Tuning porosity in macroscopic monolithic metal-organic frameworks for exceptional natural gas storage

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Widespread access to greener energy is required in order to mitigate the effects of climate change. A significant barrier to cleaner natural gas usage lies in the safety/efficiency limitations of storage technology. Despite highly porous metal-organic frameworks (MOFs) demonstrating record-breaking gas-storage capacities, their conventionally powdered morphology renders them non-viable. Traditional powder shaping utilising high pressure or chemical binders collapses porosity or creates low-density structures with reduced volumetric adsorption capacity. Here, we report the engineering of one of the most stable MOFs, Zr-Uio-66, without applying pressure or binders. The process yields centimetre-sized monoliths, displaying high microporosity and bulk density. We report the inclusion of variable, narrow mesopore volumes to the monoliths’ macrostructure and use this to optimise the pore-size distribution for gas uptake. The optimised mixed meso/microporous monoliths demonstrate Type II adsorption isotherms to achieve benchmark volumetric working capacities for methane and carbon dioxide. This represents a critical advance in the design of air-stable, conformed MOFs for commercial gas storage.
With global energy usage predicted to exponentially increase over the next 50 years, widespread access to clean fuels is imperative. Natural gas (NG), mainly composed of methane, is a favourable fuel due to its abundant natural reserves and reduced pollutant emissions relative to other fossil fuels. Although liquefied NG at 113 K and compressed NG (CNG) at 250 bar are already in use, cryogenic and high-pressure storage methods have severely limited practical applications. For example, the higher pressures required for liquefaction can only be achieved using complex and expensive multi-stage compressors. To counteract these limitations, the U.S. Department of Energy (DOE) sets the ambitious volumetric NG storage target of 263 cm³ (STP) cm⁻³ at 65 bar, which is equal to that of CNG at 250 bar and 298 K. The moderate 65 bar pressure targeted by the DOE is highly practical, being achieved using inexpensive compressors and light-storage tanks. This offers not only safety benefits but also improvements in large-scale industrial economics. Adsorbed NG (ANG) stored at relatively low pressure on porous materials has emerged as a safe and cost-effective method of achieving this ambitious target. Furthermore, advances in gas storage technology are critical for multiple energy applications, including pollutant capture, such as CO₂ capture. Technological advances in adsorption are clearly vital for environmental fuel usage, both in this century and the future economy.

Over the last 20 years, metal–organic frameworks (MOFs), obtained through the crystalline self-assembly of metal atoms/ clusters and organic molecules, have massively extended the use of porous materials in adsorption applications. Indeed, they show promise for both dense NG storage, and selective CO₂ capture. Microporous MOFs, with pore sizes below 2 nm, can exhibit outstanding total volumetric CH₄ uptake, reported to exceed 200 cm³ (STP) cm⁻³ at the DOE target pressure of 65 bar (e.g., NU-111, PCN-14 and HKUST-1). Meanwhile, an extraordinary CO₂ capacity of 320 cm³ (STP) cm⁻³ (35 bar) was calculated for MOF-177.

However, despite the immense potential of MOFs evident from these benchmark results, each of these quoted volumetric uptakes are only theoretical storage maxima that do not take into account the working capacity or the real density of the material. Figure 1 illustrates these ideas. Firstly, the working capacity, in contrast with the total uptake, represents the true volume of gas available under practical working conditions. Volumetric working capacity is defined as the volume adsorbed at the maximum working pressure minus the uptake at the minimum desorption pressure (typically ca. 5 bar). Thus, the Type I isotherm shape of typical microporous MOFs leads to a low working capacity due to high uptake at low pressure and plateauing at high pressure (Fig. 1a). An example is HKUST-1, which shows an outstanding, theoretical, total volumetric capacity of 270 cm³ (STP) cm⁻³ (65 bar) using single-crystal density, but exhibits an accessible working capacity of 190 cm³ (STP) cm⁻³, measured between 5 and 65 bar. Type II and IV isotherms do not plateau at high pressures, but still show a relatively high uptake at low pressure (Fig. 1b). For this reason, adsorbents that maximise working capacity via Type V S-shaped isotherms, e.g., flexible but also rigid MOFs with unusual adsorption behaviour, are of significant interest (Fig. 1c). For example, Long et al. reported an outstanding theoretical 197 cm³ (STP) cm⁻³ volumetric working capacity in the flexible MOF Co(bpd) and a theoretical volumetric capacity of 203 cm³ (STP) cm⁻³, both calculated using the single-crystal density of the MOF.

In addition to the shape of the isotherms, although these exceptional, theoretical, volumetric capacities were determined experimentally via the measurement of gas isotherms, it is common practice to convert the obtained gravimetric uptake (cm³ g⁻¹) to volumetric capacity (cm³ cm⁻³) using the MOFs ideal single-crystal density. This neglects the detrimental effect of extensive interstitial space that exists between the synthesised MOF particles in the powder (Fig. 1d). Experimentally, the bulk or tap density of such finely powdered materials is very low, and this loose packing of the MOF particles is widely observed to reduce the adsorbents volumetric capacity. Although a 25% reduction in packing efficiency is widely reported, experimentally compacted MOF pellets have even been reported with a bulk density 50% lower than the theoretical crystal density. Taking into account the real density of the powder, the reported benchmark working capacities of flexible MOFs can be expected to fall between 100 and 150 cm³ (STP) cm⁻³. With this loss of storage capacity in mind, the volumetric DOE target for unpacked and undensified NG adsorbents becomes a staggering 350 cm³ (STP) cm⁻³, making it clear that, in terms of practical volumetric working capacity, powdered MOFs have not yet achieved industrially viable NG storage capacities.

Attempts to overcome the low densities of MOF powders have led to densification using pressure, with chemical binders added to improve the mechanical properties of the shaped pellets. However, the application of high pressures to MOFs provokes devastating and irreversible collapse of the internal porosity, while binders might block pores and the use of milder pressures prevent efficient densification. The result of these traditional pelletization procedures has therefore been low-density pellets with diminished volumetric capacity. Furthermore, many MOFs are incompatible with this pelletization process. For example, flexible Co(bpd) undergoes a staggering 94% increase in unit cell-volume upon transition from its collapsed to expanded state during CH₄ adsorption. In addition to issues with the mechanical properties of flexible MOF pellets, they would require highly voluminous tanks to allow the expansion of these constrained volumes. Long et al. reported that, upon densification of Co(bpd) powder to only 68% of the maximum crystal density, 11% of collapsed Co(bpd) crystals were no longer able to expand in the constrained volume. Clearly, the commercialisation of gas-storing MOFs has been hugely limited by the non-optimised volumetric capacities in the conformed materials.

Much effort has been applied to finding alternative ways to pelletise, densify and shape MOFs. As a significant advancement in this direction, we reported the sol–gel synthesis of centimetre-scale monolithic MOFs (monoMOFs) mono-ZIF-8 and mono-HKUST-1 without using supports, applied pressures or binders. In particular, the high microporosity and bulk density of mono-HKUST-1 enabled a record total CH₄ storage capacity of 259 cm³ (STP) cm⁻³, making it the first conformed material to reach the U.S. DOE target. Although this material has laid the groundwork for MOF densification with retention of physical properties, from an industrial perspective, it failed to address significant practical barriers. Again, its high microporosity and a strong physical interaction with NG at low pressure leads to a working capacity that falls short of the DOE target. As a result of the classical Type I isotherm this MOF exhibits (Fig. 1a), moderately increasing the maximum pressure to a still industrially viable 100 bar fails to achieve the working capacity target of the Advanced Research Projects Agency-Energy (ARPA-E). This is a persistent characteristic of purely microporous MOFs: micropores rapidly saturate at low pressure with only marginal gains achieved by applying higher pressures. Finally, the high water affinity of the metal nodes in HKUST-1 incurs irreversible loss of crystallinity and adsorption performance under moisture in ambient...
conditions\textsuperscript{30,31}. This makes long-term usage of the adsorbent problematic. It is the inadequate working capacity and poor chemical stability of even benchmark mono-\textit{HKUST-1} that has driven us to further develop a synthetic procedure for enhancing the volumetric working capacity of high-stability MOFs with tuneable mesoporosity.

Among all the MOFs, UiO-66 (Zr\textsubscript{6}O\textsubscript{4}(OH)\textsubscript{4}(1,4-benzenedi-carboxylate)\textsubscript{6} (Fig. 2a) represents the prototypical structure for high porosity and thermo-chemical/mechanical stability\textsuperscript{32}. This high-stability MOF has typically been overlooked as a NG adsorbent as a result of its exclusive microporosity and relatively poor physical interaction with CH\textsubscript{4}—especially when compared with MOFs with more exotic surface chemistry. However, in our view, this weak interaction at low pressure can be utilised to enhance its working capacity. Through the development of a synthetic protocol that introduces tuneable volumes of mesoporosity into the monolith macrostructure, we modify and optimise pore-size distribution to convert this MOFs undesirable Type I adsorption isotherm into a promising Type II isotherm (Fig. 1b). The result is a mixed micro-/mesoporous monolith with a volumetric working capacity that surpasses the theoretical maximum for the traditional, microporous MOF. Using grand canonical Monte Carlo (GCMC) simulations, we are then able to rationalise our observations and to account for the outstanding values recorded for volumetric NG and CO\textsubscript{2} adsorption.

**Results**

**Synthesis of monolithic MOFs.** In our previous syntheses of mono\textit{ZIF-8} and mono\textit{HKUST-1}\textsuperscript{27,28}, MOF primary nanoparticles (70 and 50 nm, respectively) were densified during drying to yield centimetre-scale monoliths. We demonstrated that both mild drying conditions using a low-surface tension solvent and small primary particles were critical to monolith formation. For mono\textit{UiO-66}, we have modified a literature synthesis for UiO-66 gel\textsuperscript{33} to produce 10 nm primary MOF particles in a viscous gel phase (Fig. 2c). We then washed and dried the MOF gel under four different conditions (Supplementary Table 1) to obtain macroscopic monoliths (Fig. 2d–g). mono\textit{UiO-66_A} was prepared by the existing literature procedure\textsuperscript{33}, whereby reaction solvent (DMF) and impurities were washed from the primary particles with ethanol before drying at 200 °C. This fails to create large, conformal monoliths, giving exclusively sub-mm-sized MOF fragments (Fig. 2d).

We evaluated the role of drying temperature in monolith formation. In the case of mono\textit{ZIF-8} and mono\textit{HKUST-1}, high temperatures induced fast removal of solvent from the interstitial spaces between primary particles. This stress at the vapour–liquid meniscus interface destroyed the materials’ gel macrostructure, resulting in standard powders. We decided therefore to synthesise mono\textit{UiO-66_B} by again washing the gel in ethanol, but instead drying at 30 °C. This resulted in centimetre-sized, opaque monoliths (Fig. 2e), supporting the view that the drying temperature is fundamental to controlling the monolithic macrostructure. We further studied the influence of washing solvent on monolith physical properties by next washing the DMF synthesised gel in further DMF before drying at 30 °C; this produced optically transparent mono\textit{UiO-66_C} (Fig. 2f). This solvent-induced alteration in transparency demonstrates the complex range of solvent–particle interactions that exist. We have previously proposed that slow evaporation of the reaction solvent, coupled with the presence of residual precursors, facilitates primary particle interaction by effectively extending the reaction time\textsuperscript{28}. We propose that epitaxial growth of the primary particles reduces the electron density contrast and therefore reduces the optical visibility of the interparticle barrier, giving a transparent material\textsuperscript{34}. According to this view, the use of ethanol to wash UiO-66 particles quenches the reaction, whereas the use of DMF facilitates its continuation. Furthermore, while the surface tension of DMF is higher than that of ethanol, the boiling point of DMF (153 °C) is also significantly higher (78 °C), meaning that the evaporation of DMF from the primary particles is slower. Given the high mechanical strength of UiO-66, the balance between surface tension and drying speed permits the gel macrostructure to be maintained throughout the drying process via gradual solvent evaporation. Finally, we used a similar synthesis for mono\textit{UiO-66_D} (Fig. 2g), but with an extended (180 min) centrifugation step. This was done to better understand the effects of primary particle densification prior to drying. These relatively minor changes to the synthetic procedure incurred fascinating changes in the physical properties of the resulting monoliths.

The powder X-ray diffraction (PXRD) patterns for each of mono\textit{UiO-66_A–D} show significant Scherrer line broadening. This stems from the non-convergence of diffraction peaks in nanocrystallites (Fig. 2b)\textsuperscript{35}. Transmission electron microscopy (TEM) of mono\textit{UiO-66_D} further confirms that the monoliths comprise densely packed MOF nanoparticles with particle interstitial space visibly reduced compared with that in the MOF gel (Supplementary Fig. 1a–d). Low-magnification scanning electron microscopy (SEM) shows the smooth surface of the macrostructure, which...
Fig. 2 Crystalline structure and optical images of UiO-66 gel and monoliths. a Graphical representation of the microporous crystal structure of UiO-66 with purple, sky blue, navy blue and white sticks representing zirconium, oxygen, carbon and hydrogen atoms, respectively. b Comparison of simulated XRD pattern of UiO-66 generated from its crystal structure; black, with PXRD patterns of, monoUiO-66 samples (monoUiO-66_A; blue, monoUiO-66_B; red, monoUiO-66_C; purple, monoUiO-66_D; green) confirming successful synthesis in each case. c UiO-66 gel used for synthesising monoliths. d UiO-66 washed in ethanol and dried at 200 °C (monoUiO-66_A). e UiO-66 washed in ethanol and dried at 30 °C (monoUiO-66_B). f UiO-66 washed in DMF and dried at 30 °C (monoUiO-66_C). g UiO-66 washed in DMF with extended centrifugation and then dried at 30 °C (monoUiO-66_D). d g (lower left corner, inset), symbols used to represent each material in Figs. 4 and 5.

resolves into a homogenous array of densely packed nanoparticles at high magnification (Supplementary Fig. 1c, f). These combined data support the proposed mechanism of monolith formation via primary particle densification. Elemental analysis showed that all four monoliths have compositions closely matching the crystal structure of defect-free UiO-66 (Supplementary Table 2). The high thermal stability of the monoliths is demonstrated by thermal decomposition above 500 °C (Supplementary Fig. 2), which also matches literature values. In addition, the characteristically high mechanical strength of UiO-66 was reproduced by the four monoliths (E = 4.2–14.3 GPa, H = 0.11–0.48 GPa) (Supplementary Fig. 3). These outstanding values are also comparable with those of the robust monoliths we have previously reported, monoZIF-8 (E = 3.6 ± 0.2 GPa, H = 0.43 ± 0.03 GPa) and monoHKUST-1 (E = 9.3 ± 0.3 GPa, H = 0.46 ± 0.03 GPa).

To further elucidate the synthetic origins of their different textural properties, we studied monoUiO-66 using fluorescence lifetime imaging microscopy (FLIM). FLIM utilises spatially resolved fluorescence lifetime decays to investigate the nanoscopic environment of a material, such as its morphology and defects. FLIM reveals the samples to be comprising smaller particle aggregates with distinct fluorescence lifetimes (Fig. 3a, b). Interestingly, monoUiO-66_A shows high homogeneity, being comprised entirely of quazispherical aggregates with uniform fluorescent lifetimes of ~4.7 ns (orange), whereas monoUiO-66_B-D show two distinct morphologies: small, circular particles and large rod-like particles. The small, circular particles have a long autofluorescence lifetime (~4.5 ns, orange), whereas the larger aggregates show a faster fluorescent decay (~3 ns, blue). Figure 3c shows the FLIM data analysis by the phasor approach, graphically translating fluorescence lifetime into Fourier space (Supplementary Figs. 4–7). Here, mono-exponential decays fall along an arc of radius 0.5 with long lifetime components located near the origin (0, 0) and short lifetime components near (1, 0). Multi-exponential decays comprise a weighted vector of the constituent phasors, meaning that all decay pathways in phasor space lie within the arc. In our case, each monoUiO-66 sample occupies phasor space within the arc, indicating multicomponent exponential decays. A single population was recorded for monoUiO-66_A whereas plots for monoUiO-66_B-D are heterogeneous showing at least two populations. This can be correlated with their biphasic morphology as described above and supports the proposed relationship between monolith textual properties and synthetic parameters. Since all monoliths are synthesised from the same primary particles (ca. 10 nm), any changes in photophysical properties must be caused by the way these identical particles interact with each other under different drying conditions. monoUiO-66_B-D show a statistically greater prevalence of larger, rod-like aggregates within the monolith macrostructure than monoUiO-66_A. To incur these differences in fluorescence lifetime, the observed aggregates cannot be an ensemble of completely discrete particles, as they would be in a powdered MOF. Instead, the primary particles of which each aggregate is comprised must be in close physical proximity and the decrease in fluorescence lifetime could be an indication of chemical interactions. These FLIM measurements thus reinforce our understanding of the monolith formation mechanism by confirming what morphology-only SEM measurements cannot: alterations to the synthetic procedure influence primary particle interaction.
Adsorption properties, porosity and density of monoliths. We analysed the porosity of the monoMOFs through N₂ adsorption at 77 K. Figure 4a, b and Supplementary Fig. 8 show the adsorption and desorption isotherms, respectively; Table 1 shows the BET areas ($S_{\text{BET}}$) calculated using Rouquerol’s consistency criteria (Supplementary Figs. 9–12) as well as the micro ($W_o$) and the total ($V_{\text{tot}}$) pore volumes. These experimental values are lower than, but consistent with, the theoretical maximum for defect-free UiO-66 ($S_{\text{BET}} = 1644 \text{ m}^2 \text{ g}^{-1}$), calculated using GCMC simulations as well as closely matching the original report of UiO-66 by Lillerud et al. ($1187 \text{ m}^2 \text{ g}^{-1}$). For all monoliths, we observed Type IV N₂ isotherms, with high gas uptake below 0.1 $P/P_o$ indicating extensive microporosity. The shape of each isotherm (Fig. 4b) is characteristic of the sequential filling of the discrete tetrahedral and octahedral (8 and 11 Å diameters, respectively) cavities of UiO-66. Extensive N₂ uptake at higher relative pressures was also recorded, indicating the existence of mesoporosity. After micropore filling, capillary condensation of the gas takes place within these wider cavities. The extent of the mesoporosity, obtained from the difference between the micro and the total pore volume (Table 1), varies considerably between the materials. The NLDFT pore-size distributions (PSD) highlight the substantial micropore volume (Supplementary Fig. 13), whereas the BJH analysis (Supplementary Fig. 14) confirms significant volumes of wide mesoporosity (varying between 2 and 20 nm for monoliths UiO-66_A-D). Small mesopores have previously been observed in UiO-66, on account of the enlargement of micropores due to missing linker/cluster defects. Crucially, both the size and volume of the mesopores obtained in this study vary with drying conditions. The observed meso/macroporosity is not the result of crystalline defects within the MOF primary particles and instead corresponds to void space in-between them, enforced by their arrangement in the macrostructure. The synthetic origin of the tuneable mesoporosity thus lies in the variations to primary particle drying conditions which alter particle packing/densification. Overall, the mesopore volumes follow the trend $\text{monoUiO-66_A} > \text{monoUiO-66_B} > \text{monoUiO-66_C} > \text{monoUiO-66_D}$.

We analysed the adsorption behaviour of the samples using computational simulations of mixed micro-/mesoporous UiO-66 by artificially creating a mesopore between two purely...
microporous UiO-66 layers (Supplementary Fig. 15). We were able to both match the condensation of N₂, i.e., the relative pressure at which N₂ uptake into the mesopores occurs and the characteristic step in N₂ uptake seen in Type IV isotherms (Fig. 4d; Supplementary Fig. 16). Although pore-shape is known to significantly influence gas adsorption behaviour, we found that, by tuning the pore width in a model slit-shaped pore between 2.3 and 2.75 nm, we could predict computational isotherms that closely resembled those obtained experimentally.

In this case, we found that a slit pore is representative of the wide mesoporous gap between two adjacent primary MOF particles—the origin of the mesoporosity in the current materials. Moreover,

**Table 1 Textural and adsorption properties of monolithic UiO-66**

|        | S\text{BET} (m² g⁻¹) | S\text{BET (v)} (m² cm⁻³) | W\text{o} (cm³ g⁻¹) | V\text{tot} (cm³ g⁻¹) | V\text{tot (v)} (cm³ cm⁻³) | ρ\text{b} (g cm⁻³) | CO₂ 40 bar\textsuperscript{v} (g g⁻¹) | CH₄ 65 bar\textsuperscript{v} (g g⁻¹) | CH₄ 100 bar\textsuperscript{v} (g g⁻¹) |
|--------|---------------------|--------------------------|---------------------|----------------------|--------------------------|-------------------|-----------------------|-----------------------|-----------------------|
| UiO-66_A | 1177                | 506                      | 0.46                | 1.62                 | 0.697                    | 0.430             | 0.670                 | 149                   | 0.180                 | 109                   | 0.252                 | 153                   |
| UiO-66_B | 994                 | 431                      | 0.39                | 1.43                 | 0.616                    | 0.434             | 0.648                 | 142                   | 0.160                 | 98                    | 0.228                 | 142                   |
| UiO-66_C | 1065                | 903                      | 0.42                | 0.81                 | 0.687                    | 0.848             | 0.635                 | 265                   | 0.170                 | 202                   | 0.243                 | 289                   |
| UiO-66_D | 982                 | 1032                     | 0.38                | 0.57                 | 0.601                    | 1.051             | 0.537                 | 284                   | 0.143                 | 211                   | 0.203                 | 296                   |
| Simulation | 1644                | 2033                     | 0.49                | 0.49                 | 0.602                    | 1.237             | 0.375                 | 236                   | 0.103                 | 178                   | 0.116                 | 200                   |

\text{S\text{BET}} area, \text{S\text{BET (v)}}, \text{W\text{o}}, \text{V\text{tot}}, \text{V\text{tot (v)}}, \text{ρ\text{b}}, \text{CO₂ 40 bar\textsuperscript{v}}, \text{CH₄ 65 bar\textsuperscript{v}}, \text{CH₄ 100 bar\textsuperscript{v}}.

\*\text{Obtained at } P/P\text{º} = 0.1; ¹\text{Obtained at } P/P\text{º} = 0.98; ²\text{Quantified using Hg-porosimetry; } ³\text{the total absolute uptake.}

Fig. 4 N₂ adsorption isotherms and Hg-porosimetry pore-size distributions of UiO-66 monoliths. a Linear and b, semi-log isotherm plots of gravimetric N₂ uptake at 77 K for monolithic UiO-66_A (blue triangles), UiO-66_B (red diamonds), UiO-66_C (purple squares) and UiO-66_D (green circles). The theoretical isotherm (white squares) was simulated from the crystal structure of UiO-66 (Supplementary Fig. 15). The experimental isotherms indicate extensive microporosity, which is comparable with the simulated isotherm, as well as variable mesoporosity, indicated by N₂ uptake at higher relative pressure. c pore-size distributions (PSD) obtained by Hg-porosimetry showing the variations in meso- (2–50 nm diameter) and macro- (> 50 nm diameter) porosity amongst the materials. d Comparison of experimental and simulated micro-/mesoporous UiO-66 (black cross), indicating the good match obtained when using an appropriate ratio of porosities (see the Methods section). e-f The density distribution and a snapshot, respectively, of simulated N₂ adsorption (navy blue spheres) at 0.7 P/Po (i.e., before capillary condensation—the micropores and the mesopore walls are completely filled by N₂, whereas the centre of the mesopore remains empty) between two UiO-66 crystals (Zr; blue; O; red; C; grey and H; white) separated by a 2.3 nm mesopore (representative of monoUiO-66_D).
by defining the ratio of micro-/mesoporosity, we achieved an excellent match of the whole experimental adsorption isotherms. The micro-/mesoporosity ratios obtained from the simulations were 0.45, 0.43, 0.71 and 0.85 for monoUiO-66_A-D respectively. Calculation of the density distributions and snapshots during N₂ adsorption let us elucidate the most probable regions for adsorption and visualise how the pores are filled. Figure 4e and f show that, at 0.7 \( P/P₀ \), i.e., before the onset of capillary condensation — the micropores and the mesopore walls are completely filled by N₂, whereas the centre of the mesopore remains empty.

To further study the monolith density and PSD in the meso- and macroporous range, we utilised Hg-porosimetry. Figure 4c shows that the experimental PSDs for the four samples match well those calculated by BJH (Supplementary Fig. 14). These data establish the importance of the materials showing both variable meso- and macroporosity. Although larger pore volumes are generally associated with enhanced adsorption capacities on a gravimetric basis, they also incur lower volumetric adsorption. When we quantified the bulk density (\( ρ_b \)) of the samples, we found that, as expected, those with greater meso- and macropore volumes showed lower densities (Table 1). Thus, \( ρ_b \) in the monolithic MOFs varies according to UiO-66_D > UiO-66_C > UiO-66_B > UiO-66_A. Excitingly, \( ρ_b \) of monoUiO-66_D (1.05 g cm\(^{-3}\)) approaches the theoretical crystal density of UiO-66 (1.237 g cm\(^{-3}\)). We postulate that this relatively high density derives from the efficient packing of small primary particles within the monolithic macrostructure, with the extraneous interparticle space, which reduces \( ρ_b \) in e.g., powdered materials/pellets, being minimised\(^{44,45}\). For example, Dhainut et al. previously reported the densification of UiO-66 powder at 18 MPa to obtain a UiO-66 pellet with 0.43 g cm\(^{-3}\) density\(^{46}\). This pressure was selected as a compromise between maximising industrially significant physical properties, such as pellet density and mechanical strength, while minimising compressive loss of \( S_{\text{BET}} \). Crucially, monoUiO-66_D exhibits not only exceptional \( ρ_b \) but also high \( S_{\text{BET}} \) and relatively low but significant mesopore volume.

The simple modifications made to the original synthetic protocol (discussed above) account for the differences in physical properties between these materials. The near identical densities of highly mesoporous monoUiO-66_A (\( ρ_b = 0.430 \) g cm\(^{-3}\)) and monoUiO-66_B (\( ρ_b = 0.434 \) g cm\(^{-3}\)), dried at 200 and 30 °C, respectively, suggest that \( ρ_b \) is not strongly dependent on drying temperature. In contrast, the high density of monoUiO-66_C (\( ρ_b = 0.834 \) g cm\(^{-3}\)) demonstrates a significant reduction in interstitial space/mesoporosity, with the only synthetic difference being the washing solvent (i.e., DMF). The slow evaporation of this solvent during drying enables both primary particle densification and continued primary particle interaction (as supported by the FLIM data), controlling both the density and porosity of the monolith. Finally, at 1.05 g cm\(^{-3}\), monoUiO-66_D reveals the highest \( ρ_b \). In this case, the extended centrifugation period applied prior to drying (30 °C) evidently facilitates better primary particle compaction and minimises meso-/macroporosity. These observations are especially significant when the high \( S_{\text{BET}} \) area and microporosity of each monolith is considered. Pore collapse in materials obtained through traditional densification procedures (e.g., applied pressures) renders them unsuitable for physiosorptive applications (e.g., dense gas storage)\(^{16}\). We have thus demonstrated that both the density and PSD of pure monolithic MOFs can be synthetically controlled without significant collapse/blocking of microporosity. The high thermal and mechanical stability of these robust and high density UiO-66 monoliths points strongly to their viability for commercial gas storage.

**Gas storage and selectivity.** We evaluated the gas adsorption performance of monoUiO-66_A-D (Supplementary Figs. 17–20). Figure 5 shows the adsorption isotherms for CH₄ and CO₂; Table 1 compares the gas uptake of CO₂ (40 bar) and CH₄ (65 and 100 bar). Rapid, industrially viable equilibration was reached for both CO₂ and CH₄ (<270 s for all monoliths, comparable with monoHKUST-1\(^{28}\)) with no trend discernible related to monolith density or porosity (Supplementary Fig. 21). In addition, no significant differences in CH₄/CO₂ selectivity were observed between monoUiO-66_A-D (Supplementary Figs. 22, 23), with each variant demonstrating high preferential uptake of CO₂.

Instead of the expected Type I isotherms, we observed surprising Type II isotherms. The presence of a quasi-linear performance in the high-pressure adsorption isotherms, compared with the traditional Type I isotherm in purely microporous samples (i.e., monoHKUST-1, Fig. 5b, i), is of paramount importance from a technical point of view in vehicles under driving conditions—i.e., for a constant supply of gas–fuel upon a pressure change. The gravimetric uptake capacities recorded do not vary substantially across monoUiO-66_A-D, reaching values of 0.252 g g\(^{-1}\) (298 K, 100 bar) for CH₄ and 0.670 g g\(^{-1}\) (298 K, 40 bar) for CO₂. For comparison, Wu et al. reported CH₄ and CO₂ uptakes of 0.11 g g\(^{-1}\) (300 K, 63 bar) and 0.38 g g\(^{-1}\) (300 K, 30 bar), respectively. Notably, the exclusively microporous character of their powder UiO-66 meant that the porosity became saturated at relatively low pressures yielding plateaued Type I isotherms. In contrast, isotherms obtained for our mixed micro-/mesoporous monoUiO-66 do not saturate at low pressures, demonstrating continued gas uptake even at the maximum pressures tested in this study. These promising Type II isotherms yield significant improvements in the total gas-storage capacity amongst UiO-66_A-D; 0.14–0.18 g g\(^{-1}\) (298 K, 63 bar) for CH₄ and 0.43–0.54 g g\(^{-1}\) (298 K, 30 bar) for CO₂, which we attribute to the narrow mesopore filling mechanism.

These results raise the question: Can the synthetic addition of mesoporosity be used to enhance gas adsorption capacity? While the presence of mesoporosity in the monoliths resulted in Type II isotherms with increased gas loadings at higher pressures, we observed little difference between the samples in terms of their gravimetric capacity (Fig. 5a, c). Yet the dramatic effect that these pores have on monolith density (\( \rho_b \), Table 1) incurred significant changes to the volumetric adsorption capacity. Figure 5b, d and Supplementary Figs. 18, 20 show the volumetric adsorption isotherms for CO₂ and CH₄. First of all, each monolith displays an outstanding improvement in volumetric gas storage relative to a pressurised empty tank. Small differences in porosity and BET surface area between the samples have a minor influence on the total volumetric uptake, while the different densities of the monoliths cause outstanding changes. Volumetric gas uptake for both CH₄ and CO₂ follows the same trend: monoUiO-66_D ≈ monoUiO-66_C >> monoUiO-66_B ≈ monoUiO-66_A (Table 1). Remarkably, this is the trend we found for the micro-/mesoporosity ratio analysis during our molecular simulations described above, where monoUiO-66_D had the largest relative amount of microporosity of the four experimental samples.

Overall, monoUiO-66_D showed outstanding total gas uptakes for both CH₄ (211 and 296 cm\(^3\) (STP) cm\(^{-3}\) at 65 and 100 bar) and CO₂ (284 cm\(^3\) (STP) cm\(^{-3}\) at 40 bar) in a conformed material. Comparison with microporous UiO-66 (Table 1) shows that these results are significantly higher than the theoretical maximum. We attribute the performance of monolithic UiO-66 to the tuneable physical properties of these dense materials: high microporosity but weak CH₄ interaction facilitate moderate uptake at low pressures while mesopores permit Type II isotherms and enhanced gas condensation at higher pressures. Density distributions and snapshots of gas adsorption (Fig. 5e, f
and Supplementary Fig. 25) demonstrate this phenomenon, showing gas condensation in optimised mesopores at high pressure, which thus leads to an overall enhancement in volumetric gas-uptake capacity relative to the purely microporous material. If mesoporosity is too extensive, such as in monoUiO-66_A-B, the material’s low density translates into low volumetric gas storage. Figure 5g clearly demonstrates the existence of this maximum performance in terms of gas-uptake capacity, correlated with an optimal amount of mesoporosity. In monoUiO-66_C-D, we achieved a finely tuned balance between surface area, porosity and density for optimised gas uptake, highlighting the power of molecular simulations to identify trends in this area.
When benchmarking our data against available literature, we first compared the CH₄ isotherms of monoUiO-66-D with that of powdered UiO-66[5] (Fig. 5h). The isotherms of both UiO-66 materials show similar uptake up to ca. 30 bar, attributable to the filling of comparable microporosity in each material. However, above this pressure, CH₄ uptake by monoUiO-66-D continues to increase, whereas that of powdered UiO-66 plateaus. For powdered UiO-66 was not reported, preventing comparison in terms of volumetric capacity. Using GCMC simulations of defect-free microporous UiO-66, we obtained a theoretical CH₄ isotherm that closely matched the results for UiO-66 powder (Supplementary Fig. 24). It is well reported that defects i.e., missing linkers, missing clusters and non-porous phases, are common amongst experimentally obtained UiO-66[7,8]. The similarity of these isotherms demonstrates that, at relatively high temperature, i.e., 300 K, the potential errors in the force field and pore volume estimation using a pristine crystalline UiO-66 with perfect activation on the one hand, versus a real UiO-66 with missing linkers and potential non-porous phases on the other hand, counter-balance. At the end of the day, crystalline defects, typical to UiO-66, incur only a minor influence on methane adsorption capacity compared with the non-crystalline mesoporous defects in monoUiO-66. Using the single-crystal density of the MOF, we found that the simulated volumetric CH₄ capacity of theoretical microporous UiO-66 again matches the volumetric isotherm for UiO-66-D up to only ca. 50 bar (Fig. 5i). The fact that mixed micro-/mesoporous monoUiO66-D closely matches both the theoretical and experimental UiO-66 isotherms at lower pressures, while exceeding both at higher pressures, supports the hypothesis that enhanced gas uptake occurs through condensation in the synthetically introduced mesoporous cavities.

As described above, one of the most important practical engineering parameters for an optimal NG adsorbent is the working capacity. This is the uptake at maximum storage pressure minus the uptake at release pressure (typically ca. 5 bar)—i.e., the real volume of accessible gas in the storage system[9]. At the DOE’s target pressure of 65 bar, monoUiO-66-D shows a working capacity of 172 cm³ (STP) cm⁻³ using real bulk density. This can be compared with the theoretical benchmark ca. 200 cm³ (STP) cm⁻³ working capacity of powdered UTSA-76a, which, under packing, would be expected to display a 25–50% reduction in volumetric capacity down to 100–150 cm³ (STP) cm⁻³. This means that, at 172 cm³ (STP) cm⁻³, densely UiO-66-D surpasses this benchmark significantly. Furthermore, by assuming a Langmuir fitting and using single-crystal density, the volumetric working capacity (5–100 bar) of UTSA-76a will be 236 cm³ (STP) cm⁻³. This theoretical maximum value will fall to 118–177 cm³ (STP) cm⁻³ in a standard pellet. Our monolith, UiO-66-D shows a volumetric working capacity (5–100 bar) of 261 cm³ (STP) cm⁻³.

When comparing with the 191 cm³ (STP) cm⁻³ (5–65 bar) working capacity of the chemically unstable monoHKUST-1, this result is, however, 10% lower. Although 65 bar is considered an optimal storage pressure, being easily obtained by low-cost single-stage compressors, higher pressures are increasingly being considered both industrially viable and safe. For example, the Toyota Mirai fuel-cell vehicle utilizes a hydrogen tank stored under 700 bar pressure[29]. In the current case, a maximum pressure of 100 bar, though above the DOE target, represents significantly milder storage conditions than the 250 bar required for CNG. Yet, even at these higher pressures, the monoHKUST-1 working capacity increases only up to 235 cm³ (STP) cm⁻³ (5–100 bar). This small increment is commonly observed amongst Type I microporous MOFs (Fig. 1a) that saturate at low pressure; substantial increases in gas uptake are prevented even at increased pressures. Interestingly at ca. 90 bar, monoUiO-66-D overtakes monoHKUST-1 and reaches a volumetric working capacity of 261 cm³ (STP) cm⁻³ (5–100 bar).

This outstanding result is a consequence of the material’s finely tuned physical properties i.e., the unique combination of weak CH₄ interaction at low pressure and its Type II isotherm character, which enhances gas uptake at high pressure. Due to its extrinsic mesoporosity, UiO-66_D does not saturate even at 100 bar, representing an 11% improvement in working capacity relative to benchmark densified monoHKUST-1 (5–100 bar). Furthermore, this significant improvement in volumetric working CH₄ storage capacity has been achieved with a densified, air-stable monolith. The working capacity of 261 cm³ (STP) cm⁻³ (5–100 bar) for monoUiO-66-D is, to the best of our knowledge, the highest recorded for a chemically stable, conform MOF over this pressure range.

We selected Zr-MOF UiO-66 for this study due to its industrially valued physical/chemical properties. However, this is just one of an extensive range of promising Zr-MOFs with different pore sizes, surface areas and chemical properties, making the entire family of Zr-MOFs industrially interesting[50]. To demonstrate the generality of the reported synthetic procedure for monoZr-MOFs, we further synthesised and fully characterised both mono[51,52]- and bi-functionalised monoUiO-66-NH₂ [Zr₂O₂(OH)₂(2-amino-1,4-benzenedicarboxylate)]ₙ with a range of different PSDs (Supplementary Figs. 26–36) and monoNU-1000 (Zr₆(μ₂-O)₆(1,3,6,8-tetakis(p-benzoate)pyr- eenc)ₙ, Supplementary Figs. 37–43).

Discussion

We have reported the synthesis of high density, centimetre-scale monoliths of UiO-66 without the use of high pressures or chemical binders. The obtained monoliths show high thermal, mechanical and chemical stability, characteristic of industrially viable Zr-MOFs. Crucially, we have developed a synthetic procedure that enables modulation of the extrinsic pore-size distribution within the monolithic macrostructures. Via the controlled variation of synthetic parameters, we have demonstrated that precise volumes of meso- and macroporosity, external to the MOFs crystalline structure, can be built into the material. Through the subsequent optimisation of both PSD and density, we have achieved benchmark results for gas storage. We studied CH₄ and CO₂ uptake capacity in a selection of monoUiO-66 samples with high microporosity and varied mesoporosity/density, demonstrating Type II isotherms, which yield improvements in working capacity compared with previous work on UiO-66[47]. We used GCMC simulations to demonstrate that the physical origin of this enhanced uptake capacity lies in substantial gas condensation in the mesopores at high pressure.

The use of UiO-66, which demonstrates a relatively poor interaction with CH₄ at low pressure, combined with optimisation of its PSD to include finely tuned volumes of narrow mesoporosity, resulted in a volumetric CH₄ working capacity of 172 cm³ (STP) cm⁻³ at 65 bar and 261 cm³ (STP) cm⁻³ at 100 bar, an 11% improvement over the benchmark of monoHKUST-1. Although a higher, yet still industrially reasonable, maximum working pressure is required, this result represents a step further in the design of materials for maximised CH₄ working capacity, making it unique among air-stable MOFs. This result not only expands our understanding of the experimental capabilities of porous MOFs but has major implications for real-world applications of MOFs in the crucial field of environmental fuel distribution.

Methods

Synthesis of UiO-66 gel. Benzene-1,4-dicarboxylic acid (1.20 g, 7.25 mmol) and zirconium(IV) oxychloride octahydrate (1.61 g, 5.0 mmol) were dissolved in N,N-dimethylformamide (30 ml, 99 %). Concentrated hydrochloric acid (1.5 ml, 37 %) and glacial acetic acid (2.0 ml) were added with vigorous stirring. The resulting solution was sealed in a 100 ml Pyrex Schott bottle and heated to 100 °C for 2 h. This yielded UiO-66 as a thick white gel.
Preparation of UiO-66_A-D

N,N-diethylformamide (50 mL) was added to the UiO-66 gel as synthesized above and vigorously mixed. The diluted UiO-66 suspension (75 mL per 1 g of UiO-66) was centrifuged (3 min, 5000 rpm) and the supernatant decanted. The gel was washed, centrifuged (5500 rpm) and dried to produce a range of monoliths (Supplementary Table 1). The obtained monolith was soaked in acetone (3 × 5 mL, 24 h) and methanol (3 × 5 mL, 24 h) and then dried at room temperature overnight. It was then activated by heating to 110 °C under vacuum for 8 h.

Characterisation. TEM was performed using an FEI Philips Tecnai 20 and FEI Osiris STEM operated in scanning mode (accelerating voltage of 200 kV). Primary MOF particles were prepared for analysis by diluting undried MOF gel in acetone and briefly sonicating before coating onto a copper grid. Dried monoliths were prepared for analysis by crushing with a spatula and pressing a copper grid into the resulting powder. Images were processed with Image J software. Scanning electron microscope images were collected using a TESCAN VIRA3 FEG-SEM and processed with Image J software. PXRD patterns were collected using a PANalytical Empyrean diffractometer with an X’celerator detector (Cu-Kα, source, λ = 1.5406 Å). Monolith powders were prepared for PXRD analysis by gently crushing with a pestle and mortar before being placed on a zero-background silicon wafer. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) and C, H and N elemental analyses were performed using a Thermo Scientific ICP 7400 ICP-OES analyser and an Exeter analytical CE 440 elemental analyser (975 °C), respectively. Thermogravimetric analysis was collected using a Mettler Toledo/SDTQ600 thermobalance with alumina crucible. Low pressure N2, isotherms (adsorption and desorption) were collected using a Micromeritics 3Flex at 77 K. Prior to analysis, samples were degassed in a vacuum oven at 110 °C for 8 h. In situ (adsorption and desorption) were collected using a Micromeritics 3Flex at 77 K and 298 K.

Computational details. Grand canonical Monte Carlo (GCMC) simulations were employed to obtain adsorption isotherms for N2, CO2 and CH4 at 77 K and 298 K. Simulations were based on a model that included Lennard–Jones (LJ) interactions for the guest–guest and guest–host interactions. The LJ potential parameters for the framework atoms were taken from the Universal Force Field (UFF)29. The interactions involving N2, CO2 and CH4 were described by the TraPPE force field. An atomistic representation was used for the MOF, starting from its crystal structure. The simulation cells consisted of 8 (2 × 2 × 2) unit cells for microporous UiO-66, and a single unit cell for all micro-/mesoporous structures, with a LJ cut-off radius of 12.8 Å and no tail corrections. For CO2, long-range electrostatic interactions were handled using the Ewald summation technique. Periodic boundary conditions were applied in all three dimensions. For each pressure point, GCMC simulations consisted of 50,000 Monte Carlo cycles to guarantee equilibration, followed by 50,000 production cycles to calculate the ensemble averages. All simulations included insertion/deletion, translation and rotation (for N2 and CO2) with equal probabilities. GCMC simulations were run on five models; one corresponding to defect-free microporous UiO-66 and four corresponding to the micro-/mesoporous materials (monoUiO-66_A-D). To obtain micro-/mesoporous materials, the microporous UiO-66 supercell (of eight unit cells) was modified by artificially creating a gap between two purely microporous UiO-66 layers, increasing the simulation cell length. The appropriate mesoporous gap lengths to match the experimental N2 isotherms were 2.75 nm (for monoUiO-66_A and B), 2.50 nm (for monoUiO-66_C) and 2.30 nm (for monoUiO-66_D).

The ideal adsorbed solution theory (IAST) can accurately predict multicomponent isotherms from pure-component isotherms36. We employed the Python package pyIAST37 to estimate the CO2–CH4 IAST selectivities for monoUiO-66_A-D at 298 K and at different pressures from experimental pure-component CO2 and CH4 adsorption isotherms by using the BET and the quadratic model fittings for CO2 and CH4 respectively (Supplementary Figs. 22, 23).

Data availability

The experimental dataset generated and/or analysed during the current study are available from the corresponding authors on reasonable request.

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