Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

An Anionic Metal-Organic Framework Constructed from a Triazole-Functionalized Diisophthalate Featuring Hierarchical Cages for Selective Adsorptive C_2H_2/CH_4 and CO_2/CH_4 Separation

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Calculation of Isosteric Heats of Adsorption

The isosteric heats of adsorption (Q_{st}) were calculated using the Clausius-Clapeyron equation based on pure-component isotherms collected at three different temperatures of 278 K, 288 K and 298 K. The Q_{st} was defined as

$$Q_{st} = -R\left(\frac{\partial Inp}{\partial(1/T)}\right)_q$$

where p is the pressure, T is the temperature, R is the gas constant, and q is the adsorption amount. These calculations are done through the "Heat of Adsorption" function embedded in the software supplied by Micromeritics ASAP 2020 HD88 surface-area and pore-size analyzer machine. The isostere plots for C_2H_2, CO_2 and CH_4 adsorption in the title MOF compound were provided in Fig. S7.

Fitting of Pure-Component Isotherms

The pure-component C_2H_2, CO_2 and CH_4 adsorption isotherms measured at 278 K, 288 K and 298 K were fitted with the single-site Langmuir-Freundlich model

$q = \frac{q_{sat} b p^{v}}{1 + b p^{v}}$, with T-dependent parameter $b = b_o \exp(\frac{E_a}{RT})$

where q is the adsorbed amount (mmol g^{-1}), q_{sat} is the monolayer adsorption capacity (mmol g^{-1}), p is the equilibrium pressure (kPa), , and b and v is the Langmuir and Freundlich constants. The corresponding fitting parameters are provided in Table S2. Fig S6 provides a comparison of the experimental isotherm data for C_2H_2, CO_2 and CH_4 in the title MOF compound with the isotherm fits.

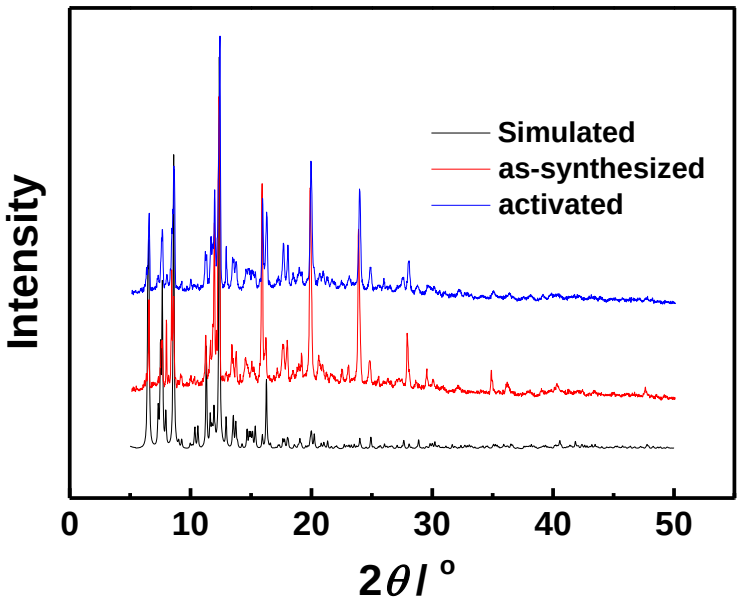


Fig. S1 PXRD patterns of the as-synthesized (red) and activated (blue) MOF compound (red) together with the simulated one (black).

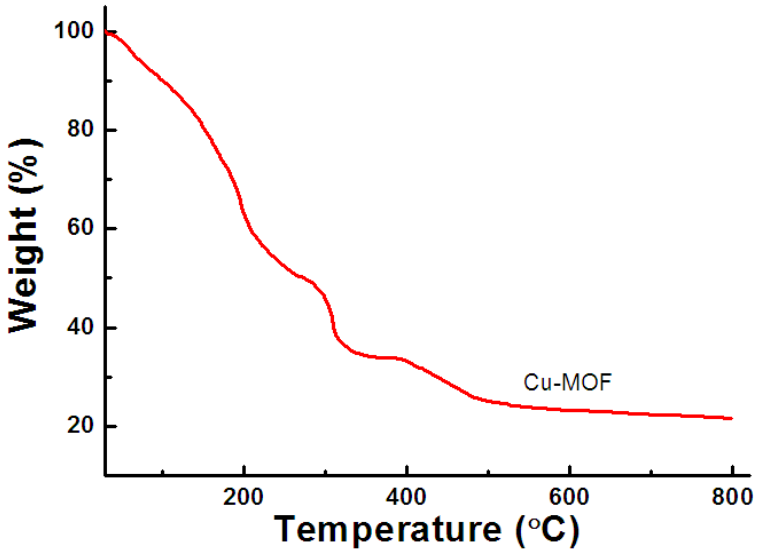


Fig. S2 TGA curve of the as-synthesized title MOF compound under nitrogen atmosphere.

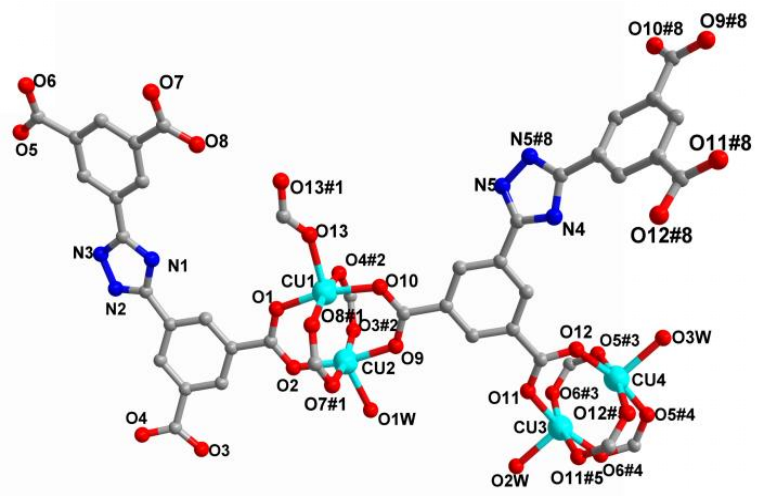


Fig. S3 Coordination environment of the Cu(II) ions. Hydrogen atoms and lattice water molecules are omitted for clarity.

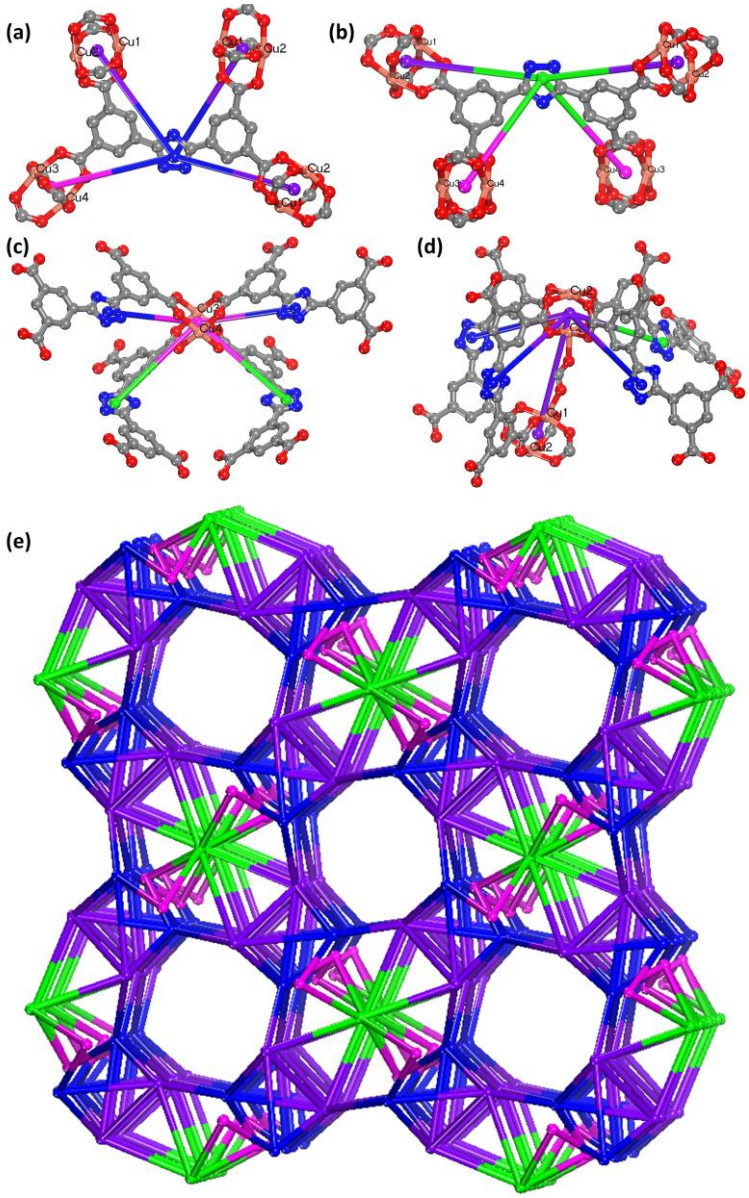
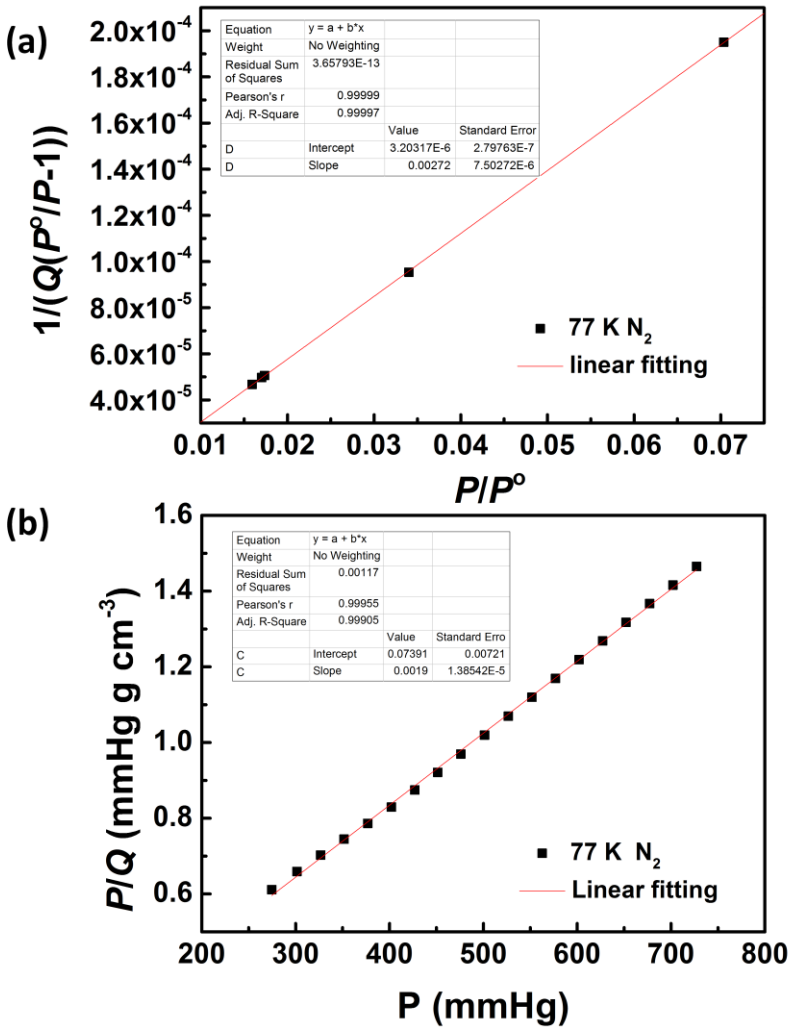


Fig. S4 Topological analyses of the title MOF compound. (a) View of 4-connected λ-L^{4-} ligand; (b) view of 4-connected τ-L^{4-} ligand; (c) view of 4-connected $Cu3Cu4(COO)_4$ SBU; (d) view of 5-connected $Cu1Cu2(COO)_4$ SBU, and (e) schematic representation of the (4,5)-c 4-nodal net with the point symbol $\{3\cdot5\cdot6^4\}_2\{3^2\cdot4\cdot5^2\cdot6^5\}_2\{4\cdot5^2\cdot6^3\}\{4\cdot5^2\cdot7^2\cdot8\}$



S_{BET} = 1/(3.20317 ×10^{-6}+ 0.00272)/22414 ×6.023 ×1023 ×0.162 ×10^{-18}=1599 m^2 g^{-1}

$S_{Langmuir}$ = 1/(0.0019)/22414 ×6.023 ×1023 ×0.162 ×10^{-18}=2291 m^2 g^{-1}

Fig. S5 BET (a) and Langmuir (b) plots for the activated title MOF compound.

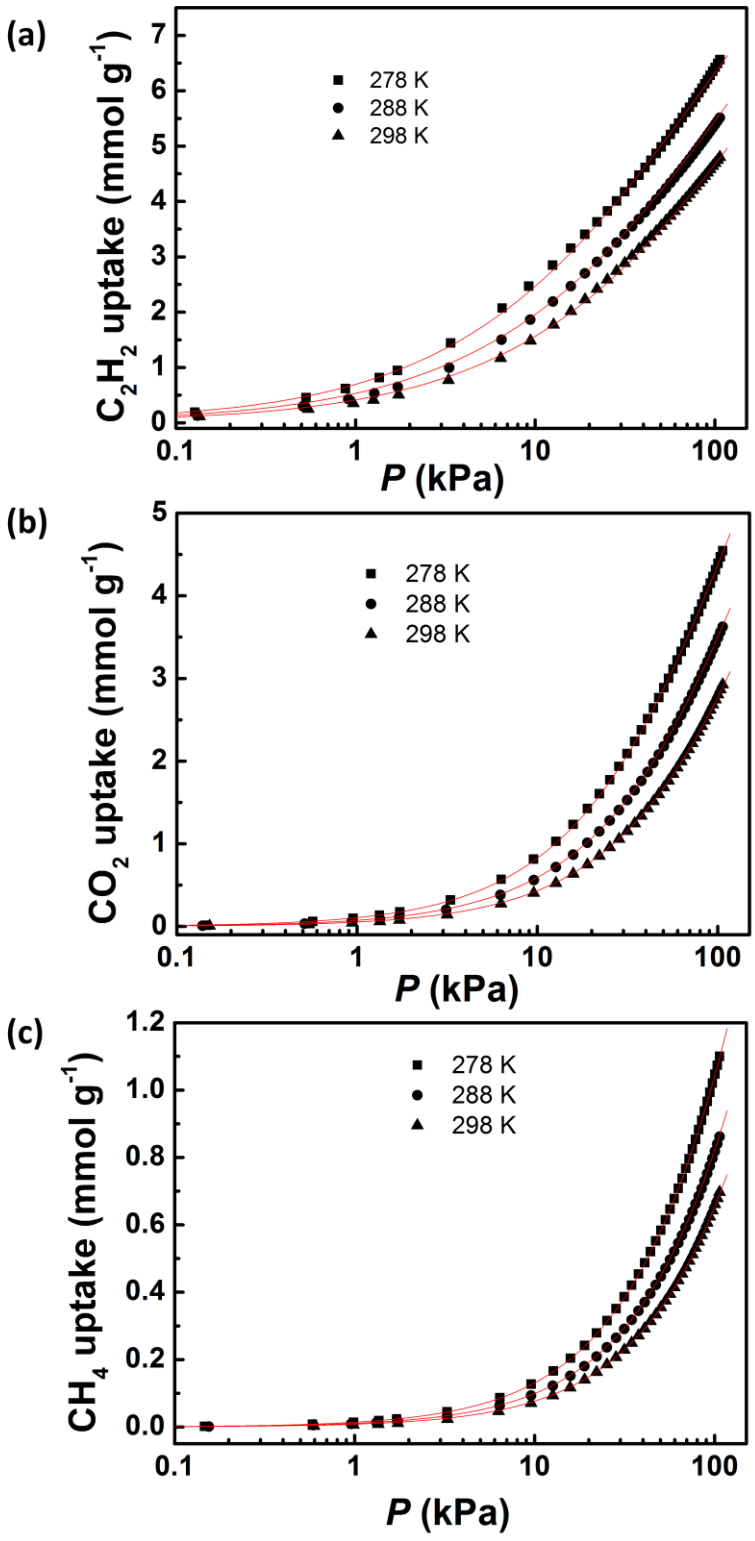


Fig. S6 Comparison of the pure-component C_2H_2 (a), CO_2 (b) and CH_4 (c) isotherm data with the fitted isotherms.

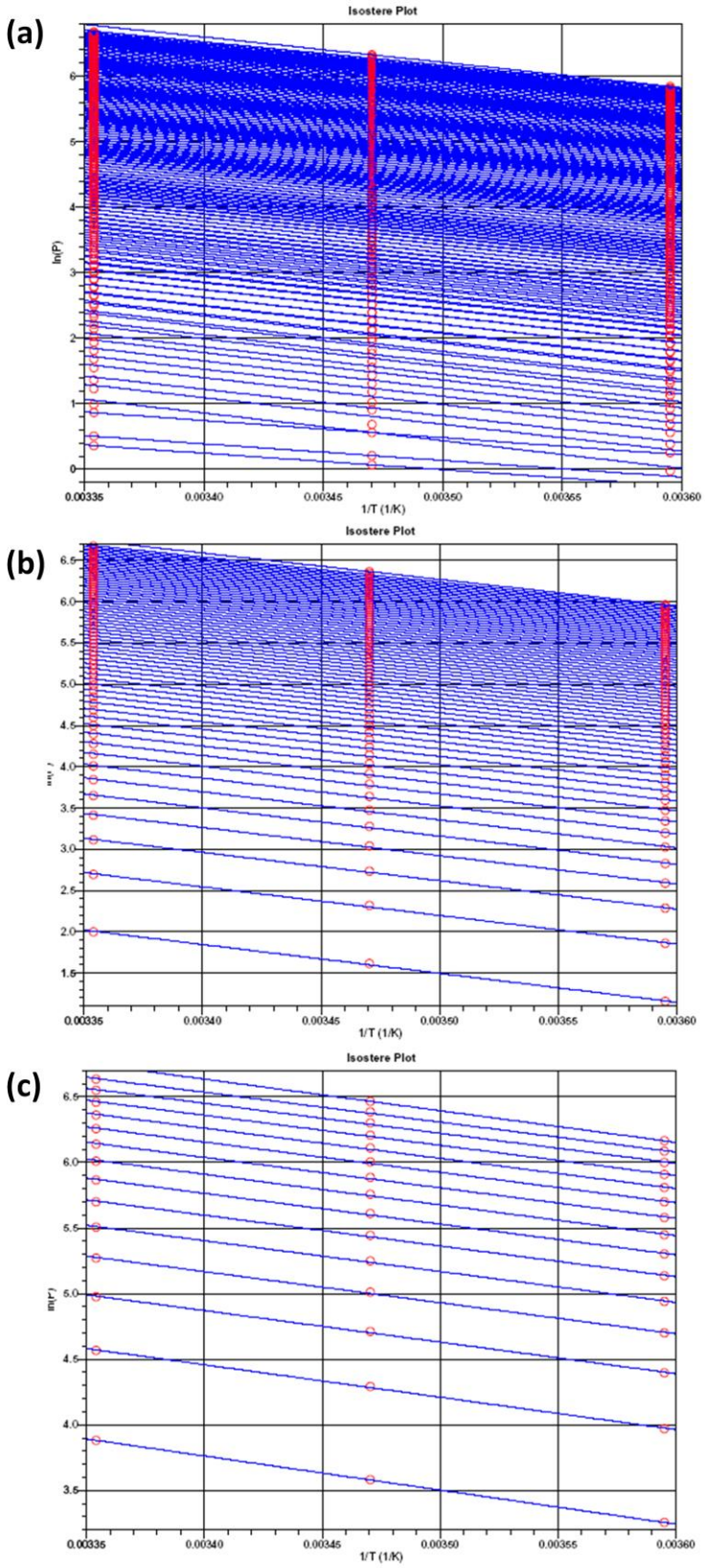


Fig. S7 Isostere plots for C_2H_2 (a), CO_2 (b) and CH_4 (c) adsorption in the title MOF compound.

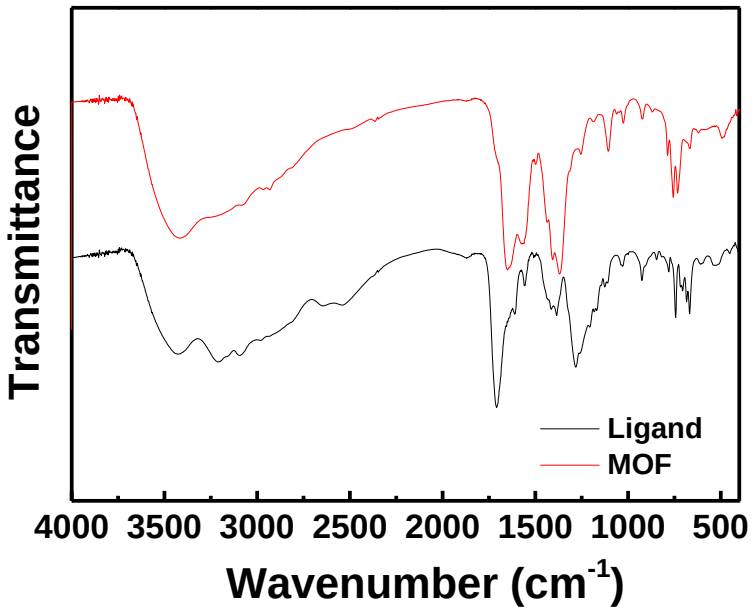


Fig. S8 FTIR spectra of the organic ligand (black) and the as-synthesized title MOF compound (red).

Table S1 Crystal data and structure refinement

Empirical formula	$C_{117}H_{178}N_{30}O_{50}Cu_6$	F (000)	13309
Formula weight	3186.19	Crystal colour	blue
Crystal system	Tetragonal	θ_{min} / θ_{max} (°)	0.9004 / 0.7858
Space group	*P4/mnc*	Reflections collected	196752
a (Å)	26.9768(15)	Unique reflections (R_{int})	16651(0.1509)
b (Å)	26.9768(15)	Data with $I > 2\sigma(I)$	16651
c (Å)	39.206(3)	Parameters refined	458
V (Å^3)	28532(3)	R_1 / wR_2 [$I > 2\sigma(I)$]	0.0576/0.1436
Z	8	R_1 / wR_2 (all data)	0.1119/0.1583
D_c (g·cm^{-3})	1.483	Goodness-of-fit (on F^2)	1.083
μ (mm^{-1})	0.974	$\Delta\rho_{max}$ / $\Delta\rho_{min}$ (e·Å^{-3})	1.800 / -0.715

Table S2 Langmuir-Freundlich parameters for adsorption of C_2H_2, CO_2, and CH_4 in the title MOF compound

	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v
C_2H_2	12.4574	1.81076×10^{-5}	18.702	0.62087
CO_2	10.55342	3.71544×10^{-7}	23.624	0.92016
CH_4	6.032	7.34757×10^{-7}	18.657	0.97384