Conformational isomerism controls collective flexibility in metal-organic framework DUT-8(Ni)

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Abstract

Metal-organic frameworks (MOFs) are coordination networks with organic ligands containing potential voids. Some MOFs show pronounced structural flexibility that may result in closing and re-opening these pores. Here, we show that collective flexibility in a MOF – DUT-8(Ni) – is controlled by conformational isomerism. DUT-8(Ni), a pillared-layer MOF with Ni_2 paddle-wheels, **dabco** pillars and naphthalene dicarboxylate (**ndc**) linkers, can crystallize in many conformational isomers that depend on the orientation of the non-linear **ndc** linkers with respect to each other. While the open form is compatible with several of these conformations, only one of them, with alternating linker orientations, is stable as closed form. We show, by means of first principles calculations, that in the stable closed form, the appreciable lattice strain is compensated by London-dispersion between the **ndc** linkers that arrange with maximum overlap in a stacking order similar to the stacking in graphite. We substantiate these results by well-tempered metadynamics calculations at the DFT-based Born-Oppenheimer potential energy surface, by refined X-ray diffraction data and by nitrogen adsorption data obtained by experiment and Grand-Canonical Monte-Carlo simulations based on the DFT-optimized and PXRD-derived geometries. While the reported origin of flexibility cannot be generalized to all flexible MOFs, it offers a rational design concept of folding mechanisms in switchable MOFs by exploitation of the stabilization effect of linker stacking in the closed form.

Introduction

Metal-Organic Frameworks (MOFs)[1] are materials where molecular building blocks are stitched together by coordination bonds to form a periodic lattice, and where the spatially separated building blocks often result in large pores and high internal surface areas.[2] Some MOFs show remarkable structural flexibility and are capable to perform pronounced reversible structural transformations, many of them triggered by the chemical potential of guest molecules.[3] The simultaneous structural transformation of a MOF maintaining the lattice translational symmetry is called collective flexibility and associated with the so-called “breathing” phenomenon. This has first been demonstrated for MIL-53(Cr),[4] where opening and closing motions of the flexible MOF lattice resembling wine rack architectures. Further development of novel flexible MOF materials, their adsorption properties and application potential are described in recent reviews of Férey and Serre[5] and Schneemann *et al*.[6] One of the important applications of flexible MOFs is gas storage and release, where the gas is loaded in the fully open form whereas at lower pressure, the MOF “folds” together, reducing the pore volume and releasing the entire residual gas molecules from the structure, allowing for maximal improvement of working capacity and heat management.[7]

In the recent years, several groups reported approaches for explanation and prediction of the flexibility in MOFs. For example, the flexibility triggers in MIL-53[8] and in ELM-11[9] have been explained in atomistic detail. The most recent advances in the computational techniques that can be applied to explain the collective flexibility in MOFs are reviewed by Coudert.[10] All these techniques help to explain or to predict the breathing in well-known, strictly defined crystal structures. However, structures solved from X-ray diffraction data average over disorder in the MOF, which can originate from conformational isomerism of the linkers: non-linear linkers can arrange in different orientations with respect to each other, resulting in distinct crystal structures, as displayed for the example of DUT-8[11] in Figure 1.

Linker-based conformational isomerism and its influence on the adsorption properties of hypothetical, fully ordered structures has been discussed in the literature from a theoretical point of view.[12] However, to date it was not known that conformational isomerism of the linkers can have an impact on the collective flexibility of the framework. This effect is different from the opening/closing mechanisms in the most prominent flexible MOFs, including MIL-53 and ELM-11 which both have rigid linear linkers. For example, while MIL-53 **lt** (i.e. the closed form) and **ht** (i.e. the open form) are representatives of conformational framework isomers, the isomerism in this case is due to the change of the coordination parameters of the metal centre, and does not depend on the linker orientation.[13]

One striking example of a flexible material, where pronounced linker-based conformational isomerism is possible, is DUT-8(Ni), consisting of a nickel paddle-wheel (**pw**) connected by non-linear naphthalene dicarboxylate (**ndc**) linkers and forming 2D grids. The grids are pillared by 1,4-diazabicyclo[2.2.2]octane (**dabco**) forming an open framework with **pcu** topology and possessing 1D channels. DUT-8(Ni) has first been reported by Klein *et al.* in 2010[11] and afterwards thoroughly characterized by experiment and theory.[14,15,16,17]

Careful inspection of the structures reported in the literature reveals that DUT-8(Ni) is referring to two different frameworks. They are identical in their stoichiometry, topology, and show a very similar powder X-ray diffraction (PXRD) pattern of their open forms (see below), but they differ by the orientation of their non-linear **ndc** linkers, that is, they are conformational isomers (Figure 1). As we will show below, the linker orientation has a decisive influence on the London-dispersion interactions in the closed form and hence becomes the crucial element in stabilizing the closed form in this and potentially other MOF materials with collective flexibility. While different conformers of DUT-8(Ni) can hardly be distinguished in their open (as synthesized) forms, they strongly differ in structure and energy in the closed forms. As only one closed form is thermodynamically stable and compatible with experimental PXRD (the other spontaneously open), only one of the DUT-8(Ni) conformers shows collective flexibility.

Results and discussion

Among the many possibilities of arranging the **ndc** linkers, only two conformational isomers of the open structure, labelled here as **A** and **B,** and shown in Figure 1a,b, are compatible with the open structure that has been obtained from PXRD analysis. In structure **A,** the four **ndc** linkers are arranged in such a way around the Ni paddle-wheel that their ends are pointing in one and same direction (alternatingly all up or all down), while in structure **B** the **ndc** ends alternate in their orientation (Fig 1a). The open structures, indicated **(op)**, can be transformed into closed ones **(cl)** following a so-called "wine-rack mode". As in a wine rack, there are two modes possible to close it, which point in orthogonal directions (i.e. closing it by pulling either at the top and bottom or pulling at the left and right-hand sides). It is important to note that those different modes are equivalent in conformer **A** of

DUT-8(Ni), but differ for conformer **B**, resulting in two different closed structures. In the first one, **B(cl)^a**, the orientation of the **ndc** linkers is *aligned* (as it is the case for conformer **A(cl)**), but in the second one, **B(cl)^o** they have *opposite* orientation (Figure 1c). The atomistic structure of conformers **A** and **B** in open and closed forms are shown in Figure S1.

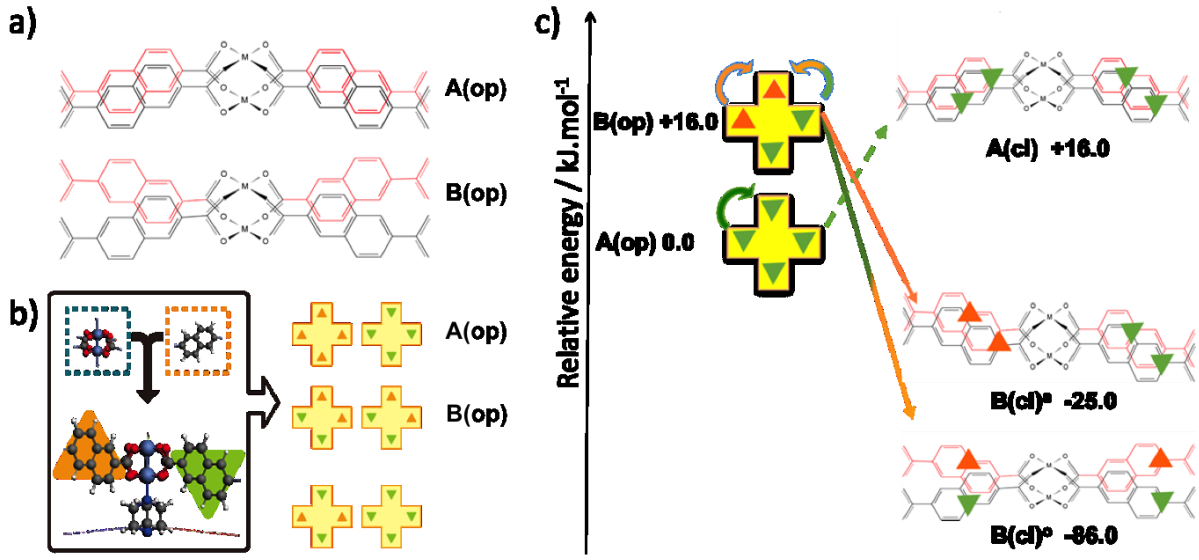


Figure 1: a) Metal paddle wheel unit with attached linkers of two conformational DUT-8(Ni) isomers (**A and B**) resulting in the most stable open forms of DUT-8(Ni). b) Many more conformational isomers of DUT-8(Ni) can be constructed. c) Transformation of **A(op)** to its closed form **A(cl)** and transformation of **B(op)** to its two inequivalent closed forms **B(cl)^a** and **B(cl)^o**, as indicated by the curved arrows on the left-hand side. The graph shows the interrelation of the three forms. Relative energies for the periodic structure are given per unit cell.

In the open form, without any solvent in the pores, conformers **A** and **B** are very similar: they are close in energy, **A(op)** being slightly more stable by 16 kJ mol^{-1} per unit cell (uc) one uc contains one Ni_2 paddle-wheel (**pw**), one **dabco**, and two **ndc** linkers. The accessible surface area calculated with a nitrogen-sized probe molecule is practically the same (2249 m^2 g^{-1} for **A(op)** and 2407 m^2 g^{-1} for **B(op)**). Their pore size (9.75 Å for **A (op)** and 9.95 Å for **B(op)**, see Figure S10) and their solvent accessible volumes[18] (66.2 % and 66.6 %, respectively) are also very similar. Thus, at first glance the two structures appear to be similar, which is also reflected by similar powder X-ray Diffraction (PXRD) patterns (Figure 2b) and GCMC simulations of nitrogen adsorption at 77 K which give very similar isotherms (**Figure S2**).

a) b)

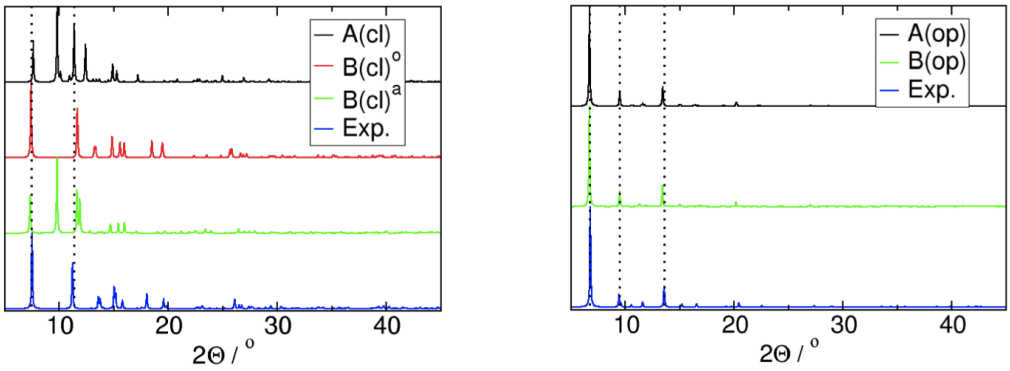


Figure 2. a) PXRD patterns of DUT-8(Ni) **cl** simulated from crystal structures obtained experimentally (Exp)[14] and from calculated optimized structures **A(cl), B(cl)°** and **B(cl)ª** in closed form. b) Simulated PXRD patterns of DUT-8(Ni) taken from experimentally obtained coordinates (Exp)[11] and calculated from optimized structures of **A(op)** and **B(op)** in open forms.

In the absence of guest molecules, however, both conformers behave very differently. Surprisingly, **A(op)** is more stable than **A(cl)**, even in the absence of guest molecules. Closing the structure costs about 16 kJ mol^{-1} per uc. In contrast, upon closure conformer **B** is stabilized, with significant energy gain of 86 kJ mol^{-1} per uc for the structure **B(cl)°** (with opposite linker orientation), and even the less favourable isomer **B(cl)ª** gets stabilized by 25 kJ mol^{-1} per uc. In order to understand this very different behaviour for two apparently very similar structures, we decompose the energy difference between open and closed forms into two components: The electronic energy difference gives, in absence of changes in the bonding pattern, the strain energy E_{str}, associated with the transformation from unstrained open to closed form. The remaining part of the total energy is the London dispersion contribution. Its difference between closed and open structures, ΔE_{disp}, reflects the increased interactions between the linkers in the closed structures. The numerical values of these energies are given in Table 1. In summary, closing the DUT-8(Ni) pores gives a large strain energy penalty of 60 to 135 kJ mol^{-1} per uc, while the gain in London dispersion energy ranges from 85 to 188 kJ mol^{-1} per uc.

The balance between E_{str} and ΔE_{disp} is the key to understand the collective switching in DUT-8(Ni). In conformer **A**, the cost in strain energy of 105 kJ mol^{-1} per uc that is required to close the pore is not compensated by the gain in ΔE_{disp} (-89 kJ mol^{-1}). Thus, DUT-8(Ni) conformer **A** should not possess flexibility, and its pores remain open even without the presence of any adsorbate. In contrast, conformer **B** has a very interesting energy balance upon closure. If closing follows the mode towards the aligned linker stacking to conformer **B(cl)ª** (see Figure 1c), the cost in strain energy is only 60 kJ mol^{-1} per uc. However, the gain in London dispersion energy is relatively small, i.e. 85 kJ mol^{-1} per uc, leading to a small stabilization of 25 kJ mol^{-1} per uc upon closure. The other wine-rack mode requires about twice the strain energy to go to **B(cl)°**, 102 kJ mol^{-1} per uc, but results in a much stronger London dispersion stabilization of 188 kJ mol^{-1} per uc (Table 1).

Table 1. Relative energy (ΔE) of the transformation of open to closed forms of conformer A and B, change of strain energy E_{str} and change of London dispersion energy ΔE_{disp}. All values are in kJ mol^{-1} per uc. The relative energy contains the PBE energy (without dispersion correction) and the additive London dispersion component. E_{str} is estimated as relative energy at the PBE level without London dispersion correction, while ΔE_{disp} is the relative energy of the D3 correction.

	A(op) → A(cl)	**B(op) → B(cl)°**	**B(op) → B(cl)[a]**
ΔE	+16	-86	-25
E_{str}	+105	+102	+60
ΔE_{disp}	-89	-188	-85

Closely inspecting the structure of the closed DUT-8(Ni) conformers sheds some light on these puzzlingly large differences in strain and London dispersion energies. Closing conformer **A** requires bending every second linker, and this bending is associated with a strong penalty in strain energy (Figure S1b, Table 1). On the other hand, the linkers are not overlapping strongly, so the gain in London dispersion energy is not sufficient to undergo a structural transition. The smallest strain penalty is observed for closing **B(op)** to **B(cl)[a]**, where the relatively small E_{str} value is due to the fact that **B(cl)[a]** has a cell volume that is about 30% larger than that of the other closed forms **A(cl)** and **B(cl)°**. Finally, **B(cl)°**, where the **ndc** linkers are in opposite direction, mark the lowest energy structure of the observed DUT-8(Ni) conformers. Here, the linkers show the slipped stacking pattern that is known from molecular crystals and graphite (Figure S1b), the phenyl rings are on top of one another, but slipped by about 1.4 Å (C-C bond length in aromatic systems), arranging in sp^2 carbon's favourite stacking that is known, for example, also from covalent-organic frameworks (COFs).[19,20] If we take into account the zero-point energy and thermal corrections for the **B(op) → B(cl)°** transition, the energy difference between the open and closed states is reduced to 69 kJ mol^{-1}, essentially due to the higher zero-point energy of conformer **B(cl)°**, while the difference in vibrational entropy contributions is small, favouring **B(cl)°** by 8 J mol^{-1} K^{-1}.

While the observed stacking in **B(cl)°** is the key to understand the stability of the closed structure, it also suggests strong differences in the electronic properties of open and closed form of DUT-8(Ni). Stacking of linkers has already been identified as means to introduce ballistic transport in MOFs, as for example for a derivative of SURMOF-2,[21] and the tight stacking of **ndc** linkers suggests even stronger impact on the band structure. The calculated band structures of **A(op)**, **B(op)** and **B(cl)°** are shown in Figure S3. While the open MOFs show only flat bands at the band edges, which indicate very low charge carrier mobilities, the **B(cl)°** shows distinct dispersive features in the valence and conduction bands, indicating ballistic charge carrier transport if doped or photo-excited.

While these results explain the peculiar relationship between the stability of the open and closed forms of DUT-8(Ni) and the conformational isomerism of this material, they only provide a static picture and do not shed light on the flexible nature of this material. To find out if the transition from open to closed form (and vice versa) is more likely in one of the conformers we carried out Born-Oppenheimer Molecular Dynamics simulations (BOMD), within the constant number of particles, constant pressure, constant temperature (NPT) ensemble (see Methods section).

When starting from the **A(cl)** structure, during the BOMD simulation at room temperature the structure spontaneously opens and transforms to **A(op)**. Thus, there is no free energy barrier for opening this MOF from its closed form, and we can conclude that the closed form is not stable at room temperature (Figure S4, black curve). In contrast, **A(op)** remains open for the time scale of the simulation (12 ps), which is consistent with the higher thermodynamic stability of the A(op) in

comparison to A(cl), with a wine rack vibration in the THz regime, 0.57 THz or approximately 18 cm^{-1}, being clearly visible in the potential energy profile of the BOMD run (Figure S5), and which is in agreement with experiment as discussed elsewhere.[16] In contrast, **B(cl)** remains stable in the closed form during a BOMD run, showing that the closed form is also a free energy minimum, while **B(op)** spontaneously closes to **B(cl)°** during the BOMD simulation, thus relaxing straight to the most stable conformer of DUT-8(Ni) in the absence of adsorbates (Figures S4 and S5).

The process of opening and closing the pores of conformer **B** is studied using metadynamics (MTD) in its well-tempered variant, again using DFT energies and gradients (BOMD) (for details, see Methods). We start from the most stable conformation **B(cl)°** and run the MTD in order to reach its open state, **B(op)**. The pore opening is controlled by two independent collective variables as shown in Figure 3b. Figure 3a shows that the free energy barrier to convert **B(cl)°** to its open state **B(op)** along each collective variable is roughly 30 $kJ.mol^{-1}$ per uc (one Ni **pw**, two **ndc** linkers and one **dabco**) in the absence of adsorbates.

a) b)

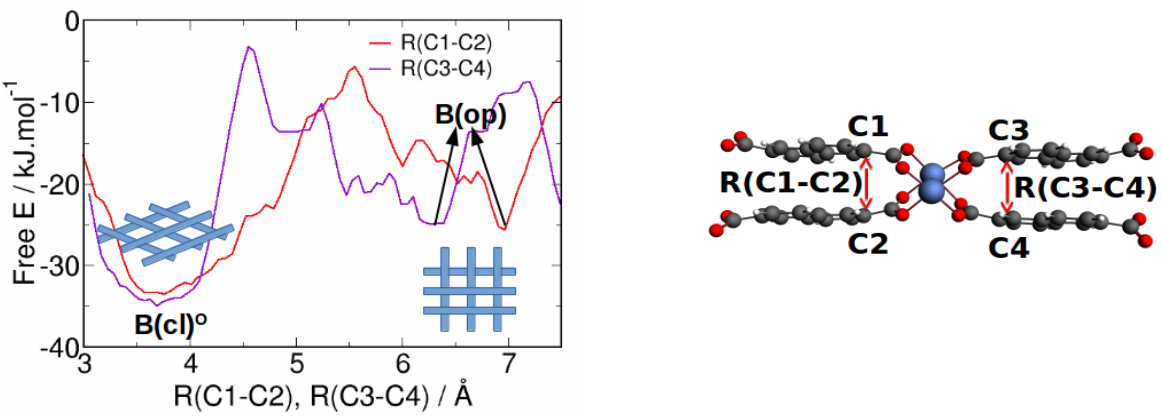


Figure 3. a) Free energy profile of the transformation of **B(cl)°** to **B(op)**. The energy is given in kJ mol^{-1} per uc. b) Definition of the collective variables.

We have attributed the flexibility in DUT-8(Ni) conformer **B** to the non-linear **ndc** linkers. To support this hypothesis, we studied the opening and closing for two derivatives of this material, one with anthracene dicarboxylate (**adc**) linkers, which are longer than **ndc** and also non-linear, and another one with biphenyl dicarboxylate (**bpdc**) linkers, which are only slightly longer than **ndc**, but linear. While the **adc**-substituted DUT-8(Ni) shows the same flexibility as the parent material (Figure S6), the **bpdc**-based MOF is rigid, with the lattice being destroyed if forced into the closed form (Figure S7).

So far we have shown that conformers **A** and **B** behave contrary in terms of collective flexibility. As the relative energy of their open forms is small, an important question is if it is possible to transform DUT-8(Ni) conformers into each other. To answer this question, we study the conversion of **A(op)** to **B(op),** which is particularly interesting as **A(op)** is thermodynamically somewhat more stable than **B(op)** and thus may serve as metastable open form of empty DUT-8(Ni). This transformation does not involve any bond breaking, but is associated with the rotation of **ndc** linkers. The MTD simulation, carried out for a super cell with two Ni paddle-wheel units with four **ndc** linkers, describes the simultaneous transformation of an infinitely large entire DUT-8(Ni) structure and thus only can serve as upper estimate of the transformation barrier. The rotational angle between **ndc** linker and paddle- wheel is selected as a collective variable. The free energy surface and corresponding profile, indicated in Figure 4, shows that the two linkers can be rotated independently (as low-energy paths are uncorrelated

between the two collective variables NDC1 and NDC2), and that the free energy barrier of a linker rotation is ~20 kJ mol^{-1} per uc at room temperature. This value is very close to the relative energy between **A(op)** and **B(op)** conformers (16 kJ mol^{-1}), and indicates that such interconversions are possible at ambient conditions.

a) b)

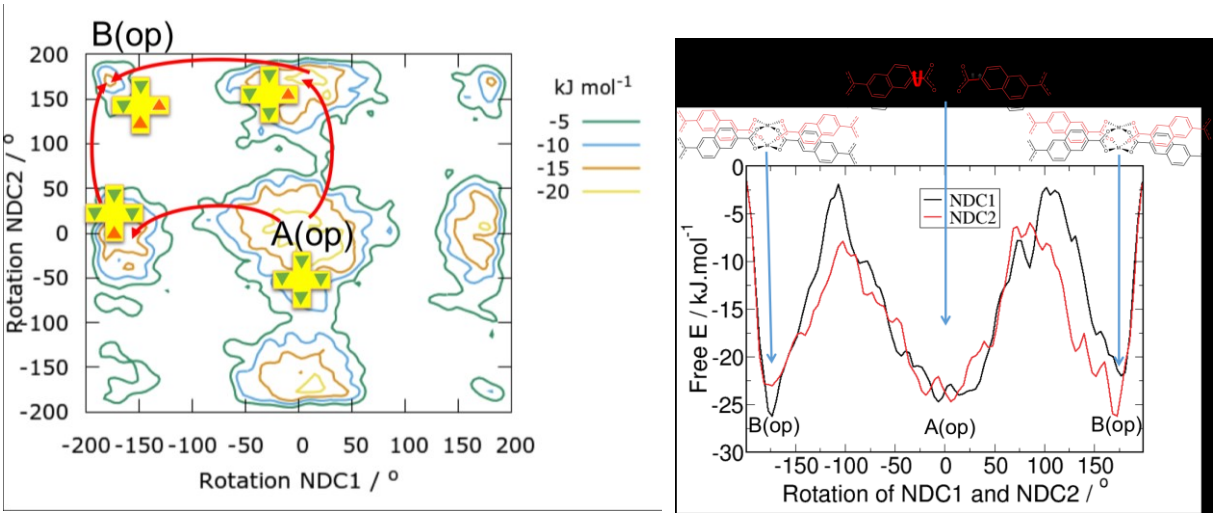


Figure 4. a) 2D contour plot of the free energy for a linker rotation, starting from **A(op)** (centre of the plot) and arriving at **B(op**) (corners of the plot). The collective variables are defined as a rotation along the alpha-C – carbonyl-C bond. The isolines on the contour plot connect regions with constant free energy; energy difference between two isolines is 5 kJ mol^{-1}. b) Free energy profile for the linker rotation, starting from **A(op)** (centre of the plot) and arriving at **B(op**) (left and right side of the plot), along the angle between the collective variables. Energies are in kJ mol^{-1} per uc.

A conclusion of the structural and MTD calculations is that the interconversion between conformers is energetically possible at ambient conditions, and that these calculations are not sufficient for the unambiguous structural assignment of the open form of DUT-8(Ni). To compare our structural predictions with experimental structures, we calculated their corresponding PXRD patterns and compared them with the reported structures. The numerical values of the lattice parameters are collected in Table S1.

Up to now, two experimental crystal structures have been reported in the literature: A closed structure with *P*1 symmetry and an alternating stacking of **ndc** molecules around the Ni-paddle-wheel as in the theoretically predicted **B(cl)°** structure[14] (see also Figure 2). An open structure, apparently the conformational analogue of **A(op)**,[11] crystallizes in *P*4/*n* space group. While the closed form, **B(cl)°**, is unambiguously identified and its cell parameters, no clear assignment is possible for the open structure due to the similarity of **A(op)** and **B(op)** (see cell parameters in Table S2 and comparison of simulated and experimental PXRD pattern in Figure 2). We further note that **A(op)** and **B(op)** conformers can interconvert by flipping of **ndc** linkers, subject to a modest energy penalty.

This prompted us to reinvestigate the crystal structure of the open DUT-8(Ni) structure by single crystal X-ray diffraction. Figures of merit for the tetragonal crystal structure of open pore phase, derived from the single crystal X-ray diffraction experiment performed in 2010,[11] are relatively high (Table S2) and therefore, the reliability of the structure in terms of the conformational isomerism is ambiguous. Therefore, we collected a room temperature single crystal X-ray diffraction dataset from the single crystal of DUT-8(Ni), pretreated by post-synthetic exchange of the guest molecules to dichloromethane

for one month. Just before the experiment, the crystal was soaked in dimethylformamide again to protect it from rapid solvent evaporation and transformation. The analysis of the crystal symmetry suggests a monoclinic base-centred cell with monoclinic angle of 97.545(9)° and a unit cell volume, comparable to that of the reported **A(op)** structure.[11] The coordination geometry of the paddle- wheel unit shows alternating orientations of the adjacent **ndc** molecules in the same way as in theoretically predicted **B(op)** conformer (Fig. S8b). In the previously reported tetragonal **A(op)** structure, Ni-paddle-wheels are surrounded by four equally orientated **ndc** ligands (Fig. S8a).[11] Such differences in the local geometry have an impact on the 3D structure of the resulting framework. Namely, in the case of **A(op)** structure, Ni-paddle-wheels form zig-zag-like chains along the *a* axis arranged in two alternating height (z) levels of the SBU in the unit cell (Fig. S8c). A view along the same crystallographic direction of **B(op)** structure indicates infinite unidirectional stair-like chains running along *a* (Fig. S8d), showing shifts of the paddle-wheels caused by the non-linear structure of the **ndc** molecule. Thus, we conclude that solvent exchange can interconvert DUT-8(Ni) conformational isomers in the open form, allowing the transformation between two polymorphs.

Experimental and predicted structures of the open forms of DUT-8(Ni) are apparently similar in terms of their crystallographic structure. What is the impact of the subtle differences on adsorption properties? To answer this question, we calculate the N_2 adsorption isotherms at 77K at predicted **A(op)** and **B(op)** and on the corresponding experimental frameworks from which all guest molecules have been removed. The isotherms, calculated after refinement of the collected datasets, are shown in Figure S2 (see also Table S3), and are very similar for **A(op)** and **B(op)**, independent if theoretical or experimental data are used, again not allowing the unambiguous assignment of the structures based on adsorption data. There are quantitative differences between experiment and theory that are within the range of expected accuracy of both theoretical and experimental approaches to assess the solvent-free structures. Details of the adsorption calculations are given in the Electronic Supplementary Information (ESI). The experimental N_2 adsorption isotherms for open and closed forms have been published earlier.[17]

Conclusion

We have shown that collective flexibility in DUT-8(Ni) is controlled by conformational isomerism. Stabilization of the closed pore by London dispersion interactions between organic linker molecules, which crucially depend on the arrangement of non-linear linkers, is identified as driving force to compensate the strain energy that is needed to close the framework of DUT-8(Ni). The observed linker stacking in the close form is the well-known motif that is found in graphite, but also, for example, in layered COFs.[19] These results are substantiated by relative energy calculations, well-tempered metadynamics, both on grounds of first-principles energies and gradients, as well as by a refined experimental structural analysis of the DUT-8(Ni) open forms. Simulated DUT-8(Ni) derivatives further support our hypothesis, non-linear **adc**-based DUT-8(Ni) is flexible, while a MOF with linear **bpdc**-linkers is found to be rigid in our structural and BOMD investigations. The stacking in the closed form of DUT-8(Ni) results in an appreciable dispersion of conduction and valence bands, and thus suggest band transport if charge carriers are generated by doping or photo-excitation. Two principal conformers have been identified, but many others are in principle possible. The flexible variant is by 16 kJ mol^{-1} per uc less stable in open form compared to its rigid counterpart and closes spontaneously in the absence of guest molecules, gaining a substantial energy of 86 kJ mol^{-1} per uc. Rotation of linkers, subject of a free energy barrier estimated to be in the order of 20 kJ mol^{-1} per uc, interconverts the conformers, and besides the two principal ones, many of the mathematically possible structural arrangements could exist. While it is straight forward to distinguish between closed and open forms the identification of open forms remains challenging due to very similar PXRD patterns, formation of domains of conformers in the crystallites and impact of the solvent molecules. The similarity is further

reflected by simulated N_2 adsorption isotherms at 77K. However, given the distinct geometry of closed **B(cl)°**, we conclude that the flexible form of DUT-8(Ni) is associated with conformational isomer **B** (see Figure 1).

Thus, we have demonstrated that structural design of closed frameworks, where linker interactions are maximized by means of London dispersion forces, can be exploited as means for the rational design of molecular framework compounds (MOFs, but also COFs) with collective flexibility. In this approach, London dispersion interactions, which can accumulate to significant amounts (here up to ~90 kJ mol^{-1} per linker), must be in the same order as the strain energy of the deformed, closed framework.

Methods

Computational Methods.

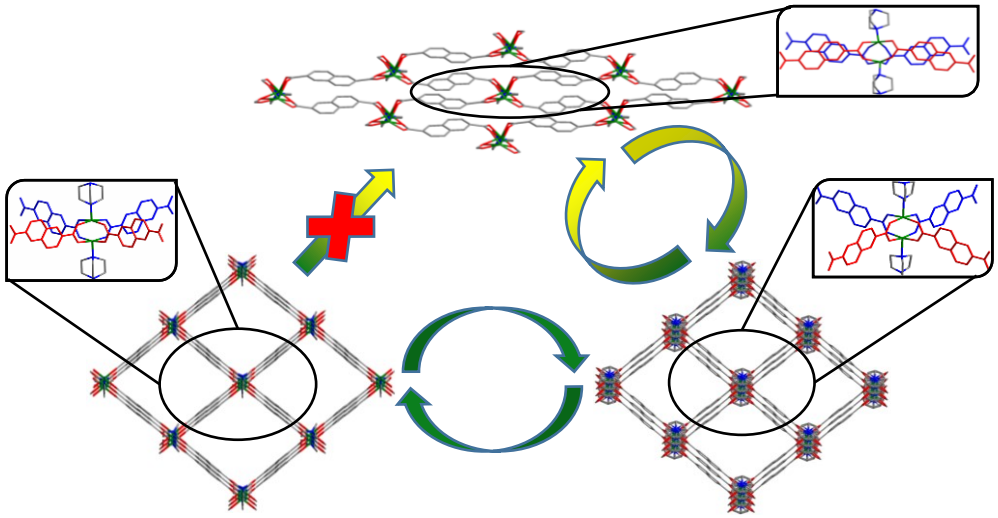
All geometry optimizations have been carried out within periodic boundary conditions using density-functional theory (DFT) employing the QUICKSTEP[22] module of CP2K.[23,24] We used the PBE functional,[25] Goedecker–Teter–Hutter (GTH) pseudopotentials[26] incorporating scalar-relativistic core corrections, and contracted Gaussian basis sets of DZVP quality, with a grid cutoff of 300 Ry for the BOMD simulations and 360 for the geometry optimization,[27] with Grimme's DFT-D3 dispersion correction.[28] Well-tempered metadynamics based on Born-Oppenheimer molecular dynamics (BOMD) employing DFT energies and gradients has been used to study the dynamical processes within the NPT ensemble at T = 300K and P = 1.0 bar. Electronic band structures and densities of states have been refined using the PBE0 hybrid functional[25,29] with the POB-TZVP basis set[30] as implemented in the CRYSTAL17 code.[31] N_2 Gas adsorption was simulated using grand canonical Monte Carlo (GCMC) simulations, implemented in the multipurpose code MuSiC.[32] More details are given in the ESI.

Single crystal X-ray diffraction

Single crystal of DUT-8(Ni), suitable for single crystal XRD experiment was selected from the sample, synthesized using earlier reported procedure.[17] After the synthesis, the solvent was exchanged to ethanol for three days with further exchange to dichloromethane for four weeks. Prior to the XRD measurement, the solvent was exchanged again to DMF. A single crystal was prepared in a glass capillary with d = 0.5 mm using an optical microscope and polarized light. A small amount of the mother liquid was deposited into the capillary before closing with wax in order to prevent the desolvation of the MOF during the experiment. Diffraction images were collected at room temperature using a Bruker KAPPA APEX2 diffractometer, equipped with 4-circle goniometer, Mo-K_α radiation (λ = 0.71073 Å, graphite monochromator) and APEX2 CCD-camera. The unit cell parameters were determined based on three short scans, performed on the different crystal orientations. Although a *C*-centred monoclinic unit cell was suggested, one-half of the Ewald sphere was scanned. The images were integrated using SAINT routine.[33] Further correction on Lorentz, polarization and absorption effects was performed with the help of SADABS software.[33] Since no systematic absences indicating the presence of screw axis or glide planes were found, the *C*2/*m* space group was used for the solution of the structure, performed *ab initio* by direct methods implemented in SHELXS-2016/4 program.[34] The obtained model was refined by full matrix least-squares on F^2 using SHELXL-2016/4.[34] All non-hydrogen atoms were refined in anisotropic approximation. Hydrogen atoms were refined in geometrically calculated positions using a "riding model" with $U_{iso}(H)$=1.2$U_{iso}(C)$. Anisotropic displacement parameters of the carbon atoms of **dabco** molecule were treated by using SIMU and DELU instructions in the refinement. Because of relatively high reliability parameters, the dataset was checked for twinning using the *TwinRotMat* routine, implemented in PLATON.[18] The program suggested the presence of two domains, related to each other by a 2-fold axis about (100). Therefore, the combination of TWIN (rotation matrix 1 0 0.5 0

-1 0 0 0 -1) and BASF instructions were used in both cases for the further refinement. All experimental details for this single crystal X-ray diffraction experiment as well as experimental data from earlier published tetragonal structure[11] are given in Table S2. CCDC-1857107 contains the experimental data for crystal structure of **B(op)**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table of Contents Graphics (ToC)



ToC text

The linker orientation in conformational isomers of DUT-8(Ni) determines the flexibility of this metal-organic framework.

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