ABSTRACT

DESIGN, SYNTHESIS AND CHARACTERIZATION OF *m*-PHENYLENE ETHYNYLENE-BASED MACROCYCLES AS DISCOTIC LIQUID CRYSTALS

by Ashley Nicole Scioneaux

Many organic materials that have liquid crystalline properties have found applications in liquid crystal displays and photovoltaics. For this reason, it is highly likely that novel discotic liquid crystals will play a significant role in the next generation of electronics. A stepwise synthesis for discotic alkyloxy-substituted tetrabenzo[18]cyclynes (TBCs), which contain hexyloxy, decyloxy, and dodecyloxy side chains, is reported. Our TBCs are a set of shape persistent macrocycles designed for charge transport across the cross-conjugated backbone. With a structured backbone and flexible side units, the macrocycles should theoretically possess liquid crystalline properties and exhibit self-assembly via intermolecular $\pi-\pi$ stacking and/or van der Waals interactions. Recrystallized **12a-c** macrocycles were tested for liquid crystallinity with differential scanning calorimetry and polarized optical microscopy. Results suggest that none of the *meta*-phenylene ethynylene-based macrocycles possess thermotropic columnar liquid crystallinity; further explanations of these results are given.
DESIGN, SYNTHESIS AND CHARACTERIZATION OF \textit{m}-PHENYLENE ETHYNYLENE-BASED MACROCYCLES AS DISCOTIC LIQUID CRYSTALS

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<tr>
<td>DABCO</td>
<td>1,4-Diazabicyclo[2.2.2]octane</td>
</tr>
<tr>
<td>DIPA</td>
<td>Diisopropylamine</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N’-Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl Sulfoxide</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel Permeation Chromatography</td>
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<tr>
<td>HABA</td>
<td>2-(4’-Hydroxybenzeneazo)benzoic acid</td>
</tr>
<tr>
<td>HMBC</td>
<td>Heteronuclear Multiple Bond Correlation</td>
</tr>
<tr>
<td>HMQC</td>
<td>Heteronuclear Multiple Quantum Coherence</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>J</td>
<td>Coupling Constant (Hz)</td>
</tr>
<tr>
<td>LC</td>
<td>Liquid Crystal</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic Light-Emitting Diode</td>
</tr>
<tr>
<td>POM</td>
<td>Polarized Optical Microscopy</td>
</tr>
<tr>
<td>SPM</td>
<td>Shape-Persistent Macrocycle</td>
</tr>
<tr>
<td>TBAB</td>
<td>Tetrabutylammonium Bromide</td>
</tr>
<tr>
<td>TBAF</td>
<td>Tetrabutylammonium Fluoride</td>
</tr>
<tr>
<td>TBC</td>
<td>Tetrabenzo[18]cyclyne</td>
</tr>
<tr>
<td>TIPS</td>
<td>Triisopropylsilyl</td>
</tr>
<tr>
<td>TIPSA</td>
<td>Triisopropylsilyl Acetylene</td>
</tr>
<tr>
<td>TMS</td>
<td>Trimethylsilyl</td>
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<td>TMSA</td>
<td>Trimethylsilyl Acetylene</td>
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I dedicate this manuscript to the late Dr. Jim Hershberger, Ms. Valerie Robinson, my fiancé Joel Spells, my parents Alvin and Yevette Scioneaux, and my siblings Alvin, Ariel, Ashton, Austin, Asia, and Aaron for providing constant love and encouragement during my time at Miami University; you all have made my time in Oxford, Ohio more productive and enjoyable than I could have imagined.
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Chapter 1: Introduction

1.1 States of Matter

Atoms make up all matter, and they can be organized in a variety of ways within a given substance. It is this arrangement that dictates what properties will be expressed for a given substance. In General Chemistry we are introduced to two basic concepts: “matter is composed of various types of atoms” and “one substance changes to another by reorganizing the way the atoms are attached to each other.”

Matter is anything that occupies space and has mass, and it exists primarily in three states: solid, liquid, and gas (Figure 1.1). A solid is a rigid substance that does not flow under moderate stress because it has a fixed volume and shape. Molecules of a solid are usually stacked close together in a three-dimensional periodic lattice and exhibit long-range positional and orientational order. Crystals can be either isotropic or anisotropic depending on the crystal lattice, but liquids are isotropic. A liquid is a substance that has definite volume, but no specific shape because the constituent molecules are allowed to flow freely. A gas is a substance that has no fixed volume or shape. When a substance does not fit neatly into one of these three states of matter, new phases are discovered (e.g., liquid crystal phases).

![Figure 1.1 Abstract representation of the three states of matter: a) solid; b) liquid; c) gas](image)

A liquid crystal (LC) phase (i.e., mesophase or mesomorphic phase) is between the crystalline solid phase and the isotropic liquid phase and therefore exhibits properties of both; they have long-range order, but are fluids. The anisotropic behavior of LCs includes their permittivity, refractive index, elasticity, absorbance, conductivity, flow behavior, and response to
electric fields. Liquid crystalline molecules tend to have an ordered, rigid core with aliphatic solubilizing groups (e.g., alkyl or alkoxy groups) for the purpose of promoting fluidity. Like molecules in a crystal lattice, mesophases may have long-range positional and orientational order, which is attributed to the intermolecular interactions between the constituent molecules.

1.2 Liquid Crystals: Discovery, Development, and Characterization

The discovery for the liquid crystal phase of matter is credited to an Australian botanist by the name of Friedrich Reinetzer. In 1888, Reinetzer was studying a derivative of cholesterol, known today as cholesteryl benzoate, and he was intrigued when he found it had two melting points. In collaboration, Otto Lehmann, a professor of natural philosophy in Germany, checked the crystallization properties of cholesteryl benzoate under a polarizing microscope. Lehmann called this new class of substances a variety of names (e.g., soft crystals and crystalline fluids), but he ultimately settled on the name “liquid crystals.”

Since technology was not advanced enough to fully examine these novel mesophases, understanding liquid crystal phases was moderately slow. The lack of interest in mesophases was probably due to the fact that these molecules were not discussed in textbooks and reasonable applications for these molecules had not yet been found.

Glenn Brown, an American chemist, was one of the pioneers to resurrect research interest in LCs through publication of several manuscripts (from 1955-1987) on liquid crystalline molecules. Once physicists and chemists observed LCs in biological systems, detergents, and polymers, LCs began to appear in several commercial products. Biological materials that possess a liquid crystal phase include the tobacco mosaic virus and myelin, which is a fatty material from nerve cells.

Liquid crystalline phases were traditionally investigated by optical means with instruments such as the polarizing optical microscope and the x-ray diffractometer, which has been most useful in studying their microscopic structure. Polarizing optical microscopy is commonly considered a required technique when analyzing LCs, because it gives information about the structure, orientation, and type(s) of LC phases present at various temperatures. This
technique involves sandwiching a thin sample of the material between a glass slide and glass coverslip, which are then placed in the temperature-controlled stage of the microscope. As the temperature is increased, a magnified view of the sample between two crossed polarizers (perpendicular to one another) may display various liquid crystalline textures and/or colors. These colors and textures are results of the birefringence of the material.

LC birefringence (i.e., double refraction) produces different refractive indices due to the anisotropy of LCs, which in turn changes the polarization of polarized light to give colored or black illustrations of the bulk material. The appearance of blackness occurs when there is no sample or when the polarized light passes through an isotropic liquid in which there is no director. A director ($n$) is a dimensionless unit vector that designates the preferred direction of the molecules. In other words, the polarized light is unaffected so it is not transmitted through the other polarizer.

New instrumental techniques including differential thermal analysis and nuclear magnetic resonance (NMR) spectroscopy made it possible to effectively evaluate the intermolecular forces of LCs. Differential scanning calorimetry (DSC) is a type of differential thermal analysis technique that is usually coupled with another complimentary technique, such as x-ray analysis, to classify LC phases adequately. DSC measures the enthalpy change associated with a crystal-liquid phase transition or any other phase transition, and it can give some sense of the degree of order (proportionally) within the mesophase. DSC operates by measuring the energy required to maintain identical temperatures for two pans: a reference (empty) pan and the sample pan. The instrument measures the enthalpy change for a sample of material with a particular weight. Once mesophases are fully characterized and analyzed, then they can be tested within various systems for plausible applications based on their properties.

1.3 Liquid Crystals: Advantages and Applications

Applications for LCs took off in the 1970s beginning with liquid crystal displays (LCDs), which became a multi-million dollar industry by the early 1980s. Devices that involve LCDs,
such as calculators and wristwatches, are attractive because they are cost- and energy-efficient. These devices are often small and durable, and they require low power to operate.9

1.3.1 Types of Designs: Calamitic and Discotic LCs

Applications for calamitic (i.e., rod-shaped) molecules have been studied since the early 1900s. Temperature sensors,10 natural silk,11 and high-strength materials (e.g., Kevlar10) are examples of calamitic applications, but LCDs are the most profitable and researched application of all. Portable computers and flat panel televisions make up a large portion of this market. The most popular LCD technology is the twisted nematic LCD, which operates with homogeneous alignment.12 When considering materials for LCDs, the following features are evaluated: stability for long periods of time; liquid crystalline behavior within the appropriate temperature range; low viscosity, anisotropy, dielectric and mechanical properties (allowing fast switching); and optical properties.2,13 Although displays are more complicated than what is being mentioned, finding the right LC properties is significant in the manufacturing of efficient displays. Often mixtures of liquid crystalline compounds are required to obtain the desired performance within displays. Good (primarily homogeneous) alignment of the molecules on the glass substrate makes for a good LC display.14,15

As a result of the success of LCDs, research skyrocketed on the investigation of structure-property relationships of LCs, which raised questions regarding discotic (disc-shaped and often planar) molecules. Figure 1.2 shows a discotic LC (mesophase is within 88.6-145.6 °C) and the columnar structure it forms. Discotic LCs are not yet understood as well as calamitic LCs, but significant progress has been made since the 1977 discovery3 of discotic mesophases.
Various publications have reported that discotic LCs have potential applications in organic light-emitting diodes (OLEDs),\textsuperscript{3,16} sensors,\textsuperscript{17} field effect transistors,\textsuperscript{18} and photovoltaics.\textsuperscript{13,19} Charge transfer in OLEDs is improved with $\pi$-$\pi$ stacking, but if the spacing between the discs is too large then charge-carrier mobility will be reduced.\textsuperscript{20} In addition, having too large of a ring system may disrupt the LC phase altogether because it will be difficult to fill the space necessary to promote the liquid crystal phase.\textsuperscript{21}

1.4 Phase Transitions

Calorimetry is the science of measuring heat and it is “based on observing the temperature change when a substance absorbs or discharges energy as heat.”\textsuperscript{1} The phase transition from solid to liquid for organic materials is not limited to a single transition, but may undergo a series of transitions involving phases that are intermediate phases between crystal and liquid phases.\textsuperscript{2,9} The enthalpy for the transition from a liquid crystal to a liquid is about 5 J/g, which can be translated to 0.3-6 kJ/mol.\textsuperscript{2} When there is no evidence that a mesophase exists, the enthalpy for the transition from a crystal to a liquid is about 250 J/g, which can be translated to 30-50 kJ/mol.\textsuperscript{2}

1.4.1 Thermotropic and Lyotropic LCs

Phase transitions do not necessarily depend on temperature; some mesophases depend on other conditions (e.g., solvent). There are two classes of LCs: thermotropic and lyotropic. The

Figure 1.2 Discotic LC: Hexabutoxyltriphenylene\textsuperscript{10}
presence or absence of thermotropic LC phases depends on temperature, whereas lyotropic LCs depend on concentration\(^9\) (and temperature). Thermotropic LCs are further split up into calamitic (rod-shaped) and discotic (disc-shaped) LCs. Most discotic LCs are thermotropic LCs because they have a functional LC phase within a specific temperature interval, but some have been found to be lyotropic based on their amphiphilic design (e.g., derivatives of phthalocyanines)\(^{22-24}\). Lyotropic LCs are more relevant to biological applications, so they will not be discussed in great detail here.

### 1.5 Liquid Crystals: Phases and Ordering

The two basic types of mesophases for calamitics are “nematic” and “smectic,” and each of these terms were coined by Georges Friedel in 1922.\(^9\) In Greek, “nematic” means thread and “smectic” means soap; these names were given based on the appearance of the phases under the microscope.\(^9,25\) The molecules of the nematic phase are orientationally ordered, but not positionally ordered.\(^3\) Meanwhile, the molecules of the smectic phase are orientationally and positionally ordered (layered).\(^3\) The two main types of mesomorphic phases for discotics are “nematic” and “columnar.” Columnar phases are so named because the molecules arrange themselves into columns via intermolecular forces according to microphase segregation (e.g., aromatic vs. aliphatic). LCs tend to have positional order in one or two dimensions, but never all three.\(^9\) As a result, no liquid crystalline material will exhibit all liquid crystal phase types.\(^2\)

If molecules are aligned along their long axes in one direction where they appear more or less parallel to one another, then they are called “nematics.” In the nematic phase there is orientational order, but no positional order.\(^9\) It is the simplest LC phase; the degree of order within this phase is very similar to the degree of order of an isotropic liquid. Therefore, the nematic phase usually occurs at a higher temperature than smectic or columnar phases. A nematic phase will usually appear slightly opaque or cloudy.

The alignment of calamitic molecules is also an essential aspect to consider. The alignment of liquid crystalline molecules is either homeotropic, where the long axis of the molecules is perpendicular to the glass surface, or homogeneous/planar, where the long axis of
the molecules is parallel to the glass surface.\textsuperscript{2,12,14} Many applications are designed in such a way to permit control of the alignment of the molecules so that the desired results may be achieved.

Although there is only one nematic phase, there are many different types of smectic phases. Since 1965, interest in nematics has grown at a rapid pace, but smectic mesophases have gained little attention from industry because of their high viscosities.\textsuperscript{9} Smectics are layered structures that are more ordered than nematics. Molecules with this phase tend to arrange themselves parallel to one another.\textsuperscript{25} Recall the director ($n$) is the preferred direction a molecule points, and if the director is pointed perpendicular to the layers it is known as smectic A, but if the molecules are tilted slightly then it is smectic C (Figure 1.3).\textsuperscript{2,7}

![Smectic A and Smectic C Phases](image)

**Figure 1.3** Abstract representation of smectic A and smectic C phases

Disc-like molecules are designed to form “discotic” LCs, which may have the following phases: N\textsubscript{D}, Col\textsubscript{h}, and Col\textsubscript{r} (smectic is very rare) (Figure 1.4).\textsuperscript{26} The discotic nematic phase (N\textsubscript{D}) is considered the simplest phase of disc-like molecules; they have one axis shorter than the others and the molecules are sporadically arranged in the direction of the director ($n$).\textsuperscript{2} Discotic LCs have the potential to arrange in columns (i.e., columnar phases). Columnar phases exhibit positional order and possess a two-dimensional lattice that is perpendicular to the plane of the columns.\textsuperscript{2} These columns may arrange in a hexagonal (Col\textsubscript{h}) or rectangular (Col\textsubscript{r}) fashion (Figure 1.4). According to these columns, if the column axis is perpendicular to the glass surface then it has homeotropic alignment (i.e., the shortest axis of the discotic molecule is perpendicular
to the surface). If the columns are parallel to the glass surface then it has homogeneous alignment (i.e., the shortest axis of the discotic molecule is parallel to the surface).

![Diagram of ND, Colh, and Colr phases]

Figure 1.4 Abstract representation of ND, Colh, and Colr phases

Some discotic molecules may have both columnar and nematic phases, but others may possess only one of these phases. When trying to find a balance between the makeup of the core and the substituents, space filling is a key concept to keep in mind. It will promote stacking of discotic molecules. Steric effects and electron repulsion will inhibit or weaken the intermolecular interactions for columnar stacking of discotic structures. For example, when the functional groups have acetylene linkages to the core, this will lower the melting point and generate a nematic phase; consequently, the columnar phase will be sacrificed due to repulsion of the acetylene units (if there are too many acetylene linkages). There are also instances where intermolecular interactions are only strong enough to allow a nematic phase to occur. Discotic materials are more sensitive than calamitic materials when it comes to slight structural changes, which may be attributed to the molecular arrangement along the short molecular axis rather than the long molecular axis.

1.6 Liquid Crystalline Designs

A multidisciplinary approach is needed to fully design, develop, and evaluate a meaningful and logical synthesis of liquid crystals, which means adequate knowledge from diverse fields serves as an advantage. The findings of chemists are only part of the whole understanding of LCs. As chemists, examining the correlation between structure-property
relationships\textsuperscript{27} and monitoring how small changes to the structure affect the phase properties and phase transitions is an important contribution to the field.

### 1.6.1 Discotic LCs: Core and Substituents

The core of discotic LC molecules is usually based on (but not limited to) benzene, triphenylene, phthalocyanine or truxene with six to eight hydrocarbons attached to the periphery. If all the substituents are identical, it is more likely that the desired discotic architecture will form.\textsuperscript{2} Symmetrical designs are attractive due to their ability to create discotic liquid crystals, but unsymmetrical designs have yielded discotic LCs as well.\textsuperscript{24} Figure 1.5 shows some of the substituents often used when synthesizing discotic LCs.

![Figure 1.5](image)

Figure 1.5 Typical substituents attached to the core of a discotic liquid crystal\textsuperscript{2}

Making minor changes to either the core or the solubilizing groups around the periphery can drastically change the presence or absence of a liquid crystalline mesophase. If the anisotropy of the long or short axis of the molecules is changed, it will consequently affect the thermal stability of the mesophase.\textsuperscript{28} Nevertheless, the scope of discotic LCs will continue to expand as a result of innovative (unsymmetrical) designs and syntheses.

### 1.6.2 Shape Persistent Macrocycles and Self-Assembly

A shape-persistent macrocycle (SPM) is a molecule that has a relatively rigid backbone that cannot collapse;\textsuperscript{31-33} SPMs are often used in supramolecular chemistry since they are capable
of self-assembly within supramolecular systems that require highly organized networks. SPMs can be challenging and time-consuming to synthesize, especially when they are unsymmetrical. They are synthesized under kinetic control or thermodynamic control. Kinetically controlled reactions involve irreversible bond formations, such as Sonogashira-couplings. Thermodynamically controlled reactions produce the more thermodynamically stable product through reversible bond formations, such as alkyne metathesis. Many successful macrocyclizations are a result of highly dilute conditions, which favor cyclic products versus acyclic oligomers. A schematic representation of the self-assembly of SPMs into columnar structures is shown in Figure 1.6.

![Figure 1.6 Stacking illustration of SPMs with an internal void](image)

SPMs are synthesized with a particular structural motif, molecular design, size, and configuration in mind. They have been successfully used in supramolecular self-assemblies, host-guest systems, solution state aggregation, and liquid crystals. In regards to liquid crystals, Moore and coworkers created a phenylacetylene macrocycle (PAM: A) that forms a tubular liquid crystal within a hexagonal columnar lattice in the absence or presence of silver ions (Figure 1.7). PAM A has an internal void that can be occupied by silver ions; therefore, it can serve as channel conduction material (i.e., ion conductors). According to powder x-ray diffraction, A will maintain columnar phases at 1% and 2% of (doped) silver triflate. Results
suggest the stacking pattern involves any of the following: alternating orientations, alternating tilts about inequivalent axes, periodic distortions of the side chains, etc.\textsuperscript{32}

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{Discotic LC that has a Col\textsubscript{h} phase – Moore (A)\textsuperscript{32} (Hex = -C\textsubscript{6}H\textsubscript{13})}
\end{figure}

Höger and coworkers\textsuperscript{27} took it upon themselves to investigate if a mesophase would form if the flexible side chains filled the void of a (semi) rigid core rather than having extraanular side chains around the core. This sub-class of molecules is called inverted liquid crystals, which are synthesized using an acetylenic homocoupling reaction. Figure 1.8 shows an example of one of Höger’s inverted LCs (B). The aryls that are para-linked to the ring backbone have the option of rotating to allow the long alkylxoy chains to occupy the space of the internal void for an inverted conformation, which means the alkylxoy chains are at adaptable positions of the ring. The filling of space promotes the formation of a stable thermotropic mesophase via an intraanular orientation of the alkylxoy chains: crystal phase $\rightarrow$ 185 °C (N\textsubscript{D}) 207 °C $\rightarrow$ isotropic liquid phase.\textsuperscript{27} Similarly, C (Figure 1.9), which has a different substitution pattern than B, exhibits a thermotropic (discotic nematic) mesophase (134-159 °C).\textsuperscript{40}
Tew and coworkers\textsuperscript{41} reported on \textit{ortho}-phenylene ethynylene cyclic trimers, and they found that the symmetry of D and E (Figure 1.10) allows these molecules to self-assemble into columnar structures. In contrast, F (Figure 1.10) does not form columnar structures because the stacking pattern is less ordered due to asymmetry.
Figure 1.9 Liquid Crystalline SPM – Höger (C)⁴⁰ (Pr = -C₃H₇)

Figure 1.10 Macrocycles that self assemble into columnar structures – Tew (D, E, F)⁴¹
1.7 Previous Work

Amanda Ponsot, a former graduate student of Miami University and Dr. Hartley, began a study on the electron transport across the molecular axis of a series of macrocycles referred to as "tetrabenzo[18]cyclynes" (TBCs). Figure 1.11 shows an example of one of the macrocycles within that study. The design for these macromolecules was based on the following characteristics: cross-conjugation, shape persistent core, and self-assembly potential. Cross-conjugation (i.e., meta-substitution) promotes intermolecular charge transport and involves “three unsaturated groups, two of which although conjugated to a third unsaturated center are not conjugated to each other.” On the contrary, para-substitution and ortho-substitution are implemented for linear-conjugation. A shape persistent core will not collapse, but will promote self-assembly in response to π–π stacking, van der Waals forces, dipole-dipole, hydrogen bonding, and hydrophobic interactions.

Hence, synthesizing a series of molecules that have a meta-phenylene bridge was chosen for the design to meet these parameters. Amanda Ponsot developed a methodology to synthesize these molecules and investigated the charge mobility across the cross-conjugated backbone in response to various donor and acceptor groups. These columnar architectures are fairly new compared to rod-like structures, but they are promising in single-molecule electronics and other advanced materials.

![Figure 1.11 Example of macrocycle used in electron transport study](image-url)
1.8 Goal of Study

As a branch from Amanda Ponsot’s project, the TBC design was altered toward the synthesis of potential liquid crystals with various alkyloxy groups attached to the rigid core. An investigation of various cross-conjugated designs that will exhibit LC phases began in this study, but it is to be continued. Figure 1.12 shows the three macrocycles that were synthesized and tested in this study along with two plausible macrocycles that are more likely to have liquid crystalline behavior. If the macrocycles (12a-c) are found to have liquid crystal properties, then the electron push-pull effect will be introduced into later designs. Another project is working on the charge transport aspect. Ultimately, we hope to eventually study intramolecular charge transfer in the liquid crystal phase, which may someday be incorporated into photovoltaics and other electronic devices.

**Figure 1.12** Design of TBC macrocycles
Chapter 2: Results and Discussion

2.1 Syntheses

2.1.1 Synthetic Intermediates for Methodological Study

In order to synthesize a series of alkoxy-substituted TBCs, an efficient methodology had to be developed. Amanda Ponsot tested various catalysts for the Sonogashira coupling reactions\textsuperscript{42,50} and her results were used as the starting point for the methodological study herein. The two main monomers for the study are shown below in Scheme 2.1 and Figure 2.1. Compound 3 will be referred to as the “bridge unit” because figuratively it is in the middle of the cross-conjugated network and it bridges the gap between the two “end units” (i.e., diiodo-monomers). These molecules were the building blocks for the SPM construction, in which the final Sonogashira coupling of the macrocyclization was the key step to be optimized.

![Scheme 2.1](image)

**Scheme 2.1** Overview of synthetic scheme to make bridge unit 3

![Figure 2.1](image)

**Figure 2.1** Diiodo-Monomer (end unit)

Since the steps prior to the synthesis of 3 were discussed in Amanda Ponsot’s thesis,\textsuperscript{42} only the Sonogashira couplings will be discussed. However, information regarding the procedure and results for intermediate molecules can be found in the Experimental (Chapter 4).
Since the catalysts are oxygen-sensitive, all Sonogashira couplings were done in an inert argon atmosphere. Compounds 3, 4, and 5 were stored in the freezer because it was expected that would decrease the rate of degradation by light and/or heat.\textsuperscript{20} Compound 6 (Figure 2.2) was chosen for the methodological study because its synthetic route is well established for the intermediates.

![Figure 2.2 OMe-t-butyl-OMe Tetrimer (6)](image)

**2.1.2 Optimization of Sonogashira Couplings**

The reaction to synthesize trimer 4 is shown in Scheme 2.2. Attempts toward the most efficient conditions to synthesize trimer 4 are summarized in Table 2.1. The Sonogashira coupling of 3 and 1,2-diiodo-4,5-dimethoxybenzene required a combination of copper(I) iodide, palladium(II) acetate, and triphenylphosphine to yield 4 (92%). Although the palladium-catalyzed cross coupling reaction gave the desired product, evidence of acetylenic homocoupling of 3 (Figure 2.3) was found in the proton NMR spectrum, which is not unusual in Sonogashira couplings.
Scheme 2.2 Synthesis of trimer 4

Table 2.1 Reaction Conditions for the Synthesis of Trimer 4

<table>
<thead>
<tr>
<th>Starting Material: (3) (2.2 equiv)</th>
<th>Starting Material: diiododimethoxy (1.0 equiv)</th>
<th>Pd(OAc)$_2$</th>
<th>CuI</th>
<th>PPh$_3$</th>
<th>DIPA</th>
<th>Product</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 195.6 mg</td>
<td>106.4 mg</td>
<td>2.5 mg</td>
<td>2.4 mg</td>
<td>12.7 mg</td>
<td>5 mL</td>
<td>79.9 mg*</td>
<td>36%</td>
</tr>
<tr>
<td>(2) 184.1 mg</td>
<td>97.7 mg</td>
<td>3.0 mg</td>
<td>1.7 mg</td>
<td>12.6 mg</td>
<td>5 mL</td>
<td>42.2 mg*</td>
<td>21%</td>
</tr>
<tr>
<td>(3) 219.1 mg</td>
<td>114.9 mg</td>
<td>5.6 mg</td>
<td>2.4 mg</td>
<td>31.7 mg</td>
<td>3.2 mL</td>
<td>97.2 mg*</td>
<td>41%</td>
</tr>
<tr>
<td>(4) 2.0076 g</td>
<td>1.0510 g</td>
<td>48.7 mg</td>
<td>22.8 mg</td>
<td>282.8 mg</td>
<td>12.4 mL</td>
<td>2.0227 g*</td>
<td>92%</td>
</tr>
</tbody>
</table>

*reaction temp = 95°C  #reaction temp = 80°C

Figure 2.3 Acetylenic homocoupling product of 3
Comparing the crude proton NMR spectra of entry 1 and 2 showed that entry 2 gave higher yield, but purification did not reflect these results. In relationship to entry 3, all three of the reagents were increased in addition to increasing substrate concentration. As a result, the proton NMR spectrum of entry 3 had fewer impurities and relatively more product than entries 1 and 2. These improvements are represented from the yield (41%). Although 3 was in excess for each of the three entries, unreacted alkyne in the crude proton NMR spectra was not observed. The lack of recovered starting material (3) may be attributed to various byproducts, such as homocoupling and/or decomposition due to high temperature (95 °C).

The conditions of entry 4 correspond to pushing the reaction forward by increasing the substrate (3) concentration. As a result, the temperature was decreased to 80 °C to compensate for the increased concentration, which gave a clean crude proton NMR spectrum and very good yield (92%). Therefore, not only was the reaction optimized, but the practicality of scaling up was proven.

The next reaction is very common and it involves deprotecting the TIPS groups to give the terminal acetylenes (Scheme 2.3). This reaction was straightforward and yields were consistently between 90%-99%.

![Scheme 2.3 Deprotection of TIPS to give trimer 5](image-url)
The purification of the Sonogashira coupling of 5 and the diiodo-monomer proved to be extremely challenging as a result of the decreased solubility of 6 in various solvents. Scheme 2.4 briefly lists the three conditions attempted to synthesize 6. Various purification techniques were evaluated in addition to modifying the reaction conditions; therefore, yields were not an accurate representation of the efficiency of each condition. Instead, the crude proton NMR spectra were the basis for qualitatively comparing the efficiency of each reaction condition.

**Scheme 2.4** Macrocyclization via Sonogashira coupling of 5 and diiodo-monomer

**Condition 1:** In addition to the starting materials, the initial conditions for the macrocyclization required Pd(P’Bu₃)₂ (0.10 equiv) and toluene/triethylamine (2.2:1), which stirred overnight at room temperature. The isolated yield was ~50%, but it was not reproducible. This may be from the degradation of the catalyst over time. It was found that under the same initial conditions, increasing the temperature or dilution made little to no improvement in the yield. Only a combination of increased temperature (45 °C) and dilution yielded more consumption of trimer 5 and only slightly more production of 6. The best results involved 0.4 equiv of Pd(P’Bu₃)₂ and (1:2) toluene:triethylamine while stirring for 24 hours at room temperature.
**Condition 2:** Since the conditions to synthesize trimer 4 proved to be very efficient, they were attempted for the macrocyclization. When trimer 5 and diodo-monomer (2.2:1.0) were allowed to react overnight at 40 °C in the presence of CuI and PdII catalysts, the product was not produced (possibly because of CuI). The reaction was repeated with excess trimer 5 and 0.32 equiv of Pd(OAc)2 rather than 0.16 equiv. As a result, the product was produced in moderate yield (~40%), yet was not repeated due to limited amounts of trimer 5. Lowering the ratio of the starting materials to 1:1 and decreasing the amount of Pd(OAc)2 (0.2 equiv) produced either a trace of the product or no product at all, regardless of temperature (room temp or 40 °C).

**Condition 3:** Using DABCO instead of Et3N for the macrocyclization was found to be more effective by Dr. Wade Leu; hence, Condition 3 was implemented. The two starting monomers were allowed to react in 1:1 ratio in the presence of 0.10 equiv of Pd(P(t-Bu)3)2. As a result, cleaner crude proton NMR spectra and more of 6 were obtained. When varying ~20% (w/v) DABCO and substrate (5) concentration from 8.18 mM to 1.64 mM, results suggest 1.64 mM gave slightly better crude proton NMR spectra with fewer impurities.

After evaluating the three conditions mentioned above, Condition 3 clearly gave the best results. Therefore, these conditions were implemented with the target molecules, which are designed in such a way that solubility and intermolecular π-π stacking should improve. Compound 6 is not a liquid crystal due to short alkyloxy groups and the inhibition of π-stacking from the sterically encumbered t-butyl substituent on 3.

### 2.1.3 Mono-Alkyloxy Bridge Units

The first mono-alkyloxy bridge unit to be synthesized was the mono-hexyloxy bridge. The first step is brominating 1,3-dinitrobenzene,51 which is commercially available. Recrystallization gave the product in 50% yield (Scheme 2.5). Next, was an SNAr reaction, which involved replacing one of the nitro groups with hexyloxy (Scheme 2.5). It is important to note that although DMF and hexanol both have boiling points greater than 150 °C, it is better to still attach a condenser to the reaction flask; failure to do so leads to poorer yields (30% on
average). Experimentation using other sources of base, such as 60% NaH (2.5-5.4 equiv) and 98% KO\textsubscript{t}Bu (3.3 equiv), did not give the correct product.

![Scheme 2.5](image)

Scheme 2.5 Bromination of 1,3-dinitrobenzene followed by S\textsubscript{N}Ar substitution

One of the key intermediates was the 1-alkyloxy-3-bromo-5-iodobenzene. The procedure to synthesize 1-bromo-3-hexyloxy-5-iodobenzene was straightforward (Scheme 2.6). The nitro group was reduced with tin(II) chloride dihydrate to obtain the amine, which was substituted with iodine by diazotization followed by iodination.\(^5\)

![Scheme 2.6](image)

Scheme 2.6 Reduction of nitro group and diazotization/iodination

To produce the decyl- and dodecyl-versions of 1-alkyloxy-3-bromo-5-iodobenzene, a shortcut was needed to shorten the synthesis. Therefore, Amanda Wilson, an undergraduate lab assistant, synthesized large quantities of 1-bromo-3-iodo-5-methoxybenzene. This material could be deprotected and easily alkylated with various alkyl halides via nucleophilic substitution. Using 1-bromo-3-iodo-5-methoxybenzene, the following conditions were tested to find which would give the most effective and cleanest deprotection of the alcohol (Scheme 2.7). Condition 1\(^5\) gave only 30%-35% yield and Condition 3\(^5\) gave 25%-30%, which differs from what was reported (96%). Perhaps the yield for Condition 3 was low because it was not heated high
enough (as a result of safety concerns). The traditional method, Condition 2, proved to give the best yields.

Scheme 2.7 Deprotection of alcohol

For all trials in Condition 2, the substrate concentration (0.0525 M) was not changed. Surprisingly, 2.5 equiv of BBr$_3$ proved insufficient to yield the desired product, but an increase to 7.5-8.5 equiv of BBr$_3$ gave nearly reaction completion (with only 2%-4% starting material). Although the highest isolated yield was 80% with 8.5 equiv of BBr$_3$, 7.5 equiv gave satisfactory results (64%) as well. Scheme 2.8 illustrates the alkylation conditions/results following the deprotection.

Scheme 2.8 Deprotection of alcohol and alkylation
Once 1-alkyloxy-3-bromo-5-iodobenzene was synthesized, trimethylsilyl acetylene and triisopropylsilyl acetylene were attached via Sonogashira couplings. Selective deprotection of TMS in the presence of TIPS gave the terminal alkyne in 9 after workup (Scheme 2.9).

Scheme 2.9 Synthesis of 9

Once derivatives of 9 were synthesized, the diiodo-monomer with matching alkyloxy chain was synthesized, which was produced in moderate to good yields (Scheme 2.10). Yields for the alkylation step were found to be lower than the reported yields, possible due to the following: variable concentration, not using dry DMF, and shorter reaction times. Extractions were done with diethyl ether rather than DCM because ether allowed the DMF to partition into the aqueous layer. The mono-alkylated product for hexyl-catechol was not re-alkylated, which is
the reason the yield is lower than the others. Decyl-catechol led to a complete di-alkylated product after 48 hours, but dodecyl-catechol was re-alkylated to afford maximum yield.

Optimizing the iodination step was time-consuming, but there were two major findings: increasing the equivalents of periodic acid and iodine will push the reaction further to completion, but decreasing the concentration causes a slower reaction and more mono-iodinated product will result. NMR data suggested there was no instance of starting material remaining, which means the first iodination occurs rather quickly, but the second iodination is slow. The delay of the second iodination may be influenced by steric hinderance and slight deactivation of the benzene ring after the first iodination.

2.1.4 Tetramer Macrocyclization

\[ \text{Scheme 2.11 Synthesis of trimers 10 and 11} \]
Due to the methodological study previously, the syntheses of 10-12 were relatively simple. Once the two monomers are constructed, trimers 10 were synthesized and then deprotected to give 11. Both 10 and 11 were recovered with good yields. The final step was adding another end unit (diiodo-monomer) to produce the tetramer macrocycle (Scheme 2.13). Originally, 12 were purified by flash chromatography (12a in particular), but poor solubility made this an unreasonable purification method. Al Ouahabi and coworkers\textsuperscript{20} came across similar solubility problems when purifying long oligomers with several TIPS groups as well. The long alkyl chains were meant to increase solubility, but the rigid, conjugated backbone of 12 makes these compounds sparingly soluble in most solvents. Toluene was found to be the best solvent for 12, but solubility was still limited – an observation found during chromatography. Fortunately, the GPC semi-preparative column purified 12 in 59%-65% yield (i.e., 12b and 12c). There was good separation between polymers, product, and excess starting material. Once purified from other organic and/or inorganic materials, 12 were recrystallized from benzene to remove grease and other small contaminants prior to characterization.

\begin{center}
\includegraphics[width=\textwidth]{scheme_2.12.png}
\end{center}

**Scheme 2.12** Synthesis of macrocycles 12

### 2.2 Characterization

In addition to NMR spectroscopy, utilization of MALDI-TOF MS further characterized and supported the findings of the study. Literature\textsuperscript{56-57} supports that phenylene ethynlenes form
complexes with Ag⁺ and Cu⁺ ions. Al Ouahabi detected a loss of the TIPS substituents using Ag ion, but obtained cleaner spectra when Cu was used.²⁰ Therefore, we doped our trimers with Cu⁺ using CuI salt, and as a result obtained high intensity signals for [M + Cu⁺] ions for 10-12.

The following techniques were used to characterize and test for liquid crystalline properties: differential scanning calorimetry (DSC) and polarized optical microscopy (POM). In DSC, 1-3 mg of each macrocycle (12) was weighed out on the microbalance in aluminum pans, which will be referred to as the “sample pans” for clarity. A sharp downward peak represents an endothermic phase transition, while a sharp upward peak represents an exothermic phase transition. Figure 2.4 shows that 12a has a crystal-isotropic phase transition (downward peak) at 182.88 °C and then crystallizes (upward peak) at 179.75 °C (due to super-cooling effect). Recall the enthalpy for a liquid crystal-isotropic liquid phase transition will be around 5 J/g. In Figure 2.4, there is only one phase transition for 12a, which does not involve a liquid crystal phase based on its intensity and the lack of other peaks (transitions). The main difference in 12a and 12c is the length of alkyl chains; longer alkyl chains will result in lower melting points (see Table 2.2). DSC measurements showed that 12a had the greatest stability to heat, but not the greatest endothermic/exothermic energy. Instead, 12b exhibited the largest change in energy upon heating and cooling. Results of DSC found that 12a is stable to at least 200 °C, and 12b and 12c to at least 150 °C. Significantly heating past the melting temperature usually results in irreversible decomposition of the material, but instrumentation to measure this occurrence was not available for study. In conclusion, all of the tetramers 12a-c exhibited a single endothermic/exothermic peak, indicative of a crystal-isotropic liquid phase transition or vice-versa, which proves there was no crystal-to-liquid crystal phase transition.
Table 2.2: DSC Results for 12a-c

<table>
<thead>
<tr>
<th>Compound (see pg. 26)</th>
<th>T_m (°C)</th>
<th>Heating ΔH (J/g)</th>
<th>T_f (°C)</th>
<th>Cooling ΔH (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12a-C_6H_{13}</td>
<td>182.88</td>
<td>97.34</td>
<td>179.75</td>
<td>101.20</td>
</tr>
<tr>
<td>12b-C_{10}H_{21}</td>
<td>115.07</td>
<td>102.00</td>
<td>102.60</td>
<td>103.60</td>
</tr>
<tr>
<td>12c-C_{12}H_{25}</td>
<td>99.66</td>
<td>64.01</td>
<td>91.89</td>
<td>66.40</td>
</tr>
</tbody>
</table>

T_m: melting temp; T_f: freezing temp; Cr: crystal; Iso: isotropic liquid; Peak temperatures in the DSC traces obtained during the second heating and cooling cycles at a rate of 5 deg/min.

The DSC gives only preliminary data about the presence or absence of liquid crystal phases, but POM provides more concrete evidence of liquid crystalline phases. When POM is coupled with a camera, a sample may be monitored in real time as it is heated/cooled. This
observation allows pictures to be taken of the interesting LC phase transitions, if any take place. In Figures 2.5 there are examples of some of the pictures taken for 12a-c during crystalline solid phase.

![12a](image1.png) ![12b](image2.png) ![12c](image3.png)

**Figure 2.5** POM crystal phases of 12a-c

The reason(s) for the absence of liquid crystalline behavior is not certain, but there are several possibilities. Perhaps the discotic molecules did not stack properly into a columnar phase, which would have been affected by the following: poor microphase segregation, electron-rich core’s repulsion forces, or an imbalance between the peripheral solubilizing groups and the rigid core. If there are not enough alkyl units around the periphery to take up space (volume), then the columnar phase will not occur. As a result, the most logical approach is adding more alkyloxy substituents to the bridge unit of the core in an effort to induce a liquid crystal phase transition. In addition, adding electron withdrawing groups may significantly promote π-π stacking if the electron density is spread out across the cross-conjugated system (i.e., opposing donor sites and opposing withdrawing sites).
Chapter 3: Conclusion

The goals of this study were to design, synthesize, and characterize molecules that would possess discotic and columnar phases in the liquid crystal state. An efficient synthetic method to create planar, cross-conjugated, shape persistent macrocycles based on the TBC motif was generate successfully, but the design needs alterations. It is suspected that the design, which involves meta-substituted bridge units with one alkyloxy substituent on each, may be the reason for the absence of liquid crystalline phases amongst macrocycles 12a, 12b, and 12c (Figure 3.2).

![Figure 3.1 Tetramer macrocycles studied](image)

3.1 Future Work

Therefore, a design to incorporate more alkyloxy substituents on the bridge units is being pursued (Figure 3.3). A balance between the core system and the aliphatic units will usually promote liquid crystal phases because of aggregation (i.e, discotic molecules will stack into columnar structures via π-stacking). Work towards this design has been hindered by poor solubility during the macrocyclization step. Solubility tests in various organic solvents are the next phase of this study because favorable conditions for purification are still needed.
Figure 3.2 Future Work: Di-alkyloxy bridge unit (e.g., 13a) and hexylester bridge unit (14a)

In addition, we will test whether distributing the electron density around the system by integrating electron-withdrawing (ester) groups onto the bridge units will promote intermolecular $\pi-\pi$ stacking (Figure 3.4). The reasoning behind this design stems from Moore’s work. Moore and coworkers$^{32}$ found that a conjugated phenylacetylene macrocycle with hexylester and hexyloxy substitution not only had a liquid crystalline phase, but also self-assembled into a hexagonal columnar phase. A possible arrangement of A is shown in Figure 3.5, which involves approximately $180^\circ$ rotation (about the column axis) with each additional molecule in the column.
Figure 3.3 Possible stacking pattern of A

A
Chapter 4: Experimental

All reagents were purchased and used as received from commercial sources. Reactions were carried out open to the atmosphere unless stated otherwise. Thin-layer chromatography was carried out on glass plates precoated with silica gel, and column chromatography was carried out on silica gel P60 (230-400 mesh). Gel permeation chromatography (GPC) was performed on a Waters Breeze 2 HPLC system (RI-2414, UV/Vis-2489) with an Ultrastyragel 500 Å column (19 x 300 mm), using THF as the eluent, a flow rate of 5mL/min, and approximately 1 mL injections. The $^1$H NMR and $^{13}$C NMR spectra were obtained using Bruker spectrometers (DPX-200 MHz, DPX-300 MHz, and AV-500 MHz) and referenced to traces of CHCl$_3$ (7.26 ppm or 77.16 ppm). The mass spectroscopy measurements were the cleanest and strongest when the trimers and tetramers were coupled with CuI salt within a HABA or Dithranol MALDI matrix, unless stated otherwise, to give the [M + Cu$^+$] molecular ion.

The differential scanning calorimetry (DSC) measurements were performed on a TA Instruments Q20 DSC, which was coupled to a TA Refrigerated Cooling System 40. The tests were run with 1-3 mg of each sample in aluminum pans at heating and cooling rates of 5 deg/min (three cycles) unless otherwise noted. Polarized optical microscopy was performed on an Olympus BX51 Microscope with a Linkam LTS 350 hot stage that was controlled by a Linkam TMS94 Temperature Controller.
Scheme 4.1 Overview of Optimization of Methodology

4-tert-butyl-N-acetanilide\(^{58}\)

A solution of 4-tert-butyl aniline (20.64 g, 138 mmol), pyridine (30 mL), and THF (15 mL) was cooled in an ice bath for approximately 10 minutes. Then acetic acid anhydride (35 mL) was
added dropwise via an addition funnel, which resulted in the formation of a pink precipitate. The solution was allowed to stir overnight at room temperature. The mixture was vacuum filtered and the precipitate was rinsed with cold MeOH (57 mL). The product was dried in vacuo, which gave 17.13 g (89.5 mmol, 64%) of the titled compound as white crystals. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.40 (m, 2H), 7.34 (m, 2H), 7.07 (br. s, 1H), 2.17 (s, 3H), 1.30 (s, 9H). $^1$H NMR was in agreement with published data.$^{58}$

![Reaction Scheme](image)

**2-bromo-4-tert-butyl-N-acetanilide$^{58}$**

To a stirred solution of 4-tert-butyl-N-acetanilide (17.13 g, 89.5 mmol) and acetic acid (70 mL), bromine (7 mL) dissolved in acetic acid (55 mL) was added dropwise via an addition funnel. The reaction was allowed to stir at room temperature for 3 days, resulting in an orange solution. Then the solution was poured into saturated sodium thiosulfate solution and allowed to stir overnight. The product was isolated by vacuum filtration and washed with water, which gave 44.59 g of wet product. The product was used for the next step without further purification. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 8.19 (d, 1H, $J = 9.2$ Hz), 7.51 (m, 2H), 7.33 (dd, 1H, $J = 2.2$ Hz, $J = 8.7$ Hz), 2.22 (s, 3H), 1.29 (s, 9H). $^1$H NMR was in agreement with published data.$^{58}$

![Reaction Scheme](image)

**2-bromo-4-tert-butyl aniline$^{58}$**
A suspension of 2-bromo-4-tert-butyl-N-acetanilide (44.59 g, still wet), conc. HCl (85 mL), and EtOH (165 mL) was refluxed overnight while stirring, then allowed to cool. The suspension was neutralized with 30% NaOH (70 mL), and then poured into ether and water in a separatory funnel. The aqueous phase was extracted with ether twice; then the combined organics were washed with water and brine, dried over MgSO₄, and filtered. The solvent was removed in vacuo, which gave a yellow oil and a small amount of impurity precipitated out. The precipitate was gravity filtered and washed with ether, and the filtrate was concentrated, which gave 17.69 g (77.5 mmol, 86%) of an oil that was used without any further purification. ¹H NMR (300 MHz, CDCl₃) δ: 7.40 (d, 1H, J = 2.2 Hz), 7.13 (dd, 1H, J = 2.2 Hz, J = 8.3 Hz), 6.74 (d, 1H, J = 8.4 Hz), 4.14 (br. s, 2H), 1.27 (s, 9H). ¹H NMR was in agreement with published data.⁵₈

2-bromo-4-tert-butyl-6-idoaniline⁵⁹

A solution of 2-bromo-4-tert-butyl aniline (2.03 g, 8.9 mmol), water (10 mL), MeOH (20 mL), and CaCO₃ (1.32 g, 13.19 mmol) was vigorously stirred at room temperature. Then ICl (1.89 g, 11.64 mmol) dissolved in MeOH (2 mL) was added to the solution dropwise. The solution became warm, and was allowed to stir for two hours. The reaction mixture was poured into a separatory funnel, followed by EtOAc and saturated sodium thiosulfate. The organic phase was washed with water twice and brine twice, dried over MgSO₄, and filtered. The product was concentrated under reduced pressure and distilled using a Kugelrohr (115 °C), which gave 2.73 g (7.71 mmol, 86%) of the titled compound as an oil. ¹H NMR (300 MHz, CDCl₃) δ: 7.58 (d, 1H, J = 2.2 Hz), 7.41 (d, 1H, J = 2.2 Hz), 4.49 (br s, 2H), 1.27 (s, 9H). ¹H NMR was in agreement with published data.⁵₈
1-bromo-3-tert-butyl-5-iodobenzene

To a solution of 2-bromo-4-tert-butyl-6-iodoaniline (2.73 g, 7.71 mmol) dissolved in benzene (4.1 mL), EtOH (13 mL) and concentrated sulfuric acid (1.2 mL) was added. The solution was cooled to 0 °C, then NaNO₂ (1.17 g, 16.95 mmol) was added, and the reaction mixture was allowed to warm up to room temperature. Then the solution was heated to reflux and stirred until completion while monitored by TLC. When minimum starting material remained, the solution was cooled to room temperature and diluted with water and extracted with ether twice. The combined organics were washed with water twice and brine twice, dried over MgSO₄, and filtered. Most of the solvent was removed in vacuo and the remaining product distilled under reduced pressure via Kugelrohr (100 °C, 45 mtorr), which gave 1.98 g (4.1 mmol, 75%) of the titled compound as an oil. ¹H NMR (300 MHz, CDCl₃) δ: 7.67 (t, 1H, J = 1.5 Hz), 7.62 (t, 1H, J = 1.5 Hz), 7.46 (t, 1H, J = 1.7 Hz), 1.28 (s, 9H). ¹H NMR was in agreement with published data.

1-bromo-3-tert-butyl-5-{(trimethylsilyl)ethynyl}benzene (I)

In a Schlenk vacuum tube charged with a stir bar, CuI (120 mg, 0.63 mmol) and Pd(PPh₃)Cl₂ (217 mg, 0.31 mmol) were added and the tube was evacuated and backfilled with argon three times. Then 1-bromo-3-tert-butyl-5-iodobenzene (3.54 g, 10.44 mmol), TMSA (2.2 mL, 15.66 mmol), and Et₃N (36 mL) were added under a positive pressure of argon. The suspension was degassed three times, sealed under an argon atmosphere, and stirred at room temperature for two
hours. The suspension was then diluted with EtOAc and washed with NH₄Cl, water, and brine. The organic phase was dried over MgSO₄, filtered, and the solvent was removed in vacuo. Purification via column chromatography using hexanes gave 2.47 g (7.98 mmol, 76%) of 1 as a colorless liquid. \(^1\)H NMR (300 MHz, CDCl₃) δ: 7.46 (m, 1H), 7.44 (m, 1H), 7.40 (m, 1H), 1.29 (s, 9H), 0.25 (s, 9H). \(^1\)H NMR was in agreement with published data.\(^{60}\)

\[
\begin{align*}
\text{CuI, Pd(PPh₃)Cl}_2, \\
\text{TIPSA, Et}_3\text{N} \\
\text{overnight, 70°C} \\
\end{align*}
\]

\[
\begin{align*}
\text{TMS} & \quad \text{Br} & \quad \text{1} \\
\text{TMS} & \quad \equiv & \quad \equiv & \quad \text{2} \\
\end{align*}
\]

\(1\text{-}\text{tert-butyl-3-}[(\text{trimethylsilyl})\text{ethynyl}]\text{-5-}(\text{triisopropylsilane})\text{ethynylbenzene (2)}\)

In a Schlenk vacuum tube charged with a stir bar, CuI (27.7 mg, 0.14 mmol) and Pd(PPh₃)Cl₂ (95 mg, 0.13 mmol) were added and the tube was evacuated and backfilled with argon three times. Then a solution of 1 (840 mg, 2.71 mmol) and Et₃N (9.4 mL), followed by TIPSA (0.73 mL, 3.27 mmol) was added to the tube under a positive pressure of argon. The solution was degassed three times, sealed under an argon atmosphere, and stirred overnight at 70°C in an oil bath. The tube was cooled and diluted with EtOAc and washed with NH₄Cl, water, and brine. The organic phase was dried over MgSO₄, filtered, and the solvent was removed in vacuo. Purification via column chromatography using hexanes gave 1.03 g (2.51 mmol, 92%) of 2 as a colorless oil. \(^1\)H NMR (500 MHz, CDCl₃) δ: 7.42 (m, 1H), 7.41 (m, 2H), 1.30 (s, 9H), 1.13 (s, 21H), 0.25 (s, 9H). \(^1\)H NMR was in agreement with published data.\(^{60}\)
To a stirred solution of 2 (1.03 g, 2.51 mmol) in THF/MeOH (8mL/8mL), K₂CO₃ (400.5 mg, 2.89 mmol) was added. The flask was purged with argon for ten minutes and stirred overnight at room temperature. The solution was diluted with ether and poured into water in a separatory funnel. The aqueous phase was extracted with ether twice and the combined organics were washed with water twice, and then dried over MgSO₄ and filtered. The solvent was removed in vacuo and purification via column chromatography using hexanes gave 0.36 g (1.06 mmol, 42%) of 3 as a yellow oil. ¹H NMR (300 MHz, CDCl₃) δ: 7.45 (m, 3H), 3.05 (s, 1H), 1.31 (s, 9H), 1.13 (s, 21H). ¹H NMR was in agreement with published data.⁶⁰

In a Schlenk vacuum tube charged with a stir bar, CuI (22.8 mg, 0.11 mmol), Pd(OAc)₂ (48.7 mg, 0.21 mmol), PPh₃ (282.8 mg, 1.07 mmol), and 1,2-diiodo-4,5-dimethoxybenzene (1.05 g, 2.69 mmol) were added and the tube was evacuated and backfilled with argon three times. Then
a solution of 3 (2.00 g, 5.91 mmol) and diisopropylamine (12.4 mL) was added to the tube under a positive pressure of argon. The suspension was degassed three times, sealed under an argon atmosphere and was stirred overnight at 80 °C in an oil bath, then allowed to cool to room temperature. The suspension was diluted with EtOAc and washed with brine twice. The organic phase was dried over MgSO₄, filtered, and the solvent was removed in vacuo. Purification via column chromatography (5% DCM/hexanes then 10% EtOAc/hexanes) gave 2.02 g (2.49 mmol, 92%) of 4 as brown crystals. ¹H NMR (500 MHz, CDCl₃) δ: 7.48 (m, 4H), 7.41 (m, 2H), 7.04 (s, 2H), 3.93 (s, 6H), 1.24 (s, 18H), 1.12 (s, 42H); ¹³C NMR* (125 MHz, CDCl₃) δ: 151.60, 149.28, 132.07, 129.14, 129.09, 123.66, 123.24, 118.95, 114.17, 106.98, 92.19, 90.55, 88.24, 56.17, 34.68, 31.19, 18.83, 11.48; MALDI-TOF-MS* (dithranol) calc’d for C₅₄H₇₄CuO₂Si₂ (M+Cu⁺) m/z = 873.45, found 873.42.

In a scintillation vial, a solution of 4 (97.2 mg, 0.12 mmol), 1M TBAF in THF (0.08 mL), and THF (2.8 mL) was stirred for two hours at room temperature. The solution was diluted with water and extracted with EtOAc twice. The combined organics were dried over MgSO₄, filtered, and the solvent was removed in vacuo. Purification via column chromatography (2:3

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*Provided by Dr. Wade Leu
DCM:hexanes) gave 61.8 mg (0.12 mmol, ~99%) of 5 as a yellow flaky powder. m.p. 166-167 °C. (Dr. Wade Leu). $^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.54 (m, 2H), 7.51 (m, 2H), 7.47 (m, 2H), 7.04 (s, 2H), 3.93 (s, 6H), 3.04 (s, 2H), 1.28 (s, 18H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 151.81, 149.33, 132.17, 129.37, 129.34, 123.47, 122.28, 118.88, 114.18, 92.03, 88.47, 83.53, 77.27, 56.17, 34.76, 31.20; MALDI-TOF-MS$^+$ (dithranol) calc’d for C$_{36}$H$_{34}$O$_2$ (M$^+$) $m/z$ = 498.26, found 498.14.

$^{5,5'}$-(4,5-dimethoxy-1,2-phenylene)bis(ethyne-2,1-diyl)bis(1-tert-butyl-3-ethynylbenzene) (6)

In a Schlenk vacuum tube charged with a stir bar, Pd(P$_{3}$Bu$_3$)$_2$ (2.8 mg, 0.005 mmol) and 1,2-diiodo-4,5-dimethoxybenzene (11.6 mg, 0.029 mmol) were added and the tube was evacuated and backfilled with argon three times. Then 5 (14.8 mg, 0.029 mmol) dissolved in toluene (2.1 mL) was added followed by Et$_3$N (0.9 mL) under positive argon pressure. The solution was degassed three times, sealed under an argon atmosphere, and allowed to stir for 24 hours at room temperature. The solution was then diluted with EtOAc and washed with water and brine. The aqueous washings were combined and extracted with EtOAc. The combined organics were dried over MgSO$_4$, filtered, and the solvent was removed in vacuo. Purification via column chromatography (2:1 DCM:hexanes) gave 5.8 mg (0.009 mmol, 31%) of 6 as a yellow solid. $^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.85 (t, 2H, $J = 1.5$ Hz), 7.55 (d, 4H, $J = 1.2$ Hz), 7.08 (s, 4H), 3.96 (s, 12H), 1.37 (s, 18H). m.p. > 300 °C. $^{*}$ 1H NMR (300 MHz, CDCl$_3$) $\delta$: 7.85 (s, 2H), 7.56 (s,

* Provided by Dr. Wad Leu
4H), 7.08 (s, 4H), 3.96 (s, 12H), 1.37 (s, 18H); $^{13}$C NMR $^\ast$ (75 MHz, CDCl$_3$) $\delta$: 152.04, 149.88, 132.94, 128.25, 123.92, 119.57, 115.01, 92.48, 88.91, 56.42, 35.02, 31.41; MALDI-TOF-MS $^\ast$ (dithranol) calc'd for C$_{44}$H$_{40}$O$_4$ (M$^+$) $m/z = 632.29$, found 632.29.

**Scheme 4.2** Overview of Methodology

1-bromo-3,5-dinitrobenzene$^\ast$
In a round bottom flask charged with a stir bar, 1,3-dinitrobenzene (15.80 g, 93.98 mmol) was dissolved in concentrated nitric acid (30 mL). The solution was cooled to 0 °C using an ice bath and bromine (2.6 mL, 50.74 mmol) was added dropwise using a syringe. While stirring, sulfuric acid (105 mL) was added dropwise to the solution using an addition funnel. The flask was coupled with a condenser and allowed to stir for two hours in a 90 °C oil bath. The flask was cooled to nearly room temperature and the solution was poured into a beaker of ice; as a result, a yellow solid crashed out, which was isolated by vacuum filtration. The crude product was washed with water until neutral, and purified by recrystallization from 95% ethanol. The recrystallized product was isolated by vacuum filtration and dried under vacuum, which gave 11.67 g (47.24 mmol, 50%) of the titled compound as off-white flaky crystals. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 9.00 (t, 1H, \(J = 1.9\) Hz), 8.71 (d, 2H, \(J = 1.9\) Hz). \(^1\)H NMR was in agreement with published data.\(^{51}\)

\[
\text{HOC}_6\text{H}_{13} \quad \text{KOH, DMF} \quad \text{overnight, 65°C} \quad \text{HOC}_6\text{H}_{13}
\]

1-bromo-3-hexyloxy-5-nitrobenzene

Using a mortar and pestle, 85% KOH pellets (0.5736 g, 10.22 mmol) were crushed to form a powder that was stirred for five minutes in hexanol (2.2 mL, 17.65 mmol) in a round bottom flask charged with a stir bar. Then 1-bromo-3,5-dinitrobenzene (2.3083 g, 9.34 mmol) dissolved in DMF (9.2 mL) was added. A condenser was coupled to the flask and the solution was allowed to stir overnight at 65 °C in an oil bath. Then the solution was poured into water in a separatory funnel and “gently” extracted with ether three times. The combined organics were dried over MgSO\(_4\), filtered, and the solvent was removed in vacuo. Purification via column chromatography using hexanes gave 1.3265 g (4.39 mmol, 47%) of the titled compound as a yellow oily liquid. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 7.94 (t, 1H, \(J = 1.9\) Hz), 7.66 (t, 1H, \(J = 2.2\) Hz), 7.36 (t, 1H, \(J = 1.9\) Hz), 4.02 (t, 2H, \(J = 6.4\) Hz), 1.81 (qu, 2H \(J = 7.0\) Hz), 1.46 (m, 2H), 1.35 (m, 4H), 0.92 (t, 3H, \(J = 6.9\) Hz). \(^1\)H NMR was in agreement with published data.\(^{61}\)
1-amino-3-bromo-5-hexyloxybenzene

In a round bottom flask charged with a stir bar, SnCl₂·2H₂O (4.947 g, 21.93 mmol), 1-bromo-3-hexyloxy-5-nitrobenzene (1.323 g, 4.38 mmol) and 100% EtOH (15.1 mL) were stirred. The flask was coupled with a condenser and refluxed for an hour while stirring. The solution was cooled and poured into aqueous NaOH (3.16 g in 52 mL) at 0 °C to basify the solution. After a solid crashed out, brine was added and the mixture was extracted with ether four times. The combined organics were dried over MgSO₄, filtered, and the solvent was removed in vacuo. The product, which was 1.16 g (4.26 mmol, 97%) as a white flaky solid, was used in the next step without any further purification. ¹H NMR (300 MHz, CDCl₃) δ: 6.46 (m, 1H), 6.43 (m, 1H), 6.14 (m, 1H), 3.87 (t, 1H, J = 6.5 Hz), 3.61 (br s, 2H), 1.73 (qu, 2H, J = 6.9 Hz), 1.42 (m, 2H), 1.33 (m, 4H), 0.90 (t, 3H, J = 6.7 Hz). ¹H NMR was in agreement with published data.⁶¹

1-bromo-3-hexyloxy-5-iodobenzene

In a round bottom flask charged with a stir bar, 1-amino-3-bromo-5-hexyloxybenzene (161.1 mg, 0.59 mmol) and KNO₂ (648.8 mg, 7.62 mmol) was dissolved in DMSO (4.6 mL). A solution of CuI (42.8 mg, 0.22 mmol) and 57% aq HI (0.95 mL, 7.42 mmol) in DMSO (4.6 mL) was added to the flask dropwise while stirring. The round bottom was capped with a rubber septum that had a syringe needle in it and the solution was allowed to stir for an hour in a 40 °C oil bath. Then the solution was poured into aqueous K₂CO₃ (1.13 g in 25 mL) and extracted with ether four times. The combined organics, which appeared as a dark red solution, were washed with
saturated sodium sulfite and brine, in which the organic phase turned an orange color. The organic phase was then dried over MgSO$_4$, filtered, and the solvent was removed in vacuo. Purification via column chromatography using 5% DCM/hexanes gave 142.9 mg (0.37 mmol, 63%) of titled compound as a slightly yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.41 (t, 1H, $J = 1.5$ Hz), 7.17 (m, 1H), 7.01 (t, 1H, $J = 1.9$ Hz), 3.90 (t, 2H, $J = 6.5$ Hz), 1.75 (qu, 2H, $J = 6.6$ Hz), 1.43 (m, 2H), 1.32 (m, 4H), 0.91 (t, 3H, $J = 6.7$ Hz). $^1$H NMR was in agreement with published data.$^{36}$

![Chemical structure](attachment:chemical_structure.png)

**3-bromo-5-iodophenol**

In a round bottom flask charged with a stir bar, 1-bromo-3-iodo-5-methoxybenzene (97.4 mg, 0.31 mmol) was purged with argon for ten minutes and dissolved in DCM (6.0 mL). Then 1 M BBr$_3$ in DCM (2.3 mL) was added dropwise via syringe, which resulted in an exothermic reaction and the solution turned an orange color. The solution was allowed to stir overnight at room temperature. The reaction was quenched by adding water, which caused the solution to become warm. The solution and water was vigorously stirred for an hour, and then extracted with DCM three times. Purification via column chromatography using 60% DCM/hexanes gave 59.8 mg (0.20 mmol, 64%) of the titled compound as a light yellow solid. $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.43 (t, 1H, $J = 1.5$ Hz), 7.15 (t, 1H, $J = 1.8$ Hz), 6.98 (t, 1H, $J = 1.9$ Hz), 4.94 (br s, 1H). $^1$H NMR was in agreement with published data.$^{62}$

![Chemical structure](attachment:chemical_structure.png)

**1-alkyloxy-3-bromo-5-iodobenzene**
Taking 1-bromo-3-dodecyloxy-5-iodobenzene as an example: To a stirred mixture of 5-bromo-3-iodophenol (128.3 mg, 0.42 mmol), K$_2$CO$_3$ (132.8 mg, 0.96 mmol), KI (3.5 mg, 0.02 mmol), and DMF (2.2 mL) in a round bottom flask, 1-bromododecane (0.11 mL, 0.45 mmol) was added dropwise. With a condenser attached, the flask was then purged with argon for ten minutes. The reaction was allowed to stir overnight at 80 °C using an oil bath under an argon atmosphere. Then the reaction was quenched by pouring the solution into a beaker of ice cold water. The solution was extracted with ether three times and the combined organics were washed with brine twice. The organic phase was then dried over MgSO$_4$, filtered, and the solvent was removed in vacuo. Purification via column chromatography using hexanes gave 180.0 mg (0.38 mmol, 90%) of 1-bromo-3-dodecyloxy-5-iodobenzene as white needle-like crystals. $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.41 (t, 1H, J = 1.4 Hz), 7.17 (t, 1H, J = 1.7 Hz), 7.01 (t, 1H, J = 1.8 Hz), 3.90 (t, 2H, J = 6.5 Hz), 1.75 (qu, 2H, J = 6.8 Hz), 1.40 (m, 4H), 1.27 (~s, 14H), 0.88 (t, 3H, J = 6.6 Hz). $^1$H NMR was in agreement with published data.63

Using the above procedure for 1-bromo-3-dodecyloxy-5-iodobenzene, 5-bromo-3-iodophenol (172.2 mg, 0.57 mmol) and 1-bromodecane (0.14 mL, 0.67 mmol) were allowed to react to give a brown residue. Purification via column chromatography using hexanes gave 208.2 mg (0.47 mmol, 82%) of 1-bromo-3-decyloxy-5-iodobenzene as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.41 (~t, 1H), 7.17 (~t, 1H), 7.01 (~t, 1H), 3.90 (t, 2H, J = 6.2 Hz), 1.75 (qu, 2H, J = 6.7 Hz), 1.42 (m, 4H), 1.28 (~s, 12H), 0.88 (t, 3H, J = 6.7 Hz).

**Compounds 7**

Taking 1-bromo-3-hexyloxy-5-trimethylsilylacetylenebenzene (7a) as an example: In a Schlenk vacuum tube charged with a stir bar, CuI (45.0 mg, 0.23 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (80.4 mg, 0.11
mmol) were added and the tube was evacuated and backfilled with argon three times. Then 1-bromo-3-hexyloxy-5-iodobenzene (1.4520 g, 3.78 mmol) dissolved in Et₃N (12.5 mL) was added to the tube followed by TMSA (0.80 mL, 5.69 mmol) under a positive pressure of argon. The suspension was degassed three times, and sealed under an argon atmosphere. The yellow suspension was allowed to stir at room temperature for two hours. Dilution of the suspension with EtOAc was followed by washing with NH₄Cl, water, and brine. The organic phase was dried over MgSO₄, filtered, and the solvent was removed in vacuo. Purification via column chromatography using hexanes gave 1.1535 g (3.26 mmol, 86%) of 7a as a bright yellow oil. ¹H NMR (300 MHz, CDCl₃) δ: 7.19 (~t, 1H), 7.01 (~t, 1H), 6.91 (~t, 1H), 3.91 (t, 2H, J = 6.5 Hz), 1.75 (qu, 2H, J = 6.9 Hz), 1.43 (m, 2H), 1.33 (m, 4H), 0.92 (t, 3H, J = 6.5 Hz), 0.25 (s, 9H). ¹H NMR was in agreement with published data.³⁶

7b: Using the above procedure for compound 7, 1-bromo-3-decyloxy-5-iodobenzene (206.0 mg, 0.47 mmol) and TMSA (0.1 mL, 0.70 mmol) were allowed to react to give a brownish-orange residue. Purification via column chromatography using hexanes gave 177.5 mg (0.43 mmol, 92%) of 7b as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 7.18 (~t, 1H), 7.01 (~t, 1H), 6.90 (~t, 1H), 3.91 (t, 2H, J = 6.4 Hz), 1.75 (qu, 2H, J = 6.9 Hz), 1.42 (m, 2H), 1.27 (~s, 12H), 0.88 (t, 3H, J = 6.6 Hz), 0.24 (s, 9H).

7c: Using the above procedure for compound 7, 1-bromo-3-dodecyloxy-5-iodobenzene (228.1 mg, 0.48 mmol) and TMSA (0.1 mL, 0.70 mmol) were allowed to react to give a brownish-orange residue. Purification via column chromatography using hexanes gave 192.9 mg (0.44 mmol, 90%) of 7c as a colorless oil. ¹H NMR (300 MHz, CDCl₃), δ: 7.18 (~t, 1H), 7.01 (t, 1H, J = 2.01 Hz), 6.90 (dd, 1H, J = 1.2 Hz, J = 2.1 Hz), 3.91 (t, 2H, J = 6.5 Hz), 1.75 (qu, 2H, J = 6.7 Hz), 1.44 (m, 2H), 1.26 (~s, 16H), 0.88 (t, 3H, J = 6.7 Hz), 0.24 (s, 9H).
Compounds 8

Taking 1-hexyloxy-3-triisopropylsilylacetylene-5-trimethylsilylacetylenebenzene (8a) as an example: In a Schlenk vacuum tube charged with a stir bar, CuI (33.3 mg, 0.17 mmol) and Pd(PPh₃)Cl₂ (115.7 mg, 0.16 mmol) were added and the tube was evacuated and backfilled with argon three times. Then 7a (1.14 g, 3.22 mmol) dissolved in Et₃N (11.6 mL) was added to the tube followed by TIPSA (0.87 mL, 3.88 mmol) under a positive pressure of argon. The suspension was degassed three times and sealed under an argon atmosphere. The suspension was allowed to stir overnight at 70°C in an oil bath. Then the dark gray suspension was cooled to room temperature and diluted with EtOAc. The organic phase was washed with NH₄Cl, water, and brine. The organic phase was dried over MgSO₄, filtered, and the solvent was removed in vacuo. Purification via column chromatography using hexanes gave 1.29 g (2.83 mmol, 88%) of 8a as a light yellow oil. ¹H NMR (200 MHz, CDCl₃) δ: 7.16 (~t, 1H), 6.94 (~t, 2H), 3.93 (t, 2H, J = 6.4 Hz), 1.76 (qu, 2H, J = 6.8 Hz), 1.43 (m, 2H), 1.34 (m, 4H), 1.11 (s, 21H), 0.91 (m, 3H), 0.24 (s, 9H). ¹H NMR was in agreement with published data.³⁶

8b: Using the above procedure for compound 8, 1-bromo-3-decyloxy-5-trimethylsilylacetylenebenzene (7b) (172.8 mg, 0.42 mmol) and TIPSA (0.11 mL, 0.49 mmol) were allowed to react. Purification via column chromatography using hexanes gave 158.6 mg (0.31 mmol, 74%) of 8b as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 7.16 (~t, 1H), 6.94 (~t, 2H), 3.92 (t, 2H, J = 6.4 Hz), 1.75 (qu, 2H, J = 6.3 Hz), 1.42 (m, 2H), 1.27 (~s, 12H), 1.11 (s, 21H), 0.88 (t, 3H, J = 6.6 Hz), 0.24 (s, 9H).

8c: Using the above procedure for compound 8, 1-bromo-3-dodecyloxy-5-trimethylsilylacetylenebenzene (7c) (186.8 mg, 0.42 mmol) and TIPSA (0.12 mL, 0.53 mmol) were allowed to react. Purification via column chromatography using hexanes gave 200.6 mg (0.37 mmol, 87%)
of 8c as a colorless oil. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 7.16 (~t, 1H), 7.00-6.98 (m, 1H), 6.94 (m, 1H), 3.92 (t, 2H, \(J = 6.7\) Hz), 1.76 (m, 2H), 1.43 (m, 2H), 1.26 (~s, 16H), 1.11 (s, 21H), 0.88 (t, 3H, \(J = 6.4\) Hz), 0.24 (s, 9H).

Compounds 9

Taking monomer 9a as an example: In a scintillation vial charged with a stir bar, 8a (133.5 mg, 0.29 mmol) was dissolved in THF (0.81 mL). A suspension of K\(_2\)CO\(_3\) (50.7 mg, 0.36 mmol) in MeOH (0.81 mL) was sonicated and added to the starting material. The reaction was allowed to stir overnight at room temperature with a cap loosely fitted on the vial. The reaction was quenched by pouring it into water. The vial was rinsed out with water and ether, and the aqueous phase was extracted with ether twice. The combined organics were dried over MgSO\(_4\), filtered, and the solvent was removed in vacuo. The crude product was absorbed onto silica gel and purification via column chromatography using hexanes gave 101.1 mg (0.26 mmol, 90%) of 9a as a light yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 7.19 (~t, 1H), 6.98 (t, 1H, \(J = 1.8\) Hz), 6.96 (t, 1H, \(J = 1.9\) Hz), 3.93 (t, 2H, \(J = 6.5\) Hz), 3.04 (s, 1H), 1.76 (qu, 2H, \(J = 7.0\) Hz), 1.44 (m, 2H), 1.33 (m, 4H), 1.12 (s, 21H), 0.90 (t, 3H, \(J = 6.6\) Hz). \(^1\)H NMR was in agreement with published data.\(^{36}\)

9b: Using the above procedure for compound 9, 8b (155.7 mg, 0.30 mmol) and K\(_2\)CO\(_3\) (50.1 mg, 0.36 mmol) were allowed to react overnight. Purification via column chromatography using hexanes gave 119.4 mg (0.27 mmol, 89%) of 9b as a colorless oil. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 7.19 (~t, 1H), 6.96 (m, 2H), 3.93 (t, 2H, \(J = 6.4\) Hz), 3.04 (s, 1H), 1.76 (qu, 2H, \(J = 6.9\) Hz), 1.43 (m, 2H), 1.27 (~s, 12H), 1.12 (s, 21H), 0.88 (t, 3H, \(J = 6.6\) Hz).
Using the above procedure for compound 9c, 8c (198.8 mg, 0.37 mmol) and K$_2$CO$_3$ (63.9 mg, 0.46 mmol) were allowed to react overnight. Purification via column chromatography using hexanes gave 133.5 mg (0.28 mmol, 77%) of 9c as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.19 (~t, 1H), 6.98 (~t, 1H), 6.96 (~t, 1H), 3.93 (t, 2H, $J = 6.4$ Hz), 3.04 (s, 1H), 1.76 (qu, 2H, $J = 6.8$ Hz), 1.43 (m, 2H), 1.27 (~s, 16H), 1.12 (s, 21H), 0.88 (t, 3H, $J = 6.7$ Hz).

$\text{n H}_{13}\text{C}_6\text{Br}, K_2\text{CO}_3, K\text{I, DMF}}$

overnight, 80°C

$\text{47%}$

![Reaction Diagram]

$1,2$-$\text{dihexyloxybenzene}$

Catechol (5.0089 g, 45.49 mmol), KI (0.3789 g, 2.28 mmol), anhydrous K$_2$CO$_3$ (26.3579 g, 190.71 mmol), and DMF (133 mL) were stirred in a round bottom flask. To the light turquoise suspension, 1-bromohexane (14.6 mL, 103.92 mmol) was slowly added. Then a condenser was attached to the flask and the suspension was purged with argon for ten minutes, resulting in a light brown suspension. The reaction was allowed to stir overnight under an argon atmosphere in an 80 °C oil bath. The suspension was poured into cold water and extracted with ether three times. The combined organics were washed with water and brine. Then the organic phase was dried over MgSO$_4$, filtered, and the solvent was removed in vacuo. Purification via column chromatography using 2% EtOAc/hexanes gave 5.9588 g (21.40 mmol, 47%) of 1,2-dihexyloxybenzene as a colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 6.89 (s, 4H), 3.99 (t, 4H, $J = 6.7$ Hz), 1.82 (qu, 4H, $J = 7.1$ Hz), 1.48 (m, 4H), 1.34 (m, 8H), 0.91 (t, 6H, $J = 6.7$ Hz). $^1$H NMR was in agreement with published data.$^{26}$
1,2-didecyloxybenzene

Catechol (1.0001 g, 9.08 mmol), KI (78.6 mg, 0.47 mmol), anhydrous K$_2$CO$_3$ (6.2765 g, 45.41 mmol), and DMF (46 mL) were stirred for 20 minutes in a round bottom flask. To the maroon suspension, 1-bromodecane (4.7 mL, 22.70 mmol) was added dropwise via syringe. A condenser was attached to the flask and the suspension was purged with argon for ten minutes before allowed to stir for 48 hours in an 80 °C oil bath under an argon atmosphere. The brown suspension was poured into cold water and extracted with ether three times. The combined organics were washed with water twice and the combined aqueous phases from the washings were extracted with ether once. The combined organics were dried over MgSO$_4$, filtered, and the solvent was removed in vacuo. Purification via column chromatography using 4% ether/hexanes gave 2.8738 g (7.35 mmol, 81%) of 1,2-didecyloxybenzene as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) δ: 6.89 (s, 4H), 3.99 (t, 4H, $J = 6.6$ Hz), 1.81 (qu, 4H, $J = 7.0$ Hz), 1.46 (m, 8H), 1.27 (m, 20H), 0.88 (t, 6H, $J = 6.5$ Hz). $^1$H NMR was in agreement with published data.$^{64}$

1,2-didodecyloxybenzene

Catechol (3.002 g, 27.26 mmol), KI (0.2214 g, 1.33 mmol), anhydrous K$_2$CO$_3$,(15.7862 g, 114.22 mmol) and DMF (101 mL) were stirred in a round bottom flask. To the green suspension, 1-bromododecane was added dropwise via syringe. Then a condenser was attached and the purple suspension was purged with argon for ten minutes and allowed to stir for 65 hours in an 85 °C oil bath under an argon atmosphere. The warm suspension was poured into cold water and extracted with ether three times. The combined organics were washed with water and
brine. Then the organic phase was dried over MgSO₄, filtered, and the solvent was removed in vacuo. The crude brown product was recrystallized from 100% EtOH (150 mL). Vacuum filtration gave 6.8162 g (15.25 mmol, 56%) of 1,2-didodecylbenzene as an off-white solid. ¹H NMR (300 MHz, CDCl₃) δ: 6.88 (s, 4H), 3.99 (t, 4H, J = 6.5 Hz), 1.81 (qu, 4H, J = 6.7 Hz), 1.38 (m, 36H), 0.88 (m, 6H). ¹H NMR was in agreement with published data.⁶⁵

\[
\begin{array}{c}
\text{H}_{3}\text{IO}_{6}, \text{I}_2, \text{MeOH} \\
\text{5 hrs, 70}^\circ\text{C} \\
R = \text{C}_6\text{H}_{13} \ 79\% \\
R = \text{C}_{10}\text{H}_{21} \ 56\% \\
R = \text{C}_{12}\text{H}_{25} \ 92\%
\end{array}
\]

1,2-diiodo-4,5-diheptyloxybenzene

In a round bottom flask charged with a stir bar, a solution of H₅IO₆ (1.9556 g, 8.58 mmol) and MeOH (13 mL) was stirred for 15 minutes at room temperature. Then I₂ (4.3322 g, 17.07 mmol) was added to the solution, which was vigorously stirred for ten minutes. Next, 1,2-dihexyloxybenzene (5.9480 g, 21.36 mmol) was slowly added to the solution. With a condenser attached, the solution was allowed to stir for five hours at 70 °C. The hot solution was poured into dilute sodium thiosulfate. Instead of a solid crashing out of solution, the crude product remained an oil. Therefore, the mixture was extracted with EtOAc twice. The combined organics were dried over MgSO₄, filtered, and the solvent was removed in vacuo. Monoiodinated product was re-subjected to the conditions above. Purification via column chromatography using 3% EtOAc/hexanes gave 8.9566 g (16.89 mmol, 79%) of 1,2-diiodo-4,5-dihexyloxybenzene as a light yellow oil. ¹H NMR (300 MHz, CDCl₃) δ: 7.24 (s, 2H), 3.92 (t, 4H, J = 6.7 Hz), 1.78 (qu, 4H, J = 7.1 Hz), 1.44 (qu, 4H, J = 7.3), 1.32 (m, 8H), 0.90 (t, 6H, J = 7.1 Hz).

1,2-diiodo-4,5-didecyloxybenzene

In a round bottom flask charged with a stir, a solution of H₅IO₆ (209.6 mg, 0.92 mmol) and MeOH (2.6 mL) was stirred for 15 minutes at room temperature. Then I₂ (457.6 mg, 1.80 mmol) was added to the solution, which was vigorously stirred for ten minutes. Then 1,2-
didecyloxybenzene (581.2 mg, 1.48 mmol) was slowly added to the solution. A condenser was attached and the solution was allowed to stir for five hours at 70 °C. The hot solution was poured into dilute sodium thiosulfate and extracted with DCM three times. The combined organics were dried over MgSO₄, filtered, and the solvent was removed in vacuo. Prior to characterization the compound was recrystallized from 100% EtOH. Vacuum filtration gave 543.3 mg (0.84 mmol, 57%) of 1,2-diiodo-4,5-dihexyloxybenzene as a white solid. \( ^1H \) NMR (300 MHz, CDCl₃) \( \delta \): 7.24 (s, 2H), 3.92 (t, 4H, \( J = 6.6 \) Hz), 1.78 (qu, 4H, \( J = 6.9 \) Hz), 1.43 (m, 8H), 1.27 (m, 20H), 0.88 (t, 6H, \( J = 6.0 \) Hz).

**1,2-diiodo-4,5-didodecyloxybenzene**

In a round bottom flask charged with a stir, a solution of H₅IO₆ (0.8181 g, 3.59 mmol) and MeOH (14 mL) was stirred for 15 minutes at room temperature. Then I₂ (1.8068 g, 7.12 mmol) was added to the solution, which was vigorously stirred for ten minutes. Then 1,2-didodecyloxybenzene (1.9782 g, 4.42 mmol) was slowly added to the solution. A condenser was attached and the solution was allowed to stir for five hours at 75 °C. The hot solution was poured into dilute sodium thiosulfate and extracted with EtOAc three times. The combined organics were dried over MgSO₄, filtered, and the solvent was removed in vacuo. Prior to characterization the compound was recrystallized from 100% EtOH (100 mL). Vacuum filtration gave 2.8471 g (4.07 mmol, 92%) of 1,2-diiodo-4,5-hexyloxybenzene as a tan solid. \( ^1H \) NMR (300 MHz, CDCl₃) \( \delta \): 7.24 (s, 2H), 3.92 (t, 4H, \( J = 6.3 \) Hz), 1.78 (~qu, 4H), 1.35 (m, 36H), 0.88 (~t, 6H).
Compounds 10

Taking 10a as an example: In a Schlenk vacuum tube charged with a stir bar, CuI (3.8 mg, 0.02 mmol), Pd(OAc)$_2$ (5.6 mg, 0.02 mmol), and PPh$_3$ (32.0 mg, 0.12 mmol) were added and the tube was evacuated and backfilled with argon three times. Then 9a (246.3 mg, 0.64 mmol) and 1,2-diiodo-4,5-dihexyloxybenzene (167.4 mg, 0.31 mmol) were weighed out in scintillation vials and dissolved in diisopropylamine (1.6 mL). Both monomers were added to tube while under a positive pressure of argon. The suspension was degassed three times, and the tube was sealed under an argon atmosphere. The suspension was allowed to stir overnight at 80°C in an oil bath. Then the reddish-brown suspension was cooled to room temperature and diluted with EtOAc and washed with water and brine. The combined aqueous layers were extracted with EtOAc twice. The combined organics were dried over MgSO$_4$, filtered, and the solvent was removed in vacuo. The crude product was absorbed onto silica gel and purification via column chromatography using 1:2 DCM:hexanes gave 206.1 mg (0.20 mmol, 63%) of 10a as a reddish-orange viscous oil, which became an orange solid when allowed to sit at room temperature. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.23 (~t, 2H), 6.99 (s, 2H), 6.97 (~t, 2H), 6.94 (~t, 2H), 4.02 (t, 4H, $J = 6.5$ Hz), 3.79 (t, 4H, $J = 6.3$ Hz), 1.84 (qu, 4H, $J = 6.8$ Hz), 1.70 (qu, 4H, $J = 6.5$ Hz), 1.48 (m, 4H), 1.35 (m, 20H), 1.10 (s, 42H), 0.90 (m, 12H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 159.17, 149.97, 127.60, 125.09, 124.95, 119.28, 117.57, 116.95, 106.69, 91.82, 91.23, 89.04, 69.83, 68.58, 31.78, 29.44, 25.87, 22.73, 18.84, 14.03, 11.69; MALDI-TOF-MS (dithranol) calc’d for C$_{68}$H$_{102}$O$_4$Si$_2$Cu (M+Cu$^+$) $m/z = 1101.66$, found 1101.38.
10b: Using the above procedure for compound 10, 9b (119.0 mg, 0.27 mmol) and 1,2-diodo-4,5-didecyloxybenzene (68.8 mg, 0.10 mmol) were allowed to react for 24 hours in an 80 °C oil bath. The crude product was absorbed onto silica gel and purified by column chromatography using 15% DCM/hexanes, which gave 98.1 mg (0.07 mmol, 72%) of 10b as an orange solid. $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.25 (~t, 2H), 7.01 (s, 2H), 6.99 (~t, 2H), 6.95 (~t, 2H), 4.03 (t, 4H, $J = 6.3$ Hz), 3.81 (t, 4H, $J = 6.1$ Hz), 1.85 (m, 4H), 1.71 (m, 4H), 1.49 (m, 4H), 1.38 (m, 8H), 1.28 (~s, 44H), 1.12 (s, 42H), 0.90 (t, 12H, $J = 6.5$); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 158.90, 149.41, 127.38, 124.83, 124.64, 119.06, 118.74, 117.04, 115.84, 106.33, 91.63, 91.04, 88.86, 69.32, 68.23, 32.07, 29.73, 29.57, 29.54, 29.51, 29.35, 29.25, 26.16, 26.13, 22.85, 18.79, 14.26, 11.44; MALDI-TOF-MS (HABA) calc’d for C$_{84}$H$_{134}$O$_4$Si$_2$Cu (M+Cu$^+$) $m/z = 1325.91$, found 1325.98.

10c: Using the above procedure for compound 10, 9c (114.0 mg, 0.24 mmol) and 1,2-diodo-4,5-didodecyloxybenzene (75.8 mg, 0.10 mmol) were allowed to react overnight in an 80 °C oil bath. Purification via column chromatography using 10% DCM/hexanes gave 115.6 mg (0.08 mmol, 77%) of 10c as an orange solid. $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.24 (~t, 2H), 7.00 (s, 2H), 6.98 (~t, 2H), 6.95 (~t, 2H), 4.03 (t, 4H, $J = 6.5$ Hz), 3.80 (t, 4H, $J = 6.4$ Hz), 1.85 (qu, 4H, $J = 6.7$ Hz), 1.71 (qu, 4H, $J = 6.4$ Hz), 1.48 (m, 4H), 1.27 (~s, 68H), 1.12 (s, 42H), 0.89 (t, 12H, $J = 6.5$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 158.90, 149.42, 127.39, 124.84, 124.65, 119.07, 118.75, 117.06, 117.02, 115.87, 106.35, 91.63, 91.05, 88.86, 69.34, 68.25, 32.10, 29.85, 29.82, 29.78, 29.59, 29.54, 29.37, 29.25, 26.17, 26.14, 22.85, 18.80, 14.27, 11.46; MALDI-TOF-MS (HABA) calc’d for C$_{92}$H$_{150}$O$_4$Si$_2$Cu (M+Cu$^+$) $m/z = 1438.04$, found 1437.81.
Taking 11a as an example: In a 10 mL round bottom charged with a stir bar, 10a (168.5 mg, 0.16 mmol) was added and the flask was purged with argon for ten minutes. Then 1 M TBAF in THF (0.11 mL) was added via syringe, followed by THF (4.0 mL). The solution was allowed to stir for two hours at room temperature. Then it was diluted with EtOAc, and washed with water and brine. The combined aqueous layers were extracted with EtOAc twice. The combined organics were dried over MgSO₄, filtered, and the solvent was removed in vacuo. The crude orange solid was absorbed onto silica gel and purified by column chromatography using 1:3 DCM:hexanes, which gave 113.2 mg (0.15 mmol, 96%) of 11a as a yellow powder. ¹H NMR (300 MHz, CDCl₃) δ: 7.26 (~s, 2H), 7.03 (~t, 2H), 7.00 (s, 2H), 6.97 (~t, 2H), 4.03 (t, 4H, J = 6.7 Hz), 3.87 (t, 4H, J = 6.6 Hz), 3.03 (s, 2H), 1.84 (qu, 4H, J = 6.9 Hz), 1.73 (qu, 4H, J = 6.8 Hz), 1.41 (m, 24H), 0.91 (m, 12H); ¹³C NMR (75 MHz, CDCl₃) δ: 159.34, 150.20, 127.90, 125.26, 123.83, 119.34, 119.21, 118.39, 117.35, 91.70, 89.27, 83.27, 77.34, 70.03, 68.80, 31.78, 29.54, 29.46, 25.90, 22.74, 13.99; MALDI-TOF-MS (HABA) calc’d for C₅₀H₆₂O₄Cu (M+Cu⁺) m/z = 789.39, found 788.98.

11b: Using the above procedure for compound 11, 10b (97.9 mg, 0.07 mmol) and 1 M TBAF in THF (0.05 mL) were dissolved in THF (2.0 mL) and allowed to react for two hours at room temperature. The crude yellow crystals were purified by column chromatography using gradient elution (10% DCM/hexanes then 20% DCM/hexanes), which gave 59.6 mg (0.06 mmol, 81%) of 11b as light yellow granular crystals. ¹H NMR (300 MHz, CDCl₃) δ: 7.26 (~t, 2H), 7.03 (~t, 2H), 7.00 (s, 2H), 6.97 (~t, 2H), 4.02 (t, 4H, J = 6.6 Hz), 3.86 (t, 4H, J = 6.4 Hz), 3.02 (s, 2H), 1.84 (qu, 4H, J = 6.9 Hz), 1.73 (qu, 4H, J = 6.9 Hz), 1.38 (m, 56H ), 0.88 (t, 12H, J = 6.5 Hz);
$^{13}$C NMR (75 MHz, CDCl$_3$) δ: 158.96, 149.48, 127.53, 124.86, 123.47, 118.89, 118.67, 117.75, 115.91, 91.44, 89.05, 82.97, 77.50, 69.36, 68.35, 32.06, 29.77, 29.73, 29.54, 29.51, 29.31, 29.25, 26.13, 22.84, 14.26; MALDI-TOF-MS (HABA) calc’d for C$_{66}$H$_{94}$O$_4$Cu (M+Cu$^+$) m/z = 1013.64, found 1013.75.

11c: Using the above procedure for compound 11, 10c (113.0 mg, 0.082 mmol) and 1 M TBAF in THF (0.06 mL) were dissolved in THF (2.05 mL) and allowed to react for two hours at room temperature. Purification via column chromatography using gradient elution (10% DCM/hexanes then 20% DCM/hexanes) gave 81.0 mg (0.078 mmol, 93%) of 11c as yellow crystals. $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.26 (~t, 2H), 7.04 (~t, 2H), 7.00 (s, 2H), 6.97 (~t, 2H), 4.03 (t, 4H, $J$ = 6.5 Hz), 3.87 (t, 4H, $J$ = 6.4 Hz), 3.03 (s, 2H), 1.84 (qu, 4H, $J$ = 6.8 Hz), 1.73 (qu, 4H, $J$ = 6.7 Hz), 1.38 (m, 72 H), 0.88 (t, 12H, $J$ = 6.4 Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 158.97, 149.49, 127.55, 124.86, 123.47, 118.89, 118.67, 117.77, 115.93, 91.44, 89.05, 82.98, 77.50, 69.36, 68.35, 32.08, 29.86, 29.82, 29.81, 29.78, 29.52, 29.32, 29.25, 26.14, 22.85, 14.26; MALDI-TOF-MS (HABA) calc’d for C$_{74}$H$_{110}$O$_4$Cu (M+Cu$^+$) m/z = 1125.77, found 1125.68.

Compound 12a
In a Schlenk vacuum tube charged with a stir bar, Pd(P$^t$Bu$_3$)$_2$ (3.6 mg, 0.007 mmol) and 11a (34.1 mg, 0.047 mmol) were added and the tube was evacuated and backfilled with argon three times. Then DABCO (5.526 g, 49.264 mmol) and 1,2-diiodo-4,5-dihexyloxybenzene (31.1 mg, 0.058 mmol) were dissolved in toluene (24.0 mL) and each was added to the tube under positive
argon pressure. (Note: all of DABCO will not dissolve in toluene.) The solution was degassed three times and sealed under an argon atmosphere. Sonication provided a homogeneous solution that was allowed to stir overnight at room temperature. The solution was then diluted with fresh toluene and washed with water and brine. The aqueous washings were combined and extracted with toluene twice. The combined organics were dried over MgSO₄, filtered, and the solvent was removed in vacuo. Purification via column chromatography using gradient elution (50% toluene/hexanes then 70% toluene/hexanes) gave 15.5 mg (0.015 mmol, 33%) of 12a as a light brown solid. The product was recrystallized from benzene to give an off-white powder prior to characterization. ¹H NMR (500 MHz, CDCl₃) δ: 7.58 (~s, 2H), 7.03 (~d, 8H), 4.04 (t, 8H, J = 6.54 Hz), 4.00 (t, 4H, J = 6.4 Hz), 1.85 (qu, 8H, J = 7.1 Hz), 1.76 (m, 4H), 1.49 (m, 12H), 1.36 (m, 24H), 0.92 (~t, 18H); m.p. = 182.88 °C; ¹³C NMR (125 MHz, CDCl₃) δ: 159.09, 149.46, 128.09, 124.83, 118.71, 117.18, 116.05, 91.57, 89.12, 69.35, 68.43, 31.71, 29.30, 29.22, 25.84, 25.81, 22.76, 14.170; MALDI-TOF-MS (dithranol) calc’d for C₆₈H₈₈O₆ (M⁺) m/z = 1000.66, found 1000.27.

**Compound 12b**

In a Schlenk vacuum tube charged with a stir bar, Pd(P^tBu₃)₂ (3.6 mg, 0.007 mmol) and 11b (57.5 mg, 0.060 mmol) were added and the tube was evacuated and backfilled with argon three times. Then DABCO (7.130 g, 63.594 mmol) and 1,2-diiodo-4,5-didecyloxybenzene (40.5 mg, 0.063 mmol) were dissolved in toluene (30.0 mL) and each was added to the tube under positive argon pressure. (Note: all of DABCO will not dissolve in toluene.) The solution was degassed three times and sealed under an argon atmosphere. Sonication provided a homogeneous solution that was allowed to stir overnight at room temperature. The solution was then diluted with fresh toluene and washed with water and brine. The aqueous washings were combined and extracted with toluene twice. The combined organics were dried over MgSO₄, filtered, and the solvent was removed in vacuo. Purification via GPC gave 52.9 mg (0.39 mmol, 65%) of 12b as a light orange powder. Prior to characterization, the product was recrystallized from benzene, which gave an off-white powder. ¹H NMR (500 MHz, CDCl₃) δ: 7.58 (~s, 2H), 7.03 (~d, 8H), 4.04 (t, 8H, J = 6.2 Hz), 3.99 (t, 4H, J = 6.3 Hz), 1.85 (~qu, 8H), 1.79 (m, 4H), 1.47 (m, 12H), 1.33 (m, 72H), 0.92 (t, 18H, J = 6.5 Hz); m.p. = 115.07 °C; ¹³C NMR (125 MHz, CDCl₃) δ: 159.09, 149.47, 128.09, 124.83, 118.73, 117.18, 116.10, 91.57, 89.12, 69.36, 68.44, 32.07, 29.78, 29.73,
29.54, 29.51, 29.48, 29.35, 29.27, 26.15, 22.84, 14.26; MALDI-TOF-MS (HABA) calc’d for C_{92}H_{136}O_6Cu (M+Cu^{+}) m/z = 1399.96, found 1399.53.

**Compound 12c**

In a Schlenk vacuum tube charged with a stir bar, Pd(P^tBu_3)_2 (3.3 mg, 0.006 mmol) and 11c (60.5 mg, 0.057 mmol) were added and the tube was evacuated and backfilled with argon three times. Then DABCO (6.7325 g, 60.020 mmol) and 1,2-diiodo-4,5-didodecyloxybenzene (40.8 mg, 0.058 mmol) were dissolved in toluene (27.0 mL), and each was added to the tube under positive argon pressure. (Note: all of DABCO will not dissolve in toluene.) The solution was degassed three times and sealed under an argon atmosphere. Sonication provided a homogeneous solution that was allowed to stir overnight at room temperature. The solution was then diluted with fresh toluene and washed with water and brine. The aqueous washings were combined and extracted with toluene twice. The combined organics were dried over MgSO_4, filtered, and the solvent was removed in vacuo. Purification via GPC gave 51.1 mg (0.034 mmol, 59%) of 12c as a light yellow powder. Prior to characterization, the product was recrystallized from benzene to give an off-white powder. \(^{1}H\) NMR (500 MHz, CDCl_3) \(\delta\): 7.58 (~s, 2H), 7.03 (~d, 8H), 4.04 (t, 8H, \(J = 6.6\) Hz), 4.00 (t, 4H, \(J = 6.3\) Hz), 1.83 (m, 12H), 1.47 (m, 12H), 1.32 (m, 96H), 0.88 (t, 18H, \(J = 6.9\) Hz); m.p. = 99.66 °C; \(^{13}C\) NMR (extracted from HMBC and HMQC, CDCl_3) \(\delta\): 158.83, 149.25, 127.88, 125.48, 118.56, 117.00, 115.98, 91.40, 88.98, 69.18, 68.18, 31.79, 29.44, 28.99, 25.83, 22.67, 22.50, 14.06; MALDI-TOF-MS (HABA) calc’d for C_{104}H_{160}O_6Cu (M+Cu^{+}) m/z = 1568.15, found 1567.61.
Chapter 5: References


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Chapter 6: Spectroscopic Data

\[ ((\text{3-tert-butyl-5-ethynylphenyl})\text{ethynyl})\text{triisopropylsilane} \ (3) \]

\[ ((\text{3-tert-butyl-5-ethynylphenyl})\text{ethynyl})\text{triisopropylsilane}-\text{homocoupling} \]

\[ ((\text{3-tert-butyl-5-ethynylphenyl})\text{ethynyl})\text{triisopropylsilane} \]
5,5’-(4,5-dimethoxy-1,2-phenylene)bis(ethyne-2,1-diyl)bis(3-tert-butyl-5,1-phenylene)bis(ethyne-2,1-diyl)bis(triisopropylsilane) (4)
5,5'-(4,5-dimethoxy-1,2-phenylene)bis(ethyne-2,1-diyl)bis(3-tert-butyl-5,1-phenylene)bis(ethyne-2,1-diyl) (5)
5,5’-(4,5-dimethoxy-1,2-phenylene)bis(ethyne-2,1-diyl)bis(1-tert-butyl-3-ethynylbenzene) (6)
Trimer TIPS-mono-hexyloxy (10a)

![Chemical Shift Graph]

- Chemical Shift (ppm)
- Normalized Intensity
- CDCl3
- H2O
- EtOAc

![13C NMR Graph]

- Chemical Shift (ppm)
- Normalized Intensity
- CDCl3

10a
Trimer TIPS-mono-decyloxy (10b)

Chemical Shift (ppm)

Normalized Intensity

CDCl₃
Trimer TIPS-mono-dodecyloxy (10c)
Trimer Alkyne-mono-hexyloxy (11a)

Chemical Shift (ppm)
Trimer Alkyne-mono-decyloxy (11b)
Trimer Alkyne-mono-dodecyloxy (11c)

![Chemical Structure](image)

**Chemical Shift (ppm)**

**Normalized Intensity**
Tetramer Macrocycle -OC₆H₁₃ (12a)

C₆H₁₃O

OC₆H₁₃

C₆H₁₃O

OC₆H₁₃

OC₆H₁₃

12a

Chemical Shift (ppm)

Normalized Intensity

CDCL₃

H₂O

Acetone

Normalized Intensity

CDCL₃

H₂O

Acetone
Tetramer Macrocycle –OC$_{10}$H$_{21}$ (12b)
Tetramer Macrocycle –OC_{12}H_{25} (12c)