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Synthesis and Review of Polymer Structures Ranging from 1D to 3D

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## ABSTRACT

In today's industrial world, polymers can be considered one of the most prevalent materials. Most of polymers fall under three structure categories, ranging from one dimensional (1D) to three dimensional (3D), resulting from the growth direction of the monomer and/or overall assembly of the polymer within a given environment (i.e., solvent). This thesis works to synthesize and also review different types of polymers that fall within these structural categories. Within the 1D category, the focus will be on the controlling the backbone with sequence precision. The reviewed methods include iterative synthesis for forming oligomers with controlled sequence, electronic influenced donor-acceptor copolymer synthesis using Kumada catalyst transfer polymerization, and both electronically governed and sterically influenced sequence-controlled copolymers using ROMP. In the 2D category, a triarylpyrylium photocatalyst that could be incorporated into covalent-organic frameworks was investigated and designed; however, the final product was not synthesized as planned. While a different route of converting the TPT unit into katritzky unit was developed, the research was not completed owing to limited access during the COVID-19 pandemic. Toward 3D structures, a polymer that incorporated **C4P** and dye complex that is capable of sensing and capturing anion was synthesized and the anion binding affinity was investigated. The final anion (fluoride ion) binding affinity for the polymer was  $1.8 \times 10^4 \text{ M}^{-1}$ , which is on par with the small molecule. This research started the foundation for developing structure specific 3D anion capturing polymer network. This summation of this thesis work provides an overall fundamental view for of polymers varying in structure and discusses target applications of each. The overall goal is to provide a fundamental viewpoint of synthetic polymers to the readership.

## TABLE OF CONTENTS

LIST OF FIGURES .....	i
ACKNOWLEDGEMENTS .....	ii
Chapter 1 Introduction .....	1
1.1 Polymer Background .....	1
1.2 Structure Specific Polymers and Applications .....	2
1.3 Introduction to Small Molecules of Interest .....	4
1.4 Thesis Overview .....	6
Chapter 2 Sequence Control on Donor-Acceptor Conjugated Polymer .....	7
2.1 Sequence Control Introduction .....	7
2.2 Sequence Control in Polymers.....	8
2.3 Multistep-Synthesis-Driven Sequence.....	9
2.4 Catalyst-Dictated Sequence Control.....	11
2.5 Electronically Governed Sequence Control.....	12
Conclusion .....	13
Chapter 3 Covalent Organic Framework .....	15
3.1 Introduction.....	15
3.2 Experimental.....	17
3.3 Review and Discussion.....	18
Conclusion .....	23
Chapter 4 Calix [4] Pyrrole Polymer .....	25
Introduction.....	25
Review and Discussion.....	26
Conclusion .....	28
Chapter 5 Final Remark .....	30
Overall Conclusion .....	30
Appendix A NMR Spectrum .....	31

**LIST OF FIGURES**

Figure 1. Unsymmetrical D-A Cyclophanediene.....	4
Figure 2. 2,4,6-triphenylpyrylium (TPT) Salt Photocatalyst .....	5
Figure 3. Calix[4]Pyrrole .....	5
Figure 4. Route to obtain sequence-controlled conjugated oligomers and polymers ..	8
Figure 5. Iterative Synthesis of Conjugated D–A Oligomers with Controlled Sequence	10
Figure 6. Donor-Acceptor Copolymer Synthesis Using KCTP.....	11
Figure 7. Schematic Depicting Design for Donor-Acceptor Sequenced Polymer.....	12
Figure 8. Synthesis of MEH-BT pCpd isomers .....	13
Figure 9. COFs Building Blocks and Their Corresponding Architecture. ....	15
Figure 10. TPT Catalytic Cycle .....	16
Figure 11. TPT Photocatalyst Synthesis .....	18
Figure 12. Suzuki Coupling Synthesis Probing .....	19
Figure 13. Prep-TLC of Suzuki Coupling with TPT Salt .....	20
Figure 14. One Step TPT COF Synthetic Scheme.....	21
Figure 15. Katritzky Salt Formation .....	22
Figure 16. Addition of Functional Group to the katritzky Salt.....	23
Figure 17. C4P Monomer Synthesis Route .....	26
Figure 18. C4P Polymer Formation .....	27
Figure 19. Fluorescence spectra of C4P (Left) and UV/Vis spectrum (Right) of C4P27	
Figure 20. UV/Vis Titration of C4P Polymer.....	28

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## Chapter 1 Introduction

### 1.1 Polymer Background

A polymer is defined as a macromolecule consisting of small repeating units, usually possessing high molecular weight. The two major categories of polymer include natural polymers and synthetic polymers both of which are now prevalent in our daily life. Some of the major polymer applications include biomedical materials applications (e.g., drug delivery, biosensor devices and implantable and wearable sensors<sup>1,2</sup>), industrial materials applications (e.g., lubricant additives for better performance<sup>3</sup>), and consumer applications such as biodegradable packaging materials.<sup>4</sup> Scientists have been investigating each of these unique properties and are on the path of perfecting the products. Some of the unique properties includes high strength, light weight, resistance to corrosion, lack of conductivity, and low cost.<sup>5</sup> Many of the properties arise from the polymer structure and the nature of the repeating units. The two main parts of a polymer system are the backbone chain and side chain. The backbone of the polymer dictates the primary structure of the macromolecule, forming from the repeating units covalently bonding together. The chain can be bi-directionally or tri-directionally grown (or even higher than that, pending monomer units), which results in different global structure. The different polymer growth directions lead to linear or network structure. Changing the covalently-linked backbone often results in different mechanical properties. Such properties include tensile strength and compressive properties.<sup>6</sup> The side chain often depends on target functions, as the decoration can be specific to application. By changing the side chain functional group, different polymer functional properties can be selectively chosen to fit for the application. The selectivity allows versatile (and modular) application seen in

modern polymer science, such as side chain variation leading to mechanical strength difference for 3D printing,<sup>7</sup> electronic structure difference in conjugated polymer,<sup>8</sup> and hole mobility difference in polymer semiconductors.<sup>9</sup>

## 1.2 Structure Specific Polymers and Applications

Polymer structure can be categorized into three groups: one dimensional (1D), two dimensional (2D) and three dimensional (3D). Each group can also be divided into multiple subgroups. Within the 1D structure, there are linear polymers with no molecule decoration and branched polymers that carries specific functional groups. When the functional group possess the ability to form covalent bond with nearby polymer side chains, the polymer can be extended to 2D direction and form a sheet-like network. This 2D structure can also be formed during the polymerization steps, when two or more monomers contain multiple reaction sites. The process allows the polymer to become a covalent bonded network. Using a 1D structure with functionalized side chains, it can also form covalent or noncovalent bonds with itself, resulting in a confined 3D structure.

Many polymer applications currently are utilizing the 1D structure and its side chain to apply functionality to the final material. Specific modification usually performed on the backbone and the side chain. Much research has been conducted to mimic nature's biological system, synthesizing a sequence defined polymer backbone.<sup>9,10</sup> The main difficulty arises from enforcing atomic level of precision during polymerization. In a later chapter, a few methods for synthesizing sequence defined polymer, including stepwise iterative synthesis techniques and step-growth

methods will be compared and a new method using ring-opening metathesis polymerization will be introduced.<sup>11</sup>

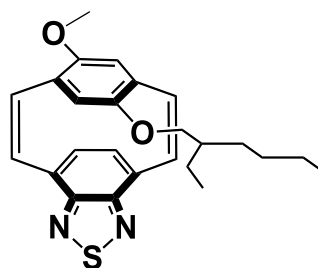
In addition to the 1D backbone design, 2D polymeric sheets are among popular research topics. The 2D sheet can be formed through either crosslinking of a 1D polymer chain (this can also lead to higher dimensionality, pending polymer structure) or two comonomers with at least three reaction sites. The two forms of the polymer sheet can yield to two different products: polymer networks derived from polymer chain crosslinking and covalent organic framework (COFs). Most of polymer network syntheses involves simultaneous polymerization and leads to poorly controlled structure.<sup>12</sup> On the other hand, employing different methods and building blocks COFs, more well-defined structure with high crystallinity, have been reported;<sup>13</sup> further methods to form functional COFs were investigated in this thesis. The research herein also investigated the possibility of incorporating multifunctionality into the framework, borrowing ideas from 1D polymer side chain decorations.

Building on the simple 1D polymer, functionalities have been added to the polymer material through modification on the side chain.<sup>71</sup> Using multiple comonomers with different functional pedants during the polymerization process expands utilities of the previous polymer material. The side chain also possesses the ability to form covalent bond with each other. When the polymers formed intermolecular linkage, it becomes a 2D sheet; when one polymer strand forms intramolecular linkages within the strand, the polymer will start to fold onto a specific shape, thus achieving a 3D network. This folding process is similar protein folding and presents the potential on create synthetic protein mimicking material.<sup>72</sup> One such example of a material is a single-chain polymer nanoparticle (SCNP).



The polymer nanoparticle involves using single polymer chains, to mimic the folding of biomolecules in structure.<sup>14</sup> Such polymer chain undergoes intra-chain cross-linking. The intra-chain cross-linking is promoted by dilute solution condition that minimizes specific interactions between each polymer chain and maximizes chain-solvent and intra-chain interactions.<sup>15</sup> This type of 3D structure is prevalent in nature (i.e., as enzymes), where many of the SCNPs take inspiration from. The specific folding pattern enables the possibility for more efficient catalytic result, like the protein enzymatic mechanism. Many applications utilize the folded structure for building nanoreactor,<sup>16</sup> green chemistry application with dynamic covalent bond.<sup>17</sup> These applications use co-monomers to add the functionality into the folded system, allow the modular modification. The potential of this category of material is high.

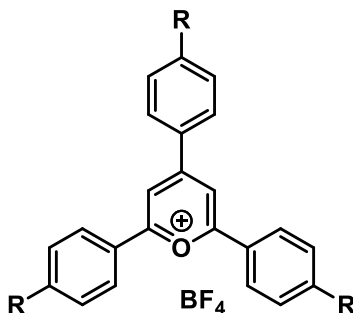
### 1.3 Introduction to Small Molecules of Interest



**Figure 1.** Unsymmetrical D-A Cyclophanediene

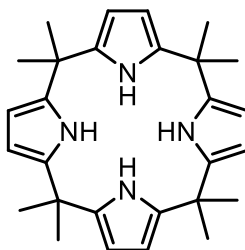
All the polymers mentioned above formed from small monomers, and there are a few critical monomers and functional small molecules to be mentioned in this thesis, including unsymmetrical donor acceptor cyclophane for sequence control polymerization,<sup>11,18</sup> pyrylium photocatalyst for 2D COFs synthesis, C4Ps for anion sensing polymer. In **figure 1**, the monomer synthesized by the Elacqua group, is used in synthesizing sequence controlled electronic donor and acceptor polymers.<sup>18</sup> The reactive alkene formed from organic electronic donor and acceptor

building block also possess the functional group that allows the specific polymerization method to be steric and electronic directed.



**Figure 2.** 2,4,6-triphenylpyrylium (TPT) Salt Photocatalyst

In **figure 2**, a photoredox catalyst, triphenylpyrylium (TPT) is synthesized through condensation of an aldehyde and ketone. It absorbs in visible light range and is strongly oxidizing in both the singlet and triplet excited states. The R functional group are easily modified by changing the starting material with different functional groups.<sup>21</sup> The targeted TPT salt provides the possibility to participate in forming a polymeric COF network as a tri-functionalized building block.



**Figure 3.** Calix[4]Pyrrole

In **figure 3**, calix[4]pyrrole (C4P), synthesized through pyrrole and aldehyde condensation, is a macrocycle that can participate in host-guest chemistry through its crown shape structure. The positively polarized cavity provides space and interaction with the guest molecules. Through hydrogen bonding provided by the N-H functional group, it possesses the ability to bind

an array of anions, especially fluoride ion.<sup>22</sup> Small molecule studies and modification have been reported with C4Ps,<sup>23</sup> but only few studies exist with it as a polymer side chain decoration.

#### **1.4 Thesis Overview**

Diving into the three polymer structures (e.g., 1D, 2D, and 3D), the thesis will present an overview of each structure and fundamental synthetic designs to reach each. Chapter 2 provides insight on using sequence control polymerization methods of 1D conjugated polymers and is founded on an extensive literature search. Chapter 3 will shift to discussion on synthesizing photocatalyst incorporated 2D COFs. In chapter 4, the investigation will revolve around synthesizing polymers with C4P side chains and their future direction on forming structure defined 3D single chain nanoparticles. The conclusion chapter, chapter 5, summarizes and provides a useful overview that hopefully sparks inspiration for those who wish to invest into the versatile modification methods and applications of synthetic polymers.

## Chapter 2

### Sequence Control on Donor-Acceptor Conjugated Polymer

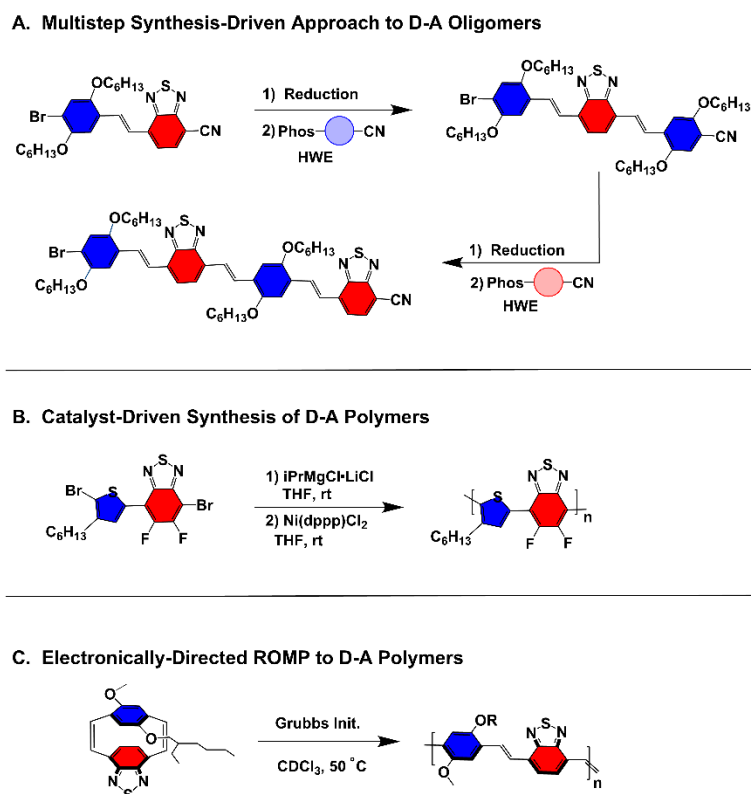
This chapter was compiled during the remote period of the Covid-19 Pandemic, and solely involves literature review and discussion. The work was completed by Stephen Koehler, Dr. Elizabeth Elacqua and me. A corresponding review paper was published on Synlett, and the majority of the content in this chapter is from the paper. The figures in this chapter are adapted with permission from the publisher (Stephen J. Koehler, Jinzhen Hu, and Elizabeth Elacqua, Electronically Governed ROMP: Expanding Sequence Control for Donor-Acceptor Polymers, *Synlett*, **2020**, *31*, 1435-1442; Copyright 2020, Thieme Publishing).<sup>11</sup>

#### 2.1 Sequence Control Introduction

Drawing inspiration from nature, a system that uses seemingly simplistic iterative routes to produce well-defined system with controlled sequence,<sup>24</sup> organic chemists have been wanting to synthesize material that mimic natural material's structure precision.<sup>25</sup> Though many efforts have been applied to compete with nature's ability on sequence-controlled material synthesis, few reached the level of precision as nature. Seeking viable method to apply to the polymer system, scientists started with methods that are capable applying control over small molecules sequence synthesis.<sup>26-30</sup> The main aspect on controlling small molecule reactivity is the combination of both steric and electronic effects. Some other effects also include molecular orbital overlap and orientation, and thermodynamics influence. It is still difficult to translate these small molecule synthesis aspects to polymer sequencing.

## 2.2 Sequence Control in Polymers

The first method to be mentioned in synthesis sequence control is stepwise iterative strategies. They are commonly used in synthesizing small strand of peptides. This method presents high control over the sequence but failed to achieve high molecule weight at reasonable time and cost.<sup>31,32</sup> Step-growth methods are able to yield high molecular weight polymer with certain degree of sequence control (periodically), but the products length usually are not uniformly distributed (high dispersity). The two strategies are still requiring improvement on balancing precise monomer placement and controlled polymerization.



**Figure 4.** Route to obtain sequence-controlled conjugated oligomers and polymers

Recent methods based on chain-growth polymerization have focused on ring-opening metathesis polymerization (ROMP).<sup>33</sup> ROMP uses a strained cycloalkene and driving by the relief of the ring strain. Because of the requirement of a strained cycloalkene, it possesses limitation, but

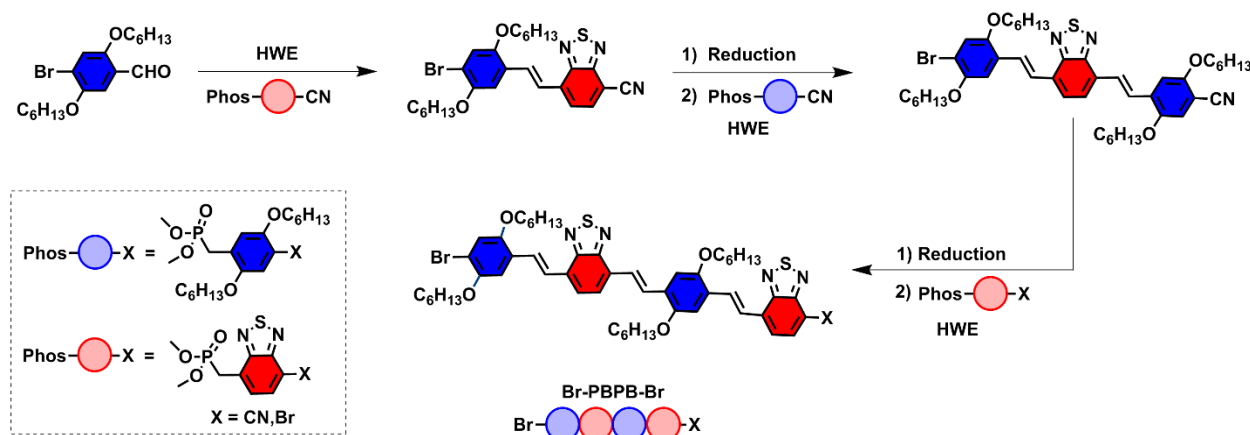
this strain driven polymerization method shows promises in producing sequence-controlled polymers. Much work in the sequence control polymerization features nonconjugated species, and only a few invested sequence controls in conjugated system. The few mainly uses chain-growth methods that affords oligomers and polymer, shown in **Figure 4, A**. Another method was using Kumada catalyst-transfer polymerization, shown in **Figure 4, B**, to yield donor-acceptor sequences, under the chain growth mechanism. And finally, using ROMP, shown in the **Figure 4, C**, vinylene units can be installed into the backbone and form the conjugation. The investigation of linear chain extends the understanding on sequence control for 1D polymer chain.

### 2.3 Multistep-Synthesis-Driven Sequence

The conjugate system usually synthesized via cross-coupling reactions such as Suzuki-Miyaura coupling, Stille, and Kumada polymerization.<sup>34</sup> The iterative synthesis starts from the first monomer units, applies coupling techniques, then isolate the first product. The first product contains a functional group that will be able to be further functionalized with the second sets of monomers, then the second products will be isolated, and the process goes on. This process similar to strand each molecule together and repeat. It provides complete sequence control on the products, but it is time consuming and are not sustainable. The main use of the method was synthesizing sequence specific oligomers,<sup>35-37</sup> and enable the study the effect of altering sequence on conducting and optical properties. The specific order of each monomer unit in the conjugating network presents distinct charge transport path and enhanced the conductance more than tenfold.<sup>40</sup> Further research shows promising properties on electron-rich and electron-deficient aromatic ring system (donor-acceptor frameworks). The precise sequences enable specific molecular orbital overlap for

enhancing material performance, this is also applicable for the HOMO and LUMO energy value.<sup>41,42</sup> One example of achieving precise sequence of oligomer is the synthesis of Donor-Acceptor oligomer, containing 2,5-dihexyloxy-p-phenylenevinylene (P, electronic donor) and benzothiadiazole (B, electronic acceptor), shown in **Figure 5**, done by Meyer and Hutchison.<sup>39</sup>

Furthermore, Meyer and Hutchison were able to incorporate the small strand of sequence specific oligomer into a polymer chain.<sup>38</sup> They observed almost identical absorption and emission

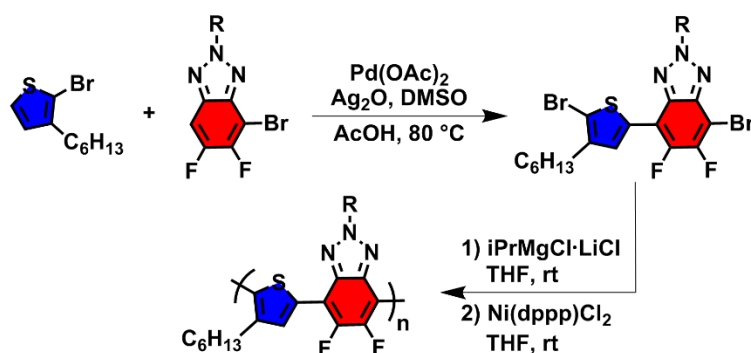


**Figure 5.** Iterative Synthesis of Conjugated D–A Oligomers with Controlled Sequence

for the polymer as the oligomer (with the corresponding monomer unit sequence), but the two oligomer systems show significant different adsorption profile because of the difference in sequence. The polymer systems also show difference in the emission intensity, and present the evidence of the influence of 1D polymer backbone on the material properties. This research presents the methods to extend the unique electronic, optical properties in sequence defined oligomer to a polymeric system, and allows the material to possess both of the properties by the oligomer and the polymer.

## 2.4 Catalyst-Dictated Sequence Control

Many of the cross-coupling based polymerizations present high dispersity and have less power on the polymer sequence.<sup>34</sup> Recent studies applied Kumada catalyst transfer polymerization (KCTP) in the synthesis of conjugated polymers and showed potential for producing well defined conjugated polymer.<sup>43</sup> The low tolerance of the starting material due to the use of Grignard reagents do pose potential limitation on the type of reaction it can perform, but it can still be a power tool after careful monomer design and catalyst selection. A single example of synthesizing donor-acceptor polymer sequence (to date) with well-defined sequence was reported by



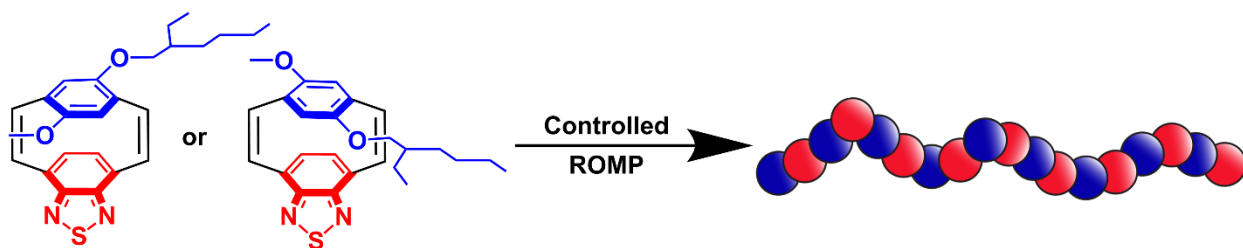
**Figure 6.** Donor-Acceptor Copolymer Synthesis Using KCTP

Bielawski,<sup>44</sup> shown in **Figure 6**. During the catalytic cycle, the magnesium-halogen exchange is more rapid in the electron-deficient system, and lead to selection preference when adding the new monomer, thus achieves sequence alternating with relatively uniform polymer length. This study presents the electronic bias effect on the sequence control using the KCTP method and opens a new pathway on creating preference for the polymer synthesis. Many other methods using varying halogenation,<sup>45</sup> ligand diversification<sup>46</sup> and changing steric hindrance to influence the sequence have also been studied extensively.



## 2.5 Electronically Governed Sequence Control

The KCTP method for synthesizing sequence-controlled polymers opened the door of employing electronic bias for sequence control. Yet, further research that improving the strategy to a more flexible and mild method are few. The existing method has been limited to aryl-aryl connectivity. Recently, the Elacqua group developed a monomer system that incorporated the electronic bias and donor and acceptor moieties for dictating the polymer sequence using ROMP (**Figure 7**).<sup>28</sup> Such system should experience both steric and electronic bias through careful design.

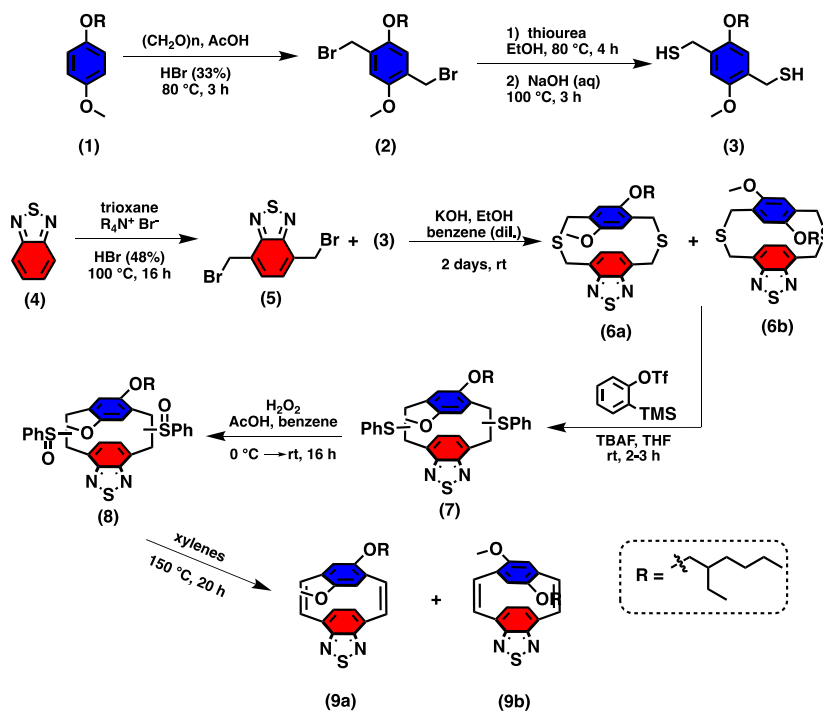


**Figure 7.** Schematic Depicting Design for Donor-Acceptor Sequenced Polymer

The side chain design and the strain within the ring will be able to pose a steric preference, and the donor-acceptor monomer unit will lead to the electronic bias.

Comparing to KCTP, the ROMP provides more flexible condition for installing functional groups, as the ruthenium's relatively high tolerance when comparing to the Grignard reagent. In addition to the new functional group, the addition of the vinylene unit into the polymer can also expand the scope of the conjugated system. The design of the monomer features two parts, the electronically deficient species with sterically hindered olefin subunit, and the electronically activated subunit. The combination of electronically deficiency and the steric hindrance allows the

selective metathesis. Through this design, a preferred catalysis polymerization pathway was then formed. A synthetic scheme is shown in **figure 8**.



**Figure 8.** Synthesis of MEH-BT pCpd isomers

## Conclusion

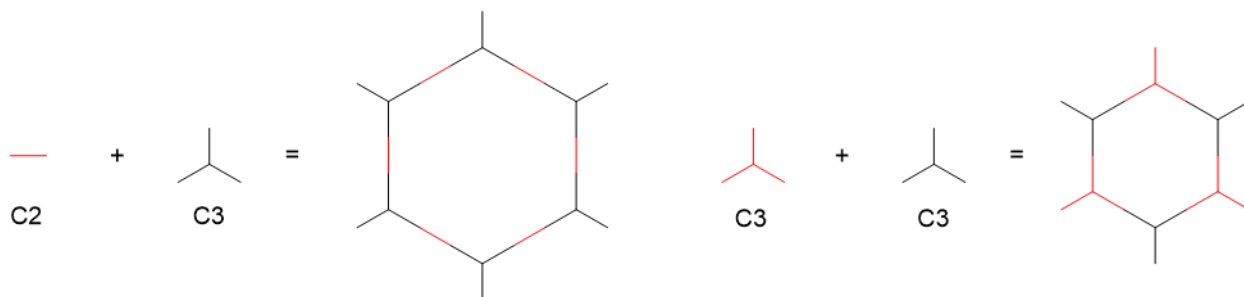
The synthesis of sequence-defined polymers remains a grand challenge in polymer chemistry as scientists try to map macromolecular structure and function in a manner akin to nature. The Elacqua group introduced a ROMP-based methodology to realize well-defined donor acceptor polymers; The monomer is capable of electronically directed cross metathesis and subsequent polymerization. Upon polymerization, the growing chains all demonstrate ‘sequence fidelity,’ as illustrated by NMR spectroscopic measurements in situ that verify the strict D–A alternation. The resultant polymers displayed enhanced (red-shifted) excitation and emission spectra in comparison to ‘sequence-ill-defined’ conjugated polymers from cross-coupling or

polycondensation methods. The research done by the Elacqua group allows for ROMP as a powerful avenue to target electronically diverse and well-defined polymers through a modular design. And this sequence design on the backbone provided new methodology for engineering future 1D polymer.

## Chapter 3 Covalent Organic Framework

### 3.1 Introduction

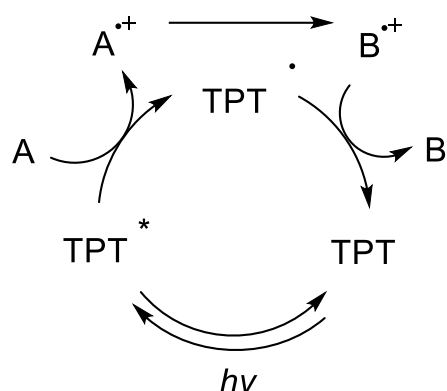
Included in the 2D category of polymeric systems, covalent organic frameworks (COFs) have received increasing attention for yielding lightweight material properties, synthesized from light elements (H, C, N, O).<sup>47</sup> COFs also possess high thermal stability and chemical stability, resulting in stable pore size and crystallinity.<sup>48</sup> In comparison to 1D polymeric materials, COFs are synthesized from building blocks with multiple reactive sites, which results in 2D architectures and even three-dimensions in some cases.<sup>73</sup> The periodic repeating pattern results in an ordered skeletal structure with applications including ion membrane separation,<sup>49</sup> enzyme performance enhancement,<sup>50</sup> novel catalysis frameworks,<sup>51</sup> and as novel capsules for creating microenvironments for enzymes.<sup>52</sup> The versatility in COF building blocks provides various options for tuning properties including the pore size. Common building blocks can be divided into three main categories: C2 elements, C3 elements and C4 elements. Each of these correspond to the number of active sites, two, three, and four. Changing which components are used in COF



**Figure 9.** COFs Building Blocks and Their Corresponding Architecture.

synthesis can allow you to tune the pore size or alter the shape in general.<sup>53</sup> For example, COFs synthesized from C3 and C2 building blocks, or a C3 and C3 combination will form hexagonal architectures as shown in **figure 9**. Using bigger or smaller building blocks can help precisely

design a specified pore size. COF building blocks frequently possess aromatic rings and form a  $\pi$ -conjugated network.<sup>74</sup> This has led to investigations probing the use of COFs in relation to charge transfer as it pertains to applications like semiconductors and catalysis. While COFs have demonstrated the ability to catalyze reactions, no research to date has studied the inclusion intrinsically photocatalytic building blocks into COF frameworks. This research aims to incorporate an organic photocatalyst building block, TPT salt, into COFs. In terms of photoredox



**Figure 10.** TPT Catalytic Cycle

chemistry, the TPT salt has been shown to catalyze cyclobutane formation via alkene dimerization using photoinduced electron transfer methods.<sup>54</sup> TPT first absorbs light, varying in wavelength depending on its substituents, and an electron is promoted to an excited state. The excited electron is then undergoes internal conversion followed by an electron transfer to oxidize the substrate. After a back electron transfer after the desired organic transformation has occurred, the TPT is regenerated (**Figure 10**).<sup>54</sup> Radicals generated on TPT throughout the catalytic cycle are stabilized via many resonance contributors. By changing the substituents, this stability can also be affected and consequently change properties like UV/Vis absorption, oxidation potential, and reaction rate.<sup>54</sup> Because of the fully conjugated network present in most COFs, including a TPT building

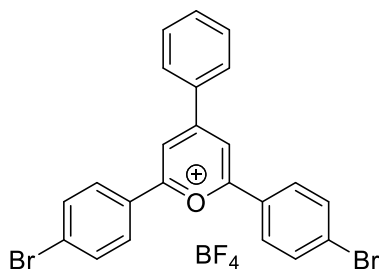
block could still allow for the catalytic cycle to proceed and could further stabilize the generated radicals. This can potentially result a more efficient photocatalytic cycle.

### 3.2 Experimental

#### Brominated 2,4,6-triphenylpyrylium (TPT) General Synthesis Procedure

To 10 ml of dichloromethane, 4-bromo-benzaldehyde (1.74 g, 9.42 mmol) or regular aldehyde and para-bromoacetophenone or regular ketone (4.69 g, 23.6 mmol) were added and dissolved. The reaction mixture was then heated to 50 °C. Boron trifluoride etherate (4.01g, 28.3 mmol) was then added into the reaction mixture at moderate rate. The reaction was allowed to stir overnight. Upon cooling to room temperature, the reaction mixture was added into diethyl ether (200 ml) while stirring. Yellow precipitate formed. The yellow solid was then filtered and dissolved in DCM. The separated solid was added into another diethyl ether ((200 ml). The purified solid was then separated using vacuum filtration and washed with DCM. The solid was left to dry overnight and yield yellow solid (1.13 g, 22%). <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) δ (ppm) 8.04 (m,6H), 8.53 (m, 6H), 9.22 (s, 2H).

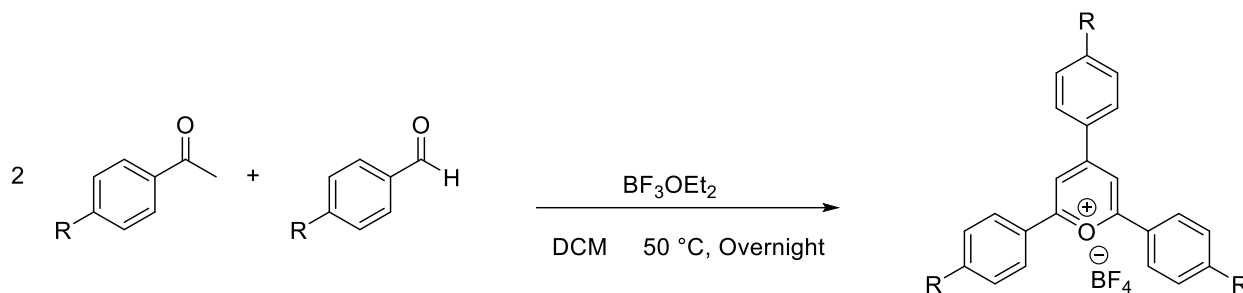
#### Brominated 2,4,6-triphenyl katritzky salt synthesis



To 20 ml of anhydrous ethanol, Di-Br-TPT (0.5 g, 1.07 mmol) and aniline (0.100 g, 1.07 mmol) were added and dissolved. Sodium acetate (0.351 g, 4.28 mmol) was added into the previous solution and dissolved. The solution was brought to boil and refluxed for 8 hours. The final precipitate was filtered and washed with water and ether, yield a white solid. (0.093 g, 16%).  $^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 7.27 (m, 3H), 7.37 (d, 4H), 7.48 (m, 2H), 7.61 (d, 4), 7.70 (m, 3H), 8.35 (d, 2H), 8.71 (s, 2H)

### 3.3 Review and Discussion

TPT salts are synthesized a condensation reaction between ketone and aldehyde. A general reaction pathway is shown in **figure 11**. By altering functional groups in the starting materials,

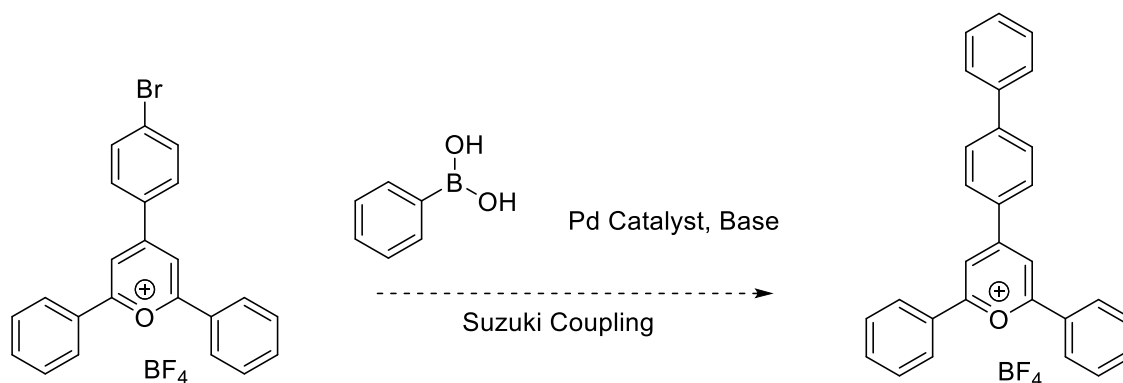


**Figure 11.** TPT Photocatalyst Synthesis

the TPT salt can be readily modified. Substrate selections can affect the condensation reaction for its rather complex mechanism and the resulting properties of the TPT salts.<sup>55</sup> Many TPT salts with different functional groups at the para position have been previously synthesized.<sup>54</sup> The typical yield for the condensation reactions reported in the literature is around 13% -38% depending on the substrates.<sup>55</sup> It would be considered a low yield reaction. However, given the one step nature of the reaction and the ease for purification, the condensation reaction is desirable for obtaining sufficient functionalized C3 elements.

As the less complex element in the system, there are more flexibility in choosing the C2 elements. It requires the presence of symmetric functional groups, such as 1,4-substitution pattern, for producing a uniform framework. Many of the C2 elements can be either purchased or synthesized easily. Some common functional groups the C2 component are  $-B(OH)_2$ ,  $-NH_2$ ,  $-CHO$ , and  $-CN$  groups.<sup>53</sup> Different functional groups attached can accommodate different coupling techniques to give some versatility in the COF synthesis. Combining the design goal to incorporate the photocatalyst into the framework, the final coupling technique selected for forming the COFs is a Suzuki-Miyaura coupling.<sup>56</sup> Suzuki-Miyaura coupling utilizes a palladium metal catalyst to couple a boronic acid or ester to an aryl halide resulting in a C-C bond. Through this C-C bond, the resulting COF would be existed as a conjugated system, capable of the hypothesized resonance stabilization.<sup>57</sup>

Before synthesizing the final C3 element, trial reactions were done on a model system. This included the synthesis of mono- and di-substituted brominated TPT salt. The idea was to subject the mono-substituted bromide TPT salt to standard Suzuki coupling conditions with benzene boronic acid. The reaction scheme is shown in **figure 12**.

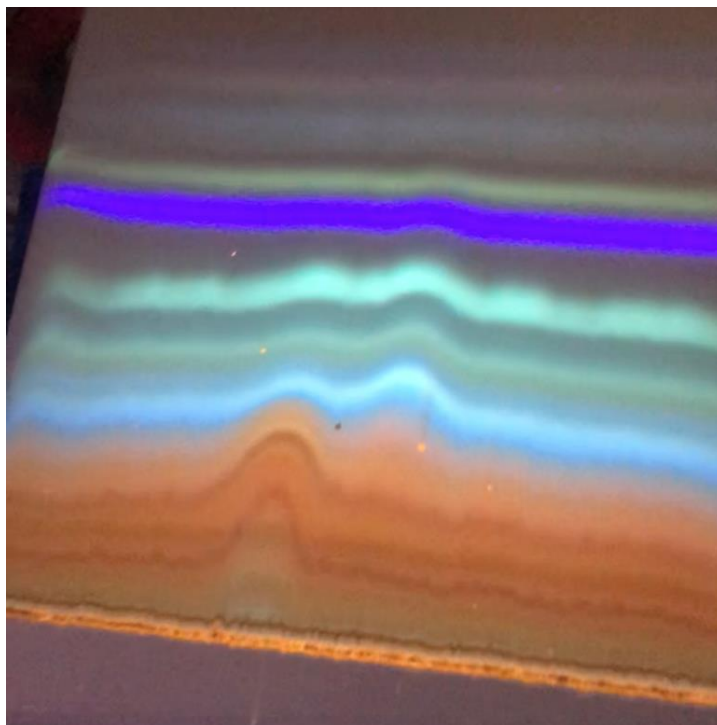


**Figure 12.** Suzuki Coupling Synthesis Probing

If successful and through optimization, this could provide a basis, as well as proof of concept for the eventual Suzuki reaction for the synthesis of the COF system. It is important to



note that a Suzuki-Miyaura coupling generally requires a base to complete the reaction. However, certain bases have been shown to decompose TPT salts from some preliminary tests. Less



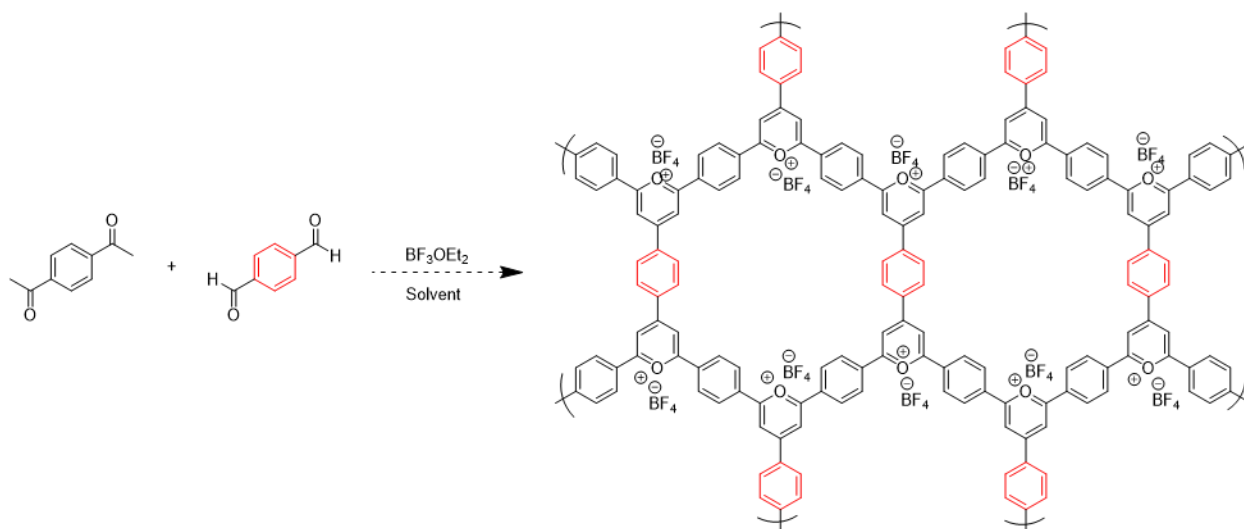
**Figure 13.** Prep-TLC of Suzuki Coupling with TPT Salt

nucleophilic or sterically hindered bases such as *tert*-butoxide or even base-free conditions may need to be used or to prevent this. Nevertheless, the coupling reaction under typical condition was performed, and the result was not optimal. The crude mixture was purified by preparative thin layer chromatography (prep-TLC). The result of the prep-TLC shows a likelihood of decomposition of the TPT salt, shown in **figure 13**. The prep TLC showed the formation of multiple fluorescent band, and each band represented a different compound in the reaction mixture. The  $^1\text{H-NMR}$  data for each band did not correspond to a desired compound and the reasonable conclusion is that the reagent in the coupling caused the decomposition of TPT salt.

Additional attempts using the bulky base, *tert*-butoxide, were conducted. Due to its steric bulk, it was hypothesized that electrophilic sites on the TPT salt site will not be as accessible, and

the decomposition reaction could be avoided. The base will still be strong enough to activate the palladium catalyst and yield a successful result.<sup>75</sup> Unfortunately, the result was similar to the previous Suzuki coupling attempt. The reason for this is not yet clear and would require further investigation to determine the cause.

One step formation of a TPT COF was also attempted. Taking inspiration from extending the TPT size by using longer ketone/aldehyde, this method uses di-functionalized starting building

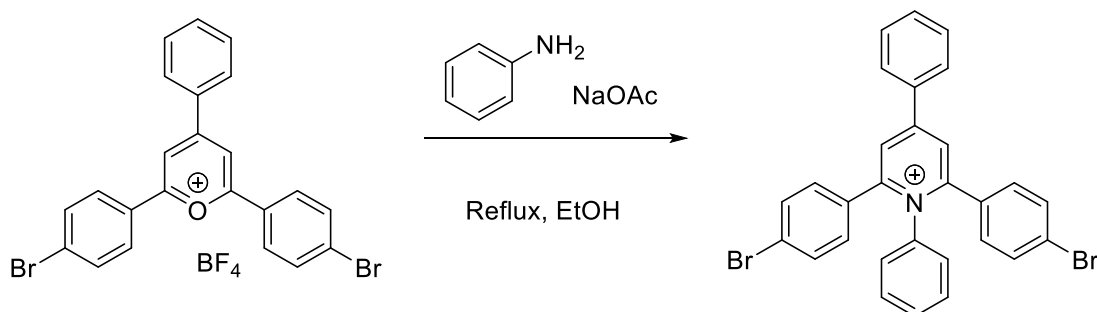


**Figure 14.** One Step TPT COF Synthetic Scheme.

blocks and the condensation is allowed to proceed until the solubility reaches the limits. A simple schematic is shown in the **figure 14**. The two di-functionalized carbonyls can undergo condensation in the presence of Lewis acid similar to a traditional TPT salt formation. The difference is that after the initial condensation, there will still be additional active sites for further condensation reactions, thus forming a COF continuously. This method would eliminate the need of transition metal coupling techniques, removing the potentially prohibitive base, and shortens the synthesis into a single step. I predict this reaction would be rather uncontrolled and proceed most-similarly to other polycondensation reactions. The condensation degree can be varying due to the uncontrollable nature of this reaction. However, this method was also unsuccessful. It is not

clear whether the resulting product is not soluble enough for preliminary characterization, or if the di-functionalization is incompatible. Purification was also a concern. There is lack of evidence to prove the growth of a high molecular weight material.

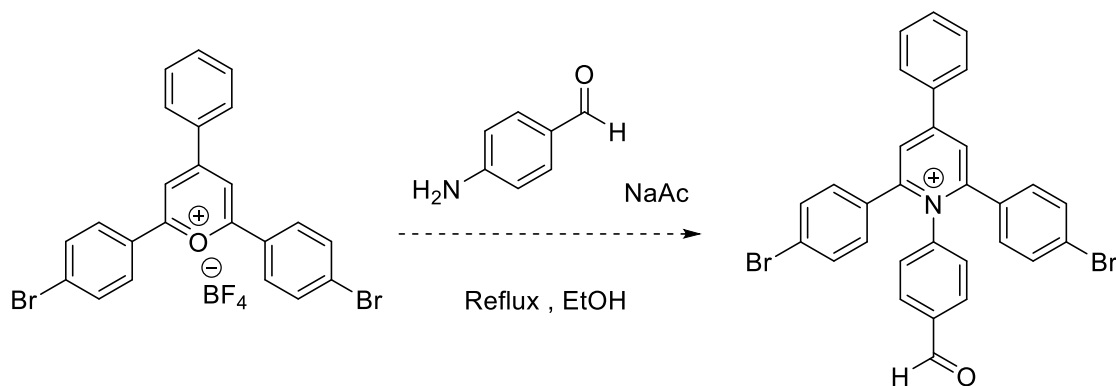
A modified direction was used to form the COFs. TPT is shown to react with a primary amine to form what is known as a katritzky salt. The katritzky salt shows higher tolerance with Suzuki coupling and was able to form a conjugated network.<sup>59</sup> The reference work was able to use di-substituted TPT salt as the base model and convert it to katritzky salt. It also shows the viability of using Suzuki coupling on the katritzky system. This provided a new opportunity to synthesize stable COFs based on a photocatalyst. The conversion of the katritzky salt was successful, the scheme for which is shown in **figure 15**. Further pursuit of this method was cut short by the



**Figure 15.** Katritzky Salt Formation

ongoing pandemic and department regulations for undergraduate research. But this method demonstrated a promising method to form the described COFs if given the opportunity.

With the simple conversion of TPT salt to the katritzky salt and the potential of forming COFs using Suzuki Coupling after the fact, many of the previously described goals could be



**Figure 16.** Addition of Functional Group to the katritzky Salt.

realized using this route. Additionally, further functionality could be added with the inclusion of a new aromatic ring off of the nitrogen. One such example would be to use a bi-functionalized primary amine that also possesses an aldehyde. This can enable post functionalization on the COF to add a TPT unit after incompatible reactions (Suzuki coupling) have already been performed. This could finally allow for the formation of a TPT catalyst within a COF network. (Scheme shown in **figure 16**).

## Conclusion

This research explored the possibility of extending the polymer dimension through utilizing monomer elements with multiple reactive sites. Despite the success of synthesizing the C3 building block with photocatalytic properties, the final formation of the 2D polymer sheet was not able to form due to the instability of the C3 element, pyrylium salt, in the coupling conditions. Another route was attempted, by converting the TPT units into a katritzky salt, which worked for preliminary steps. The research was cut short due to the lack of time and undergraduate research

restriction. It still provided the foundation for expanding the scope of photocatalyst enabled COFs at a preliminary level. The results and ideology can help pave the path for further experiments. One possible application for these materials can be using the COF as a versatile tool for attaching enzyme/protein with primary amine functional group built in and use the product to engineer materials with the ability to facilitate localized biological catalytic reactions.

## Chapter 4

### Calix [4] Pyrrole Polymer

Note: This work was done by graduate student, Tanner Geibel, with the assistance of Mitchell Giordano and myself. Tanner conducted the majority of the final synthesis pathway with limited undergraduate lab access at the onset of the pandemic. This chapter presents a foundation toward the 3D aspect of polymer structure, based on the work I completed at Penn State.

#### Introduction

The exploration of the sidechain functional group has been prevalent within the polymer research community. Sidechains on polymers have altered many of their resulting properties. The development and incorporation of functionalized sidechains have had wide ranging applications, many of which pertain to some form of sensing.<sup>76</sup> In battling with anion pollution in the environment, the known anion binding properties of **C4P** attracted researchers to explore its potential on applications pertaining to sustainability. Studies to improve the anion binding strength and anion binding selectivity have emerged recent years.<sup>65-68</sup>

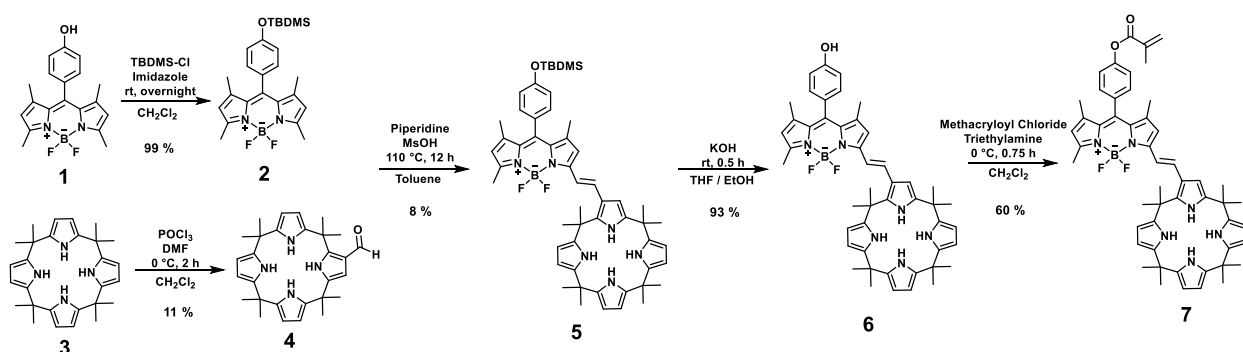
Through functionalizing **C4Ps** with chromophores, the combined small molecule can be used as a colorimetric sensor for the presence and concentration of various anions.<sup>66</sup> Establishing conjugation between the calixpyrrole allows for changes in electron density to be delocalized into a chromophore portion of a small molecule complex. When the crown shape of **C4P** detects an anion, the electron density will change resulting from noncovalent interactions between the anion and the calixpyrrole. When attached to a chromophore, this will lead to a color change.<sup>69</sup> Different

anions will result in different color shift due to the slight difference in the electronic interaction and allow for anion recognition.

The inclusion of calixpyrrole in a polymer has been achieved before by Sessler and coworkers,<sup>69</sup> but incorporating the calixpyrrole with a colorimetric sensor into the polymer has not been achieved. The polymer with the **C4P** complex has the potential to detect, collect, and be recycled all at once. Such material can provide a useful contribution to efforts related to green chemistry and environmental remediation for solving anion pollution issues.

## Review and Discussion

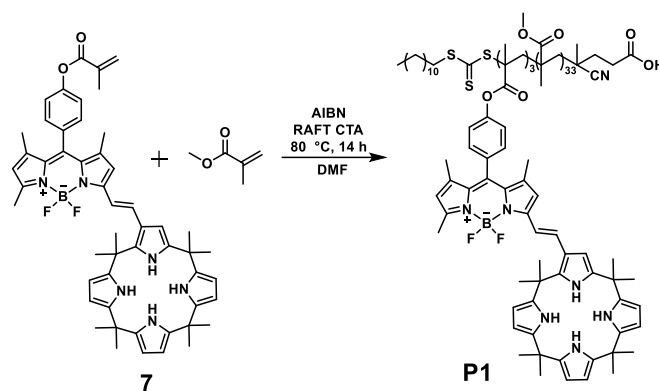
My research contributions mainly involved the synthesis of the **C4P** incorporated polymer and the full synthetic route is shown in **figure 17**. This began with synthesizing the calix pyrrole through a condensation reaction between pyrrole and acetone with moderate yield. Next, the **C4P** was functionalized using a Vilsmeier-Haack formylation reaction. The added aldehyde group was



**Figure 17.** **C4P** Monomer Synthesis Route

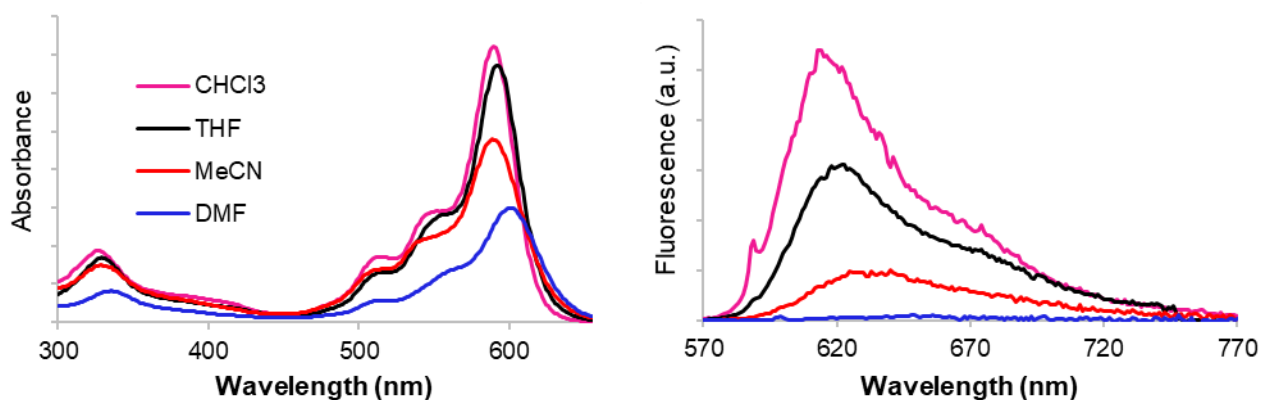
able to link with the protected boron-dipyrromethene (BODIPY) dye to form the dye-anion-recognition complex molecules. The deprotection of the complex freed the alcohol functional group to be transformed into a monomer unit that can be polymerized and yield to the final

polymer. This was polymerized using reversible addition-fragmentation chain transfer (RAFT) polymerization, the synthetic steps are shown in **figure 18**.



**Figure 18.** C4P Polymer Formation

Additional UV/Vis study was conducted on the C4P polymer to test its interaction with different solvents and sensor properties (**Figure 19**). As the solvent increases in polarity, the



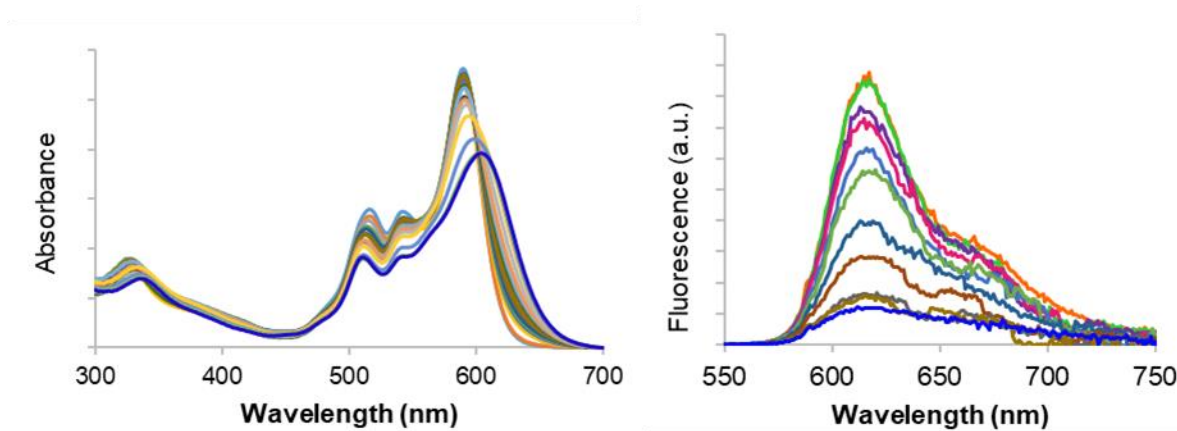
**Figure 19.** Fluorescence spectra of C4P (Left) and UV/Vis spectrum (Right) of C4P

absorbance decreased with the same concentration added. The color of the polymer solution was also red shifted. The intensity of the fluorescence spectrum showed quenching of fluorescence when in the polar solvent as well. This can be the result of the **C4Ps** unit binding with the neutral polar species.<sup>65</sup>

The **C4P** polymer was investigated for its fluoride anion binding affinity, and was titrated with tetrabutylammonium fluoride (TBAF). The concentration of **C4P** polymer in is 0.1 mg/mL



and titrated with TBAF from (0M to  $3.44 \times 10^{-4}$  M). It was determined through the two graphics that the association constant was  $1.8 \times 10^4 \text{ M}^{-1}$ , a little lower than the small molecule complex,  $7 \times 10^4 \text{ M}^{-1}$ .<sup>69</sup> This can be the result of Hofmeister bias. But the binding affinity is still strong for practical applications. **(Figure 20)**



**Figure 20.** UV/Vis Titration of C4P Polymer

The successful synthesis of the **C4P** polymer allows for further studies to improve its utilities. One advance can be converting the polymer chain into a single chain nanoparticle that contains reversible covalent bonds, allowing the polymer to change its solubility and hopefully make it recyclable. With future experiments, this intra-molecular crosslinking can be used to tune and design the proposed nanoparticle structure. If the **C4P** unit remains on the external portion of this resulting nanoparticle it could possess a higher transport constant. This can also maximize the probability for anion binding. More improvements can be realized as the research focuses on designing a structure specific for the **C4P** polymer continues.

## Conclusion

The synthesis of copolymer with **C4P** sensor built-in started with the synthesis of the two subunits. The two subunits, with moderated product yield, were then covalently attached to form

a conjugated system. The complex was then transformed into monomer unit and polymerized using RAFT polymerization techniques. The resulting polymer had a molecular weight of 16,670 with a molecular weight distribution of 1.15. The anion binding affinity with fluoride ion of the **C4P** polymer,  $1.8 \times 10^4 \text{ M}^{-1}$ , which is lower than the small molecule complex but still high enough for practical use.<sup>69</sup> Future studies will focus on designing a co-polymer that allows self-folding into designed structure can be beneficial for improving the recyclability and even the binding of the polymer.

## Chapter 5

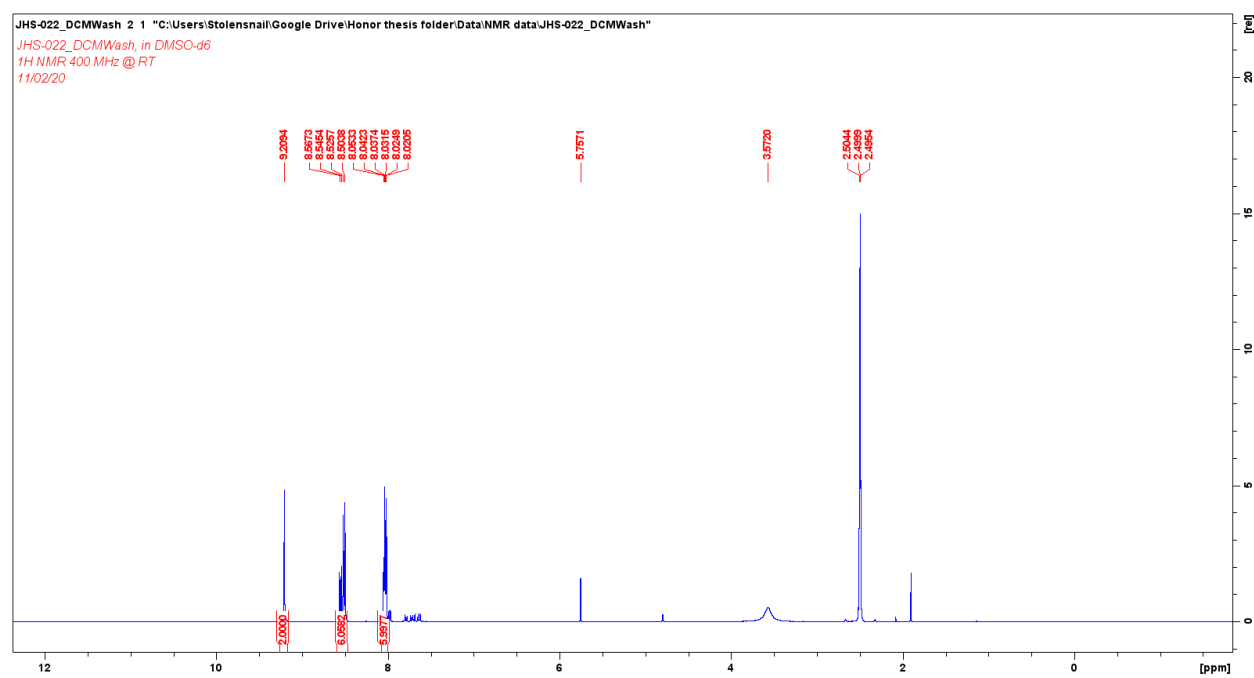
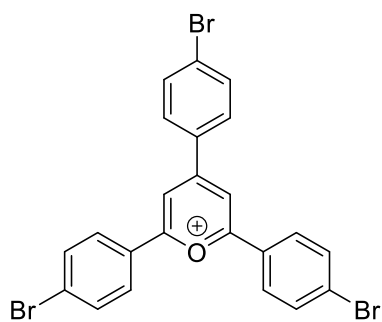
### Final Remark

#### Overall Conclusion

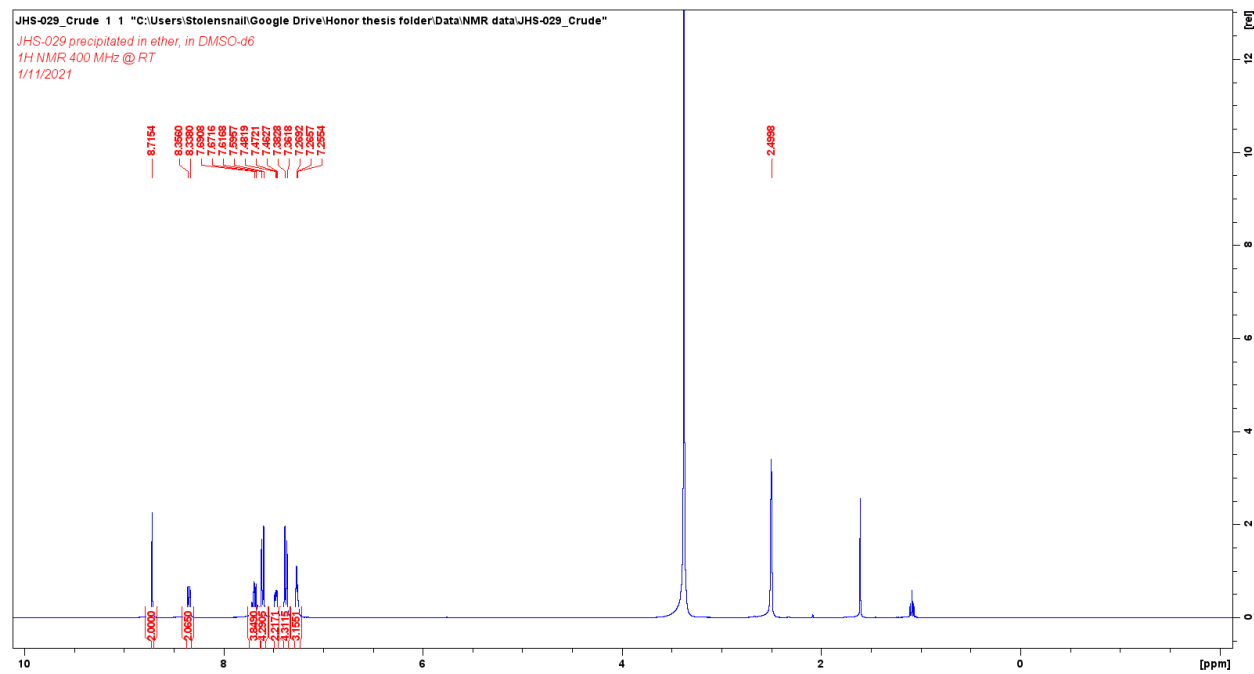
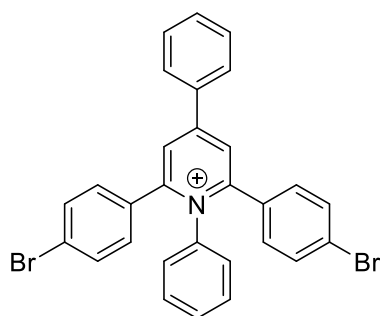
With polymeric materials prevalent in our daily life, having the fundamental understanding about their structures systematically is beneficial for pursuing materials in this area. This thesis followed the structure category pattern, starting with a discussion on 1D chains with simple polymer backbone. The 1D polymer section covered an overview of research on sequence control for conjugated donor-acceptor polymers, highlighting the research done by Elacqua group on designing unsymmetrical donor-acceptor monomer system, and introduced the potential of using steric and electronic bias on controlling polymer sequence. This extended the techniques within the 1D polymer synthesis area. The 2D polymer section covered the synthesis of COFs with the goal of producing high performance 2D sheet for material application. Even though the original research goal was not met owing to the pandemic, the research still provided the basis and benefit for further modification on the TPT-COFs concept, especially the post-function of the TPT and use the TPT unit as a reaction site for additional functionality. The 3D polymer section covered the research of synthesizing a copolymer with the ability to sense and capture anions. The application concept opens the possibility to incorporate a specific 3D structure into the polymer and motivate the research on structural polymer.

## Appendix A

## NMR Spectrum



<sup>1</sup>H-NMR Spectrum of Tri-functionalized TPT salt



<sup>1</sup>H-NMR Spectrum of Tri-functionalized TPT salt in DMSO-6d

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## ACADEMIC VITA

**Jinzheng Hu**

### Education

**The Pennsylvania State University, Schreyer Honor College** University Park, PA  
Bachelor of Science in Chemical Engineering, minor and Honor in Chemistry May 2021

### Research Experience

**The Pennsylvania State University, Chemistry; Undergraduate Research Project, University Park, PA**

Undergraduate Research Student, Elacqua Research Group; Feb 2018- Present

- Conducted and scaled up (10 times higher) synthetic experiments to produce anion sensors compound
- Assisted in dye sensor subunit synthetic process for a novel anion binding single chain nano particle
- Experimented and optimized various reaction designs for the anion binding polymer synthesis

**Schreyer Honor Thesis Projects:** Synthesis of heterogeneous photoredox catalysts for oxidative small molecule and polymer synthesis

- Synthesizing and studying various triphenylpyrylium salt (TPT) photocatalyst for 2+2 cycloadditions reaction
- Designing novel TPT-incorporated covalent organic framework (TPT-COF) with tunable porous catalytic pocket
- Characterizing synthesized compound via UV/Vis and NMR spectroscopy
- Proposing XRD, porosity measurement, TEM imaging characterization technique on TPT-COF

**The Pennsylvania State University, Summer Research Fellowship** University Park, PA

Undergraduate Research Assistant, Chemical Engineering, *Kim Research Group*  
Summer 2019

- Designed Simplified model for supporting and optimizing cellulose nanocrystals (CNC) reaction.
- Utilized EDC coupling reaction for dye tagging on CNCs for reaction confirmation.
- Applied chemical modification on CNCs for crystals alignment and piezoelectric property study.
- Collaborated and assisted research faculty on cellulose polarization data processing.
- Fitted and Analyzed X-ray diffraction (XRD) data for Cellulose III to Cellulose Ib kinetic study.
- Participated and presented in 11<sup>th</sup> REU final symposium through an oral presentation and poster presentation.

### Publication

S. J. Koehler, **J. Hu**, and E. Elacqua\*, “Electronically-Governed ROMP: Expanding Sequence Control for Donor-Acceptor Polymers”, *Synlett*, 2020, 31(15), 1435-1442.

### Technical Presentation & Fellowship

**11th Annual Research Experience for Undergraduates (REU) Symposium** University Park, PA  
*Bio and Chemical engineering Fellowship \$4,000* Summer 2019

*Presentation Title:* Selective Functionalization of Reducing End of Cellulosic sugar for parallel arrangement of cellulose nanocrystals.

*Contributor:* **J. Hu**, I. Chae, S. Kim.

## **Teaching Experience**

**The Pennsylvania State University**

University Park, PA

Instrument Room Teaching Assistant, Chemistry

September 2018-January 2020

- Assisted and trained undergraduate students with organic chemistry characterization machines including NMR spectrometer, infrared spectrometer, and gas chromatography spectrometer.
- Guided and enhanced students' knowledge on data analysis and working principles of characterization instruments.