Electronic Supplementary Information

"Click"-Extended Nitrogen-Rich Metal-Organic Frameworks and Their High Performance on CO₂-Selective Capture

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General information

All the reagents and solvents employed were commercially available and used without further purification unless specifically mentioned: copper (II) nitrate hemi(pentahydrate) (Cu(NO₃)₂·2.5H₂O, 98%, Alfa Aesar), copper (II) sulphate pentahydrate (CuSO₄·5H₂O, 99%, Alfa Aesar), *N*,*N*-dimethylacetamide (DMA, \geq 99%, Sigma-Aldrich), dimethyl 5-aminoisophthalate (98%, Sigma-Aldrich), dimethyl 5-ethynylisophthalate (97%, Sigma-Aldrich), *N*,*N*-dimethylformamide (DMF, 99.8%, Sigma-Aldrich), 1,4-diethynylbenzene (96%, Sigma-Aldrich), 1,3-diethynylbenzene (97%, Sigma-Aldrich), hydrochloric acid (HCl, 37w%, MSR), sodium nitrite (NaNO₂, \geq 97%, Sigma-Aldrich), sodium azide (NaN₃, \geq 99.5%, Sigma-Aldrich), and sodium *L*-ascorbate (\geq 98%, Sigma-Aldrich).

¹H NMR measurements were conducted on Bruker AV 300 NMR Spectrometer, JEOL ECA400 NMR spectrometer, and JEOL ECA400 SL NMR spectrometer at ambient temperature. All ¹H NMR spectra were reported as chemical shift δ in units of parts per million (ppm) downfield with reference to deuteratred solvent (2.50 ppm for DMSO-*d*₆, 7.26 ppm for CDCl₃) or TMS (0.00ppm). Multiplicities were presented as: s (singlet); d (doublet); t (triplet); and m (multiplet). Coupling constants *J* values were expressed in Hz and the number of protons was expressed as *n*H. ¹³C NMR spectra were obtained from a JEOL ECA400 SL NMR spectrometer at ambient temperature. Spectra were reported as chemical shift δ in units of parts per million (ppm) downfield with reference to deuteratred solvent (DMSO-*d*₆ relative to 39.81 ppm or CDCl₃-*d*₁ relative to 77.16 ppm). High resolution mass spectrometry analysis (HR-MS) was performed on a Waters LCT Classic TOF Mass Spectrometer. FT-IR spectra were recorded as KBr pellets on a SHIMADZU IRPrestige-21 spectrometer.

Single Crystal X-ray diffraction measurements were performed on a SuperNova X-ray Diffraction System from Agilent Technologies. Powder X-ray diffraction (PXRD) data were collected at 40keV, 30 mA on a SHIMADZU XRD-6000 Labx diffractometer using Cu-K α radiation ($\lambda = 1.5418$ Å) over 2θ range of 2.5° - 40° at room temperature. Thermogravimetric analyses (TGA) were carried out on a TGA-Q500 thermoanalyzer with a heating rate of 10 °C min⁻¹ under N₂ flow (60 mL/min) from room temperature to 700 °C. Gas sorption analyses were conducted using Quantachrome Instruments Autosorb-iQ (Boynton Beach, Florida USA) with extra-high pure gases.

Experimental section



Scheme S1. Synthetic routes for the preparation of ligand H_4L1 .

Synthesis of tetramethyl 5,5'-(1*H*-1,2,3-triazole-1,4-diyl)diisophthalate (Me₄L1). Me₄L1 was synthesized in accordance to the method reported by Sharpless et. al. with slight modifications.^{S1-S3} Starting materials, dimethyl 5-ethynylisophthalate (0.24 g, 1.10 mmol) and dimethyl 5-azidoisophthalate (1, 0.26 g, 1.10 mmol), were added into a

mixture solution of THF/H₂O (50 mL/20 mL), and then CuSO₄·5H₂O (0.0125 g, 0.05 mmol) and excess sodium *L*-ascorbate (0.1 g, 0.41 mmol) were added. The solution was stirred at room temperature under N₂ for 3 days. Then, the mixture was poured into water (50 mL) and extracted with CH₂Cl₂ (100 mL × 2). The combined organic layer was dried over Na₂SO₄ and the solvent was evaporated under vacuum. The crude product was purified by silica gel flash column chromatography (CH₂Cl₂/CH₃OH, 100/1) to give **Me₄L1** as a white solid (0.46 g, 1.01 mmol, yield: 87%). ¹H NMR (300 MHz, CDCl₃- *d*₁) δ 8.79-8.78 (m, 3H), 8.70-8.69 (m, 3H), 8.49 (s, 1H), 4.03 (s, 6H), 4.00 (s, 6H). ¹³C NMR (100 MHz, CDCl₃- *d*₁) δ 166.0, 165.0, 147.3, 137.3, 132.7, 131.6, 130.9, 130.8, 130.6, 125.1, 118.5, 53.1, 52.7. ESI-TOF-HRMS: *m/z* calcd for C₂₂H₁₉N₃O₈: 454.1250, found: 454.1252 [M+H]⁺.

Synthesis of 5,5'-(1*H*-1,2,3-triazole-1,4-diyl)diisophthalic acid (H₄L1). The ester Me₄L1 (0.56 g, 1.24 mmol) was hydrolyzed with excess NaOH (0.85 g, 21.3 mmol) in a mixture solution of THF/H₂O (60 mL/30 mL) at room temperature overnight. Then, H₂O (50 mL) was added into the above solution, which was washed by Et₂O (100 mL × 2). The aqueous layer was acidified with HCl to pH 1. The solid was collected by filtration, rinsed several times with distilled water, and dried to give H₄L1 (0.48 g, 1.21 mmol, yield: 98%). ¹H NMR (300 MHz, DMSO-*d*₆) δ 13.59 (br, 4H), 9.96 (s, 1H), 8.77 (dd, *J* = 4.8, 1.4 Hz, 4H), 8.54 (t, *J* = 1.4 Hz, 1H), 8.47 (t, *J* = 1.5 Hz, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 166.4, 165.7, 146.1, 137.1, 133.3, 132.2, 131.1, 130.0, 129.5, 129.4, 123.8, 121.0. ESI-TOF-HRMS: *m/z* calcd for C₁₈H₁₁N₃O₈: 398.0624, found: 398.0623 [M+H]⁺.



Scheme S2. Synthetic routes for the preparation of ligand H₄L2.

Synthesis of tetramethyl (5,5'-(benzene-1,4-diyl)di(1*H*-1,2,3-triazole-1,4-diyl))diisophthalate (Me₄L2). Me₄L2 was also prepared in accordance to the method reported by Sharpless et. al. with slight modifications.^{S1-S3} 1,4-Diethynylbenzene (0.13g, 1.03 mmol) and dimethyl 5-azidoisophthalate (1, 0.60 g, 2.55 mmol) were added in a mixture solution of THF/H₂O (50 mL/20 mL) followed by the addition of CuSO₄·5H₂O (0.0125 g, 0.05 mmol) and excess sodium *L*-ascorbate (0.1 g, 0.41 mmol). The yellow mixture was stirred at room temperature under N₂ for 3 days to yield yellow precipitate. The precipitate was obtained by filtration and washed with water (20 mL × 3). Subsequently, the residue was washed twice with THF/H₂O (20 mL/8 mL) to yield **Me₄L2** as a pale yellow solid (0.55 g, 92%). ¹H NMR (400 MHz, CDCl₃- *d*₁): δ 8.77 (t, *J* = 1.3 Hz, 2H), 8.70 (d, *J* = 1.3 Hz, 4H), 8.40 (s, 2H), 8.07 (s, 4H), 1.55 (s, 12H). ¹³C NMR (100 MHz, CDCl₃- *d*₁) δ 165.2, 148.6, 137.6, 132.7, 130.6, 130.2, 126.7, 125.2, 117.8, 53.1. ESI-TOF-HRMS: *m/z* calcd for Mr of C₃₀H₂₅N₆O₈: 597.1734, found 597.1741 [M + H]⁺.

Synthesis of 5,5'-(benzene-1,4-diyl)di(1*H*-1,2,3-triazole-1,4-diyl)diisophthalic acid (H₄L2). The compound Me₄L2 (0.60 g, 1.00 mmol) was hydrolyzed with excess NaOH (0.24 g, 6 mmol) in a solution of THF/H₂O (60 mL/30 mL). The mixture was stirred at room temperature overnight. THF in the reaction mixture was then removed under reduced pressure to yield a yellow aqueous solution. Then, the resulting solution was acidified with HCl (1M) to pH 1. The solid was collected by filtration, rinsed several times with distilled water, and dried to yield yellow solid H₄L2 (0.51 g, 94%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 13.73 (br, 4H), 9.68 (s, 2H), 8.72 (d, *J* = 1.5 Hz, 4H), 8.53 (t, J = 1.5 Hz, 2H), 8.11 (s, 4H). ¹³C NMR (100 MHz, CDCl₃- *d*₁) δ 166.3, 147.8, 137.6, 133.9, 130.4, 129.9, 126.5, 124.3, 120.6. ESI-TOF-HRMS: *m/z* calcd for Mr of C₂₆H₁₇N₆O₈: 541.1108 [M⁺], found 541.1105 [M + H]⁺.



Scheme S3. Synthetic routes for the preparation of ligand H₄L3.

Synthesis of tetramethyl (5,5'-(benzene-1,3-diyl)di(1H-1,2,3-triazole-1,4-diyl))diisophthalate (Me₄L3). Me₄L3 was prepared in accordance to the method reported by Sharpless et. al. with slight modifications.^{S1-S3} 1,3-Diethynylbenzene (0.13g, 1.03 mmol) and dimethyl 5-azidoisophthalate (1, 0.60 g, 2.55 mmol) were added in a mixture solution of THF/H₂O (50 mL/20 mL) followed by the addition of sodium CuSO₄·5H₂O (0.0125 g, 0.050 mmol) and excess *L*-ascorbate (0.1 g, 0.4 mmol). The yellow mixture was stirred at room temperature under N₂ for 3 days to yield yellow precipitate. The precipitate was obtained by filtration and washed with water (20 mL × 3). Subsequently, the residue was washed twice with THF/H₂O (20 mL/8 mL) to yield **Me₄L3** as a pale yellow solid (0.52 g, 87%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.77 (m, *J* = 0.6 Hz, 2H), 8.78 (m, *J* = 0.6 Hz, 4H), 8.49 (s, 1H), 8.47 (d, *J* = 0.6 Hz, 2H), 8.00 (dd, *J* = 1.2 Hz, 2H), 7.61 (m, *J* = 7.8 Hz, 1H), 1.57 (s, 12H). ¹³C NMR (100 MHz, CDCl₃- *d*₁) δ 165.2, 148.6, 137.5, 132.7, 130.7, 130.6, 130.0, 126.3, 125.1, 123.5, 118.0, 53.0. ESI-TOF-HRMS: *m/z* calcd for Mr of C₃₀H₂₅N₆O₈: 596.1734, found 597.1741 [M + H]⁺.

Synthesis of 5,5'-(benzene-1,3-diyl)di(1*H*-1,2,3-triazole-1,4-diyl)diisophthalic acid (H₄L3). The compound Me₄L3 (0.60 g, 1.00 mmol) was hydrolyzed with excess NaOH (0.24 g, 6 mmol) in a mixture of THF/H₂O (60 mL/30 mL). The mixture was stirred at room temperature overnight. THF in the reaction mixture was then removed under reduced pressure to yield a yellow solution. Then, the resulting solution was acidified with HCl (1M) to pH 1. The precipitate was collected by filtration, rinsed several times with distilled water, and dried to yield yellow solid H₄L3 (0.49 g, 91%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 13.74 (br, 4H), 9.72 (s, 2H), 8.74 (d, *J* = 1.5 Hz, 4H), 8.66 (s, 1H), 8.54 (t, *J* = 1.5 Hz, 2H), 8.00 (dd, *J* = 1.7 Hz, 2H), 7.64 (t, *J* = 7.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃- *d*₁) δ 166.3, 147.9, 137.6, 134.1, 131.4, 130.3, 130.0, 125.8, 124.2, 124.0, 120.8. ESI-TOF-HRMS: *m*/z calcd for Mr of C₂₆H₁₇N₆O₈: 541.1108 [M⁺], found 541.1104 [M + H]⁺.

Synthesis of NTU-111. H_4L1 (20 mg, 0.05 mmol) and $Cu(NO_3)_2 \cdot 2.5H_2O$ (25 mg, 0.11 mmol) were dissolved in DMF (10 mL), then drops of HNO₃ was added into the mixture solution. The mixture was placed in a capped 20 mL vial and heated at 75°C in an oven for 3 days. The blue block crystals of NTU-111 suitable for X-ray diffraction were obtained after cooling down to room temperature. The crystals were washed by fresh DMF for three times and dried naturally at room temperature to yield NTU-111 (33.8 mg).

Synthesis of NTU-112. H₄L2 (20 mg, 0.03 mmol) and $Cu(NO_3)_2 \cdot 2.5H_2O$ (20 mg, 0.09 mmol) were dissolved in DMF/DMA (8 mL / 2 mL). Then, HNO₃ (0.1 mL, 1M) was added into the reaction mixture. The mixture was placed in a capped 20 mL vial and heated at 75°C in an oven for 3 days. The regular hexagonal-shaped blue crystals of NTU-112 suitable for X-ray diffraction were obtained after cooling down to room temperature. The crystals were washed by fresh DMF for three times and dried naturally at room temperature to yield NTU-112 (34.2 mg).

Synthesis of NTU-113. H₄L3 (20 mg, 0.03 mmol) and $Cu(NO_3)_2 \cdot 2.5H_2O$ (20 mg, 0.09 mmol) were dissolved in DMF/DMA (8 mL / 8 mL). Then, HNO₃ (1.2 mL) was added into the reaction mixture. The mixture was placed in a capped 20 mL vial and heated at 75°C in an oven for 3 days. The blue crystals of NTU-113 suitable for X-ray diffraction were obtained after cooling down to room temperature. The crystals were washed by fresh DMF for three times and dried naturally at room temperature to yield NTU-113 (30.2 mg).

X-ray crystallography. The single crystals of **NTU-111**, **112**, **113** for X-ray analyses were picked up under a microscope from freshly synthesized solutions, respectively, and then mounted to the glass fibers immediately. The diffraction data were collected at 295 K using graphite-monochromated Cu- $K\alpha$ radiation ($\lambda = 1.54178$ A) for **NTU-111** and **113**, and Mo- $K\alpha$ radiation ($\lambda = 0.71073$ A) for **NTU-112** on a SuperNova (Dual Source) X-ray Diffraction System from Agilent Technologies. The program SAINT was used for integration of the diffraction profiles,^{S4} and the data were corrected for absorption by using the SADABS program.^{S5} The structures were solved by the direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares analyses on F^2 (SHELXTL-97).^{S6} Metal atoms in each complex were located from the *E*-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses. The hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The solvent molecules in all three MOFs were highly disordered and cannot be modeled, thus the SQUEEZE routine of PLATON was applied to remove the contributions of the solvent molecules to the scattering.^{S7} Further details of crystallographic data and structural analyses for three MOFs are summarized in Table S1. CCDC 957323, 957324 and 957458 contains the supplementary crystallographic data for **NTU-111**, **112**, **113**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Gas sorption. Low-pressure gas sorption measurements were performed by using Quantachrome Instruments AutosorbiQ (Boynton Beach, Florida USA) with the extra-high pure gases. The as-synthesized MOF crystals were immersed in CH_2Cl_2 (30 mL) for 3 days, respectively, during which CH_2Cl_2 was replaced for three times. Then, the samples were 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, total pore volume and pore size distribution were calculated from the N₂ sorption isotherms at 77 K. The pore size distribution was calculated based on the Non-Local Density Functional Theory (NL-DFT, a zeolite/silica model containing spherical/cylindrical pores) model in the Quantachrome ASiQwin 2.01 software package. The isosteric heats of adsorption (Q_{st}) for CO₂, defined as

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

were determined by using the CO₂ adsorption isotherms at 273 and 298 K, respectively (ASiQwin 2.01).

Molecular simulation models and methods. The MOF structure used in simulation was constructed from the experimental determined crystallographic data. The charges of the framework atoms were calculated by the extended charge equilibration (EQeq) method, which has been used to rapidly assign the atomic charges of periodic MOFs without intensive computational expense.^{S8} Table S2 lists the atomic charges with the atoms labeled in Fig. 4a. The dispersion interactions of the framework atoms were represented by Lennard-Jones potential with parameters from the Universal Force Field (UFF).^{S9} The UFF is commonly adopted to simulate sorption in MOFs.^{S10-S13}

CO₂ was represented by the elementary physical model (EPM), which was fitted to reproduce the experimental vaporliquid equilibrium data of bulk CO₂.^{S14} The partial charges on C and O atoms were $q_C = 0.6645e$ and $q_O = -0.33225e$ ($e = 1.6022 \times 10^{-19}$ C is the elementary charge), respectively. The C-O bond length was 1.161 Å and the bond angle $\angle OCO$ was 180°. The CO₂-CO₂ interactions were mimicked by the additive Lennard-Jones (LJ) and Coulombic potentials

$$u_{ij}(r) = \sum_{\substack{\alpha \in i \\ \beta \in j}} \left\{ 4\varepsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}} \right)^{6} \right] + \frac{q_{\alpha}q_{\beta}}{4\pi\varepsilon_{0}r_{\alpha\beta}} \right\}$$

where $\sigma_{\alpha\beta}$ and $\varepsilon_{\alpha\beta}$ are the collision diameter and well depth, respectively; the cross LJ interaction parameters were calculated by the Lorentz-Berthelot combining rules; $\varepsilon_0 = 8.8542 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$ is the permittivity of the vacuum and q_{α} is the charge on atom α . N₂ was considered as a two-site rigid molecule with the N-N bond length of 1.10 Å. The N₂-N₂ interactions were modeled by the LJ potential with parameters fitted to the experimental data of bulk N₂.^{S15} H₂ was mimicked as a three-site model with explicit charges.^{S16} The H-H bond length was 0.74 Å, the charge on H atom was +0.468*e*, and the center-of-mass (COM) was a LJ core with a charge of -0.936*e*. Table S3 lists the LJ parameters and charges of CO₂, N₂ and H₂.

Grand Canonical Monte Carlo (GCMC) method was implemented to simulate gas adsorption in **NTU-113**. As the chemical potentials of adsorbate in adsorbed and bulk phases are identical at thermodynamic equilibrium, GCMC allows one to directly relate the chemical potentials in both phases and is thus widely used to simulate adsorption. The simulation box contained four $(2 \times 2 \times 1)$ unit cells of the MOF and the periodic boundary conditions were used in all three dimensions. The framework was assumed to be rigid and the framework atoms were fixed during simulation. The *LJ* interactions were evaluated using a spherical cutoff of 15 Å with long-range corrections added, while the Coulombic interactions were calculated using the Ewald sum method.^{S17} The real/reciprocal space partition parameter and the cutoff for reciprocal lattice vectors were 0.2 Å^{-1} and 10, respectively. The number of trial moves in a typical GCMC simulation was 2×10^7 , with the first 10^7 moves for equilibration and the subsequent 10^7 moves for ensemble averages. Five types of trial moves were randomly attempted in the GCMC simulation: displacement, rotation, and partial regrowth at a new position, and swap with reservoir including creation and deletion. The

simulated adsorption isotherms of CO_2 , N_2 and H_2 in **NTU-113** are shown in the Fig. S18, which are consistent very well with the experimental isotherms of CO_2 , N_2 and H_2 .

Breakthrough predication. Typically, adsorptive process is carried out in a fixed-bed packed with adsorbent. To mimic post-combustion CO₂ capture from a flue gas, the breakthrough curves for a CO₂/N₂ mixture in **NTU-113** were predicted by using the isotherms of pure CO₂ and N₂. The prediction involves the estimation of adsorbate concentration at the outlet after a step change in adsorbate concentration is introduced at the inlet. As outlined in the previous study,^{S18} simulation of the separation of a CO₂/N₂ mixture in a fixed-bed of length L_b and bed voidage ε_b was carried out (Fig. S19).

For an axially-dispersed plug flow along the *z*-direction, the concentration of adsorbate at any position can be obtained as a function of time *t* by solving the overall and component mass-balance equations:

$$c_{\mathrm{T}} \frac{\partial v}{\partial z} = -\frac{(1-\varepsilon_{\mathrm{b}})}{\varepsilon_{\mathrm{b}}} \sum_{i} \frac{\partial q_{i}}{\partial t}$$
$$D_{L} \frac{\partial^{2} c_{i}}{\partial z^{2}} - \frac{\partial (c_{i}v)}{\partial z} - \frac{\partial c_{i}}{\partial t} = \frac{(1-\varepsilon_{\mathrm{b}})}{\varepsilon_{\mathrm{b}}} \frac{\partial q_{i}}{\partial t}$$

where v is the interstitial fluid velocity, c_T is the total concentration of fluid, $q_i(z,t)$ is the loading of component *i* in adsorbent, $c_i(z,t)$ is the concentration of component *i* in the fluid phase, and DL is the axial dispersion coefficient.

The mass transfer rate in the adsorbent is expressed using the linear driving force (LDF) model:

$$\frac{\partial q_i}{\partial t} = k_i (q_i^* - q_i)$$

where q_i^* is the equilibrium loading calculated from the Langmuir isotherm, and k_i is the LDF rate constant or the overall effective mass transfer coefficient of component *i*. The LDF rate constant is related to external film, macropore, and micropore resistances:

$$\frac{1}{k_i} = \frac{1}{k_{\text{film}}} + \frac{1}{k_{\text{macro}}} + \frac{1}{k_{\text{micro}}} = \frac{R_{\text{p}} q_{i0}^*}{3k_{\text{f}} c_{i0}} + \frac{\tau_{\text{p}} R_{\text{p}}^2 q_{i0}^*}{15\varepsilon_{\text{p}} D_{\text{m}} c_{i0}} + \frac{r_{\text{c}}^2}{15D_{\text{c}}}$$

where $k_{\rm f}$ is the mass transfer coefficient across the external film around adsorbent particles, c_{i0} is the concentration of component *i* in the feed, q_{i0}^* is the equilibrium loading at feed concentration, $D_{\rm m}$ and $D_{\rm c}$ are molecular and intracrystalline diffusivities, $r_{\rm c}$ is crystal size, and $R_{\rm p}$, $\varepsilon_{\rm p}$ and $\tau_{\rm p}$ are particle radius, porosity and tortuosity, respectively. It is commonly acceptable to assume that the micropore (intracrystalline diffusion) resistance is negligible, particularly when $r_{\rm c}$ is small and $D_{\rm c}$ is large.

To predict the breakthrough for a CO₂/N₂ mixture in a bed packed with **NTU-113**, the set of partial differential were made dimensionless by introducing scaling factors, and then solved numerically by reducing into a set of ordinary differential equations via the finite difference technique for spatial terms. Finally, the ordinary differential equations subjected to appropriate initial and boundary conditions were solved. In the prediction, typical values, $L_b = 0.4$ m, $\varepsilon_b =$ 0.4, $v_0 = 0.02$ m s⁻¹, $R_p = 0.15$ cm, $\varepsilon_b/\tau_p = 0.1$, used in the absence of more specific information were assumed. D_L , D_m and k_f were calculated using the Edwards–Richardson correlation,^{S19} the Chapman–Enskog equation,^{S20} and the Wakao– Funazkri correlation,^{S21} respectively. The fixed-bed is assumed to be free of adsorbate initially, and the inlet CO₂/N₂ mixture is set at 273 K and 100 kPa with the CO₂/N₂ molar ratio of 0.15:0.85 for mimicing a flue gas. The calculated breakthrough curves for a CO₂/N₂ mixture in a fixed-bed packed with **NTU-113** as adsorbent shows that there are three characteristic regimes: (1) initially CO₂ is adsorbed and almost pure N₂ is exited from the bed; (2) CO₂ breakthrough occurs after a certain time; (3) both CO_2 and N_2 at the outlet reach their feed compositions. The breakthrough times, defined as the time when the composition at the outlet is 0.01%, are 13.8 for N_2 and 181.2 for CO_2 .

Tables

	NUTLAN		
	NTU-III	NTU-112	NTU-113
Formula	C54 H33Cu6N9O30	C13H8CuN3O5	C13H7CuN3O5
Mr	1669.16	807.67	348.77
Temperature (K)	293(2)	293(2)	293(2)
Wavelength	1.54178 Å	0.71073 Å	1.54178 Å
Crystal system	Monoclinic	Trigonal	Orthorhombic
Space group	C2/m	P321	Fmmm
a,b,c/Å	a = 49.1880(6) Å,	a = 18.140(1) Å,	a = 24.9933 (13) Å,
$\alpha, \beta, \gamma / °$	b = 37.4243(4) Å,	b = 18.140(1) Å,	b = 28.2078 (12) Å,
	c = 16.0489 (2) Å,	c = 18.114 (2) Å.	c = 38.8733 (18) Å.
	$\beta = 103.491 (1)^{\circ}$		
V, Å ³	28728.0(5)	1202.7(4)	27406(2)
Ζ	8	6	32
Dcalc (g·cm ⁻³)	1.133	0.668	0.676
Crystal size,(mm)	0.16 * 0.15 * 0.14	0.15 * 0.15 * 0.06	0.16 * 0.12 * 0.10
Theta range (deg)	3.06 to 73.17	1.72 to 29.12	3.13 to 73.21
Reflections	11542/2766	9222/3778	7050 / 4136
collected/unique			
Rint	0.1251	0.1082	0.0487
Goodness-of-fit on F ²	1.068	1.121	1.375

Table S1. Crystallographic data and structural refinement summary for NTU-111, 112, 113.

Table S2. Atomic charges in NTU-113.

Atom	Charge (e)	Atom	Charge (e)	Atom	Charge (e)
Cu	0.895	C7	-0.011	H7	0.067
0	-0.404	C8	0.035	H8	0.027
C1	0.356	C9	0.005	H9	0.035
C2	-0.039	C10	0.037	N1	-0.093
C3	-0.082	C11	0.067	N2	-0.042
C4	0.106	Н3	0.087	N3	-0.076
C5	-0.119	Н5	0.098		
C6	-0.114	Н6	0.077		

Table S3. Potential Parameters of CO_2 , N_2 and H_2 .

Adsorbate	Site	$\sigma(\text{\AA})$	$\varepsilon/k_{\rm B}({ m K})$	<i>q</i> (<i>e</i>)
	С	2.785	28.999	+0.6645
CO_2	0	3.064	82.997	-0.33225
N_2	Ν	3.32	36.4	-
	Н	-	-	+0.468
H ₂	СОМ	2.958	36.7	-0.936



Fig. S1. Photographs of as-synthesized crystals of (a) NTU-111, (b) NTU-112 and (c) NTU-113.



Fig. S2. Structure of **NTU-111**: (a) square-planar 4-connected paddle-wheel Cu_2 cluster, (b) square-planar 4-connected Ligand L1 moiety, (c) 2D layers with Cu_2 clusters arranging alternately in equilateral triangle and regular hexagon geometries, (d) 3D framework of **NTU-111** showing the "clicked" uniform location of nitrogen-rich triazole rings, and (e) NbO-type network with $6^4 \cdot 8^2$ topology of **NTU-111**.



Fig. S3. Structure of **NTU-112**: (a) square-planar 4-connected paddle-wheel Cu_2 cluster, (b) 4-connected Ligand L2 moiety, (c) 2D layers with Cu_2 clusters arranging alternately in equilateral triangle and regular hexagon geometries, (d) 3D framework of **NTU-112** showing the "clicked" uniform location of nitrogen-rich triazole rings, and (e) *acs* network of **NTU-112**.



Fig. S4. Structure of **NTU-113**: (a) square-planar 4-connected paddle-wheel Cu₂ cluster, (b) 4-connected Ligand L3 moiety, (c) 2D layers with Cu₂ clusters arranging alternately in quadrilateral lattice, (d) 3D framework of **NTU-113** showing the "clicked" uniform location of nitrogen-rich triazole rings, and (e) *PtS*-type network with $4^{2} \cdot 8^{4}$ topology of **NTU-113**.



Fig. S5. Powder XRD patterns of NTU-111, indicating the framework was retained after the activation process.



Fig. S6. Powder XRD patterns of NTU-112, indicating the framework was retained after the activation process.



Fig. S7. Powder XRD patterns of NTU-113, indicating the framework was retained after the activation process.



Fig. S8. TGA plot of naturally dried NTU-111, indicating the framework was stable up to ~260 °C.



Fig. S9. TGA plot of naturally dried NTU-112, indicating the framework was stable up to ~260 °C.



Fig. S10. TGA plot of naturally dried NTU-113, indicating the framework was stable up to ~260 °C.



Fig. S11. Pore-size distribution plot of NTU-111 calculated from experimental N_2 adsorption isotherm using the nonlocal density functional theory (NLDFT).



Fig. S12. Pore-size distribution plot of NTU-112 calculated from experimental N_2 adsorption isotherm using the nonlocal density functional theory (NLDFT).



Fig. S13. Pore-size distribution plot of NTU-113 calculated from experimental N_2 adsorption isotherm using the nonlocal density functional theory (NLDFT).



Fig. S14. CO_2 adsorption isotherms (left) of activated NTU-111 and isosteric heat of CO_2 adsorption (right) calculated from the adsorption isotherms at 273 K and 298 K.



Fig. S15. CO_2 adsorption isotherms (left) of activated NTU-112 and isosteric heat of CO_2 adsorption (right) calculated from the adsorption isotherms at 273 K and 298 K.



Fig. S16. CO_2 adsorption isotherms (left) of activated **NTU-113** and isosteric heat of CO_2 adsorption (right) calculated from the adsorption isotherms at 273 K and 298 K.



Fig. S17. H₂ adsorption isotherms of activated (1) **NTU-111**, (2) **NTU-112**, (3) **NTU-113** at 77 K. The three MOFs also showed good H₂ adsorption capabilities presenting adsorption values of 163.7, 214.9 and 239.8 cm³ g⁻¹ for **NTU-111**, **112**, **113**, respectively, at 1atm and 77K.



Fig. S18. Simulated adsorption isotherms of NTU-113 on CO_2 (273 and 298 K), N_2 (273 K) and H_2 (77 K), which are consistent well with the experimental isotherms.



Fig. S19. (a) Illustration of adsorptive separation of a CO_2/N_2 mixture in a fixed-bed packed with adsorbent; (b) breakthrough curves for CO_2 and N_2 through a fixed-bed packed with **NTU-113**. The inlet CO_2/N_2 mixture (0.15/0.85) is at 273 K and 100 kPa.





¹³C NMR spectrum of tetramethyl 5,5'-(1H-1,2,3-triazole-1,4-diyl)diisophthalate (Me₄L1) in CDCl₃.



HRMS spectrum of tetramethyl 5,5'-(1H-1,2,3-triazole-1,4-diyl)diisophthalate (Me₄L1)



FT-IR spectrum of tetramethyl 5,5'-(1H-1,2,3-triazole-1,4-diyl)diisophthalate (Me₄L1)



¹³C NMR spectrum of 5,5'-(1H-1,2,3-triazole-1,4-diyl)diisophthalic acid (H₄L1) in DMSO-d₆



HRMS spectrum of 5,5'-(1H-1,2,3-triazole-1,4-diyl)diisophthalic acid (H₄L1)



FT-IR spectrum of 5,5'-(1H-1,2,3-triazole-1,4-diyl)diisophthalic acid (H₄L1)



 $\label{eq:main_spectrum} \begin{tabular}{l} $1H NMR spectrum of tetramethyl (5,5'-(benzene-1,4-diyl)di(1$$H-1,2,3-triazole-1,4-diyl)$$) diisophthalate ($$Me_4L2$) in CDCl_3$. \end{tabular}$



 $\label{eq:main_spectrum} ^{13}C \ \text{NMR spectrum of of tetramethyl} \ (5,5'-(benzene-1,4-diyl)) \\ \text{di}(1H-1,2,3-\text{triazole-1},4-diyl)) \\ \text{disophthalate} \ (\textbf{Me_4L2}) \ \text{in } CDCl_3.$



HRMS spectrum of tetramethyl (5,5'-(benzene-1,4-diyl)di(1H-1,2,3-triazole-1,4-diyl))diisophthalate (Me₄L2)



FT-IR spectrum of tetramethyl (5,5'-(benzene-1,4-diyl)di(1H-1,2,3-triazole-1,4-diyl))diisophthalate (Me₄L2)



¹H NMR spectrum of 5,5'-(benzene-1,4-diyl)di(1*H*-1,2,3-triazole-1,4-diyl)diisophthalic acid (H₄L2) in DMSO-*d*₆





¹³C NMR spectrum of 5,5'-(benzene-1,4-diyl)di(1*H*-1,2,3-triazole-1,4-diyl)diisophthalic acid (H₄L2) in DMSO-d₆



HRMS spectrum of 5,5'-(benzene-1,4-diyl)di(1H-1,2,3-triazole-1,4-diyl)diisophthalic acid (H₄L2)



FT-IR spectrum of 5,5'-(benzene-1,4-diyl)di(1*H*-1,2,3-triazole-1,4-diyl)diisophthalic acid (H₄L2)



¹H NMR spectrum of tetramethyl (5,5'-(benzene-1,3-diyl)di(1H-1,2,3-triazole-1,4-diyl))diisophthalate (Me₄L3) in CDCl₃.



¹³C NMR spectrum of tetramethyl (5,5'-(benzene-1,3-diyl)di(1H-1,2,3-triazole-1,4-diyl))diisophthalate (Me₄L3) in CDCl₃.



HRMS spectrum of tetramethyl (5,5'-(benzene-1,3-diyl)di(1H-1,2,3-triazole-1,4-diyl))diisophthalate (Me₄L3)



FT-IR spectrum of tetramethyl (5,5'-(benzene-1,3-diyl)di(1H-1,2,3-triazole-1,4-diyl))diisophthalate (Me₄L3)



¹H NMR spectrum of 5,5'-(benzene-1,3-diyl)di(1*H*-1,2,3-triazole-1,4-diyl)diisophthalic acid (H₄L3) in DMSO-*d*₆

166.34	147.90	137.60 134.14 134.14 130.30 129.92 125.81 124.03 124.03 124.03
1		$\mathbb{K} = \mathbb{K} = $



¹³C NMR spectrum of 5,5'-(benzene-1,3-diyl)di(1*H*-1,2,3-triazole-1,4-diyl)diisophthalic acid (H₄L3) in DMSO-d₆



HRMS spectrum of 5,5'-(benzene-1,3-diyl)di(1H-1,2,3-triazole-1,4-diyl)diisophthalic acid (H₄L3)



FT-IR spectrum of 5,5'-(benzene-1,3-diyl)di(1H-1,2,3-triazole-1,4-diyl)diisophthalic acid (H₄L3)

References

- S1 V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem. Int. Ed.*, 2002, 41, 2596–2599.
- S2 X.-J. Wang, P.-Z. Li, L. Liu, Q. Zhang, P. Borah, J. D. Wong, X. X. Chan, G. Rakesh, Y. Li and Y. Zhao, *Chem. Commun.*, 2012, 48, 10286–10288.
- S3 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.
- S4 SAINT V6.1, Bruker Analytical X-ray Systems, Madison, WI, 1999.
- S5 G. M. Sheldrick, *SADABS*, Empirical Absorption Correction Program, University of Göttingen, Göttingen, Germany, **1997**.
- S6 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112.
- S7 Spek, A. L. J. Appl. Crystallogr. 2003, 36, 7.
- S8 C. E. Wilmer, K. C. Kim and R. Q. Snurr, J. Phys. Chem. Lett., 2012, 3, 2506–2511.
- S9 A. K. Rappé, C. J. Casewit, K. S. Colwell, W. A. Goddard III and W. M. Skiff, J. Am. Chem. Soc., 1992, 114, 10024– 10035.
- S10 R. Babarao, Z. Hu, J. Jiang, S. Chempath and S. I. Sandler, *Langmuir*, 2007, 23, 659–666.
- S11 R. Babarao and J. Jiang, *Langmuir*, 2008, 24, 6270-6278.
- S12 G. Garberoglio, A. I. Skoulidas and J. K. Johnson, J. of Phys. Chem. B, 2005, 109, 13094-13103.
- S13 A. I. Skoulidas and D. S. Sholl, J. Phys. Chem. B, 2005, 109, 15760-15768.
- S14 J. G. Harris and K. H. Yung, J. Phys. Chem., 1995, 99, 12021-12024.
- S15 C. S. Murthy, K. Singer, M. L. Klein and I. R. McDonald, Mol. Phys., 1980, 41, 1387-139.
- S16 F. Darkrim and D. J. Levesque, Chem. Phys., 1998, 109, 4981-4984.
- S17 M. P. Allen and D. J. Tildesley, Computer Simulation of Liquids. Oxford University Press: Oxford, 1987.
- S18 K. Zhang, A. Nalaparaju, Y. F. Chen and J. W. Jiang, *RSC Adv.*, 2013, **3**, 16152-16158.
- S19 M. F. Edwards and J. F. Richards, Chem. Eng. Sci., 1968, 23, 109-123.
- S20 E. L. Cussler, Diffusion, Mass Transfer in Fluid Systems, Cambridge University Press, New York, 1984.
- S21 N. Wakao and T. Funazkri, Chem. Eng. Sci., 1978, 33, 1375-1384.