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Supporting Information

3D Hydrogen-Bonded Porous Metal-Organic Framework for Natural Gas Separation with High Selectivity

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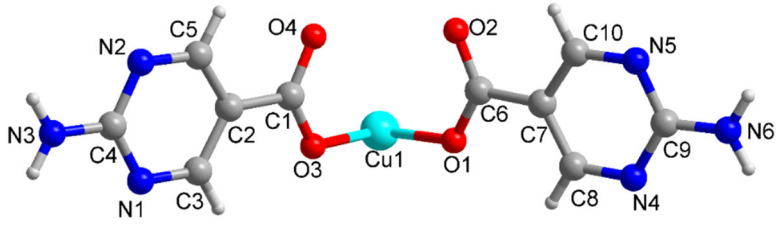

Figure S1. The asymmetric unit of compound **TJU-Dan-5**.

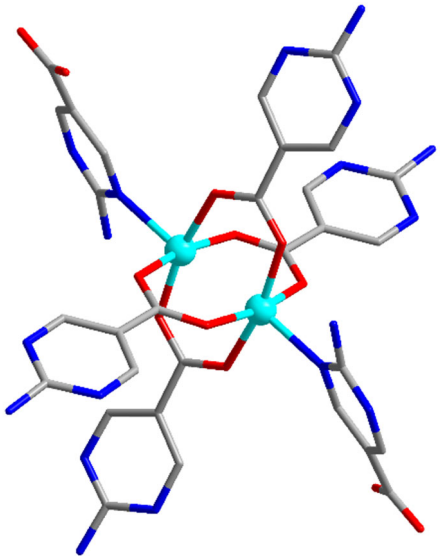

Figure S2. The coordinated environment around the metal center of **TJU-Dan-5** (Color code; Carbon: grey, oxygen: red, nitrogen: blue, copper: blue).

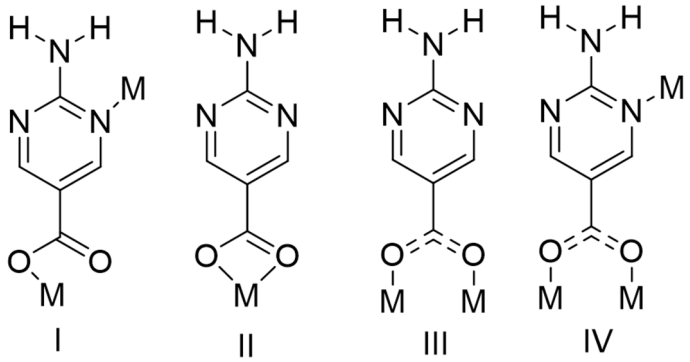

Figure S3. The coordination mode of Hapc.

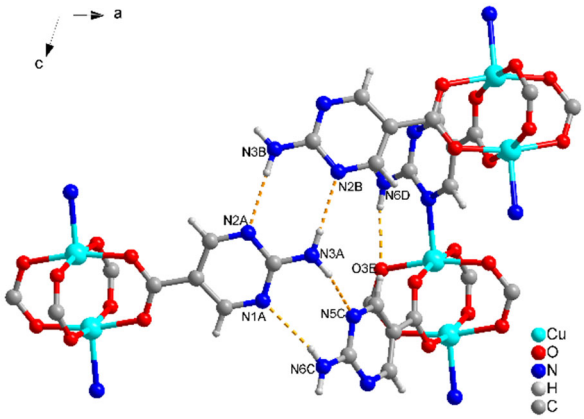

Figure S4. Hydrogen bonds in **TJU-Dan-5** (Symmetry codes: A: 1.5-x, 1.5-y, 1-z; B: 0.5+x, 1.5-y, -0.5+z; C: 2-x, 1-y, 1-z; D: 2-x, y, 0.5-z; E: 0.5+x, -0.5+y, z; orange dotted lines are added to highlight the Hydrogen bonds).

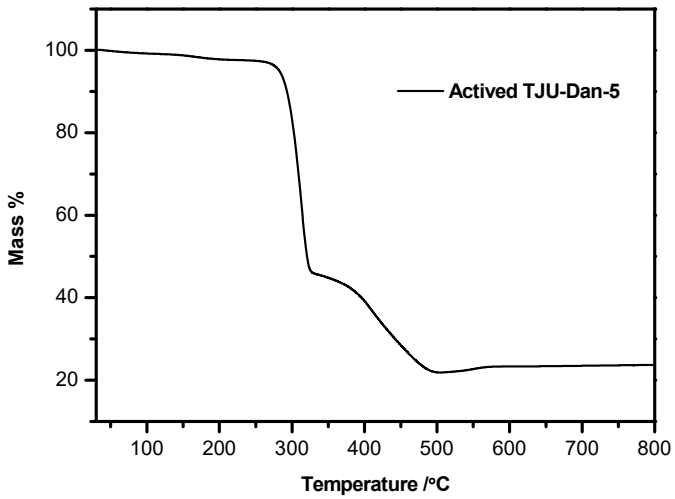

Figure S5. TGA curve of active **TJU-Dan-5**.

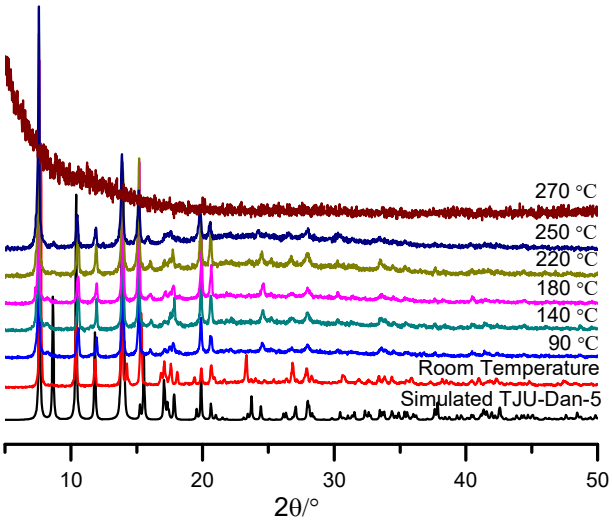

Figure S6. PXRD patterns of **TJU-Dan-5** in air from room temperature to 270 °C.

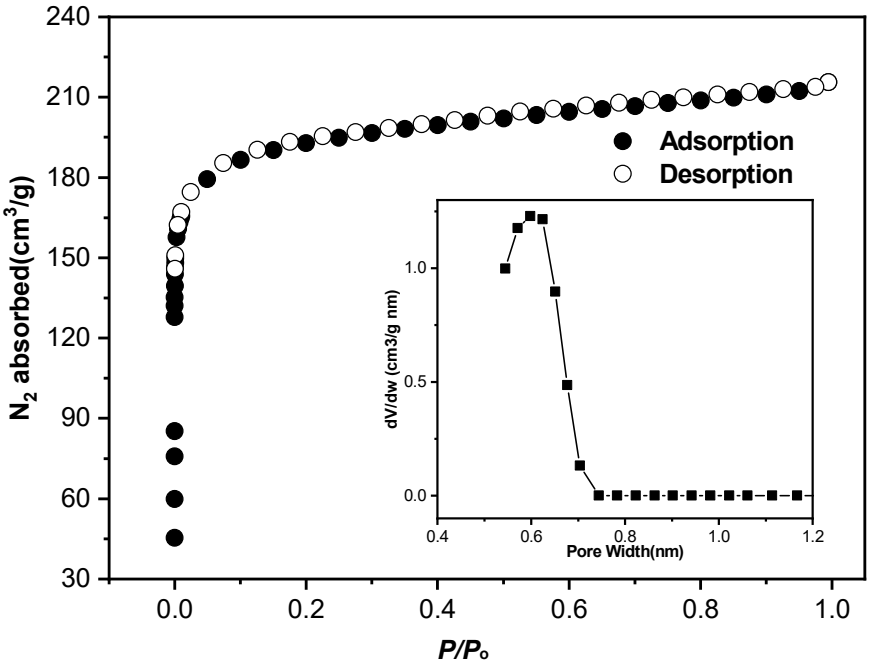

Figure S7. Nitrogen sorption isotherm of **TJU-Dan-5** at 77 K. The inset graph indicates the pore size distribution.

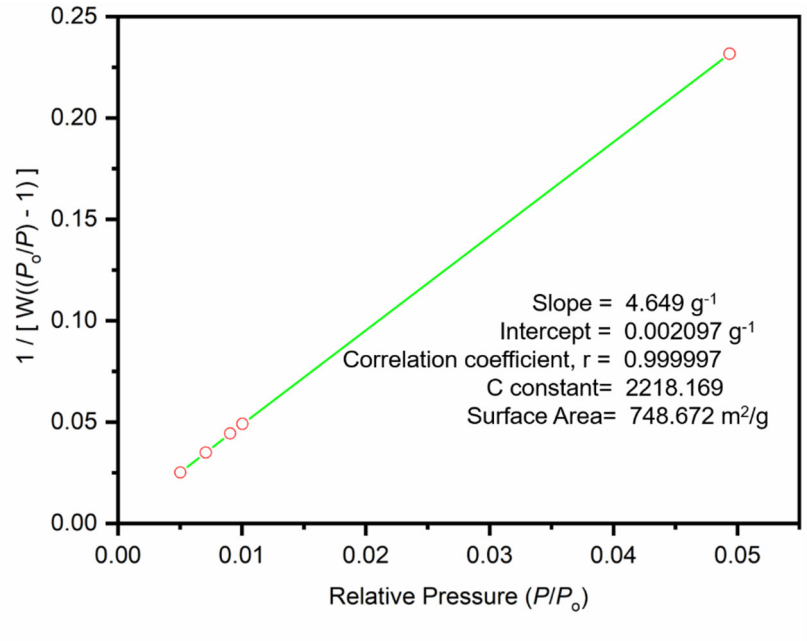

Figure S8. BET surface area plot for **TJU-Dan-5**

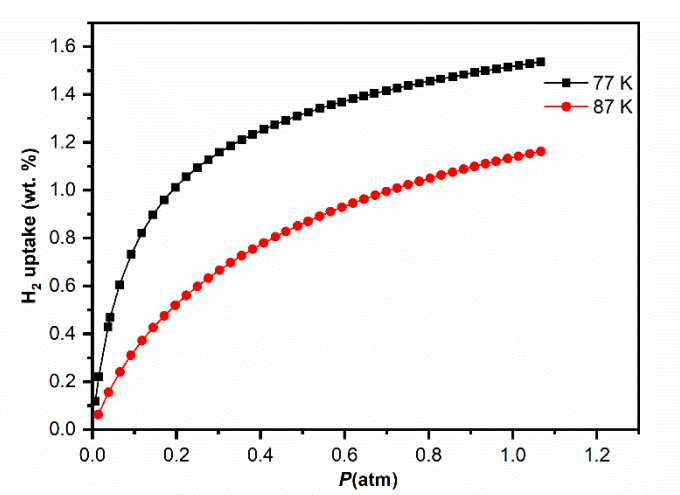

Figure S9. Hydrogen sorption isotherm of **TJU-Dan-5** at 77 K and 87 K.

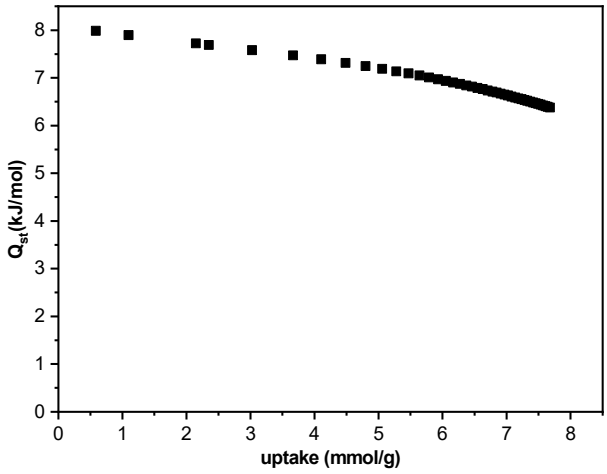

Figure S10. Isosteric heat of adsorption *Qst* of H_2 for **TJU-Dan-5**.

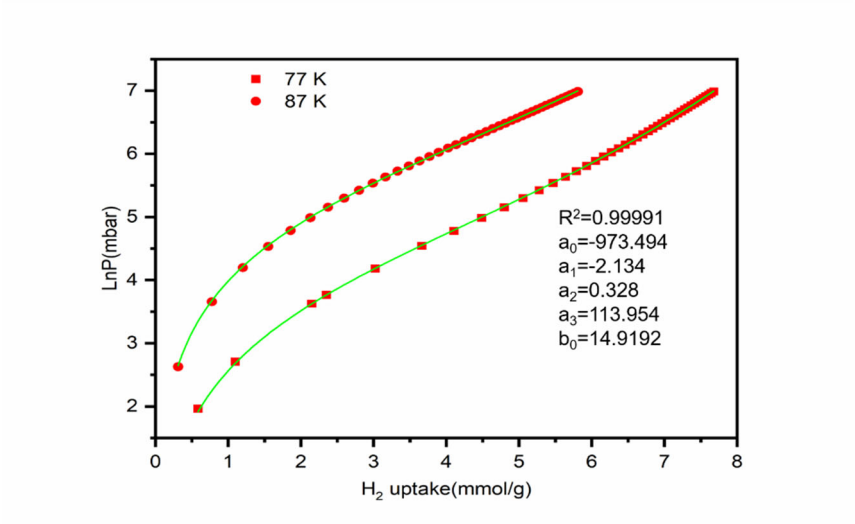

Figure S11. The H_2 isotherms at 77 K and 87 K (symbols) and the Virial equation fits (lines) for **TJU-Dan-5**

To perform the IAST calculations, an adsorption model is needed in order to fit a discrete set of adsorption data from single-component isotherms with a continuous function. Herein, we used a Dual-site Langmuir-Freundlich (DSLF, Equation (S1)) model for the fitting of the adsorption isotherms.

$$q = \frac{a \cdot b \cdot P^{x}}{1 + b \cdot P^{x}} + \frac{g \cdot k \cdot P^{y}}{1 + g \cdot P^{y}} \quad \text{(S1)}$$

P is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mmol/g), *a* and *q* are the saturation capacities of sites 1 and 2 (mmol/g), *b* and *k* are the

affinity coefficients of sites 1 and 2 (1/kPa), and *c* and *t* represent the deviations from an ideal homogeneous surface. R is the universal gas constant.

The adsorption selectivity for binary mixtures defined by Equation (S2).

$$S_{ij} = \frac{x_i/x_j}{y_i/y_j} \quad \text{(S2)}$$

where *S* is the selectivity factor, x_i represents the quantity adsorbed of component *i,* and y_i represents the partial pressure of component *i*.

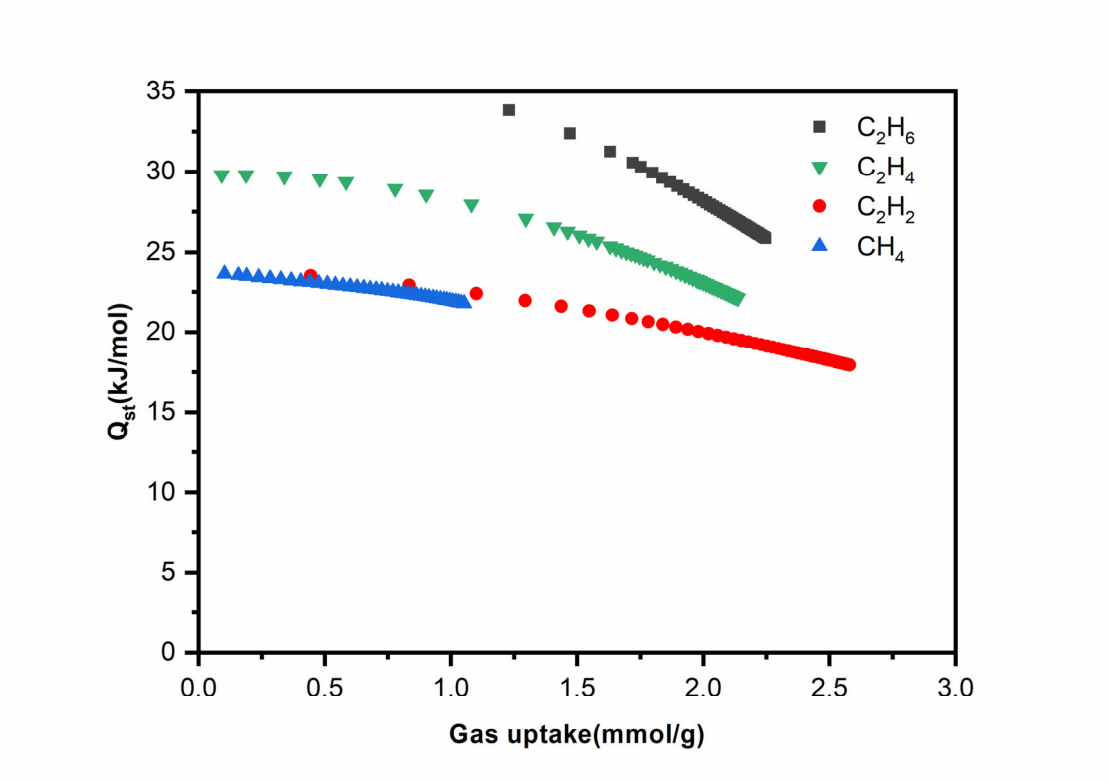

Figure S12. Isosteric heat of adsorption *Q*st of C_2H_6, C_2H_4, C_2H_2, CH_4 for **TJU-Dan-5**.

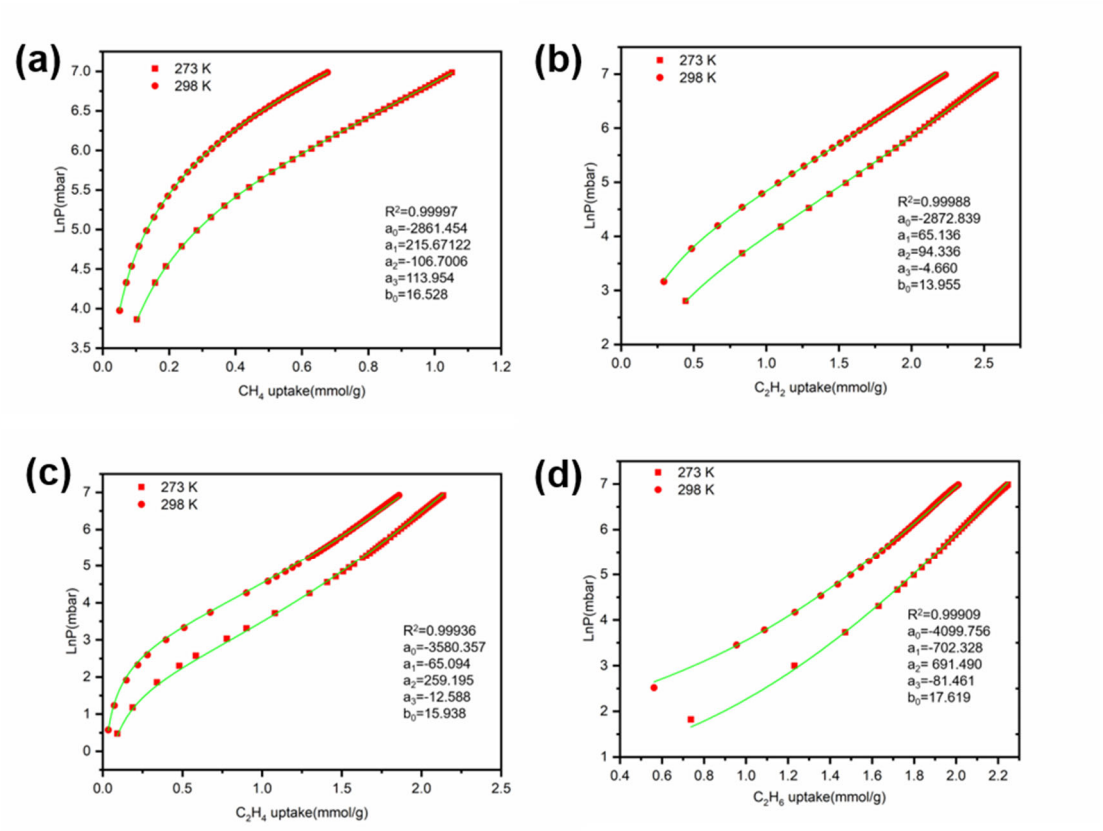

Figure S13. The gas isotherms at 273 K and 298 K (symbols) and the Virial equation fits (lines) for **TJU-Dan-5**: (a) CH_4, (b)C_2H_2, (c) C_2H_4, (d)C_2H_6.

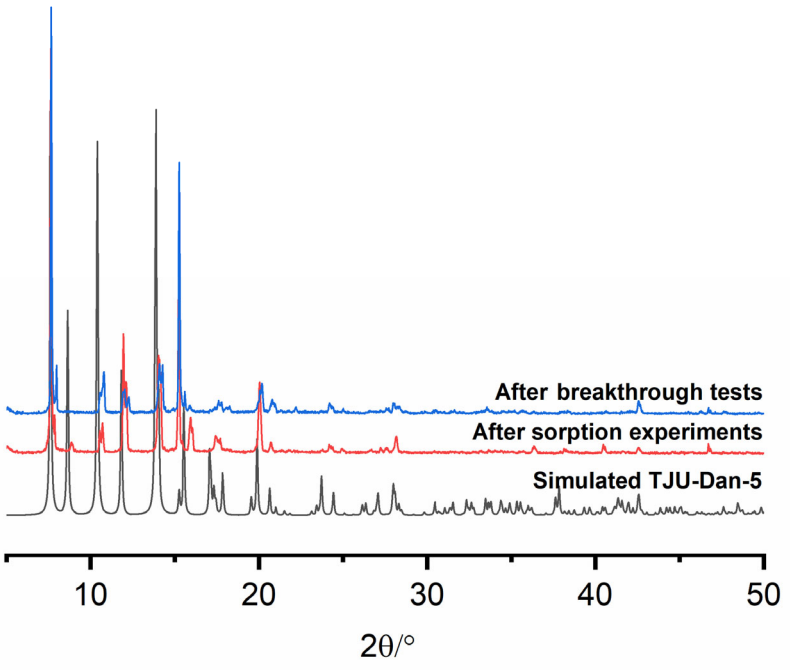

Figure S14. PXRD patterns of **TJU-Dan-5** after sorption experiments and breakthrough tests.

Table S1. Crystal data and structure refinement of **TJU-Dan-5**.

Entry	**TJU-Dan-5**
Empirical formula	$C_{10}H_8CuN_6O_4$
Formula weight	339.75
Temperature [K]	296(2)
Crystal system	monoclinic
Space group (number)	*C*2/*c* (15)
a [Å]	24.306(6)
b [Å]	11.394(3)
c [Å]	13.189(3)
α [°]	90
β [°]	107.218(7)
γ [°]	90
Volume [Å^3]	3489.1(15)
Z	8
ρ_{calc} [g·cm^{-3}]	1.294
μ [mm^{-1}]	1.272
F(000)	1368
Crystal size [mm^3]	0.200×0.120×0.030
Crystal colour	blue
Crystal shape	plate
Radiation	MoK_α (λ=0.71073 Å)
2Θ range [°]	6.47 to 51.46 (0.82 Å)
Index ranges	$-29 \le h \le 29$
	$-13 \le k \le 13$
	$-16 \le l \le 16$
Reflections collected	28193
Independent reflections	3277
R_{int}	0.0646
R_{sigma}	0.0379
Completeness to Θ = 25.242°	99.6 %
Data / Restraints / Parameters	3277/0/190
Goodness-of-fit on F^2	1.059
Final *R* indexes	R_1 = 0.0555
[$I \ge 2\sigma(I)$]	wR_2 = 0.1544
Final *R* indexes	R_1 = 0.0674
[all data]	wR_2 = 0.1623
Largest peak/hole [e·Å^{-3}]	1.12/-0.47

Table S2. Selected bond lengths (Å) and angles (º) for **TJU-Dan-5**.

TJU-Dan-5			
Cu1–O3	1.972(4)	Cu1–O1	1.976(4)
Cu1–O2$^{\#1}$	1.973(4)	Cu1–N4$^{\#2}$	2.177(4)
Cu1–O4$^{\#1}$	1.975(4)	C1–O4	1.258(6)
O1–C6	1.264(6)	C1–O3	1.265(6)
N1–C3	1.314(7)	C1–C2	1.485(7)
N1–C4	1.348(7)	C2–C3	1.397(7)
O2–C6	1.254(6)	N3–C4	1.322(7)
N2–C5	1.328(7)	N5–C9	1.356(7)
N2–C4	1.356(7)	C6–C7	1.494(7)
C2–C5	1.375(7)	N6–C9	1.334(7)
N4–C8	1.341(6)	C7–C10	1.399(8)
N4–C9	1.357(7)	N5–C10	1.322(8)
O3–Cu1–O2	88.92(18)	C6–O1–Cu1	123.1(3)
O3–Cu1–O4	168.06(14)	C6–O2–Cu1	122.7(4)
O2–Cu1–O4	90.49(18)	C1–O3–Cu1	120.0(3)
O3–Cu1–O1	89.24(18)	C1–O4–Cu1	125.9(3)
O2–Cu1–O1	168.04(15)	C8–N4–Cu1	116.8(3)
O4–Cu1–O1	88.87(18)	C9–N4–Cu1	125.4(3)
O3–Cu1–N4	99.74(15)	O4–Cu1–N4	92.17(15)
O2–Cu1–N4	96.63(16)	O1–Cu1–N4	95.33(16)

Table S3. Hydrogen bonds for **TJU-Dan-5**.

D–H···A [Å]	**d(D–H) [Å]**	**d(H···A) [Å]**	**d(D···A) [Å]**	**<(DHA) [°]**
N3–H3A···N5$^{\#1}$	0.86	2.32	3.051(7)	142.5
N3–H3B···N2$^{\#2}$	0.86	2.13	2.984(6)	169.5
N6–H6B···O3$^{\#3}$	0.86	2.18	2.988(6)	155.3
N6–H6A···N1$^{\#4}$	0.86	2.33	3.054(6)	142.3

Symmetry transformations used to generate equivalent atoms:

#1: -0.5+X, 0.5+Y, +Z; #2: 1-X, +Y, 1.5-Z; #3: 1.5-X, -0.5+Y, 0.5-Z; #4: 0.5+X, -0.5+Y, +Z;

Table S4. Parameters for DSLF isotherm fits at 298 K.

	a	b	c	q	k	t	R^2
CH_4@TJU-Dan-5	0.07245	0.05856	0.97662	1.66511	0.00324	1.10952	0.9999
C_2H_2@TJU-Dan-5	1.10086	0.13390	1	1.81175	0.001683	1	0.9988
C_2H_4@TJU-Dan-5	1.40516	0.16663	1.09161	1.15993	0.01219	0.89703	1
C_2H_6@TJU-Dan-5	1.26825	0.43525	1.10229	1.59914	0.06749	0.55141	0.9999