Electronic Supplementary Material (ESI) for Dalton Transactions.

CO_2 Adsorption of Three Isostructural Metal-Organic Frameworks Depending on the Incorporated Highly Polarized Heterocyclic Moieties

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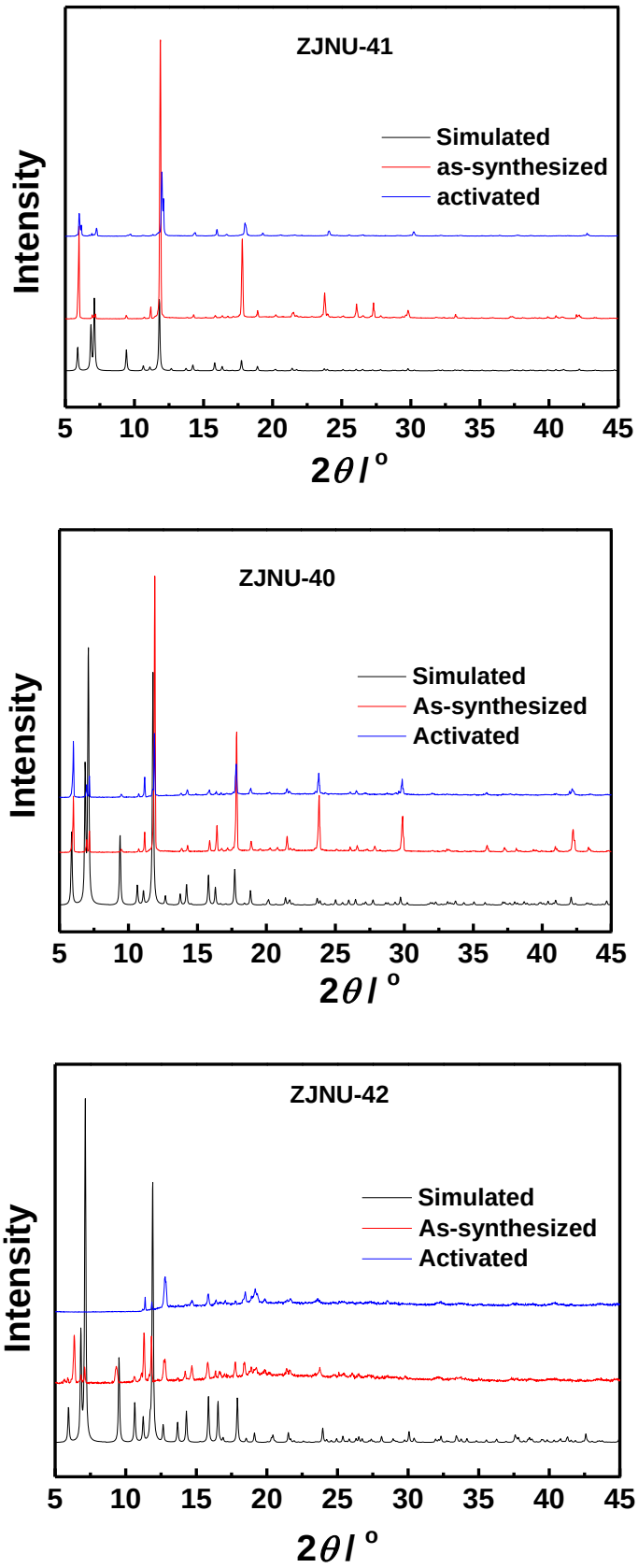


Fig. S1 PXRD patterns of as-synthesized MOFs (**ZJNU-41**, **ZJNU-40** and **ZJNU-42**) together with the ones simulated from cif files. Calculated PXRD patterns were generated using Mercury 1.4.1.

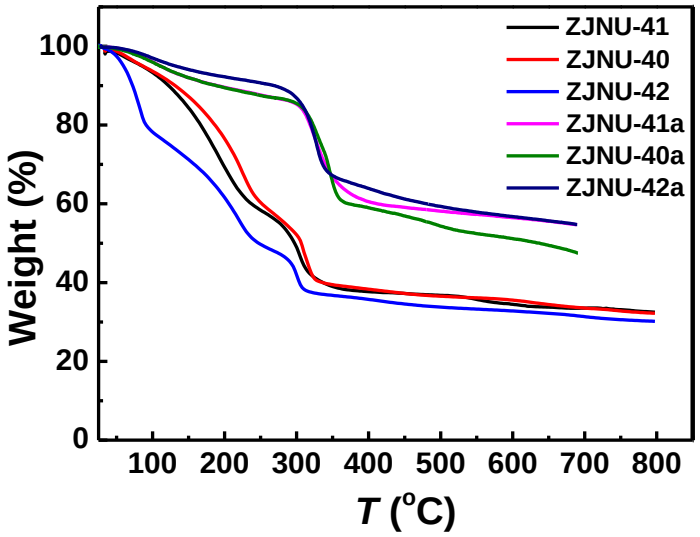
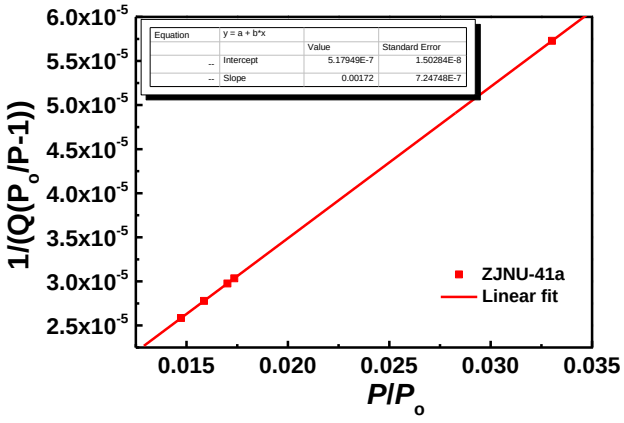
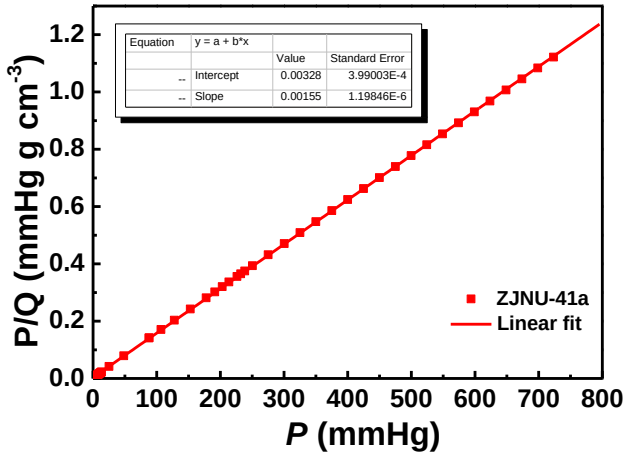


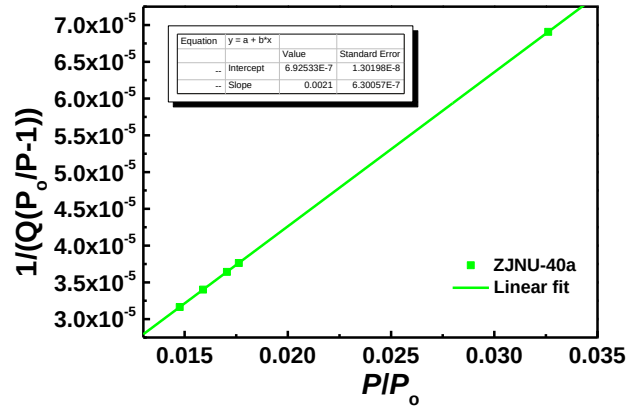
Fig. S2 TGA curves of as-synthesized MOFs (**ZJNU-41** (red), **ZJNU-40** (green) and **ZJNU-42** (blue)), as well as activated MOFs (**ZJNU-41a** (magenta), **ZJNU-40a** (olive) and **ZJNU-42a** (navy)) under a nitrogen atmosphere with a heating rate of 5 ^{o}C min^{-1}.

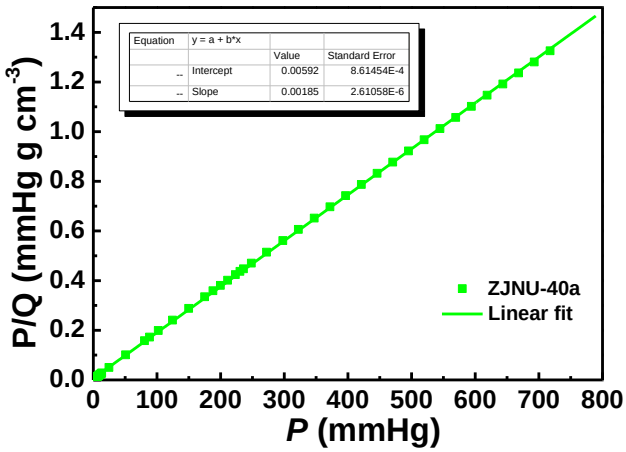




S_{BET} = 1/(5.17949 ×10^{-7}+0.00172)/22414 ×6.023 ×10^{23} ×0.162 ×10^{-18} = 2530 m^2 g^{-1}
$S_{Langmuir}$ = (1/0.00155)/22414 ×6.023 ×10^{23} ×0.162 ×10^{-18} = 2809 m^2 g^{-1}

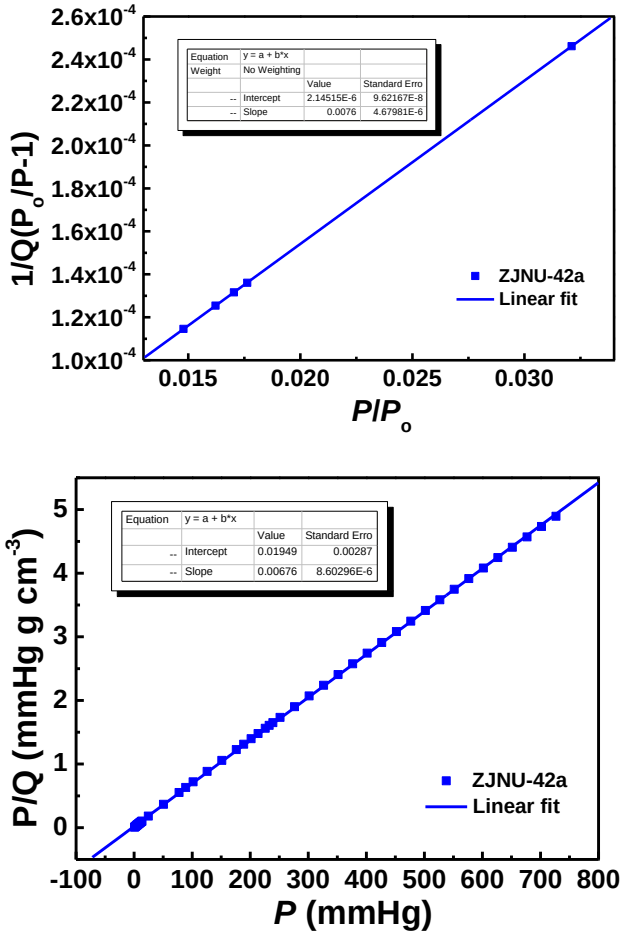
Fig. S3 BET and Langmuir plots for **ZJNU-41a**.





S_{BET} = 1/(6.92533×10^{-7}+0.0021)/22414×6.023×10^{23}×0.162×10^{-18} = 2072 m^2 g^{-1}
$S_{Langmuir}$ = (1/0.00185)/22414×6.023×10^{23}×0.162×10^{-18} = 2353 m^2 g^{-1}

Fig. S4 BET and Langmuir plots for **ZJNU-40a**.



$S_{BET} = (1/(2.14515\times10^{-6}+0.0076)/22414)\times6.023\times10^{23}\times0.162\times10^{-18} = 572\ m^2\ g^{-1}$

$S_{Langmuir} = (1/0.00676)/22414\times6.023\times10^{23}\times0.162\times10^{-18} = 644\ m^2\ g^{-1}$

Fig. S5 BET and Langmuir plots for **ZJNU-42a**.

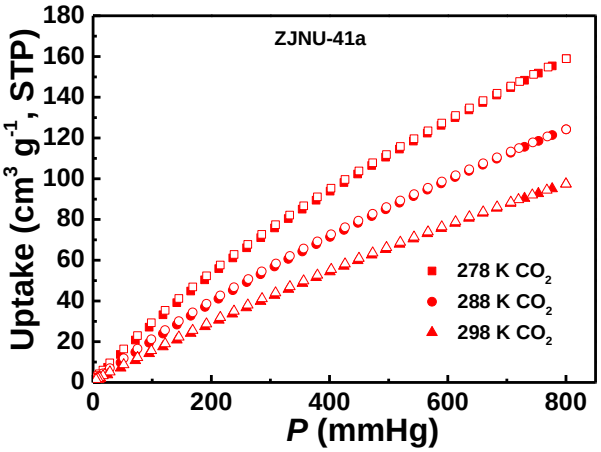


Fig. S6 CO_2 adsorption-desorption isotherms of **ZJNU-41a** at 278 K, 288 K and 298 K. Solid and open symbols represent adsorption and desorption, respectively.

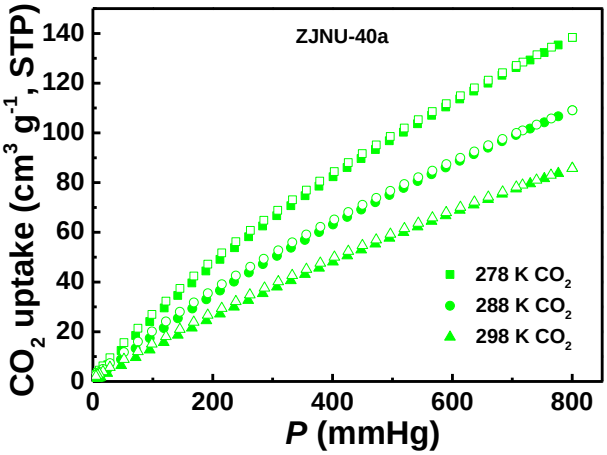


Fig. S7 CO_2 adsorption-desorption isotherms of **ZJNU-40a** at 278 K, 288 K and 298 K. Solid and open symbols represent adsorption and desorption, respectively.

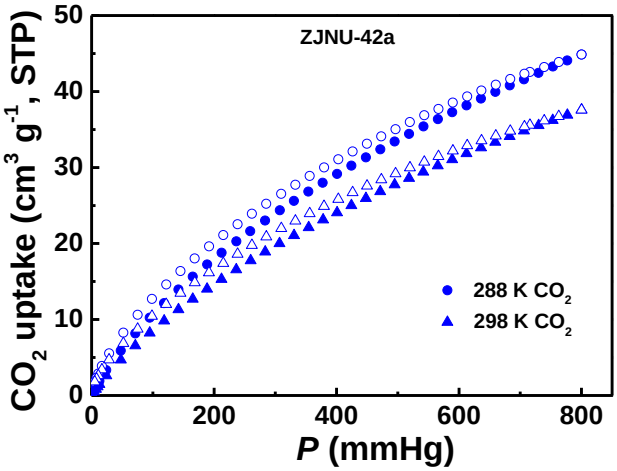


Fig. S8 CO_2, CH_4 and N_2 adsorption-desorption isotherms of **ZJNU-42a** at 288 K and 298 K. Solid and open symbols represent adsorption and desorption, respectively.

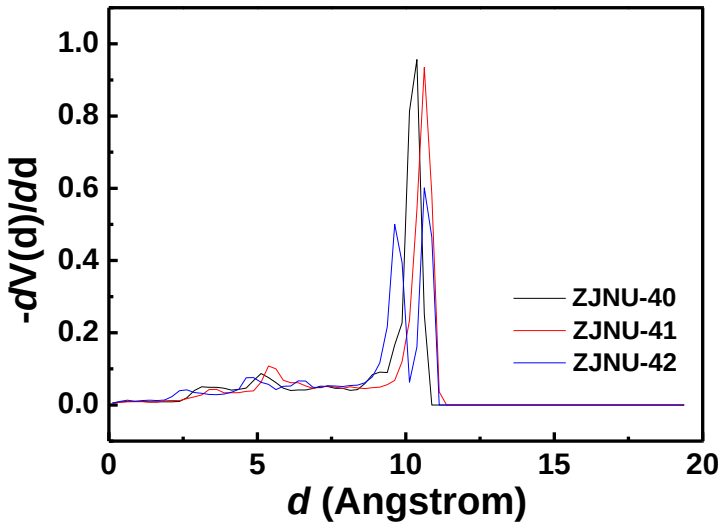


Fig. S9 Geometric PSD as a function of the pore diameter *d* (Å) for **ZJNU-40** (black line), **ZJNU-41** (red line), and **ZJNU-42** (blue line), which were calculated using poreblazer_v3.0.2 software.[1]

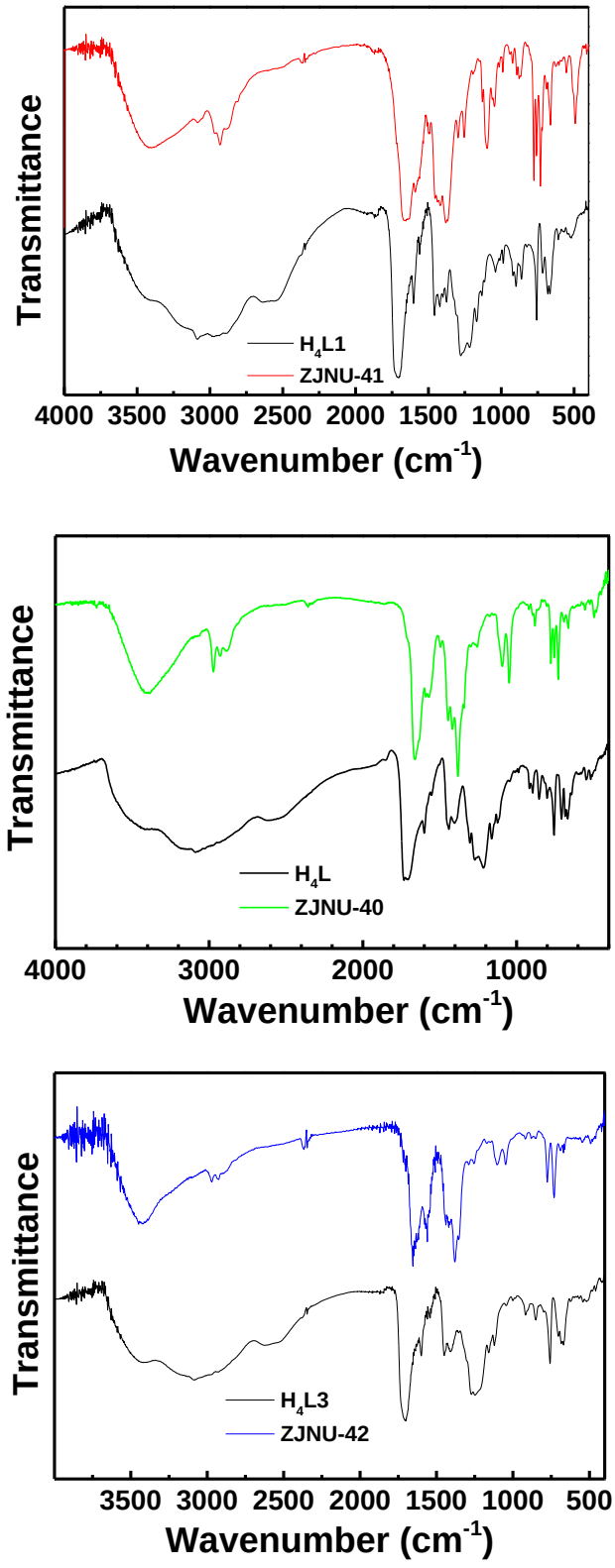


Fig. S10 FTIR spectra.

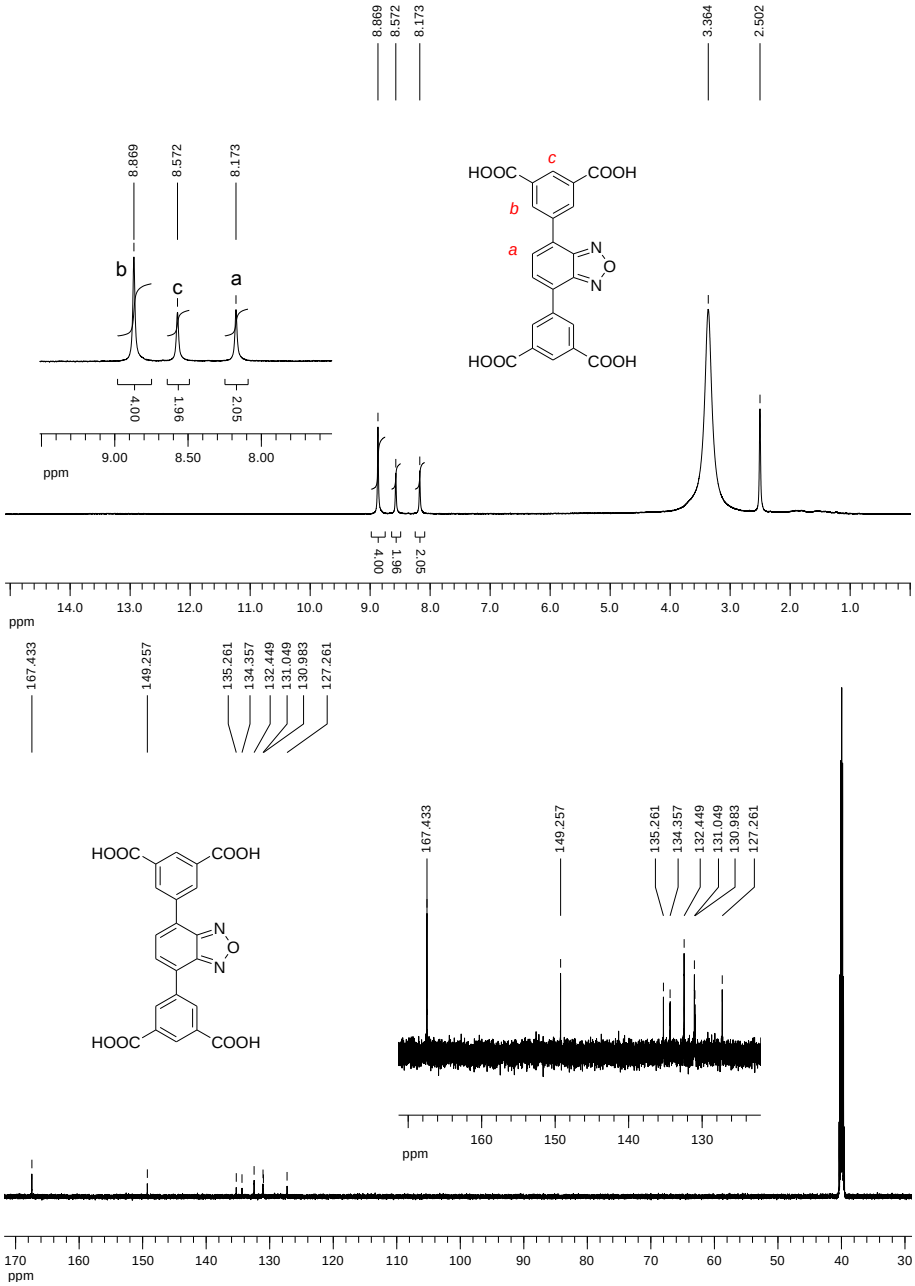


Fig. S11 ^{1}H NMR spectra (DMSO-d_6, 600.1 MHz) and ^{13}C NMR (DMSO-*d*6, 150.9 MHz) of the organic building blocks H_4L1.

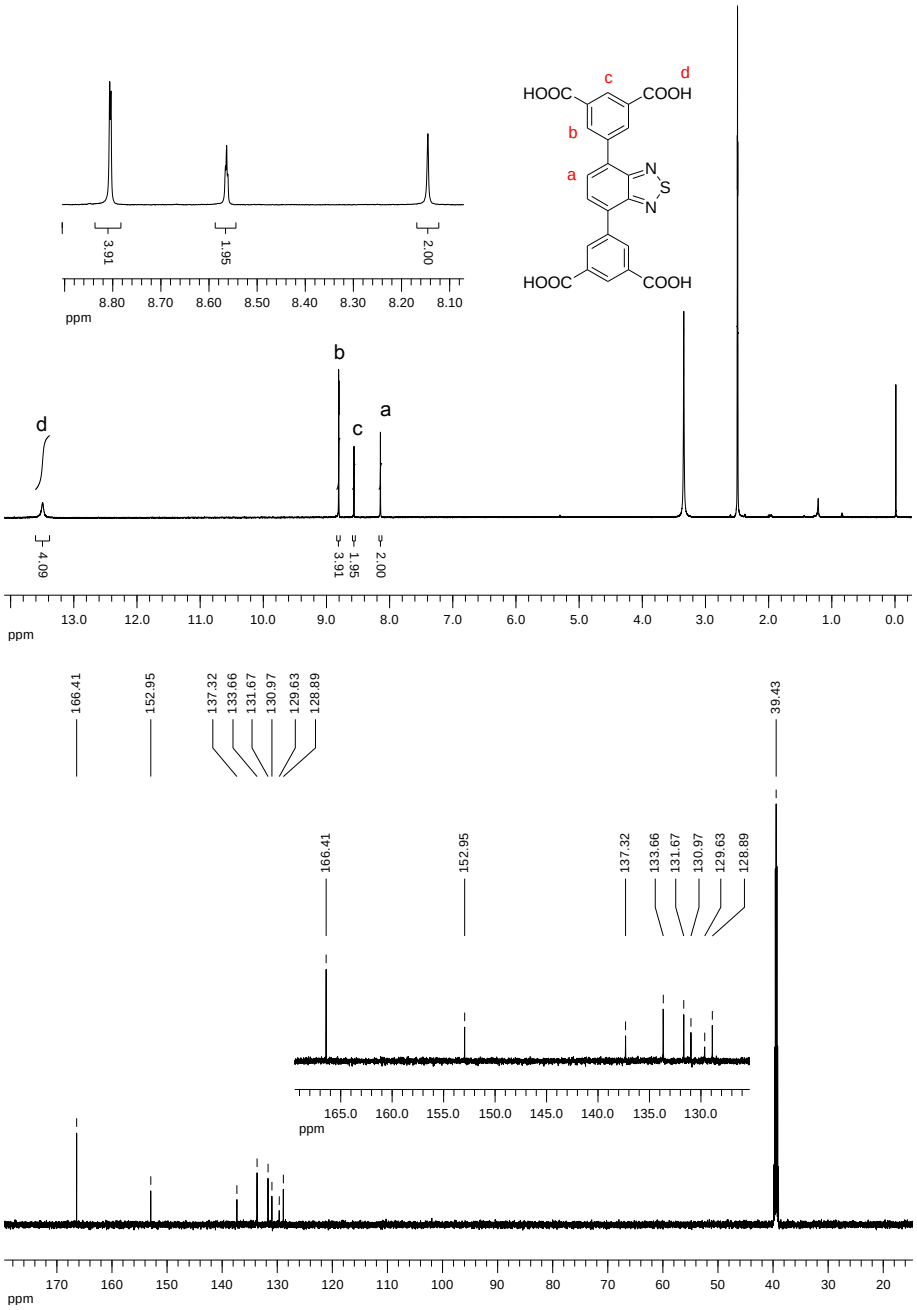


Fig. S12 ^{1}H NMR (DMSO-d_6, 600.1 MHz) and ^{13}C NMR (DMSO-d_6, 150.9 MHz) spectra of the organic linker H_4L2.

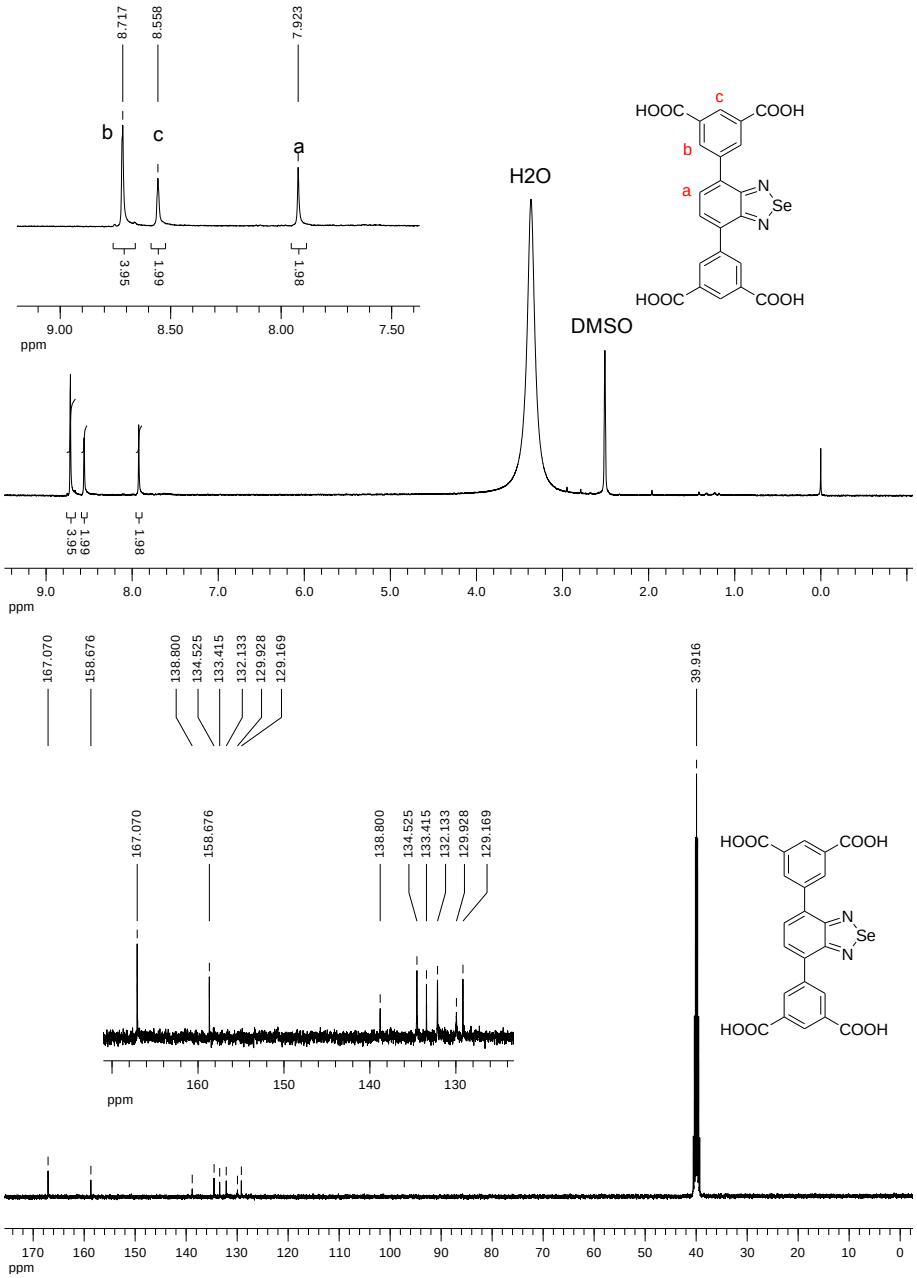


Fig. S13 ^{1}H NMR (DMSO-d_6, 600.1 MHz) and ^{13}C NMR (DMSO-d_6, 100.6 MHz) spectra of the organic linker H_4L3.

Table S1 Crystal data and structure refinement for **ZJNU-41** and **ZJNU-42.**

MOFs	**ZJNU-41**	**ZJNU-42**
Empirical formula	$C_{11}H_6CuNO_{5.5}$	$C_{22}H_{12}Cu_2N_2O_{10}Se$
Formula weight	303.72	670.39
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Trigonal	Trigonal
Space group	*R*-3m	*R*-3m
Unit cell dimensions	a = 18.7632(7) b = 18.76320(10) c = 38.6558(13) $\alpha = 90^o$ $\beta = 90^o$ $\gamma = 120^o$	a = 18.554(5) b = 18.554(5) c = 38.822(8)) $\alpha = 90^o$ $\beta = 90^o$ $\gamma = 120^o$
Volume (Å^3)	11785.8(6)	11574(5)
Z	18	9
Calculated density (g cm^{-3})	0.770	0.866
Absorption coefficient (mm^{-1})	0.845	1.562
F(000)	2804	522
θ range for data collection (^{o})	1.36 to 28.33	3.29 to 27.49
Limiting indices	$-23 \le h \le 25$, $-25 \le k \le 19$, $-51 \le l \le 39$	$-20 \le h \le 24$, $-24 \le k \le 24$, $-50 \le l \le 50$
Reflections collected / unique	28573 / 3569 [R(int) = 0.0747]	37278 / 3226 [R(int) = 0.1544]
Completeness to θ	θ = 28.33, 99.9 %	θ = 27.49, 99.6 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3569 / 20 / 135	3226 / 27 / 145
Goodness-of-fit on F^2	1.026	1.619
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0399, wR_2 = 0.1272	R_1 = 0.1500, wR_2 = 0.4195
R indices (all data)	R_1 = 0.0481, wR_2 = 0.1317	R_1 = 0.1619, wR_2 = 0.4287
Largest diff. peak and hole (e.Å^{-3})	0.885 and -0.261	1.142 and -0.724
CCDC	1413736	1413737

Reference

1. Sarkisov, L.; Harrison, A., Computational structure characterisation tools in application to ordered and disordered porous materials. *Molecular Simulation* **2011,** *37*, 1248-1257.