Adsorption Contraction Mechanics: Understanding Breathing Energetics in Isoreticular Metal-Organic Frameworks

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In this article we report the synthesis and detailed analysis of the highly porous metal-organic framework DUT-48, isoreticular to DUT-49 a material which shows an adsorption-induced structural transition. DUT-48 has impressive porosity and methane storage capacity, however displays conventional adsorption behaviour. The contrasting flexibility of DUT-48 and DUT-49 were analysed and rationalised using a combination of novel experimental and computational techniques. Microcalorimetry measurements, in conjunction with molecular simulations, demonstrate that DUT-48 has a significantly lower adsorption enthalpy difference and a higher framework stiffness which leads to an absence of adsorption-induced transitions and negative gas adsorption (NGA). However, by analysing the mechanical behaviour of both DUT-48 and DUT-49, employing mercury porosimetry experiments, we discovered that both materials exhibit large volume changes under hydrostatic compression, demonstrating noteworthy potential as shock absorbers, and directly linking internal adsorption-induced contraction to external hydrostatic compression.
Adsorption contraction mechanics: Understanding breathing energetics in isoreticular metal–organic frameworks

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A highly porous metal-organic framework DUT-48, isoreticular to DUT-49, is reported with a high surface area of 4560 m² g⁻¹ and methane storage capacity up to 0.23 g g⁻¹ (164 cm³ cm⁻³) at 6.5 MPa and 298 K. The flexibility of DUT-48 and DUT-49 under external and internal (adsorption-induced) pressure is analyzed and rationalized using a combination of advanced experimental and computational techniques. While both networks undergo contraction by mechanical pressure, only DUT-49 shows adsorption-induced transitions and negative gas adsorption of n-butane and nitrogen. The adsorption behaviour was analyzed by microcalorimetry measurements and molecular simulations to provide an explanation for the lack of adsorption-induced breathing in DUT-48. It was revealed that for DUT-48 a significantly lower adsorption enthalpy difference and a higher framework stiffness prevent adsorption-induced transitions and negative gas adsorption. The mechanical behavior of both DUT-48 and DUT-49 was further analysed by mercury porosimetry experiments and molecular simulations. Both materials exhibit large volume changes under hydrostatic compression, demonstrating noteworthy potential as shock absorbers.

Introduction

Application of pressure to even the hardest materials, such as diamond, will generate changes in structure. For some applications, pressure-induced structural transitions are an important prerequisite, exemplified in zirconia ceramics where crack propagation is stopped by incorporating a metastable phase which undergoes a phase transition to absorb energy. Moreover, where such transitions are large in magnitude and in a defined area and direction they can be leveraged for novel shock absorbers. Amorphous materials often lack these properties due to their disordered structure. Alternatively, many ordered and crystalline materials show defined and large structural changes upon application of pressure, however, the prediction and tuning of the transitions remain challenging. Metal-organic frameworks (MOFs) are a class of crystalline materials with a wide spectrum of potential applications, in particular for mechanics-related fields. The high porosity in MOFs allows for very large volume changes upon mechanical compression.

Many “softer” MOFs have shown distinct structural transitions with large changes in structure upon exposure to mechanical pressure but also temperature, irradiation, or exposure to guest molecules. Several of these flexible MOFs are excellent candidates for mechanical shock absorbers. Upon the application of hydrostatic pressure, MIL-53(Al)(DUT-48) and MIL-47(V) can switch from a large pore to a contracted pore state. Due to this large change in unit cell volume upon compression MIL-47(V) is regarded as one of the best shock absorber materials. More recently, the fumarate version of MIL-53 in its Ga and Al forms has shown even higher mechanical energy absorption performances. Moreover, adsorption-induced stress, which acts similarly to internal pressure, can also cause contraction of MIL-53. Upon exposure to guest molecules such as water, methane, carbon dioxide or xenon, the guest-free framework contracts at low pressures and expands again at higher pressures to its original state, filled with guest molecules. This transition which is also referred to as breathing can be manipulated by functionalization of the terephthalate linker.

A entirely new type of breathing transition in a mesoporous MOF has been recently observed in DUT-49 (DUT = Dresden University of Technology), which contracts from an open pore (op) structure to a contracted pore (cp) form under adsorption-induced stress of methane, n-butane or xenon.

A novel aspect of this mesoporous breathing MOF is the passage through a metastable state during adsorption causing a counterintuitive phenomenon called negative gas adsorption (NGA). With increasing gas pressure, DUT-49 releases previously adsorbed gas from its pore upon structural contraction in the cp state causing a negative step in the isotherm (∂Nads / ∂P < 0). The NGA phenomenon implies the material acts as a pressure amplifier, which is an interesting conceptually novel function of adsorbents. The structural transitions responsible for the NGA behaviour have been extensively investigated by in situ diffraction and spectroscopic methods as well as theoretical calculations. However, the question of the molecular origins and construction principles of such pressure amplifying materials is still an open one. In particular the development of rational concepts to further extend this class of materials requires a better understanding of their intrinsic mechanics for tuning NGA and mechanical energy storage in materials.
In this contribution we report DUT-48 as a new highly porous MOF isoreticular to DUT-49 with reduced ligand length (9,9ʹ-(1,4-phenylene)bis(9H-carbazole-3,6-dicarboxylate,cpcdc) (Scheme 1). A series of experimental techniques including adsorption, microcalorimetry and mercury intrusion were coupled to explore the guest and mechanically-induced flexible behaviour of this new MOF. An important finding is that both DUT-48 and DUT-49 materials can be termed “flexible” since both undergo structural transformations under external pressure, showing potential as shock absorbing materials. However, the enhanced stiffness of DUT-48 caused by the shorter linker prevents adsorption-induced breathing. This difference in behaviour was further interpreted and rationalized by a combination of force field and quantum-based molecular simulations.

Results and discussion

The ligand H4cpcdc (Scheme 1) used for the synthesis of DUT-48 was obtained in a large-scale 5-step synthesis with high yield based on inexpensive starting materials and 9H-carbazole (synthetic protocol in ESI). The ligand was used in a solvothermal reaction with Cu(NO3)2·3H2O in DMF or NMP to yield DUT-48 as blue powder. Zhou and co-workers have reported the synthesis of PCN-81, isomorphous to DUT-48 but crystallizing in the cubic space group Pm3m, and PCN-82, bearing two additional methoxy groups on the linker and crystallizing in Fm3m. However, attempts to reproduce the reported structure of PCN-81 by replicating and also modifying the reaction conditions (see ESI) always yielded phase pure DUT-48, crystallizing in cubic space group Fm3m. From three different synthesis protocols the reaction of H4cpcdc with Cu(NO3)2·3H2O in DMF with acetic acid as modulator (for details see ESI) yielded the best result and was thus used for the further experiments. The structure of DUT-48 was determined by synchrotron based single crystal diffraction experiments (see Tab. S2). DUT-48 is isoreticular and isosymmetrical to DUT-49, while the linker is slightly buckled in PCN-81 (Fig. S9). PCN-82 in contrast to PCN-81 retains its structure upon removal of solvent by freeze-drying and shows permanent porosity for gases.

To analyse the adsorption behaviour of DUT-48 a well-
established activation protocol for removal of solvent from the pores, involving supercritical CO$_2$ drying, was applied.\textsuperscript{28,29} The resulting deep blue powder was activated additionally at 120 °C in dynamic vacuum (p < 10\textsuperscript{-3} mbar). PXRD analysis showed structural preservation of DUT-48 upon activation which is stable up to 350 °C similar to DUT-49, as determined by thermal analysis (Fig S10).

The pore volume and apparent BET area of DUT-48 were determined on the basis of a N$_2$ adsorption isotherm at 77 K. A high BET area of 4560 m$^2$ g$^{-1}$ and specific pore volume of 1.98 cm$^3$ g$^{-1}$ could be determined improving values for isoreticular PCN-82 (4480 m$^2$ g$^{-1}$, 1.7 cm$^3$ g$^{-1}$)\textsuperscript{27} but lower compared to DUT-49 (5476 m$^2$ g$^{-1}$, 2.68 cm$^3$ g$^{-1}$)\textsuperscript{30} due to the reduced pore size.

The high BET area and specific pore volume motivated us to investigate the storage capacity of CH$_4$, H$_2$ and CO$_2$ at high pressures (ESI). As expected, the maximum gravimetric excess uptake (CH$_4$ 0.23 g g$^{-1}$, CO$_2$ 1.23 g g$^{-1}$; H$_2$ 80 mg g$^{-1}$), as well as the pressure, at which the maximum capacity is reached (CH$_4$ 100 bar, CO$_2$ 45 bar; H$_2$ 50 bar) are lower for DUT-48 in comparison to DUT-49 due to the reduced porosity. The total CH$_4$ adsorption capacity at 6.5 MPa and 25 °C is 164 cm$^3$ cm$^{-3}$ (0.27 g g$^{-1}$).

Neither the high-pressure adsorption experiments nor the N$_2$ adsorption isotherm at 77 K showed hysteresis or unusual steps as indications for structural transitions similar to DUT-49 (Figure 1). From our previous studies of DUT-49 it is known that adsorption-induced transitions occur at temperatures close to the respective boiling point of the adsorbate. Nitrogen at 77 K was found to be a very sensitive adsorbate only initiating structural transitions for DUT-49 crystals larger than 1 - 2 µm.\textsuperscript{31} Consequently, adsorption isotherms close to ambient temperature were recorded using n-butane at the respective boiling point of 273 K and also at 295 K and 303 K (Figure 1 and Figure 2). These conditions were previously found to induce a contraction from DUT-49 to DUT-49cp independent of particle size, which has been well studied by in situ PXRD in parallel to adsorption and derived from multiple steps, hysteresis and spikes in the adsorption isotherms.\textsuperscript{24}

**Figure 2** n-Butane adsorption isotherm of a) DUT-48 and b) DUT-49 at 303 K (blue circles) including GCMC simulations for the predicted op and cp phases (green and purple, respectively), enthalpy of adsorption for n-butane in c) DUT-48 and d) DUT-49 determined by calorimetry (blue circles), calculated by GCMC simulations for open pore (green) and contracted pore (purple) structures.
In the case of DUT-48 neither adsorption of nitrogen or n-butane induced a structural transition, illustrated by the lack of steps or hysteresis in the isotherms (Figure 2). PXRD measurements after the adsorption experiments showed no sign of structural transitions or decomposition from the pristine material, in contrast to DUT-49 (Fig. 59).

Analysis of adsorption and structure thermodynamics

Upon contraction in DUT-49 the enthalpy of adsorption rises from 29.4 kJ mol\(^{-1}\) for the \(op\) structure to over 50 kJ mol\(^{-1}\) for the \(cp\) structure for \(n\)-butane, due to the reduction of porosity and increased gas-surface interactions.\(^{24}\) This increase in adsorption enthalpy which was calculated in our original study for DUT-49 as \(\Delta H = 153 \text{ kJ mol}^{-1}\) per ligand, which compensates for the energy required for the endothermal structural transition that occurs upon NGA.\(^{24}\) To investigate the effect of a smaller pore structure we monitored the pressure dependence of the adsorption enthalpies for \(n\)-butane at 303 K for both DUT-48 and DUT-49 (Figure 2).\(^{32}\) This provides access to experimental analysis of the isosteric \(\Delta H_{ads}\) of the \(cp\) phase in DUT-49 as well as the full profile of DUT-48. The experimentally obtained enthalpies match the values calculated with the Van’t Hoff equation well (ESI) indicating the validity of the data. A large increase in enthalpy is observed for DUT-49 after NGA due to the stronger interactions of \(n\)-butane with the microporous \(cp\) phase of DUT-49. However, we are unable to measure isosteric adsorption enthalpies for both, the \(op\) and \(cp\) phases because the \(op\) and especially the \(cp\) phase is only experimentally present in a constrained pressure region. Thus enthalpies of adsorption for \(op\) and \(cp\) phases of DUT-48 and DUT-49 were calculated for adsorption of \(n\)-butane using energy/particle fluctuations with grand canonical Monte Carlo (GCMC) methods (Figure 2). A representative model for a \(cp\) phase of DUT-48 was generated from classical molecular dynamics simulation (additional details for the model of DUT-48\(cp\) is described later).

Simulated adsorption enthalpies match well with the experimental values allowing for an accurate analysis of the adsorption enthalpies for all structures involved. There is a systematic underestimation of \(\Delta H_{ads}\) by simulation by ca. 20\% as sampling the energetics of flexible \(n\)-butane is challenging by Monte Carlo methods — we note here that we used a readily available force field with no adjustment. The experimental \(\Delta H_{ads}\) of DUT-49 shows a clear discontinuity after NGA with a significant increase in adsorption enthalpy. This change corresponds well to the disparate GCMC adsorption enthalpies calculated for the \(op\) and \(cp\) phases (43.7 and 21.6 kJ mol\(^{-1}\), respectively). The \(cp\) phase of DUT-49 has a significantly higher enthalpy of adsorption owing to the drastic reduction in pore size that leads to a significant increase of the host/guest interactions.

Contrastingly, the adsorption enthalpy of DUT-48 follows the behaviour of the \(op\) phase corresponding to the behaviour expected for a nanoporous material matching the profile predicted by simulation. The values obtained from calculation, \(in\ situ\) experiment and GCMC simulations are summarized in Table 1.

| Method            | \(\Delta H_{ads}\) \((\text{kJ mol}^{-1})\) |
|-------------------|-----------------------------------------|
| DUT-48\(op\)      | 34.6                                    |
| DUT-48\(cp\)      | n. a.                                   |
| DUT-49\(op\)      | 29.4                                    |
| DUT-49\(cp\)      | 51 (±4)                                 |
| \(\Delta H_{ads}\) DUT-48 | n. a.                                   |
| \(\Delta H_{ads}\) DUT-49 | 149 (±26)                               |

The simulated adsorption enthalpy for the \(op\) and \(cp\) phases can be used to determine the energy gain, \(\Delta H_{ads}\) (equation 1), for a transition from \(op\) to \(cp\) phase.

\[
\Delta H_{ads} = n_{ads}(cp) \cdot |\Delta H_{ads}(op) - \Delta H_{ads}(cp)|
\]

In agreement with the previous study\(^{34}\), we find \(\Delta H_{ads}\) for \(n\)-butane and DUT-49 at ~39 kPa and 303 K to be at around 150 kJ mol\(^{-1}\) per ligand. In contrast for DUT-48, at ~10 kPa, the potential energy gain is around 80 kJ mol\(^{-1}\), significantly lower than DUT-49.

In addition to understanding the thermodynamics of adsorption, we have applied molecular simulations to examine the thermodynamics of the DUT-48 framework itself. Total energies were calculated using several constant-volume (\(N\), \(V\), \(T\)) molecular dynamics (MD) simulations and free energies were calculated using thermodynamic integration.\(^{33}\) The
resulting energy profiles show two minima for both DUT-49 and DUT-48 (Figure 3), as expected for bistable breathing MOFs.\textsuperscript{19} The minima at large volumes correspond to the observed crystal structure of the materials (op phase). The second minimum, at small cell volumes, owing to the conformational strain on the ligand is greater in energy than the op phase. Importantly, these simulations highlight that a \textit{cp} phase for DUT-48 exists with a cell parameter of 32.8 Å, compared to 40.5 Å for the experimental op phase. The \textit{cp} phase for DUT-48 is approximately 5 kJ mol\textsuperscript{-1} per ligand higher in energy than for DUT-49. Additionally, the energy barrier for the \textit{op}-\textit{cp} transition is also greater.

The comprehensive thermodynamic analysis described here exposes two key differences between DUT-48 and DUT-49 that prevent DUT-48 from undergoing an adsorption-induced transition to a \textit{cp} phase:

Firstly, the differences in adsorption enthalpies (\(\Delta \Delta H_{\text{ads}}\)) are significantly smaller than observed for DUT-49. Secondly, the proposed \textit{cp} phase requires a greater unfavourable strain of the building units resulting in a significantly higher energy state. Although the combination of these two factors results in the rigid adsorption profiles observed for DUT-48 we expect that these factors can be tuned using alternative ligands to produce a stimuli-responsive framework and thus providing the basis for further modification of DUT-49.

Analysis of mechanical stability

The adsorption-induced stress on the framework is limited by the extent of the host–guest interactions, as described above. As a result, the presented adsorption experiments for DUT-48 exhibit no structural contraction as the stress is not large enough to compensate for the energy required for a transition to the \textit{cp}-phase, which presence is indicated by the MD simulations. Thus, we further investigated the mechanical behaviour of DUT-48 and DUT-49 in the absence of adsorbates to analyse if it is possible to contract DUT-48 by external stress, i.e. applying mechanical pressure.

Crystal structures of DUT-49, \textit{op} and \textit{cp} feature a copper paddlewheel environment that is mostly undeformed in the \textit{cp} structure.\textsuperscript{24, 26} However, the ligand is significantly bent with deformation localized to the biphenyl unit, showing considerable similarity to the buckling behaviour of macroscopic columns under load.\textsuperscript{14} Density functional theory (DFT) optimizations of the single isolated building unit with a series of fixed decreasing N-atom-to-N atom (N–N) distances has provided excellent insight into the mechanical force required to produce the \textit{op}-\textit{cp} transition in DUT-49. We have employed these simulations for the ligands used to form DUT-48 and DUT-49 and the resulting energy-strain curve was used to obtain the stress-strain profiles depicted in Figure 4. The bending of the ligands can be characterized by a “deflection” parameter, which is the N-centroid-N angle. The ligands exhibit two distinct regimes with the application of strain.

Firstly, the elastic regime corresponds to small deformations resulting in no deflection to the ligand. However, larger deformations produce a buckling phenomenon resulting in a sudden large deflection of the ligand. We find here that the smaller ligand of DUT-48 requires almost three times the pressure to produce the buckling event than DUT-49. We note that this result is expected from Euler’s column formula where the stress required to produce buckling is inversely proportional to the length of the column.\textsuperscript{15} Nevertheless, these results pertain to only a single molecule. To investigate the response of the entire periodic lattice we consult the constant-volume (\(N, V, T\)) MD simulations discussed previously (Figure 5).

Notably, the pressure-profiles resulting from these simulations confirm the conclusions gained from the study of the adsorption case. DUT-48 requires a transition pressure of \(\sim 150\ \text{MPa}\) significantly greater than that of DUT-49, \(\sim 60\ \text{MPa}\). This transition pressure, while greater than DUT-49, is similar to other flexible frameworks and is achievable experimentally by applying hydrostatic pressure to provide an alternative pathway to adsorbate-induced \textit{op}-\textit{cp} transition.

The pressure-induced structural behaviour of DUT-48 and DUT-49 was further explored by mercury intrusion which has been established to ensure application of pressure under hydrostatic conditions.\textsuperscript{8, 17} In addition, Hg is a non-wetting fluid that is expected to not enter mesopores in the range of pressure [0-400 MPa] following the Washburn equation to

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{a) Deflection angle for the ligands used to produce DUT-48 and DUT-49, defined as the N-centroid-N angle, for increasing strain. b) Stress-strain curve of the ligands with increasing axial compression.}
\end{figure}
In both cases the first part of the intrusion curve (<1 MPa) corresponds to the compaction of the powder and filling of the interparticle porosity. Subsequently, there is a second step corresponding to a volume variation of ~1.5 mL g\(^{-1}\) and 2.3 mL g\(^{-1}\) for DUT-48 and DUT-49, respectively. This is assigned to an abrupt significant contraction of the solids since the non-wetting Hg cannot penetrate the mesoporosity of both solids at this pressure. Thus, we assign this change in volume to the contraction of DUT-48 and DUT-49 at ~65 MPa and ~35 MPa, respectively. This supports the transition pressures obtained from the MD simulations which are estimated to be higher but within the margin of error of the method, since a generic force field was used to describe the flexibility of the MOF architectures, and the pressure differences involved here are very small compared to the usual GPa scale of mechanical properties of stiff materials. Furthermore, we observe that this structural transition is irreversible once the applied pressure is released and a loss of crystallinity and deformation of the cubic crystals was observed from the samples recovered after the measurement (see ESI). No additional changes in volume can be detected upon release of the pressure down to 1 MPa. The contraction of the two solids can be determined from the mercury intrusion curves based on the Hg volume change observed between the two plateaus. This leads to relative volume variations (ΔV/V) of 27% and 25% for DUT-48 and DUT-49 respectively which are both lower than the predicted volume changes as well as the previously guest-induced contraction of DUT-49. This deviation suggests that in both cases, only a fraction of the solid initially present in its open form can be converted into its contracted version. The so-observed pressure-induced behaviour for the two solids corresponds to the scenario of a shock-absorber due to the irreversibility of the structural conversion.\(^3\) From the transition pressures and associated volume changes experimentally evidenced, we can derive work energies (W = P x ΔV) of 43 J g\(^{-1}\) and 25 J g\(^{-1}\) for DUT-48 and DUT-49, respectively. These performances are amongst the highest reported so far for the family of MOF materials.\(^3, 33\)

Conclusions
In this study we have synthesized and characterized DUT-48, a highly porous MOF isoreticular to DUT-49 with reduced ligand length. DUT-48 can store up to 0.23 g g\(^{-1}\) of methane due to its high surface area and pore volume. In contrast to DUT-49, DUT-48 does not undergo a structural transition upon adsorption of N\(_2\) or n-butane.

We have analysed the adsorption energetics by microcalorimetry and GCMC simulations and determined the adsorption energy gain by contraction of the pores in DUT-48 is not sufficient for compensating the energy required for this transition thus preventing an adsorption-induced structural transition. As a result, neither guest-assisted structural contraction or NGA is observed in DUT-48. Furthermore, we have analysed the mechanical behaviour of DUT-48 and DUT-49 by MD and DFT simulations and found that it takes approximately three-times the stress to contract DUT-48 which we relate to the shorter ligand length. In addition, this trend was confirmed by mercury intrusion experiments showing that a higher pressure is required for DUT-48 (65 MPa) than DUT-49 (35 MPa) to induce a structural transition. Furthermore, the measured work energies of 43 J g\(^{-1}\) and 25 J g\(^{-1}\) for DUT-48 and DUT-49, respectively, highlight their outstanding potential as future shock-absorbers.

The presented findings provide fundamental insight into structural transition in DUT-49 type structures and importantly link external hydrostatic compression to the energetics of internal adsorption-induced contraction.

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**Figure 5** a) Profiles of internal pressure for DUT-48 and DUT-49 obtained from (N, V, T) molecular dynamics simulations as a function of unit-cell volume at 300 K. The transition pressure for an op-op transition is marked by a dotted line. b) Cumulative volume of intruded mercury in two intrusion-extrusion cycles as a function of the applied pressure for the activated DUT48 and DUT49 (blue and orange, respectively). Circles and diamonds correspond to the compression and decompression of the first cycle respectively and the black line to the compression decompression curves of the second cycle.
Experimental

Synthesis of organic ligands and MOF materials

The ligand H4bbdcd was synthesized according to a previously reported procedure. The ligand H4dpdecd was synthesized according to a similar carbazole-containing ligand. Both MOF materials were synthesized according to a previously mentioned procedure. Detailed synthesis procedures, activation of the MOF materials and characterization are provided in the ESI.

Gas adsorption experiments

Low pressure adsorption experiments were performed on a BELSORP-max, high pressure adsorption on a BELSORP-HP instrument. Gases of purity 99.9% or higher were used. Detailed information about the adsorption measurements are provided in the ESI.

Intrusion experiments

Mercury intrusion experiments were carried out in the range of pressure atm - 415 MPa available with the Hg-porosimeter Micromeritics Autopore 9240. Details of sample preparation are provided in the ESI.

Crystallography

Single crystal structure of DUT-48: C48H40C4N40O32, 743.6 g mol⁻¹, cubic, Fm3m, a = 40.490(5) Å, V = 66381(23) Å³, Z = 24, ρcal = 0.444 g cm⁻³, 3870 independent reflections observed, R₁ = 0.0748 [/>2θ(I)], wR₂ = 0.2286 (all data) and GOF 1.121.

Simulation details

The behaviour and mechanical properties of the representative ligands were investigated for the corresponding acid via DFT optimizations using the CRystal14 software with localized TZVP basis sets and the hybrid exchange-correlation functional PBE0. Long-range dispersion corrections were included via the Grimme “D2” approach. Stress-strain curves were subsequently produced using the methodology described previously. GCMC simulations were employed using the RASPA2.0 code and with frameworks treated by the UFF forcefield and n-butane the united-atom TraPPE force field recently adapted to lammps by Boyd et al. to describe the flexibility of the materials. Further details can be found in the supporting information. Representative input files for molecular simulations are available online in our data repository at https://github.com/fxoudert/citable-data.

Conflicts of interest

There are no conflicts to declare.

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1 Methods and Materials

Materials and gases used in the synthesis and analysis of ligands, DUT-49, and DUT-48 samples were of high purity. Cu(NO$_3$)$_2$·3H$_2$O (Sigma Aldrich, 99.5%), acetic acid (AcOH) (AppliChem, 99%), (N-methyl-2-pyrrolidone (NMP) (AppliChem, 99%), N,N Dimethylformamid (DMF) (Fischer Scientific, 99%), anhyd. ethanol (VWR Prolabo, 99%) were used for the synthesis and activation of DUT-49 (C$_{40}$H$_{20}$N$_8$O$_8$Cu$_2$) and DUT-48. The ligand Habbcdic (9,9'-[(1,1'-biphenyl)-4,4'-diyl]bis(9H-carbazole-3,6-dicarboxylic acid)) incorporated in DUT-49 was used following a previously reported study by our group$^1$. The synthetic protocol and analytic data can be obtained from reference 1.

Powder X-ray diffraction (PXRD) patterns were collected in transmission geometry with a STOE STADI P diffractometer operated at 40 kV and 30 mA, with monochromatic Cu-K$_{α1}$ ($λ = 0.15405$ nm) radiation, a scan speed of 20 s per step and a step size of 0.1° 2$Θ$. Activated samples were prepared under inert atmosphere.

Thermogravimetric analysis (TGA) was carried out in synthetic dry air using a NETZSCH STA 409 thermal analyzer at a heating rate of 5 K min$^{-1}$.

Elemental analysis (C, H, N, S) was performed for ligand and MOF materials with a HEKATECH EA 3000 Euro Vector CHNS analyzer.

Scanning electron microscopy (SEM) images of DUT-49 and DUT-48 were taken with secondary electrons in a HITACHI SU8020 microscope using 1.0 kV acceleration voltage and 10.8 mm working distance. The powdered samples were prepared on a sticky carbon sample holder under inert atmosphere.

Volumetric adsorption experiments were carried out on a BELSORP-max instrument and gases with high purity were used (N$_2$: 99.999%, n-butane: 99.95%, He: 99.999%, CH$_4$: 99.999%). For volumetric adsorption experiments the measuring routine of BELSORP-max was used. Targeted relative pressures in the range of 0.001 – 100 kPa were defined and limits of excess and allowance amount were set to 10 and 20 cm$^3$ g$^{-1}$, respectively. For high resolution isotherms of n-butane limits of excess and allowance amount were set to 2 and 4 cm$^3$ g$^{-1}$, respectively. Equilibration conditions for each point were set to: 1% pressure change within 350 s. The dead volume was routinely determined using helium. Values for the adsorbed amount of gas in the framework are all given at standard temperature and pressure (STP), except the high pressure measurements. Liquid nitrogen was used as coolant for measurements at 77 K and a Julabo thermostat was used for measurements at 298 K. Measurements at 111 K and 121 K were carried out using a closed cycle He-cryostat setup described in reference $^1$. Samples of DUT-48 and DUT-49 were installed in the measuring set up under inert atmosphere.

High pressure H$_2$ adsorption measurement at 77 K up to 110 bar was performed on a volumetric BELSORP-HP apparatus. High pressure CH$_4$ and CO$_2$ adsorption was studied using a magnetic suspension balance (Rubotherm Co.). The total gas uptake was calculated as follow: $N_{\text{total}} = N_{\text{excess}} + \rho_{\text{bulk}} V_{\text{pore}}$, where $\rho_{\text{bulk}}$ equals to the density of compressed gases at the measuring temperature and pressure, and $V_{\text{pore}}$ was obtained from the N$_2$ sorption isotherm at 77 K.
2 Synthesis of \( \text{H}_4\text{pbcdc} \) \( \text{(9,9'-(1,4-Phenylene)bis(9H-carbazole-3,6-dicarboxylic acid))} \)

![Chemical structure of \( \text{H}_4\text{pbcdc} \)]

**Scheme S 1.** Synthesis of \( \text{H}_4\text{pbcdc} \) a) N-Bromosuccinimide, THF, 40 °C, 20 h. b) 1. \text{n-butyllithium}, trimethylsilyl chloride, diethyl ether, -78 °C, 1 h; 2. tert-butyllithium, -78 °C, 2h, \( \text{CO}_2 \), 20min. c) 1,4 Diiodobenzene, \text{CuI}, L-prolin, \( \text{K}_2\text{CO}_3 \), DMSO, 90 °C, 48 h. d) KOH, THF/\( \text{H}_2\text{O}/\text{MeOH} \), 60 °C, 24 h.

2.1 3,6-Dibromo-9H-carbazole

To a solution of 150 g (0.9 mol) 9H-carbazole in 2 l of THF 351 mg (1.97 mol) N-bromosuccinimide are slowly being added at 40 °C over 30 min. The light brown solution is stirred over 20 h at 40 °C. Afterwards the THF is being removed in vacuum and the solid washed thoroughly with water. The resulting pale white solid is recrystallized in a mixture of Dichloromethane (DCM) and \text{n-hexane} to yield 209.9 g (0.65 mol, 75%) of the pure white product.

Elemental analysis: \( \text{C}_{12}\text{H}_7\text{Br}_2\text{N} \) (325.00 g mol\(^{-1}\))

- **calculated:** C: 44.35 %  H: 2.17 %  N: 4.34 %  Br: 49.17 %
- **experimental:** C: 44.27 %  H: 2.09 %  N: 4.41 %
2.2 Diethyl 9H-carbazole-3,6-dicarboxylate

In a dried Schlenk flask 26.5 g (58.8 mmol) 3,6-dibromo-9H-carbazole are dissolved in diethyl ether at 0 °C under Ar-atmosphere. To the solution 35 ml of a 2.5 M n-butyllithium solution in n-hexane were slowly added over 30 min, the solution stirred for 1 h at 0 °C and 11.1 ml of trimethylsilyl chloride were slowly added over 10 min. The suspension was stirred for 1 h at 0 °C, cooled to -78 °C and 202 ml of a 1.7 M tert butyllithium solution in pentane were added over 40 min. After stirring the solution for 2 h at -78 °C dry CO₂ was bubbled through through the reaction mixture for 20 min. The reaction mixture was allowed to warm to room temperature overnight. The white suspension was quenched with 50 ml water and the diethylether was removed in vacuum. The resulting suspension was stirred in 500 ml 1 M hydrochloric acid at 90 °C, filtered and dried at 80 °C. The off white product was suspended in 1 l ethanol, 2 ml of concentrated sulfuric acid were added and the suspension was stirred under reflux for 24 h. The ethanol was removed in vacuum, the resulting solid dissolved in ethylacetate and washed with saturated sodium carbonate solution. The organic solution was dried over MgSO₄ and the solvent removed in vacuum. The solid was purified by chromatography in a DCM/ethylacetate mixture of 15:1 to yield 12.27 g ester.

¹H-NMR (600 MHz, d₆-DMSO):

δ (in ppm) = 1.37 (tr, J = 7.0 Hz, 6H), 4.35 (q, J = 7.0 Hz, 4H), 7.61 (dd, J = 8.5 Hz, J = 0.6 Hz, 2H), 8.06 (dd, J = 8.5 Hz, J = 1.7, 2H), 8.89 (dd, J = 1.7 Hz, J = 0.6 Hz, 2H), 12.09 (s, 1H).

¹³C-NMR und DEPT (150 MHz, d₆-DMSO):

δ (in ppm) = 14.38 (CH₃), 60.39 (CH₂), 111.31 (CH), 121.24 (Cq), 122.29 (Cq), 122.77 (CH), 127.46 (CH), 143.25 (Cq), 166.33 (Cq).

Elemental analysis: C₁₈H₁₇NO₄ (311.33 g mol⁻¹)

Calculated: C: 69.44 %  H: 5.50 %  N: 4.50 %.

Experimental: C: 69.71 %  H: 5.63 %  N: 4.37 %.

2.3 9,9'-{(1,4 Phenylen)bis(3,6-diethoxycarbonyl)carbazol

In a Schlenk tube 6 g (19.27 mmol) 3,6-diethoxycarbonylcarbazole, 2.89 g (8.76 mmol) 1,4 diiodobenzene, 334 mg (1.75 mmol) copper(I)iodine, 403 mg (3.5 mmol) L-prolin and 4,84 g (35 mmol) potassiumcarbonate are dissolved in 80 ml of DMSO under inert atmosphere. The suspension is subsequently degassed by dynamic vacuum at 10⁻² mbar and heated to 90 °C for two days. After addition of 300 ml water and 2 ml 2M hydrochloric acid the precipitate was filtered off, washed with water and dissolved in DCM. The DCM solution was extracted with water, the organic solution dried over MgSO₄ and removed in vacuum. The obtained white powder was recrystallized from ethyl acetate to obtain 4.58 g (6.57 mmol, 75 %) white powder.
**1H-NMR (600 MHz, CDCl₃):**

δ (in ppm) = 1.49 (tr, J = 7.3 Hz, 12H), 4.48 (q, J = 7.3 Hz, 8H), 7.56 (d, J = 8.5 Hz, 4H), 7.88 (s, 4H), 8.23 (dd, J = 8.5 Hz, J = 1.6 Hz, 4H), 8.97 (d, J = 1.6 Hz, 4H).

Elemental analysis: C₄₂H₃₈N₂O₈  (696.74 g mol⁻¹)
calculated:  C: 72.40 %  H: 5.21 %  N: 4.02 %.
experimental: C: 72.49 %  H: 5.33 %  N: 4.03 %.

**2.4  9,9′-(1,4-Phenylene)biscarbazol-3,6-dicarboxylic acid**

![Chemical structure](image)

4 g (5.74 mmol) 9,9′-(1,4 phenylene)bis(3,6-die thoxycarbonyl)carbazole are dissolved in a solvent mixture of 100 ml THF, 50 ml methanol and 50 ml water at 60 °C. To the solution 1.93 g (34.44 mmol) potassiumhydroxide were added and the solution was stirred for 24 h at 60 °C, the organic solvents were then removed in vacuum and the solution diluted with 50 ml water. The pH was adjusted to 4 by addition of 2M hydrochloric acid and a white precipitate was formed which was filtered off, washed 3 times with fresh water and dried at 80 °C to obtain 3.33 g (5.7 mmol, 99%) of the pure product as white powder.

**1H-NMR (600 MHz, d₆-DMSO):**

δ (in ppm) = 7.69 (d, J = 8.5 Hz, 4H), 8.04 (s, 4H), 8.16 (dd, J = 8.5 Hz, J = 1.3 Hz, 4H), 9.03 (d, J = 1.3 Hz, 4H), 12.88 (s br, 4H).

**13C-NMR und DEPT (150 MHz, d₆-DMSO):**

δ (in ppm) = 110.06 (CH), 123.10 (Cq), 123.54 (CH), 124.07 (Cq), 128.78 (CH), 129.38 (CH), 136.03 (Cq), 143.88 (Cq), 168.09 (Cq).

Elemental analysis: C₃₄H₂₀N₂O₈  (584.53 g mol⁻¹)
calculated:  C: 69.86 %  H: 3.45 %  N: 4.79 %.
experimental: C: 69.76 %  H: 3.41 %  N: 4.62 %.
3 Synthesis of \( H_{4}bbcdc \) (9,9'-((1,1'-biphenyl)-4,4'-diyl)bis(9H-carbazole-3,6-dicarboxylic acid))

The ligand \( H_{4}bbcdc \) (9,9'-((1,1'-biphenyl)-4,4'-diyl)bis(9H-carbazole-3,6-dicarboxylic acid)) was used from a synthesis previously reported by our group. The synthetic protocol including the analytic data can be obtained from reference [1].

4 Synthesis of DUT-48 and DUT-49 samples

For the described experiments DUT-48 and DUT-49 were synthesized on larger scale based on a solvothermal reaction of the regarding ligands with \( Cu(NO_{3})_{2} \cdot 3H_{2}O \) in NMP at 80 °C for 48 h similar to what has been previously descried for DUT-49 in reference[1]. The synthesis conditions for PCN-81 were used in a second synthesis according to reference 2. In addition, a synthetic approach using larger amounts of DMF and acetic acid to avoid reduction of the \( Cu^{2+} \) by NMP was used. All reaction conditions and yields are listed in Table S 1.

Table S 1 Conditions used for the synthesis of DUT-48

| Reference | \( m_{Cu(NO_{3})_{2} \cdot 3H_{2}O} \) (mg) | \( m_{ligand} \) (mg) | modulator | solvent | \( T \) (°C) | \( t_{reaction} \) (h) | Yield (%)a |
|-----------|---------------------------------|----------------|-----------|-------------------|------|-------------|--------|
| 2         | 2440                            | 840            | 1.68 ml 48% HBF4 | 84 ml DMSO + 168 ml DMA | 85   | 96          | 52     |
| This work | 515                             | 500            | AcOH      | NMP              | 80   | 24          | 64     |
| This work | 1030                            | 1000           | AcOH 12 ml | DMF 800 ml       | 80   | 72          | 51     |

a based on the amount of ligand, determined after activation, actual yield of reaction is larger

PXRD patterns obtained for the reaction products are given in Figure S 1-Figure S 7, \( N_{2} \) adsorption isotherms at 77 K are given in Figure S 12. Due to the best adsorption performance of DUT-48(3) all further adsorption and Hg-intrusion experiments were carried on this sample.
5 Washing and activation of DUT-48 and DUT-49 Samples

The blue precipitates obtained after the solvothermal synthesis of DUT-48 and DUT-49 (conditions under Table S 1) were washed 6 times with fresh DMF over a period of two days at room temperature. The NMP was exchanged by anhyd. ethanol 10 times over 4 days. The respective blue precipitates of DUT-48 and DUT-49 were subjected to an activation procedure involving supercritical CO$_2$ previously described for DUT-49$^3$: The samples which were suspended in ethanol were placed in filter frits into a Jumbo Critical Point Dryer 13200J AB (SPI Supplies) which was subsequently filled with liquid CO$_2$ (99.995% purity) at 15 °C and 50 bar. To ensure a complete substitution of ethanol by CO$_2$, the liquid in the autoclave was exchanged with fresh CO$_2$ 18 times over a period of 5 days. The temperature and pressure were then risen beyond the supercritical point of CO$_2$ (35 °C and 100 bar) and kept until the temperature and pressure was constant at least for 1 h. The supercritical CO$_2$ was steadily released over 3 h. The dry powder was further subjected to additional thermal activation by heating the sample under dynamic vacuum ($p < 10^{-3}$ mbar) at 100 °C for 24 h. The dark blue powders were transferred and stored in an argon filled glove box (H$_2$O content < 1 ppm).
6 Characterization of DUT-48 and DUT-49

6.1 Powder X-ray Diffraction

Figure S 1. PXRD pattern calculated for DUT-48op (blue), DUT-48cp (green), PCN-81 (orange), PCN-82 (red), and experimental pattern for activated DUT-48 (purple) from bottom to top, respectively.

Figure S 2. PXRD pattern of DUT-48op simulated from single crystal structure (blue), activated DUT-48(1) (green), activated DUT-48(2) (orange), activated PCN-82 (red), from bottom to top, respectively.
Figure S 3. PXRD pattern of DUT-48op simulated from single crystal structure (blue), as made DUT-48(1) (green), as made DUT-48(2) (orange), as made PCN-82 (red), from bottom to top, respectively.

Figure S 4. PXRD pattern of DUT-48op simulated from single crystal structure (blue), as made DUT-48(1) (green), DUT-49op simulated from single crystal structure (orange), as made DUT-49 (red), from bottom to top, respectively.
Figure S 5 PXRD pattern of DUT-48op simulated from single crystal structure (blue), activated DUT-48(1) (green), DUT-49op simulated from single crystal structure (orange), activated DUT-49 (red), from bottom to top, respectively.

Figure S 6. PXRD pattern of DUT-48op simulated from single crystal structure (blue), DUT-48(3) after adsorption-desorption of nitrogen at 77 K (green), DUT-49(3) after adsorption-desorption of n-butane at 298 K (orange), DUT-49(3) after adsorption-desorption of n-butane at 273 K (red), from bottom to top, respectively.
Figure S 7. PXRD pattern of DUT-49op simulated from single crystal structure (blue), DUT-49 after adsorption-desorption of nitrogen at 77 K (green), and DUT-49 after adsorption-desorption of n-butane at 298 K (orange) from bottom to top, respectively.

Figure S 8. PXRD pattern calculated for DUT-48op (blue), DUT-48(3) after Hg-intrusion (green), DUT-48op theor (orange), calculated for DUT-49op (red), and empty capillary (purple) from bottom to top, respectively.
6.2 Single crystal X-ray diffraction
Cubic single crystal of DUT-48 was prepared in the closed glass capillary (d = 0.3 mm) with small amount of the mother liquor. The capillary was mounted on the 1-axis goniometer of BL14.2 beamline of the MX-facility at BESSY-II synchrotron, operated by Helmholtz-Zentrum Berlin für Materialien und Energie. The beamline is equipped with 1-axis goniometer and MX-225 CCD detector from Rayonix. All diffraction experiments were performed at room temperature using synchrotron radiation with E = 14 keV (λ = 0.88561 Å). The φ-scan with oscillation range of 1° was used for data collection. The diffraction images were processed using CCP4 software. The crystal structure was solved by direct methods and refined by full matrix least-squares on F2 using SHELX-2016/4 program package. All non-hydrogen atoms were refined in anisotropic approximation. Hydrogen atoms were refined in geometrically calculated positions using “riding model” with Uiso(H)=1.2Uiso(C). Atom C9 shows disorder by symmetry near the mirror plane and therefore was treated with occupancy factor 0.5. High symmetry of the crystal system as well as mobility of the solvent molecules in the pores make the localization of the guest molecules complicated, therefore the SQUEEZE procedure was applied to the dataset in order to correct reflection intensities, corresponding to disordered solvent molecules. CCDC-1827897 contains the supplementary crystallographic data for DUT-48. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif
Table S 2 Crystallographic data for DUT-48 and PCN-81.

|                      | DUT-48op                      | PCN-81 (Reference 2) |
|----------------------|-------------------------------|----------------------|
| **Empirical formula** | $\text{C}_{34}\text{H}_{20}\text{Cu}_{2}\text{N}_{2}\text{O}_{10}$ | $\text{C}_{34}\text{H}_{20}\text{Cu}_{2}\text{N}_{2}\text{O}_{10}$ |
| **Formula weight, g mol$^{-1}$** | 743.60                        | 743.60               |
| **Crystal system, space group** | cubic, $\text{Fm\bar{3}m}$ | cubic, $\text{Pa\bar{3}}$ |
| **Unit cell dimensions, Å** | $a = 40.490(5)$ | $a = 39.4840(16)$ |
| **Volume, Å$^3$** | 66381(23)                     | 61555(4)             |
| **Z** | 24                            | 24                   |
| **Calculated density, g·cm$^{-3}$** | 0.444                         | 0.481                |
| **Temperature, K** | 296                           | 173                  |
| **Wavelength, Å** | 0.88561                       | 0.41328              |
| **Absorption coefficient, mm$^{-1}$** | 0.728                         | 0.230                |
| **$F(000)$** | 8928 (after SQUEEZE)          | 9024 (after SQUEEZE)  |
| **Limiting indices** | $-42 \leq h \leq 40$ | $-49 \leq h \leq 25$ |
| | $-48 \leq k \leq 50$ | $-43 \leq k \leq 49$ |
| | $-50 \leq l \leq 12$ | $-47 \leq l \leq 49$ |
| **Reflections collected / unique** | 40089 / 3870                   | 543624 / 21027       |
| **$R_{int}$** | 0.0700                        | 0.0945               |
| **Data / parameters** | 3870 / 84                      | 21027 / 433          |
| **$\text{GooF on } F^2$** | 1.121                         | 1.236                |
| **Final $R$ indices [$I/2\sigma(I)$]** | 0.0748                        | 0.1125               |
| **$wR$ indices (all data)** | 0.2286                        | 0.2983               |
| **Largest diff. peak / hole, eÅ$^3$** | 1.273 / -1.376                | 1.134 / -1.849       |
6.3 Thermogravimetric analysis

![Graph showing thermogravimetric analysis](image)

*Figure S 11. Thermogravimetric analysis of activated DUT-48(3) (blue) and DUT-49 (orange)*

6.4 Elemental Analysis

The DUT-49 samples used in this study were taken from synthesis previously reported by our group.

Elemental analysis DUT-48 activated: Cu$_2$C$_3$H$_{16}$N$_2$O$_8$ (707.59 g mol$^{-1}$)

calculated: C: 57.71% H: 2.28 % N: 3.96 %. O: 18.09 Cu: 17.96.

experimental: C: 56.93 % H: 2.07 % N: 3.91 %
6.5 Gas Adsorption Experiments

Figure S 12. Nitrogen adsorption-desorption isotherms at 77 K for DUT-48(3) including inlet with semilogarithmic plot (a), DUT-49 including inlet with semilogarithmic plot (b), DUT-48(2) (c), and DUT-49(3) (d), closed symbols adsorption, open symbols desorption.
Figure S 13. Hydrogen high pressure excess adsorption (filled symbols) and desorption (empty symbols) isotherm of DUT-48 (blue) and DUT-49 (red) at 77 K.

Figure S 14. CO$_2$ high pressure excess adsorption (filled symbols) and desorption (empty symbols) isotherm of DUT-48 (blue) and DUT-49 (red) at 298 K.
Figure S 15. Methane high pressure excess (blue) and total (red) adsorption (filled symbols) and desorption (empty symbols) isotherm of DUT-48 at 298 K. Gravimetric methane high pressure excess (blue) and total (red) adsorption isotherms are shown as dashed lines and only corresponds to the values displayed on the left y-axis.
7 Enthalpy of adsorption

For microcalorimetric experiments, all isotherms and enthalpies were measured using a Tian-Calvet type microcalorimeter coupled with a home-made manometric gas dosing system⁸. This apparatus allows the simultaneous measurement of the adsorption isotherm and the corresponding differential enthalpies. Gas is introduced into the system using a step-by-step method and each dose is allowed to stabilize in a reference volume before being brought into contact with the adsorbent located in the microcalorimeter. The introduction of the adsorbate to the sample is accompanied by an exothermic thermal signal, measured by the thermopiles of the microcalorimeter. The peak in the calorimetric signal is integrated over time to give the total energy released during this adsorption step. At low coverage the error in the signal can be estimated to around ± 0.2 kJ mol⁻¹. Around 400 mg of sample is used in each experiment. For each injection of gas, equilibrium was assumed to have been reached after 90 minutes. This was confirmed by the return of the calorimetric signal to its baseline (<5 µW). The gases used for the adsorption were obtained from Air Liquide and were of minimum N47 quality (99.997 % purity).

Figure S16. Isosteric adsorption enthalpy determined by the VAN'T HOFF equation (filled symbols) and by in situ calorimetry (empty symbols) for DUT-49 (a) and DUT-48 (b).

8 Hg-intrusion experiments

Mercury intrusion experiments were performed on a Hg-porosimeter Micromeritics Autopore 9240 (P≤413 MPa) to explore the pressure-induced structural contraction of the DUT-48 and -49. The intruded volume of mercury (which is assumed to not penetrate the mesoporosity of both solids) corresponds to the volume compressed under hydrostatic conditions. The powder was previously activated under secondary vacuum at 150°C for 8 hours to obtain the large pore version of the materials as starting form. The obtained activated powders were transferred into a glove box (Jacomex, P-BOX under argon atmosphere, H₂O<5 ppm, O₂<5 ppm) where the samples were loaded into a penetrometer (Type 14 Micromeritics, 3 Bulb, 0.4120 mL stem and 3.1126 mL total volume powder penetrometer). Before the experiment the cell was then evacuated under primary vacuum to outgas the argon for 10 minutes.
9 Scanning electron microscopy

Figure S 17. SEM images of DUT-49 before (a,b,c) and after (d,e,f) Hg intrusion at different magnifications.
Figure S18. SEM images of DUT-48(3) before (a,b) and after (c,d) Hg intrusion at different magnifications.
10 Simulation of adsorption isotherms

Adsorption isotherms were simulated using the grand canonical Monte Carlo approach, implemented by the RASPA2.0 code. For each adsorption pressure $5 \times 10^5$ cycles were used for equilibration and the subsequent $1 \times 10^6$ cycles were sampled. The van der Waals interactions were treated for the framework by the UFF forcefield and $n$-butane the united-atom TraPPE forcefield. Parameters for framework—gas interactions were obtained by Lorentz-Berthelot mixing rules. No charges were considered for the framework atoms.

11 Simulation of mechanical behavior

The behavior and mechanical properties of the representative ligands were simulated for the corresponding acid via DFT optimizations using the CRYSTAL14 software with localized TZVP basis sets and the hybrid exchange-correlation functional PBE0. Long-range dispersion corrections were included via the Grimme “D2” approach. The ligand structure was strained by a decrease in the N–N length from the local minimum to 9.227 and 5.232, for DUT-49 and DUT-48 respectively, in 40 steps. At each step, the structures were optimized with the N–N length fixed. Consequently, a stress-strain curve relative to this axial deformation of the ligand was generated; stress is defined by the gradient of the energy, and strain is the relative decrease in N–N length.

Classical simulations of the periodic systems used an adapted MOF-FF force field by Boyd et al implemented using lammps. To investigate the energy landscape a series of $(N, V, T)$ simulations at varying volumes $V$ were conducted. Constant-volume simulations, with an initial 1 ns for equilibration and a final 1 ns for obtaining a converged value of internal pressure, were used to compute the average internal pressure for a given volume. From this series of constant-volume simulations, we integrated the internal pressure to find free-energy profiles as a function of volume. All classical molecular-dynamics simulations used a time step of 1 fs and the Nosé-Hoover thermostat.
12 Simulation of DUT-48 contracted pore structure

A structural model for DUT-48cp (contracted pore) was simulated based on the unit cell parameters derived from the mechanical MD simulations (See Fig. 5). A starting geometry was taken from of (N, V, T) simulations at the cp minima and the energy was minimized iteratively adjusting the coordinates and cell parameters using the lammps minimize and box/relax commands with default convergence criteria.

Table S 3 Crystallographic data for DUT-48op, DUT-48cp, and PCN-81.

|                      | DUT-48op          | DUT-48cp          | PCN-81 (ref 2)   |
|----------------------|-------------------|-------------------|------------------|
| Empirical formula    | C_{34}H_{20}Cu_{2}N_{2}O_{10} | C_{34}H_{20}Cu_{2}N_{2}O_{10} | C_{34}H_{20}Cu_{2}N_{2}O_{10} |
| Formula weight, g mol\(^{-1}\) | 743.60            | 743.60            | 743.60           |
| Crystal system, space group | cubic, Fm\(\overline{3}\)m | cubic, P1 | cubic, Pa\(\overline{3}\) |
| Unit cell dimensions, Å | \(a = 40.490(5)\) | \(a = 32.8\) | \(a = 39.4840(16)\) |
| Volume, Å\(^3\)     | 66381(23)         | 35287            | 61555(4)         |
| Z                    | 24                | 24               | 24               |

Figure S 19 Comparison of linker configuration in DUT-48op (red), PCN-81 (blue), and DUT-48cp (green).
13 Author Contributions

S. Krause and U. S. synthesized and characterized the ligands and MOF materials, S. Krause, V. B. and I. S. performed adsorption experiments, V. B. measured and refined the crystal structure of DUT-48. S. E. performed SEM measurements. P. Y and G. M performed and analyzed the mercury intrusion experiments. S. Kaskel advised and interpreted the in situ characterization experiments. J. D. E. and F.-X. C. performed and interpreted the DFT, GCMC, MD simulations on DUT-48 and DUT-49. All authors contributed to writing and reviewing the manuscript.
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