ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF ORTHO-PHENYLENE Oligomers

by Jason L. Crase

ortho-Phenylene oligomers are a class of organic molecules that are both chemically and synthetically interesting. Similar molecules have found uses in organic light emitting diodes and organic semiconductors as well as other applications. They are also potential precursors to graphene-like nanoribbons. Little work has been done with ortho-phenylene oligomers, as para-phenylene oligomers have received most of the attention. We have developed a synthesis based on alternating Suzuki-Miyaura couplings and activation of hydroxyls. The ortho-phenylene oligomers are also structurally interesting as there are indications that they assume helical conformations in solution.
SYNTHESIS AND CHARACTERIZATION OF ORTHO-PHENYLENE Oligomers

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Introduction

The focus of this project is ortho-phenylene oligomers, an interesting, fundamental class of conjugated oligomers that has received very little attention. When it was discovered in the late 1960’s\(^1\) and early 1970’s\(^2\) that organic polymers can be conducting and semiconducting, the field of organic electronics was born. As a result, new reactions were discovered that have furthered the studies of this field and have found uses in other fields as well. With the increasing demand for better yet affordable technology, organic electronics are becoming increasingly important. Organic molecules have found uses as organic light emitting diodes (OLED’s),\(^1,3\) field effect transistors (FET’s),\(^3\) thin-film transistors,\(^4\) and organic (semi)conductors\(^5\) among others. They are also finding uses in photovoltaic and solar cells.\(^6,7,8\) Organic electronics are versatile in the size of the device they can be used for, from large area displays to personal identification tags,\(^3,8\) uses that are cost-prohibitive for silicon. In addition to these uses, polycyclic aromatic hydrocarbons (PAHs), which include ortho-phenylene oligomers, are being used to study the effects they have on biological systems as they are believed to be carcinogenic. Also, if sufficiently long, they can serve as models for macromolecules,\(^9\) foldamer models for biological systems,\(^9,10\) and enzyme mimics.\(^11\)

ortho-Phenylene oligomers are also interesting chemically, both in the conformations they can assume and in the manner in which they can be synthesized, and because they have been almost completely ignored. This is due to the fact that most of the work that has been done on \(\pi\)-conjugated systems has been done on \textit{meta} and \textit{para} linked oligomers, with \textit{para} receiving the most attention. While there are numerous compounds similar to the oligomers we synthesized, in that they are all \(\pi\)-conjugated, the closest similarities are \textit{para}-phenylene oligomers, commonly used as blue OLEDs,\(^12\) and \textit{ortho}-phenylene ethynylene oligomers, Figure 1.
Figure 1. Examples of a para-phenylene (l.) and an ortho-phenylene ethynylene oligomer (r.).

The published work that has been done with ortho-linked oligomers has been primarily by two groups. The first is the King group in their investigation of the Scholl reaction and its use in the synthesis of graphitic nanoribbons.\textsuperscript{13,14,15} The second group is the Simpkins group,\textsuperscript{16} who worked with a series of genuine ortho-phenylene oligomers, such as 1. The Simpkins group first became interested in o-phenylene oligomers during their study of atropisomeric amide synthesis.\textsuperscript{16} This interest was spurred by the fact that ortho and meta phenylenes have been virtually ignored versus para-phenylenes, largely due to the para isomers’ potential as materials for electronic devices.\textsuperscript{16} Also, from the work of other groups, they learned that meta-linked oligomers, in the crystal state, adopted a helical structure with five rings per turn. This led the Simpkins group to perform molecular modeling on ortho-polyphenylene structures, which suggested that these structures should adopt a tight helix having three rings per turn.\textsuperscript{16} This, combined with the fact that helical molecules had started to attract attention for their potential in materials and polymers\textsuperscript{16} led the Simpkins group to continue their investigation. To validate their models, they synthesized several oligomers, containing three to nine rings, and looked at the x-ray crystal structures of several of them.\textsuperscript{16} They found that larger oligomers, specifically the hexamer 1 (the longest for which an X-ray structure was obtained), adopted a conformation with a tight helix. They found that this helix had a pitch of approximately 3.8 angstroms; by comparison, the pitch of the DNA helix is approximately 5.2 to 5.4 angstroms. This equates to a stack such that the first ring in the turn overlaps the fourth ring, or a twist having three rings per turn.\textsuperscript{16} The distances between these rings is around 3.2 angstroms and was interpreted as a result of the tight twist adopted by the molecule and not due to π-π stacking.\textsuperscript{1} These distances though suggest that π-π stacking interactions could be possible.\textsuperscript{16} Therefore, it is conceivable that our
synthetic targets, substituted ortho-phenylene oligomers (e.g., 2), should also assume similar helical conformations.

![Molecule 1](image1.png)

![Molecule 2](image2.png)

What is also noticeably different between our target molecules (e.g., 2) and the Simpkins molecule (1) are the methoxy groups present on each ring. We had specific reasons for targeting this molecule. First, the methoxy groups (or longer-chain alkoxy derivatives) would aid in solubility. This would be more important if these oligomers could be converted to graphene-like molecules (see below). Second, they serve as points of attachment. This means that altogether different functional groups could be attached, allowing the electronic properties (e.g., oxidation potentials) of the oligomers to be tuned. Third, the methoxy groups could aid in the Scholl reaction by serving as ortho/para directors.\(^\text{15}\) In Figure 2, the highlighted groups determine where the bonds will form.
Figure 2. Target \( o \)-phenylen hexamer. The highlighted \( \text{OCH}_3 \) groups were designed to direct the Scholl reaction toward the formation of graphene nanoribbons.

In order to create their molecules, the Simpkins group used a series of iterative Suzuki-Miyaura couplings. The Suzuki-Miyaura (S-M) coupling is a palladium-catalyzed reaction that takes place primarily between an aryl halide, or some equivalent, and a boronic acid derivative. A phosphine-containing ligand is usually added. This is especially true, and its presence is important, if an aryl chloride is used as one coupling partner,\(^{17}\) as chloride is the least reactive of the halides, or halide equivalents, in the S-M coupling. **Scheme 1** is the general form of a Suzuki-Miyaura coupling.

![Scheme 1 General form of a S-M coupling](image)

The Simpkins group began synthesizing their oligomer by reacting commercially available 4-methoxyphenyl-boronic acid with 1-bromo-2-iodobenzene. By doing this, they took advantage of the differential reactivity of aryl iodides and bromides to control the oligomer
growth. They then performed a metal-halogen exchange to form the boronic acid and followed that with a second Suzuki coupling to form the terphenylene derivative. At times, during their synthesis, they would use 2,2'-dibromobiphenyl in place of the 1-bromo-2-iodobenzene to increase the length of the molecule by two rings. This can be seen in Scheme 2.

Scheme 2 Simpkins group synthesis
Using the above synthesis, they were able to synthesize oligomers from the trimer to the nonamer. Our synthetic strategy was informed by the one reported by the Simpkins group, mainly in the use of the Suzuki-Miyaura coupling and a biphenyl-based monomer as in Scheme 2.\textsuperscript{16} However, for our system we used the 2,2’-dibromo-5,5’-dimethoxy biphenyl, 3. This simple modification was predicted to help us in two ways. First, it would enable us to synthesize the oligomers two rings at a time, thereby speeding up the process. Second, it would fulfill our need of having a functional group present on each ring, regardless of the final length.

![Image of compound 3]

During the course of the synthesis, we investigated various reagents and techniques. This was done in the hopes of making the Suzuki-Miyaura coupling and other reactions easier to use. We examined the use of masking agents, for both the boronic acid and hydroxyl groups, in order to control the S-M coupling. During the synthesis, we also synthesized monomers with longer alkyl chains, such as the 5,5’-didodecyloxy biphenyl derivative 4.

![Image of compound 4]

In regards to the Suzuki coupling, there are two reactive sites, the bromine and the boronic acid. In order to prevent the boronic acid from reacting intramolecularly or polymerizing, two masking groups were examined. As it is generally thought that the Lewis acidity of the boron atom controls the reactivity in the S-M couplings, it is necessary to lower this acidity.\textsuperscript{18} One way to do this is through donation of a lone pair of electrons to the $p$-orbital of the boron atom.\textsuperscript{18} The masking groups that were examined both contain nitrogen, and it is the
nitrogen that is responsible for the donation of the lone pair of electrons.\textsuperscript{18} The first masking group to be examined was diaminonaphthalene (DAN), which was pioneered by the Suginome group. In addition to lowering the acidity of the boron atom, it also increases the overall chemical stability.\textsuperscript{18} One potential drawback is that removal of the DAN group requires strongly acidic conditions.

\begin{center}
\includegraphics[width=0.5\textwidth]{DAN.png}
\end{center}

The second masking group we examined was N-methylimidodiacetic acid (MIDA).\textsuperscript{19} Like the DAN group, MIDA is able to form a pseudo-cyclic aminoborane,\textsuperscript{19} and an example is shown in Figure 3. In addition to protecting the boronic acid, the MIDA group has a second advantage. It is highly selective in not reacting in the presence of other boronic acids. Burke and Gillis demonstrated this by performing a S-M coupling with a 1:1 mixture of a MIDA protected and an unprotected boronic acid. The unprotected acid reacted preferentially to the protected one in a 24:1 ratio.\textsuperscript{19} This is consistent with a strong preference of reacting with the sp\textsuperscript{2}-hybridized boronic acid.\textsuperscript{19} What also made the use of MIDA attractive were the conditions used to remove it, typically a mild, aqueous base.

\begin{center}
\includegraphics[width=0.5\textwidth]{MIDA.png}
\end{center}

\textbf{Figure 3} MIDA protected $p$-tolylboronic acid
The final masking strategy we investigated was the use of masked hydroxyls. Again, because of the flexibility in the S-M coupling, numerous molecules can participate. One of these is the triflate group. A triflated hydroxyl can act as a pseudo halide and its use was also examined. This method was previously used by Ishikawa and Manabe, in the investigation of the pinacol esters, and was the one we ended up adopting. Scheme 3 is the scheme that was used by Ishikawa and Manabe to produce their ortho-phenylene oligomer.

Due to the versatility of reactants that can participate in the S-M coupling, time was taken to explore some of the lesser-used ones to see if they proved better than the aryl halide or boron species. The first to be examined was the boronate ester. These are known to react in a similar fashion as boronic acids but are more easily purified. One that showed promise was the pinacol esters of boronic acids. Ishikawa and Manabe used pinacol esters to perform a stepwise synthesis of functionalized oligoarenes. Shown in Figure 4 are three of the molecules they synthesized using this process, which includes an ortho-phenylene pentamer. In their work, the pinacol ester proved to be very versatile in the types of functional groups that could be present, from hydroxyls to a carboxylic acid ester. Both of these aspects were appealing as our compounds have both an alkyl ether and a phenyl group present. Its use was also appealing, as it was used to synthesize an ortho-phenylene oligomer, (top left structure, Figure 4), and was more easily purified.

Figure 4. Selected oligoarenes synthesized by Manabe
Scheme 3  Ishikawa and Manabe synthetic scheme
There are many characteristics that make organic molecules ideal for use in electronics. These include ease of processibility, versatility of chemical synthesis, cost, and the physical properties of the molecules themselves. These include solubility, structure, and length. Another advantage in using organics over their inorganic counterparts is that the physical and electronic properties can be tailored by the synthetic chemist. Much of the cost of electronics comes during the manufacturing process and from the packaging (e.g. the protective packaging or the housing of the electronics themselves). Therefore, savings during manufacturing is highly desirable. The savings during processing/manufacturing are primarily a result of the solubility of the molecule in various solvents. This characteristic has two main advantages: (1) the molecule can be deposited by using either the vapor or solution phase and (2) the compatibility of the molecule with different substrates. These qualities enable electronic devices to be produced from organics on a larger scale and at a lower temperature than silicon. This ability is most likely a result of the fact that organic molecules/PAH’s have high thermal and chemical stability. This quality is never more evident than during the production of an organic semiconductor. The organic molecule is dissolved in a solvent and then cast onto the substrate of choice. The substrate could be glass, plastic, metal or a combination of these. As a result, organic based semiconductors are both easier and less expensive than producing standard silicon semiconductors. Taking advantage of the solubility has also given rise to new methods in creating these products. One method that has seen a lot of use, recently, is using an inkjet printer and simply printing the molecule onto the desired substrate, typically plastic. While the ability of these molecules to act as molecular models are purely a result of the size and shape of the molecule, the organic-electronics, and other uses, take advantage of the structure and length of the oligomers. Optical properties, in particular, depend upon the length of the oligomer. There are numerous examples where for a particular molecule; the oligomer has the same properties as that of the polymer. The advantage of this is that the oligomer is a monodisperse material, and as a result, its optoelectronic properties are purer.

When organic molecules are utilized for electronics, the π-conjugation of the molecule allows for electron and energy delocalization. However, with o-phenylene oligomers, due to the helical conformation they may assume, we may observe through-space delocalization for the oligomer, as in Figure 5.
The through space movement of electrons is a result of the arene stacking of the molecule and the proximity of the rings to each other. This arene stacking and subsequent through-space

Figure 5. Model of a helical oligophenylene, showing electron transfer between stacked aromatic rings
π-π interactions can also lead to substantially lower oxidation potentials when compared to their linear counterparts. The helical structures that these ortho-phenylenes may assume also have alternative uses. Depending upon the size of the inner void, they may be able to accommodate ions or small molecules. This can lead to their use as synthetic ion channels. Additionally, the arene stacking could result in the alignment of the chromophores. This occurrence is of interest to the field of molecular electronics, such as photovoltaics and FET’s. If these molecules were synthesized to include some type of donor and acceptor molecules, on opposite ends, then by tuning the secondary structure, the electronic interactions between the donor and acceptor molecules could be modulated. It is this characteristic that makes molecules like ortho-phenylene oligomers attractive for future use in photolytic reactions or solar light energy conversion.

One of our original goals for this project was the planarization of ortho-phenylenes to graphene-like nanoribbons. At the time, graphene was an emerging material and is similar to carbon nanotubes. Unlike the nanotubes though, graphenes are two-dimensional and are an excellent candidate for use in circuits. However, there are uses of graphenes besides the standard electric ones. These include being made into single molecule gas detectors and the potential creation of biodevices that include biobatteries, biodetection, tools and biodriven electronic devices. Graphene has the structure shown in Figure 6. It is a unit of graphite and as such is a single layer of $sp^2$ hybridized carbons. While the ortho-phenylenes will never be this large, they can lead to graphene-like ribbons with a structure similar to the one shown below, Figure 7.
There are many methods used to create graphenes, including physical exfoliation of graphite\textsuperscript{31} or chemical conversion of silicon carbide,\textsuperscript{32} and it is believed that the markings left by a pencil are in fact graphenes.\textsuperscript{33} While we will never produce oligomers the size of those in Figure 6, using a bottom-up approach would allow us to do things not possible with these other
methods. First it would enable us to produce small graphenes, much smaller than those produced by lithographic techniques, similar to the one shown above in Figure 7. It will also allow us to have more precision in the graphenes produced. This means that we will be able to control the chemical aspects of the molecule. As mentioned before, the first is solubility. By adding sufficiently long functional groups during the synthesis, the solubility of the molecule should remain useful regardless of length. This solubility is one of the main reasons organic molecules are attractive for use in the production of electronics, as it aids in manufacturing. Also, by manipulating the type of functional group, whether electron donating or withdrawing, the electronic properties can be adjusted. Finally, the length of the graphene-like ribbon itself can be altered. This is done by simply increasing the number of aryl units present. The last two characteristics, the functional groups that are present and length, are highly desirable for use in organic electronics as well. By simply altering one or both of them, the molecule can be tuned to fit specific needs.

When comparing the ortho-phenylene oligomers and the graphene-like ribbon, 2, and Figure 7, respectively, the only difference between them is that the graphene is planar, while the ortho-phenylene oligomer is not. This planarity could be introduced via the Scholl reaction, an oxidative coupling of two aryl compounds. It is done using both a Lewis acid and an oxidant. In addition to being the crucial reaction in the synthesis of graphene-like materials, it is also chemically interesting. Without this reaction, the bonds that planarize the ortho-phenylene would need to be done individually and could prove to be a difficult task. Thanks to Müllen and his extensive work with the Scholl reaction, numerous conditions have been established that will form multiple bonds in a single step. This is never more apparent than in Figure 8 below, where thirty bonds are formed with one step.
If the formation of thirty bonds is possible, then, given the proper conditions, the formation of two, four, or six bonds should not be a problem. However, this turned out not to be the case. While the Scholl reaction has been around for nearly a century, debate is still ongoing as to its exact mechanism: a radical cation versus an arenium cation mechanism. The King group believes it is the arenium cation mechanism that is the correct one, whereas other groups favor the radical cation mechanism. Regardless of the exact mechanism, the King group’s findings suggest that rearrangements are prevalent in the Scholl reaction. It is these rearrangements, discovered after we began our study, that prohibit its use to synthesize complex architectures such as graphene-like nanoribbons. The King group made a second discovery during this study. It dealt with the type of functional groups present. They found that methoxy groups actually promote rearrangements in the Scholl reaction. An example of this can be seen in Figure 9. They also concluded that any electron-donating substituent in the meta or para position tended to increase the migratory potential. In fact, the second functional group they tested, the methyl group, caused a rearrangement two times during the reaction.

With the varied methods to synthesize them and the conformations they assume, ortho-phenylene oligomers are indeed a class of conjugated polymers that deserve more attention.

Figure 8 Formation of thirty bonds via the Scholl reaction
Additionally, if in the future we are able to find successful conditions for the Scholl reaction, then graphene-like ribbons will be within reach. If these structures do assume a helical conformation then the through space movement of electrons should be possible. If this is indeed true, then the electronic properties dependent upon it are also possible. With the emerging fields of nano materials and organic electronics, both molecules deserve further investigation. While ortho-phenylene oligomers and other organic molecules will never replace silicon, they are finding niches they can fill and may someday be a viable alternative to silicon.

Figure 9. The phenyl shift and rearrangement as proposed by the King group.
Results/Discussion

Synthesis

The route to synthesize ortho-phenylenes involves several aspects that ultimately lead to iterative Suzuki-Miyaura (S-M) couplings. First was a series of steps leading to the creation of the aryl halide monomer. It began with the readily available starting material, o-dianisidine. Then through the use of diazonium chemistry, the o-dianisidine was deaminated to yield the dimethoxy- biphenyl $5$. It was then brominated to yield 2,2’-dibromo-5,5’-dimethoxy biphenyl $3$ as white, needle-like crystals. These reactions are shown in Scheme 4.

\[
\begin{align*}
\text{H}_3\text{CO} & \quad \text{H}_3\text{CO} \\
\text{H}_2\text{N} & \quad \text{H}_3\text{CO} \\
\text{OCH}_3 & \quad \text{OCH}_3 \\
\text{NH}_2 & \quad \text{OCH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{CO} & \quad \text{H}_3\text{CO} \\
\text{OCH}_3 & \quad \text{Br} \\
\text{Br} & \quad \text{OCH}_3 \\
\end{align*}
\]

Scheme 4

Due to the directing effects of both the methoxy and phenyl groups, the bromine is added at the positions indicated, adding para to the methoxy group and ortho to the phenyl group. ortho-Phenylenes like the ones we are synthesizing are expected to be soluble. However, when they are planarized to form graphene-like nanoribbons, they should become much less soluble. To overcome this issue, our synthesis ensures that functional groups will be present on each ring and should increase the solubility in the graphene-like materials. The plan was initially to deprotect the methoxy, groups essentially protected hydroxyls, and then alkylate them to a longer...
chain. The first step was to convert the methyl ethers, on each ring, to hydroxyls. Methyl ethers are one of the most effective protecting groups for phenols, but their robustness and the difficulty in removing them are, at times, a major drawback.\textsuperscript{37} Many of the currently accepted methods for deprotecting them are flawed in some way. They may produce impurities or react more slowly upon scaling up, like LiI/2,4,6-collidine.\textsuperscript{37} They may decompose or not react with the starting material like AlCl\textsubscript{3}/EtSH, BBr\textsubscript{3}, and others.\textsuperscript{37} The Magano group encountered these problems during the course of a synthesis and devised a method to deal with them. They believed the problem was solved when they used the previously reported combination of NaH and ethanethiol in refluxing DMF.\textsuperscript{37} This method provided both good yields and purity, however, the odor that was produced during workup made this route impractical. They then searched for an alternative that gave similar performance but without the smell. The hydrochloride salt of 2-(diethylamino)-ethanethiol fulfilled both of these requirements.\textsuperscript{37} Not only is this compound commercially available, but it gave good yields when used in combination with the appropriate base.\textsuperscript{37} This method also turned out to be compatible with numerous functional groups present on an aromatic ring. Most importantly, during workup under slightly acidic conditions, the odor was avoided.\textsuperscript{37} With the brominated compound in hand, the methyl ethers were removed to yield the phenol 6. Once completed, the phenol groups were then alkylated to the desired length using bromododecane and potassium carbonate in N,N-dimethylformamide (DMF). These reactions yielded the biphenyl 7 with the –C\textsubscript{12}H\textsubscript{25} side chain, as shown in Scheme 5.
With this compound in hand, the next step was to synthesize a reactant that serves two purposes, initiating and ending the oligomer. It was in the form of a boronic acid and was synthesized from 4-bromophenol. **Scheme 6** shows the alkylation of the phenol to the dodecyloxy and subsequent conversion to the boronic acid.

**Scheme 5**

**Scheme 6**
Following the Simpkins group approach, we also employed a stepwise growth of the oligomer. However, in order to accelerate the process we used the dibromo bidodecyloxy biphenyl 7, the molecule that was produced in Scheme 5. It began by creating a boronic acid on one of the aryl rings and started with a single lithium-halogen exchange, Scheme 7. It was with this molecule that testing of the boronic acid masking agents, DAN and MIDA began, again to prevent intramolecular reactions. Scheme 8 shows the boronic acid reacting with each of these protecting groups.
**DAN** and **MIDA** may be effective in preventing boronic acids from reacting, but for us they proved ineffective. The products of coupling with the **MIDA**-protected boronic acids proved difficult to purify, were low yielding, and difficult to characterize. As a result, the use of **DAN** and **MIDA** was abandoned.

While testing with the **DAN** and **MIDA** groups was underway, testing with the pinacol commenced. Rather than use the pinacol protecting group with the biphenyl, it was used with the alkoxy phenyl boronic acid. **Scheme 9** shows the reaction of the pinacol with the phenyl boronic acid. As with the **DAN** and **MIDA**, a similar problem was also encountered with the use of the pinacol, but only in the fact that it was low yielding. However, it was used in a S-M coupling, as in **Scheme 10**.

![Scheme 9](image1.png)

![Scheme 10](image2.png)
The molecule synthesized in Scheme 10 is an ortho-phenylene oligomer, and as stated previously, it may serve as a precursor to graphenes or graphene-like nanoribbons. The key difference between a graphene nanoribbon and an o-phenylene oligomer are bonds between adjacent aryl rings as shown in the figure on the right in Scheme 11. In order to create these bonds, the Scholl reaction was used. The Scholl reaction couples arenes using a Lewis acid and an oxidant. Alternatively, a strong protic acid and an oxidant can be used in the Scholl reaction instead of the Lewis acid/oxidant combination. Instead of using the Scholl reaction, other groups have utilized UV light and iodine\(^{38}\) in a photochemical ring closure in an attempt to planarize similar molecules. Intramolecular reactions perform better than intermolecular reactions, and Scheme 11 shows the Scholl reaction, with our molecule, using FeCl\(_3\) as the Lewis acid.

![Scheme 11](image)

Ideally, the product formed in Scheme 11 is the one that is supposed to be created, but this particular set of reaction conditions failed to form both bonds. Numerous other conditions were tried, and all gave similar results. It is believed that the Scholl reaction proceeds through an arenium cation or radical ion mechanism. Additionally, the presence of the methoxy groups should aid in forming the bond between the rings and is done by directing intramolecular bond formation and preventing intermolecular bond formation. In a paper published after our numerous attempts at planarizing these molecules, the King group examined the Scholl reaction using a molecule similar to the ortho-phenylene oligomers. The initial purpose of the paper was to determine the exact mechanism by which the Scholl reaction occurs. Upon completion of their work, they proposed that the mechanism is an arenium cation mechanism. They also discovered that a rearrangement occurs during the reaction and found that this rearrangement involves a phenyl shift. This rearrangement could explain why two bonds never formed in our reactions. Our first indication that the Scholl reaction did not work was from the MALDI mass
spectrum of the product. The mass of the fully planarized tetramer should be 1,038.84; however the mass as measured by MALDI was 1,040.95 m/z. This measured value indicates a loss of two protons, as opposed to a loss of four protons for a successful Scholl reaction. The second indication comes when looking at a $^1$H-NMR of the Scholl reaction product. Initially it appears the reaction has worked as the multiplet at 6.5 ppm is no longer present, as shown in Figure 10. The loss of this signal is significant as it represents the protons that are lost when adjacent aryl rings are bonded in a successful reaction. Upon closer examination of the aromatic region of the spectrum, however, it is apparent that this is not the case, as shown in Figure 11.
Figure 10. $^1$H-NMR of the Scholl reaction product
Figure 11. The aromatic region of $^1$H-NMR of the Scholl reaction product.

Structure A

Structure B

Figure 12. The possible products of the Scholl reaction.
A tetramer that has successfully undergone a Scholl reaction would have five sets of protons and therefore five signals, and this is clearly not the case as there are six clusters of peaks representing the twelve aromatic protons. The two possible structures that could be formed are shown in Figure 12. However, based upon the theory the King group put forth that a phenyl shift occurs,\textsuperscript{14} and data from the MALDI and the \textsuperscript{1}H-NMR (i.e., $J$ values), the product that we believe formed is Structure B. If the King group’s theory is correct and a phenyl shift does occur, then Structure A is immediately eliminated as a possibility as no shift has occurred. Additionally, if A is the structure, then the second bond should be able to form based on the proximity of ring 2 to ring 4. This is also not the case, as increased time or excess FeCl$_3$ led only to dimerization, as determined by MALDI.

A closer examination of the aromatic region of the spectrum (Figure 11) and the structure on the right is further confirmed as the product that is formed. The evidence for this is based upon ring 3. In Structure A, the protons on ring 3 should appear as two doublets with similar $J$ values to the ones at 7.0 ppm and 7.6 ppm (which correspond to the four protons on ring 4). However, in Structure B, these protons would appear as two separate singlets (or tight doublets) and are lost as part of the multiplet at approximately 7.9-8.0 ppm. Based upon this, Structure B seems like the obvious choice given the evidence at hand. Whatever mechanism the Scholl reaction proceeds through, it did not work for us. If the King group’s findings are true and the methoxy/alkoxy functionalities do promote an aryl shift, then their prescence is the reason for the shift.

With the failure of the Scholl reaction, the primary goal of the synthesis then became the creation of longer ortho-phenylene oligomers. For that, an alteration to our current synthetic scheme was needed. For simplification, to speed up the process and because we no longer needed solubilizing groups, all subsequent work was done using the original methoxy side chains. It was at this point, that the use of masked hydroxyls as triflates was used. The obvious modification of our existing strategy is to make use of a 10-hydroxy-10,9-boroxarophenanthrene-based monomer 8, which had been previously shown to undergo S-M couplings by the Zhou group.\textsuperscript{39}
With this knowledge, the final route was established. The synthesis would remain the same up to the point of brominating the biphenyl and foregoing the deprotection of the methyl ethers and subsequent alkylation. We then developed a synthesis of boroxarophenanthrenes based on a series of metal-halogen exchanges. The dimethoxy biphenyl 3 was subjected to a single lithium-halogen exchange and was then oxidized to the hydroxyl 9 upon treatment with a solution of sodium hydroxide in hydrogen peroxide. The resulting hydroxyl 9 was then protected using dihydropyran to form the tetrahydropyran protected biphenyl 10. A second lithium-halogen exchange was then performed on the THP protected biphenyl 10 and the resulting aryl lithium was quenched with triisopropyl borate. Then during workup with 1 M HCl the boroxarene 11 was formed as shown in Scheme 12.
The resulting boroxarene 11 was then used in a Suzuki coupling. For every S-M coupling used in our synthesis, a phosphine ligand was present. In addition to activating aryl chlorides, they are also useful when biaryls are present,\(^\text{40}\) as in our case. The specific ligand used, Figure 13, is one of Buchwald’s and is commonly referred to as SPhos.\(^\text{40}\)
Figure 13. Buchwald’s ligand, SPhos.

In addition to these qualities, this particular ligand, of Buchwald’s many, allows lower catalyst levels to be used, and is particularly good for Suzuki-Miyaura couplings of sterically hindered systems. As before, the first step was to begin the growth of the oligomer. To start the oligomer chain, the boroxarene 11 was reacted with commercially available 4-bromoanisole. This yielded the hydroxyl 12 that was subsequently triflated to 13, as shown in Scheme 13.

This triflated trimer 13 was then reacted with readily available 4-methoxyphenyl boronic acid to form the tetramer 14, shown in Scheme 14.
Alternatively, the tetramer can be synthesized by the reaction of an excess of 4-methoxyphenylboronic acid with biphenyl 3 in a S-M coupling, using these same conditions. The triflated product 13 can also be reacted with additional boroxarene 11, in another Suzuki-Miyaura coupling to yield the pentamer 15, Scheme 15.

From this point, the synthesis becomes a series of alternating reactions. The resulting hydroxyl was first triflated, and then used in a subsequent Suzuki coupling to increase the oligomer length by two aryl units. With this method, it is possible to create an oligomer with as
few as three rings or as many rings as is desired. To create a molecule with an odd number of rings it would simply be a matter of removing the hydroxyl group. In order to make an oligomer with an even number of rings, a final Suzuki coupling was done using the 4-methoxyphenylboronic acid and the triflated compound as in Scheme 16, this time going from the triflated pentamer 16 to the hexamer 17. The final scheme, Scheme 17, is the synthesis of the ortho-phenylene octamer 20 from the triflated pentamer 16. Continued work by Dr. Jian He has produced the [10]-mer and the [12]-mer. He has also continued trying various reaction conditions in an attempt to planarize some of these compounds. A number of interesting features have been discovered, including bathochromic shifts in the UV/Vis spectra with increasing length, hypsochromic shifts in fluorescence spectra, and evidence of a stacked helical conformation in solution.

![Scheme 16](image)

**Scheme 16**
Scheme 17
Results/Discussion

As none of these ortho-phenylenes had been previously synthesized, we relied on mass spectrometry and $^1$H-NMR to verify that the products were indeed synthesized. MALDI mass spectrometry was used to confirm the calculated weights of the oligomers synthesized and would have been particularly important had the Scholl reaction worked. Table 1 is a comparison of the expected masses of the various ortho-phenylenes, [4]-mer to the [12]-mer, with those as determined by MALDI. $^1$H-NMR was the most important tool for characterizing these oligomers. It was the $^1$H-NMR of the tetramer that first led us to believe that these molecules can assume a helical conformation as described by the Simpkins group.\(^{16}\) The tetramer, with protons and rings labeled, is shown in Figure 14. Based upon empirical substituent effects\(^{41}\) the tetramer could have the following $^1$H-NMR chemical shifts as in Table 2. However, a $^1$H-NMR of the tetramer, Figure 15, did not match the expected values.

Table 1

<table>
<thead>
<tr>
<th>Ortho-phenylene</th>
<th>Calculated mass m/z</th>
<th>Measured mass m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>[4]-mer</td>
<td>426.18</td>
<td>425.97</td>
</tr>
<tr>
<td>[6]-mer</td>
<td>638.27</td>
<td>638.23</td>
</tr>
<tr>
<td>[8]-mer</td>
<td>850.35</td>
<td>850.43</td>
</tr>
<tr>
<td>[10]-mer*</td>
<td>1062.43</td>
<td>1062.51</td>
</tr>
<tr>
<td>[12]-mer*</td>
<td>1274.52</td>
<td>1274.66</td>
</tr>
</tbody>
</table>

*Values provided by Dr. Jian He
Figure 14. *ortho*-Phenylene tetramer with rings and protons labeled.

### Table 2

<table>
<thead>
<tr>
<th>Proton</th>
<th>Chemical shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Multiple signals from 0.92 – 3.80</td>
</tr>
<tr>
<td>B</td>
<td>7.00</td>
</tr>
<tr>
<td>C/C'</td>
<td>7.59</td>
</tr>
<tr>
<td>D</td>
<td>7.20</td>
</tr>
<tr>
<td>E</td>
<td>7.07</td>
</tr>
<tr>
<td>F</td>
<td>7.67</td>
</tr>
</tbody>
</table>
Notable is the multiplet at approximately 6.5 ppm. This signal corresponds to the protons labeled C’. Recall that the Simpkins group, using ortho-phenylene oligomers, showed that these molecules do assume a helical conformation in the solid state.\textsuperscript{16} Though their molecules were unsubstituted, there is no reason to believe our molecules will not behave similarly in solution. This belief is based in part on the $^1$H-NMR of the tetramer, and specifically, the signal at 6.5 ppm. From Table 1, the protons labeled C/C’ are predicted to have the same chemical shift of 7.59 ppm. If the tetramer does indeed assume the helical conformation then as a result of the twisting ring #1 is above ring #4 while ring #2 and ring #3 are at a roughly 70 degree angle to each other. As a result of this shifting, the proton labeled C’ of ring #1 lies within the induced magnetic field of the ring #3 and the C’ proton of ring #4 lies within the magnetic field of ring #1 and both are therefore more shielded. This shielding causes them to be shifted upfield, appearing at the observed value of 6.5 ppm. It is well known from the literature that cofacial stacking of
aromatic rings leads to upfield shifts in NMR spectra. An example is the work the Shudo group did with the structure in Figure 16. It is the similarities in the values of the chemical shift of aromatic protons they observed that is evidence for the helical conformations. They found that the three protons (indicated by the asterisks) were all shifted upfield from the expected values, to 6.04. Further evidence for the tetramer possibly assuming a helical conformation comes from work done by the Nelson group. They demonstrated that the chemical shifts of protons within seven angströms of an aromatic ring are shifted upfield to a smaller value. When combined with the observation made by the Simpkins groups that in a helix the rings are separated by 3.2 angströms, it is reasonable to believe these ortho-phenylene oligomers can assume helical conformations. The $^1$H-NMR spectra of the hexamer and the octamer also led us to believe that these molecules assume helical conformations. The evidence we believe supports the proposed helical conformations comes primarily from two groups of the many examples available. The first is based upon work done by the Rathore group. They studied $\pi$-stacked polyfluorenes, and the structures of their molecules are shown in Figure 17. They found that as the number of fluorene units increases, going from $\text{F1}$ to $\text{F4}$, and as the $\pi$-stacking increases, the proton signals move further upfield. For example, the lowest value, for the aromatic protons of $\text{F1}$ was at approximately 7.25 ppm, conversely the lowest value for the aromatic protons of $\text{F4}$ was at approximately 6.05 ppm. The $^1$H-NMR spectra of these structures resembled those of the hexamer and the octamer. These are shown in Figures 18 and 19.

\[\text{X} = \text{O} \]
\[\text{X} = \text{NH}_2^+\text{Cl}^-\]
Figure 16. Adaptation of the Shudo group molecule.

Figure 17. The Rathore group polyflouorenes F1 to F4.

Figure 18. $^1$H-NMR spectrum of the ortho-phenylene hexamer
A comparison of the Rathore group NMR spectra and ours show similarities in the observed positions of the aromatic protons; however, our values are shifted even further upfield. As with the tetramer, these shifts are a result of anisotropic shielding due to the π-stacking of the aryl rings in these molecules. What is also noticeably different for our molecules is the broadening of the peaks. Unlike the Rathore molecules, which are rigid, the hexamer and octamer are more dynamic at room temperature and are able to assume different conformers. This broadening is a result of these different conformers these molecules have in solution that slowly interchange on the NMR timescale. The second piece of evidence is from work done by Prest, Prince, and Moore. They found that long chain oligomers adopt helical conformations and as a result they aggregate and cause a broadening of the NMR signal. This is similar to the broadening we observed for the hexamer and octamer.
Conclusion:

With the successful synthesis of the tetramer, hexamer, and octamer, ortho-phenylene oligomers are ready for closer examination and further experimentation. If these molecules do assume helical conformations as the current results indicate they do, then through-space charge transport may be possible. Additionally, their use as ion transport channels, or in the presence of donor and acceptor molecules, other uses would also be possible. With these uses, they can be tuned to specific needs, by increasing the length or changing the functional groups present, and as a result, their physical and electronic properties will change as well. With the successful creation of these oligomers we have also demonstrated an efficient method of synthesizing ortho-phenylenes in general. This process was done using various aspects of previous methods. Our method allowed us to create these molecules using functionalized biaryls in a previously unreported way. As organic molecules continue to be refined, their uses will continue to expand. While they will never full replace it, they may someday become a viable alternative for or a helpful addition to silicon.

The obvious continuation would be to optimize the current synthetic scheme. Work should continue in an attempt at synthesizing these molecules with longer alkoxy groups present, or synthesizing them with different and/or multiple functional groups present. Work should continue to investigate the electronic properties of these oligomers, as well as any future oligomers that are synthesized, i.e. those with different functional groups. Finally, a continued effort should be made to find the appropriate conditions to planarize these molecules.
Experimental:

Unless noted, all the starting materials, reagents, and solvents were from commercially available sources and used without further purification. Anhydrous THF was obtained by distillation from Na0/benzophenone. Melting points were determined using a Thermal Analysis Q20 differential scanning calorimeter at a heating rate of 10 °C/min. NMR spectra were measured in CDCl3 solutions using the Bruker Avance 300 or 500 MHz NMR spectrometers. Chemical shifts are reported in δ (ppm) relative to TMS, with the residual solvent protons used as internal standards (CDCl3: 7.26 for 1H, 77.16 for 13C). Mass spectra were recorded on Bruker Esquire ESI or Ultraflex MALDI spectrometers. MALDI spectra were acquired using dithranol as the matrix.

3,3’-Dimethoxy biphenyl (5).35 o-Dianisidine (20g, 81.9 mmol) was added to a boiling solution of 12 N HCl (15.5 mL) in water (200 mL), and stirred until nearly dissolved. The solution was then cooled in an ice bath until the temperature dropped to between 10–15 °C. At this point, additional 12 N HCl (17.5 mL) was added and stirring was continued until the temperature reached 10 °C. A solution of sodium nitrite (11.65 g, 16.5 mmol) in water (25 mL) was added dropwise over 10 minutes and the reaction mixture was stirred for an additional 20 minutes. The solution was then suction filtered and the filtrate added to an ice cold 50% hypophosphorous acid solution and allowed to slowly warm to room temperature overnight. The organic layer was separated with and the aqueous layer washed with Et2O (2x60 mL). The combined organic layers were washed with 20% sodium hydroxide solution, dried over K2CO3, filtered and concentrated. Purification by distillation gave 5 as a yellow oil, 14.4 g, 82%: 1H-NMR (CDCl3, 300 MHz) δ 7.39 (t, 2H), 7.21 (d, 2H), 7.17 (s, 2H), 6.95 (dd, 2H), 3.90 (s, 6H)

2,2’-5,5’-Dibromo-dimethoxy biphenyl (3).36 Bromine (2.5 g, 15.6 mmol) was added to a solution of biphenyl (5) (1 g, 4.8 mmol) in acetic acid (10 mL) and stirred 2 h. The crude was collected via suction filtration, washed with water and recrystallized from ethanol to give white needle-like crystals, 1.04g, 60%: 1H-NMR (CDCl3, 300 MHz) δ 7.53 (d, 2H), 6.82 (m, 4H), 3.81 (s, 6H)

2,2’-5,5’-Dibromo-dihydroxy biphenyl (6). A solution of 2-Diethylamino-ethanethiol hydrochloride (4.1 g, 24.3 mmol) in DMF (40.5 mL) was cooled to 0 °C. Potassium tert-
butoxide (5.8 g, 51.8 mmol) was added and stirred for 15 min at 0°C and then at room temperature for 15 min. The biphenyl (3) (3.0 g, 8.1 mmol) was added and the reaction mixture was refluxed for 24 h. The reaction mixture was then poured into water and acidified with 1 M HCl to a pH of 2 as measured by universal pH paper. The organic layer was then separated and the aqueous layer washed with Et₂O (2x20 mL). The combined organic layers were washed with brine, dried MgSO₄, filtered and concentrated. Recrystallization from toluene gives white needle-like crystals, 2.19 g, 79%: ¹H-NMR (CDCl₃ 300 MHz) δ 6.77 (t, 2H), 7.49 (t, 2H), 8.10 (d, 2H)

2,2’-5,5’-Dibromo-dodecyloxy biphenyl (7). A solution of dibromo-dihydroxy biphenyl (6) (2.5 g, 7.3 mmol), bromododecane (4.6 g, 4.4 mL, 18.3 mmol), and potassium carbonate (3.0 g, 21.9 mmol) in DMF (26.0 mL) was stirred at 85°C overnight under argon. The organic layer was then separated and the aqueous layer extracted with Et₂O (2x40 mL). The combined organic layers were washed with water, brine, then dried over MgSO₄, filtered and concentrated. Purification by flash chromatography (9:1 Hexanes:CH₂Cl₂) gave a white solid, 2.03 g, 41%: ¹H-NMR (CDCl₃, 300 MHz) δ 0.87 (m, 6H), 1.40-1.24 (m, 28H), 1.52 (m, 8H), 1.75 (m, 4H), 3.91 (t, 4H), 6.77 (t, 2H), 7.49 (t, 2H), 8.10 (d, 2H); MS (ESI) calculated for C₃₆H₅₆Br₂O₂ 678.26, found 687.25.

2-Bromo-2'-hydroxy-5,5'-dimethoxy biphenyl (9). To a flame dried round bottomed flask, under Ar, a solution of biphenyl (3) (5 g, 13.4 mmol) was dissolved in anhydrous THF (60 mL) and cooled to -78 °C (CO₂(s)/IPA). A solution of n-butyllithium in hexanes (1.6 M, 10.9 mL) was added dropwise and the aryllithium was stirred for 30 minutes. The aryllithium was then quenched with triisopropyl borate (6.2 mL) and allowed to warm to room temperature overnight. The reaction mixture was treated with a solution of sodium hydroxide (3.8 g, 95.0 mmol) in 30% hydrogen peroxide (40 mL), stirred for 3 h and then partitioned with ether. The organics were collected, washed with brine, dried over MgSO₄, filtered and concentrated. Purification by flash chromatography (3:1 Hexanes: EtOAc) gave 9 as a white solid, 3.03 g, 73%: m.p. 98.4 °C; ¹H-NMR (CDCl₃, 300 Mhz) δ 3.78 (s, 3H), 3.79 (s, 3H), 4.69 (br s, 1H), 6.71 (d, 1H, J = 2.8 Hz), 6.83 (dd,1H, J = 8.8, 3.1 Hz), 6.88 (dd, 1H, J = 9.0, 3.1 Hz), 6.89 (d, 1H, J = 2.9 Hz), 6.92 (d, 1H, J = 8.9 Hz), 7.57 (d, 1H, J = 8.8 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 55.8, 56.1,
2-Bromo-5,5’-dimethoxy-2’-tetrahydropyranoloxybiphenyl (10). A solution of 9 (4.0 g, 12.9 mmol), dihydropyran (1.63 g, 19.4 mmol), and pyridinium p-toluenesulfonate (0.33 g, 1.30 mmol) in CH₂Cl₂ (50 mL) was stirred overnight at room temperature. The reaction mixture was diluted with CH₂Cl₂ and the organic layer separated. The aqueous layer was extracted with CH₂Cl₂ (2x60 mL). The combined organic layers were washed with brine, dried over MgSO₄, filtered and concentrated. Purification by flash chromatography (85:15 Hexanes:EtOAc) gave 10 as a colorless oil, 4.43 g, 87 %. ¹H-NMR (CDCl₃, 500 MHz) δ 1.51-1.68 (m, 6H), 3.55 (m, 1H), 3.79 (s, 6H), 3.84 (m, 1H), 5.22 (s, 1H), 6.76 (d, 1H, J = 3.0 Hz), 6.78 (d, 1H, J = 3.1 Hz), 6.81-6.93 (br m, 1H), 6.88 (dd, 1H, J = 9.0, 3.1 Hz), 7.18 (d, 1H, J = 9.0 Hz), 7.51 (d, 1H, J = 8.7 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 18.3, 18.9, 19.9, 25.4, 30.6, 55.6, 55.8, 61.7, 62.2, 94.7, 97.5, 98.4, 114.3, 115.0, 116.2, 117.0, 117.4, 132.4, 133.0, 140.7, 148.5, 154.1, 158.5; MS (ESI) calculated for C₁₉H₂₁BrO₄+Na 415.0, found 415.1.

2,9-Dimethoxydibenzo[c,e][1,2]oxaborinin-6-ol (11). A flame dried round bottomed flask was purged with Ar and then charged with a solution of 10 (4.0 g, 10.2 mmol) in anhydrous THF (70 mL) and cooled to -78 °C (CO₂(s)/IPA). A solution of n-butyllithium in hexanes (1.6 M, 8.3 mL) was added dropwise and stirred for 30 minutes. The aryllithium was then treated with triisopropyl borate (4.7 mL, 20.34 mmol) in one portion and the reaction mixture was allowed to slowly warm to room temperature overnight. The reaction mixture was treated with 1M HCl and stirred for 4 h. The organic layer was then separated and the aqueous layer was extracted with Et₂O (2x30 mL). The combined organic layers were washed with water, brine, dried MgSO₄, filtered and concentrated. Purification by flash chromatography (7:3 Hexanes:EtOAc) gave 11 as a white solid, 2.11 g, 81 %. ¹H-NMR (CDCl₃, 300 MHz) δ 3.89 (s, 3H), 3.96 (s, 3H), 4.57 (br s, 1H), 6.96 (dd, 1H, J = 8.9, 3.0 Hz), 7.05 (dd, 1H, J = 8.3, 2.3 Hz), 7.19 (d, 1H, J = 8.9 Hz), 7.53 (m, 2H), 7.99 (d, 1H, J = 8.3 Hz); ¹³C NMR (CDCl₃) δ 55.3, 55.9, 106.2, 108.0, 114.2, 115.3, 120.2, 123.3, 135.2, 142.2, 145.9, 154.8, 163.2; MS (ESI) calculated for C₁₅H₁₅BO₄+Na (methyl ester of 1—spectrum run in MeOH) 293.1, found 293.1.
**ortho-Phenylene hydroxy trimer (12).** A Schlenk tube was charged with 11 (0.5 g, 2.0 mmol), Pd(OAc)$_2$ (0.44 g, 0.2 mmol), SPhos (1.0 g, 2.4 mmol), K$_3$PO$_4$ (0.8 g, 3.9 mmol) and flushed/backfilled with argon (3x). A solution of 4-bromoanisole (1.1 g, 5.9 mmol) in anhydrous THF (10 mL) was added to the vacuum tube. The reaction mixture was then degassed (freeze/pump/thaw) (3x), sealed and then heated at 85-90 °C overnight. The reaction mixture was diluted with EtOAc (20 mL), the organic layer was separated and the aqueous layer was extracted with EtOAc (2x20 mL). The combined organic layers were washed with water, brine, dried over MgSO$_4$, filtered and concentrated. Purification by flash chromatography (9:1 Hexanes:EtOAc) gave 12 as a pale yellow solid, 0.46 g, 70%: $^1$H-NMR (CDCl$_3$, 500 MHz) δ 3.70 (s, 3H), 3.76 (s, 3H), 3.86 (s, 3H), 4.47 (br s, 1H), 6.68 (d, 1H, $J = 2.8$ Hz), 6.71 (d, 1H, $J = 8.7$ Hz), 6.73–6.77 (m, 3H), 6.91 (d, 1H, $J = 2.8$ Hz), 7.01 (dd, 1H, $J = 8.6$, 2.8 Hz), 7.39 (d, 1H, $J = 8.6$ Hz); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 55.1, 55.4, 55.7, 113.6, 114.5, 114.6, 116.0, 116.2, 116.6, 128.8, 130.1, 131.7, 132.6, 133.5, 136.4, 146.4, 153.3, 158.5, 158.9; MS(MALDI) calculated for C$_{21}$H$_{20}$O$_4$ 336.14, found 335.83.

**Triflated ortho-phenylene trimer (13).** A solution of 12 (0.45 g, 1.3 mmol) and pyridine (0.16 mL, 2.0 mmol) in CH$_2$Cl$_2$ (4 mL) was cooled to 0 °C. Trifluoromethane sulfonic anhydride (0.3 mL, 1.6 mmol) was added dropwise and the reaction mixture was allowed to slowly warm to room temperature overnight. The reaction mixture was diluted with EtOAc. The organic layer was washed with 1 M HCl, water, brine, dried over MgSO$_4$, filtered and concentrated. Purification by flash chromatography (4:1 Hexanes:EtOAc) gave 13 as a pale yellow solid, 0.49 g, 78%: m.p. 108.9 °C; $^1$H-NMR (CDCl$_3$, 300 MHz) δ 3.73 (s, 3H), 3.77 (s, 3H), 3.87 (s, 3H), 6.76 (m, 2H), 6.82 (dd, 1H, $J = 8.9$, 3.1 Hz), 6.86 (d, 1H, $J = 3.0$), 6.98 (d, 1H, $J = 2.6$ Hz), 7.01–7.10 (m, 4H), 7.36 (d, 1H, $J = 8.5$ Hz); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 55.2, 55.6, 55.7, 114.3, 114.8, 116.4, 117.5, 122.7, 130.5, 131.5, 133.2, 134.0, 134.9, 136.6, 140.3, 158.4, 158.5, 158.6; MS(MALDI) calculated for C$_{22}$H$_{19}$F$_3$O$_6$S 468.09, found 467.92.

**ortho-Phenylene tetramer (14).** A Schlenk tube was charged with 13 (0.2 g, 0.43 mmol), 4-methoxy phenylboronic acid (0.2 g, 1.3 mmol), Pd(OAc)$_2$ (0.01 g, 0.04 mmol), SPhos (0.2 g, 0.05 mmol), K$_3$PO$_4$ (0.3 g, 1.3 mmol) and then flushed/backfilled with Ar. A solution of THF/H$_2$O (4:1, 4 mL) was added and then degassed (freeze/pump/thaw) (3x). The tube was then sealed and heated at 85-90 °C overnight. The reaction mixture was cooled and then diluted
with EtOAc. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with water and brine, dried MgSO₄, filtered and concentrated. Purification by flash chromatography (4:1 Hexanes:EtOAc) gave 14 as a white solid, 0.15 g, 81%: m.p. 168.2 °C; ¹H-NMR (CDCl₃, 500 MHz) δ 3.75 (s, 6H), 3.82 (s, 6H), 6.56 (m, 8H), 6.87 (dd, 2H, J = 8.4, 2.7 Hz), 6.95 (d, 2H, J = 2.7 Hz), 7.08 (d, 2H, J = 2.7 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 55.4, 55.5, 113.0, 113.4, 116.7, 130.2, 131.1, 133.5, 133.6, 141.2, 157.9, 158.4; MS (MALDI) calculated for C₂₈H₂₆O₄ 426.18, found 425.96; anal. calculated for C₂₈H₂₆O₄ C 78.85, H 6.14, found C 78.56, H 6.26.

ortho-Phenylenedioxy pentamer (15). A Schlenk tube was charged with a solution of 13 (0.40 g, 0.85 mmol), 11 (0.28 g, 1.10 mmol), Pd(OAc)₂ (0.02 g, 0.09 mmol), SPhos (0.04 g, 0.10 mmol) and K₃PO₄ (0.36 g, 1.70 mmol) in THF/H₂O (4:1) (10.0 mL) and flushed/backfilled with argon. The reaction mixture was then degassed (freeze/pump/thaw) (3x), the tube was sealed and heated overnight at 85-90 °C. The reaction mixture was diluted with EtOAc (20 mL), the organic layer was separated and the aqueous layer was extracted with EtOAc (2x20 mL). The combined organic layers were washed with water, brine, dried over MgSO₄, filtered and concentrated. Purification by flash chromatography (9:1 Hexanes:EtOAc) gave 15 as a pale yellow solid, 0.39 g, 83%: ¹H-NMR (CDCl₃, 500 MHz) δ 3.55 (br s, 3H), 3.74 (br s, 3H), 3.78 (s, 3H), 3.80 (s, 3H), 3.84 (br s, 3H), 4.23 (br s, 1H), 6.03 (br s, 1H), 6.08 (br s, 1H), 6.19 (br s, 1H), 6.5–6.8 (br m, 8H), 6.85–6.95 (br m, 3H), 7.05 (br s, 1H), 7.13 (br s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 54.8, 55.1, 55.2, 77.4, 112.8, 113.0, 113.5, 114.4, 115.4, 116.0, 116.7, 116.8, 128.5, 130.0, 130.1, 132.2, 132.4, 132.5, 132.8, 133.3, 133.5, 136.4, 140.1, 142.1, 146.5, 152.8, 157.8, 158.1, 158.7; MS (MALDI) calculated for C₃₅H₃₂O₆ 548.22, found 548.20.

Triflated ortho-phenylene pentamer (16). A solution of 15 (0.40 g, 0.73 mmol) and pyridine (0.07 mL, 0.87 mmol) in CH₂Cl₂ (5.0 mL) was cooled to 0 °C. Trifluoromethane sulfonic anhydride (0.18 mL, 1.10 mmol) was added dropwise and reaction mixture was allowed to slowly warm to room temperature overnight. The reaction mixture was diluted with EtOAc. The organic layer was washed with 1 M HCl, water, brine, dried over MgSO₄, filtered and concentrated. Purification by flash chromatography (9:1 Hexanes:EtOAc) gave 16 as a pale yellow solid, 0.35 g, 77%: m.p. 175.0 °C; ¹H-NMR (CDCl₃, 500 MHz) δ 3.71 (br s, 3H), 3.74
(br s, 3H), 3.79 (s, 6H), 3.86 (s, 3H), 5.92 (br s, 1H), 5.99 (br s, 1H), 6.07 (br s, 1H), 6.5–6.7 (br m, 6H), 6.75 (br m, 1H), 6.79 (br s, 2H), 6.92 (br s, 2H), 6.99 (br m, 1H), 7.15 (br s, 1H); \( ^{13} \text{C} \) NMR (CDCl\(_3\), 125 MHz) \( \delta \) 54.8, 55.3, 55.4, 112.76, 112.85, 113.2, 114.1, 115.8, 116.2, 116.5, 116.8, 117.0, 119.6, 121.7, 129.6, 130.1, 130.7, 132.6, 132.9, 133.7, 134.0, 135.1, 136.6, 139.8, 140.7, 141.2, 157.8, 158.0, 158.2, 158.8; MS (MALDI) calculated for C\(_{36}\)H\(_{31}\)F\(_3\)O\(_8\)S 680.17, found 680.27.

**ortho-Phenylene hexamer (17).** A Schlenk tube was charged with a solution of 16 (0.20 g, 0.32 mmol), 4-methoxyphenylboronic acid (0.15 g, 0.97 mmol), Pd(OAc)\(_2\) (0.01 g, 0.03 mmol), SPhos (0.02 g, 0.04 mmol) and K\(_3\)PO\(_4\) (0.21 g, 0.97 mol) in THF/H\(_2\)O (4:1) (4.0 mL) and flushed/backfilled with Ar. The reaction mixture was then degassed (freeze/pump/thaw) (3x), the tube was sealed and heated overnight at 85-90 °C. The reaction mixture was cooled and then diluted with EtOAc. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with water and brine, dried over MgSO\(_4\), filtered and concentrated. Purification by flash chromatography (9:1 Hexanes:EtOAc) gave 17 as a white solid, 0.16 g, 77%; m.p. 176.2 °C; \(^1\)H-NMR (CDCl\(_3\), 500 MHz, -5 °C) \( \delta \) 3.74 (s, 6H), 3.75 (s, 6H), 3.80 (s, 6H), 5.68 (d, 2H, \( J = 8.5 \) Hz), 5.94 (d, 2H, 2.7 Hz), 6.35–6.42 (br m, 6H), 6.49 (d, 4H, \( J = 8.6 \) Hz), 6.65 (d, 2H, \( J = 2.7 \) Hz), 6.76 (dd, 2H, \( J = 8.5, 2.7 \) Hz), 6.93 (br d, 2H, \( J = 8.3 \) Hz); MS (MALDI) calculated for C\(_{42}\)H\(_{38}\)O\(_6\) 638.27, found 638.22; anal. calculated for C\(_{42}\)H\(_{38}\)O\(_6\) C 78.97, H 6.00, found C 78.38, H 6.21.

**ortho-Phenylene hydroxy heptamer (18).** A Schlenk tube was charged with a solution of 16 (0.20 g, 0.32 mmol), 11 (0.17 g, 0.65 mmol), Pd(OAc)\(_2\) (0.01 g, 0.03 mmol), SPhos (0.02 g, 0.04 mmol) and K\(_3\)PO\(_4\) (0.42 g, 0.65 mol) in THF/H\(_2\)O (4:1) (4.0 mL) and flushed/backfilled with Ar. The reaction mixture was then degassed (freeze/pump/thaw) (3x), the tube was sealed and heated overnight at 85-90 °C. The reaction mixture was diluted with EtOAc (20 mL), the organic layer was separated and the aqueous layer was extracted with EtOAc (2x20 mL). The combined organic layers were washed with water, brine, dried over MgSO\(_4\), filtered and concentrated. Purification by flash chromatography (9:1 Hexanes:EtOAc) gave 18 as a pale yellow solid, 0.18 g, 72%; MS (MALDI) calculated for C\(_{49}\)H\(_{44}\)O\(_6\) 760.30, found 760.39.
**Triflated ortho-phenylene heptamer (19).** A solution of 18 (0.15 g, 0.20 mmol) and pyridine (0.05 mL, 0.57 mmol) in CH\(_2\)Cl\(_2\) (5.0 mL) was cooled to 0 °C. Trifluoromethane sulfonic anhydride (0.10 mL, 0.49 mmol) was added dropwise and the reaction mixture was allowed to slowly warm to room temperature overnight. The reaction mixture was diluted with EtOAc. The organic layer was washed with 1 M HCl, water, brine, dried over MgSO\(_4\), filtered and concentrated. Purification by flash chromatography (9:1 Hexanes:EtOAc) gave 19 as a pale yellow solid, 0.13g, 80%, m.p. 154.3 °C; MS (MALDI) calculated for C\(_{50}\)H\(_{43}\)F\(_3\)O\(_{10}\)S 892.25, found 892.37.

**ortho-Phenylene octamer (20).** A Schlenk tube was charged with a solution of 19 (0.10 g, 0.12 mmol), 4-methoxyphenylboronic acid (0.06 g, 0.37 mmol), Pd(OAc)\(_2\) (0.01 g, 0.01 mmol), SPhos (0.01 g, 0.01 mmol) and K\(_2\)PO\(_4\) (0.08 g, 0.37 mol) in THF/H\(_2\)O (4:1) (4.0 mL) and flushed/backfilled with Ar. The reaction mixture was then degassed (freeze/pump/thaw) (3x), the tube was sealed and heated overnight at 85-90 °C. The reaction mixture was cooled and then diluted with EtOAc. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with water and brine, dried over MgSO\(_4\), filtered and concentrated. Purification by flash chromatography (9:1 Hexanes:EtOAc) gave 20 as a white solid, 0.09 g, 85%, m.p. 177.1°C; \(^1\)H-NMR (CDCl\(_3\), 500 MHz) \(\delta\) 3.64 (s, 6H), 3.68 (s, 6H), 3.72 (s, 6H), 3.83 (s, 6H), 5.52 (d, 2H, \(J = 2.7 \text{ Hz}\)), 5.62 (d, 2H, \(J = 8.4 \text{ Hz}\)), 5.73 (d, 2H, \(J = 2.7 \text{ Hz}\)), 6.01 (d, 2H, \(J = 8.4 \text{ Hz}\)), 6.20 (dd, 2H, \(J = 8.4, 2.9 \text{ Hz}\)), 6.22 (d, 4H, \(J = 8.6 \text{ Hz}\)), 6.41 (d, 4H, \(J = 8.7 \text{ Hz}\)), 6.43 (dd, 2H, \(J = 8.0, 2.8 \text{ Hz}\)), 6.60 (d, 2H, \(J = 2.6 \text{ Hz}\)), 6.62 (dd, 2H, \(J = 9.0, 2.8 \text{ Hz}\)), 6.77 (d, 2H, \(J = 8.4 \text{ Hz}\)); MS (MALDI) calculated for C\(_{56}\)H\(_{50}\)O\(_8\) 850.35, found 850.42; anal. calculated for C\(_{56}\)H\(_{50}\)O\(_8\) C 79.04, H 5.92, found C 79.21, H 6.12.
References:
