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A sol-gel monolithic metal-organic framework with enhanced methane uptake

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Contents

S1 Elemental analysis	S2
S2 High-resolution powder X-ray diffraction	S3
S3 FTIR	S4
S4 Transmission electron microscopy (TEM) and electron diffraction	S4
S5 Formation mechanism for monolithic MOF	
S6 Scanning electron microscopy (SEM)	
S7 N2 adsorption and BET representation	
S8 Mercury porosimetry and density evaluation	
S9 High pressure adsorption	
S10 Nanoindentation	S17
S11 TGA-MS	S18
S12 References	S19

S1. Elemental analysis

Elemental analysis for experimental powder and monolithic samples did not show any important differences (Supplementary Table 1). When comparing the composition with the molecular formula of HKUST-1, it is clear that the analysed materials were hydrated, with ca. one molecule of water per Cu atom. A repeated experiment on a dry sample was closer to the calculated composition of HKUST-1.

Sample	% C	% Н	% O	% Cu
monoHKUST-1	33	3	37	27
monoHKUST-1 (repeat)	35	2.5	33.5	29
powdHKUST-1	32	3	37	28
Calc. HKUST-1	36	1	32	31
Calc. HKUST-1 – hydrated	33	2	36	29

Supplementary Table 1. Elemental analysis of *mono*HKUST-1 compared with calculated HKUST-1.

S2. High-resolution powder X-ray diffraction

PXRD analysis and Pawley fitting shows that the crystalline phase of both the monolith and the powder is the same, and that it is HKUST-1 (Supplementary Figure 1). No extra crystalline phases were observed.



Supplementary Figure 1. PXRD of **a**, *powd*HKUST-1 and **b**, *mono*HKUST-1. Observed (black symbols), Pawley fitting (red line) and difference (grey line).

S3. FTIR

FTIR showed essentially identical peaks in both *mono*HKUST-1 and *powd*HKUST-1 samples (Supplementary Figure 2). This indicates that there are no new chemical functionalities in the monolith.



Supplementary Figure 2. FTIR of *mono*HKUST-1 (red) and *powd*HKUST-1 (black).

S4. Transmission electron microscopy (TEM) and electron diffraction



Supplementary Figure 3. TEM images and primary particle size distribution of HKUST-1 synthesis at **a**, room temperature, 20 °C; **b**, 40 °C and **c**, 60 °C.



Supplementary Figure 4. TEM images of the aggregation of *powd*HKUST-1 particles – synthesis at room temperature.

Both the powder and the monoHKUST-1 samples show some bright spots of ca. 5 nm uniformly distributed in the samples (Supplementary Fig. 5). These bright spots have been observed previously in HKUST-1 samples; see for example Bradshaw *et al.*¹; Liu *et al.*²; Srimuk *et al.*³ EDX elemental analysis in both powdHKUST-1 and monoHKUST-1 confirmed the existence of Cu (mainly), O and C in the bright spots (Figure 2). We attribute these spots to denser, non-crystalline defects probably caused by the fast synthesis of HKUST-1 – this would explain the higher density of the monolith. Importantly, both the powder and the monolith present them, and therefore cannot be related to the "binder" itself.



Supplementary Figure 5. TEM images of a-b, monoHKUST-1, and c-d, and powdHKUST-1.



Supplementary Figure 6. Electron diffraction of *mono*HKUST-1 and *powd*HKUST-1.

S5. Formation mechanism for monolithic MOF

Supplementary Table 2. Effects of particle size and drying conditions on the morphology of obtained materials. M represents monolithic structure, P represents powdered structure, M/P represents partial monolithic partial powdered structure.

Drying Temp (°C)	Particle size (nm)			
	51	73	145	
20	М	М	Р	
30	М	М	Р	
40	М	M/P	Р	
50	M/P	M/P	Р	
60	Р	Р	Р	
70	Р	Р	Р	
80	Р	Р	Р	

S6. Scanning electron microscopy (SEM)



Supplementary Figure 7. SEM images of **a**, *mono*HKUST-1, and **b**, *powd*HKUST-1. There is a clear difference in the way the material is packed: *powd*HKUST-1 is a simple agglomeration of particles with a large amount of interstitial space, whereas *mono*HKUST-1 surface is much more compact and with minimal amount of interstitial space.

S7. Sample activation, N2 adsorption and BET representation

We first dried the samples at 120 °C under vacuum overnight first, at which stage the samples were fully dried and activated, please see TGA-MS discussion below. This allows measuring the weight unequivocally. The samples were then quickly transferred to the equipment and degassed in situ at 120 °C for 8 hours under vacuum.

BET area was calculated by Rouquerol's consistency criteria.^{4,5} The representation in Supplementary Fig. 9a was used to select the maximum P/P_0 for BET calculation.



Supplementary Figure 8. a, **b**, linear and semi-log plot, respectively, of N_2 adsorption isotherms on *mono*HKUST-1 at 77 K; **c**, determination of maximum P/P₀ by applying Rouquerol's consistency criteria; and **d**, BET representation of N_2 isotherms for *mono*HKUST-1.

S8. Mercury porosimetry and density evaluation

Mercury porosimetry is a well-established method to determine envelope (i.e. bulk) densities and macro- and mesoporosity.⁶ In contrast to capillary condensation where the pore fluid wets the pore walls (i.e. the contact angle is $<90^{\circ}$), mercury is a non-wetting liquid (i.e. contact angle $>90^{\circ}$) that must be forced to enter a pore by application of external pressure. The surface tension of mercury and the interfacial tension between mercury and the solid surface results in mercury bridging the openings to pores, cracks, and crevices until sufficient pressure is applied to force entry. At atmospheric pressure, mercury will resist entering pores smaller than ca. 6 μ m diameter and therefore can be used to calculate envelop (bulk) volume. Therefore, when an object is surrounded by mercury, the mercury forms a closely fitting liquid envelope around the object. Thus, a progressive increase in hydrostatic pressure is applied to enable the mercury to enter the pores in decreasing order of width (i.e. first large macropores, then mesopores). At a pressure of 60,000 psi (414 MPa) mercury has been forced to enter pores of diameters down to 0.003 micrometer.

In a typical mercury porosimetry experiment, the exact volume of the sample cell is known. The cell containing the activated sample is evacuated and filled with mercury. In the case of a monolithic sample, mercury surrounds the sample, but, at ambient pressure, does not enter small cracks and crevices in the surface smaller than ca. $6 \mu m$ diameter, nor into pores in the structure of the material. Reweighing the filled sample containers and subtracting from this the weight of the empty sample cell plus sample, yields the weight of the surrounding mercury from which the volume of mercury is to be calculated. The fact that mercury presents a high density allows minimising errors in the evaluation of volume from mass. At ambient pressure, the difference in the volume of the sample. When increasing the pressure, the mercury will start invading the open pore space, starting with larger macropores and following with mesopores. This will allow the evaluation of a pore size distribution of the macro- and mesopore region.

In the case of a powdered sample, the procedure follows essentially the same preliminary steps as when the sample is a single piece (monolith). A powdered sample is a bulk mass of grains, in which the bulk of the sample also contains interparticle space as void volume. Initially, the mercury envelope forms around the bulk mass and not around the individual particles, so the *bulk* or *envelope volume* of the entire sample mass is displaced. Only when the pressure is increased will mercury invade the interparticle space and envelope individual particles. A further increase in pressure will force mercury into the voids within the individual particles (i.e. the macro- and mesopores).

To calculate the bulk density of both monoliths and powder samples, we therefore used the volume of mercury displaced at ambient pressure, i.e. before mercury penetrates any kind of interparticle space and/or porosity. Whereas the "particle density" of the monolithic sample can be the exactly the same to the one of a powder particle, the "bulk density" (i.e. the *envelop density* or *mercury density*)^{6b} of the powder will be much smaller than the monolith due to the existence of interparticle spaces.

In this work, we used in the same activation conditions for density and gas adsorption: i.e. vacuum oven at 120 °C overnight to fully dry them. This allows measuring the weight unequivocally. Note that high temperature and lengthy in situ activation is not necessary for mercury porosimetry since the technique measures the macro- and mesoporosity as well as the envelop volume, which is not affected by the presence of adsorbed gas/moisture in the microporosity. However, high vacuum and long times are required for gas adsorption in order to start the adsorption isotherms at really low pressure (1E-8 P/P₀ in the case of N₂ isotherms at 77 K). This is common for the characterisation of MOFs and other porous materials, and although some gas molecules (N₂, CO₂) can be removed during this extra step, we can also confirm that the weight of samples before and after using high vacuum was not affected. In this work, we first activated the samples (vacuum oven, rotatory pump, at 120 °C overnight) before measuring the mass, and then we degassed the samples in situ thoroughly before the mercury porosimetry. Maximum pressure used in the mercury porosimetry was 206 MPa. The density of *mono*HKUST-1 at ambient pressure was 1.04 ± 0.06 g/cm³.

Supplementary Figure S10 shows the pore size distributions obtained from mercury porosimetry up to 206 MPa (i.e. equivalent to 60 Å). From the pressure versus intrusion data, the instrument generates volume and size distributions using the Washburn equation.⁶ The volume of mercury intruded for *mono*HKUST-1 and *powd*HKUST-1 were 0.037 and 1.922 cm³/g, respectively. In particular, the volume of mercury intruded for *powd*HKUST-1 is coming from the interparticle space rather than any real porosity.



Supplementary Figure 9. Pore size distribution (PSD) of the macroporosity for *mono*HKUST-1 (red line) and *powd*HKUST-1 (black line), obtained through mercury porosimetry. Note the absence of macroporosity in *mono*HKUST-1.

Alternative methods for density evaluation include i) tap density, valid for powders, and ii) geometrical density and iii) Archimedes' principle, valid for monolithic samples. However, these methods cannot be used in both monoliths and powders, and therefore the comparison is not

straightforward. In our case, when measuring the geometrical density assuming that the monolith had a truncated cone shape (Supplementary Figure 11), the derived density was $1.26 \pm 0.06 \text{ g/cm}^3$, higher than the bulk density from mercury porosimetry ($1.04 \pm 0.06 \text{ g/cm}^3$). We assume these important differences are a result of the uncertainties in the measurement of height and radii, and the existence of minor cracks that are difficult to take into account in the real shape compared with an ideal body. For Archimedes' principle, we immersed our monolith in silicone oil – not able to penetrate the microporosity network – with a 0.967 g/cm^3 density, allowing the monolith to sink (Supplementary Figure 12). The sample was preactivated at 120 °C under vacuum, overnight, and the weight of the samples was measured before immersion. The obtained density of monolithic HKUST-1 by this method is 1.10 g/cm^3 , confirming the high value obtained through mercury.

Taking into account the mercury density $(1.04 \pm 0.04 \text{ g/cm}^3)$ and the Archimedes' principle using silicon oil (1.10 g/cm^3) , we get an average value of $1.06 \pm 0.05 \text{ g/cm}^3$ (Supplementary Table 3); note that we are not including the very large density obtained through the geometrical method $(1.26 \pm 0.06 \text{ g/cm}^3)$ due to the large discrepancies.

Supplementary Table 3. Density of monoHKUST-1 measured by different methods.

	Mercury - Cambridge	Mercury - Micromeritics	Archimedes' Principle	Archimedes' Principle	Average
Density (g/cm ³)	1.08	1.00	1.10	1.095	1.06 ± 0.05
Degas conditions ^a	overnight	3 h	3 h	overnight	

^aAll samples were activated at 120 °C and vacuum overnight. The degas conditions only describe the second stage. An additional sample (not included) was degassed under high vacuum and 120 °C overnight to measure any potential changes in the weight; we confirm that no changes were observed.



Supplementary Figure 10. monoHKUST-1 with truncated core shape.



Supplementary Figure 11. The height of silicone oil before (left) and after (right) adding the monoHKUST-1.

S9. High-pressure adsorption

The experimental data of high-pressure gas adsorption was obtained as excess gravimetric adsorption capacity (N_{Exc}). The gravimetric uptake can be transferred to volumetric capacity by multiplying the bulk density of the adsorbent. The experimentally measured values are excess amounts adsorbed (N_{Exc}), which are transformed into absolute uptakes (N_{Abs}) by using equation [1]:

$$N_{Abs} = N_{Exc} + \rho V_{pore}$$
[1]

where ρ is the density of the gas at the given adsorption pressure and temperature, obtained from NIST, and V_{pore} is the pore volume of the adsorbent.



Supplementary Figure 12. Comparison of absolute gravimetric CH₄ adsorption isotherms at 298 K on *mono*HKUST-1 (red solid circles), excess gravimetric uptake on *mono*HKUST-1 (red empty circles), and powder HKUST-1 (black squares) from Peng *et al.*⁷

Supplementary Table 4. Methane adsorption isotherm on monoHKUST-1 at 298 K.

Excess adsorption					Absolute a	dsorption
Pressure	wt. %	Gravimetric	Volumetric	Methane density	Gravimetric	Volumetric
bar		(g/g)	(cm ³ /cm ³)	g/ml	(g/g)	(cm ³ /cm ³)
0.36	0.6	0.006	8	0.0002	0.006	9
0.72	1.0	0.010	15	0.0005	0.010	16
1.52	1.9	0.019	28	0.0010	0.019	29
3.08	3.3	0.033	50	0.0020	0.034	52
4.10	4.2	0.042	63	0.0026	0.043	65
5.10	4.9	0.049	74	0.0033	0.051	77
7.10	6.2	0.062	94	0.0046	0.065	98
10.12	7.9	0.079	119	0.0066	0.082	124
15.11	9.8	0.098	148	0.0100	0.103	156
20.08	11.2	0.112	170	0.0134	0.119	180
25.04	12.4	0.124	188	0.0169	0.133	201
30.08	13.2	0.132	199	0.0205	0.142	215
39.96	14.1	0.141	213	0.0278	0.155	234
49.88	14.5	0.145	219	0.0353	0.163	246
59.79	14.6	0.146	220	0.0430	0.168	254
69.76	15.1	0.151	227	0.0510	0.177	267
79.57	15.3	0.153	231	0.0592	0.184	278
89.35	15.4	0.154	232	0.0676	0.189	285
99.38	14.3	0.143	215	0.0761	0.182	275

In order to identify the nature of the secondary phase present in the monolith, we have simplified the problem assuming the existence of two phases only. The properties of the phases are then given by Supplementary Table 5, where x is the volumetric percentage of phase of pure HKUST-1, w_1 and w_2 are the weight percentage of phase of pure HKUST-1 and secondary denser phase, respectively, ρ is the volumetric methane uptake of the unknown phase, a_1 and a_2 are the volumetric methane uptake of pure HKUST-1 and secondary phases, respectively. The equations required for the calculations are:

$0.88x + \rho(1-x) = 1.08$	$0 \leq x < 1$	eq. 1
$a_1x + a_2(1-x) = 259$		<i>eq</i> . 2
$w_1 = 0.88 x / 1.06$		eq. 3

Supplementary Table 5. Methane uptake, percentage and densities of phases in monoHKUST-1.

Phase	V %	Uptake (cm³/cm³)	Uptake (cm ³ /g)	Density (g/cm³)	wt%
HKUST-1	х	a 1	a ₁ /0.88	0.88	W 1
Unknown denser phase	1-x	a ₂	a₂/p	ρ	W 2
monoHKUST-1	-	259	244	1.06	-

The values are therefore based not only on the densities of HKUST-1 single crystal and monoHKUST-1 (0.88 and 1.06 g/cm³, respectively), but also on the volumetric uptake from HKUST-1 single crystal. Molecular simulations are generally used to predict maximum capacities on perfect crystals, but due to the presence of unsaturated open metal sites they tend to under-predict adsorption capacities for HKUST-1.⁸ If we take Peng et al. experimental data,⁷ HKUST-1 capacity at 65 bar is $270 \pm 8 \text{ cm}^3(\text{STP})/\text{cm}^3$. Also, this theoretical value can be potentially increased if even higher purity is achieved or due to the existence of defects that can enhance the adsorption capacity of a MOF.⁹ Regarding denser phases the presence of a mixture of BTC (density = 1.7 g/cm^3) and CuO (density = 6.31 g/cm^3) can be hypothesized. Keeping the stoichiometry of HKUST-1 (Cu₃(BTC)₂), a final density of a mixture of CuO+BTC secondary phases would be ca. 4.47 g/cm^3 , and would satisfy equation 2 (Supplementary Table 6).

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	Phase	V %	Uptake	Uptake	Density	wt%
			(cm ³ /cm ³)	(cm³/g)	(g/cm ³)	
	HKUST-1	0.950	272	309	0.88	0.789
	CuO+BTC	0.050	13	3	4.47	0.211
	monoHKUST-1		259	244	1.06	

Supplementary Table 6. Methane uptake, percentage and densities of phases in monoHKUST-1.

A different possibility is the presence of a dense copper benzene-1,3,5-tricarboxylate (CuBTC) xerogel phase with a density of 2.81 g/cm³. In this case equation 2 will be satisfied if the theoretical uptake of non-defective HKUST-1 reaches 280 cm³/g (Supplementary Table 7), only slightly higher than previously reported data, and therefore a realistic value.

Phase	V %	Uptake	Uptake	Density	wt%
		(cm³/cm³)	(cm³/g)	(g/cm ³)	
HKUST-1	0.907	280	318	0.88	0.753
CuBTC xerogel	0.093	46	16	2.81	0.247
Average		259	244	1.06	

Supplementary Table 7. Methane uptake, percentage and densities of phases in monoHKUST-1.

S10. Nanoindentation experiments



Supplementary Figure 13. Indentation modulus (*I*) of $_{mono}$ HKUST-1 plotted as a function of surface penetration depth. The average value determined from 200 to 2000 nm is 11.5 ± 0.4 GPa. Each error bar arises from the standard deviation of 60 indents. Note that the indentation modulus, *I*, was obtained by assuming the sample Poisson's ratio *v* to be zero. This meant that the values shown here are representing the *upper bound* of the Young's modulus (*E*). HKUST-1 single crystal has not being included here due to its high anisotropy in terms of elastic response.¹⁰

S11. Thermogravimetric analysis (TGA-MS)

TGA-MS of $_{powd}$ HKUST-1 shows that the degradation takes place at the same temperature as for $_{mono}$ HKUST-1 (i.e. 330 °C);¹¹ the small differences are in the initial stage at low temperature, where $_{powd}$ HKUST-1 and $_{mono}$ HKUST-1 lose ca. 16 and 20 wt.%, respectively (Supplementary Figure 14). Mass spectroscopy analysis of the gases show that the initial step is provoked by loss of water and ethanol adsorbed, whereas the 330 °C step is related to the decomposition of the sample, BDC and CO₂ (Supplementary Figure 15).

A further TGA-MS was carried on a *mono*HKUST-1 sample previously activated at 120 °C under vacuum for 8 hours. This time, after activation the sample was heated up to 120 °C, kept for 8 hours at this temperature, and then heated again up to 900 °C. This experiment tried to replicate the heating activation procedure – with the obvious limitation of the absence of vacuum and the inevitable presence of small amounts of moisture in the chamber of the TGA at room temperature. The TGA showed a very small initial mass loss (ca. 1.5 %) related to water desorption below or at 120 °C (Supplementary Figure 14). Mass spectroscopy proved the absence of ethanol after the activation sample, and the successful removal of water at 120 °C without vacuum (Supplementary Figure 14).



Supplementary Figure 14. Thermogravimetric analysis of *mono*HKUST-1, black line; activated *mono*HKUST-1, grey dotted line; and *powd*HKUST-1, red line. Vertical red dotted line shows the 8 h activation at 120 °C for activated *mono*HKUST-1.



Supplementary Figure 15. Mass spectroscopy from TGA of **a**, $_{mono}$ HKUST-1, **b**, $_{powd}$ HKUST-1, and **c-d**, activated $_{mono}$ HKUST-1. H₂O, blue line; ethanol, red line; CO₂, green line; BTC, purple line. Vertical red dotted line and red dotted square in **c** - **d**, respectively, shows the 8 h activation at 120 °C.

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