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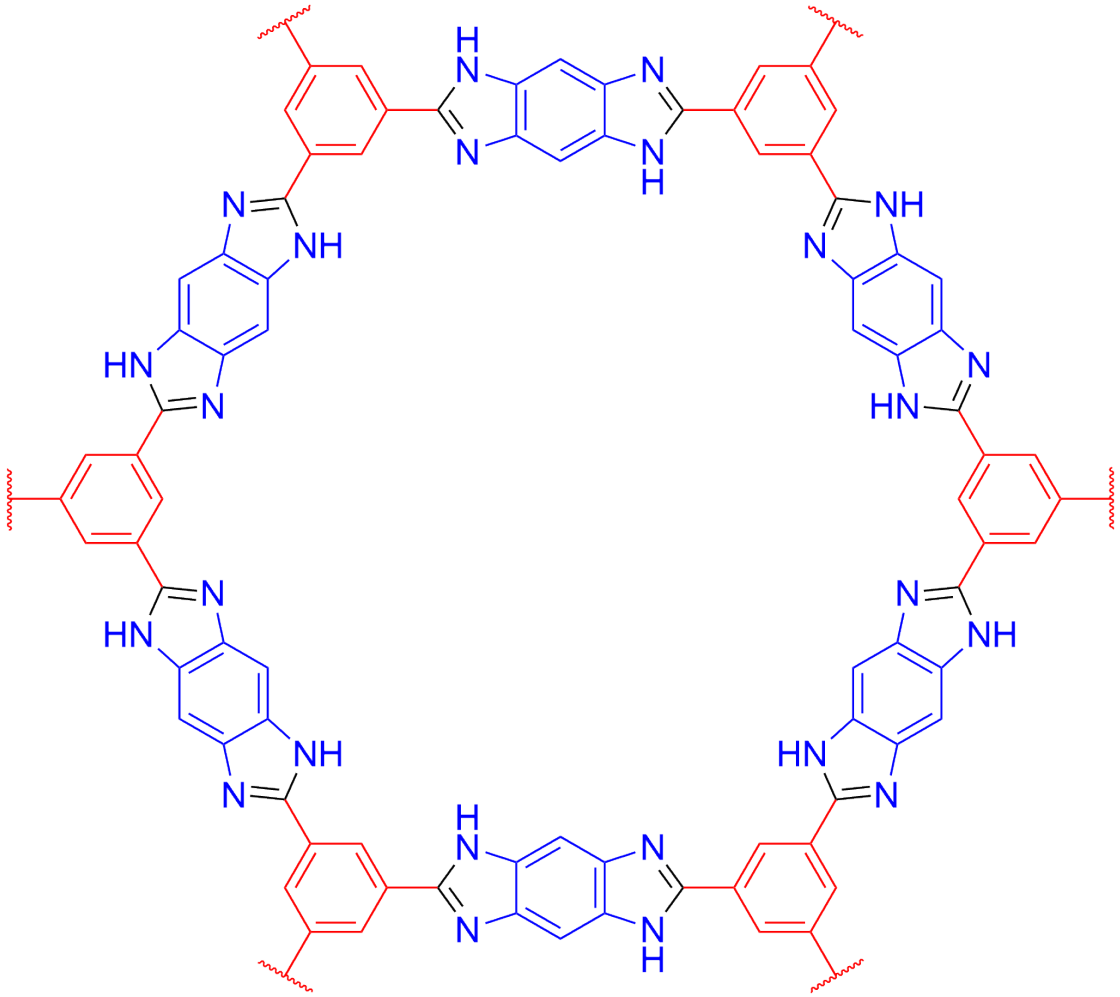

2D imidazole- and thiazole-based COFs

Syntheses parameters using linker exchange

Master's thesis in Material Chemistry

MARKUS LINDER

DEPARTMENT OF APPLIED CHEMISTRY

CHALMERS UNIVERSITY OF TECHNOLOGY
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Cover: Visualization of imidazole COF ring.

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Abstract

Constructing new materials for proton conduction above 100 °C is vital for the development of robust proton-exchange membrane fuel cells. Utilizing the remarkable proton conducting properties of polybenzimidazole and the tunable properties of covalent organic frameworks (COF), it is possible to create chemically stable structures that can be used as scaffolds for dopants. This thesis aimed to shed light on both how to increase the crystallinity of imidazole and thiazole COFs, and how to construct a reversible, highly crystalline imine-based COF that can be used as a pre-network (PN) for the irreversible COF synthesis. The PN underwent linker exchange in order to create imidazole COFs with crystallinity equal to that of the PN. Different configurations of temperature, modulator, oxidant, excess reagent, and time were tested to examine their impact on the PN and imidazole COFs. The results indicate the successful creation of crystalline imidazole COFs when synthesized with modulators, pressured air and excess reagent during linker exchange. Modulators were shown to have low impact on the crystallinity of the PN and a high impact on the crystallinity of the imidazole COF, making their use vital during imidazole COF synthesis.

Keywords: COF, imidazole, thiazole, pre-network, linker exchange, modulator

Acknowledgements

I would most of all want to thank my supervisor Eva Dahlqvist for being an excellent supervisor and guiding me through this project. Eva was always available and answered any questions I had. Had it been possible to insert knowledge by whacking my head with a book, I have no doubt that she would (rightfully) have done so. I want to thank my examiner Anna Martinelli for taking time out of her busy schedule to have regular meetings to guide the project, and buying me a beer to celebrate my successful thesis presentation.

I also want to thank everyone on floor 2 and 3 and especially those in the masters room for socializing during this period, otherwise I would not have made it through mentally. And of course I have to thank my family and friends who helped me through these five years.

Lastly, I want to dedicate my thesis to my late grandpa Ingemar Larsson who supported me and eagerly wanted to know how every single exam went until his passing during the summer of 2024. We all wish you were here.

Markus Linder, Gothenburg, June 2025

List of Acronyms

Below is the list of acronyms that have been used throughout this thesis listed in alphabetical order:

COF	Covalent Organic Framework
PN	Pre-network
PEM	Proton exchange membrane
FC	Fuel cell
PBI	Polybenzimidazole
PFAS	Polyflouroalkyl substances
BTT	Benzene-1,2,4,5-tetrayltetraamine tetrahydrochloride
BTB	1,3,5-Benzenetricarboxaldehyde
PPD	P-phenyldiamine
DBD	2,5-Diaminobenzene-1,4-dithiol
PPA	Polyphosphoric acid
CMR	Carcinogenic, Mutagenic or Reprotoxic

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Introduction

Covalent Organic Frameworks (COFs) are a type of crystalline organic polymer that forms a long-range, ordered structure and has gained a lot of popularity since its introduction in 2005 by Yaghi *et al.* [1]. This popularity can be explained by its versatility and broad range of applications which include proton conduction, adsorption, separation and catalysis [2]. The possibility to create highly structured proton-conducting COF with tunable properties makes it very interesting for use in proton exchange membrane (PEM) fuel cells (FC), seen in illustration Figure 1.1 from Ren Weiqun *et al.* [3], as an electrolyte [4]. The electrolyte used today is the fluorinated carbon chain polymer Nafion, but due to its optimal operation temperature being around 80 °C and below, which is relatively low compared to the desired temperature range of above 100 °C, and its classification as a polyflouroalkyl substance (PFAS), a new material that can both act as a substitute to Nafion and work in higher temperatures is desired [5]. Imidazole and thiazole-based materials are of particular interest due to their high proton exchange capabilities combined with their high thermal and chemical stability [4]. Polybenzimidazole (PBI) is a linear polymer that can be impregnated with, for example, phosphoric acid or water, for high proton conduction and has been tested as a potential alternative for high temperature PEM FC applications. However, the impregnation of phosphoric acid reduces the interplay of the polymeric chains, resulting in leakage of the dopant. Phosphoric acid-doped PBI also experience high swelling when in contact with water, leading to contact issues between the PEM and electrode catalyst inside the PEMFC. To potentially address these problems, it is possible to use imidazole or thiazole-based COFs.

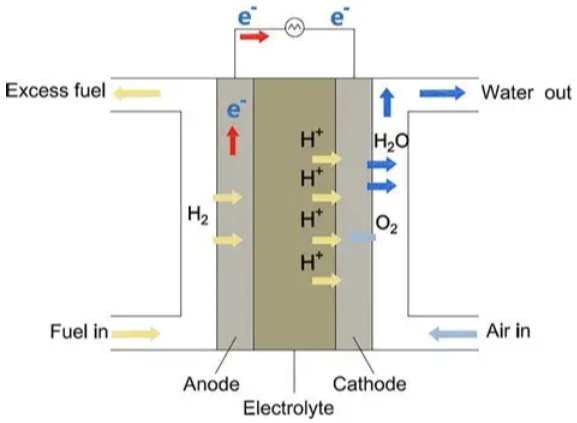

Figure 1.1: Illustration of PEMFC from Ren Weiqun *et al.*.

COFs consist of long-range crystalline polymers in an ordered two- or three-dimensional structure [6], whose properties depend on the monomers used and functionalization [7]. The created structures have the potential to be more stable than previous porous materials, but have a trilemma where crystallinity, stability and functionality are hard to achieve simultaneously [8]. Extensive research is necessary to improve the crystallinity, robustness and stability of COFs [9, 10]. A common way to achieve crystallinity is by using reversible reactions, which allows monomers to rearrange into a more crystalline structure over time [10]. However, COFs made with reversible imine bonds are prone to hydrolysis reactions, giving the structure poor physiochemical properties and often require further stabilization of the linkages [9, 10].

One way to escape the trilemma is through COFs created with irreversible reactions, which generally create more robust structures but suffer from poor crystallinity, forming amorphous or polycrystalline products [8, 9, 10]. Several pathways are being researched to increase the crystallinity of irreversible COFs, and three pathways have emerged as especially promising[8].

The first one is single reaction pathway which consists of using monomers with low degrees of freedom, limiting the functional group of the linker to only react with a functional group of the node, effectively limiting the ways in which the COF can be assembled [8]. The second pathway is linker exchange, where a network with high crystallinity is first made from reversible bonds before the linkers are exchanged for irreversible bonds. The third pathway utilizes modulators that slow the reaction and give it more time to crystallize [8, 11].

1.1 Aim

The aim of this master's thesis is to use linker exchange to synthesize imidazole and thiazole-linked COFs with high crystallinity and stability. The primary focus is to try to increase crystallinity and stability in comparison to previous research by testing different solvents, temperatures, modulators and reaction times. The main problem that will be addressed is how to create stable irreversible structures with thiazole and imidazole with high crystallinity. Most reports today have not achieved a satisfactory percentage of crystalline structure in irreversibly bonded COFs. Without a proper crystalline structure, there will be problems with desired properties such as stability, adsorption, proton exchange and directionality of proton transfer. This thesis will focus on synthesis, crystallization, and optimization of imidazole- and thiazole-based COFs in a two-dimensional structure.

1.2 Limitations

The report will not test the COFs properties related to pore size and transport properties. Different node molecules, up-scaled production, environmental, and ethical impact will not be tested or evaluated.

2
Theory

Increasing crystallinity is vital for the future applications of COFs, and different strategies such as reversible reactions, linker exchange, modulators, and single reaction pathways have been explored in recent years [8]. Each pathway comes with different advantages and disadvantages and can be used in combination to compensate for each others weaknesses.

2.1 Proton exchange membrane fuel cell

Proton exchange membranes or polymer electrolyte membranes (PEM) FC have in recent years become a contender against conventional power-generating alternatives, for example in transportation, and are seen as an imperative part in the energy transition towards cleaner energy [5, 12]. The electrolyte in the fuel cell needs to have good proton exchange properties and separate anode and cathode gases [5]. Today, a big part of fuel cell electrolytes are made with Nafion, which has been studied extensively. Nafion is a PFAS material, and is therefore banned in Europe in any application that is not deemed essential for society due to their toxicity [12]. However, the use of Nafion in PEM fuel cells is allowed because of the importance of cleaner energy sources. Nafion is chemically inert in both oxidizing and reducing environments and is highly acidic, making it excellent for proton conduction when used with water [5]. It is also very stable and efficient around 80 °C and below, making it possible to run many cycles before needing to change the material. However, due to its limited thermal range of operation to around 80 °C, high osmotic drag at higher temperatures, high cost, and being hard to recycle, a substitute material is highly sought after. Currently, it is possible to increase the temperature range of the electrolyte by increasing the pressure of the system to approximately 3 atm and hydrating the electrolyte by humidifying the gas feed. This approach leads to a working temperature of around 135 °C. Increasing the working temperature of the fuel cells improves a number of parameters, such as increased proton conductivity and increased tolerance to carbon monoxide. Higher operating temperatures require the development of a water-free approach and new electrolytes.

2.2 Reversible reaction

It is important to clarify that no bond or reaction is truly irreversible, however, the equilibrium can be heavily shifted toward the product in a ratio that makes it acceptable to call the reaction irreversible [13]. The most common way to synthesize

COFs is through reversible bonds, which can rearrange in a self-healing process until a thermodynamic minimum is reached, resulting in a crystal structure [8]. In the case of imine based COFs, there is generally a quick formation of amorphous polymers before a slower rearrangement into a highly crystalline structure occurs. This reformation happens due to imine linkages created through a reversible Schiff base condensation reaction between aldehydes and amines [4]. Reversible linkages in COFs are the oldest technique and were used by Yaghi *et al.*. in their original work in 2005 when synthesizing crystalline boroxine rings [8, 14]. The main disadvantage of reversible reactions is low chemical stability amid changes in temperature, pH and chemical composition [10].

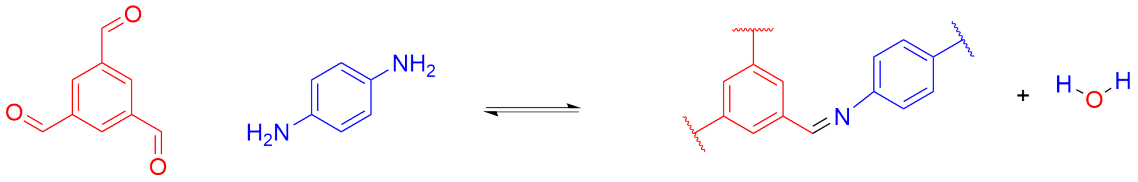

Figure 2.1: Reversible reaction pathway of imine condensation.

2.3 Linker exchange

A novel way to make COFs that are both sturdy and crystalline is to start the reaction with a monomer that uses a reversible reaction in order to create a crystalline structure, called a pre-network (PN), before substituting the linker for one that forms an irreversible bond. The monomers with reversible reactions can then be replaced over time with monomers that undergo an irreversible reaction [6, 10]. Hence, the pre-formed crystalline structure can be irreversibly replaced, forming a stable yet crystalline framework [9]. Yaghi *et al.* used linker exchange in 2018 to produce thiazole- and oxazole-based COF from a imine linked COF which resulted in higher crystallinty than previously recorded for these types of structures [15]. The results show that achieving crystalline structures through linker exchange is possible but things like atmosphere, temperature, solvent, *etc* had a major impact on the products crystallinity. Therefore, further studies were necessary to optimize reaction parameters to improve the structure of the COF. Fang *et al.*. developed a two-step bottom-up synthesis in 2025 where the first step uses an aldehyde and acyl chloride to form an imine bond [6]. The imine bond is then replaced in the second step to form an imide bond, making the irreversible crystalline network. The way it would work in a reaction between 1,3,5-carboxaldehyde and P-phenyldiamine can be seen in Figure 2.2. The reaction Fang that used is autocatalytic and shows a lot of promise as a quick way to form robust structures with high crystallinity.

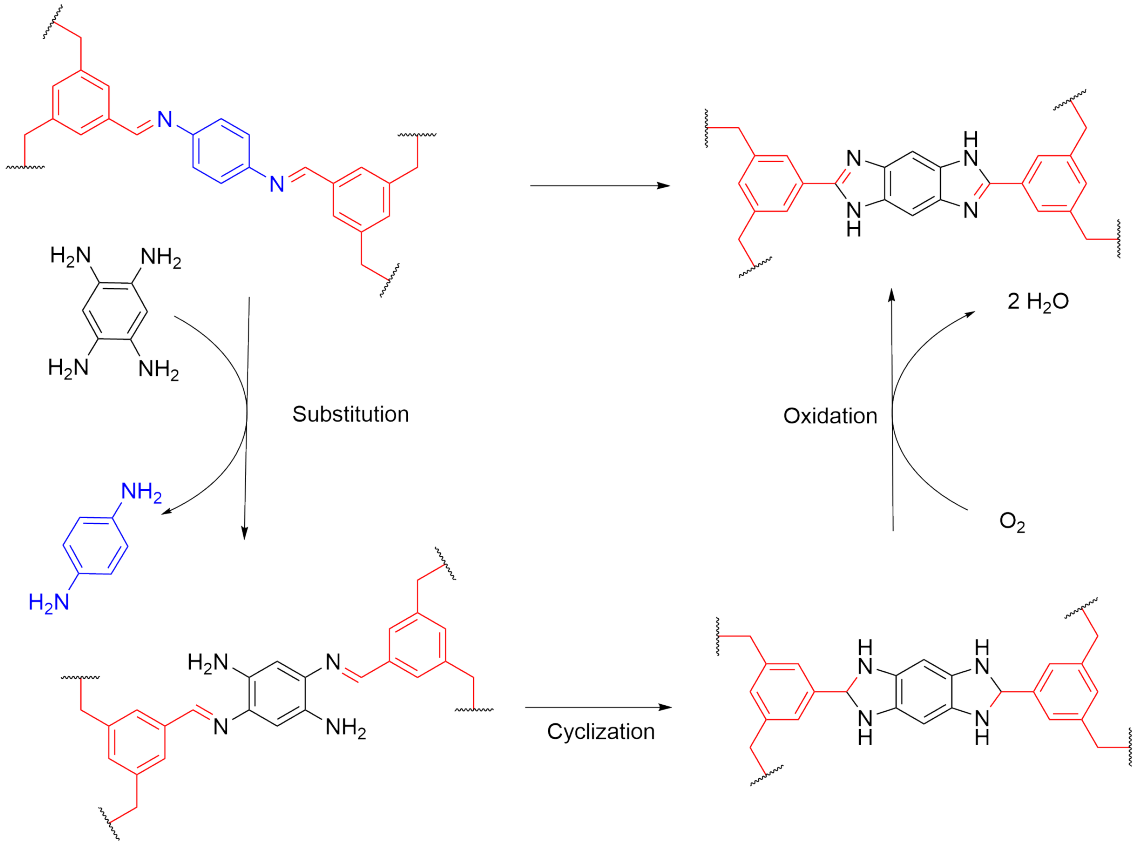

Figure 2.2: Reaction steps for linker exchange in imidazole where the oxidation step is irreversible.

2.4 Modulators

Modulators are additive molecules that can enhance crystallization by slowing down and/or changing the reaction steps through competitive and reversible bonds [8]. This equilibrium can be further altered by adding a strong acid in order to favor the hydrolysis instead of the imine formation [8]. It is important to use the correct modulator since modulators without similar reactivity as the linkers tend to decrease crystallinity or create amorphous materials. Aniline is an example of a good modulator in an imine condensation reaction and can possibly be used when constructing imidazole, as is visualized in Figure 2.3.

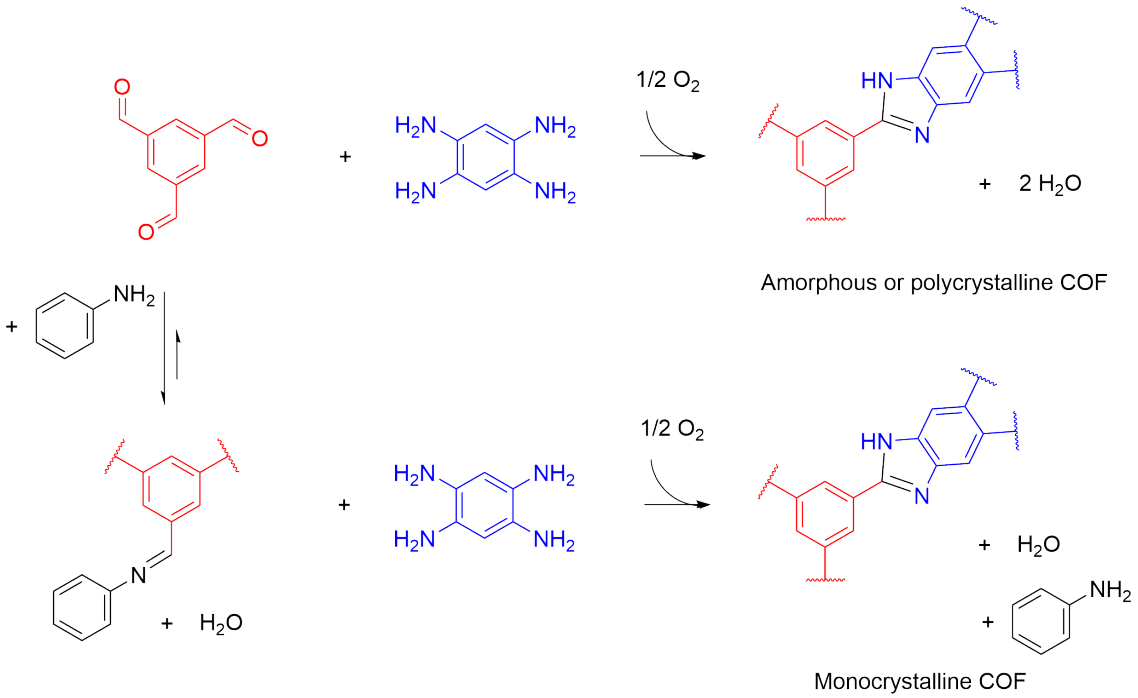

Figure 2.3: Aniline used as a competing reaction to slow down the formation of imine-based COF linkage, giving it time to crystallize.

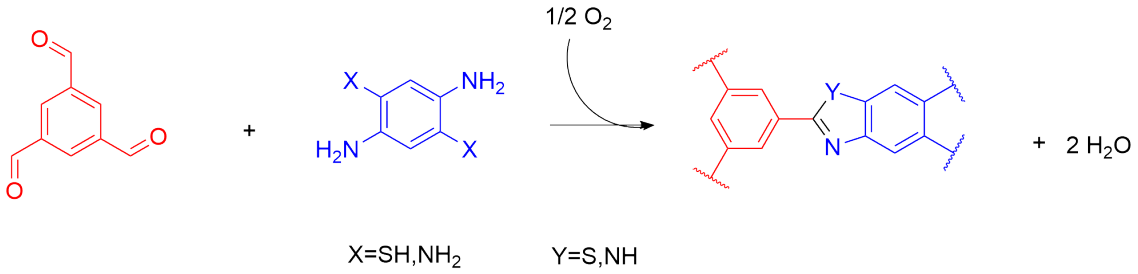

Figure 2.4: Synthesis pathway of imidazole and thiazole COF linkage.

2.5 Single reaction pathway

Single reaction pathway utilizes monomers with a low number of conformational degrees of freedom, leading to fewer synthetic options [8]. The monomers of this reaction pathway ideally have only one way to polymerize, leading to an ordered network even if irreversible bonds are used. The advantage of this method is its simplicity, which reduces the need for additional chemicals. Defects can arise when a monomer is added interstitially in a way that disrupts the ordered matrix, as can be seen in Figure 2.5. Depending on the bond flexibility, these defects may create connected lattices which disrupts the ordered structure of the COF. This is because more flexible bonds may turn away from the intended position and react into other directions. One way to prevent this is by slow addition of one monomer in order to give more time for the COF to assemble with the correct configuration.

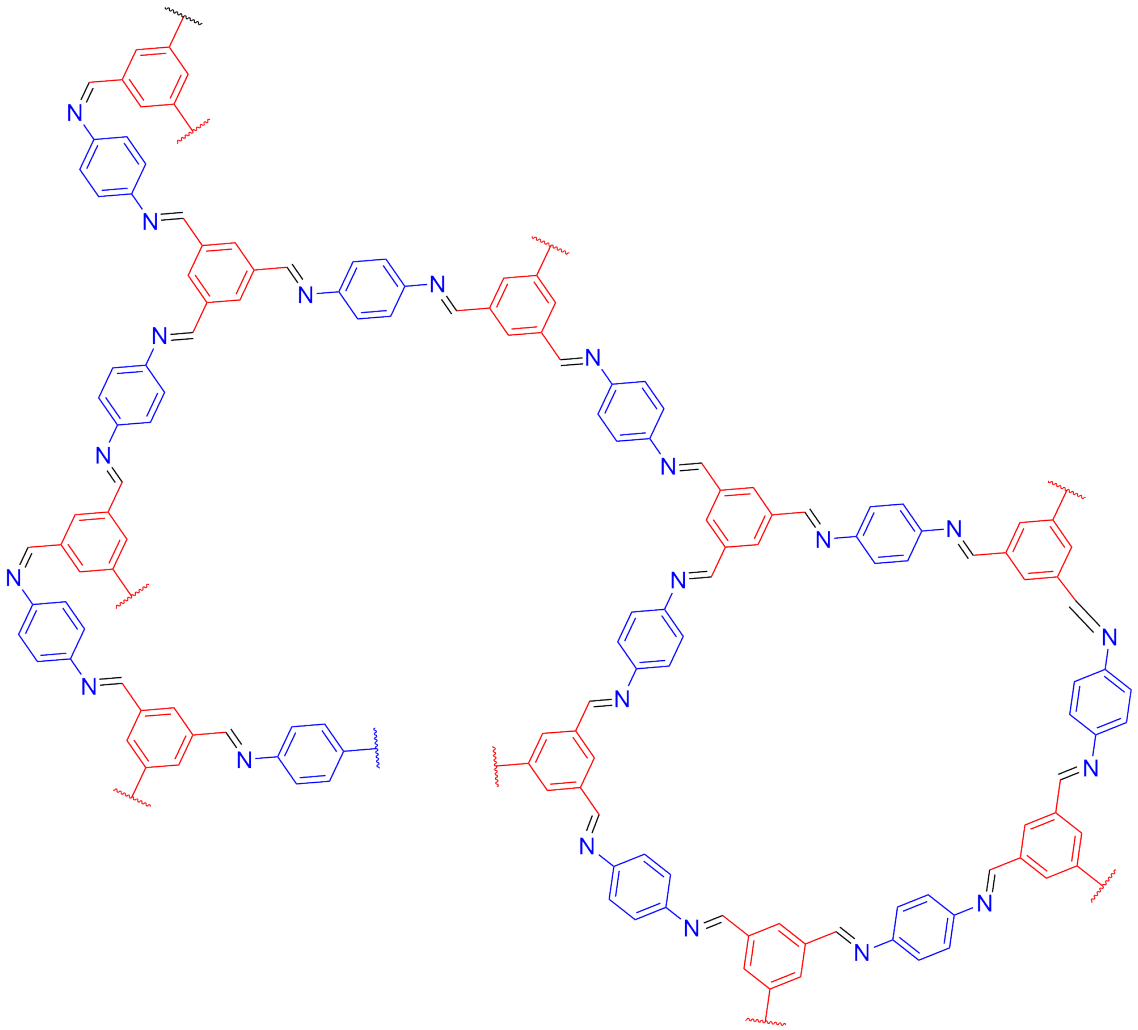

Figure 2.5: Defective COF structure, resulting in low-crystalline arrangement.

2.6 Reaction pathways

2.6.1 Imine

The imine condensation reaction will be central in the synthesis of imidazole and thiazole based COFs in this thesis. Imine bonds are often used in the synthesis of COFs because of their reversibility and tunable formation rate in different solvents [2]. Imine bonds can be produced by aldehydes and amines in a Schiff base condensation reaction and display high stability under normal circumstances [16]. The imine bond is also stable in both aqueous and organic solvents, making it versatile for a wide variety of different syntheses. Imines are, however, unstable under acidic conditions due to dissociation into carbonyls and primary amines [17]. The theoretical structure of the imine COF can be seen in Figure 2.6.

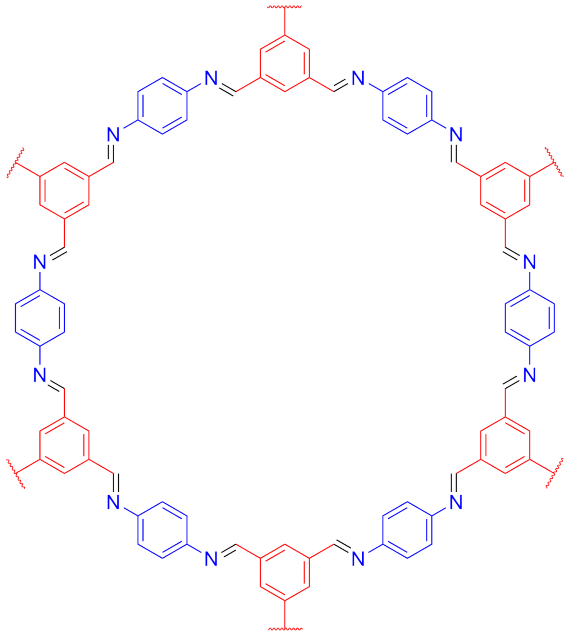

Figure 2.6: Imine COF ring structure in cis conformation.

2.6.2 Imidazole

Imidazole-based COFs have shown great potential as a proton-conducting material with a robust structure and high tolerance against acids and bases [4, 7]. The synthesis steps can be observed in Figure 2.4. In 2022 Zhang *et al.*. tried to synthesize an imidazole-based COF using benzene-1,2,4,5-tetrayltetraamine tetrahydrochloride (BTT) and benzene-1,3,5-tricarboxyling acid [4]. The PXRD showed very low crystallinity, indicating that carboxylic acids, together with amines, are insufficient in producing highly crystalline imidazole-based COFs on their own. Zhang *et al.* tried, in 2024, a four-component approach in order to synthesize and functionalize an imidazole based COF [7]. The structure showed relatively high crystallinity but still had a lot of residues left.

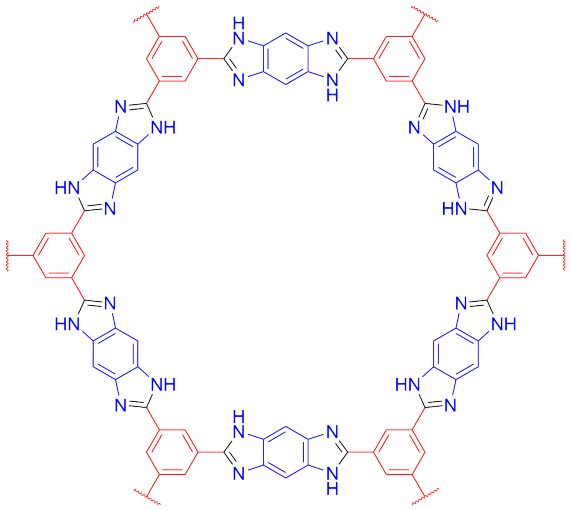

Figure 2.7: Imidazole COF ring structure.

2.6.3 Thiazole

Thiazole based COFs have a similar structure as imidazole, which can be seen in Figure 2.4 but may have even better electron-conducting properties due to sulfurs empty d-orbital, improved delocalization within the π-orbitals and decreased energy of the π-π* transitions [18]. Yaghi *et al.*'s study from 2018 regarding thiazole linkages, created through linker exchange, in COFs and their findings on its synthesis, found a multitude of constraints which reduces the products cyrstallinity [15]. Their most vital discovery was the change from imines to amines under reducing conditions, which could not be made into thiazole, leading to a product containing a mix of amine and thiazole linkages as seen in Figure 2.8. An oxygen rich atmosphere was tested, which resulted in improved thiazole crystallization. Different oxidants, such as p-chloranil, and benzoquinone, were also tested but resulted in poor or no crystallinity.

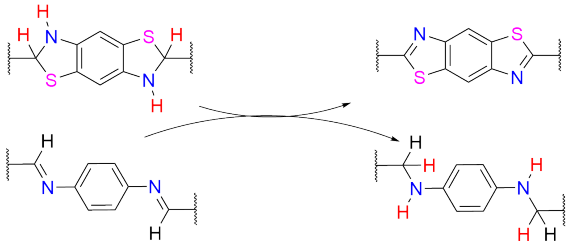

Figure 2.8: Reduction of imines between layers under reducing conditions.

3

Results

3.1 Synthesis of pre-network

Although imine-bonded COFs, used here as a PN, have been previously reported in literature [19, 20], we performed further optimization to obtain improved crystallinity and a yield of 85.9 %. From the results of **PN-solvent** and **PN-solvent-2**, seen in Figure 3.1 and Figure 3.2, it became clear that the choice of solvent is an important aspect to consider when creating the PN. Today, most research groups uses dioxane [19, 20, 21] to make imine-COFs. Dioxane is a CMR (carcinogenic, mutagenic or reprotoxic) substance and therefore should be avoided when possible. The results of **PN-solvent**, seen in Figure 3.1, indicate that dioxane and mesitylene perform worse than the alternatives when synthesizing PN. Due to their suboptimal performance and toxic properties, they were excluded from further testing. o-Dichlorobenzene, chloroform, and 2-metyltetrahydrofuran (2MTHF) from **PN-solvent** and water from **PN-water** showed promising results and were therefore tested again in **PN-solvent-2** with a longer reaction time at 80 °C to allow the PN to self-correct and create a more crystalline structure. The results of **PN-solvent-2** showed improved crystallinity for all solvents except water, indicating a clear dependence on time to create crystalline imine-linked COF. The COF created with water as the solvent did not follow the trend, leading to decreased crystallinity compared to the first PN created in **PN-water**. The most likely reason is the time it took to wash the samples. The first time water was used was in the first experiment (**PN-water**), where the reaction took place at room temperature. The washings were then performed by letting the suspended powder go through sedimentation until the solution was clear enough to be extracted. In the later test (for example, **PN-solvent-2**) a centrifuge was used to speed up the process, leading to considerable less time for the reactant to be suspended in solution. Since it was clear from **PN-water** that the reaction could occur at room temp, it is reasonable to assume that the reaction continued through the whole washing process which took a few days in the case of **PN-water**, leading to a considerably longer reaction time, with decreasing hydrogen chloride concentration after each wash, that allowed the COF-network to self-correct and become more crystalline. Another important factor that should be further tested when considering water as a solvent, is the change in temperature between the experiments. In **PN-water** the reaction took place at room temperature while in **PN-solvent-2** the sample was placed in an oilbath at 80 °C which led to lower crystallinity.

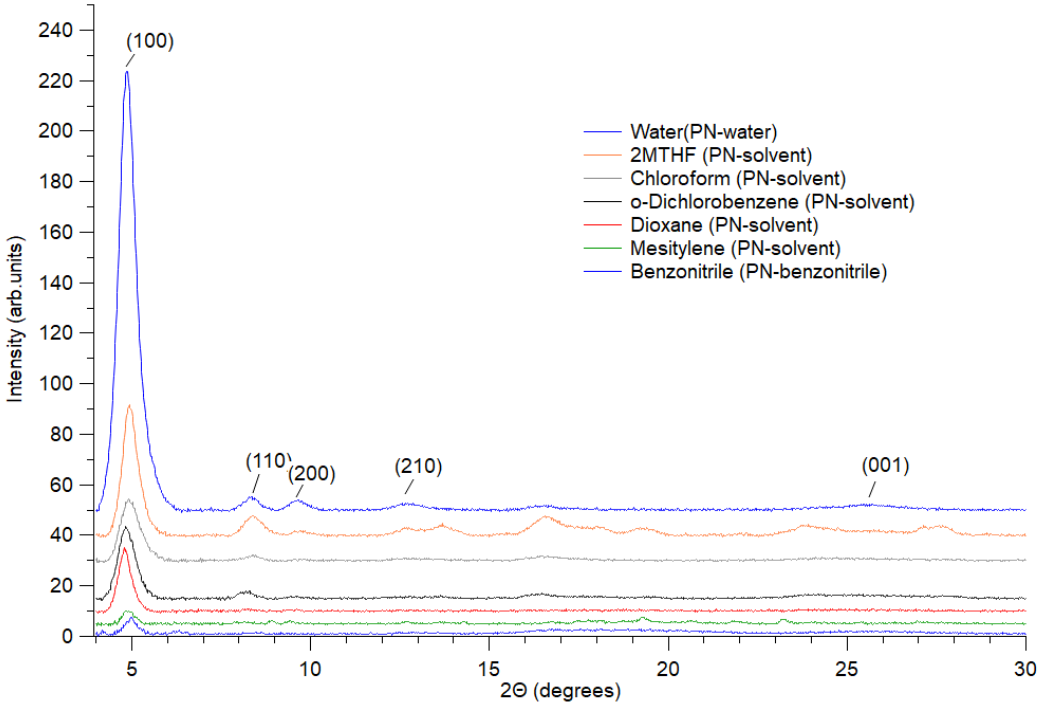

Figure 3.1: Comparison of PXRD spectra between PN synthesized using different solvents for 24 hours.

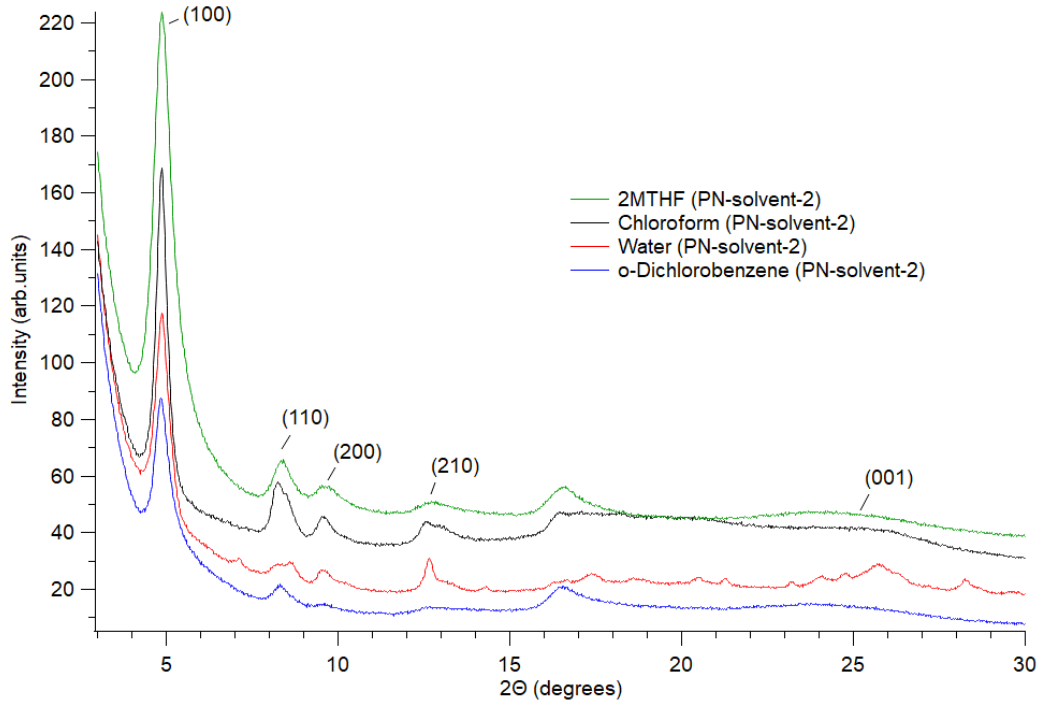

Figure 3.2: Comparison of PXRD spectra between improved PN synthesized using different solvents based on the results on **PN-solvent**. The reaction time was increased to 72 hours.

Experiment **Im-PPA** failed to produce a PN when using PPA as solvent. This result is consistent with the literature which states that imine bonds are unstable in acidic environment, leading to the network breaking down. Highly acidic solvents were not further tested when synthesizing PN.
Benzonitrile was tested as a solvent in experiment **PN-benzonitrile** together with benzoic acid to try to produce a PN. The resulting crystallinity, seen in Figure 3.1, was underwhelming compared to the alternative solvents and was therefore not further tested.

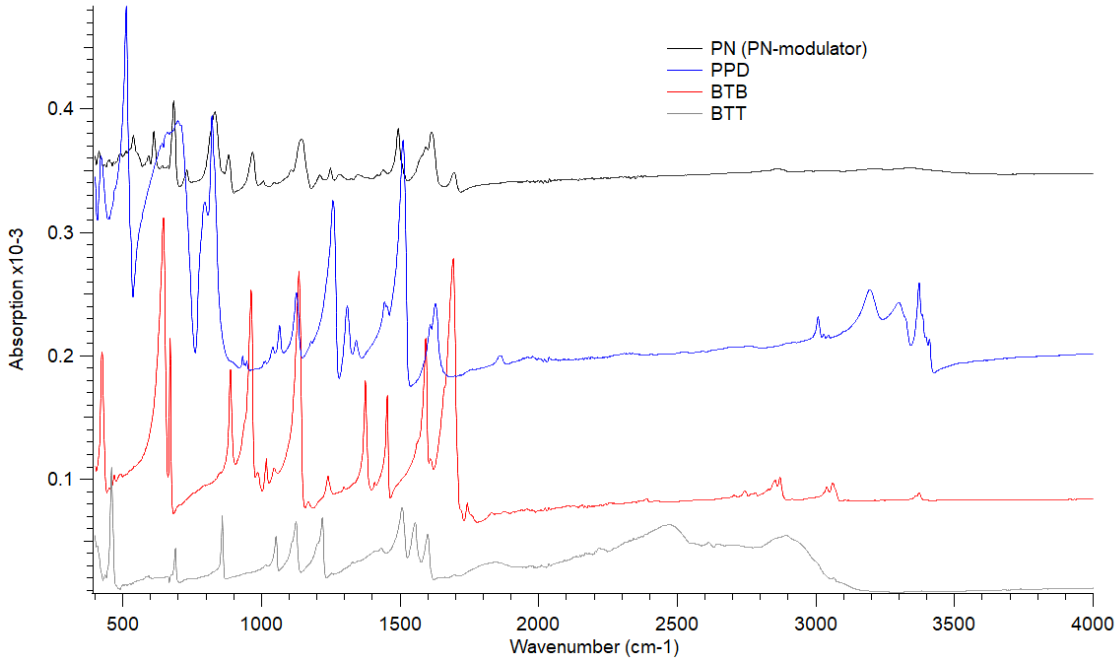

Figure 3.3: FT-IR spectra up to 4000 cm^{-1} of PN and the three reagents used in this project.

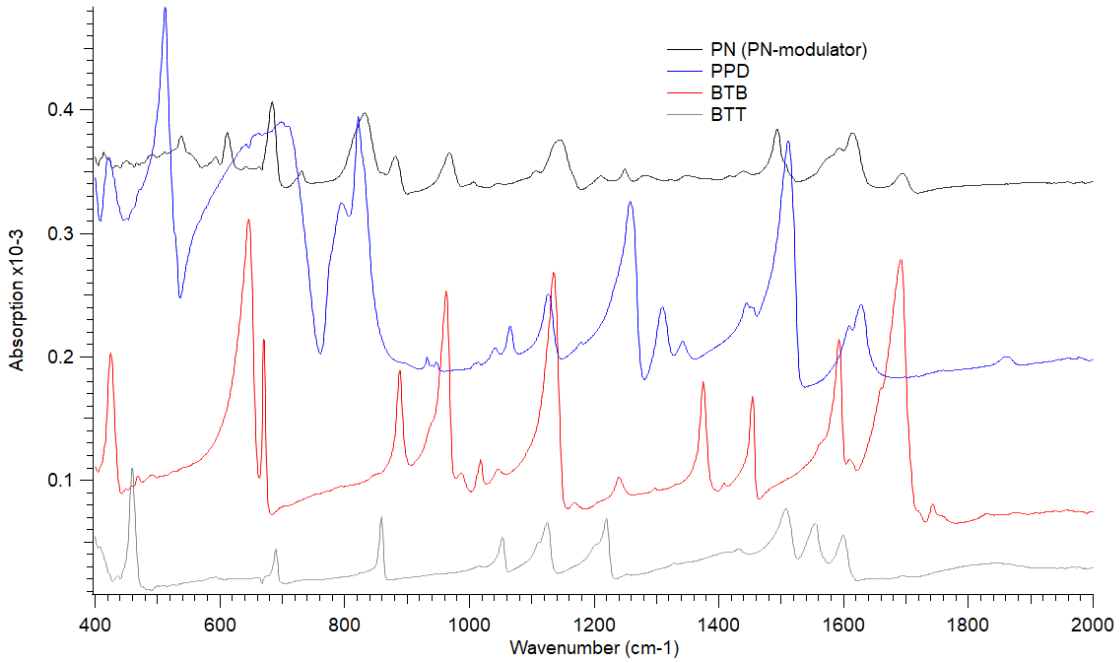

Figure 3.4: FT-IR spectra up of 2000 cm^{-1} of PN and the three reagents used in this project.

From the spectra in Figure 3.3 and Figure 3.4, it is clear that the desired imine linkages have been formed due to the apperance of the peak at 1615 cm^{-1}, representing a C=N bond, and the decrease in the peak at 1693 cm^{-1}, representing a C=O bond, compared to the BTB spectra [20]. The aldehyde bond should have ideally been gone in the PN but remaining aldehydes might be due to unreacted end-groups in the crystal boundary. The imine peak at 1615 cm^{-1} can also be due to unreacted PPD in the crystal boundary, which also displays a peak in the area. However, since the peak at 1615 cm^{-1} is supposed to be there, in the combination with the decrease of the the aldehyde peak, strongly suggests that the desired structure has been formed.

3.2 Synthesis of imidazole and thiazole

Imidazole based COFs are being researched to varying degrees of success in literature [4, 7, 11]. This thesis has tried to shed more light on what factors are important and how to tune them when creating imidazole and thiazole-based COFs using linker exchange. In the synthesis of imidazole and thiazole in experiment **Im-water** and **Th-COF**, a color change was immediately observed when adding BTT or DBD to either BTB or PN, suggesting a quick reaction. A picture of imidazole COF compared to the PN used to create it, can be seen in Figure A.1. The PXRD Figure 3.8 spectra of the imidazole created through direct addition from **Im-water** also showed a complete loss of crystallinity compared to the PN used for the reaction (**PN-water**), indicating that the ring structures of the PN-COF breaks too quickly for the BTT to align itself and retain the ring formation. Based on this, it is

improbable that the resulting crystalline structure seen in PXRD in experiment **Im-slow-addition**, Figure 3.10 is unreacted PN. Another reason to assume that the reaction has occurred successfully is that the structures are more crystalline when they undergo slower addition, as can be seen in Figure 3.10 and will be further discussed under **Addition time**. However, no conclusions can be drawn since the FT-IR spectra, seen in Figure 3.5 and Figure 3.6, of **Im-slow-addition** and **Im-air** are nearly identical to that of the PN.

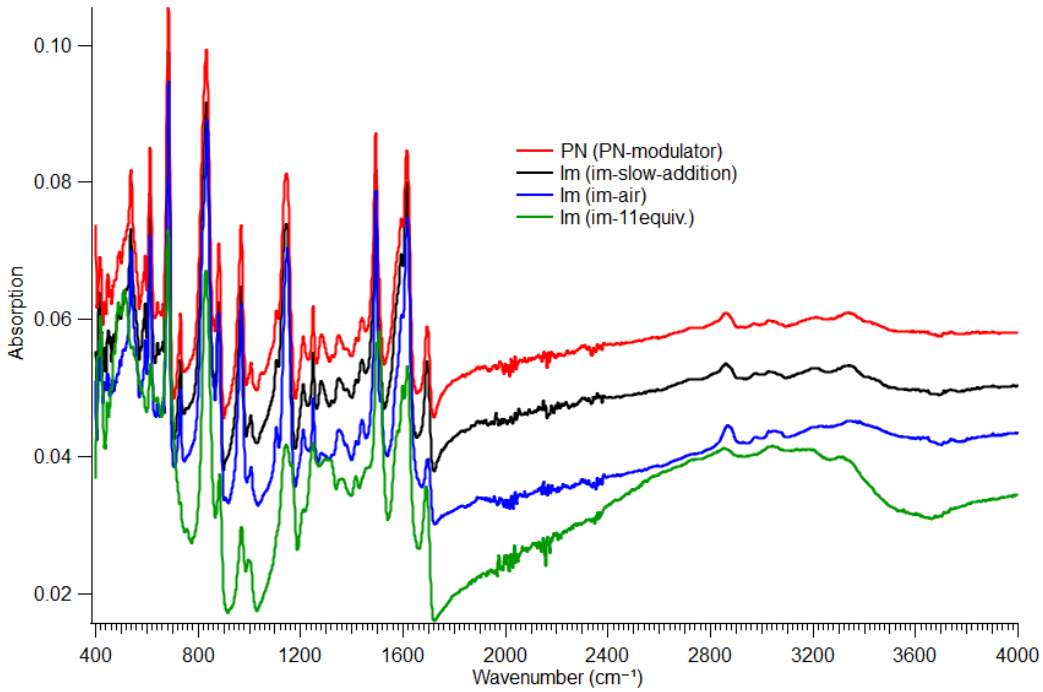

Figure 3.5: Comparison of FT-IR spectra up to 4000 cm^{-1}, between imidazole synthesized during three different experiments and PN.

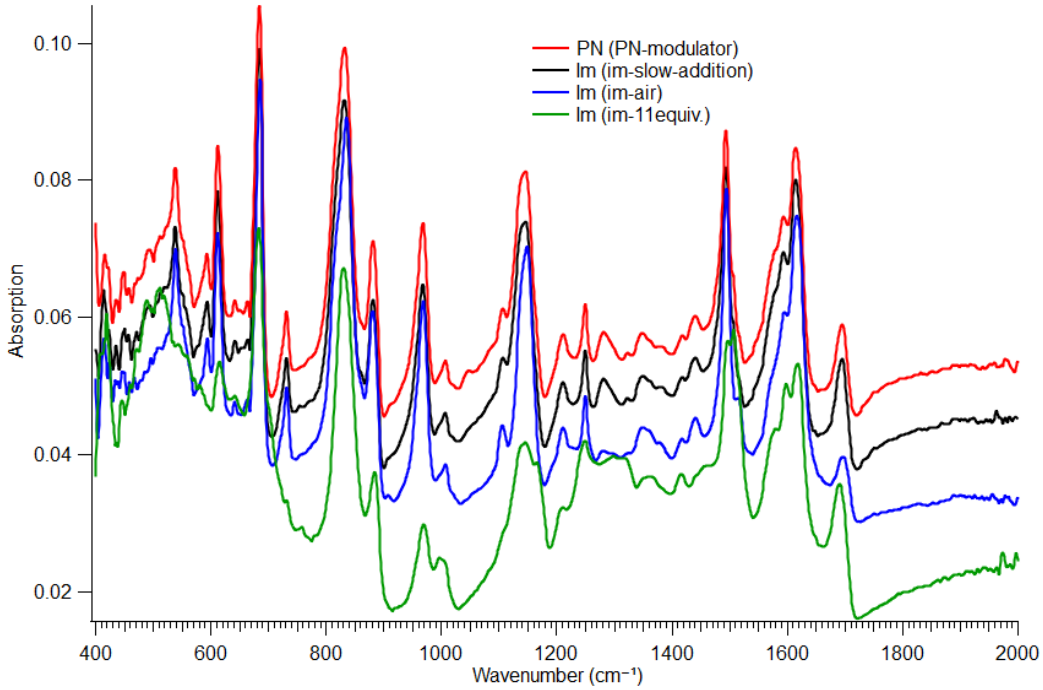

Figure 3.6: Comparison of FT-IR spectra p to 2000 cm^{-1}, between imidazole synthesized during three different experiments and PN.

The matter is further complicated when analyzing the results of **Im-11equiv.**, where crystallinity, seen in Figure 3.10, was partly retained during the exchange and the FT-IR spectra, seen in Figure 3.5, changed when 11 equiv. of BTT was used, where the peaks at 731, 1106 and 1144 are clearly different, indicating a successful linker exchange. However, because of time constraints and the lack of clear FT-IR reference spectra in the literature, it is unknown if this new FT-IR spectra show the desired structure or something else.

An important source of error that could have left large amounts of unreacted reagent or residues in the samples from **Im-11equiv.**, is that the samples were not washed with water. Later experiments gave a clear indication that using water when washing the samples extracted a lot more residue than what was already extracted with ethanol or 2MTHF.

Another important factor that could greatly impact the results is that the BTT reagent was a salt with hydrogen chloride. The solvent used to create imidazole was a mixture of water and DMF, leading to the formation of hydrochloric acid when hydrogen chloride comes into contact with water, leading to a low pH in the solution. Because **Im-11equiv.** had highly excessive amounts of BTT added, it is reasonable, without any pH tests, to assume a lower pH in the solution compared to the other tests. This low pH could have helped increase crystallinity by slowing down the reaction by preventing the cyclic intermediate (Figure 2.2) from undergoing irreversible oxidation, giving the structure more time to self-arrange. However, the results of **Im-PPA**, seen in Figure 3.7, contradict this theory, since none of

the imidazole products displayed crystallinity when polyphosphoric acid (PPA) was used as a solvent. Because of the low number of tests done with pH as a reaction parameter, it becomes difficult to draw any conclusions regarding the impact of pH on imidazole formation. However, it is possible to hypothesize that PPA is not a viable solvent for the synthesis based on other factors, such as being a polymer which might sterically hinder the COF formation. It is therefore uncertain whether it is the pH, solvent or excessive reagent that made the samples from **Im-11equiv.** have crystallinity while none of the samples from **Im-PPA** did.

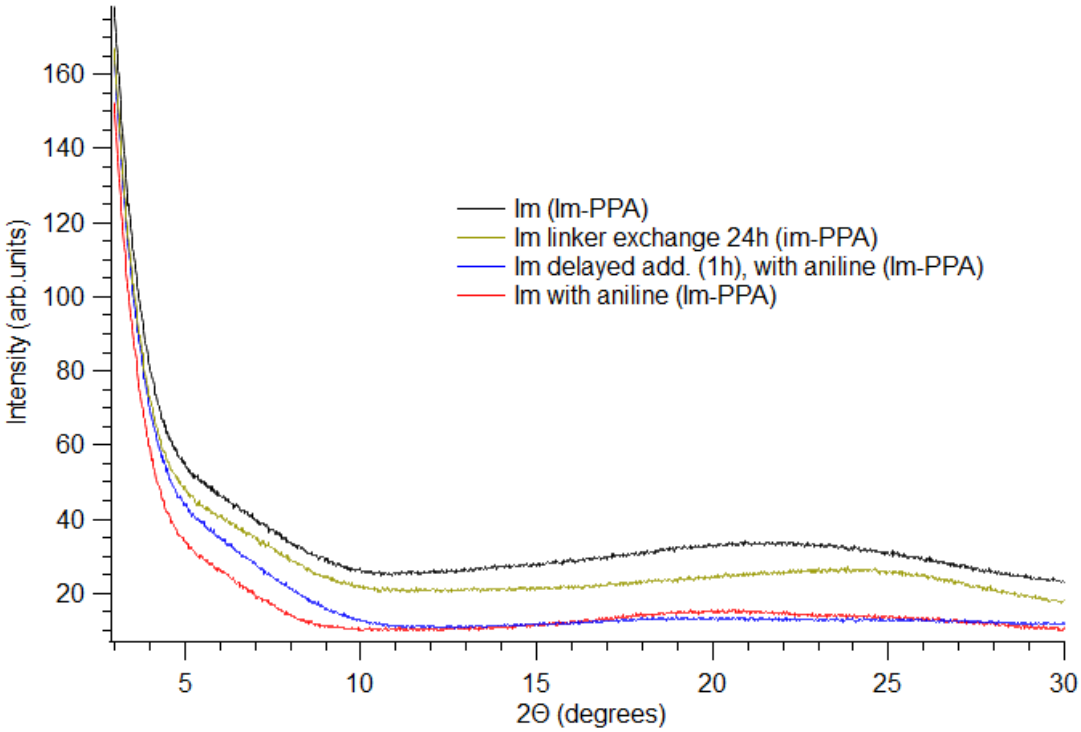

Figure 3.7: Comparison of PXRD spectra between different imidazole samples synthesized with PPA as solvent, in experiment **Im-PPA**.

3.3 Oxidant supply

Yaghi *et al.* tested in 2008 using an oxygen atmosphere as an oxidant to increase crystallinity [15]. From experiment **Th-COF** there seems to be a clear indication that, when synthesizing thiazole-based COFs, the addition of pressurized air during linker exchange makes the product more crystalline than when pure oxygen is used, which can be seen in Figure 3.8. This increase in crystallinity can be explained by oxygen helping the oxidation of the intermediate, as seen in Figure 2.2. It is not clear why oxygen performed worse than air. It can be speculated that if the oxidized too quickly, it may increase the reaction speed by removing hydrogen from the intermediate, as seen in Figure 2.2, too quickly, resulting in a less ordered structure. This increase in reaction rate might decrease crystallinity as previously mentioned. Later experiments continued to use pressurized air, since the spectra of thiazole,

seen in Figure 3.9, shows different peaks compared to PN at, for example, 1303, 1401 and 1507 cm^{-1}, strongly indicating different bonds. It was also assumed that, in future experiments, thiazole and imidazole are similar enough to draw conclusions from each other. The spectra in Figure 3.9 do not give any indication that oxidant supply determines the success of the linker exchange when imidazole is formed. It is speculated that the linker exchange to create imidazole is more dependent on other factors, such as modulators and addition time, but the addition of pressurized air helps the reaction by providing an oxidant to both speed up the oxidation step and avoid the amine side-reaction, if the other parameters are met and the reaction occurs correctly.

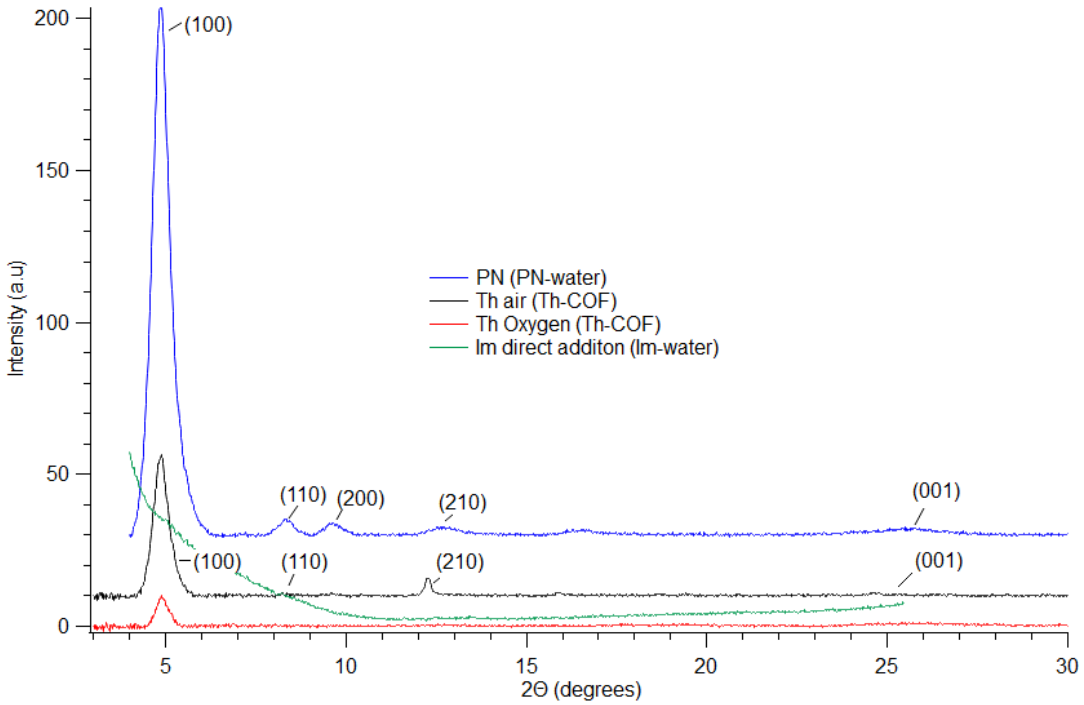

Figure 3.8: Comparison between PXRD spectra of thiazole COFs made under pressurized air or oxygen atmosphere, with the PN used to create them, all with the background subtracted. The spectra of imidazole when directly adding BTT to form imidazole is also seen with background.

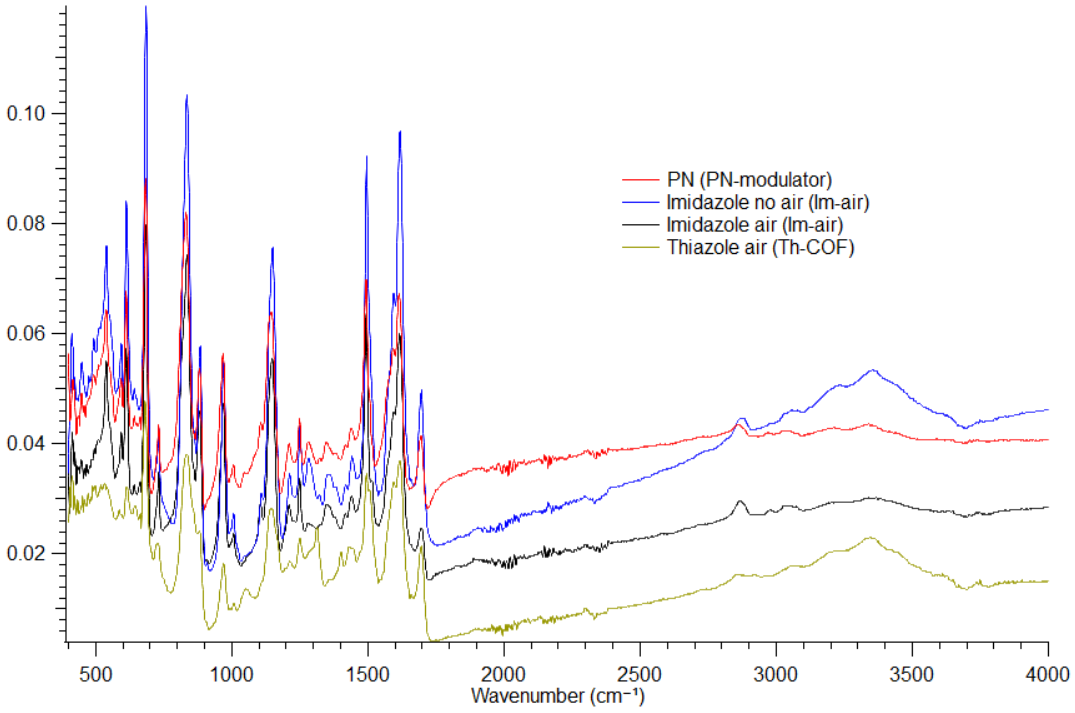

Figure 3.9: FT-IR spectra between **Im-air** and **PN-modulator** shows no clear difference, indicating no linker exchange. Th-COF shows some peak difference at 1303, 1401 and 1507 cm^{-1}, indicating different bonds.

3.4 Rate of addition

The addition time was tested in experiments **Im-11equiv.** and **Im-slow-addition**. **Im-11equiv.** showed a clear difference between sample one (all the BTT was added simultaneously) and sample 2 (1/6 of the BTT was added every half hour), indicating a correlation between addition time and crystallinity as seen in Figure 3.10. In **Im-slow-addition** a small increase of crystallinity could be observed with longer addition time up to vial 3, which had an addition time of 1/5 of the total BTT every 15 minutes, while vial 4 had 1/5 added every 30 minutes. The reason why vial 4 did not show higher crystallinity is probably because after 15 minutes the linker exchange is done, making waiting any longer to add more BTT unnecessary. More tests are needed to examine why the crystallinity in vial 4 actually decreased compared to vial 3. This might be within the margin of error, but it might also point to an optimal point of addition, which needs to be further examined. Further tests should also examine whether slower stepwise addition with lower concentrations per addition increases the crystallinity.

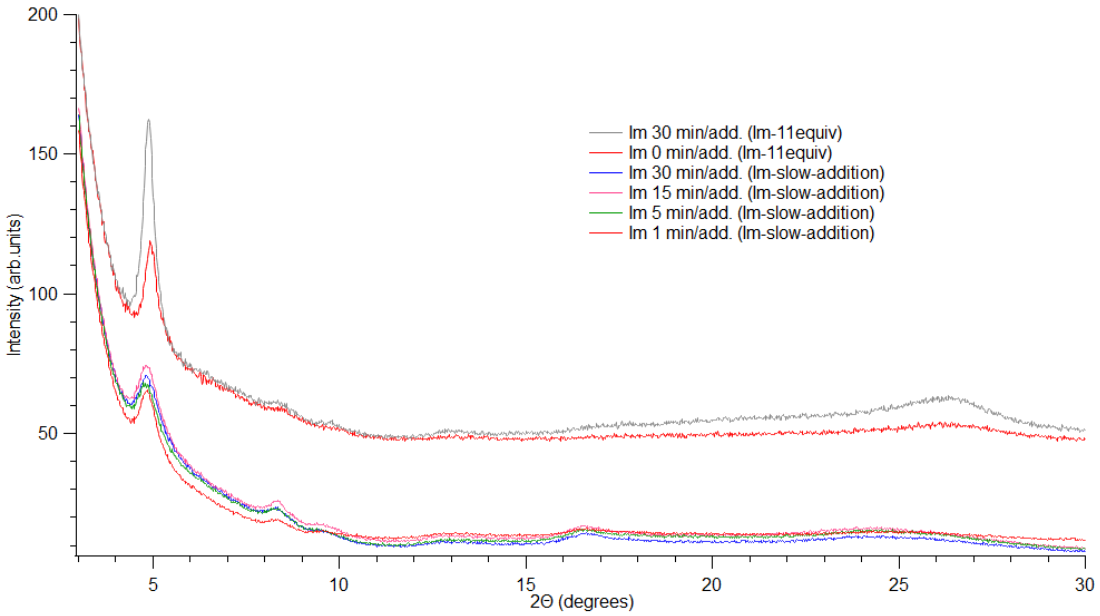

Figure 3.10: PXRD showing the crystallinity between different addition times i **Im-11equiv.** and **Im-slow-addition.**

3.5 Modulators

The use of modulators was briefly studied when synthesizing PN and imidazole COFs. From the PXRD spectra seen in Figure 3.11, it becomes clear that minor improvements are possible when PN is synthesized with the help of a modulator. Modulators used in the reaction has to be extracted afterwards, which might lead to more extensive washes and higher costs. Because of this it is unclear if slightly higher crystallinity is worth the trouble brought by the modulator. When a modulator was used at high rates (109.52 and 219.04 equiv.) in **PN-benzonitrile**, no powder was produced at all, strongly indicating that too much modulator slows the reaction to a stop.

In contrast, the results of using a modulator when constructing an imidazole COF through linker exchange, as seen in Figure 3.11, strongly indicates that the product becomes more crystalline when using a modulator. However, as mentioned previously, it is still unclear if this crystallinity is due to the successful creation of an imidazole COF or leftover residues of unreacted PN. In the event of successfully creating imidazole COF it seems vital to use a modulator to increase the crystallinity. If the imidazole COF was not produced it seems that modulators stop the conversion of PN to imidazole COF from happening. If this is correct, then the reaction might need a longer reaction time than one day, higher temperature or, based on **Im-11equiv.**, higher concentration of BTT. However, the reaction gaining benefits from having a longer reaction time is seen as unlikely since the reaction has been observed to be very quick, making it unlikely for 3 equivalents of modulator to stop the reaction for 24 hours. Crystallinity was observed in **Th-COF** even if no modulator was present, indicating that modulators might help but are not necessary when

forming thiazole COFs. This suggests that thiazole COFs are better at forming crystalline structures than imidazole COFs and therefore do not need modulators to the same extent. The hypothesis is that the oxidation step might be slower because of the sulfur in thiazole, but this is purely speculative and more studies are needed. Due to time constraints, the optimal amount of modulator was not found.

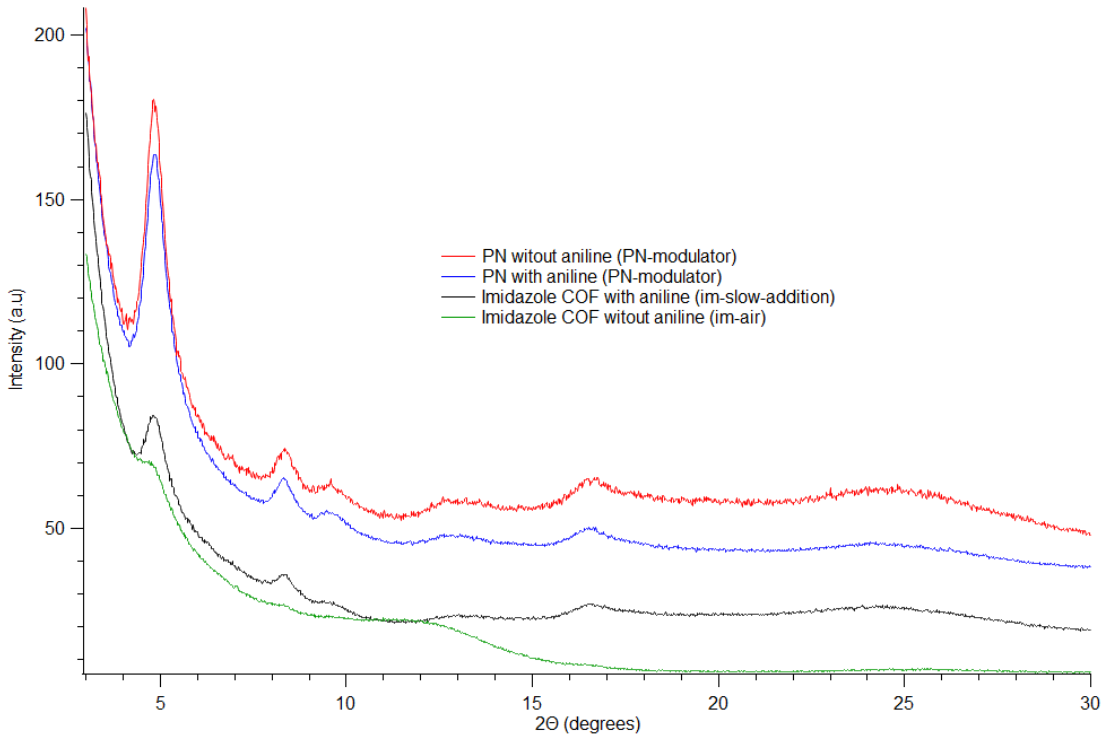

Figure 3.11: Comparison of PXRD spectra in using aniline as a modulator when synthesizing PN and imidazole based COF.

3.6 Raman spectroscopy

Raman spectroscopy was tried during analysis to find complementary data to FT-IR. Three different wavelengths (522 nm, 633 nm, 785 nm) were tested but none resulted in a good spectrum since the spectra kept increasing during the measurement, possibly hiding the smaller peaks midst the background noise. Some peaks were visible and could be improved by using static mode, but the disappearance of smaller peaks meant that Raman spectroscopy was not fit for further analysis.

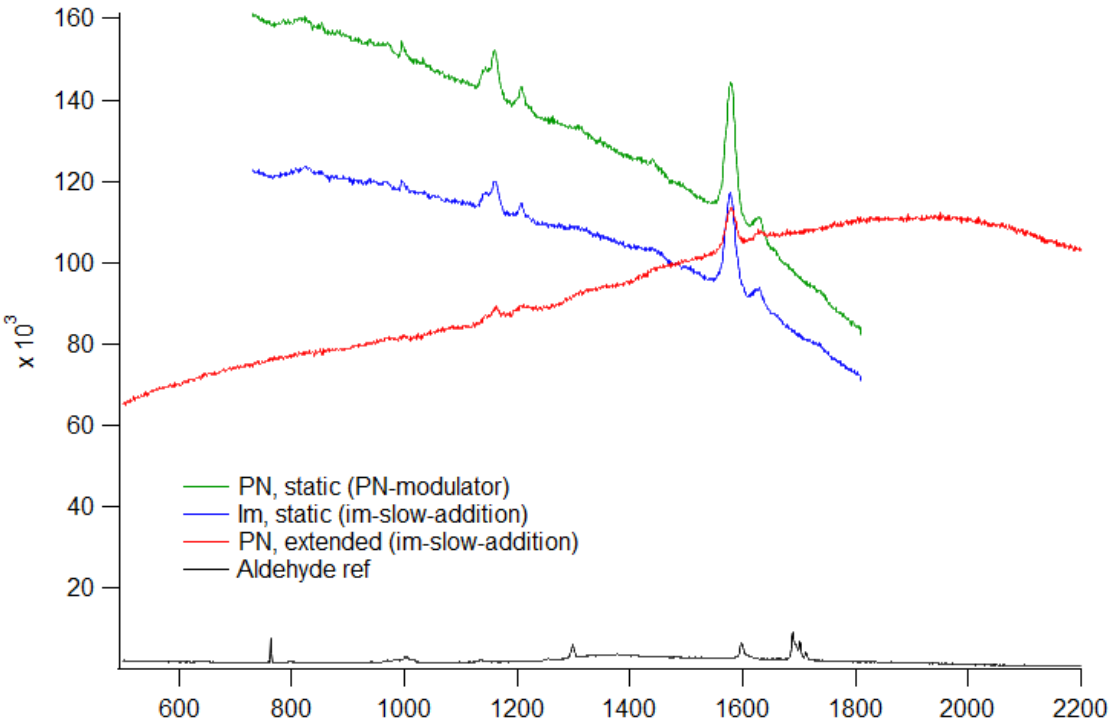

Figure 3.12: Raman spectroscopy used to analyze PN (from experment PN-modulator, vial 2 with no modulator) in both extended and static mode, imidazole (from experiment Im-slow-addition, vial 3 with 15 min/addition) in static mode, and aldehyde as a reference sample.

4

Conclusion

The PN was further optimized with high yields and more information regarding the parameters was discovered to optimize the synthesis. Different solvents, time, and the use of modulators were tested to understand their impact on the PN. Modulators were found to have a low impact on the resulting structure, while the choice of solvent and reaction time was critical to produce crystalline PN. Different factors such as the addition time, modulators, amount of reagent, oxidant, and direct addition to a PN have all been briefly examined for imidazole COFs. It appears that imidazole COF was successfully synthesized when excessive amounts (11 equiv.) of BTT was used with modulators (3 equiv.) and bubbling pressurized air (as an oxidant) through the samples. The other experiments that tried to synthesize imidazole all seem to have failed because they either lost crystallinity completely, or the FT-IR spectra were too similar to those of the PN to rule out the possibility of failed linker exchange. IR-references are needed to more accurately determine if the resulting structure is imidazole COF or unreacted imine PN. Alternatively, another experimental method, such as solid state NMR, could be used to determine whether there is hydrogen bonded to nitrogen, indicating an imidazole instead of an imine. Modulators need to be further tested since there are clear indications that they help form crystalline structures in linker exchange. Slower addition should be tested to investigate the reaction speed and how to increase the crystallinity. More tests regarding excess BTT needs to be done to confirm if excess reagent works better in a linker exchange reaction. Factors such as temperature and pH have only been briefly tested and seems to have an impact on the crystallinity of the COF, further studies are needed to investigate their exact impact on the synthesis. More tests are also needed to find the differences between imidazole and thiazole COFs and their requirements during synthesis, and if it is possible to assume that they work under the same requirements.

5

Experimental section

5.1 Yield calculation

The yield was calculated from the linker reagent since one mole of linker should create one mole of COF. If the node was the limiting reagent, the amount of linker that would theoretically react was calculated by the equivalent balance where 2 equiv. node would react with 3 equiv. linker, making the equation $n_{linker} = 2/3 * n_{node}$. One equiv. of COF included the linker and 1/3 of each connected node as seen in Figure 5.1. The amount of substance was then converted to the mass that would have been created if 100% yield occurred. The measured mass was divided by the theoretical mass to get the yield.

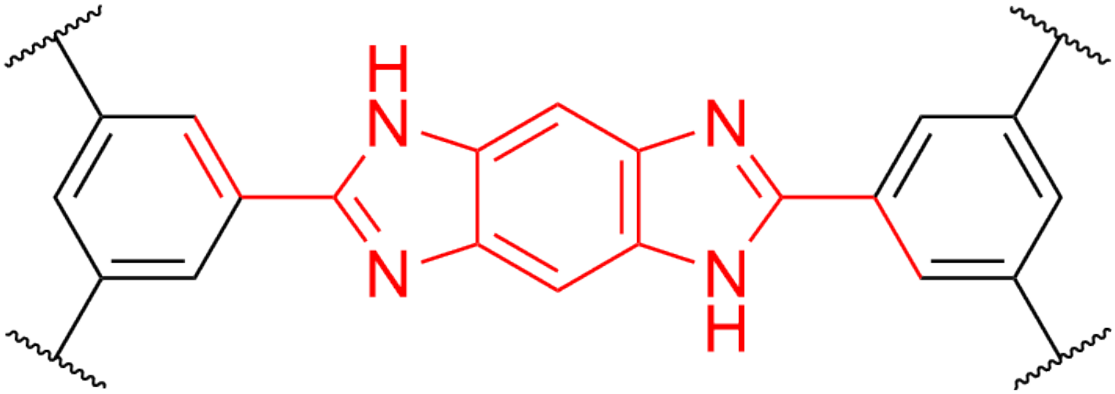

Figure 5.1: Illustration of one equivalent (red) in a COF when calculating yield.

5.2 Instruments

PXRD, FT-IR and Raman spectroscopy were used to analyze the samples compositions and investigate the crystallinity of the COFs. PXRD is excellent for analysis regarding crystallinity in a sample and was used both for qualitative and quantitative analysis. FT-IR and Raman were used as qualitative analysis methods to determine the chemical composition of samples to determine if the product had been successfully synthesized.

5.2.1 PXRD

PXRD was used to determine crystallinity of samples. The machine D8 Discover with a Cu source (λ =1.54178 Å) was used. Three different settings were used depending on requested range of operation and scanning speed. For long scans the range was 3-40 2 with a scan speed of 1 s/step and 1851 steps total. Medium scans were performed in the range of 3-30 2, 0.4 s/step and 1500 steps. Fast scans were done in the range of 3-40 2, 0.25 s/step and 1851 steps.

5.2.2 FT-IR

FT-IR was used to determine the chemical composition of samples. A "ParkinElmer spectrum 3" machine with Pike GladiATR "module" was used. The samples were measured in absorbance with a resolution of 4 cm^{-1} and 64 accumulations.

5.2.3 Raman Spectroscopy

Raman was tried as an alternative to FT-IR spectroscopy using a Renishaw InVia, switching between magnification 50x and 20x in a Leica objective. Three different lasers were tested; 1. 522 nm, 2400 groves/mm 2. 633 nm, 1800 groves/mm 3. 785 nm, 1200 groves/mm. A silicon-wafer was used as a reference sample and both static and extended modes were tested.

5.3 Chemicals

1,3,5-Benzenetricarboxaldehyde (BTB) served as the node when creating the different COFs in this thesis while p-phenyldiamine (PPD) was used as a linker when creating an imine-linked PN. The imidazole-based COFs were made by either reacting Benzene-1,2,4,5-tetrayltetraamine tetrahydrochloride (BTT) with the node or with a PN in a linker-exchange reaction. Thiazole based COFs were made by reacting 2,5-Diaminobenzene-1,4-dithiol (DBD) with the node or PN in the same way as imidazole. When a modulator was added, it was in the form of aniline since it was close to the linkers in terms of properties.

5.4 Synthesis

PN-water synthesized PN in water solvent according to the steps of the previous work of Kong *et al.* [2]. BTB (32.428 mg, 0.2 mmol, 2 equiv) was added to a vial together with an aqueous acetic acid solution (2 ml, 8.75 M) and stirred for 30 minutes. PPD (32.442 mg, 0.3 mmol, 3 equiv) was added to a separate vial together with water (2 ml) and placed in lukewarm water to dissolve. The PPD was added to the BTB and left for 2 hours to react and form PN. The product was washed with acetone in rounds of 10 ml/wash, up to a total of 50 ml. The washing process consisted of adding a solvent and letting the product sediment before extracting as much solvent as possible without removing any product. The vials were filled with

15 ml and rested during the night before being washed until the solution became clear (70 ml). The flasks were filled and allowed to rest for 1.5 hours. The samples were left in a full vial for three days. The solution was washed with acetone once. The wash process was repeated with chloroform (10 ml/ wash) 3 times before the product was transferred to a 4 ml sample vial and dried under a flow of nitrogen. The samples were placed in a vacuum oven overnight at 50 °C. The products were analyzed with PXRD and the spectra can be seen in Figure 3.8.

PN-benzonitrile tested using benzonitrile as a solvent with benzoic acid as the acid to create PN similar to another study [22]. Benzonitrile (4.5 ml) and benzoic acid (8 mmol, 0.97696 g) were added to four glass vials and capped before being placed in a 90 °C oil bath to dissolve the benzoic acid. BTB (8.107 mg, 0.05 mmol, 2 equiv.) was added to four separate vials with benzonitrile (0.5 ml) to dissolve. (8.1105 mg, 0.075 mmol, 3 equiv.) was in a similar manner placed in four vials with benzonitrile (0.5 ml). After the benzoic acid had dissolved, aniline (0.5 ml, 5.476 mmol 219.04 equiv. in vial 1 and 4; 0.25ml, 5.476 mmol, 109.52 equiv. in vial 3) and the BTB solutions were added, which quickly formed powder. PPD was added and the vials were capped without shaking or stirring. Vials 1-3 was placed in 90 °C oilbath for 5 minutes before being left at room temperature for 20 hours. The samples were moved to centrifuge tubes with the help of ethanol (5 ml) and centrifuged (1048 G) for 5 min. The products were washed two more times with ethanol (10 ml) and centrifuged before it became evident that there was no product in vials 1,3,4 and so they were discarded. The Remaining vial was centrifuged one more time with ethanol for 10 minutes. 2-Methyltetrahydrofuran (2MTHF) (10 ml) was used to wash the sample three times before two final washes of ethanol and extraction to a smaller vial. The sample was placed in a vacuum-oven at 70 °C for 16 hours to dry. The sample was weighed and the yield was calculated to 80.75%. The PXRD spectra can be seen in Figure 3.1.

PN-solvent tried using different solvents to determine their impact upon the formation of PN. BTB (21.1 mg, 0.13 mmol, 2 equiv.) and PPD (21.1 mg, 0.195 mmol, 3 equiv.) was added togheter in a microwave vial. The different solvents (1. Dioxane, 2. Mesitylene, 3. Dichlorobenzene, 4. chloroform, 5. 2MTHF) were added (4 ml), which resulted in a yellow solution. Aqueous acetic acid (6 M, 0.5 ml) was added before the vials were capped and placed in a 80 °C oilbath with stirring for 24 hours. The solutions were transferred to centrifuge tubes with ethanol (7 ml) before being washed at intervals with different solvents as seen in table 5.1. The washes contained adding solvent, centrifuging (1509 G, 10 min) the samples before removing and readding new solvent. Problems occured when using DCM since the powder had trouble settling so the centrifuge time was increased to 15 min for the second and third DCM wash and the force was increased to 2958 G. The samples were washed until the solution was clear for both the organic and inorganic solvent. The suspended powders were transferred to scintillation vials with ethanol (2 ml) and dried with nitrogen gas. The mostly dry powder was put in a vacuum oven at 80 °C but was interrupted after 3.5 hours since it started to smell of amines. It was determined that 80 °C is too high and it should be kept at 50 °C. The samples were

weighed and the yield calculated in realtion to the limiting reactant. The yield was: 1. 34.9%, 2. 64.6%, 3. 74%, 4. - (sample was used in PXRD before being weighed which makes it impossible to calculate yield.), 5. 43.67 %. PXRD spectra seen in Figure 3.1.

Solvent	volume	number of additions
Ethanol	7 ml	1
Ethanol	10 ml	3
DCM	5 ml	3
Ethanol	10 ml	1
Ethanol	2 ml	1

Table 5.1: Washes to clean the different solvents in **PN-solvent**.

PN-solvent-2 synthesized pre-network based on the results of **Th-COF** and **PN-solvent**. PPD (42.17 mg, 0.39 mmol, 3 equiv) and BTB (42.16 mg, 0.26 mmol, 2 equiv) was added to separate 4 ml scintillation vials with 4 ml of respective solvent (1. Water 2. o-Dichlorobenzene, 3. Chloroform, 4. 2MTHF) before being added to a microwave vial. Aqueous acetic acid (6 M, 1 ml) was added to the vial and a yellow powder quickly started to form. The vials were capped and placed in an 80 °C oilbath fr 72 hours with stirring. After 15 hours 1 and 4 had turned more orange and all vials had become more cloudy. After 39 hours 1,2 and 4 had turned different shades of brown. The solution was after 72 hour transferred to centrifugation vials and centrifuged at 1509 G for 5 minutes. The order of solution used to wash the samples can be seen in 5.2. The samples were transferred with ethanol (4 ml) to scintillation vials and dried with nitrogen before being placed in a vacuum oven at 50 °C for 17 hours. The samples were weighed to calculate the yield: 1. 68%, 2. 83.8%, 75.2%, 4 84.8%. PXRD spectra can be seen in Figure 3.2.

Solvent	volume	number of additions
Ethanol	10 ml	4
2MTHF	10 ml	2
Ethanol	10 ml	2
Ethanol	4 ml	1

Table 5.2: Washes to clean the different solvents in **PN-solvents-2**.

PN-modulator tested the use of modulators when synthesizing the pre-network from **PN-solvent-2**. PPD (42.17 mg, 0.39 mmol, 3 equiv) and BTB (42.16 mg, 0.26 mmol, 2 equiv) was added to two microwave vials. 2MTHF (8 ml) and aqueous acetic acid (6 M, 1 ml) was added to both vials while aniline (59.35 µl, 0.65 mmol, 5 equiv) was added to vial 1. The vials were capped and placed in 80 °C oilbath for 72 hours with stirring. The solutions were transferred to centrifuge vials with ethanol (4 ml) before being washed multiple times as seen in Table 5.3. The solution in vial 1 was observed as redder than vial 2. The vials were placed under nitrogen to dry before being placed in a vaccuum oven at 50 °C for 14 hours. The samples were weighed to calculate the yield 84.9% in vial 1 and 85.9% in vial 2. PXRD seen in Figure 3.11.

Solvent	volume	number of additions
Ethanol	4 ml	1
Ethanol	10 ml	3
2MTHF	10 ml	1
Ethanol	10 ml	2

Table 5.3: Washes to clean the different solvents in **PN-modulator**.

Im-water had PN synthesized according to the steps in **PN-water** before BTT (97.98345 mg, 0.345 mmol, 3.45 equiv) was put into water (2 ml) for 5 minutes to dissolve before being added to the PN to react for 2 hours. The addition happened before the PN had been washed in an attempt to use direct addition to create imdazole COF. The sample was washed the same as the PN in **PN-water** except using 10 ml acetone to clear the solution instead of 70 ml. PXRD seen in in Figure 3.8.

Th-COF was based on a synthesis from a previous study [15]. The experiment used PN from **PN-water** to synthesize thiazole via linker-exchange. Three vials were prepared with PN (5 mg, 0.013mmol, 1 equiv) and different amounts of 2,5-Diaminobenzene-1,4-dithiol (3.36 mg, 0.195 mmol, 1.5 equiv. in vial 1; 8.96 mg, 0.052 mmol, 4 equiv. in vial 2 and 3) were added to a scintillation vial with a mix of dimetylformamide (DMF) and water (3:1 % (V/V) 3 ml). The vials were capped and either pressurized air (vial 1 and 2) or oxygen (vial 3) was bubbled through a needle into the solution for approximately 20 h, with an additional needle for pressure release. The samples were later washed by filling the vials with acetone before removing it and any potential residue still suspended in the solution. Vial number 2 was accidentally dropped. Remaining vials placed in vacuum oven for 16 h at 50 °C to dry. PXRD seen in Figure 3.8.

Im-PPA imidazole COF was made based on a previous study [4], using polyposphoric acid (PPA) as a solvent at 150 °C for 48 hours. The goal was to test different ways to synthesize imidazole COF. BTB (16.214 mg, 0.1 mmol, 2 equiv.) was added to microwave vials with 3 ml PPA and vial 1 and 2 had aniline (0.137 ml, 3 equiv.) added. BTT (42.6 mg, 0.15 mmol, 3 equiv in vial 1,2 and 3. 48.99 mg, 0.1725 mmol, 3.45 equiv in vial 5) was added after the time given in Table 5.4. PPD (0.15 mmol, 16.221 mmol, 3 equiv) was added to vial 4 and 5 before the vials were capped with nitrogen atmosphere and placed in the oil-bath. The samples had turned dark after 20 hours. The samples were removed after 24 hours and left to cool for 1 hour before 5 ml sodium bicarbonate saturated water (SBW) was added to the solution. Vial 1,2 and 4 had aggressive foam formation upon addition. The samples were washed until the solution was clear and stopped foaming, the total umber of washes can be seen in Table 5.5. Vial 5 turned pink in ethanol and afterwards there was barely anything left in vial 4. Water (5 ml) was first used to transfer the samples to sample vials, however, due to the slow evaporation of water the samples were transferred back to centrifuge vials and water extracted before transferring the samples to sample vials with ethanol (5 ml). The samples were placed under nitrogen gas to dry before being placed in a vacuum oven (60 °C) for 16 hours. The samples, except the

PN in vial 4, were analyzed with PXRD, seen in Figure 3.7.

Vial	product	aniline	BTT added after	linker exchange
1	Imidazole	yes	0 hours	no
2	Imidazole	yes	1 hour	no
3	Imidazole	no	0 hours	no
4	PN	no	-	no
5	Imidazole	no	24 hours	yes

Table 5.4: Different reaction conditions in experiment **Im-PPA**.

Solvent	volume	number of additions
SBW	5 ml	1
SBW	10 ml	5 (+7 for vial 1 and 2)
Water	10 ml	1
SBW	10 ml	1 (in vial 3 and 5)
Ethanol	10 ml	7
water	10 ml	6
Ethanol	10 ml	2
water	5 ml	1
Ethanol	5 ml	1

Table 5.5: Washes to clean the different solvents in **Im-PPA**.

Im-slow-addition used the synthesis from **Th-COF** to make imidazole COF from pre-network in a linker-exchange reaction. The goal of this test was to see if the addition time had an impact on the crystallinity of the imidazole-based COF. A stock solution of BTT (35 mg, 0.12188 mmol) and DMF/water (4 ml) was created and sonicated to dissolve. Pre-network (**PN-modulator** vial 2, 5 mg, 0.0277 mmol, 1 equiv) was added to a scintillation vial with a DMF/water solution (75/25%, 5 ml) together with aniline (7.59 µl, 0.0831 mmol, 3 equiv) and had pressured air bubble through it while being stirred. Four syringes were prepared with 1 ml of tetraamine stock each but there was too little left after filling the first three syringes. More tetraamine (8.6 mg, 0.03047 mmol, 1.1 equiv) and dmf/water solution (1 ml) was added to the stock, which was used in vial 1. The addition (0.2 ml) was done with the following intervals: 1. 1 minute, 2. 5 minutes, 3. 15 minutes, 4. 30 minutes. From the first addition there was a total reaction time of 23 hours before the samples were transferred to centrifuge vials with ethanol (2 ml). The samples were washed multiple times as seen in Table 5.6 with the help of centrifugation (1509 G, 5 min/wash) before being transferred to new sample vials with ethanol (2 ml). The samples were dried with nitrogen before being placed in a vacuum oven (50 °C) for 17.5 hours. PXRD seen in Figure 3.10.

Solvent	volume	number of additions
Ethanol	2 ml	1
Ethanol	10 ml	2
2MTHF	10 ml	1
Ethanol	10 ml	2
Ethanol	1 ml	1

Table 5.6: Washes to clean the different solvents in **Im-slow-addition**.

Im-11equiv. used 11 equivalents of BTT because of the results from **Im-slow-addition**, in an attempt to increase crystallinity. The BTT (86.5348 mg, 0.3047 mmol, 11 equiv.) added to a vial together with DMF/water solution (3:1 3 ml) and sonicated to dissolve. PN from **PN-solvent-2**-4 (5 mg, 0.0277 mmol, 1 equiv.) was put in a scintillation vial with DMF/water solution (3:1, 3 ml) before adding aniline (7.59 µl, 0.0831 mmol, 3 equiv.). The BTT solution was added through stepwise addition (0.5 ml/step) and the time between each addition was different between the vials (1. all at once, 2. 5 min, 15 min, 30 min). The reaction time was 17 hours from the first addition before the samples were moved into centrifuge vials with ethanol (2 ml) and extra ethanol (2 ml) in vial 1 and 4. The samples were washed (order and number of washes seen in 5.7 with the help of a centrifuge (1509 G, 5 min/wash) before being transferred to sample vials before being dried with nitrogen. The samples were placed in a vacuum oven (50 °C) for 18 hours. PXRD seen in Figure 3.10.

Solvent	volume	number of additions
Ethanol	4 ml	1
Ethanol	10 ml	3
2MTHF	10 ml	1
Ethanol	10 ml	2

Table 5.7: Washes to clean the different solvents **Im-11equiv.**.

Im-air aimed to see the impact of bubbling pressurized air through samples with different amounts of BTT and different solvents. Four scintillation vials were prepared with PN from **PN-water**4-2 (5 mg, 0.0277 mmol, 1 equiv) before adding the solvents. In vials 1,2 and 4 a mixture of DMF/water (3:1 4 ml) were added while in vial 3, 2MTHF (4 ml) was used. The vials were placed under stirring and vial 1,2 and 3 had pressured air bubbled through. BTT (8.6534 mg, 0.03047 mmol, 1.1 equiv) was added to separate sample vials 1 and 4 while vials 2 and 3 had 4 times the amount. The solvents (2 ml) were added to the BTT and sonicated to dissolve. The BTT in vial 3 did not dissolve in 2MTHF and so it was dried with nitrogen gas before DMF/water (3:1 2 ml) was added to the sample vial. The BTT solutions were taken up by syringe and 0.2 ml were added every 15 minutes. The total reaction time was 24 hours before the samples were transferred to centrifuge vials with ethanol (4 ml). Most of the 2MTHF solution in vial 3 had evaporated during the reaction, leaving a smaller volume. Extra ethanol (4 ml) was added to vial 3 to balance the vials during centrifugation (1509 G, 5 min/wash). The samples

were washed in the order seen in Table 5.8. The powders were transferred to sample vials and dried under nitrogen gas. Some of the powder in vial 4 was lost due to too high nitrogen flow. The samples were placed in a vacuum oven (50 °C) for 17 hours. The samples were weighed to calculate the yield: 1. 45.4%, 2. 47.1%, 3. 56.5%, 4. 34.3%.

Solvent	volume	number of additions
Ethanol	4 ml	1
Ethanol	5 ml	3
2MTHF	5 ml	1
Water	5 ml	8
Ethanol	5 ml	2

Table 5.8: Washes to clean the different solvents **Im-air**.

Bibliography

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A

Appendix

Figure A.1: Picture of PN from **PN-water** (yellow) and Im from **Im-water**

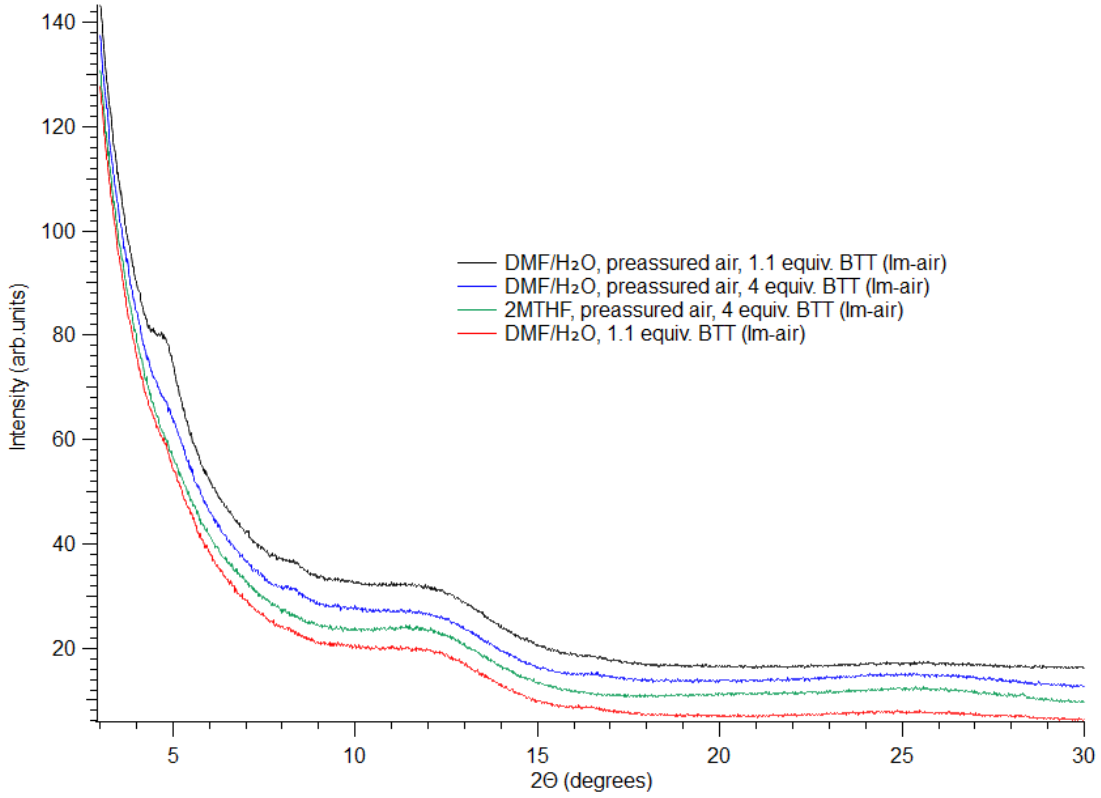

Figure A.2: Comparison of PXRD spectra between different imidazole samples synthesized in experiment **Im-air**.

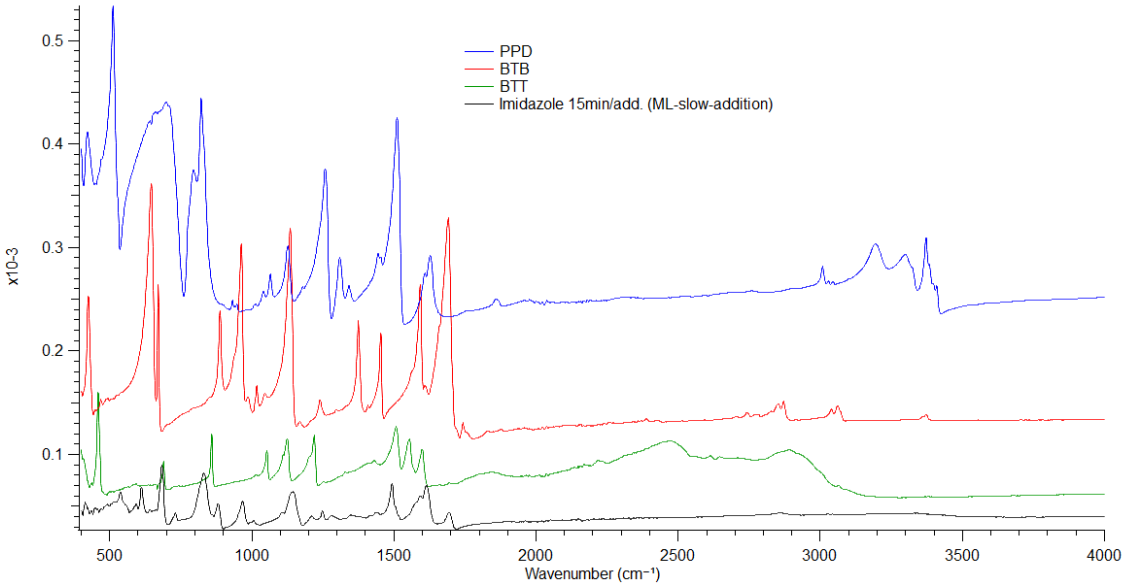

Figure A.3: Comparison of PXRD spectra between imidazole and reagents.

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