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A Metal-Organic Framework Based on Cyclotriphosphazene Functionalized Hexacarboxylate for Selective Adsorption of CO_2 and C_2H_6 from CH_4 at Room Temperature

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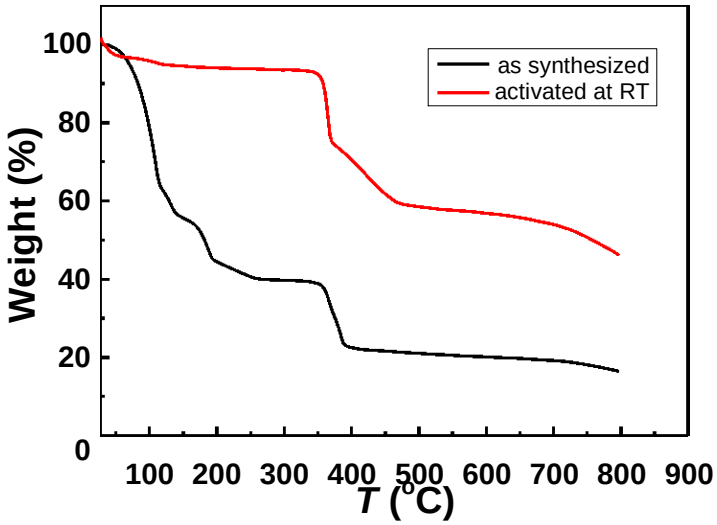


Fig. S1 TGA curve of as-synthesized **ZJNU-60** and activated **ZJNU-60a** under a nitrogen atmosphere at a heating rate of 5 ^{o}C min^{-1}.

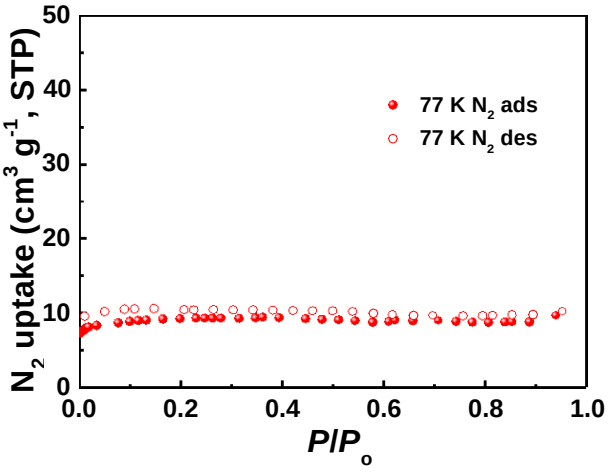


Fig. S2 N_2 adsorption-desorption isotherm of **ZJNU-60a** at 77 K. Solid and open symbols represent adsorption and desorption, respectively.

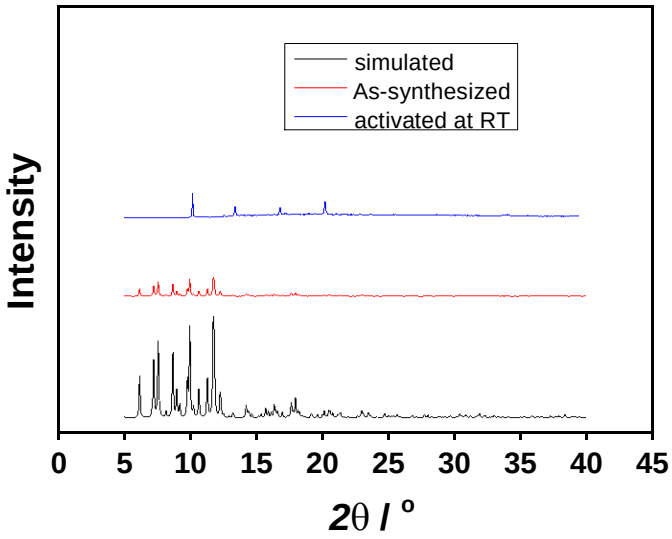


Fig. S3 PXRD patterns of as-synthesized **ZJNU-60** and activated **ZJNU-60a** together with the simulated one.

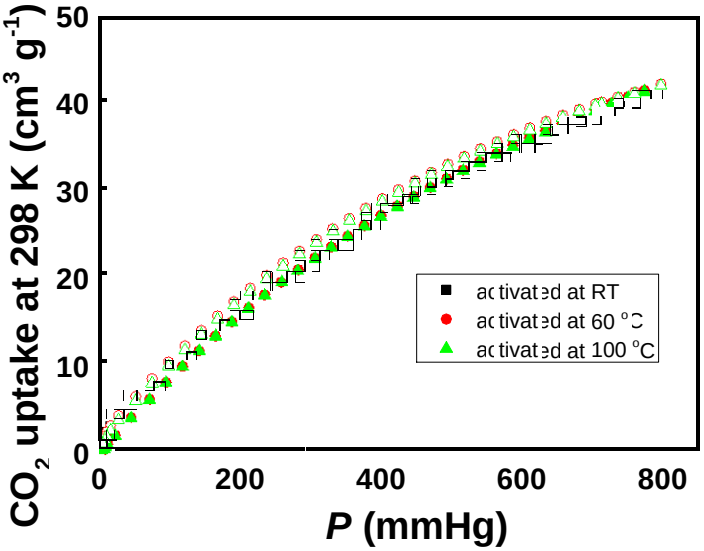


Fig. S4 CO_2 adsorption isotherms at 298 K of the samples activated at RT (black), 60 ^oC (red) and 100 ^oC (green), respectively. Solid and open symbols represent adsorption and desorption, respectively.

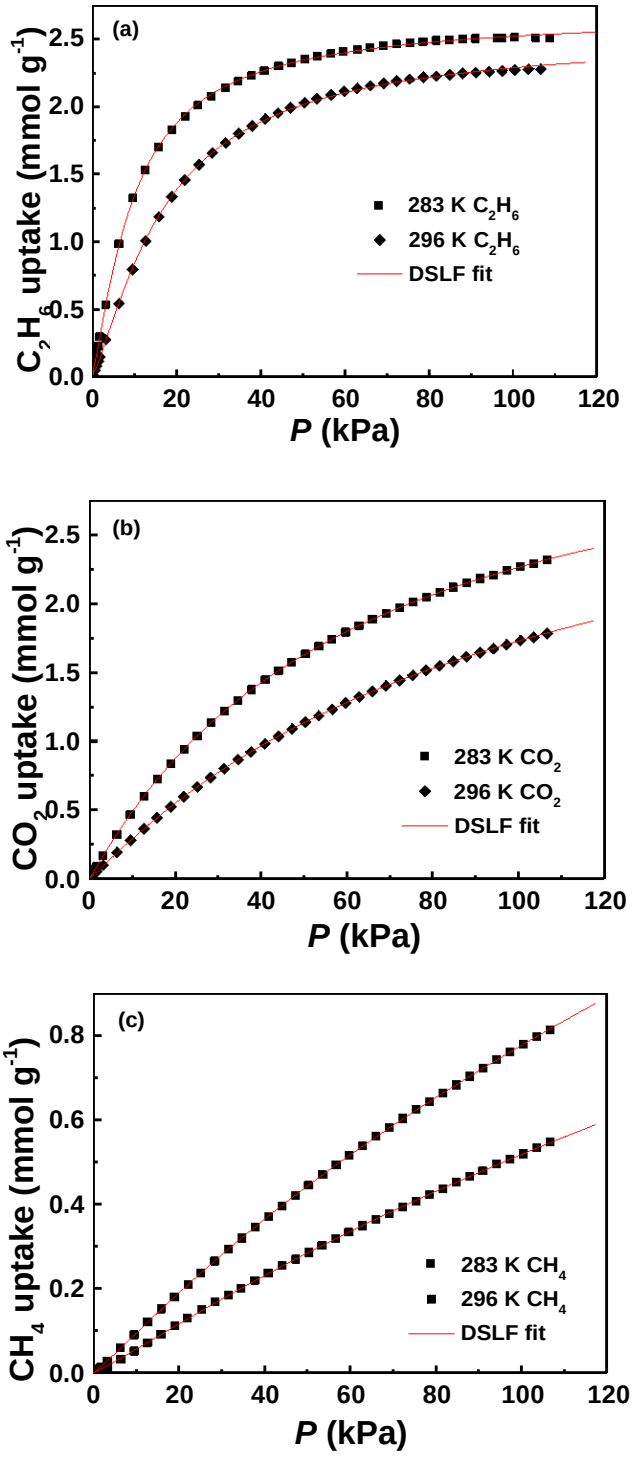


Fig. S5 Comparison of the pure-component isotherm data for (a) C_2H_6, (b) CO_2, and (c) CH_4 in **ZJNU-60a** with the fitted isotherms shown by continuous solid lines at 283 K, and 296 K.

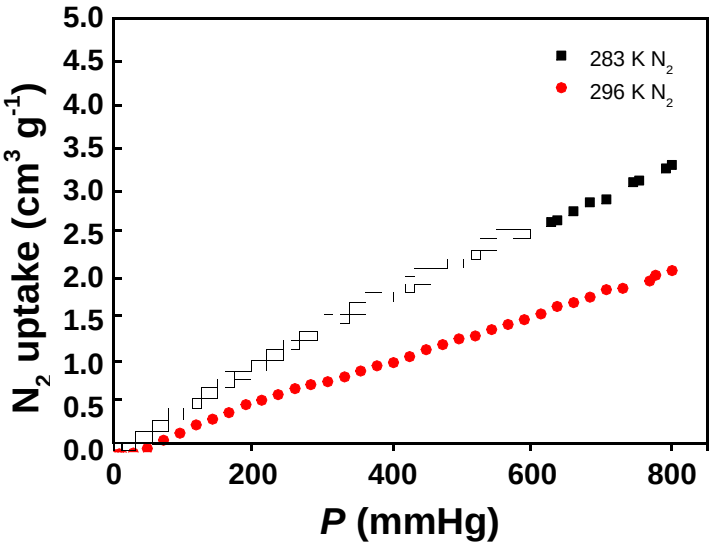


Fig. S6 N_2 adsorption isotherms of **ZJNU-60a** at 283 K and 296 K, respectively.

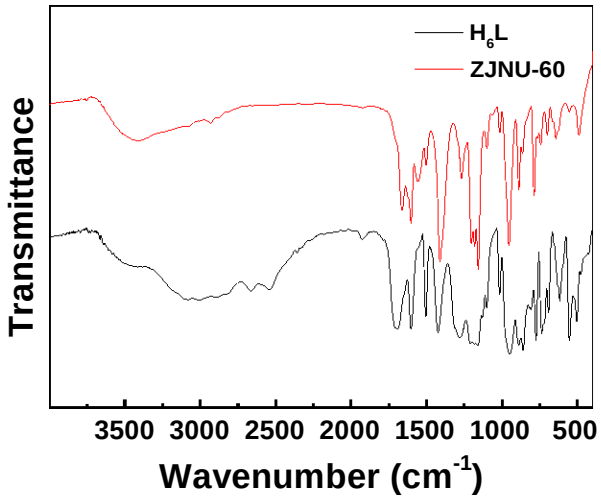
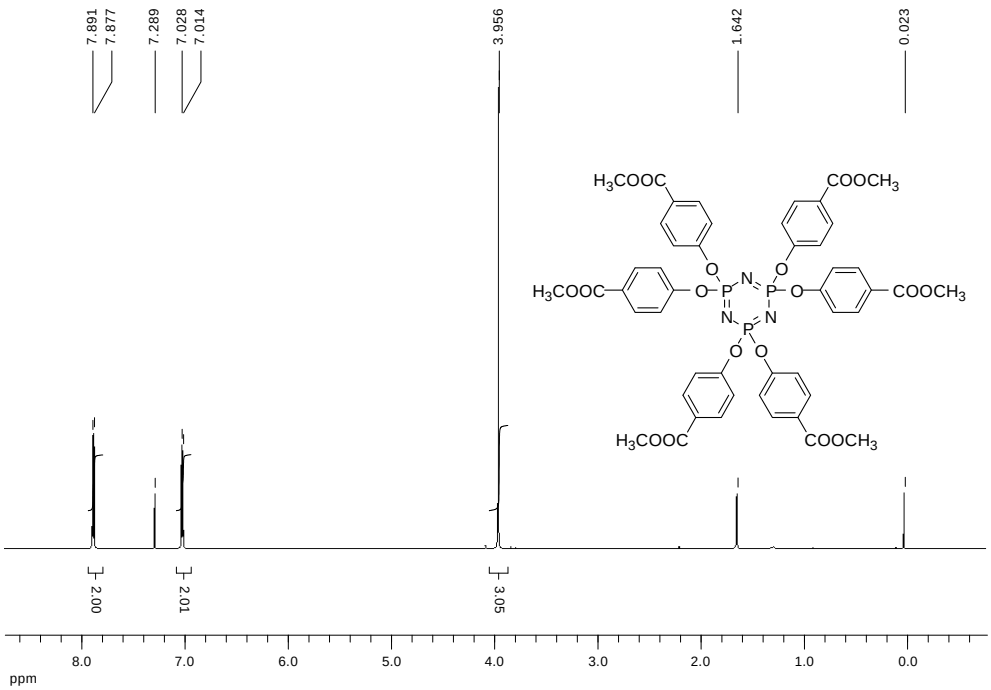


Fig. S7 FTIR spectra of organic ligand (black) and the as-synthesized **ZJNU-60** (red).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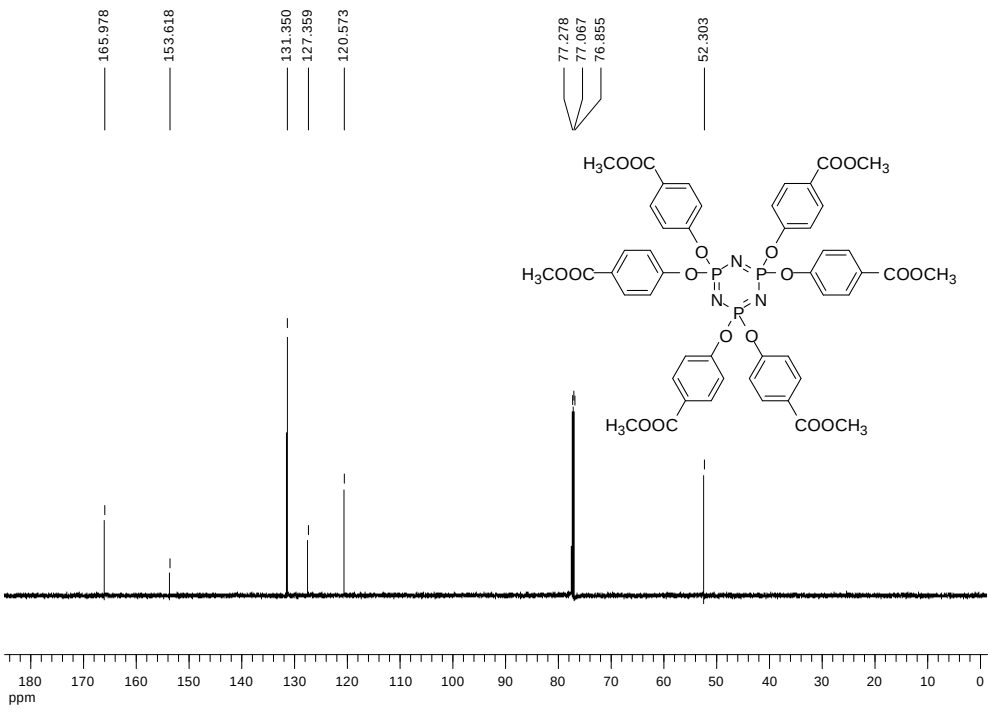
7.877
7.289
7.028
7.014
3.956
1.642
0.023
2.00
2.01
3.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm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153.618
131.350
127.359
120.573
77.278
77.067
76.855
52.303
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

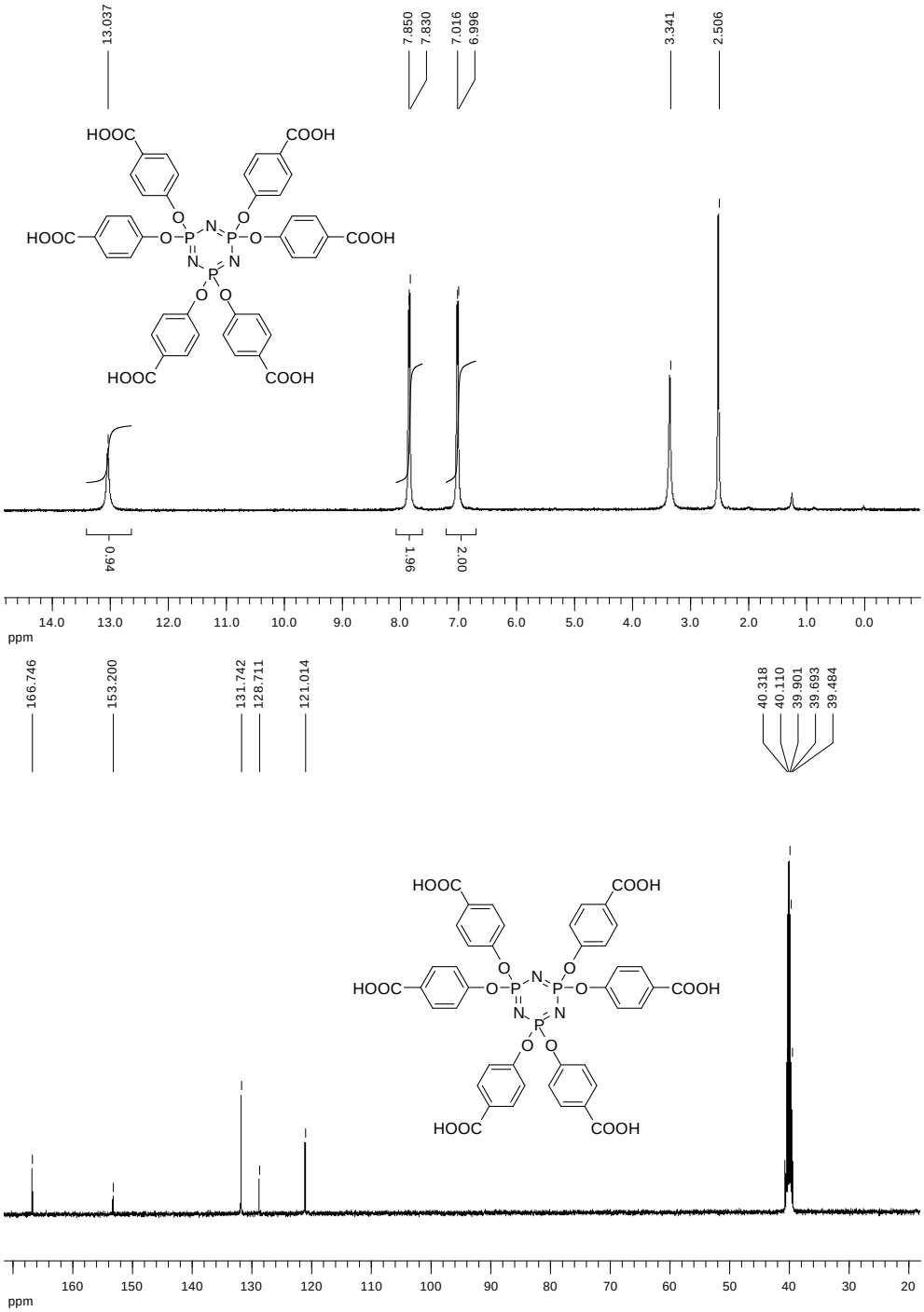

Fig. S8 ^{1}H NMR and ^{13}C NMR spectra.

Table S1 Dual-site Langmuir-Freundlich fit parameters for **ZJNU-60a**.

	Site A				Site B			
	$q_{A,sat}$ (mmol g^{-1})	b_{A0} ($kPa^{-\nu A}$)	E_A (kJ mol^{-1})	ν_A	$q_{B,sat}$ (mmol g^{-1})	b_{B0} ($kPa^{-\nu B}$)	E_B (kJ mol^{-1})	ν_B
C_2H_6	4.79	2.56×10^{-13}	57.815	0.27	2.44	2.41×10^{-9}	39.66	1.31
CO_2	3.13	6.59×10^{-9}	34.511	0.98	0.57	9.01×10^{-6}	16.46	1.25
CH_4	5.67	4.68×10^{-9}	29.031	1	0.35	5.54×10^{-8}	27.36	1.24

Table S2 Crystal and structural refinement data for **ZJNU-60**

Empirical formula	$C_{42}H_{30}Cu_3N_3O_{21}P_3$
Formula weight	1196.25
Temperature (K)	100 K
Wavelength (Å)	1.54184
Crystal system, space group	Triclinic, *P*-1
Unit cell dimensions	*a* = 12.6305(12) Å *b* = 14.5753(7) Å *c* = 22.114(3) Å α = 93.228(6)^o β = 100.746(9)^o γ = 98.776(6)^o
Volume (Å^3)	3937.7(7)
Z, Calculated density (g cm^{-3})	2, 1.009
Absorption coefficient (mm^{-1})	1.967
F(000)	1146
Crystal size (mm)	0.06 ×0.04 ×0.04
θ range for data collection (^{o})	3.08 to 74.73
Limiting indices	-15≤*h*≤14, -17≤*k*≤18, -26≤*l*≤27
Reflections collected / unique	41838 / 15694 [R_{int} = 0.1860]
Completeness to θ = 27.56	97.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	21.966 and 2.1075
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15694 / 108 / 547
Goodness-of-fit on F^2	1.106
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.1921, wR_2 = 0.4431
R indices (all data)	R_1 = 0.2527, wR_2 = 0.4910
Largest diff. peak and hole (e.Å^{-3})	5.647 and -1.090
CCDC	1060803