

Kurzzusammenfassung

Seit einigen Jahren ist das Problem des Klimawandels nun verstärkt in den Fokus der Öffentlichkeit geraten, dabei wird schon seit längerem intensiv an der Umstellung von fossilen Energieträgern wie Benzin und Diesel auf umweltfreundliche und regenerative Energieträger geforscht. Im Zuge dessen ist auch die effiziente Speicherung großer Mengen gasförmiger Energieträger notwendig, wie beispielsweise Wasserstoff oder Methan die unter anderem aus Power-to-Gas Verfahren gewonnen werden können. Poröse Materialien mit einer hohen spezifischen Oberfläche, großer Stabilität und möglichst geringer Dichte sind hochinteressante Kandidaten für diese Aufgabe. Gleichzeitig können solche Materialien unter anderem auch als heterogene Katalysatoren, Filtersysteme für Gasgemische und in der Optoelektronik Anwendung finden.

COFs (Covalent Organic Frameworks) als kristalline organische Netzwerke, stellen eine solche Materialklasse dar, und werden aus symmetrischen, hochfunktionalisierten Bausteinen mit starrer Geometrie zusammengesetzt. Die Nitroxid-Austausch-Reaktion stellt dabei einen neuen Ansatz dar, für welchen im Rahmen der vorliegenden Arbeit die passenden Bausteine synthetisiert wurden. So gelang es zehn mehrfach-funktionalisierte Alkoxyamine mit verschiedenen Geometrien darzustellen und ein robustes Verfahren für ihre Synthese zu etablieren. Als Gegenstücke wurden ein Dinitroxid, mehrere Trinitroxide und zwei Tetranitroxide dargestellt, sodass sich über 50 Kombinationsmöglichkeiten der in dieser Arbeit dargestellten Bausteine für die Synthese von COFs ergeben. Weiterhin wurde an einer Bibliothek aus Alkoxyaminen der Einfluss verschiedener Seitenketten und Nitroxideinheiten auf die Dissoziationsenergie untersucht.

Neben COFs können auch andere, nicht kristalline Netzwerke wie POPs (Porous Organic Polymers) als Speichermedium für Gase dienen. In einem zweiten Projekt wurden daher starre, mehrfach-funktionalisierte Azide dargestellt, die anschließend über Thermolyse in poröse Polymere überführt wurden. Dabei bildeten sich stark expandierte Netzwerke, die je nach Geometrie der Azidbausteine ein anderes Erscheinungsbild aufweisen. Außerdem konnte gezeigt werden, dass sich die spezifische Oberfläche dieser Materialien über die Thermolysetemperatur einstellen lässt.

Abstract

Recently, the problem of climate change has increasingly attracted public attention; however, in the scientific community, intensive research has already been conducted for several years on the transition from fossil fuels, such as gasoline and diesel, to more environmentally friendly, renewable energies. As a result, it is imperative to investigate more efficient methods of storing large quantities of gaseous energy carriers, which can be obtained from power-to-gas processes, such as hydrogen or methane. Porous materials with a high specific surface area, high stability, and a density as low as possible, are highly interesting candidates for this task. Furthermore, such materials can also be used as heterogeneous catalysts, filter systems for gas separation, and optoelectronic applications.

COFs (Covalent Organic Frameworks), as crystalline organic frameworks, represent such a class of materials and are assembled of symmetric, highly functionalized building blocks with rigid geometry. The nitroxide exchange reaction represents a new approach, for which the appropriate building blocks were synthesized in the present thesis. Thus, ten multi-functionalized alkoxyamines with different geometries were successfully obtained and a robust procedure for their synthesis was established. As counterparts, a dinitroxide, several trinitroxides, and two tetranitroxides were synthesized, resulting in more than 50 possible combinations of the building blocks, synthesized in this thesis, for the synthesis of COFs. Furthermore, the influence of different side chains and nitroxide units on the dissociation energy was investigated using a library of alkoxyamines.

In addition to COFs, other non-crystalline networks such as POPs (Porous Organic Polymers) can also serve as storage platforms for gaseous energy carriers. Therefore, in a second project, rigid, multi-functionalized azides were prepared, which were subsequently converted into porous polymers *via* thermolysis. In this process, strongly expanded frameworks were formed, which, depending on the geometry of the azide building blocks, had a different appearance. Moreover, it was also demonstrated that the specific surface area of these materials could be adjusted *via* the thermolysis temperature.

1 Introduction¹

On the 4th of November 2020, one day after the US presidential election, the USA, one of the main contributors to the ongoing climate change, withdrew from the Paris Agreement until the new US president JOE BIDEN, fortunately, rejoined the agreement in February 2021. The Paris Agreement is the successor of the Kyoto Protocol. It was signed by all of the members of the United Nations Framework Convention on Climate Change (UNFCCC) and went into effect in 2016.^[1–3]

The main goal of the Paris Agreement, besides increasing resilience against and adaption to adverse effects of global warming, is to limit global warming to well below 2 °C above pre-industrial limits and to ensure a maximum of 1.5 °C with all effort.^[4] Despite this agreement, the World Meteorological Organization’s (WMO) annual report on the “State of the Global Climate in 2019” indicated that we will probably not achieve this goal without further efforts. In 2019, the global mean temperature was already around 1.1 °C above pre-industrial levels with 2016 and 2019 being the two warmest years and this decade being the warmest decade since recording started.^[5]

One of the highest priorities to help stop climate change is to reduce the overall global greenhouse gas (GHG) emissions and therefore, the transition from fossil fuels to environmentally friendly, sustainable energy sources. Additionally, the efficient storage of GHGs, carbon dioxide in particular, could be necessary to achieve the goals of the Paris Agreement and to stop the acidification of the oceans.^[6] During the transition towards renewable energy carriers, methane is a preferable fuel as it has the highest hydrogen content of all hydrocarbon fuels like petrol or diesel. Combined with the high heat of combustion, a favorable ratio of carbon dioxide emission to generated energy is achieved.^[7] Ultimately, hydrogen could be the energy source of the future, as it is abundant, has a high energy density, and exhibits clean combustion. These properties make methane and hydrogen, which can be obtained from power-to-gas processes, interesting for mobile applications such as the transport sector.^[6–13]

However, for this application, safe and efficient storage of large quantities of gaseous energy carriers has to be found.^[14] Porous materials with a high specific surface area, are highly interesting candidates for this task.^[9,15–19]

¹ This chapter contains sections and schemes based on the content of the own master’s thesis.^[170]

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Porous materials can be divided into several subclasses, based on the connection between their building blocks. Some of these subclasses are shown in Figure 1 and will be presented in the following sections.

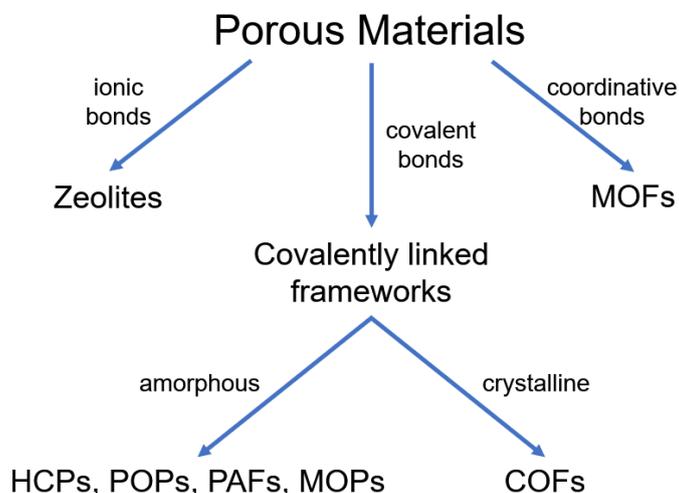


Figure 1: Illustration of the different subclasses of porous materials. MOF (Metal-Organic Framework), HCP (Hyper Crosslinked Polymer), POP (Porous Organic Polymer), PAF (Porous Aromatic Framework), MOP (Microporous Organic Frameworks).

1.1 Zeolites and Metal-Organic Frameworks

CRONSTEDT, a Swedish mineralogist who also discovered the element nickel, was the first to describe zeolites around 250 years ago in 1756.^[20] Zeolites are naturally-occurring, three-dimensional, microporous, hydrated aluminosilicates, that are assembled from edge- and corner-connected $[\text{SiO}_4]^{4-}$ -tetrahedra, which are partly replaced by $[\text{AlO}_4]^{5-}$ -tetrahedrons. According to LOEWENSTEIN'S rule, two $[\text{AlO}_4]^{5-}$ -tetrahedra cannot be connected, so that zeolites can only contain a maximum of 50% $[\text{AlO}_4]^{5-}$ -tetrahedra. Their negatively charged crystalline framework is constructed from channels that form pores at the intersection points. These channels are filled with cations, which are required to counterbalance the negative charge of the framework, and water molecules. When zeolites are heated, the adsorbed water is evaporated, which gave zeolites their name; "boiling stone" from the Greek words "zéō" for "to boil" and "líthos" for "stone".^[21,22] Although zeolites possess the pores and channels necessary for efficient adsorption of gases, investigations regarding hydrogen uptake revealed that their capacity is limited.^[21,23] Nevertheless, they are produced and mined in several million tons annually, to find widespread application in the concrete industry, as ion exchangers in detergents, as catalysts, and for drying, purifying, and separating chemicals in refineries.^[21,22,24]

Although zeolites already represent an interesting approach, their chemistry is limited to comparatively few structures due to the use of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ -tetrahedra. An extension of the “chemical construction kit”, could therefore allow a more targeted adjustment of the properties of such frameworks. The combination of inorganic chemistry, by retaining the metal centers, and organic chemistry, by using an organic linker, led to the discovery of crystalline, hybrid framework structures. The first example of such a hybrid material can be traced back to the beginning of the 18th century when “Prussian Blue” was discovered by DIPPEL and DIESBACH in Berlin.^[25]

HOSKIN and ROBSON proposed in 1989, that a new class of “scaffold-like materials” could be created, by linking metal centers with an octahedral or tetrahedral valence with an organic “rod-like” connector. They could prove their claim by crystallizing tetrakis(4-cyanophenyl)methane and $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$, which resulted in an infinite 3D framework with a diamond-like crystal lattice.^[26,27] HOSKIN and ROBSON continued to work on such structures^[28] and presented a 3D layered porphyrin framework in 1994. Although the porous structure collapsed when the solvent was removed from the pores, they could establish the concept of connecting simple organic building blocks into complex framework structures.^[29]

Eventually, Yaghi introduced the term “MOF” (Metal-Organic Framework) for this class of materials in 1995, which was quickly established in the scientific community.^[30] MOFs are crystalline, periodic materials with pores and channels, formed by connecting inorganic metal centers (SBU, Secondary Building Unit) and organic building blocks (“linkers”) *via* coordinative bonds.^[31,32] Using a metal ion as an inorganic center and a simple organic linker will not necessarily lead to robust, crystalline materials since metal ions do not contain any directional information and do not allow for high control of the MOF structure. Therefore, the metal ions have to be forced into rigid, directional metal clusters, e.g. *via* chelating functionalities on the linker. These clusters are commonly referred to as SBUs.^[31,33] The concept of SBUs led to the targeted design of new MOFs based on already successfully utilized SBUs, by simply altering the organic linker while retaining the original topology (isorecticular principle).^[31,34–36] Elongation of the organic linker but retaining their shape allows control of the pore size of the resulting series of isorecticular MOFs (Figure 2).^[34–37]

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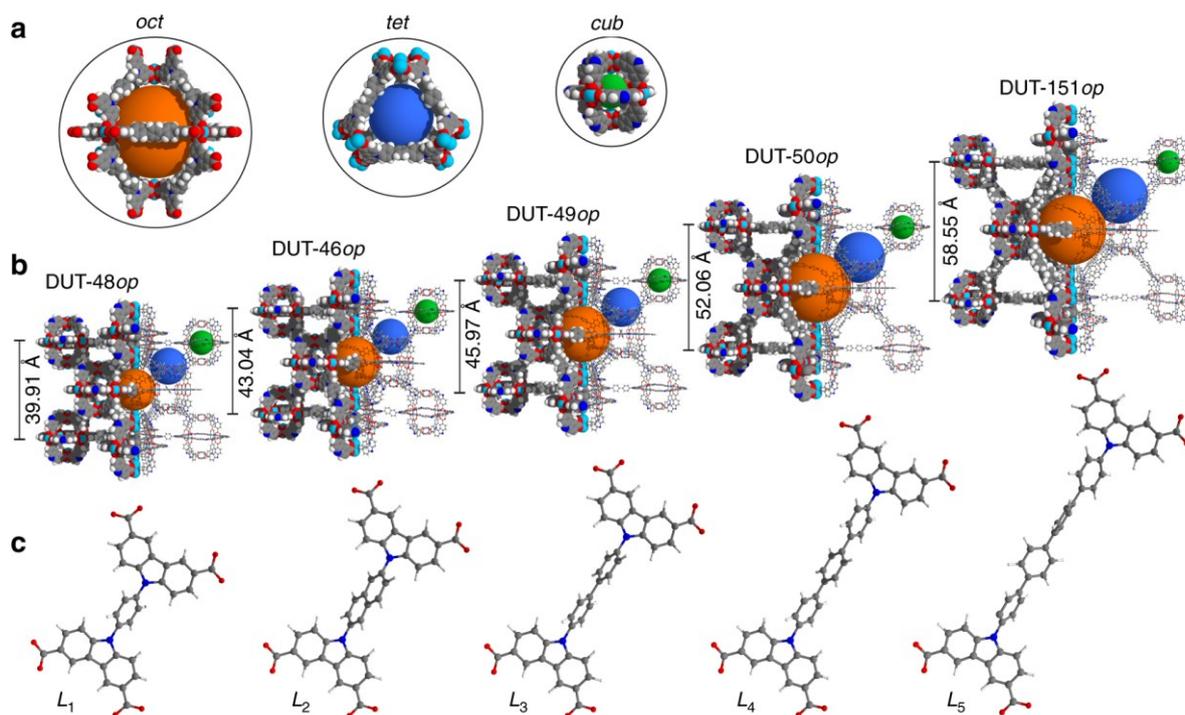


Figure 2: Organic linkers used to generate isorecticular MOFs and their crystal structure with pore volume highlighted in orange, blue, and green. Adapted from Figure 1 in “Towards general network architecture design criteria for negative gas adsorption transitions in ultraporous frameworks”. S. Krause, J. D. Evans, V. Bon, I. Senkowska, P. Iacomi, F. Kolbe, S. Ehrling, E. Troschke, J. Getzschmann, D. M. Töbrens, A. Franz, D. Wallacher, P. G. Yot, G. Maurin, E. Brunner, P. L. Llewellyn, F.-X. Coudert, S. Kaskel, *Nat. Commun.* **2019**, *10*, 3632. DOI 10.1038/s41467-019-11565-3. This material is licensed under CC BY 4.0.^[36]

In the last 26 years since the discovery of MOFs, more than 70.000 crystal structures have been added to the Cambridge Structural Database and over 90.000 MOFs have been synthesized, which highlights the overwhelming interest in these materials.^[38,39]

This unbroken interest in MOFs can be explained mainly by their extremely high specific surface areas.^[40] For a long time, a surface area of about 10500 m²/g was considered the theoretical maximum,^[41] but this was revised upwards in 2012 by HUPP *et al.* to a theoretical limit of around 14600 m²/g. At the same time, HUPP *et al.* set a new record for the largest surface area in MOFs with the MOFs **NU-109E** (7010 m²/g) and **NU-110E** (7140 m²/g).^[40] This record was set in 2018 by KASKEL *et al.*; according to current knowledge, their material **DUT-60** is the record holder in terms of surface area (7839 m²/g) and accessible pore volume (5.02 cm³/g). Figure 3 illustrates the highly ordered structure and pore system of **DUT-60**, which consists of smaller channels connecting larger pores.^[42]

Due to the high surface area, crystallinity, and variability of MOFs, they are investigated for the storage of carbon dioxide or energy carriers such as hydrogen and methane.^[35,43–50] Furthermore, MOFs can be used for catalysis, biomedical applications, water harvesting, or in the field of energy applications.^[51–59]

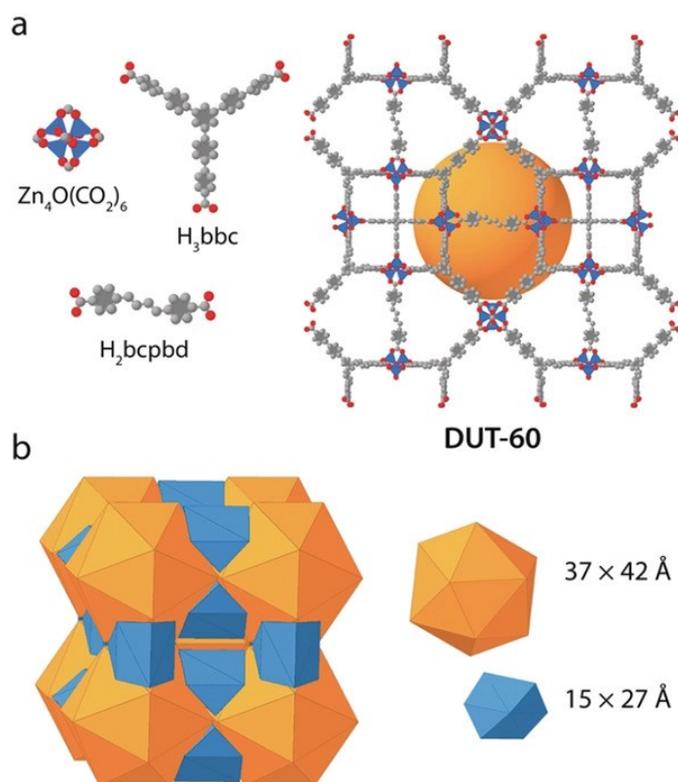


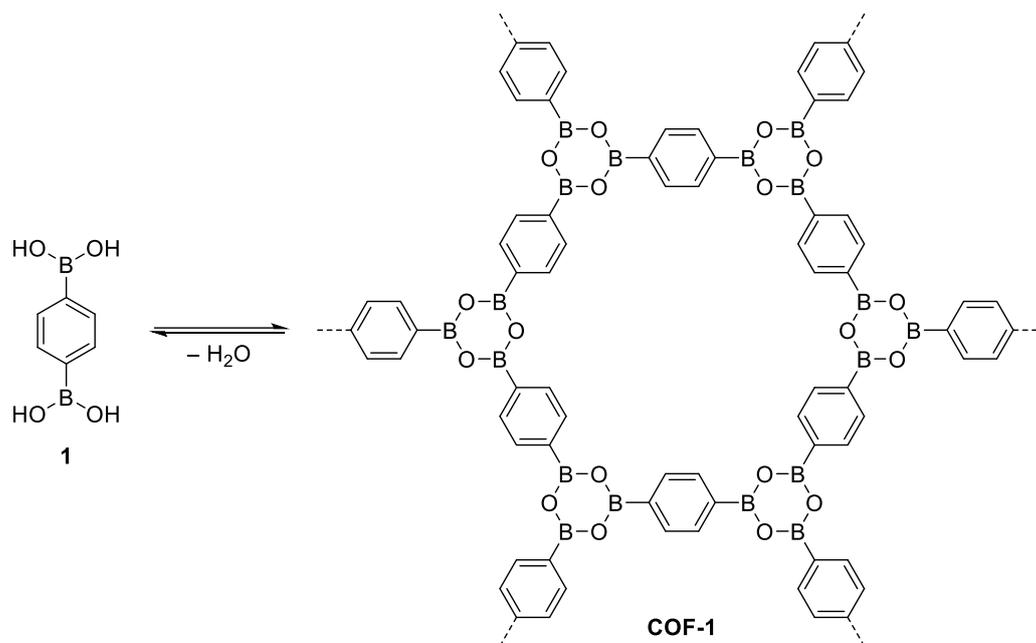
Figure 3: a) Structure of **DUT-60** and b) pore system of **DUT-60** highlighted with orange and blue polygons. Reprinted with permission from I. M. Hönicke, I. Senkowska, V. Bon, I. A. Baburin, N. Bönisch, S. Raschke, J. D. Evans, S. Kaskel, *Angew. Chem. Int. Ed.* **2018**, *57*, 13780. Copyright (2018) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

However, MOFs are not only present in research but have also found their way into commercial applications. The BASF, one of the largest companies pioneering in MOFs, presented a heavy-duty truck in 2013, which was modified with MOF-filled fuel storage tanks. This truck runs on natural gas, which is adsorbed in the MOF material. Thereby, a lower storage pressure could be achieved while retaining the driving range.^[60] MOF Technologies, a spin-off from the Queen's University Belfast, developed TruPick, a MOF material used in the food market. TruPick stores 1-methylcyclopropene, which is a competitor to ethylene, and is used to prevent the undesired ripening of fruits during storage and transport.^[61] NuMat Technologies, another spin-off company, developed ION-X, a MOF-based storage solution for toxic gases (arsine, phosphine, or boron trifluoride) used in the semiconductor industry.^[61–63]

As mentioned above, an incredible number of MOF structures exist due to the variety of available organic linkers. If the remaining SBUs are now also replaced by an organic building block, similar to the transition from zeolite to MOF, then far more combination possibilities arise. These purely organic frameworks are held together solely by covalent bonds. As can be seen in Figure 1, a further distinction can be made between crystalline and amorphous networks, which both received increasing attention in the last years.

1.2 Crystalline Organic Frameworks

Ten years after the discovery of MOFs, YAGHI established another new class of materials in 2005. Self-condensation of benzene-1,4-diboronic acid (**1**) led to the formation of **COF-1**, a boroxine-connected framework with permanent porosity and a surface area of ~ 1600 m²/g (Scheme 1). This material was designated as Crystalline Organic Framework (COF).^[64]



Scheme 1: **COF-1** formed by the self-condensation of the boronic acid **1** according to YAGHI *et al.*^[64]

COFs are built entirely from light atoms such as hydrogen, boron, carbon, nitrogen, and oxygen, which are linked by strong covalent bonds.^[64] Due to the close relationship between MOFs and COFs, the structure of their building blocks must meet the same requirements; symmetry, rigidity, and a discrete direction of bond formation. These requirements are met by aromatic systems, that are easy to functionalize and offer diverse chemistry. Figure 4 shows a selection of such aromatic systems, that were successfully applied for the formation of COFs.^[6,8,9,64-66]

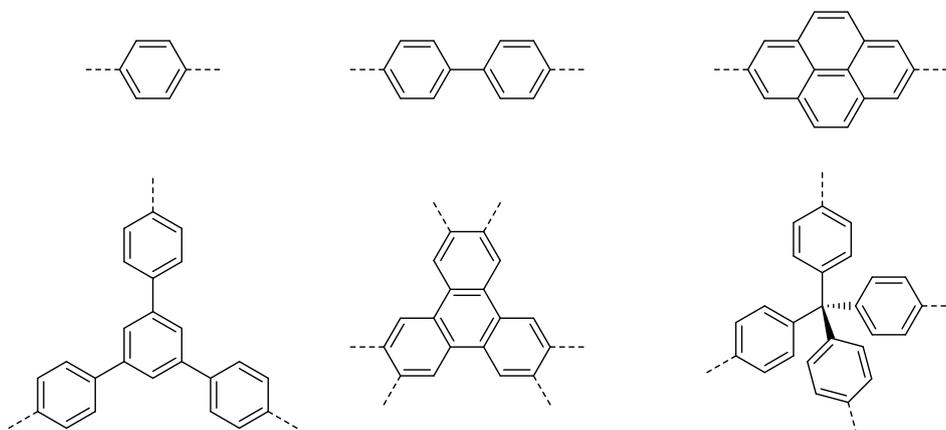
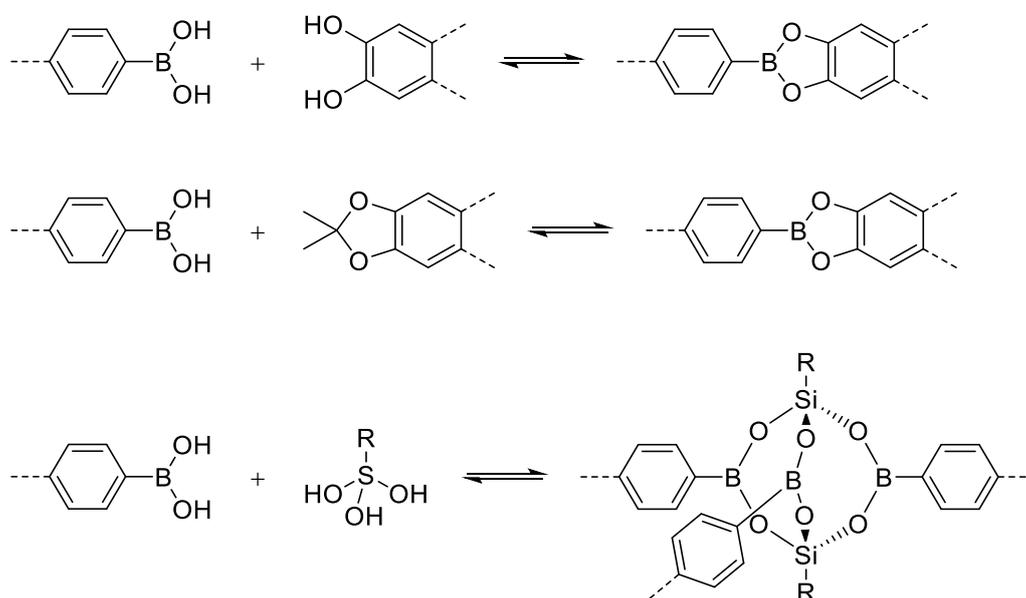


Figure 4: Selection of aromatic systems that were successfully applied for the formation of COFs.^[6,8,9,64-66]

1.2.1 Classification of COFs

The connection between these building blocks must be formed by thermodynamically controlled, reversible reactions. Thereby, defects in the framework, such as faulty linkages or loose ends, can be cured during the synthesis by a reverse reaction of the incorrectly attached building blocks and subsequent correct incorporation.^[6,8,67,68] The use of reversible reactions is therefore crucial for the successful synthesis of COFs. This criterion limits the available reactions to only a few types, some of which have so far stood out as very successful. The resulting COFs can therefore mostly be classified into one of three major categories: (1) boron-containing COFs, (2) triazine-based COFs, and (3) imine-based COFs.^[6,8,67]

The first COF (**COF-1**) synthesized by YAGHI *et al.* in 2005, is linked *via* boroxine rings and was formed by the self-condensation of a boronic acid thus belonging to the first category (Scheme 1).^[64] Frameworks of the first category can also be obtained when boronic acid-functionalized building blocks are reacted with diols or ketals to form boronate esters. Further possibilities are the reaction between boronic acids and organosilanols to form borosilicates or the formation of borazine-linked frameworks (Scheme 2).^[6,8,67,69–75]



Scheme 2: Condensation of boronic acids with diols (upper), ketals (middle), and organosilanols (lower).^[8]

Most reactions leading to COFs of the first category are condensation reactions that occur under the loss of water; therefore, boron-containing COFs exhibit an intrinsic instability toward water and humidity.^[15,76] However, an advantage of boron-containing COFs is their high thermal stability.^[64,66,69,70,72] Moreover, boron-containing COFs exhibit high surface areas and low densities. **COF-103** had the largest surface area (4210 m²/g) and **COF-108** the lowest density (0.17

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g/cm^3) for almost ten years. In 2016, **DBA-3D-COF 1** broke both records simultaneously with a surface area of $5083 \text{ m}^2/\text{g}$ and a density of 0.13 g/cm^3 .^[66,77]

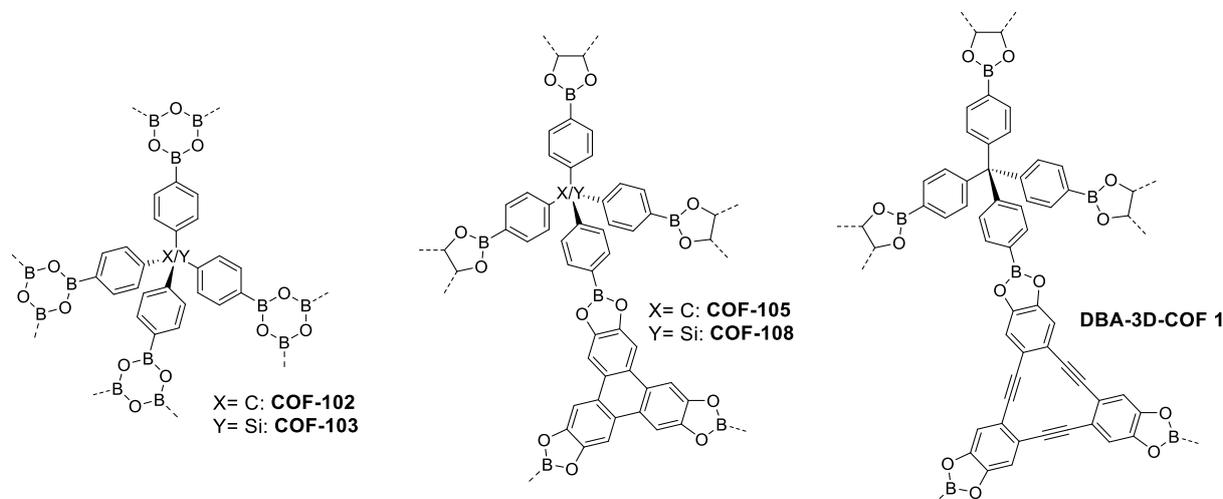
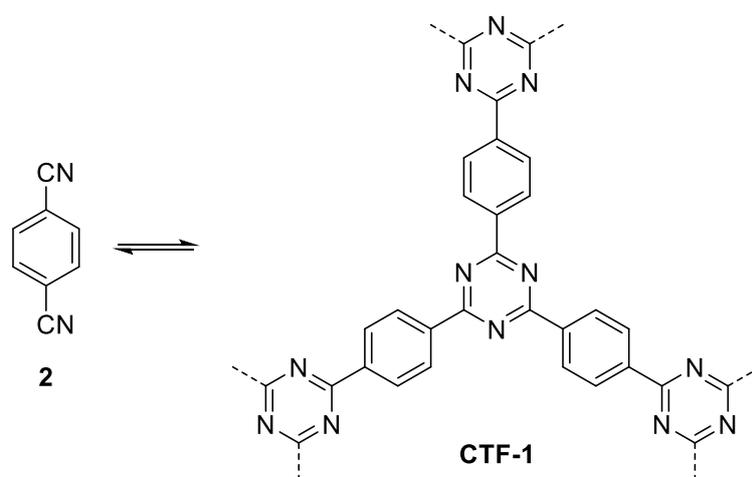


Figure 5: Boron-containing **COF-102**, **COF-103**, **COF-105**, **COF-108**, and **DBA-3D-COF 1**.^[66,77]

The structure of these record-breaking COFs can be found in Figure 5. Interestingly, all of these high-performing COFs are based on the tetraphenylmethane/silane structural motif, which indicates the immense potential of these tetrahedral aromatic building blocks.^[78]

The second class of COFs, the Covalent Triazine Frameworks (CTFs), can be synthesized *via* cyclotrimerization of aromatic nitriles in molten ZnCl_2 (ionothermal conditions) (Scheme 3). THOMAS *et al.* prepared the first **CTF-1** in 2008, starting from 1,4-dicyanobenzene (**2**). Since high temperatures of $400 \text{ }^\circ\text{C}$ are required for this process, CTFs exhibit excellent thermal stabilities (more than $600 \text{ }^\circ\text{C}$).^[6,8,79–81]

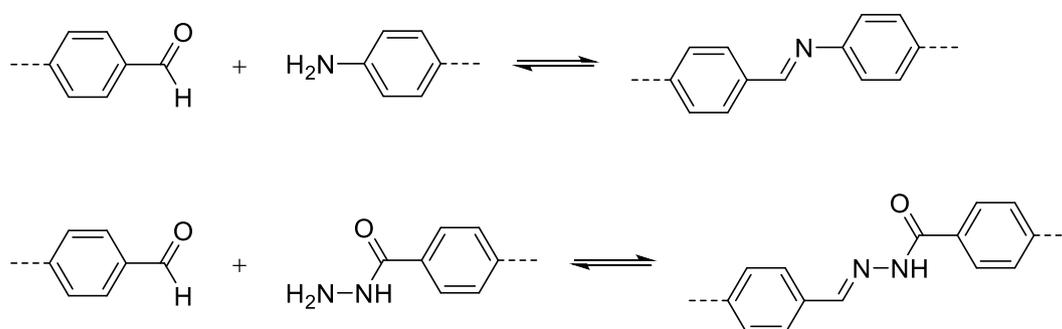


Scheme 3: Synthesis of **CTF-1** *via* cyclotrimerization of nitrile **2**. The overall structure of CTFs resembles the structure of **COF-1** with triazines instead of boroxines.^[79]

However, a tradeoff is that not many functional groups are tolerated during the harsh synthesis. Due to the low reversibility of the cyclotrimerization, CTFs often lack a high crystallinity. Moreover, the surface areas of CTFs are often not very high. Interestingly, the surface area increases drastically, when the crystalline CTFs are transformed into amorphous CTFs, through treatment at temperatures above 400 °C.^[6,8,79–81]

Lately, new developments in the field of CTFs involved low-temperature condensations of aldehydes and amidines,^[82] condensation of triazine-containing building blocks,^[83] or condensation of melamines.^[84] These approaches are much easier to perform and seem to give better crystallinity than the ionothermal approach.^[85]

Imine-based architectures form the third class of COFs and were developed by YAGHI *et al.* in 2009. Condensation of tetrakis(4-aminophenyl)methane and benzene-1,4-dialdehyde gave imine-linked **COF-300** with a diamond structure.^[86] In general, this class can be subdivided into two types. The first type can be synthesized *via* condensation of amines and aldehydes to give imines, as demonstrated by Yaghi for **COF-300**, and is therefore called the “Schiff base” type (Scheme 4). The second “hydrazine” type is obtained through condensation of aldehydes and hydrazides (Scheme 4).^[6,8,85–88]



Scheme 4: Formation of “Schiff base” (upper) and “hydrazine” (lower) type COFs.^[6,8]

In contrast to boron-containing COFs with their inherent instability towards moisture or water and CTFs with their low crystallinity, imine-based COFs are highly crystalline and possess good stability in water.^[8,85,89] However, they are susceptible to hydrolysis under acidic conditions.^[90] Attempts to stabilize the imine bonds were undertaken by oxidative cyclization^[91] or aza-DIELS-ALDER reactions.^[90]

Apart from these three classes, other reactions are also suitable for the generation of COFs. The MICHAEL addition-elimination reaction for example yields crystalline, π -conjugated COFs with

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improved hydrolytic stability and efficient π -electron delocalization.^[92] Moreover, the formation of imides was used to generate PI COFs (polyimide COFs) with good thermal stability (above 450 °C), high surface areas (~2350 m²/g) and one of the largest pore sizes reported to date.^[93,94]

In addition to the classification of COFs according to their chemical structure, they are often also classified according to their topology as 2D COFs or 3D COFs. Every combination of linear, trigonal-planar, or square/rectangular building blocks with themselves, leads to the formation of 2D COFs. However, when building blocks with an sp³ carbon or silane atom, like the already discussed tetraphenylmethane/silane, are used, 3D COFs are formed. Figure 6 shows some combinations of building block geometries and the resulting framework topology. 2D COFs consist of single layers that stack on top of each other, thereby forming channels perpendicular to the layer structure as can be seen in Figure 6 for the hexagonal and square topology. Since the building blocks in COFs are mainly aromatic systems, the layered structure forms an ordered π -system, which allows using 2D COFs for optoelectronics and photovoltaics. In contrast, 3D COFs do not form layers but are connected in every direction. Their already mentioned high surface area and their low density (5083 m²/g and 0.13 g/cm³ for **DBA-3D-COF 1**) make them ideal candidates for gas storage applications.^[6,77]

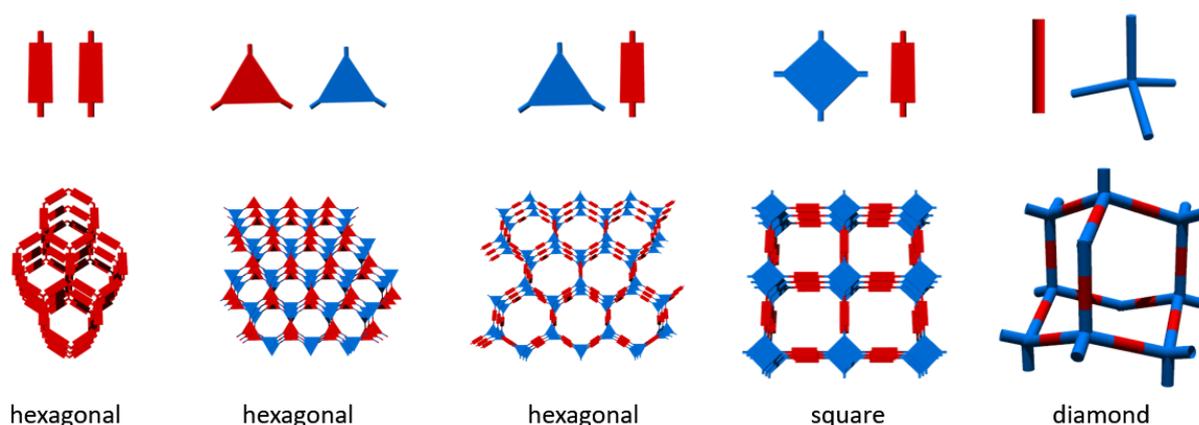


Figure 6: Combination of different building block geometries and their resulting framework topology. This image was kindly offered for use in this thesis by Dr. MANUEL TSOTSALAS (Institute of Functional Interfaces, KIT).

1.2.2 Applications

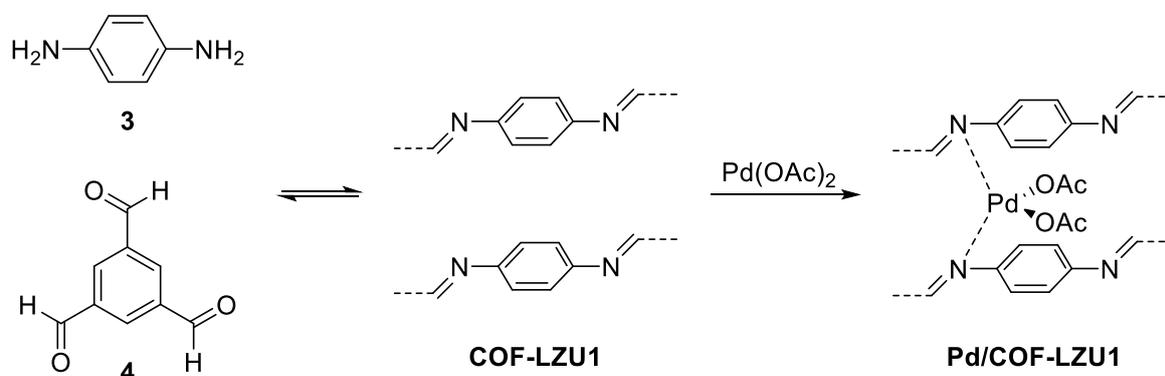
The outstanding properties of COFs, i.e. crystallinity, high chemical and thermal stability, low densities, the possibility to modify post-synthetically, and high surface areas, render them suitable candidates for many applications. Gas storage is by far the most prominent application.

1.2.2.1 Gas Storage

The absence of heavy metal centers in COFs, paired with their high surface areas and low density could provide COFs with a favorable gravimetric storage capacity for gases.^[95] In general, due to their higher surface area, 3D COFs show a higher gas uptake than 2D COFs. The US Department of Energy defined the storage capacity target of hydrogen as 5.5wt% at an operating pressure of a maximum of 100 atm and a temperature range of $-40\text{ }^{\circ}\text{C}$ to $60\text{ }^{\circ}\text{C}$ until 2017.^[8] FURUKAWA and YAGHI investigated several COFs for their uptake of hydrogen, methane, and carbon dioxide. The highest hydrogen uptakes were found for **COF-102** and **COF-103** (Figure 5) with 7.24wt% and 7.05wt%, respectively. These capacities can compete with other porous materials such as MOFs (**MOF-177**: 7.5wt%, **MOF-5**: 7.6wt%) or amorphous frameworks (**PAF-1**: 7.5wt%) and demonstrate the potential of COFs as hydrogen storage systems. However, these uptakes were determined at 77K, which is not in accordance with the DOE targets, meaning that practical application in the transport sector is not yet possible.^[6,8,9,95] Besides hydrogen, also the storage of methane is interesting and was evaluated by FURUKAWA and YAGHI. Again, the 3D COFs **COF-102** (187 mg/g) and **COF-103** (175 mg/g) surpass or come close to the DOE target of 180 mg/g at 35 bar, while the 2D COF **COF-5** only reached 89 mg/g. Although some COFs can meet the DOE target for methane uptake, their synthesis remains too expensive for a practical application.^[8,9]

1.2.2.2 Catalysis

As discussed above, zeolites and MOFs can both be used as catalysts due to their stability, large surface area, and porosity. As these properties can also be found in COFs, it is rational to assume that COFs can also be used for catalytic applications. WANG *et al.* were the first to investigate COFs for catalytic applications in 2011.^[96]



Scheme 5: Synthesis and proposed structure of **COF-LZU1** and **Pd/COF-LZU1**.^[96]

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They synthesized the imine-linked 2D COF **COF-LZU1** and post-functionalized it with Pd(OAc)₂ to achieve a Pd-loading of around 7%. The palladium was coordinated by the lone pairs on the nitrogen atoms and was located between the layers of the COF, thereby connecting them (Scheme 5). The resulting **Pd/COF-LZU1** was then used for SUZUKI-MIYAURA cross-couplings, showed excellent stability, and provided high yields (96-98%).^[85,96] Furthermore, YAN *et al.* developed 3D imine-based COFs which were used for base-catalyzed Knoevenagel condensations. These COFs possessed good recyclability and conversion and showed a high selectivity determined by the pore size of the COFs and the substrate size.^[85,97] Further examples include catalytic CO₂ reduction^[98] and photocatalytic hydrogen production.^[99]

1.2.2.3 Other Applications

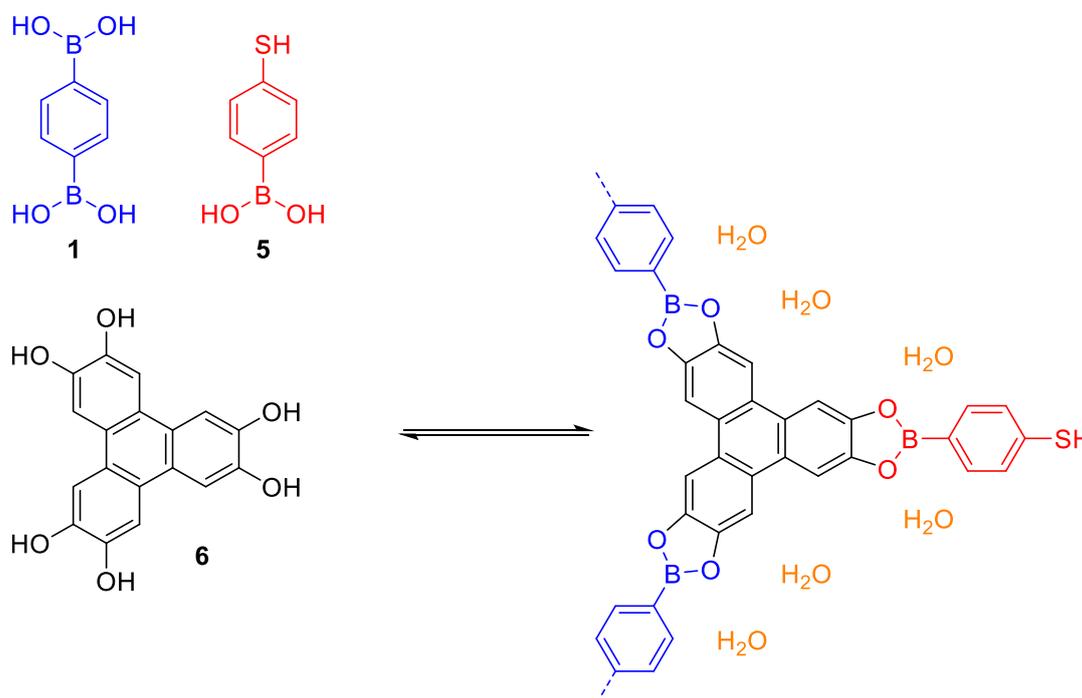
As described above, 2D COFs have a layered structure with periodically aligned columns that is formed by the π -interactions between the aromatic systems in the building blocks. These interactions are responsible for the electronic coupling between the π -orbitals and allow the transport of charge carriers and excitons through the frameworks.^[6] JIANG *et al.* produced **PPy-COF** and **TP-COF** from self-condensation of pyrene-2,7-diboronic acid or co-condensation with hexahydroxytriphenylene (HHTP, **6**), respectively. **TP-COF** absorbs photons from the UV to the visible region, shows a blue luminescence, and is semiconducting.^[100] **PPy-COF** also shows a blue luminescence and exhibits photoconductivity with a quick response to irradiation.^[101] Thereafter, further, COFs were investigated regarding their photoelectrical properties.^[88,102-105]

Furthermore, COFs can be used for electrode modifications,^[106] sensing,^[107-109] drug delivery,^[94] proton conduction,^[110] and many other applications.^[6,8,85,95]

1.2.3 Controlling Crystallinity

In most cases, a high crystallinity of the COFs is a prerequisite for the success of the desired application. However, using strong covalent bonds usually makes it difficult to obtain crystalline structure, as described by YAGHI with the “crystallization problem”. To overcome this problem, the utilization of thermodynamically controlled, reversible reactions is crucial for the formation of COFs. Thereby, defects in the framework, such as faulty linkages or loose ends, can be cured during the synthesis and the thermodynamically most stable product is formed.^[6,8,67,68,92,111] Modulating a reaction can further enhance the control over the crystallinity. A modulator either reopens already formed bonds, thereby exerts pressure on the system

and forces it closer to the thermodynamic minimum or it reversibly captures reactive sites on the framework surface. Both approaches slow down the framework formation and allow to heal defects that would otherwise move the framework away from its thermodynamic minimum. For condensation reactions that cleave off water molecules, these can serve as modulator (Scheme 6), while it is also possible to add an external modulator into the system.^[111,112] BEIN *et al.* could enhance the crystallinity of **COF-5** by adding a monofunctional boronic acid **5** as an external modulator into the reaction mixture (Scheme 6). Thereby, they could raise the surface area and the pore volume as well as obtain larger crystals.^[112]



Scheme 6: Formation of **COF-5** using a monofunctional boronic acid **5** (red) as an external modulator. This boronic acid reversibly blocks a reaction site and slows down the reaction. Furthermore, the water molecules cleaved off during the condensation reactions (orange) can also serve as a modulator, as they can hydrolyze the boronate esters, thereby reopening wrong connections between the building blocks.^[111,112]

In summary, COFs have a range of interesting properties and applications, however, access to this class of materials is limited to only a few reaction types. In order to make them more accessible and thus create an opportunity for market readiness, it is necessary to develop further synthetic methods. The nitroxide exchange reaction (NER) is a new approach for the formation of covalent organic frameworks and will be discussed in the next section.

1.2.4 Nitroxide Exchange Reaction

The nitroxide exchange reaction (NER) is a fully reversible, thermodynamically controlled reaction between an alkoxyamine and a nitroxide. Alkoxyamines are a class of compound which, formally seen, belong to the ethers of disubstituted hydroxylamines. They are commonly used as initiators of the nitroxide-mediated polymerization (NMP).^[113] Nitroxides are disubstituted NO radicals, commonly used as spin labels and closely related to alkoxyamines as can be seen in Figure 7.^[114–116]

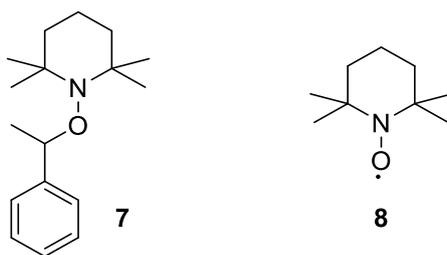
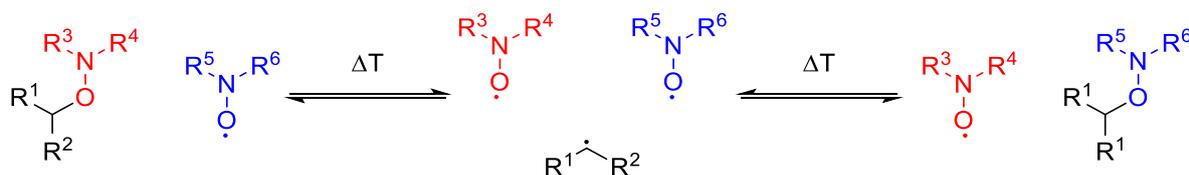


Figure 7: Structures of 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine (**7**) and (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO, **8**) as examples for an alkoxyamine and a nitroxide.

Nitroxides without protons in α -position like TEMPO **8** (Figure 7) are bench stable compounds. This unusual stability arises from the fact that the electron is shielded by the substituents and is additionally distributed over the oxygen and nitrogen, which results in a bond order of 1.5 for the N–O bond. For the delocalization of the unpaired electron, an energy of 96–125 kJ/mol is reported, which is responsible for the fact that nitroxides do not dimerize, as the formation of a weak O–O bond would result in an energy loss. Interestingly, nitroxides can undergo reactions without the participation of the unpaired electron, provided that the electron is sterically shielded and that the reacting group is isolated.^[115,117,118]

The mechanism of the NER can be described as follows: The C–O bond in alkoxyamines is relatively weak compared to other C–O bonds and can be cleaved upon heating, which results in the formation of a C-centered radical and a persistent nitroxide. In the presence of a second nitroxide, both nitroxides compete for the recombination with the C-centered radical. Since the NER is fully reversible and thermodynamically controlled, the reaction ultimately yields the thermodynamic product (Scheme 7).^[119]

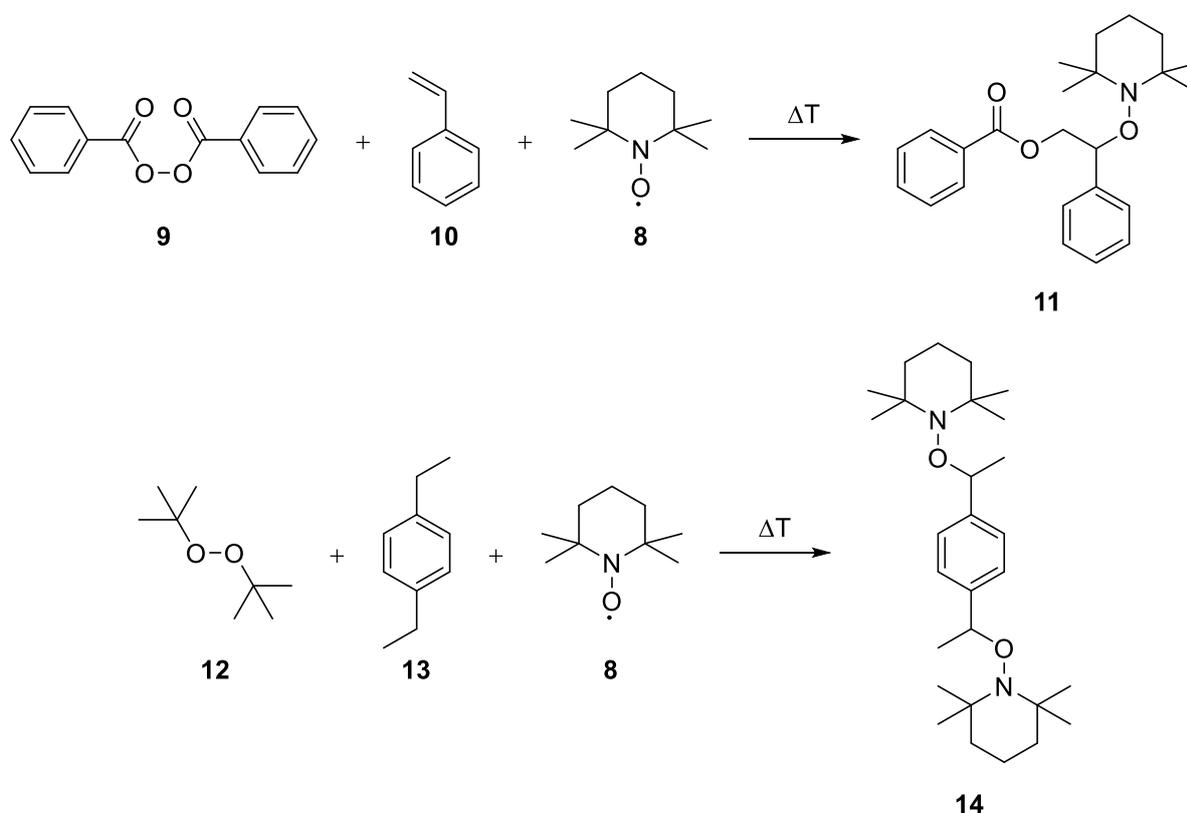


Scheme 7: Mechanism of the nitroxide exchange reaction.

The NER is capable of producing chemically stable frameworks and can be controlled with the addition of a modulator; e.g. the nitroxide, that is cleaved off during the reaction. Moreover, the NER tolerates many functional groups and allows to functionalize the building blocks for desired applications before the assembly of the frameworks. A detailed description of such NER frameworks and their unique properties can be found in chapter 3.2.3. Furthermore, due to the involved unpaired electrons, the NER can be monitored in-situ *via* EPR spectroscopy. This allows an unprecedented insight into the defect density without destroying the framework, which is difficult to achieve for other reaction types. Therefore, the NER is highly promising for the generation of COFs.^[119–123]

1.2.4.1 Synthesis of Alkoxyamines

The most important way to synthesize alkoxyamines is the scavenging of C-centered radicals with a nitroxide. As described above, nitroxides do not form O–O bonds due to the involved energy loss. Therefore, one of the easiest ways to generate these C-centered radicals is the use of a radical initiator.

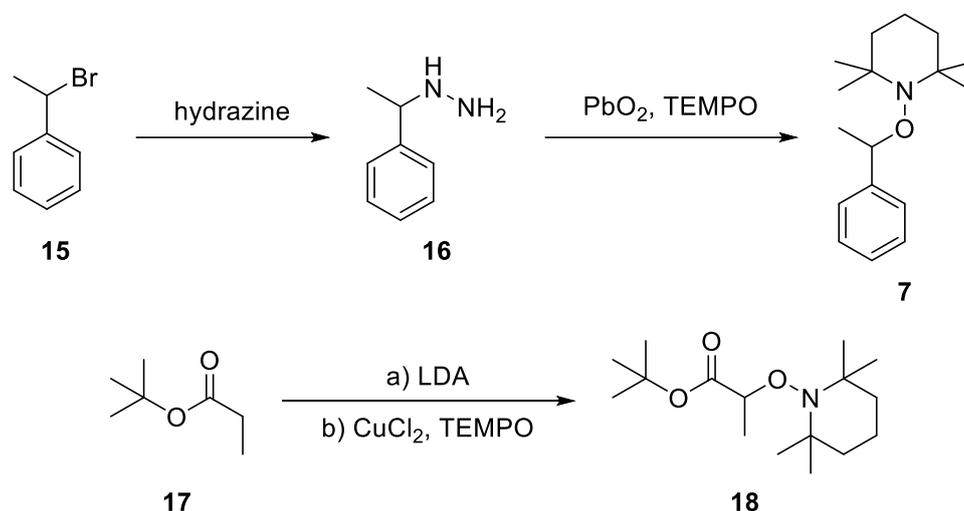


Scheme 8: Early method of HAWKER *et al.* for the synthesis of alkoxyamines (upper) and synthesis of the bifunctional alkoxyamine **14** *via* proton abstract from 1,4-diethylbenzene (**13**) (lower).^[124,125]

Introduction

HAWKER *et al.* demonstrated in 1994, that reaction of benzoyl peroxide (**9**) with styrene (**10**) and TEMPO **8**, allowed to isolate the resulting alkoxyamine **11** in a yield of 42%.^[114,124] Since the resulting alkoxyamines are derivatives of benzoates, saponification gives the free hydroxy group, which allows a further functionalization.^[126] Another method that makes use of radical initiators, like di-*tert*-butyl peroxide **12**, was developed by various groups to abstract protons from alkanes and ethers to form alkoxyamines.^[125–130] PRIDDY *et al.* could demonstrate that it is also possible to obtain a bifunctional alkoxyamine **14** with this procedure, however, a large excess of di-*tert*-butyl peroxide (**12**) was necessary (Scheme 8).^[125]

Moreover, C-centered radicals can be generated by the oxidation of hydrazines with PbO₂ or *via* Cu(II)-mediated oxidation of carbanions (Scheme 9) as demonstrated by MAHAL *et al.*^[130] as well as by photochemical cleaving of C–Br bonds.^[127]

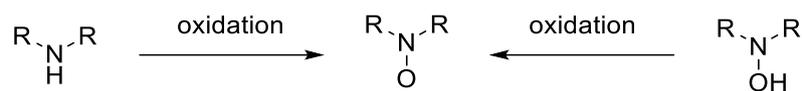


Scheme 9: Synthesis of alkoxyamine **7** and **18** *via* oxidation of hydrazine **16** (upper) and oxidation of carbanions with Cu(II) salts (lower).^[130]

Another interesting pathway involves the addition of oxo-manganese compounds to alkenes, leading to C-centered radical intermediates, which can be trapped by TEMPO **8**. Originally, the expensive JACOBSEN catalyst was used but could be replaced by the cheaper $\text{Mn}(\text{OAc})_3$ ultimately.^[114,131,132] Further methods for the generation of alkoxyamines include the use of GRIGNARD reagents,^[126] alkylation of hydroxylamine anions,^[133] addition of C-centered radicals to nitroso compounds or nitrones,^[134–136] and addition of oxoammonium salts to olefines leading, to functionalized alkoxyamines.^[137] However, the most prominent method is the generation of C-centered radical from alkyl halides with elemental copper and subsequent scavenging with TEMPO **8** according to Matyjaszewski *et al.*^[138] This method was also employed in this thesis and will be described in detail in chapter 3.2.1.4.

1.2.4.2 Synthesis of Nitroxides

Nitroxides are synthetically accessible *via* several routes, with the oxidation of secondary amines being the most frequently used method (Scheme 10).^[115,139] The oxidizing agent can either be an organic peroxy acid, e.g. *meta*-chloroperoxybenzoic acid (*m*CPBA),^[123,140–142] or a combination of hydrogen peroxide and a metal catalyst based on tungstate, molybdate, or vanadate.^[115,117,143,144]



Scheme 10: Preparation of nitroxides *via* oxidation of secondary amines (left) or hydroxylamines (right).^[115]

Another possibility is the oxidation of hydroxylamines to the corresponding nitroxide (Scheme 10),^[115] using milder oxidizing agents like lead oxide^[145,146] or silver oxide.^[147] Further, rarely used methods involve the reaction of nitrones and metal-organic reagents with subsequent oxidation.^[115,148] In this thesis, the first and second method illustrated in Scheme 10 were used.

1.3 Amorphous Organic Frameworks

The formation of amorphous, porous networks, in contrast to the COF formation, does not require reversible reactions, which allows for a wide range of possible connections between the building blocks. The resulting frameworks can be assigned to a variety of classes, based on their topology or the structure of the building blocks used for their construction. However, a sharp definition for each class does not exist, so that one material can be assigned to multiple classes. These are for example: HCPs (Hyper Crosslinked Polymers), POPs (Porous Organic Polymers), PAFs (Porous Aromatic Frameworks), PIMs (Polymers of Intrinsic Microporosity), CMPs (Conjugated Microporous Polymers), and PPNs (Porous Polymer Networks).^[149]

The class of CMPs, which are fully conjugated porous materials with a high surface area and high stability, was developed by COOPER *et al* in 2007. SONOGASHIRA-HAGIHARA cross-couplings between trigonal planar and linear building blocks gave rise to the **CMPs 1-4**, which possess chemical and thermal robustness. Despite the lack of long-range order (crystallinity), the pore size and surface area could be influenced by the length of the linkers, which was previously thought to be a feature of crystalline materials.^[150] Although the initial surface areas were comparably low (834 m²/g for **CMP-1**)^[150], COOPER *et al.* could achieve surface areas of up to 3200 m²/g for “**network 1**” when connecting tetrahedral building blocks like tetraphenylmethane *via* YAMAMOTO coupling.^[151] The groups of ZHOU and ZHU/QIU reported the same

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material under different names and achieved surface areas even higher (5600 m²/g for **PAF-1** and 4023 m²/g for **PPN-6**).^[152,153] Due to its high surface area and excellent stability, **PAF-1** went into the focus of many research groups and various derivatives were reported.^[154] As the tetrahedral building blocks seemed to be a prerequisite for high-performing frameworks, all three groups started to investigate further derivatives.

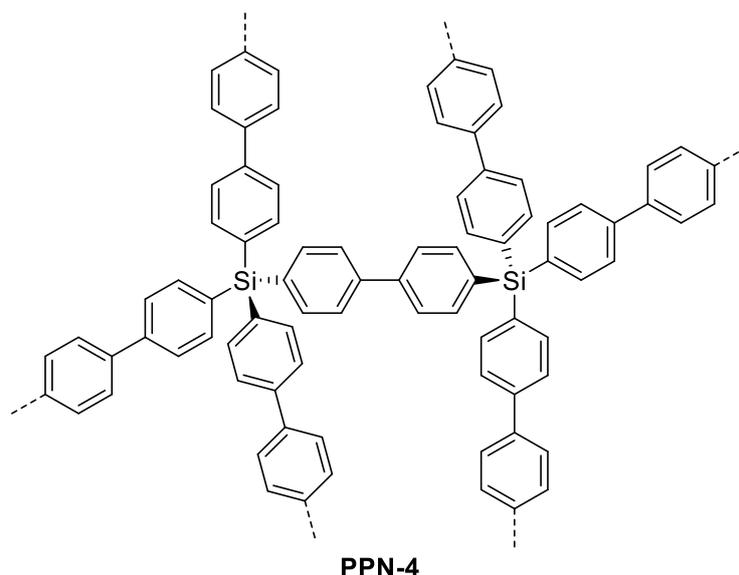
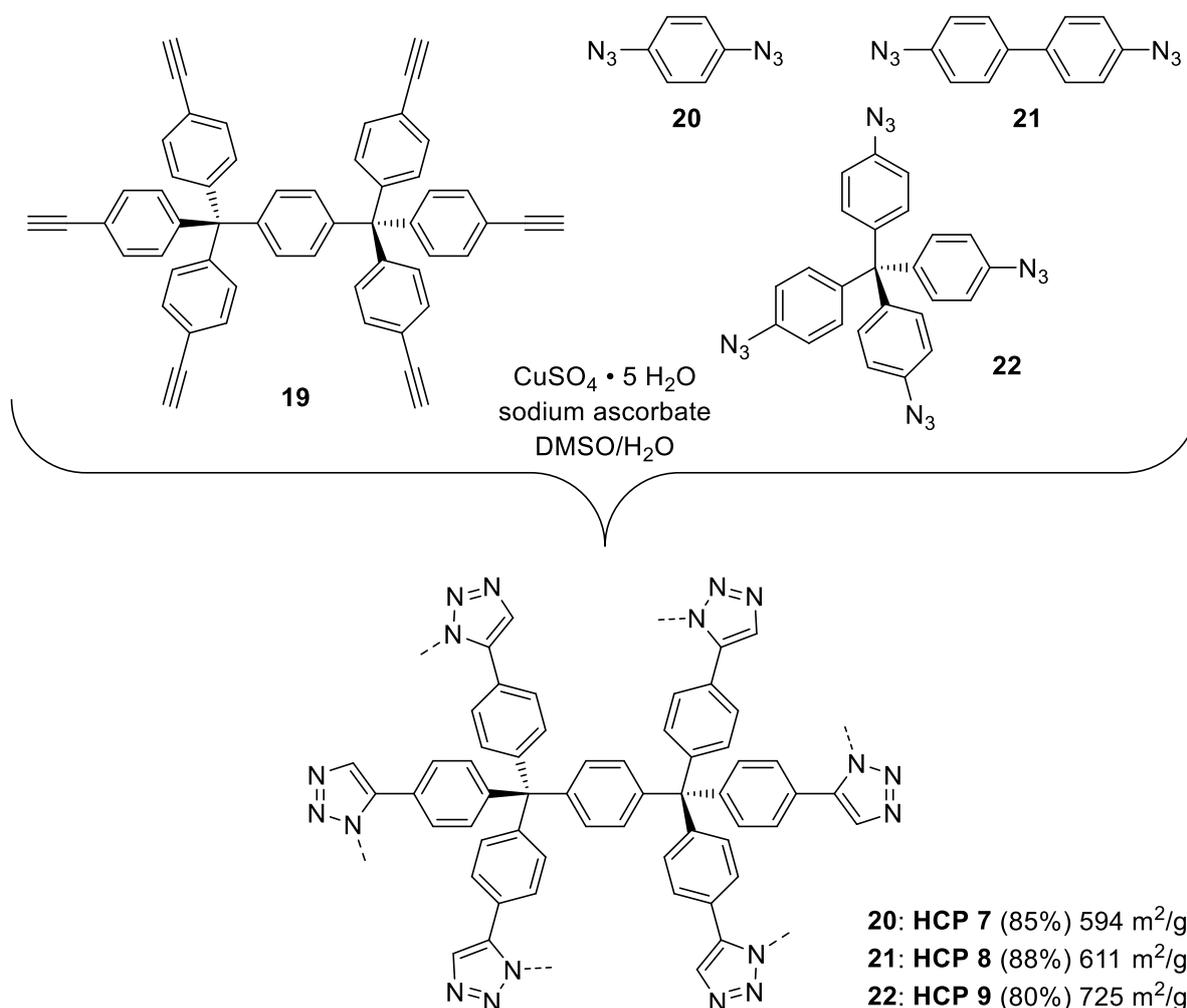


Figure 8: Structure of **PPN-4** based on tetraphenylsilane building blocks.

This led to the discovery of **PPN-4** (Figure 8) with a surface area of more than 6400 m²/g, which is the highest known for any porous organic material, surpasses COFs, and can compete with high-performing MOFs.^[155] Moreover, **PPN-4** and **PAF-1** are high-performance materials regarding the storage of hydrogen, as they reach uptakes of 9.10wt% and 7.0wt% at 77 K, respectively.^[149,152,155] Due to their fully conjugated π -system, CMPs were investigated for sensing,^[156] as antennas for light-harvesting,^[157] and energy applications.^[158]

Besides YAMAMOTO and SONOGASHIRA-HAGIHARA (cross-)couplings, amorphous porous materials are also accessible through many other reactions, like sulfur-based reactions,^[159] SUZUKI-MIYAJI cross-couplings,^[160] FRIEDEL-CRAFTS alkylations,^[161] or “click” reactions, such as the copper-catalyzed azide-alkyne cycloaddition (CuAAC). This was demonstrated in 2010 by the groups of COOPER and NGUYEN who converted tetrakis(4-azidophenyl)methane (**22**) and tetrakis(4-ethynylphenyl)methane (**63**) *via* CuAAC into porous organic polymers, achieving surface areas of up to 1440 m²/g. The resulting frameworks were stable under basic and acidic conditions and thermally robust.^[151,162]

The research group of Prof. BRÄSE has extensive knowledge about rigid, aromatic building blocks and their functionalization for many years. We are especially experienced in the field of azides,^[163,164] so that our group has been working with such materials since 2007. Dr. CHRISTINE SCHILLING reported the synthesis of azide building blocks based on tetrahedral geometries as high-energy materials and investigated their potential for the CuAAC.^[165] In 2011, Dr. OLIVER PLIETZSCH incorporated such tetraphenylmethane and -adamantane-based building blocks into HCPs. Although the surface area was not exceptionally high, the adamantane-derived HCP showed an efficient CO₂ uptake at low pressures.^[166]



Scheme 11: First examples of HCPs based on hexakis(phenyl)-*para*-xylene.^[167]

Dr. ALEXANDRA SCHADE “clicked” the alkyne-derivative **19** of hexakis(phenyl)-*para*-xylene with different azides (**20-22**) to generate three new HCPs (**HCP 7-9**) (Scheme 11), demonstrating that the geometry of the linkers influences the framework properties.^[167] In the same year, BRÄSE and WÖLL could enhance the processability of these insoluble HCPs with a layer-by-

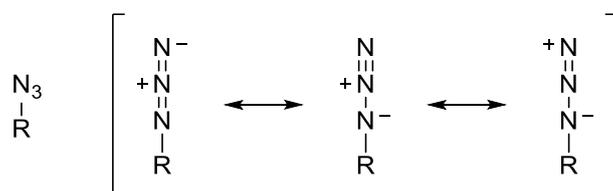
Introduction

layer approach to produce freestanding nanomembranes.^[168] Dr. LAURE MONNEREAU could further proof, that the incorporation of germanium nodes offers an easy way to tune the porosity and adsorption properties of such HCPs.^[169]

This brief historical outline demonstrates the knowledge that exists in the working group of Prof. BRÄSE about rigid, aromatic building blocks. However, with many reactions established and studied in the field of HCPs and CMPs, our focus turned to the development of new methods. Recently, it was discovered that multifunctional azides can be transformed into porous organic materials without any additional reagents *via* simple thermolysis.^[170] This method shall be further investigated in this thesis, therefore the next section describes the synthesis of aryl azides and the chemistry of nitrenes thereof.

1.4 Azides and Nitrenes

Azides are a highly versatile class of 1,3-dipoles, which can undergo several reactions that have been extensively studied in the past. Their reactivity with electrophiles and nucleophiles can be explained by their structure, which is illustrated in Scheme 12.^[163,164,171–173]



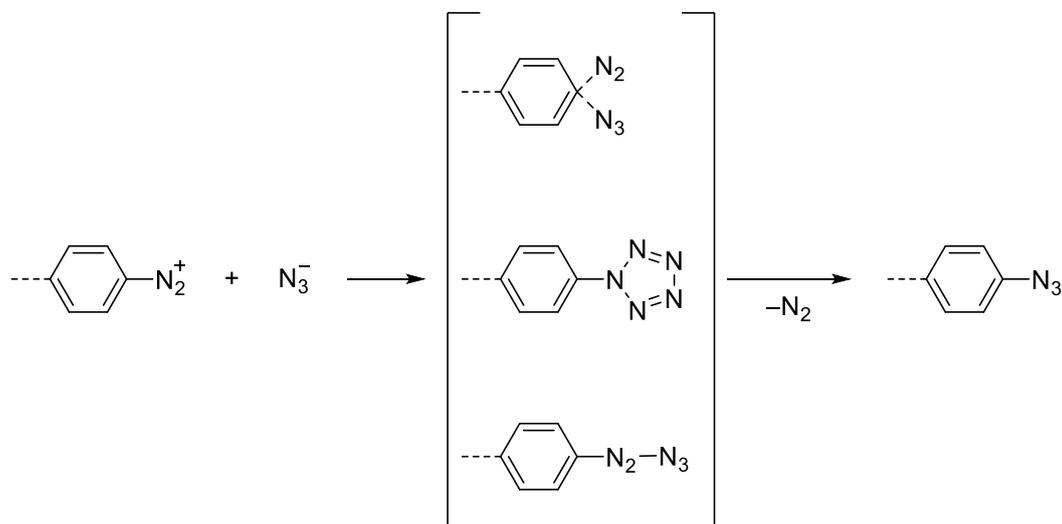
Scheme 12: Structure of organic azides. Reaction with nucleophiles occurs at the N³, while the N¹ attacks electrophiles.^[163]

However, organic and inorganic azides are also considered to be potentially explosive compounds, which lead to a kind of “azidophobia” strongly limiting their use (see chapter 5.2.5 for safety information).^[164]

1.4.1 Synthesis of Azides

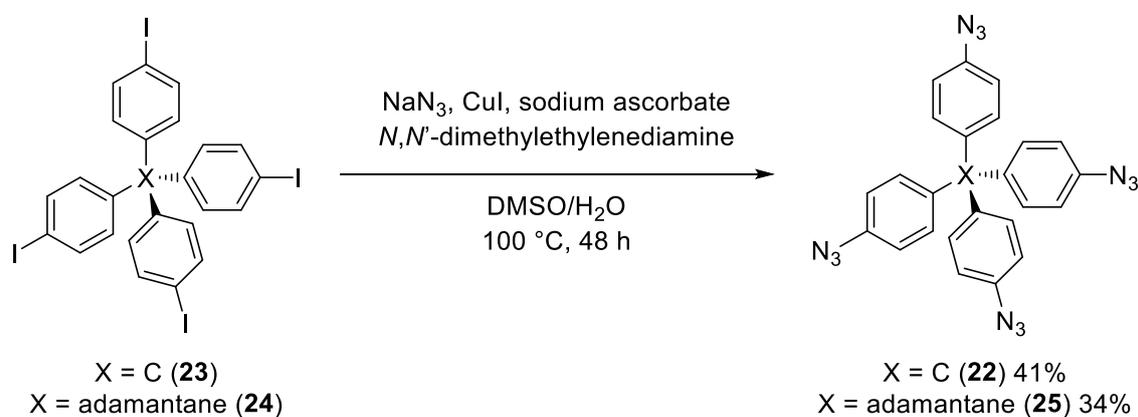
Aromatic azides, with phenyl azide being the simplest representative, can be prepared *via* three main synthetic routes. Starting from aromatic amines, the formation of the diazonium salt and subsequent reaction with sodium azide or trimethylsilyl azide is the first method to give the desired aromatic azides.^[163,164,174–177] Regarding the mechanism of this reaction, three plausible possibilities were identified and controversially discussed. The first mechanism would imply a substitution of the diazonium functionality (Scheme 13, upper intermediate), while the second and third involve the formation of cyclic pentazoles and acyclic pentazenes, respectively

(Scheme 13, middle and lower intermediate). Theoretical studies and experiments with radio-labeled compounds indicate that the former mechanism does not occur and identified the second and, predominantly, the third one as the preferred mechanisms.^[163,164,178,179]



Scheme 13: Mechanisms of the azide formation starting from diazonium salts.^[178,179]

Nucleophilic aromatic substitutions are the second method for the generation of aromatic azides. Pentafluorobenzenes, substituted with electron-withdrawing groups, or other electron-deficient (hetero)-aromatic systems readily react with azide transfer reagents to give the respective azides in good to excellent yields.^[163,164,180–185] Electron-rich systems can be substituted, when they have been thallated (introduction of thallium) before, to create a good leaving group.^[163,164,186] ZHU and MA presented a mild procedure for the conversion of aryl iodides, irrespective of their electronic structure, using a copper(I) iodide/proline system in the presence of sodium azide.^[187,188] A closely related procedure was adapted in our group for the synthesis of the polyazides **22** and **25** on the tetraphenylmethane and -adamantane scaffold starting from the respective iodides **23** and **24** (Scheme 14).^[165]

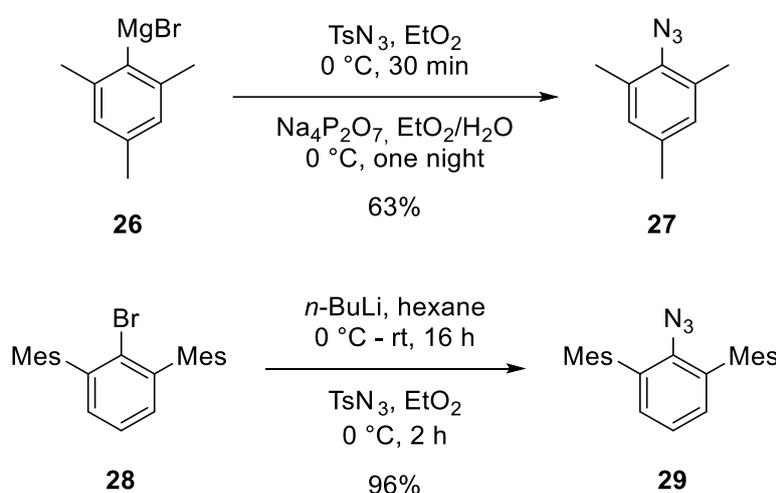


Scheme 14: Synthesis of polyazides **22** and **25** based on tetraphenylmethane and -adamantane.^[165]

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Another mild procedure for electron-rich and deficient systems is the copper-mediated conversion of boronic acids, which tolerates a broad range of functional groups and can achieve excellent yields.^[189,190]

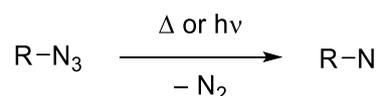
The third method for the formation of aromatic azides includes all routes carried out with the aid of organometallic reagents.^[163,164,191–194] For instance, mesityl azide (**27**) and 2,6-dimesitylphenyl azide (**29**) can be obtained by reacting the corresponding GRIGNARD or organolithium reagents with tosyl azide.^[195,196] However, this procedure is not limited to hydrocarbons but can also be used for heteroaromatic systems.^[197–199] This third method was also used in this thesis and will be discussed in chapter 3.3.1.



Scheme 15: Synthesis of azides **27** and **29** using GRIGNARD and organolithium reagents.^[195,196]

1.4.2 Nitrene Chemistry

Nitrenes are highly reactive monovalent, neutral nitrogen functionalities, structurally related to carbenes. Nitrenes can be generated by photolysis and thermolysis of azides (Scheme 16), which leads, depending on the structure of the azide and the applied conditions, to nitrenes in the singlet or triplet state.^[163,164,200–207]

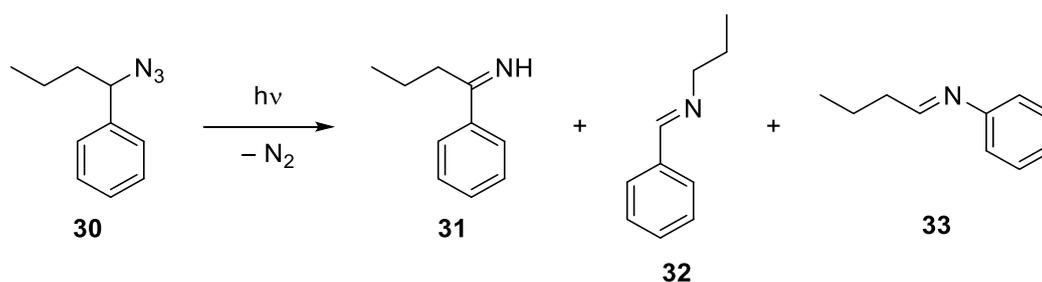


Scheme 16: Thermal or photochemical generation of nitrenes.

According to HUND'S rule, the triplet state is the ground state. In the case of phenylnitrene, the difference between triplet and singlet state amounts to 75 kJ/mol, which is much larger than the difference of the corresponding carbene (12-16 kJ/mol).^[200,202] Due to the high reactivity of nitrenes, they undergo a broad range of reactions, which cannot be covered in the present thesis.

Therefore, only a selection of reactions of alkyl nitrenes and aryl nitrenes crucial for the present thesis will be discussed, while a comprehensive discussion can be found in the literature.^[163,164,200,208,209]

Regarding the thermal decomposition of azides, the decomposition temperature decreases from alkyl and aryl azides to sulfonyl azides and acyl azides, mirroring the relative stabilities of such compounds.^[200] Alkyl nitrenes can, depending on their structure and the conditions, stabilize through the formation of amines and pyrrolidines,^[210] as well as imidazoles, and in a special case, even indigo is formed.^[211–213] Nevertheless, the stabilization through migration of hydrogen, alkyl, and aryl substituents to form imines is most prominent and proceeds cleanly for most alkyl nitrenes.^[163,164,200,214,215] MORIARTY and REARDON investigated the decomposition of several azides for the migration ratios of different substituents (Scheme 17). They found that hydrogen atoms migrate up to five times faster than alkyl chains. When aryl substituents are present, their migration rate is similar to alkyl chains.^[216]

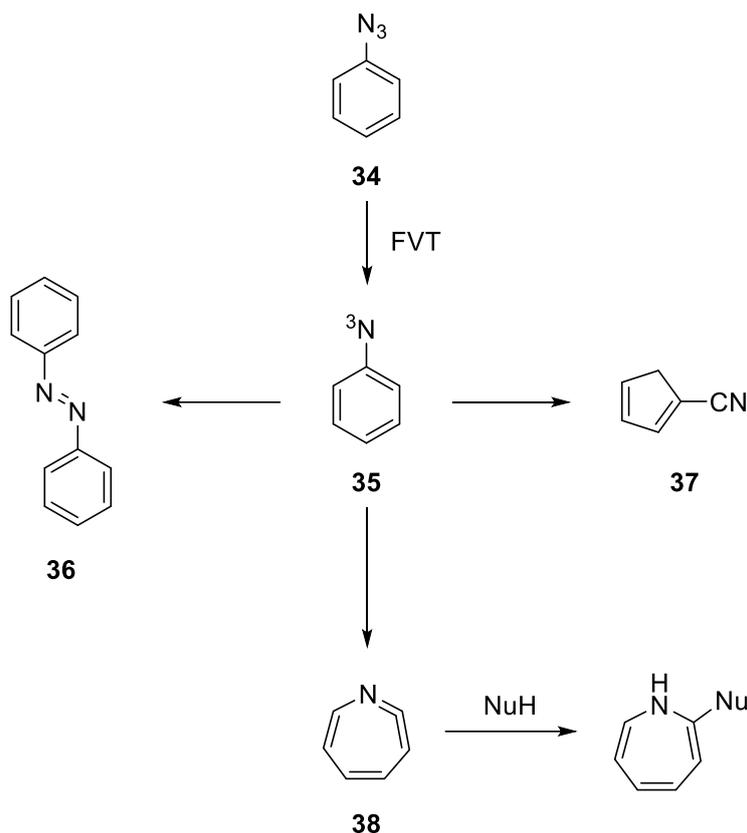


Scheme 17: Photolysis of (1-azidobutyl)benzene (**30**) resulting in the formation of imines by the migration of hydrogen (**31**), the alkyl chain (**32**), and the aryl substituent (**33**).^[216]

This migration mechanism even allowed the synthesis of highly strained imines, as demonstrated for the decomposition of 1-azidonorbornane.^[217] Triplet-sensitized photolysis of 1-azidoadamantane led to the respective alkyl nitrene that stabilized through hydrogen abstraction, dimerization to form azo-compounds or reaction with the respective solvent.^[218] Furthermore, vinylic azides form the corresponding azirines upon thermal or photochemical decomposition.^[219–222]

Aryl nitrenes, like phenyl nitrene (**35**), can undergo a variety of rearrangements that are, to some extent, illustrated in Scheme 18 for the flash vacuum thermolysis of phenyl azide (**34**). SANDER *et al.* found that the product ratios heavily depend on the applied conditions (temperature, oven diameter, length of the heating zone). However, the three main products are nitrile **37**, azobenzene **36**, or ketenimine **38**, which can further react with nucleophiles.^[163,164,202]

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Scheme 18: Flash vacuum thermolysis (FVT) of phenyl azide (**34**) mainly results in nitrile **37**, ketenimine **38**, or azobenzene **36**.^[202]

Further investigations regarding the thermal decomposition of aryl azides confirm the formation of ketenimines, nitriles, and azo compounds, among others.^[200,223–227]

Another highly important reaction of thermally generated aryl nitrenes is the insertion into sp^2 and sp^3 hybridized C–H bonds to form secondary amines. Through intramolecular insertion, various indoles,^[228–231] indolines,^[200,201] and carbazoles^[200,232–234] are accessible.

This thesis aims to thermolyze rigid, aromatic azides into porous framework materials. This method was discovered during the own master's thesis and will be investigated in greater detail in chapter 3.3. The reactions of the aryl nitrenes presented above, namely the formation of nitriles, azo compounds, ketenimines, or C–H insertion, are suitable for the connection of aromatic building blocks. While the formation of azo compounds links the building blocks directly, nitriles can trimerize to give triazine and ketenimines can react with water to form ether-bridged azepines as linkages (see chapter 3.3.2).

2 Objective

Porous, organic frameworks represent an interesting class of materials due to their special properties, such as high specific surface area^[151,152,155,235,236] at simultaneously low density^[66,77] and high stability.^[6,8,19,66,78,159] Although these materials are mainly used in gas storage and separation^[9,15–19] because of their high surface area, they are also suitable as catalysts^[19,96–99,237–240] and for photoelectric applications.^[88,100–105] Due to their crystallinity, COFs (Covalent Organic Frameworks), a subclass of such materials, are of particular interest and can be prepared with several reaction types.^[6,8,241] The nitroxide exchange reaction, between highly functionalized alkoxyamines and nitroxides, represents a new approach, which is particularly noteworthy due to its reversibility^[119] and the possibility of *in-situ* reaction monitoring *via* EPR spectroscopy.^[123] Since the geometry, rigidity, and size/length of the building blocks have a critical influence on the framework formation, rigid aromatic systems are the most common core structures.^[6,8] In the context of the present thesis, such rigid aromatic alkoxyamines and nitroxides should be synthesized for the exchange reaction (Figure 9).

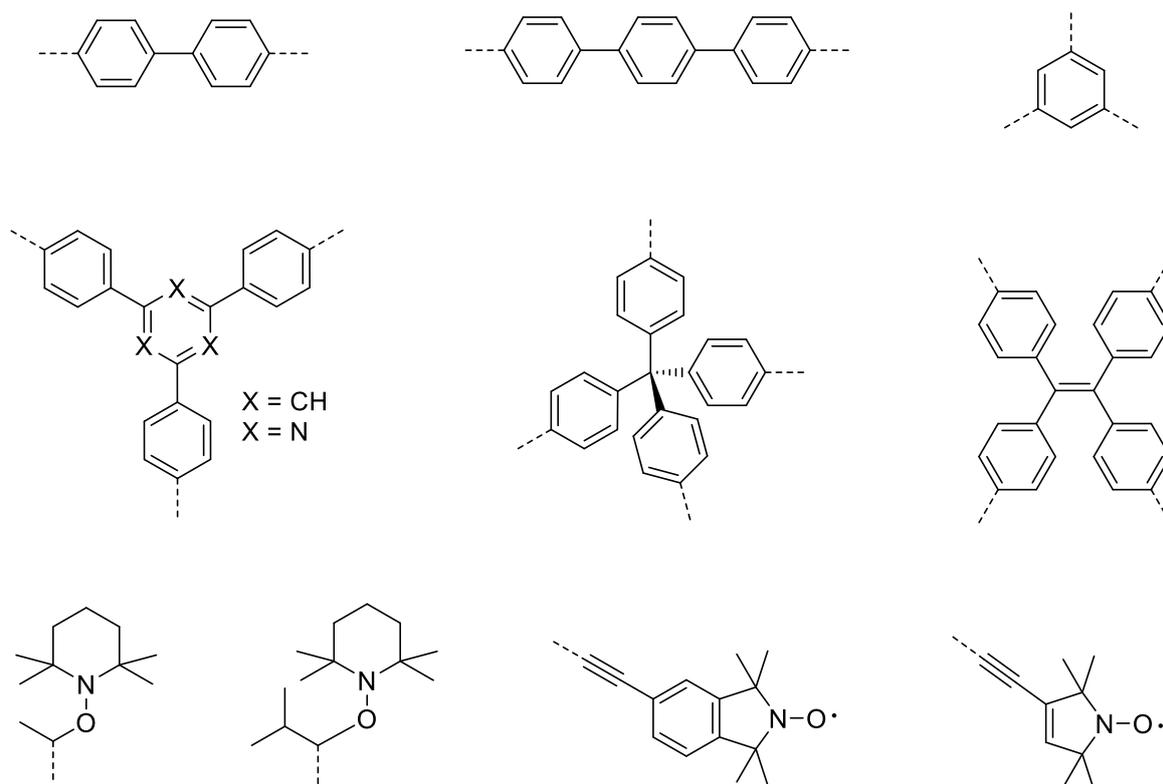


Figure 9: Selection of suitable alkoxyamines and nitroxides for the NER.

The alkoxyamines should be prepared from the unsubstituted aromatic core structures in a linear, multistep synthesis. As counterparts, iodine-functionalized nitroxides should also be synthesized, and then attached to an aromatic core *via* cross-coupling reactions or click chemistry.

Objective

Finally, in order to gain a better understanding of the NER, the influence of sterically demanding side chains and nitroxide units on the stability of the alkoxyamine should be investigated on a library of monoalkoxyamines.

In addition to crystalline COFs, amorphous, porous materials such as POPs, HCPs, or PAFs are also of great interest, since reversible reactions are not required for their synthesis. Therefore, cross-couplings, thiol-ene/-yne reactions, or copper-catalyzed azide-alkyne cycloadditions have been used in the BRÄSE group in the past.^[166,169,236,242–246] A completely new approach is the linkage of rigid, aromatic azides with themselves, *via* thermolysis. In a second project, therefore, various multifunctional azides should be synthesized as building blocks, and subsequently thermolyzed into amorphous, porous frameworks (Figure 10).

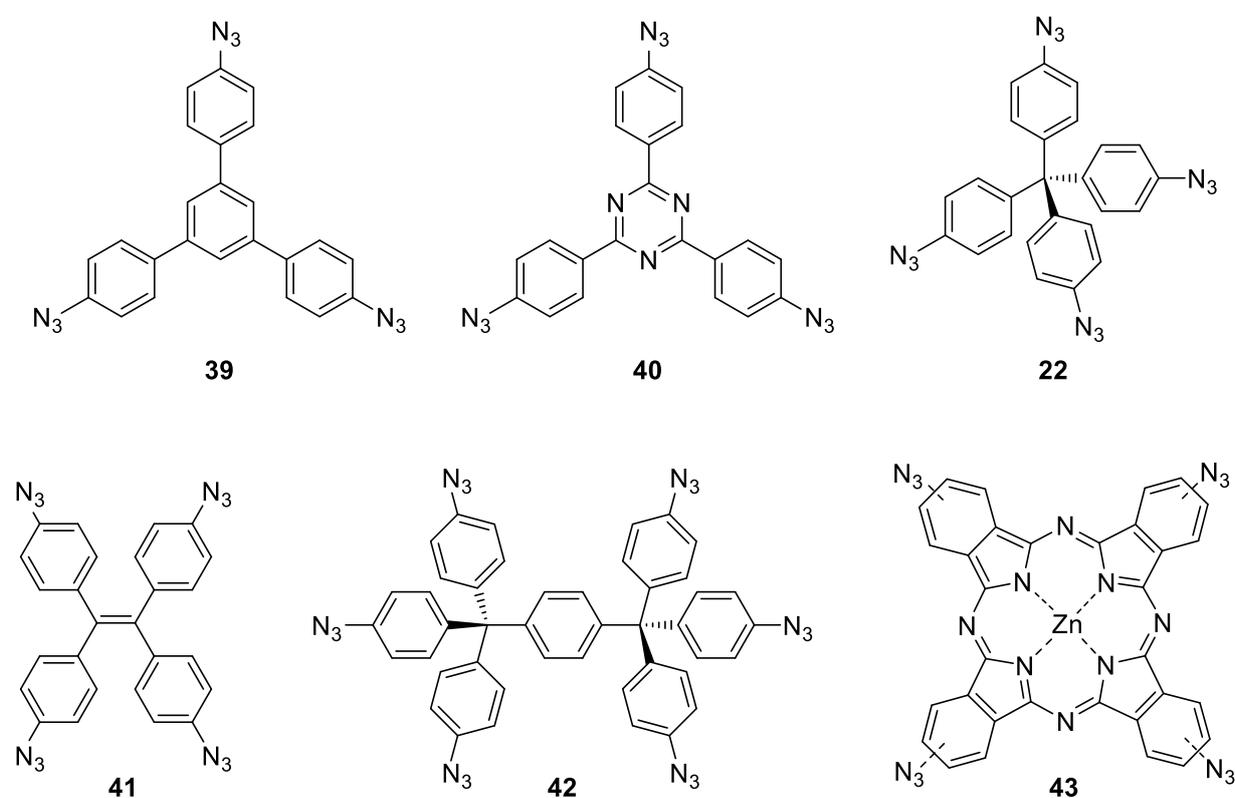


Figure 10: Multifunctional azides for the generation of amorphous frameworks.

During a research stay in the group of Prof. Dr. NEIL B. MCKEOWN, additional azido-substituted porphyrins and phthalocyanines should be synthesized. These compounds allow the incorporation of different metals so that exchangeable metal centers for catalytic applications can be integrated into the frameworks. The frameworks obtained by thermolysis should then be examined in detail, concerning their composition and linkage, by IR spectroscopy and elemental analysis. Furthermore, the influence of the thermolysis temperature on the properties of the frameworks, e.g. specific surface area and pore size, should also be investigated.