Supporting Information

Solvents regulated packing porosity of a bilayer metal-organic cage

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General procedures and materials

All the solvents and materials were purchased from chemical vendors and without further depuration before used. The instrument used for the ^{1}H-NMR test was a Bruker Advance III 600 MHz nuclear magnetic resonance spectrometer. Powder X-Ray Diffraction (PXRD) pattern was tested with Rigaku SmartLab (test conditions: 40 kV, 40 mA, CuKα, λ = 1.5418 Å, scanning range 5-50°). Infrared (FT-IR) spectra were tested on the VECTOR 22 spectrometer using KBr tableting method in the range of 4000-400 cm^{-1}. Thermogravimetric analysis (TGA) measurements were performed on a STA 209 F1 instrument under astatic N_2 atmosphere with a heating rate of 10 °C/min at the range of 30-700 °C.

Ligand synthesis

3,5-di(pyridin-3-yl)-4H-1,2,4-triazole was prepared according to previous literature.[1-3]

Crystal analysis

Single-crystal X-ray diffraction data was collected by Rigaku XtaLAB Synergy diffractometer at room temperature using graphite monochromator Mo Kα radiation (λ = 0.71073 Å). Data reduction was made with the Saint program. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The structure was solved by direct methods and refined with full-matrix least-squares technique using the SHELXTL package.[4] 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 × Ueq of the attached atom. We have employed PLATON/SQUEEZE[5, 6] 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.

Sample activation

Prior to adsorption measurement, the samples were prepared by immersing the as-synthesized samples in dry acetone for three days to remove non-volatile solvents, and the extract was decanted every 8 h and replaced with fresh acetone. The completely activated sample was obtained by heating the solvent-exchanged sample at atmospheric temperature under a dynamic high vacuum for 24 h.

Single gas adsorption

In the gas adsorption measurement, ultra-high-purity grade of CO_2, C_2H_2 and C_2H_4, gases were used throughout the adsorption experiments. Gas adsorption isotherms were collected using a Belsorp-mini volumetric adsorption instrument from BEL Japan Inc, using the volumetric technique.

Breakthrough Measurements.

The breakthrough experiments were performed on the Beifang Gaorui CT-4 system. The initial activated samples were tightly packed into a stainless-steel column (φ = 0.30 cm, L = 20 cm). Then, the column was activated under vacuum at corresponding temperature and then swept with N_2 flow to remove impurities. Until no signal was detected, the gas flow was dosed into the column. Breakpoints were determined by gas chromatography. Between cycling experiments, re-generation can be achieved under vacuum at 323 K for half hour. Pressure of the feed gas is 1 bar.
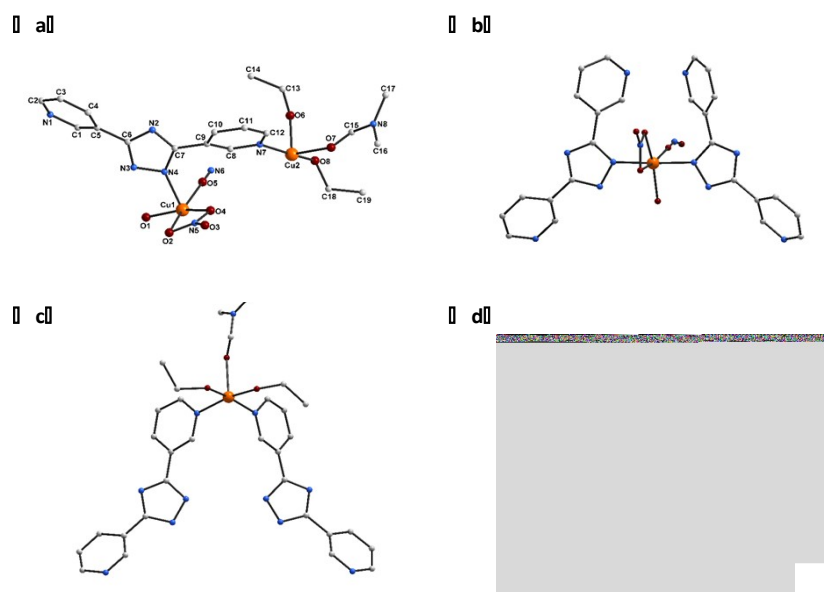
Structures.
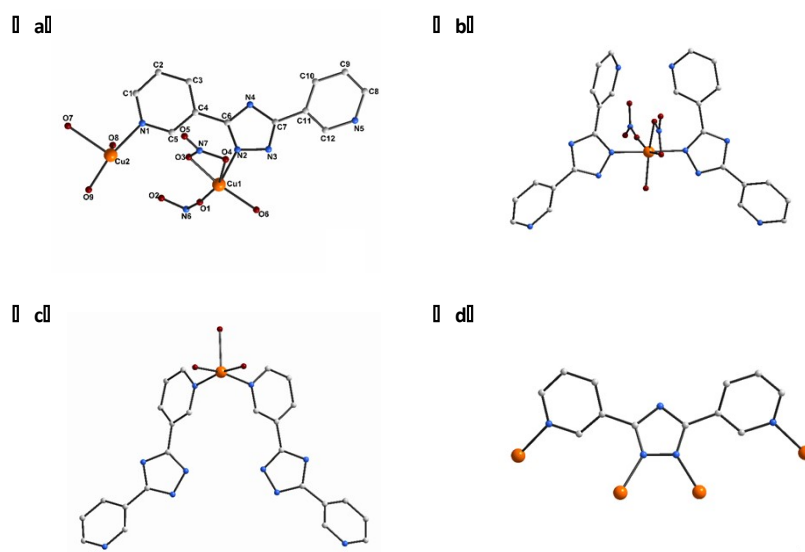
Fig S1. Structure of **NTU-93**: Asymmetric unit (a), Coordination configuration of Cu1 center (b), Coordination configuration of Cu2 center (c) and Ligand connection (d). Color codes: C, grey; N, blue; O, dark red; Cu, orange.
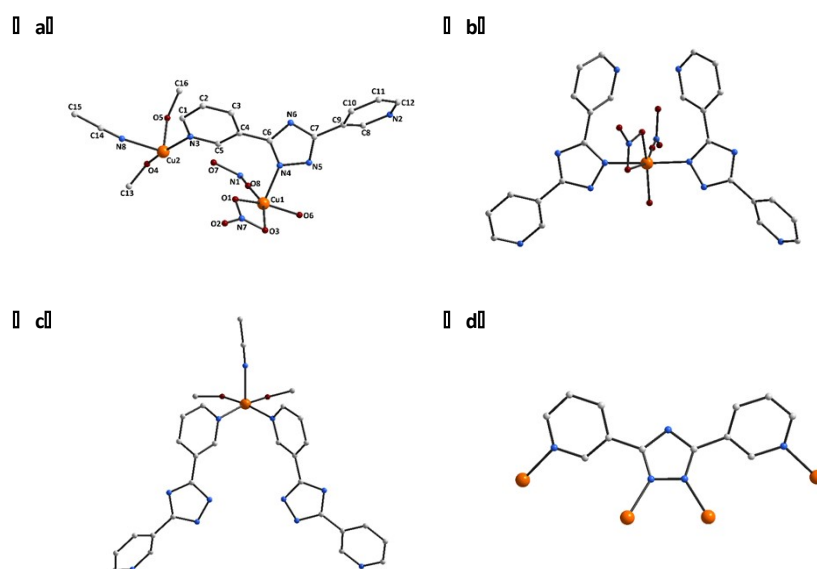

Fig S2. Structure of **NTU-94**: Asymmetric unit (a), Coordination configuration of Cu1 center (b), Coordination configuration of Cu2 center (c) and Ligand connection (d). Color codes: C, grey; N, blue; O, dark red; Cu, orange.

Fig S3. Structure of **NTU-95**: Asymmetric unit (a), Coordination configuration of Cu1 center (b), Coordination configuration of Cu2 center (c) and Ligand connection (d). Color codes: C, grey; N, blue; O, dark red; Cu, orange.

3.203 Å
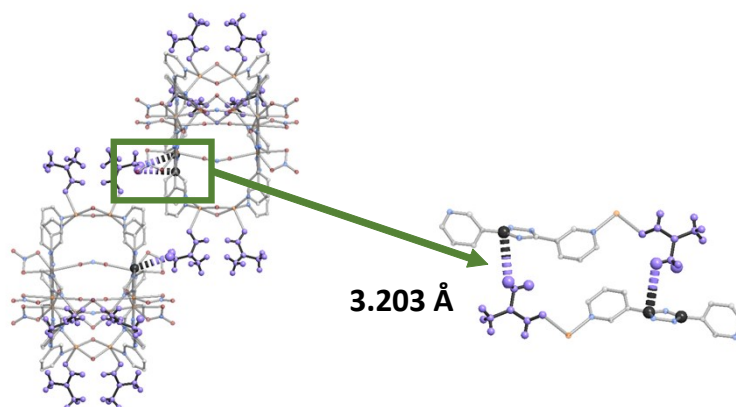
Fig S4. Weak hydrogen bonding connections in **NTU-95**.

Characterizations.
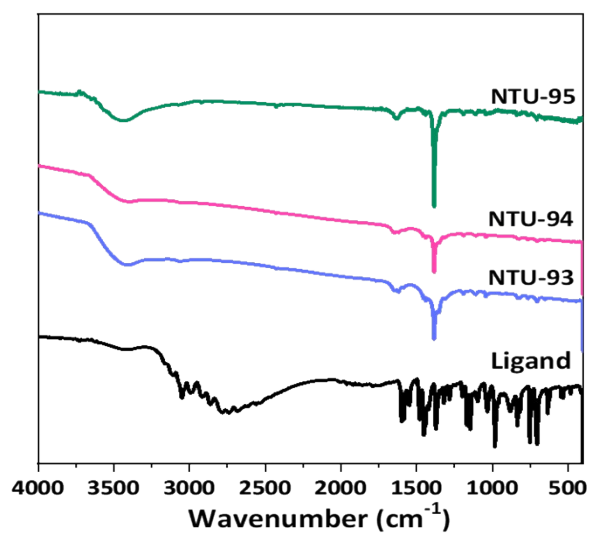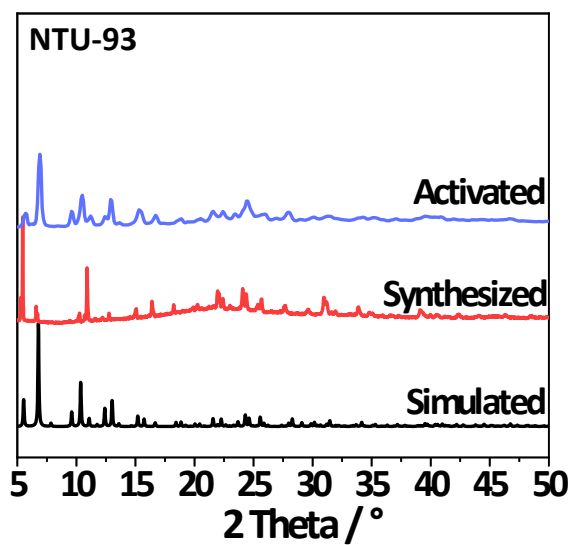

Fig S5. FT-IR spectra for the three MOCs and ligand.
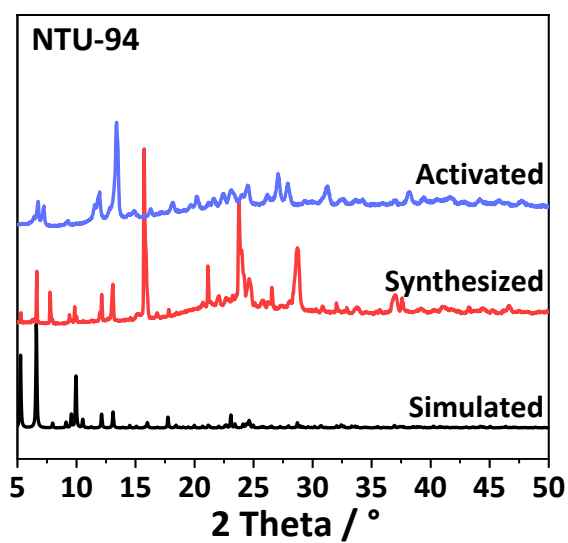

Fig S6. PXRD patterns of **NTU-93**.

Fig S7. PXRD patterns of **NTU-94**.
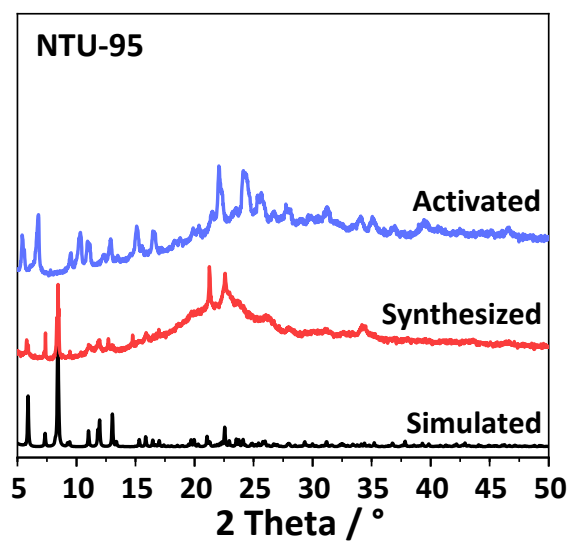
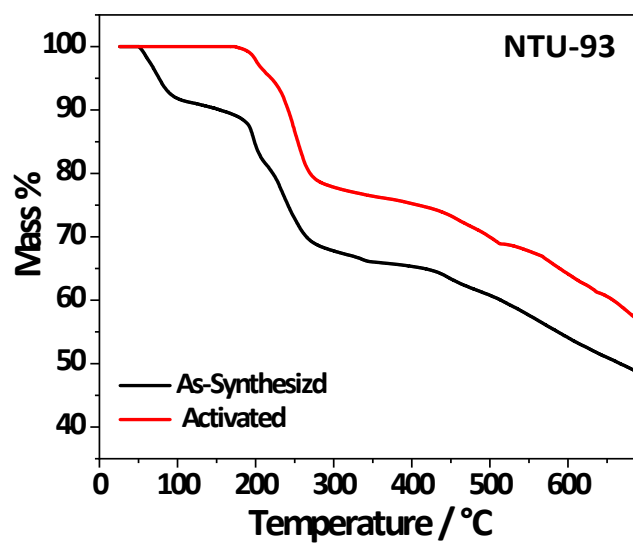**Fig S8.** PXRD patterns of **NTU-95**.

Fig S9. TG curves of as-synthesized and activated of **NTU-93**.
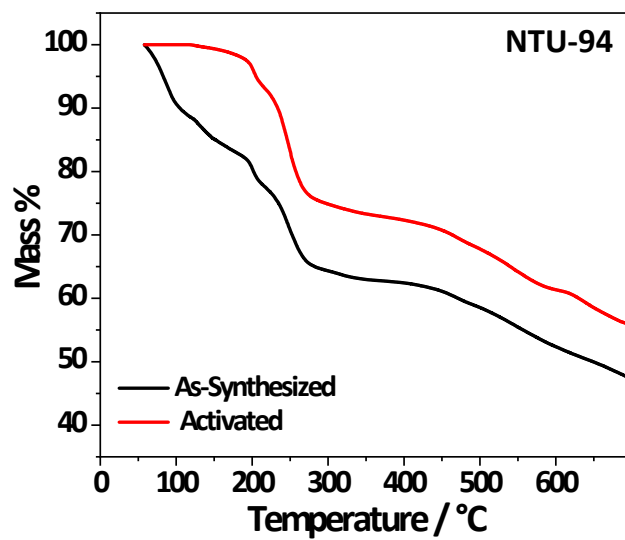

Fig S10. TG curves of as-synthesized and activated of **NTU-94**.
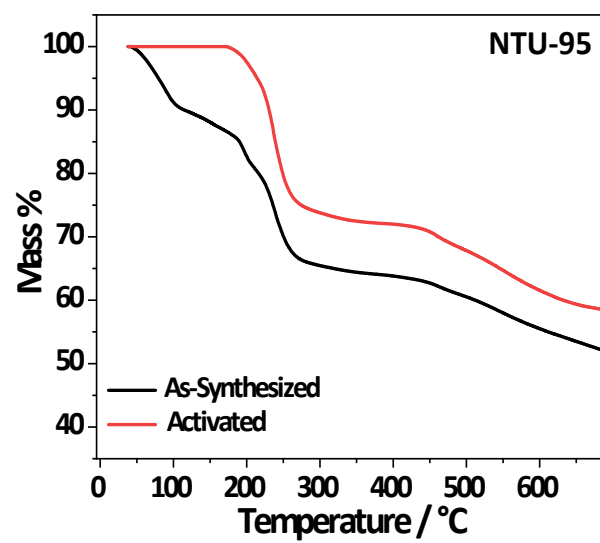
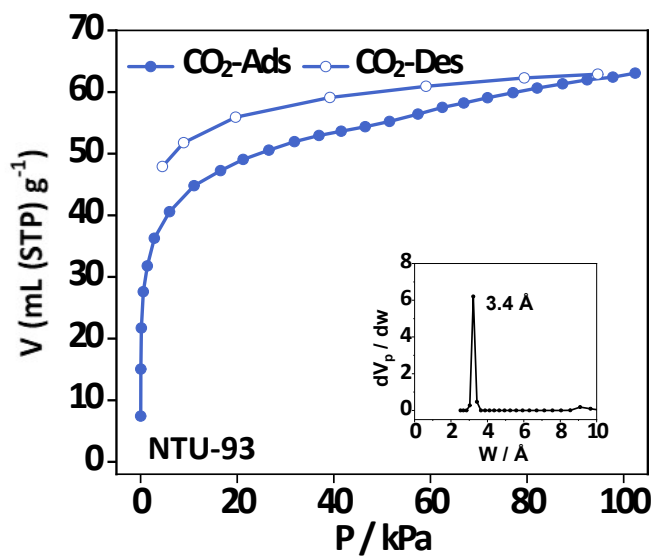**Fig S11.** TG curves of as-synthesized and activated of **NTU-95**.

Adsorption

Fig S12. CO_2 adsorption at 195 K for **NTU-93** and calculated pore size distribution.
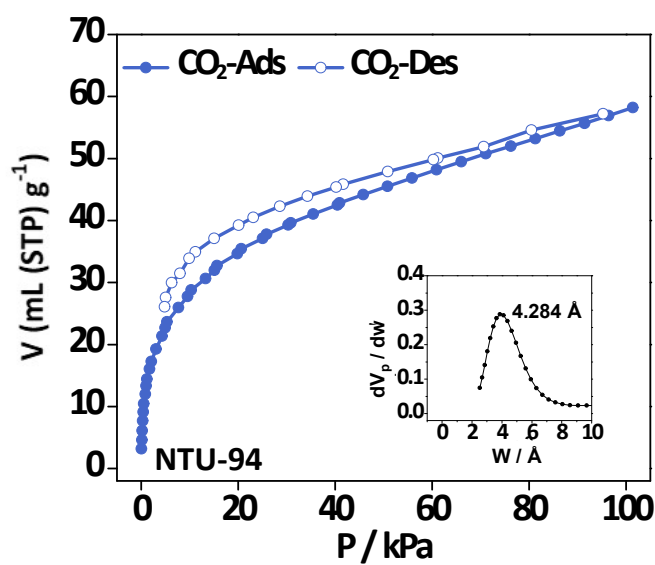

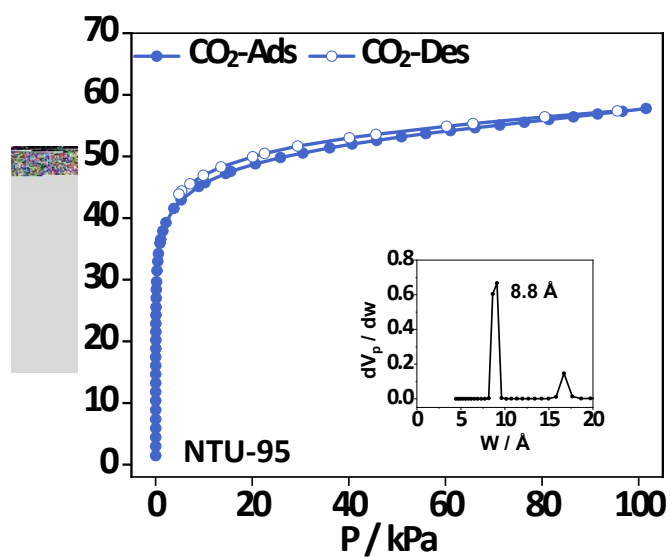**Fig S13.** CO_2 adsorption at 195 K for **NTU-94** and calculated pore size distribution.

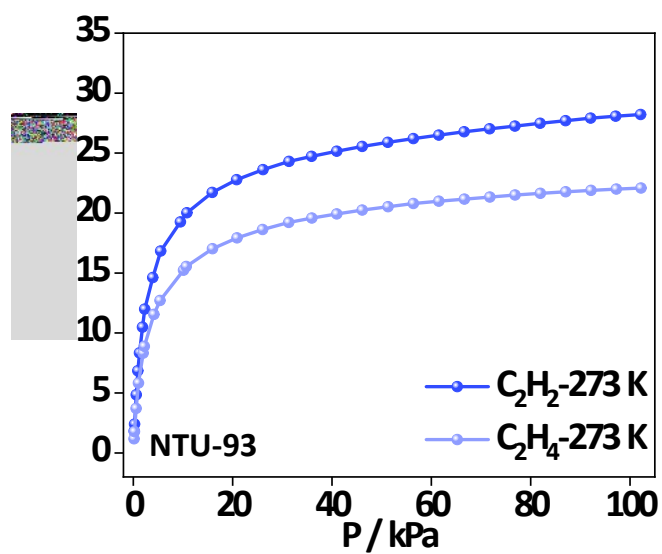**Fig S14.** CO_2 adsorption at 195 K for **NTU-95** and calculated pore size distribution.

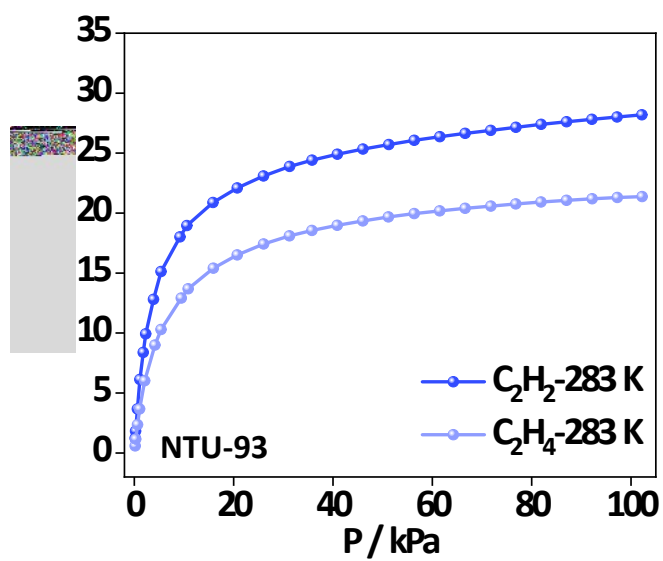**Fig S15.** C_2H_2 and C_2H_4 gas adsorption isotherms of **NTU-93** at 273 K.

Fig S16. C_2H_2 and C_2H_4 gas adsorption isotherms of **NTU-93** at 283 K.
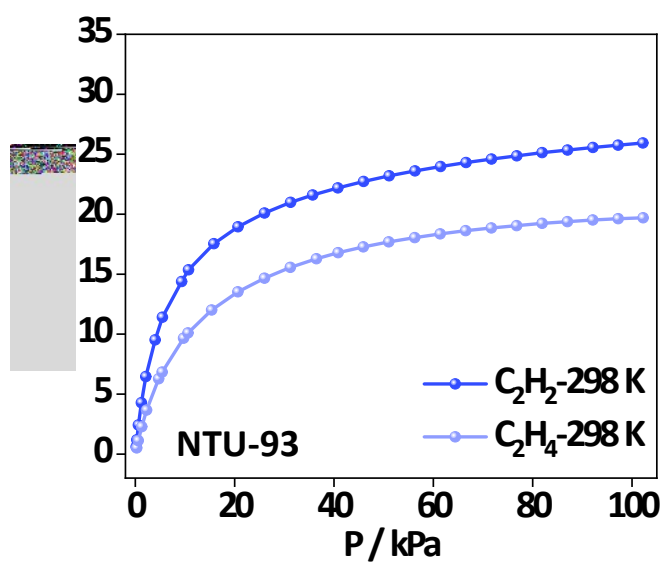
Fig S17. C_2H_2 and C_2H_4 gas adsorption isotherms of **NTU-93** at 298 K.
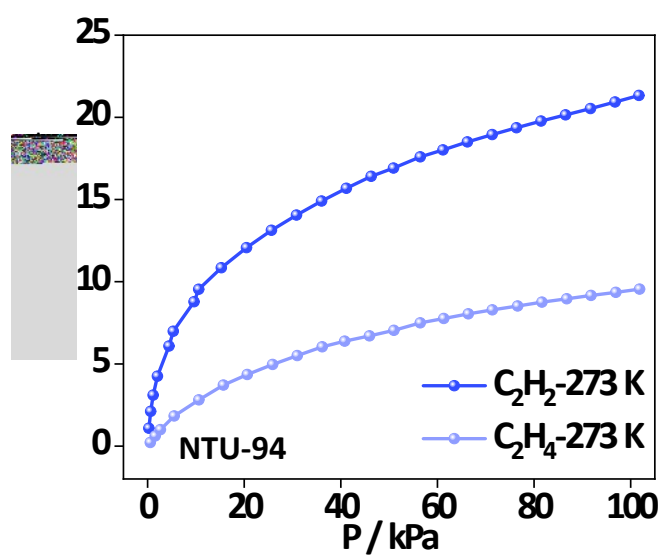
Fig S18. C_2H_2 and C_2H_4 gas adsorption isotherms of **NTU-94** at 273 K
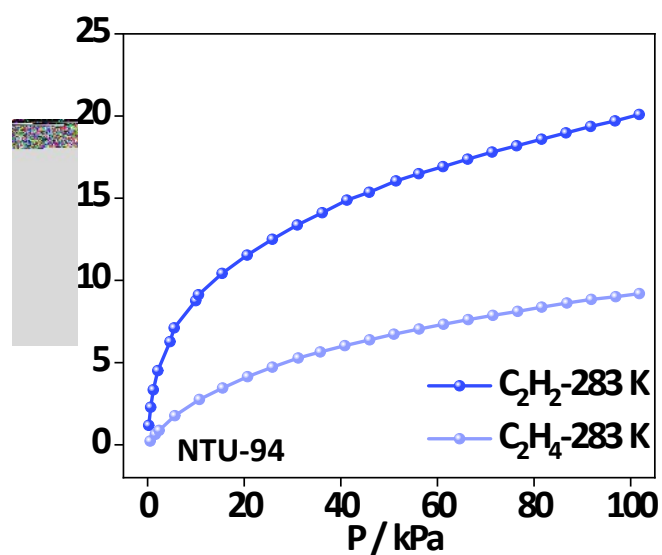
Fig S19. C_2H_2 and C_2H_4 gas adsorption isotherms of **NTU-94** at 283 K.

Fig S20. C_2H_2 and C_2H_4 gas adsorption isotherms of **NTU-94** at 298 K.

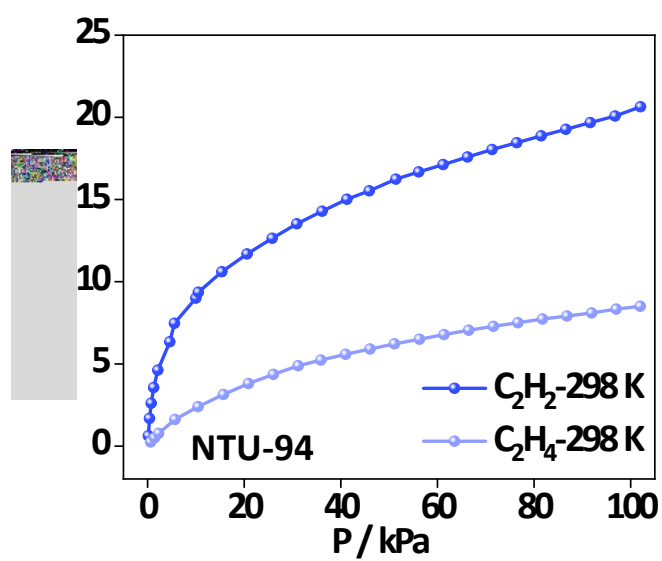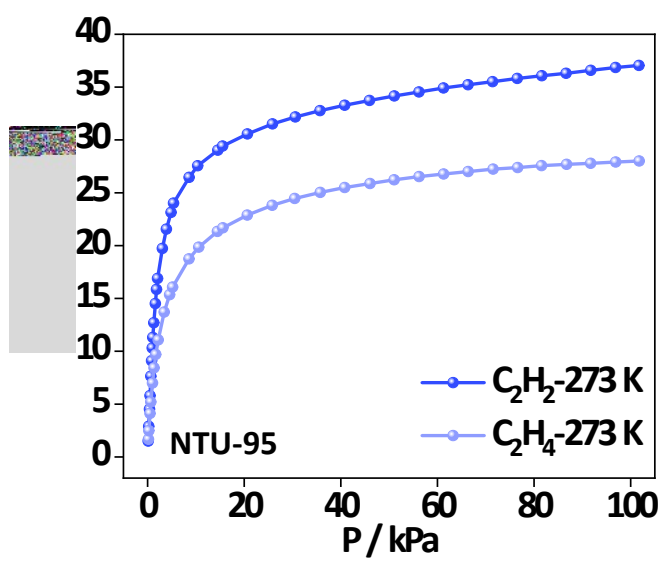**Fig S21.** C_2H_2 and C_2H_4 gas adsorption isotherms of **NTU-95** at 273 K.
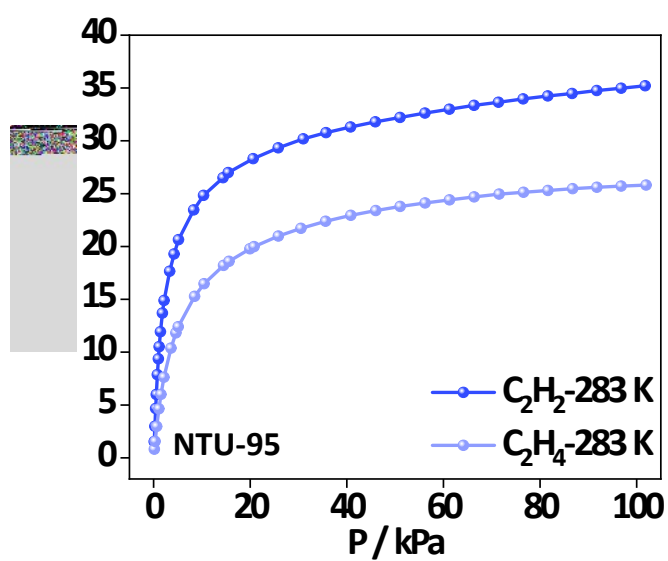
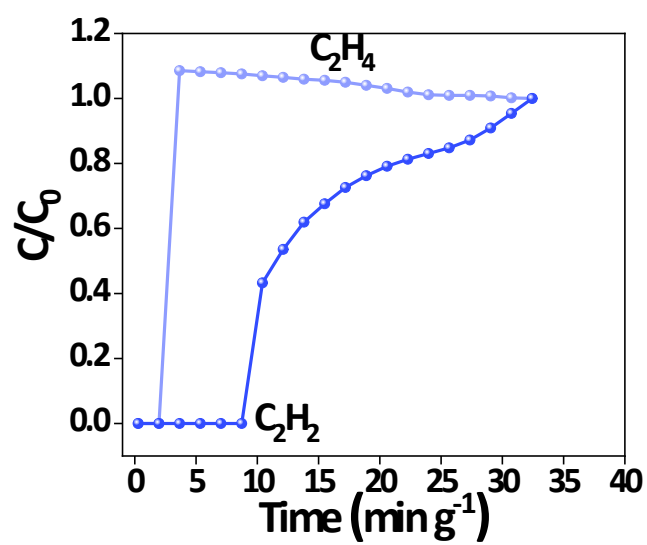**Fig S22.** C_2H_2 and C_2H_4 gas adsorption isotherms of **NTU-95** at 283 K.

Fig S23. Compare of breakthrough curves of **NTU-95** for a C_2H_2/C_2H_4 mixture (1/99, v/v) at 298 K, 1 bar at 5 mL min^{-1}

Table S1 Crystal data and structure refinements for **NTU-93-series**.

Compound	NTU-93	NTU-94	NTU-95
Formula	$C_{72}H_{67}Cu_{12}N_{39}O_{61}$	$C_{96}H_{105}Cu_{12}N_{48}O_{35}$	$C_{102}H_{120}Cu_{12}N_{45}O_{41}$
Formula weight	3217.12	3253.75	3394.90
Crystal system	hexagonal	hexagonal	hexagonal
Space group	$P6_3/m$	$P6_3/m$	$P6_3/m$
a (Å)	18.4268 (6)	19.3815 (10)	24.0593 (12)
b (Å)	18.4268 (6)	19.3815 (10)	24.0593 (12)
c (Å)	22.5112 (11)	22.130 (2)	21.519 (2)
V (Å^3)	6619.6 (5)	7199.2 (11)	10787.5 (15)
Z	2	2	2
Density / g cm^{-3}	1.614	1.501	1.045
Index ranges	$-21 \leq h \leq 15$	$-23 \leq h \leq 23$	$-28 \leq h \leq 28$
	$-21 \leq k \leq 21$	$-21 \leq k \leq 23$	$-28 \leq k \leq 27$
	$-26 \leq l \leq 24$	$-26 \leq l \leq 26$	$-25 \leq l \leq 24$
R_1	0.0715	0.0538	0.0765
$wR_2[I > 2\sigma(I)]$	0.2294	0.1663	0.2524
F (000)	3216	3290	3446
GOOF	1.02	1.03	1.02

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$ and $w = 1/[\sigma^2(F_o^2) + (0.1452P)^2]$ where $P = (F_o^2+2F_c^2)/3$.

Table S2 Formed hydrogen bonds in **NTU-93, NTU-94 and NTU-95**.

NTU-93			
D-H...A	D-H (Å)	H...A (Å)	∠D-H...A (°)
O7--H7A...O10	0.929	3.260	142.065
O7--H7A...O12	0.929	3.247	125.582
O7--H7B...C9	0.931	3.663	139.258
NTU-94			
D-H...A	D-H (Å)	H...A (Å)	∠D-H...A (°)
C15--H15B...C10	0.960	2.861	152.437
C15--H15C...O2	0.960	2.651	121.543
NTU-95			
D-H...A	D-H (Å)	H...A (Å)	∠D-H...A (°)
C16--H16B...O6	0.960	2.605	161.033
C16--H16B...N6	0.960	2.845	152.862
C16--H16C...C7	0.959	3.203	116.745

References

1. Q. Wei, C. Qiao, Z. Xia and S. Chen, *Synth Commun*, 2013, **43**, 3181-3191.
2. P. Howlader, P. Das, E. Zangrando and P. S. Mukherjee, *J. Am. Chem. Soc.*, 2016, **138**, 1668-1676.
3. J. Tang, Y. Shen, X. He, M. Chen, H. Zhao, Y. Wang, J. Jiang, P. Liu, R. Dang, M. Zhang, G. Qin, J. Bai and J. Duan, *Inorg. Chem.*, 2024, **63**, 3667-3674.
4. G. M. Sheldrick, *Acta Crystallogr. Sec. A*, 2008, **64**, 112-122.
5. P. Vandersluis and A. L. Spek, *Acta Crystallogr. Sec. A*, 1990, **46**, 194-201.
6. A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.