Electronic Supplementary Information (ESI)

Interpenetrated Metal Organic Frameworks and Their Uptake of CO_2 at Relatively Low Pressures

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Thermogravimetric Analysis (TGA)

TGA was performed on a Perkin Elmer TGA 7 analyzer to study the thermal stability and the quantity of solvent guest molecules present in the SUMOFs. The SUMOFs were heated from 30 °C to 700 °C at a heating rate of 10 °C/min in a platinum holder under a continuous flow of dry air. TGA curves for the interpenetrated MOFs are given in Fig. S1.

SUMOF-2: it lost all solvents (DMF and water) with a mass loss of 25.8% before 250 °C. During this process, the entrapped zinc species, $Zn(OH)_2$, in the pores would be dehydrated to ZnO. There is no mass loss between 250 and 450 °C. Upon heating to 480 °C in air, it starts to decompose to give 31.8% ZnO. The observed mass loss for the activated SUMOF-2 upon decomposition to ZnO is 57.1%, which matches very well with the calculated theoretical mass loss, 57.0%, suggesting that the sample is pure.

SUMOF-3: it lost all solvents (DMF and water) with a mass loss of 34.0% before 200 °C. There is no mass loss between 200 and 400 °C. Upon heating to 420°C in air, it starts to decompose to give 23.2% ZnO. The observed mass loss for the activated SUMOF-3 upon decomposition to ZnO is 64.9%, which matches very well with the calculated theoretical mass loss 64.6%, suggesting that the sample is pure.

SUMOF-4: it lost all solvents (DMF and water) with a mass loss of 31.8% before 220 °C. There is no mass loss between 220 and 420 °C. Upon heating to 420°C in air, it starts to decompose to give 26.4% ZnO. The observed mass loss for the activated SUMOF-4 upon decomposition to ZnO is 61.3%, which matches very well with the calculated theoretical mass loss 61.5%, suggesting that the sample is pure.

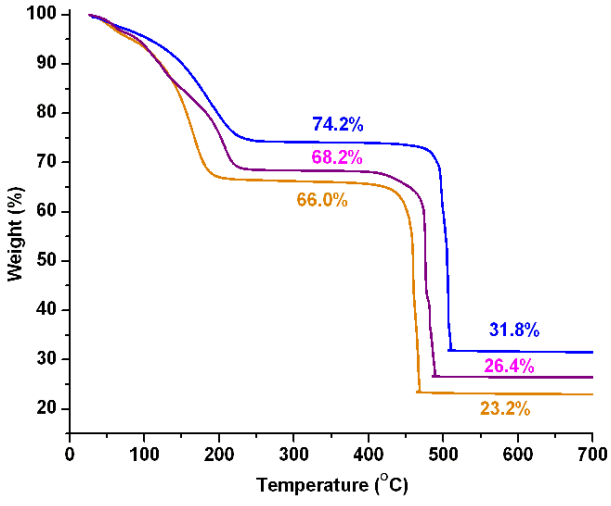


Figure S1. TGA curves for SUMOF-2 (blue line), SUMOF-3 (orange line) and SUMOF-4 (purple line). The mass of the activated SUMOFs and the remaining mass after decomposition of the SUMOFs are indicated.

Electronic Supplementary Information (ESI)

Nitrogen adsorption isotherms at 77 K

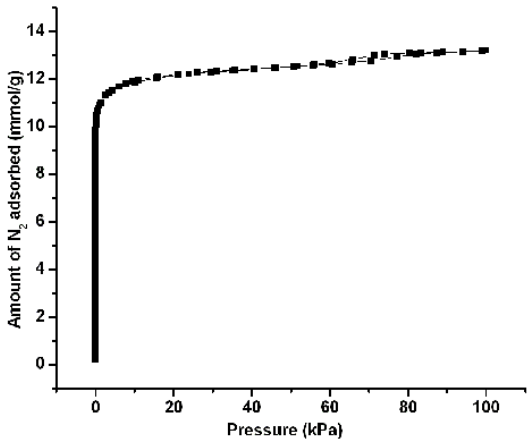


Figure S2 Nitrogen adsorption isotherm of SUMOF-2 at 77 K.

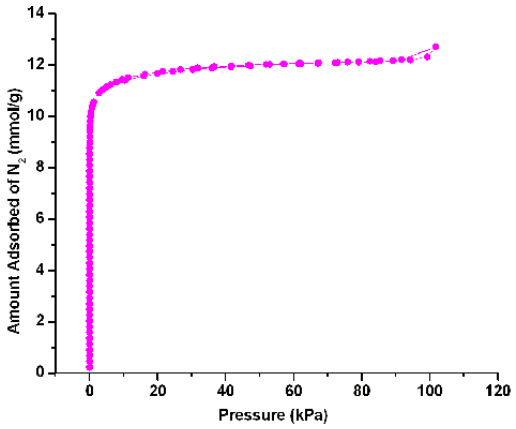


Figure S3 Nitrogen adsorption isotherm of SUMOF-3 at 77 K.

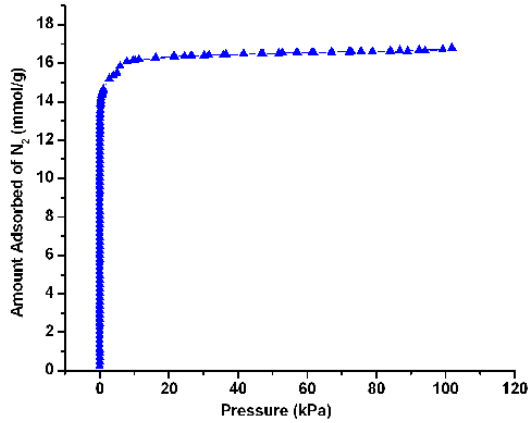


Figure S4 Nitrogen adsorption isotherm of SUMOF-4 at 77 K.

Electronic Supplementary Information (ESI)

Stability of activated sample in open air

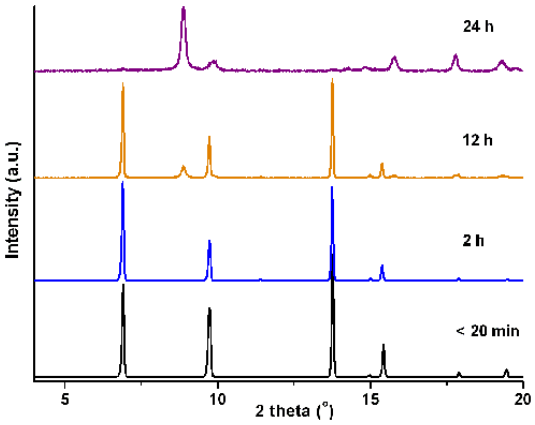


Figure S5. PXRD patterns for activated SUMOF-2 subjected to open air for various time periods. The activated sample was stable in air for at least 2 hours. After being exposed to open air for 12 hours, a new line appears at 2 θ = 8.9°, indicating partial conversion to a second phase. After further being exposed in air for 24 hours, two additional lines appear at 2 θ = 15.8 and 17.8°, suggesting formation of a second phase isostructural to MOF-69C.[1] Similar results were observed for MOF-5 in humid air.[2]

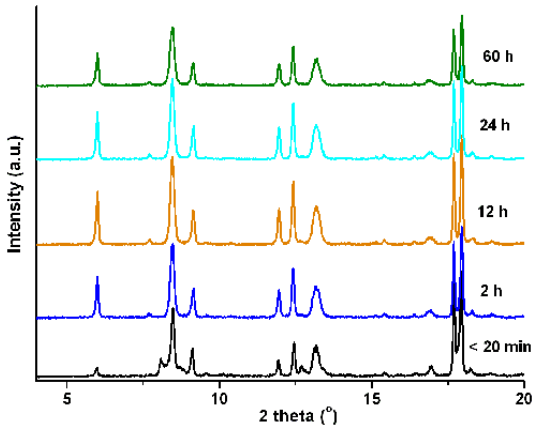
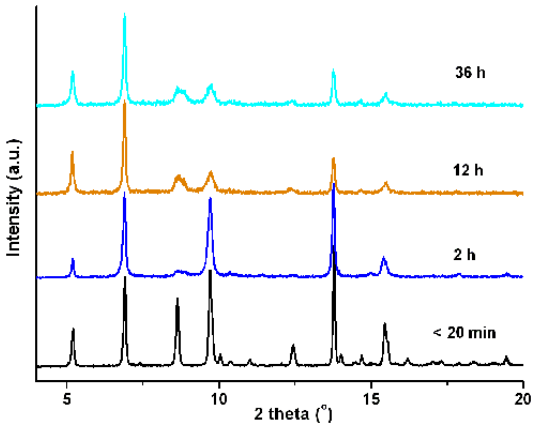


Figure S6. Powder X-ray diffraction patterns for activated SUMOF-3 subjected to open air for various amount of time. The activated sample can be stable in air at least for two and half days.



Electronic Supplementary Information (ESI)

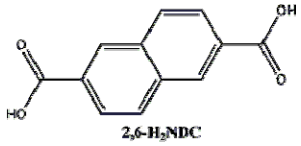
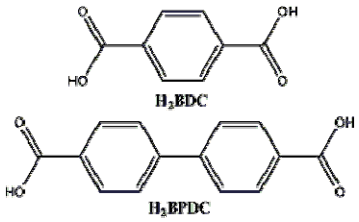
Figure S7. Powder X-ray diffraction patterns for activated SUMOF-4 subjected to open air for various amount of time. The activated sample can stand to be subjected to open air for a long time, although some of the diffraction lines got broadened rather rapidly.

Table S1. Crystal data and structure refinements[3,4] for SUMOF-2, SUMOF-3 and SUMOF-4.

Identification code	SUMOF-2	SUMOF-3	SUMOF-4
Empirical formula	$C_{24}H_{12.25}O_{14}Zn_{4.125}$	$C_{75}H_{50}NO_{31.7}Zn_8$	$C_{33}H_{24}NO_{15}Zn_4$
Formula weight	794.24	1995.32	936.01
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Trigonal	Triclinic	Orthorhombic
Space group	*R-3m*	*P*-1	*Pnnm*
Unit cell	a = 18.4010(10) Å c = 44.057(3) Å	a = 18.6086(8) Å b = 20.2422(7) Å c = 20.8135(7) Å α = 70.421(3) ° β = 68.955(3) ° γ = 68.031(4) °	a = 18.3770(6) Å b = 17.3043(4) Å c = 17.9565(5) Å
Volume (Å^3)	12918.9(14)	6600.7(4)	5710.2(3)
Z	12	2	4
Density (calculated)	1.225 g/cm^3	1.004 g/cm^3	1.089 g/cm^3
Absorption coefficient	2.314	1.479	1.705
F(000)	4704	2001	1876
Crystal size (mm^3)	0.30 × 0.30 × 0.25	0.20 × 0.15 × 0.15	0.25 × 0.20 × 0.20
Crystal color	colorless	colorless	colorless
Theta range for data collection	4.13° < θ < 26.37°	4.14° < θ < 26.37°	4.20° < θ < 26.37°
Index ranges	$-22 \le h \le 18$, $-21 \le k \le 22$, $-55 \le l \le 44$	$-23 \le h \le 23$, $-25 \le k \le 22$, $-19 \le l \le 26$	$-22 \le h \le 13$, $-21 \le k \le 12$, $-22 \le l \le 22$
Reflections collected	29350	45520	19462
Unique reflections	3211 ($R_{(int)}$= 0.1114)	26227 ($R_{(int)}$= 0.0490)	5966 ($R_{(int)}$= 0.0419)
Completeness to theta	0.992	0.973	0.986
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Min. and max. transmission	0.96827 and 1.00000	0.92284 and 1.00000	0.85492 and 1.00000
Observed reflections	2326	15115	4341
Goodness-of-fit on F^2	1.098	1.002	1.086
Final R indices [I>2sigma(I)]	$R1$ = 0.0890, $wR2$ = 0.2153	$R1$ = 0.0590, $wR2$ = 0.1616	$R1$ = 0.0545, $wR2$ = 0.1828
R indices (all data)	$R1$ = 0.1143, $wR2$ = 0.2308	$R1$ = 0.0916, $wR2$ = 0.1745	$R1$ = 0.0738, $wR2$ = 0.1937

Electronic Supplementary Information (ESI)

Table S2. Comparison of the unit cells and voids of the non-interpenetrated analogues of SUMOF-2 to SUMOF-4.

	SUMOF-2	SUMOF-3	SUMOF-4
Ligand	 H_2BDC	 $2,6\text{-}H_2NDC$	 H_2BDC H_2BPDC
Unit cell	a= b=12.9Å, c=12.9Å, α=90.8°, β=90.8°, γ=90.8°	a=b=15.1Å, c=15.0Å, α=92.7°, β=76.5°, γ=84.3°	a=b=12.9Å, c=17.3Å, α=88.8°, β=88.8°, γ=88.6°
Cell volume ($Å^3$)	2417	3300	2876
Void (%)	44.2	58.3	54.4

References

1. Rosi, N. L; Kim, J.; Eddaouddi, M.; Chen, B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* 2005, ***127***, 1504.
2. S. S. Kaye, A. Dailly, O. M. Yaghi and J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 14176.
3. Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112-122.
4. Spek, A. L. *J. Appl. Cryst.* **2003**, *36*, 7-13.