

Reactive metal-organic frameworks for highly selective gas sensing applications

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Abstract

Metal-organic frameworks (MOFs) are a new class of hybrid compounds which are characterized by their high crystallinity and by well-defined pore systems in the microporous range. Due to their modular structure of inorganic metal-oxo clusters and organic linker molecules, these compounds exhibit a high variety of possible structures. As a result, it is possible to produce tailored frameworks that can be optimized for specific applications.

In this work, the synthesis of novel MOFs was investigated with respect to their application as selective materials for the use in sensors. The approach was based on the incorporation of organic molecules as linkers in a MOF which have specific interactions with only one specified analyte. Thus, the molecular properties of the linkers are combined with the porosity and high thermal and chemical stability of Zr-based MOFs. An outstanding representative of molecules with such specific interactions is the class of calix[4]arenes. These cup-shaped molecules have an intrinsic cavity in which guests can be encapsulated. Especially, the specific interaction with the toxic gas NO_2 has to be emphasized. This gas is present in the gas phase in an equilibrium with its dimer N_2O_4 which can decompose into its ionic components NO^+ and NO_3^- in a dissociation reaction. The electron-poor NO^+ is preferably hosted in the π -electron-rich cavity of a calix[4]arene, forming a deep blue coloured charge-transfer complex. Until now, this complex formation has only been possible either in solutions of the calix[4]arene with NO^+ -donating reagents or with the calix[4]arene bound to silica gels and NO_2 . By using calix[4]arene-containing molecules as organic linkers for the synthesis of a MOF, the complex formation with gaseous NO_2 could be transferred to a solid for the first time. The pore system of the MOF makes the cavities of the immobilised calix[4]arene accessible. Partially unsaturated sites on the metal clusters serve as LEWIS acid sites to stabilize the complex. Thus, a high stability of the sensor material against the highly aggressive gas NO_2 was guaranteed and a reversibility of the sensory process was achieved.

In the second part of this thesis, the synthesis of MIL-140 structured MOFs was systematically investigated and reaction conditions were determined that allow their synthesis at lower temperatures in glass vessels. By further reducing the reaction temperature down to $80\text{ }^\circ\text{C}$, linkers with more delicate functional groups can now be used which was impossible for the original syntheses carried out at high temperatures. In this context, a MIL-140 structured MOF based on 4,4'-stilbenedicarboxylic acid, the MIL-140D-*sdc*, was presented for the first time. With the aid of post-synthetic modifications, the linkers of the prepared MIL-140D-*sdc* could be partially replaced by 4,4'-azostilbenedicarboxylic acid. Hence, a mixed-linker MOF could be obtained. The special chemistry of the azo groups makes it possible to coordinate copper ions and store them in the framework. As a result, these framework compounds could be used for the detection of H_2S , which forms CuS with the coordinated copper ions in the framework. This reaction thus imparts a high degree of selectivity of this sensor material for H_2S .

Keywords: metal-organic frameworks • sensor material • molecular recognition • selectivity • calix[4]arene

Kurzzusammenfassung

Metal-organische Gerüste (*engl.*: metal-organic frameworks, MOF) sind eine neue Klasse von Hybridverbindungen, welche sich durch ihre hohe Kristallinität und gut definierten Porensystemen im mikroporösen Bereich auszeichnen. Durch ihren modularen Aufbau aus anorganischen Metall-Oxo-Clustern und organischen Linkermolekülen, weisen diese Verbindungen eine hohe Vielfalt an möglichen darstellbaren Strukturen auf. Daraus folgend ergibt sich die Möglichkeit zur Herstellung von maßgeschneiderten Systemen, die auf spezielle Anwendungen hin optimiert sind.

Im Rahmen dieser Arbeit wurde die Synthese von neuartigen MOFs im Hinblick auf die Anwendung als selektive Materialien für den Einsatz in Sensoren untersucht. Der Ansatz basierte auf der Integration von organischen Molekülen als Linker in einen MOF, die spezifische Wechselwirkungen mit nur einem spezifischen Analyten aufweisen. Somit werden die molekularen Eigenschaften der Linker mit der Porosität und hohen thermischen sowie chemischen Stabilität von Zr-basierten MOFs kombiniert. Ein herausragender Vertreter von Molekülen mit solchen spezifischen Interaktionen bildet die Klasse der Calix[4]arene. Diese kelchförmigen Moleküle weisen eine intrinsische Kavität auf, in die Gäste eingelagert werden können. Vor allem hervorzuheben ist die spezifische Wechselwirkung mit dem toxischen Gas NO_2 . Dieses liegt in der Gasphase in einem Gleichgewicht mit seinem Dimer N_2O_4 vor, das in einer Dissoziationsreaktion in seine ionischen Komponenten NO^+ und NO_3^- zerfallen kann. Das elektronenarme NO^+ wird bevorzugt in die π -elektronenreiche Kavität eines Calix[4]arens aufgenommen, wodurch sich ein tiefblau gefärbter *charge-transfer* Komplex bildet. Bislang war die Komplexbildung nur in Lösungen des Calix[4]arens mit NO^+ -donierenden Reagenzien oder mit dem an Silicagelen angebondenen Calix[4]arenen und NO_2 realisierbar. Durch die Nutzung von Calix[4]aren-haltigen Molekülen als organische Linker für die Synthese von einem MOF konnte die Komplexbildung mit gasförmigen NO_2 erstmals auf einen Feststoff übertragen werden. Das Porensystem des MOFs macht die Kavitäten der immobilisierten Calix[4]arene zugänglich. Teilweise ungesättigte Stellen an den Metall-Clustern dienen bei dieser Reaktion als LEWIS-saure Stellen zur Stabilisierung des Komplexes. Dadurch konnte eine hohe Stabilität des Sensormaterials gegenüber dem hochaggressiven Gas NO_2 gewährleistet und eine Reversibilität des sensorischen Prozesses erzielt werden.

Im zweiten Teil dieser Arbeit wurde die Synthese von MIL-140-strukturierten MOFs systematisch untersucht und Reaktionsbedingungen ermittelt, die ihre Synthese bei niedrigeren Temperaturen in Glasgefäßen ermöglichen. Durch die weitere Absenkung der Reaktionstemperatur auf $80\text{ }^\circ\text{C}$ können nun Linker mit empfindlicheren funktionellen Gruppen eingesetzt werden, was für die ursprünglich durchgeführten Synthesen bei hohen Temperaturen unmöglich war. In diesem Zusammenhang wurde auch erstmals ein MIL-140 strukturierter MOF auf Basis von 4,4'-Stilbendicarbonsäure, der MIL-140D-*sd*c, vorgestellt. Unter Zuhilfenahme von post-synthetischen Modifikationen, konnten die Linker des fertigen MIL-140D-*sd*c teilweise durch 4,4'-Azostilbendicarbonsäure ausgetauscht werden. So konnte ein *mixed-linker* MOF dargestellt werden. Die besondere Chemie der Azogruppen ermöglicht es, Kupferionen zu koordinieren und diese in das Gerüst einzulagern. Dadurch konnten diese Gerüstverbindungen für den Nachweis von H_2S verwendet werden, das mit den koordinierten Kupferionen im Gerüst CuS bildet. Dadurch verleiht diese Reaktion diesem Sensormaterial eine hohe Selektivität für H_2S .

Stichworte: metall-organische Gerüste • Sensormaterial • molekulare Erkennung • Selektivität • Calix[4]arene

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1 Introduction

The scientific advancement of porous matter is driven by an increasing demand of functional materials which exhibit a high degree of tuneability. Zeolites are a well-established and studied class of porous materials, which possesses pore sizes on a scale of less than one nanometre.^[1] With the porous carbons, materials were found the pore size of which reaches far into the mesoporous range.^[2] The resulting gap between these two materials could be closed by metal-organic frameworks (MOFs). These materials belong to the material class of inorganic-organic hybrid compounds.^[3] Additionally, due to their modular design, these materials can overcome existing limits such as lack of flexibility or functionality of existing zeolitic frameworks.

The first reports on these frameworks originate from HOSKINS and ROBSON and the term MOF was introduced for the first time by YAGHI et al. in 1995.^[4] These solids are characterized by metal-oxo clusters which are connected by so-called organic linkers. The coordinating functionalities on the linker molecule are often based on nitrogen or oxygen atoms like in amino or carboxylate groups. Using a linker with at least two functional groups, these clusters can be linked to each other, resulting in one- to three-dimensional highly-crystalline frameworks.^[5]

The modular structure of metal cations and linker molecules provides a strong contrast to conventional porous materials. Thus, the large number of theoretically accessible MOF structures can already be recognized here by the endless combination possibilities of the two types of building blocks. With the synthesis of an isoreticular MOF series, EDDAOUDI *et al.* impressively demonstrated that with the same metal source and the addition of different linkers, a variety of frameworks sharing the same topology but with different properties, such as inner surface area or density, can be obtained.^[6] As a result, a high degree of control over the synthesis can be ensured by the choice of precursors, and properties such as pore size or pore functionality can be systematically adjusted. This offers the possibility of a tailored synthesis of MOFs for a previously defined application.^[7]

With surfaces areas of up to $7000 \text{ m}^2 \text{ g}^{-1}$, these materials are ideal for gas storage.^[8] In times of global warming and climate change, the high storage capacity for hydrogen as a potential fuel is particularly worth mentioning.^[9] Furthermore, the harvesting of drinking water in desert regions is an interesting field of application.^[10] Moreover, MOFs are used in electrochemical processes,^[11] heterogeneous catalysis,^[12] gas separation membranes^[13] and drug delivery systems.^[14]

Despite the many advantages of MOFs over other materials and their broad application possibilities, many of these materials suffer from a lack of thermal or chemical stability, which restricts their use in industrial processes.^[15,16] With the synthesis of the first Zr-based MOF, CAVKA *et al.* were able to provide a framework with especially high stability and resistance to a variety of common reagents.^[17] This isoreticular series yields the compounds UiO-66 and UiO-67,

in which the length of the linker is extended by one phenylene unit and thus the pore size and the inner surface also increase. However, the more longer linker molecules make the UiO-67 more susceptible to moisture, which can either attributed to rotational or steric effects or destructive capillary forces.^[15,18] Additional functional groups on the linker can increase the moisture tolerance at the cost of porosity.^[19] The same precursors and higher temperatures allowed GUILLERM et al. to describe a new isorecticular series of Zr-MOFs.^[20] With thermal stability of over 500 °C, these MOFs are outstanding representatives of this class of material.

Based on this research, one focus of this work was the synthesis of new Zr-based frameworks. The objective was to closely combine functionality and stability in order to develop highly selective sensor materials for hazardous gases. Current sensor devices often consist of semiconducting metal oxides or carbon materials such as CNTs.^[21] Although these are characterized by a very high sensitivity, cross-sensitivities to other molecules and interfering influences of humidity often occur. The stability of MOFs against a variety of aggressive or toxic gases has already been well investigated.^[22] In addition, there are already many reports on MOFs as luminescent or photonic sensor materials for the detection of gases or vapours.^[23] A small disadvantage is the applicability of these MOFs for the detection of an entire analyte group and not of single molecules.

In order to improve the selectivity, a new approach for the production of highly selective or specific sensors is chosen in this thesis. Here, organic molecules that exhibit a very selective or specific interaction with a particular gas are explored. Some specific interactions are described in the literature, such as the colorimetric detection of SO₂ with an indicator-displacement assay based on porphyrins.^[24] However, most of these reactions were conducted in solution. By functionalising such molecules with carboxylates, they can be incorporated into MOFs. As porous solids, they are much more suitable for the practical use as sensing material for gases.

A main part of this thesis focuses on calix[4]arenes, which were firstly described in the 1940s by the German chemists ZINKE and ZIEGLER.^[25] Later, these molecules were mainly characterized by the work of GUTSCHE.^[26] The ring structures of these molecules are constructed from phenolic units that are linked by methylene groups. Due to the possibility of rotation around the methylene bridges, different conformational isomers can be obtained. Due to their intrinsic porosity and a non-dense packing in the crystal, these molecules already have a certain degree of porosity as solid.^[27] Nevertheless, calix[4]arenes show a special reaction behaviour towards NO₂ only in solution, since the cavities are only accessible here.^[28] As a result of this reaction, a deep blue coloured charge-transfer complex forms.^[29] Furthermore, this complex is stabilized by the addition of LEWIS acids and retains its colour over months.

A combination of these organic molecules with zirconium salts results in a framework structure which inhibits a three-dimensional network with large inner surfaces area. The cavities of the

calix[4]arenes become accessible by their presentation in the porous solid and consequently transfers the unique properties of the calix[4]arene into a MOF. With this approach, the formation of a charge-transfer complex can also take place in the solid state. Before this work, only a few MOFs based on calix[4]arenes as linkers had been published.^[30] The first challenge was to find a suitable calix[4]arene as linker for MOF synthesis and to equip this with carboxylic acid groups. Calix[4]arenes in the *1,3-alternate*-conformation possess an appropriate shape for this purpose. In comparison to linear linkers such as terephthalic acid, these correspond to tetrahedral building blocks. By introducing open metal sites into the framework, LEWIS acidity is generated and prevents the nitration of the calix[4]arenes by the highly corrosive NO₂.^[31] This further guarantees long-term stability of the MOF and enables the possibility for a reversible sensing process. For application as sensor material, characteristic parameters such as response time or detection limit have to be specified for the novel compound.

A further topic this thesis deals with is the systematic investigation of the crystallisation of MIL-140 structured MOFs. A major drawback of the synthesis of Zr-based MOFs with the MIL-140 structure is the high synthesis temperatures of above 200 °C and the fact that often product mixtures of UiO-66 and MIL-140 phases result. Especially, adequate reaction parameters are required to permit a phase-pure synthesis of a desired MIL-140 structured MOF. In the scope of these investigations, the synthesis conditions for the systems MIL-140A and MIL-140C with terephthalic acid and biphenyl dicarboxylic acid, respectively, as linkers, which were already described in the literature, are examined in detail. In addition, another new MOF with the MIL-140 structure based on stilbene dicarboxylic acid (*H₂sdc*) was described for the first time. The synthesis of the MIL-140D-*sdc*-MOF was adapted from the original synthesis of MIL-140D, the framework of which is constructed with the dichloro azostilbene dicarboxylic acid (*H₂abdcCl₂*), which is similar in length. Furthermore, the reaction temperature needs to be lowered in order to use linkers with delicate functional groups. To achieve this, special synthesis techniques can be applied. On the one hand, the use of crystals in a seed-mediated synthesis would be conceivable.^[32] On the other hand, there is the possibility of post-synthetic modifications of previously presented compounds.^[33] Functional groups of incorporated linkers can be modified or entire linker molecules can be exchanged for others. In this way, the generation of a mixed-linker MOF is also possible.^[34] By incorporating *H₂abdc* into a MIL-140D-*sdc* framework, functionality of the azo-group and stability of the carbon-based stilbene backbone can be combined. The introduction of the functional azo group is of crucial importance, because different metals have the possibility of coordination to this group.^[35] For the detection of H₂S, copper can be incorporated into the framework between two azo linkers and the formation of CuS can be exploited to achieve high selectivity. A similar principle was used years ago for semiconducting metal oxides as sensors doped with CuO.^[36] Here, a mixed-linker MOF for the detection of gaseous H₂S is presented.

In the following chapters of this thesis, a theoretical foundation is given at the beginning for the work accomplished here. Afterwards, the three publications prepared are introduced with a brief preface and then finally presented as a result. A concluding chapter is also given in which perspectives on further studies are given.

2 Theoretical background

2.1 Metal-organic frameworks (MOFs)

Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) are a class of inorganic-organic hybrid materials. These crystalline, microporous materials are based on organic linker molecules which connect two or more inorganic nodes to infinite one- to three-dimensional frameworks. The inorganic nodes consist of or metal-oxo clusters and are generally referred to as secondary building units (SBUs), or more precisely as inorganic building units (IBUs). The connecting bricks or linker molecules need two or more coordination sites which are often carboxylate groups or nitrogen-heterocycles for the complexation of the metal nodes. Widely used are rigid benzene-di- or tri-carboxylate linkers but more and meanwhile more flexible linkers are used in MOF synthesis.^[37]

By the combination of various metal cations and linker molecules, a variety of differently structured frameworks is accessible. Due to this modular setup of MOFs, a tailored design for desired applications is possible. The coordination pattern of the IBUs depends on the used metal cation and its free coordination sites and is one essential brick for the building concept of MOFs.^[38] This can be illustrated by the example of the linear linker terephthalic acid which forms different IBU geometries depending on the used metal type, as it is shown in Figure 1. In the Al-based MIL-53, the octahedral IBUs are connected via four linker molecules, resulting in one-dimensional pores.^[39] With the use of chromium or zinc as metal source (MIL-101 or MOF-5), IBUs with six points of extension occur.^[40,41] A 12-fold coordination of the IBUs is realized in the titanium- and zirconium-based MOFs MIL-125 and UiO-66.^[17,42]

Beside different geometries of IBUs, the shape of the bridging linker molecules and their number of linking sites ensures further combination possibilities. Moreover, the length of the linker molecules can be varied, which is often realized by the introduction of additional phenylene units. This extension of the linker molecules is in most cases accompanied by an enlargement of the pore system of the MOF. With retention of the original structure of the network, the compounds are considered as isorecticular.^[6,43] With increasing linker length, the tendency of interpenetration rises, mainly due to π -stacking interactions.^[37,44] The pore chemistry of MOFs can furthermore be fine-tuned by the systematic attachment of functional groups to the linker. Depending on the nature of the functionalisation, this affects the pore size in most cases, the hydrophobicity and polarity without altering the framework topology.^[45] Additional functional groups can also have an influence on the thermal and chemical stability.^[46]

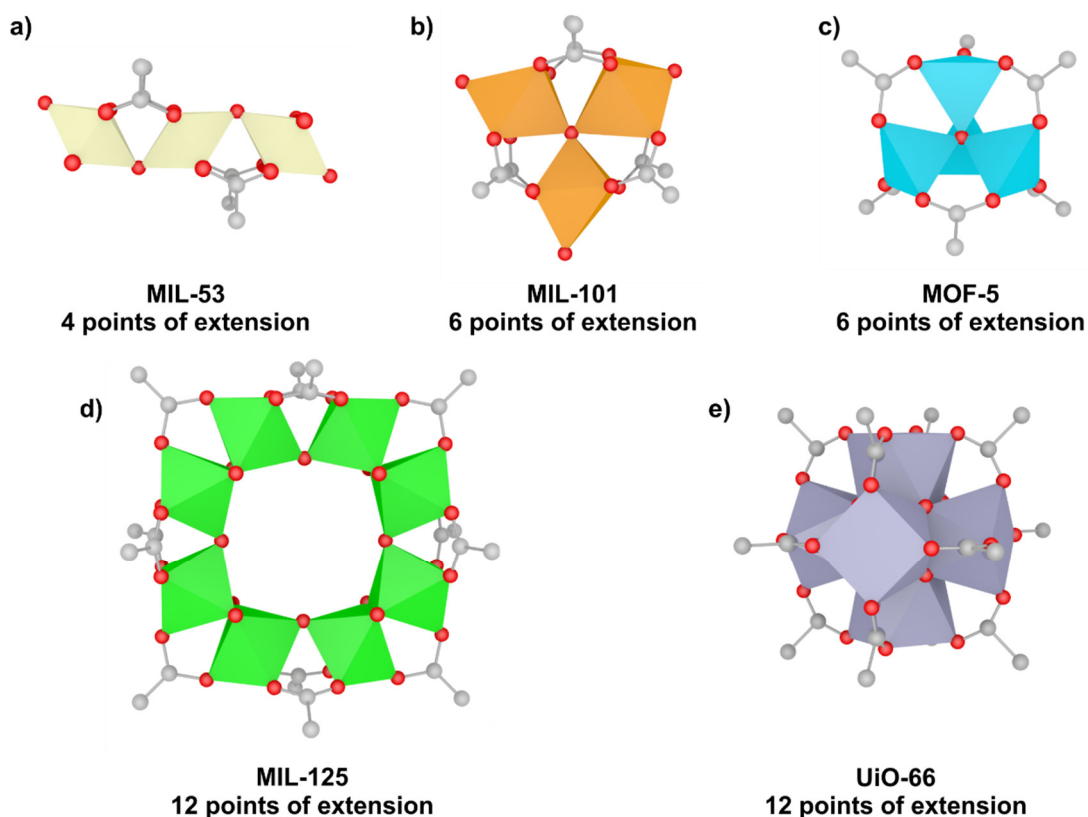


Figure 1. Illustration of typical IBUs of common MOFs with regard to the different numbers of points of extension (carbon: grey, oxygen: red, aluminium: pale yellow, chromium: orange, zinc: blue, titanium: green, zirconium: purple). a) chain-like IBU of Al-based MIL-53;^[39] b) trimeric IBU of Cr-based MIL-101;^[41] c) tetranuclear IBU of Zn-based MOF-5;^[40] d) ring-like IBU of Ti-based MIL-125^[42] and e) hexanuclear IBU of Zr-based UiO-66.^[17]

Knowledge about the preferred geometry of the IBU and the shape of the linker is important to design MOFs, but there are several more factors that need to be considered. By changing the synthesis conditions, like reaction temperature or solvents, different coordination geometries and numbers can be realized for the same metal ion.^[47] Using novel organic linkers or delicate functional groups, the synthesis temperature needs to be mild enough to maintain the functionalisation but still high enough to form coordinative bonds with the IBU.^[48]

The term MOF was firstly established by YAGHI for a compound containing metal ions linked by organic molecules.^[49] According to YAGHI, only materials which have certain features like a strong metal-oxygen bond, modifiable linker molecules and a defined structure as well as a high crystallinity should be designated as MOF.^[48] With the description of the zinc-based isorecticular IRMOF-*n* series (*n* = 1-16), YAGHI and co-workers presented prototypes of this new material class.^[6] Based on geometric consideration, the isorecticular synthesis combines different linkers with the same tetranuclear ZnO₄-IBU to cubic primitive structures. As a result, the pore sizes range from 4 to 29 Å and the free volume from 55 to 91%. Although the IRMOF series reveal high specific surface areas, the strength of the zinc-oxygen bond is relatively weak. For this

reason, most zinc-based MOFs exhibit a poor thermal or chemical stability limiting their potential in applications, like for example as a material for gas storage.^[50]

An example for chemically and thermally more stable zinc-based MOFs are the zeolitic imidazole frameworks (ZIFs). This class of porous materials crystallizes in zeolite-like nets, by formally exchanging tetrahedrally coordinated Si or Al atoms with transition metal ions like Zn^{2+} or Co^{2+} . The bridging oxygen species are replaced by imidazolate links.^[51] Due to this arrangement, the bridging angle of a metal-imidazolate-metal unit is close to 145° , showing similarity to the O-Si-O angle in zeolites. Due to their high tolerance towards moisture and acidic media, ZIFs are desirable materials for CO_2 separation applications in industry.^[52]

Despite their often high thermal stability of $250^\circ C$ and more a major disadvantage of MOFs is their low chemical stability towards humidity as well as acidic or basic media.^[6,46,51] Since the chemical stability of the framework is mainly dictated by the strength of the coordinative bonds between the IBU and the linker, high-valent metal cations with high oxidation states, like Ti^{4+} or Zr^{4+} , can be used as a route for the synthesis of stable MOFs. These cations obtain high charge densities and the higher affinity towards oxygen results in stronger coordination bonds. Furthermore, the inorganic nodes tend to have a higher connectivity, because they need more ligands to balance their charge.^[53] However, the number of titanium-carboxylate-based MOFs is low owing to highly reactive titanium sources and a lack of control over the crystallisation behaviour of Ti-MOFs.^[42,53,54] Contrary to the work with Ti-based MOFs, the Zr-based MOFs are widely known and the synthesis methods are already well-established.^[55]

2.2 Synthesis and modification methods

In addition to solvent, linker molecules and metal salts, other additives, so-called modulators, are used for the synthesis of MOFs. Depending on the nature of the modulator, a distinction is made between coordination and deprotonation modulation.^[56,57] The basic principle of the coordination modulation is the competition between linker and modulator. In the case that dicarboxylic acids are used as linkers, monocarboxylic acids are often used as modulators, such as formic or acetic acid as well as more complex ones like amino acids.^[58] In this process, the modulator complexes the metal cations and needs to be exchanged with the linker molecules to build up a framework. The complexation reduces the supersaturation in the reaction mixture and decelerates the formation of crystal nuclei. The exchange with the linker molecules is a dynamic and reversible process leading to a more ordered crystal growth and the lower number of seeds often results in larger crystals. Another benefit of an excess of modulator is the saturation of the crystal surfaces with these monocarboxylic acids which reduces the attractive interactions between these particles. For these reason as well as by steric or charge effects, the level of intergrowth of the particles is lowered which increases the probability of single crystal growth (Figure 2).^[57]

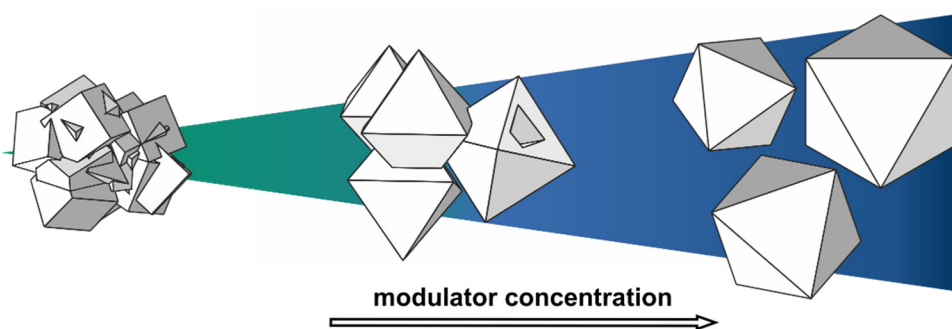


Figure 2. Schematic presentation of the influence of the amount of modulator on the crystal size and shape as well as on the degree of aggregation. Reproduced and edited from ref. ^[59].

The aid of modulators in MOF syntheses does not only influence the particle size and the crystal growth.^[60] The preparation of some compounds, especially those with longer linker molecules than terephthalic acid, tends to be more difficult and not reproducible without modulating agents.^[61]

A factor not to be neglected is the relationship between the amount of modulator and its acidity on the pH-value which has a decisive influence on the solubility of the linker molecules. Thus, it also has a considerable influence on crystallinity, morphology and several other properties.^[62] Furthermore, modulators can act as structure-directing agents affecting the crystal structure by reducing the connectivity of the IBU.^[63]

However, the influence of modulators on the resulting MOF structure is even more pronounced. In spite of the high crystallinity, the idea of ideal MOF crystals is false, many of them rather show

quite a large number of defects.^[64,65] The concentration and the identity of the modulator as well as the reaction time or temperature can be varied to tune linker vacancies.^[66,67] This behaviour can be explained with regard to the crystallization process. If the modulator is not exchanged with a linker molecule and still remains coordinated to the IBU, it acts as defect-compensating ligand. A linker molecule in the MOF can consequently be replaced by two modulator molecules (Figure 3a). Correspondingly, there are also cluster defects where a large number of linkers has been replaced by modulator molecules and no connection can be established (Figure 3b).^[68] These defects can provide higher surface areas and a more porous structure but can also enhance the robustness and stability of the frameworks, especially if trifluoroacetic acid is used as modulator.^[64,67,69,70] By subsequent removal of the molecules with heat treatment, unsaturated sites at the IBU can be obtained (Figure 3c). These unsaturated metal sites act as LEWIS acid sites and can for example increase the catalytic activity of a MOF.^[71] For example, the works of SHEARER *et al.* focus on the influence of monocarboxylic acids on the concentration of defects. The studies can be summarized as defect engineering. They show that tuning the properties of the MOFs is possible and that these defects can be functionalised by exchanging the acidic ligands.^[72,73] This process is an important part in MOF chemistry and will be discussed in the following.

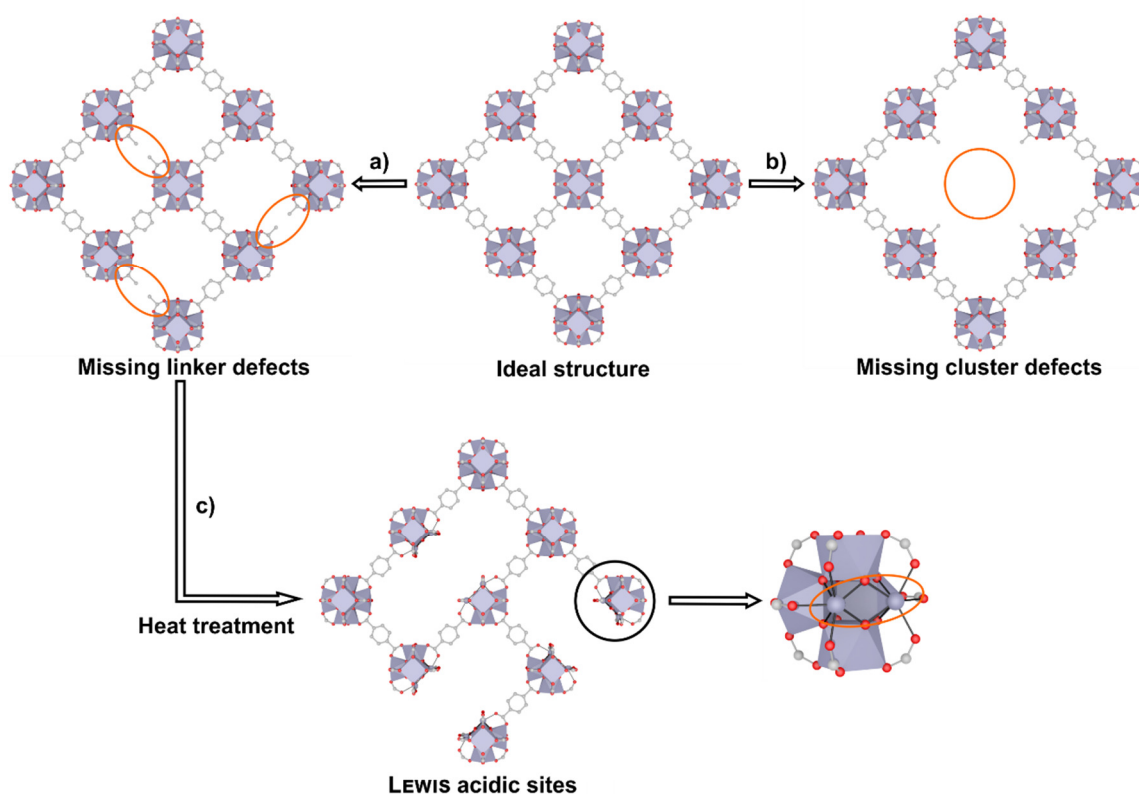


Figure 3. Illustration of defect engineering in MOFs between an ideal crystal structure and defective crystal structures obtained from modulated synthesis. Starting from the ideal structure a) shows missing linkers and b) missing clusters. After a heat treatment (c) of a defective structure, the modulators are removed and LEWIS acid sites are formed. Reproduced and edited from ref. ^[69,72], crystal structure produced from crystal data given in ref. ^[17].

Functionalities in MOFs are very important for several applications but not all functionalised frameworks are accessible through direct synthesis. For example, some functionalised linkers have poor solubilities or an insufficient thermal stability.^[74] To overcome these limits, post-synthetic approaches are developed, modifying existing functionalities or introducing new ones into preassembled MOFs. Methods like the post-synthetic modification (PSM) or the post-synthetic-exchange (PSE) extend synthetic variability without topological changes. To undergo these chemical reactions at the functional group there are some requirements that the MOF must fulfil. Certainly, the framework must be stable under the reaction conditions and exhibit a porous structure, so that the functional groups are accessible and can also react inside of the lattice. During a modification, possible by-products may occur, which have to be removed from the pore system.^[75]

In literature, various types of reactions like couplings, condensations, or click chemistry are described and above all, the amino group is particularly emphasized as a well functionalisable group. The group of COHEN is specialized in the field of post-syntheses and impressively demonstrates the possibilities this approach offers (Figure 4a).^[76,77] In some cases, a functional group can subsequently be introduced into an unfunctionalised MOF which requires exceptional chemical stability.^[78] As already mentioned, click chemistry is a popular approach in the field of PSM and often these reactions are conducted with azide groups. The direct synthesis of MOFs with azide-functionalised linkers is a difficult task due to the delicate nature of the azide group. Compounds containing this group exhibit a low thermal stability and often show a degradation of the azide group above 80 °C.^[79] Producing MOFs with more than one functional group, the tandem PSM approach is a useful method in which the functionalities are integrated step by step into the lattice.^[80] Some PSMs do not require additional reagents. These are thermally or photochemically induced, for example as a removal of protective groups or cycloadditions.^[81]

The other post-synthesis route beyond the PSM is based on exchange reactions of key components of the MOF. This PSE or building block replacement includes methods like solvent-assisted linker exchange (SALE), solvent-assisted ligand incorporation (SALI) or non-bridging ligand replacement and transmetallation.^[82] The most widely used PSE is the SALE which highlights in particular the importance of the solvent. In general, an already prepared MOF is dispersed in a solvent and an additional linker is added. During this procedure it is possible to exchange all linker molecules completely and to obtain a new MOF with the original topology but new functionality (Figure 4b).^[83] Thus, a simple control on the pore environments can be pursued. With the gradual introduction of even longer linker molecules, the pore size can be tuned by expanding the structure.^[84] Nevertheless, the linkers to be exchanged should have similar dimensions in length and coordination geometry for a more successful exchange.^[85] The SALI allows the insertion of additional molecules inside the framework. The IBUs inside the MOFs are often charge balanced with non-bridging ligands as modulators or possess unsaturated metal sites

(Figure 4c). This setup can be used to exchange existing ligands or introduce new charge compensating ligands bound directly to the metal cations.^[86] This utilisation of the metal nodes can enhance the chemical stability of the MOFs significantly.^[87] For the preparation of MOFs containing IBUs with different metal ions, syntheses can be conducted with mixed-metal salts like Ce^{4+} and Zr^{4+} .^[88] However, this is also achievable via transmetalation (Figure 4d).^[89] The process is similar to that of the SALE. But instead of a second linker other metal salts will be added to the MOF which is again dispersed in a solvent. This approach is very useful for the insertion of metal ions in existing MOF structures which cannot be used as metal salt for the synthesis due to their high reactivity like Ti^{4+} .

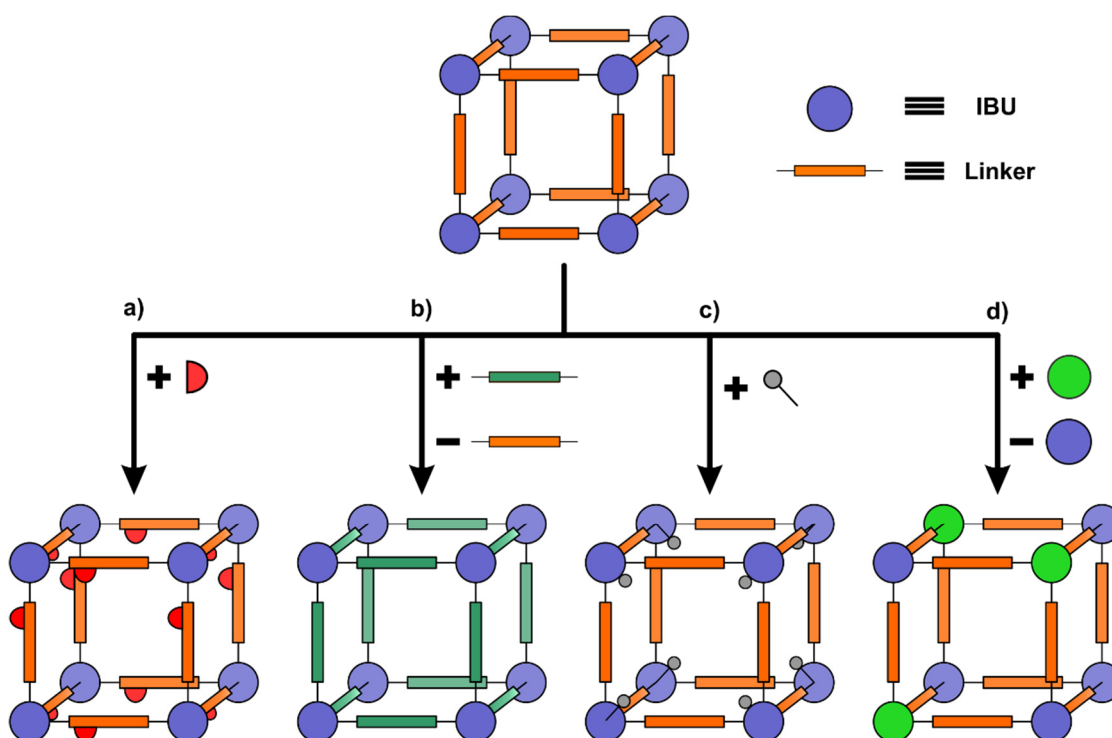


Figure 4. General scheme of different post-synthetic modification possibilities with a) post-synthetic modification; b) solvent-assisted ligand exchange; c) solvent-assisted ligand incorporation and d) transmetalation.

One last method of synthesising new functionalised materials that will be briefly explained here is the mixed-linker approach based on conventional synthesis.^[90] Either several linkers can be used in a one-pot synthesis or previously created two-dimensional MOFs can be extended to three-dimensional networks via another linker. In the second case, subsequently added ditopic linkers connect free coordination sites at the IBUs.^[91] Nevertheless, this approach offers the chance to build up multicomponent MOFs and pores with a microenvironment which can be tuned according to the later application. With the mixed-linker approach, the TELFER group established a MOF inspired from protein engineering with well-defined and enzyme-like pockets as new class of heterogenic catalysts.^[92]

Post-synthetic approaches offer the potential to create new MOF structures which are not accessible by using conventional synthesis procedures. The synthesis temperature is often considerably lower than typically required in the solvothermal pathway. Furthermore, MOFs with distinct compositions or certain properties can be obtained.

2.3 Zr-carboxylate-based MOFs

Two prominent representatives of Zr-based MOFs are the UiO-66 and the MIL-140A. In the following subchapters, the structures of both materials, as well as their isorecticular analogues, are explained in more detail. In addition, there will be also an insight into secondary phases and various synthesis possibilities to obtain phase pure materials. In the last part, the properties of these compounds are compared and possible applications discussed.

2.3.1 The UiO series

The isorecticular series of UiO-66 to UiO-68 was firstly described by the LILLERUD group in 2008.^[17] The frameworks consist of the same inorganic nodes that were previously reported as isolated clusters.^[93] It is formed by an inner core of a Zr_6 -octahedron, whose faces are capped with μ_3-O^{2-} and μ_3-OH^- alternately (Figure 5a). The resulting composition of the cluster is $[Zr_6O_4(OH)_4]^{12+}$. The free edges of the octahedron are bridged by 12 carboxylates ($-CO_2^-$) from the linker molecules, wherein each carboxylate coordinates two Zr-cations. In the formed $Zr_6O_4(OH)_4(CO_2)_{12}$ cluster, each Zr-cation is square-antiprismatic coordinated (Figure 5b). If one IBU is considered, the arrangement of the linkers and the twelvefold coordination results in a cuboctahedral coordination polyhedron built up from the other IBUs. This coordination polyhedron is usually found only in metals that crystallise in a cubic-close packing (*ccp*) and also have a 12-fold coordination (Figure 5c). Thus, the topology of the UiO-66 family can also be understood as extended *ccp*, in which the IBUs are separated from each other by the linkers. Similar to the *ccp* of metals, the structure of UiO materials contains cavities that can be regarded as tetrahedrally and octahedrally shaped pores. Both cavities are connected via triangular windows which are stretched over the linker molecules (Figure 5d).

Accordingly, the length of the linker has a direct effect on the distance of the IBUs. In the isorecticular compounds UiO-67 and UiO-68, the linker is elongated by one or two phenylene units, respectively, arising in larger pore sizes and corresponding triangular windows sizes. Naturally, isorecticular compounds of UiO-66 can be synthesised with shorter linker or derivatives of the terephthalic acid.^[94,95]

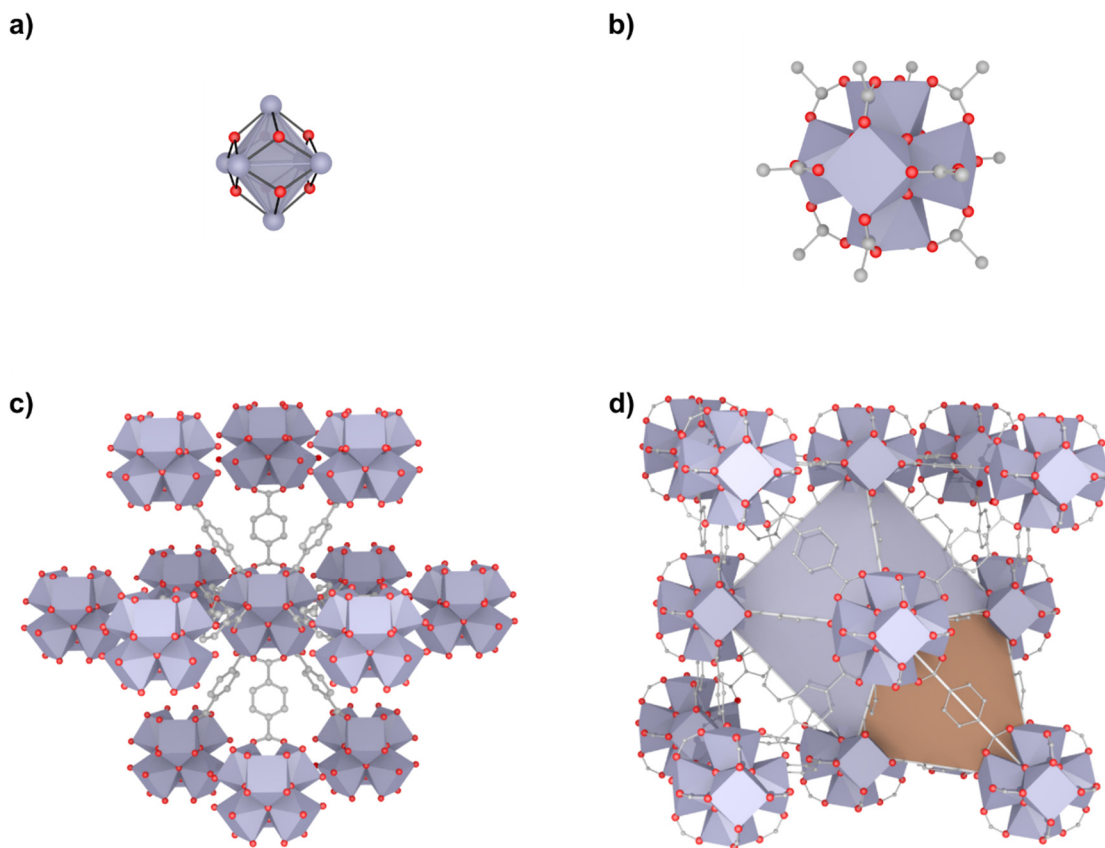
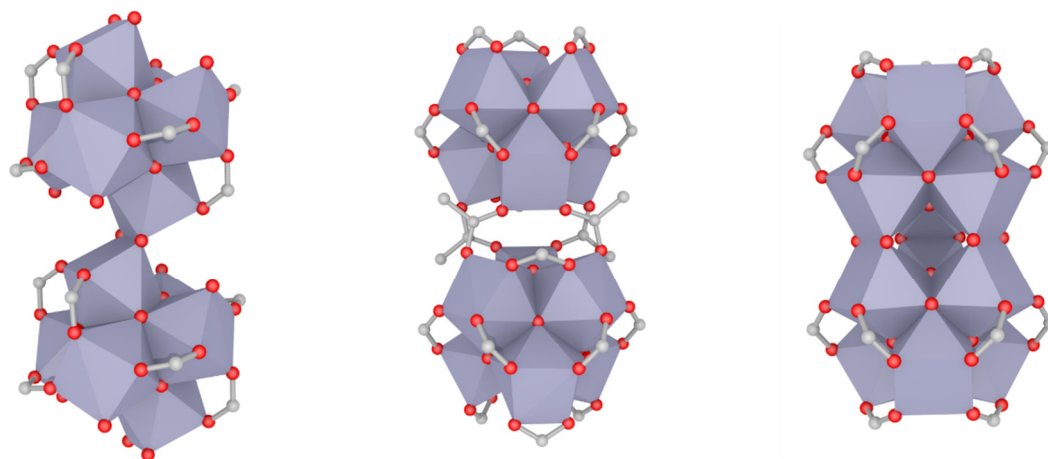


Figure 5: a) Zr_6 octahedron with oxygen capped faces, b) hexanuclear IBU of the composition $Zr_6O_4(OH)_4(CO_2)_{12}$ with the square-antiprismatic coordination of zirconium (zirconium: purple, oxygen: red, carbon: grey); c) illustration of the cuboctahedral coordination polyhedra resulting from a twelvefold coordination around a single IBU and d) crystal structure of UiO-66 with highlighted octahedral (purple) and tetrahedral void (brown). Crystal structure produced from crystal data given in ref. [17].

The crystal structure solution from CAVKA *et al.* was determined from powder data, but the hydrogen atoms could not be localized during this refinement. With the addition of monocarboxylic acids like benzoic acid, SCHAATE *et al.* could obtain single crystals of a related structure, the UiO-68-NH₂, which crystallises with the same topology like the UiO-66.^[61] With the same approach, they were able to crystallise an UiO related framework under the use of an azobenzene dicarboxylate ($abdc^{2-}$) as linker.^[96] The use of monocarboxylic acids as modulators is discussed in chapter 2.2. In another work, KATZ *et al.* described the synthesis of UiO-66 and UiO-67 as well as several isostructural compounds with functionalised linker molecules with the use of HCl as additive. They point out, that HCl enhance the solubility of the $ZrCl_4$ in DMF speeding up the formation of the products.^[97] The FÉREY group produced crystalline Zr-MOFs with *fcu*-topology using a precursor approach.^[98] In contrast to the conventional solvothermal synthesis, they prepared zirconium methacrylate oxoclusters in a first step and used them as metal source. With the addition of terephthalic acid to the synthesis, the initial methacrylate ligands were exchanged with the dicarboxylates forming frameworks with UiO-66 structure. Another example of a synthesis technique for the crystallisation of UiO-66 is the electrochemical

deposition. In this case, zirconium electrodes are used as only metal source and by applying of a current, the electrochemical film deposition could be realised.^[99]

Apart from the classical hexanuclear cluster as IBU, there are several Zr-MOFs with related clusters that have recently been published. In the CAU-22, these Zr-cluster are condensed, forming edge-linked one-dimensional chains, retaining the same coordination number as a single IBU (Figure 6a).^[100] A similar coordination geometry can be achieved by bridging two cluster with four carboxylate groups. These clusters can also be used as precursor in MOF synthesis (Figure 6b).^[101] Furthermore, dodecanuclear clusters are reported in which two Zr₆-cluster are dimerized by six bridging OH-groups (Figure 6c).^[102] This arrangement is used as building brick in hexagonal MOFs like CAU-39, which are related to the face-centred cubic UiO-MOFs.^[103] Meanwhile, many groups deal with systematic investigations of the crystallisation behaviour of MOFs.^[88,104]



a) $\text{Zr}_6\text{O}_4(\text{OH})_4(\mu\text{-OH})_2(\text{CO}_2)_8$ b) $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{10}]_2(\text{CH}_3\text{COO})_4$ c) $\text{Zr}_{12}\text{O}_8(\text{OH})_8(\mu\text{-OH})_6(\text{CO}_2)_{18}$

Figure 6: Illustration of different Zr-based clusters related to the hexanuclear IBU of the UiO-66 with their possible points of extension; a) chain-like IBU of condensed Zr₆-cluster, b) two hexanuclear cluster connected *via* four acetate ions and c) a dodecanuclear Zr₁₂-cluster with edge-sharing hydroxide groups (zirconium: purple, oxygen: red, carbon: grey, hydrogen atoms are missing for reasons of clarity). Crystal structures produced from crystal data given in ref. ^[100-102].

2.3.2 The MIL-140 series

In 2012, a new series of porous Zr-based MOFs was reported by GUILLERM *et al.* using the same linker molecules as for UiO-66 and its analogue structures.^[20] The resulting frameworks are polymorphs of the UiO series and denoted as MIL-140 series. Instead of the hexanuclear Zr₆ cluster from the UiO phase, the MIL-140 materials have infinite zirconium oxide chains as IBUs, oriented parallelly along the *c*-axis (Figure 7a). Each zirconium cation is coordinated by three μ_3 -O²⁻ oxygen ions and four oxygen ions from the carboxylate groups. Hence, the coordination number of the zirconium cations is seven in contrast to the UiO materials with a coordination number of eight but similar to the polyhedra in monoclinic ZrO₂.^[105] Due to this arrangement, the crystallographic parameter for the *c*-axis is the same for all compounds (Figure 7b). One chain is connected via dicarboxylic linkers to six other chains stretching a three-dimensional framework with the general formula [ZrO(L)] (with L as dicarboxylate linker). The one-dimensional tube-like pores are located between three zirconium oxide chains and are framed by the linkers (Figure 7c). Thus, the length of the linker has a direct influence on the pore size and the triangular window similar to the UiO series.

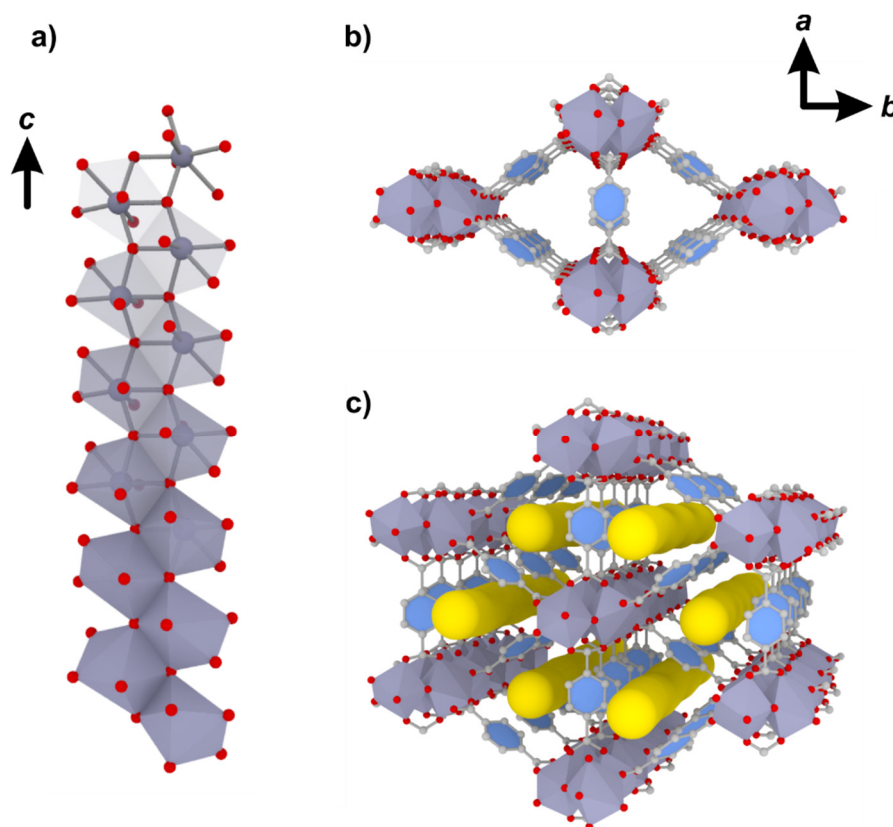


Figure 7. a) one-dimensional chain-like IBU of MIL-140 based MOFs with sevenfold coordinated Zr and b) crystal structure of MIL-140A with view along the *c*-axis with terephthalic acid as linker molecule (zirconium: purple, oxygen: red, carbon: grey, the benzene rings are filled in blue and hydrogen atoms are missing for reasons of clarity); c) three-dimensional presentation of the MIL-140A structure with highlighted tube-like pore system along the *c*-axis (yellow). Crystal structure produced from crystal data given in ref. ^[20].

In their work, GUILLERM *et al.* pointed out, that for the successful synthesis of products with MIL-140 structure high temperatures are needed, otherwise the UiO phase is obtained. For example, using the same ratio of precursors, MIL-140A crystallises at 200 °C while at 150 °C UiO-66 is obtained. Therefore, they are of the opinion that the UiO phase and their polymorph MIL-140 phase are kinetic and thermodynamic products, respectively. In this hypothesis, the UiO phase is initially formed, followed by a dissolution at higher temperatures and a recrystallisation of the MIL-140 phase over time. A possible explanation for the higher hydrothermal stability of the MIL-140 phase could be the higher hydrophobicity of the frameworks. Furthermore, the chain-like IBU show a lower susceptibility for undergoing hydrolysis of the Zr-O bonds compared to the isolated Zr₆-clusters in UiO materials. This can be explained by a better shielding of the IBU by a more compact linker arrangement.^[20]

A further problem occurring during the synthesis of MIL-140 structured MOFs is a lack of product control and phase purity. The group of D'ALESSANDRO uses microwave-assisted synthesis techniques to crystallise MIL-140 structured frameworks to enhance phase purity and the quality of the crystalline products.^[106] The advantage of microwave-assisted synthesis compared to conventional heating is for instance the more uniform heating with a faster heating rate and a higher efficiency with less reaction time. With this approach, the D'ALESSANDRO group showed that a faster heating rate improves the phase purity and crystallinity of the MIL-140 phase. Furthermore, they were able to yield different functionalised MIL-140 frameworks that had previously not been accessible via the conventional synthesis route.^[106-108]

The work of BUTOVA *et al.* deals with the selective phase formation of UiO-66 and MIL-140A, respectively.^[109] They investigated the role of water as additive in the nucleation process at two different temperatures. While all syntheses that were conducted at 120 °C yielded the UiO-66 phase, the products of the syntheses at 220 °C differed depending on the addition of water to the synthesis mixture. They argued that due to the addition of water ZrO₂ nanoparticles are formed during the nucleation step. Their local arrangement in the tetragonal phase is very similar to that of the UiO-66 IBU. This allows them to be regarded as seeds for the UiO-66 formation.

Another approach to achieve phase purity is a subsequent purification of a product mixture after the synthesis. This was published by WANG *et al.* who separated phase mixtures of UiO-66/MIL-140A nanoparticles by electrostatic adsorption onto magnetic beads.^[110] The general principle is based on different surface zeta potential of the MOF nanoparticles caused by differences in the IBUs. Contrary to MIL-140A, the UiO-66 is positively charged as a result of the discrete IBU and a high number of defects or unsaturated metal sites. Upon the addition of negatively charged magnetic beads to the synthesised phase mixture, the UiO-66 nanoparticles were electrostatically adsorbed onto the magnetic beads. This allows an effective separation of the two phases.

2.3.3 Comparison between MIL-140 and UiO series characteristics

For their later application, it is necessary for MOFs to stay stable over a wide temperature range and to show a chemical resistance towards various vapours and liquids, like humidity or water, respectively. Additionally, the accessibility of the pore system is crucial for many applications. For this reason, this chapter describes and compares the characteristics of Zr-based MOFs from the UiO and MIL-140 series. In this context, special attention is dedicated to the thermal and chemical stability of these frameworks and their functionalised derivatives.

2.3.3.1 Thermal and chemical stability

In general, each Zr-based MOF features a unique chemical and thermal stability which can be modified by the attachment of functionalities or the variation of the linker length.^[18] Starting with the unfunctionalised UiO-66, CAVKA *et al.* described this compound as a highly stable material with a thermal stability up to 450 °C in air, which is confirmed by different groups.^[17,18,94] Under ambient conditions, the material stays crystalline for months and there is no structural degradation detectable.^[111] It shows a high resistance to several organic solvents as well as acidic or neutral aqueous solutions.^[18] Only alkaline media are able to cleave the bonds between the IBU and the organic linkers resulting in a collapse of the structure. This observation can be made for UiO-66 and a large range of UiO-66 derivatives such as UiO-66-NH₂, -Br, -(COOH)₂ to name a few examples. An exception is the UiO-66-NO₂ which retains its crystalline structure.^[46,94] A clear explanation for the different stabilities has yet not been found. According to KANDIAH *et al.* there are no simple correlations between electronic or steric requirements of the functional groups which could explain the thermal stabilities. Despite the high stability, post-synthetic modifications were applied to many frameworks with UiO-66 structure. As already explained in chapter 2.2.1, the SALE is also part of this reaction repertoire. The fast going exchange of linker and metal ions suggests, that the frameworks is less inert than expected.^[46] For example, the COHEN group was able to show that the UiO-66-Br reacts in aqueous solution with a UiO-66-NH₂ or with amino-terephthalic acid. The result in each case was a UiO-66 with both NH₂- and Br-functional groups in a single particle.^[76] However, the MOF retained its full crystallinity and porosity after the SALE. This exchange phenomenon shows that the UiO-66 system can probably be both structurally stable and chemically labile. In the work of DECOSTE *et al.* they focussed on the stability and degradation mechanism of Zr-based MOFs in aqueous solutions.^[18] In presence of HCl, they observed a reversible protonation of the carboxylate groups of the linker in case of the unfunctionalised UiO-66 but not for UiO-66-NH₂. Here, the functional group is a steric barrier which impedes the access of guest molecules to the IBU and therefore prevent the breaking of the Zr-O bonds. In addition, the -NH₂ group can be protonated by itself, which provides additional protection of the Zr-O bonds against acids.

In comparison to UiO-66, the isorecticular structure of UiO-67 shows similar thermal stability with a linker decomposition above 450 °C but a lack of similar chemical stability.^[17,61] The framework is resistant to various organic solvents like acetone, methanol, pyridine or chloroform but not to aqueous solution, regardless of the pH-value.^[18] As for the degradation of UiO-66, DECOSTE *et al.* investigated the structural breakdown of UiO-67.^[18] They observed a complete amorphization in basic medium and additional diffraction peaks after exposure to water and HCl which can be aligned to the XRD pattern of monoclinic zirconia. Responsible for the decreased stability of UiO-67 are steric and rotational effects of the longer *bpd*²⁻ linker as well as the length of the linker.^[112,113] The more open structure of UiO-67 simplifies access of water molecules to the IBUs. This leads to a higher bending of the more flexible linker which weakens the bond strengths. Consequently, the framework is more susceptible to chemical degradation. As described for the UiO-66, further functional groups can enhance the chemical stability. Additional hydrophobic naphthyl groups shield and protect the IBUs over a wide pH range but reduce the pore volume drastically.^[113] With more hydrophilic groups, like hydroxides, the chemical stability is even lower.^[114]

The UiO structured MOFs and their functionalised derivatives are already quite well studied, while the MIL-140 series remains rather unexplored. Although some fundamental investigations have been reported in this field, more detailed information of the chemical decomposition or the influence of functional groups on the degradation are missing.^[20] With about 500 °C, the MIL-140 series exhibit a higher thermal stability than the UiO series. According to LIANG *et al.*, the thermal stability of microwave-assisted synthesised MIL-140A samples is slightly higher than that of conventionally produced samples.^[106] Furthermore, the introduction of functional groups (-NH₂, -NO₂, -Br, -Cl, -F) in the MIL-140A structure does not affect the thermal stability of the framework.^[107] Concerning the chemical stability, most of the unfunctionalised MIL-140 frameworks show no loss of crystallinity after a treatment with boiling water as well as the functionalised MIL-140A frameworks. This behaviour can only be found for UiO-66, but not for its analogues with longer linkers.^[20,107] However, there are some exceptions, such as the already in ambient atmosphere unstable MIL-140C-Me or MIL-140D-H, which are isostructural to the MIL-140C and MIL-140D.^[108] Unfortunately, there are no reported stability tests at different pH-values for MIL-140 structured MOFs in literature. But there are examples where MIL-140 structured MOFs are used as adsorbent of lactic acids or aromatic amino acids from aqueous solution in acidic medium (pH ≈ 2).^[115] Additionally, these frameworks are used for the separation of different phenolics in aqueous solution over multiple cycles.^[116] This leads to the conclusion, that these MOFs are stable in slightly basic medium, too. This higher tolerance of MIL-140 structured MOFs towards water can be explained with the more hydrophobic character compared to UiO structured materials. This results from the infinite Zr-oxide chains which are better protected against hydrolysis compared to the isolated Zr₆ cluster, as already discussed above.

Further improvements like the higher thermal or mechanical stability can also be attributed to the chain-like IBU especially in case of longer linkers. Due to this arrangement, the flexibility of the IBU is reduced and additional interactions between the aromatic linkers like π - π -stacking is possible along the c -axis.^[20,117] Further information about water stability of MOFs is given by the group of WALTON.^[118]

2.3.3.2 Surface properties and possible applications

As a consequence of the arrangement between IBU and linker and the resulting one-dimensional pore system in MIL-140 structured materials, the thermal and chemical stability is enhanced, but the surface area and pore sizes of these materials are reduced with respect to the UiO phase.^[20] Accordingly, the experimental accessible BET surface area (N_2 at 77K) increases from MIL-140A to MIL-140D from 415 to 700 $m^2 g^{-1}$ but is significantly lower than the experimental BET surface area of UiO-66 or UiO-67 with approximately 1100 and 2700 $m^2 g^{-1}$.^[20,97] The same applies for the pore sizes. In MIL-140A, the pore diameter as well as the pore windows is roughly 3.2 Å (Figure 7) while the UiO-66 obtains two different shaped pores with 8 and 11 Å (Figure 5). However, the corresponding triangular pore window in UiO-66 is only 6 Å, limiting the maximal size of potential guest molecules enter the pore.^[17] By the use of functionalised linker molecules, the corresponding pore sizes and BET surface areas are reduced regardless of whether MIL-140 or UiO materials are considered.^[94,107] This is attributed both to a reduction of the free volume in the framework and to a higher molar mass of the functionalised linker or rather of the MOF.

As stated out, the synthesis of MOFs can be highly versatile, their structures can be controlled and fine-tuned with focus on their properties. The result are porous and highly stable materials, such as the Zr-based MOFs of the UiO and MIL-140 series presented here.

Even differently functionalised UiO structured materials have a variety of possible applications. The LEWIS acidic sites of the IBUs can be used for the post-synthetic incorporation of lithium *tert*-butoxide which enhance the ionic conductivity leading to MOFs that are potentially suitable as solid electrolytes.^[119] Moreover, the combination of LEWIS acidic sites and alkaline groups at the ligand facilitate the use of this material as catalyst in cross-aldol condensations.^[120] The high catalytic activity of UiO-66 can also be used for the degradation of phosphate-based nerve agents or chemical warfare agents.^[121] With functionalised linkers, UiO-66 derivatives can be tuned for an effective adsorption of different gases like CO_2 or CH_4 improving the selectivity in gas separation processes.^[122] In the same way, the networks can be loaded specifically with certain drugs like ibuprofen.^[123] If other MOFs are taken into account, many more applications are possible. Thus, these frameworks can be used for various other catalytic reactions, as gas storage material for hydrogen, as molecular sieves or in photonic or electronic devices.^[12,124] Another potential scope of application is in the field of sensor technology. Since the main objective of this

work was also in the field of sensor technology with MOFs, a detailed discussion of this will be given in the next chapter.

2.4 Materials for sensing applications

In the field of gas sensing, a variety of different materials can be applied as detector. The sensing process is based on the change of certain properties of the material due to the interaction with the target gas. The most common gas sensing principles is based on semiconducting metal oxides, where a change in current or resistance is measured. In addition, there are other materials, such as carbon modifications (graphene, CNTs), in which the detection is based on the same principle.^[125] Presently, MOFs are gaining in importance as chemical sensors as a result of their tailored design in combination with the possibility of higher selectivity. In this chapter, metal oxide semiconductors and MOFs as sensors are presented as well as the chemical background for the detection. Furthermore, the requirements for sensors and the dependence of the measurement signal on external influences are discussed.

In our everyday environment there is a variety of gases emitted from different sources. Concerning the development of the industry, the emission of toxic gases like CO, CO₂ or NO_x into the atmosphere increases. These pollutants are often hazardous to the environment or human health. For the reason of polluting gases, the monitoring of industrial emissions or urban air quality is indispensable.^[126] In medical diagnostics, the detection of gases like acetone or ethanolamine in the human breath provide information on the state of health.^[127] However, these gases only occur in very small quantities, so that the sensitivity of the materials is an important aspect. Depending on the application, further characteristics as a fast response time or a real-time monitoring as well as stability or selectivity are also crucial.^[128]

2.4.1 Metal oxide semiconductors

Oxide semiconductors as detectors for gaseous components were firstly reported in 1962 and are nowadays one of the most investigated type of gas sensors and part of commercial available sensing devices.^[129] Typically, these sensors are based on porous sintered blocks or thin- or thick-film type devices consisting of mostly polycrystalline transition metal oxides as SnO₂, WO₃, ZnO or NiO.^[130] These metal oxides can be further divided into two classes, the *n*-type and *p*-type semiconductors. According to YAMAZOE *et al.* the sensing process can be explained with two key functions. First of all, there is the recognition of the gas by the oxide surface. This receptor function is explained by an interaction on the solid-gas boundary inducing a change in the electronic properties. The second step is the so-called transducer function, where the surface phenomena is transduced into a change in the electrical resistance of the material.^[130] For the second step, the mobility of the charge carriers appears to be an important factor for metal oxides used as gas sensors. Consequently, the mobility of electrons as main charge carriers in *n*-type oxides (*e.g.* SnO₂, ZnO and WO₃) is much higher than the mobility of positive holes inside *p*-type semiconductors (*e.g.* NiO, or CuO). For this reason, the number of *p*-type gas sensors utilised is

significantly lower than that of the *n*-type devices.^[131] Nevertheless, the chemical and thermal stability of the metal oxides under the operating conditions need to be guaranteed.

2.4.1.1 Sensing mechanism

The sensing of gaseous target molecules is based on the change of the equilibrium of the chemisorbed oxygen on the semiconductors surface after the reaction with the target gas. Depending on the conduction type of the metal oxide, the response of the sensing device to the same target gas is different.^[132] With regard to *n*-type semiconductors, their electrical resistance increases in an atmosphere containing an oxidizing gas as O₂ or NO₂, which acts as electron acceptor. In the opposite case, the electrical resistance decreases in absence of oxygen and upon exposure to a reducing gas, where the target gas (CO or H₂S) acts as electron donor. If a *p*-type metal is considered, the change of the electrical resistance changes in a reversed manner, as positive holes are the charge carriers. For a more detailed description of the sensing mechanism two different models can be applied.^[133] The ionosorption model considers only space-charge effects or the change of the electric potential of the surface due to the ionosorption of oxygen and the reaction of reducing gases with the surface oxygen species. In case of *n*-type semiconductors, atmospheric oxygen is adsorbed onto the surface of the metal oxide. Through an electron transfer from the conduction band, molecular and atomic oxygen ions are formed. For this reason, the electrons are trapped from the bulk on the surface reducing the free charge carrier concentration. Consequently, a band bending occurs and an electron depletion layer, the so-called space-charge layer, is formed. The thickness of this layer determines the length of the band bending region. As result, a potential barrier is present at the grain boundaries or metal oxide surface, respectively.^[132–134] In contrast to the absence of oxygen, where free electrons can flow easily through the grain boundaries, the electron flow is suppressed and the electrical resistance increases (Figure 8a). If the material is now exposed to a reducing gas like CO, the process is reversed. The CO reacts with the oxygen ions on the surface releasing an electron which can return to the conduction band. Finally, the thickness of the space-charge layer and the corresponding length of the band bending decreases. For this reason, the potential barrier between two grains is lowered which enhances the electron flow and reduces the electrical resistance (Figure 8b). However, this considerations for this mechanism can only be made in a certain temperature range, where the diffusion process is limited. In the presence of even stronger oxidising gases like NO₂, the potential barrier at the grain boundaries as well as the thickness of the space-charge layer increases further due to an interaction of NO₂ with the oxygen ions on the semiconductors surface.^[135] Hence, in this mechanism the transport of free charge carriers is dominated by the formation of the depletion layers and the formation of SCHOTTKY barriers at the grain boundaries.

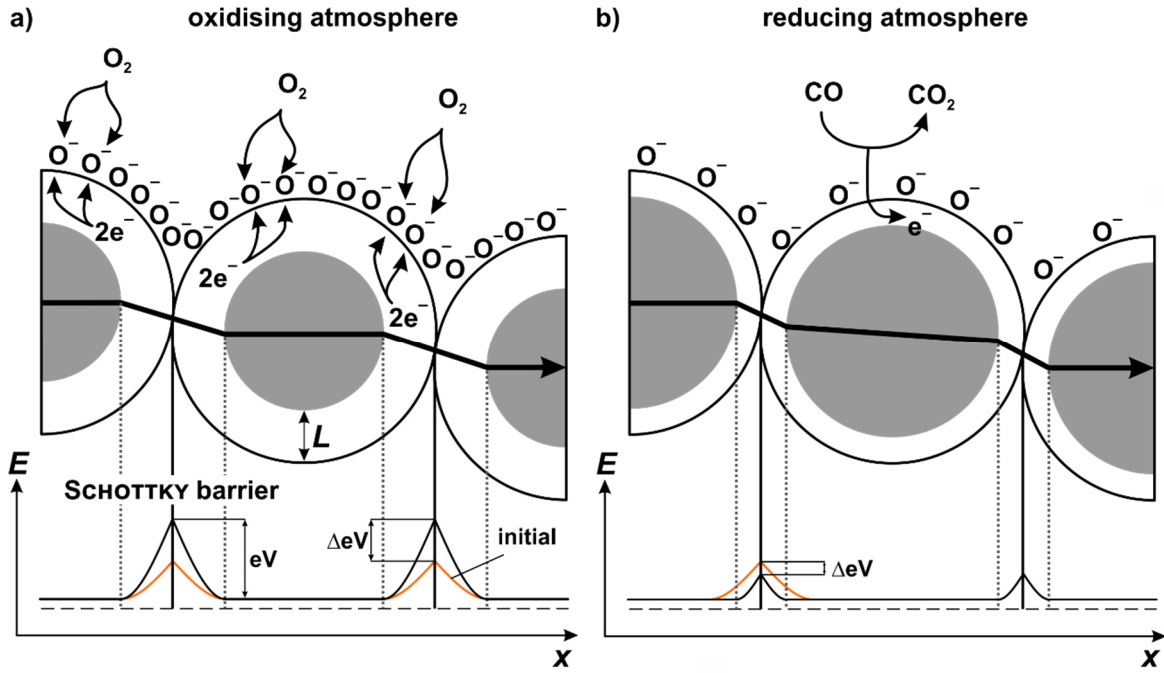


Figure 8: Schematic illustration for the ionosorption as structural and band model showing the conductive mechanism in a polycrystalline oxide semiconductor upon the reaction with a target gas in oxidising atmosphere (a) and reducing atmosphere (b). The in intergranular contacts between the particles represents the SCHOTTKY barriers with L as thickness of the electron depletion layer. The resulting increase (a) or decrease (b) of the potential barrier or the electrical resistance is shown in comparison to the initial energy (orange) and denoted as ΔeV and eV as total energy of the potential barrier. Reproduced and edited slightly from ref. [136].

The second mechanism is based on oxygen vacancies and by a change in their amount on the surface and their ionization, a sensing effect is achieved.^[133] As for the Ionosorption model, a n -type semiconductor like SnO_2 is a good example. This material is oxygen-deficient and therefore obtains oxygen vacancies, which can be considered as electron donors. According to the MARS-VAN-KREVELEN mechanism, gaseous oxygen reduces and re-oxidises the surface. This alternate reaction is used to describe the surface conductivity and the sensing properties. In an oxidising atmosphere, these vacancies are filled with additional oxygen for which one or more electrons from the conduction band are required. A measurable result is the increase of the resistance. Upon the reaction with a reducing gas like CO , oxygen is removed from the surface of the material producing CO_2 and a vacancy. The oxygen vacancy is ionised and the released electron accumulates in the conductive band. Accordingly, the electrical resistance decreases.

2.4.1.2 Control of sensitivity and selectivity

It should be noted that these are only models and that the experimental and theoretical data do not agree completely.^[133] For instance, the mechanism can be influenced drastically by the composition of the material itself or by several external stimuli. As already mentioned, the resulting change of the electrical resistance upon the detection of a target gas seems to be dependent on the film thickness or the particle sizes, respectively. Since the SCHOTTKY barriers at the grain boundaries limit the electron flow, the sensitivity of the material should be adjustable by a specific size adjustment. Indeed, a reduction of the particle size leads to a significant increase

of the sensors response.^[137–139] The formation of the space-charge layer is an effect of the concentration of free charge carriers and constant for one certain material. As a result, the thickness of this layer (L) is also constant but its proportion changes relative to the particle size (d). For large crystals with grain sizes $d > 2L$, the reaction on the surface do not affect the conductivity of the whole bulk material (Figure 9a). Consequently, the depletion layer is only present on the bulk surface and the occurring SCHOTTKY barriers at the grain boundaries limit the electrical conductivity. For this reason, the response and sensitivity of the material is independent of d , if surface area effects are neglected.^[132] For smaller particles with $d = 2L$ the grain size is comparable to the depletion layer thickness and conductive necks between the particles are present (Figure 9b). Therefore, the sensitivity increases with the amount of necks. In the last case ($d < 2L$), the electron depletion area is completely extended over the particle leading to a grain-control of the sensitivity (Figure 9c). Obviously, other material properties such as the surface area or pore size of the material have decisive effects on the sensitivity in addition to the particle size.^[132] By this factors, the diffusion can be enhanced and the reaction rate of the target gas with the metal-oxides surface increases, too.

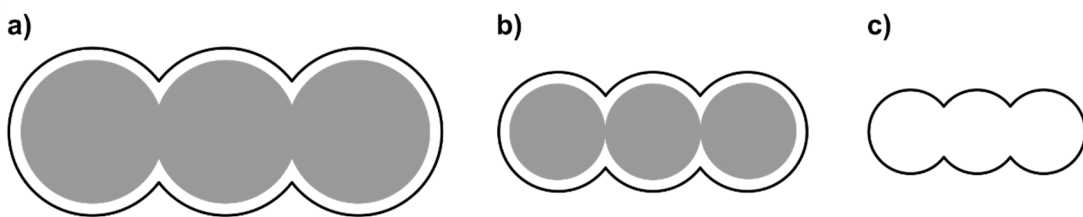


Figure 9: Schematic illustration of the conductance mechanism in semiconducting metal oxides. The space-charge layer (L , high resistance) is shown in white and the core region (low resistance) in grey for different proportions of intergrown particles with the size d : a) $d > 2L$, b) $d = 2L$ and c) $d < 2L$. Reproduced and edited slightly from ref. ^[137].

Another possibility to take control over the sensitivity of the semiconducting metal oxides is doping with other metal oxides.^[130,140] These impurities act as additional donor or acceptors and change the thickness of the space-charge layer. For example, SnO_2 doped with Al_2O_3 obtains an increase of the layer thickness by the factor 30, whereas a doping with Sb_2O_5 reduces the thickness slightly. An enhancement of the sensitivity can also be obtained by doping the surface with noble metals like Pd or Pt, which act as catalysts on the sensors surface.^[130,134] The interaction between metal additive and oxide semiconductor can be explained by two concepts, namely the electronic or chemical sensitization. In the first case, the additive acts as strong electron acceptor inducing an extended space-charge layer. Upon oxygen adsorption and desorption, the oxidation state of the noble metal changes which results in a large difference of the barrier potential of the semiconductor and an increase of the sensing response. The latter chemical mechanism is based on the catalytic activation of the gas by the metal additive. The dissociated fragments localise around the additive, which act as collect zones. This enhances the oxygen ionosorption and hence the sensibility. In some cases, metal oxide additives react with the target gas and are converted

into metals or sulfides. After this reaction, the electronic interaction disappears leading to a very high sensitivity at the expense of reusability. One example for this reaction is the selective detection of H₂S with CuO doped SnO₂ sensor. Here, the CuO react with the H₂S to CuS under the disappearance of the electronic interaction. This exhibits an extremely high response to H₂S in contrast to other gases based on the chemical affinity between CuO and H₂S.^[141] A major disadvantage is the lack of reversibility in this process.

Increasing the sensitivity of the sensor material, the operating temperature is an important factor, too. Typically, the sensitivity firstly rises with increasing temperature, reaching a maximum and then decrease again.^[130,134,142] In general, this can be explained combining kinetical effect at lower temperatures and desorption processes at higher temperatures. With increasing temperature, the adsorption of the oxygen species is the dominant process and simultaneously the reaction rate on the oxide surface rises. This makes the material more sensitive to the target gas. At the temperature where the sensitivity maximum is reached, the gas has the optimal reactivity for diffusion through the sensor material and the interaction between the gas and the oxide surface is strongest. At higher operating temperatures, the desorption of the ionic oxygen species prevails which leads to a decrease in the sensitivity.

Even though metal oxide semiconductors have advantages by adjusting their high sensitivity, there are some disadvantages or disturbances which are caused by the detection mechanism. Most metal oxides sensors operate at high temperatures of 200 °C and more which results in high power consumption and a decreased long-term stability.^[131,143] Especially with increasing sensor life, a recalibration of the baseline is necessary to maintain the sensing properties.^[144,145] For sensing devices operating at room temperature, the response times as well as the recovery times are often very high, due to slow kinetics.^[145,146] Nevertheless, the main challenge is to provide a high selectivity and to prepare a material which is selective only to one target gas and exhibits no cross-sensitivity to other gases.^[135,139,147] The lack of selectivity is usually compensated by the correct temperature, by doping with other metals or by a combination of different sensors. The achievement of an absolute selectivity is practically impossible, since there is at least a cross-sensitivity to water or humidity, respectively.^[139] The sensitivity of the metal oxide sensor suffers due to the adsorption of water molecules on the surface. This can be explained by a general decrease of the basic resistance upon water adsorption and a reduced ionosorption rate of the oxygen species due to a decreased surface area. Additionally, adsorbed water molecules block the adsorption of a target gas on the surface and limit the superficial diffusion of already adsorbed gas molecules.^[134] Furthermore, the long-time exposure to humidity or repeated measurements of humidity pulses cause a progressive deterioration of the sensitivity and a full recovery of the initial resistance level is thus prohibited.^[148] The same disruption of the sensor response occurs in presence of ozone or other volatile organic compounds, leading to false measurements. These

compounds are present in traces in almost all environments.^[149] For this reason, most sensing devices are tuned for a certain application in a well-defined environment.

In addition to metal oxides semiconductors as chemiresistors, there are other detection methods that will be briefly described using the example of NO₂ as target gas. Some commercially available sensor devices use electrochemical cells and reduce NO₂ between two electrodes. The concentration of NO₂ in the environment is proportional to the produced electrons by the reduction and consequently to the measured current flow.^[140] Other sensors are based on chemiluminescence, where light is emitted after a chemical reaction and detected.^[150] However, for the detection of NO₂, first it must be catalytically converted into NO before it reacts with ozone to form an excited NO₂ species. The emission of radiation results from the return into the ground state and is proportional to the NO concentration.

2.4.2 MOFs as sensor materials

In a wide range of applications, a need for selectivity and sensitivity is indispensable for the detection of hazardous and toxic gases or vapours. The commercially used metal oxide semiconductors as chemiresistive sensors are influenced by many factors. Usually they operate at high temperatures of above 200 °C and suffer by cross-sensitivities as well as by a baseline drift over time. Additionally, they are susceptible to poisoning with other gases that frequently occur side by side with the target gas. As a result, the common sensors are calibrated to a specific working environment.^[151] Specifically in the areas of selectivity and cross-sensitivity, MOFs can provide solutions and overcome the limits which plague many other sensor materials. A variety of MOFs are thermally robust and remain stable at temperatures up to 300 °C, allowing them to be used in similar applications.

One benefit of MOFs is their responsive nature in presence of detectable gases and vapours which results in a change of their physical or chemical properties. This rather unique behaviour is based on the modular character of MOFs and the ordered structure by controllable linkers and metal nodes. This porosity provides appropriate host-guest interactions, as the gases or vapours can be effectively concentrated in the framework.^[152] This is a key property for a high sensitivity and to generate specific responses of these materials. By the combination of different metals and linkers as well as different post-synthetic approaches, there is an unlimited number of possible structures with well-designed pore channels or pockets. In addition to the large amount of experimental data, theoretical calculations for predicting the structure can also be considered. Thus, frameworks can be routinely pre-configured to increase affinity to certain guests and build a MOF with desired properties. This possible characteristic change in certain properties qualifies MOFs as a unique class of chemosensory materials. The signal triggered by the guest can then be monitored using various analytical methods.^[153] Nevertheless, the development of MOFs with desired properties

and the integration of these materials into sensing devices is at least as challenging as a sufficient signal transduction capacity.^[154]

2.4.2.1 Fundamental properties for MOFs as sensors

In general, there are numerous properties of MOFs which can be used for the signal transduction and makes these materials promising for sensing. Beside macroscopic changes, such as colour changes upon the host-guest interaction,^[155] electrical or electrochemical as well as mechanical transduction methods can be realised.^[156,157] Basically, any measurable property change can be used to generate a measurement signal. MOF sensors that show a change in their magnetic properties when a certain guest is present are also conceivable.^[158]

The majority of MOFs consist of organic linkers, most of which have aromatic subunits or extended conjugated π -systems, which are subject to luminescence upon irradiation making them attractive for photoluminescent sensing devices.^[159] Basically, the excitation of the linker provokes the temporal population of the linkers lowest unoccupied molecular orbital (LUMO) with an additional electron and consequently the formation of a hole in the highest occupied molecular orbital (HOMO). Obviously, the luminescence intensity can be diminished by adsorbed guest molecules which can be easily reduced or oxidised. Furthermore, additional functional groups of the linker can enhance the chemical interactions between the MOF and a target molecule leading to a different luminescent response.^[160] Unfortunately, there is a limitation for these types of MOF sensor materials due to a low and often insufficient selectivity towards a certain target gas. Beyond that, most luminescent sensor materials are so-called „*turn-off*” sensors and show a complete loss of the signal after the interaction with the guest.^[154]

The term luminescence includes the emission of light caused by the absorption of energy in form of photons and not of heat. In general, two cases of luminescence can be distinguished.^[161] The first case is described as fluorescence. Here, an electron is lifted into the excited singlet state and then relaxes back into the singlet ground state by emitting a photon. This radiation transition is spin-allowed and as a consequence, its lifetime in the order of 1 ns is relatively short. The emitted fluorescent light is often subject to a red shift, which is understood as a STOKES shift. The second case is described as phosphorescence and is insignificantly more complicated. Just as in the fluorescence process, an electron is excited from the singlet ground state and moved to an excited singlet state. At this point there is a quantum mechanical, spin-forbidden transition into an electronically excited state, into the triplet state. The recovery of the electron from this state to the ground state is therefore also spin-forbidden and very slow. Compared to fluorescence, phosphorescence can still be observed after much longer periods of time of minutes or hours.

The STOKES shift mentioned is even more pronounced in most MOFs due to various factors.^[153] In addition to the arrangement of the linkers, which can show π - π interactions due to stacking of the aromatic rings, guest molecules can also broaden the emission spectrum and shift it into the

red range compared to the individual components.^[162,163] The metal ions themselves also influence the luminescence. Thus, the emission of lanthanides is regulated differently by the selection rules than by the usual *d*-elements. This often leads to a weak and long-lived emission, which is also spin-forbidden and can most likely be described as phosphorescence.^[164]

A detailed overview of the luminescence in MOFs is given in a review by ALLENDORF *et al.*^[153] Here 5 modes are mentioned to achieve a luminescence in MOFs. The simplest possibility is the incorporation of luminescence via the linkers, which can either emit on themselves or involve a charge transfer with the metal nodes. Another possibility are the previously described metal ions. In addition to the sharp but weak emission bands of lanthanoid ions, *d*¹⁰-transition metal ions without unpaired electrons can be used to increase linker-based emission.^[165] In addition, adsorbed guests can provide a so-called antenna effect and increase the luminescence of the metal ion due to a charge transfer from the strong absorbing linker to the metal node.^[166] Furthermore, the π - π -interactions between neighbouring linkers or linkers and guests are discussed, which can form a luminescent complex.^[163] ALLENDORF *et al.* also lists the adsorption of lumophores as the last possibility, whereby luminescent molecules can be trapped in non-emitting MOFs or lumophores bind to the MOF surface and thus exhibit emitting properties.^[167]

2.4.2.2 Requirements for MOFs as sensors

A MOF can be used as a sensor material if it exhibits a change in property during interaction with an analyte, as described above. Ideally, this change is specific to a certain analyte, but most MOFs only have a very high selectivity for a certain analyte or group of analytes. Two examples are the selective detection of nitroaromatic compounds as an analyte group^[168] or the selective detection of sulphur-containing amino acids such as histidine.^[169] Sensory selectivity is a necessary condition for the successful detection of specific analytes, but is not sufficiently developed. There are several conceivable ways to improve the selectivity of a MOF. For example, the pore system can be used as a molecular sieve to separate larger molecules from the smaller analytes, which then adsorb inside the MOF.^[170] Separation is also possible on the basis of the surface properties of the MOF. Its surface can be adjusted or chemically modified in such a way that only hydrophilic or hydrophobic analytes can penetrate the pore system.^[171]

A much more elegant approach is based on specific chemical interactions between an analyte and the sensor material. This selectivity is based on specific chemical interactions between the analyte and the MOF or its functional groups that other molecules do not have. Such behaviour can be achieved by specific formation of hydrogen or covalent bonds, as well as donor acceptor interactions.^[154,172] A good example for these interactions is the separation between cyclohexane and benzene in a zinc-based MOF with an anhydride-based linker.^[173] The framework exhibits a high benzene uptake at room temperature while the cyclohexane uptake is not worth mentioning. This behaviour can be attributed to the dynamic character of the framework and to the electron-

deficient pore surface which interacts strongly with the electron-rich benzene rings in contrast to the cyclohexane. The benefit of MOFs is that the linkers or functional groups required for detection can be directly integrated into the network design.^[174] In addition to the interaction with the linkers, the structure of MOFs also enables the reaction of potential analytes with the metal centres or their open metal sites.^[175] The MOF-74 is a prominent member with open metal sites which can be used for the selective coordination of benzene over cyclohexane.^[176] The underlying mechanism for the effective complexation of the electron-rich benzene is presumably based on LEWIS acid-base interactions. However, other molecules can also coordinate at open metal sites, which shows the integration of NO in different frameworks.^[177] For the design of a MOF with highly selective or even specific sensing properties it may be helpful to study the existing literature regarding adsorption preferences of MOFs and functional groups.^[178]

A reversibility in the detection reaction is also desirable, which makes a sensor usable several times. The regeneration process of a sensor is dependent on kinetics and thermodynamics, as is the detection process. Most analytes are only physisorbed in the MOFs and should then be removable by applying a vacuum at ambient temperatures. However, if chemical reactions take place at free functional groups in the MOF, simple regeneration by heating is no longer possible. This is often used, for example, for quenching in the fluorescence „*turn-off*” samples.^[179]

Finally, the change in the property must also be measurable in the presence of very small amounts of analyte. The detection limit or sensitivity of a MOF depends strongly on the signal transduction. For luminescent MOFs it has been shown that the response to an external stimulus can be influenced by the composition.^[180] For MOFs, however, this means that the stronger an analyte can interact with the framework or bind to certain functionalities, the stronger the expected response should be.^[170] For the transmission of the signal and a fast response time, the transport of the analyte via the pore system is also essential. If the pore system is too small for the analyte or the diffusion of the analyte to the recognition sites takes too long, the response signal may be significantly delayed or completely absent.^[154] The maximum response signal, on the contrary, is limited by the possible total capacity of the framework.

Like other nanoporous materials, MOFs also show a very high affinity for the absorption of water from the environment. This makes them very interesting as sensor and storage materials for water.^[181] Nevertheless, this also has disadvantages, since water is a frequently occurring interfering molecule as already discussed for the metal oxide semiconductors. It disturbs a lot of MOF-based sensor devices regarding their sensing properties or stability. Again, hydrophobic MOFs can be used to reduce the interaction with water.

To ensure good signal transmission, an interface between the MOF and the receiver unit is required. Conductive MOFs can be arranged as pressed pellets between two electrodes.^[156] However, MOFs are typically deposited as thin films on various substrates such as silicon, glass

or metals.^[182] There are different approaches for the synthesis of MOFs on surfaces or generally as thin layers. A quite simple method is direct growth on a substrate which is placed in the synthesis solution. For this purpose, the substrate surface can be functionalised prior to the synthesis. The materials used for functionalisation often carry terminal carboxylic acid or amine functions, which improve the adhesion of the MOF layer.^[183] The film thickness can be adjusted by repeated growth cycles and can thus be tailored to the later application.^[184] In some cases, these surface functionalisation also influence the growth of the layer in specific oriented directions.^[185] Small MOF crystals are also used as seeds to nucleate the growth of the MOF in a second solvothermal step.^[186] Another approach is the production of MOF nanoparticles which are subsequently deposited on the substrates surface using various deposition techniques, like dip- or spray-coatings.^[187] Many working groups are concerned with the investigation of the production of MOF films. At this point it is referred to a detailed review by BÉTARD and FISCHER.^[188]

Since a part of this work deals with the detection of hydrogen sulphide (H_2S), a short overview of literature-known MOFs which discusses the measurement of H_2S is given below. Hydrogen sulphide is a colourless gas occurring in the environment or in industrial processes such as oil and gas production.^[189] In general, H_2S is considered as a toxic and dangerous gas. Many studies prove the harmful effect on organisms and also on human health. The typical smell of rotten eggs is perceived in concentrations of 20 to 30 ppm. Already from 50 to 100 ppm irritations of the respiratory tract can occur. Above 500 ppm, it can be deadly for humans after only a few breaths.^[190] However, it turned out that H_2S also plays a vital role in small doses. Besides NO and CO, it is the third endogenous gaseous signalling molecule found. Depending on the concentration, it has cytotoxic or cytoprotective properties and acts, for example, in the cardiovascular system vasodilatory to regulate blood pressure.^[191] A malfunction in the human H_2S metabolism is held responsible for a variety of diseases, such as liver cirrhosis.^[192] For this reason, many studies are focusing on the detection of H_2S under physiological conditions. Various MOFs with different metal nodes are used as sensor materials. Although the frameworks differ in structure, most of them are based on terephthalic acid with $-\text{NO}_2$ or $-\text{N}_3$ functionalities as linker molecules.^[193,194] The sensor principle uses the above mentioned fluorescence „*turn-on*” probe. Both groups attached on the linker can quench the fluorescence effectively due to their electron-withdrawing effect. As a result of the reaction with H_2S , these groups can be reduced to form a highly fluorescent amino group. For the sake of completeness, it must be mentioned that all reactions take place in buffered, aqueous or ethanolic solution. The H_2S source is not the natural gas, but sulphide-containing salts such as Na_2S or NaHS , instead of gaseous H_2S the actual detected HS^- ion is present in solution. Since the weak base H_2S is also present as HS^- under physiological conditions, this choice of sulphide source seems to be reasonable, but these systems are not suitable for the detection of H_2S from the gas phase. Depending on the system, the required response times until fluorescence occurs are a few minutes and the detection limit is between 2

and about 100 μM . All studies concerning the selectivity of HS^- are consistent. Thus, competing biomolecules or other anions also seem to be able to act as reducing agents, but only in much higher concentrations than they occur in the body.^[194] The fluorescence enhancement after the exposure to HS^- is several times stronger than that of the other analytes tested. Although the fluorescence „*turn-on*” probe is the most common method for the detection of H_2S , the underlying reaction mechanism is as yet largely unexplained. A mechanistic insight was carried out by HENTHHORN *et al.* using experimental data and computational investigations on the reaction between H_2S and aryl azide.^[195] Here, it was shown that HS^- is the active species in the reduction and not H_2S . Furthermore, they showed that two molecules HS^- per azide group are necessary for a complete reduction. Consequently, a sensor for gaseous H_2S seems to be inaccessible by this route (compare chapter 3.3).

2.5 Calixarenes as molecules for specific sensing of NO₂

Within the scope of this work, a focus was placed on the preparation of MOFs with carboxylic acid functionalised calixarenes as new non-linear linker molecules. Calixarenes are porous organic solids with a special chemistry regarding their reaction with NO₂. In this chapter, a fundamental knowledge of the synthesis and the structure of these cyclic molecules will be given. On the other hand, the special properties such as intrinsic porosity and above all the reaction with nitrosating agents or gaseous NO₂ are to be explained. Finally, on the basis of this special reaction behaviour, the unique feature of Calixarenes as materials for highly specific NO₂ sensors is described.

2.5.1 Synthesis and structure

Due to the cup-shaped conformation of these molecules, GUTSCHE introduced the name Calixarene (calix, *Greek*: cup).^[196] This name already indicates the possibility of the storage of guests in the structure. The first studies on the controlled synthesis of these macrocycles date back to ZINKE and ZIEGLER in the 1940s.^[25] They were able to obtain high-melting resins from a simple condensation reaction of formaldehyde and phenol derivatives. Due to the possibilities at that time only a molecular mass determination could be carried out and the cyclic tetrameric arrangement was only an assumption. Only ten years later, CORNFORTH *et al.* have structurally proven this assumption by X-ray crystallographic data.^[197] Depending on the reaction conditions, oligomers with four, six or eight phenolic units are accessible, which are linked by methylene bridges (Figure 10). The number of monomers the product consists of is indicated by a *n* in Calix[*n*]arene. By using *para*-substituted phenols, further functionalities can be introduced into the ring structure. However, modifications to the opposite phenolic group are also possible. Similar to the reaction with phenol, resorcinol or pyrogallol as starting materials also provide cyclic condensation products, which are referred to as resorcinol[*n*]arene and pyrogallol[*n*]arene.^[198]

The most common starting material for the synthesis of calix[*n*]arenes is *p-tert*-butylphenol. Condensation with formaldehyde is realized in the presence of an acid or base that acts as a catalyst. The reaction conditions for the targeted one-step synthesis of calix[*n*]arenes with a certain number of phenol building blocks are also based on the work of GUTSCHE.^[199] Through complex extraction steps, even ring compounds with up to sixteen phenolic units are accessible.^[200] Although the reaction conditions are quite well known, the reaction mechanism that leads to the product is still unclear. Thus, it remains questionable why certain calix[*n*]arene are preferentially formed. Similarly, the simple production of these compounds is surprising because covalent bonds are specifically formed, which lead to a few cyclic compounds in very high yields and not to many smaller ether molecules.^[26]

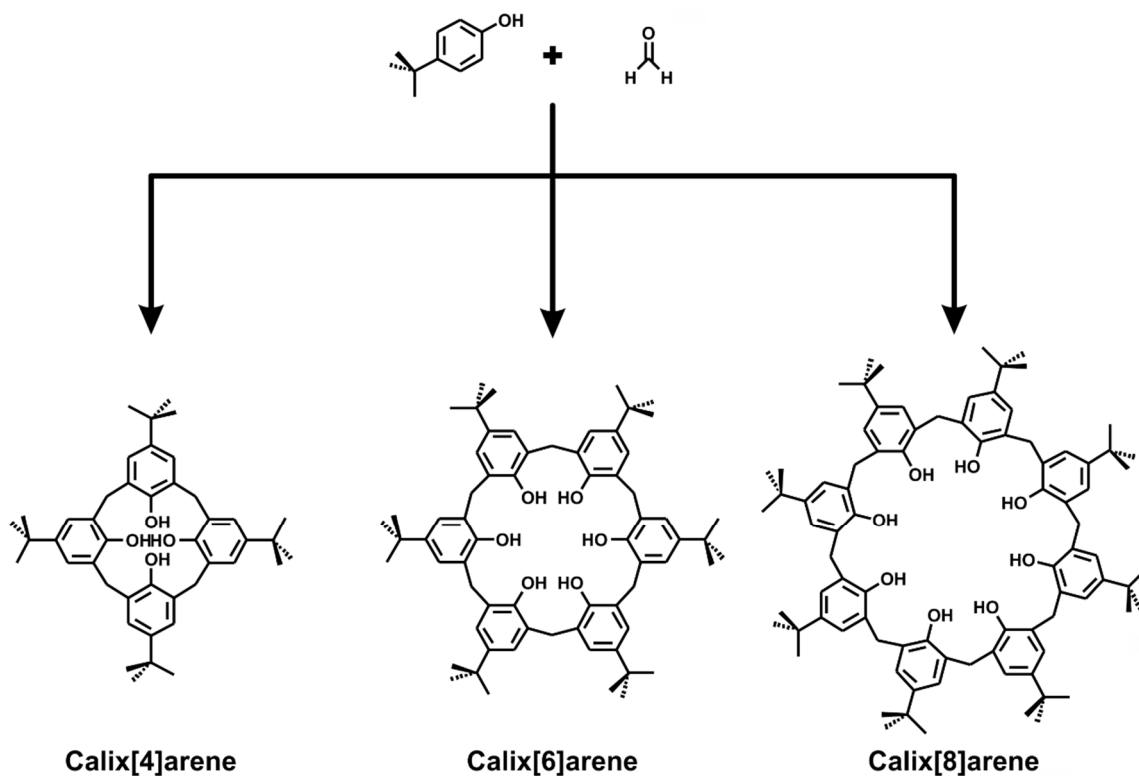


Figure 10: Schematic representation of the condensation reaction of butylphenol and formaldehyde for the synthesis of different calix[n]arenes with four to eight phenolic units.

The decisive factor for the ring size of the resulting product is the quantity and type of base used. There is an optimum concentration of NaOH in the preparation of calix[4]arene. If the amount of base increases, the hexamer is preferably obtained under the same reaction conditions. Similar to the amount, the type of cation also has an influence on the product. While LiOH is rather unsuitable for synthesis, KOH and CsOH can also be used to produce the hexamer in very high yields.^[199] However, the tetramer appears to be the most thermodynamically stable product, since larger rings can be converted into it at higher temperatures. Depending on the used educts different Calix[n]arene are accessible. Thus, also bridged or double Calix[n]arenes can be synthesised.^[201] Sulphur or nitrogen bridges between the rings can also occur instead of methylene bridges.^[202]

As indicated above, Calix[n]arene is the name of a large number of possible compounds due to the ring sizes and various substituents. In addition, calix[n]arenes also exhibit conformational isomers which can be converted into each other by the rotation of the phenyl-methyl bonds or by rotation through the circular ring.^[203] Obviously, the number of possible conformational isomers increases with the number of phenolic units that compose the ring.^[199] In the following, only the structural diversity of the calix[4]arene will be discussed and explained. In the solution, this compound has four different conformational isomers which are accessible through ring inversion. Depending on the position of the phenolic groups in up or down direction, the four compounds are described according to GUTSCHE with the prefixes *cone*, *partial cone* (*paco*), *1,2-alternate*

and *1,3-alternate* (Figure 11).^[200] A distinction of the four conformers is possible for example by ¹H-NMR examinations. Here, the signal of the two protons of the methylene groups is used for closer examination. In the *cone*-conformation this signal is split into two duplets and in the *paco*-conformation into four duplets. In the *1,2-alternate* and *1,3-alternate*-conformation the same signal is split into a singlet and a doublet pair or into only one singlet.^[204,205] Due to favourable intramolecular hydrogen bonds, the cone conformation in solution is thermodynamically preferred to the other.^[206] During NMR analysis, it is possible that the signals of the protons are broadened. This coalescence of the signals is caused by the inversion of the hydroxy groups through the ring. Depending on the solvent, the energy barrier for the ring inversion is different. Thus, the doublet pair of the *cone*-conformation in nonpolar solvents only converts into a sharp singlet at about 90 °C, in the case of polar solvents already at room temperature.^[199,207] In addition to lower temperatures, other *para*-substituents can also prevent ring inversion.

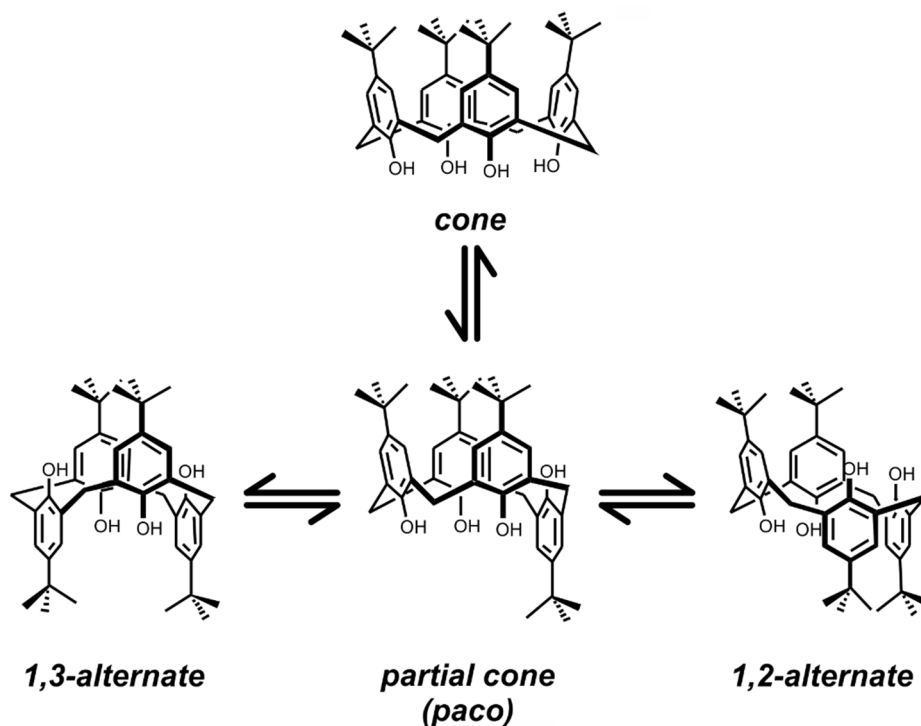


Figure 11: Schematic illustration of the structural diversity of a *p-tert*-butylcalix[4]arene and the conformational isomers accessible through ring inversion.

The resulting conformation can already be adjusted in the system by different factors and can be fixed in the desired position by additional modifications to the ring. The most commonly used method for fixing calix[4]arene in a particular conformation is an alkylation of the phenolic group. However, introducing a methyl or ethyl group at this position is not sufficient to completely prevent ring inversion.^[205] This only influences the equilibrium of the conformational isomers. In methylation, for example, the *paco* conformation is the most thermodynamically stable, since the cone conformation is no longer favoured by intramolecular hydrogen bonds. The calix[4]arene

can only be fixed in the desired position by a fourfold propylation.^[208,209] The present conformation can be influenced not only by the alkylation reagent but also by the used solvents and bases. When sodium-containing bases are used, *cone*-conformers are usually obtained. For bases with larger cations such as Cs₂CO₃ there is usually a mixture of *1,2*- and *1,3-alternate*-conformers.^[199,208] A possible explanation for the different behaviour can be a template effect of the larger cations.^[210]

MOFs or zeolites consist of up to three-dimensional pore systems that are in the order of smaller molecules. In comparison, individual molecules in the solid tend to pack themselves with as little free space as possible. This results in non-porous materials. Nevertheless, there are some organic molecules that have a certain porosity even in the solid state, although there are no accessible pores in the material.^[211] For example, an inefficient packing of the molecules can lead to free spaces in the structure, which is referred as extrinsic porosity. If, in contrast, the structure of the molecule provides permanent pores or permanent porosity, this is referred to as intrinsic porosity. Due to the cup-shaped design of the calix[*n*]arenes, these molecules also have intrinsic and extrinsic porosities in the solid. The incorporation of very large amounts of guests can be described by a cooperative diffusion mechanism between the guest molecule and the intrinsically porous calix[*n*]arenes.^[212] Hence, the term porous does not imply the presence of connected pores. Instead, materials with discrete pores such as calix[*n*]arene are referred to as zero-dimensional porous substances according to IUPAC.^[27,213] Despite this, the fact that gas sorption occurs at this point is due to temperature or pressure-induced gating effects or to conformational dynamics in the structure, which can lead to a temporary opening of the pore windows and thus to diffusion of the guests.^[214]

Due to their zero-dimensional porosity, calix[4]arenes can absorb small molecules such as CH₄ or CO₂ and include them in their structure.^[215] Since the storage and detection of several gases is becoming more and more important, these porous materials are an ideal starting material for the production of new porous materials. Thus, there is an opportunity to use these substances for the sorption of harmful gases or other volatile organic compounds.^[216] For this reason, the very special properties of the Calix[4]arene for the storage and detection of NO₂ will be discussed in the next section.

2.5.2 Calix[4]arenes as specific NO₂ recognition sites

The abbreviation NO_x is often used to describe nitrous gases and the sum of nitric oxides. Besides nitrogen monoxide (NO), nitrogen dioxide (NO₂) is one of the main components of these gaseous pollutants and it is of particular interest because they are harmful substances in everyday life. Apart from natural sources, these gases are mainly released by anthropogenic processes, such as the combustion of fossil fuels or industrial emissions.^[217] Nitrous gases are responsible, among other gases such as SO₂ or CO₂, for the formation of ground-level ozone and acid rain and also contribute to global warming. Moreover, NO₂ is a dangerous gas with toxic to lethal effects on human health already after short exposure. Concentrations of more than 10 ppm are sufficient to cause lasting damage to the respiratory system.^[218]

The storage and release of nitrous gases, in particular NO, is a well-studied area in the MOF field.^[219] As described in chapter 2.4.1, the detection of these substances is mostly based on electrochemical sensors. Optical sensors for the colorimetric detection of NO₂ offer better possibilities for selectivity due to various interfering factors.^[220] Calix[4]arenes show a specific reaction with NO₂. They are able to encapsulate a nitrosonium cation (NO⁺) in their cavities and form a deep blue coloured complex. This special reaction behaviour was first discovered by the RUDKEVICH group.^[221] NO₂ is present in a temperature-dependent equilibrium with its dimer N₂O₄. The latter can disproportionate into its ionic components NO⁺ and NO₃⁻ if it reacts with aromatic compounds.^[222]

A closer look at the conformational isomers reveals two fundamentally different forms. Where the *cone*-conformer looks cup-shaped, the *1,3-alternate*-conformation reminds rather of a very short nanotube. This results in the possibility for ions to enter the cavity of the calix[4]arene from both sides. This is possible because the *1,3-alternate*-conformation also offers two possible binding sites. Each consist of two „hard” phenolic hydroxy groups and two „soft” π -basic benzene rings. The two binding sites also have two cofacial arranged pairs of aromatic rings, forming a cylindrical π -electron-rich tunnel. This tunnel has a diameter of about 5-6 Å and is large enough for metal cations like Li⁺ or Cs⁺ to tunnel through it.^[223] The electron-rich cavity thus also allows the electron-poor NO⁺ cation to penetrate deep into the cavity of these hosts. The work of Rathore et al. dealt extensively with the penetration of NO⁺ into the cavity of the calix[4]arene. They used calix[4]arene derivatives dissolved in dichloromethane and produced strongly coloured complex compounds by adding NOSbCl₆. These solutions proved not only to be very stable over several months, they were even able to grow single crystals to determine the structure of the complexes with all four conformational isomers.^[28,224] This has proven that between these cofacial arranged aromatic ring pairs the NO⁺ molecule is equally distributed. The corresponding counterion for charge balance (SbCl₆⁻) is outside the cavity but in close contact to the calix[4]arene (Figure 12). Furthermore, the structural determination shows that the distance between the NO⁺ ions and the

aromatic rings is only 2.4 Å. This is significantly shorter than the typical van der Waals distance of 3.2 Å.^[225] This shortened distance indicates strong charge-transfer interactions and could be found repeatedly in several calix[4]arene-NO⁺-complexes.^[28,224] The fact that the encapsulation of NO⁺ into the cavity results in the formation of a [cal,NO⁺]-complex and not a bound NO⁺ is also shown by the vibration bands of the N-O stretching vibration in IR-spectroscopy.^[226]

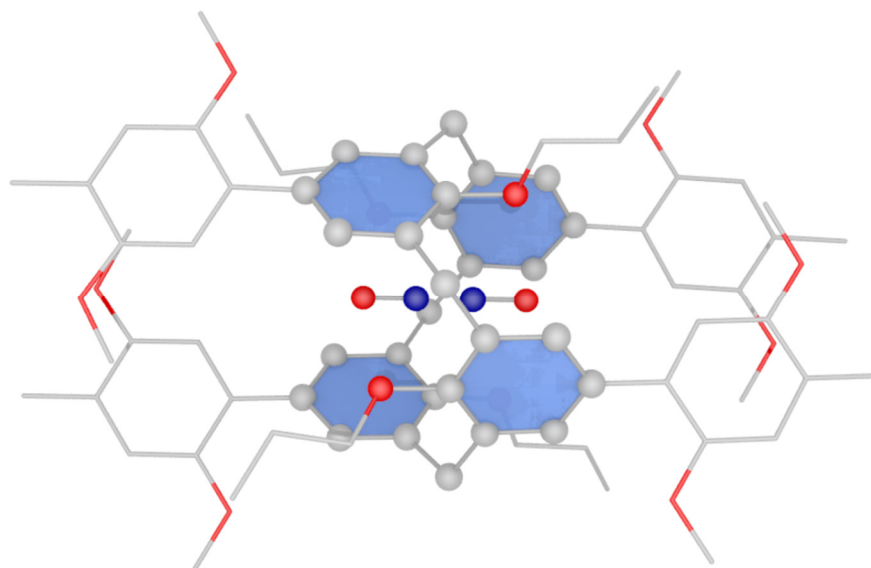


Figure 12: Illustration of the molecular structure of NO⁺ encapsulated in a functionalised calix[4]arene in the *1,3-alternate*-conformation. The NO⁺ molecule is equally distributed between the π -electron-rich aromatic rings at each site of the cylindrical tube (oxygen: red, carbon: grey, nitrogen: dark blue, the benzene rings are filled in blue and hydrogen atoms as well as the hexachloroantimonate counter ion are missing for reasons of clarity); Crystal structure produced from crystal data given in ref. ^[28].

The investigations by the group of RUDKEVICH correspond very well with those of RATHORE *et al.* A solution of a calix[4]arene in chloroform changed its colour to dark blue due to the insertion of NO₂. However, it came to a rapid (1-2 h) discolouration to a pale-yellow solution. Since NO₂ is a strong nitrosating agent, *p*-nitrated calix[4]arenes were formed.^[221] Only the addition of a LEWIS acid, such as SnCl₄, could prevent this *p*-nitration and increase the stability of the blue solution. Furthermore, non-cyclic aromatics show only a weak interaction with NO⁺. This proves once again the importance of the existing cavities of the calix[4]arene, into which exactly one NO⁺ molecule fits.^[227] Even larger ring systems (calix[5]arenes or wider) do not permit encapsulation of NO⁺.^[228] The enclosed NO⁺ can also be released as NO gas by reacting with hydroquinone in an electron reduction process.^[229] The Calix[4]arene is recovered and serves only as a molecular container.

This special and rather unique reaction behaviour of calix[4]arene and NO₂ is ideal for use as optical sensor material. Other atmospheric gases such as H₂O, SO₂, CO₂, NH₃ and even NO do not disproportionate and form charge-transfer complexes, ensuring detection without cross-selectivity.^[221] Furthermore, the encapsulation of NO⁺ inside the cavity and the formation

of the charge-transfer complex is a reversible process which can be reversed in solution, for example by the addition of ethanol or chloride anions.^[230] Unfortunately, complexation is only possible in solution and not with the calix[4]arenes as solid, since the cavities do not appear to be accessible. This problem can be avoided by immobilizing calix[4]arene derivatives on porous silica.^[231] The material produced in this way shows again a reaction with NO₂ by a colour change from white to blue. However, even in this case a rapid decolouration occurs. The same material that was previously moistened with CHCl₃, on the contrary, is much longer coloured. OHIRA *et al.* used this reaction behaviour after immobilization to develop a colorimetric sensor for NO₂ on calix[4]arene basis.^[232] After a few minutes, the sensor produced in this way showed an increase in absorbance in the presence of a few ppm NO₂, which indicates colour change and thus complex formation. A closer look at the reversibility shows that the sensor can be used several times, but the sensitivity decreases with each cycle. Here, the calix[4]arene also tends to change to the *p*-nitrated form. Based on this research a MOF with calix[4]arene-based linker molecules should be produced. Calix[4]arene-based linkers are already described in the literature and also some MOF structures are known. However, they either show hardly any porosity or are not suitable for use as sensor material due to their chemical and thermal stability.^[233] For this reason it has been attempted to create a Zr-based *cal*MOF, which is described in more detail in chapter 3.1.

2.6 References

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3 Results

3.1 A Novel Calixarene-based MOF for highly selective NO₂ detection

Preface

This work has been published as a communication in “Angewandte Chemie – International Edition” and deals with highly selective sensing in MOFs due to a specific reaction of the linker molecules with NO₂. The aim of this investigation was to create a highly selective sensor material by transfer of a well-known, highly specific reaction of an organic molecule into MOFs, thus solving the problem of the often low selectivity of many sensor materials in spite of high sensitivity. In this case, the specific reaction between a calix[4]arene and NO₂ was used to exclude cross-sensitivities with other gases that occur in the environment. The formation of deep blue coloured charge-transfer complexes based on the incorporation of NO⁺ inside the calix[4]arene cavities was firstly investigated by the RUDKEVICH group. Here, the complexation was realised in solution with the addition of SnCl₄ as LEWIS acids and a NO⁺ donating species. In the solid-state no reaction between a calixarene species and NO₂ could be observed. Moreover, without the addition of LEWIS acids the complexation is not stable and the calix[4]arene undergoes nitration.

The result of the work is a new Zr-based MOF with a tetra-carboxylate functionalised calix[4]arene in the *1,3-alternate* conformation. This conformation favours especially the complexation with NO⁺, since there are two possible binding sites. The modulated synthesis of the new MOF produced single crystals suitable for SXRD and structure determination. The elucidated structure reveals a hexanuclear IBU as in UiO-66 but with only six coordinated linker molecules. The other coordination sites are saturated with formate molecules. ¹H-NMR spectroscopy as well as IR spectroscopy uncover defective IBUs with missing formate molecules, resulting in LEWIS acidic sites. These vacancies stabilise the formation of the [cal-NO⁺]-complex and prevent the nitration of the aromatic units. The benefit of the arrangement of calixarenes inside the MOF is the accessibility of the cavities through the porous system allowing the detection of gaseous NO₂ using the bulk of a solid material. During this process, the colour of the material changed from white to dark blue. In cooperation with the group of Prof. ZIMMERMANN (Institute of Electrical Engineering and Measurement Technology, Leibniz University Hannover) a proof-of-concept sensing device for the colorimetric detection of NO₂ was built.

The author conducted or supervised all experiments concerning the synthesis of the calix[4]arene linker and the Zr-based *cal*-MOF. The product was analysed with PXRD, SXRD and IR spectroscopy. The structure determination was carried out by Dr. ANDREAS SCHAATE. The physisorption measurements were carried out by Dr. MANDY JAHNS and Dr. ALEXANDER MOHMEYER. TG-analysis was performed by MARC KREY and SEM investigation by HENDRIK SCHULZE. The ¹H-NMR spectroscopy was performed at the Institute of Organic Chemistry of the

Leibniz University Hannover. The investigations concerning the quantitative detection of NO₂ were carried out together with ADRIAN GEHL (Institute of Electrical Engineering and Measurement Technology, Leibniz University Hannover).

The author wrote the manuscript on his own and it was edited by Dr. ANDREAS SCHAATE.

A novel Calixarene-based MOF for highly selective NO₂ detection

M. Schulz, A. Gehl, J. Schlenkrich, H. A. Schulze, S. Zimmermann, A. Schaate

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Supplementary material is available online from the publisher.

3.2 A Low-Temperature Approach for the Phase-Pure Synthesis of MIL-140 Structured Metal-Organic Frameworks

Preface

This work has been published as full paper in “Chemistry – A European Journal”. It focusses on the low temperature synthesis of MIL-140 structured frameworks and the control of the product purity which enables the easier accessibility of these compounds and the introduction of more delicate functional groups. The MIL-140 series was firstly published by GUILLERM *et al.* and its structure and properties are described in chapter 2.3.2 in this work. In the first publication of these materials, the synthesis was described to take place with the same precursors as the UiO MOFs, but at high temperatures of more than 200 °C. In this work, the reaction temperature to synthesise MIL-140-structured frameworks was decreased down to 150 °C and the phase purity of the obtained products was systematically investigated. For this reason, the synthesis of MIL-140A and MIL-140C was revisited and conducted in highly concentrated reaction mixtures with acetic acid as modulator. Furthermore, the influence of the reaction temperature and reaction time on the formation of MIL-140 frameworks was investigated. As a result, synthetic parameters were found which produce a phase-pure product at a reaction temperature of only 120 °C. Due to the commercially availability of the stilbene dicarboxylic acid in contrast to the originally used dichloro azostilbene dicarboxylic acid ($H_2abcdCl_2$) in MIL-140D, a new MOF, the MIL-140D-*sdc*, was firstly described. As before, the crystallisation behaviour of this compound was systematically investigated and phase-pure materials were obtained at 150 °C under certain reaction parameters. Together with MALTE SCHÄFER a structural model of this MOF was developed.

The author conducted or supervised all experiments including the synthesis of the MOFs and the analysis with PXRD. The structural model for MIL-140D-*sdc* was designed by MALTE SCHÄFER; also, the physisorption measurements were conducted by him. The TGA experiments were performed by KATHARINA NOLTE. SEM investigations were carried out by SASKIA ZAILSKAS and the TEM investigation by DAWID WARWAS in cooperation with the LNQE Hannover.

The author wrote the manuscript on his own and it was edited by Dr. ANDREAS SCHAATE.

A Low-Temperature Approach for the Phase Pure Synthesis of MIL-140 Structured Metal-Organic Frameworks

M. Schulz, N. Marquardt, M. Schäfer, D. P. Warwas, S. Zailskas, A. Schaate

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3.3 Solvent-assisted linker exchange as tool for the Design of mixed-linker MIL-140D structured MOFs for highly selective detection of gaseous H₂S

Preface

This work has been submitted as communication in “Chemical Communications”. It is a further development of the previous publication and is based on the recently discovered synthesis of MIL-140D-*sdc*. This thermally and chemically highly stable framework is used as a backbone to integrate a new linking device into the network by using the solvent-assisted linker exchange (SALE) as post-synthetic modification. The new linker is azostilbene dicarboxylic acid, which is very similar to the initial used 4,4'-stilbene dicarboxylic acid. The exchange in the MOF was monitored by ¹H-NMR spectroscopy and maximum 50% of the linkers could be replaced. Through this exchange, azo groups are added to the framework as new functionalities. These new azo groups now serve as coordination sites for copper cations. This reaction behaviour has already been demonstrated at molecular level for various copper-azo complexes. The coordination of the copper ions to the azo groups also causes the reddish colour of the MOF to turn green. With physisorption measurements it could be proven that the surface of the materials is barely reduced by this incorporation, so that the pore channels are still accessible for guests. Using thermogravimetric analyses and EDX spectroscopy, an evaluation of the amount of copper present in the sample could be made. With the incorporated copper ions, these materials are used to detect H₂S. Upon reacting with this gas, the MOF turned black, a consequence of the formation of CuS, that was confirmed by Raman spectroscopy. Using UV/Vis spectroscopy, the exposure of H₂S to the absorption spectrum of the sample could be measured *in operando* and the response time could be determined. For the examination of the selectivity, the copper incorporated MOF was exposed to other gases such as CO, CO₂ or NO₂.

The author conducted or supervised all experiments including the syntheses of the MOFs and the analysis with PXRD, Raman-, IR- and UV/Vis-Spectroscopy. The physisorption measurements were conducted by SONGÜL NOYUN. The TGA experiments were performed by KATHARINA NOLTE and ARNE SCHIERZ. SEM investigations and the EDX spectroscopy were done by THEA HEINEMEYER. The ¹H-NMR spectroscopy was performed at the Institute of Organic Chemistry of the Leibniz University Hannover.

The author wrote the manuscript on his own and it was edited by Dr. ANDREAS SCHAATE.

Solvent-assisted linker exchange as tool for the Design of mixed-linker MIL-140D structured MOFs for highly selective detection of gaseous H₂S

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Supplementary material is available online from the publisher.

4 Conclusion and Outlook

The present thesis deals with the synthesis of new MOFs, which show particular reactivities. Linkers have been used which, as molecules in solution, show selective reactions with certain analytes. By immobilisation of these linkers in porous frameworks, it should be possible to transfer the reactive properties of these molecules to the solid state. This should make the corresponding MOFs applicable for the selective or specific sensing of the corresponding analyte gases, exemplified here by H₂S or NO₂.

The first project of this thesis focuses on calix[4]arenes as linker molecules. The pioneering work concerning the special chemistry between calix[4]arenes and NO₂ or NO⁺ donating agents was provided by RATHORE¹ and RUDKEVICH². They investigated the complex formation and the selectivity of this reaction with different calix[4]arenes derivatives in the molecular state in solution. In this work, a calix[4]arene derivative in the *1,3-alternate*-conformation was equipped with four carboxylate functionalities at the phenolic oxygen atoms. The pseudo-tetrahedral shape of this tetracarboxylate was favourable for the synthesis of MOF. Some MOFs have already been presented with this linker, but without any porosity. For the synthesis of the compound described here, monocarboxylic acids were used as modulators (formic, acetic and propionic acid). By using a formic acid-modulated synthesis, single crystals were obtained which were suitable for single crystal X-ray diffraction and for elucidating the structure. The MOF crystallizes in a cubic crystal system. The structure has two chiral pore systems, similar to the pore structure of MCM-48, a silica-based mesoporous material³. These pore systems are only connected by the tunnel-like cavities of the calix[4]arene molecules. In combination with the crystal structure, Ar physisorption measurements proved the highly porous three-dimensional pore system. It allows guest molecules to reach the cavities of the immobilized calix[4]arene. The thermogravimetric analysis confirms a high thermal stability which is typical for Zr-based frameworks. The single crystal structure solution also shows that - besides its modulating effect - formic acid is also coordinated at the IBUs of the MOF. Parts of this saturating formate molecule are missing, which means that the IBU exhibits LEWIS acid sites. This observation was confirmed by ¹H-NMR investigations and IR-spectroscopy.

In the reaction with gaseous NO₂ it was demonstrated for the first time that the formation of *charge-transfer* complexes is also possible in the solid. Already after a very short time, an intensive blue colouration could be observed. The absorption maximum was determined with UV/Vis-measurements and a home-made sensor cell was built in cooperation with the ZIMMERMANN Group (Institute of Electrical Engineering and Measurement Technology, Leibniz

¹ R. Rathore, S. V. Lindeman, K. S. S. P. Rao, D. Sun, J. K. Kochi, *Angew. Chem. Int. Ed.* **2000**, *39*, 2123.

² G. V. Zyryanov, Y. Kang, S. P. Stamp, D. M. Rudkevich, *Chem. Commun.* **2002**, 2792.

³ V. Alfredsson, M. W. Anderson, *Chem. Mater.* **1996**, *8*, 1141.

University Hannover). With this setup, NO₂ concentrations in the lower ppm range could be successfully measured.

Further experiments to be carried out in this field would be the verification of selectivity and thus the measurement of NO₂ in competition against different gases. These include CO₂, SO₂ or other nitric gases such as NO, since these gases are often accompanying NO₂. The influence of water on the sensor system must also be examined, since in conventional sensor materials humidity often interferes the measuring signal. If this is the case, post-synthetic modifications could be used to improve the hydrophobicity of the material and thus reduce interaction with water.

In addition, the decomplexation reaction should be further investigated. A possible reaction pathway for the encapsulated NO⁺ species could be the reaction with water to nitrous acid. This would make the system suitable for both the storage and degradation of NO₂, which could reduce air pollution. The NO⁺-loaded MOF could also be used for nitrosylation reactions in organic chemistry. The Rudkevich Group has already published reactions in this context.⁴ The pore system of the MOF described here could further improve the selectivity of such reactions. If one of the two chiral pore systems could be blocked, even enantioselectively nitration reactions might be possible.

The second part of this thesis dealt with the systematic investigation of the synthesis of MIL-140-structured MOFs. This phase was published for the first time by Guillerm *et al.* and was regarded as the thermodynamically stable phase of the zirconium-organic frameworks for linkers of intermediate length.⁵ The competing structures are of UiO-type topology. The MIL-140 frameworks with similar linkers were typically produced from the same starting materials, but at higher temperatures. Also, the Zr-O building units are connected in one dimension in the MOF-140 structures whereas UiO-type frameworks feature quasi-zero-dimensional building units. Both facts point to a higher thermodynamical stability of the MOF-140 topology. However, in our work we were able to obtain, for all MOF compositions investigated phase-pure products at lower temperatures, namely between 120 and 150 °C, a temperature range in which usually MOFs with UiO structure are synthesized. The resulting product phase can be controlled by the synthesis parameters. In this case the correct ratio between DMF and acetic acid is crucial. However, the synthesis mixtures are also significantly higher concentrated than is usually observed in MOF synthesis. The highly concentrated syntheses also have the benefit that a large amount of product is obtained. This means that less harmful solvent is used and the synthesis is more economic. If this approach for the preparation of MOFs can be further developed, one might also be detected unknown phases in other MOF systems. According to the results found here, such new phases

⁴ G. V. Zyryanov, Y. Kang, D. M. Rudkevich, *J. Am. Chem. Soc.* **2003**, 125, 2997.

⁵ V. Guillerm, F. Ragon, M. Dan-Hardi, T. Devic, M. Vishnuvarthan, B. Campo, A. Vimont, G. Clet, Q. Yang, G. Maurin, G. Férey, A. Vittadini, S. Gross, C. Serre, *Angew. Chem. Int. Ed.* **2012**, 51, 9267.

might be obtained under the same reaction conditions but from much more concentrated reaction mixtures.

At this point, syntheses with terphenylene dicarboxylic acid (*tpdc*) derivatives would be of interest, enabling the synthesis of a potential “MIL-140E” as an additional Zr-*tpdc*-MOF to UiO-68. The lower reaction temperature of 120 °C for the synthesis of MIL-140 MOFs will make this family more interesting for other groups, since the accessibility has been significantly improved. In addition, other linkers, such which possess functional groups with a delicate nature which might let them decompose at higher temperatures, can also be used. The synthesis of MIL-140D-*sdc* is particularly highlighted in this work and published for the first time. For this purpose, stilbene dicarboxylic acid (*H₂sdc*) was used as a linker consisting of a pure carbon-based backbone. This molecule shows a strong similarity to the dichloro azostilbene dicarboxylic acid (*H₂abdcCl₂*) which was originally used for the synthesis of MIL-140D. This analogy is also reflected in the very similar chemical properties of both compounds.

With the use of the *H₂sdc*, a new possibility is offered to integrate functional groups into the network. For example, amino, nitro or azide functionalised stilbenes are easily accessible and differ significantly from each other by electron-withdrawing or electron-pushing effects. In the context of this work, these compounds have already been successfully synthesised, but are not described within the present publications. For example, a framework could be tailored to more specific applications, or the uptake of a particular gas could be significantly enhanced by interactions with the respective functional group in competition with other gases. For example, it was possible to use the nitro or azide functionalised stilbene compounds for sensing H₂S through a fluorescence „*turn-on*” probe, as presented in chapter 2.4.2.1.

This synthesis of the new MIL-140D-*sdc* compound was used as preliminary work for the last part of this thesis, which also focuses on the detection of H₂S and combines different synthesis techniques for the production of MOFs. In addition to conventional solvothermal syntheses, a post-synthetic modification in form of a SALE was applied to the framework. This allowed certain parts of the *sdc*²⁻ to be substituted by the *abdc*²⁻. This step is required because a framework based purely on the *abdc*²⁻ is not stable under ambient atmosphere and consequently not suitable as sensor material. The exchange is not complete, which means that the high chemical stability of the MIL-140D-*sdc* can still be maintained. The efficient SALE can be monitored by ¹H-NMR spectroscopy, but also a colour change of the material from white to red suggests a successful exchange as well. The surface of the MOF decreases due to the exchange as the new linker *abdc*²⁻ is slightly shorter. Taken together, the retained stability and the implemented azo groups can be used to achieve a further possibility of functionalisation. In this way, azo groups tend to coordinate

metal ions.⁶ Copper ions, which bind to the azo linker and cause a further colour change from red to green, can be introduced into the *mixed-linker* MOF. At this point, a successful incorporation of copper can be investigated by EDX spectroscopy. Due to the incorporation, it is possible to use this MOF as H₂S sensor material, since the incorporated copper ions have a high affinity to react with H₂S. Following this reaction, the colour of the MOF changes again from green to black-grey, due to the formation of CuS. The colour changes can be examined more closely with UV/Vis spectroscopy. The response time of this system is very short, as even the human eye can observe the colour change from green to black immediately. However, other important parameters for sensing applications need to be investigated at this point. For example, the detection limit has not yet been determined exactly and it must be verified whether the material can be regenerated. One possibility could be the recovery of the MOF as a starting material to perform a re-storage of copper ions. Another interesting aspect would be the identification of the chemical surrounding of the copper ions. Although there are sufficient literature reports on complexes of copper ions and organic azo compounds, there are no reports of their storage in azo-functionalised MOFs available yet. Further tasks would also be the construction of another measuring cell, similar to the one used for NO₂ detection, for the determination of cross-sensitivities and to obtain a quantitative detection limit.

All in all, these here presented new, reactive MOFs have been functionalised successfully in such a way that they can be used in the field of sensor technology. The approach to transfer already investigated and highly selective reactions of organic molecules into three-dimensional solids, is a promising method to achieve a high selectivity or even specificity for analytes in these materials.

⁶ M. S. Masoud, E. A. Khalil, A M. Hinawy, A. E. Ali, E. F. Mohamed, *Spectrochim. Acta. A.* **2004**, 60, 2807.

5 List of Publications

5.1 Articles Presented in this work

A novel Calixarene-based MOF for highly selective NO₂ detection

M. Schulz, A. Gehl, J. Schlenkrich, H. A. Schulze, S. Zimmermann, A. Schaate
Angewandte Chemie – International Edition **2018**, *57*, 12961–12965

A Low-Temperature Approach for the Phase Pure Synthesis of MIL-140 Structured Metal-Organic Frameworks

M. Schulz, N. Marquardt, M. Schäfer, D. P. Warwas, S. Zailskas, A. Schaate
Chemistry – A European Journal **2019**, *25*, 13598–13608

Solvent-assisted linker exchange as tool for the Design of mixed-linker MIL-140D structured MOFs for highly selective detection of gaseous H₂S

M. Schulz, N. Marquardt, Malte Schäfer, Thea Heinemeyer, A. Schaate
RCS Advances **2020**, *10*, 12334–12338

5.2 Further articles

Reversible Cation Exchange on Macroscopic CdSe/CdS and CdS Nanorod Based Gel Networks

Franziska Lübke, Pascal Rusch, Malte Schäfer, Marcel Schulz, Bastian Hoppe, Peter Behrens, Nadja C. Bigall, Dirk Dorfs
Nanoscale **2020**, *12*, 5038–5047

5.3 Oral presentations

Highly specific molecules as linkers in MOFs: a solid state sensor for the selective detection of NO₂

M. Schulz, A. Gehl, J. Schlenkrich, H. A. Schulze, S. Zimmermann, A. Schaate
6th International Conference on Multifunctional, Hybrid and Nanomaterials, March 11-15,
2019, Sitges, Spain

Revisiting the Synthesis of Metal-Organic Frameworks with MIL-140 Structure

M. Schulz, N. Marquardt, A. Schaate
31. Deutsche Zeolith Tagung, March 6-8, **2019**, Dresden, Germany

5.4 Poster presentations

Functionalised MOFs with MIL-140 structure as sensing materials

M. Schulz, N. Marquardt, M. Schäfer, F. Lübke, P. Rusch, A. Schaate

3rd International Conference on Metal Organic Frameworks and Porous Polymers, October 27-30, **2019**, Paris, France

A Novel Calixarene-based MOF for highly selective NO₂ detection

M. Schulz, A. Gehl, J. Schlenkrich, H.A. Schulze, S. Zimmermann, A. Schaate

6th International Conference on Metal-Organic Frameworks, December 9-13, **2018**, Auckland, New Zealand

A Novel Calix[4]arene-based MOF for NO₂ Sensing Applications

M. Schulz, A. Gehl, J. Schlenkrich, H. A. Schulze, S. Zimmermann, A. Schaate

30. Deutsche Zeolith Tagung, Februar 28 – March 2, **2018**, Kiel, Germany

A Novel Calix[4]arene-based Metal-Organic Framework for the Detection and Storage of NO₂

M. Schulz, J. Schlenkrich, H. A. Schulze, A. Schaate

2nd International Conference on Metal Organic Frameworks and Porous Polymers, October 29 – November 1, **2017**, Delft, Netherland

Calix[4]arene based Metal-organic frameworks for sensing applications

M. Schulz, A. Schaate, P. Behrens

29. Deutsche Zeolith Tagung, March 1-3, **2017**, Frankfurt, Germany

6 Curriculum Vitae

Name	Marcel Schulz
geboren am	10. August 1993
geboren in	Stadthagen
11/2016-12/2019	Beginn der Promotion zum Dr. rer. nat in Chemie in der Arbeitsgruppe von Prof. Dr. Peter Behrens Am Institut für Anorganische Chemie Der Leibniz Universität Hannover Thema: Reactive Metal-organic frameworks for highly selective gas sensing applications
04/2016-09/2016	Masterarbeit in der Arbeitsgruppe von Prof. Dr. Peter Behrens Am Institut für Anorganische Chemie Der Leibniz Universität Hannover Thema: Synthese von Metall-organischen Gerüstverbindungen unter Verwendung von organischen Molekülen mit intrinsischer Porosität
10/2011-03/2016	Studium im Fach Chemie (Bachelor) und Master (Material- und Nanochemie) An der Leibniz Universität Hannover
2011	Abitur
2004-2011	Gymnasium Bad Nenndorf, Bad Nenndorf
2003-2004	Orientierungsstufe Stadtschule Rodenberg, Rodenberg
1999-2003	Grundschule Albert-Schweizer Schule, Lauenau