Electronic Supplementary Information (ESI)

A new *mfj*-tpye Metal-Organic Framework Constructed from Methoxyl Derived V-shaped Ligand and Its H_2, CO_2 and CH_4 Adsorption Properties

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SECTION S1. Crystal structure

Table S1. Crystal Data for NJFU-3.

	NJFU-3
CCDC number	1532967
Empirical formula	$C_{69}\ H_{36}\ Cu_6\ O_{33}$
Formula weight	1774.28
crystal system	orthorhombic
Space group	*Cmc2₁*
a [Å]	24.742(3)
b [Å]	33.475(3)
c [Å]	18.4621(19)
α [deg]	90
β [deg]	90
γ [deg]	90
V [Å^3]	15291(3)
Z	4
T [K]	296(2)
ρ_{calc} [g cm^{-3}]	0.771
R1, wR2[a] [$I>2\sigma(I)$]	0.0729; 0.1842
R1, wR2[a] [all data]	0.1022; 0.1967

[a] $R1 = \Sigma||F_o| - |F_c||/|F_o|$; $wR2 = [\Sigma w(\Sigma F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

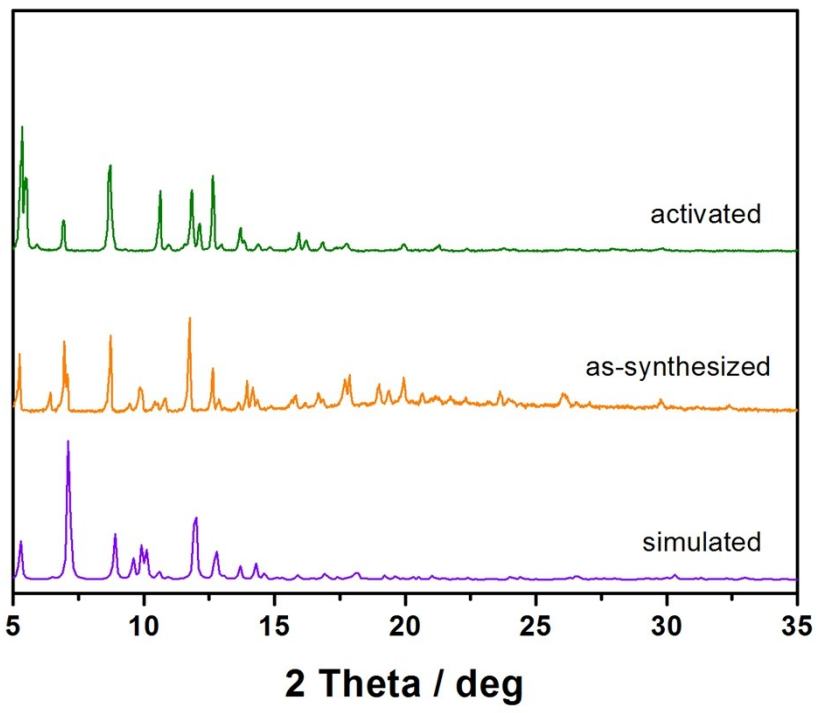

Figure S1. PXRD patterns of NJFU-3.

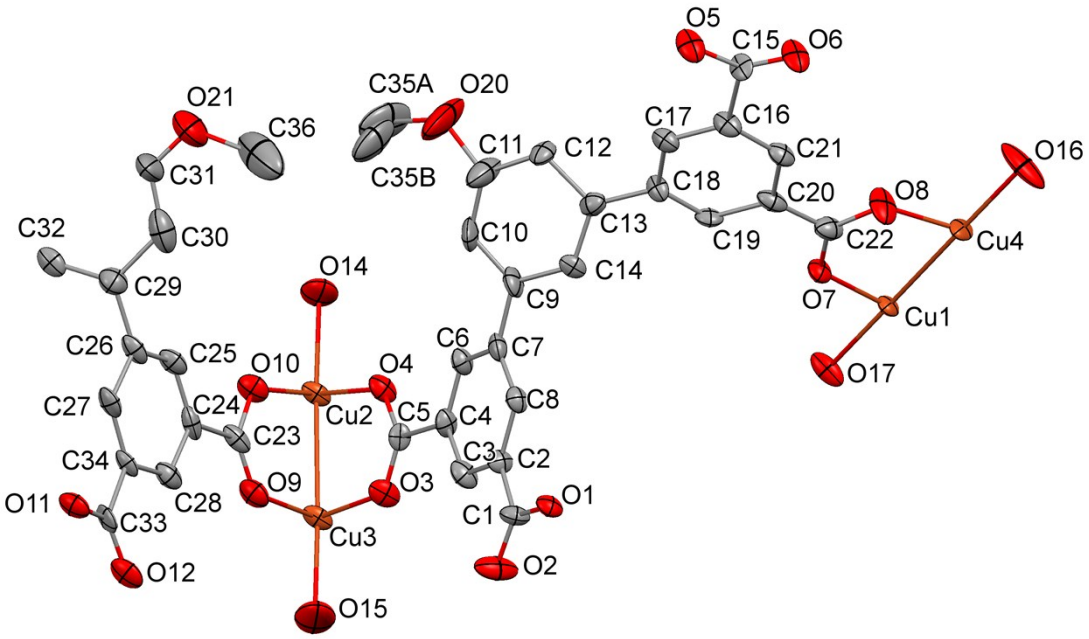

Figure S2. The asymmetric structural unit of NJFU-3.

SECTION S2. BET Surface Area Analysis

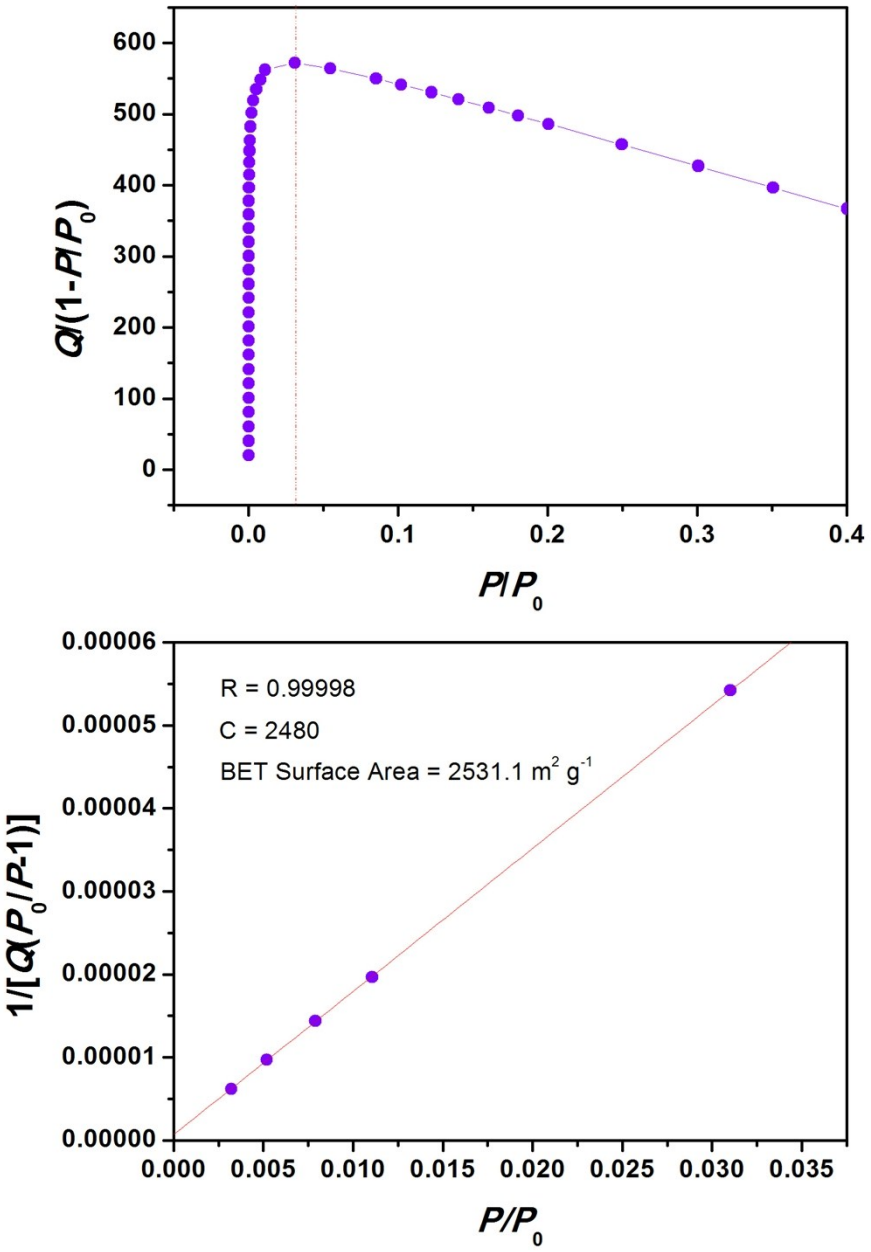

Figure S3. Top: $Q(1-P/P_0)$ vs. P/P_0 for simulated N_2 isotherm in NJFU-3. Only the range below $P/P_0 = 0.04$ satisfies the first consistency criterion for application of the BET theory. Bottom: Plot of the linear region for the BET equation, which satisfies the second criterion for application of the BET theory.

SECTION S3. Langmuir Surface Area Analysis

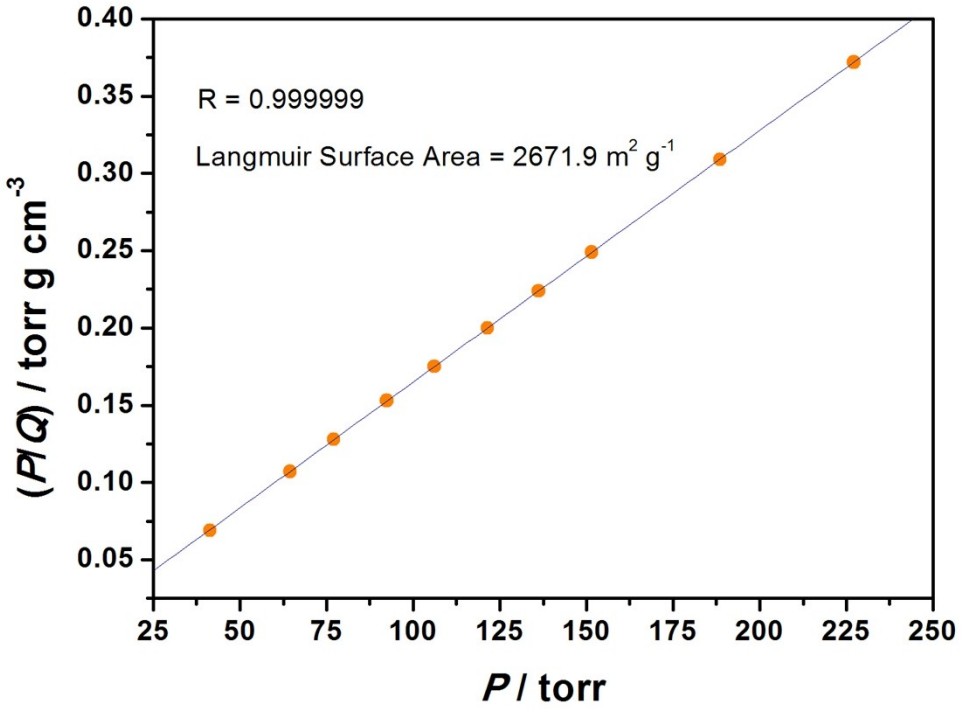

Figure S4. Langmuir equation fitting curve for NJFU-3's N_2 isotherm (adsorption branch data points, P/P0 = 0.1–0.3).

SECTION S4. Estimation of the isosteric heats of gas adsorption.

A virial-type expression comprising the temperature-independent parameters a_i and b_i was employed to calculate the enthalpies of adsorption for H_2 (at 77 and 87 K) and CO_2 (at 273 and 298 K). The data were fitted using the equation:

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \quad (1)$$

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_i 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).

$$Q_{st} = -R\sum_{i=0}^{m} a_i N^i \quad (2)$$

Here, Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant.

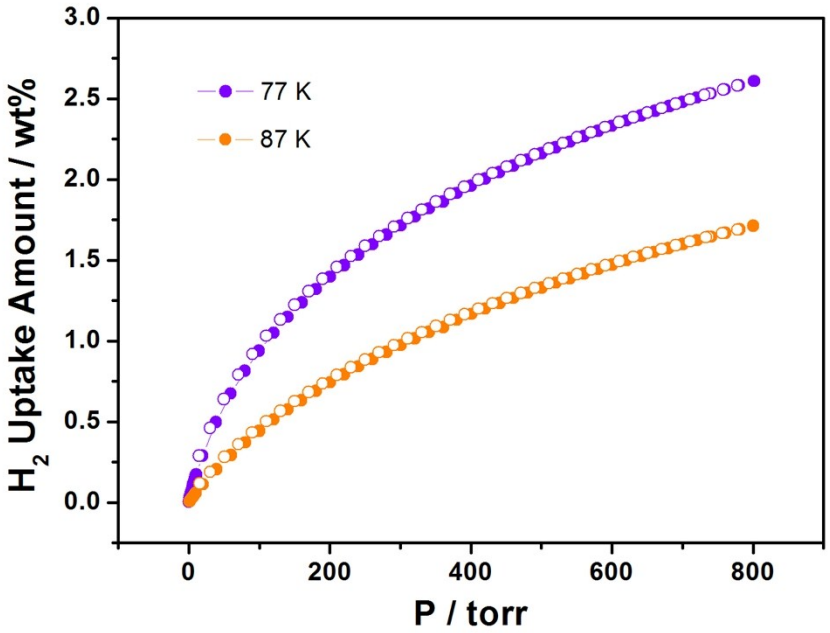

Figure S5. The H_2 adsorption isotherms of NJFU-3 at 77 K and 87 K.

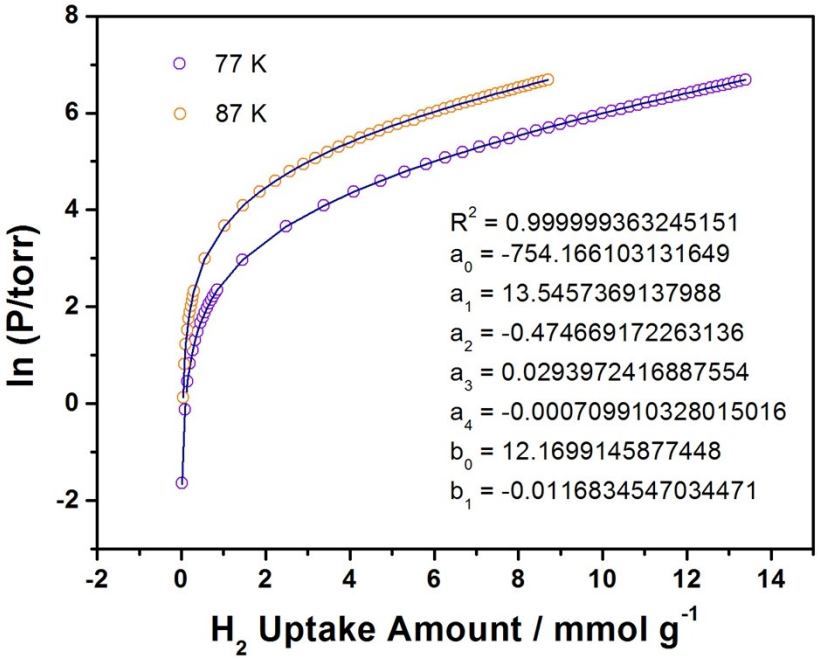

Figure S6. The details of virial equation (solid lines) fitting to the experimental H_2 adsorption data (symbols) for NJFU-3.

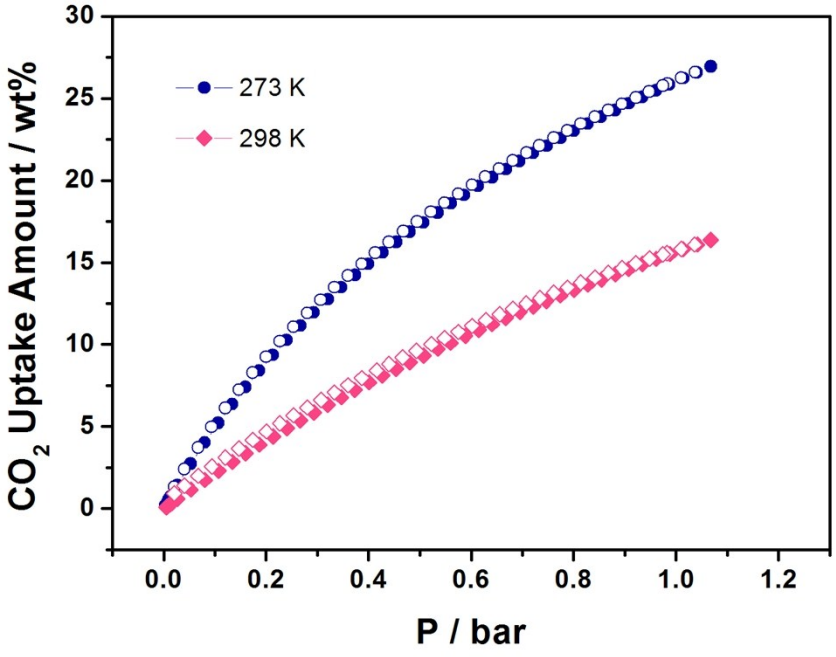

Figure S7. The CO_2 adsorption isotherms of NJFU-3 at 273 K and 298 K.

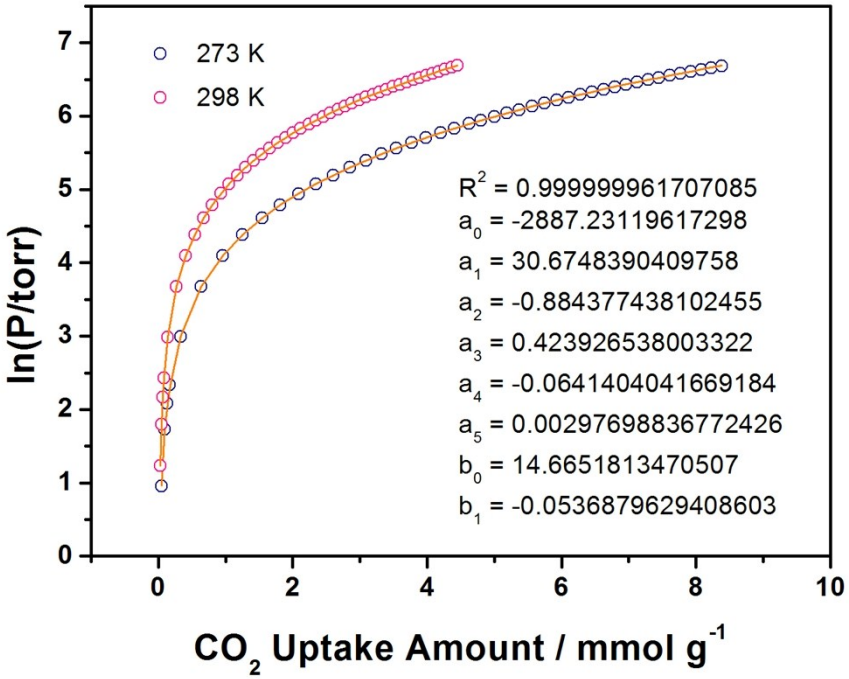

Figure S8. The details of virial equation (solid lines) fitting to the experimental CO_2 adsorption data (symbols) for NJFU-3.

SECTION S5. IAST adsorption selectivity calculation.

Dual site Langmuir-Freundlich model for CO_2/CH_4 adsorption isotherms:

$$N = \frac{N_{m,1} b_1 p^{1/n_1}}{1 + b_1 p^{1/n1}} + \frac{N_{m,2} b_2 p^{1/n_2}}{1 + b_2 p^{1/n_2}}$$

Where p (unit: KPa) is the pressure of the bulk gas at equilibrium with the adsorbed phase, N is the adsorption quantity, $N_{m,1}$ and $N_{m,2}$ are the saturation capacities of sites 1 and 2, b_1 and b_2 (unit: 1/KPa) are the affinity coefficients of sites 1 and 2, and n_1 and n_2 represent the deviations from an ideal homogeneous surface. Here, the single-component CO_2 and CH_4 adsorption isotherms have been fit to enable the application of IAST in simulating the performance of NJFU-3a under a mixed component gas. The fitting parameters of DSLF equation are listed in Table S2.

Table S2 Dual site Langmuir-Freundlich fitting parameters for gas adsorption for NJFU-3a.

Adsorbates	$N_{m,1}$	b_1	$1/n_1$	$N_{m,2}$	b_2	$1/n_2$
CO_2 (273 K)	64.8928	0.0016246	0.92159	1.7460	0.01169	1.2662
CH_4 (273 K)	0.38390	0.015170	0.99193	15.909	0.000715	1.0430

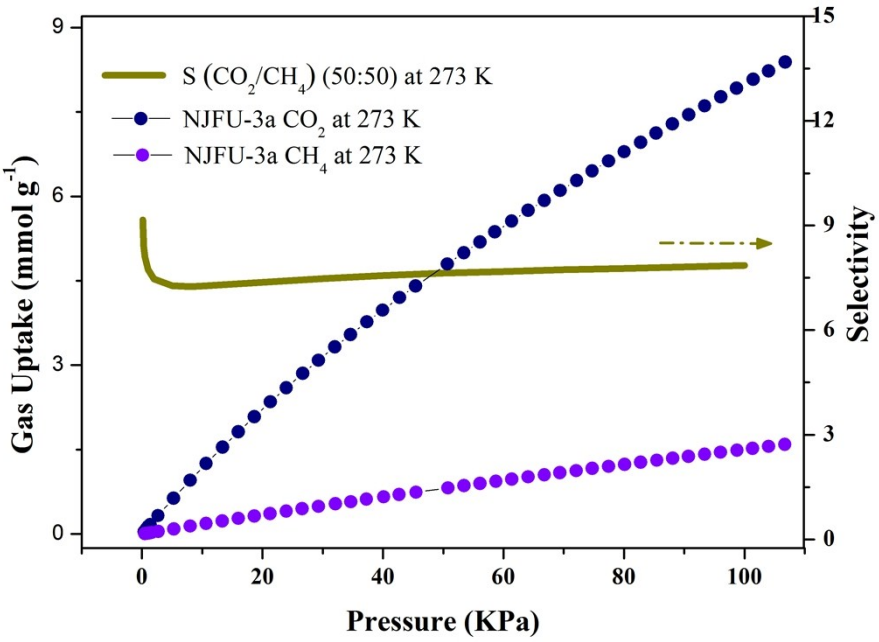

Figure S9. Mixture adsorption isotherms and adsorption selectivity predicted by IAST of NJFU-3a for CO_2 (50%) and CH_4 (50%) at 273 K.

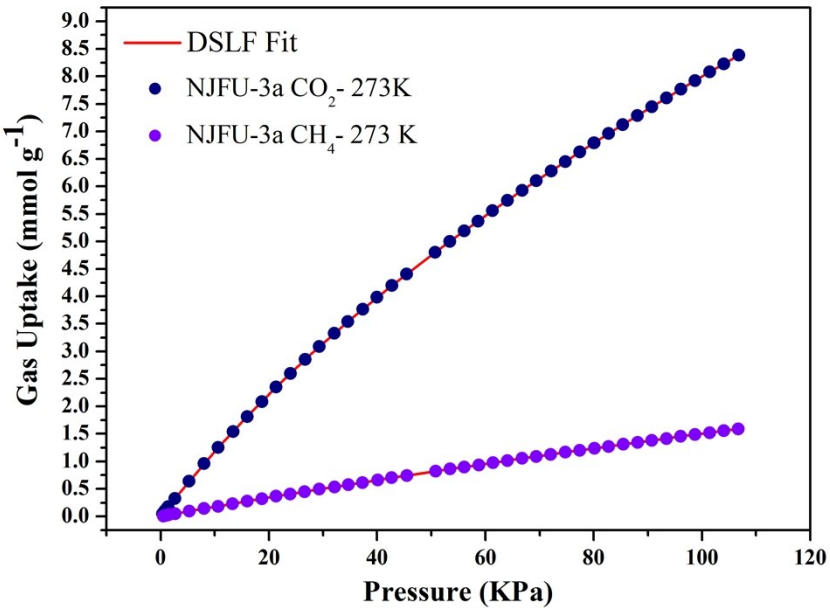

Figure S10. DSLF models fitting for the CO_2 and CH_4 adsorption isotherms of NJFU-3a. Dots are experimental data; lines are fitting curves.

SECTION S6. Thermal stability.

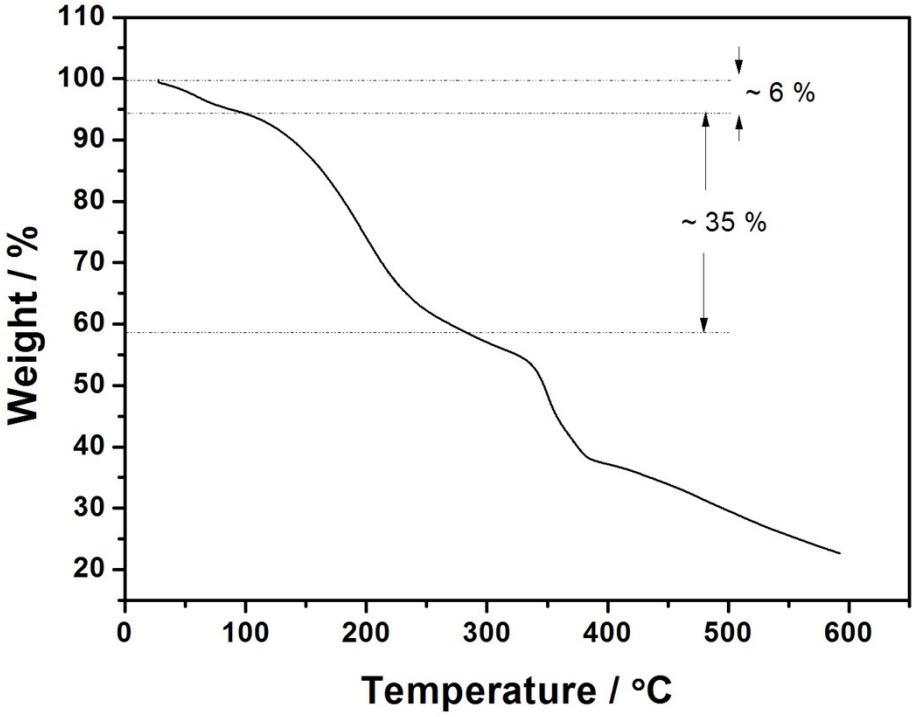

Figure S11. TG curve of NJFU-3.