## **Electronic Supplementary Information**

## Porous NbO-type metal-organic framework with inserted acylamide groups exhibiting highly selective CO<sub>2</sub> capture

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## **Experimental Details**

All reagents were obtained from commercial vendors and, unless otherwise noted, were used without further purification. The organic linker Bis(3,5-dicarboxyphenyl)terephthalamide<sup>[1]</sup> (H<sub>4</sub>BDPT) was prepared according the literatures and characterized by IR and <sup>1</sup>H NMR. Data for H<sub>4</sub>BDPT: Selected IR (KBr, cm<sup>-1</sup>): 3383 (br,s), 1719 (s), 1677 (m), 1554 (s), 1510 (m), 1406 (m), 1337 (m), 1255 (m), 1201 (m), 758 (m), 665 (m). <sup>1</sup>H NMR (DMSO- $d_6$ ,  $\delta$  ppm): 13.363 (broad peak, COO<u>H</u>), 10.972 (s, 3H, CON<u>H</u>), 8.855 (s, 3H, Ar<u>H</u>), 8.745 (s, 6H, Ar<u>H</u>), 8.269 (s, 3H, Ar<u>H</u>); MP: > 300 °C.

 $[Cu_2(BDPT^{4-})(H_2O)_2]$ ·xG (G=guest molecule), HNUST-1. H<sub>4</sub>BDPT (12.3 mg, 0.025 mmol) and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (24 mg, 0.1mmol) in 2 mL DMF/ethanol/water (5:3:1) with 2 mL 2.7 M HNO<sub>3</sub> (in DMF) were stirred for a few minutes in air and the clear solution was transferred into a autoclave Teflon-line stainless vessel (20 mL). The vessel was sealed and heated to 65 °C for 2 days and then cooled to room temperature at a rate 5 °C/hour. Pale blue block crystals of HNUST-1 were filtered and washed with DMF. Yield 12.5 mg, (~ 77 % based on the ligand). Selected IR (cm<sup>-1</sup>): 3412 (br, s), 1654 (vs), 1570 (s), 1419 (m), 1371 (vs), 1239 (m), 1101 (m), 914 (w), 837(m), 773 (m), 727 (m), 661 (m), 544 (m).

**Sample activation.** The solvent-exchanged sample was prepared by immersing the as-synthesized samples in anhydrous acetone for 3 days to remove the nonvolatile solvates, 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 100 °C under a dynamic high vacuum for 24 hours. During this time, the pale blue sample changed to a deep purple-blue color indicative of the presence of unsaturated metal Cu<sup>II</sup> sites (Figure S1). The similar color change upon activation was observed for other frameworks that constructed from copper paddlewheel clusters<sup>[2]</sup>. The completely-activated samples were moisture sensitive and a few minutes of exposure to air could change the sample's color back to pale blue. Anal. Calcd. for activated HNUST-1 (C<sub>24</sub>H<sub>12</sub>Cu<sub>2</sub>N<sub>2</sub>O<sub>12</sub>, Mw = 647.45 g·mol<sup>-1</sup>): C 44.52, H 1.87, N 4.33; found: C 44.41, H 1.98, N 4.71. Selected IR (KBr, cm<sup>-1</sup>): 3415 (br, s), 1660 (vs), 1620 (m) 1571 (s), 1421 (m), 1373 (vs), 1239 (m), 1102 (m), 914 (w), 837(m), 773 (m), 727 (m), 661 (m), 544 (m).

**X-ray Crystallography.** Single-crystal X-ray diffraction data were measured on a Bruker Smart Apex CCD diffractometer at 298 K using graphite monochromated Mo/K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Crystals were sealed in capillaries containing a small amount of mother liquor to prevent desolvation during data collection. Data reduction was made with the Bruker SAINT program. The structures were solved by direct methods and refined with full-matrix least squares technique using the SHELXTL

package<sup>[3]</sup>. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to  $1.2 \times U_{eq}$  of the attached atom. The hydrogen atoms of the ligated water molecules could not be located, but are included in the formula. The unit cell includes a large region of disordered solvent molecules, which could not be modelled as discrete atomic sites. We employed PLATON/SQUEEZE<sup>[4]</sup> to calculate the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities; structures were then refined again using the data generated.

In the structure, the middle benzene ring moiety and acylamdie groups in the ligand is highly disordered over several positions. CCDC 881431 contains the supplementary crystallographic data for HNUST-1. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK.

Low pressure gas sorption measurements. Low-pressure gases (N<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>) sorption isotherms (up to 1 bar) were performed on Micromeritics ASAP 2020 M+C surface area and pore size analyzer. Before gases sorption measurements, about 150 mg samples were activated by using the "outgas" function of the surface area analyzer. For all isotherms, warm and cold free space correction measurements were performed using ultra-high purity He gas (UHP grade 5.0, 99.999% purity). 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. The pore size distribution (PSD) was obtained from the DFT model in the Micromeritics ASAP2020 software package (assuming cylinder pore geometry) based on the N<sub>2</sub> sorption isotherm.

High pressure gravimetric gas sorption measurements. High pressure excess adsorption of  $H_2$ ,  $CH_4$ ,  $CO_2$  and  $N_2$  were measured using an IGA-003 gravimetric adsorption instrument (Hiden-Isochema, UK) over a pressure range of 0-20 bar at 77 K (liquid nitrogen bath) or 273 K and 298 K after an activation procedure same to that in low-pressure volumetric gas adsorption measurement. Before measurements, about 150 mg acetone-exchanged samples were degassed at 100 °C for 24 h under a dynamic high vacuum to obtain about 75 mg fully desolvated samples. During the gases sorption measurements, the sample mass was monitored until equilibrium was reached (within 15 minutes) at each pressure. The total amount of gases stored in the adsorbent was calculated as previously described<sup>[5]</sup>.

Estimation of the isosteric heats of gas adsorption. A virial-type<sup>[6]</sup> expression comprising the temperature-independent parameters  $a_i$  and  $b_j$  was employed to calculate the enthalpies of adsorption for CO<sub>2</sub> and CH<sub>4</sub> (at 273 and 298 K) on HNUST-1. In each case, the data were fitted using the equation:

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{j=0}^{n} b_j N^j \qquad (3)$$

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  $b_j$  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 heat of adsorption using the following expression.

$$Q_{st} = -R \sum_{i=0}^{m} a_i N^i \qquad (4)$$

 $Q_{st}$  is the coverage-dependent isosteric heat of adsorption and *R* is the universal gas constant. The heat of CO<sub>2</sub> and CH<sub>4</sub> sorption for HNUST-1 in the manuscript is determined by using the excess sorption data measured in the pressure range from 0-20 bar (273 and 298 K), which is fitted by the virial-equation very well (R<sup>2</sup>>0.9999, see Figure S8).

Other Physical Measurements. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240 analyzer. The IR spectra were obtained on a VECTOR TM 22 spectrometer with KBr pellets in the 4000~400 cm<sup>-1</sup> region. <sup>1</sup>H NMR spectra were recorded on a Bruker DRX-500 spectrometer with tetramethylsilane as an internal reference. Thermal gravimetric analyses (TGA) were performed under N<sub>2</sub> atmosphere (100 ml/min) with a heating rate of 5 °C/min using a 2960 SDT thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were collected over the 20 range 5 ~ 30° on a Bruker axs D8 Advance diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) with a routine power of 1600 W (40 kV, 40 mA) in a scan speed of 0.2 s/deg at room temperature.



*Figure S1.* Upper: Structure of the ligand H<sub>4</sub>BDPT and a photograph of the single crystals of HNUST-1. Down: Visual observation of color change in HNUST-1 upon activation. Acetone-exchanged HNUST-1 (A) and activated HNUST-1 (B).



*Figure S2.* The PXRD patterns of HNUST-1. A simulated PXRD pattern from the single-crystal structure; as-synthesized, and activated samples, respectively.



Figure S3. TGA-DSC data of as-synthesized HNUST-1.



*Figure S4.* The  $N_2$  sorption isotherm at 77 K for activated HNUST-1, filled and open symbols represent adsorption and desorption, respectively. Inset: pore size distributions calculated from the  $N_2$  sorption isotherm.



*Figure S5.* The infrared spectra for HNUST-1. (a) ligand, (b) as-synthesized, (c) acetone-exchanged and (d) activated MOF materials. Note the absence of the vibration frequencies of the solvent DMF and acetone molecules in activated samples. The frequencies at 1663 cm<sup>-1</sup> in (b) and 1706 cm<sup>-1</sup> in (c) attribute to the v (CO) vibration of the DMF and acetone, respectively. The presence of the v (OH) stretching frequencies at 1620 cm<sup>-1</sup> in both (c) and (d) may result from the rapid re-adsorption of trace moisture during the IR measurements.



*Figure S6.* The BET plots for HNUST-1 in the chosen range ( $P/P_0 = 0.001 - 0.03$ ). This range was chosen according to two major criteria established in literatures<sup>[7]</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 S7.* The fitting initial slope for  $CO_2$ ,  $CH_4$  and  $N_2$  isotherms for HNUST-1 collected at 273 K ( $N_{ads}$  = gases uptake; R = related coefficient). The calculated selectivity of  $CO_2/CH_4$  and  $CO_2/N_2$  is 7.2 and 39.8, respectively.



*Figure S8.* Details of virial equation (solid lines) fitting to the experimental  $CO_2$  a) and CH4 b) adsorption data (symbols) for HNUST-1 collected at 273 K (blue symbols) and 298 K (red symbols).



*Figure S9.* Gases sorption properties at 298 K of HNUST-1. a) low-pressure volumetric total  $CO_2$ ,  $CH_4$  and  $N_2$  isotherms; b) High-pressure gravimetric excess  $CO_2$ ,  $CH_4$  and  $N_2$  isotherms. Filled and open symbols represent adsorption and desorption, respectively.

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