Engineering Micromechanics of Soft Porous Crystals for Negative Gas Adsorption

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Framework materials at the molecular level, such as metal-organic frameworks (MOF), were recently found to exhibit exotic and counterintuitive micromechanical properties. Stimulated by host-guest interactions, these so-called soft porous crystals can display counterintuitive adsorption phenomena such as negative gas adsorption (NGA). NGA materials are bistable frameworks where the occurrence of a metastable overloaded state leads to pressure amplification upon a sudden framework contraction. How can we control activation barriers and energetics via functionalization of the molecular building blocks that dictate the frameworks' mechanical response? In this work we tune the elastic and inelastic properties of building blocks at the molecular level and analyze the mechanical response of the resulting frameworks. From a set of 11 frameworks, we demonstrate that widening of the backbone increases elasticity, while elongation of the building blocks results in a decrease in critical yield stress of buckling. We further functionalize the backbone by incorporation of sp3 hybridized carbon atoms to soften the molecular building blocks, or stiffen them with sp2 and sp carbons. Computational modeling shows how these modifications of the building blocks tune the activation barriers within the energy landscape of the guest-free bistable frameworks. Only frameworks with free energy barriers in the range of 800 to 1100 kJ mol−1 per unit cell, and moderate yield stress of 0.6 to 38 1.2 nN for single ligand buckling, exhibit adsorption-induced contraction and negative gas adsorption. Advanced experimental in situ methodologies give detailed insights into the structural transitions and the adsorption behavior. The new framework DUT-160 shows the highest magnitude of NGA ever observed for nitrogen adsorption at 77 K. Our computational and experimental analysis of the energetics and mechanical response functions of porous frameworks is an important step towards tuning activation barriers in dynamic framework materials and provides critical design principles for molecular building blocks leading to pressure amplifying materials.
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Engineering micromechanics of soft porous crystals for negative gas adsorption

Simon Krause1,2*, Jack D. Evans1*, Volodymyr Bon1, Irena Senkovska1, Sebastian Ehrling1, Paul Iacomi3,5, Daniel M. Többens4, Dirk Wallacher4, Manfred S. Weiss4, Bin Zheng5,6, Pascal G. Yot5, Guillaume Maurin5, Philip L. Llewellyn3, François-Xavier Coudert7, Stefan Kaskel1*

1. Faculty of Chemistry and Food Chemistry, TU Dresden, Bergstrasse 66, 01069, Dresden, Germany
2. Centre for Systems Chemistry, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
3. Aix-Marseille Univ., CNRS, MADIREL (UMR 7246), 13013, Marseille, France
4. Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109, Berlin, Germany
5. ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, France
6. School of Materials Science and Engineering, Xi’an University of Science and Technology, Xi’an 710054, PR China
7. Chimie ParisTech, PSL University, CNRS, Institut de Recherche de Chimie Paris, 75005, Paris, France

Correspondence to:
Simon Krause: simon.krause@rug.nl
Jack D. Evans: jack.evans@tu-dresden.de
Stefan Kaskel: Stefan.kaskel@tu-dresden.de

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Abstract
Framework materials at the molecular level, such as metal-organic frameworks (MOF), were recently found to exhibit exotic and counterintuitive micromechanical properties. Stimulated by host-guest interactions, these so-called soft porous crystals can display counterintuitive adsorption phenomena such as negative gas adsorption (NGA). NGA materials are bistable frameworks where the occurrence of a metastable overloaded state leads to pressure amplification upon a sudden framework contraction. How can we control activation barriers and energetics via functionalization of the molecular building blocks that dictate the frameworks’ mechanical response? In this work we tune the elastic and inelastic properties of building blocks at the molecular level and analyze the mechanical response of the resulting frameworks. From a set of 11 frameworks, we demonstrate that widening of the backbone increases elasticity, while elongation of the building blocks results in a decrease in critical yield stress of buckling. We further functionalize the backbone by incorporation of sp3 hybridized carbon atoms to soften the molecular building blocks, or stiffen them with sp2 and sp carbons. Computational modeling shows how these modifications of the building blocks tune the activation barriers within the energy landscape of the guest-free bistable frameworks. Only frameworks with free energy barriers in the range of 800 to 1100 kJ mol⁻¹ per unit cell, and moderate yield stress of 0.6 to 1.2 nN for single ligand buckling, exhibit adsorption-induced contraction and negative gas adsorption. Advanced experimental in situ methodologies give detailed insights into the structural transitions and the adsorption behavior. The new framework DUT-160 shows the highest magnitude of NGA ever observed for nitrogen adsorption at 77 K. Our computational and experimental analysis of the energetics and mechanical response functions of porous frameworks is an important step towards tuning activation barriers in dynamic
framework materials and provides critical design principles for molecular building blocks leading to pressure amplifying materials.

Introduction

Designer materials on the macro and nanoscale have taken the spotlight in recent years with fantastical properties approaching those described in science fiction. Macro- and microscopic mechanical metamaterials have captured the imagination of many researchers with many demonstrating unnatural properties, such as negative effective bulk modulus and negative effective mass density. This has poised their utilization in seemingly absurd applications, including unfeelable cloaks. Mechanical metamaterials derive their interesting properties primarily from specific framework architectures and topologies combined with the mechanical properties of the construction materials such as polymers, ceramics or metals fabricated into struts and nodes on the length scale of millimetres to sub-micrometres. In comparison, the construction of ordered 3D frameworks by self-assembly of molecular building blocks represents a straightforward bottom-up methodology for building framework architectures at the nanoscale (in the range of 0.5 to 5 nm). As such, metal-organic frameworks (MOFs) or covalent organic frameworks (COFs) can be understood as molecular analogues to macroscopic framework materials. Interestingly, many of these crystalline frameworks demonstrate unusual mechanical properties including negative Poisson’s ratio or negative linear compressibility and are thus considered nanoscopic mechanical metamaterials. Notably, the molecular-scale architecture of these “meta-MOFs” routinely produces responses difficult to engineer on the macroscale, such as negative thermal expansion (NTE) and other optical phenomena. While most of these properties are based on elastic deformations of the crystal lattice, several MOFs are known to undergo large scale inelastic transitions under preservation of the framework connectivity. These so-call soft porous crystals (SPCs) or flexible MOFs exhibit strong deformation of the lattice in particular upon adsorption or desorption of guest species. Such guest-induced transitions are specific to nanoscopic metamaterials, as they rely on enhanced host-guest interactions due to confinement at the molecular scale. As a consequence, SPCs can exhibit exotic adsorption properties with application in the area of gas storage, separation and sensing. Despite extensive knowledge about the mechanical properties of polymers and metals typically used in the construction of macroscopic metamaterials and the advancing understanding of the mechanical properties of nanoscopic materials such as poly(ethylene glycol), DNA, or carbon nanotubes, little is known regarding the mechanical behaviour of individual small molecules and their influence on the elastic and inelastic response of molecular crystalline frameworks.

In 2016, we discovered the counterintuitive adsorption phenomenon termed negative gas adsorption (NGA) in the flexible MOF named DUT-49 (Dresden University of Technology Nr. 49). NGA occurs during the course of guest adsorption with increasing gas pressure when a metastable overloaded state suddenly collapses by cooperative adsorption-induced buckling of molecular struts throughout the framework, resulting in framework contraction. In the process of this pore contraction, gas adsorbed in the overloaded metastable state is expelled from the solid, resulting in the counterintuitive release of gas with increasing pressure upon adsorption. Computational analysis showed that this behaviour can in principle be observed for other porous materials if their mechanical properties allow for bistability. We subsequently investigated molecular changes to the DUT-49 structure in an effort to tune or change the inelastic mechanical response involved in this phenomenon. Motivated by the macroscopic understanding of columnar buckling, in recent studies we considered shortening and elongation of the molecular struts. We demonstrated by density functional theory (DFT) calculations and experimental investigations that the characteristic yield stress could be tuned, leading to three frameworks with rigid characteristics in the gas physisorption experiments and a new framework, DUT-50, that also exhibits NGA. However, all these materials are based on 1,4 phenylene backbones which are buckled in the process of structural compression (Figure 1).
Figure 1. a) Unstrained fcu topology based on 12-connective cuboctahedral building blocks (green) and linear struts in the framework backbone (blue), b) strained fcu topology with bent struts (blue) in the framework backbone, c) open pore (op) form of DUT-49 with corresponding ligand L_{49} and ligand backbone (pores are indicated as orange, blue, and green spheres), and d) contracted pore (cp) form of DUT-49 with strained ligand and ligand backbone.

In NGA materials such as DUT-49 and DUT-50, the linker plays the key role of a molecular hinge enabling the dynamic framework transformation. It is therefore essential, for a rational design of novel NGA materials, to balance the linkers micromechanics as being stiff enough to stabilize the op structure of the guest-free and metastable overloaded state, but also soft enough to allow for the guest-induced contraction.

In order to identify linker backbones providing the ideal mechanical properties for NGA, we apply in the present study a combined computational and experimental approach to probe the elastic and inelastic properties of a series of molecular building units with different chemical bond-motifs typical for molecular frameworks. We link the single molecule buckling behaviour to the mechanical properties of a series of 11 isoreticular metal-organic frameworks. Both their mechanical and adsorption-induced inelastic structural transitions are unravelled by advanced in situ characterization, and their structural behaviour is rationalized using computational methods. Based on these results we quantify the essential micromechanical features of the molecular building blocks leading to new NGA frameworks, of which three are presented in this work.

Results

Computational analysis of mechanical properties of different ligand motives

To investigate the effect of various chemical bonding-motifs on the elastic properties, independently of the framework topology, we selected the framework type of DUT-49. The DUT-49 network is constructed by the linkage of tetra-connective carbazole-based ligands (L_{49}) to a copper paddle wheel to result in a framework with composition Cu_2(L_{49}) and fcu topology. When exposed to hydrostatic pressure via a pressure transmitting medium such as mercury, which is unable to penetrate the pores in the operating range of pressure, the open pore form of DUT-49 (op) exhibits volumetric compression by over 50% in a contracted pore (cp) state and beyond. A guest-induced response is observed when DUT-49 is exposed to various gases, close to their respective standard boiling points. In this case, the adsorption stress of the confined adsorbate imposes an internal contractive pressure which also leads to an inelastic but reversible contraction of the framework. In contrast to hydrostatic compression, this transition was found to be fully repeatable and can be followed via in situ diffraction and spectroscopic methods. Experimental observations were
combined with computational modelling to establish the molecular mechanism of this unusual structural contraction. The linear ligand-backbone (Figure 1b) is observed to undergo buckling upon contraction of the framework. Recently, we have demonstrated that the length of this phenylene-based building unit in L\textsuperscript{49} dictates the inelastic response of the framework.\textsuperscript{36} This behaviour can be rationalized by Euler’s formula of critical load, $P_{\text{crit}}$, commonly applied in the characterisation of macroscopic columns,

$$P_{\text{crit}} = \frac{\pi^2 E I}{L^2} \quad (1)$$

where the buckling of a column depends on its length $L$, elastic modulus $E$, and moment of inertia $I$.

Interestingly, the previously investigated ligands (Figure 2a) exhibit similar elastic moduli and illustrate the expected length dependence of yield stress (Figure 2d) which is attributed to the chemical similarity of the 1,4-substituted phenylene backbone.

![Figure 2](image.png)

**Figure 2.** a) Biscarbazol ligand subunits used in previously reported DUT-49-type frameworks, b) biscarbazol ligand subunits that are novel in this work. c) Stress-strain profiles for the ligands in DUT-49 (L\textsuperscript{49}), DUT-147 (L\textsuperscript{147}) and DUT-160 (L\textsuperscript{160}) with the elastic response region and yield stress labelled, d) correlation of the yield stress (calculated by DFT) and ligand length illustrated by the N-N distance in the ligand backbone. Dashed line represents a fit of equation (1) with varying length, e) comparison of the yield stress and elastic modulus of the ligands investigated in this study (filled symbols) and previously reported ligands (open symbols), L\textsuperscript{159} not included.

Based on these observations we were interested in how the mechanical response of DUT-49-type frameworks can be rationally tuned by changing the elastic properties of the ligand backbone via chemical functionalization. Intuitively, to increase stiffness and $P_{\text{crit}}$ in a macroscopic column one would increase its thickness or use a stiffer material, but how can these properties be manipulated on the molecular level? We deliberately chose to follow two approaches. First, by enhancing the ligand “thickness” by increasing the area of $sp^2$ conjugated backbone and introduction of alkane side groups which is expected to enhance stiffness. Second, by breaking the $sp^2$ conjugation and introducing $sp^3$ hybridised carbon atoms to increase softness. To investigate these effects of chemical functionalisation we introduced a para-substituted 9,10-dihydrophenanthrene-derived (L\textsuperscript{148}) and pyrene-derived (L\textsuperscript{147}) backbone which is expected to rigidify the central C–C bond in the backbone of the
biphenylene-based ligand L in DUT-49. Additionally, to analyse the impact of hybridization of the carbon atoms in the ligand backbone, we introduced alkynyl (L), alkenyl (L) and alkane (L, L) functionalities (Figure 2b). While L and L exhibit the same length as L, the other ligands are comparable in length to L. DFT calculations were employed to study the application of axial strain on these ligands, generating characteristic stress-strain profiles. These simulations indicate the elastic modulus (or stiffness), within the elastic regime, and the yield stress related to the non-elastic buckling behaviour of the ligands (Figure 2c). As expected, in the series of biphenylene-derived ligands, L exhibits the highest elastic modulus of 110 nN while L only shows a slight increase in elasticity over L around 80 nN. In the series of different hybridisation L (with 84 nN) exhibits a twofold increase in elasticity compared to L, and L shows the lowest elasticity, in the range of 30 nN. Interestingly, the yield stress of functionalized ligands is found to be in a rather small range of 0.5 to 2 nN compared to the series of elongated ligands, with phenylene-based backbone, which spans from 0.8 to 3.5 nN. Consequently, the functionalisation of the ligand backbone allows to rationally tune the elastic properties with comparable yield stress (horizontal trend in Figure 2e) while elongation of a phenylene-based ligand allows to manipulate the yield stress independent of the elastic properties (vertical trend in Figure 2e). This analysis demonstrates how the elastic and inelastic properties of molecular building blocks can be manipulated by both elongation and chemical exchange of the backbone constituents leading to stiffening and softening. Notably, the loss of linearity and sp hybridization in the backbone has the biggest influence on both elasticity and yield stress producing an extremely soft molecular unit to an extent where the ligand no longer exhibits a linear conformation, as in L (Supplementary Figure 20).

Synthesis and characterisation of metal-organic frameworks

To link the elastic and inelastic behaviour of the molecular ligands to the mechanical properties of the corresponding frameworks, the proposed ligands and their corresponding Cu(II)-based MOFs (DUT-147, DUT-148, DUT-159, DUT-160, DUT-161, DUT-162) were synthesized based on procedures previously described for DUT-49 and elongated derivatives. With the exception of DUT-159 all frameworks are found to crystallize in cubic symmetry with the fcu topology expected for DUT-49-type structures. The ligand backbones are found to be disordered over two (in case of DUT-147 and DUT-160) and four (DUT-148, DUT-161 and DUT-162) positions consistent with the symmetry of Fm space group. Interestingly, while introduction of two CH groups in the backbone of L results in the formation of a framework with fcu topology and linear backbone, the introduction of two CH groups adjacent to the carbazole nitrogen in L distorts the linear conformation and results in the formation of a drastically different structure. The substituted carbazole-3,6-dicarboxylate units in DUT-159 no longer form cuboctahedral cages as in DUT-49 but 2D kagome-type sheets that are pillared by the 1,4-bismethylenebenzene backbones in L. DUT-159 thus represents a 3D framework based on kagome lattices previously reported in DUT-158 (composition Cu(cdc), cdc = 9H-carbazole 3,6-dicarboxylate) (Supplementary Figure 20). This demonstrates that the incorporation of sp hybridized carbon atoms in the spacing unit not only softens the ligand backbone but also affects the formation of highly symmetrical supermolecular building blocks.

Crystal size and shape are important parameters to control as they significantly impact adsorption-induced structural transitions in flexible MOFs in general and DUT-49 in particular. A representative size distribution obtained via scanning electron microscopy is shown in Supplementary Figure 9 - Supplementary Figure 14. Crystal morphologies range from cubic to cuboctahedral with mean sizes in the range of 4–7 μm, similar to those previously chosen to analyse NGA in DUT-49 and DUT-50 samples. Bulk powders of the MOFs were further characterized by powder X-ray diffraction (Supplementary Figure 3 to Supplementary Figure 8), elemental analysis (Supplementary Table 3), and thermogravimetric analysis (Supplementary Figure 2).

To characterize the mechanical properties independently of the guest species, MOF samples were desolvated by applying a supercritical activation protocol previously used on DUT-49 and related materials. With the exception of DUT-159, all other materials show preservation of the op structure upon solvent removal investigated by PXRD (Supplementary Figure 3 to Supplementary Figure 8). DUT-159 was found to lose long-range structural ordering upon removal of the solvent from the pores indicating that the previously discussed soft nature of the ligand is transferred to the framework, which in this case seems to be stabilized by the
presence of solvent in the pore space. The lack of crystallinity does not allow further characterization in the context of this work and DUT-159 is thus not further considered in the following discussion. In the remaining series of five new DUT-49-type structures, the experimentally observed ligand lengths of the respective open phases obtained by MD simulations correspond well to the values derived from DFT simulations of the free single ligand molecules (Table 1).

Table 1. Selected structural parameters for the series of frameworks and ligands in the open (op) and contracted pore (cp) state derived from the experimental (exp) and MD-based simulated (sim) crystal structures. Data for DUT-49 and -50 was taken from reference.36

| Material | Ligand N...N spacing op (Å) (exp) | Ligand N...N spacing cp (Å) (exp) | Ligand N...N spacing op (Å) (sim) | Ligand N...N spacing cp (Å) (sim) | Unit cell volume (Å³) op (exp) | Unit cell volume (Å³) cp (exp) | Unit cell volume (Å³) op (sim) | Unit cell volume (Å³) cp (sim) | Contraction (%) (exp) | Contraction (%) (sim) |
|----------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|---------------------|---------------------|
| DUT-49   | 9.945(4)                         | 9.22                            | 9.630(2)                         | 9.31                             | 101117(19)                    | 47281(5)                     | 97153                         | 46287                         | 53                  | 53                  |
| DUT-147  | 9.868(5)                         | 9.85                            | 9.535(3)                         | 9.34                             | 100221(35)                    | 48998(7)                     | 99781                         | 48300                         | 51                  | 51                  |
| DUT-148  | 9.907(4)                         | 9.91                            | 9.720(2)                         | 9.14                             | 100804(35)                    | 47979(8)                     | 98806                         | 48971                         | 52                  | 52                  |
| DUT-160  | 12.438(4)                        | 12.4                            | 11.455(4)                        | 11.6                             | 125627(44)                    | 51866(10)                    | 125669                        | 59127                         | 59                  | 59                  |
| DUT-161  | 12.215(4)                        | 12.3                            | 11.105(4)                        | 11.1                             | 123209(43)                    | 45898(8)                     | 119947                        | 53082                         | 63                  | 63                  |
| DUT-162  | 12.128(6)                        | 12.2                            | n.a.                             | 9.82                             | 121950(42)                    | 42839                         | 122682                        | n.a.                           | 61                  | 61                  |
| DUT-50   | 14.273(7)                        | 14.4                            | 13.593(3)                        | 13.2                             | 145781(51)                    | 58062(4)                     | 141092                        | 58557                         | 60                  | 60                  |

Computational and experimental analysis of mechanical properties of metal-organic frameworks

To explore the dynamics of the framework materials, we performed classical molecular dynamics (MD) simulations similar to our previous studies on DUT-49,35,36 The simulations employed established forcefields,46 not specially produced or optimized for the systems at hand, which qualitatively reproduce the lattice parameters observed experimentally (Table 1). We computed a series of pressure-volume curves at 300 K, which represent the response of the framework under increasing hydrostatic compression, using previously reported protocols.35 The pressure-volume curves thus give access to the underlying free energy surface of the frameworks with respect to volume. All materials presented in this work demonstrate a bistable nature with a local minimum, \(\Delta F_{cp}\), at reduced unit cell volume and estimated activation barriers, \(\Delta F^\dagger (op \rightarrow cp)\), in the range of DUT-49 (\(\Delta F^\dagger = 1000\) kJ mol\(^{-1}\) (UC = unit cell), \(\Delta F_{cp} = 950\) kJ mol\(^{-1}\)) with the exception of DUT-162 (\(\Delta F^\dagger = 580\) kJ mol\(^{-1}\), \(\Delta F_{cp} = 220\) kJ mol\(^{-1}\)) and DUT-147 (\(\Delta F^\dagger = 1420\) kJ mol\(^{-1}\), \(\Delta F_{cp} = 1240\) kJ mol\(^{-1}\), Figure 3).
This analysis demonstrates structural bistability, as in each case a second minimum is identified with significantly reduced unit cell and pore volume. This is a key prerequisite for NGA materials, but it also requires the presence of sufficiently large activation barriers promoting the metastable overloaded state. In order to experimentally probe the mechanical response and bistability of these MOFs, compression via mercury intrusion was performed on desolvated crystalline MOF powders of the series of functionalized MOFs (Supplementary Figure 18 and Supplementary Figure 19). From the intrusion curves the inelastic transition pressure for hydrostatic compression of the op-phases can be estimated as a first approach to quantify and rationalize the framework micromechanics as predicted by computer simulations. The computational analysis of the inelastic yield stress of the ligands is well reflected in the experimental transition pressure for structural contraction of the corresponding MOF materials, and also agrees well with the computationally predicted values (Figure 3c) confirming the generality of the microscopic mechanism at play. DUT-160 and -161 exhibit transition pressures comparable to DUT-50 in the range of 24 MPa while DUT-148 and 147 exhibit a slight increase with 32 MPa and 35 MPa, respectively over DUT-49 (30 MPa). DUT-162, however, exhibits by far the lowest transition pressure of all materials tested (less than 10 MPa). From a molecular perspective the application of sp² hybridized carbon atoms in the backbone not only severely softens the framework but can also prevent the formation of the desired framework topology due to enhanced degrees of freedom in the ligand structure. Extended aromatic systems on the other hand were found to yield the most stable configurations with a slight decrease in stability upon introduction of stilbene-type motives.

Analysis of adsorption properties by experiment and simulation

In the published literature, DUT-49 and DUT-50 are so far unique in their ability to sustain a guest-overloaded metastable state before they undergo adsorption-induced structural contraction leading to NGA and pressure amplification. According to previous experimental and computational studies, tuning and balancing the activation barrier and energetic separation of the two states is essential to maintain the overloaded metastable state without disabling the adsorption-induced contraction. Mechanically and energetically this means DUT-
148, 160, 161, 162 are promising materials for NGA, having activation barriers in the same range as DUT-49 and 50 (around 1000 kJ mol⁻¹).

To test the porosity of the bulk materials and potential occurrence of adsorption-induced transitions, the desolvated MOF powders were analysed using nitrogen physisorption at 77 K, Grand Canonical Monte Carlo (GCMC) simulations for op and cp phase greatly facilitate the interpretation of the experimental adsorption isotherms (description of the simulation procedures and CIF files in ESI) (Figure 4).

![Figure 4. Nitrogen physisorption isotherms at 77 K for a) DUT-49, b) DUT-148, c) DUT-147, d) DUT-159, e) DUT-50, f) DUT-160, g) DUT-161, and h) DUT-162. Closed symbols adsorption, open symbols desorption, simulated isotherm for op phase as purple line, cp phase as orange line.]

DUT-160 and DUT-161 stand out as highly porous materials with specific pore volumes up to 3.38 and 3.2 cm³g⁻¹ and geometrically accessible surface areas of 5342 and 5229 m²g⁻¹, respectively determined by Zeo++ calculations from the simulated crystal structures (Supplementary Table 11).

With regard to adsorption-induced transitions, the recorded N₂ adsorption isotherms at 77 K reflect three different scenarios. The rigid DUT-147 exhibits a reversible type IVb isotherm without any indication of structural contraction (and, in particular, no hysteresis loop typically associated with such structural transition). DUT-148, 160 and 161 are dynamic and exhibit characteristic NGA steps around 10-20 kPa, followed by a plateau at intermediate pressures and a steep increase in uptake at approximately 50 kPa. Upon desorption a wide hysteresis in the pressure range of 50-20 kPa is observed. This is a remarkable finding as so far, NGA steps induced by N₂ at 77 K were only observed for DUT-49. Hence, DUT-148, 160, and 161 represent three new NGA materials demonstrating counterintuitive N₂ pressure amplification at 77 K. Of the three DUT-148 and DUT-161 exhibit incomplete contraction of the bulk sample upon NGA evident by the deviation in uptake of experimental and simulated isotherm at intermediate pressure and previously described for DUT-50. Further softening of the backbone as in DUT-162, leads to a different scenario and significantly decreased uptake. Crumbled crystals are detected in SEM indicating deformation upon solvent removal (Supplementary Figure 14). However, PXRD do not confirm complete collapse of the crystals. The remaining porosity in the bulk sample and comparison to the simulated isotherm indicate that ca. 60% of the DUT-162 bulk undergoes collapse likely upon solvent removal. Whether this collapse occurs partially in individual crystals or the bulk powder consists of a mixture of completely collapsed and non-collapsed crystals could not be determined. The reduced porosity explains the gradient slope and low volumetric compression of DUT-162 in the mercury intrusion experiments (Supplementary Figure 19). Hence, in this system backbone softening exceeds a critical value to maintain the open porosity. Similarly, DUT-159 exhibits a strong decrease in uptake compared to the simulated isotherm which further supports the framework collapse upon solvent removal. Replication of the
synthesis and activation procedure on a second sample of DUT-159 and DUT-162 supported these findings rendering DUT-162 the lower limit of stability required to obtain a non-collapsed guest free DUT-49-type framework. Upon desorption DUT-49, 148, 50, 160 and 161 exhibit an inverse hysteresis in which the desorption branch intersects the adsorption branch indicating desorption-induced contraction. The good agreement of low-pressure desorption branches with the simulated isotherms of the \textit{cp} phases indicates complete structural contraction upon desorption in contrast to the adsorption behaviour. NGA in DUT-49 was initially observed upon adsorption of methane at 111 K and \textit{n}-butane at 298 K\textsuperscript{32} and strongly depends on the adsorption temperature and nature of the adsorbate\textsuperscript{49}. The magnitude of NGA, which is proposed to be correlated to the barrier of structural transformation\textsuperscript{49}, is defined by the released amount of gas upon structural contraction, $\Delta NGA$, which is the difference in uptake of gas in the \textit{op} phase before contraction, $n_{\text{op}}$, minus the uptake in the \textit{cp} phase after contraction, $n_{\text{cp}}$. Methane adsorption at 111 K in DUT-49 yields a relatively large NGA step of 6.3 mmol g\textsuperscript{-1}, adsorption of \textit{n}-butane at 273 K was found to result in structural contraction without NGA due to enhanced adsorption-induced stress. Conversely, nitrogen adsorption at 77 K yielded an intermediate NGA step of 4.4 mmol g\textsuperscript{-1} due incomplete contraction caused by lower adsorption-induced stress partly reflected by the adsorption enthalpy\textsuperscript{39,50}. To further investigate the response of the series of materials in this study against increased adsorption-induced stress, adsorption experiments with methane adsorption at 111 K and \textit{n}-butane adsorption at 273 K were conducted (Figure 5).

Interestingly, under these conditions even DUT-147 as the most rigid framework shows a narrow hysteresis in the pressure range of 10-60 kPa for both adsorption of methane at 111 K and \textit{n}-butane at 273 K, indicating a partial contraction. Isotherms of DUT-148, 160 and 161 exhibit wide hysteresis at intermediate pressures for both methane and \textit{n}-butane adsorption. Interestingly, only methane isotherms at 111 K of DUT-148 and DUT-
160 show NGA steps similar to DUT-49.\textsuperscript{32} The absence of NGA steps in DUT-161 upon adsorption of methane at 111 K and \(n\)-butane at 273 K is consistent with the observations made for DUT-50.\textsuperscript{36} These findings reflect the close energetic relationship of DUT-50 and DUT-161 which exhibit the lowest activation barriers of the series and the relationship of DUT-49 with DUT-148 and DUT-160 with slightly enhanced barriers (Figure 3).

The fundamental driving force of the adsorption-induced contraction in DUT-49-type frameworks is the enhanced interactions of the fluid inside the contracted pore diameter in the \(cp\) phase.\textsuperscript{35} In a previous study we could correlate the non-monotonic enthalpy profile to the pore filling mechanism in the \(op\) phase by \textit{in situ} calorimetry experiments and computational analysis.\textsuperscript{35, 36, 50} While elongation of the ligand backbone was found to strongly influence the adsorption energetics due to the change in pore size,\textsuperscript{36} the effect of chemical functionalization on the adsorption enthalpy profile is less clear. \textit{In situ} calorimetry experiments in parallel to the adsorption of \(n\)-butane at 303 K for DUT-148, 147 and 160 (Supplementary Figure 34) show that the enthalpy curves of DUT-148 and DUT-147 match the previously reported data of DUT-49 demonstrating that the functionalization of the ligand backbone does not impact the solid-fluid interactions in the \(op\) phase. This is further confirmed by comparing enthalpy curves of DUT-160 to DUT-49 and DUT-50: the average adsorption enthalpy in the \(op\) phase is found to decrease with increasing pore size. This finding is also supported by adsorption enthalpy curves simulated for methane adsorption at 111 K for the \(op\) and \(cp\) phases (Supplementary Figure 35). Thus, the applied ligand functionalization has negligible influence on the adsorption energetics of the \(op\) and \(cp\) phase and the observed adsorption behavior and adsorption-induced contraction can be attributed primarily to the mechanical characteristics of the solid. Structures that exhibit enhanced mechanical stability (DUT-48, 47, 147) are found to be non-contractable under these conditions while the structure of softened MOFs (DUT-159, 162) cannot be retained upon solvent removal. In the intermediate range of mechanical stability (DUT-49, 148, 160, 161, 50) adsorption-induced structural contraction and in some cases NGA occurs. This finding underpins the importance of balancing mechanical stiffness for pressure amplifying materials towards adsorption-responsive transitions.

**Elucidation of adsorption-induced structural transitions by \textit{in situ} powder X-ray diffraction**

The interpretation of adsorption-induced transformations is also supported by \textit{in situ} PXRD studies in parallel to the adsorption of \(n\)-butane at 273 K for DUT-147 and DUT-148 (full datasets Supplementary Figure 21, selected patterns in Figure 5) and methane at 111 K for DUT-160 and DUT-161. Remarkably, DUT-147 undergoes partial contraction around 10 kPa and incomplete reopening at increased pressure up to 95 kPa. Upon desorption, the DUT-147 sample undergoes partial contraction in the pressure range of 12-9 kPa and complete contraction is observed at pressures below 1 kPa. Interestingly, the desorption-induced stress can trigger phase transitions which are otherwise not observed during adsorption, revealing a different mechanism for the adsorption and desorption processes in these bistable systems. As phase mixtures occur during adsorption but not upon desorption this indicates that gas loading, in addition to previously mentioned crystal size effects,\textsuperscript{39} can have a strong influence on the bulk adsorption properties in DUT-49-type systems. DUT-148 shows complete contraction of the bulk sample at intermediate pressures upon adsorption of \(n\)-butane at 273 K.

Experimental crystal structures of DUT-147\(cp\) and DUT-148\(cp\) could be refined by Rietveld methods based on PXRD pattern collected at 15 kPa loading with \(n\)-butane at 273 K (Supplementary Figure 28, Supplementary Figure 30). The unit cell parameters and conformational changes in the ligand are very similar to DUT-49\(cp\) (Table 1) and the modelled values. However, in both, DUT-148 and 147 incomplete reopening of the \(cp\) phase is observed even at pressures close to saturation. This indicates a high barrier for the \(cp\)-\(op\) transformation in these systems possibly caused by the strong host guest interactions.

\textit{In situ} PXRD patterns recorded for DUT-160 in parallel to adsorption of \(n\)-butane at 273 K show complete transformation of the \(op\) phase (Supplementary Figure 25). However, the quality of the PXRD pattern is drastically reduced with severe loss in intensity and broadening of the remaining peaks. Similar observations for DUT-50 were attributed to the relatively high adsorption temperature in which the increased mobility of the elongated ligands causes increased disorder in the framework of the strained \(cp\) phase.\textsuperscript{36} \textit{In situ} PXRD patterns recorded for DUT-160 and DUT-161 (Supplementary Figure 26 and Supplementary Figure 24, selected patterns...
in Figure 5) in parallel to methane adsorption at 111 K show improved quality but still severe broadening compared to patterns collected for DUT-148cp. Both materials show complete op-cp transition at 17 kPa and presence of cp phase in the pressure range of 17-35 kPa. At elevated pressures the samples undergo reopening with phase pure op phases at saturation pressure. PXRD patterns obtained for DUT-161cp during adsorption are different from the pattern obtained for DUT-160cp during desorption for which the patterns of DUT-161cp are comparable to DUT-160cp at pressures below 10 kPa. In both cases the quality of the PXRD patterns did not allow for Rietveld refinement. Instead, structural models for DUT-160cp and DUT-161cp were simulated based on the unit cell parameter, obtained from the Le Bail fit of the PXRD patterns and show good agreement with the simulated models. The fact that the cp phase in DUT-160 and 161 shows only few reflections with low intensity in PXRD but still can transform back in a crystalline op phase at elevated pressures (Figure 5 k,l) demonstrates the preservation of framework connectivity and the cooperativity of the transition.

In situ PXRD patterns recorded during adsorption of nitrogen at 75 K in DUT-148 shows that at 10 kPa the op phase transforms to a mixture of op, cp and intermediate pore (ip) structures. These observations were previously also made for nitrogen adsorption in DUT-49. With increasing pressure in the range of 12 to 20 kPa the ip phases expand gradually to the op phase thus producing multiple steps in the isotherm. The cp phase of the remaining phase mixture, is only completely reopened at around 50 kPa forming phase pure DUT-148op at pressures beyond 70 kPa (Supplementary Figure 33).

The magnitude of negative gas adsorption

Adsorption-induced contraction and the resulting adsorption behavior, including NGA, can be thought of as a response of the framework to different levels of adsorption-induced stress. From the adsorption experiments reported above, we can derive that softer frameworks contract at lower adsorption-induced stress levels present upon adsorption of N₂ at 77 K. On the other hand, stiffer frameworks only undergo contraction at increased stress levels that can be present during n-butane adsorption at 273 K. However, in order for NGA transitions to occur, the framework not only needs to undergo adsorption-induced contraction, but that contraction needs to occur at a pressure/loading beyond the intersection of the op and cp. So far, three scenarios have been observed for the investigated materials upon gas adsorption of nitrogen (77 K), methane (111 K) and n-butane (273 K): (i) absence of structural transitions indicated by the lack of hysteresis; (ii) structural contraction without NGA transition indicated by a wide hysteresis; and (iii) structural contraction with NGA transition indicated by the presence of a drop in uptake at intermediate pressure. Interestingly, NGA is only found to occur in materials with free energy barriers and yield stress of single ligand buckling in the range of 800 to 1100 kJ mol⁻¹ and 0.6 to 1.2 nN, respectively (Figure 6).
Figure 6. a) NGA parameter $\Delta n_{\text{NGA}}$ for the series of materials and different gases, d) their respective free energy barriers and g) single ligand yield stress for buckling. b,e,h) $\Delta n_{\text{NGA}}$ as a function of the free energy barrier and c,f,i) as a function of the yield stress of the single ligand.

The similar three scenarios were also found to occur for DUT-49 upon changing the adsorption temperature. There, NGA was only found to occur in a narrow range of temperature for a given adsorbate. In fact, while structural contraction in the absence of NGA was observed for DUT-49, 148, 160, 161, 50 upon adsorption of $n$-butane at 273 K, NGA is observed in DUT-49 and 148 at 298 K (Supplementary Figure 15), DUT-161 only exhibits NGA upon adsorption of nitrogen at 77 K and methane at 111 K. DUT-50 is found to show NGA only upon adsorption of methane at 111 K. DUT-160 exhibits NGA upon adsorption of methane at 111 K, as well as a very large NGA step of almost 12 mmol g$^{-1}$ upon adsorption of nitrogen at 77 K: this is the highest value reported, almost twice compared to the largest value found so far in DUT-49. However, we cannot from this dataset establish a clear and direct correlation between the magnitude of $\Delta n_{\text{NGA}}$, the adsorption conditions, and the mechanical properties of the frameworks.

For DUT-49 we previously found that, in the 91–150 K temperature range, the maximum adsorption-induced stress increases with decreasing adsorption temperature promoting adsorption-induced contraction at lower adsorption temperature. We also showed that the critical stress for contraction is shifted towards lower adsorption pressure closer to the intersection of the $op$-$cp$ isotherm and as a consequence $\Delta n_{\text{NGA}}$ is found to decrease with decreasing adsorption temperature. To test whether this behavior is universal and present in other DUT-49-type systems, and whether a correlation between $\Delta n_{\text{NGA}}$ and the mechanical properties of the framework can be made, we conducted variable methane adsorption in the range of 90-140 K for DUT-50 (Supplementary Figure 17) and DUT-160 (Supplementary Figure 16). For each isotherm parameters important to NGA are derived and shown in Figure 7.
Both DUT-50 and DUT-160 exhibit a similar temperature dependence of $\Delta \rho_{NGA}$ upon adsorption of methane. In all cases $\Delta \rho_{NGA}$ reaches a maximum with a more defined maximum in DUT-150 and 160 compared to DUT-49. Interestingly, the temperature at which $\Delta \rho_{NGA}$ reaches its maximum is governed by the mechanical characteristics of the corresponding framework. For DUT-49 which is the most robust of the three, a maximum is observed in the range of 110-115 K while DUT-50 and 160 a maximum is observed at 120-125 K. This is in line with the previously discussed correlation between the adsorption temperature, the critical adsorption stress and the framework rigidity. To investigate the influence of the variation in pore volume present upon elongation of the ligand, $\Delta \rho_{NGA}$ was normalized to the excess uptake of the $\rho_{op}$ phase, $n_{excess}$, at 0.95 relative pressure. Interestingly, each material exhibits a maximum of $\Delta \rho_{NGA}$ around 10%. Considering the total uptake of the $\rho_{op}$ phase is around 30% of $n_{excess}$ of the $\rho_{op}$ phase there would still be a lot of theoretical potential for an increase in $\Delta \rho_{NGA}$ under these conditions. Thus, we investigated the evolution of $\Delta \rho_{NGA}$ as a function of $n_{op}$ and $n_{sp}$. The analysis clearly shows that the increase in $\Delta \rho_{NGA}$ with increasing temperature is a result of the increase in $n_{op}$ before contraction while $n_{sp}$ is almost constant in the analyzed temperature range. Although the variable temperature analysis in DUT-50 and 160 supports the earlier findings of DUT-49, a wider dataset potentially involving different adsorbates is still needed to derive a quantitative relationship of the framework micromechanics and their NGA response.

Conclusion

In summary, by controlled tuning of the elastic and inelastic characteristics of a series of ligands under uniaxial strain and implementation into a DUT-49-type fcu network, it is possible to manipulate the counterintuitive negative gas adsorption response and pressure amplification behaviour in adsorption induced structural transformations. Shortening and widening of the ligand backbone is observed to increase stiffness while incorporation of acetylene, ethylene, and $sp^3$ hybridized groups in the ligand backbone increases softness. The inelastic transition of the frameworks and metastable states controlled by free energy barriers for framework compression and yield stress for single ligand buckling lead to NGA. According to computational estimations, these free energy barriers are in the range of 800 to 1100 kJ mol$^{-1}$ per unit cell or 33 to 46 kJ mol$^{-1}$ per linker with moderate yield stress (0.6 to 1.2 nN) which is essential to preserve an overloaded metastable state without suppressing the framework transformation. By balancing the elasticity of the ligand, the magnitude of gas expulsion ($\Delta \rho_{NGA}$) from the metastable state is boosted, as demonstrated for the new framework DUT-160. However, the degree of metastability and pressure amplification is also critically affected by the gas composition, the adsorption temperature and porosity of the porous solid.
These new findings provide fundamental insights for understanding the impact of chemical constitution on the mechanical properties of molecular building blocks. While the mechanical properties of more rigid but also structurally flexible porous solids have recently gained interest, this study provides fundamental design principles towards softening and rigidifying molecular building blocks. The deliberate design of transformation barriers has important implications for applications of flexible porous frameworks as mechanical actuators, valves, selective adsorbents, sensors and switchable catalysts. Yet, the current study only probes molecular mechanical effects and transformations in a single framework topology and the striking analogy to macro and microscopic mechanical metamaterials may serve as an inspiration for the future design of novel counterintuitive framework response functions. In this sense topological engineering and the art of building block design enable unforeseen opportunities at different length scales.

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Conflict of interest:

The authors have no conflict of interest to declare.

Notes:

MOF materials are abbreviated DUT (Dresden University of Technology) followed by a serial number, Corresponding ligands are abbreviated L with the corresponding DUT serial number as superscript, Open, contracted, and intermediate pore states are abbreviated op, ip, and cp, respectively. Energy values for framework contraction are given in kJ mol⁻¹ per unit cell which is abbreviated to kJ mol⁻¹ uc⁻¹ (UC = unit cell).

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Supplementary Materials for

Engineering micromechanics of soft porous crystals for negative gas adsorption

Simon Krause\textsuperscript{a,b}, Jack D. Evans\textsuperscript{a*}, Volodymyr Bon\textsuperscript{a}, Irena Senkovska\textsuperscript{a}, Sebastian Ehring\textsuperscript{a}, Paul Iacomi\textsuperscript{c,e}, Daniel M. Többens\textsuperscript{d}, Dirk Wallacher\textsuperscript{d}, Manfred S. Weiss\textsuperscript{d}, Bin Zheng\textsuperscript{e,f}, Pascal G. Yot\textsuperscript{e}, Guillaume Maurin\textsuperscript{e}, Philip L. Llewellyn\textsuperscript{c}, François-Xavier Coudert\textsuperscript{g}, Stefan Kaskel\textsuperscript{a*}

\textsuperscript{a} Faculty of Chemistry and Food Chemistry, TU Dresden, Bergstrasse 66, 01069, Dresden, Germany
\textsuperscript{b} Centre for Systems Chemistry, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
\textsuperscript{c} Aix-Marseille Univ., CNRS, MADIREL (UMR 7246), 13013, Marseille, France
\textsuperscript{d} Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109, Berlin, Germany
\textsuperscript{e} ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, France
\textsuperscript{f} School of Materials Science and Engineering, Xi'an University of Science and Technology, Xi'an 710054, PR China
\textsuperscript{g} Chimie ParisTech, PSL University, CNRS, Institut de Recherche de Chimie Paris, 75005, Paris, France

Correspondence to:
Simon Krause: simon.krause@rug.nl
Jack D. Evans: jack.evans@tu-dresden.de
Stefan Kaskel: Stefan.kaskel@tu-dresden.de

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1 Instruments and methods

The description of instruments and methods has been previously published by our group in reference 1 and is a literal adaption.

Solution/liquid-state NMR

Nuclear magnetic resonance (NMR) spectra were acquired on a BRUKER Avance III 500 spectrometer (500.13/600.16 MHz and 125.77/150.91 MHz for \(^1H\) and \(^13C\) respectively) and/or on a VARIAN Mercury (300 MHz, 282 MHz and 75.5 MHz for \(^1H\) and \(^13C\), respectively). All \(^1H\) and \(^13C\) NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the residual signals of the solvents at 7.26 ppm (CHCl\(_3\)) or 2.54 ppm (DMSO). Data for \(^1H\) NMR spectra are described as following: chemical shift (δ ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad signal), coupling constant \(J\) (Hz), integration corresponding to amount of C or CH. Data for \(^13C\) NMR spectra are described in terms of chemical shift (δ ppm) and functionality were derived from DEPT spectra.

Mass spectrometry

Matrix-assisted laser desorption/ionization (MALDI) time of flight (TOF) mass spectrometry analysis was performed on a BRUKER Autoflex Speed MALDI TOF MS using dithranol as matrix. Atmospheric-pressure solid analysis probe (ASAP) mass spectrometry was performed on an ADVION expression LCMS with an APCI ion source.

Elemental analysis

Elemental analysis was carried out on a VARIO MICRO-cube Elemental Analyzer by Elementar Analysatorsysteme GmbH in CHNS modus. The composition was determined as the average of three individual measurements on three individually prepared samples.

DRIFT Spectroscopy

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was performed on a BRUKER VERTEX 70 with a SPECAC Golden Gate DRIFT setup. Prior to the measurement 2 mg of sample were mixed with 10-15 mg dry KBr in a mortar and pressed in the DRIFT-cell. Assignments of peaks in wavenumber ν (cm\(^{-1}\)) were categorized by strong (s), medium (m), weak (w).

Thermogravimetric analysis

Thermal analysis (TGA) was carried out in synthetic dry air using a NETZSCH STA 409 thermal analyser at a heating rate of 5 K min\(^{-1}\). Air sensitive MOF samples were prepared in an Ar-filled glovebox and inserted in the instrument with little exposure to ambient conditions.

X-Ray Diffraction

Powder X-ray diffraction (PXRD) patterns were collected in transmission geometry with a STOE STADI P dифрактометр operated at 40 kV and 30 mA with monochromatic Cu-Kα (λ = 0.15405 nm) radiation, a scan speed of 30 - 15 s/step and a detector step size of 2θ = 0.1 – 2 °. The samples were placed between non-diffracting adhesive tape or in a glass capillary. “As made” samples were analysed while suspended in DMF. Desolvated samples were prepared under inert atmosphere. Theoretical PXRD patterns were calculated on the basis of crystal structures using Mercury 3.9 software package.

SEM analysis of crystal size and morphology
Scanning electron microscopy (SEM) images of DUT-49 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. To avoid degradation upon exposure to air, the samples were prepared under argon atmosphere. For each sample a series of images was recorded at different magnifications and for each sample three different spots on the sample holder were investigated. The crystal size refers to the edge length of the cubic crystals as they are the easiest to measure. The analysis of the SEM images was performed with ImageJ Software package. Values for mean crystal size, as well as relative standard deviation (RSD) were obtained by using the ImageJ Analyse-Distribution function.
2 Materials and Ligand synthesisi

For the synthesis and characterisation the following commercial chemicals were used: 2,7-Dibromopyrene (CAS:102587-98-4, >97%, TCI), 4,4′-Diiodo-2,2′-dimethyl-1,1′-biphenyl (CAS:69571-02-4, 97%, Sigma Aldrich), 9,10-Hydrophenanthrene (Cas: 776-35-2, 99%, ABCR), Bis(4-Bromophenyl)acetylene (2789-89-1, >98%, TCI), Copper(II) nitrate trihydrate (10031-43-3, 98%, Sigma Aldrich), Dibromo-p-xylene (623-24-5, 98%, Sigma Aldrich), 4,4′-Dibromo-trans-stilbene (CAS: 18869-30-2, 99%, TCI).

Synthesis procedures

General procedures for the synthesis of the ligands described below were previously published by our group1 The Synthesis is based on n-butyl ester 1 which can be obtained in a 5 step synthesis from 9H-carbazole following procedures published in reference 1,3.

Supplementary Figure 1. Chemical structure of n-butyl ester 1. The general synthesis of the ligands is based on Ullmann coupling of the ester 1 with different iodides and bromines. The following procedures which were previously published in reference 1 were used:

Ullmann coupling with iodides

This procedure is based on synthesis previously used for carbazole based ligands4. A Schlenk flask was charged with indicated amounts of ester 1, the corresponding iodine, potassium carbonate, copper (I) iodine, and L-proline under inert atmosphere. To the mixture indicated amounts of degassed DMSO or DMF were given and Ar was bubbled through the suspension for 30 min. The reaction mixture was stirred at 90 – 120 °C for 24 h to 10 d and the reaction was cooled down to room temperature. The suspension was quenched with diluted (< 0.02 M) Hydrochloric acid and extracted with chloroform. He organic phases were collected, dried over MgSO$_4$, and the solvent removed in vacuum. The crude product was purified by flash column chromatography using indicated mixtures of chloroform, DCM, iso-hexane and ethyl acetate. Corresponding amounts of the chemicals added and used for the synthesis and purification are provided for each coupling product.

Ullmann coupling with bromines

This procedure is based on synthesis previously used for carbazole based ligands5. A Schlenk flask was charged with indicated amounts of ester 1 the corresponding bromine, potassium carbonate, copper (I) iodine, and N,N′-dimethylethylenediamine under inert atmosphere. To the mixture indicated amounts of degassed anhydrous 1,4-dioxane were given and Ar was bubbled through the suspension for 30 min. The reaction mixture was stirred at 80 – 110 °C for 24 h to 12 d and the reaction was cooled down to room temperature. The solvent was removed in vacuum and the obtained powder was dissolved in chloroform and extracted with diluted (< 0.02 M) hydrochloric acid. He organic phases were collected, dried over MgSO$_4$, and the solvent removed in vacuum. The crude product was purified by flash column chromatography using indicated mixtures of chloroform, DCM, iso-hexane and ethyl acetate. Corresponding amounts of the chemicals added and used for the synthesis and purification, reaction times and temperatures are provided for each coupling product.

General procedure for ester hydrolysis

To hydrolyse the ester groups the corresponding coupling products were dissolved in indicated volumes of THF, methanol, and water at 85 °C. To the solution potassium hydroxide was added and the mixture was stirred at 85 °C for 12 h– 5 d. In case a precipitation formed from the previous clear solution (most
likely the potassium salt of the hydrolysed ester which is insoluble in THF) small amounts of water were added until a clear solution formed again. After the indicated reaction time the THF and methanol were removed in vacuum, the resulting solution was filtered, and neutralized with 2 M hydrochloric acid. The precipitate was filtered off and dried in vacuum at room temperature. Corresponding amounts of the chemicals added and reaction times are provided for each hydrolysis product.

**Tetrabutyl 9,9'- (pyrene-2,7-diyl)bis(9H-carbazole-3,6-dicarboxylate)**

\[
\text{Synthesis conditions: } 3.76 \text{ g (10.2 mmol) n-butyl ester 1, 1.23 g (3.41 mmol) 2,7-dibromopyrene, 1.84 g (13.3 mmol) potassium carbonate, 323 mg (1.7 mmol) copper(I) iodine, 0.1 ml (0.91 mmol) N,N'-dimethylethylenediamine, 60 ml anhydr. 1,4 dioxane, 100 °C for 11 d; Flash column chromatography chloroform : iso-hexane : ethyl acetate – 1 : 0.33 : 0.03 (Rf 0.41); Yield: 0.7 g (20%) white powder.}
\]

**1H NMR (500 MHz, CHLOROFORM-d):** δ (ppm): 1.05 (t, J=7.41 Hz, 3 H) 1.49 - 1.64 (m, 2 H) 1.78 - 1.92 (m, 2 H) 4.44 (t, J=6.62 Hz, 2 H) 7.53 (d, J=8.51 Hz, 1 H) 8.22 (dd, J=8.51, 1.58 Hz, 1 H) 8.29 (s, 1 H) 8.47 (s, 1 H) 9.03 (d, J=0.95 Hz, 1 H).

**13C NMR (126 MHz, CHLOROFORM-d):** δ (ppm): 14.11 (s, 1 CH₃) 19.64 (s, 1 CH₂) 31.19 (s, 1 CH₂) 65.17 (s, 1 CH₂) 109.90 (s, 1 CH) 123.41 (s, 1 C) 123.57 (s, 1 C) 123.72 (s, 1 CH) 123.97 (s, 1 CH) 124.05 (s, 1 C) 128.63 (s, 1 CH) 128.66 (s, 1 C) 133.04 (s, 1 C) 134.93 (s, 1 C) 144.91 (s, 1 C) 167.32 (s, 1 C).

**MALDI-TOF-MS (m/z):** Calculated for C₆₀H₅₆N₂O₈: 859; found 859 [M - C₄H₉OH]+.

Elemental analysis: Calculated: C: 77.23%; H: 6.05%; N: 3%; found: C: 77.27%; H: 6.144%; N: 2.88%.

**9,9'- (Pyrene-2,7-diyl)bis(9H-carbazole-3,6-dicarboxylic acid), H_{2}(L^{147})**

\[
\text{Synthesis conditions: } 1.6 g (1.71 mmol) Ester 2, 2.5 g (43.9 mmol) potassium hydroxide, 300 ml THF, 1 ml methanol, 2 ml H₂O + 1 ml H₂O after 1 d, 85 °C for 5 d; Yield: 650 g (91%) white powder.
\]

**1H NMR (500 MHz, CHLOROFORM-d):** δ (ppm): 7.63 (d, J=8.51 Hz, 1 H) 8.15 (dd, J=8.83, 1.58 Hz, 1 H) 8.48 (s, 1 H) 8.77 (s, 1 H) 9.08 (d, J=1.26 Hz, 1 H).

**13C NMR (126 MHz, DMSO-d₆):** δ (ppm): 110.06 (s, 1 CH) 122.67 (s, 1 C) 122.94 (s, 1 C) 123.18 (s, 1 CH) 123.66 (s, 1 C) 123.75 (s, 1 CH) 128.39 (s, 1 CH) 128.66 (s, 1 C) 133.04 (s, 1 C) 144.03 (s, 1 C) 167.67 (s, 1 C).

**MALDI-TOF-MS (m/z):** Calculated for C₄₄H₂₃N₂O₈: 707; found 707 [M-H]+.

Elemental analysis: Calculated: C: 69.46%; H: 3.83%; N: 3.68%; found: C: 69.50%; H: 3.907%; N: 3.63%.

**DRIFT, KBr, 298 K (cm⁻¹):** 3074 (w, br), 2628 (w), 1905 (w), 1694 (s), 1630 (m), 1604 (s), 1479 (s), 1454 (m), 1409 (m), 1345 (m), 1288 (s), 1236 (s), 1159 (m), 1138 (w), 1028 (w), 1001 (w), 905 (w), 880 (w), 826 (m), 765 (s), 734 (w), 710 (m), 666 (w).

**2,7-Dibromo-9,10-dihydrophenanthrene (3)**
In a 250 ml flask 2 g (11.1 mmol) 9,10-hydrophenanthrene and 0.09 g (0.5 mmol) iron(III) chloride are suspended in 150 ml water. Over 30 min a solution of 1.26 ml (49.2 mmol) bromine in 50 ml water is added in dark conditions and stirred for 16 h at room temperature. The precipitate is filtered off, washed thoroughly with water, 30 ml 1 M aqueous sodium hydroxide solution, and again water. The yellow solid is recrystallized from 20 ml ethyl acetate to yield 2.7 g (71%) white powder.

**Rf**: 0.52 in iso-hexane.

**1H NMR** (500 MHz, CHLOROFORM-d) δ (ppm): 2.84 (s, 2 H) 7.39 (d, J=1.89 Hz, 1 H) 7.43 (dd, J=8.28, 1.89 Hz, 1 H) 7.56 (d, J=8.28 Hz, 1 H).

**13C NMR** (151 MHz, CHLOROFORM-d) δ (ppm): 28.53 (s, 1 CH) 76.79 (s, 1 CH) 77.00 (s, 1 C) 77.21 (s, 1 C) 121.50 (s, 1 C) 125.17 (s, 1 CH) 130.14 (s, 1 CH) 131.09 (s, 1 CH) 132.59 (s, 1 C) 139.09 (s, 1 C).

MALDI-TOF-MS (m/z): Calculated for C14H10Br2: 337; found: 337 [M]+.

Elemental analysis: Calculated: C: 49.74%; H: 2.98%; found: C: 48.63%; H: 3.021%.

**Tetrabutyl 9,9’-(9,10-dihydrophenanthrene-2,7-diyl)bis(9H-carbazole-3,6-dicarboxylate) (4)**

Synthesis conditions: 4.89 g (13.3 mmol) n-butyl ester 1, 1.5 g (4.4 mmol) 2,7-dibromo-9,10-dihydrophenanthrene (3), 2.36 g (17.1 mmol) potassium carbonate, 400 mg (2.1 mmol) copper(I) iodine, 0.1 ml (0.91 mmol) N,N’-dimethylethylenediamine, 80 ml anhydr. 1,4-dioxane, 95 °C for 9 d; Flash column chromatography chloroform : iso-hexane : ethyl acetate – 1 : 0.33 : 0.03 (Rf 0.49); Yield: 1.8 g (45%) white powder.

**1H NMR** (500 MHz, CHLOROFORM-d) δ (ppm): 1.05 (t, J=7.41 Hz, 6 H) 1.49 - 1.67 (m, 4 H) 1.77 - 1.93 (m, 4 H) 2.21 Hz, 1 H) 8.11 (d, J=8.20, 2.1 Hz, 1 H) 4.43 (t, J=6.78 Hz, 4 H) 7.49 - 7.51 (m, 1 H) 7.51 - 7.54 (m, 2 H) 7.58 (dd, J=8.20, 1.73 Hz, 2 H) 8.21 (dd, J=8.67, 1.26 Hz, 2 H).

**13C NMR** (126 MHz, CHLOROFORM-d) δ (ppm): 13.60 (s, 1 CH3) 19.13 (s, 1 CH3) 28.59 (s, 1 CH3) 30.67 (s, 1 CH3) 64.62 (s, 1 CH3) 109.61 (s, 1 CH) 122.77 (s, 1 C) 122.93 (s, 1 CH) 125.37 (s, 1 CH) 125.48 (s, 1 CH) 126.36 (s, 1 CH) 127.95 (s, 1 CH) 133.52 (s, 1 C) 135.69 (s, 1 C) 139.24 (s, 1 C) 143.85 (s, 1 C) 166.83 (s, 1 C).

MALDI-TOF-MS (m/z): Calculated for C58H58N2O8: 837.3540; found: 837.2457 [M-C4H9OH]+.

Elemental analysis: Calculated: C: 76.46%; H: 6.42%; N: 3.07%; found: C: 76.45%; H: 6.083%; N: 2.78%.

**9,9’-(9,10-Dihydrophenanthrene-2,7-diyl)bis(9H-carbazole-3,6-dicarboxylic acid) (H4(L148))**

**1H NMR** (500 MHz, DMSO-d6) δ (ppm): 3.08 (s, 2 H) 7.57 (d, J=8.51 Hz, 2 H) 7.68 (dd, J=8.04, 2.05 Hz, 1 H) 7.71 (d, J=8.20 Hz, 2 H) 7.84 (dd, J=8.67, 1.73 Hz, 2 H) 8.21 (dd, J=8.67, 1.26 Hz, 2 H).
(d, J=1.89 Hz, 1 H) 8.13 (dd, J=8.30, 1.80 Hz, 2 H) 8.28 (d, J=8.51 Hz, 1 H) 9.00 (d, J=1.58 Hz, 2 H) 12.81 (br. s., 2 H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ (ppm): 27.97 (s, 1 CH$_3$) 110.16 (s, 1 CH) 122.58 (s, 1 C) 123.08 (s, 1 CH) 123.46 (s, 1 C) 125.55 (s, 1 CH) 125.94 (s, 1 CH) 126.50 (s, 1 CH) 128.33 (s, 1 CH) 132.29 (s, 1 C) 135.26 (s, 1 C) 139.57 (s, 1 C) 143.44 (s, 1 C) 167.66 (s, 1 C).

Elemental analysis: Calculated (C$_{42}$H$_{26}$N$_2$O$_8$·2.75H$_2$O): C: 68.52%; H: 4.31%; N: 3.81%; found: C: 68.56%; H: 4.302%; N: 3.7%.

DRIFT, KBr, 298 K (cm$^{-1}$): 3073 (w, br), 2639 (w), 1902 (w), 1693 (s), 1630 (m), 1600 (s), 1491 (s), 1362 (m), 1292 (s), 1235 (m), 1138 (m), 1027 (w), 769 (s), 734 (m), 696 (w), 640 (m), 597 (w), 573 (w).

Tetrabutyl 9,9'-(Ethyne-1,2-diylbis(4,1-phenylene))bis(9H-carbazole-3,6-dicarboxylate) (5)

Synthesis conditions: 9.83 g (26.8 mmol) n-butyl ester 1, 3 g (8.93 mmol) bis(4-bromophenyl)acetylene, 4.93 g (35.7 mmol) potassium carbonate, 4.46 mmol N,N'-dimethylethylenediamine, 847 mg (4.46 mmol) copper(I) iodide, 0.1 ml (0.91 mmol) 1,4-dioxane, 108 °C for 7 d; Flash column chromatography DCM : iso-hexane : ethyl acetate – 1 : 0.3 : 0.017 (R$_f$ 0.51); Yield: 5.3 g (65%) white powder.

$^1$H NMR (500 MHz, DMSO-$d_6$) δ (ppm): 1.05 (t, J=7.41 Hz, 3 H) 1.53 - 1.61 (m, 2 H) 1.82 - 1.89 (m, 2 H) 4.43 (t, J=6.62 Hz, 2 H) 7.46 (d, J=8.83 Hz, 1 H) 7.62 (d, J=8.51 Hz, 1 H) 7.88 (d, J=8.20 Hz, 1 H) 8.20 (dd, J=8.83, 1.58 Hz, 1 H) 8.94 (d, J=1.26 Hz, 1 H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ (ppm): 14.10 (s, 1 CH$_3$) 19.62 (s, 1 CH$_2$) 31.17 (s, 1 CH$_2$) 65.16 (s, 1 CH$_2$) 109.93 (s, 1 CH) 123.30 (s, 1 CH) 123.56 (s, 1 CH) 123.69 (s, 1 C) 127.27 (s, 1 C) 128.55 (s, 1 CH) 129.72 (s, 1 CH) 133.74 (s, 1 CH) 134.46 (s, 1 C) 136.81 (s, 1 C) 144.08 (s, 1 C) 167.25 (s, 1 C).

MALDI-TOF-MS (m/z): Calculated for C$_{58}$H$_{56}$N$_2$O$_8$: 835; found 835 [M-C$_2$H$_5$OH]$^+$. 

Elemental analysis: Calculated: C: 76.63%; H: 6.21%; N: 3.08%; found: C: 75.8%; H: 6.093%; N: 3.01%.

9,9'-((Ethyne-1,2-diylbis(4,1-phenylene))bis(9H-carbazole-3,6-dicarboxylic acid) (H$_4$L$^{160}$))

Synthesis conditions: 1 g (1.1 mmol) Ester 5, 5 g (87.8 mmol) potassium hydroxide, 80 ml THF, 1 ml methanol, 5 ml H$_2$O, 90 °C for 16 h; Yield: 740 mg (98%) white powder.

$^1$H NMR (500 MHz, DMSO-$d_6$) δ (ppm): 7.53 (d, J=8.83 Hz, 1 H) 7.80 (d, J=8.51 Hz, 1 H) 7.96 (d, J=8.51 Hz, 1 H) 8.12 (dd, J=8.51, 1.58 Hz, 1 H) 9.00 (d, J=1.58 Hz, 1 H) 12.88 (br. s., 1 H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ (ppm): 90.07 (s, 1 C) 110.35 (s, 1 CH) 122.38 (s, 1 C) 123.05 (s, 1 C) 123.42 (s, 1 CH) 124.00 (s, 1 C) 127.70 (s, 1 CH) 133.84 (s, 1 CH) 136.52 (s, 1 C) 143.53 (s, 1 C) 167.94 (s, 1 C).

MALDI-TOF-MS (m/z): Calculated for C$_{42}$H$_{26}$N$_2$O$_8$: 684; found 684 [M$^+$].
Elemental analysis: Calculated (C_{58}H_{60}N_{2}O_{8}): C: 76.29%; H: 6.62%; N: 3.07%; found: C: 76.2%; H: 5.93%; N: 2.8%.

**DRIFT, KBr, 298 K (cm^{-1}):**
3065 (w, br), 2641 (w), 1689 (s), 1630 (m), 1598 (s), 1516 (s), 1477 (m), 1415 (s) 1352 (m), 1273 (s), 1171 (m), 1134 (m), 1026 (w), 904 (m), 821 (m), 768 (s), 725 (m), 693 (w), 659 (w), 611 (w), 575 (w), 538 (w), 497 (w), 460 (w), 418 (m), 385 (s), 353 (s), 327 (s), 285 (w), 258 (w).

**MALDI-TOF-MS (m/z):** Calculated for C_{58}H_{60}N_{2}O_{8}: 839; found 839 [M-C_{2}H_{5}OH]+.

A 50 ml Schlenk flask was charged with 600 mg (0.66 mmol) acetylene 5 and 100 mg 10% Pd on carbon and flushed with hydrogen. 30 ml anhydr. THF was added, hydrogen was bubbled through the suspension for 10 min. and stirred with 1.05 bar hydrogen pressure at room temperature for 48 h. The THF was removed in vacuum, the residual powder dissolved in chloroform and the suspension filtered over silica. The chloroform was removed in vacuum to yield 580 mg (97%) white powder.

**1H NMR (500 MHz, BENZENE-d_{6})** δ (ppm): 1.04 (t, J=7.41 Hz, 3 H) 1.53 - 1.60 (m, 2 H) 1.81 - 1.89 (m, 2 H) 3.21 (s, 1 H) 4.42 (t, J=6.62 Hz, 2 H) 7.40 (d, J=8.83 Hz, 1 H) 7.53 (d, J=3.78 Hz, 1 H) 8.16 (dd, J=8.67, 1.73 Hz, 1 H) 8.94 (d, J=1.26 Hz, 1 H).

**13C NMR (126 MHz, BENZENE-d_{6})** δ (ppm): 13.83 (s, 1 CH_{3}) 19.36 (s, 1 CH_{2}) 30.92 (s, 1 CH_{2}) 37.49 (s, 1 CH_{2}) 64.83 (s, 1 CH_{2}) 77.56 (s, 1 CH_{2}) 109.71 (s, 1 CH) 122.99 (s, 1 CH) 123.04 (s, 1 C) 127.13 (s, 1 CH) 128.12 (s, 1 CH) 130.17 (s, 1 CH) 134.49 (s, 1 C) 141.85 (s, 1 C) 144.26 (s, 1 C) 167.10 (s, 1 C).

**MALDI-TOF-MS (m/z):** Calculated for C_{42}H_{28}N_{2}O_{8}: 688; found 688 [M]+.

Elemental analysis: Calculated: C: 76.29%; H: 6.62%; N: 3.07%; found: C: 76.2%; H: 5.93%; N: 2.8%.

A 50 ml Schlenk flask was charged with 600 mg (0.66 mmol) acetylene 5 and 100 mg 10% Pd on carbon and flushed with hydrogen. 30 ml anhydr. THF was added, hydrogen was bubbled through the suspension for 10 min. and stirred with 1.05 bar hydrogen pressure at room temperature for 48 h. The THF was removed in vacuum, the residual powder dissolved in chloroform and the suspension filtered over silica. The chloroform was removed in vacuum to yield 580 mg (97%) white powder.

**1H NMR (600 MHz, DMSO-d_{6})** δ (ppm): 3.20 (s, 1 H) 7.45 (d, J=8.66 Hz, 1 H) 7.63 - 7.67 (m, 1 H) 7.73 (m, 1 H) 8.11 (dd, J=8.66, 1.88 Hz, 1 H) 9.00 (d, J=1.51 Hz, 1 H).

**13C NMR (151 MHz, DMSO-d_{6})** δ (ppm): 36.63 (s, 1 CH_{2}) 109.86 (s, 1 CH) 122.39 (s, 1 C) 123.00 (s, 1 CH) 123.26 (s, 1 C) 126.89 (s, 1 CH) 128.26 (s, 1 CH) 130.36 (s, 1 CH) 133.64 (s, 1 C) 142.17 (s, 1 C) 143.61 (s, 1 C) 167.62 (s, 1 C).

**MALDI-TOF-MS (m/z):** Calculated for C_{42}H_{28}N_{2}O_{8}: 688; found 688 [M]+.

Elemental analysis: Calculated: C: 68.87%; H: 3.99%; N: 3.82%; found: C: 68.39%; H: 2.35%; N: 3.71%.
Tetrabutyl 9,9′-(ethene-1,2-diylbis(4,1-phenylene))(E)-bis(9H-carbazole-3,6-dicarboxylate) (7)

Synthesis conditions: 6.56 g (17.8 mmol) n-butylester 1, 1.93 g (5.95 mmol) 4,4′-dibromo-trans-stilbene, 3.2 g (23.7 mmol) potassium carbonate, 475 mg (2.49 mmol) copper(I) iodine, 0.1 ml (0.91 mmol) N,N′-dimethylethlenediamine, 60 ml anhydr. 1,4-dioxane, 108 °C for 10 d; Flash column chromatography chloroform: iso-hexane : ethyl acetate – 1 : 0.17 : 0.003 (Rf 0.49)

Yield: 3.8 g (70%) white powder

\[ ^1H \text{ NMR (500 MHz, CHLOROFORM-}d^6 \text{)} \delta (ppm): 1.05 (t, J=7.41 Hz, 6 H) 1.50 - 1.66 (m, 4 H) 1.79 - 1.91 (m, 4 H) 4.43 (t, J=6.62 Hz, 4 H) 7.36 (s, 1 H) 7.46 (d, J=8.83 Hz, 2 H) 7.61 (d, J=8.51 Hz, 2 H) 7.85 (d, J=8.51 Hz, 2 H) \]

13C NMR (126 MHz, CHLOROFORM-\textit{d}_6) \delta (ppm): 13.83 (s, 1 CH3) 19.36 (s, 1 CH2) 64.87 (s, 1 CH2) 109.77 (s, 1 CH) 123.02 (s, 1 CH) 123.20 (s, 1 C) 123.24 (s, 1 C) 127.32 (s, 1 CH) 128.21 (s, 1 CH) 128.24 (s, 1 CH) 128.83 (s, 1 CH) 135.91 (s, 1 C) 137.12 (s, 1 C) 144.06 (s, 1 C) 167.06 (s, 1 C).

HRMS-MALDI (m/z): Calculated for C_{58}H_{58}N_2O_8: 837.3540; found 837.42787 [M-\text{C}_2\text{H}_5\text{OH}]^+.

Elemental analysis: Calculated: C: 76.46%; H: 6.42%; N: 3.07%; found: C: 76.33%; H: 6.14%; N: 2.82%.

(E)-9,9′-(Ethene-1,2-diylbis(4,1-phenylene))bis(9H-carbazole-3,6-dicarboxylic acid) (H_4L^{161})

Synthesis conditions: 2.7 g (2.63 mmol) Ester 7, 2.3 g (40.4 mmol) potassium hydroxide, 200 ml THF, 2 ml methanol, 10 ml H_2O, 85 °C for 48 h.

Yield: 2 g (99%) yellow powder

\[ ^1H \text{ NMR (500 MHz, DMSO-}d_6 \text{)} \delta (ppm): 6.66 (d, J=8.51 Hz, 2 H) 6.76 (s, 1 H) 6.88 (d, J=8.51 Hz, 2 H) 7.16 (d, J=8.51 Hz, 2 H) 7.26 (dd, J=8.51, 1.58 Hz, 2 H) 8.14 (d, J=1.26 Hz, 2 H) 11.96 (br. s., 2 H) \]

13C NMR (126 MHz, DMSO-\textit{d}_6) \delta (ppm): 110.03 (s, 1 CH) 122.55 (s, 1 C) 123.04 (s, 1 CH) 123.44 (s, 1 C) 127.26 (s, 1 CH) 128.32 (s, 1 CH) 128.44 (s, 1 CH) 128.78 (s, 1 CH) 135.07 (s, 1 C) 137.18 (s, 1 C) 143.42 (s, 1 C) 167.46 (s, 1 C) 167.63 (s, 1 C).

Elemental analysis: Calculated: C: 73.46%; H: 3.82%; N: 4.08%; found: C: 68.43%; H: 3.78%; N: 4.05%;

DRIFT, KBr, 298 K (cm⁻¹): 3064 (w, br), 2643 (w), 1905 (w), 1689 (s), 1630 (m), 1600 (s), 1518 (s), 1476 (m), 1412 (m), 1365 (m), 1286 (s), 1236 (s), 1182 (m), 1170 (m), 1137 (w)1108 (w), 1028 (m), 948 (w), 905 (w), 826 (m), 771 (s), 739 (w), 728 (w), 693 (w).

Tetrabutyl 9,9′-(1,4-phenylenebis(methylene))bis(9H-carbazole-3,6-dicarboxylate) (8)
Synthesis conditions: 8.34 g (22.7 mmol) n-butyl ester 1, 2 g (7.58 mmol) dibromo-p-xylene, 4.93 g (35.7 mmol) potassium carbonate, 686 mg (3.62 mmol) copper(I) iodine, 0.1 ml (0.91 mmol) N,N'-dimethylethlenediamine, 150 ml anhydr. 1,4 dioxane, 95 °C for 5 d; Flash column chromatography DCM : iso-hexane : ethyl acetate – 1 : 0.4 : 0.01 (Rf 0.6); Yield: 1.2 g (19%) white powder.

\[ \text{1H NMR (500 MHz, CHLOROFORM-}d) \delta (ppm): 1.02 (t, J=7.41 Hz, 2 H) 1.54 (dq, J=14.94, 7.42 Hz, 2 H) 1.82 (quin, J=7.17 Hz, 2 H) 4.39 (t, J=6.62 Hz, 2 H) 5.51 (s, 1 H) 7.01 (s, 1 H) 7.34 (d, J=8.51 Hz, 1 H) 8.16 (dd, J=8.51, 1.26 Hz, 1 H) 8.88 (d, J=1.26 Hz, 1 H). \]

\[ \text{13C NMR (126 MHz, CHLOROFORM-}d) \delta (ppm): 13.56 (s, 1 CH$_3$) 19.09 (s, 1 CH$_2$) 30.66 (s, 1 CH$_2$) 46.22 (s, 1 CH$_2$) 64.54 (s, 1 CH$_2$) 108.52 (s, 1 CH) 122.44 (s, 1 C) 122.65 (s, 1 C) 122.80 (s, 1 C) 126.69 (s, 1 CH) 127.89 (s, 1 CH) 135.48 (s, 1 C) 143.44 (s, 1 C) 166.83 (s, 1 C). \]

MALDI-TOF-MS (m/z): Calculated for C$_{52}$H$_{56}$N$_2$O$_8$: 763; found: 763 [M-C$_4$H$_9$OH]+.

Elemental analysis: Calculated: C: 74.62%; H: 6.74%; N: 3.35%; found: C: 74.3%; H: 6.725%; N: 3.28%.

\[ \text{9,9'-}(1,4\text{-Phenylenbis(methylene))bis(9H-carbazole-3,6-dicarboxylic acid) (H$_4$L}^{159}\text{))} \]

Synthesis conditions: 900 g (1.08 mmol) Ester 8, 2.6 g (45.7 mmol) potassium hydroxide, 100 ml THF, 1 ml methanol, 2 ml H$_2$O, 90 °C for 24 h; Yield: 480 mg (73%) white powder.

\[ \text{1H NMR (500 MHz, DMSO-}d$_6$) \delta (ppm): 5.68 (s, 1 H) 7.08 (s, 1 H) 7.70 (d, J=8.51 Hz, 1 H) 8.04 (dd, J=8.51, 1.58 Hz, 1 H) 8.87 (d, J=1.58 Hz, 1 H) 12.67 (br. s., 1 H). \]

\[ \text{13C NMR (126 MHz, DMSO-}d$_6$) \delta (ppm): 45.62 (s, 1 CH$_2$) 109.79 (s, 1 CH) 122.09 (s, 1 C) 122.55 (s, 1 C) 122.81 (s, 1 CH) 127.06 (s, 1 CH) 127.80 (s, 1 CH) 135.48 (s, 1 C) 143.44 (s, 1 C) 167.70 (s, 1 C). \]

Elemental analysis: Calculated (C$_{36}$H$_{24}$N$_2$O$_8$ 7.3-H$_2$O): C: 58.11%; H: 5.23%; N: 3.76%; found: C: 57.44%; H: 4.56%; N: 3.74%.

DRIFT, KBr, 298 K (cm$^{-1}$): 3062 (w, br), 2643 (w), 1682 (s), 1630 (m), 1598 (s), 1515 (w), 1482 (m), 1416 (m), 1385 (m), 1308 (s), 1203 (s), 1147 (m), 1119 (m), 1052 (w), 1026 (w), 904 (w), 855 (w), 819 (m), 769 (s), 722 (m), 642 (w), 597 (w).
3 Synthesis of Metal-Organic Frameworks

Synthesis of MOF Single Crystals

For the synthesis of crystals large enough to allow for SCXRD higher amounts of DMF (N,N-Dimethylformamide) as well as acetic acid as modulator were used. The reactions were generally carried out according to the following procedure. The reaction conditions are listed in. The solvothermal reactions were carried out in a 10 ml Pyrex® tube. The organic ligand was dissolved in indicated amounts of DMF and acetic acid by sonication at room temperature. Indicated amounts of Cu(NO$_3$)$_2$·3H$_2$O were added and dissolved by sonication. The sealed tube was placed in an oven at 80 °C for the indicated timeframe. Synthesis conditions are summarized in Supplementary Table 1.

Supplementary Table 1. Reaction conditions for the synthesis of MOF single crystals (> 100 µm). No yield was determined and all reactions were carried out at 80 °C.

| Material ID | $m_{\text{Ligand}}$ (mg) | $n_{\text{Ligand}}$ (µmol) | $m_{\text{Cu(NO}_3\text{)$_2$·3H}_2\text{O}}$ (mg) | $n_{\text{Cu(NO}_3\text{)$_2$·3H}_2\text{O}}$ (µmol) | $V_{\text{Acetic acid}}$ (µl) | Eq.per ligand | $V_{\text{DMF}}$ (ml) | $t_{\text{Reaction}}$ (d) | Morphology |
|-------------|---------------------------|----------------------------|-------------------------------------------|---------------------------------------------|----------------------------|----------------|-------------------|-----------------|------------|
| DUT-49      | 10                        | 15.1                       | 9.5                                       | 39.3                                        | 0.5                        | 8.7            | 577               | 4               | 5          | Cubic         |
| DUT-147     | 5                         | 7.1                        | 8.5                                       | 35.2                                        | 0.2                        | 3.5            | 495               | 10              | 6          | Cubic         |
| DUT-148     | 10                        | 14.6                       | 8.8                                       | 36.4                                        | 0.08                       | 1.4            | 96                | 3               | 3          | Cubic         |
| DUT-159     | 5                         | 8.2                        | 4.8                                       | 19.9                                        | 0.2                        | 3.5            | 428               | 3               | 4          | hex. Plates   |
| DUT-160     | 10                        | 14.6                       | 8.8                                       | 36.4                                        | 0.33                       | 5.8            | 395               | 4               | 2          | Cuboct.       |
| DUT-161     | 10                        | 14.6                       | 8.8                                       | 36.4                                        | 0.33                       | 5.8            | 395               | 4               | 2          | Cuboct.       |
| DUT-162     | 10                        | 14.5                       | 8.8                                       | 36.4                                        | 0.8                        | 14.0           | 963               | 5               | 5          | Cuboct.       |
Synthesis of MOF powders

Synthesis of large-scale MOF powders was conducted in DMF (with the exception of DUT-162 where L^{162} was found to be insoluble in higher concentrations; N-Methylpyrrolidone (NMP) was used in the synthesis of DUT-162). The reaction was carried out in a round bottom flask, and the reaction mixture was stirred and heated at 80 °C using an oil bath. All reactions were conducted in the following manner: The linker was dissolved in the indicated amount of solvent; corresponding amounts of modulator were added and the solution was stirred at 80 °C. To this solution indicated amounts of Cu(NO\(_3\))\(_2\)·3H\(_2\)O were added and dissolved, the flask was closed and the reaction mixture stirred for the indicated time at 80 °C. Afterwards the MOF powders were separated from the mother liquid via centrifugation and washed with fresh DMF for at least three times over three days. The powder was kept solvated with DMF at all times. The reaction conditions are summarized in Supplementary Table 2.

Supplementary Table 2. Reaction conditions for the synthesis of DUT-49 and analogous MOF powders synthesis at 80 °C.

| Material ID | \(m_{\text{ligand}}\) (mg) | \(n_{\text{ligand}}\) (mmol) | \(m_{\text{Cu(NO}_3)_2\cdot3\text{H}_2\text{O}}\) (mg) | \(n_{\text{Cu(NO}_3)_2\cdot3\text{H}_2\text{O}}\) (mmol) | \(V_{\text{Acetic acid}}\) (ml) | \(n_{\text{Acetic acid}}\) (mmol) | \(V_{\text{DMF}}\) (ml) | \(t_{\text{reaction}}\) (h) | Yield [%][a] | Mean crystal size/ SD (nm) |
|-------------|-------------------|----------------|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|------------------|
| DUT-49      | 150               | 0.23           | 140             | 0.58           | 7.5            | 131.1          | 60             | 144            | 39              | 14861±5069       |
| DUT-147     | 250               | 0.35           | 215             | 0.89           | 6              | 104.9          | 230            | 96             | 68              | 8385±5279        |
| DUT-148     | 100               | 0.15           | 87.9            | 0.36           | 2              | 35.0           | 30             | 48             | 81              | 7872±4500        |
| DUT-159     | 250               | 0.41           | 202             | 0.84           | 0.5            | 8.7            | 40             | 48             | 40              | n. a.            |
| DUT-160     | 1000              | 1.46           | 880             | 3.64           | 10             | 174.8          | 200            | 48             | 47              | 4475±1969        |
| DUT-161     | 500               | 0.74           | 441             | 1.82           | 4              | 70.1           | 95             | 48             | 48              | 6241±3103        |
| DUT-162     | 120               | 0.17           | 100             | 0.41           | 0.3            | 5.2            | 20*            | 48             | 71              | 4517±3223        |

[a] yield based on \(n_{\text{ligand}}\) after activation, actual yields of reaction may be higher. *NMP was used instead of DMF
4 Supercritical Activation of MOF Powders

All MOF samples analyzed in this work were activated using this protocol which is based on previous reports\(^1,6\). Activation in this context refers to the removal of the solvent or guest molecules from the pores of the MOF. After synthesis the MOF powders were suspended in fresh solvent used for the synthesis (DMF or NMP) and the solvent was exchanged at least 9 times over a period of at least two days. Afterwards the solvent was replaced by anhydr. ethanol (for DUT-49) or anhydr. acetone (for DUT-49(17) and all other MOF materials) in multiple washing cycles (at least 6 times over three days). The material was then dried (solvent removal) using a previously well described protocol involving supercritical CO\(_2\).\(^{217}\) The ethanol/acetone suspended MOF powder was placed in glass filter frits in a Jumbo Critical Point Dryer 13200J AB (SPI Supplies) which was subsequently filled with liquid CO\(_2\) (99.995% purity) at 288 K and 5 MPa. To ensure a complete substitution of the solvent by CO\(_2\), the liquid in the autoclave was exchanged with fresh CO\(_2\) at least 18 times over a period of 5 days using a valve at the bottom of the autoclave. The temperature and pressure were then risen beyond the supercritical point of CO\(_2\) to 308 K and 10 MPa and kept until the temperature and pressure was constant. The supercritical CO\(_2\) was steadily released over 3 h and the dry powder was transferred and stored in an argon filled glove box. To ensure complete removal of the solvent (especially from the open metal sites of the Cu-paddle-wheels) additional activation at 120 - 423 K in a Schlenk-tube under dynamic vacuum of 10\(^{-4}\) kPa for at least 24 h was performed.
5 Elemental Analysis of MOF samples

For elemental analysis the desolvated powders were placed in Sn-sample holders under inert atmosphere in a glove box and sealed to avoid contamination with humidity. The given results are the mean values obtained from three individual measurements. Results are summarized in Supplementary Table 3.

Supplementary Table 3. CHNS elemental analysis of activated MOF powders.

| Material ID | Calculated (%) | Experimental (%) |
|-------------|----------------|------------------|
|             | C   | H   | N   | S   | C   | H   | N   | S   |
| DUT-49      | 61.3| 2.57| 3.57| 0   | 59.85| 2.542| 3.64| 0   |
| DUT-147     | 63.54| 2.42| 3.37| 0   | 60.78| 2.397| 3.5 | 0   |
| DUT-148     | 62.3 | 2.74| 3.46| 0   | 61.49| 2.539| 3.75| 0   |
| DUT-159     | 58.78| 2.74| 3.81| 0   | 62.66| 3.677| 4.88| 0   |
| DUT-160     | 62.45| 2.5 | 3.47| 0   | 61.04| 2.752| 5.05| 0   |
| DUT-161     | 62.03| 2.81| 3.11| 0   | 60.66| 3.165| 4.09| 0   |
| DUT-162     | 62.14| 2.98| 3.45| 0   | 61.29| 3.382| 3.71| 0   |
Supplementary Figure 2. Thermogravimetric analysis of a) DUT-147, b) DUT-148, c) DUT-159, d) DUT-160, e) DUT-161 and, f) DUT-162.
Supplementary Figure 3. PXRD patterns of DUT-147 under different conditions.

Supplementary Figure 4. PXRD patterns of DUT-148 under different conditions.
Supplementary Figure 5. PXRD patterns of DUT-159 under different conditions.

Supplementary Figure 6. PXRD patterns of DUT-160 under different conditions.

Supplementary Figure 7. PXRD patterns of DUT-161 under different conditions.
Supplementary Figure 8. PXRD patterns of DUT-162 under different conditions.
Supplementary Figure 9. Scanning electron microscopy images of a, b) DUT-147, c) Experimental crystal size distribution (red histogram) and distribution curve (black dashed line).

Supplementary Figure 10. Scanning electron microscopy images of a, b) DUT-148, c) Experimental crystal size distribution (red histogram) and distribution curve (black dashed line).
Supplementary Figure 11. Scanning electron microscopy images of activated DUT-159 at different magnifications.

Supplementary Figure 12. Scanning electron microscopy images of a,b) DUT-160, c) Experimental crystal size distribution (red histogram) and distribution curve (black dashed line).
Supplementary Figure 13. Scanning electron microscopy images of a,b) DUT-161, c) Experimental crystal size distribution (red histogram) and distribution curve (black dashed line).

Supplementary Figure 14. Scanning electron microscopy images of a,b) DUT-162, c) Experimental crystal size distribution (red histogram) and distribution curve (black dashed line).
Supplementary Figure 15. n-Butane physisorption isotherms at 298 K of a) DUT-160, b) DUT-161, c) DUT-147, and d) DUT-148. Closed symbols adsorption, open symbols desorption.
Supplementary Figure 16. Methane adsorption/desorption isotherms on DUT-160 at 91 K (a), 111 K (b), 115 K (c), 120 K (d), 125 K (e), 130 K (f), 135 K (g) and 140 K (h). Adsorption in closed symbols, desorption in open symbols. i) Evolution of $\Delta n_{NGA}$ at different temperatures in comparison to DUT-49(4) and DUT-50.
Supplementary Figure 17. Methane adsorption (closed symbols) /desorption (open symbols) isotherms on DUT-50 at a) 105 K, b) 111 K, c) 115 K, d) 120 K, e) 125 K, f) 130 K, and g) 135 K. h) Evolution of ΔNGA at different temperatures in comparison to DUT-49(4).
Hg intrusion of MOF samples

Mercury intrusion has been successfully used in the past to provoke the contraction of microporous metal organic frameworks\textsuperscript{1,7}. MOF powders were preliminary outgassed under secondary vacuum at 110°C overnight. The so-obtained powders were loaded into a powder penetrometer of 3.1126 cm\textsuperscript{3} volume with a stem volume of 0.4120 cm\textsuperscript{3} using a glove box (Jacomex P-BOX) under argon atmosphere H\textsubscript{2}O < 5 ppm. The mercury intrusion experiments were carried out using a Micromeritics AutoPore IV 9500 allowing a range of pressure applied from 0.003 to 413 MPa. Before the compression experiment, the powders were outgassed at ~6.5 Pa for 15 minutes. The collected volume of intruded mercury was corrected by a blank recorded in the same conditions of temperature and pressure using the same penetrometer to obtain the absolute contracted volume as a function of the pressure.

Supplementary Figure 18. Mercury intrusion curves (pressure increase red, pressure release blue) for a) DUT-147, b) DUT-148, c) DUT-49 (taken from reference\textsuperscript{1}), and d) comparison of the three intrusion curves. Pressure for unit cell compression indicated as dashed line.
Supplementary Figure 19. Mercury intrusion curves (pressure increase red, pressure release blue) for a) DUT-160, b) DUT-161, c) DUT-162, and d) comparison of the three intrusion curves. Pressure for unit cell compression indicated as dashed line.

The bulk modulus $K$ of the pristine phase for the studied solids can be estimated from the compression curves obtained by mercury intrusion using the following equation $K = V_0 \left( \frac{dp}{dV} \right)$.

Where $V_0$ is the volume of the initial phase. The bulk modulus is then related to the slope of the linear domain of the cumulative volume of intruded mercury as a function of the applied pressure (Supplementary Figure 19, Supplementary Figure 18) which is defined by $\alpha = \left( \frac{dV}{dp} \right)$. In mercury intrusion experiments $V$ is expressed in volume of Hg intruded per gram of sample. Hence this volume correspond to $V_{Hg} = \frac{V_0 \times N_A}{Z \times M_{sample}}$. Table S1 contains the results of the linear fitting and bulk moduli estimation following the relation defined by Henke et al. as

$$K = \frac{V_0 \times N_A}{\alpha \times Z \times M_{sample}}$$
Supplementary Table 4. Unit cell volumes, formula per unit cell, molar mass, slope of the mercury intrusion curves and bulk moduli determined form both DUT-49, -147, -148, -160, -161 and -162 and 147.

|                  | DUT49  | DUT-147 | DUT-148 | DUT-160 | DUT-161 | DUT162 |
|------------------|--------|---------|---------|---------|---------|--------|
| \( V_0 \) unit cell volume (Å³) | 100071 | 100221  | 100804  | 125827  | 123209  | 121950 |
| \( Z \), number of formula per unit cell | 24     | 24      | 24      | 24      | 24      | 24     |
| \( M \), molar mass (g.mol⁻¹) | 783.70 | 863.70  | 809.77  | 839.68  | 814.69  | 843.71 |
| \( \alpha \), slope of the mercury intrusion curve (mL.g⁻¹.MPa⁻¹) | 3.80x10⁻³ | 2.19x10⁻³ | 2.67x10⁻³ | 6.92x10⁻³ | 4.16x10⁻³ | 6.79x10⁻³ |
| \( K \), Bulk modulus (MPa) | 843    | 1518    | 1170    | 543     | 883     | 534    |
11 Single crystal X-ray diffraction

Single crystals of DUT-147, DUT-148 and DUT-159, DUT-160, and DUT-161 with dimensions ranging from 30 μm to 80 μm were prepared in a borosilicate glass capillary (d = 0.3 mm) with small amount of DMF. The capillaries were sealed with wax from both sides in order to avoid contact with ambient atmosphere. The datasets were collected at BESSY MX BL14.2 and BL14.3 beamlines of Helmholtz-Zentrum Berlin für Materialien und Energie at 298 K. After short test scans, the crystal symmetry and scan range were determined in each particular case using iMosflm program. The ϕ-scans with oscillation step of 0.5° were used for data collection. All datasets were processed automatically using XDSAPP 2.0 software. Crystal structures were solved by direct methods and refined by full matrix least-squares on F^2 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 \( U_{iso}(H) = 1.2U_{iso}(C) \). In the crystal structures of DUT-147 and DUT-160, the pyrene and phenyl rings are disordered over two positions. Dihydrophenanthrene, stilbene and dibenzyl backbones in DUT-148, DUT-161, and DUT-162 structures, respectively are disordered over four positions, which were refined with corresponding reduced occupancies. During the refinement of DUT-148, DUT-161, and DUT-162 distance restraints were used to fix the geometry of dihydrophenanthrene, stilbene and dibenzyl fragments. Disordered guest molecules could not be refined unambiguously from the difference Fourier map, hence, SQUEEZE routine in PLATON was used to generate the reflection intensities with subtracted solvent contribution.

CCDC-2003150-2003155 contain the supplementary crystallographic data for DUT-147, DUT-148, DUT-159, DUT-160 and DUT-161 correspondingly. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
Supplementary Table 5. Experimental data on single crystal X-ray diffraction for as made phases of DUT-147, DUT-148 and DUT-159.

|                  | DUT-147                                      | DUT-148                                      | DUT-159                                      |
|------------------|----------------------------------------------|----------------------------------------------|----------------------------------------------|
| Empirical formula | C₄₄H₂₀Cu₂N₂O₈·2H₂O                         | C₄₂H₂₂Cu₂N₂O₈·2H₂O                         | C₃₆H₂₀Cu₂N₂O₁₀·2H₂O                        |
| Formula weight, g mol⁻¹ | 867.76                                      | 845.75                                      | 767.62                                      |
| Crystal system, space group | cubic, Fm3m                                 | cubic, Fm3m                                 | trigonal, R3m                               |
| Unit cell dimensions, Å  | a = 46.450(5)                               | a = 46.540(5)                               | a = 23.110(3)                              |
|                      | a = 46.450(5)                               | a = 46.540(5)                               | c = 49.600(10)                             |
| Unit cell volume, Å³   | 100221(35)                                  | 100804(35)                                  | 22941(8)                                   |
| Z                  | 24                                           | 24                                           | 9                                           |
| Calculated density, g·cm⁻³ | 0.343                                       | 0.333                                        | 0.500                                       |
| Temperature, K       | 293                                          | 293                                          | 293                                         |
| Wavelength, Å        | 0.88561                                      | 0.88561                                      | 0.89499                                    |
| Absorption coefficient, mm⁻¹ | 0.5                                           | 0.497                                        | 0.814                                       |
| F(000)              | 8928 (after SQUEEZE)                         | 10224 (after SQUEEZE)                        | 3492 (after SQUEEZE)                        |
| θ range, °          | 0.956 – 33.070                               | 0.954 – 36.062                               | 1.382 – 33.930                             |
|                      | -45 ≤ h ≤ 52                                 | -50 ≤ h ≤ 44                                 | -28 ≤ h ≤ 28                               |
|                      | -56 ≤ k ≤ 48                                 | -58 ≤ k ≤ 48                                 | -28 ≤ k ≤ 28                               |
|                      | -55 ≤ l ≤ 17                                 | -58 ≤ l ≤ 18                                 | -61 ≤ l ≤ 51                               |
| Reflections collected / unique | 46235 / 4582                                 | 53443 / 5638                                 | 48209 / 5577                               |
| Rint               | 0.0681                                       | 0.0486                                       | 0.0653                                      |
| Data / parameters   | 4582 / 106                                   | 5638 / 106                                   | 5577 / 124                                  |
| GooF on F²          | 0.981                                        | 1.021                                        | 0.972                                       |
| Final R indices [I>2σ(I)] | R₁ = 0.0626/ wR₁ = 0.1862                   | R₁ = 0.0676 / wR₁ = 0.2043                   | R₁ = 0.0579 / wR₁ = 0.2003                 |
|                     | R₁ = 0.1082 / wR₁ = 0.2344                  | R₁ = 0.1102 / wR₁ = 0.2490                  | R₁ = 0.0745 / wR₁ = 0.2252                 |
| wR indices (all data) | R₁ = 0.0626/ wR₁ = 0.1082                   | R₁ = 0.0676 / wR₁ = 0.2344                  | R₁ = 0.0579 / wR₁ = 0.2003                 |
|                     | R₁ = 0.1082 / wR₁ = 0.2344                  | R₁ = 0.1102 / wR₁ = 0.2490                  | R₁ = 0.0745 / wR₁ = 0.2252                 |
| Largest diff. peak / hole, eÅ⁻³ | 0.465 / -0.522                              | 1.102 / -0.417                              | 0.357 / -0.274                             |
Supplementary Table 6. Experimental data on single crystal X-ray diffraction for as made phases of DUT-160, DUT-161 and DUT-162.

| DUT-160 | DUT-161 | DUT-162 |
|---------|---------|---------|
| Empirical formula | C\textsubscript{42}H\textsubscript{20}Cu\textsubscript{2}N\textsubscript{2}O\textsubscript{8} · 2H\textsubscript{2}O | C\textsubscript{42}H\textsubscript{22}Cu\textsubscript{2}N\textsubscript{2}O\textsubscript{8} · 2H\textsubscript{2}O | C\textsubscript{42}H\textsubscript{24}Cu\textsubscript{2}N\textsubscript{2}O\textsubscript{8} · 2H\textsubscript{2}O |
| Formula weight, g mol\textsuperscript{-1} | 843.74 | 841.69 | 847.77 |
| Crystal system, space group | cubic, \textit{Fm\textbar m} | cubic, \textit{Fm\textbar m} | cubic, \textit{Fm\textbar m} |
| Unit cell dimensions, Å | \(a = 50.110(6)\) | \(a = 49.760(6)\) | \(a = 49.590(6)\) |
| Unit cell volume, Å\textsuperscript{3} | 125827(44) | 123209(43) | 121950(42) |
| \(Z\) | 24 | 24 | 24 |
| Calculated density, g·cm\textsuperscript{-3} | 0.266 | 0.272 | 0.276 |
| Temperature, K | 293 | 293 | 293 |
| Wavelength, Å | 0.89499 | 0.89499 | 0.88561 |
| Absorption coefficient, mm\textsuperscript{-1} | 0.398 | 0.406 | 0.411 |
| \(F(000)\) | 10176 (after SQUEEZE) | 10224 (after SQUEEZE) | 10272 (after SQUEEZE) |
| \(\theta\) range, \(^\circ\) | 0.886 – 28.112 | 0.893 – 30.832 | 0.896 – 33.535 |
| Limiting indices | \(-52 \leq h \leq 51\) | \(-24 \leq h \leq 56\) | \(-61 \leq h \leq 27\) |
| | \(-52 \leq k \leq 50\) | \(-56 \leq k \leq 55\) | \(-59 \leq k \leq 61\) |
| | \(-52 \leq l \leq 52\) | \(-56 \leq l \leq 27\) | \(-59 \leq l \leq 16\) |
| Reflections collected / unique | 140813 / 3736 | 56402 / 4651 | 58786 / 5731 |
| \(R_{int}\) | 0.0578 | 0.0994 | 0.0648 |
| Data / parameters | 3736 / 101 | 4651 / 106 | 5731 / 106 |
| \text{GooF on } F^2 | 1.083 | 1.021 | 0.917 |
| Final \(R\) indices [\(I>2\sigma(I)\)] | \(R_I = 0.0577 / wR_2 = 0.0555 / wR_2 = 0.0670 / wR_2 = 0.1921\) | \(R_I = 0.0555 / wR_2 = 0.0869 / wR_2 = 0.1467 / wR_2 = 0.2254\) | \(R_I = 0.0670 / wR_2 = 0.1932\) |
| \text{wR} indices (all data) | \(0.0522 / -0.350\) | \(0.0347 / -0.341\) | \(0.451 / -0.285\) |
| Largest diff. peak / hole, eÅ\textsuperscript{3} | \(0.522 / -0.350\) | \(0.347 / -0.341\) | \(0.451 / -0.285\) |
Supplementary Figure 20. a) L$^{159}$ in the conformation present in DUT-159, b) Unit cell along $c$-direction of DUT-159 and c) DUT-158, d) DUT-159 along $a$-direction, individual Cu(cdc) layers are coloured in orange, red, purple and blue. e) Unit cell along $b$-direction of DUT-159 and f) DUT-158, g) DUT-158 along $a$-direction, individual Cu(cdc) layers are coloured in orange, red, purple and blue. Colour code: Hydrogen (white), carbon (grey), nitrogen (blue), oxygen (red), and copper (turquoise).
**In situ Powder X-ray Diffraction**

*In situ*-PXRD studies and parallelised gas adsorption were measured at KMC-2 beamline of the BESSY II synchrotron\textsuperscript{14}, operated by Helmholtz-Zentrum Berlin für Materialien und Energie. Self-designed automated instrumentation, based on the volumetric adsorption instrument and closed-cycle Helium cryostat, equipped with adsorption chamber with beryllium domes was used in all experiments\textsuperscript{15}. PXRD patterns were measured at constant wavelength $\lambda = 0.15406$ nm ($E = 8048$ eV) in transmission geometry. Because of the bulky cryostat, the sample holder cannot rotate during experiments, however an average crystallite size in the range of 2-15 µm and using an area 2D detector (Vantec 2000, Bruker) allowed to record diffraction images with reasonable particle statistics. Each 2D image was measured with 31 s exposure. For each experiment 10-12 mg of sample were used. In order cut off reflections coming from the crystalline Be-dome, tungsten slits with 5 mm aperture were mounted on the detector cone. The obtained diffraction images were integrated using DATASQUEEZE 2.2.9\textsuperscript{16} with further processing in FITKY 0.9 software\textsuperscript{17}. For all automated measurements the physisorption isotherms were measured using equilibrium settings for pressure change of 0.1% within 300 s. In case of the manual measurements, each pressure was set manually and PXRD patterns were measured after the pressure in the cell was stabilized for at least 300 s. PXRD patterns during adsorption and desorption of methane at 111 K on DUT-161 (Supplementary Figure 24) and nitrogen at 75.5 K on DUT-148 (Supplementary Figure 23) were measured in the automatic mode. PXRD patterns, measured during adsorption and desorption of $n$-butane at 273 K on DUT-147 (Supplementary Figure 21) and DUT-148 (Supplementary Figure 22) and DUT-160 (Supplementary Figure 25) and PXRD patterns with methane loading at 111 K on DUT-160 (Supplementary Figure 26) were measured in manual mode.

Supplementary Figure 21. *In situ* PXRD in parallel to $n$-butane physisorption at 273 K of DUT-147: a) Adsorption-desorption isotherm, selected points are labeled by numbers. Filled symbols correspond to adsorption, empty symbols to desorption. b) PXRD patterns, color code: DUT-147*op* (orange), DUT-147*cp* (purple), simulated pattern *op* (red) and *cp* (black).
Supplementary Figure 22. In situ PXRD in parallel to \textit{n}-butane physisorption at 273 K of DUT-148: a) Adsorption-desorption isotherm, selected points are labeled by numbers. Filled symbols correspond to adsorption, empty symbols to desorption. b) PXRD patterns, color code: DUT-148\textit{cp} (orange), DUT-148\textit{op} (purple), simulated pattern \textit{op} (red) and \textit{cp} (black).
Supplementary Figure 23. *In situ* PXRD in parallel to nitrogen physisorption at 75.5 K of DUT-148: a) Adsorption-desorption isotherm, selected points are labeled by numbers. Filled symbols correspond to adsorption, empty symbols to desorption. b) PXRD pattern recorded during adsorption and c) PXRD pattern recorded during desorption, color code: DUT-148cp (orange), DUT-148ip (green), DUT-148op (purple), and simulated pattern op (red).
Supplementary Figure 24. *In situ* PXRD in parallel to methane physisorption at 111 K of DUT-160: a) Adsorption-desorption isotherm, selected points are labeled by numbers. Filled symbols correspond to adsorption, empty symbols to desorption. b) PXRD patterns color code: DUT-160cp (orange), DUT-160op (purple).

Supplementary Figure 25. *In situ* PXRD in parallel to *n*-butane physisorption at 273 K of DUT-160: a) Adsorption-desorption isotherm, selected points are labeled by numbers. Filled symbols correspond to adsorption, empty symbols to desorption. b) PXRD patterns, color code: DUT-160cp (orange), DUT-160op (purple).
Supplementary Figure 26. In situ PXRD in parallel to methane physisorption at 111 K of DUT-161: a) Adsorption-desorption isotherm, selected points are labeled by numbers. Filled symbols correspond to adsorption, empty symbols to desorption. b) PXRD patterns, color code: DUT-160cp (orange), DUT-160cp (purple), mixtures or unidentified intermediate phases (green).
Refinement of DUT-147\textit{cp} and DUT-148\textit{cp} structures

\textit{In situ} PXRD patterns, measured during the adsorption of methane at 111 K on DUT-160 and DUT-161, nitrogen at 75.5 K on DUT-148 and \textit{n}-butane at 273 K on DUT-160 and DUT-161 were indexed and profile was refined using Le Bail fit\textsuperscript{18}, implemented into the FullProf software\textsuperscript{19}. The evolution of the unit cell volume during adsorption of fluids on above mentioned MOFs is given in Supplementary Figure 33.

PXRD patterns measured in vacuum on DUT-147, DUT-148, DUT-160, DUT-161 were used for the Rietveld analysis of the desolvated structures. The refinement was performed using Reflex tool of Materials Studio 5.0. Structural models of corresponding MOFs in artificially reduced symmetry (Pa-3 space group) were used in order to eliminate the disorder. Because of low data / parameter ratio, rigid body refinement was used, in which copper atoms, carboxylates, carbazole moieties and corresponding backbone (pyrene – DUT-147, dihydrophenanthrene – DUT-148, phenyl rings and acetylene group – DUT-160 and phenyl rings + ethylene moiety – DUT-161) were defined as rigid bodies. Rietveld refinement with energy (contribution of UFF ~1\%) was used in refinement.

PXRD patterns measured in vacuum at 273 K after \textit{n}-butane physisorption on DUT-147 and PXRD patterns measured after reaching adsorption equilibrium at 40 kPa of \textit{n}-butane at 273 K on DUT-148 were used for Rietveld refinement of the corresponding contracted phases. Structural models in Pa-3 space groups with 6 molecules of \textit{n}-butane per paddle-wheel in the pores were used as initial model. The rigid body Rietveld refinement with energy contribution (UFF ~1\%) was performed and both framework and \textit{n}-butane molecules were refined.

The Rietveld plots are given in Supplementary Figure 27 and experimental data on refinements are summarized in the Supplementary Table 7 and Supplementary Table 8.

![Rietveld plot of DUT-147\textit{cp} (vacuum 273 K).](image-url)
Supplementary Figure 28. Rietveld plot of DUT-147cp (desorption <1 kPa n-butane 273 K).

Supplementary Figure 29. Rietveld plot of DUT-148op (vacuum 273 K).
Supplementary Figure 30. Rietveld plot of DUT-148cp (adsorption 40 kPa n-butane 273 K).

Supplementary Figure 31. Rietveld plot of DUT-160op (vacuum 111 K).
Supplementary Figure 32. Rietveld plot of DUT-161op (vacuum 111 K).
Supplementary Figure 33. Evolution of the unit cell volume upon as adsorption: a) n-butane on DUT-147 at 273 K; b) n-butane on DUT-148 at 273 K; c) nitrogen on DUT-148 at 75.5 K; d) methane on DUT-160 at 111 K; e) methane on DUT-161 at 111 K.
Supplementary Table 7. Experimental data on Rietveld refinement of DUT-147 and DUT-148 structures.

|                  | DUT-147\_op vacuum 273 K | DUT-148\_op vacuum 273 K | DUT-147\_cp n-butane 273 K | DUT-148\_cp n-butane 273 K |
|------------------|---------------------------|---------------------------|-----------------------------|-----------------------------|
| Formula unit     | C\textsubscript{44}H\textsubscript{20}Cu\textsubscript{2}N\textsubscript{2}O\textsubscript{8} | C\textsubscript{42}H\textsubscript{22}Cu\textsubscript{2}N\textsubscript{2}O\textsubscript{8} | C\textsubscript{44}H\textsubscript{20}Cu\textsubscript{2}N\textsubscript{2}O\textsubscript{8} \( \supset \) 6C\textsubscript{4}H\textsubscript{10} | C\textsubscript{42}H\textsubscript{22}Cu\textsubscript{2}N\textsubscript{2}O\textsubscript{8} \( \supset \) 6C\textsubscript{4}H\textsubscript{10} |
| Z                | 24                        | 24                        | 24                          | 24                          |
| Symmetry, space group | cubic, \( P\bar{a}\bar{3} \) | cubic, \( P\bar{a}\bar{3} \) | cubic, \( P\bar{a}\bar{3} \) | cubic, \( P\bar{a}\bar{3} \) |
| Unit cell parameter, \( a \) (\( \text{Å} \)) | 46.3743 (11) | 46.4426(8) | 36.5924(15) | 36.337 |
| Unit cell volume, (\( \text{Å}^3 \)) | 99731.4 | 100173.0 | 48997.8 | 47978.6 |
| Wave length (\( \text{Å} \)) | 1.5406 | 2 - 50 | 4 - 40 | 2 - 50 |
| Instrument geometry | Debye-Scherrer | | | |
| Zero point line shift (\( ^\circ \)) | 0 | 0 | 0 | 0 |
| Profile function | Thompson-Cox-Hastings | | | |
| \( U \) | 0.18752 | 0.25181 | 0.03173 | -0.13854 |
| \( V \) | -0.03441 | -0.03780 | -0.00390 | 0.14424 |
| \( W \) | 0.00505 | 0.00654 | 0.00408 | -0.00040 |
| \( X \) | 0.03457 | -0.00064 | 0.36644 | 0.28784 |
| \( Y \) | 0.02425 | 0.02095 | 0.01411 | 0.03139 |
| Asymmetry correction | Berar-Baldinozzi | | | |
| \( P1 \) | -0.01281 | -0.01288 | 0.00463 | 0.00653 |
| \( P2 \) | -0.00010 | 0.00021 | 0.00100 | 0.00013 |
| \( P3 \) | -0.01092 | -0.00589 | 0.00930 | 0.00119 |
| \( P4 \) | -0.00209 | -0.00114 | 0.00164 | 0.00021 |
| Final \( R_{wp} \) | 0.1732 | 0.11187 | 0.1455 | 0.0878 |
| Final \( R_p \) | 0.1328 | 0.0881 | 0.1092 | 0.0675 |
Supplementary Table 8. Experimental data on Rietveld refinement of DUT-160op and DUT-161op structures.

|                      | **DUT-160op**                      | **DUT-161op**                      |
|----------------------|------------------------------------|------------------------------------|
|                      | vacuum 111 K                       | vacuum 111 K                       |
|                      | Supplementary Figure 31            | Supplementary Figure 32            |
| Formula unit         | C₄₂H₂₀Cu₂N₂O₈                     | C₄₂H₂₀Cu₂N₂O₈                     |
| Z                    | 24                                 | 24                                 |
| Symmetry, space group| cubic, Pa3                          | cubic, Pa3                          |
| Unit cell parameter, a (\(\text{Å}\)) | 50.1601(2)                       | 49.8406(13)                       |
| Unit cell volume, (\(\text{Å}^3\)) | 126200                            | 123809                            |
| Wave length (\(\text{Å}\)) | 1.5406                             |                                    |
| 2\(\theta\) range (\(°\)) | 2 - 50                             | 2 - 50                             |
| Instrument geometry  | Debye-Scherrer                     |                                    |
| Zero point line shift (\(°\)) | 0                                 | 0                                 |
| Profile function     | Thompson-Cox-Hastings              |                                    |
| U                    | 0.01559                            | 0.01000                            |
| V                    | -0.01579                           | -0.01587                           |
| W                    | 0.00579                            | 0.00522                            |
| X                    | 0.13872                            | 0.27949                            |
| Y                    | 0.00587                            | 0.00063                            |
| Asymmetry correction |                                    |                                    |
| P₁                   | -0.01626                           | -0.01263                           |
| P₂                   | -0.00055                           | -0.00009                           |
| P₃                   | -0.00419                           | -0.00090                           |
| P₄                   | -0.00056                           | -0.00018                           |
| Final \(R_{wp}\)     | 0.1730                             | 0.1489                             |
| Final \(R_p\)        | 0.1207                             | 0.1056                             |
Calorimetric analysis of gas adsorption

In situ calorimetric adsorption studies were performed using a protocol previously applied in the characterisation of DUT-49 and related solids.\textsuperscript{1, 7} The following description is a literal adaption from reference\textsuperscript{1}:

For microcalorimetry, all isotherms and enthalpies were measured experimentally using a Tian-Calvet type microcalorimeter coupled with a home-made manometric gas dosing system\textsuperscript{20}. 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. Around 0.05 g of sample is used in each experiment. For each injection of gas, equilibrium was assumed to have been reached after 130 minutes. This was confirmed by the return of the calorimetric signal to its baseline (\(< 5 \mu W\)). The gases used for the adsorption experiment were obtained from Air Liquide and were of minimum N47 quality (99.997 % purity).

To obtain the experimental errors, the procedure described in the Guide to the Expression of Uncertainty in Measurement was used. The quantity, enthalpy or pressure, is first expressed as a function \(f(y)\) of other physical measured quantities. The standard uncertainty \(u_c(y)\) is then calculated on the basis of, where \(u_i(x_i)\) is the standard uncertainty in each input quantity. Here it is assumed that the input quantities are independent and uncorrelated. The error margins \(a_i\) for each quantity were taken from manufacturer specifications of the equipment used for recording. They were then divided by a value \(k_i\) chosen to cover the expected variance in that quantity, as each variable is assumed to be characterized by a probability distribution. The error introduced by the equation of state used (NIST REFPROP\textsuperscript{21}) were assumed to be minor compared to the error introduced by the physical quantities, with the same to be said regarding the error in the calorimetric heat signal, which represents less than 1% of the error in enthalpy. Finally, the expanded uncertainty was calculated by choosing a suitable coverage factor of 1.645, corresponding to a 95% confidence interval.

\[
\begin{align*}
\frac{df(y)}{dx_i} &\times u_i(x_i) \\
\sum &\rightarrow
\end{align*}
\]

\[
\begin{align*}
uc(y) &\equiv \sqrt{\sum_{i=1}^N \left(\frac{\partial f(y)}{\partial x_i} \times u_i(x_i)\right)^2} \\
&\rightarrow
\end{align*}
\]

Supplementary Table 9. Parameters used to estimate the errors of in situ calorimetric analysis.

| Variable \((i)\) | \(a_i\) | \(k_i\) |
|----------------|--------|--------|
| Pressure, \(p\) (Pa) | 20 | \(\sqrt{3}\) |
| Temperature, \(T\) (K) | 0.1 | 3 |
| Sample mass, \(m\) (g) | \(1 \times 10^{-4}\) | \(\sqrt{3}\) |
| Reference volume, \(V_r\) (m\(^3\)) | \(1 \times 10^{-6}\) | \(\sqrt{6}\) |
| Cell volume, \(V_c\) (m\(^3\)) | \(6 \times 10^{-7}\) | \(\sqrt{6}\) |
Supplementary Figure 34. Adsorption (filled symbols) and desorption (empty symbols) isotherms of \( n \)-butane at 303 K (left), corresponding adsorption/desorption enthalpies with error bars (middle), and isosteric adsorption enthalpy profiles with semi-transparent error region (right) of a–c) DUT-49, d–f) DUT-147, g–i) DUT-148, j–l) DUT-160.
Computational methods

Adsorption energetics and isotherm simulation

Grand canonical Monte Carlo (GCMC) simulations were carried out at 77 K and 111 K to compute the adsorption isotherms and enthalpies for nitrogen and methane in DUT-49, DUT-50, DUT-147, DUT-148, DUT-160, DUT-161 and DUT-162 for respective cp and op forms by employing the Complex Adsorption and Diffusion Simulation Suite (CADSS) code. The simulation box was made of 1 conventional unit cell for all DUT phases. The fugacities for methane at a given thermodynamic condition were computed using the Peng–Robinson equation of state. For each state point, $10^8$ Monte Carlo steps were used for both equilibration and production runs. The guest/DUT and guest/guest interactions were treated using a van der Waals contribution with a cutoff of 12 Å. The Lennard-Jones (LJ) potential parameters for the atoms of the inorganic and organic parts of the DUT frameworks were derived from the universal force field (UFF) and DREIDING, respectively. Methane was represented by a single LJ site described by the TraPPE force field. Lorentz–Berthelot (LB) combination rules were used to calculate the cross LJ potential parameters.

Supplementary Table 10. LJ potential parameters for adsorbate-adsorbate and adsorbate-DUT-49 interactions used.

| Atoms   | Guest | Framework |
|---------|-------|-----------|
|         | N₂    | CH₄       | C   | H   | N   | O   | Cu |
| σ (Å)   | 3.31  | 3.730     | 3.47| 2.85| 3.66| 3.12| 3.30|
| $\epsilon/k_B$ (K) | 36.00 | 148.00     | 47.86| 7.65| 38.98| 30.20| 2.52|

Supplementary Figure 35. a,d,g) Simulated methane adsorption isotherm at 111 K, b,e,h) corresponding simulated adsorption enthalpy profile and c,f,i) corresponding isosteric adsorption enthalpies of DUT-49 (blue), DUT-147 (red), and DUT-148 (orange) (a,b,c), DUT-160 (pink), DUT-161 (yellow), and DUT-162 (green) (d,e,f) and DUT-49, DUT-160, and DUT-50 (grey) (g,h,i). Data for op phases in solid and corresponding cp phases in dashed lines.

Pore characteristic simulations
Pore characteristics such as density, specific pore volume, and specific accessible surface area were calculated using Zeo++.\textsuperscript{25}

Supplementary Table 11. Specific surface area, pore volume and density of the series of materials determined by Zeo++ based on simulated crystal structures of $op$ and corresponding $cp$ phases. Experimental pore volumes were determined from nitrogen adsorption isotherms at 77 K and a relative pressure of 0.95.

| Material | Specific geometric surface area simulated (m$^2$ g$^{-1}$) | Specific pore volume simulated (cm$^3$ g$^{-1}$) | Specific pore volume experimental (cm$^3$ g$^{-1}$) | density |
|----------|----------------------------------------------------------|-------------------------------------------------|-------------------------------------------------|---------|
| 49$op$   | 4950                                                     | 2.61                                            | 2.73                                            | 0.321   |
| 50$op$   | 5354                                                     | 3.59                                            | 3.52                                            | 0.242   |
| 147$op$  | 4853                                                     | 2.51                                            | 2.68                                            | 0.332   |
| 148$op$  | 4995                                                     | 2.58                                            | 2.71                                            | 0.323   |
| 160$op$  | 5375                                                     | 3.38                                            | 3.41                                            | 0.256   |
| 161$op$  | 5229                                                     | 3.20                                            | 3.19                                            | 0.269   |
| 162$op$  | 5342                                                     | 3.26                                            | 1.32                                            | 0.263   |
| 159$op$  | 4727                                                     | 1.53                                            | n. a.                                           | 0.500   |
| 49$cp$   | 3324                                                     | 0.95                                            | n. a.                                           | 0.674   |
| 50$cp$   | 3533                                                     | 1.16                                            | n. a.                                           | 0.585   |
| 147$cp$  | 3318                                                     | 0.93                                            | n. a.                                           | 0.686   |
| 148$cp$  | 3331                                                     | 0.97                                            | n. a.                                           | 0.658   |
| 160$cp$  | 3969                                                     | 1.29                                            | n. a.                                           | 0.544   |
| 161$cp$  | 3552                                                     | 1.10                                            | n. a.                                           | 0.607   |
| 162$cp$  | 3242                                                     | 0.93                                            | n. a.                                           | 0.669   |

Ligand mechanics simulations

Ligand Buckling simulations were performed according to a strategy previously applied on related ligands.\textsuperscript{1} The ligands were simulated as the corresponding acids using density functional theory (DFT) simulations employed by the NWChem software. The 6-31G+* basis set the hybrid exchange-correlation functional PBE0 were used. Dispersion corrections were included using the Grimme “D3” approach. The optimised structures were subsequently strained by decreasing the N–N length from this local minimum to a compressive strain of 0.06, in 40 steps. For each step, the structure was optimised with default convergence criteria and with this N–N length fixed. Subsequently, a stress-strain curve relative to this axial compression of the ligand is generated; where stress is defined by the gradient of the energy, and strain is the relative decrease in N–N length.
Framework dynamics simulations

Molecular dynamics simulations to produce the free energy surfaces relative to different volumes used a modified MOF-FF force field adapted to lammps to describe the bonds, angles, dihedrals and improper dihedrals present in the frameworks. Representative input files for molecular simulations are available online at the data repository https://github.com/jackevansadl/supp-data. The established protocol to compute the pressure-volume equation of states was applied, however, a cubic symmetric cell was fixed. The energetic contribution per Ligand can be determined by dividing $\Delta F^\ddagger$ with the number of ligands per unit cell which in both the op and cp phase is 24.

Supplementary Figure 37. Free energy profile of guest free a) DUT-49 and DUT-50, b) DUT-147, c) DUT-148, d) DUT-160, e) DUT-161, and f) DUT-162. In b-f) DUT-49 and DUT-50 are given as dashed lines for reference.
Structural models of the op and cp phases were generated based on the minima observed in the energy landscapes. Structural models were additionally geometrically optimized which may lead to slight deviations in unit cell volume compared to the actual minimum in the energy surfaces.

Supplementary Table 12. Energy and unit cell parameter derived from free energy profiles and structural models.

| Material | $\Delta F_{\text{op}}$ (kJ mol$_{\text{uc}}$)$^{-1}$ | $V_{\text{UC}}$ (Å$^3$) | $\Delta F_{\text{cp}}$ (kJ mol$_{\text{uc}}$)$^{-1}$ | $V_{\text{UC}}$ (Å$^3$) | minimum | structural model |
|----------|-----------------|-----------------|-----------------|-----------------|---------|-----------------|
| DUT-49   | 0               | 100267          | 950             | 47061           | 46287   |
| DUT-147  | 0               | 100004          | 1240            | 48453           | 48300   |
| DUT-148  | 0               | 100144          | 860             | 49280           | 48654   |
| DUT-160  | 0               | 126118          | 850             | 55444           | 59127   |
| DUT-161  | 0               | 118544          | 780             | 54317           | 53082   |
| DUT-162  | 0               | 1220925         | 220             | 51686           | 48339   |
| DUT-50   | 0               | 139361          | 670             | 58478           | 58557   |

Throughout the discussion of the manuscript unit cell volumes derived from the structural models of the cp phases (CIF of structural model provided as supplementary information) are used.

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Other files

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