Amplification of Negative Gas Adsorption in a multivariate framework

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The approach of multivariate MOFs was used to fine-tune the mechanical properties of the flexible framework DUT-49. In situ XRD, NMR and physisorption studies showed that the partial incorporation of a more rigid linker into DUT-49 framework enables a stabilization of the metastable open pore phase which led to a twofold amplification of ΔNGA.

Bistable Metal-Organic Frameworks show reversible guest-induced phase transitions upon physisorption of gases and vapours. These solids have a remarkable performance in gas storage and separation, but are also discussed as sensors and actuators. In particular, flexible frameworks demonstrate potential towards CO2/CH4, C2H6 (x = 2, 4, 6) and even hydrogen isotopologues separation. A while ago we discovered a phenomenon in a mesoporous DUT-49 framework with hierarchical pore structure, coined as “Negative Gas Adsorption”. The solid expels gas upon outer pressure increase after the adsorption of subcritical gases, caused by a structural contraction from a gas-loaded metastable open pore phase to a contracted pore phase with reduced porosity. This unusual effect leads to pressure amplification in a closed system. Further filling of the structure leads to reopening to open pore phase and can be characterized as breathing, previously described in MIL-53 structures. The nature of the effect is now well understood from experimental and theoretical standpoints, indicating the importance of mechanical properties of the ligand molecule, crystal size effects, nature of guest molecules and temperature. The complete thermodynamic description of DUT-49 is charted by Evans and co-authors in the form of the free energy landscape describing the dependence of osmotic potential from the pressure and unit cell volume. Using carbon dioxide as adsorbing fluid at 230-240 K, the pressure amplifiers could be designed working far above atmospheric pressures. One of the most important characteristics of pressure amplification materials is ΔNGA, describing the amount of the gas, expelled from the framework at the defined pressure and temperature. This value can be manipulated by variation of experimental conditions such as guest molecule and adsorption temperature or adjustment of the mechanical properties of the host structure such as the length of the strut connecting the carboxazole units. A more sophisticated approach is to enhance the ΔNGA by keeping above mentioned conditions constant and engineer the micromechanics of the host structure, more specifically to design the ligand molecules with the desired stress/strain properties, namely the buckling of the ligand should happen at maximum possible loading or in another words to stabilize the overloaded metastable open pore phase until highest possible loading before buckling. This strategy was applied in DUT-147, DUT-148 and DUT-160 framework series, containing the struts with different mechanical stiffness and the highest ΔNGA of 12 mmolg⁻¹ was reached for DUT-160 upon nitrogen physisorption at 77K. Nevertheless, the targeted design of the frameworks showing NGA at desired guest/gas pressure/temperature condition is still challenging because of lacking of organic struts with desired stiffness. Therefore, the design of multivariate NGA frameworks, containing ligands with different stiffness may allow to tune ΔNGA at desired experimental conditions. It is well known that MOF structures show a certain geometrical tolerance towards implementation of the ligands. Zhou and co-authors proposed kinetically guided synthesis for obtaining multicomponent hierarchical MOFs. Telfer and co-authors demonstrated the high tolerance of ith-d MOFs towards systematic ligand substitution. In our previous work we also demonstrated the tolerance of n frameworks towards the variation of the cross–ligand length.

Inspired by the above mentioned reports, we selected DUT-49, known as the first NGA framework, and its isoreticular analogue DUT-46, based on shorter, yet more rigid ligand for the synthesis of multivariate MOFs by varying the ratio of 9,9’-(naphthalene-2,6-diyl)bis(9H-carbazole-3,6-dicarboxylic acid) (H2NBCDC) and 9,9’-[(1,1’-biphenyl)-4,4’-diyl]bis(9H-carbazole-3,6-dicarboxylic acid) (H2BBCDC) ligands. From previous publications it is known that large crystals of DUT-49 show NGA reaching ΔNGA values of 8.62 mmolg⁻¹ upon physisorption of methane at 111 K, whereas DUT-46 shows a reversible type-Ib isotherm. Calculations of stress/strain properties for H2NBCDC and H2BBCDC ligands indicate that the first one shows higher stress/strain yield, which may potentially increase the stability of the overloaded metastable states compared to networks based on pure H2BBCDC. The strain/stress yield can be then finely tuned by variation of the NBCDC/BBCDC ligand ratio. In terms of experimental feasibility, the N...N spacing in the ligands vary by 2.113 Å and based on the previous reports, the crystal structures may tolerate such geometrical mismatch. As a proof of principle, we synthesized three samples with ligand ratio NBCDC/BBCDC of 2:1 (MTV-DUT-49-1), 1:1 (MTV-DUT-49-2) and 1:2 (MTV-DUT-49-3). H NMR spectra of the digested MOFs have been investigated to determine the actual ratio of the two linkers. The determined ratio NBCDC/BBCDC built into the lattice of the material amounts to 3:1 (MTV-DUT-49-1), 1:2:1 (MTV-DUT-49-2) and 1:2 (MTV-DUT-49-3) (Fig. S7, ESI). This discrepancy between the used linker ratio for the synthesis and the resulting ratio suggest the network of DUT-46 to be less adaptive because of its rigid structure and therefore
does not accept a high amount of the longer BBCDC-Linker. In contrast to this, the DUT-49 network accepts a higher amount of the shorter NBCDC-linker due to its greater softness. DUT-49 is known for elastic contraction/reopening between op and ip phases showing unit cell parameters in the range 44-46 Å and introduction of shorter NBCDC ligand obviously helps to stabilize intermediate phases, observed in DUT-49. In all cases the single crystals were available and synchrotron datasets were collected suggesting the cubic symmetry and Fm̅3m space group, as in the pristine frameworks. Although the solution of the crystal structure was not possible for MTV-DUT-49, the unit cell parameters of MTV-DUT-49 could be determined unambiguously indicating a smooth transition between DUT-46 and DUT-49 structures. In order to confirm the formation of MTV-MOFs with average DUT-49 structure, we simulated distorted crystal structures containing desired ratio of the ligand molecules, however the simulated regular distorted structures contain different ratio of NBCDC and BBCDC ligands (Fig.S12, ESI). The frameworks were desolvated using supercritical CO₂ activation procedure and integrity of the structures was confirmed by PXRD patterns (Fig.2b). Comparison of simulated PXRD patterns disapproves such a

Figure 1. Schematic representation of DUT-46 and DUT-49 structures (a); Experimental PXRD patterns of DUT-46 and DUT-49 (b); Stress/strain curves for NBCDC and BBCDC ligands (c); Geometrical pore size distribution for DUT-46 and DUT-49 (d); Methane physisorption isotherms for DUT-46 and DUT-49 at 111 K (e).

Figure 2. Crystal structures of DUT-46, DUT-49 and MTV-DUT-49 MOFs with various ligand ratio (a); PXRD patterns of the desolvated structures of DUT-46, DUT-49 and MTV-DUT-49 with magnified low-angle range (b); Methane physisorption experiments at 111 K with magnified NGA range (c).
the possibility of the formation of other structures than DUT-49, indicating that ligands are randomly distributed and the structure well tolerates the random combination of longer and shorter ligands. Detailed analysis of PXRD patterns by Le Bail method indicates single phases with gradual increasing of the linear unit cell dimension in MTV-DUT-49 frameworks from 44.18 Å in MTV-DUT-49-1 to 45.46 Å in MTV-DUT-49-3. These values are exactly within the range of unit cell parameters, experimentally obtained for pure DUT-46(Cu) op (α = 43.55 Å) and DUT-49(Cu) op (α = 46.59 Å) frameworks in open phase (Fig.2a). SEM images show large cubic and cuboctahedral crystals, typical for DUT-49 with a broad crystal size distribution in all samples ranging between 5 and 50 μm (Fig. S5, ESI). In order to prove the hypothesis on the tuning of the stiffness in multivariate frameworks proposed above we conducted physisorption of methane at 111 K on all synthesized solids (Fig.2c). In case of MTV-DUT-49-1 and MTV-DUT-49-2 we observed the reversible type-Ib isotherm, similar to DUT-46, however, in case of MTV-DUT-49-3, both NGA and hysteresis between adsorption and desorption branches, typical for DUT-49 isotherm was observed (Fig.2c). The detailed analysis of the isotherm confirmed a NGA event observable at π\text{DUT-49} = 9 kPa, namely lower than in case of DUT-49 (π\text{DUT-49} = 11.5 kPa). Moreover, the NGA event starts at higher absolute loading at n\text{CH}_{4} = 35.9 mol\text{g}^{-1}, compared to DUT-49 structure contracting at n\text{CH}_{4} = 32.1 mol\text{g}^{-1}. Comparison of the isotherms slope indicate the gradual shift towards higher pressure with increasing amount of BBCDC ligand in the structure. In terms of porosity this means the gradual increasing of tetrahedral and octahedral pore-sizes, which are responsible for NGA transitions. Obviously, in MTV-DUT-49-3, we could optimize the pore size and average ligand stiffness, which allows the metastable state of the op phase to resist more adsorption stress and therefore reach a higher loading, compared to pure DUT-49 framework. After NGA transitions, both structures contract to the cp phase showing comparable uptake of 24.6 mol\text{g}^{-1} along with adsorption isotherm. Thus, the difference in the metastable overloaded state leads to nearly doubling of the Δπ\text{NGA} from 6.34 mmol\text{g}^{-1} in DUT-49 to 11.26 mmol\text{g}^{-1} in MTV-DUT-49-3 which is quite remarkable. The cp phase of MTV-DUT-49-3 starts reopening at 28 kPa, which is less than 46 kPa in DUT-49, indicating a smaller energy barrier. The relative stabilization of the op phase may also play a role here. In desorption, the op-cp transition for both frameworks happens in very similar pressure range of 16-18 kPa, whereas in the case of MTV-DUT-49-3 no additional step, known as op-ip transition, is observed. In order to corroborate these observations, in situ-PXRD in parallel to methane physisorption on MTV-DUT-49-3 at 111 K was conducted with the DYNADIFF® system to achieve a better mechanistic understanding of the phase transitions (Fig. 3, Figs.S13-S18, ESI).

PXRD patterns, measured in vacuum were indexed in \textit{Fm\textbar{3}m} space group indicating op phase of MTV-DUT-49-3 structure (α = 45.348(2) Å). After NGA transition at equilibrium pressure of 12 kPa, PXRD patterns could be indexed in the \textit{Pa\textbar{3}} symmetry, which is known for DUT-49 cp phase. Interestingly, in case of DUT-49, the unit cell axis contracts from 46.427(4) Å in op phase to 36.1603(2) Å in cp phase. In case of MTV-DUT-49-3, the stronger contraction of cp phase is observed reaching the value of 35.887(2) Å. Increasing the methane pressure to 95 kPa demonstrates reopening of the structure to a guest-filled op phase with α = 45.412(1) Å. In desorption, the structure contracts to the cp phase, previously observed after NGA transition. These experimental observations suggest that embedding 33% of NBCDC in DUT-49 shifts both minima in a free energy landscape towards smaller unit cells. Because of the disordered structure containing two ligands, modelling of the structure and \textit{in silico} calculations are challenging in case of MTV-DUT-49 frameworks and thermodynamic quantities could not be estimated.

In summary, we applied a mixed-ligand approach to synthesized a series of multivariate MTV-DUT-49 frameworks showing gradual expansion of the unit cell between DUT-46 and DUT-49 resulting in a remarkable guest-responsive behaviour. Methane physisorption, conducted at 111 K indicates that in the framework MTV-DUT-49-3, the ΔΔπ\text{NGA} could be boosted to 11.26 mmol\text{g}^{-1} due to the implementation of 33 % of more rigid NBCDC linker. This stabilized the metastable overloaded state of the op phase and allowed higher overloading. In the future, this approach can be used for the design of pressure amplifiers at desired pressure, temperature and guest conditions.

F.W. synthesised and characterized the materials by PXRD, NMR and gas physisorption and analysed the results. A.D. conducted SEM measurements and analysed the images. V.B. conducted in situ PXRD experiments, analysed the results and wrote the manuscript. V.B. and S.K. conceptualized and supervised the project. All authors discussed the results and contributed to the manuscript.

Conflicts of interest
There are no conflicts to declare.

Data availability
The data that support the findings of this study are available from the corresponding author upon request. Adsorption isotherms are enclosed as .aif files. Structural models of ordered structures are provided as .cif files.

References