a sample cell and dried under vacuum at 60 °C and 120 °C by using the "outgasser" function for 12 h and 5 h before the measurements, respectively. The Brunauer−Emmett−Teller (BET) surface area and total pore volume were calculated from the N_2 sorption isotherms at 77 K by using the Quantachrome ASiQwin 2.01

software package. The isosteric heat of adsorption (Q_{st}) for H_2 and CO_2, defined as

$$Q_{st} = RT^2\left(\frac{\partial \ln p}{\partial T}\right)_q \quad \text{(Clausius-Clapeyron equation)}$$

was determined by using the H_2 and CO_2 absorption isotherms at 77 and 87 K as well as 273 and 298 K, respectively (ASiQwin 2.01).

X-Ray crystallography.

The single crystal MOF **Cu-UBTA** for X-ray analysis was picked up under a microscope from a freshly synthesized solution and then mounted immediately. The diffraction data were collected at room temperature using micro-focus graphite-monochromated Cu-$K\alpha$ radiation (λ = 1.5418 Å) on an Agilent Technologies Super Nova diffractometer. The structure was solved by the direct methods and refined by full-matrix least-squares analyses on F^2 (SHELXTL-97[S3]). In the structure, the urea group is highly disordered in three position of the ligand, therefore, it was treated as a triaozle unit for refinement. The solvent molecules in MOF are highly disordered and cannot be modeled, thus the SQUEEZE routine[S4] of PLATON was applied to remove the contributions of the solvent molecules to the scattering. Crystallographic data for **Cu-UBTA** is summarized in Table S1.

CCDC 1056256 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and structure refinement for MOF **Cu-UBTA**

Empirical formula	$C_{36}H_{18}Cu_3N_9O_{15}$	
Formula weight	1007.24	
Wavelength	1.54184 Å	
Crystal system	Tetragonal	
Space group	*I4/m*	
Unit cell dimensions	a = 31.4206(3) Å	α = 90°.
	b = 31.4206(3) Å	β = 90°.
	c = 44.8239(5) Å	γ = 90°.

Volume	44252.6(10)Å^3
Z	16
Density (calculated)	0.605 mg/m^3
Absorption coefficient	0.932 mm^{-1}
F(000)	8064
Crystal size	0.17 x 0.19 x 0.21 mm^3
Index ranges	-38<=h<=22, -38<=k<=35, -48<=l<=55
Reflections collected	72811
Independent reflections	22413 [R(int) = 0.044]
Absorption correction	Multi-scan
Max. and min. transmission	0.822 and 0.853
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.060
Final R indices [I>2sigma(I)]	R_1 = 0.0554, wR_2 = 0.1772

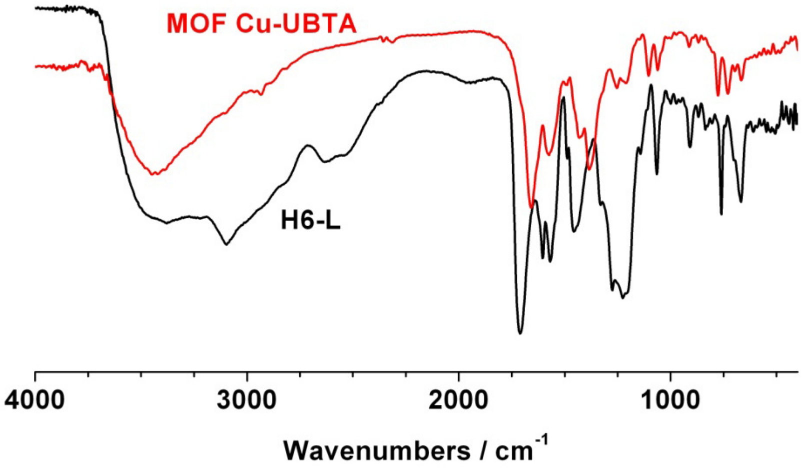
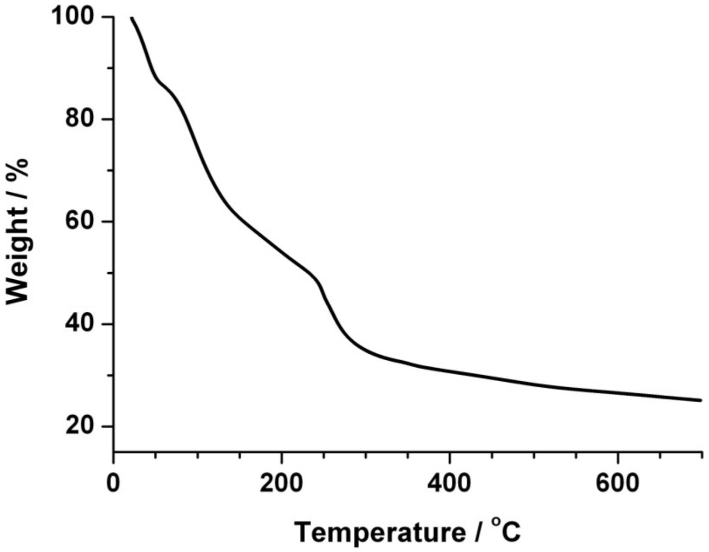


Fig. S1 FT-IR spectra of ligand **H6-L** and as-synthesized MOF **Cu-UBTA**.



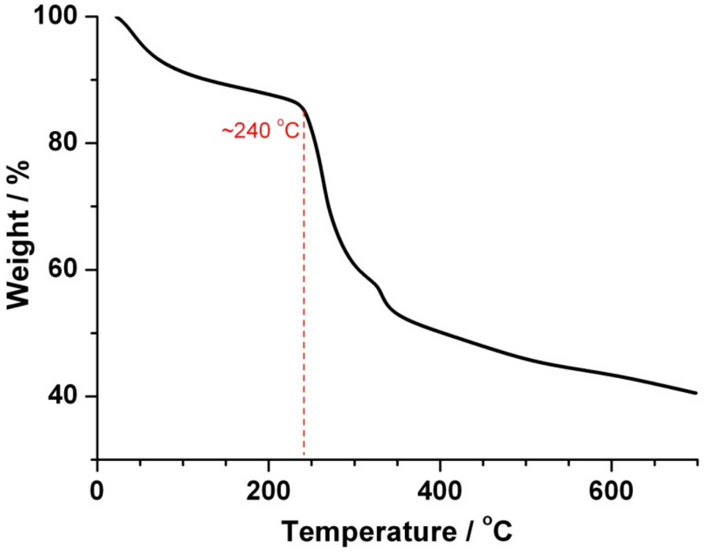


Fig. S2 TGA plot of as-synthesized (upper) and desolvated (bottom) MOF **Cu-UBTA**. The initial weight loss of activated sample can be attributed to the re-adsorbed water during sample weighing (bottom). This suggests the framework was stable up to ~240 °C, which is slightly lower than that of MOF **NTU-105** (~260 °C). The slightly lower thermal stability of MOF **Cu-UBTA** probably was caused by the flexible urea group in the framework.

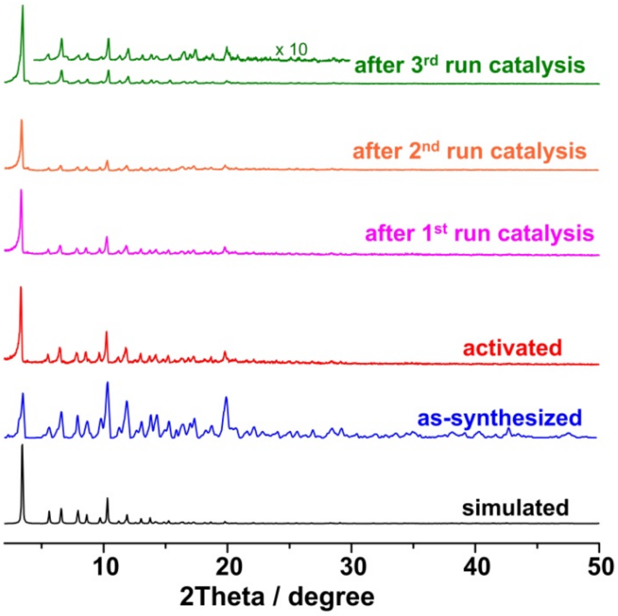


Fig. S3 Powder XRD patterns of MOF **Cu-UBTA**, indicating the framework was retained after activation and catalysis for model reaction.

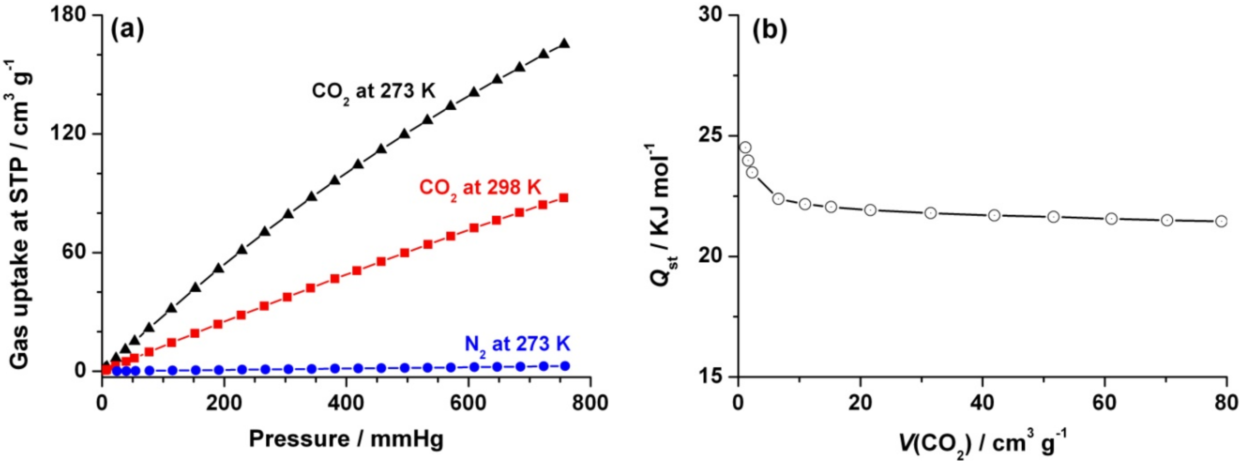


Fig. S4 CO_2 adsorption isotherms (a) and isosteric heat of CO_2 absorption (b) for activated **Cu-UBTA** calculated from the adsorption isotherms at 273 K and 298 K.

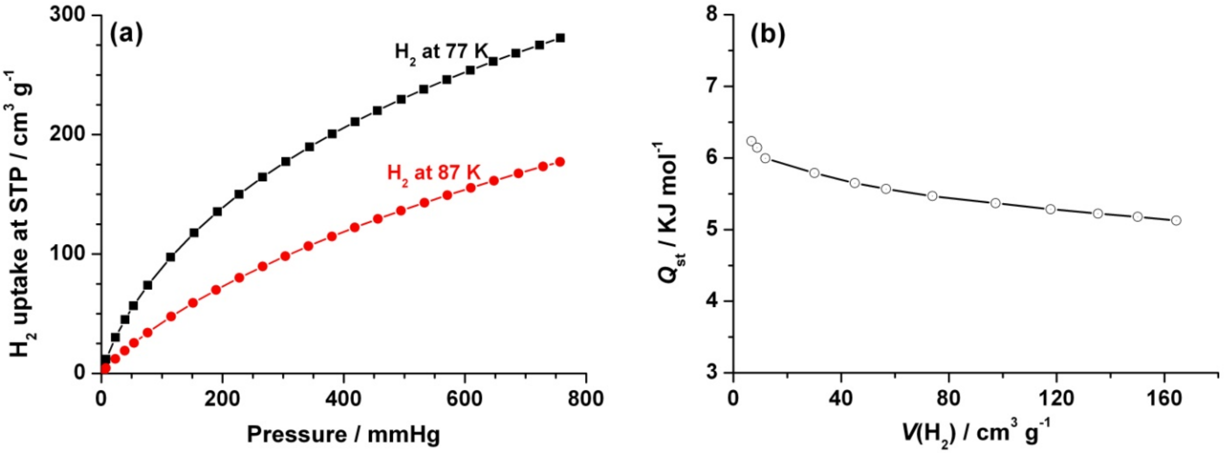
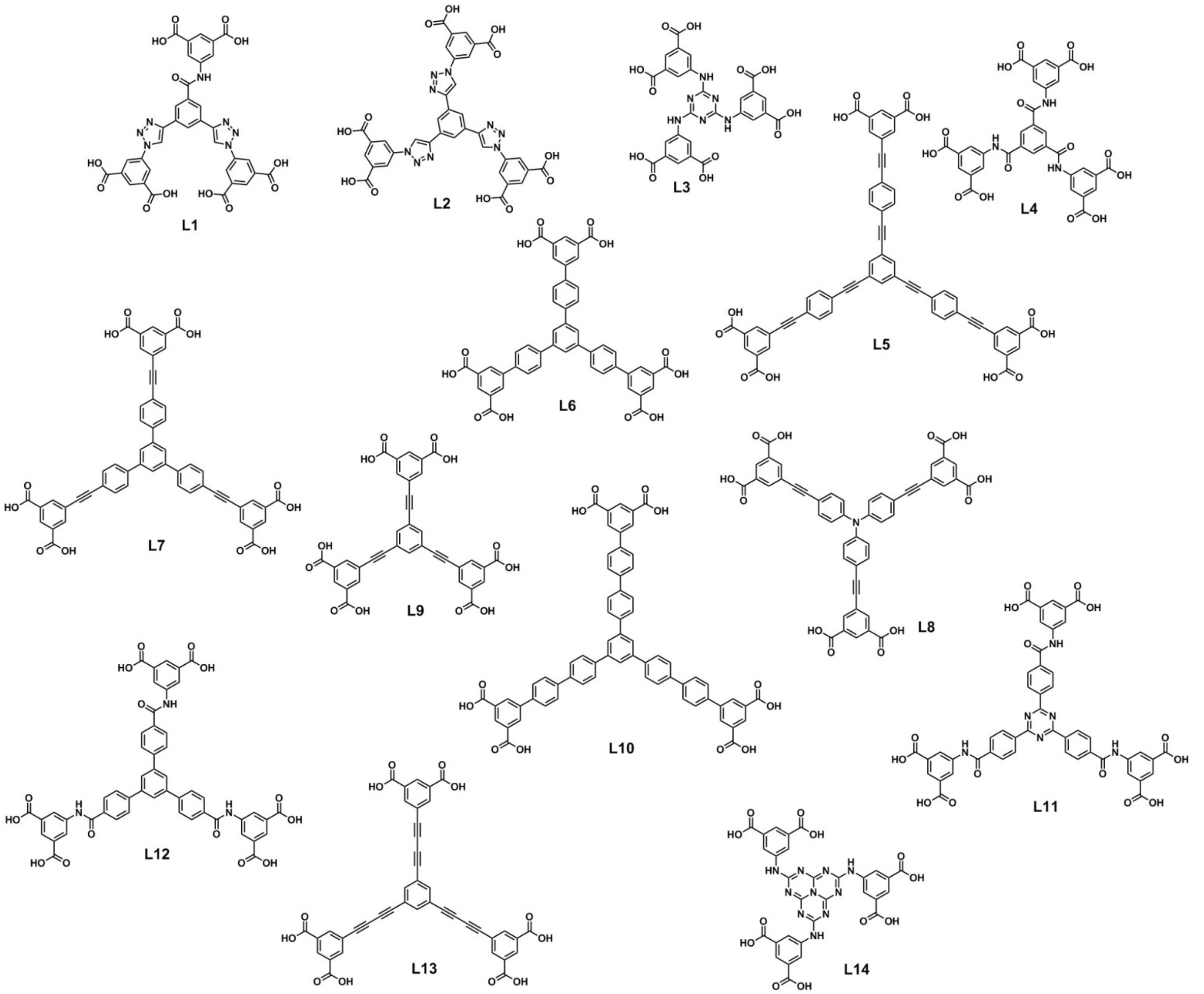


Fig. S5 H_2 adsorption isotherms (a) and isosteric heat of H_2 adsorption (b) for activated **Cu-UBTA** calculated from the adsorption isotherms at 77 K and 78 K.



Scheme S2. The chemical structure of reported hexa-carboxylate ligands used in constructing *rht*-type MOFs.

Table S2. Summary of the porosities, and gas uptake capacities of various *rth*-type MOFs.

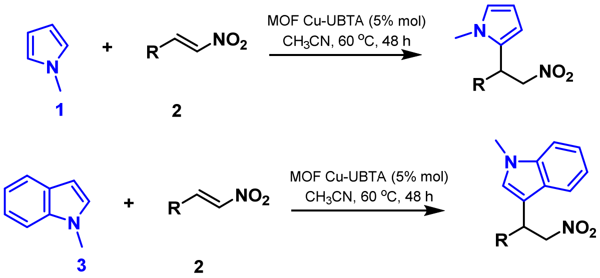
MOF [ligand]	S_{BET} [m^{2} g^{-1}][a]	V_{pore} [cm^{3} g^{-1}][a]	H_2 uptake [wt%][b]	CO_2 uptake [wt%][c]	ref.
Cu-UBTA [H6-L]	3134	1.23		32.4	This work
Cu-ABTA [L1]	2840	1.19	2.75	30.1	S5
NTU-105[d] [**L2**]	3543	1.33	2.75	36.7	S2
Cu-TDPAT[e] [**L3**]	1938	0.93	2.65	44.5	S6
Cu-TPBTM [**L4**]	3160	1.27	—	42.6	S7
NU-100[f] [**L5**]	6143	2.82	1.82	12.3[g]	S8
NOTT-112 [**L6**]	3800	1.62	2.3	—	S9
PCN-68[h][**L7**]	5109	2.13	1.87	—	S10
PCN-66 [**L8**]	4000	1.63	1.79	—	S10,S11
PCN-61 [**L9**]	3000	1.36	2.25	—	S10,S11
PCN-69[i] [**L10**]	3989	2.17	1.72	—	S12
Cu-TATB [**L11**]	3360	1.91	—	17.3	S14
Cu-BTB [**L12**]	3288	1.77	—	17.2	S13
NU-111 [**L13**]	5000	2.38	2.1	—	S14
rht-MOF-9 [**L14**]	2420[j]	1.01[j]	2.72	25.3	S15

[a]calculated from N_2 isotherms at 77 K; [b]at 77 K, 1 atm; [c]at 273 K, 1 atm; [d]also known as NOTT-122[S16] or NU-125[S17]; [e]also known as rth-MOF-7[S18]; [f]also known as PCN-610[S10]; [g]data at 298 K, 1 atm, due to the absence of the data at 273 K, 1 atm; [h]also known as NOTT-116[S19]; [i]also known as NOTT-119[S20]; [j]calculated from Ar isotherms at 87 K.

General Procedure for Catalysis

The weighed as-synthesized MOF **Cu-UBTA** crystals were exchanged with CH_3OH and CH_3CN for 2 days, respectively. During the period, fresh solvent was exchanged several times a day. To a solution of nitroalkenes (0.1 mmol) and *N*-methyl pyrrole or indole (0.2 mmol) was added 5% molar MOF catalyst in a vial. Then, the vial was placed in a vortex mixer and shook at 60 °C for 48 h. ^1H NMR spectroscopy with mesitylene as an internal standard was employed to determine the yield. The catalyst for cyclic reaction was recycled by centrifugation at 10 000 rpm and washed by fresh CH_3CN two times.

Table S3. MOF **Cu-UBTA** catalyzed Friedel-Craft reaction



Entry	R	Yield [b](%)	
		1+2	**3+2**
1	4-Me-Ph	88	76
2	4-^{t}Bu-Ph	93	63
3	4-MeO-Ph	92	76
4	4-F-Ph	91	83
5	4-Cl-Ph	91	79
6	4-CF_3-Ph	92	91
7	2-furanyl	86	47
8	2-thiophenyl	87	66

[a] Reactions were carried out with **1** or **3** (0.2 mmol), **2** (0.1 mmol) and catalyst MOF **Cu-UBTA** (5% mol) in CH_3CN.

[b] Determined using ^1H NMR.

References:

S1. J. M. Roberts, B. M. Fini, A. A. Sarjeant, O. K. Farha, J. T. Hupp and K. A. Scheidt, *J. Am. Chem. Soc.*, 2012, **134**, 3334.

S2. X.-J. Wang, P.-Z. Li, Y. Chen, Q. Zhang, H. Zhang, X. X. Chan, R. Ganguly, Y. Li, J. Jiang and Y. Zhao, *Sci. Rep.*, 2013, **3**, 1149.

S3. G. Sheldrick, *Acta Cryst.*, 2008, **64**, 112.

S4. A. Spek, *Acta Crystallogr., Sect. D*, 2009, **65**, 148.

S5. J. Li, P.-Z. Li, Q.-Y. Li, Y. Cao, H. Lu, H. Wu, F. Li, Y. Shi, X.-J. Wang and Y. Zhao, *RSC Advances*, 2014, **4**, 53975.

S6. B. Li, Z. Zhang, Y. Li, K. Yao, Y. Zhu, Z. Deng, F. Yang, X. Zhou, G. Li, H. Wu, N. Nijem, Y. J. Chabal, Z. Lai, Y. Han, Z. Shi, S. Feng and J. Li, *Angew. Chem. Int. Ed.*, 2012, **51**, 1412.

S7. B. Zheng, J. Bai, J. Duan, L. Wojtas and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2011, **133**, 748.

S9. O. K. Farha, A. Özgür Yazaydın, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr and J. T. Hupp, *Nat Chem*, 2010, **2**, 944.

S9. Y. Yan, X. Lin, S. Yang, A. J. Blake, A. Dailly, N. R. Champness, P. Hubberstey and M. Schroder, *Chem. Commun.*, 2009, 1025.

S10. D. Yuan, D. Zhao, D. Sun and H.-C. Zhou, *Angew. Chem. Int. Ed.*, 2010, **49**, 5357.

S11. D. Zhao, D. Yuan, D. Sun and H.-C. Zhou, *J. Am. Chem. Soc.*, 2009, **131**, 9186.

S12. D. Yuan, D. Zhao and H.-C. Zhou, *Inorg. Chem.*, 2011, **50**, 10528.

S13. B. Zheng, Z. Yang, J. Bai, Y. Li and S. Li, *Chem. Commun.*, 2012, **48**, 7025.

S14. O. K. Farha, C. E. Wilmer, I. Eryazici, B. G. Hauser, P. A. Parilla, K. O'Neill, A. A. Sarjeant, S. T. Nguyen, R. Q. Snurr and J. T. Hupp, *J. Am. Chem. Soc.*, 2012, **134**, 9860.

S15. R. Luebke, Ł. J. Weseliński, Y. Belmabkhout, Z. Chen, Ł. Wojtas and M. Eddaoudi, *Cryst. Growth Des.*, 2014, **14**, 414.

S16. Y. Yan, M. Suyetin, E. Bichoutskaia, A. J. Blake, D. R. Allan, S. A. Barnett and M. Schroder, *Chem. Sci.*, 2013, **4**, 1731.

S17. C. E. Wilmer, O. K. Farha, T. Yildirim, I. Eryazici, V. Krungleviciute, A. A. Sarjeant, R. Q. Snurr and J. T. Hupp, *Energy Environ. Sci.*, 2013, **6**, 1158.

S18. R. Luebke, J. F. Eubank, A. J. Cairns, Y. Belmabkhout, L. Wojtas and M. Eddaoudi, *Chem. Commun.*, 2012, **48**, 1455.

S19. Y. Yan, I. Telepeni, S. Yang, X. Lin, W. Kockelmann, A. Dailly, A. J. Blake, W. Lewis, G. S. Walker, D. R. Allan, S. A. Barnett, N. R. Champness and M. Schröder, *J. Am. Chem. Soc.*, 2010, **132**, 4092.

S20. Y. Yan, S. Yang, A. J. Blake, W. Lewis, E. Poirier, S. A. Barnett, N. R. Champness and M. Schroder, *Chem. Commun.*, 2011, **47**, 9995.