SYNTHESIS OF THE FLUORINATED ARYLENE ALKYLENE ETHER AND RESEARCH ON ITS POTENTIAL THERMOTROPIC BEHAVIOR UNDER PHOTOCHEMICAL CROSSLINK REACTION

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SYNTHESIS OF THE FLUORINATED ARYLENE ALKYLENE ETHER AND RESEARCH ON ITS POTENTIAL THERMOTROPIC BEHAVIOR UNDER PHOTOCHEMICAL CROSSLINK REACTION

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ABSTRACT

A series of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((n-
alkoxy)benzene)) (n = 1 to 12) were synthesized by a three step strategy. Thermotropic
behaviors of 5 in 12 molecules were studied by differential scanning calorimetry. With
the enhancement of arene-perfluoroarene interaction, this series of molecules will be used
for copolymerization with 1,4-bis((E)-n-alkoxy-2,3,5,6-tetrafluorostyryl)benzene via
photo[2+2] cycloaddition reaction. In contrast to benzene, the lowest temperature phase
of the benzene/hexafluorobenzene dimer generates face-to-face stacks structure and this
non-covalent interaction between benzene and hexafluorobenzene is called an arene-
perfluoroarene interaction. Those n-alkoxy-bis-stillbenes are supposed to have
thermotropic liquid crystallinity, because thermotropic liquid crystals are based on a
mesogenic core (bis-stillbene part) coexisting with a tail (alkoxy part) in the same
molecules. We deduced that these bis-stilbene dimers can be aligned in the liquid
crystalline state, and the orientation will be locked by photo[2+2]cycloaddition reaction
to generate a macro-ordered film through a roll-to-roll assembly process.
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CHAPTER I
INTRODUCTION

In contrast to pure benzene,\textsuperscript{1,2,3} which crystallizes primarily by an edge-to-face interaction, hexafluorobenzene forms a transient complex with aromatic hydrocarbons by a face-to-face style. This interaction\textsuperscript{4,5} is known as arene-perfluoroarene interaction. The arene-perfluoroarene interaction is the electrostatic interaction with electron-deficient aromatic ring and the electron-rich aromatic ring of the hydrocarbon. This interaction directs the geometry of crystallization and contributes to photo-active crystals:\textsuperscript{6} fluorinated arylene alkylenes can be photo-polymerized easily and generate highly regular and rigid structures by photo [2+2] cycloaddition reaction. The bis-stilbene bonds are close enough to react with each other under the mediation by the $\pi-\pi$ interaction between perfluoroarene and arene. Those $n$-alkoxy-bis-stillbenes are supposed to have thermotropic liquid crystallinity, because thermotropic liquid crystals require a mesogenic core (bis-stillbene part) coexisting with a flexible tail (alkoxy part) in the same molecules. Based on that, two series of fluorinated (n= 1~ 12) are supposed to be photopolymerized easily in a 1:1 ratio and further generate macro-ordered film by locking orientation at the liquid crystalline phase under a roll-to-roll assembly process. This work primarily focus on synthesis and thermotropic study for one of two designed $n$-alkoxy-bis-stillbenes: \((4,4'-(1E,1'E)-(\text{perfluoro-1,4-phenylene})\text{bis(ethene-2,1-diyl)})\text{bis(}(n\text{-alkoxy})\text{benzene})\).
CHAPTER II

LITERATURE BACKGROUND

2.1 Thermotropic Liquid Crystalline Behaviors

Liquid crystallinity, first discovered by Friedrich Reinitzer at 1888, describes the state of molecules that can flow like liquid molecules and orient like crystalline molecules either in a particular solvent or over a range of temperatures. Liquid crystals exist in both nature and in modern technologies. Many proteins and membranes are reported to have liquid crystalline structure. Cholesterol and its derivatives are also famous for their liquid crystal behavior. The display field and biomedical applications (e.g. biosensors, biomimicry) are current robust areas of liquid-crystal materials research.

Generally two basic classifications are used in liquid crystal field: lyotropic and thermotropic. The morphological behaviors of lyotropic liquid crystals depend on both concentration and temperature. Over a certain range of temperatures, a variety of molecular mixtures, such as water, oil and surfactants generate long range orientational order in response to changes in concentration.

Lyotropic liquid crystal molecules are generally amphiphilic molecules consisting two parts that repel each other or possess different solubilities in a particular solvent (e.g. water). For molecules that are amphiphilic in water (e.g. phospholipids and sodium
dodecyl sulfate) the hydrophilic part is called the “head” and the hydrophobic part is called the “tail”. With increasing concentration of liquid crystal molecules in water, the phase frequently shows a sequence of micellar phase, hexagonal phase, and cubic phase, and finally a lamellar phase.

Thermotropic liquid crystals are the most common type of liquid crystals and relate more close to this work. In contrast to lyotropic liquid crystals, thermotropic liquid crystals are molecules that form a liquid crystalline phase in bulk as a function of temperature. At lower temperatures, the molecular movement is blocked and the molecules are oriented in a crystalline phase. With increasing temperature, if the movement of molecules is activated and the orientation of the molecules is completely disrupted, the molecules will melt into an isotropic melt. However, there may be an intermediate range of temperatures, at which the movement of the molecules is activated, while some orientation of molecules is retained, this is the liquid crystalline phase mentioned above.

Thermotropic liquid crystalline molecules generally consist of two parts: the mesogenic core and the flexible tail. The mesogenic core generally has a rigid molecular structure due to aromatic rings and is oriented in the liquid crystalline phase. The tail refers to a flexible chain such as an alkoxy group, which lowers the melting temperature and increases the movement of molecules in the liquid crystalline phase. A balance between the rigid and flexible parts of the molecule gives it a liquid crystalline phase over a particular temperature range.

Two general kinds of thermotropic liquid crystalline phases exist: nematic and smetic phases. In the nematic phase, the long axes of the mesogens are oriented parallel
to each other, although the molecular centers arrange randomly, and there is no positional order. The smectic phases occur at lower temperature than a nematic phase, and have an additional type of order: the molecules are arranged in layers and the mesogens are oriented parallel.\textsuperscript{17} The different types of smetic phase differ by the amount of positional order and the extent of long range order.

Literature uses short, e.g. “k number 1 s number 2 n number 3 i”, to describe the thermotropic liquid crystalline behavior. “k” refers to the crystalline phase; “s” and “n” refer the smetic and nematic liquid crystalline phase respectively; “i” refers to the isotropic melt. The numbers in between describe the temperatures (°C) at which the phase transition takes place. For example, “k 18 n 48 i” for N-(4-methoxybenzylidene)-4-butylaniline molecule means that it exhibits a nematic liquid crystalline phase between 18 °C and 48 °C.\textsuperscript{18}

We are using the thermotropic liquid crystalline phase of bis-stilbene dimers to ideally orient them into a macroscopic order in a roll-to-roll assembly process. The thermotropic liquid crystals for this research should also be arranged to undergo for a photo [2+2] cycloaddition due to arene-perfluoroarene interactions as described in chapter 2.2 and 2.3.

2.2 Arene-perfluoroarene Interactions and Their Applications

Pure benzene\textsuperscript{1,2,3} crystallizes in an edge-to-face style in the solid state (Scheme 2.1a). This interaction between an electron-rich aromatic ring and an electron-deficient proton minimizes the total interaction energy in the solid state. In 1960, Patrick and Prosser reported\textsuperscript{19} that a 1:1 mixture of benzene (m.p. 5.0 °C) and hexafluorobenzene
(m.p. 5.4 °C) generates a complex that melts at a higher temperature (23.7 °C). In contrast to benzene, the lowest temperature phase of the benzene/hexafluorobenzene dimer generates face-to-face stacks by a non-covalent interaction is called an arene-perfluoroarene interaction.\textsuperscript{4,5} This face-to-face stacking arrangement is the result of van der Waals forces and electrostatic π-π stacking interactions, not from charge-transfer interactions.\textsuperscript{20} Hexafluorobenzene and benzene have large molecular quadrupole moments of similar magnitude. However the charge distribution on fluorinated benzene is the opposite of that of benzene,\textsuperscript{5} and it therefore forms an electrostatic interaction with benzene. Theoretical calculations\textsuperscript{21} of the interactions between benzene and hexafluorobenzene result in an energy of stabilization energy of 3.7 kcal/mol and an interplane separation distance of 3.6 Å.

![Scheme 2.1. Interaction between Benzene Dimer and Benzene/Hexafluorobenzene Dimer.](image)

These interactions influence the properties of compounds in the solution, liquid crystalline and solid states. In solution, Kilbinger and Grubbs\textsuperscript{22} used these arene-perfluoroarene interactions to aggregate PEG. They synthesized 1-pyrene butyroyl chloride end capped poly(ethylene glycol)s (PEGs) with a degree of polymerization of 180. By mixing this end-cap polymer with octafluoronaphthalene (OFN) in a 1:2 ratio in
water, the solution had higher viscosities than the end-caped polymers in the absence of OFN (Figure 2.1).

Figure 2.1. Arene-perfluoroarene Interactions Between End-Capped Pyrene and OFN Aggregate PEGs in Solution State.

Arene-perfluoroarene interactions are also used to stabilize the liquid crystalline state. Dai et al. reported\(^2\) expand the temperature range of liquid crystallinity via arene-perfluoroarene interaction (Figure 2.2). 1,4-Bis(phenylethynyl)benzene shows only a short monotropic liquid crystalline temperature range (5 °C approximately) on cooling (k\(\text{181.7 i; i 164.3 n 159.5 k on cooling}\)). 1,4-Bis(pentafluorophenylethynyl)tetrafluorobenzene shows no liquid crystalline behavior (k 226.1 i). However, 1:1 co-crystals of these two molecules show a nearly 54 °C temperature range of liquid crystallinity (k 178.5 \(\text{s b 196.2 bi n/i 231.5 i}\)).

Figure 2.2. Arene-perfluoroarene Interaction between 1,4-Bis(phenylethynyl) and 1,4-Bis(pentafluorophenylethynyl)tetrafluorobenzene Stabilize the Liquid Crystalline State.
In a bio-application, Pace et al.\textsuperscript{24,25} utilized this face-to-face arene-perfluoroarene interactions to stabilize secondary structure of peptide system (Figure 2.3). They studied peptide system which consists of aromatic residues and had a dimeric helix structure. The position 10 of each peptide chain stacks in a face-to-face style with those of position 29 on the other chain. A fluorinated phenylalanine (Phe) analogue was incorporated into the α2D at position 10 and/or position 29 and replace the phenylalanine Phe. With both amino acids of position 10 and position 29 are replaced by fluorinated analogues Phe, Peptide system show obvious improvement of the α2D structural stability. The new peptide system has a decrease of free energy by 6.7 kcal/mol and an increase of meting point from 29 °C to 79 °C.

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<th>T\textsubscript{m} (°C)</th>
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<tbody>
<tr>
<td>Phe</td>
<td>28.9</td>
<td>-5.9</td>
<td>0</td>
</tr>
<tr>
<td>F-Phe</td>
<td>78.3</td>
<td>-12.6</td>
<td>6.7</td>
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Figure 2.3. Arene-perfluoroarene Interaction Stabilize the α2D Peptide System.\textsuperscript{25}
Scheme 2.2. Topology Photo Oligmerization between Diphenylbutadiyne and Decafluorodiphenylbutadiyne.

Arene-perfluoroarene interactions have been used to align molecules in the crystalline state to enable the photochemical reactions. Diphenylbutadiyne (mp 87 °C) and decafluorodiphenylbutadiyne (mp 114 °C) are both colorless crystals. Diphenylbutadiyne is photostable and decafluorodiphenylbutadiyne generate only trace (< 4%) materials with slight degree of polymerization under UV irradiation. Cocrystallization of both molecules from ethanol generates 1:1 complex of long colorless crystals. This complex has a melting point (154 °C) higher than either of the components (Scheme 2.2). Photo[2+2] cycloaddition under UV irradiation shattered the crystals immediately and generates a red-brown oligomer after 18 hours, presumably with a zigzag displacement structure. Similarly, trans-stilbene (124 °C) molecules and trans-decafluorostilbene molecules (103 °C) form a 1:1 complex that can be recrystallized from ethanol. This complex, which is colorless crystal, also has a higher melting point (139 °C) than either of the components (Scheme 2.3). Photocyclo [2+2] addition under UV irradiation for 5 hours gives 98% yield of heterodimer only, with no homo-dimerized product. Phenyl and perfluorophenyl groups are cis to each other in the product as shown in Scheme 2.3.
Scheme 2.3. Photodimerization of Trans-stilbene and Decafluoro-trans-stilbene in the Solid State.

Scheme 2.4. Trans,trans-1,4-bis(2-phenylethenyl)-2,3,5,6-tetrafluorobenzene (A) and trans, trans-1,4-bis(2-pentafluorophenylethenyl)benzene (B)

These arene-perfluoroarene interactions are useful for supramolecular construction. Similar to the reaction between bis-stilbene and perfluoro-bis-stilbene, trans,trans-1,4-bis(2-phenylethenyl)-2,3,5,6-tetrafluorobenzene (Scheme 2.4a) and trans, trans-1,4-bis(2-pentafluorophenylethenyl)benzene (Scheme 2.4b) were also synthesized and reacted photochemically to undergo oligomerization. Cocrystallization of the compounds A and B (1:1 solution in tetrahydrofuran) by solvent evaporation gives light green crystals. These crystals are proved by NMR spectroscopy to be the 1:1 complexes of compound A and B. The complex melts at 227 °C, which is higher than either of the compound (208 °C and 216 °C respectively). Photolysis of this complex for 20 hours gives polymeric product (an average degree of polymerization of 22) with quantitative yield (67%). Photopolymerization resulted in polymers with a zigzag type and rigid
structure. The stereochemistry of the product is influenced by the arene-perfluoroarene interactions. The backbone is stabilized by cyclobutane rings generated from photopolymerization and arene-perfluoroarene interactions. This arrangement of phenyl and perfluorophenyl groups should be a general supramolecular motif, as shown in Scheme 2.5.

Scheme 2.5. Proposed Solid-state Packing and Polymerization Stereochemistry of the A and B Cocrystals.

2.3 Designed Monomers, Polymer Structure and Processing Procedures.

Scheme 2.7 presents the new type of polymers that are being generated from the liquid crystalline bis-stilbene dimer in this project. The target monomers are 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diy1))bis(n-alkoxybenzene) and 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diy1))bis(n-alkoxybenzene). Their thermotropic behaviors will be characterized at first. Then we design to study their ability to align and undergo photopolymerization in the new roll-to-roll assembly system.
reported\textsuperscript{27} by Cakmak (Figure 2.4). This novel process is designed to produce nanostructured materials continuously with the aid of external field, e.g. electric field, magnetic field, and/or thermal gradient.

Those molecules should have liquid crystalline phase. The liquid crystalline phase will enable the bis-stilbene monomers to be aligned with the magnetic or electric field. Photo[2+2]cycloaddition at the liquid crystalline temperature is deduced to result in a rigid supramolecular structure with the lock of orientation.

![Figure 2.4. Cakmak’s Electromagnetic Processing Line.\textsuperscript{27}](image)

Those molecules should have liquid crystalline phase. The liquid crystalline phase will enable the bis-stilbene monomers to be aligned with the magnetic or electric field. Photo[2+2]cycloaddition at the liquid crystalline temperature is deduced to result in a rigid supramolecular structure with the lock of orientation.

![Scheme 2.6. Designed Monomers and Polymer Structure.](image)
In this thesis, synthesis and thermotropic behavior of one of two series of monomers, 1,4-bis((E)-2,3,5,6-tetrafluoro-4-alkoxystyryl)benzene, will be discussed. To achieve the liquid crystallinity in at least the monomers, and to find an optimum temperature for macroscopic alignment during photopolymerization, the bisalkoxy derivatives will be synthesized with the length of the alkoxy groups ranging from n=1 to n=12. The synthetic route of this series of molecules will be shown in section 2.4.

2.4 Synthetic Route

Fluorinated bis-stilbene structures are generally synthesized by transition metal catalyzed reactions\(^6\,^28\) or Wittig reactions.\(^{29}\) Our group\(^30\) recently developed a synthetic route to the bis-stilbene dimers that uses a palladium-catalyzed oxidative olefination reaction.\(^31,\,^32\) This method does not require a special preparation of functionalized highly fluorinated benzene, such as with a Heck reaction or a Negishi reaction, and is therefore very convenient and efficient for the synthesis of our molecules.

The synthetic strategy is a 3-step strategy. The first step is to synthesize 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(tert-butoxybenzene) (tBu-FHF-tBu). At second step, tert-butoxy groups will be deprotected to generate 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))diphenol (HO-FHF-OH). With the hydroxyl groups on both sides of molecules, a Williamson reaction is a useful route to attach alkyl groups with different length onto the molecules at the final step.
The first step of the synthesis is the synthesis of 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(tert-butoxybenzene) (tBu-FHF-tBu) from 4-tert-butoxystyrene and 2,3,4,5- tetrafluorobenzene by the oxidative olefination reaction (Scheme 2.7).

Scheme 2.7. Synthetic Procedure of 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(tert-butoxybenzene)

The second step is to deprotect of tert-butoxy groups via trifluoroacetic acid (TFA). TFA is widely used to deprotect tert-butoxy and tert-butoxycarbonyl groups (Scheme 2.8).

Scheme 2.8. Synthetic Procedure of 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))diphenol.

Williamson reactions are used as the final step to synthesize the 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(n-alkoxybenzene). For alkyl groups ranging from n 3 to 12, alkyl bromides are used; for methoxyl and ethoxyl groups, dimethyl sulfate and diethyl sulfate are used (Scheme 2.9).
Scheme 2.9. Synthetic Procedure of 1,4-bis((E)-2,3,5,6-tetrafluoro-4-alkoxystyryl)benzene.

(a) Via Dialkyl Sulfate for n = 1, 2:

(b) Via Alkyl Bromide for n from 3 to 12:

R = CH₃ and CH₃CH₃

Scheme 2.9. Synthetic Procedure of 1,4-bis((E)-2,3,5,6-tetrafluoro-4-alkoxystyryl)benzene.
CHAPTER III
EXPERIMENTS SECTION

3.1 Materials

1-Bromobutane (Aldrich, 99 %), 1-bromododecane (Aldrich, 97%), 1-bromoheptane (Lancaster, NA), 1-bromohexane (Acros, 99.9+ %), 1-bromononam (99% Alfa Aesar), 1-bromooctane (Aldrich, 99 %), 1-bromopentane (Aldrich, 98 %), diethyl sulfate (Janssen Chemical, 99 %), dimethyl sulfate (Aldrich, > 99.8 %), palladium (II) acetate (Aldrich, 99 %), potassium carbonate (Fisher Scientific, Crystal), potassium hydroxide (Aldrich, > 85% pellets) and silver carbonate (Aldrich, 99%), and 1,2,4,5 – tetrafluorobenzene (Oakwook Product Inc., 99 %) were used as received. 1-Bromodocane (98%, Aldrich) and 1-bromoundecane (Lancaster, NA) were dried by refluxing over and distilling from CaH$_2$ under N$_2$. N,N-dimethylformamide (DMF, Aldrich, 99.8 %) was dried by distilling from CaH$_2$ under vacuum at 40 °C. Dimethyl sulfoxide (DMSO, Fisher Scientific, 99.9 %) dried by distilling from CaH$_2$ under vacuum at 80 °C. 4-tert-Butoxystyrene (Aldrich, 99 %) was passed through a short basic alumina column before use. Trifluoroacetic acid (Aldrich, 99%+) was dried by refluxing over and distilling from 4Å molecular sieves under N$_2$. All of the other chemicals and solvent were used as received.
3.2 Techniques

All reactions were performed under a N\textsubscript{2} atmosphere using a Schlenk line unless noted otherwise. Thin-layer chromatography (TLC) was performed using silica gel plates (Sorbent Technologies, 200 μm particle size w/UV254) with polyester backing. Elemental analyses were performed on a PE 2400 Series II CHNS/O Analyzer.

\textsuperscript{1}H (300 MHz), \textsuperscript{13}C (75 MHz) and \textsuperscript{19}F NMR (282 MHz) spectra were recorded on a Varian Mercury 300 instrument. Unless noted otherwise, all spectra were recorded in CDCl\textsubscript{3}. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet and br = broad. The resonances in \textsuperscript{1}H spectra were measured relative to residual solvent resonances and referenced to tetramethylsilane. The resonances in \textsuperscript{19}F spectra were measured relative to residual solvent resonances and referenced to trifluoroacetic acid unless noted otherwise.

A Perkin-Elmer Pyris 1 differential scanning calorimeter was used to study the thermotropic behavior of the sample. Both enthalpy changes and transition temperatures were determined using indium and zinc as calibration standards. All heating and cooling rates were 10 °C/min.

3.3 Synthesis of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(tert-butoxybenzene) (Scheme 2.7)

4,4'-(1E,1'E)-(Perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(tert-butoxybenzene) was synthesized in 58% to 62% yield as in the following example. A mixture of 1,2,4,5-tetrafluorobenzene (1.0023 g, 6.7 mmol, 1 eq), 4-tert-butoxybenzene
(2.927 g, 16.6 mmol, 2.5 eq), silver carbonate (4.4964 g, 16.6 mmol, 2.5 eq), Pd(OAc)$_2$ (0.1513 g, 0.67 mmol, 0.1 eq) and 4 Å molecular sieves (0.5 g, 5 wt % to the volume of DMF) in dry DMF (10 mL) and dry DMSO (0.5 mL) were added into 100 mL Schlenk flask. The mixture was degassed by 6 freeze-pump-thaw (5 - 15 - 10 minutes) cycles. The mixture was then stirred at 120 °C for 24 hours. The resulting dark mixture was diluted with THF (150 mL) and filtered to remove the silver and 4 Å molecular sieves. THF was removed by rotary evaporation and ethanol (100 mL) was added to precipitate the product for overnight. Large amount of yellow solid precipitated. The solid was collected via filtration under reduced pressure and dried in vacuum oven for overnight to yield 2.0078 g yellow solid (60.5%). Melting point: 204 °C-207 °C. $^1$H-NMR: 1.40 (s, $-C(CH_3)_3$, 18H), 7.00 (d, $^1J = 16.9$ Hz, =CH-, 2H), 7.02 (d, $^1J = 8.3$ Hz, aromatic protons ortho to the double bonds, 4H), 7.44 (d, $^1J = 17.4$ Hz, -CH=, 2H), 7.48 (d, $^1J = 8.5$ Hz, aromatic protons ortho to the tert-butoxy group, 4H). $^{19}$F-NMR (C$_6$H$_5$F as intern reference): 144.98 (s, ArF, 4F).

3.4 Synthesis of 4,4'-(((1E,1'E)-(Perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))diphenol
(Scheme 2.8)

4,4'-(((1E,1'E)-(Perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))diphenol was synthesized in 80% to 85% yield as in following example. A solution of 4,4'-(((1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(tert-butoxybenzene) (2.0032 g, 4.01 mmol) in dry trifluoroacetic acid (20.0 mL) in a 100 mL round bottom flask was stirred at room temperature for 24 h. The resulting solid product was collected in a fritted glass funnel and washed with chloroform, after dried in vacuum oven at room temperature for
overnight, yield 1.258 g (81.2 %) of a dark yellow solid. $^1$H-NMR (d$_6$-DMSO): 6.80 (d, $^1$J = 8.2 Hz, aromatic protons ortho to the double bonds, 4H), 6.87 (d, $^1$J = 16.7 Hz, =CH-, 2H), 7.35 (d, $^1$J = 16.7 Hz, -CH=, 2H), 7.49 (d, $^1$J = 8.5 Hz, aromatic protons ortho to hydroxyl groups, 4H), 9.86 (s, -OH, 2H). $^{19}$F-NMR: 148.38 (s, ArF, 4F).

3.5 Synthesis of 4,4’-((1E,1’E)-(Perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(methoxybenzene) (1C-HFH-1C) and 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(ethoxybenzene) (2C-HFH-2C) via Dialkyl Sulfate. (Scheme 2.9 (a))

14,4’-((1E,1’E)-(Perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(methoxybenzene) and 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(ethoxybenzene) were synthesized in 38.1% and 31.6% yield respectively. Synthesis of 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(methoxybenzene) via dimethyl sulfate is used as example to illustrate the synthetic procedure. A solution of dimethyl sulfate (1.00 mL, 10.5 mmol, 10.5 eq) in THF (1.0 mL) was added dropwisely over 8 minutes into the 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))diphenol (404.2 mg, 1.04 mmol, 1 eq), KOH (254.6 mg, 4.54 mmol, 4.3 eq) in THF (10 mL) and methanol (5 mL). The mixture was then stirred for another 38 hours under room temperature. The mixture became turbid with yellow solid. The resulting mixture was poured into ice water (100 mL), and then extracted once with Et$_2$O (100 mL). The organic layer was washed 3 times with saturated NaHCO$_3$ (50 mL ea.) and 3 times with saturated NaCl (50 mL ea.). The organic layer was separated using a separation funnel. The mixture dried with sodium sulfate or magnesium sulfate to
yield clear light yellow solution. Rotary evaporated the organic layer and dried in the vacuum oven at room temperature to yield 432.5 mg (99.4%) light yellow solid as the crude product.

For 4,4′-((1E,1′E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(methoxybenzene): The solid was then recrystallized from a mixture of ethanol (45 mL) / toluene (27 mL) and a mixture of hexane (25 mL) / dichloromethane (35 mL) to yield 164.9 mg fine yellow crystal (38.1%). $^1$H-NMR : 3.86 (s, -CH$_3$), 6.94 (d, $^1$J = 8.7 Hz, aromatic protons ortho to the double bonds, 4H), 6.96 (d, $^1$J = 16.4 Hz, =CH-, 2H), 7.46 (d, $^1$J = 16.2 Hz, -CH=, 2H), 7.50 (d, $^1$J = 8.5 Hz, aromatic protons ortho to methoxy groups, 4H). $^{19}$F-NMR: 148.32 (s, ArF, 4F).

For 4,4′-((1E,1′E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(ethoxybenzene): The solid was recrystallized from a mixture of ethanol (50 mL) and toluene (37 mL) to give fine yellow crystals. $^1$H-NMR: 1.45 (t, $^2$J = 6.9 Hz, -CH$_3$, 6H), 4.09 (q, $^2$J = 6.9 Hz, -CH$_2$-, 4H), 6.92 (d, aromatic protons ortho to the double bonds, $^1$J = 8.8 Hz, 4H), 6.96 (d, $^1$J = 14.33 Hz, =CH-, 2H), 7.46 (d, $^1$J = 16.4 Hz, =CH-, 2H), 7.50 (d, $^1$J = 8.5 Hz, aromatic protons ortho to the ethoxy groups, 4H). $^{19}$F-NMR: 148.32 (s, ArF, 4F). Anal. (C$_{26}$H$_{22}$F$_4$O$_2$): calcd 70.50, 5.01; found: 70.32, 4.68.

3.6 Synthesis of 4,4′-((1E,1′E)-(Perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis($n$-alkoxybenzene) via Alkyl Bromide (Scheme 2.9 (b))

A series of 4,4′-((1E,1′E)-(Perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis($n$-alkoxybenzene) (n from 3 to 12) was synthesized in 35% to 72.2% yield. 4,4′-((1E,1′E)-(Perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((n-propoxy)benzene) (n=3) is used as
an example to illustrate the synthetic procedure. A solution of 1-bromopropane (434.5 mg, 3.5 mmol, 3.25 eq) in ethanol (15 mL) was added dropwisely over 2 hours into the refluxing dark red clear solution of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))diphenol (402.4 mg, 1.04 mmol, 1 eq), K$_2$CO$_3$ (447.8 mg, 3.25 mmol, 3 eq) in ethanol (25 mL) and water (5 mL). The mixture was stirred at reflux for another 48 hours and yellow precipitation appeared. The resulting mixture was poured into ice water (100 mL), and then extracted once with Et$_2$O (120 mL). The organic layer was washed 3 times with saturated NaHCO$_3$ (50 mL ea.) and 3 times with saturated NaCl (50 mL ea.). The organic layer was separated using a separation funnel. The mixture was heated up to 50 °C to increase the solubility of the sample and then dried with sodium sulfate or magnesium sulfate to yield clear light yellow solution. Rotary evaporated the organic layer and dried in the vacuum oven at room temperature to yield light yellow solid.

For 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(n-propoxybenzene): The solid was recrystallized firstly from a mixture of ethanol (45 mL) and toluene (27 mL) and then saturated chloroform to yield 246.8 mg fine yellow crystal (50.4%). $^1$H-NMR: 1.07 (t, $^2$J = 7.3 Hz, -CH$_3$, 6H), 1.84 (m, -CH$_2$-, 4H), 3.97 (t, $^2$J = 6.6 Hz, -CH$_2$-, 4H), 6.92 (d, aromatic protons ortho to the double bonds, $^1$J = 8.5 Hz, 4H), 6.95 (d, =CH-, $^1$J = 16.9 Hz, 2H), 7.46 (d, -CH=, $^1$J = 16.0 Hz, 2H), 7.50 (d, aromatic protons ortho to the propoxy groups, $^1$J = 8.6 Hz, 4H). $^{19}$F-NMR: 148.49 (s, ArF, 4F).

For 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(n-butoxybenzene): The solid was recrystallized firstly from a mixture of ethanol (55 mL) and toluene (35 mL) and then saturated chloroform to yield 379.3 mg fine yellow crystal (70.4%). $^1$H-NMR: 1.00 (t, $^2$J = 7.3 Hz, -CH$_3$, 6H), 1.52 (m, -CH$_2$-, 4H), 1.80 (m, -CH$_2$-,
4H), 4.01 (t, $^2J = 6.6$ Hz, -CH$_2$-, 4H), 6.92 (d, aromatic protons ortho to the double bonds, $^1J = 8.8$ Hz, 4H), 6.95 (d, =CH-, $^1J = 16.7$ Hz, 2H), 7.46 (d, -CH=, $^1J = 16.4$ Hz, 2H), 7.50 (d, aromatic protons ortho to the butoxy groups, $^1J = 8.8$ Hz, 4H). $^{19}$F-NMR: 148.45 (s, ArF, 4F).

For 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((n-pentyloxy)benzene): The solid was recrystallized from a mixture of ethanol (25 mL) and toluene (17 mL) to yield 319.4 mg fine yellow crystals (51.9 %). $^1$H-NMR: 0.96 (t, $^2J = 7.0$ Hz, -CH$_3$, 6H), 1.35 - 1.52 (m, -CH$_2$-, 8H), 1.83 (quin, $^4J = 7$ Hz, -CH$_2$-, 4H), 4.00 (t, $^2J = 6.6$ Hz, -CH$_2$-, 4H), 6.92 (d, aromatic protons ortho to the double bonds, $^1J = 8.7$ Hz, 4H), 6.96 (d, =CH-, $^1J = 16.9$ Hz, 2H), 7.46 (d, -CH=, $^1J = 16.4$ Hz, 2H), 7.48 (d, aromatic protons ortho to the pentyloxy groups, $^1J = 8.9$ Hz, 4H). $^{19}$F-NMR: 148.42 (s, ArF, 4F).

For 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((n-hexyloxy)benzene): The solid was recrystallized from a mixture of ethanol (50 mL) and toluene (35 mL) to yield 305.8 mg fine yellow crystals (53.0 %). $^1$H-NMR: 0.93 (t, $^2J = 6.7$ Hz, -CH$_3$, 6H), 1.36 - 1.53 (m, -CH$_2$-, 12H), 1.81 (quin, $^4J = 6.9$ Hz, -CH$_2$-, 4H), 4.00 (t, $^2J = 6.6$ Hz, -CH$_2$-, 4H), 6.92 (d, aromatic protons ortho to the double bonds, $^1J = 8.8$ Hz, 4H), 6.96 (d, =CH-, $^1J = 16.1$ Hz, 2H), 7.46 (d, -CH=, $^1J = 16.4$ Hz, 2H), 7.49 (d, aromatic protons ortho to the hexyloxy groups, $^1J = 8.4$ Hz, 4H). $^{19}$F-NMR: 148.45 (s, ArF, 4F).

For 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((n-heptyloxy)benzene): The solid was recrystallized from a mixture of ethanol (50 mL) and toluene (35 mL) to yield 323.1 mg fine yellow crystals (51.3 %). $^1$H-NMR: 0.91 (t, $^2J =
6.4 Hz, -CH$_3$, 6H), 1.33 - 1.53 (m, -CH$_2$-, 16H), 1.81 (quin, $^4$J = 7 Hz, -CH$_2$-, 4H), 4.00 (t, $^2$J = 6.4 Hz, -CH$_2$-, 4H), 6.92 (d, aromatic protons ortho to the double bonds, $^1$J = 8.2 Hz, 4H), 6.96 (d, =CH-, $^1$J = 16.2 Hz, 2H), 7.46 (d, -CH=, $^1$J = 16.0 Hz, 2H), 7.48 (d, aromatic protons ortho to the heptyloxy groups, $^1$J = 8.5 Hz, 4H). $^{19}$F-NMR: 148.43 (s, ArF, 4F).

For 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((n-octyloxy)benzene): The solid was recrystallized from a mixture of ethanol (50 mL) and toluene (35 mL) to yield 323.1 mg fine yellow crystals (51.3 %). $^1$H-NMR: 0.90 (t, $^2$J = 6.4 Hz, -CH$_3$, 6H), 1.30 - 1.53 (m, -CH$_2$-, 20H), 1.80 (quin, $^4$J = 7 Hz, -CH$_2$-, 4H), 3.99 (t, $^2$J = 6.4 Hz, -CH$_2$-, 4H), 6.92 (d, aromatic protons ortho to the double bonds, $^1$J = 8.5 Hz, 4H), 6.96 (d, =CH-, $^1$J = 16.4 Hz, 2H), 7.46 (d, -CH=, $^1$J = 16.5 Hz, 2H), 7.48 (d, aromatic protons ortho to the octyloxy groups, $^1$J = 8.5 Hz, 4H). $^{19}$F-NMR: 148.48 (s, ArF, 4F).

For 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((n-nonyloxy)benzene): The solid was recrystallized from a mixture of hexane (25 mL) and chloroform (30 mL) to yield 350.1 mg fine yellow crystals (54.8 %). $^1$H-NMR: 0.90 (t, $^2$J = 6.7 Hz, -CH$_3$, 6H), 1.30 - 1.53 (m, -CH$_2$-, 24H), 1.81 (quin, $^4$J = 7 Hz, -CH$_2$-, 4H), 4.00 (t, $^2$J = 6.6 Hz, -CH$_2$-, 4H), 6.92 (d, aromatic protons ortho to the double bonds, $^1$J = 8.5 Hz, 4H), 6.95 (d, =CH-, $^1$J = 16.4 Hz, 2H), 7.46 (d, -CH=, $^1$J = 16.4 Hz, 2H), 7.48 (d, aromatic protons ortho to the nonyloxy groups, $^1$J = 8.8 Hz, 4H). $^{19}$F-NMR: 148.43 (s, ArF, 4F).

For 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((n-nonyloxy)benzene): The solid was recrystallized from a mixture of ethanol (60 mL) and
toluene (43 mL) to yield 378.1 mg fine yellow crystals (54.5 %). $^1$H-NMR: 0.90 (t, $^2$J = 6.7 Hz, -CH$_3$, 6H), 1.29 - 1.53 (m, -CH$_2$-, 28H), 1.81 (quin, $^4$J = 7 Hz, -CH$_2$-, 4H), 4.00 (t, $^2$J = 6.6 Hz, -CH$_2$-, 4H), 6.92 (d, aromatic protons ortho to the double bonds, $^1$J = 8.5 Hz, 4H), 6.95 (d, =CH-, $^1$J = 16.7 Hz, 2H), 7.46 (d, -CH=, $^1$J = 16.6 Hz, 2H), 7.48 (d, aromatic protons ortho to the nonyloxy groups, $^1$J = 8.8 Hz, 4H). $^{19}$F-NMR: 148.43 (s, ArF, 4F).

For 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((n-undecyloxy)benzene): The solid was recrystallized from a mixture of ethanol (50 mL) and toluene (65 mL) to yield 522.5 mg fine yellow crystals (72.3 %). $^1$H-NMR: 0.90 (t, $^2$J = 6.3 Hz, -CH$_3$, 6H), 1.29 - 1.53 (m, -CH$_2$-, 32H), 1.81 (quin, $^4$J = 6.8 Hz, -CH$_2$-, 4H), 4.00 (t, $^2$J = 6.6 Hz, -CH$_2$-, 4H), 6.92 (d, aromatic protons ortho to the double bonds, $^1$J = 8.1 Hz, 4H), 6.96 (d, =CH-, $^1$J = 16.3 Hz, 2H), 7.46 (d, -CH=, $^1$J = 16.3 Hz, 2H), 7.48 (d, aromatic protons ortho to the undecyloxy groups, $^1$J = 8.2 Hz, 4H). $^{19}$F-NMR: 148.51 (s, ArF, 4F).

For 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((n-dodecyloxy)benzene): The solid was recrystallized from a mixture of hexane (50 mL) and chloroform (23 mL) and a mixture of ethanol (50 mL) and toluene (45 mL) to yield 266 mg fine yellow crystals (35.4 %). $^1$H-NMR: 0.89 (t, $^2$J = 6.7 Hz, -CH$_3$, 6H), 1.27 - 1.52 (m, -CH$_2$-, 36H), 1.80 (quin, $^4$J = 6.8 Hz, -CH$_2$-, 4H), 3.99 (t, $^2$J = 6.4 Hz, -CH$_2$-, 4H), 6.92 (d, aromatic protons ortho to the double bonds, $^1$J = 8.7 Hz, 4H), 6.94 (d, =CH-, $^1$J = 16.3 Hz, 2H), 7.45 (d, -CH=, $^1$J = 16.3 Hz, 2H), 7.48 (d, aromatic protons ortho to the dodecyloxy groups, $^1$J = 8.4 Hz, 4H). $^{19}$F-NMR: 148.31 (s, ArF, 4F).
CHAPTER IV
RESULTS AND DISCUSSION

4.1 Synthesis of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(tert-butoxybenzene).

Figure 4.1. Stacked $^1$H-NMR Spectra of (1) 2,3,4,5-Tetrafluorobenzene, (2) 4-tert-Butoxy styrene and (3) 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(tert-butoxybenzene).
We used $^1$H-NMR (Figure 4.1) spectroscopy to demonstrate that 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(tert-butoxybenzene) (tBu-FHF-tBu) was synthesized successfully via direct oxidative olefination between 4-tert-butoxystyrene and 1,2,4,5-tetrafluorobenzene. The 1,2,4,5-tetrafluorobenzene resonance at $\delta = 7.08$ ppm disappears, indicating that those carbons have been reacted with 4-tert-butoxystyrene. The resonance at $\delta = 1.40$ ppm at the spectra of the tBu-FHF-tBu is consistent with the resonance of $\delta = 1.37$ ppm from 4-tert-butoxystyrene with a slight downfield shift. This demonstrates that the success of attaching tert-butoxy styrene groups onto the molecule. The disappearance of the H$_1$ resonance on 4-tert-butoxystyrene indicates that the 4-tert-butoxystyrene is coupled with 2,4,5,6-tetrafluorobenzene via double bonds. The integrals demonstrate that the product is the desired bis-substituted products.

The use of molecular sieves (5 wt % to the volume of DMF) increases the yield of the reaction sharply from 20% to 60%. Evidently the activity of Pd(OAc)$_2$ decreases in the presence of water, which is generated from the oxidative reaction between Ag$_2$CO$_3$ and a proton from each reactant. Using activated 4 Å molecular sieves maintains the activity of the catalyst, and ensures a high yield bis-alkenylated product. This yield is much higher than the reported$^{32}$ oxidative olefination between styrene and 1,2,4,5-tetrafluorobenzene (26% in bis-alkenylated product) . The complete $^1$H and $^{19}$F-NMR spectra are attached in the appendix chapter.
4.2 Synthesis of 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))diphenol.

We used $^1$H-NMR (Figure 4.2) spectroscopy to demonstrate that trifluoroacetic acid deprotects the tert-butoxy groups of 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(tert-butoxybenzene) (tBu-FHF-tBu) to generate 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))diphenol (HO-FSF-OH) successfully. The disappearance of the resonance at $\delta = 1.40$ ppm demonstrates the successful deprotection of the tert-butoxy groups and the resonance at $\delta = 9.86$ ppm indicates the generation of hydroxyl groups. The resonances of aromatic protons shift to upfield are due to the higher electron density of hydroxyl groups. The complete $^1$H and $^{19}$F-NMR spectra are attached in the appendix chapter.

Figure 4.2. Stacked 1H-NMR for (1)4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(tert-butoxybenzene) and (2) 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))diphenol.
Figure 4.3. Stacked $^1$H-NMR for (1) 1-Bromopropane (2) 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))diphenol and (3) 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(propoxybenzene).

4.3 Synthesis and Thermotropic Behavior of 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(n-alkoxybenzene).

Figure 4.3 presents the $^1$H-NMR spectroscopy of 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(n-propoxybenzene) as an example to demonstrate that the successful syntheses of 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(n-alkoxybenzene). The resonances on $\delta = 1.07, 1.85$ and 3.97 ppm are due to protons from alkoxy groups. Their multiplicities patterns are the same as the resonances of 1-bromopropane, and their position shifts downfield. This is because the oxygen atoms are more electronegative than bromine. The integrals (3.96) of the resonance “k” (protons
of methylene groups) at $\delta = 3.97$ ppm and the disappearance of the resonance “d” (protons of hydroxyl groups) at $\delta = 9.85$ ppm demonstrate that both of the hydroxyl groups on HO-FHF-OH were converted into $n$-propoxy groups. The complete $^1$H and $^{19}$F-NMR spectra of all 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis($n$-alkoxybenzene) are attached in the appendix chapter.

Figure 4.4. Differential Scanning Calorimetry Traces of 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(ethoxybenzene) On (A) Heating and (B) Cooling

Figure 4.4 presents the DSC traces of 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(ethoxybenzene) (2C-HFH-2C) on both heating and cooling, at the temperatures ranging from 20 °C to 250 °C. The DSC traces reveal two 1st order phase transitions. At 158 °C on heating (109 °C on cooling) the molecules show a phase transition between two crystalline phases. At 208 °C on heating (203 °C on cooling), the molecules undergo a phase transition from the crystalline to the isotropic melt.
Figure 4.5. Differential Scanning Calorimetry Traces of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(n-propoxybenzene) On (A) Heating and (B) Cooling.

Figure 4.5 presents the DSC traces of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(n-propoxybenzene) (3C-HFH-3C) on both heating and cooling, at temperatures ranging from 70°C to 250°C. The DSC traces reveal one 1st order phase transition at 203°C on heating and 182°C on cooling. At 203°C on heating (182°C on cooling cycle) the molecules melt from a crystalline phase to an isotropic melt.

Figure 4.6. Differential Scanning Calorimetry Traces of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(n-butoxybenzene) On (A) Heating and (B) Cooling.

Figure 4.6 presents the DSC traces of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(n-butoxybenzene) (4C-HFH-4C) on both heating and cooling, at temperatures ranging from 60°C to 260°C. The traces reveal two 1st order
phase transitions. At 167 °C on heating (163 °C on cooling) the molecules show a phase transition between two crystalline phases. At 188 °C on heating cycle (184 °C on cooling cycle) the molecules melt from a crystalline phase to an isotropic melt.

Figure 4.7. Differential Scanning Calorimetry Traces of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((n-pentyloxy)benzene) On (A) Heating and (B) Cooling.

Figure 4.7 presents the DSC traces of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((n-pentyloxy)benzene) (5C-HFH-5C) on both heating and cooling, at temperatures ranging from 20°C to 240 °C. The traces reveal one 1st order phase transition at 186 °C on heating and 182 °C on cooling. At 186 °C on heating cycle (182 °C on cooling cycle) the molecules melt from crystalline phase to the isotropic melt.

Figure 4.8 Differential Scanning Calorimetry Traces of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((n-octyloxy)benzene) On (A) Heating and (B) Cooling.
Figure 4.8 presents the DSC traces of 4,4'-((1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((n-octyloxy)benzene) (8C-HFH-8C) on both heating and cooling, at temperatures ranging from 20 °C to 250 °C. The traces reveal three 1st order phase transitions. At 136 °C on heating (131 °C on cooling) the molecules show a phase transition between two crystalline phases. At 158 °C on heating (154 °C on cooling) the molecules show a phase transition between a crystalline phase and a liquid crystalline phase. At 181 °C on heating cycle (180 °C on cooling cycle) the molecules show phase transition between a liquid crystalline phase and the isotropic melt.
Table 4.1. Thermo Transition and Thermodynamic Parameters 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(n-alkoxybenzene) On Heating and Cooling.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase Transition, °C (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2C-HFH-2C</td>
<td>k1 158 (9.57) k2 208 (25.67) i [i 203 (11.12) k2 110 (25.08) k1]</td>
</tr>
<tr>
<td>3C-HFH-3C</td>
<td>k 202 (29.80) i [i 194 (28.80) k]</td>
</tr>
<tr>
<td>4C-HFH-4C</td>
<td>k1 167 (6.21) k2 188 (21.82) i [i 164 (6.22) k2 185 (21.93) k1]</td>
</tr>
<tr>
<td>5C-HFH-5C</td>
<td>k 186 (35.31) i [i 182 (32.98) k]</td>
</tr>
<tr>
<td>8C-HFH-8C</td>
<td>k1 136 (10.25) k2 158 (21.07) (n) 181 (1.24) i [i 180 (1.21) (n) 154 (21.21) k2 131 (10.70) k1]</td>
</tr>
</tbody>
</table>

Table 4.1 summarizes the phase transitions and corresponding thermodynamic parameters of five molecules on heating and cooling. The melting temperatures decrease with increasing length of the alkoxy groups. This is consistent with previous study concerning 1,4-bis[(4’-n-alkoxybenzoyl)oxy]toluenes. Of these five compounds, only the molecule with n=8 (8C-HFH-8C) exhibits a (nematic) liquid crystalline phase.
A series of 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(n-alkoxybenzene), with n = 1 to 12, were synthesized by a three step strategy. The use of 4Å molecular sieves (5 wt % to the volume of DMF) sharply increases the yield of the first step reaction. Thermotropic behaviors of 5 out of 12 molecules (n=2~5, 8) were studied via differential scanning calorimetry. The melting temperature decreases with increasing length of the alkoxy groups until a liquid crystalline phase is revealed. 4,4’-((1E,1’E)-(Perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((n-octyloxy)benzene) shows a 23 °C temperature range of liquid crystalline behavior.
REFERENCES


1. $^1$H and $^{19}$F NMR Spectra of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(tert-butoxybenzene)
2. $^1$H and $^{19}$F NMR Spectra of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))diphenol
3. $^1$H and $^{19}$F NMR Spectra of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(methoxybenzene)
4. $^1$H and $^{19}$F NMR Spectra of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(ethoxybenzene)
5. $^1$H and $^{19}$F NMR Spectra of 4,4'-(1E,1' E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(propoxybenzene)

![NMR spectra](image)

$^{1}$H-NMR

$^{19}$F-NMR

Chemical Shift (ppm)

$^3$COOH

ArF
6. $^1$H and $^{19}$F NMR Spectra of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(butoxybenzene)
7. $^1$H and $^{19}$F NMR Spectra of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(pentyloxybenzene)
8. $^1$H and $^{19}$F NMR Spectra of 4,4'-(((1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(hexyloxybenzene)
9. $^1$H and $^{19}$F NMR Spectra of 4,4'-(1E,1′E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis(heptyloxybenzene)
10. $^1$H and $^{19}$F NMR Spectra of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((octyloxy)benzene)
11. $^1$H and $^{19}$F NMR Spectra of 4,4'-((1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((nonyloxy)benzene)
12. $^1$H and $^{19}$F NMR Spectra of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((decyloxy)benzene)
13. $^1$H and $^{19}$F NMR Spectra of 4,4'-(1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((undecyloxy)benzene)
14. $^1$H and $^{19}$F NMR Spectra of 4,4’-((1E,1’E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))bis((undecyloxy)benzene)