PARTIALLY FLUORINATED POLYCYCLIC AROMATIC COMPOUNDS: SYNTHESIS AND SUPRAMOLECULAR BEHAVIOR

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ABSTRACT OF THESIS

PARTIALLY FLUORINATED POLYCYCLIC AROMATIC COMPOUNDS:
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The field of organic electronics has received much attention over the last few years, and engineering of organic crystals to grow with pi-electron systems arranged in a face-to-face motif has been shown to be beneficial in electronic devices. The effects of combining aromatic and perfluorinated aromatic derivatives have shown that the intramolecular stacking pattern can be changed from an edge-to-face arrangement to that of a face-to-face motif. Before the work described herein, there were no reported studies of the supramolecular behavior of fused polycyclic aromatic compounds with partial peripheral fluorination, inducing the desired face-to-face behavior. This is the main focus of the thesis. Furthermore, by exploiting the interactions between the fluorinated and non-fluorinated faces of the molecule, columnar liquid crystalline behavior can be achieved through variations of the alkyl substituents on the molecule.

KEYWORDS: Partial Fluorination, Polycyclic Aromatic Compounds, Pi Stacking, Columnar Liquid Crystals, Organic Materials

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December 19, 2006
PARTIALLY FLUORINATED POLYCYCLIC AROMATIC COMPOUNDS:
SYNTHESIS AND SUPRAMOLECULAR BEHAVIOR

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THESIS

Don Mark Cho

The Graduate School
University of Kentucky
2006
PARTIALLY FLUORINATED POLYCYCLIC AROMATIC COMPOUNDS:
SYNTHESIS AND SUPRAMOLECULAR BEHAVIOR

THESIS

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the College of Arts and Sciences at the University of Kentucky

By

Don Mark Cho
Lexington, Kentucky

Director: Dr. Mark D. Watson, Assistant Professor of Chemistry
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2006

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This thesis is dedicated to my family: to my parents who have been most supportive of me throughout my life, and to my wife, Trinity, who has been patient and understanding through everything.
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Chapter One – Introduction

Inorganic materials have long dominated the field of electronic circuits and devices. Over the past few years, there has been increasing attention given to the use of organic materials for these purposes.\(^1\) The reason for this growing interest lies in the potential advantages offered by organics that cannot currently be realized by their inorganic counterparts. For example, inorganic displays and circuits require high processing temperatures whereas the organic counterparts are soluble in common solvents, so the device can be made through spin coating, drop casting, doctor blading, or “printed” using an ink jet printer. Among the possible applications for organic electronics are field effect transistors (OFETs),\(^2\) light emitting diodes (OLEDs),\(^3\) photovoltaics,\(^4\) radio frequency identification (RFIDs),\(^5\) and thin film transistors (OTFTs).\(^6\)

A majority of polycyclic aromatic hydrocarbons (PAHs) tend to assemble in an edge-to-face fashion in the crystalline state.\(^7\) It is generally believed that face-to-face contact is better for organic electronics as there is the possibility for increased π-π overlap between the faces of adjacent molecules. This would allow significant π-overlap between molecules to facilitate the carrier pathway. This is not to say, however, that edge-to-face interactions have no π-π overlap as it can be seen in the crystal packing found in pentacene,\(^8\) which has been shown to have excellent device properties.

![Figure 1.1: X-ray crystal packing of anthracene\(^9\) (left) and naphthalene\(^10\) (right).](image)

Research in modern small molecule organic electronics has focused on aromatic systems (or conjugated systems at the very least). Of primary importance in developing a suitable candidate for an electronic system such as a field effect
transistor or a photovoltaic device lies in designing a molecule such that its interactions with adjacent molecules will achieve optimal charge carrier ability. It is for this reason that co-facial \( \pi \)-stacking motifs are sought in the development of potential organic electronic materials. Co-facial \( \pi \)-stacking for organic small-molecules with continuous, uninterrupted stacks currently can be placed into two very general categories based upon stacking motifs: 1-D and 2-D.\(^{11}\) One-dimensional \( \pi \)-\( \pi \) stacking indicates that the electronic packing occurs along one axis; this motif can be columnar or can be arranged in a slip stack,\(^{12}\) which can be seen in the first example in Figure 1.2. Two-dimensional materials can be represented by a “brick wall” type arrangement as can be seen in the second example in Figure 1.2. In both cases below, these molecules are designed with substituents which partly preclude edge-to-face interactions; face-to-face stacking is achieved by default.

![Figure 1.2: 1-D\( \pi \) slip-stack exhibited by rubrene\(^{12}\) (left) and 2-D\( \pi \) stack exhibited by tri-isopropylsilylethynylated pentacene\(^{11}\) (right).](image)

Design of an organic electronic system leads to the formation of an n-type (negative charge or electron carrier) or p-type (positive charge or hole carrier) material. Ideal systems are those where the n- and p-type materials have similar electrical and physical properties but possess different charge carriers. To this end, it has been shown that pentacene (a fused aromatic, or \( \pi \) system) can be converted from its characteristic p-type behavior to an n-type material by perfluorination of its periphery (a perfluorinated fused aromatic system, or \( \pi F \)).\(^{13}\) The strong electron-withdrawing effects fluorine atoms possess pull electron density away from the core of the pentacene molecule, essentially lowering the lowest occupied molecule orbital (LUMO) and facilitating electron injection. It should be pointed out, however, that it
is not necessary to fully fluorinate the molecule and that the relative location of the fluorine atoms about the $\pi$ system may be important. Tobin Marks, Antonio Facchetti, and co-workers synthesized variations of sexithiophene, replacing some of the thiophene rings with perfluorinated phenyl rings.\textsuperscript{14}

![Figure 1.3: Marks' and Facchetti's $\pi$-$\pi$F systems.\textsuperscript{15}](image)

They found that by placing the fluorinated phenyl rings on opposite ends of four $\alpha$-connected thiophene rings (for a total of six aromatic rings), an n-type material could be made. Interestingly, the molecule with the best device characteristics was the top left molecule in Figure 1.3; it stacks in a 2-dimensional fashion with a thin film transistor mobility of $0.4\text{cm}^2/\text{Vs}$ with an on/off current ratio of $10^8$.

Designing an aromatic system that will stack in a face-to-face fashion requires that one overcome favorable edge-to-face interactions. Adjusting a molecule or in some way modifying it to behave in a specific manner has been appropriately dubbed “crystal engineering” and interest in this field has been high. One way commonly used to accomplish this is to build aromatic systems with a sufficiently large ratio of pi-surface-to-circumference such that a perfect herringbone packing, that is all intermolecular contacts being edge-to-face interactions, is impossible due to space filling requirements. One of the possible ways of doing this is to create ever larger $\pi$ systems such that a herringbone pattern is not possible; the extreme example of this would be graphite, but a more conventional example is superphenalene systems; these are large, disklike molecules consisting of many fused benzene rings ($\sim$96 carbons or greater).\textsuperscript{16}

The addition of side chains can also be used to induce this behavior; unsubstituted hexa-\textit{peri}-hexabenzocoronene (HBC) stacks in a herringbone-like
arrangement\textsuperscript{17} whereas the addition of bulky side chains yield face-to-face interactions with liquid crystalline behavior.\textsuperscript{18} These large side chains also allowed for a decrease in isotropization temperature ($T_i$) and the inclusion of an ether in the side chain induced control of self-assembly by allowing the molecule to interact with the polar substrate surfaces.

![Figure 1.4: X-ray crystal structure of HBC.\textsuperscript{17}](image)

Related to this method of adding side chains is to add substituents to the molecule which force face-to-face interactions that similarly create steric effects and do not allow for efficient edge-to-face interactions. Anthony and co-workers sought to overcome the edge-to-face interactions and increase the slight face-to-face interactions seen in pentacene by adding bulky silyl-alkynyl groups to the peri positions.\textsuperscript{19} For most of these pentacene derivatives, an edge-to-face motif would be an extremely inefficient way for these molecules to stack in the solid state as these long and bulky groups would create a considerable amount of empty space. Furthermore, the size of the “ball” (silyl group) and length of the “rod” (alkynyl group) can dictate whether the co-facial packing adopts a 1D or 2D motif. Kobayashi and coworkers synthesized anthracenes with OCH$_3$, SCH$_3$, and TeCH$_3$ substituents placed at the peri positions of anthracene to investigate the ability of pendant chalcogens to force face-to-face stacking.\textsuperscript{20} They were able to show that while methoxy groups on anthracene do not lead to face-to-face $\pi$ stacking, this motif can
be observed by substitution of a methylthio or methyltelluro group on the peri position of anthracene. S-S or Te-Te close contacts were observed at a distance of 3.638Å and 3.747Å, respectively, whereas the O-O distance was 4.236Å. The sum of the Van der Waals radii for O-O is 3.04, S-S is 3.3 and Te-Te is 4.12.\textsuperscript{21}

There are further reported examples on the usage of substituents to induce co-facial packing. In 1986, Sarma and Desiraju published a paper explaining why a number of chloroaromatic compounds exhibit face-to-face stacking in the crystalline state.\textsuperscript{22} They were able to determine that the number of chlorines added to an aromatic system increased the chances for face-to-face interactions. This was interesting at the time because when chlorine is compared to methyl groups, they fill nearly the same volume; conventional thinking was that chlorosubstituted products should stack similarly to methyl substituted products in the crystalline state (the Cl-Me rule).\textsuperscript{23} However, while hexamethylbenzene stacks in a herringbone fashion, hexachlorobenzene stacks in a face-to-face pattern. They concluded that there was a weak attraction between nearby chlorines in aromatic systems which resulted in edge-to-edge interactions, ultimately leading to ribbons or sheets of molecules which stack in a co-facial manner. This edge-to-edge interaction was found to be rather weak and was limited by the fact that any stronger interactions would disrupt this packing pattern.

Cocrystallizations of H-bond donor/acceptor systems have also been investigated as a way of inducing face-to-face interactions. MacGillivray and coworkers were able to cocrystallize resorcinol (1,3-dihydroxybenzene) derivatives with anthracene and thiophene, each functionalized such that end groups would contain an H-bond acceptor (pyridine)\textsuperscript{24}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{resorcinol.png}
\caption{Hydrogen bonding acceptors co-crystallized with resorcinol.}
\end{figure}

While each molecule does not experience face-to-face interactions when in the crystalline state by themselves, the interaction of the lone pair of electrons from the
pyridine with the hydroxyl groups from resorcinol results in the formation of dimer pairs, each of which crystallize in a slipped 1-D column. The main advantage here is that hydrogen bonding is a relatively strong interaction and is quite favorable.

Figure 1.6: Co-crystallization of 2,5-bis(4-pyridylethynyl)thiophene and 1,3-dihydroxy5-iodobenzene.$^{24}$

More recently there has been some effort in exploiting the attractive nature of $\pi$-$\pi$F interactions. In 1999, Grubbs and coworkers showed that arene/perfluoroarene co-crystals could be formed that exhibit liquid crystalline behavior through self assembly$^{25}$. The 1:1 mixture of arene/perfluoroarene led to a complete loss of characteristics for each single compound and the combination behaved as if it was a completely new substance, showing different transitions in differential scanning calorimetry and a different UV/VIS spectrum.

Another example was shown by Uwe Bunz and Volker Enkelmann through an investigation during their successful elucidation of the Eglinton-Galbraith dimer$^{26}$.

Figure 1.7: Eglinton-Galbraith dimer (left) and co-crystallization with hexafluorobenzene (right).
This was a molecular system consisting of dibenzodehydro[12]annulene molecules in the crystalline state, known for its instability in ambient conditions and tendency to explode when mildly heated. It was found to co-crystallize with hexafluorobenzene and form a rather stable complex which could be left out in air for a number of weeks (the naked dimer would decompose in a matter of a few hours). What was unexpected was they found that hexafluorobenzene did not interact as predicted with the benzene rings but rather with the butadiyne groups. They were best able to explain this through electrostatic potential calculations, finding that while hexafluorobenzene has a characteristic positive ring charge with partial negative charges for each fluorine, there is a similar partial negative charge on the butadiyne carbons. Face-to-face ring packing and interaction between benzene rings would require unfavorable interactions between the fluorines and the butadiyne carbons.

In 1960, Patrick and Prosser reported the structure of a 1:1 complex between benzene and hexafluorobenzene.\textsuperscript{27} This work showed that benzene and hexafluorobenzene align themselves in an alternating, co-facial manner. This is quite different than the crystal structure of pure hexafluorobenzene\textsuperscript{28} or benzene,\textsuperscript{29} each of which crystallize in an edge-to-face motif.

\begin{figure}[h!]
\centering
\includegraphics[width=\textwidth]{benzene_hexafluorobenzene_structure.png}
\caption{X-ray crystal structures of benzene\textsuperscript{29} (left, with hydrogens removed for clarity) and an illustration of the quadrupole interactions experienced in the crystalline state.\textsuperscript{30}}
\end{figure}
Figure 1.9: X-ray crystal structure of hexafluorobenzene\textsuperscript{28} and an illustration of the quadrupole interactions experienced in the crystalline state.

While both are liquids at room temperature, the mixture yields a solid with a melting point of 23.7 °C. A definitive crystal structure was obtained in 1992\textsuperscript{31} and a number of monocyclic and polycyclic aromatic cores have been co-crystallized with hexafluorobenzene to demonstrate this face to face behavior\textsuperscript{32}. The tendency to co-crystallize in a face-to-face manner can be explained via quadrupole moments or by examining the molecular electrostatic potential (MEP) maps of both hexafluorobenzene and benzene.

Figure 1.10: MEP maps of benzene (left) and hexafluorobenzene (right) (MEP maps generated using Viewerlite).

The MEP maps are color coded according to electrostatic potential, where blue indicates repulsion to an approaching proton and red indicates attraction to an approaching proton. The slight positive nature of the face of hexafluorobenzene is established due to the high electronegativity of fluorine. Furthermore, the quadrupole of hexafluorobenzene has been determined to be large and positive, whereas the
quadrupole for benzene has been established as large and negative, further explaining
the preference for face-to-face interaction between the two arenes.$^{33}$

![Figure 1.11: Crystal packing of a 1:1 mixture of benzene and hexafluorobenzene viewed down the c-axis$^{34}$ (left) and an illustration of quadrupole moments (right).]

![Figure 1.12: Packing of co-crystallized hexafluorobenzene and anthracene$^{35}$. Double headed arrows indicate the spacing between the two parallel best planes defined by the carbon atoms of anthracene and hexafluorobenzene.]

**Discotic Liquid Crystals (DLCs)**

Disk shaped molecules which assemble into a liquid crystalline mesophase are referred to as discotic liquid crystals.$^{36}$ These typically form mesophases which can be described as lamellar, columnar, or nematic, but the focus here will only be on the
columnar-type materials. Thermotropic liquid crystals are the most common and are defined as a material that passes among its different phases (liquid, solid, and liquid crystalline) as a function of temperature. While there are a number of ways the columns of specific molecules can pack to achieve the greatest space filling requirements (rectangular, oblique, helical, etc) dependant upon the architecture of the molecule; a hexagonal arrangement ($D_h$) is the most common. When in “solid” or “plastic” phases, columnar liquid crystals have been shown to have charge-carrier mobilities similar to those seen in crystalline materials. Single crystals, however, are limited in size and processing can lead to defects on the crystal at the electrode; columnar liquid crystals have the advantage of the ability to form large and oriented domains. Growth of the columns can be directed normal to a substrate (homeotropic), or parallel to a substrate (planar).

![Figure 1.13: Columnar hexagonal packing](image)

It is known that single crystals deliver superior charge carrier mobilities, but the prospect of producing mass amounts of a single crystal device is daunting. If these characteristics could be seen in a liquid crystalline device, processability becomes much more feasible. For this reason, there is considerable interest in the factors governing self assembly in columnar discotic liquid crystals. Self-assembly is an elegant process by which life could not exist and allows for some of the outstanding advantages of columnar liquid crystals, such as self healing devices, cheap processing costs, and the potential for photoconductive materials with good charge carrying ability. Self-assembly with DLCs has been demonstrated by using
the effects from a magnetic field\textsuperscript{40} and through intermolecular interactions among the molecules.\textsuperscript{41}

**Summation**

The following chapters will describe the synthesis and supramolecular structure of fused, partially fluorinated π-systems. Synthetic approaches to targeted molecules will include oxidative cyclization via hv and iodine and by iron trichloride. An alternate synthetic approach will also be shown utilizing the bis-lithiation of biaryls and their subsequent double nucleophilic attack on a perfluorinated arene. Appropriate characterizations were performed to demonstrate all of the hypothesized behaviors that were exhibited by the target molecules.
Chapter Two – Synthesis and Characterization of Janus Materials

This chapter details the synthesis and characterization of a number of Janus-type materials. There are two primary goals that were made during the course of this investigation; the first goal was to engineer self-assembly by utilizing the $\pi$-$\pi$F interactions described in the previous chapter. While a number of systems have been synthesized for electronic applications exploiting $\pi$-$\pi$F aromatic systems and their tendency for face-to-face stacking, what is lacking is a fused system manipulating these effects. The second goal in this project was to find a convenient, efficient method to prepare these fused $\pi$-$\pi$F aromatic systems that could be applied to a large number of targeted molecules.

The first question addressed by this project was whether partial fluorination on a polycyclic aromatic compound would achieve the desired face-to-face $\pi$-$\pi$ stacking. The first compound made in this series was a partially fluorinated napthodithiophene. Napthodithiophenes were shown to have some promise in organic electronics by Swager and coworkers as they had previously synthesized napthodithiophene polymers and non-fluorinated small molecules, finding that naphtho[2,1-b:3,4-b']dithiophene (NDT1) had a fully reversible redox state whereas a shuffling of the thiophene rings (NDT2) (bottom example, Scheme 2.1) led to only partially reversible redox states, and even this diminished over time.\(^{42}\)

\[
R= n\text{-}C_{14}H_{29}, \text{Ar}=2,5\text{-}Me_{2}C_{6}H_{3}.
\]

**Scheme 2.1:** Swager’s synthetic scheme towards napthodithiophenes.\(^{42}\)
The question that begged to be answered was whether $\pi$-$\pi F$ interactions could be seen on a partially fluorinated fused aromatic system as opposed to systems containing multiple singly-bonded aromatic rings (see Figure 1.3). Examination of calculated MEP maps of a non-fluorinated and fluorinated NDT2 suggest that blue and red areas of the $\pi$-surface should be mutually attractive and lead to anti-parallel, face-to-face stacking.

![Figure 2.1: MEP maps of fluorinated and nonfluorinated naphthodithiophenes.](image)

The fluorinated NDT2 target can be described as a Janus material, aptly named after the Roman god having two faces. In the fluorinated naphthdithiophene pictured above, one face is described as the top ring containing the fluorine atoms and possessing a partial positive face whereas the lower bithiophene containing half is the other face with a partially negative charged face.

![Figure 2.2: Statue depicting Janus.](image)
Another example of a Janus system includes a ribbon-like polythiophene derivative by David Collard and co-workers which contain alternating alkyl and perfluoroalkyl chains. These side chains nano-phase separate with R and Rf on opposing sides of the polythiophene ribbon, resulting in a dual face macromolecule. These molecules result in unique thermo-chromic properties and a blue shift in the UV-VIS spectrum versus the non-fluorinated polythiophene derivative.

Synthesis of Partially Fluorinated Napthodithiophenes and Triphenylenes

Napthodithiophenes 2a-c were prepared from readily available starting materials using modified published procedures (Scheme 2.2). The Stille coupling to precursors 1 yielded almost no product at 110 °C after three days, but increasing the temperature to 150 °C in a sealed vessel resulted in near quantitative yields after just 12 hours.

Attempts to accelerate the Stille coupling leading to 1 utilizing microwave heating were found to be no more advantageous than traditional heating methods. Throughout the last two decades, copious amounts of research have focused on the effects of microwaves in organic synthesis, and the Stille reaction has similarly received ample attention. Typical microwave synthetic work involves placing a sealed pressure tube into a microwave chamber where microwaves increase the kinetic energy of a polar solvent and result in increased temperature. While studies are able to conclude that microwave synthesis does indeed result in faster reaction times, these studies often do not contain reasonable comparisons to reactions run in a similarly sealed vessel and heated to well above the boiling point of the solvent. In this particular case, the reaction was found to be sluggish at temperatures near the boiling point of toluene but was greatly accelerated in super-heated toluene in a sealed vessel.

Separation of 1a and 1b from organotin byproducts by column chromatography proved difficult. However, through physisorption onto dry silica gel prior to loading the column, greater resolution was achieved. While the column appeared to have been successful by thin layer chromatography, NMR showed continued presence of at least one type of organostannane. When the crude product
was dry-loaded onto the column, a cleaner product was realized, although the tin byproduct was never completely removed. The conditions required for oxidative cyclization to produce compounds 2 differed according to ring system. Initial attempts in the synthesis of 2a involved oxidative cyclization similar to Swager’s approach using FeCl₃ but resulted only in an insoluble solid, most likely a polymer. FeCl₃ treatment of 1b resulted in no reaction. Mallory-type cyclizations⁴⁸ utilizing catalytic amounts of iodine and exposure to 300nm light were successfully implemented in the formation of 2a and 2b whereas 2c was synthesized using FeCl₃.

Scheme 2.2: Synthesis of 2a-c and 3. Reaction conditions: (i) Pd[PPh₃]₄, toluene, 150°C, (ii) C₆H₆, cat I₂, hv, (iii) FeCl₃, CH₂Cl₂, MeNO₂, RT, (iv) a) tBuLi, Et₂O, -78°C b) C₆F₆, DME, RT. Yields for 2 are over two steps.

The biggest disadvantage to synthesizing these compounds through Mallory-type cyclizations is the necessity to perform these reactions at very low concentrations. At higher concentrations, intermolecular interactions become increasingly possible and the surfaces of the vessel become coated with the poorly soluble products, diminishing further light influx. Also, since the targets require intermediate synthesis through Stille coupling, it can be troublesome to completely remove the organostannane by-products. It is well known that perfluorinated aromatics undergo nucleophilic substitution,⁴⁹ and for hexafluorobenzene, attack by...
two nucleophiles typically results in para-disubstitution. However, it was hypothesized that a doubly lithiated biaryl could form the desired fused aromatic product by a 1,2 nucleophilic attack on hexafluorobenzene. Following the lithium-halogen exchange of 1,2-dibromobiphenyl and subsequent addition of hexafluorobenzene in the synthesis of compound 3, there was no evidence of reaction taking place by fluorescence of the molecule and was supported by GC-MS. DME\textsuperscript{50} (dimethoxyether) was then added to the solution as a chelating agent and resulted in the reaction mixture becoming immediately hot and rapid appearance of strong blue fluorescence under illumination at 366nm. Isolation resulted in product 3 in good yield. To our knowledge, this is the first instance of forming polycyclic aromatic systems in this fashion, and since the publication of this work, other investigators have used this approach to prepare helicenes\textsuperscript{51} and napthalenes\textsuperscript{52}.

Scheme 2.3: Synthetic routes to helicenes\textsuperscript{51} and napthalenes\textsuperscript{52} using a bilithio biaryl and related 1,4-dilithio-butadiene approach.

Crystallographic Studies on Partially Fluorinated 2a-c and 3

X-ray crystallography on compounds 2 and 3 verify the hypothesis that the π-πF interactions in these Janus materials should lead to face-to-face anti-parallel stacking. Compound 2a (Figure 2.3) shows close π-stacking with an intermolecular distance perpendicular to the planes of the molecules at 3.37 Å.
Compound 2c was synthesized as a non-fluorinated reference to 2a and 2b and stacks as predicted in a herringbone-like arrangement. Triphenylene is a known compound; it is the non-fluorinated analogue to compound 3 and is known to pack in a herringbone-like motif in the crystalline state.\textsuperscript{53}

**Figure 2.3:** X-ray crystal structure packing of 2a parallel to the molecular plane (left) and perpendicular to the molecular plane (right).

**Figure 2.4:** X-ray crystal structure packing of 2c.

**Figure 2.5:** X-ray crystal structure packing of 3 parallel to the molecular plane (left) and perpendicular to the molecular plane (right). Distance shown on the left is 3.47 Å between molecular planes.
Compound 2b was the first attempt at making a columnar liquid crystal (LC) exploiting this molecular design. A common belief in the LC field is that a minimum of three side chains are required to form columnar liquid crystals. This belief stems from the fact that a sheath of solubilizing side chains must surround columns of the disk. This would not be necessary, however, if one can induce the molecules to assemble in such a way to make this sheath. It might normally be expected that the side-chains and aromatic cores of 2b would normally self-assemble with nanophase-separated domains of aliphatic and aromatic parts. This would not give the traditional description of a columnar D_h phase; however, it was hypothesized that antiparallel stacking would lead to the required sheath of alkyl chains surrounding the column. This topic will be revisited in further detail with successful examples later in this chapter.

The problem faced here was that although face-to-face stacking was seen by x-ray crystallography, the side chains were found to interdigitate the π-stacks, severely limiting π-overlap between every second and third disk, resulting only in dimer pairs. The π-system does appear to be continuous, however, although overlap between dimer pairs is diminished. Future studies on this class of molecule should include the preparation of derivates with branched alkyl chains which should prevent the crystallization of side chains seen in 2b and result in the desired liquid crystalline behavior.
Figure 2.7: View perpendicular to the molecular plane of compound 2b. The view on the left is of a dimer pair and the right is between a non-dimer pair. The red arrow on the right indicates minimal π-system overlap.

It is of interest to note here the packing arrangement exhibited between columns of compound 2b. The electron rich sulfur atoms are located in a close proximity to electron rich fluorines. This might seem counter-intuitive but can be explained not only by space filling arguments but also through a resonance structure of thiophene; lone-pair electrons from the sulfur are donated into the π-system and result in a slight positive charge. Furthermore, one can think of sulfur as a “soft,” highly polarizable atom and of fluorine as a “hard,” highly polarizing atom. This creates an intermolecular attraction between molecules in adjacent stacks and forces a tighter inter-stack packing arrangement. The sum of the Van der Waals radii of sulfur and fluorine is 3.27Å;$^{54}$ the S-F distances exhibited here are considerably smaller (3.14 Å).
Figure 2.8: X-ray crystal structure packing showing S-F short contacts for 2b.

A molecule produced by John Reynold’s laboratories exhibits close intramolecular sulfur-oxygen contacts. In the example shown in Figure 2.9 below, coplanarity of the aryl rings is achieved through the close interaction between the sulfur of the ethylenedioxythiophene (EDOT) group and the oxygen on the alkoxy chain. One might have expected significant torsion angles between the adjacent aryls if the electron rich sulfur atoms from thiophenes were repelled by the electron rich oxygen atoms; however, it is more likely the case that the electrons on the oxygen are attracted to the partial positive nature of the sulfur.

Figure 2.9: X-ray crystal demonstrating close S-O contacts (left), the molecule shown on the right
Furthermore, carbonyl-carrying bithiophene derivatives were synthesized which were found to be planar.\textsuperscript{56} Ab initio calculations were then performed on a number of bithiophene derivatives which justified close contacts of sulfur and oxygen (Figure 2.10), and these were found to be planar.\textsuperscript{57} Removal of the oxygen from the immediate vicinity of the sulfur results in a large change in the dihedral angle between the two thiophene rings.

![Figure 2.10: Diagram of planar vs. non-planar bithiophene derivatives](image)

**Synthesis and Structure Properties of Partially Fluorinated Naphdithiophenes from Dilithiated Bithiophene**

The next series of naphdithiophenes synthesized involved a shifting of the thiophene attachment to the fluorinated benzene ring to form NDT1 rather than NDT2. The syntheses of these products were significant in that they led to broadening the scope of the double nucleophilic attack method as seen in the formation of triphenylene 3.

![Synthesis reaction](image)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>4a</td>
<td>82%</td>
</tr>
<tr>
<td>ii</td>
<td>4b</td>
<td>67%</td>
</tr>
<tr>
<td>iii</td>
<td>5a: R=TMS</td>
<td>87%</td>
</tr>
<tr>
<td></td>
<td>5b: R=TIPS</td>
<td>92%</td>
</tr>
<tr>
<td>iv</td>
<td>6a: R=TMS</td>
<td>73%</td>
</tr>
<tr>
<td></td>
<td>6b: R=TIPS</td>
<td>69%</td>
</tr>
</tbody>
</table>
Scheme 2.4: Synthesis of 6. Reaction conditions: (i) Mg, Et₂O, Ni(dppp), rt (iii) NBS, CHCl₃, reflux (iii) n-BuLi, followed by TMSCl, Et₂O, -78 °C, or n-BuLi, followed by TIPSCl, THF, 60 °C (iv) a) n-BuLi, b) C₆F₆.

Mallory-type cyclizations and ring fusion using iron trichloride were attempted and found to be ineffective (Scheme 2.5). However, since compound 5a was known, a double lithiation approach similar to that used to make compound 3 was attempted and found to be successful. This and all subsequently described π-systems were prepared by reacting dilithio biaryls with fluorinated arenes.

Scheme 2.5: Attempted synthesis of NDT1. Reaction conditions: (i) 1,2-diiodotetrafluorobenzene, K₂CO₃, 5% Pd[η-Bu₃P], toluene, and H₂O; (ii) neither FeCl₃ in CH₂Cl₂ nor I₂ and hv in benzene were found to be effective.

Compound 6a (and subsequently synthesized higher dithienoacenes) were poorly soluble and therefore triisopropylsilyl (TIPS)-substituted 6b was prepared. After lithium-halogen exchange reactions with 4, nucleophilic attack on TMSCl occurred either at -78 °C or during its subsequent warming to room temperature, whereas the reaction with TIPSCl required mild heating (60 °C) to achieve any formation of product; this was attributed to higher steric hindrance caused by the bulkier isopropyl groups. Compounds 6 are potentially very versatile building blocks following reaction at the four remaining fluorinated sites and/or by conversion of the silyl groups to iodides using ICl. Compound 6a was easily converted to 758 and 8a59. Conversion to compound 7 was carried out simply to show the ability to functionalize this compound in a manner to make it a reactive substrate for a host of transition-metal catalyzed reactions.
Scheme 2.6: Synthesis of 7 and 8. Reaction conditions: (i) ICl, CH₂Cl₂, rt (ii) HI, toluene, rt.

X-ray crystallography of 6a confirms the formation of product and indicates anti-parallel face-to-face stacking similar to that observed for the isomeric naphthodithiophenes (2a-c) with a distance of 3.39Å in-between molecular planes.

Figure 2.11: Crystal structure packing of 6a parallel to the molecular planes (left, with hydrogens removed for clarity) and perpendicular to the molecular planes (right).

Packing between columns was not as close as was seen previously in compound 2b. These compounds were synthesized with bulky trialkyl-silyl groups
attached at the 5,5’ positions of bithiophene to act as a protecting group. Failure to include these would result in lithiation at the 5,5’ positions and not at the desired 3,3’ positions on bithiophene. The biggest advantage created by this is the ability for post-functionalization of the disk. The resulting intermolecular interactions following desilylation will be studied and exploited in future work on these molecules.

It should also be noted that hexafluorobenzene has six sites reactive towards nucleophilic aromatic substitution, and there are therefore a number of different possible products, illustrated in Figure 2.11.

![Figure 2.12: Possible products resulting from nucleophilic attack on hexafluorobenzene. 1,2 attack shown on left, 1,2,3,4 attack shown in the middle, and 1,2,4,5 shown on the left (6c).](image)

Attempts at crystal growth for compound 6b yielded needles too thin for x-ray crystallography; however, in addition to the needles there were a number of plates which were analyzed and shown to be compound 6c (Figure 2.12, right). Therefore, the forcing conditions required to cause reaction between 5b and hexafluorobenzene led also to the 1,2,4,5 product, a tetrathienoanthracene.
The ratio of products 6b and 6c was not determined. Repeating the reaction with a 1.2:1 rather than 1:1 molar ratio of hexafluorobenzene to the bithiophene precursor resulted in complete suppression of side-product 6c. The packing arrangement of this molecule was a herringbone motif and can be seen in Figure 2.13. The four bulky silyl groups totally preclude face-to-face $\pi$-stacking and result in the herringbone pattern seen in the crystal structure.

**Synthesis of Anthradithiophenes and Tetrathienotetracenes**

It was hypothesized that more extended $\pi$-systems could be produced by replacing hexafluorobenzene with octafluoronapthalene; subsequent work led to double nucleophilic attack from the bithiophene precursor to octafluoronapthalane in an attempt to make partially fluorinated anthradithiophenes (10) and tetrathienotetracenes (9) in relatively few synthetic steps. Another goal here is to investigate the selectivity in the reaction of 3,3’-dilithiobithiophenes with octafluoronapthalene.
Scheme 2.7: Synthesis of 9 and 10. Reaction conditions: (i) a) 2eq. 5a or 5b in THF, n-BuLi, followed by C_{10}F_{8}, -78 °C b) gradually warmed to 60 °C (ii) a) 10% excess 5a or 5b in THF, n-BuLi, C_{10}F_{8}, -78 °C b) gradually warmed to 60 °C.

Initial efforts produced mixtures containing both 9 and 10. Analysis by GC-MS showed that little reaction occurred between the lithiated bithiophenes and octafluoronapthalene after four hours at room temperature but readily proceeded to completion after increasing the temperature to 60 °C. The resulting mixtures could not be completely separated following several attempts via column chromatography. A combination of multinuclear NMR and GC-MS indicated that the products were simply isomers, the formation of which is outlined in Figure 2.13. A similar problem was seen during attempted synthesis of the tetracenes (9) as the number of possible isomers is doubled. Furthermore, it has been previously reported that octafluoronaphthalene is susceptible to its first nucleophilic attack not only at the 2 position, but yields as high as 20% have been reported for the 1-substituted position using sodium methoxide as the nucleophile. Coupled with the illustration given in Figure 2.14, it is easy to see the possibility for multiple isomers.
Figure 2.14: Mechanism of alternate attack on octafluoronapthalene. Red arrow indicates free rotation, 2nd formation of Meisenheimer complex not shown for brevity.

An x-ray crystal structure was obtained for compound 10b but suitable crystals could not be grown from 9a, 9b, and 10a. The x-ray experiment showed the desired packing pattern and showed some promise as the π-face overlap between molecules in a given column is nearly maximized, and this is continuous throughout a column. The anthradithiophenes and the tetradithiophenes appeared to be sensitive to light and/or air, complicating electrochemical experiments.
Figure 2.15: X-ray crystal structure of compound 10b parallel to the molecular planes (left) and perpendicular to the molecular planes (right).

**Synthesis of Dibenzoanthracenes**

Questions needing to be answered were whether selectivity could be controlled with a dilithio-biaryl nucleophilic attack on octafluoronapthalene and if the molecular design could be exploited to lead to thermotropic liquid crystals. 2,2’dibromo-4,4’,5,5’-tetramethoxybiphenyl was previously synthesized for a different project and was a good candidate for study as the tetramethoxy groups could be readily converted to longer alkoxy chains in just two steps. If these target molecules carrying 4 alkoxy chains stack in a columnar, face-to-face antiparallel fashion, the columns could take on a cylindrical shape despite not being substituted with an insulating sheath of flexible side chains regularly around the entire periphery.
Figure 2.16: Chem3D depiction of dibenzoanthracene parallel to the molecular planes (left) and perpendicular to the molecular planes (right) illustrating alkoxy chains along the periphery of a dimer pair.

During the course of this investigation, Williams and coworkers reported a number of azatriphenylenes, dibenzophenazines, and tribenzophenazines\textsuperscript{61} with molecular frameworks similar to those described herein. In that study, a relatively large number of compounds (Figure 2.17) were prepared and the authors by chance observed columnar LC behavior.

![Chem3D depiction of dibenzoanthracene](image)

**Figure 2.17:** Dibenzophenazine derivatives showing LC behavior and those which do not.\textsuperscript{61}

As pointed out in Figure 2.17, the substituents located at X and Y dictate the LC behavior in these derivatives. Those that drive anti-parallel columnar stacking are those which exhibit columnar liquid crystalline mesophases; X and Y are electron withdrawing groups which lead to Janus-type materials similar to those described here. It is also helpful to note here that a single fluorine atom is not sufficient to
induce the desired behavior, adding to the evidence that there are a minimal number of fluorines needed to force columnar stacking.

Synthesis of partially fluorinated tetraalkoxydibenzoanthracenes began with commercially available 4-bromoveratrole. Formation of compounds \( \text{12} \) and \( \text{13} \) were completed with few problems by a modified published procedure. GC-MS showed that conditions (i) produced three isomeric biphenyls. Following recrystallization, only one peak remained and the product was verified by NMR as the desired product \( \text{12} \).

![Scheme 2.8: Synthesis of partially fluorinated dibenzoanthracenes: (i) FeCl₃ and CH₂Cl₂, MeOH (ii) BBr₃ in CH₂Cl₂, followed by H₂O (iii) K₂CO₃, RBr, DMF, 90 °C (iv) n-BuLi, THF, -78 °C followed by C₁₀F₈.](image)

The high solubility of \( \text{13} \) in water complicated its separation from boronic acid produced during the reaction. The tetraol was found to have limited solubility in water until the water reached a temperature at approximately 80 °C, at which point it was readily soluble. Cooling of the solution did not result in precipitation of the intended product until the solution reached a temperature approaching 0 °C. This made recrystallization of the product convenient and high yielding.

Reaction of \( \text{13} \) with various alkyl halides under basic conditions (Williamson ether synthesis) led to alkylated biphenyls \( \text{14b-d} \) in high yields. For the synthesis of \( \text{15a-d} \), low regioselectivity was observed in the initial reactions with octafluoronaphthalene, similar to reactions involving lithiated bithiophenes. It was
reasoned that a lower temperature would increase selectivity, so the experiments were repeated and the temperature was maintained at -78 °C and resulted in only the product of 2,3 attack on octafluoronapthalene. This observation led to a re-evaluation of the synthesis of the dithienoanthracene and dithienotetracene derivatives, so these experiments were repeated while holding the temperature at -78 °C. Lithiated bithiophene was found not to react with octafluoronapthalene at such a low temperature, but selectivity could possibly be increased in these systems through optimization of the reaction conditions, possibly by utilizing a chelating agent such as DME or TMEDA or adding substituents to generate a less stable anion, allowing the reaction temperature to be lowered. Purification of 15b-d by flash chromatography was facile and yielded the intended products as evidenced by NMR and elemental analysis (EA).

In order to calculate $E_{\text{gap}}$ and $E_{\text{HOMO}}$, UV-VIS and cyclic voltammetry (CV) were performed on 15b-15d. UV-VIS data for each compound was nearly identical, with each compound showing multiple absorbances and $\lambda_{\text{max}}$ for each was shown to be nearly the same at 306 nm.

![Figure 2.18](image)  

**Figure 2.18**: UV/VIS spectra for 15b-15d (1 x 10^{-6}, THF).
The UV-VIS plot shows a $\lambda_{\text{max}}$ at about 306 nm, with two small peaks at 382 nm and 404 nm. It was uncertain if the smaller peaks were arising from the compound itself or if they were the result of an impurity possibly resulting from double nucleophilic attack to form a tetrabenzotetracene. Photoluminescence (PL) experiments were performed to verify if these peaks were arising from 15 or impurities. Excitation at 306 nm, 382 nm, or 404 nm produced the same PL profile with $\lambda_{\text{max}} \approx 465$ nm. This type of absorbance profile is typical of highly fluorinated $\pi$-systems. The absorbance profile of perfluorinated pentacene\textsuperscript{13} is dominated by intense high-energy bands. It also exhibits a lower-energy progression of bands similar in shape and energy to its non-fluorinated parent, but with relatively low molar absorptivity.

Figure 2.19: PL Measurements of 15c (left) and 15d (right).

Cyclic voltammetry showed single reversible oxidations for compounds 15b-15d. No reduction was detected in the range of measurement (less than 2000 mV), providing some (but not conclusive) evidence that these are p-type materials.
Figure 2.20: Oxidation potential for 15b-15d

The onset of the UV-VIS absorption for each compound was used in determining $E_{\text{gap}}$ based on the formula $E_{\text{gap}} = \frac{hc}{\lambda}$. $E_{\text{HOMO}}$ (eV) was calculated from the CV plot and used the premise that the energy level for Fc/Fc+ was -4.8 eV below the vacuum level.\(^{64}\)

**Table 1:** Electrochemical and UV-Vis onsets along with calculated HOMO, LUMO, and HOMO/LUMO gap

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{ox}}$ (V)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>HOMO (eV)</th>
<th>$E_{\text{gap}}$ (eV)</th>
<th>LUMO (eV)</th>
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<tbody>
<tr>
<td>15b</td>
<td>0.950</td>
<td>420</td>
<td>-5.75</td>
<td>2.95</td>
<td>-2.80</td>
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<td>420</td>
<td>-5.76</td>
<td>2.95</td>
<td>-2.81</td>
</tr>
<tr>
<td>15d</td>
<td>0.990</td>
<td>420</td>
<td>-5.79</td>
<td>2.95</td>
<td>-2.84</td>
</tr>
</tbody>
</table>

The thermal stabilities in air of compounds 15b-d were determined by thermogravimetric analysis (TGA). Each compound underwent a two-step weight loss, the second of which resulted in complete volatilization. The magnitude of the percent weight lost in the first step, which began at approximately 200 °C, increased
with relative weight-fraction of the side chains. This percent weight loss corresponds to $\beta$-cleavage of the side chains.

![TGA results from 15b-15d.](image)

**Characterization of Thermotropic Liquid-Crystalline Behavior**

The thermotropic liquid-crystalline behavior of 15b-d was investigated by differential scanning calorimetry (DSC), variable temperature polarized optical microscopy (VT-POM), and wide angle x-ray diffraction (WAXD). The thermal transitions and their nature were revealed by DSC and VT-POM, respectively. Unlike 15b, both 15c and 15d underwent reversible second-order transitions at approximately -50 to -60 °C (Figure 2.22). These are likely glass transitions ($T_g$) arising from cessation (on cooling) and onset (on heating) of thermal motion within a non-crystalline ordered phase (liquid-crystalline). The branched, racemic side chains preclude crystallization. The only other observable transitions are endothermic ones occurring near 260 °C and 270 °C for 15d and 15c, respectively. These transitions
were confirmed by VT-POM to be the isotropization temperatures ($T_i$) or complete loss of all order. In subsequent heating scans, the $T_i$ occurred at progressively lower temperatures as a consequence of thermal decomposition already observed by TGA. The thermal windows for LC behavior are remarkably large (>300 °C), which was attributed to the strong attractive intermolecular interactions between electron-rich and electron poor segments of the molecules. It was initially expected that $T_i$ for 15c (ethylhexyl side-chains) would be lower than that of 15d (3,7-dimethyloctyl side-chains). The larger ethyl branches, closer to the aromatic core, should require less thermal energy to disrupt packing. In this case, however, the surprising contradiction might be explained by some interlocking of side chains which would be influential with increased volume swept out by mobile side chains. The $T_i$ for 15d, however, occurs above those of 15b,c as would normally be expected.

Virgin (as isolated) compound 15b underwent a large endothermic transition near 80 °C during the first heating scan, suggestive of a crystal or plastic crystal to liquid crystal transition. This transition does not appear in subsequent heating and cooling scans but instead is replaced by a new reversible transition at 47 °C (heating) and 34 °C (cooling). This behavior suggests self assembly to different (meso)phases from solution (isolation of product) and from elevated temperatures (melt). The significant hysteresis of the new transition also suggests that reorganization is a kinetically slow, involving, and complex process.
Figure 2.22: DSC plot for 15b-d from -90 °C to -20 °C.

Figure 2.23: DSC plot for 15b-d from 230 °C to 280 °C.
Isotropization temperatures were confirmed by variable temperature polarized optical microscopy (VT-POM). Samples were prepared by drop-casting solutions of each compound onto a glass slide. These samples displayed significant birefringence between cross-polars below their respective $T_i$ during initial heating scans. Clearing temperatures were observed to be similar to those seen by DSC and resulted in a loss of birefringence. Samples were then slowly cooled and held at a temperature just below $T_i$, during which time nuclei with roughly hexagonal shapes appeared (Figure 2.25a). The hexagonal shape is typical of the most favorable packing arrangement for cylinders: hexagonal. This is the first indication that the Janus design principle is effective. The elliptical-shaped molecules assemble face-to-face with regular alternating anti-parallel orientation, giving rise to cylindrical columns. The features show essentially no birefringence because the columns are aligned perpendicular to the surface (homeotropic alignment). The anisotropic optical elements (columns) minimally affect the plane-polarized light, thus appearing relatively dark and colorless in the images. Any “bright” features correspond to domains with columnar alignment deviating from normal to the surface.

Figure 2.24: DSC plot for 15b showing initial endothermic transition and its disappearance upon the second heating.
Figure 2.25: VT-POM pictures featuring nucleation (top), growth (middle), and impingement (bottom).
Homeotropic alignment is the most thermodynamically favored state for columns to pack, and all that is required is to form a hexagonal columnar phase from the melt. \textsuperscript{65} What is remarkable about the formation of these perpendicular columns was that they were formed on a single glass slide. Typically, two slides are needed for this type of growth as a single slide would most often lead to columnar growth parallel to the plane of the slide.

The columnar packing arrangements of \textbf{15b-d} were confirmed by wide angle x-ray diffraction (WAXD) experiments. Measurements of oriented samples, using an area detector, greatly simplify the interpretation as scattering perpendicular, parallel, and oblique to the columns results in intensity maxima in different areas of the detector. Oriented fibers were prepared by forcing each material through a 0.5 mm circular orifice. The samples were mounted vertically and perpendicular to the beam. Scattering from repeating elements along the columns occurs on the meridian, while reflections resulting from lateral packing of the columns occur on the equator. Any off-meridional reflections must indicate some 3-dimensional registry among molecules in different columns.

The WAXD pattern from compound \textbf{15b} is shown in Figure 2.26. A large number of relatively sharp reflections suggested long-range order bordering on crystalline. The most intense meridional arcs occur with d-spacing near 3.4 Å, the expected $\pi$-$\pi$ stacking distance between face-to-face molecules within columns. Additional horizontal rows of reflections forming layer lines indicate 3-dimensional order. Variations in intensity within these layer lines faintly suggest an “X” shape, typical of helical structures. This can result from a regular rotational translation of successive molecules within the columns.
Following the x-ray experiments, the fiber of 15b was saved. After 2 months at room temperature, a dramatically different, yet equally complex diffraction pattern was collected. Some features of the new pattern were present in that of the as-extruded fiber, suggesting polymorphism. The DSC profile measured after 2 months equilibration was similar to the as-isolated powder, while that of the as-extruded fiber corresponded to subsequent heating scans of the as-isolated powder. This clear polymorphism has so far precluded assignment of a unit cell. The fiber was originally extruded at 100 °C and slowly brought to 40 °C where it was annealed for 45 minutes. This resulted in a predicted loss of the transition at ca. 76 °C and showed its only transition upon heating at just under 50 °C. However, after allowing the fiber to rest for two months, it relaxes to a more stable configuration and the transition between 40 °C and 50 °C is not seen on first heating and the transition at 76 °C has returned. The original diffraction pattern therefore does not likely represent the equilibrium structure.
Figure 2.27: DSC results for a fiber of 15b after 2 months of equilibration (top) and freshly annealed (bottom).
It was therefore hypothesized that columnar alignment goes through at least two different phases; the first, lower melting phase (hereafter referred to as D\text{h1}) being a columnar stack with a disordered helix and, with time and energy permitting, relaxes into a more stable, more ordered helical configuration with a higher melting point (hereafter referred to as D\text{h2}). Additional DSC experiments were performed and involved annealing an aligned fiber of 15b at 40 °C, 45 °C, 50 °C, 60 °C, and 68 °C for varying amounts of time to investigate the kinetics of relaxation to D\text{h2} from D\text{h1}. It was found that D\text{h2} could only be formed through D\text{h1} as annealing at temperatures above the melting point of D\text{h1} was not able to result in a DSC observed melting point of D\text{h2}. Annealing the fiber of 15b at 40 °C for 10 hours allows for nearly complete conversion from D\text{h1} to D\text{h2}.

Reasoning for why it is believed that the supramolecular structure of 15b is that of a helical motif lies primarily in WAXD pattern. All helices, including single molecule helices like DNA and multi-molecular helices, form an ‘X’ figure in the x-ray diffraction patterns. This is attributed to the planes of symmetry in a given helix which work to diffract the x-ray beam into this shape as exhibited in Figure 2.28.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure228.png}
\caption{Diagram showing planes of a helix resulting in an X pattern.}
\end{figure}

WAXD patterns for 15b,c clearly confirm hexagonal columnar mesophases (Figure 2.27). A series of equatorial reflections with relative d-spacings of 1, \sqrt{3}, \sqrt{4}, \sqrt{7}, etc indicated hexagonal packing of columns. Intense meridional arcs with d-spacing of \( \sim 3.4 \text{Å} \) arise from the intracolumnar packing of molecules. Compound 15c gives diffuse off-meridional reflections, forming layer lines in somewhat similar
fashion to the diffraction pattern for \(15b\). These can be attributed to some 3-dimensional order as well, but their broad, diffuse nature suggests that this order is short range. A greater number of higher-order equatorial reflections for \(15c\) shows that its columns are more regularly arranged (see Figure 2.29). The higher dimensionality and longer-range order of \(15c\) relative to \(15d\) can explain its initially unexpected higher \(T_i\). Homeotropic alignment in a thin film of \(15c\) on mica was also confirmed by WAXD measurement with the film mounted perpendicular to the beam. Five sharp spots (the sixth is missing due to misalignment of the sample relative to the beam) are seen equidistant from the center of the pattern (Figure 2.31).

![Figure 2.29: WAXD results for \(15c\) (right) and \(15d\) (left)](image)

Relative scattering intensity distributions are provided in Figures 2.29 and 2.30 to make clearer the proof of a 2D hexagonal lateral packing of columns. Series of intensity maxima, labeled with appropriate Miller indices, occur at d-spacings with values predicted by the equation below. The relative intensities decrease with increasing scattering angle for \(15d\) as expected. However, the intensities vary for \(15c\) suggesting a super-lattice which may accommodate screw-like helical columns.

\[
d = \left[ \frac{4}{3a^2} \left( h^2 + k^2 + h k \right) + \frac{l^2}{c^2} \right]^{\frac{1}{2}}
\]
Figure 2.30: Equatorial intensity distributions integrated from the 2D-diffactrom of the fiber produced from 15c. Labels correspond to Miller indeces (h,k,l).

Figure 2.31: Equatorial intensity distributions integrated from the 2D-diffactrom of the fiber produced from 15d. Labels correspond to Miller indeces (h,k,l).
Figure 2.32: Homeotropically aligned sample of 15d on mica.
Chapter Three - Conclusions and Future Work

There is considerable interest in the organic materials sector of chemistry in polycyclic aromatic compounds, and this work has led to a number of conclusions of potential utility in this field. Most notably, a new route to fused polycyclic aromatic compounds has been established through the utilization of double nucleophilic attack on perfluoroarenes. This is a single-step reaction resulting in the desired product, whereas most other procedures require multi-step, sometimes complicated syntheses. Furthermore, it has been shown that the quadrupole moments induced upon the compounds by the partial fluorination causes sufficient attraction to cause co-facial, columnar packing. This head-to-tail design has been exploited by adding solubilizing side-chains to just one half of the periphery, resulting in a sheath of alkyl chains to surround a given column of the molecules, ultimately resulting in columnar liquid crystals which pack in a hexagonal motif.

There is significant potential for future work based on the results outlined in this document. Most notably, any number of partially fluorinated aromatic systems can be made by double nucleophilic attack on strategically placed (ortho-positioned) fluorines on an aromatic system. Attempts were only made on hexafluorobenzene and octafluoronapthalene, but a number of perfluorinated aromatic systems are in existence, including perfluorotriphenylene, perfluoroanthracene, perfluoropentacene, perfluorophenanthrene, and many others. It will be interesting to find out if higher tetrathienoacenes or tetrabenzoacenes with varied side chains could similarly form columnar or 2-D π stacks. In the case of the triphenylene derivative (see Figure 3.1), the remaining fluorines are in the bay positions of the ring system. This would presumably create ring strain and would distort the disk-like molecule from planarity. Partially fluorinated tetrabenzopentacene is also a possibility (Figure 3.1). Pentacene has already shown to be an excellent molecule for organic thin film transistors. A question needing to be answered for this molecule, aside from the synthetic plausibility, is if there is sufficient fluorination and enough space for quadrupolar interactions to induce co-facial stacking.
Figure 3.1: Possible targets from perfluorotriphenylene (left) and perfluoroanthracene (right).

Furthermore, there are a number of unanswered questions remaining with some of the materials presented in this document. In the case of the napthodithiophenes, branched alkyl chains could be added to preclude crystallization of the side chains and make a columnar liquid crystal with less than three side chains. Also, optimization of the reaction conditions for nucleophilic attack on octafluoronapthalene by lithiated bithiophene could lead to increased selectivity and ease difficulties in the purification of the molecule.

The most important future work to be done is device measurements of these molecules. For this to occur, purity levels of all of these molecules will need to improve dramatically. While increased selectivity should help to some degree, there is room to improve on purification techniques. Crude vacuum sublimation was found to be unsuccessful on dithienoanthracenes, but such techniques as vapor phase sublimation and fractional sublimation were not attempted and could prove to greatly improve the quality of the materials.
Chapter Four - Experimental

Materials and Methods. 2-Tributylstannyl thiophene, 2-\textit{n}-hexyl thiophene, 4-bromoveratrole, \textit{n}-hexylbromide, 2-ethylhexylbromide, 3,7-dimethyloctylbromide, 2-bromothiophene, magnesium turnings, \textit{n}-bromosuccinimide, TMSCl, TIPSCl (Aldrich), 1,2-diiodotetrafluorobenzene, octafluoronaphthalene (Apollo Scientific), Pd(PPh$_3$)$_4$ (Strem) were used as purchased. Hexafluorobenzene, toluene, ether, and THF were distilled from the appropriate drying agents and stored over molecular sieves. Compound 2c$^{66}$ was prepared analogously to 2a below strictly for comparison of crystal packing, without further characterization. Unless otherwise stated, all manipulations and reactions were carried out under argon atmosphere using standard Schlenk techniques. High-resolution electron impact (EI) ionization mass spectra were recorded at 25eV on a JEOL JMS-700T MStation (magnetic sector instrument) at a resolution of greater than 10000. Samples were introduced via heatable direct probe inlet. Perfluorokerosene (pfk) was used to produce reference masses. High resolution mass spectra experiments performed at the Mass Spectroscopy Center at the University of Kentucky. $^1$H, $^{13}$C, and $^{19}$F NMR spectra were recorded on a Varian INOVA 400MHz spectrometer. Chemical shifts were referenced to solvent signals, except for $^{19}$F spectra, where CCl$_3$F was added as internal standard. Photocyclizations were conducted in a Rayonet photochemical reactor equipped with 300 nm lamps. Differential scanning calorimetry was performed on a Mettler Toledo DSC822 under an ultra pure nitrogen atmosphere. UV-VIS data was recorded on a CARY 1 UV-Visible spectrophotometer.

Synthetic procedures

![Synthetic procedure diagram]

Compound 2a. In an oven dried vacuum flask, 1,2-diiodotetrafluorobenzene (2 g, 4.98 mmol), 2-tributylstannyl thiophene (3.9 g, 10.45 mmol), Pd(PPh$_3$)$_4$ (0.287 g, 5mol%) and 11 mL dry toluene were combined. The solution was sparged with argon, the flask was sealed, and then heated to 150 °C for 12 hours. The solvent was
then removed through rotary evaporation and the remaining non-volatiles run through a pad of silica with hexane to yield colorless microcrystals (1.44 g, 4.75 mmol, 92% yield). 20 mg (0.064 mmol) of this product was then placed in a quartz tube with 6 mL of benzene and I$_2$ (0.8 mg, 5 mol %). This was then irradiated for 30 minutes in an air atmosphere. Solvents were removed and the product was recrystallized from hexane to yield a white solid (17 mg, 86%). mp 239°C. $^1$H NMR (C$_6$D$_6$) δ: 7.22 (m, 2 H), 7.08 (d, 2 H, J=4.8Hz) $^{13}$C NMR (CDCl$_3$, 40 °C) δ: 154.35, 144.90 (dm, $^1$J$_D$=122Hz), 139.93 (dm, $^1$J$_D$=233 Hz), 131.34, 130.65, 127.98, 125.42. $^{19}$F NMR (C$_6$D$_6$) δ: -138.06, -155.95. HR-MS: 311.9694 +/- 0.0005 (1.6 ppm) versus a calculated value of 311.9691, error is 0.0003 (0.8 ppm).

**Compound 2b.** In an oven dried Schlenk flask, n-butyl lithium (1.94 mL, 1.6M in hexanes) was added dropwise to 2-n-hexyl thiophene (0.523 g, 3.1 mmol) dissolved in 5 mL dry THF while cooling to -25 °C. After stirring for 45 min, $t$-Bu$_3$SnCl (1.01g, 3.1mmol) was added dropwise and the solution was brought to room temperature and stirred for one hour. The mixture was then diluted with CH$_2$Cl$_2$ and washed with saturated NH$_4$Cl (aq) and water, dried over MgSO$_4$, and concentrated using rotary evaporation to yield a brown oil which was used without further purification (1.29 g, 2.8 mmol, 90%)$^{67}$. This product was combined with 1,2-diiodotetrafluorobenzene (0.5 g, 1.2 mmol), 5 mL dry toluene, and Pd(PPh$_3$)$_4$ (72 mg, 5 mol %) in an oven dried vacuum flask. The flask was deaerated for 5 minutes with argon, sealed, and brought to 150°C for 12 hr. The solvent was removed by rotary evaporation and the nonvolatiles run through a column of silica gel with hexanes to yield a colorless oil (0.55 g, 92%). 20 mg (0.042 mmol) of this product was then
placed in a quartz tube with 6 mL benzene and I₂ (0.5mg, 5 mol %) and irradiated for 30 minutes in an air atmosphere. Solvents were removed and the product was recrystallized from boiling ethanol to yield a white solid (16mg, 79%). mp 86.5°C. 

\(^1\)H NMR (C₆D₆) δ: 7.20 (s, 2H), 2.807 (t, 4 H), 1.71 (p, 4H), 1.30 (m, 12 H), 0.91 (t, 6H) 

\(^{13}\)C NMR (CDCl₃) δ: 149.60 (m), 142.34 (dm \(^1\)J\(_d\)=249.3 Hz), 137.46 (dm 138.70 \(^1\)J\(_d\)=171 Hz), 134.541, 126.143, 118.52, 112.82 (m), 31.58, 30.52, 29.02, 28.81, 22.57, 14.14. 

\(^{19}\)F NMR (C₆D₆) δ: -138.71, -156.96. HR-MS: 480.1574 +/- 0.0006 (1.2ppm), versus a calculated value of 480.1569, error is 0.0005 (1.0ppm).

Compound 3. \(t\)-BuLi (7.0 mL of a 1.65M solution in hexanes, 4 eq) was slowly added via syringe to 2,2’-dibromobiphenyl (0.90 g, 2.9mmol) in 60 mL dry ether, while maintaining the temperature below -70°C. After allowing the solution to slowly warm to RT over 3 hours, C₆F₆ (0.50 mL, 1.5 eq) and 10 mL DME were added in rapid succession and the vessel was sealed. After 15 minutes, copious precipitate had formed and GC-MS indicated ~90% conversion. After stirring overnight, the mixture was stirred vigorously with 10% HCl (aq) (2 x 50 mL). Volatiles were evaporated under reduced pressure and the remaining solid was washed repeatedly with pentane. The pale tan solid was >98% pure by GC-MS (0.610g, 68% yield). An analytical sample was prepared by recrystallization from hot CHCl₃. 

\(^1\)H NMR (CDCl₃, 58°C) δ: 8.89 (m, 2H), 8.60 (m, 2H), 7.68 (m, 2H), 7.63 (m, 2H). 

\(^{19}\)F NMR (CDCl₃, 58°C) δ: -138.62, -158.07. HR-MS: 300.0562 +/- 0.0004 (1.5ppm) versus a calculated value of 300.0562, error is 0.0000 (0.0ppm)
Compound 4a. To a 1000mL Schlenk flask containing magnesium turnings (9.84g, .405mol) and 200mL dry ether was added a solution of 2-bromothiophene (60g, .368 mol) in 300mL of dry ether. This solution was canula transferred to an addition funnel attached to a 1000mL 3-neck flask cooled to 0 °C containing 200mL of dry ether and Ni(dppp) (2.0g, 1 mol %). The solution was added over a period of 30 minutes and allowed to stir for an additional 30 minutes. 60g of 2-bromothiophene in 200mL of ether was added dropwise by syringe and the mixture was allowed to slowly warm to room temperature and stirred for an additional 12 hours. This solution was then poured into a separatory funnel and shaken with 200 mL of 10% HCl three times. The organics were extracted with ether and dried with MgSO₄ followed by filtration. Ether was removed under reduced pressure and the crude product was pushed through a pad of silica gel using hexane eluent to yield 50.42g of a green solid as the intended product (82%) and was used in the next reaction.

Compound 4b. To a solution of bithiophene (10g, .06mol) in 160mL of 1:1 acetic acid to chloroform was added NBS (42.34g, .24mol). The reaction stirred at 60 °C and followed by GC-MS. After 24 hours the reaction mixture was poured into 10% HCl and extracted with chloroform. The organic layer was dried with MgSO₄ and the solvent was removed under reduced pressure. The resulting crude product was pushed through a pad of silica gel with hexane eluent to yield 19.24g (67%) of tetrabromobithiophene as an off white powder. 

$^1$H NMR (CDCl₃) δ: 7.05 (s, 2H); $^{13}$C NMR (CDCl₃, rt) δ: 112.1, 114.8, 129.5, 133.0.
**Compound 5a.** Tetrabromobithiophene (1.0 g, 0.002 mol) was added to an oven dried argon filled 50mL Schlenk flask. Dry ether was added (25 mL) and the mixture was brought to -78 °C by a dry ice/isopropanol bath. 2.6 mL of 1.6M n-butyllithium was added dropwise. The solution was then brought to 0 °C and maintained at this temperature for 6 hours. TMSCl (0.55 mL, 0.004 mol) was added and the solution was raised to room temperature. This was stirred overnight and poured into a separatory funnel containing 25 mL of HCl. The organic layer was washed twice and the organic layer was dried under MgSO₄. The solvent was removed under reduced pressure and pushed through a pad of silica gel with hexane eluent to yield 0.85 g (87%) of the intended product as an off-white powder. ¹H NMR (CDCl₃, rt) δ: 7.140 (h, 2H), 1.054 (m, 18H).

**Compound 5b.** Tetrabromobithiophene (7.5 g, 0.0156 mol) was added to an oven dried 100 mL argon filled vacuum flask. 25 mL of dry THF was added and the mixture was brought to -78 °C by a dry ice/isopropanol bath. 19.5 mL of 1.6M n-butyllithium was added dropwise. The solution was then brought to 0 °C and maintained at this temperature for 6 hours. TIPSCl (6.17 g, 0.032 mol) was added slowly. Following addition, the temperature was raised to 60 °C and the solution was allowed to stir for 12 hours. The solvent was removed under reduced pressure and re-dissolved in ether. The mixture was then washed with 10% HCl three times and dried under MgSO₄. The solvent was removed under reduced pressure and the crude product was pushed through a pad of silica gel with hexane eluent to yield the intended product as an off-white powder (9.2 g, 92%). ¹H NMR (CDCl₃, rt) δ: 7.154 (s, 2H), 1.317 (septet, 6H), 1.143 (d, 36H). ¹³C NMR (CDCl₃, rt) δ: 137.497, 135.447, 133.522, 111.879, 12.845.
Compound 6a. Into an oven dried reaction flask with an argon atmosphere was placed 5a (100mg, .213mmol) and 1mL of dry THF. The mixture was brought to -78 °C using a dry ice/isopropanol bath and 1.6M n-butyllithium was added (.266 mL, .426 mmol) in a dropwise fashion. The mixture was allowed to warm to room temperature by removing the cold bath and hexafluorobenzene was added (.047g, .256 mmol) and there was no immediate evolution of fluorescence. 1mL of DME was added and fluorescence evolved in under a minute. The reaction mixture was heated to 60 °C and allowed to stir two hours. The solvent was removed by rotary evaporation under reduced pressure and dissolved into ether, washed with 5mL 10% HCl three times, dried under MgSO₄, and removed the ether by rotary evaporation for a crude yield of 87mg of 6a (86%). 50mg of this was recrystallized in chloroform and resulted in small colorless crystals with a total mass of 18mg (36%). ¹H NMR (CDCl₃, rt) δ: 8.188 (s, 2H), 0.456 (s, 18H). ¹³C NMR (CDCl₃, rt) δ:145.173, 142.685, 141.295, 138.771, 132.304, 129.854, 125.110, 0.186. ¹⁹F NMR: -141.774, -160.543
Compound 6b. Followed the same general procedure as above using 1.026g of 5b (1.61 mmol), 1.3 mL 2.5M n-butyllithium (3.22 mmol), 0.36g hexafluorobenzene (1.93 mmol), 15mL dry THF, and 5mL of dry DME. The crude product was pushed through a pad of silica gel with pentane to yield 743mg of 6b as a white powder (74%). $^1$H NMR (CDCl$_3$, rt) δ: 8.378 (s, 2H), 1.156 (s, 6H), 0.744 (m, 18H). $^{13}$C NMR (CDCl$_3$, rt) δ: 146.157, 143.478, 140.478, 137.418, 131.479, 128.178, 124.178, 22.174, 16.547. $^{19}$F NMR: -140.874, -159.178.
Compound 7. In an oven dried Schlenk flask was added 6a (300mg, .657mmol) and 20mL of dry methylene chloride. The solution was brought to 0°C and 2.62 mL of 1.0M ICl was added dropwise. The solution was allowed to stir for 3 hours and the solvent was evaporated under reduced pressure. The crude product was recrystallized using ethanol to retrieve a fluffy off white powder (268mg, 72%). $^1$H NMR (C$_6$H$_6$, 80°C) δ: 8.07 (s, 2H); $^{13}$C NMR: 175.014, 171.697, 163.058, 152.478, 138.228, 129.563, 120.207. $^{19}$F NMR: -141.84 (d, 2F), -159.002 (d, 2F).
Compound 8. To 50mL of toluene in a round bottom flask was added 6a (300mg, 0.657mmol). A solution of hydroiodic acid (50% by weight in water) (.336g, 1.314mmol), was added dropwise to the solution at room temperature. The mixture was stirred for 24 h. and an additional two equivalents of HI were added to the solution. This was allowed to stir for an additional 24 hours. The mixture was then poured into deionized water and extracted with ether. The ether layer was then washed with 15mL of 1M NaOH and followed with a wash with brine. This layer was then dried under MgSO₄, filtered, and then the solvent was removed by rotary evaporation to yield a quantitative amount of the crude product (203mg). 50mg of this was recrystallized using ethanol to yield 37mg (74%) of colorless needles. The product was only checked by GC-MS for evidence of product formation.

General procedure for compounds 9a, 9b, 10a, 10b. Bithiophene 5a or 5b was placed into an oven dried vacuum flask with an argon atmosphere. Dry THF was added (10mL per gram of bithiophene) and the temperature was reduced to -78 °C using a dry ice/isopropanol bath. After reaching this temperature, n-butyllithium was added dropwise and allowed to stir for one hour during which time the solution was slowly brought to room temperature. Octafluoronaphthalene was then added (0.5 eq for 9a,b and 1.2eq for 10a,b) and the temperature was increased to 60 °C. The
reaction was allowed to proceed an additional 6 hours. The THF was removed under reduced pressure and the crude product was then either pushed through a column of silica gel with pentane eluent followed by recrystallization with hexane (for those compounds with TIPS groups) or recrystallized in hot chloroform (for those compounds with TMS groups).

**Compound 9a.** Octafluoronaphthalene (200mg, .735mmol) added to lithiated 5a (1.83mL 1.6M n-butyllithium to 689mg, 1.47mmol 5a) to yield 312mg (26%) of 9a as an orange solid. $^1$H NMR (CDCl$_3$, rt) δ: 8.562 (s, 4H), 0.521 (m, 36H);

**Compound 9b.** Octafluoronaphthalene (300mg, 1.10mmol) added to lithiated 5b (2.75 mL n-butyllithium added to 1.404g, 2.20mmol 5b) resulting in 115mg (9%) of 9b as a yellow solid. $^1$H NMR (CDCl$_3$, rt) δ: 8.610 (s, 4H); 1.535 (m, 12H), 1.236 (d, 72H); $^{13}$C NMR (CDCl$_3$) δ: 147.796, 139.141, 135.894, 134.136, 130.119, 115.190, 18.667, 11.918. $^{19}$F NMR (CDCl$_3$, rt) δ: -119.0181.

**Compound 10a.** Octafluoronaphthalene (.240mg, .881mmol) added to lithiated 5a (.92mL 1.6M n-butyllithium to 344mg, .734mmol 5a) resulting in 178mg (45%) of
10a as a yellow solid. $^{1}$H NMR (CDCl$_3$, 40 °C) δ: 8.335 (t, 2H), 0.492 (s, 18H). $^{19}$F NMR (CDCl$_3$, 40 °C) δ: -120.222, -146.443, -156.788.

**Compound 10b.** Octafluoronapthalene (360mg, 1.32mmol) added to lithiated 5b (1.37mL 1.6M n-butyllithium in 702mg, 1.10mmol of 5b) resulting in 338mg (43%). 100mg placed into a vial with hexanes and heated. After cooling to room temperature, the liquid was filtered away to retain 12mg of 10b as a reddish-orange solid. $^{1}$H NMR (CDCl$_3$, rt) δ: 8.482 (s, 2H), 1.520 (septet, 6H), 1.207 (m, 36H) $^{13}$C NMR (CDCl$_3$) δ: 145.036, 142.652, 139.141, 138.771, 135.894, 134.136, 130.119, 125.486, 18.667, 11.918. $^{19}$F NMR (CDCl$_3$, rt) δ: -120.008, -146.350, -156.843.
Compound 12. 4-bromoveratrole (50g, 0.23mol) was added to a 500mL 3-neck flask. 250mL of dry methylene chloride was added and a slow but steady stream of nitrogen was continuously bubbled through the solution. In three parts separated by five minute intervals, ferric chloride (37.36g, .023mol) was added to the solution and the flask was sealed with a septum. The solution was allowed to stir for 12 hours and 100mL of methanol was added and the solution was allowed to stir an additional hour. This solution was then poured into water and extracted with chloroform. This layer was separated, dried with MgSO₄, and the solvent was removed under reduced pressure. The dark colored crude material was dissolved into chloroform and boiled with decolorizing charcoal for an hour. This was then filtered and the solvent was once again removed under reduced pressure. The crude product was then recrystallized from boiling ethanol to yield 22.61g (45%) of 11 as a white powder and used directly in the next step.

\[
\text{H}_3\text{CO} - \text{Br} - \text{OCH}_3 \\
\text{H}_2\text{CO} - \text{Br} - \text{OCH}_3 \\
\text{Br} - \text{OCH} - \text{Br} - \text{OH}
\]

Compound 13. Compound 12 (2.0g, 5.32mmol) was dissolved in 50mL of dry methylene chloride in a 100mL Schlenk flask. The air atmosphere was removed and replaced with argon. The reaction was brought to -78 °C using a dry ice/isopropanol bath and a 1.0M solution of BBr₃ (18.5 mL, 21.28mmol) was added dropwise. The mixture was allowed to very slowly return to room temperature by sublimation of the dry ice. The reaction was allowed to stir 12 hours and 25mL of degassed H₂O was then added to quench the reaction. The solvent was removed by reduced pressure and additional degassed water (50mL) was added to the crude product. This was heated to 80 °C and allowed to stir until the product was completely dissolved. The mixture was then cooled with an ice bath to 0 °C and the product was then immediately filtered and used without further purification. Recrystallization yielded 1.50g (86%) as a gray solid. ¹H NMR (D₂O) δ: 7.141 (s, 4H), 6.753 (s, 4H).
**Compound 14a.** To a 100mL 3-neck flask equipped with a condenser was added compound 13 (1.0g, 2.66mmol), 1-hexylbromide (1.93g, 11.7mmol), and potassium carbonate (4.41g, 31.9mmol) in 30mL of dry DMF. The mixture was raised to 90 °C and allowed to stir for 24 h. The reaction was followed by TLC and upon completion the reaction mixture was washed with water and extracted with ether. The organic layer was separated and dried under MgSO₄, and the solvent was removed under reduced pressure. The crude product was pushed through a column using pentane eluent to yield 1.75 (92%) of the intended product as a colorless oil. ¹H NMR (CDCl₃, rt) δ: 7.107 (s, 2H), 6.775 (s, 2H), 4.0108 (t, 4H), 3.971 (t, 4H), 1.829 (m, 8H), 1.486 (m, 2H), 1.351 (m, 16H), 0.901 (m, 12H). ¹³C NMR (CDCl₃, rt) δ: 149.180, 147.800, 133.934, 116.856, 116.273, 113.790, 69.345, 31.491, 29.059, 25.618, 25.580, 22.522, 13.932.

**Compound 14b.** To a 100mL 3-neck flask equipped with a condenser was added compound 13 (1.51g, 4.02mmol), 2-ethylhexylbromide (3.41g, 17.7mmol), and potassium carbonate (6.67g, 48.2mmol) in 40 mL of dry DMF. The mixture was raised to 90 °C and allowed to stir for 24 h. The reaction was followed by TLC and upon completion the reaction mixture was washed with water and extracted with ether (3x 50mL). The organic layer was separated and dried under MgSO₄, filtered, and the solvent was removed under reduced pressure. The crude product was pushed through a column using pentane eluent to yield 2.00 (60%) of the intended product as a colorless oil. ¹H NMR (CDCl₃, rt) δ: 7.107 (s, 2H), 6.771 (s, 2H), 1.777 (m, 4H), 1.494 (m, 16H), 1.336 (m, 16H), 0.937 (m, 24H). ¹³C NMR (CDCl₃, rt) δ: 149.580, 148.223, 133.887, 116.561, 116.087, 113.709, 71.850, 39.488, 30.568, 29.095, 23.914, 23.045, 14.054, 11.183.

**Compound 14c.** To a 100mL 3-neck flask equipped with a condenser was added compound 13 (1.72g, 4.57mmol), 3,7-dimethyloctylbromide (4.45g, 20.1mmol), and
potassium carbonate (7.59g, 54.9mmol) in 40mL of dry DMF. The mixture was raised to 90 °C and allowed to stir for 24 h. The reaction was followed by TLC and upon completion the reaction mixture was washed with water and extracted with ether. The organic layer was separated and dried under MgSO₄, and the solvent was removed under reduced pressure. The crude product was pushed through a column using pentane eluent to yield 2.94 (67%) of the intended product as a colorless oil. ¹H NMR (CDCl₃, rt) δ: 7.114 (s, 2H), 6.783 (s, 2H), 4.045 (8H), 1.881 (m, 4H), 1.661 (m, 8H), 1.534 (m, 4H), 1.337 (m, 12H), 1.176 (m, 12H), 0.967 (m, 12H), 0.877 (m, 12H). ¹³C NMR (CDCl₃, rt) δ: 149.220, 147.824, 133.943, 116.788, 116.228, 113.818, 67.747, 39.215, 37.278, 36.050, 29.857, 27.962, 24.689, 22.680, 22.581, 19.673.

**Compound 15a.** To a 50mL argon filled reaction flask was added compound 12 (1.00g, 2.31mmol) and 10mL of dry THF. The reaction solution was brought to -78 °C and n-butyllithium (1.85mL of a 2.5M solution, 4.63mmol) was added dropwise. The solution was allowed to stir at this temperature for an additional hour at which time octafluoronapthalene (0.76g, 2.78mmol) was added. A blue fluorescence is noted almost immediately upon the addition of octafluoronapthalene. The mixture was allowed to stir an additional four hours and following this time the solvent was removed under reduced pressure. The product was found to be only very slightly soluble in hot chloroform or toluene, making separation from the lithium bromide very difficult. The resulting suspension was washed with 10% HCl, extracted with chloroform, and filtered to yield 0.96g (82%) as a yellow powder. Recrystallization in boiling 1,2-dichloroethane was found to be minorly successful, but the product was found to decompose over the course of a few hours at high temperature. ¹H NMR (C₂D₂Cl₄, 80 °C) δ: 9.618 (t, 2H), 8.916 (s, 2H), 5.384 (s, 6H), 5.324 (s, 6H). ¹³C
NMR (C$_2$D$_2$Cl$_4$, 80 °C) δ: 153.733, 152.122, 145.364, 142.842, 140.303, 128.965, 122.563, 120.766, 114.669, 111.719, 108.333, 59.231. $^{19}$F NMR (C$_2$D$_2$Cl$_4$, 80 °C) δ: -117.687, -144.102, -155.272.

**Compound 15b.** To a 50mL argon filled reaction flask was added compound 14b (1.00g, 2.31mmol) and 10mL of dry THF. The reaction solution was brought to -78 °C and n-butyllithium (1.12mL of a 2.5M solution in hexanes, 4.62mmol) was added dropwise. The solution was allowed to stir at this temperature for an additional hour at which time octafluoronapthalene (0.49g, 1.68mmol) was added. A blue fluorescence is noted almost immediately upon the addition of octafluoronapthalene. The mixture was allowed to stir an additional four hours and following this time the solvent was removed under reduced pressure. The crude product was redissolved in ether and washed with 3x10mL portions of 10% HCl and the organic layer was separated. Following the extraction, the mixture was dried with MgSO$_4$ and the solvent was removed using a rotary evaporator. The crude material was then pushed through a column of silica gel using a mixture of 30% methylene chloride in pentane to yield 712mg (64%) of 15b as a yellow powder. $^1$H NMR (C$_6$D$_6$) δ: 8.155 (t, 2H), 7.623 (s, 2H), 4.093 (t, 4H), 4.002 (t, 4H), 1.879 (m, 4H), 1.556 (m, 4H), 1.362 (m, 20H), 0.970 (m, 16H). $^{13}$C NMR (C$_6$D$_6$) δ: 149.673, 148.448, 142.054, 139.494, 136.977, 124.662, 118.606, 116.456, 110.978, 107.900, 104.817, 68.832, 32.380, 29.88., 26.300, 23.150, 14.366. $^{19}$F NMR (C$_6$D$_6$) δ: -118.622, -146.379, -157.599. Elemental analysis – calculated: 70.21 %C, 7.17 %H; found: 70.63 %C, 7.44 %H.

**Compound 15c.** Followed the same procedure as 15b using 14c (1.00g, 1.21mmol), octafluoronapthalene (396mg, 1.45mmol), and n-butyllithium (0.97mL of a 2.5M solution in hexanes) to yield 544mg (50%) of a soft bright yellow solid. $^1$H NMR (C$_6$D$_6$) δ: 8.773 (t, 2H), 7.987 (s, 2.00H), 4.14 (dd, 8H), 1.831 (m, 4H), 1.628 (m, 12H), 1.495 (m, 4H), 1.373 (m, 16H). $^{13}$C NMR (C$_6$D$_6$) δ: 151.493, 149.988, 142.739, 140.081, 137.554, 126.171, 120.007, 118.225, 112.593, 109.088, 108.912, 106.732, 71.799, 40.356, 31.454, 29.851, 24.707, 23.833, 23.804, 14.619, 11.858. $^{19}$F NMR (C$_6$D$_6$) δ: -119.252, -145.739, -157.167. Elemental analysis – calculated: 72.13 %C, 8.07 %H; found: 72.01 %C, 8.44 %H.
**Compound 15d.** Followed the same procedure as 15b using 14d (1.01g, 1.08mmol), octafluoronapthalene (352mg, 1.29mmol), and n-butyllithium (0.86mL of a 2.5mL solution in hexanes, 2.16mmol) to yield 648mg (59%) of a very soft bright yellow solid. H NMR (C₆D₆) δ: 8.253 (t, 2H), 7.680 (s, 2H), 4.243 (t, 4H), 4.170 (t, 4H), 2.061 (m, 4H), 1.879 (m, 4H), 1.773 (m, 4H), 1.595 (m, 4H), 1.461 (m, 12H), 1.280 (m, 12H), 1.124 (m, 12H), 0.984 (m, 24H). ¹³C NMR (C₆D₆) δ: 150.807, 149.436, 142.734, 140.150, 137.627, 125.952, 119.682, 117.694, 112.226, 108.868, 106.226, 67.847, 40.100, 38.422, 37.201, 30.863, 28.799, 25.712, 23.372, 20.314. ¹⁹F NMR (C₆D₆) δ: -118.851, -146.095, -157.497. Elemental analysis – calculated: 73.63 %C, 8.77 %H; found: 74.00 %C, 9.37 %H.


44. Wikipedia Janus (November 20, 2006),


Vita

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