Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

A Rare Pb_9 Cluster-Organic Framework Constructed from a Flexible Cyclotriphosphazene-Functionalized Hexacarboxylate Exhibiting Selective Gas Separation

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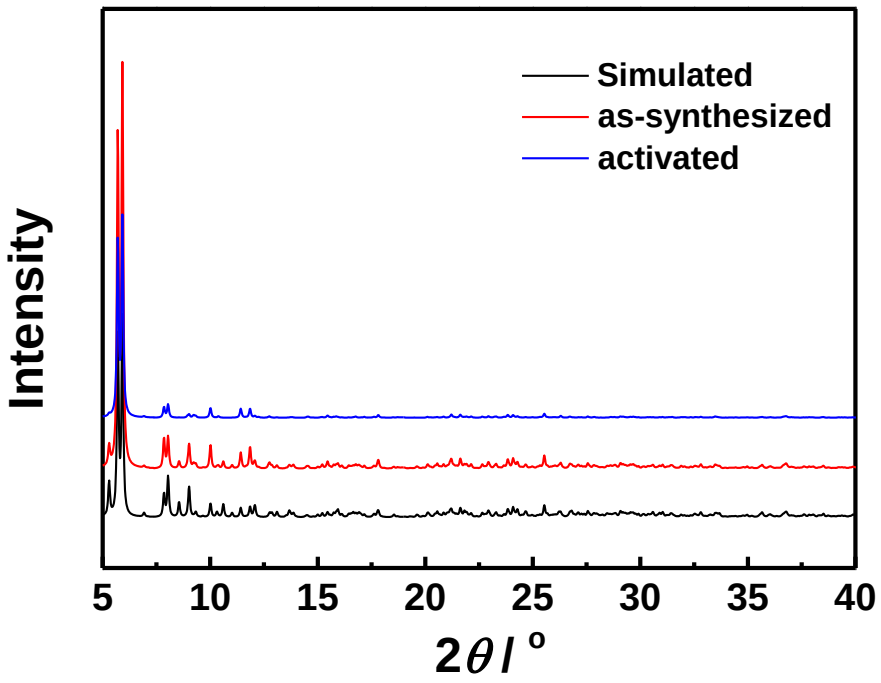


Fig. S1 PXRD patterns for as-synthesized **ZJNU-62** (red) and activated **ZJNU-62a** (blue) together with the simulated one (black).

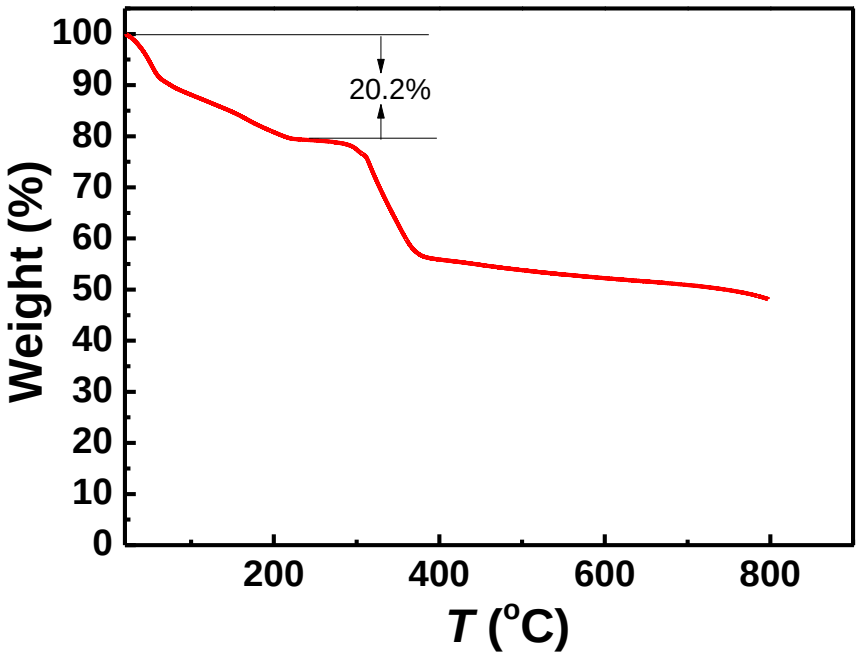


Fig. S2 TGA curve of the as-synthesized **ZJNU-62** under N_2 atmosphere

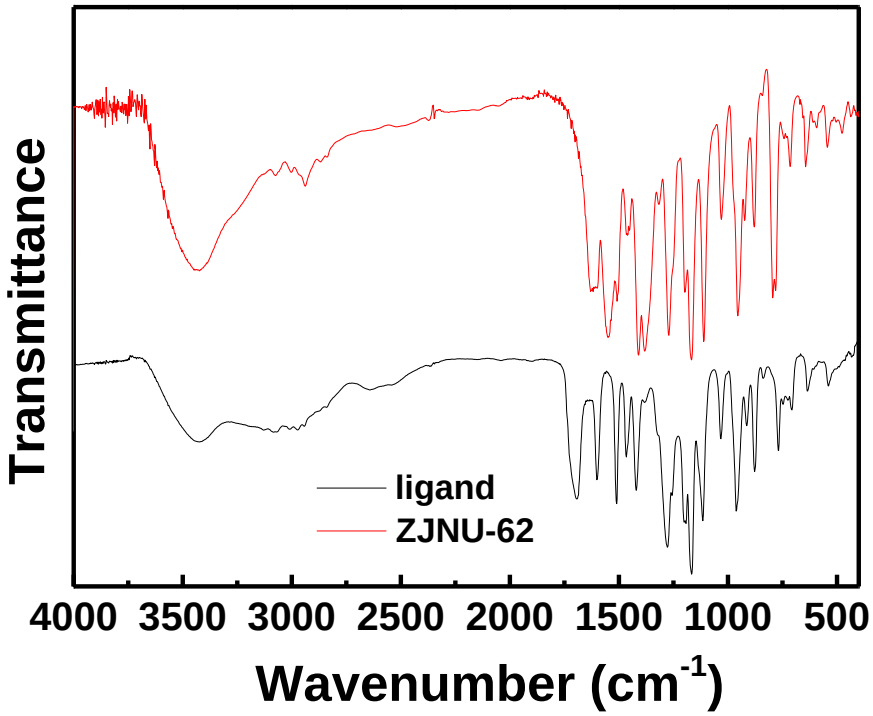


Fig. S3 FTIR spectra of the organic ligand (black) and the as-synthesized **ZJNU-62** (red)

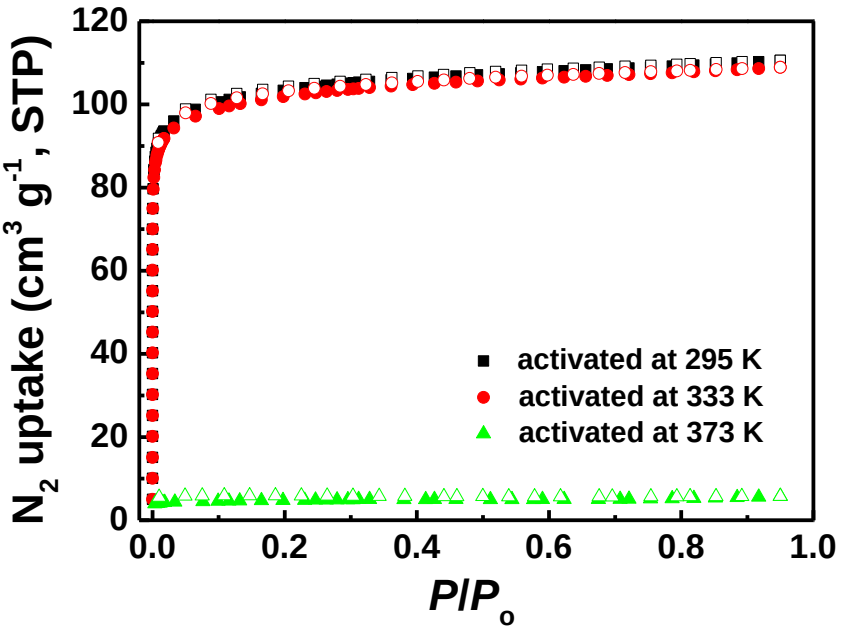
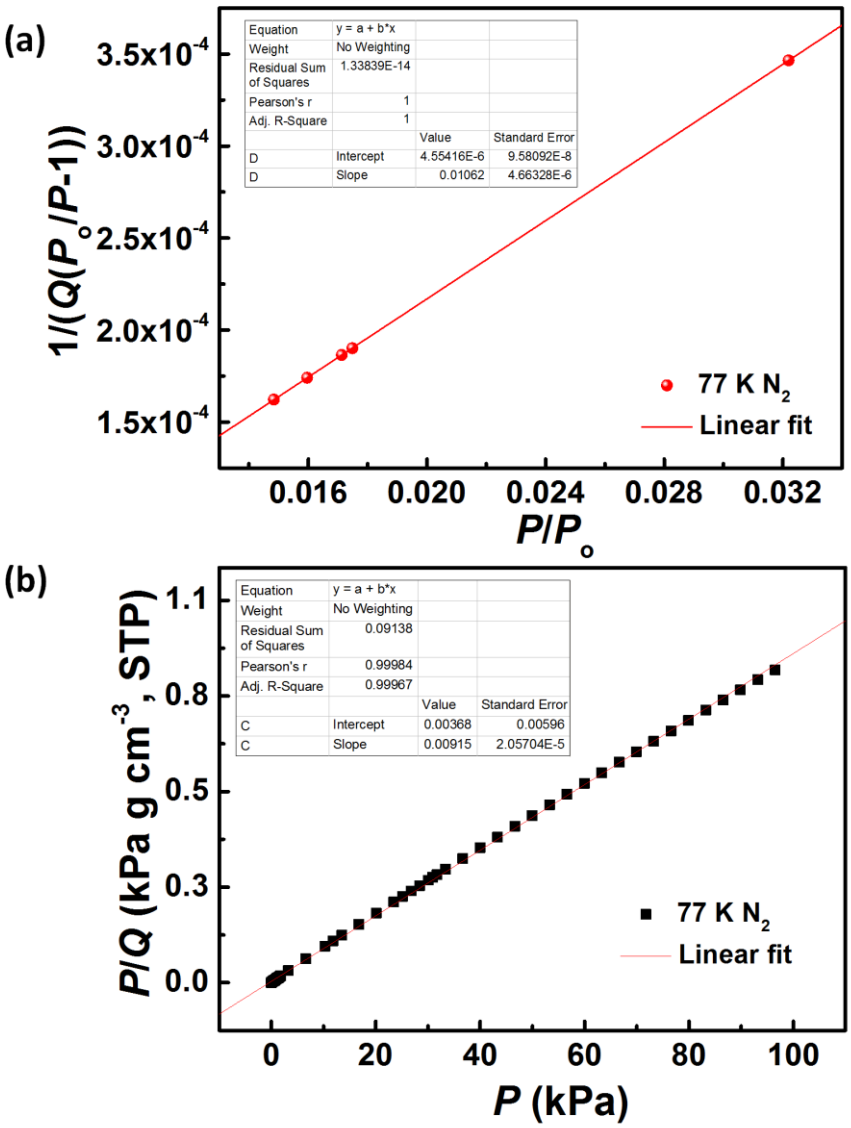


Fig. S4 N_2 adsorption-desorption isotherms at 77 K of **ZJNU-62** after activation under dynamic vacuum at 295 K, 333 K and 373 K. The solid and open symbols represent adsorption and desorption, respectively. STP = standard temperature and pressure.



S_{BET} = 1/(4.55416 ×10^{-6} + 0.01062)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 410 m^2 g^{-1}

$S_{Langmuir}$ = (1/0.00915)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 476 m^2 g^{-1}

Fig. S5 BET (a) and Langmuir (b) plots for **ZJNU-62a**

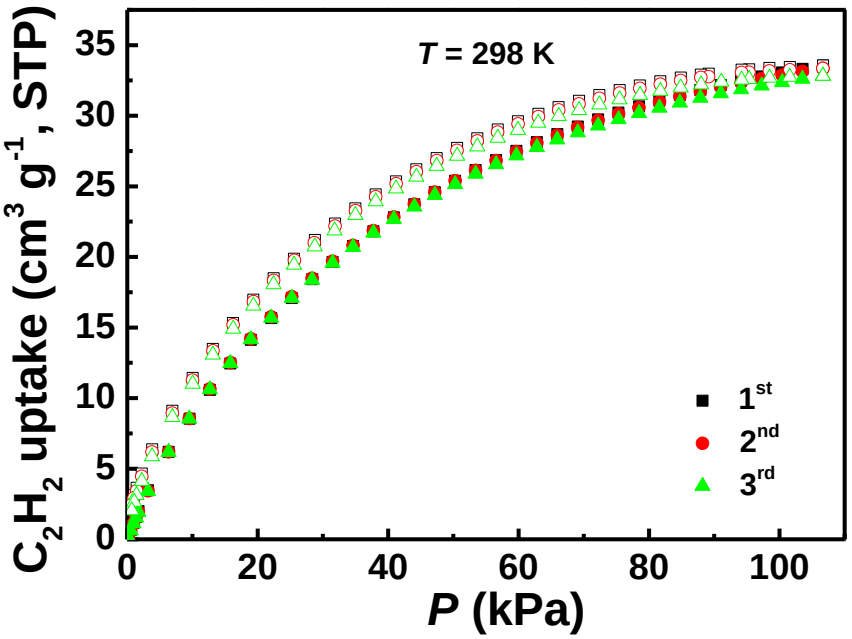


Fig. S6 Three cycles of C_2H_2 isotherms at 298 K of **ZJNU-62a.** The reactivation process was not applied between each run. The solid and open symbols represent adsorption and desorption, respectively. STP = standard temperature and pressure.

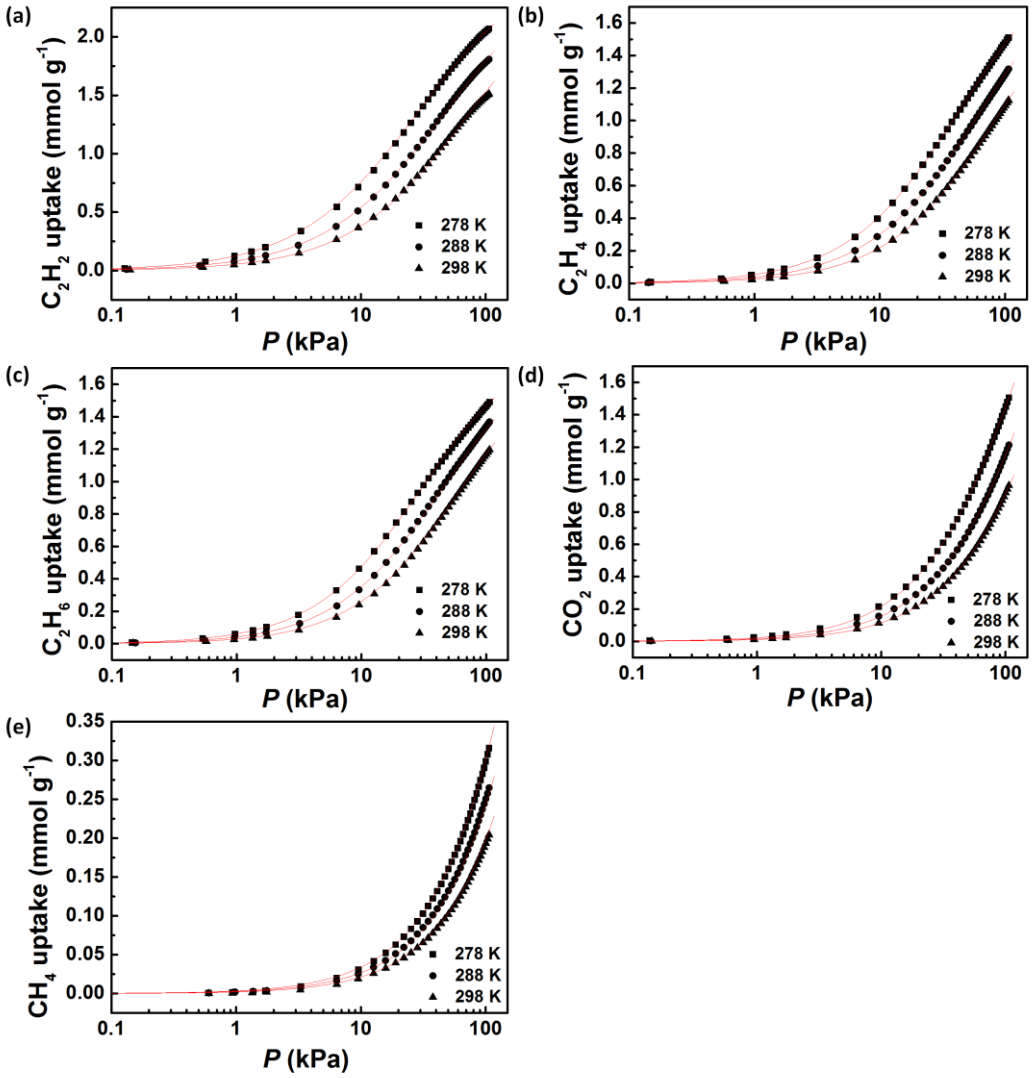


Fig. S7 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) C_2H_4, (c) C_2H_6, (d) CO_2, and (e) CH_4 in **ZJNU-62a** with the fitted isotherms (shown by continuous solid lines) at 278 K, 288 K and 298 K.

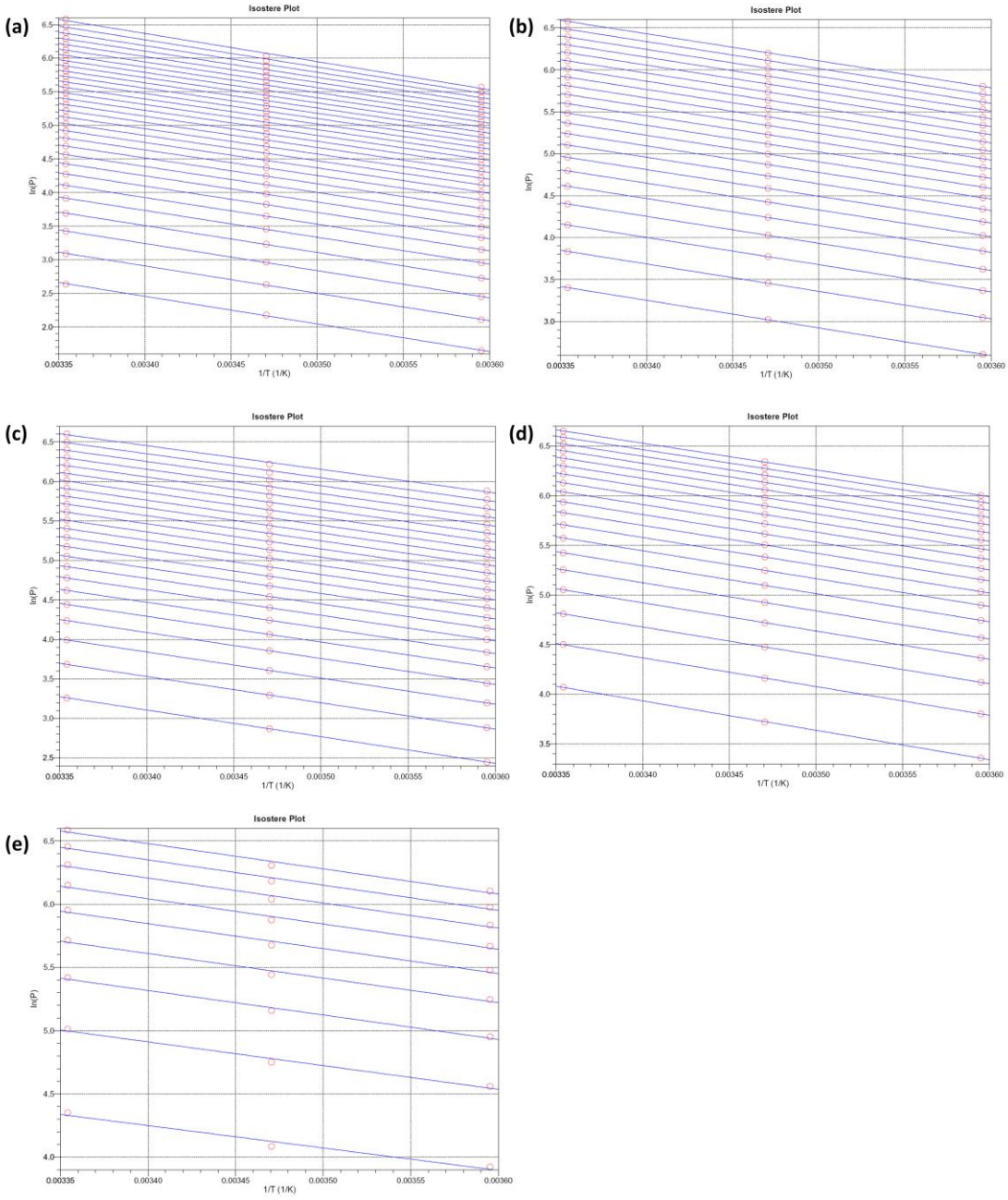


Fig. S8 Isostere plots for (a) C_2H_2, (b) C_2H_4, (c) C_2H_6, (d) CO_2 and (e) CH_4 adsorption in **ZJNU-62a**.

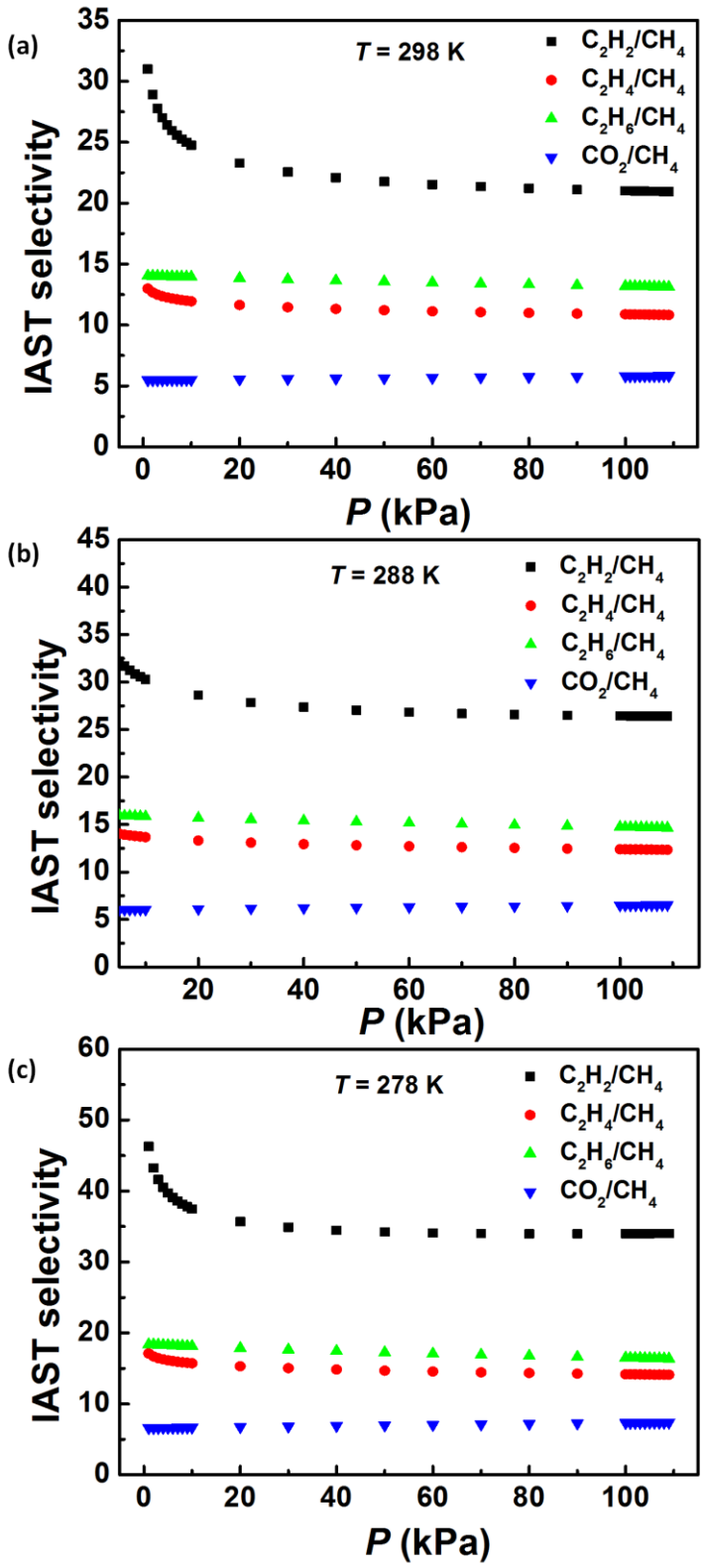


Fig. S9 The IAST-predicted adsorption selectivities for the equimolar C_2H_2/CH_4, C_2H_4/CH_4, C_2H_6/CH_4 and CO_2/CH_4 gas mixtures at 298 K (a), 288 K (b) and 278 K (c).

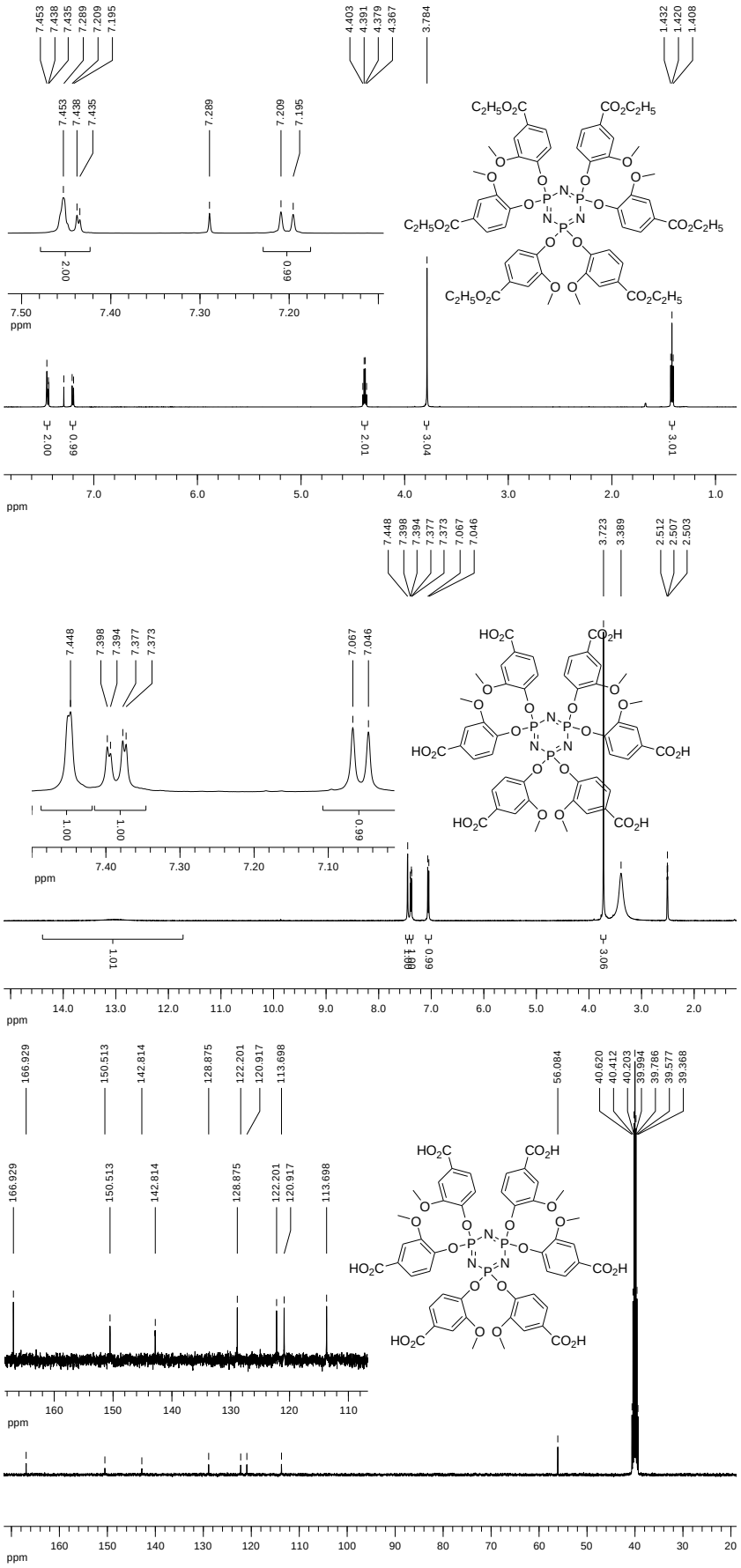


Fig. S10 ^{1}H and ^{13}C NMR spectra of the organic ligand.

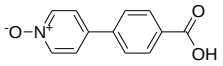
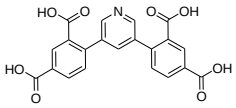
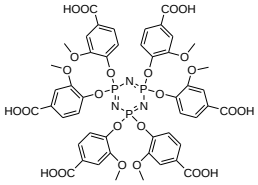
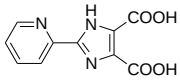
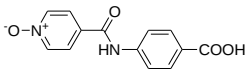
Table S1 Crystal data and structure refinement for **ZJNU-62**.

Empirical formula	$C_{148}H_{122}N_9O_{78}P_9Pb_9$
Formula weight	5449.99
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic,
Space group	*C*2/c
Unit cell dimensions	a = 31.5688(7) Å b = 30.9664(6) Å c = 22.7830(4) Å α = 90° β = 98.981(2)° γ = 90°
Volume (Å^3)	21999.0(8)
Z	4
Calculated density (g cm^{-3})	1.646
Absorption coefficient (mm^{-1})	7.007
F(000)	10344
Crystal size (mm)	0.14 × 0.10 × 0.10
θ range for data collection (°)	1.60 to 26.29
Limiting indices	-38 ≤ h ≤ 32 -34 ≤ k ≤ 37 -28 ≤ l ≤ 26
Reflections collected / unique	63410 / 21809
R_{int}	0.0471
Completeness to θ = 27.60	97.6 %
Max. and min. transmission	0.5409 and 0.4404
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	21809 / 126 / 1048
Goodness-of-fit on F^2	1.019
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0999, wR_2 = 0.2900
R indices (all data)	R_1 = 0.1073, wR_2 = 0.3133
Largest diff. peak and hole (e·Å^{-3})	18.437 and -8.340
CCDC	1551676

Table S2 Langmuir-Freundlich parameters for adsorption of C_2H_2, C_2H_4, C_2H_6, CO_2, and CH_4 in **ZJNU-62a**.

Adsorbate	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v
C_2H_2	2.7065	1.22039×10^{-7}	29.836	0.89777
C_2H_4	2.13726	3.97441×10^{-7}	25.636	0.96456
C_2H_6	1.90692	5.52098×10^{-7}	25.440	1
CO_2	3.95295	3.249×10^{-7}	22.619	1
CH_4	2.34842	1.38122×10^{-6}	16.107	1

Table S3 Summary of gas adsorption properties of the reported Pb-based MOFs.

Pb-MOFs	Ligand structure	$S_{BET}/S_{Langmuir}$ ($m^2\ g^{-1}$)	V_p ($cm^3\ g^{-1}$)	CO_2 uptake (condition)	$Q_{st}(CO_2)$	*Ref.*
Pb-L		725/NA[a]	0.47	NA	NA	[1]
Pb-L		669.3/800.5[b]	NA	56.9 cm^3 (STP) g^{-1} (298 K and 1 bar)	53.9	[2]
ZJNU-62		410/476[a]	0.171	21.6 cm^3 (STP) g^{-1} (298 K and 1 atm)	25.6	This work
Pb-L		374.3/492.3[a]	0.15	28.4 cm^3 (STP) g^{-1} (293 K and 1 atm)	27.5	[3]
Pb-L		NA/NA	NA	16.3 cm^3 (STP) g^{-1} (273 K and 0.95 atm)	NA	[4]

[a] based on N_2 isotherm at 77 K; [b] based on CO_2 isotherm at 195 K; NA = not available

References:

1. Hu, L.; Lin, X.-M.; Mo, J.-T.; Lin, J.; Gan, H.-L.; Yang, X.-L.; Cai, Y.-P., Lead-Based Metal-Organic Framework with Stable Lithium Anodic Performance. *Inorg. Chem.* **2017,** *56*, 4289-4295.

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3. Li, J.; Yang, G.; Hou, L.; Cui, L.; Li, Y.; Wang, Y.-Y.; Shi, Q.-Z., Three new solvent-directed 3D lead(II)–MOFs displaying the unique properties of luminescence and selective CO_2 sorption. *Dalton Trans.* **2013,** *42*, 13590-13598.

4. Lin, X.-M.; Li, T.-T.; Chen, L.-F.; Zhang, L.; Su, C.-Y., Two ligand-functionalized Pb(II) metal-organic frameworks: structures and catalytic performances. *Dalton Trans.* **2012,** *41*, 10422-10429.