

Electronic Supplementary Information

A New Methyl-embedded (3,36)-connected *Txt*-type Metal-Organic Framework Exhibiting High H₂ Adsorption Property

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Section S1. Experimental Section

1. Materials and General methods.

All chemical reagents were obtained from commercial sources and, unless otherwise noted, were used as received without further purification. The IR spectra were recorded in the 400-4000 cm^{-1} on a VECTOR TM 22 spectrometer using KBr pellets. ^1H NMR spectra were recorded on a Bruker DRX-500 MHz spectrometer with tetramethylsilane as an internal reference. Thermal gravimetric analyses (TGA) were performed under N_2 atmosphere (100 ml/min) with a heating rate of 5 $^\circ\text{C}/\text{min}$ using a 2960 SDT thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 ADVANCE X-ray diffractometer with $\text{Cu K}\alpha$ radiation.

2. Synthesis of the ligand

Preparation of 3,5-bis(3,5-dicarboxylphenylethynyl)-4-methylpyridine (H_4DCPEMP): Into a flask flushed with N_2 , 3,5-dibromo-4-methylpyridine (5 g, 20 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (1.47 g, 2.1 mmol) and CuI (0.78 g, 8.4 mmol) were added to a solution of tetrahydrofuran (50 mL) and Et_3N (50 mL). After stirring for half an hour, trimethylsilylacetylene (8 mL, 51.0 mmol) was added. Then the solution was refluxed at 50 $^\circ\text{C}$ overnight under nitrogen atmosphere. The resultant mixture was evaporated to dryness and taken up in CH_2Cl_2 and washed with brine for three times. The organic layer was dried over MgSO_4 and filtered. The volatiles were removed by evaporation under reduced pressure, and then the crude dark product was purified by column chromatography on silica gel with 4:1 $\text{CH}_2\text{Cl}_2/\text{hexane}$ to give dark brown solid. 4.22 g (14.8 mmol) of the product was then dissolved in $\text{MeOH}/\text{H}_2\text{O}$ ($v/v = 2:1$, 30 mL), and KOH (2 g, 32.5 mmol) was added with stirring overnight. The volatiles were removed by evaporation under reduced pressure. The residue was dissolved in CH_2Cl_2 and washed with water. The organic layer was dried over MgSO_4 and filtered. After evaporation under reduced pressure, the crude yellow product obtained was further purified by column chromatography on silica gel with CH_2Cl_2 to give pale yellow solid of 3,5-diethynyl-4-methylpyridine with yield of 1.5 g (53.4%).

Into a flask flushed with N_2 , diethyl 5-iodoisophthalate (5.92 g, 17.0 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.43 g, 0.61 mmol) and CuI (0.193 g, 1.02 mmol) were added to a solution of tetrahydrofuran (40 mL) and Et_3N (40 mL). After stirring for half an hour, 3,5-diethynyl-4-methylpyridine (1.14 g, 8.1 mmol) was added. Then the solution was stirring overnight under nitrogen atmosphere. The resultant mixture was evaporated to dryness and taken up in CH_2Cl_2 and washed with brine for three times. The organic layer was dried over MgSO_4 and filtered. The volatiles were removed by evaporation under reduced pressure, and then the crude yellow product was slightly washed with PE/EA ($v/v = 9:1$) to give pale yellow solid of 2 g (42.5 %). The product was then dissolved in $\text{THF}/\text{H}_2\text{O}$ ($v/v = 5:3$, 160 mL), and KOH (2.40 g, 42.8 mmol) was added with stirring under reflux overnight. The volatiles were removed by evaporation under reduced pressure. The residue dissolved in 100 mL of water was acidified to $\text{pH} \approx 2 \sim 3$ using 1.0M HCl and stirred for 3 hours. The precipitate was separated by filtration, washed with water, and dried. Yield=1.50g (93.2%). ^1H NMR (500 MHz, $\text{DMSO}-d_6$, δ ppm): 13.55 (s, 4H, COOH), 8.77 (s, 2H, ArH), 8.47 (s, 2H, ArH), 8.31 (s, 4H, ArH), 2.71 (s, 3H, CH_3). IR (KBr, cm^{-1}): 3142, 2931, 2858, 1758, 1640, 1617, 1587, 1479, 1399, 1384, 1256, 1141, 1118, 1065, 990, 950, 861.

3. Synthesis of NJFU-4 $[\text{Cu}_2(\text{DCPEMP})\cdot\text{H}_2\text{O}]_n\cdot x(\text{solv})$

A mixture of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (19.3 mg, 0.12 mmol), H_4DCPEMP (5.63 mg, 0.012 mmol), HNO_3 (60 μL , 16 mol/L) and $\text{DMF}/\text{H}_2\text{O}$ (5: 1 in volume) (2 mL) was stirred for 10 min in air and sealed in a 20 mL Teflon-lined autoclave, which was heated at 65 $^\circ\text{C}$ for 72 h. After cooling to the room temperature, green octahedron-shaped crystals were obtained. The crystals of NJFU-4 were filtered and washed with fresh DMF. Yield: $\sim 60\%$ based on the ligand. Selected IR (KBr, cm^{-1}): 3432, 3075, 2929, 1663, 1595, 1558, 1421, 1374, 1289, 1254, 1194, 1150, 1097, 1049,

1031, 915, 887, 801, 775, 730, 700.

Section S2. Crystal Structure

Single crystal suitable for X-ray structure determination were selected and sealed in a capillary under a microscope. The X-ray diffraction intensity data were measured on a Bruker Smart Apex CCD diffractometer at room temperature using graphite monochromated Mo/K α radiation ($\lambda = 0.71073 \text{ \AA}$). 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. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atom. The unit cell includes a large region of disordered solvent molecules, which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE 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. Crystal data and refinement conditions are shown in Table S1. The crystal data for NJFU-4 have been deposited in CSD database, and labeled as 1509051. Copies of the data can be obtained, free of charge, on application to the CCDC (e-mail: deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinement for NJFU-4.

Identification code	NJFU-4
CCDC number	1509051
Empirical formula	C ₂₆ H ₁₁ Cu ₂ N O ₉
Formula weight	608.46
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	<i>I</i> <i>m</i> -3 <i>m</i>
<i>a</i>	31.0977(16) Å
<i>b</i>	31.0977(16) Å
<i>c</i>	31.0977(16) Å
α	90°
β	90°
γ	90°
Volume	30074(5) Å ³
<i>Z</i>	24
Density (calculated)	0.806 g cm ⁻³
Absorption coefficient	0.876 mm ⁻¹
F(000)	7296
Crystal size	0.20 × 0.1 × 0.1 mm
Theta range for data collection	0.93 to 28.29 °
Limiting indices	-41 ≤ <i>h</i> ≤ 31, -39 ≤ <i>k</i> ≤ 41, -36 ≤ <i>l</i> ≤ 41
Reflections collected unique	110179 / 3543 [R(int) = 0.1554]
Completeness	100 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.916 and 0.9

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3543 / 18 / 107
Goodness-of-fit on F^2	1.054
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0539, wR2 ^a = 0.1382
R indices (all data)	R1 = 0.1020, wR2 ^a = 0.1491
Largest diff. peak and hole	1.030 and -0.600 e. \AA^{-3}

$$^a R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}.$$

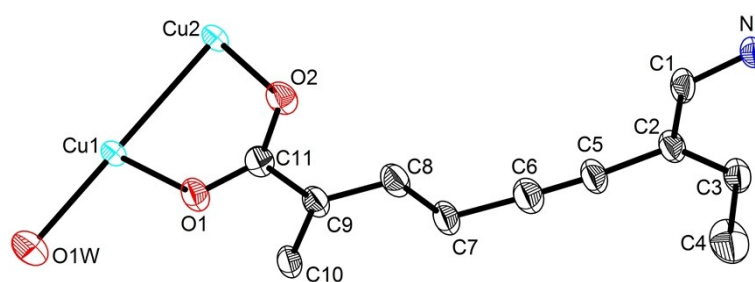


Figure S1. The asymmetric structural unit of NJFU-4.

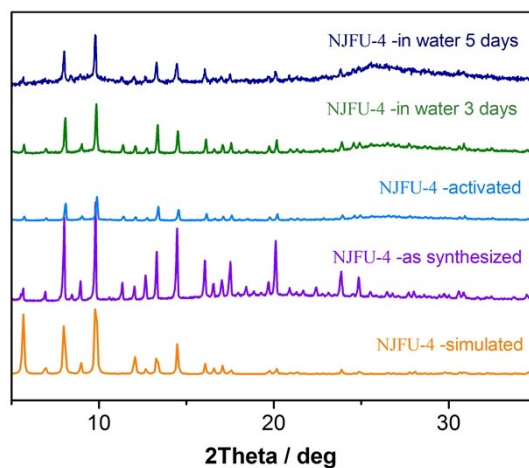


Figure S2. PXRD patterns of NJFU-4: the simulated (orange), as-synthesized (violet), activated (sky blue) and in water 3 days (olive).

Section S3. BET Surface Area Analyses

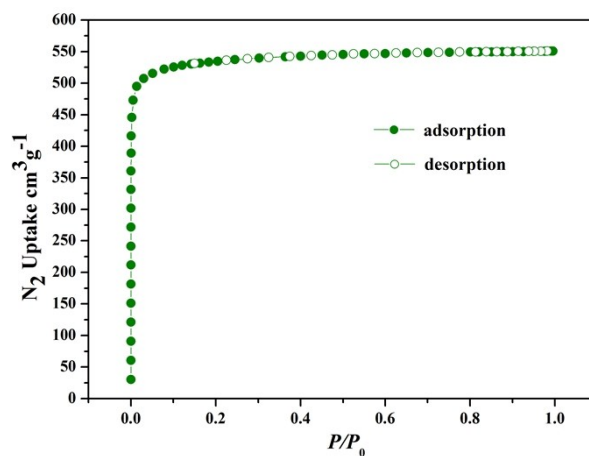


Figure S3. Nitrogen adsorption isotherm at 77 K. Adsorption (filled circles), desorption (open circles).

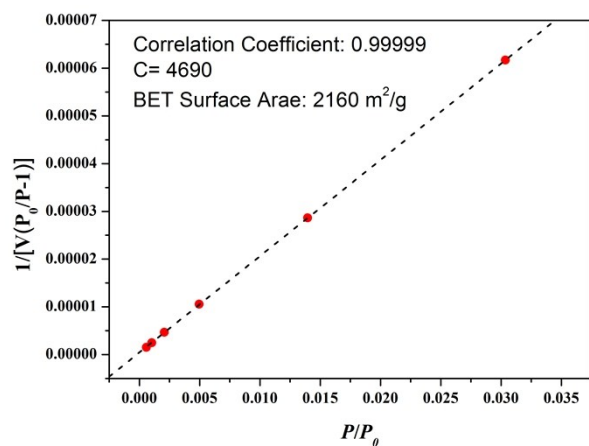


Figure S4. Plot of the linear region for the BET equation, which satisfies the second consistency criteria for application of the BET theory: (1) The pressure range selected should have values of $Q(P_0-P)$ increasing with P/P_0 . (2) The y intercept of the linear region must be positive to yield a meaningful value of the c parameter, which should be greater than zero.

Section S4. Gas Adsorption Isotherms

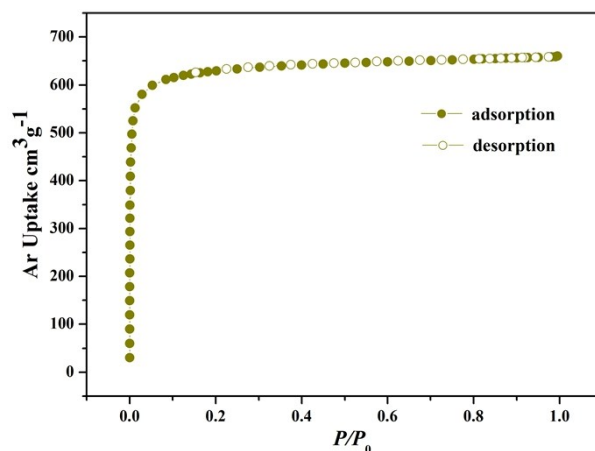


Figure S5. Ar sorption isotherm at 87 K. Adsorption (filled circles), desorption (open circles).

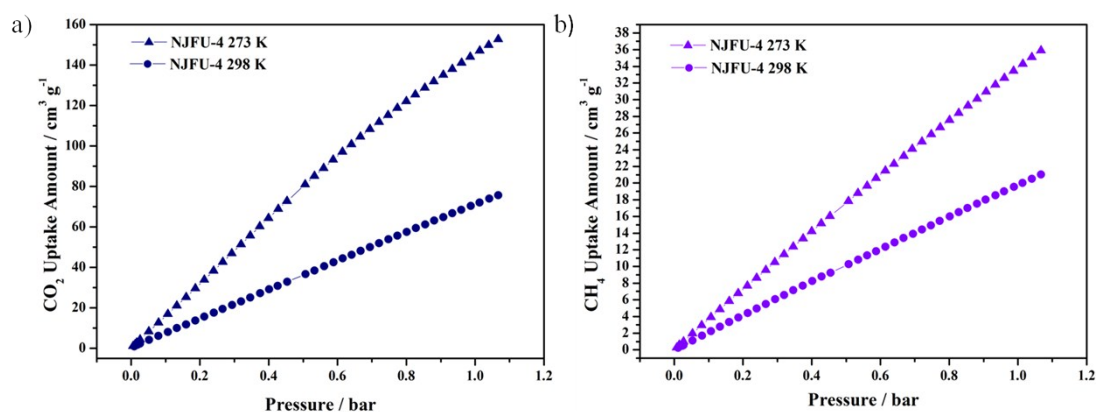


Figure S6. CO₂ a) and CH₄ b) adsorption isotherms of NJFU-4 at low pressure range (0~1 bar).

Section S5. Estimation of the Isothermic 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 H₂, CO₂ and CH₄. 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.

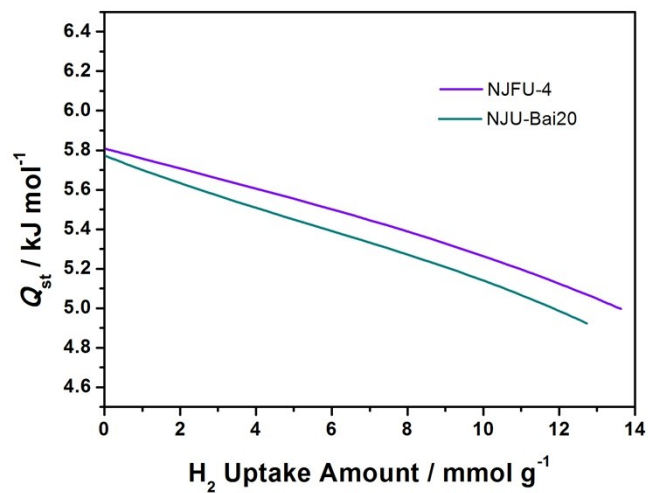


Figure S7. The H₂ adsorption enthalpies for NJFU-4 and NJU-Bai20 calculated from the adsorption isotherms at 87 K and 77 K through the virial method.

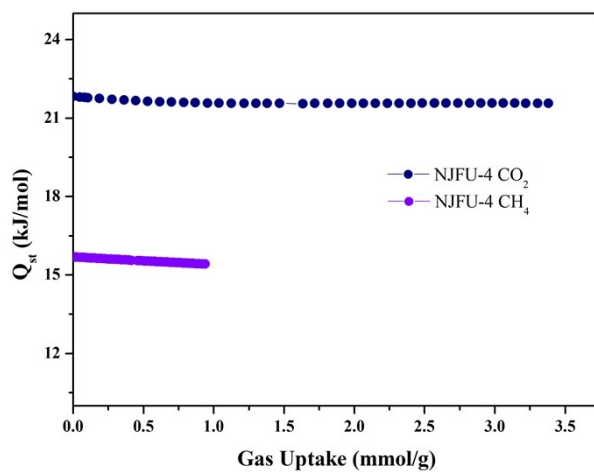


Figure S8. The CO₂ and CH₄ adsorption enthalpies for NJFU-4 calculated from the adsorption isotherms at 298 K and 273 K through the virial method.

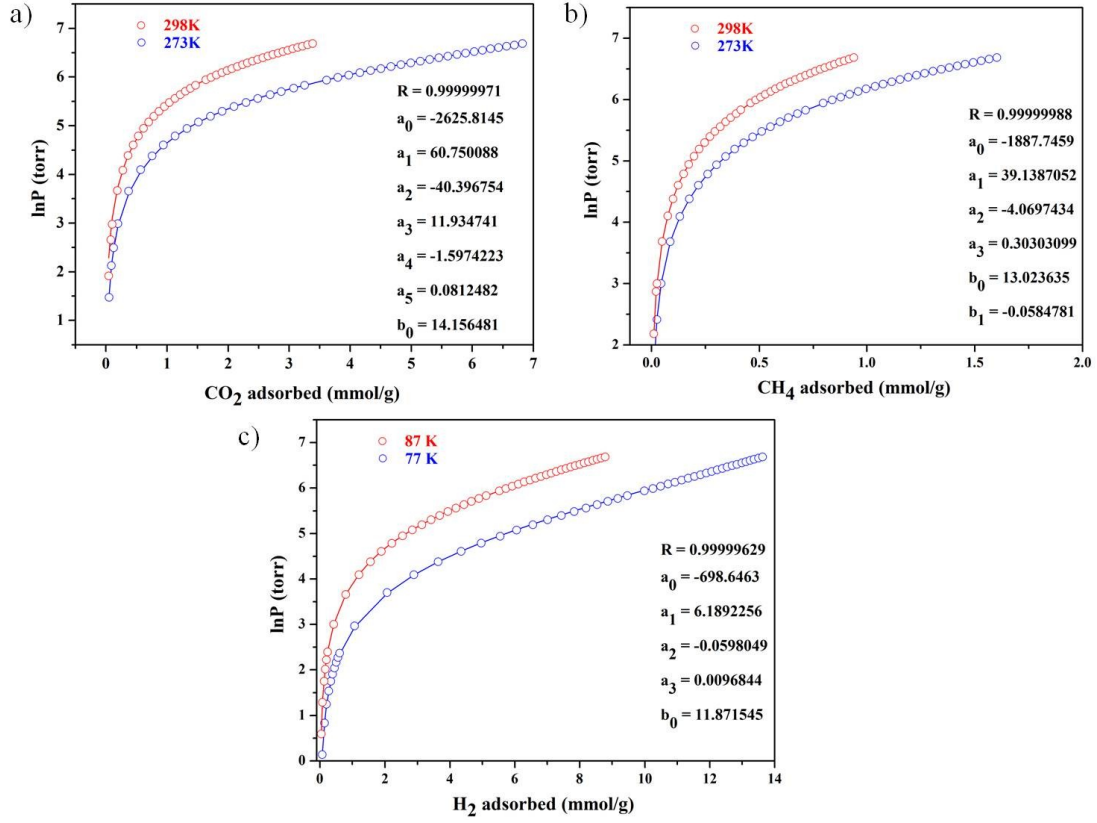


Figure S9. The gas isotherms (red and blue symbols, respectively) and the corresponding virial equation fits (red and blue lines, respectively) for NJFU-4. (a-b): CO₂ and CH₄ at 273 K and 298 K; (c): H₂ at 77 K and 87 K.

SECTION S6. Dual-site Langmuir-Freundlich (DSLFF) Fits of Pure Component Isotherms.

The pure component isotherm data for CO₂ and CH₄ in NJFU-4 were fitted with dual-site Langmuir-Freundlich isotherm model.

$$q = q_{m1} \cdot \frac{b_1 \cdot P^{1/n_1}}{1 + b_1 \cdot P^{1/n_1}} + q_{m2} \cdot \frac{b_2 \cdot P^{1/n_2}}{1 + b_2 \cdot P^{1/n_2}} \quad (3)$$

Here, P is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mol/kg), q_{m1} and q_{m2} are the saturation capacities of sites 1 and 2 (mol/kg), b_1 and b_2 are the affinity coefficients of sites (1/kPa), and n_1 and n_2 represent the deviations from an ideal homogeneous surface. Figure S11 show that the dual-site Langmuir-Freundlich equation fits the single-component isotherms extremely well. The R^2 values for all the fitted isotherms were over 0.99999. Hence, the fitted isotherm parameters were applied to perform the necessary integrations in IAST. The binary mixture of CO₂/CH₄ is calculated as a 50/50 composition. The adsorption selectivity defined by

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \quad (4)$$

can be determined using the IAST theory.

In equation (4), q_1 and q_2 are the absolute component loadings of the adsorbed phase in the mixture. In all the

calculations to be presented below, the calculation of S_{ads} is based on the use of the Ideal Adsorbed Solution Theory of Myers and Prausnitz.

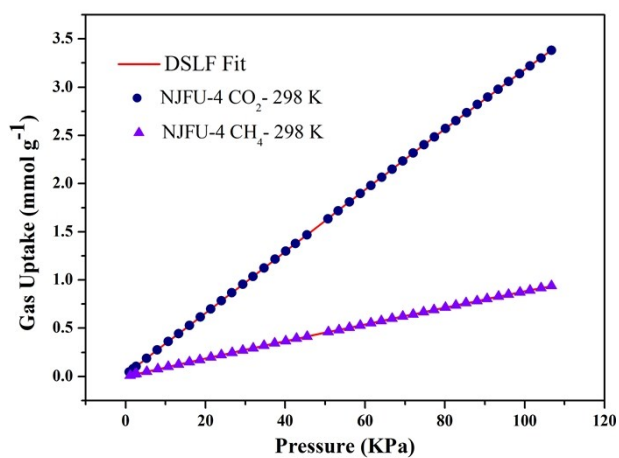


Figure S10. DSLF models fitting for the CO₂ and CH₄ adsorption isotherms of NJFU-4. Dots are experimental data; lines are fitting curves.

Table S2 Dual site Langmuir-Freundlich fitting parameters for gas adsorption for NJFU-4.

Adsorbates	$N_{m,1}$	b_1	$1/n_1$	$N_{m,2}$	b_2	$1/n_2$
CO ₂	1.15922	0.031981	0.69241	19.95486	0.000551	1.22419
CH ₄	0.37510	0.020018	0.98857	5.44853	0.000267	1.34755

SECTION S7. Thermal stability.

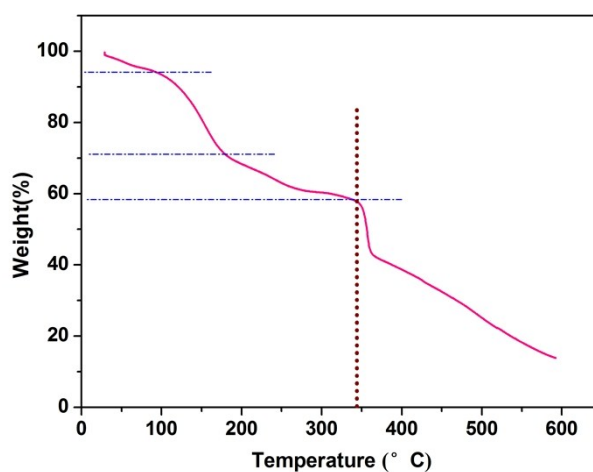


Figure S11. TG data of as-synthesized sample of NJFU-4.