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Synthesis of Phosphonate-Based Diimide Ligands

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SYNTHESIS OF PHOSPHONATE-BASED DIIMDE LIGANDS

by

Kenya V. Medina

HONORS THESIS

Presented in Partial Fulfillment of the Requirements for
Graduation from the Honors Progam of
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San Antonio, Texas

Approved by:

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Director, Honors Progam

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Abstract

by

Kenya V. Medina

There has been a resurged interest in the synthesis of metal-organic frameworks because of their potential applications in energy production and drug delivery. Although diimides are insoluble in aqueous solutions, the addition of phosphonic acid allows the complex to be water soluble, which greatly increases their application. Therefore, the creation of a hybrid metal-organic complex by the addition of phosphonic groups to diimide ligands can result in a polar porous compound. In this project the ligand design included the use of dianhydrides including pyromellitic dianhydride, naphthalenetetracarboxylic dianhydride, perylenetetracarboxylic dianhydride, and biphenyl-tetracarboxylic acid dianhydride. These dianhydride precursors were refluxed under argon with aminomethyl phosphonic acid. The methods were repeated with imidazole and dimethylformamide as the solvents and subsequently purified. The results of the IR spectroscopy, ^{1}H NMR, ^{13}C-NMR, and absorbance indicated successful design of the ligands.

This thesis is dedicated to Dr. Adelani for all his help in my research journey. Additionally, special thanks go out to all my professors at St. Mary’s University and family members who have encouraged me to continue my education.

CONTENTS

FIGURES

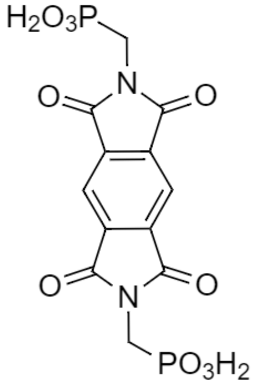
ACKNOWLEDGEMENTS

I wish to thank the funding organizations, the San Antonio Livestock and Exposition Scholarship and the Welch Departmental Research Grant Program (grant No. U-0047). Special regards to the department of Chemistry at the University of Texas at San Antonio for allowing the use of their equipment for NMR analysis, and to Dr. Adelani for all his guidance throughout these years.

CHAPTER 1: INTRODUCTION

There are many crystalline compounds that are gaining recognition in the scientific community. Amongst them, metal-organic frameworks (MOFs) are of high interest. With their inorganic and organic properties, they are able to perform a wide range of functions[1]. These family of compounds is characterized by the formation of highly porous networks with an organic backbone and a metal center[2]. While three-dimensional compounds render the largest variety of functions, even MOFs with two-dimensional properties have been explored for a multitude of uses. One of the emphases in this area is on the ability to control the pore size and surface area of the compounds. Such abilities allow for potential uses in drug delivery[2,3], as well as in the arrangement of proton carriers, making it a subject of interest for energy production[4].

In this instance, the ligand design includes the use of dianhydrides including pyromellitic dianhydride, naphthalenetetracarboxylic dianhydride, perylenetetracarboxylic dianhydride, and biphenyl-tetracarboxylic acid dianhydride (Figure 1). These aromatic diimides are highly fluorescent compounds with excellent photochemical[5] and electrochemical properties, provided by the strong π-stacking interactions[6]. Their high thermal stability[7.8] and rigidity make them excellent candidates to be used as organic ligands for coordination polymers (CPs) and metal-organic frameworks (MOFs). Previous experiments have also explored the formation of thin films of these aromatic compounds and their use as insulators[8].



N,N´-bis
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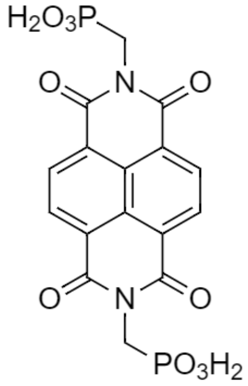
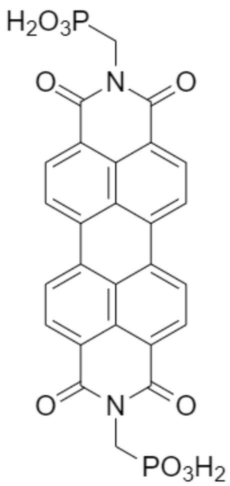
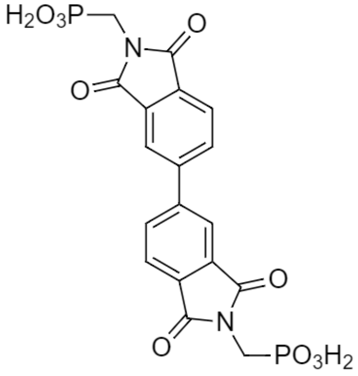
-pyromellitimide
(PPMI)



N,N´-bis
(phosphonomethyl)
-1,4,5,8-
naphthalenediimide
(PNDI)



N,N´-bis
(phosphonomethyl)
-3,4,9,10-
perylenediimide
(PPDI)



N,N´-bis
(phosphonomethyl)-
3,3′,4,4′-
biphenylenediimide
(PBDI)

Figure 1. Chemical structure of ligands synthesized by addition of aminomethyl phosphonic acid to the dianhydride derivatives.

The purpose of this project is to explore the reaction of aminomethyl phosphonic acid with various aromatic dianhydride compounds. The dianhydrides selected have shown an extensive use as semiconductors due to their high electron affinities and conjugation[9]. In order to incorporate the ligands into organized materials, the aromatic rings are held in a π-stacked arrangement favoring radical stabilization, since the lone electron can be delocalized over several aromatic rings[5]. Although these characteristics make these diimides potential candidates for light harvesting devices, the size of their framework provides some challenges when making complexes such as poor yield. Although most diimides are insoluble in aqueous solutions, the addition of phosphonic acid allows the complex to be water soluble, which greatly increases their application.[10] Their solubility in aqueous media, allows for spectroscopic studies under more affordable resources and in a timely manner. In addition, previous experiments have found that di-substituted phosphonic acid derivatives of the diimides have yielded highly thermal and solvolitically stable ligands, resisting temperatures up to 200°C.[11] This is especially important for the synthesis of MOFs and CPs with high thermal stability. Since not only are the synthesis of MOFs completed at high temperatures (80-100 °C) but are also aimed to work in very diverse environments, a large temperature range for survival without decomposition is being sought[4].

CHAPTER 2: EXPERIMENTAL SECTION

Synthesis: All the reagents, benzene-1,2,4,5-tetracarboxylic dianhydride (97 %, Sigma-Aldrich), perylene-3,4,9,10-tetracarboxlic dianhydride (98 %, Sigma -Aldrich), 1,4,5,8-naphthalenetetracarboxylic dianhydride (97 %, Sigma-Aldrich), 3,3',4,4'-biphenyltetra-carboxylic dianhydride (97 %, Aldrich), imidazole (99.5%, Sigma-Aldrich) and dimethylformamide (99.8% anhydrous, Sigma-Aldrich) were used as received. The (aminomethyl)phosphonic acid was prepared by refluxing diethyl (aminomethyl)phosphonate (97 %, Epsilon Chimie) in concentrated HCl.

N,N´-bis (phosphonomethyl)-pyromellitimide (PPMI). Benzene-1,2,4,5-tetracarboxylic dianhydride (349.0 mg, 1.6 mmol) and (aminomethyl)-phosphonic acid (563.2 mg, 3.2 mmol) were refluxed in dimethylformamide (35.0 mL) at 110°C for 28 hours. The resulting white solid product (714.9 mg) was isolated by removing the solvent. The residue was washed with 30.0 mL of deionized water and 20.0 mL of cold ethanol. Thereafter, the product was dissolved in 80.0 mL of deionized water using 4.0 mL of 0.20 M NaOH while stirring on a hot plate. The solution was placed in a desiccator with concentrated HCl for 2 weeks. The final product was a white crystal-like solid with a yield of 225.9 mg.

Alternatively, the synthesis can be performed with imidazole (1.00 g) as solvent. The reflux was performed under nitrogen gas in a paraffin oil bath at 130°C for 30 minutes. The product was washed with 30.0 mL of a mixture of 2 M HCl and Ethanol solution (1:1 ratio), and had a crude yield of 294.4 mg. After drying for a day, it was dissolved in 40.0 mL deionized water using 3.0 mL of 0.2 M NaOH, and the solution was placed in a desiccator with concentrated HCl for a week. The product was a crystal-like off-white solid with a yield of 141.9 mg.

N,N´-bis (phosphonomethyl)-3,4,9,10-perylenediimide (PPDI). Perylene-3,4,9,10-tetracarboxlic dianhydride (392.4 mg, 1.0 mmol), (aminomethyl)-phosphonic acid (351.9 mg, 2.0 mmol), and imidazole (2.00 g) were refluxed at ~130°C for 20 min under nitrogen gas in a hot paraffin oil bath. The product was washed with 30 mL of a mixture of 2 M HCl and ethanol solution (1:1 ratio). The solution (dark red) was gravity filtered and washed with an additional 10.0 mL of ethanol. The product was allowed to dry in an oven and the crude yield was 765.0 mg. The crude product was dissolved in 400.0 mL of water using 0.2 M NaOH to bring the pH to 9.5. Afterwards, the solution was filtered twice, and then 2 M HCl was added to bring the solution to a pH of ~1.5 according to the procedure recorded in the literature.[3, 12] Finally, the product was filtered and dried to give off a burgundy chromatic color with a yield of 111.8 mg.

N,N´-bis (phosphonomethyl)-1,4,5,8-naphthalenediimide (PNDI). 1,4,5,8-Naphthalenetetracarboxylic dianhydride (217.7 mg, 0.80 mmol), (aminomethyl)-phosphonic acid (281.2 mg, 1.6 mmol), and imidazole (1.01 g) were refluxed at ~130°C for 30 min (the temperature fluctuated between 117°C and 148°C). A dark brown precipitate product was isolated. The sample was allowed to cool to room temperature for 3 hours. Thereafter, the solid was washed with 30.0 mL of an ethanol and 2 M HCl solution (1:1 ratio). After drying in an oven, the yield of the crude product was 332.9 mg. The re-crystallization of the crude product was done by dissolving in 50.0 mL of deionized water using 4.0 mL of 0.20 M NaOH. The mixture was stirred and warmed on a hot plate until the compound completely dissolved. Afterwards, it was re-crystallized in a desiccator with concentrated HCl for 3 days. The final product precipitated and was gravity filtered. The result was a bronzy solid with a 242.8 mg yield. The synthesis was scaled-up by doubling the amount of starting reactants and resulted in a 459.5 mg yield.

N,N´-bis(phosphonomethyl)-3,3′,4,4′-Biphenyltetracarboxyl (PBDI). 3,3’,4,4’-Biphenyltetracarboxylic dianhydride (441.3 mg, 1.5 mmol) and (aminomethyl)-phosphonic acid (527.9 mg, 3.0 mmol) was refluxed in 40.0 mL dimethylformamide under liquefied N_2 at ~120°C for 24 hours. The product was gravity filtered and washed with 20.0 mL of cold ethanol. It was dried over 2 days in an oven at 100°C. The crude product was dissolved in 120.0 mL deionized water and 7.0 mL of 0.20 M NaOH. The solution was placed in a desiccator with concentrated HCl for 2 days. The re-crystallized solid was washed with 15.0 mL of cold water, then with 15.0 mL of a mixture of cold ethanol and deionized water solutions (1:1 ratio), and lastly with cold ethanol. The product was a white solid with a yield of 497.3 mg.

An alternative synthetic procedure was performed with a scale-up reactants. 3,3’,4,4’-Biphenyltetracarboxylic dianhydride (588.6 mg, 2.0 mmol), (aminomethyl)-phosphonic acid (704.1 mg, 4.0 mmol), and imidazole (2.00 g). The reactants were refluxed under liquefied nitrogen gas in a paraffin oil bath at 130°C. Since the reaction failed to start, 20.0 mL of dimethylformamide was added after 30 minutes. The product was washed with 20 mL of cold ethanol and gravity filtered. The crude yield was 1.10 g. After drying for 2 days in an oven, the product was mixed with 100 mL of deionized water and 4.0 mL of 0.2 M NaOH. Afterwards, the solution was placed in a desiccator with concentrated HCl for a week. After re-crystalized product was filtered and washed with 10.0 mL of cold water, followed by 10.0 mL of cold ethanol. The product was a white solid with a yield of 431.9 mg.

Figure 2. Set-up diagram for the refluxing apparatus.

MOFs Synthesis: The MOFs were prepared under hydrothermal conditions with the phosphonate-based diimide ligands, metal salts, sodium hydroxide, and hydrofluoric acid as a mineralizing agent in an autoclave for a week. The samples were kept at 100°C for 2 days, then they were subsequently cooled down for 3 days from 100°C to 80°C, 60°C, and lastly 20 °C.

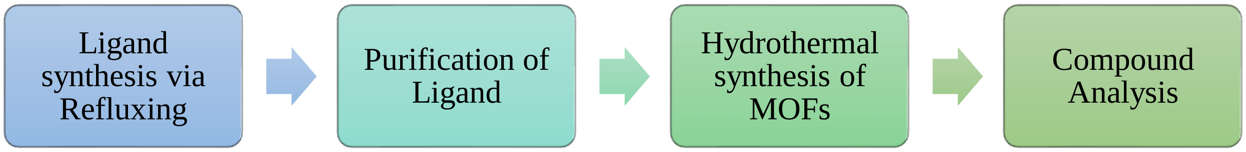


Figure 3. Schematic diagram for MOFs synthesis and analysis.

CHAPTER 3: RESULTS AND DISCUSSION

PNDI showed an average yield of 0.45 g, PPMI had a mean yield of 0.25 g, PBDI had a yield of approx. 0.45 g, and PPDI of 0.12 g, making it the lowest. Contrary to our predictions, the yield of the re-crystallized product was seen to be higher for ligands refluxed with dimethylformamide than for those refluxed with imidazole. However, dimethylformamide is limited to use in smaller molecules, as it is not an adequate solvent for molecules like PNDI and PPDI which have larger aromatic rings. Furthermore, PPDI had a very low recovery rate. Immediately after re-crystallization, the volume of PPDI increased immensely and gained a foam-like morphology. However, once left to dry in the oven the product decreased greatly.

PNDI showed visual inconsistencies in a couple of synthesis. Some samples were more copper tone while others more bronze, nonetheless, the analyses performed supported the chemical structures being the same. These variations may be due to contaminants or side products that may have remained in the product. Similarly, PPMI synthesized with dimethylformamide was a slightly brighter white color than PPMI synthesized with imidazole. Further purifications could be carried out to ensure no other substance is present.

Results of ^{1}H NMR and ^{13}C-NMR for PNDI were inconsistent with the expected chemical structure (Figure 4). However, the X-ray crystallographic structure (see Figure 13) confirmed that the phosphonic acid and the dianhydride precursors were fully imidized. The ^{13}C-NMR showed symmetry and possible overlap due to the benzene rings, but the ^{1}H NMR indicated there were more hydrogen molecules than expected. Therefore, it is possible that either the sample was contaminated or that the signals came from the solvent chosen. For instance, the imidazole molecule co-crystallized with the PNDI crystal in Figure 13(a).

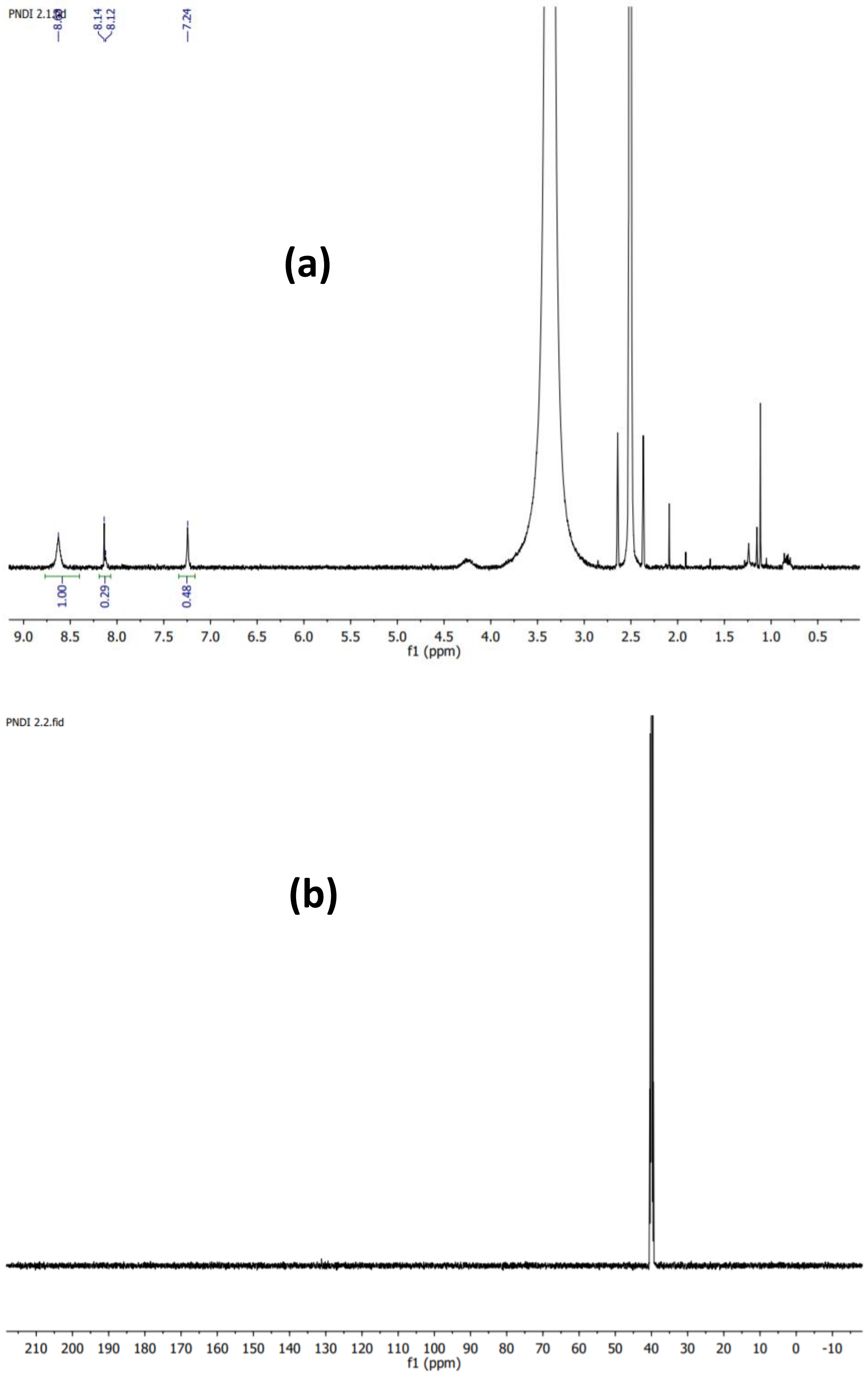


Figure 4. ^{1}H NMR (b) and ^{13}C-NMR (a) for PNDI

Figure 5 of the ^{1}H NMR and ^{13}C-NMR for PPMI supports the proposed chemical structure. The ^{13}C-NMR had an expression of three signals corresponding to the three different types of bonding carbon is present in the molecule. Similarly, the ^{1}H NMR showed that the proton signals correspond to peaks expected for PPMI. Furthermore, X-Ray crystallographic structure of the PPMI molecule confirmed its chemical structure, as shown in Figure 14.

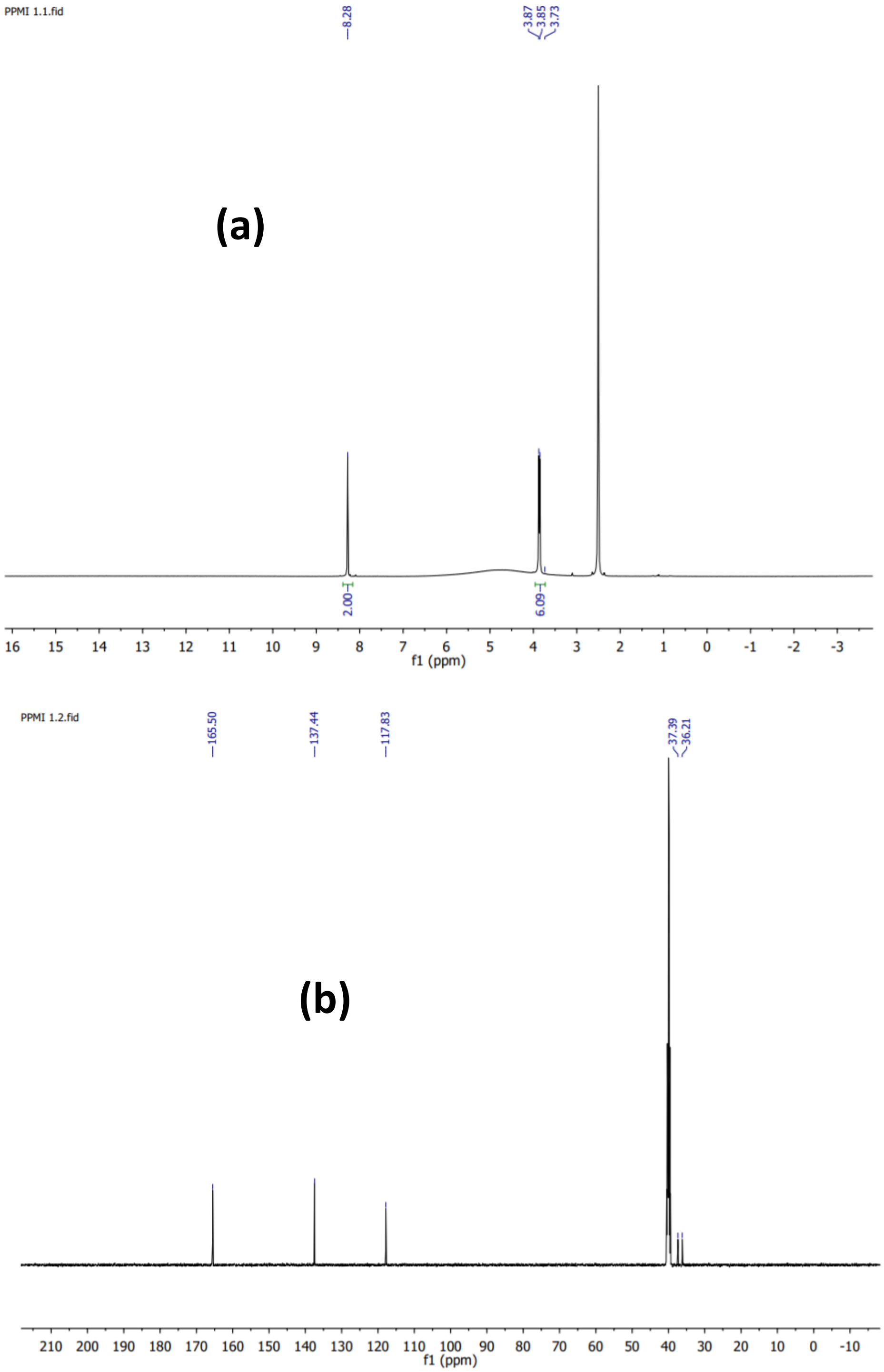


Figure 5. ^{1}H NMR (a) and ^{13}C-NMR (b) for PPMI

Unfortunately, results for PBDI were not clear and there is a suspicion of both contaminants and/or unsuccessful synthesis. Although, the ^{1}H NMR shown in Figure 6(a) did not contain as much noise signals, the peaks did not match the expected imide structure. As can be seen in Figure 6(b), the ^{13}C-NMR for PBDI had plenty of noise and significant solvent traces. Such problems made it difficult to recognize the chemical structure of the compound synthesized. In the future this compound could be further purified and dried for a longer period of time to eliminate traces of contaminants. The synthesis could also be repeated, and the method revised to obtain better results.

PPDI was not analyzed via ^{13}C-NMR or ^{1}H NMR because the compound had not been purified nor dried when samples were taken. A sample of PPDI could be prepared and analyzed in the future but the method should still be revised since it had poor yield and inconsistent results over multiple syntheses rounds.

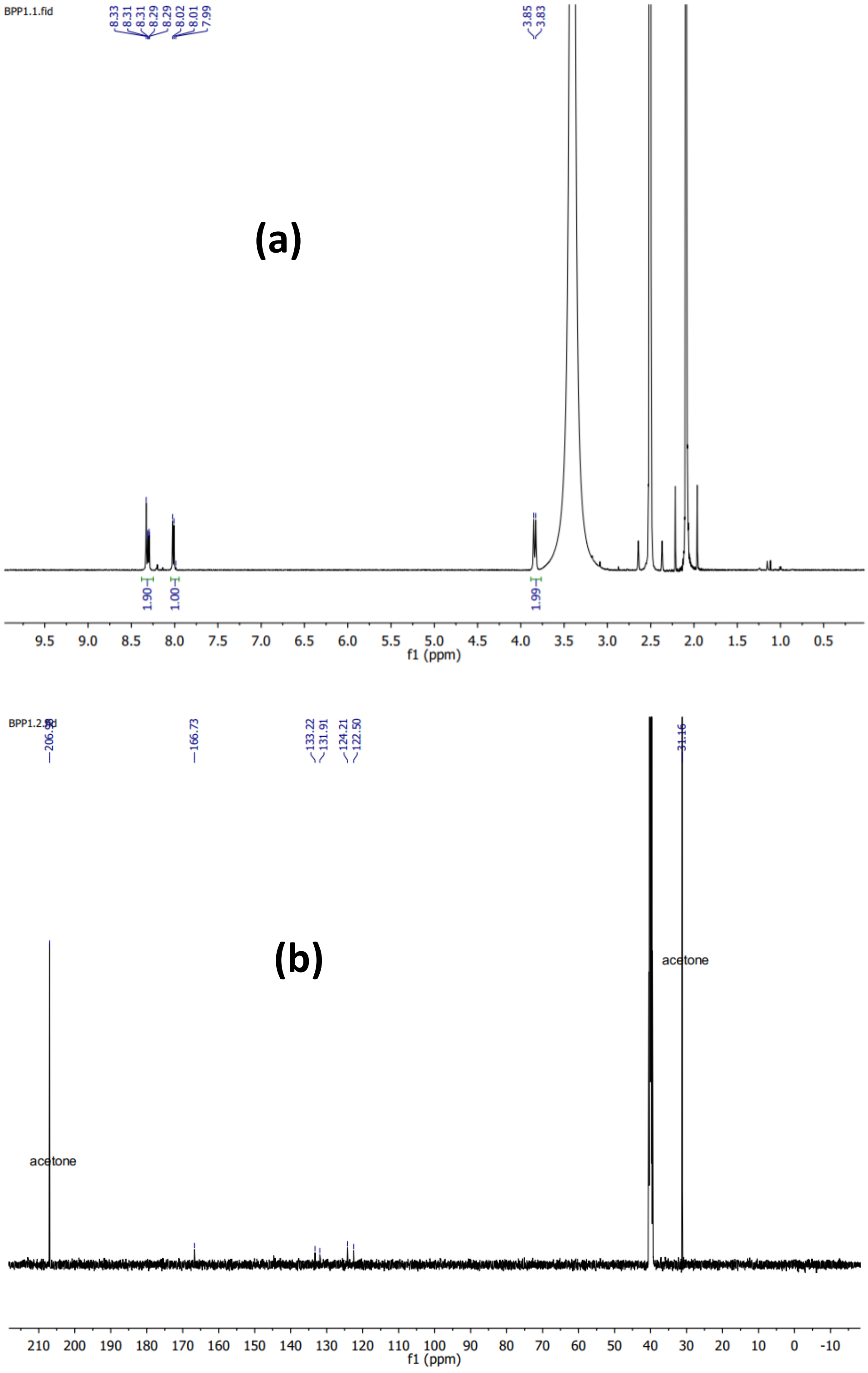


Figure 6. ^{1}H NMR (a) and ^{13}C-NMR (b) for PBDI

IR Spectroscopy results for PPMI (Figure 7), support the proposed structure. The IR showed signs of benzene around 1600 cm^{-1}, as well as nitrogen at 1250 cm^{-1}. There are also signs of a carbonyl group around 1750 cm^{-1}. However, traces of water molecules were also observed at about 3500 cm^{-1}. The compound's IR was taken days later after drying but the spectrum remained the same.

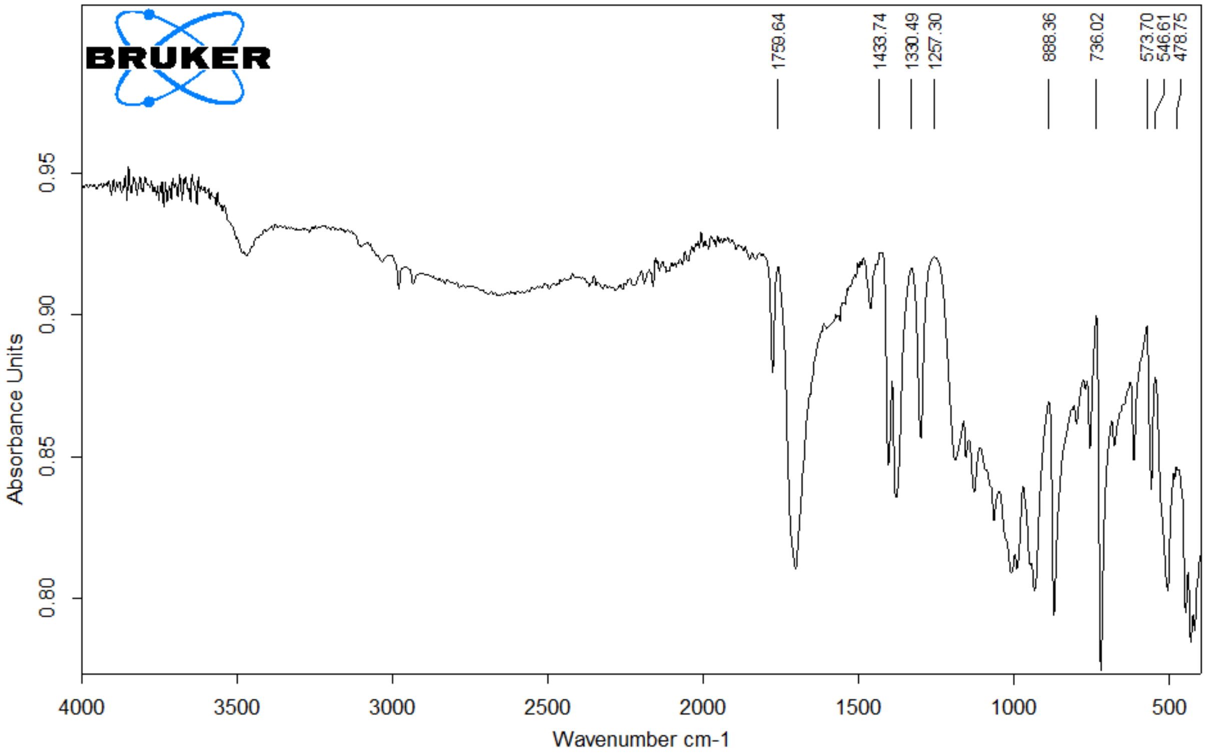


Figure 7. IR Spectroscopy of PPMI

PBDI's IR spectroscopy analysis (Figure 8) indicated the presence of benzene with peaks around 1600 and 1500 cm^{-1}, as well as a carbonyl group with a peak around 1740 cm^{-1}. However, the efficiency of the addition of phosphonic groups to the dianhydride remains unknown and requires further analysis. As previously mentioned, there might be a need for re-crystallization of the compound to discern impurities.

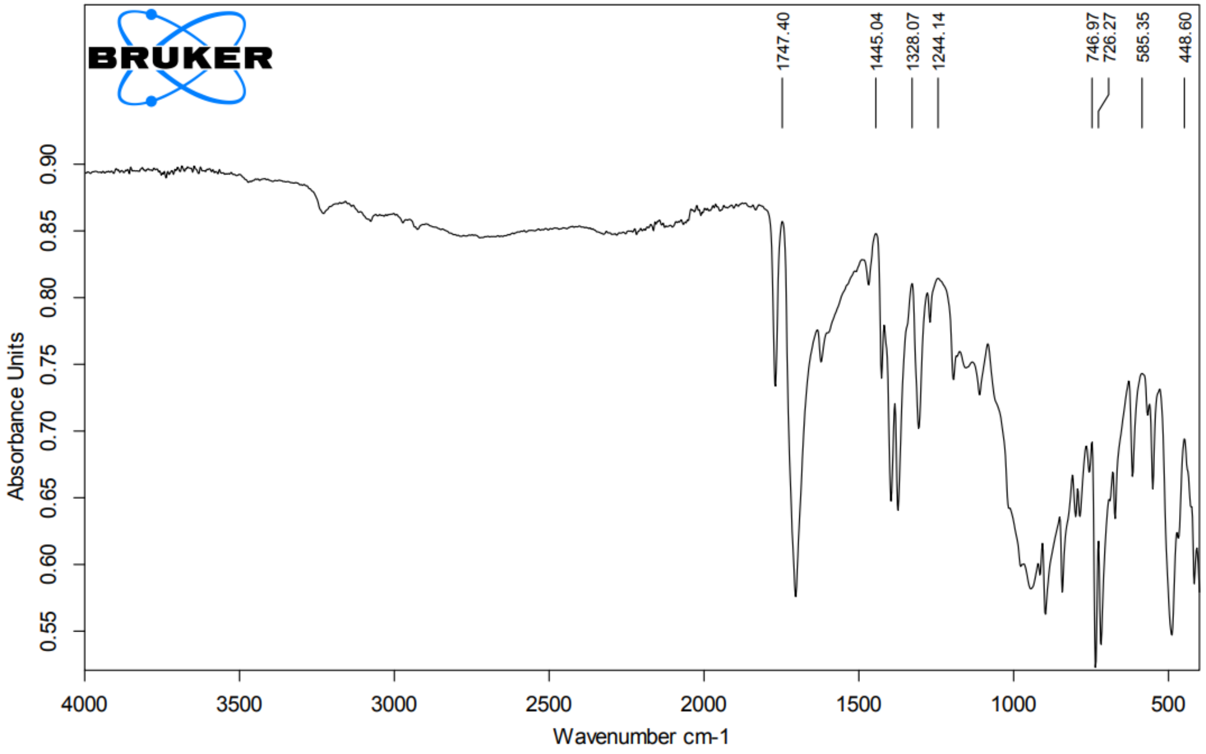


Figure 8. IR Spectroscopy of PBDI

The IR Spectroscopy of PPDI (Figure 9) had a significant presence of noise and was difficult to interpret. Different samples from different batches of syntheses were collected and analyzed and they all gave inconclusive and even inconsistent results. Although there are strong signals at around 1600 and 1500 cm^{-1}, which indicates the presence of benzene. The regions outside of the fingerprint mostly suggest the presence of alcohol or water. Even when the samples were dried for days, the data remained unreliable. Additionally, without NMR analysis and an inconclusive IR, there was no conclusively evidence that I synthesized the target compound. Perhaps X-ray diffraction measurement could provide better information. Nevertheless, we need to modify the procedure since the yield was poor thus making the current procedure to be wasteful and very labor intensive.

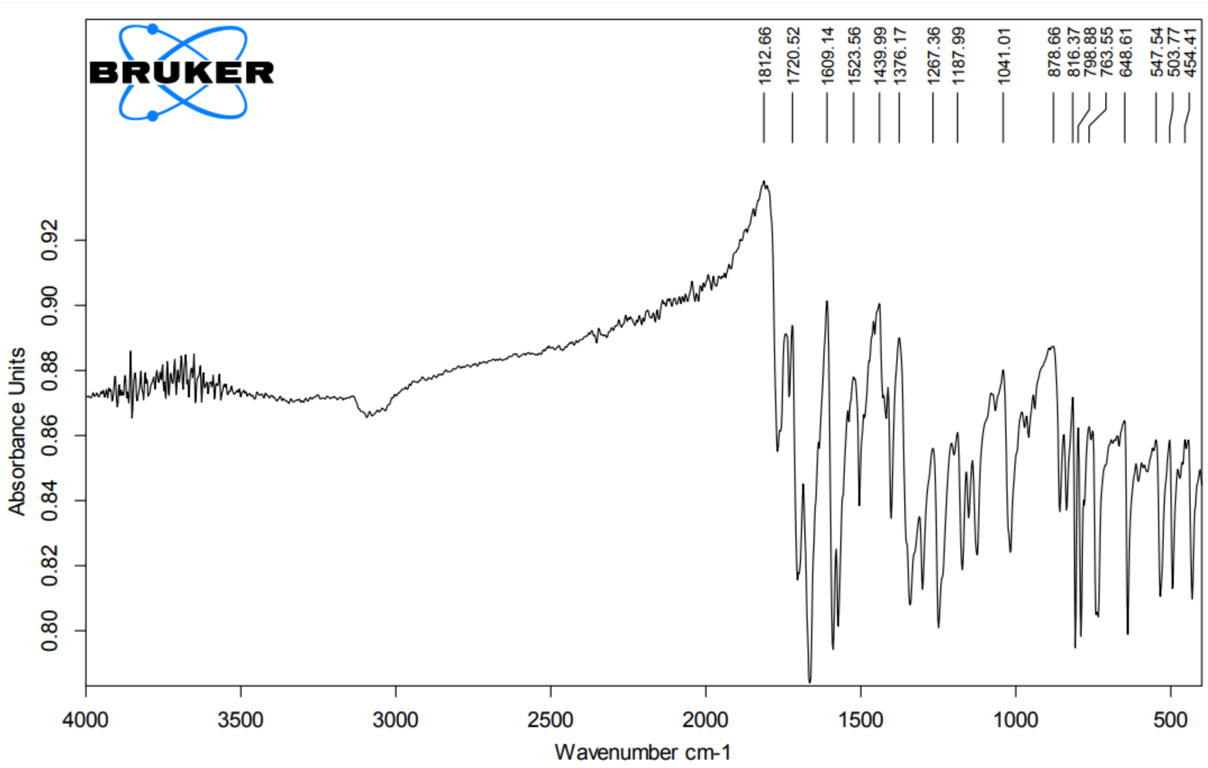


Figure 9. IR Spectroscopy of PPDI

Figure 10 demonstrates the presence of benzene with peaks around 1680 and 1590 cm^{-1}. A signal around 1740 cm^{-1} indicates that there is a carbonyl group and around 1250 there are signs of a carbon-nitrogen bond. Such signals support the proposed structure for PNDI, though there might be some water in the compound as was seen with other molecules.

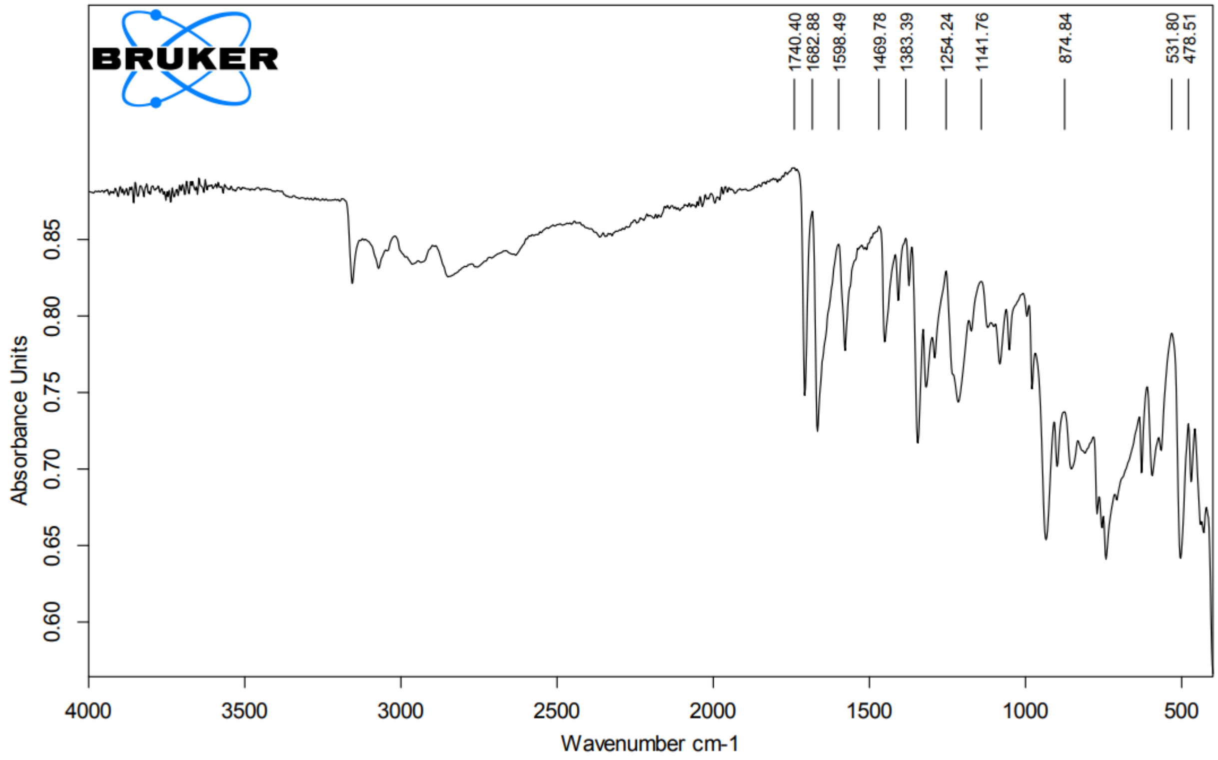


Figure 10. IR Spectroscopy of PNDI

The absorbance spectrum of PNDI (Figure 11) had maximum absorption wavelengths at 343.20 nm, 362.00 nm, and 383.20 nm in agreement with the spectrum reported in the literature.[11] All of these values fall within the ultraviolet light region and not in the visible spectrum. Furthermore, these wavelengths would be useful in detecting PNDI concentrations for quantification since they would give the highest absorptivity values, and therefore magnify absorbance signals and experimental accuracy.

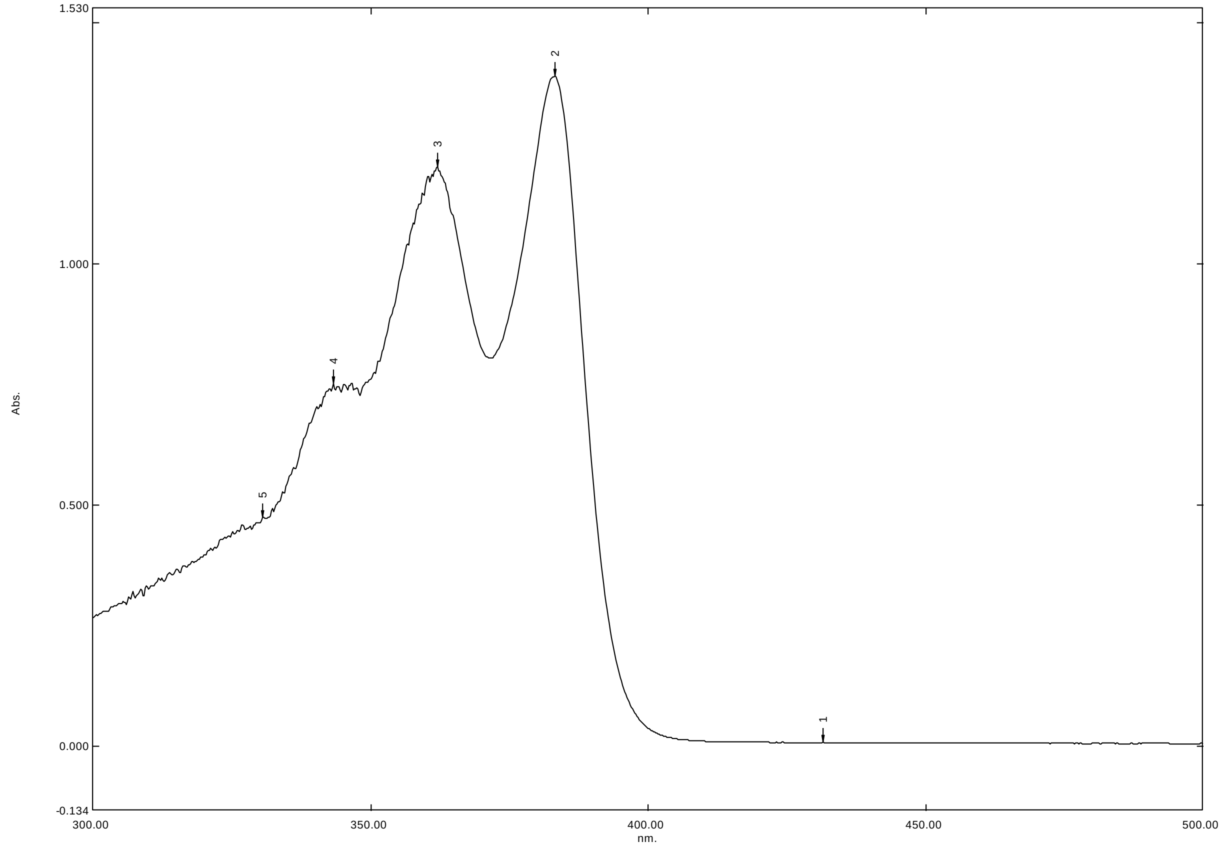


Figure 11. PNDI UV Absorbance Spectrum

As shown in Figure 12, unlike the PNDI, the PPDI spectrum revealed light absorption in the visible light region. The maximum wavelengths observed were at 494.00 and 523.00 nm. Such wavelengths correspond with the colors cyan and green, meaning that the compound absorbed such light colors and reflected the complimentary ones. In this case, the complimentary colors are violet and red, which is consistent with the tone-shifting burgundy color observed. Cited references have also encountered similar absorbance spectrums when analyzing both PNDI and PPDI.[11]

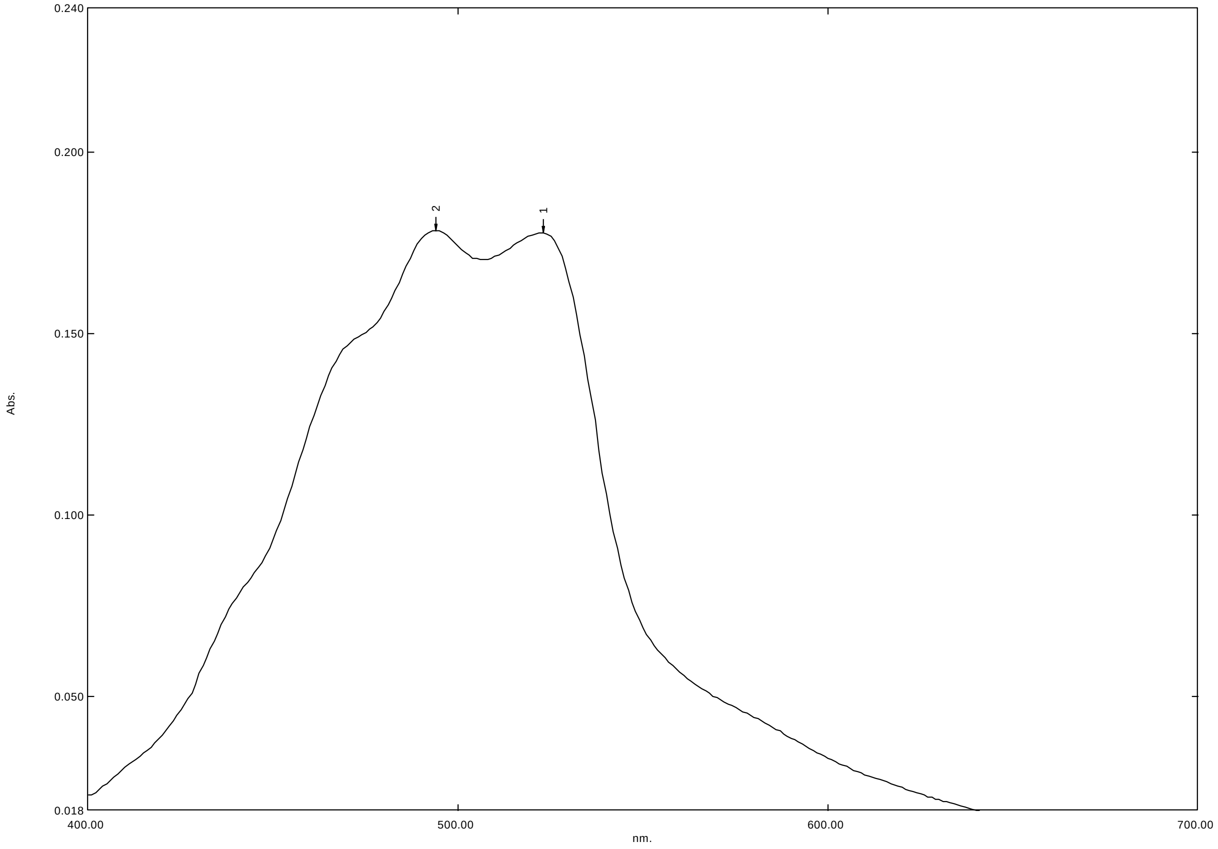


Figure 12. PPDI UV-Vis Absorbance Spectrum

Recent X-ray crystallography data for PNDI and PPMI (Figure 13 and 14) confirm the proposed synthesis of addition of a phosphonic group to the naphthalene-1,4,5,8-tetracarboxylic dianhydride and pyromellitic dianhydride. There is also a presence of water molecules which supports the initial hypothesis that addition of the phosphonic group increased water solubility of the ligands. While MPC data has not been collected, the confirmation of PNDI and PPMI's structure will be of much value when designing and analyzing the complexes. Furthermore, these properties will now be able to be explored.

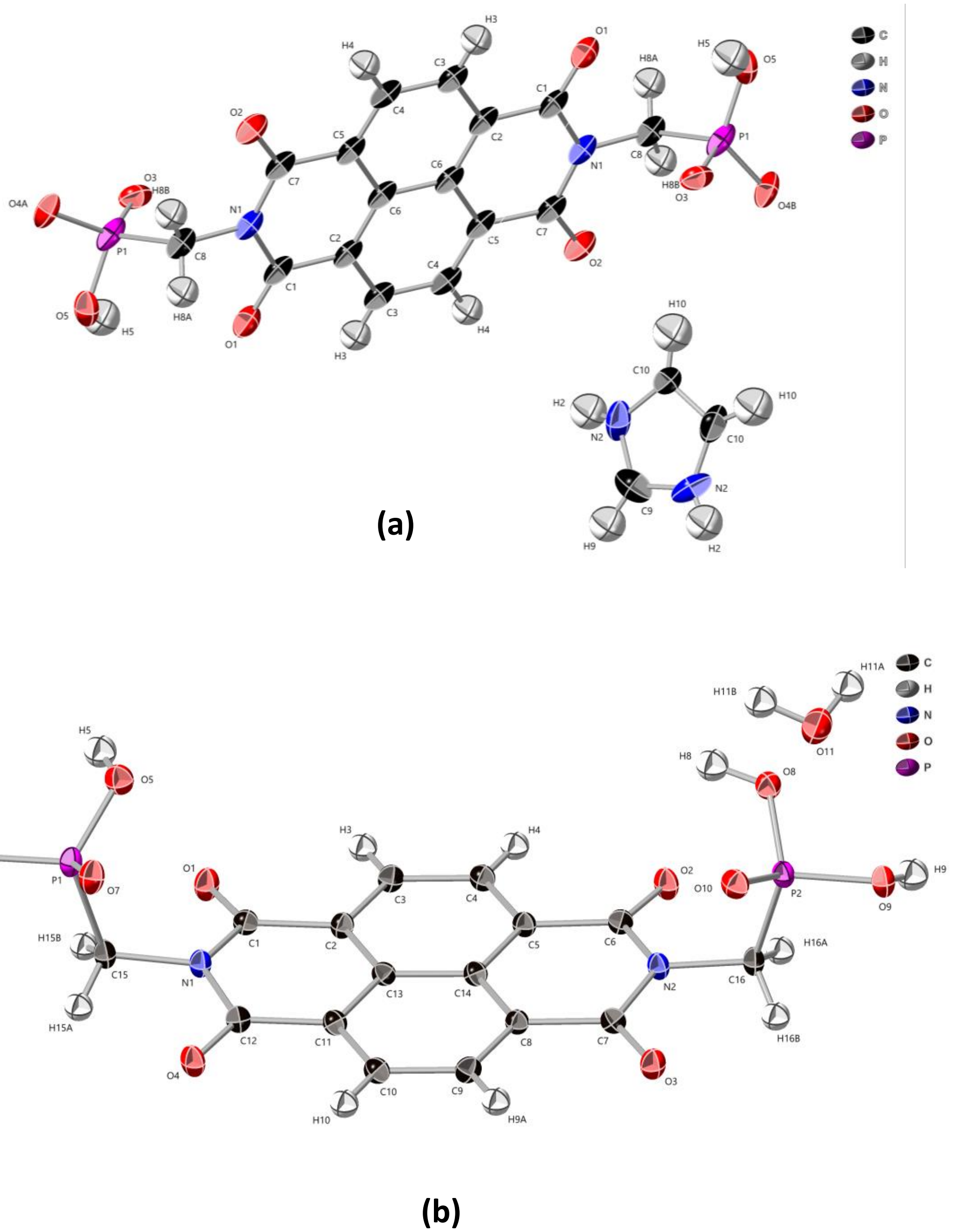


Figure 13. The molecular structure of N,N´-bis (phosphonomethyl)-1,4,5,8-naphthalenediimide (PNDI) with and without imidazole. Thermal ellipsoid are drawn at 50% probability level.

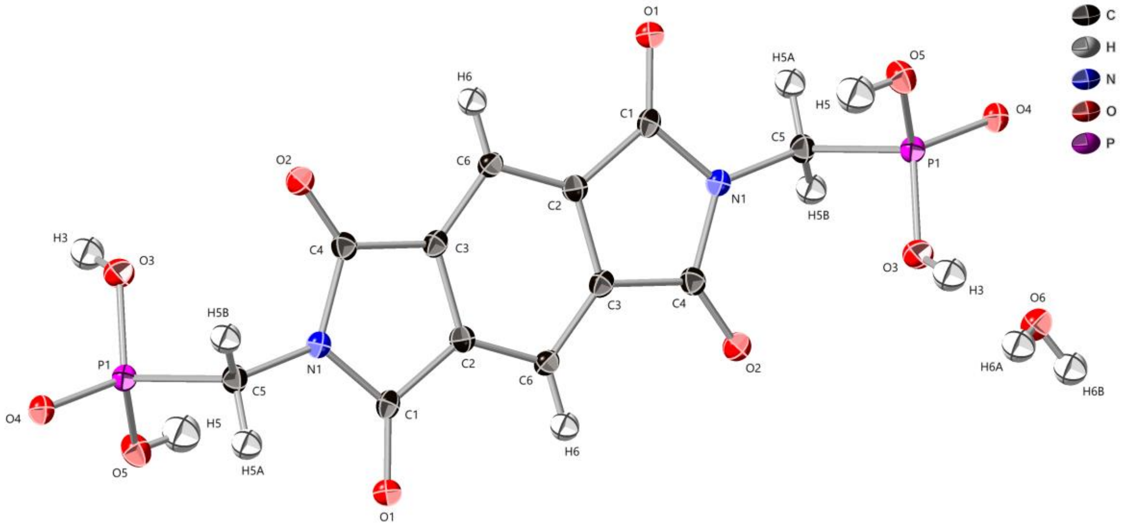


Figure 14. The molecular structure of N,N´-bis (phosphonomethyl)-pyromellitimide (PPMI). Thermal ellipsoid are drawn at 50% probability level.

CHAPTER 4: CONCLUSION

The results of the NMR, IR spectroscopy, absorbance and X-ray diffraction studies corroborate the successful design of the PPMI and PNDI ligands. PPMI and PNDI showed patterns of high crystallinity which encouraged subsequent synthesis, and is currently being explored for the design of phosphonate-based MOFs. PPDI will require further work in both method development, re-crystallization and characterization. The smaller aromatic diimide complex, PPMI, is more favorable in growing suitable crystals for X-ray analysis. The PNDI and PPDI molecules have larger rigid phenyl rings and are more promising for building MOFs. Future research efforts will focus on the spectroscopic characterization of the compounds and their use in investigating proton conduction in MOFs.

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