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Tailoring Responsiveness of Metal-Organic Frameworks

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„Vielleicht gibt es hinter der gedruckten

Geschichte eine andere, viel größere Geschichte,

die sich ebenso wandelt, wie unsere Welt es tut?

Und die Buchstaben verraten uns darüber gerade

so viel wie ein Blick durch ein Schlüsselloch.

Vielleicht sind sie nicht mehr als der Deckel zu einem Topf,

der viel mehr enthält als wir lesen können."

Tintenherz

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FÜR MEINE ELTERN

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LIST OF ABBREVIATIONS

1D	one-dimensional
2D	two-dimensional
3D	three-dimensional
abtc	3,3′,5,5′-azobenzene-tetracarboxylate
BA	bisallyloxy
bbcdc	9,9′-([1,1′-biphenyl]-4,4′-diyl)bis(9H-carbazole-3,6-dicarboxylate)
bdc	1,4-benzenedicarboxylate
bdp	1,4-benzenedipyrazolate
BET	Brunauer-Emmett-Teller
bIm	benzimidazolate
BME	bis-(2-methoxyethoxy)
BPy	bispropynyloxy
btc	benzene-1,3,5-tricarboxylate
btca	benzotriazolide-5-carboxylate
cp	closed pore
CSD	Cambridge Structural Database
CUS	coordinatively unsaturated sites
dabco	1,4-diazabicyclo[2.2.2.]octane
DAC	diamond anvil cell
DB	dibutoxy
DE	diethoxy
DMA	diemthylammonium
DMF	N,N-dimethylformamide
dobdc	2,5-dioxido-1,4-benzenedicarboxylate
DiP	diisopropoxy
DP	dipropoxy
DUT	Dresden University of Technology
EtOH	ethanol
fu-bdc	2,5-functionalized-1,4-benzenedicarboxylate

HKUST	Hongkong University of Science and Technology
HPPXRD	high-pressure powder X-ray diffraction
IAST	ideal adsorbed solution theory
Im	imidazolate
ip	intermediate pore
IRMOF	isoreticular metal-organic framework
IUPAC	International Union of Pure and Applied Chemistry
L	linker
lp	large pore
M	metal
MeOH	methanol
MIL	Matériaux de l'Institut Lavoisier
mIm	2-methylimidazolate
MOF	metal-organic framework
ndc	2,6-naphthalenedicarboxylate
NGA	negative gas adsorption
NLC	negative linear compressibility
np	narrow pore
NU	Northwestern University
OMS	open metal site
op	open pore
P	pillar
PCN	porous coordination polymer
PIA	pressure-induced amorphisation
PSD	post-synthetic deprotection
PSE	post-synthetic exchange
PSM	post-synthetic modification
PTM	pressure transmitting medium
PXRD	powder X-ray diffraction
SALE	solvent-assisted linker exchange
SBU	secondary building unit
TPD	temperature programmed desorption
UiO	Universitetet i Oslo
ZIF	zeolitic imidazolate framework

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ABSTRACT

In the last three decades, highly porous and crystalline metal-organic frameworks (MOFs) have emerged as a fascinating material class. Built from metal nodes that are connected by organic linkers, their modular building principle gives rise to a vast number of combinations leading to almost 100,000 already reported MOFs in the Cambridge Structural Database. Their modularity, allowing for the targeted design of properties, make MOFs an intensively studied material family that shows large promises in many applications such as gas separation and gas storage processes, catalysis and drug delivery, to name just a few. Furthermore, MOFs show interesting and useful responses to external stimuli such as host-guest interactions, light, changes in temperature or pressures, making them auspicious candidates as smart (or intelligent) materials. The responses shown involve static and dynamic responsiveness, where the prior describes interactions between the MOF and guest molecules without structural changes, whereas the latter comprises structural changes triggered by any stimulus. In turn, these responses are very useful, *e.g.* static responses like size exclusion or specific interactions between the MOF and a guest molecule that enable the selective adsorption of guest molecules. However, using pressure as an external stimulus to trigger a dynamic response is relatively new and there is a need to uncover the underlying thermodynamics that drive these dynamic responses.

The work within this thesis is divided into two parts. In the first part, the role of intrusive gases on the separation performance of the MOF Co_2dobdc (dobdc^{4-} = 2,5-dioxidobenzenedicarboxylate) which has open metal sites (OMSs) was explored. This MOF is particularly known for its high sorption selectivities towards olefins over paraffins in mixtures of light hydrocarbons. The OMSs play a crucial role in adsorption process because of the strong π-complexation of the electron rich π-bonding orbital in the olefin and the vacant σ-like orbital of the metal centre. If this preferential adsorption site is blocked by water molecules or carbon dioxide (that could be present as traces in the gas stream under realistic conditions in the industry), the material could lose its high selectivity and its use in application. Therefore, we investigated the separation performance of hydrated Co_2dobdc (*i.e.* water molecules coordinated to the OMSs) in multi-component adsorption measurements with mixtures of propene and propane and showed that, while initially surprising, the selectivity towards propene is retained. Based on simulations of binding energies it was assumed that this unexpected result is a consequence of the water molecules acting as a new binding site for propene due to π-H interactions and therefore compensating the blocked preferential adsorption site.

The second part of this thesis deals with the mechanical properties of MOFs. For the first time, a hydrostatic set-up was used to investigate MOFs that allows to apply high pressures in very small steps of Δp = 0.005 GPa in the pressure range p = ambient – 0.4 GPa. We demonstrated that this set-up is well suited to study soft materials like MOFs that show interesting dynamic responses such as phase transitions in this 'low' high-pressure region. Here, two well-studied examples, namely ZIF-4 ($ZnIm_2$ with Im^- = imidazolate) and ZIF-8 ($Zn(mIm)_2$ with mIm^- = 2-methylimidazolate), were reinvestigated and their structural responses extensively studied. Another MOF subclass known for its structural flexibility when triggered by external stimuli are the pillared-layer MOFs $M_2(fu-bdc)_2dabco$ (fu-bdc = 2,5-functionalised-1,4-benzenedicarboxylate and dabco = diazabicyclo[2.2.2]octane). Previous works have shown that the unfunctionalised parent MOFs can be rendered structurally flexible through the introduction of a conformationally flexible sidechain into the linker backbone and a whole library of these functionalised linkers and the respective MOF exist. We investigated their responsiveness to pressure for the first time and compared the response of the functionalised pillared-layer MOF $Cu_2(DB-bdc)_2dabco$ (DB = dibutoxy) to the unfunctionalised parent $Cu_2(bdc)_2dabco$. Here, it was shown that the unfunctionalised MOF amorphises at high pressures, while the functionalised MOF undergoes a phase transition from an open pore to a closed pore phase, known as breathing. Molecular dynamics simulations revealed that the open pore form of the functionalised MOF is stabilised by configurational entropy, a parameter so far overlooked in the design and manipulation of stimuli-responsive MOFs.

ZUSAMMENFASSUNG

Hochporöse und kristalline Metallorganische Gerüstverbindungen (metal-organic frameworks, MOFs haben sich in den letzten drei Jahrzehnten zu einer faszinierenden Materialklasse entwickelt. Ihr modulares Bauprinzip aus Metallknoten, die mittels organischer Linker verbunden sind, erlaubt eine nahezu unbegrenzte Anzahl an Kombinationen, welche sich in den fast 100.000 publizierten Strukturen in der Cambridge Structural Database (CSD) widerspiegelt. Auch erlaubt diese Modularität das gezielte Design und Einstellen von Eigenschaften, wodurch MOFs zu einer vielbeachteten und vielversprechenden Materialklasse wurden, die Potential für eine Vielzahl an Anwendungen zeigen, unter anderem für Gasspeicherung und -trennung, Katalyse und Arzneimittelabgabe. MOFs zeigen interessante und nützliche Reaktionen auf externe Stimuli wie Wirt-Gast-Interaktionen, Licht, Temperatur- oder Druckänderungen, was sie ebenfalls zu vielversprechenden Kandidaten als intelligente (oder smarte) Materialien macht. Die gezeigten Reaktionen umfassen statisches und dynamisches Antwortverhalten, wobei ersteres die Interaktionen zwischen dem MOF und den Gastmolekülen ohne strukturelle Veränderungen beschreibt, während letzteres strukturelle Veränderungen umfasst, die durch jeden Stimulus ausgelöst werden. Dieses Antwortverhalten ist wiederum sehr nützlich, z.B. ermöglichen statische Reaktionen wie Größenausschluss und spezifische Interaktionen zwischen dem MOF und einem Gastmolekül die selektive Adsorption von Gastmolekülen. Die Verwendung von Druck als externer Stimulus zur Auslösung einer dynamischen Reaktion ist jedoch relativ neu und es besteht die Notwendigkeit, die zugrunde liegende Thermodynamik zu verstehen, die diese dynamischen Reaktionen antreibt.

Die Studien im Rahmen dieser Doktorarbeit sind in zwei Teile gegliedert. Im ersten Teil wurde die Rolle von Störgasen auf die Trennleistung des MOFs Co_2dobdc ($dobdc^{4-}$ = 2,5-Dioxidbenzoldicarboxylat) mit ungesättigten Koordinationsstellen (open metal sites, OMS) untersucht. Dieser MOF ist insbesondere für seine hohe Sorptionsselektivität für Olefinen gegenüber Paraffinen aus Kohlenwasserstoffgemischen bekannt. Die OMSs spielen eine entscheidende Rolle im Adsorptionsprozess aufgrund der starken π-Komplexierung des elektronenreichen π-Bindungsorbitals im Olefin und des vakanten π-ähnlichen Orbitals des Metallzentrums. Wenn diese bevorzugte Adsorptionsstelle durch z.B. Wassermoleküle oder Kohlenstoffdioxid blockiert wird (die unter realistischen Bedingungen in der Industrie als Spuren im Gasstrom vorhanden sein können), könnte das Material seine hohe Selektivität und seine Verwendung in der Gastrennung verlieren. Daher haben wir die Trennleistung von hydratisiertem Co_2dobdc (d.h. die freien Bindungsstellen an den OMSs sind mit Wassermolekülen abgesättigt) in Mehrkomponenten-Adsorptionsmessungen mit Mischungen aus Propen und Propan untersucht und gezeigt, dass die Selektivität

gegenüber Propen erhalten bleibt, was auf den ersten Blick überraschend scheint. Simulationen der Bindungsenergien führten zu der Annahme, dass dieses unerwartete Ergebnis eine Folge davon ist, dass die Wassermoleküle aufgrund von π-H-Wechselwirkungen als neue Bindungsstelle für Propen fungieren und somit die blockierte bevorzugte Adsorptionsstelle kompensieren.

Der zweite Teil dieser Doktorarbeit befasst sich mit den mechanischen Eigenschaften von MOFs. Zum ersten Mal wurde ein hydrostatischer Aufbau zur Untersuchung von MOFs verwendet, der es erlaubt, hohe Drücke in sehr kleinen Schritten von Δp = 0,005 GPa im Druckbereich p = Umgebungsdruck - 0,4 GPa anzuwenden. Damit haben wir gezeigt, dass dieser Aufbau gut geeignet ist, um weiche Materialien wie MOFs zu untersuchen, welche interessante dynamische Reaktionen wie Phasenübergänge in diesem "niedrigen" Hochdruckbereich zeigen. Dazu wurden hier die strukturellen Reaktionen zweier gut untersuchte Materialien, nämlich ZIF-4 ($ZnIm_2$ mit Im^- = Imidazolat) und ZIF-8 ($Zn(mIm)_2$ mit mIm^- = 2-Methylimidazolat), eingehend untersucht. Eine weitere MOF-Unterklasse, die für ihre durch externe Stimuli ausgelöste strukturelle Flexibilität bekannt ist, sind die MOFs $M_2(fu\text{-}bdc)_2dabco$ (fu-bdc = 2,5-funktionalisiertes-1,4-Benzoldicarboxylat und dabco = 1,4-Diazabicyclo[2.2.2]octan). Frühere Arbeiten haben gezeigt, dass die nicht funktionalisierten MOFs durch die Einführung einer konformativ flexiblen Seitenkette in den Linker strukturell flexible gemacht werden können, und es existiert eine ganze Bibliothek dieser funktionalisierten Linker und der entsprechenden MOFs. In dieser Arbeit untersuchten wir zum ersten Mal ihre Antwortverhalten auf Druck und verglichen die Reaktion des funktionalisierten MOFs $Cu_2(DB\text{-}bdc)_2dabco$ (DB = Dibutoxy) mit dem unfunktionalisierten MOF $Cu_2(bdc)_2dabco$. Hierbei konnte gezeigt werden, dass der unfunktionalisierte MOF bei hohen Drücken amorph wird, während der funktionalisierte MOF einen Phasenübergang von einer offenporigen zu einer geschlossenporigen Phase durchläuft, die als ‚Atmung' bezeichnet wird. Molekulardynamiksimulationen ergaben, dass die offenporige Form des funktionalisierten MOF durch die Konfigurationsentropie stabilisiert wird; ein Parameter, der bisher beim Design und der Manipulation von stimuli-responsiven MOFs übersehen wurde.

1 MOTIVATION

Towards the Design of Smart Materials

At the heart of materials science is the quest for the design and development of new materials that are highly functional, high-performing, preferably easy and cheap to produce, sustainable, resource-friendly and robust. This 'swiss army knife' would be suitable in an application of high technological relevance and in the best case also addresses current societal challenges. For instance, this material could be used in the storage of greenhouse gases like carbon dioxide or methane, illustrate a high storage capacity, low production costs and low energy consumption when the gas is released to be converted into a useful product. Other materials could specifically be designed to possess more than one function and/ or simultaneously serve as a part of a device functionality to minimize consumption of resources and energy, and as a convenient side effect reduce the device's space requirements, the weight and enhance practicability and compactness. In this context, the class of so-called smart or intelligent materials have attracted the fascination of (material) scientists and the public alike.

The term smart or intelligent materials first appeared in the late 1970s and has had an impact on decades of research activities ever since. I. AHMAD described smart materials as "*A system or material which has built-in or intrinsic sensor/s, actuator/s and control mechanism/s whereby it is capable of sensing a stimulus, responding to it in a predetermined manner and extent, in a short/ appropriate time and reverting to its original state as soon as the stimulus is removed.*"[1] Broadly speaking the term 'smart' does not describe the material itself but rather its response and adaptiveness to an external stimulus such as mechanical, thermal, chemical, magnetic and optical stimuli, which generates a useful property. Nowadays smart materials span a broad range including photochromic, thermochromic, chemochromic, self-healing, magnetic-sensitive and shape memory materials.[*] Ideas for smart materials are often inspired by examples found in nature which provides a fascinating and rich source of functional and smart materials inherently developed in the past million years.

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[*] For a detailed overview and further examples of smart materials, the interested reader is referred to Refs. 2–8.

When designing smart materials with tailored responses towards certain external stimuli, experimentalists look for design principles to guide them in development. To derive such design principles and guidelines, researchers must ask the right questions that surpass the apparent *"How can we design smart materials with useful stimuli-responsive behaviour?"* and address more detailed aspects like *"What are the fundamental parameters that drive the stimuli-responsive behaviour?"* and *"How can we manipulate the macroscopic parameters on a microscopic level via (small) chemical changes?"*. Determining the underlying fundamental parameters that drive the stimuli-responsive behaviour is crucial to derive design principles based for instance on structure-property relations. Furthermore, design principles help in manipulating (*i.e.* fine-tuning) stimuli-responsive properties and in predicting new possible stimuli-responsive materials. In this context, metal-organic frameworks (MOFs) have emerged as a tantalizing material platform in the last 20 years due to their unsurpassed chemical versatility that allows them to meet the requirements when developing and synthesising responsive, multifunctional and tuneable (*i.e.* smart) materials.[9] Their hybrid nature, built from organic and inorganic parts, in combination with their intrinsic porosity (which distinguishes them from other coordination networks) makes them possible candidates in a vast number of applications ranging from the aforementioned carbon dioxide capture, gas storage in general, gas separation, sensing, catalysis, to medical applications like drug delivery. While the number of synthesised MOFs increased rapidly since the first reports in the 90s,[10,11] researchers are seeking to uncover underlying design principles, establish structure-property relations and finally bring MOFs into application as smart materials.

2 INTRODUCTION

Metal-Organic Frameworks –
An Inorganic Chemist's Toolbox for Smart Materials?

2.1 The Development of Coordination Chemistry Towards Three-Dimensional Coordination Polymers

The development of modern coordination chemistry as known today started in the late 19th century when the first coordination compounds were synthesised. At that time, inorganic chemists like SOPUS MADS JØRGENSEN synthesised many new coordination complexes and tried to explain their spatial arrangement as chains of molecules bound to the metal atom according to concepts known from organic chemistry.[12] But it was ALFRED WERNER who proposed the right spatial arrangement for the $[Co(NH_3)_6]Cl_3$ complex and analogues in 1893, with the metal centre being coordinated by ligands in an octahedral fashion.[13] This ground-breaking work on these species, now coined as Werner-type complexes, established the principles of and decisively advanced coordination chemistry, paving the way for many important developments towards coordination polymers extending in all three dimensions. A few milestones in the development of coordination chemistry are shown in Figure 1. Although metal-cyanide coordination polymers like Prussian Blue ($Fe_4[Fe(CN)_6]_3$) have been known since the 18th century – long before WERNER's discovery – its crystal structure remained elusive until 1977,[14] and keeps fascinating scientists until today.[15] The case of the nickel-cyanide compounds studied by KARL ANDREAS HOFMANN was similar and first reported in 1897.[16] It took until the 1950s to explain that the structure of the so-called Hofmann clathrate $[Ni(CN)_2(NH_3)](C_6H_6)$ consists of a 2D square grid of octahedral and square planar coordinated Ni(II) ions linked by cyanide ligands and ammonia ligands in the axial position pushing the sheets apart with benzene molecules residing in between the sheets. [17] Based on the structural explanation it was also shown then that by replacing the ammonia ligands with organic diamines a 3D coordination network could be obtained giving rise to the development of the Hofmann-type coordination polymers.[18,19]
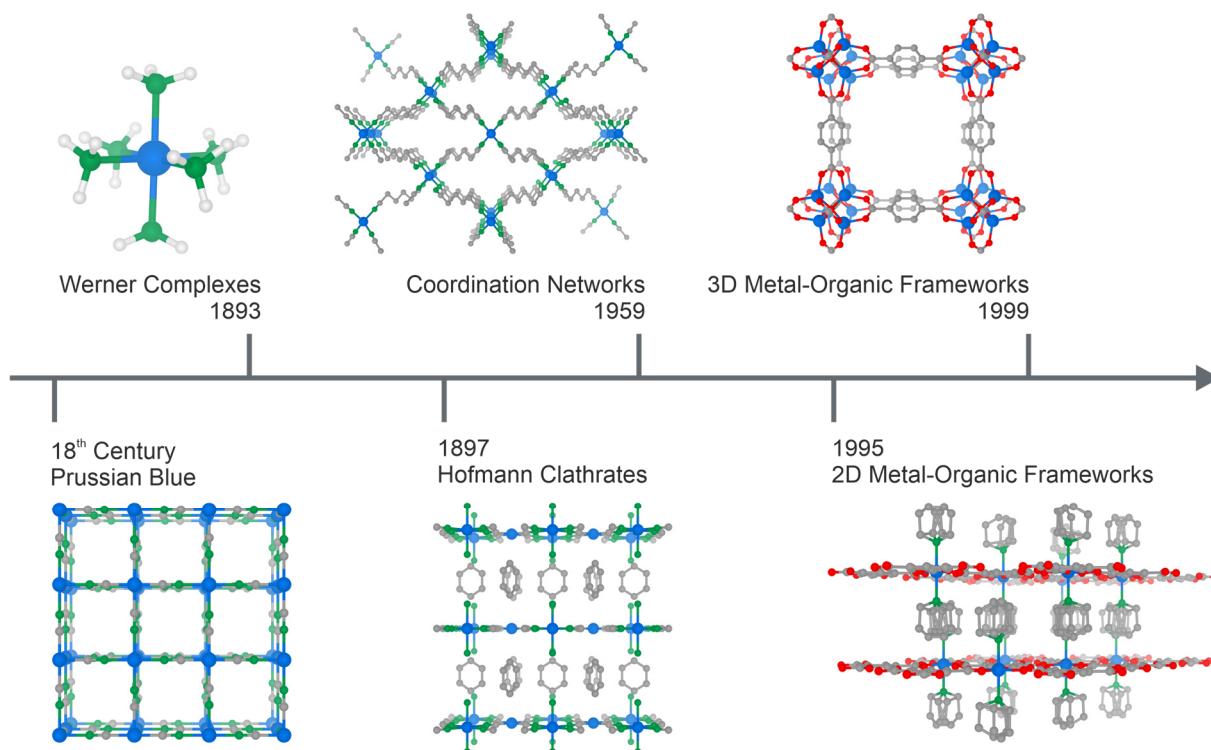
Figure 1. Milestones in the development of coordination chemistry towards MOFs. Colour code: Metal: blue, C: grey, O: red, N: green. H omitted for clarity reasons.

In the context of the advance in the last decades, the IUPAC (International Union of Pure and Applied Chemistry) defined the terminology of coordination compound, polymer and network in 2013 to avoid any misconceptions.[20] Briefly, a coordination compound is *"[...] any compound that contains a coordination entity."* with the coordination entity being an ion or neutral molecule that is surrounded by a group of atoms, so-called ligands. When extending this coordination compound into one, two or three dimensions, one ends up with a coordination polymer. It is important to note that coordination polymers do not necessarily need to be crystalline. Coordination networks are considered as a subclass of coordination polymers having additional *"[...] cross-links between two or more individual chains, loops or spiro-links [...]"*.

2.2 Metal-Organic Frameworks

The interest in 3D coordination polymers and networks finally grew when BERNARD F. HOKSINS and RICHARD ROBSON published their pioneering works on *"[...] a new and potentially extensive class of solid polymeric materials with unprecedented and possible useful properties [...]"* in the early 1990s, using a net-based approach as a synthetic strategy to design porous coordination polymers.[10,21] Their works can be seen as precursors to what OMAR M. YAGHI coined the term metal-organic framework in 1995 for when he synthesised a porous coordination network that retained its structure even upon removing the pore-filling solvent molecules (see Figure 1).[11] This discovery gave rise to a

whole new research field that rapidly increased within the last three decades. As the term metal-organic framework can be misleading – it does not consider the potential porosity – the IUPAC defined it as the following

> *"A metal–organic framework, abbreviated to MOF, is a coordination network with organic ligands containing potential voids."*[20]

Furthermore, the definition clearly differentiates between coordination networks, which MOFs are a subclass of, and porous coordination networks that are MOFs. Hence, some researchers prefer the terms porous coordination polymers or porous coordination networks to emphasise the intrinsic porosity of MOFs.[22] However, it should be noted that the nomenclature of MOFs is not systematic and mostly their trivial names are used, not revealing the nature of the metal or linker used but rather to which group (chemically but mostly laboratory wise) it belongs to.

To understand why there is so much interest in MOFs one should take a closer look at their structure. The schematic in Figure 2 shows the underlying coordination building block principle of MOFs: the inorganic secondary building units (SBUs, blue spheres) are interconnected by organic linker molecules (black rods) assembling to an infinite 3D network with a high regularity. Typically, metal ions or metal-oxo clusters are used as SBUs and multidentate organic molecules such as carboxylates, amines, hydroxides as linkers and the judicious choice thereof lead to the framework with a desired topology.[23–26] The sheer number of possible metal-linker combinations makes MOFs an extremely divers and versatile material class and the targeted design of MOFs in combination with their accessible large internal surface areas and (ultra)high porosity allows for many potential applications ranging from gas storage[27–29] and separation[30–32], to catalysis[33–35] and electro-optic applications,[36,37] to mention only a few possibilities.
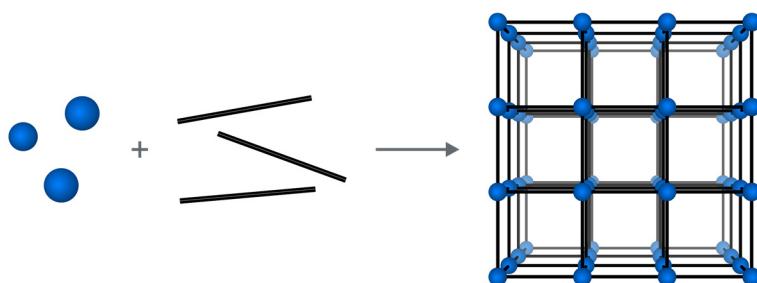
Figure 2. Schematic of a MOF unit built by inorganic SBUs (blue spheres) and organic linkers (black rods).

MOFs are commonly (but not exclusively) synthesised via solvothermal synthesis where the metal precursor, the linker and a suitable (often polar) solvent are mixed in a reaction vessel under autogenous pressures and elevated temperatures.[38–40] Thus, the crystalline as synthesised MOF contains the solvent molecules in its pores which are removed in vacuo and at elevated temperatures after the synthesis. It is important to note that not all MOFs keep their permanent porosity after the removal of solvent or generally speaking guest molecules. In 1998 SUSUMU KITAGAWA classified MOFs into three generations dependent on their structural properties, see Figure 3.[41] The 1st generation collapses upon removal of guest molecules and only a few cases are known where the collapse is

reversible. The 2nd generation is categorized by retaining its overall structure without any collapse or structural changes. Therefore, MOFs of this generation are termed rigid. MOFs of the 3rd generation undergo a (reversible) structural change when guest molecules are removed and more details about this responsive behaviour are given in chapter 2.4.
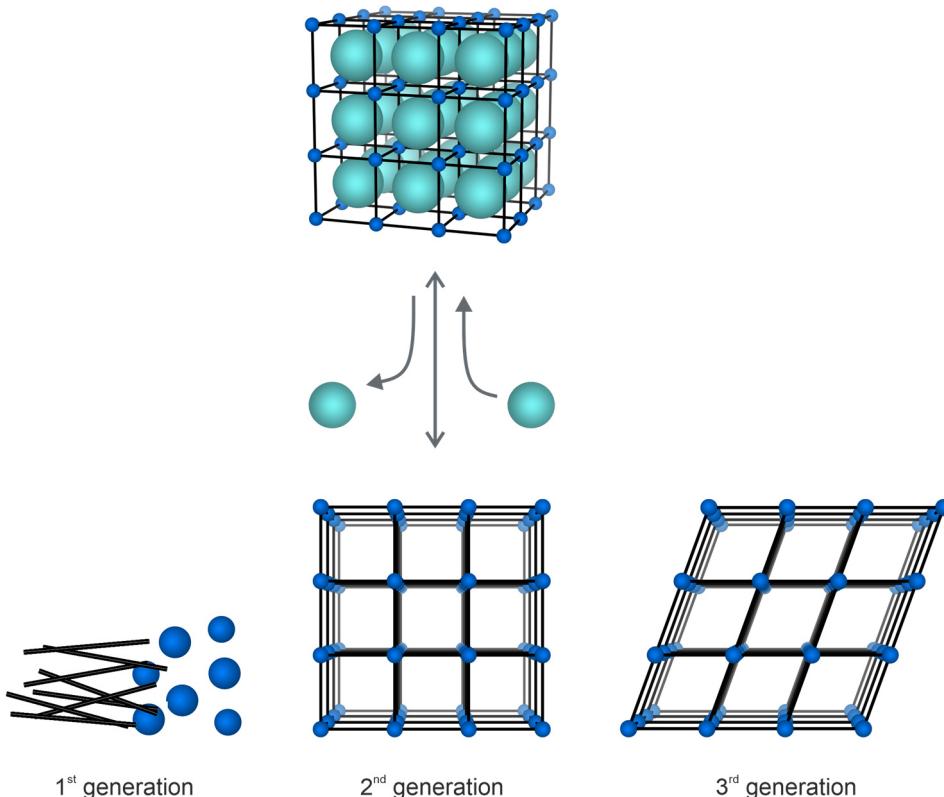
Figure 3. Illustration of the three generation of MOFs classified by KITAGAWA dependent on their structural behaviour upon solvent removal. Colour code: SBU: blue spheres, linker: black rods, solvent molecules: turquoise.

A prominent example of the 2nd generation and among the first MOFs reported by YAGHI *et al.* in 1999 is the iconic MOF-5 shown in Figure 4.[42] MOF-5 ($Zn_4O(bdc)_3$ with bdc^{2-} = 1,4-benzenedicarboxylate) is constructed from tetrahedral Zn_4O clusters that are interconnected by bdc linkers and build a primitive cubic structure. Retaining the structure after solvent removal gives rise to a high accessible surface area (S_A = 2900 $m^2 \cdot g^{-1}$), low density (ρ = 0.59 $g \cdot cm^{-3}$) and good thermal stability (T_c = 350 °C). Based on this structure, YAGHI and MICHAEL O'KEEFFE developed the concept of reticular synthesis (also known as reticular chemistry).[43–45] This concept is based on the idea that the MOF structure can be seen as a net built from linkers (organic ligands) and connectors (metal nodes) as already used in describing the topology of the purely inorganic zeolites. When for instance differently modified or expanded linkers having the same coordination geometry are assembled with the same connector, the MOFs will show the same topological features.

Applying this concept to MOF-5, the authors were able to synthesise a family of MOFs with elongated or functionalised linkers (still illustrating the same coordination geometry as the bdc linker) that are isoreticular by retaining the same primitive cubic structure as MOF-5 but with a chemically different pore space.[46] Therefore, this MOF family was named IRMOF (isoreticular MOFs, with MOF-5 = IRMOF-1) and two examples, namely

IRMOF-10 (Zn$_4$O(bpdc)$_3$ with bpdc^{2-} = biphenyl-4,4'-dicarboxylate) and IRMOF-16 (Zn$_4$O(tpdc)$_3$ with tpdc^{2-} = terphenyl-4,4''-dicarboxylate), are illustrated in Figure 4 alongside MOF-5. However, the increasing pore size may cause interpenetration of the frameworks and the degree of interpenetration was controlled in the IRMOF family by the choice of the synthesis conditions.

MOF-5
IRMOF-1   IRMOF-10   IRMOF-16
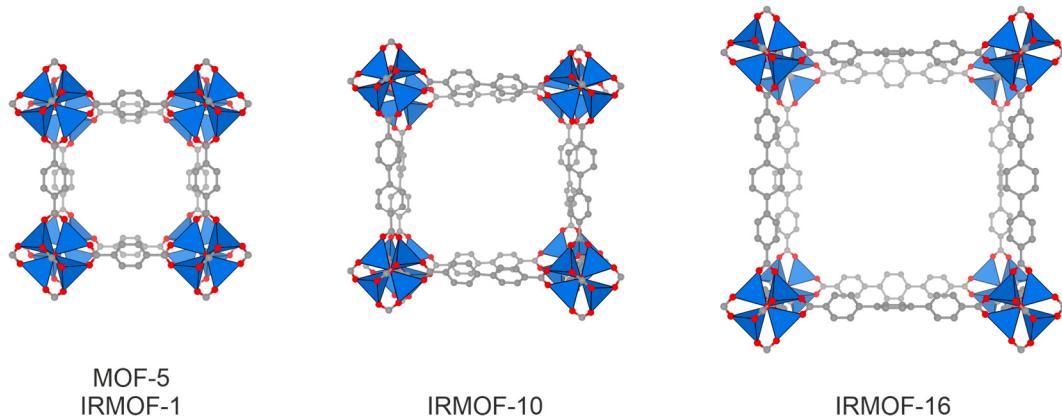
Figure 4. Crystal structure of MOF-5 and two representatives of the IRMOF family, namely IRMOF-10 and IRMOF-16, to show the increasing pore size with increasing linker length. Colour code: Zn: blue, C: grey, O: red. H omitted for clarity reasons

2.3 The Concepts of Functionalisation[†]

With the growing interest in MOFs, researchers aimed to design MOFs with fine-tuned physicochemical properties to meet the specific requirements for application for instance in hydrogen storage or carbon dioxide capture.[47,48] The concept of reticular chemistry opened the door towards introducing functional groups into the MOF by exploiting the organic nature of the linker. Mainly two approaches are known how the functionalisation of the linker is achieved and a schematic is shown in Figure 5. The first is done via functionalisation prior to the MOF synthesis and provides many possibilities to attach functional groups using knowledge from organic chemistry.[49–52] However, some aspects have to be considered. For instance, if the functional group strongly coordinates to the metal ion or reacts with the reagents during the synthesis, the formation of the framework is inhibited or a framework with a different topology than desired may form. Furthermore, if the implemented functional group changes the solubility and thermal stability of the linker, a different synthesis route might be required (*e.g.* different solvents, use of modulators, reaction temperature and time *etc.*) making time-consuming crystal engineering studies necessary. The second approach can potentially circumvent these problems by implementing the functional group after synthesis, correspondingly known as

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[†] This chapter is intended to give a general overview of the possibilities how to functionalise MOFs. For detailed examples, the reader is referred to the references given in this chapter.

I) Linker functionalisation prior to MOF synthesis
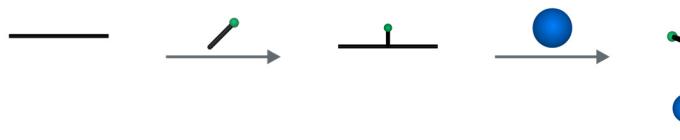
II) Post-synthetic modification
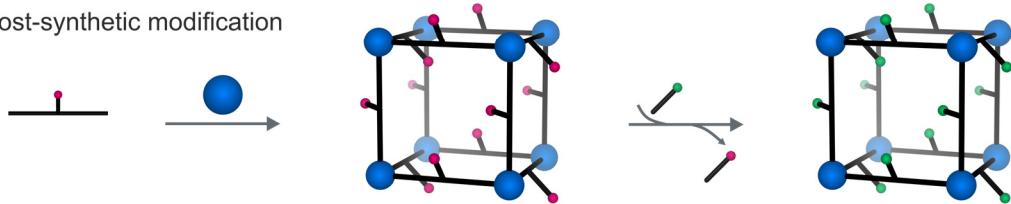
III) Post-synthetic deprotection
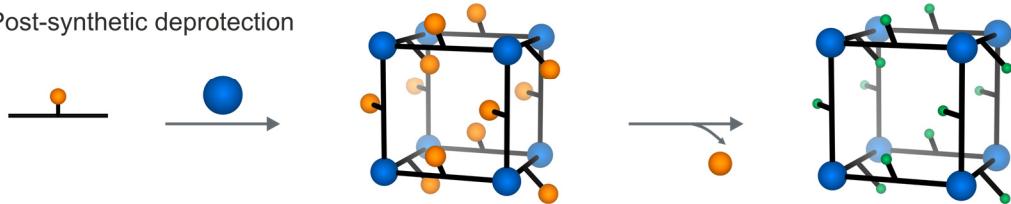
IV) Solvent-assisted linker exchange
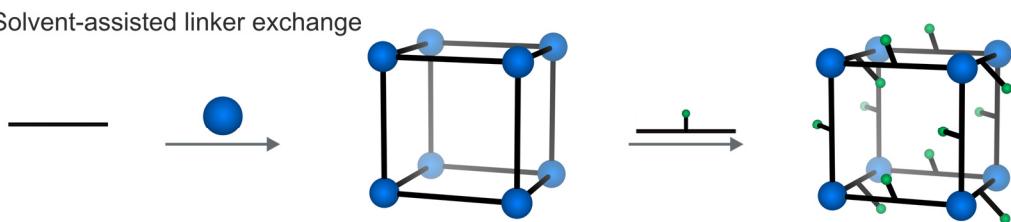
V) Metal node functionalisation
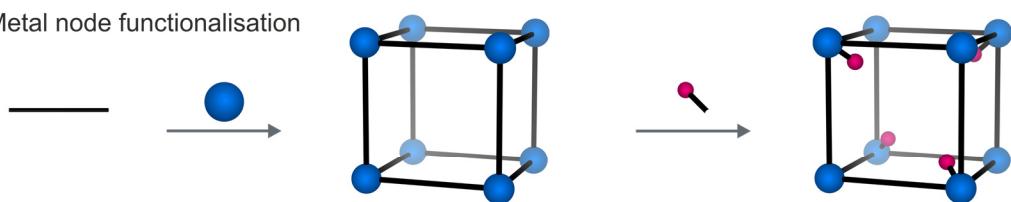
VI) Metal node exchange
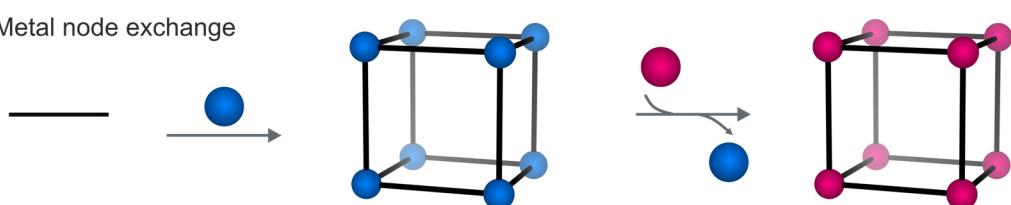
Figure 5. Schematic of the different ways to functionalise MOFs. It should be noted that the functionalisation can also occur partially despite the complete functionalisation shown in the schematics. Colour code: metal: blue and red, linker: black rods, functional groups: green and red, protection group: orange.

8

post-synthetic modification (PSM).[53] Post-synthetic linker functionalisation requires some basic functional groups attached to the linker (so-called tags *e.g.* -NH$_2$, -OH) that can undergo simple reactions like esterification or click reactions.[54–58] Because the chemical stability of some MOFs towards acids and bases is limited, only a small number of reactions operating under mild conditions are suitable. Post-synthetic deprotections (PSD) combine functionalisation of the linker prior to the synthesis bearing a protective group and its post-synthetic removal.[59–61] Another PSM method to synthesise MOFs is the solvent-assisted linker exchange (SALE or post-synthetic exchange, PSE) which is useful in cases where the direct synthesis is challenging.[62,63] Here, the synthesised MOF is soaked in a concentrated solution of the desired linkers and while the linker is replaced the material keeps its topology. It should be noted that the concepts of PSM also apply for metal nodes which for instance can be functionalised in the presence of coordinatively unsaturated sites or open metal sites (CUS or OMS), see Figure 5.[64–67] The OMSs are created if the metal ion has a lower coordination number than theoretically possible which happens due to the removal of solvent molecules coordinated during the synthesis.

The concept of solid solutions offers a different approach to fine-tune MOFs.[68–70] This concept has its origin in solid state chemistry and describes the synthesis of single-phase materials from several components with different ratios. KITAGAWA[71] and YAGHI[72] transferred this concept to MOFs and established the so-called solid solution MOFs, mixed component MOFs or multivariate MOFs. Featuring either different SBUs or differently functionalised linkers (see Figure 6), a random, alternatingly, or clustered distribution is found in the framework depending on the interactions of linkers or SBUs. It is important for the formation of the framework that the linkers or SBUs have the same connectivity, spatial expansion, and coordination environment. By varying the building block ratios, physicochemical properties, composition, pore geometry and space are controlled, and it has been found that these MOFs can have nonlinear and unusual properties that go beyond the properties of the single-component MOFs.

Mixed metal MOF   Mixed linker MOF
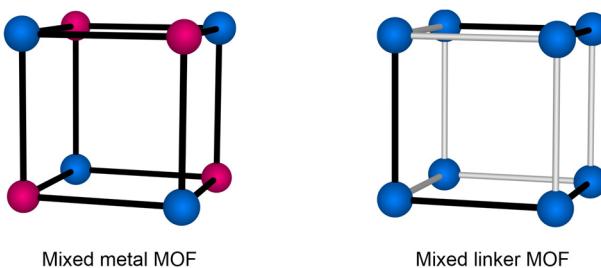
Figure 6. Representation of the concept of solid solution in MOFs featuring either two different metal nodes with alternating distribution (left, blue and red) or two different types of linkers with random distribution (right, black and grey). The concept of solid solutions can be applied to any of the six concepts of functionalisations illustrated in Figure 5.

2.4 Stimuli-Responsive MOFs: Dynamic vs. Static Responsiveness

MOFs offer a versatile material platform to design smart materials with their nearly unlimited possibilities to manipulate properties via judicious choice of linker, metal and additional functionalisation. As mentioned in chapter 1, smart materials are characterised by their useful and tailormade response to external stimuli, a behaviour that is also observed for MOFs. Early on it was observed that MOFs can undergo structural changes when the solvent is removed after the synthesis. This observation lead KITAGAWA to classify MOFs into the three generations of which the 3rd one undergoes structural changes in the presence or absence of solvent molecules (*cf.* chapter 2.2).[41] This subclass of MOFs is known as flexible or stimuli-responsive MOFs and KITAGAWA coined the term soft porous crystals to describe *"[...] porous solids that possess both a highly ordered network and structural transformability. They are bistable or multistable crystalline materials with long-range structural ordering, a reversible transformability between states, and permanent porosity. The term permanent porosity means that at least one crystal phase possess space that can be occupied by guest molecules, so that the framework exhibits reproducible guest adsorption."*[73] However, this definition limits the responsiveness of MOFs to host-guest interactions and omits that MOFs show responsiveness also in the absence of guest molecules with temperature, pressure or light as triggers and that the responsive behaviour is not always reversible.[74–76]

Rational exploration of how responsiveness can be expressed in a material requires a distinction between *dynamic* and *static* behaviour. Dynamic means that the responsive behaviour entails a significant structural change, including a phase transition to another crystalline phase,[77–81] loss of long-range order due to amorphisation,[82–84] or a flexible functional group in the linker that switches when exposed to light.[85–87] In contrast, static responsiveness does not involve structural changes of the network, but it rather considers the interactions. This responsiveness is demonstrated for example by MOFs showing a preferential adsorption of guest molecules either via size-exclusion due to the size and shape of the pores[88–91] or due to specific interactions between a functional group[92–95] or open metal site[96–99] and the guest molecule. Although both behaviours are well-known and studied in MOFs, there is only a small fraction (< 100) of dynamic stimuli-responsive MOFs known amongst the 99,075 MOFs reported in the CSD MOF subset.[100]

In the context of this thesis, MOFs were studied showing dynamic and static responsiveness in the presence of guest molecules and when pressure is applied. Therefore, the two following chapters give a more detailed insight into the state-of-the art of these two responses in the respective context.[‡]

[‡] An overview of the different stimuli-responsive behaviours not addressed in this thesis is given in references provided within the chapter.

2.4.1 Responsiveness as Function of Host-Guest Interactions§

The intrinsic porosity and reversible uptake of guest molecules intrigued researchers to address current industrial challenges in gas storage (*e.g.* hydrogen[29,102] and carbon dioxide[103–105]) or gas separation (*e.g.* olefines vs. paraffins from hydrocarbon mixtures[106,107]) by fine-tuning MOFs' responsiveness (*i.e.* selectivity) towards a certain gas. While exploiting dynamic structural features for selective sorption processes is less common and more difficult to achieve, there are more studies on how static responses can be used for selective sorption processes. Investigating the impact of different functional groups, several studies have shown that polar functional groups such as amines or hydroxides improve the uptake of polar gases such as carbon dioxide. Vice versa, non-polar functional groups like alkanes enhance the selectivity towards non-polar gases. The implementation of functional groups in the bdc linker of the Zr-based MOF UiO-66 (Universitetet i Oslo, $Zr_6O_4(OH)_4(bdc)_6$) showed that small, polar functional groups such as $-NH_2$, $-NO_2$ or $-OH$ increased the carbon dioxide uptake, whereas the nitrogen uptake of the UiO-66 analogues is more affected by the molar mass and size of the linker.[108–110]

OMSs are known to be exceptionally good adsorption sites due to the available vacant Lewis acid site and when choosing a metal centre with a higher polarity (*e.g.* Mg) – and therefore a higher positive charge and Lewis acidity – a faster uptake of polar gases and electron donating Lewis bases due to stronger adsorption sites is received.[67] Again, the sorption selectivity can be tuned towards non-polar gases when a less polar metal centre is chosen. A prominent and thoroughly studied example is the M_2dobdc (also known as CPO-27 or MOF-74; $M^{2+} = Mg^{2+}$, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}; dobdc^{4-} = 2,5-dioxidobenzenedicarboxylate, see chapter 2.5.1)[111–118] family. Caskey *et al.* studied the carbon dioxide sorption properties in dependence of the metal centre ($M^{2+} = Co^{2+}$, Mg^{2+}, Ni^{2+}, Zn^{2+}) and highlighted the metal centre polarity impact with Mg_2dobdc showing the highest and Zn_2dobdc the lowest uptake.[114] The results were shown to be transferable and a general selectivity towards olefines (*e.g.* ethene, propene) over paraffins (*e.g.* ethane, propane) due to a strong π-complexation of the electron rich π-bonding orbital in the olefin and the vacant σ-like orbital of the metal centre was determined.[119–123] The group of JEFFREY LONG replaced the linker dobdc with its meta substituted analogue *m*-dobdc (4,6-dioxido-1,3-benzenedicarboxylate) which increased the selectivity towards olefins due to an enhanced π-backbonding.[124,125]

While the examples described above rely on the interactions between the functionalised linker or OMSs to discriminate between different guest species, WANG *et al.* chose the approach of a size-exclusion based separation. Using a topology-guided approach of the SBUs, they designed the MOF $Y_6(OH)_8(abtc)_3(H_2O)_6(DMA)_2$ (Y-abtc, abtc

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§ Note, that this chapter is not intended to give a general introduction to gas adsorption in MOFs but to the specific host-guest interactions leading to static or dynamic responsiveness. For an overview of the fundamental of gas adsorption in MOFs the reader is referred to the IUPAC definition given by THOMMES *et al.* in Ref. 101.

= 3,3′,5,5′-azobenzene-tetracarboxylates; DMA = dimethylammonium) which has an optimum pore aperture (4.72 Å) that is only accessible for propene (kinetic diameter: 4.68 Å) but not for propane (kinetic diameter: 5.1 Å). The distinct feature that determines the size-exclusion separation (which is not pronounced for the Zr base analogue) is the anionic nature of the MOF requiring charge balancing cations, the DMA cations in this case. These cations reside insides the pores and were found to regulate the fine-control and adjustment of the pore dimensions.[88]

I) Swelling

IV) Breathing

II) Linker rotation

III) Subnetwork displacement
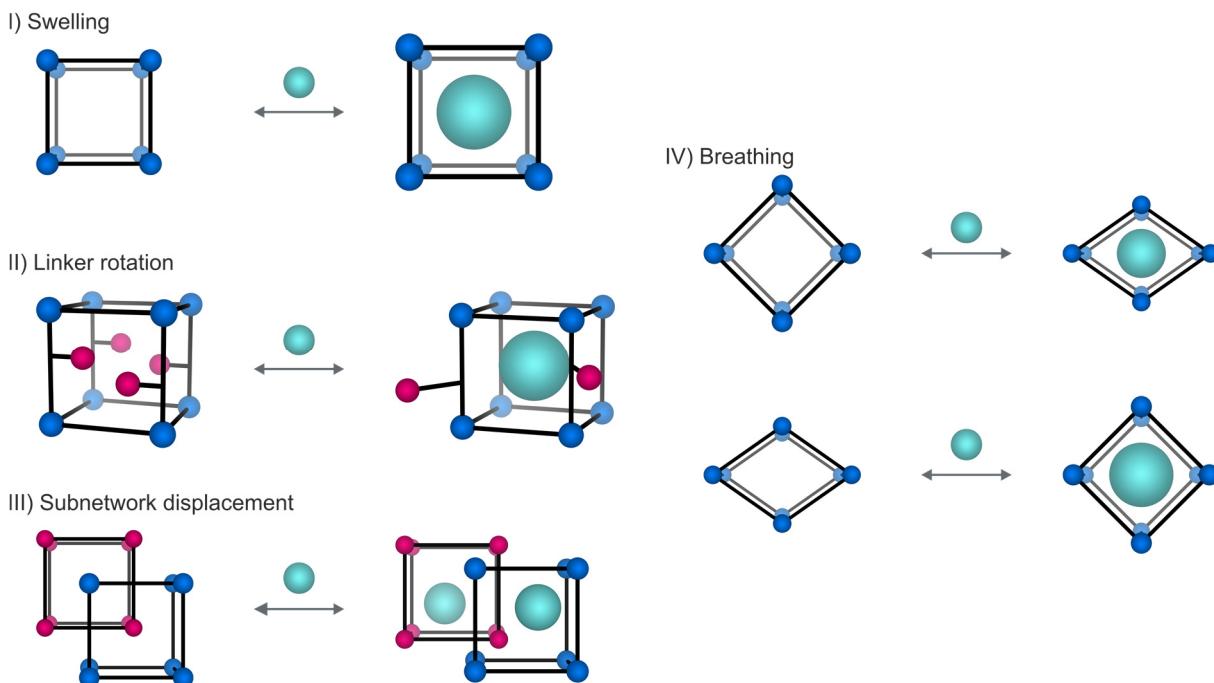
Figure 7. Flexibility as dynamic responses exhibited by MOFs when interacting with guest molecules. Colour code: metal: blue and red, linker: black rods, functional group: red, solvent molecule: turquoise spheres.

The less common but more fascinating way is to address dynamic responsiveness and here intriguing materials with unusual properties have been reported. One of these unusual properties is the negative gas adsorption (NGA) which was found in DUT-49 (DUT = Dresden University of Technology; Cu_2(bbcdc) with $bbcdc^{4-}$ = 9,9'-([1,1'-biphenyl]-4,4'-diyl)bis(9*H*-carbazole-3,6-dicarboxylate))[126] and describes the phenomenon that a material desorbs the guest molecules (methane and *n*-butane in the case of DUT-49) when a certain pressure is reached because the contraction to a closed pore (cp) phase with lower volume is energetically favourable. With increasing guest pressure, the material starts to adsorb more of the guest molecules and goes back to its open pore (op) form. Based on the structural feature characteristic of the responsiveness, the dynamic responses can be roughly divided into four categories, known as the four types of flexibility, shown in Figure 7. The simplest one is swelling that describes the enlargement of the unit cell volume when adsorbing guest molecules. The MIL-88 series (MIL = Matériaux de l'Institut Lavoisier; $M_3O(L)_3(H_2O)_2X$ with M^{3+} = Cr^{3+}, Fe^{3+}; L = fumaric acid, 2,6-naphthalenedicaboxylate, 4,4'-biphenyldicarboxylate and functionalised bdc derivatives; X^- = F^-, Cl^-, Br^-, OH^-, *etc.*)[127–129] is a prototypical example showing enlargement of the unit cell volume ranging from 60-230 % depending on the chosen linker and guest. The

interactions between the guest molecules and the linker can trigger the linker to rotate, thereby expanding or opening the pore window which increases or allows the uptake of guest molecules, respectively.[129] ZIF-8 (zeolitic imidazolate framework, $Zn(mIm)_2$ with mIm^- = 2-methylimidazolate) was expected to act as a molecular sieve for small molecules because of its small pore window (~3.40 Å). However, molecules with a larger kinetic diameter than the pore window were shown to be adsorbed, caused by the rotation of the imidazolate linker, the so-called "swing effect". It should be noted that the adsorption-induced deformation occurs gradually and in combination with packing effects of the guest molecules leads to a stepped isotherm.[130–132] Subnetwork displacement comprises the movement in MOFs built up by individual frameworks that are held together by weak van der Waals interactions. This results in MOFs having interpenetrated, interdigitated or stacked frameworks and the movements appear in various ways as the subnets can drift, relocate or shift.[133–135] Most important for this thesis is the so-called breathing behaviour. Breathing describes MOFs that undergo a distinct (reversible) phase transition from a narrow or closed pore (np or cp) to an open or large pore (op or lp) and/ or vice versa. This phase transition causes a change in unit cell volume and crystallographic space group. Among the classical examples of MOFs showing this breathing behaviour are the seminal works regarding the winerack-type MIL-53 and MIL-47 (MIL-47: V(O)(bdc); MIL-53: M(OH)(bdc); M^{3+} = Al^{3+}, Fe^{3+}, Cr^{3+})[77,136–138] family, the aforementioned NGA behaviour observed in DUT-49 and the multistep breathing in M(bdp) (M^{2+} = Co^{2+}, Fe^{2+}; bdp^{2-} = 1,4-benzenedipyrazolate).[80,139] The breathing behaviour can be tuned by different factors such as functionalisation, the metal centre and even the particle size was found to play an important role. The latter was studied in the nickel based version of DUT-8 ($M_2(2,6\text{-}ndc)_2(dabco)$, M^{2+} = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} with $2,6\text{-}ndc^{2-}$ = 2,6-naphthalenedicarboxylate, dabco = 1,4-diazabicyclo-[2.2.2]octane)[78,140] where the reversible breathing was only observed for particles > 1 mm, whereas smaller particles (500 nm – 1 mm) showed a phase transition to the cp phase but do not open upon guest adsorption and particles smaller 500 nm completely remain in the op phase.[141] The aforementioned DUT-8 belongs to the class of pillared-layer MOFs of the type M_2L_2P (with dinuclear paddle-wheels built by divalent metal ions M^{2+} and anionic dicarboxylate linkers L^{2-}, P = neutral nitrogen containing pillar; detailed structural description see chapter 2.5.3)[142] which have become well-known in the last years for its intrinsic responsiveness, especially the breathing phenomenon.[79] These pillared-layer MOFs based on functionalised bdc linkers (abbreviated as fu-bdc and the respective MOFs as fu-MOFs) and diazabicyclo[2.2.2]octane (dabco) as a pillar have evolved to one of the working horses in the FISCHER group over the past ten years. Starting from the parent framework $Zn_2(bdc)_2dabco$ (DMOF-1) that was initially considered as a 2nd generation MOF, a guest dependent dynamic response (*i.e.* linker bending or tilting) was discovered that leads to a distortion of the framework in the presence of *N,N*-dimethylformamide (DMF) or benzene.[143] Furthermore, it was later shown that the framework expands and shrinks upon the adsorption of alcohols (methanol, ethanol, isopropanol).[144] But it was the group of SETH COHEN who showed that PSM of the amino group of $Zn_2(NH_2\text{-}bdc)_2dabco$ ($NH_2\text{-}bdc^{2-}$ = 2-amino-1,4-benzenedicarboxylate) with linear alkyl anhydrides with different chain lengths to the corresponding amides gives MOFs that undergo a distinct breathing behaviour from a lp to a np phase upon guest removal.[56] This

was the first proof that linkers bearing flexible side chains pointing inside the pores cause the breathing behaviour in pillared-layer MOFs.

In his dissertation, SEBASTIAN HENKE established a library of pendant alkyl ether functionalised bdc linkers of which some undergo a lp to np phase transition upon solvent removal after the synthesis (see Figure 8.).[50,79,145] The MOF $Zn_2(BME-bdc)_2dabco$ (BME-bdc^{2-} = 2,5-bis(2-methoxyethoxy)-1,4-benzenedicarboxylate) became a showcase model during the studies done in the FISCHER group. This prototypical fu-MOF is non-porous towards nitrogen, but the polar functional groups at the linker act as molecular gates and open during the adsorption of carbon dioxide when surpassing a threshold pressure of p ≈ 0.2 GPa, leading to a stepwise adsorption isotherm typically for MOFs showing the breathing phenomenon see Figure 8b.[52] In general it can be said that the degree of flexibility is indicated by characteristics of the stepped isotherm, changes in cell volume, critical pressure or temperature (for reversible thermo-responsive breathing) of the phase transition. Furthermore, it can be influenced by the length, branching, degree of saturation and chosen functionality, but also by the packing efficiency and conformational flexibility of the side chain.[79,146] It is assumed that the flexibility originates from the attractive dipolar and dispersion interactions between the side chains, and between the side chains and guest molecules. The framework contraction is enthalpically favoured, whereas the opening is entropically favoured. Comparable to the bending of the bdc linker in the parent framework mentioned above in the presence of DMF or benzene molecules, the intermolecular framework interactions stabilize a more favourable form, here the np form. This assumption is supported by the fact that the degree of contraction becomes lower with longer side chains and MOFs with a C_5 side chain do not show a structural phase transition.[79]

a)

b)
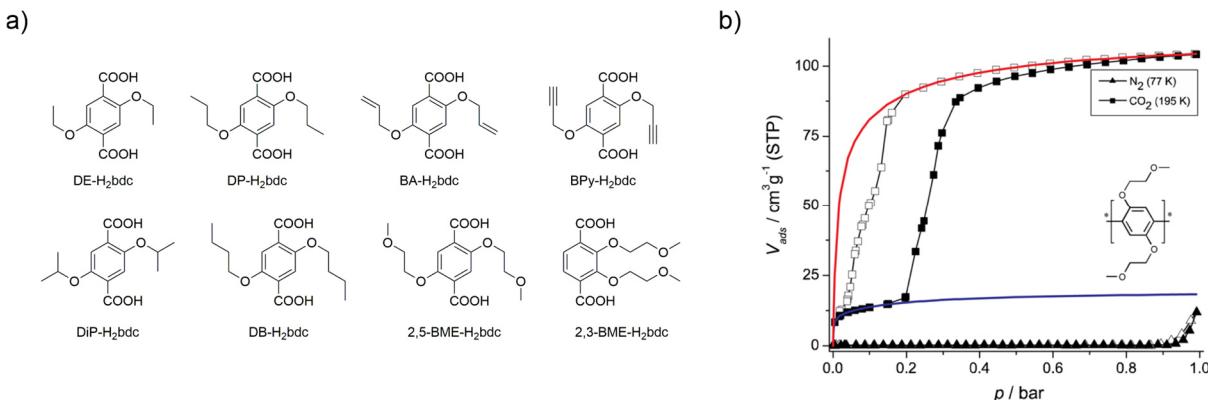
Figure 8. a) shows some of the functionalised bdc linkers used to prepare flexible MOFs. b) N_2 (77 K, triangles) and CO_2 (195 K, squares) sorption isotherms of $Zn_2(BME-bdc)_2dabco$. The filled symbols represent the adsorption and the open symbols the desorption branches. The Langmuir fits for the np and lp form are shown as blue and red lines, respectively. Reprinted with permission from S. Henke, A. Schneemann, A. Wütscher, R. A. Fischer, *J. Am. Chem. Soc.* **2012**, *134*, 9464. Copyright 2020 American Chemical Society.

Besides the functionalisation of linkers, the chosen metal centre plays a large role in the development of flexible MOFs. The bending in the parent MOF $Zn_2(bdc)_2dabco$ that is seen in the presence of guest molecules, does not happen for the Cu derivative. ROCHUS

SCHMID and co-workers attributed the more rigid behaviour of Cu(II) to the presence of orbital directing effects in 3d^9 Cu(II) centres, making it less amenable to the distortion of the coordination environment.[147] However, ANDREAS SCHNEEMANN synthesised Cu$_2$(fu-bdc)$_2$dabco MOFs which undergo a (reversible) phase transition from lp to np (fu-bdc: DE-/ DP-/ BME-bdc; DE = diethoxy, DP: 2,5-dipropoxy).[148] Furthermore, in a series of M$_2$(BME-bdc)$_2$dabco MOFs (with M^{2+} = Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) it was found that the magnitude of the pore contraction and the phase transition mechanism differ depending on the metal centre and hence on their electronic structure. The cell volume loss decreases as follows: Co(II) ≈ Zn(II) > Ni(II) > Cu(II). Despite the contraction being diverging for Zn(II) and Cu(II), they both feature a distinct switching between the np and lp phase and analysis of *in-situ* PXRD data reveal the presence of an intermediate phase (ip). This intermediate phase is abundant for Co(II) and Ni(II), in fact they gradually swell before switching to the np phase takes place.[149]

This thesis is in the line of its predecessors SEBASTIAN HENKE, ANDREAS SCHNEEMANN and INKE HANTE (née SCHWEDLER) and since the description of all their fascinating results around tuning the flexibility of pillared-layer MOFs would go beyond the scope of this introduction, reference is made at this point to their dissertations and publications.[145,150–153]

2.4.2   MOFs Under (Hydrostatic) Pressures

A material's response under high or hydrostatic pressures has long been studied in other materials classes[154–158] and subjects[159–161] because pressure as an extensive thermodynamic parameter provides insight into the underlying free energy landscape[162] via the Gibbs free energy G as a function of small chemical changes:

$$\Delta G(p,T) = \Delta U + p\Delta V - T\Delta S$$

where U is the internal energy, S the entropy, p the pressure and T the temperature. However, MOFs are relatively new in the field of high-pressure research and beyond the fundamental aspect of pressure as a thermodynamic parameter, it is important to know whether a MOF that is suitable for application as catalyst can be processed via extrusion or compression where significant stress is applied.[163,164] If the framework would collapse or undergo a phase transition when processed at high pressures, it might lose its useful property and hence knowledge of the mechanical properties is highly desired. Furthermore, the targeted synthesis of pressure-responsive (and stimuli-responsive in general) MOFs which regards the manipulation of macroscopic thermodynamics via chemical changes on a microscopic level would be desirable to receive materials showing a specific response to pressure. Unfortunately, the latter is still beyond our knowledge but in general it has been shown that macroscopic interactions such as choice of linker length[165,166] and metal node,[167–169] topology,[170–172] dispersion interactions and vibrational entropy[173–176] as determined by microscopic chemical interactions all contribute to structural flexibility (in general). When studying MOFs under high pressures, two questions

are (mostly) addressed: First, how is the MOFs' mechanical stability and are they considered as soft or hard materials? And second, what dynamic responses have been observed when compressing MOFs?

The mechanical properties are quantified by the elastic moduli that give a material's resistance to elastic deformation. Here, the Young's and bulk moduli are of interest. The Young's modulus E (also referred to as elastic modulus) gives a material's stiffness when a unidirectional strain is applied

$$E = \frac{\sigma}{\varepsilon}$$

where the tensile strength σ is given as the force per area ($\sigma = F/A$) and the relative change in length as $\varepsilon = \Delta l/l_0$ and the unit is GPa. The Young's modulus is measured using nanoindentation techniques and with that also the hardness of a material can be obtained.[177,178] The bulk modulus K extends the description of the Young's modulus into three dimensions and describes a material's resistance towards volumetric (V) changes under hydrostatic pressure and is given in the unit GPa:

$$K = -V \frac{\partial p}{\partial V}$$

The bulk modulus is obtained from pressure dependent single crystal or powder X-ray diffraction data by fitting an equation of states to the pressure dependent unit cell volume.[179] For each elastic modulus a higher value corresponds to a harder or stiffer material. When looking at the various bulk moduli of MOFs (*cf.* Table 1) it is evident that MOFs span the whole range from soft to hard materials; on the soft end ZIF-4(Zn) with a bulk modulus similar to water polymers like polyethylene or polybutadiene and on the hard

Table 1. Bulk modulus K of various MOFs derived from experiment or simulation in comparison to purely inorganic and organic materials.

Material	K / GPa	Material	K / GPa
UiO-66	12-26 [180–182]	**NaCl**	25 [183]
UiO-66	38 [166]	**Zn**	55-75 [162,184]
UiO-67	13 [180]	**H$_2$O**	2.2 [162,185]
HKUST-1	30-35 [186,187]	**Diamond**	443 [188]
MOF-5	16-18 [165,189–191]	**C$_{60}$**	14 [192]
DUT-52	17 [166]	**Polyethylene**	2.0 [193]
PCN-57	4.6 [166]	**Polybutadiene**	2.4 [193]
NU-901	7.2 [166]	**Biphenyl**	4.2 [194,195]
ZIF-4(Zn)	2-4.4 [196]	**Para-terphenyl**	7.1 [194,195]
ZIF-8	6.5 [197]	**Benzene**	8.0 [198]

side HKUST-1 (Hongkong University of Science and Technology, Cu_3btc_2 with btc^{3-} = benzene-1,3,5-tricarboxylate) and UiO-66 being in between inorganic salts and pure metals. Of course, diamond as the hardest material known is far off the chart, but for a material containing organic parts its (MOF's) resistance to compressibility is remarkable.

MOFs exhibit a variety of dynamic responses towards pressure that are depicted in Figure 9 and are extensively covered in reviews.[199–204] It should be noted that the intrinsic porosity of MOFs not only allows for the adsorption of guest molecules during gas adsorption measurements but also that the pressure transmitting medium (PTM) [205,206] can enter the pores and cause a dynamic response through host-guest interactions. Small alcohols such as methanol or ethanol are considered as penetrating PTMs, whereas long-chain and branched fluorinated hydrocarbons and silicone oils are non-interpenetrating PTMs. As this chapter discusses guest independent responses, the following examples focus on responses solely caused through the applied pressure.

When starting to compress a MOF, the first response typically observed is a compression at lower pressures. A special case of compression is the negative linear compressibility (NLC) where the crystal structure expands in at least one direction while contracting in the other direction(s). This rare anisotropic response is counterintuitive to the compression expected under hydrostatic pressures and is attributed to a hinging mechanism of the framework as was observed in $InH(bdc)_2$[207] or $Zn[Au(CN)_2]_2$[208].
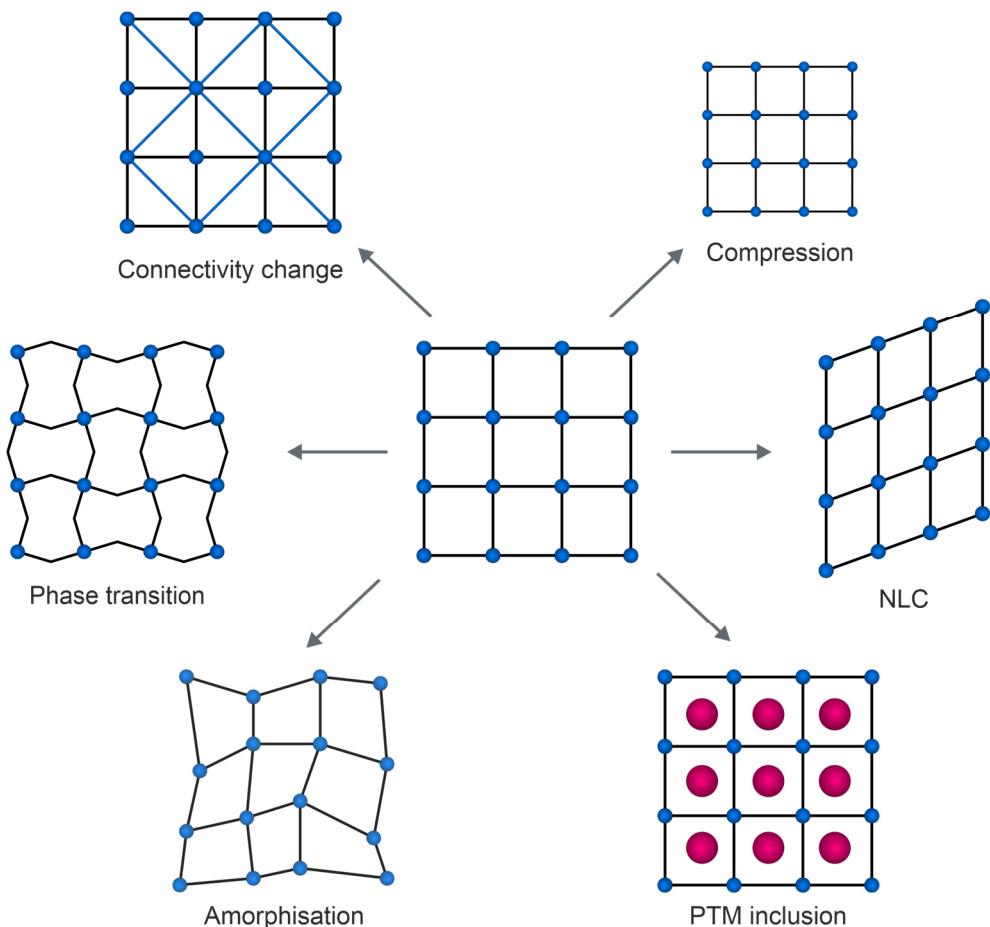

Figure 9. Representations of dynamic responses exhibited by MOFs under pressure. The figure is inspired and adopted from Ref. [204].

Going to higher pressures – noteworthy is that 'higher' is relative and depends on the chosen system but for MOFs usually pressures well below $p = 1$ GPa trigger a sufficient dynamic response – interesting dynamic phenomena such as phase transitions can be observed. Thinking about phase transitions and what is taught in the study programme of physical chemistry/ thermodynamics, usually the classical thermodynamic definitions of phase transitions after PAUL EHRENFEST come to mind. However, in the context of MOFs the definitions given by MARTIN JULIAN BUERGER seem to be more appropriate.[209] These definitions are based on the structural mechanism during the phase transition and distinguish between three types of phase transitions. Reconstructive phase transitions are characterised by breaking of chemical bonds and formation of new bonds within the metal coordination sphere and caused by changes in linker positions and orientations or connectivity. Contrary, displacive phase transitions do not involve breaking of chemical bonds and describe only slight displacement or rotation of atoms and sometimes intermolecular bonds such as hydrogen bonds are rearranged. The space groups of the low- and high-pressure phase are related by a group-subgroup relation of the space groups.

As mentioned above connectivity changes can occur as part of reconstructive phase transitions and have been observed in MOFs as well, either with or without a change of the metal centre coordination number. An example of increasing coordination number upon compression is $Co_3(OH)_2btca_2\cdot2DMF$ (with $btca^{2-}$ = benzotriazolide-5-carboxylate) where the coordination of additional DMF or MeOH molecules at the OMS leads to an increase of the coordination number from five to six.[210] The dense analogue of ZIF-4(Zn) is obtained when heating ZIF-4(Zn) to $T \approx 370$ °C[211] and has the same sum formula but another topology (zni) and is therefore known as ZIF-zni. When this MOF is compressed it transforms to another phase via a cooperative bond rearrangement but without changing the metal centre coordination number.[212] Increasing the connectivity of a MOF prior to compression was found to enhance its rigidity and mechanical stability.[213]

The winerack-type structure found in MIL-47 and MIL-53 is a common structure type of MOFs associated with flexibility and its response towards different external stimuli is well investigated both experimentally and computationally. MIL-53(Cr) was the first MOF of this family to show a lp to np phase transition of displacive nature at $p = 0.055$ GPa using mercury intrusion experiments.[214] In further works the impact of the metal centre and linker functionalisation was studied in experimental and computational studies, accessing the underlying thermodynamics of the phase transitions.[174,215–225] For instance, it was found that the metal centre determines the transition pressure and while the threshold pressure of the phase transition from the np to the very np phase (these MOFs contract upon hydration) of the Fe and Cr based analogues is around $p \approx 0.4$ GPa, the Al analogue is more resistant to pressure and switches at a threshold pressure of $p \approx 1.2$ GPa. This observation was attributed to the stronger π-π stacking interactions between the opposite pore walls because of the more contracted np phase of the Al MOF that leads to a higher resistance towards mechanical pressure. Grafting functional groups (-Cl, -CH$_3$ and -NO$_2$) to the bdc linker also impacted the mechanical properties and the -Cl functionalisation stabilised the np phase of MIL-53(Cr)-Cl due to additional intra-framework interactions

between the -Cl and the μ_2-OH groups at the surface of the MOF. Furthermore, irrespective of the functional groups grafted, the framework only contracts further to a contracted np phase instead of showing a displacive phase transition (accompanied by a change in the space group) to the very np phase.[224]

Another MOF family attracted the attention of researchers due to their widespread polymorphism, the ZIFs. For example, ZIF-4 undergoes a displacive phase transition at pressures of p(ZIF-4(Zn)) = 0.028 GPa and p(ZIF-4(Co)) = 0.050 GPa accompanied by a volume decrease of ΔV = 20 % which means that no accessible porosity remains.[226] This was the first study to show that a member of the ZIF family undergoes the breathing transition from op to cp phase under hydrostatic pressures based on rotation of the imidazolate linkers, although the high pressure phase is somewhat similar to the reported low temperature phase.[81] The differences in the threshold pressure of the isostructural Zn and Co analogues was attributed to the different chemical nature of the metal ions (Zn^{2+}: $3d^{10}$ and Co^{2+}: $3d^7$) presumably leading only to a σ-bonding of the imidazolate linkers and Zn^{2+} whereas additional stronger linker-metal π-bonding in the Co analogue might exist. Additionally, this bonding was assumed to be more covalent in the case of Co^{2+} due to its higher electronegativity. A recent study of the group of THOMAS D. BENNETT and co-workers put the low- and high-temperature/pressure phases of ZIF-4(Zn) in the broader context and established a pressure-temperature phase diagram for pressures from ambient up to p = 8 GPa and temperatures from ambient up to T = 580 °C.[227]

The pressure-induced amorphisation (PIA) can be considered as a very special case of phase transformations with a distinctive symmetry lowering, _i.e._ the full removal of periodicity. While it is not surprising that MOFs as soft materials amorphise at high pressures well below p < 1 GPa as was found for several ZIFs, some MOFs exhibit really low threshold pressures. For example, MOF-5 amorphises at pressures of p = 0.0035 GPa already.[228] Going back to the PIA of ZIFs, the amorphisation of ZIF-4,[196] ZIF-7 ($Zn(blm)_2$ with blm⁻ = benzimidazolate)[229,230] and ZIF-62 ($Zn(Im)_{1.75}(blm)_{0.25}$)[229,231] was found to be reversible and thus might be of displacive nature. Contrary, the amorphisation of ZIF-8 is not reversible,[197] most likely being a reconstructive phase transition. While it is not completely understood why some ZIFs undergo a displacive or reconstructive PIA, the influence of defects on the onset of amorphisation pressure was investigated by our group. Given that defective UiO-66 is an interesting candidate for catalysis as the defects give rise to more active sites that can be functionalised, it would lose all its application potential if it were to collapse during shaping processes. In a series of defective UiO-66, increasing defect concentration led to a lower onset of amorphisation from p > 0.4 GPa for the 'defect free' material to p ≈ 0.2 GPa for the material with the highest defect concentration. Interestingly, the bulk modulus was only decreased up to a certain defect concentration and did not show significant variation beyond this certain concentration. This unexpected behaviour might be attributed to the origin of correlated defects leading to a new and stable topology.[180,182]

The 'low' high-pressures required to trigger a response – in particular PIA and phase transition – make MOFs challenging candidates for established high-pressure set-ups like

the commonly used and well-established diamond anvil cell (DAC).[232,233] While its variability allows use in combination with different techniques besides the standard diffraction techniques, it does not allow for a small step size resolution which is needed to follow the responses at 'low' high-pressures with a high-resolution. Therefore, there is a demand for new set-ups allowing a smaller step size resolution.

2.5 Materials' Data Sheets

The following materials' data sheets give an overview on the general composition, structure and characteristics of the MOFs classes studied in this thesis. Please note that some aspects have been mentioned in the previous chapters, and the focus here is given to structural details and characteristic features. A short overview is given in

Table 2 on the characteristics of the MOFs Co_2dobdc, ZIF-4, ZIF-8 and the fu-MOFs investigated in this thesis, while a more comprehensive description is given in the following sections 2.5.1 – 2.5.3.

Table 2. Overview of the MOFs Co_2dobdc, ZIF-4, ZIF-8 and fu-MOFs studied in this thesis.

	Co_2dobdc	**ZIF-4**	**ZIF-8**	**fu-MOFs**
Composition	Co_2dobdc	$Zn(lm)_2$	$Zn(mlm)_2$	$Cu_2(fu\text{-}bdc)_2dabco$
Structure	honeycomb	cag	sod	winerack-type
Characteristic	open-metal sites	zeolite-like structure, polymorphism		tailoring responsiveness via linker functionalisation
Responsiveness	static, host-guest interactions	dynamic, pressure	dynamic, pressure	dynamic, pressure

2.5.1 The M_2dobdc Family

Co$_2$dobdc   Co$_2$dobdc·H$_2$O
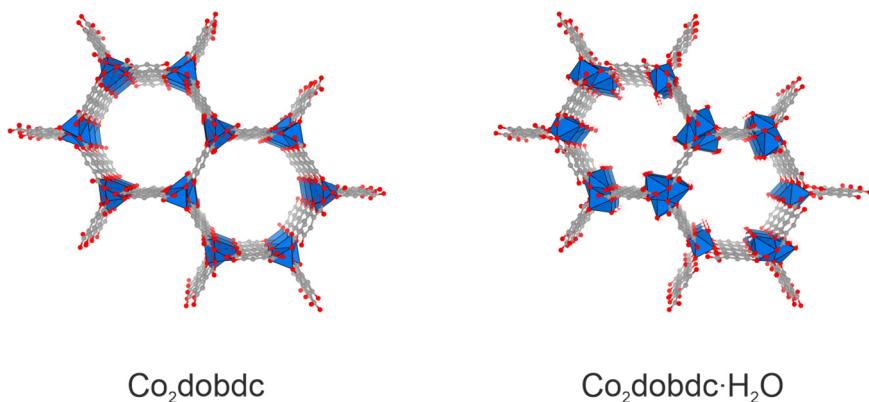
Figure 10. Crystal structures of Co$_2$dobc and the hydrated Co$_2$dobdc·H$_2$O with water molecules coordinated to the OMSs. Colour code: Co: blue, C: grey, O: red. H atoms omitted for clarity reasons.

COMPOSITION. The MOFs of this isostructural series have the general sum formula M_2dobdc with M^{2+} = Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} as divalent metals and dobdc^{4-} = 2,5-dioxidobenzenedicarboxylate as the linker.[111–118] These MOFs are also known as CPO-27(M) or MOF-74(M) in the literature.

STRUCTURE. The isostructural MOFs have a honeycomb topology with 1D, hexagonal channels. In the hydrated or as synthesized form, the metal centre has an octahedral coordination sphere. One solvent molecule (usually water) contributes with one oxygen atom to the octahedral coordination sphere and the other five positions are oxygen atoms of the carboxylate and oxide groups of the linker. Here, one oxygen atom of each carboxylate coordinates to two metal centres while the other one coordinates only to one metal centre. Thus, the edge-sharing MO_6 octahedra are alternatingly cis-linked forming helical rods. Benzene rings connect these rods in a parallel fashion giving hexagonal one-dimensional channels. After activation of the framework, it retains its overall crystal structure, but the removal of the coordinating solvent molecule leads to a square-pyramidally coordinated metal centre with an empty coordination site.

CHARACTERISTICS. The OMSs that are created when removing the solvent play an important role in gas separation processes because the OMSs offer the advantage to discriminate between saturated and unsaturated light hydrocarbons (*cf.* Refs. [96,99,117,119,121,122,234–246]). Furthermore, the OMSs offer the opportunity to graft functional groups to them and with that enhance the adsorption selectivity towards a certain guest molecule. Selected examples on this static responsiveness are described in chapter 2.4.1.

2.5.2 Zeolitic Imidazolate Frameworks

ZIF-4(Zn), cp   ZIF-4(Zn), op   ZIF-8(Zn)
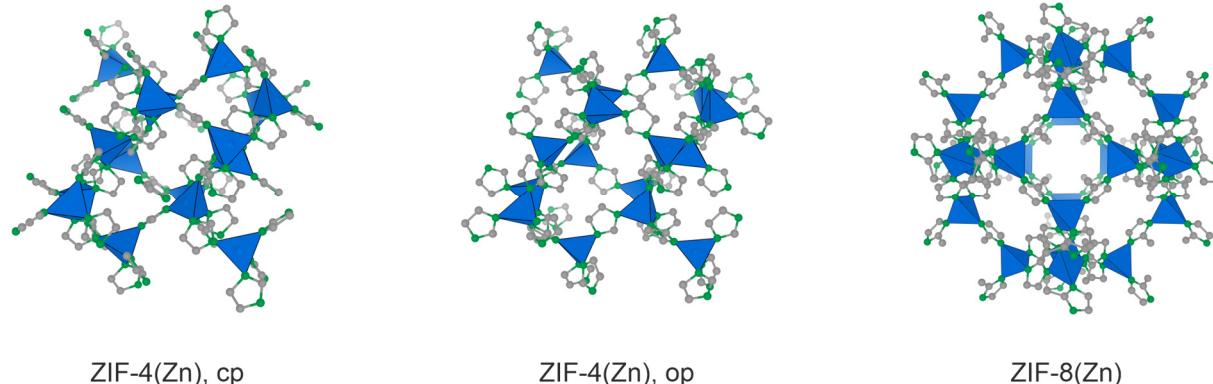
Figure 11. Crystal structures ZIF-4 in its cp and op phase and ZIF-8. Colour code: Zn: blue, C: grey, N: green. H atoms omitted for clarity reasons.

COMPOSITION. This subgroup of MOFs is usually based on the general sum formula ML_2 (note, that there are also exceptions like ZIF-5 ($In_2Zn_3(Im)_{12}$)) with divalent metals like Zn^{2+} or Co^{2+} and imidazolate (Im^-) or imidazolate derivatives as linkers. Note, that there is no systematic in the nomenclature of ZIFs and the numbers were assigned randomly. For instance, the first report of the dense ZIF-4 derivatives ZIF-zni with Co^{247} and Zn^{248} were published in 1975 and 1980, respectively, before the terms MOF or ZIF were coined.

STRUCTURE. The structure of the ZIFs is similar to what is found in the purely inorganic zeolites and therefore are considered as their hybrid siblings. The metal centre is solely coordinated by the nitrogen atoms in the 1,3 position of the imidazolate linkers bridging the metal centres. The bonding angle M-Im-M is 145° and similar to the Si-O-Si bonding angle in zeolites. Because of these structural similarities the topologies of ZIFs are described by the same three-letter code used for zeolites, *e.g.* SOD for the sodalite topology of ZIF-8. The topology of each ZIF depends on the chosen linker (*i.e.* functionalisation), metal and reaction conditions.

CHARACTERISTICS. ZIFs are known for their high thermal and chemical stability compared to most MOFs and in combination with their large structural diversity and high porosity they are auspicious candidates for application in catalysis and gas storage. Another interesting feature is the intrinsic responsiveness towards pressure and temperature changes or the gate-opening behaviour through linker rotation as was observed in ZIF-8 (see chapter 2.4).

2.5.3 Pillared-Layer MOFs (fu-MOFs)

Cu$_2$bdc$_2$dabco   Cu$_2$(DB-bdc)$_2$dabco, op   Cu$_2$(DB-bdc)$_2$dabco, np
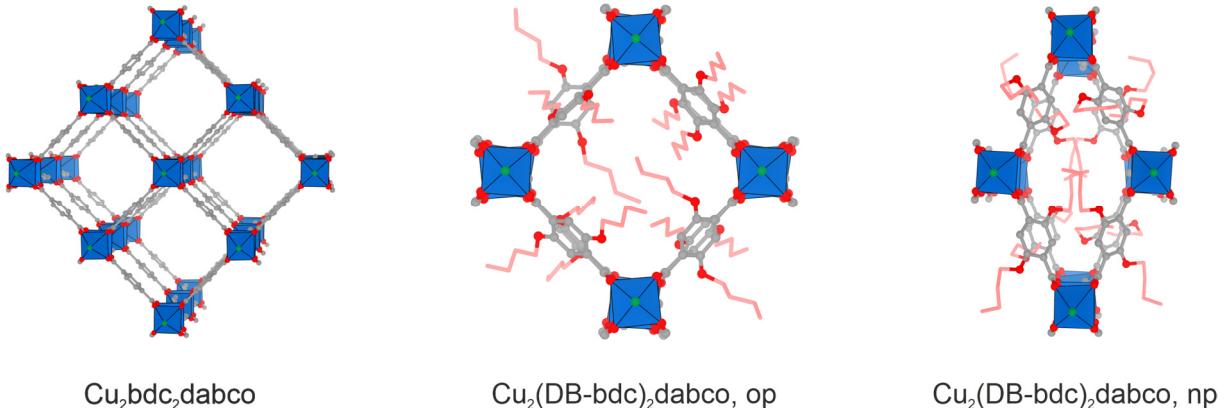
Figure 12. Representation of the crystal structures of the parent unfunctionalised Cu$_2$bdc$_2$dabco and Cu$_2$(DB-bdc)$_2$dabco in its op and cp phase at high pressures. Colour code: Zn: blue, C: grey, O: red, N: green, Butoxy side chain: rose. H atoms omitted for clarity reasons.

COMPOSITION. Pillared-layer MOFs can be described with the general sum formula M$_2$L$_2$P consisting of divalent metal ions (M^{2+} = Zn^{2+},[143] Cu^{2+},[249] Ni^{2+},[250] Co^{2+} [251] *etc.*), linear anionic dicarboxylate linkers as oxygen-donor molecules (L, *e.g. trans*-1,4-cyclohexanedicarboxylate,[249] 1,4-benzenedicarboxylicate,[143] or 2,5-functionalised-1,4-benzenedicarboxylate[79]) and neutral nitrogen containing pillars (P, *e.g.* diazabicyclo[2.2.2]octane,[143] 4,4'-bipyridine[252]). There is no consistent naming in literature and every notation of pillar(ed)-layer(ed) MOF is known. The abbreviation MLP is used and if functional groups are implemented in the linker, they are partly referred to as fu-MOFs. Furthermore, some materials are predominantly known by their trivial names, as DMOF-1 or JAST-1 for Zn$_2$bdc$_2$dabo[143] or DUT-8 for M$_2$(2,6-ndc)$_2$dabco[78].

STRUCTURE. The typical SBU motif is the paddlewheel built from dinuclear M$_2$ units where each M^{2+} is bridged fourfold by four carboxylates of four linkers to form a 2D square planar grid of {Zn$_2$bdc$_2$} motifs. The pillar molecules connect these grids in the axial position to give a 3D network. Usually these MOFs form a square net, but there also pillared-layer MOFs known with a rhombic or Kagome net.[253]

CHARACTERISTICS. What makes pillared-layer MOFs so interesting is that the formally rigid parent framework Zn$_2$bdc$_2$dabo can be rendered flexible by implementing functional groups like ether or alkoxy side chains in the linker. These fu-MOFs respond to various stimuli such as host-guest interactions, temperature, and pressure in a dynamic way by showing a phase transition from an op to a np phase. The degree of flexibility and responsiveness to a certain stimulus were found to depend on the metal centre as well as the chosen functionalisation (see chapter 2.4.1). An extensive overview on the reported pillar-layer MOFs that go beyond the ones studied in this thesis can be found in the review given in Ref. [142].

3   OBJECTIVE

While MOFs provide a tantalizing platform to design smart materials, targeted synthesis of stimuli-responsive MOFs involving the manipulation of macroscopic thermodynamics by chemical changes at the microscopic level is still elusive. To shed light on the underlying principles of stimuli-responsive MOFs is one of the tasks addressed by the research unit "FOR2433 – Switchable MOFs"[**] in which context this thesis is embedded. The projects of the research unit are related to the interplay of material synthesis, in-situ characterisation techniques and simulations. The research goal of the FOR2433 is a fundamental understanding of the underlying structural principles of dynamic responsiveness (mainly but not only triggered through host-guest interactions) in pillared-layer MOFs (fu-MOFs or DUT-8) to predict new stimuli-responsive MOFs and bring them towards application. This overarching goal is addressed in four objectives that comprise 1) development of a predictive theoretical framework, 2) development of tailored in-situ characterisation techniques, 3) impact of cooperative/ correlated phenomena and heterogeneity, disorder and defects on the stimuli-responsiveness and 4) characterisation and understanding of specific vs. non-specific responsivity in terms of host-gust interactions, functional groups, and enthalpic and entropic factors.

The studies in this thesis are set in the context of the research unit FOR2433 and explore how functionalisation either of the OMS or the linker affects the *static* or *dynamic* responsiveness of a MOF in regard to host-guest interactions or hydrostatic pressure supported by in-situ characterisation methods and computational models. Before going into the details of the studies of this thesis, the connection of each study to the FOR2433 is given. **STUDY I** addresses the investigation of host-guest interactions in sorption processes (objective 4), while **STUDY II – V** deal with the dynamic response towards hydrostatic pressure, establishing a new in-situ high-pressure set-up (objective 2) and combining high-pressure experiments with the development of computational models to gain knowledge on the thermodynamic factors driving the stimuli responsive behaviour (objective 1 and 3).

It is well established in literature, that the MOF family M_2dobdc is well suited for separation processes for light hydrocarbons due to the static responsiveness of the OMS and the guest molecules and is considered a promising candidate for industrial application. However, most of the studies published used ideal separation conditions and the high selectivities reported for the separation of propene from propane are solely derived from

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[**] Detailed information on all projects and participating groups can be found on the website of the research unit: https://tu-dresden.de/mn/chemie/ac/ac1/forschung/forschergruppe-2433.

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single-component isotherms, thereby neglecting any disturbing effects caused by guest molecules which are typically present in traces in industrial separation processes. Based on the current literature, the following question arose:

"What influence do 'interfering' guest molecules
have on the static responsiveness of MOFs with OMSs?"

This question is addressed in **STUDY I** by comparing the selectivities of fully activated Co_2dobdc to hydrated Co_2dobdc where the OMSs are saturated with water molecules. The selectivities are derived both via the ideal adsorbed solution theory from single-component adsorption measurements and from coadsorption experiments using mixtures of propene and propane. Complementary, temperature programmed desorption and density functional theory calculations are done to examine the primary adsorption sites of propane, propene and water and to shed light on the interactions (*i.e.* static response) between the OMS and the guest molecules during the adsorption process.

The second topic deals with the mechanical properties of MOFs under pressure and **STUDY II – V** comprise different aspects of it. **STUDY II** lays the foundation for the following **STUDY III – V** and addresses the following question:

"What are the current challenges in high-pressure studies of MOFs
and how can they be overcome in the future?"

An overview of the high-pressure diffraction studies of MOFs investigating structural behaviour under hydrostatic pressures is given and important aspects are discussed to advance the field, such as reporting of experimental and analytical procedures, opportunities of custom-made high-pressure diffraction setups, choice of pressure-transmitting medium and forging ties between computation and experiment.

One of the challenges found when reviewing the literature is the lack of a suitable set-up for studying MOFs under high hydrostatic pressures. MOFs as soft materials show their interesting responses to pressure in the 'low' high pressure region up to $p = 1\,GPa$, whereas established high-pressure powder X-ray diffraction (HPPXRD) set-ups like the DAC aim for high pressures of hundreds of GPa. **STUDY III** addresses this problem using a hydrostatic set-up that was established by Nicholas Brooks and co-workers for soft condensed matters.[254] This set-up allows us to apply pressures up to $p = 0.4\,GPa$ in very small steps (compared to the DAC) of $\Delta p = 0.005$ GPa, providing a fascinatingly detailed insight into the high-pressure behaviour of MOFs via HPPXRD and a precise determination of the bulk modulus. The well-studied ZIF-4(Zn) is chosen as a proof-of-principle, where the phase transition from op to cp phase is known to happen at low pressure as $p \approx 0.03$ GPa.[226]

The high-pressure behaviour of another iconic MOF is revised in **STUDY IV**. Here, again a ZIF, namely ZIF-8, is chosen because ZIFs are known for their polymorphism at elevated temperatures and pressures. In previous studies, ZIF-8 was found to undergo either a gate-opening linker rotation in presence of penetrating PTMs like methanol,[255] or PIA at $p \approx 0.34$ GPa when a non-penetrating PTM (Fluorinert) is used.[197] But upon examining the

PXRDs showing the PIA in detail, it appears to represent a phase transition (indeed with very broad peaks) and motivated us to re-examine the high-pressure behaviour of ZIF-8 in the pressure region from p = ambient – 0.4 GPa.

Given the limited knowledge about how to alter the underlying free energy surface of a MOF (see above the scope addressed by the research unit FOR2433), it is noteworthy that the free energy surface of MOFs can be quite shallow as recently highlighted by MATTHEW ROSSEINSKY and co-workers.[256] This distinguishes MOFs from purely inorganic materials and parallels enzymes that can adopt different conformations, reflected by a very shallow free energy surface with the corresponding number of minima. Knowing the underlying parameters that drive the responsiveness would allow for the tailored design of stimuli-responsive MOFs. Therefore, in **Study V** we investigated

"How does the implementation of a functional group alter
the underlying thermodynamics of a MOF obtained by its
stimuli-responsive behaviour towards pressure?"

We choose two pillared-layer MOFs that are known to be rendered flexible by implementing functional groups in the linker. One is the parent $Cu_2(bdc)_2dabco$ without any functionalisation and the other one is $Cu_2(DB-bdc)_2dabco$ (DB = dibutoxy) with two butoxy side chains attached to the linker. HPPXRD gives information on their responsiveness to pressure and molecular dynamics simulations provide detailed insights how the functionalisation alters the underlying free energy surface, guiding us to future development of synthesis guidelines for tailor-made stimuli-responsive MOFs.

4 RESULTS AND DISCUSSION

4.1 STUDY I. Coordinated Water as New Binding Sites for the Separation of Light Hydrocarbons in Metal−Organic Frameworks with Open Metal Sites

To shed light on the influence of intrusive gases in adsorption processes, we chose one of the most thoroughly investigated MOF systems with OMSs, namely Co_2dobdc (also known as MOF-74 or CPO-27). Throughout the literature, there exist numerous studies on this MOF system used in various gas separations problems, but so far these studies are based on single-component adsorption measurements and theoretical studies.[246] Here, we report the sorption properties of Co_2dobdc in the separation of propane/propene that mimics more realistic conditions by pre-adsorbing water prior to the multi-component sorption measurements with mixtures of propene and propane. Hence, the OMSs that play an important role in the adsorption process are blocked and it is therefore not surprising that the overall uptake capacity decreases. The experimentally determined selectivities do not match with the high IAST (ideal adsorbed solution theory) derived selectivities reported from single-component isotherms in the literature; however, the selectivity towards propene is retained. Considering that the water molecules block the OMSs, it might be assumed that the strong interactions between the propene molecule and the OMSs are hindered. Instead, it seems that the adsorbed water molecules add a new adsorption site for the propene molecules compensating the blocked adsorption site at the metal. Computational evaluation of the binding energies underlines that the water molecules adsorbed to the cobalt centre preferentially interact with propene over propane. Furthermore, a discrepancy between different published data is revealed, emphasizing the importance of multi-component adsorption measurements under more realistic conditions.

Comprehensive data analysis and discussion and paper writing was done by the author of this thesis through contribution and critical discussion of all co-authors. The strategy was developed by A. Schneemann and the author of this theses under supervision of R. A. Fischer S-i. Noro. The synthesis and characterization were done by the author of this thesis with support from A. Schneemann und I. Hante. The coadsorption experiments were done during the master's thesis of this author in the group and under guidance of S-i. Noro. J. Pirillo and Y. Hijikata performed the DFT calculations and provided the detailed discussion. T. Toyao did the TPD measurements.

Press release of the Hokkaido University:
https://www.global.hokudai.ac.jp/blog/metal-organic-frameworks-can-separate-gases-despite-the-presence-of-water/

P. Vervoorts, A. Schneemann, I. Hante, J. Pirillo, Y. Hijikata, T. Toyao, K. Kon, K.-I. Shimizu, T. Nakamura, S.-i. Noro and R. A. Fischer, Coordinated Water as New Binding Sites for the Separation of Light Hydrocarbons in Metal-Organic Frameworks with Open Metal Sites. *ACS Appl. Mater. Interfaces* **2020**, *12*, 9448-9456.

4.2 STUDY II. Structural Chemistry of Metal-Organic Frameworks under Hydrostatic Pressure

Within this review, we review the structural behaviour of MOFs under hydrostatic pressures with focus on bulk moduli, pressure-transmitting medium dependent properties, pressure-induced phase transitions, and amorphization processes as derived from high-pressure X-ray diffraction studies. The structural behaviour of UiO-66 depending on defect concentration, linker modification and metal exchange is highlighted as a topical example due to its well-studied nature in experiment and computation. Following on, general trends discovered so far are discussed, for example the link found between bulk moduli and linker length for two isoreticular series of MOFs with **fcu** or **scu** topology or the stabilising effect of penetrating PTMs against framework collapse like in HKUST-1. In going forward, we summarise important aspects to advance the field such as the reporting of experimental and analytical procedures, opportunities that come with custom-made high-pressure diffraction setups, the nature and impact of the pressure-transmitting medium, and the role of forging even closer ties between computation and experiment: Considering the possibility of a shallow underlying MOF free energy surface, small changes in the reaction conditions can have a great impact on the outcome and therefore it is crucial to report detailed synthetic procedures. This allows for comparison of different studies examining the same material as small chemical changes affect the mechanical properties. Furthermore, MOFs are soft materials with phase transition pressures below $p < 0.1$ GPa, which is challenging for established high-pressure set-ups such as the DAC. We raise awareness for custom-made set-ups that allow studying of phase transitions at such 'low' high pressures in great detail because a smaller step size can be achieved compared to DACs. Also, we evaluate the role of the PTM when working under hydrostatic conditions. The intrinsic porosity and therefore potential uptake of penetrating PTM has to be considered, which affects the mechanical properties. As a last point we emphasize the power of combining experimental results with computational insights on the thermodynamics of phase transitions that enhance our understanding of experimentally observed responses to pressure.

The review was written by the author of this thesis and G. Kieslich. The concept of the perspective was developed by the author of this thesis, the literature research and survey were done by J. Stebani and the author of this thesis guided by G. Kieslich and A. S. J. Méndez greatly contributed to the chapter about custom-made high-pressure set-ups.

P. Vervoorts, J. Stebani, A. S. J. Méndez, G. Kieslich, Structural Chemistry of Metal-Organic Frameworks under Hydrostatic Pressures. *ACS Materials Lett.* **2021**, *3*, 1635-1651.

4.3 STUDY III. The Zeolitic Imidazolate Framework ZIF-4 under Low Hydrostatic Pressures

Despite the large interest of researchers in the responsiveness of flexible MOFs to hydrostatic pressures, the low pressures at which such phase transitions occur have so far limited the understanding of pressure induced phase transitions and the mechanical properties of flexible MOFs in general. In this work, a high-pressure powder X-ray diffraction set-up was used that is suitable to apply small pressure steps of Δp = 0.005 GPa. The phase transition behaviour of the prototypical flexible MOF ZIF-4(Zn) was investigated, following the evolution of lattice parameters and volume as a function of pressure in the range p = ambient – 0.4 GPa. The thus obtained bulk modulus of K = 2 GPa is the lowest experimentally determined bulk modulus for a flexible MOF so far, comparable to those of liquids such as water or methanol. These results are of interest to the large inorganic chemistry community that focuses on understanding structure-property relations in (porous) coordination compounds. Furthermore, it was shown how the mechanical response of very soft crystalline materials can be probed by applying state-of-the-art methodologies and setups that are available at large scale synchrotron facilities. With that the study offers non-specialists the scope and platform to understand and follow the challenges that exist when investigating high-pressure properties of very soft materials.

The paper was written by G. Kieslich and the author of this thesis and through contribution and critical discussion of all co-authors. The strategy was developed by G. Kieslich and the author of this thesis. The synthesis and characterization were done by M. G. Ehrenreich. The high-pressure powder X-ray diffraction experiments and data analysis were done by the author of this thesis, C. L. Hobday and G. Kieslich with the help of D. Daisenberger at the Diamond Light Source, Beamline I15.

P. Vervoorts, C. L. Hobday, M. G. Ehrenreich, D. Daisenberger, G. Kieslich, The Zeolitic Imidazolate Framework under Low Hydrostatic Pressures. *Z. Anorg. Allg. Chem.* **2019**, *15*, 970-974.

4.4 STUDY IV. Revisiting the High-Pressure Properties of the Metal-Organic Frameworks ZIF-8 and ZIF-67

Within this work we revised the high-pressure responsiveness of ZIF-8 that was shown to undergo a pressure-induced amorphisation at 'low' hydrostatic pressures of $p \approx 0.3$ GPa in previous studies. Applying a hydrostatic high-pressure powder X-ray diffraction set-up that allows for a high resolution of the pressure steps, the evolution of the lattice parameters and volume as a function of pressure in the range p = ambient – 0.4 GPa was studied. These detailed experimental insights revealed that what was previously assigned as a pressure induced amorphisation is a reversible crystalline-crystalline phase transition at p = 0.3 GPa coming with a change of lattice centring from a body centred to a primitive lattice.

The paper was written by the author of this thesis and through contribution and critical discussion of all co-authors. The strategy was developed by the author of this thesis under supervision of G. Kieslich. The synthesis and characterization of the material were done by the author of this thesis. The high-pressure powder X-ray diffraction experiments were done by the author of this thesis, S. Burger, K. Hemmer and G. Kieslich with the help of D. Daisenberger at the Diamond Light Source, Beamline I15 and the data analysis by the author of this thesis.

P. Vervoorts, S. Burger, K. Hemmer, G. Kieslich, *ChemRxiv* **2020**, DOI: 10.26434/chemrxiv.13146278

Note: ChemRxiv is not a peer-reviewed journal, it is an open access preprint archive.

4.5 STUDY V. Configurational Entropy Driven High-Pressure Behaviour of a Flexible Metal-Organic Framework

In this study it was shown for the first time that configurational entropy as introduced via chemical functionalisation can superimpose effects from vibrational entropy, thus discovering a new mechanism of how to manipulate the underlying free energy landscape in flexible MOFs. This work contributes fundamental insight into the thermodynamics and the tailoring of structural flexibility of stimuli(pressure)-responsive MOFs. By applying a combination of state-of-the-art high-pressure powder X-ray diffraction and molecular dynamics simulations, the flexible pillared-layer MOF $Cu_2(DB\text{-}bdc)_2dabco$ ($DB\text{-}bdc^{2-}$ = 2,5-dibutoxy-1,4-benzendicarboxlate, dabco = 1,4-Diazabicyclo[2.2.2]octane) was identified as the first example in which configurational entropy dominates the underlying free energy landscape. Given the absence of additional examples in the literature in which configurational entropy has been identified as the dominating factor, it is suggested that configurational entropy has been an overlooked parameter in the design and manipulation of flexibility in MOFs to date. The study highlights the power of combining experiment with theory to advance understanding of chemical factors that determine the physicochemical properties of modern materials.

The paper was written by the two shared first authors and through contribution and critical discussion of all co-authors. The concept and experiments were developed by the author of this thesis under supervision of G. Kieslich and R. A. Fischer. The materials were synthesised and characterised by the author of this thesis. The high-pressure powder X-ray diffraction experiments were done by the author of this thesis, C. L. Hobday and G. Kieslich with the help of D. Daisenberger at the Diamond Light Source, Beamline I15 and the data analysis was done by the author of this thesis. J. Keupp performed the molecular dynamics simulations under supervision of R. Schmid.

[‡] These authors contributed equally.

5 CONCLUSION

Within this thesis, the responsiveness of MOFs was studied with regard to host-guest interactions (**STUDY I**) and mechanical properties (**STUDY II – V**) and are summarized plus discussed in the following two sections separately.

5.1 Static Responsiveness Through Host-Guest Interactions

Although MOFs have been proposed as auspicious candidates to tackle current challenges in gas separation and storage, as well as to replace costly energy intensive processes like the cryogenic distillation, they have not yet found a viable way into application. Exploiting OMSs for gas separation of light hydrocarbons has been proven successful with high selectivities reported towards unsaturated olefines under ideal conditions. In **STUDY I** we have shown that multi-component adsorption measurements are the key to mimic more realistic conditions and understand the role of interfering gases in systems that alter the static responsiveness. The results from the experiments and simulations on the impact of water on the propane/ propene separation performance of Co_2dobdc clearly show that, although water molecules block the OMSs and therefore the preferential binding site for propene molecules, the selectivity towards propene is retained due to $\pi-H$ interactions between the water molecules and propene. This demonstrates the importance of using multi-component studies and serves as a motivation to other groups to determine the sorption selectivities not solely based on IAST but instead use multi-component measurements also in the presence of strongly adsorbing guest molecules such as water. In the future, the combination of multicomponent adsorption measurements and simulations will serve as a blueprint to analyse other benchmark MOFs suggested to tackle real separation issues, which is necessary to study the influence of intrusive compounds disturbing the perfect binary mixtures.

5.2 MOFs under 'Low' Hydrostatic Pressures

Studying the dynamic responsiveness of MOFs towards pressure has become a topic of great interest in the last years because it allows insight on the underlying thermodynamics while developing design principles to controllably manipulate mechanical behaviour. There have been some studies published over the last years that investigate structure-property relations, but this field is still in its infancy. **STUDY II-V** within this thesis have contributed to different aspects of MOFs under pressure, ranging from general challenges of high-pressure studies to the driving force of phase transitions.

One of the challenges addressed is the 'problem' of choosing the correct set-up. The applied HPPXRD set-up in **STUDY III** and **VI** proved to be ideally suited to study the mechanical response of soft materials such as MOFs under hydrostatic pressures. The set-up has a higher pressure resolution than achievable with a standard DAC and allowed to closely follow phase transitions. In the future it will be interesting to see if such home-built set-ups can benchmark with the DACs and inspire other researchers to develop set-ups with which additional properties like fluorescence or conductivity can be studied at high-pressures. Furthermore, it will be fascinating to see if bulk moduli, which are easily obtained with this hydrostatic set-up, can be related to general aspects of their underlying structure as observed for some solid-state materials. Of course, for such general structure-property relations larger sets of bulk moduli need to be obtained. In an early study the solvent accessible volume was linked to the elastic moduli in ZIFs[257] and some recent studies show a correlation between parameters such as the solvent accessible volume, connectivity of the metal node and the linker to the mechanical properties (precisely, the bulk modulus).[166,168,213]

When going towards targeted design of intelligent materials with dynamic responses it is not only important to understand structure-property relations but to develop design rules based on the driving forces (*i.e.* the underlying thermodynamics) why a material shows a certain response to an external stimulus. These design rules can serve as guidelines for experimentalists to move away from trial-and-error synthesis. The results form **STUDY V** suggest that configurational entropy as a design parameter has so far been broadly overlooked when tuning the underlying free energy landscape, while vibrational entropy and dispersion interactions are known to drive the phase transitions for instance in the MIL-53 family.[173,174] The discovery of configurational entropy as a driving force opens new ways to tune the stimuli-responsive behaviour of MOFs via judicious choice of functionalisation. Here, the cooperation between experimentalists and theoreticians is of great importance because solely from experiment it is not possible to draw conclusions on the underlying thermodynamics which are provided by the simulations.

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7   APPENDIX

7.1   Complete List of Publications

A)   Publications as first author on which this thesis is based.

STUDY I   *Coordinated Water as New Binding Sites for the Separation of Light Hydrocarbons in Metal-Organic Frameworks with Open Metal Sites.*
P. Vervoorts, A. Schneemann, I. Hante, J. Pirillo, Y. Hijikata, T. Toyao, K. Kon, K.-I. Shimizu, T. Nakamura, S.-i. Noro, R. A. Fischer, *ACS Appl. Mater. Interfaces* **2020**, *12*, 9448-9456.

STUDY II   *Structural Chemistry of Metal-Organic Frameworks under Hydrostatic Pressures.*
P. Vervoorts, J. Stebani, A. S. J. Méndez, G. Kieslich, *ACS Mater. Lett.* **2021**, *3*, 1635-1651.

STUDY III   *The Zeolitic Imidazolate Framework ZIF-4 under Low Hydrostatic Pressures.*
P. Vervoorts, C. L. Hobday, M. G. Ehrenreich, D. Daisenberger, G. Kieslich, *Z. Anorg. Allg. Chem.* **2019**, *645*, 970-974.

STUDY IV   *Revisiting the High-Pressure Properties of the Metal-Organic Frameworks ZIF-8 and ZIF-67.*
P. Vervoorts, S. Burger, K. Hemmer, G. Kieslich, *ChemRxiv* **2020**, DOI: 10.26434/chemrxiv.13146278.

STUDY V   *Configurational Entropy Driven High-Pressure Behaviour of a Flexible Metal-Organic Framework.*
P. Vervoorts,[‡] J. Keupp,[‡] A. Schneemann, C. L. Hobday, D. Daisenberger, R. A. Fischer, G. Kieslich, *Angew. Chem., Int. Ed.* **2020**, *60*, 787-793.

[‡] Authors contributed equally to this work.

B) Publications as co-author that originated from cooperations within the research unit "FOR 2433" or that are conceptionally related to it. The contribution from the author of this thesis to each publication is listed.

1. *Different Breathing Mechanisms in Flexible Pillared-Layered Metal–Organic Frameworks: Impact of the Metal Center.*
A. Schneemann, **P. Vervoorts**, I. Hante, M. Tu, S. Wannapaiboon, C. Sternemann, M. Paulus, D.C. F. Wieland, S. Henke, R. A. Fischer, *Chem. Mater.* **2018**, *30*, 1667–1676.

Synthesis of the materials and characterisation via scanning electron microscopy.

2. *Tuning the Mechanical Response of Metal–Organic Frameworks by Defect Engineering.*
S. Dissegna, **P. Vervoorts**, C. L. Hobday, T. Düren, D. Daisenberger, A. J. Smith, R. A. Fischer, and G. Kieslich, *J. Am. Chem. Soc.* **2018**, *140*, 11581-11584.

Performing high-pressure powder X-ray diffraction measurements and contributing to manuscript writing.

3. *Probing Local Structural Changes at Cu^{2+} in a Flexible Mixed-Metal Metal-Organic Framework by in Situ Electron Paramagnetic Resonance during CO_2 Ad- and Desorption.*
M. Mendt, **P. Vervoorts**, A. Schneemann, R. A. Fischer, A. Pöppl, *J. Phys. Chem. C* **2019**, *123*, 2940-2952.

Development of the concept together with M. Mendt. Syntheses and characterisation of the materials and contribution to manuscript writing.

4. *Flexibility control in alkyl ether-functionalized pillared-layered MOFs by a Cu/Zn mixed metal approach.*
A. Schneemann, R. Rudolf, S. J. Baxter, **P. Vervoorts**, I. Hante, K. Khaletskaya, S. Henke, G. Kieslich, R. A. Fischer, *Dalton Trans.* **2019**, *48*, 6564-6570.

Contributing to the revisions of this manuscript.

5. *Experimental Evidence for Vibrational Entropy as Driving Parameter of Flexibility in the Metal–Organic Framework ZIF-4(Zn).*
K. T. Butler, **P. Vervoorts**, M. G. Ehrenreich, J. Armstrong, J. M. Skelton, G. Kieslich, *Chem. Mater.* **2019**, *31*, 8366-8372.

Performing inelastic neutron scattering experiments and contributing to manuscript writing.

C)   Further Publications as co-author. The contribution from the author of this thesis to each publication are listed.

6.   *Highly porous nanocrystalline UiO-66 thin-films via coordination modulation controlled step-by-step liquid-phase growth.*
A. L. Semrau, S. Wannapaiboon, S. P. Pujari, **P. Vervoorts**, B. Albada, H. Zuilhof, R. A. Fischer, C*ryst. Growth Des.* **2019**, *19*, 1738–1747.

Measurement and evaluation of adsorption data.

7.   *Increasing Alkyl Chain Length in a Series of Layered Metal−Organic Frameworks Aids Ultrasonic Exfoliation to Form Nanosheets.*
D. J. Ashworth, T. M. Roseveare, A. Schneemann, M. Flint, I. Dominguez Bernáldes, **P. Vervoorts**, R. A. Fischer, L. Brammer, J. A. Foster, *Inorg. Chem.* **2019**, *58*, 10837-10845.

Measurement and evaluation of adsorption data.

7.2   Conference Contributions

1. 2nd European Conference on Metal-Organic Frameworks and Porous Polymers, Delft, Netherlands, November 2017, poster presentation of STUDY I:
    Contaminants in Binary Mixtures – Impact on Sorption Selectivities in MOFs with Open Metal Sites.

2. 6th International Conference on Metal-Organic Frameworks and Open Framework Compounds, Auckland, New Zealand, December 2018, poster presentation of STUDY V:
    Flexible MOFs under Hydrostatic Pressure: Balancing Reversible Phase Transitions with Amorphization Processes.

3. 14th International Conference on Materials Chemistry (MC14), Birmingham, UK, July 2019, poster presentation of STUDY III and V:
    Flexible MOFs under Hydrostatic Pressure: Balancing Reversible Phase Transitions with Amorphization Processes.

4. Japan-Germany Bilateral Symposium on Surface-Attached Metal-Organic Framework, Sapporo, Japan, October 2019, oral presentation of STUDY I:
    Influence of Open Metal Sites and Organic Side Chains in MOFs on Their Gas Sorption Properties.

5. FlexMOF Symposium 2019, Dresden, Germany, December 2019, oral presentation of STUDY II – V:
    (Flexible) MOFs under Low Hydrostatic Pressures.

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