This doctoral thesis has been examined by a Committee of the Department of Chemistry as follows:

Professor Rick L. Danheiser: [Signature] Chairman

Professor Timothy M. Swager: [Signature] Thesis Advisor

Professor Sarah E. O'Connor: [Signature] Department of Chemistry
For Bingling and my parents
ORGANIC MATERIALS WITH ACENOID AND IPTYCENE STRUCTURES

BY

ZHIHUA CHEN

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ABSTRACT

Chapter 1. The synthesis of a group of alkoxy-substituted para-acenequinones and their photophysical properties in solution and liquid crystal are reported. Polarized absorption and fluorescence measurements demonstrate that these acenequinones have excellent alignment with nematic LC hosts, indicating their potential as dichroic dyes for guest-host liquid crystal displays. In addition, the sensitivity of emission to the substitution allows the tuning of emission by functionalization of the acenequinone chromophore.

Chapter 2. The synthesis of a series of fluorine- and alkyl/alkoxy-functionalized tetracenes using N-methyl-1,2,4,5-tetrafluoroisoindole as a synthetic building block is reported. The incorporation of fluorine functionalities was found to induce significant face-to-face molecular π-stacking in their crystal structures. Electrochemical behaviors and UV-vis absorbance spectroscopy results of these materials are also discussed. It was demonstrated that the substitution of alkyl/alkoxy groups on the main chain not only provided better solubility in common organic solvents, but also subtly tuned the crystal structures and electrochemical behaviors.

Chapter 3. A self-polymerizable AB-type monomer for Diels-Alder (D-A) polymerization was prepared, and its polymerization was carried out in the melt phase and at high pressure in solution. The former method generated only low molecular weight polymer, but the latter one offered an efficient polymerization with increased molecular weight, due to the effect of high-pressure on reactions with a negative activation volume. A pyridinium p-toluenesulfonate catalyzed dehydration reaction of the D-A polymer led to a novel aromatic ladder polymer, poly(iptycene), which is soluble in common organic solvents and stable up to 350 °C. The NMR and UV–vis spectra of these polymers match the spectra of their corresponding model compounds, and their synthesis is also reported.

Chapter 4. Two diamino functionalized iptycene monomers were successfully synthesized via two synthetic routes: a direct nitration of triptycene followed by a reduction with hydrazine and D-A reaction between a benzo-fused 1,4-endoxide and 2,6-diaminoanthracene followed by a strong acid catalyzed dehydration. Their applications in the synthesis of novel
triptycene-containing polyimides and polyureas were investigated and the resulting polymers were characterized by NMR, FT-IR, and UV-vis absorption spectroscopy.

Chapter 5. Iptycene type quinoxaline and thienopyrazine monomers were successfully synthesized via a condensation between 10-dihydro-9,10-ethanoanthracene-11,12-dione and the corresponding diamines. Copolymers based on fluorene and these new iptycene monomers were prepared via Suzuki coupling reaction, and they exhibited good solubility in appropriate organic solvents. These copolymers are fluorescent both in solution and the solid state, emitting blue, greenish-blue, and red color, due to the electronic properties of the iptycene comonomers. The difference in their absorption and emission spectra was attributed to the donor-acceptor charge transfer interactions and/or polymer backbone conformation change induced by steric effects. Moreover, the spectroscopic data clearly demonstrated the insulating effect of iptycene units, which prevented the aggregation of the polymer chains and formation of excimers in the solid state.
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CHAPTER 1

Acenequinones as Dyes for Guest-Host Liquid Crystal Displays

Adapted from:

Introduction

Liquid Crystals

The three common states of matter are solid, liquid, and gas. Crystalline solids are highly ordered and the constituting atoms or molecules stay in a fixed position and orientation with a small amount of variation from vibrations. Such arrangements result from the large attractive forces holding the molecules in place and therefore a solid is difficult to deform. On the contrary, molecules in the liquid and gas phase have no fixed position and orientation and they are free to move in a random fashion. In addition, a liquid can be easily deformed and gas molecules can spread out to fill any container that holds them. The differences between these three states can be attributed to the temperature of the substance, which is a measure of the randomness of the molecules. Increasing temperature will cause the transition from a solid to a liquid and then to a gas, and decreasing the temperature will reverse the phase transitions.  

Liquid crystals (LCs) are a class of materials that can exhibit intermediate thermodynamic phases between the crystalline solid and simple liquid. In contrast to the three common states of matter, molecules in LC phase possess orientational (and weak positional) order. Therefore, LCs reveal several physical properties of crystals, but flow like fluids. When a substance shows LC behavior in a temperature region between the solid and liquid states, this type of material is called thermotropic LCs (Figure 1.1). In blends of different components, their phase transitions may depend on both the temperature and the concentration of one component of the mixture. If the LC phase of a mixture is dependent on the concentration in a non-LC solvent, it is called lyotropic LC. While thermotropic LCs are presently mostly used for technical applications, lyotropic LCs are important for biological
Not all substances, however, can have a liquid crystal phase. It has been recognized that molecules that tend to have a thermotropic LC phase have a rigid central region and flexible ends.\textsuperscript{1,2} This leads to two major subclasses of LCs based on the molecular structures: rod-shaped and disk-shaped molecules (Figure 1.2). In addition, polymers and polymer solutions can also exhibit LC phases.\textsuperscript{1,2} Regardless of their molecular structures, LCs can also be classified according to their symmetries and degree of long-range order. In the simplest case, the molecules possess only orientational but no positional long-range order. This type of LCs is called nematic, and this name was given as a result of the thread-like textures observed under polarizing microscope.\textsuperscript{1-3} The direction of preferred alignment can be described by a unit vector, the so-called LC director. Smectics are another common type of LCs, which have a soapy texture and retains some positional order with the molecules arranged in layers. In addition, smectic phases are characterized by additional degrees of positional order, which will not be discussed here. Discotic molecules often form columnar types of LC arrangements (see examples in Figure 1.2).
Figure 1.2. Schematic illustration of nematic and semectic LC phases of rod-shaped molecules, and columnar LC phase of disk-shaped molecules.

The most remarkable features of LCs for applications are their anisotropic optical properties, which mean that the properties of LC materials depend on the direction from which the measurements are made. Since light is an electromagnetic wave, the behavior of light as it passes through a liquid crystal will also strongly depend on the direction of its propagation and polarization with respect to the director of the LC. The anisotropies of LC materials arise from the positional or orientational order in the LC phase. This kind of orientational order gives birefringence that can be manipulated by magnetic, electric or optical fields, leading to huge magneto-optical, electro-optical and opto-optical effects. For example, applying a weak electric field to a liquid crystal molecule with a permanent electric dipole will cause the dipole to align with the field. If the molecule did not originally have a dipole, then it is induced when the field is applied. Either of these situations has the ultimate effect of aligning the director of the liquid crystal with the electric field being applied. In these cases, the order of the liquid crystal has not increased, and we have only achieved alignment of the director.
**Liquid Crystal Displays**

The most successful application of liquid crystal materials is liquid crystal displays (LCDs), which are well known in pocket calculators, digital cameras, and flat screens of laptop computers. This application takes advantage of electro-optical effects of LCs. As compared to the traditional cathode-ray tube (CRT) displays, LCDs offer several advantages that make them ideal for several applications. Firstly, LCDs are flat, and they use less power than that required by CRTs. They are easier to read and more pleasant to work with for long periods of time than most ordinary video monitors. Although there were several tradeoffs, such as limited view angle, brightness, or contrast, as well as high manufacturing cost, the continuing research

![Figure 1.3](image-url)
and development has made these limitations less significant. Computer monitors using these techniques have replaced CRT monitors to a large extent, and LCD TVs that use LCD technology for its visual output have achieved satisfactory picture quality and have captured part of the TV market from traditional CRTs.\(^6\)

LCDs based on the twisted nematic (TN) mode are the most common flat panel displays.\(^5,6\) A schematic representation of a TN LCD cell is shown in Figure 1.3. Basically, each pixel of an LCD consists of a layer of molecules aligned between two transparent electrodes and two polarizing filters, the axes of polarity of which are perpendicular to each other. The surfaces of the electrodes that are in contact with the liquid crystal material are treated with rubbed polyimide films (please see Chapter 4 for more details) so as to align the liquid crystal molecules in a particular direction.\(^5\) Before applying an electric field, the orientation of the liquid crystal molecules is determined by the alignment at the surfaces. In a TN device, the surface alignment directions at the two electrodes are perpendicular to each other, and therefore, the molecules arrange themselves in a helical structure. Because the liquid crystal material is birefringent, light passing through one polarizing filter is rotated by the liquid crystal helix as it passes through the liquid crystal layer, allowing it to pass through the second polarized filter (Figure 1.3 (a)). When a voltage is applied across the electrodes, a torque acts to align the liquid crystal molecules parallel to the electric field, distorting the helical structure. If the applied voltage is large enough, the liquid crystal molecules are completely untwisted and the polarization of the incident light is not rotated at all. This light will then be polarized perpendicular to the second filter, and thus be completely blocked and the pixel will appear black (Figure 1.3 (b)). By controlling the voltage applied across the liquid crystal layer in each
pixel, light can be allowed to pass in varying amounts, correspondingly illuminating the pixel. When the electric field is turned off, LC molecules will relax back into its twisted structure and light will again be able to pass through. In some displays, the polarizers are parallel to each other, thus reversing the on and off states. If red, green, and blue colored filters are used on groups of three pixels, a color display can be created. 1

**Guest-Host Effect and Guest-Host Liquid Crystal Displays**

Guest-host liquid crystal displays (GH-LCDs) that use a LC/dye mixture as the active material have received much attention since their invention in the 1960s because of their wider viewing angle, daylight readability, and high stability in harsh environments. 7-10 Guest-host displays operate by the absorption of light by dichroic dye molecules oriented in a liquid crystal. A schematic representation of the operational principle of GH-LCD cell is shown in Figure 1.4. Similar to the TN-LCD device, a typical GH-LCD cell consists of a mixture of a dichroic dye (guest) and LC medium (host), which is sandwiched into a thin layer between two transparent plates. However, the rubbing directions of alignment layers (unidirectional rubbed polyimide film) coated on the plates are parallel with each other. This feature will lead to a homogenous alignment of the LC molecules in the cell if no voltage is applied (Figure 1.4). The dichroic dyes used in GH-LCDs are designed such that they tend to align preferentially along the director of the LC layer. When a voltage is applied, reorientation of the LC director causes a corresponding reorientation of the dissolved dye molecules (Figure 1.4). The dichroic dyes adsorb light more along one molecular axis than the others. Usually the optical transition moments of the dye also align with the LC directors, and, the color intensity of the cell can be controlled through the direction of LCs. An important difference with the widely used
TN-LCD is the fact that a TN-LCD owes its optical switching to the presence of two external polarizers, while the GH-LCD involve the LC layer in the light absorption process.

![Diagram of GH-LCD operation principle](image)

**Figure 1.4.** Schematic illustration of the operation principle of a GH-LCD cell.

Therefore, the optimal performances of GH-LCDs depend on the dichroic properties of dyes, their solubility in LC host, and stability under various environments. Anthraquinone and azo derivatives are the two major classes of dyes receiving most intensive study. 

Although the GH electro-optic effect was first filed for patent in 1965, this technology got off to a slow start owing to the poor contrast of original devices and lack of suitable LCs and dichroic dyes. The development of room-temperature LC materials and photochemically stable anthraquinone dyes with high dichroic ratios offered an opportunity of revival of interest in the 1970s. Dramatic improvement of GH technology came from the efforts of White and Taylor,
who introduced a device without polarizers and demonstrated that excellent optical performance could be achieved if dichroic dyes with higher order parameter were combined with an LC mixture that had a helical structure of small molecular pitch. In the 1980s, high-performance dichroic dyes, which combined the good photochemical stability of the early anthraquinone dyes with the high order parameters of the early azo dyes, were reported in the 8th International Liquid Crystal Conference. Many of these new anthraquinone-based dyes had high solubility in common LC hosts. Today ready-to-use black guest-host mixtures are commercially available.

The main attractive features of GH devices are a very wide viewing angle, high brightness, no need for polarizers, and ability to produce colored displays. The most common configuration for GH-LCDs at present is a display with negative contrast (light characters on a dark background). This may be considered to be identical to all emissive display technologies in common use today. Generally, the GH-LCD is best suited for display applications where a
lower information density is acceptable (direct drive applications) and a wide viewing angle, high brightness, or multiple color contrast is desired. TN-LCDs are best suited for higher information density applications such as portable terminals and other such alpha numeric or limited graphic applications. GH-LCDs have reached the point where they can begin to create their own market because they allow for the designer flexibilities previously not readily obtainable. Color can be used in more ways than increasing the “perceived value” or “fashionability” of consumer products. The use of color designation, especially in pseudoanalog meter and bar graph types of applications, greatly enhances the functionality of products. Recently, a company called AlphaMicron in Kent, OH has developed interesting ski-goggles, visors for pilots, and digital mirrors for automobiles based on GH-LCD technologies (Figure 1.5).

Recently, fluorescent dye-based GH-LCDs, which combine the excellent hues and high brightness levels of emissive displays with the desirable features of LCDs, have been proposed as a less energy consuming display for portable electronics. For fluorescent dyes in LCs, the fluorescence intensity can be controlled in a similar way as absorption. Therefore, the development of fluorescent GH-LCDs requires synthesis of fluorescent dyes with a high dichroic ratio, a high quantum yield, and a strong emission in the visible region. Additionally, the rod-like shape of nematic LC molecules favors alignment of elongated, rod-like dye molecules along the direction of long molecular axis of nematic LC molecules. In this study, we report emissive linear para acenequinone dyes with large dichroic ratios in LC mixtures. We describe the syntheses of a group of alkoxy-substituted acenequinone derivatives, their solution absorption and emission spectra, and polarized absorption and emission spectra of
their LC solutions. These compounds demonstrated strong orientation properties and have excellent potential as fluorescent dyes for GH-LCDs.

Results and Discussion

Synthetic methodologies for preparing linear para acenequinones have been previously reported, and the Diels-Alder (D-A) reaction between isobenzofurans (or their analogues) and linear 1,4-quinones is one of the more efficient approaches. In this work, we employed 3,6-di-2-pyridyl-1,2,4,5-tetrazine (DPT) and anthracene 1,4-endoxide to generate an isonaphthofuran, which is subsequently trapped by a quinone via a D-A mechanism. The D-A adducts are then easily converted into corresponding acenequinones.
This methodology avoids direct use of isobenzofuran/isonaphthofuran compounds, which are difficult to synthesize and are generally unstable. It has also allowed us to prepare various substituted acenequinones.

The synthetic route to a para pentacenequinone is outlined in Scheme 1.1. The starting 6,7-dibromo-2,3-dihydroxynaphthalene (1), which was prepared from 2,3-dihydroxynaphthalene in two steps via a literature procedure,\(^{18}\) was converted to 2 by a Williamson ether synthesis. Intermediate 2 was treated with phenyllithium (PhLi) in presence of excess of furan, at low temperature, to produce 3. The generation of 4 was successfully accomplished by treating 3 with DPT, in the presence of 1,4-naphthoquinone. Pentacenequinone 5 was then obtained from dehydration of 4, which could be realized by employing acetic acid,\(^{17b}\) \(p\)-toluenesulfonic acid (\(p\)-TsOH)/toluene\(^{15c}\) or pyridinium \(p\)-toluenesulfonate (PPTS)/acetic anhydride.\(^{19}\) We found the PPTS approach affords clean
product in a satisfactory yield by a simple filtration. Compound 5 is an orange/red solid, with high melting point and excellent thermal and photochemical stability.

**Scheme 1.3. Synthesis of tetrafluoroanthraquinone 7**

![Diagram of Scheme 1.3](image)

**Scheme 1.4. Synthesis of heptacenequinone 14**

![Diagram of Scheme 1.4](image)

Similar methodology allowed us to successfully synthesize two para hexacenequinones (10 and 11) from the corresponding 1,4-anthraquinones (6 and 7) as the dienophiles (Scheme 1.2). Dienophile 6,7,8,9-tetrafluoro-1,4-anthraquinone (7) was synthesized previously from the
oxidation of corresponding 1,4-hydroquinone. Here we report a more convenient route, as shown in Scheme 1.3. A Friedel-Crafts bis-cycloacylation of 1,4-dihydroxybenzene and 3,4,5,6-tetrafluorophthalic anhydride was conducted in a melt of aluminum chloride/sodium chloride (AlCl₃/NaCl) to give tetrafluoroquinizarin. Reduction of 12 with sodium borohydride (NaBH₄) and a subsequent dehydration with concentrated aqueous HCl afforded 7 as a dark-brown solid.

Using 1,4-benzoquinone as the limiting reagent, we prepared a tetraalkoxy-substituted heptacenequinone (14) (Scheme 1.4). Interestingly, the only detected products are exo/exo and exo/endo isomers of 13. Dehydrating both isomers yields heptacenequinone 14 as a yellow/orange solid.

A solution of the acenequinones possess a characteristic strong absorption band at 350–400 nm and a second absorption band at 420–500 nm (Figure 1.6 (A)), both of which can be assigned as \(1(\pi, \pi^*)\) absorptions. When compared to their non-substituted hydrocarbon analogues, these acenequinone compounds have broadened absorption peaks that are red-shifted by about 20–30 nm. These differences are the result of intramolecular charge transfer (ICT) character between electron-withdrawing quinoid moiety and electron-donating alkoxy sidechains.
**Figure 1.6.** Uv-vis absorption spectra (A) and fluorescence spectra (B) of acenequinones in toluene (5: red; 10: green; 11: blue; 14: black).

**Table 1.1.** Absorption and Emission Maxima and Quantum Yields of Acenequinones in Toluene

<table>
<thead>
<tr>
<th>compd</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
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<tr>
<td>14</td>
<td>376</td>
<td>484</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>470</td>
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</table>

$^a$Fluorescence quantum yield relative to coumarin 153 ($\Phi_{\text{rel}} = 0.38$).
All the acenequinone derivatives are fluorescent in solution, with the relative quantum yields ranging from 0.18 to 0.30 (Table 1.1). Figure 1.6 (B) displays the fluorescence spectra of the acenequinones in toluene. The fluorescence spectra reveal that the emission maximum ($\lambda_{em}$) of 10 has a 30 nm blue-shift as compared to that of 5. This blue shift results from the reduced ICT character of 10, because the naphtho-fused quinoid group has weaker electron-withdrawing properties than the benzo-fused quinoid group in 5.\textsuperscript{13a} Such an effect was also demonstrated by the 35 nm red-shift of the $\lambda_{em}$ of 11 and the 10 nm blue-shift of the $\lambda_{em}$ of 14, with respect to the $\lambda_{em}$ of 10. Clearly, the fluorine groups significantly enhance the ICT character in 11.\textsuperscript{13d} These results show that photophysical properties of para acenequinones can be tuned by attaching suitable functional groups.

The orientation properties of acenequinone dyes in LCs host were investigated via the measurement of polarized absorption and fluorescent spectra in aligned test cells. Samples were prepared by loading dye/LC fluids (0.1–0.5wt% dye in MLC-6884) into LC test cells. The dye/LC mixture forms a homogenously aligned structure, and the polarized UV-vis absorption and emission spectra were determined.
Figure 1.7. Polarized absorption (A) (solid line: $A_{//}$; dotted line: $A_{\bot}$) and fluorescence spectra (B) (solid line: $I_{//}$; dotted line: $I_{\bot}$) of 5 in MLC-6884. The vertical dotted-dashed lines indicate the wavelengths of dichroic ratios reported.

The polarized absorption spectra of acenequinone 5 in LC host are displayed in Figure 1.7 (A). The anisotropy of molecular absorption transition moments is in agreement with our preliminary calculations that reveal the transitions of the two major absorption bands are aligned with the long molecular axis. Therefore, dichroic ratio ($D_A$) and order parameter ($S_A$) of a dye in LC can be calculated by using the following equations:

$$D_A = A_{//} / A_{\bot}$$
$$S_A = (A_{//} - A_{\bot}) / (A_{//} + 2A_{\bot})$$

where $A_{//}$ and $A_{\bot}$ represent the absorbance for parallel and perpendicular irradiation with respect to LC director. As summarized in Table 1.2, those compounds demonstrated dichroic ratios in the range of 8–10, indicating their excellent alignment in the LC host. It has been reported
that dyes with dichroic ratio greater than 8 are appropriate for practical use.\textsuperscript{13b}

Figure 1.7 (B) shows the representative polarized fluorescence spectra. The dichroic ratio \((D_F)\) and order parameter \((S_F)\) based on polarized fluorescence can be calculated by using the following equations:

\[
D_F = \frac{I_{//}}{I_{\perp}}
\]

\[
S_F = \frac{(I_{//} - I_{\perp})}{(I_{//} + 2I_{\perp})}
\]

where \(I_{//}\) and \(I_{\perp}\) represent the emission intensity for parallel and perpendicular irradiation with respect to LC director.\textsuperscript{25} Order parameter values from the polarized fluorescence are similar

\begin{table}[h]
\centering
\caption{Spectral Characterizations, Dichroic Ratios, and Order Parameters of Acenequinones in MLC-6884}
\begin{tabular}{cccccccc}
\hline
compd & \(\lambda_{\text{max}}\) (nm) & \(D_A\) & \(S_A\) & \(\lambda_{\text{em}}\) (nm) & \(D_F\) & \(S_F\) \\
\hline
5 & 368 & 8.1 & 0.70 & 522 & 9.2 & 0.73 \\
   & 478 & 8.8 & 0.72 &  \\
10 & 373 & 8.8 & 0.72 & 504 & 10.4 & 0.76 \\
   & 470 & 9.6 & 0.74 &  \\
11 & 383 & 8.9 & 0.72 & 532 & 10.1 & 0.75 \\
   & 485 & 10.0 & 0.75 &  \\
14 & 380 & 8.7-12.8\textsuperscript{a} & 0.72-0.80\textsuperscript{a} & \_\textsuperscript{b} & \_\textsuperscript{b} & \_\textsuperscript{b} \\
   & 477 & 7.7-8.8\textsuperscript{a} & 0.69-0.72\textsuperscript{a} &  \\
\hline
\end{tabular}
\end{table}

\textsuperscript{a} The exact \(D_A\) and \(S_A\) of 14 could not be obtained due to the strong interference from test cell. \textsuperscript{b} The \(D_F\) and \(S_F\) of 14 could not be determined due to its low relative quantum yield and poor solubility in LCs.
Figure 1.8. Fluorescent images of a test cell containing 5 in E7 (A: no applied voltage; B: 9 V applied voltage). The sample was excited with a 365 nm light from a hand-held UV-lamp.

to those from the polarized absorption spectra (Table 1.2). Compounds 10 and 11 have higher aspect ratios and as expected have higher orientation properties than 5. This feature agrees with the classic model that elongation of dichroic dye molecules should enhance their orientation in nematic LCs. The fluorescence maxima of acenequinones in LCs were found to have a small blue-shift (7–13 nm) as compared to those in toluene solution. This feature is likely due to the different dielectric properties of each medium.

The reorientation of dyes under electric field was demonstrated in a test cell (Figure 1.8), containing a solution of 0.2wt% 5 in E7 (a commercial LC mixture with positive dielectric anisotropy). Because the test cell is coated with parallel rubbed polyimide films, the LC/dye mixture forms a homogeneously aligned texture, with the long molecular axis of LCs and dyes parallel with rubbing direction. Therefore, acenequinone dyes in this orientation give strong emission when they are excited by a UV light (Figure 1.8 (A)). Upon application of an electric field, the LC director and acenequinone backbones align normal to the surface of the test cell. Consequently, the transition dipole of dye compound is parallel to the direction of incident light, resulting in decreased projection of the transition dipole along the electric vector of
incident UV light and minimal absorption and emission (Figure 1.8 (B)).\textsuperscript{13e,26} The polarized fluorescence is rapidly recovered upon removal of the voltage.

**Conclusion**

In summary, we have reported a convenient synthesis of substituted para acenequinones by employing DPT and an anthracene 1,4-endoxide. The polarized absorption and fluorescence results demonstrate that acenquinones align with nematic LC hosts, indicating their potential as dichroic dyes for GH-LCDs. In addition, the sensitivity of the emission to the substitution allows the tuning of fluorescence by functionalization of the acenequinone chromophore.

**Experimental Section**

**Materials:** Anhydrous tetrahydrofuran (THF) and toluene were purchased from Mallinckrodt Baker Inc. Furan was distilled from K$_2$CO$_3$ prior to use. Starting materials, 2,3-dibromo-6,7-dihydroxynaphthalene (1)\textsuperscript{18} and 1,4-anthraquinone (6)\textsuperscript{22}, were prepared following literature procedures. All other reagent-grade starting materials were purchased from Aldrich, Lancaster, or Alfa Aesar, and used without further purification. Liquid crystal test cells with 10 μm gap and parallel rubbed polyimide coatings were purchased from E.H.C. Co. Ltd, Tokyo, Japan. MLC-6884 is a liquid crystal mixture (negative dielectric anisotropy) for active matrix addressed ECB liquid crystal displays (LCDs) and it was purchased from EMD Chemicals Inc. E7 is a liquid crystal mixture with positive dielectric anisotropy and it was donated by Merck Chemicals Ltd. (UK). The composition of E7 is shown in Chart 1.1.
**Chart 1.1. Molecular composition of E7**

General Methods and Instrumentation: Column chromatography was performed using silica gel (40–63 μm) from SiliCycle. NMR ($^1$H, $^{13}$C, $^{19}$F) spectra were recorded on Varian Mercury-300 MHz, Varian Inova-500 MHz or Bruker Advance-400 MHz spectrometers. The $^1$H and $^{13}$C chemical shifts are given in unit of $\delta$ (ppm) relative the tetramethylsilane (TMS) where $\delta$(TMS) = 0 and are referenced to the residual solvent. The $^{19}$F NMR chemical shifts are reported in ppm relative to hexafluorobenzene ($\delta$ = -164.9 ppm). High-resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APED II 3T FT-ICR-MS using electron impact ionization (EI) or electrospray ionization (ESI). Melting points were measured on a Mel-Temp II apparatus (Laboratory Devices Inc.) and were not corrected. UV-vis spectra were obtained from Hewlett-Packard 8452A diode array UV-visible spectrophotometer or Cary 50 UV/Visible spectrometer. Fluorescence spectra were measured with a SPEX Fluorolog-3 fluorometer (model FL112, 450W xenon lamp). Fourier Transform infrared (FT-IR) spectra were measured on a Perkin-Elmer model 2000 FT-IR spectrophotometer using the Spectrum v. 2.00 software package.

Polarized UV-vis absorption and fluorescence measurement: A solution of acenequinone in MLC-6884 (0.1-0.5wt%) was loaded into a LC test cell via capillary action. The test cell
consists of two glass plates coated with transparent electrodes (Indium tin oxide) (1 cm × 1 cm) and parallel rubbed polyimide thin films (Figure 1.9). The polarized UV-vis absorption spectra

![Figure 1.9. Schematic diagram of the LC test cell.](image)

Excite Vertical or Horizontal

**Light Source** → **Rub direction** → **Sample** → **Monochromator** → **Detector**

**Dichroic Ratio (N):**

\[ N_F = \frac{I_\|}{I_\perp} = \frac{I_{VV}}{G \times I_{VH}} \]

**Order Parameter (S):**

\[ S_F = \frac{I_\| - I_\perp}{I_\| + 2I_\perp} = \frac{(I_\| / I_\perp) - 1}{(I_\| / I_\perp) + 2} = \frac{N_F - 1}{N_F + 2} \]

*Figure 1.10. Schematic diagram of the measurement system used to determine the degree of polarized emission and the calculation of dichroic ratio and order parameter based on polarized fluorescence.*
were obtained by irradiating the cell with polarized lights parallel and perpendicular to the rubbing direction of the test cell. Polarized fluorescence measurements were carried out according to the procedure previously reported by Breen et al. A schematic description of the set-up for measuring polarized fluorescence is shown in Figure 1.10.

2,3-Dibromo-6,7-bis(hexyloxy)naphthalene (2): In an oven-dried 100 mL round-bottom flask equipped with a stir bar were combined 1 (2.1 g, 6.6 mmol), 1-iodohexane (3.0 mL, 20 mmol), potassium carbonate (9.8 g, 71 mmol), 18-crown-6 (0.1 g) and nitrogen-bubbled DMF (50 mL). The mixture was stirred under Ar at 85 °C for 5 d. After cooling to room temperature, the reaction mixture was poured into 200 mL water and the product was extracted with CH₂Cl₂. The organic layer was washed by dilute NH₄Cl aqueous solution and saturated NaCl aqueous solution, and then dried over MgSO₄. Solvent was removed in vacuo and the residue was purified by column chromatography on silica gel with CH₂Cl₂:hexane (1:5 up to 1:3, v/v), yielding a white solid as the product (3.2 g, 87%), which is pure enough for next step. A small portion of the product was recrystallized to obtain analytical pure sample for melting point measurement. mp 66-67 °C (methanol). ¹H NMR (300 MHz, CDCl₃) 7.92 (s, 2H), 6.96 (s, 2H), 4.08 (t, J = 6.6 Hz, 4H), 1.90 (m, 4H), 1.52 (m, 4H), 1.38 (m, 8H), 0.93 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) 150.6, 130.6, 129.4, 119.4, 106.3, 69.1, 31.8, 29.1, 25.9, 22.8, 14.2. FT-IR (KBr) v/cm⁻¹: 2956, 2925, 2852, 1506, 1466, 1405, 1381, 1347, 1250, 1164, 1043, 994, 945, 881. HRMS (EI) calcd for C₂₂H₃₀Br₂O₂ (M⁺) 484.0608, found 484.0608.

1,4-Epoxy-6,7-bis(hexyloxy)-1,4-dihydroanthracene (3): Under Ar, a stirred mixture of 2 (2.5 g, 5.1 mmol), furan (25 mL) and anhydrous THF (80 mL) was cooled by an ice-water bath.
A solution of phenyllithium (PhLi) in cyclohexane/ether (6 mL, 1.5-1.7 M) was then added dropwise over a course of 4 h. After the addition of PhLi, the mixture was stirred at 0 °C for an additional 2 h, and then allowed to warm to room temperature slowly and stirred overnight. Methanol (4 mL) was added slowly to quench the reaction. The reaction mixture was poured into water and the product was extracted by CH$_2$Cl$_2$. The organic layer was washed by saturated NaCl aqueous solution and dried over MgSO$_4$. Solvent was removed in vacuo. Purification by column chromatography on silica gel with CH$_2$Cl$_2$:hexane (2:1 up to 3:1, v/v) afforded the title compound as a white solid (1.8 g, 89%), which is pure enough for next step. A small portion of the product was recrystallized to obtain analytical pure sample for melting point measurement. mp 102-103 °C (methanol). $^1$H NMR (400 MHz, CDCl$_3$) 7.46 (s, 2H), 7.07 (s, 2H), 6.97 (s, 2H), 5.78 (s, 2H), 4.09 (t, $J = 6.4$ Hz, 4H), 1.89 (m, 4H), 1.53 (m, 4H), 1.38 (m, 8H), 0.93 (t, $J = 6.8$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) 149.4, 142.9, 142.0, 127.0, 117.8, 109.4, 82.1, 69.1, 31.8, 29.3, 25.9, 22.8, 14.2. FT-IR (KBr) v/cm$^{-1}$: 2954, 2929, 2856, 1617, 1507, 1453, 1384, 1251, 1153, 1068, 983, 866, 841. HRMS (EI) calcd for C$_{28}$H$_{34}$O$_3$ (M$^+$) 394.2503, found 394.2512.

**exo/endo-6,13-Epoxy-5a,6,13,13a-tetrahydro-9,10-bis(hexyloxy)pentacene-5,14-dione (4):**

A mixture of 3 (0.44 g, 1.1 mmol), 3,6-di-2-pyridyl-1,2,4,5-tetrazine (DPT) (0.27 g, 1.1 mmol), 1,4-naphthoquinone (0.18 g, 1.1 mmol) and toluene (50 mL) was stirred at 100 °C under Ar for 4 d. After cooling to room temperature, the reaction mixture was concentrated on a rotary evaporator. The residue was dissolved in CH$_2$Cl$_2$ and then washed in sequence with HCl aqueous solution (5%), water and saturated NaCl aqueous solution. Solvent was removed in vacuo. Purification by column chromatography on silica gel with ethyl acetate:hexane (1:6 up...
to 1:4, v/v) afforded both endo (0.12 g) and exo product (0.43 g) as a slightly yellow solid (94%). Exo: $^1$H NMR (400 MHz, CDCl$_3$) 8.15 (dd, $J = 6.0$, 3.2 Hz, 2H), 7.77 (dd, $J = 6.0$, 3.2 Hz, 2H), 7.64 (s, 2H), 7.12 (s, 2H), 5.86 (s, 2H), 4.10 (t, $J = 6.4$ Hz, 4H), 3.12 (s, 2H), 1.90 (m, 4H), 1.54 (m, 4H), 1.39 (m, 8H), 0.94 (t, $J = 6.8$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) 195.6, 149.8, 140.2, 135.6, 134.7, 128.4, 127.4, 116.9, 108.6, 85.4, 69.0, 53.1, 31.8, 29.2, 25.9, 22.8, 14.2. FT-IR (KBr) v/cm$^{-1}$: 2956, 2920, 2856, 1669, 1589, 1502, 1460, 1390, 1296, 1271, 1248, 1158, 972, 866, 850, 821. HRMS (EI) calcd for C$_{34}$H$_{38}$O$_5$ (M$^+$) 526.2714, found 526.2708; Endo: $^1$H NMR (400 MHz, CDCl$_3$) 7.63 (dd, $J = 6.0$, 3.2 Hz, 2H), 7.29 (dd, $J = 6.0$, 3.2 Hz, 2H), 7.27 (s, 2H), 6.84 (s, 2H), 5.93 (dd, $J = 3.2$, 2.0 Hz, 2H), 3.97 (t, $J = 6.8$ Hz, 4H), 3.86 (dd, $J = 3.2$, 2.0 Hz, 2H), 1.82 (m, 4H), 1.47 (m, 4H), 1.34 (m, 8H), 0.90 (t, $J = 6.8$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) 194.8, 149.4, 137.6, 134.1, 133.9, 128.2, 126.4, 118.5, 108.2, 82.9, 68.8, 50.9, 31.7, 29.1, 25.8, 22.7, 14.2. FT-IR (KBr) v/cm$^{-1}$: 2952, 2930, 2856, 1678, 1617, 1594, 1502, 1454, 1390, 1300, 1271, 1248, 1191, 1158, 1014, 985, 940, 895, 854. HRMS (EI) calcd for C$_{34}$H$_{38}$O$_5$ (M$^+$) 526.2714, found 526.2737.

9,10-Bis(hexyloxy)pentacene-5,14-dione (5): A mixture of 4 (0.31 g, 0.59 mmol), pyridinium p-toluenesulfonate (PPTS) (1.48 g, 5.9 mmol) and acetic anhydride (10 mL) was stirred at 80 °C for 16 h. After the reaction mixture was cooled to room temperature, the precipitate was collected by filtration, washed thoroughly with methanol and dried in vacuum, affording the title compound as a red/orange solid (0.23 g, 77%). A small portion of the product was recrystallized to obtain analytical pure sample for melting point measurement. mp 219-220 °C (CH$_2$Cl$_2$/methanol). $^1$H NMR (400 MHz, CDCl$_3$) 8.71 (s, 2H), 8.30 (dd, $J = 5.6$, 3.2 Hz, 2H), 8.20 (s, 2H), 7.74 (dd, $J = 6.0$, 3.2 Hz, 2H), 7.05 (s, 2H), 4.10 (t, $J = 6.4$ Hz, 4H), 1.92 (m, 4H), 1.39 (m, 8H), 0.94 (t, $J = 6.8$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) 195.6, 149.8, 140.2, 135.6, 134.7, 128.4, 127.4, 116.9, 108.6, 85.4, 69.0, 53.1, 31.8, 29.2, 25.9, 22.8, 14.2. FT-IR (KBr) v/cm$^{-1}$: 2956, 2920, 2856, 1669, 1589, 1502, 1460, 1390, 1296, 1271, 1248, 1158, 972, 866, 850, 821. HRMS (EI) calcd for C$_{34}$H$_{38}$O$_5$ (M$^+$) 526.2714, found 526.2737.
1.56 (m, 4H), 1.42 (m, 8H), 0.96 (t, J = 6.8 Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) 182.9, 151.6, 134.9, 133.9, 131.2, 130.8, 130.5, 127.8, 127.5, 127.2, 105.9, 68.9, 31.8, 29.1, 26.0, 22.8, 14.3.

FT-IR (KBr) v/cm$^{-1}$: 2953, 2929, 2854, 1665, 1570, 1489, 1432, 1324, 1300, 1223, 1152.

HRMS (EI) calcd for C$_{34}$H$_{36}$O$_4$ (M$^+$) 508.2608, found 508.2624.

**exo/endo-7,14-Epoxy-6a,7,13,13a-tetrahydro-10,11-bis(hexyloxy)hexacene-6,15-dione (8):**

This was prepared from 3 (0.72 g, 1.82 mmol), DPT (0.44 g, 1.86 mmol), and 1,4-anthraquinone (0.39 g, 1.87 mmol) in toluene (70 mL) in the same manner as described for 4, yielding 8 (0.80 g, 76%) as a yellow solid. Exo: $^1$H NMR (300 MHz, CDCl$_3$) 8.73 (s, 2H), 8.09 (dd, J = 6.3, 3.3 Hz, 2H), 7.71 (dd, J = 6.3, 3.3 Hz, 2H), 7.69 (s, 2H), 7.15 (s, 2H), 5.94 (s, 2H), 4.12 (t, J = 6.6 Hz, 4H), 3.26 (s, 2H), 1.91 (m, 4H), 1.54 (m, 4H), 1.39 (m, 8H), 0.94 (m, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) 195.9, 149.9, 140.4, 135.5, 131.4, 130.3, 129.8, 129.7, 128.5, 116.9, 108.7, 85.9, 69.1, 53.6, 31.8, 29.3, 25.9, 22.8, 14.3. FT-IR (KBr) v/cm$^{-1}$: 2954, 2925, 2856, 1677, 1614, 1507, 1456, 1390, 1295, 1276, 1251, 1191, 1153, 1093, 1021, 872, 851, 803. HRMS (ESI) calcd for C$_{38}$H$_{41}$O$_5$ (M+H$^+$) 577.2949, found 577.2939; Endo: $^1$H NMR (400 MHz, CDCl$_3$) 8.12 (s, 2H), 7.57 (dd, J = 6.0, 3.2 Hz, 2H), 7.31 (dd, J = 6.0, 3.2 Hz, 2H), 7.27 (s, 2H), 6.66 (s, 2H), 5.99 (dd, J = 3.2, 2.0 Hz, 2H), 3.92 (dd, J = 3.2, 2.0 Hz, 2H), 3.74 (m, 4H), 1.63 (m, 4H), 1.30 (m, 4H), 1.28 (m, 8H), 0.84 (t, J = 6.8 Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) 194.5, 149.1, 137.8, 134.5, 130.0, 129.5, 129.0, 128.5, 127.9, 118.3, 107.9, 82.9, 68.4, 51.0, 31.5, 28.9, 25.6, 22.5, 14.0. FT-IR (KBr) v/cm$^{-1}$: 2954, 2929, 2853, 1677, 1617, 1852, 1507, 1456, 1390, 1302, 1264, 1198, 1156, 1090, 1037, 942, 870, 854. HRMS (ESI) calcd for C$_{38}$H$_{41}$O$_5$ [M+H]$^+$ 577.2949, found 577.2960.
10,11-Bis(hexyloxy)hexacene-6,15-dione (10): A mixture of 8 (0.31 g, 0.54 mmol), p-toluenesulfonic acid monohydrate (p-TsOH \textsubscript{H\textsubscript{2}O}) (60 mg) in toluene (20 mL) was stirred at 100 °C under Ar for 13 h. After cooling to room temperature, most of solvent was removed in vacuo. The residue was dissolved in CH\textsubscript{2}Cl\textsubscript{2} and the product was washed with H\textsubscript{2}O and saturated NaCl aqueous solution, dried over MgSO\textsubscript{4}, and concentrated on a rotary evaporator. Purification by column chromatography on silica gel with CH\textsubscript{2}Cl\textsubscript{2}:hexane (2:1, slowly up to 5:1, v/v) afforded the title compound as a yellow/orange solid (0.19 g, 63%). A small portion of the product was recrystallized to obtain analytical pure sample for melting point measurement. mp 235-236 °C (CH\textsubscript{2}Cl\textsubscript{2}/methanol). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) 8.84 (s, 2H), 8.81 (s, 2H), 8.26 (s, 2H), 8.04 (dd, \textit{J} = 6.0, 3.2 Hz, 2H), 7.64 (dd, \textit{J} = 6.4, 3.2 Hz, 2H), 7.07 (s, 2H), 4.09 (t, \textit{J} = 6.8 Hz, 4H), 1.91 (m, 4H), 1.55 (m, 4H), 1.41 (m, 8H), 0.96 (t, \textit{J} = 6.8 Hz, 6H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) 183.0, 151.7, 135.3, 131.3, 131.0, 130.8, 130.2, 129.7, 129.4, 128.7, 127.1, 105.9, 69.0, 31.8, 29.1, 26.0, 22.9, 14.3. FT-IR (KBr) \textit{v}/cm\textsuperscript{-1}: 2950, 2925, 2852, 1673, 1570, 1490, 1457, 1429, 1393, 1308, 1228, 1201, 1155, 988, 930. HRMS (ESI) calcd for C\textsubscript{38}H\textsubscript{38}O\textsubscript{4}Na [M+Na]\textsuperscript{+} 581.2662, found 581.2686.

1,2,3,4-Tetrafluoro-10,11-bis(hexyloxy)hexacene-6,15-dione (11): This was prepared from 3 (0.37 g, 0.94 mmol), DPT (0.22 g, 0.93 mmol), and 6,7,8,9-tetrafluoro-1,4-anthraquinone (7) (0.26 g, 0.93 mmol) in toluene (40 mL) in the same manner as described for 8. The crude product 9 was directly used for the dehydration step as described for 5, employing PPTS (1.0 g, 4.0 mmol) and acetic anhydride (15 mL), to afford the title compound as a yellow solid (0.12 g, 20% over two steps). A small portion of the product was recrystallized to obtain analytical pure sample for melting point measurement. mp 332-334 °C (CH\textsubscript{2}Cl\textsubscript{2}/methanol). \textsuperscript{1}H NMR (300
MHz, CDCl₃) 8.78 (s, 2H), 8.68 (s, 2H), 8.10 (s, 2H), 6.91 (s, 2H), 4.07 (t, J = 6.6 Hz, 4H), 1.94 (m, 4H), 1.57 (m, 4H), 1.44 (m, 8H), 0.98 (t, J = 6.9 Hz, 6H). ¹⁹F NMR (282 MHz, CDCl₃) -144.5 (d), -151.1 (d). FT-IR (KBr) ν/cm⁻¹: 2952, 2933, 2856, 1680, 1667, 1573, 1514, 1491, 1468, 1429, 1361, 1309, 1264, 1222, 1092, 1009, 992. HRMS (EI) calcd for C₃₈H₃₄F₄O₄ (M⁺) 630.2388, found 630.2378.

**1,2,3,4-Tetrafluoro-5,8-dihydroxyanthraquinone (12):** A mixture of AlCl₃ (5.0 g) and NaCl (1.1 g) was pulverized using a mortar and pestle under a nitrogen atmosphere. The mixture was then transferred into an oven-dried 50 mL Schlenk flask under Ar, and heated to 180 °C. An intimate mixture of 3,4,5,6-tetrafluorophthalic anhydride (1.1 g, 4.8 mmol), 1,4-dihydroxybenzene (0.6 g, 5.4 mmol) and AlCl₃ (2.6 g) was added to the above melt. The heating temperature was raised to 220 °C and held there for 1.5 h. The hot mixture was poured over crushed ice and 40 mL concentrated HCl aqueous solution was then added. The resulting red/purple suspension solution was filtered, affording a brown solid as the product (1.2 g, 81%), which was used for next step, without further purification. mp 230-231 °C. ¹H NMR (400 MHz, (CD₃)₂CO) 12.37 (s, 2H), 7.45 (s, 2H). ¹⁹F NMR (282 MHz, (CD₃)₂CO) -133.0 (m), -141.8 (m). FT-IR (KBr) ν/cm⁻¹: 3448, 1632, 1605, 1510, 1449, 1412, 1379, 1301, 1264, 1210, 1118, 968, 782, 750. HRMS calcd for C₁₄H₄F₄O₄ (M⁺) 312.0040, found 312.0037.

**6,7,8,9-Tetrafluoro-1,4-anthraquinone (7):** Under Ar, sodium borohydride (NaBH₄) (0.65 g) was added in portions to a stirred solution 12 (1.0 g, 3.2 mmol) in methanol (30 mL), which was cooled by an ice-water bath. After the addition of NaBH₄, the reaction mixture was refluxed for 24 h. The reaction mixture was then cooled to room temperature and poured into water (60
mL). The resulting solution was acidified with concentrated HCl solution. The precipitate was collected by filtration and dried in a vacuum, affording the title compound as a dark/brown solid (0.67g, 75%), which was used for next step, without further purification. mp > 180 °C (decomposed). $^1$H NMR (300 MHz, CDCl$_3$) 8.87 (m, 2H), 7.16 (s, 2H). $^{19}$F NMR (282 MHz, CDCl$_3$) -145.3 (d), -151.6 (d). FT-IR (KBr) ν/cm$^{-1}$: 3064, 3022, 1661, 1674, 1605, 1512, 1472, 1375, 1300, 1123, 1066, 1056, 963, 855. HRMS (EI) calcd for C$_{14}$H$_4$F$_4$O$_2$ (M$^+$) 280.0142, found 280.0147.

(exo/endo)/(endo/endo)–[6,17],[8,15]-Diepoxy-6,6a,7a,8,15,15a,16a,17-octahydro-2,3,11,12-tetrahexyloxyheptacene-7,16-dione (13): This was prepared from 5 (0.47 g, 1.19 mmol), DPT (0.28 g, 1.18 mmol), and 1,4-benzoquinone (61 mg, 0.59 mmol) in toluene (50 mL) in the same manner as described for 4, yielding both endo/endo product (0.22 g) and exo/endo product (0.14 g) as a white solid (totally 71%). The endo/endo product was not isolated. Exo/Exo: $^1$H NMR (300 MHz, CDCl$_3$) 7.44 (s, 4H), 7.08 (s, 4H), 5.52 (m, 4H), 4.10 (t, $J$ = 6.6 Hz, 8H), 2.43 (m 4H), 1.91 (m, 8H), 1.54 (m, 8H), 1.39 (m, 16H), 0.93(m, 12H). $^{13}$C NMR (100Hz, CDCl$_3$) 206.7, 150.1, 138.0, 128.5, 118.4, 108.5, 82.7, 69.0, 52.8, 31.7, 29.2, 25.9, 22.8, 14.2. FT-IR (KBr) ν/cm$^{-1}$: 2952, 2927, 2859, 1682, 1617, 1502, 1457, 1390, 1293, 1252, 1158, 1043, 988, 937, 899, 854. HRMS (ESI) calcd for C$_{54}$H$_{68}$O$_8$Na (M+Na$^+$) 867.4806, found 867.4796; Exo/Endo: $^1$H NMR (300 MHz, CDCl$_3$) 7.56 (s, 2H), 7.46 (s, 2H), 7.06 (s, 2H), 7.05 (s, 2H), 5.78 (m, 2H), 5.67 (s, 2H), 4.06 (m, 8H), 3.93 (m, 2H), 2.20 (s, 2H), 1.86 (m, 8H), 1.50 (m, 8H), 1.36 (m, 16H), 0.91 (m, 12H). $^{13}$C NMR (100 MHz, CDCl$_3$) 207.4, 149.9, 149.7, 139.4, 138.9, 128.4, 128.3, 119.3, 116.7, 108.5, 85.0, 81.4, 69.0, 68.9, 69.0, 56.9, 53.0, 31.7, 29.2, 25.9, 22.8, 14.2. FT-IR (KBr) ν/cm$^{-1}$: 2952, 2930, 2856, 1704, 1617, 1508, 1454, 1390, 1300, 1252, 1155, 1001,
924, 873, 850. HRMS (ESI) calcd for C_{54}H_{68}O_8Na [M+Na]^+ 867.4806, found 867.4777.

2,3,11,12-Tetrahexyloxyheptacene-7,16-dione (14): This was prepared in the same manner as described for 10, employing 13 (0.18 g, 0.21 mmol), p-TsOH·H_2O (0.15 g, 0.79 mmol), and toluene (12 mL). A yellow/orange solid was obtained as the product (36 mg, 21%). A small portion of the product was recrystallized to obtain analytical pure sample for melting point measurement. mp 232-234 °C (CH_2Cl_2/methanol). \(^1\)H NMR (400 MHz, CDCl_3) 8.87 (s, 4H), 8.27 (s, 4H), 7.10 (s, 4H), 4.13 (t, J = 6.8 Hz, 8H), 1.93 (m, 8H), 1.57 (m, 8H), 1.41 (m, 16H), 0.96 (t, J = 6.8 Hz, 12H). \(^{13}\)C NMR (125 MHz, CDCl_3) 183.2, 151.7, 131.3, 131.2, 130.6, 129.3, 127.1, 106.0, 69.1, 31.8, 29.2, 26.0, 22.9, 14.3. FT-IR (KBr) v/cm\(^{-1}\): 2953, 2928, 2858, 1670, 1570, 1490, 1463, 1426, 1317, 1210, 1158. HRMS (ESI) calcd for C_{54}H_{64}O_6 (M^+) 808.4696, found 808.4706.
References and Notes


CHAPTER 2

Syntheses of Soluble, π-Stacking Tetracene Derivatives for OFETs

Adapted from:

Introduction

**Organic Field Effect Transistors**

Field-effect transistors (FETs) based on inorganic materials are the basic building units for modern digital integrated circuits and rely on an electric field to control the conductivity of “channels” in a semiconductor material.\(^1\) An FET can be constructed from a number of semiconductors and silicon is by far the most common semiconductor used. Some other materials have also been used to achieve products with unique properties. For example, gallium arsenide (GaAs) has electron mobility and drift velocities that are far higher than the standard doped silicon. Amplifiers designed with GaAs FET devices have a much higher frequency response and lower noise factor than those based on standard silicon-based FETs.\(^2\)

Organic semiconductors, including small molecules and polymers, represent a new channel material for FETs, and studies in the past two decades have achieved great advancements.\(^3\) In addition to the FETs, organic semiconductors have attracted much attention in applications, such as organic light emitting diodes (OLEDs), solar cells, electrochemical cells, and organic memories.\(^4\) This interest is based in part on their potential for lightweight, low cost, and flexible devices.

Basically, organic field effect transistor (OFET) devices are based on the conventional configuration of their inorganic counterpart.\(^1,4\) A typical device is composed of three main components: (1) source, drain, and gate electrodes; (2) a dielectric layer; and (3) an active semiconductor layer. Within the basic FET design, there are two types of device configurations: top contact and bottom contact (Figure 2.1). The former involves building the source and drain electrodes onto a preformed semiconductor layer, whereas the latter is
constructed by depositing the semiconductor layer over the source and drain electrodes. Each of these devices has particular advantages and disadvantages in the fabrication process.\textsuperscript{3-4} The FET operates by the effects of an electric field on the flow of electrons through a single type of semiconductor material.\textsuperscript{1,4} Current moves within the FET in a channel, from the source contact to the drain contact, and it is controlled by the electric field generated by a gate terminal (gate-source voltage: $V_{GS}$). The channel materials can be either $n$-type or $p$-type semiconductors. Accordingly, the device is named as either an $n$-channel or $p$-channel device (Figure 2.2), respectively. In $n$-channel devices, electrons flow so the drain potential must be higher (more positive) than that of the source (drain-source voltage: $V_{DS} > 0$). In $p$-channel devices, the flow of holes (carrier with positive charge) requires that $V_{DS} < 0$.\textsuperscript{1,4} The current

![Figure 2.1](image-url)

**Figure 2.1.** Typical field effect transistor configurations: (A) Top contact device; (B) Bottom contact device.
between source and drain electrode is measured when no voltage is applied to the gate electrode (off current) and when a voltage is applied to the gate electrode (on current). The basic relationships describing the source drain current of a FET device can be express as the following equations:

\[
(I_{DS})_{\text{lin}} = \frac{WC}{L} \mu \left( V_{GS} - V_T - \frac{V_{DS}}{2} \right) V_{SD}
\]

\[
(I_{DS})_{\text{sat}} = \frac{WC}{2L} \mu (V_{GS} - V_T)^2
\]

where \((I_{DS})_{\text{lin}}\) and \((I_{DS})_{\text{sat}}\) are the source-drain currents in the linear and saturation regimes, respectively. The value \(\mu\) is the field-effect carrier mobility of the semiconductor, \(W\) is the
channel width, $L$ is the channel length, $C_i$ is the capacitance per unit area of the insulator layer, $V_T$ is the threshold voltage, $V_{DS}$ is the source-drain voltage, and $V_{SG}$ is the source-gate voltage.\(^4\) The mobility, $\mu$, describes how easily charge carriers can move within the active layer under the influence of an electric field. Therefore, it is directly related to the switching speed of the device. This parameter can be extracted from current-voltage measurements, and is ideally as large as possible. Typical values range from 0.1-1 cm\(^2\)/Vs for amorphous-silicon devices, and the best organic materials have been reported to achieve mobilities of 1-10 cm\(^2\)/Vs.\(^4\) The on/off ratio, defined as the ratio of the on current and off current, is indicative of the switching performance of OFETs. Devices with on/off ratio higher than $10^6$ are generally suitable for most applications.

Although the current OFETs cannot compete with most conventional inorganic technologies, they should find applications in low-performance radio-frequency technology, disposable sensors, and integrated optoelectronic devices, such as pixel drives and switching
elements in displays. Polymer Vision has successfully implemented pentacene based active-
matrix backplanes in its rollable display prototypes. These organic devices have acceptable
levels of performance and stability in an introductory application and are the first devices
nearing commercialization. Many groups have also demonstrated potential utility of OFETs
for OLED backplanes on flexible substrates of fairly large size. The advantages of organic
systems include solution phase fabrication and good compatibility with flexible plastic
substrates, which meet the current requirements for developing low-cost, large area,
lightweight, and flexible devices. These requirements can not be achieved by conventional Si
technology, because it involves high-temperature and high-vacuum deposition processes and
sophisticated photolithographic patterning methods. Since the report of the first OFET in
1986, there have been great advances in materials purification, device fabrication methods,
and development of higher-performance organic semiconducting materials, which have
improved the existing technologies and expanded the scope of potentially realizable
applications. Recent improvements in device performance have rapidly expanded OFETs
from niche markets, making them targets for a wider range of applications. The numerous
applications presented thus far have already shown the potential of OFETs, which will
continue to grow. Although challenges exist for large-scale manufacturing, their rapid
development shows great promise for their future in organic electronics.

Much of this progress of OFETs has been a result of the understanding of structure-
property relationships of the active channel materials. Molecular tuning based on this
understanding has yielded materials with better solubility for spin-coating, desirable
supramolecular order for higher mobility, and improved stability towards oxygen and
In addition to the challenges presented by fabrication, particular attention must be paid to the design of materials that will meet the performance demands of a OFET in its parent applications. In well-ordered inorganics, such as single-crystal Si, the delocalization of electrons over equivalent sites leads to a band-type mode of transport, with charge carriers moving through a continuum of energy levels in the solid. In an organic transistor, the active layer is comprised of a thin film of highly conjugated small molecules or polymers, which have a different nature of charge transport than their inorganic counterpart. The well recognized mechanism is hopping between discrete, localized states of individual molecules. The presence of impurities or inconsistencies in a structure may result in “traps” that alter the relative energy levels, and inhibit the flow of charge carriers. Hence, to achieve acceptable performance, organic semiconductors must satisfy general criteria related to both the carrier injection and current-carrying characteristics. Basically, the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) energies of the individual molecules must match the Fermi levels of electrodes for efficient charge carrier injection and transport. In addition, the materials must exhibit unique molecular packing with sufficient overlap of frontier orbitals in solid state and the molecules should be preferentially oriented on the FET substrate to facilitate most efficient charge transport along the direction of intermolecular π-π stacking. Since impurity and traps in organic semiconductors have been found to significantly reduce device performance, the materials should be easily processed to achieve an extremely high purity. In the past decades, novel organic semiconductors with excellent device performances have been developed. Pentacene, α-sexithiophene, and poly-3-hexylthiophene are good examples of p-type organic semiconductors, and perfluorinated
copper-phthalocyanine, \( N,N' \)-dialkyl substituted perylenetetracarboxydiimide derivatives, and poly(benzobisimidazobenzophenanthroline), are typical \( n \)-type organic materials.\(^4,7\)

**Acenes**

Acenes or oligoacenes are a class of organic polycyclic aromatic hydrocarbons made up of linear fused benzene rings (Chart 2.1). The linear acenes from naphthalene to heptacene have been synthesized.\(^{10}\) However, higher members of this series have proved too reactive to isolate under ordinary conditions and they have been mainly the subject of many theoretical studies and controversial discussions.\(^{11}\) The larger acene representatives have potential interest in electronic applications and are actively researched in chemistry.\(^7\) In addition, the oligoacene units are a basic building unit of graphite and carbon nanotubes, and investigation of their electronic properties is helpful for understanding the structure and properties of the latter materials.\(^{7a}\) Oligoacenes, typically pentacene and tetracene, have been widely studied as the channel materials for OFETs.\(^7\) Pentacene-based devices were reported to show field effect mobilities of greater than 2 \( \text{cm}^2\text{V}^{-1}\text{s}^{-1} \), which are comparable to the performance of amorphous-silicon thin film devices.\(^{12}\) Recent reports of mobilities up to 35 \( \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) for high-purity pentacene single crystals, however, give hope that further investigation will
continue to pay off for organic semiconductors. It is generally believed that the charge carrier mobility in organic materials at room temperature is dominated by $\pi$-$\pi$ interactions between molecules via a charge hopping transport mechanism. Therefore, the molecular stacking in solid state has a strong influence on the field effect mobility. It is well recognized that the intermolecular distance and the extent of $\pi$-orbital overlap between neighboring molecules are two important parameters for investigating the electrical properties of organic semiconductors. However, the herringbone-like stacking superstructure of oligoacenes (Figure 2.4) is not the optimum packing for high mobility devices, because the edge-to-face packing reduces the $\pi$-overlap between adjacent molecules. Recently, several novel organic semiconducting compounds with cofacial $\pi$-stacking arrangement have been synthesized and their devices showed promising charge-carrier mobilities. The excellent intrinsic electrical properties of oligoacenes have also inspired chemists to design and synthesize oligoacene derivatives with improved $\pi$-stacking in the solid-state. Additionally, the often poor solubility of oligoacenes in organic solvents at room temperature has been a hurdle in fully realizing the advantages of organic electronics,
such as low-cost patterning and low-temperature processing. Therefore, it is necessary to develop new, soluble, π-stacking organic semiconductors for OFETs.\textsuperscript{21}

In this work, we report a family of partially fluorinated and alkyl/alkoxy substituted tetracene molecules that are soluble in common organic solvents and have significant π-stacking motifs in crystal lattices. Fluorine has been applied extensively to tune the electronic and structural properties of organic semiconducting materials, due to its strong electronegativity and significantly small size.\textsuperscript{17a,22} Recently, Watson and coworkers have reported that partial fluorination overcame the herringbone crystal packing of tetracyclic aromatic compounds, leading to a cofacial packing with a π-distance of 3.37 Å.\textsuperscript{22a} Partially fluorinated silylethynyl pentacenes were also found to reduce the intermolecular distances.\textsuperscript{17a} Incorporation of long alkyl or alkoxy chains is widely used to improve the solubility of small molecules and polymers, and to facilitate formation of semiconductor thin films by cost-effective solution deposition techniques.\textsuperscript{23} In our studies, we found that the regiochemistry of the side chain attachment on the tetracene backbone not only improved the solubilities, but also tuned the electrochemical properties and packing motifs. Furthermore, the incorporation of both donor and acceptor substituents to the main chain was added to induce a strong dipole moment. Strong dipole-dipole interactions between neighboring molecules were previously demonstrated to afford π-stacking with short intermolecular distance and self-assembly properties.\textsuperscript{19}
Results and Discussion

The key steps of our synthetic strategy for preparing tetracene derivatives, as outlined in Scheme 2.1, were adapted from a methodology previously reported by Gribble.\textsuperscript{24} \( N \)-methyl-4,5,6,7-tetrafluoroisoindole (2), which is a moderately stable compound and should be prepared freshly, could be easily prepared from a reaction between 1 and 3,6-di(2-pyridyl)-1,2,4,5-tetrazine, via a Diels-Alder (D-A) reaction and subsequent two thermally allowed retro D-A reactions.\textsuperscript{25} In the presence of 2, dibromonaphthalenes 3a-d were treated with phenyllithium (PhLi) at 0 °C, leading to the formation of corresponding naphthalyne, which readily reacted with 2 via the D-A reaction. Amines 4a-d were obtained as colorless or slightly yellow solids in 40-65% yields. The deamination was carried out by the treatment of an aqueous solution of NaOH (50%, w/w) to the stirred chloroform solution of 4a-d and phase-transfer catalyst benzyltriethylammonium chloride at room temperature. This reaction was proposed to proceed by way of the in situ formed dichlorocarbene, which combined with

\begin{equation}
\text{Scheme 2.1. Syntheses of 5a-d}
\end{equation}

\begin{align*}
\text{NaOH (50\%, aq)} & \quad \text{benzyltriethylammonium chloride, CHCl}_3, \text{rt} \\
\text{3,6-(Di-2-pyridyl)-1,2,4,5-tetrazine} & \quad \text{PhLi, THF, 0 °C} \\
\text{3a-d} & \quad \text{a: } R = H, \quad R' = \text{OC}_6\text{H}_{13}, \quad \text{yield (3 steps)} \quad 18\% \\
& \quad \text{b: } R = \text{OC}_6\text{H}_{13}, \quad R' = H \quad 35\% \\
& \quad \text{c: } R = H, \quad R' = \text{C}_8\text{H}_{17} \quad 21\% \\
& \quad \text{d: } R = \text{C}_8\text{H}_{17}, \quad R' = H \quad 15\%
\end{align*}
4a-d to form ammonium ylide intermediates. The aromatic acenes were then generated from the rapid cheletropic loss of methyl isocyanide dichloride. Tetracene derivatives 5a-d were obtained as red or orange crystals from recrystallization in hexane, with yields of 15-35% over 3 steps. The solubility of 5a-d in organic solvents, such as methylene chloride, chloroform and toluene, was found to be much better than their parent tetracene, owing to the long linear side chains.

Scheme 2.2. Syntheses of 3a-d
Scheme 2.2 shows the synthetic routes to dibromonaphthalenes (3a-d), which are used in Scheme 2.1. Hexyloxy-substituted naphthalenes were prepared from corresponding naphthoquinone (6 and 7) via a reduction to naphthalenehydroquinone and then alkylation under basic conditions. The bromination of 1,4-bis(hexyloxy)naphthalene (8) was carried out by a treatment of N-bromosuccinimide (NBS) in methylene chloride. Both 3a and 3b were obtained as colorless crystals. Dioctyl-substituted dibromonaphthalenes (3c-d) were obtained.

Figure 2.5. Packing diagrams of 5a-d show that the molecules stack in a slipped cofacial motif. (Left: view along the short molecular axis; Right: view along the long molecular axis.).
prepared in two steps with good yields. In the presence of an excess of the furans, tetrabromobenzenes (9a-b) were treated with n-butyllithium (n-BuLi) at low temperature, leading to the 1,4-endoxides (10a-b) via a D-A reaction between corresponding benzyne and furans.\textsuperscript{29} Low-valent Ti, prepared \textit{in situ} from a reaction between zinc and TiCl\textsubscript{4}, was applied for the deoxygenation of 10a-b,\textsuperscript{29,30} to give 3c-d as white solids.

The molecular and crystal structures of 5a-d were determined by X-ray structure analysis on single crystals, which were obtained by solvent diffusion at low temperature. The packing diagrams of 5a-d are displayed in Figure 2.5. All four compounds show primarily face-to-face slipped \( \pi \)-stacking in crystals (Figure 2.6-2.9), and the selected structural data are summarized in Table 2.1. The hexyloxy-substituted molecules, 5a and 5b, adopt anti-parallel cofacial arrangement. The \( \pi \)-stacked column has regular alternating intermolecular distances (Table 2.1), forming a face-to-face \( \pi \)-stacks of \( \pi \)-dimers.\textsuperscript{14} In the crystal structure of 5a, we found that the two hexyloxy chains are in a conformation which extends them out of the aromatic plane, holding the \( \pi \)-dimer like a shield. The remarkably short intermolecular distances (3.22 Å and 3.24 Å) indicate the existence of strong intermolecular interactions, which are expected to enhance the charge carrier mobility. The relatively large intermolecular distances in 5b may be attributed to the repulsion from the side chains, which have a kink in their otherwise extended conformation. However, the relative small roll displacement\textsuperscript{4} (0.99 Å and 0.89 Å) is suggestive of large \( \pi \)-orbital overlap.\textsuperscript{15} In contrast to the crystal structures of 5a and 5b, octyl-substituted 5c crystallizes in a parallel cofacial molecular arrangement, with the intermolecular distance of 3.35 Å and roll displacements of 1.15 Å. The molecules in each column are slipped lengthwise by about one benzene ring.
Compound 5d has a face-to-face anti-parallel $\pi$-stacking motif, similar to that of 5a and 5b. However, the stacks of 5d are packed with alternating columns that are at an angle of 141° between the short axes of the molecules in neighboring columns (Figure 2.10). Interestingly, 5d exhibits the shortest interplanar distance (3.18 and 3.20 Å) among these four compounds.

Figure 2.6. Packing diagram of 5a (view along the $a$-axis).

Figure 2.7. Packing diagram of 5b (view along the $a$-axis).
but it has the biggest pitch and roll displacement, which is expected to reduce the extent of \( \pi \)-orbital overlap.\textsuperscript{14,15} These displacements are probably due to the out of plane conformation of the octyl chains. The crystal features of 5a-d clearly demonstrate the effect of substitution regiochemistry on molecular packings.\textsuperscript{31} A close inspection of the \( \pi \)-dimers in 5a, 5b and 5d reveals that the electron-poor ring (fluorinated ring) faces to the electron-rich ring (hexyloxy- or octyl-substituted ring), indicating the effect of arene-perfluoroarene interaction on the
Table 2.1. Comparison between the Intermolecular Distances and Pitch/Roll Displacements of 5a-d

<table>
<thead>
<tr>
<th>compd</th>
<th>d (Å)(^a)</th>
<th>(d_p) (Å)(^b)</th>
<th>(d_r) (Å)(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>3.22</td>
<td>1.37</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>3.24</td>
<td>1.68</td>
<td>1.36</td>
</tr>
<tr>
<td>5b</td>
<td>3.44</td>
<td>3.41</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>3.53</td>
<td>1.21</td>
<td>0.89</td>
</tr>
<tr>
<td>5c</td>
<td>3.35</td>
<td>3.46</td>
<td>1.15</td>
</tr>
<tr>
<td>5d</td>
<td>3.18</td>
<td>1.22</td>
<td>1.45</td>
</tr>
<tr>
<td></td>
<td>3.20</td>
<td>4.68</td>
<td>1.75</td>
</tr>
</tbody>
</table>

\(^a\) Intermolecular distance.  \(^b\) Pitch displacement.  \(^c\) Roll displacement (see ref. 4).

Figure 2.10. Packing diagram of 5d, showing the 141° angle between molecules in neighboring crystal packing columns.

molecular stacking.\(^{32}\) A similar packing motif was previously observed in the crystal structure of 2,3,4,5,6-pentafluorodiphenylacetylene by Grubbs.\(^{33}\) Extensive studies on the interactions of phenyl and perfluorophenyl groups, especially the 1:1 mixture of benzene and
hexafluorobenzene, have supported that this co-facial stacking arrangement results from the electrostatic attractions between adjacent molecules.\textsuperscript{32-34} Our results suggest that the noncovalent electrostatic interactions between donor and acceptor substituted arenes can be employed to design novel $\pi$-stacking organic semiconductors.\textsuperscript{19,35}

The electrochemical behaviors of tetracene and compounds 5a-d (Figure 2.11) together with the spectroscopic data (Figure 2.12) are summarized in Table 2.2. All five compounds show one quasi-reversible reduction wave with onset reduction potentials between -2.05 and -1.84 eV (vs Fc/Fc$^+$ couple). The cyclic voltammogram (CV) of 5a exhibits two separate one-electron reversible oxidation waves at $E_{1/2} = 0.39$ V and 0.97 V.

Table 2.2. Optical Band Gap and CV Data of Tetracene and 5a-d

<table>
<thead>
<tr>
<th>compd</th>
<th>$E_g^\text{Op}$ (eV)$^a$</th>
<th>$E_{\text{ox onset}}$ (V)$^b$</th>
<th>$E_{\text{red onset}}$ (V)$^b$</th>
<th>$E_g^\text{EChem}$ (eV)$^c$</th>
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</thead>
<tbody>
<tr>
<td>tetracene</td>
<td>2.57</td>
<td>0.41</td>
<td>-2.05</td>
<td>2.46</td>
</tr>
<tr>
<td>5a</td>
<td>2.25</td>
<td>0.31</td>
<td>-1.92</td>
<td>2.23</td>
</tr>
<tr>
<td>5b</td>
<td>2.34</td>
<td>0.44</td>
<td>-1.84</td>
<td>2.28</td>
</tr>
<tr>
<td>5c</td>
<td>2.47</td>
<td>0.56</td>
<td>-1.89</td>
<td>2.45</td>
</tr>
<tr>
<td>5d</td>
<td>2.40</td>
<td>0.48</td>
<td>-1.91</td>
<td>2.39</td>
</tr>
</tbody>
</table>

$^a$ Calculated from the onset of UV-vis absorbance spectra measured in CH$_2$Cl$_2$ solution. $^b$ Performed in 0.1 M solution of TBAPF$_6$ in CH$_2$Cl$_2$, Pt electrode, scan rate of 100 mV/s, ferrocene as internal standard. $^c$ Calculated from the onset of CVs.

Similarly, 5b has two sequential oxidation waves over the range of scan rate investigated (10-100 mV/s). However, the return reduction processes were scan rate dependent, displaying the
expected two waves (0.47 and 0.66 V) at slow scan rates (10 mV/s) and an unexpected third wave with large potential shifts (0.19, 0.45 and 0.65 V) at 100 mV/s. The electrochemical irreversibility of 5b probably indicates slow electron transfer kinetics and/or strong intermolecular interactions. Both the CVs of 5c and 5d show one reversible oxidation wave and a second quasi-reversible oxidation wave, with the first waves at $E_{1/2} = 0.65$ V and $0.58$ V for 5c and 5d, respectively. We found the introduction of both fluorine and hexyloxy groups offered slight change on oxidation potentials, as compared to the $E_{1/2}$ potential of tetracene. However, 5c and 5d exhibited relatively higher oxidation potentials, due to the modest electron-donating ability of the alkyl group. Our CV studies reveal that the position of alkoxy/alkyl substituents could significantly tune the electrochemical properties of these molecules. The bandgaps, determined from the onset of oxidation and reduction (scan rate =

![Figure 2.11. CVs of compounds 5a-d and tetracene performed in 0.1 M solution of TBAPF6 in CH$_2$Cl$_2$, with a Pt electrode, a scan rate of 100 mV/s, and ferrocene as the internal standard.](image-url)
Figure 2.12. UV-vis absorption spectra of tetracene and 5a-d measured in CH$_2$Cl$_2$.

100 mV/s), correspond with the values calculated from the onset of UV-vis absorption spectra (Figure 2.12) measured in methylene chloride solution (Table 2.2). The small bandgaps of these compounds are expected to make them promising candidates for use in organic electronics.

Conclusion

In summary, we have shown the syntheses of a series of partially fluorinated tetracene derivatives with $N$-methyl-1,2,4,5-tetrafluoroisoindole as a synthetic building block. Compounds 5a, 5b and 5d were found to crystallize with antiparallel, cofacial-stacked column superstructures, while 5c exhibited a slipped parallel $\pi$-stacking arrangement in crystals. We find that the substitution of alkyl/alkoxy groups on the main chain not only provided better solubility in common organic solvents, but also subtly tuned the crystal structures and electrochemical behaviors. It will be very interesting to grow high quality
single crystals and study the intrinsic charge carrier mobilities, as well as to study the device performance of OFETs based on these tetracene derivatives.

**Experimental Section**

**Materials:** Anhydrous tetrahydrofuran (THF), toluene, acetonitrile (CH$_3$CN) and dichloromethane (CH$_2$Cl$_2$) were purchased from Mallinckrodt Baker Inc. Furan was distilled over K$_2$CO$_3$ and NBS was recrystallized from water prior to use. Known compounds 1,2,3,4-tetrafluoro-5,8-dihydro-5,8-N-methylaminonaphthalene (1)$_{38}$ 6,7-dibromo-1,4-naphthoquinone (6)$_{39}$ 1,2,4,5-tetrabromo-3,6-diocetylbenzene (9b)$_{40}$ and 2,5-diocytlfuran$_{41}$ were prepared following literature procedures. All other reagent grade starting materials were purchased from Aldrich, Lancaster, or Alfa Aesar, and used without further purification. Silica gel (40-63 μm) was obtained from SiliCycle. Neutral alumina (58 angstroms) was purchased from Alfa Aesar and basic alumina (chromatographic grade, pH: 9.0-10.5, 80-325 mesh) was purchased from EMD Chemicals Co.

**General methods and instrumentation:** NMR (1H, 13C, 19F) spectra were recorded on Varian Mercury-300 MHz, Varian Inova-500 MHz or Bruker Advance-400 MHz spectrometers. The $^1$H and $^{13}$C chemical shifts are given in unit of δ (ppm) relative the tetramethylsilane (TMS) where δ (TMS) = 0, and referenced to the residual solvent. The $^{19}$F NMR chemical shifts are reported relative to trichlorofluoromethane or hexafluorobenzene as the reference. Melting points were measured on a Mel-Temp II apparatus (Laboratory Devices INC) and were not corrected. High-resolution mass spectra (HRMS) were obtained on a Bruker Daltons APED II 3T FT-ICR-MS using electron impact ionization (EI). The X-
ray crystal structure was determined with a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (\(\lambda = 0.71073 \text{ Å}\)), performing \(\phi\)- and \(\omega\)-scans. All structures were solved by direct methods using SHELXS\(^{36}\) and refined against \(R^2\) on all data by full-matrix least squares with SHELXL-97.\(^{37}\) All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the \(U\) value of the atoms they are linked to (1.5 times for methyl groups). The electrochemistry studies were performed using Autolab PGSTAT 10 potentiostat (Eco Chemie) in a three-electrode cell configuration under nitrogen atmosphere. Cyclic voltammetry (CV) experiments were carried out in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF\(_6\)) supporting electrolyte in \(\text{CH}_2\text{Cl}_2\). A platinum button (1.6 mm in diameter) and platinum gauze were used as the working and counter electrodes, respectively. The potential was measured against a \(\text{Ag/AgNO}_3\) (10 mM) in 0.1M TBAPF\(_6\) in \(\text{CH}_3\text{CN}\). The reported potentials are versus the ferrocene/ferrocenium (Fc/Fc\(^+\)) couple with observed half-wave potentials between 250 mV and 300 mV, obtained by adding a crystal of ferrocene to the solution. UV-vis spectra were obtained from Hewlett-Packard 8452A diode array UV-visible spectrophotometer.

**General procedure for syntheses of 4a-d.\(^{24}\)**

A solution of 3,6-(di-2-pyridyl)-1,2,4,5-tetrazine (1 equiv.) and 1,2,3,4-tetrafluoro-5,8-dihydro-5,8-\(N\)-methylaminonaphthalene 1 (1 equiv.) in 50 mL \(\text{CH}_2\text{Cl}_2\) was stirred overnight under Ar at room temperature. The mixture was filtered through a short column of neutral
Al₂O₃. The filtrate was concentrated in vacuo, and the slightly yellow residue was dried under vacuum. Dibromonaphthalene 3a-d (0.8 equiv.) and anhydrous THF (50 mL) were then added. Under Ar atmosphere, a solution of phenyllithium (1.6 M in cyclohexane/ether; 1 equiv.) was then added dropwise to the above mixture at 0 °C over 3 h. After addition, the mixture was stirred at 0 °C for an additional 1 h, and then allowed to warm to room temperature slowly and stirred overnight. The mixture was poured into water and extracted by CHCl₃. The organic layer was washed by brine and dried over Na₂SO₄. Solvent was removed in vacuo. Purification by column chromatography (basic Al₂O₃) afforded colorless or slightly yellow sticky solids.

13-Methyl-1,2,3,4-tetrafluoro-7,10-bis(hexyloxy)-5,12-dihydronaphthacene-5,12-imine (4a): This compound was prepared by following the general procedure described above, employing 1 (1.7 g, 7.4 mmol), 3a (2.5 g, 5.2 mmol), phenyllithium (1.6 M in cyclohexane/ether, 4.0 mL, 6.4 mmol), THF (130 mL). The common workup and chromatography afforded 1.1 g of 4a as a white/tan sticky solid (40%). ¹H NMR (300 MHz, CDCl₃) δ 8.17 (s, 2H), 6.72 (s, 2H), 5.37 (s, 2H), 4.05 (m, 4H), 2.29 (s, 3H), 1.91 (m, 4H), 1.56 (m, 4H), 1.41 (m, 8H), 0.95 (m, 6H). ¹⁹F NMR (282 MHz, CDCl₃) δ -140.9 (br), -142.2 (br), -153.8 (br), -156.2 (br). ¹³C NMR (125 MHz, CDCl₃) δ 149.2, 125.1, 105.8, 69.8, 68.8, 36.5, 31.9, 29.6, 26.2, 22.8, 14.3. HRMS calcd for C₃¹H₃₅F₄NO₂ (M⁺) 529.2598, found 529.2590.

13-Methyl-1,2,3,4-tetrafluoro-6,11-bis(hexyloxy)-5,12-dihydronaphthacene-5,12-imine (4b): This compound was prepared by following the general procedure described above, employing 1 (0.77 g, 3.4 mmol), 3b (1.2 g, 2.5 mmol), phenyllithium (1.6 M in
cyclohexane/ether, 2.6 mL, 4.2 mmol), THF (50 mL). The common workup and chromatography afforded 0.7 g of 4b as a colorless sticky solid (55%). H NMR (300 MHz, CDCl₃) 8.12 (dd, J = 6.3, 3.3 Hz, 2H), 7.50 (dd, J = 6.3, 3.3 Hz, 2H), 5.63 (s, 2H), 4.25 (m, 2H), 4.07 (m, 2H), 2.28 (s, 2H), 1.95 (m, 4H), 1.61 (m, 4H), 1.43 (m, 8H), 3.71 (t, J = 6.9 Hz, 6H). ¹⁹F NMR (282 MHz, CDCl₃) -144.2 (br), -145.4 (br), -156.9 (br), -159.2 (br). ¹³C NMR (125 MHz, CDCl₃) 128.8, 126.6, 122.7, 74.8, 67.8, 36.5, 31.8, 30.6, 26.0, 22.8, 14.2. HRMS calcd for C₃₁H₃₅F₄NO₂ (M⁺) 529.2598, found 529.2597.

13-Methyl-1,2,3,4-tetrafluoro-7,10-dioctyl-5,12-dihydronaphthacene-5,12-imine (4c):
This compound was prepared by following the general procedure described above, employing 1 (0.73 g, 3.2 mmol), 3e (1.2 g, 2.4 mmol), phenyllithium (1.6 M in cyclohexane/ether, 2.0 mL, 3.2 mmol), THF (60 mL). The common workup and chromatography afforded 0.6 g of 4c as a white/tan sticky solid (45%). H NMR (300 MHz, CDCl₃) 8.00 (s, 2H), 7.24 (s, 2H), 5.41 (s, 2H), 3.00 (m, 4H), 2.33 (s, 3H), 1.72 (m, 4H), 1.31 (m, 20H), 0.97 (t, J = 6.9 Hz, 6H). ¹⁹F NMR (282 MHz, CDCl₃) -141.0 (br), -142.2 (br), -153.4 (br), -155.9 (br). ¹³C NMR (125 MHz, CDCl₃) 137.5, 131.1, 126.6, 70.0, 36.5, 33.5, 32.1, 31.1, 30.0, 29.7, 29.5, 22.9, 14.3. HRMS calcd for C₃₅H₄₃F₄N (M⁺) 553.3326, found 553.3334.

13-Methyl-1,2,3,4-tetrafluoro-6,11-dioctyl-5,12-dihydronaphthacene-5,12-imine (4d):
This compound was prepared by following the general procedure described above, employing 1 (0.81 g, 3.53 mmol), 3d (1.44 g, 2.8 mmol), phenyllithium (1.6 M in cyclohexane/ether, 2.1 mL, 3.4 mmol), THF (50 mL). The common workup and chromatography afforded 0.66 g of 4d as a white/tan sticky solid (42%). H NMR (300 MHz, CDCl₃) 7.96 (dd, J = 6.6, 3.6 Hz, 6H).
2H), 7.48 (dd, \( J = 6.3, 3.3 \) Hz, 2H), 5.48 (s, 2H), 3.07 (t, \( J = 7.8 \) Hz, 4H), 2.31 (s, 3H), 1.63 (m, 4H), 1.51 (m, 4H), 1.31 (m, 16), 0.91 (m, 6H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) -140.7 (br), -142.1 (br), -153.6 (br), -156.0 (br). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) 131.4, 125.9, 124.8, 69.1, 36.5, 32.1, 31.3, 30.4, 29.9, 29.7, 29.5, 22.9, 14.3. HRMS calcd for C\(_{35}\)H\(_{43}\)F\(_4\)N (M\(^+\)) 553.3326, found 553.3320.

**General procedure for the preparation of 5a-d.**

Under Ar, benzyltriethylammonium chloride (40 mg) was added in one portion to a stirred solution of amine (4a-d) (1.5 mmol) in chloroform (40 mL). An aqueous NaOH solution (50%, 2 mL) was then added dropwise. The resulting mixture was stirred at room temperature overnight. The reaction mixture was poured into an aqueous HCl solution (3 M, 80 mL) and extracted by CHCl\(_3\). The organic layer was washed by water and brine in sequence, and dried over K\(_2\)CO\(_3\). The solvent was removed in vacuo. Purification by flash column chromatography (silica gel) and recrystallization from hexane afforded red or orange crystals.

**1,2,3,4-Tetrafluoro-7,10-bis(hexyloxy)tetracene (5a):** This compound was prepared by following the general procedure described above, employing 4a (1.09 g, 2.06 mmol), benzyltriethylammonium chloride (50 mg), NaOH (50% aqueous, 1.2 mL), CHCl\(_3\) (50 mL). The common workup, chromatography and recrystallization afforded 0.45 g of 5a as red needle-like crystals (44%). mp 141-142 °C (hexane). \(^1\)H NMR (300 MHz, CDCl\(_3\)) 8.61 (s, 2H), 8.39 (s, 2H), 6.44 (s, 2H), 4.11 (t, \( J = 6.6 \) Hz, 4H), 2.02 (m, 4H), 1.67 (m, 4H), 1.50 (m, 8H), 1.02 (m, 6H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) -149.8 (m, 2F), -158.8 (m, 2F). \(^{13}\)C NMR
(100 MHz, CDCl₃) 148.3, 128.9, 126.5, 121.1, 120.0, 101.7, 68.4, 32.0, 29.6, 26.3, 23.0, 14.4.

HRMS calcd for C₃₀H₃₂F₄O₂ (M⁺) 500.2333, found 500.2325.

1,2,3,4-Tetrafluoro-6,11-bis(hexyloxy)tetracene (5b): This compound was prepared by following the general procedure described above, employing 4b (0.69 g, 1.3 mmol), benzyltriethylammonium chloride (50 mg), NaOH (50% aqueous, 0.9 mL), CHCl₃ (40 mL).

The common workup, chromatography and recrystallization afforded 0.42 g of 5b as red needle-like crystals (64%). mp 111-112 ºC (hexane). ¹H NMR (300 MHz, CDCl₃) 9.09 (s, 2H), 8.29 (dd, J = 6.8, 3.0 Hz, 2H), 7.48 (dd, J = 6.9, 3.0 Hz, 2H), 4.26 (t, J = 6.3 Hz, 4H), 2.11 (m, 4H), 1.75 (m, 4H), 1.49 (m, 8H), 1.00 (m, 6H). ¹⁹F NMR (282 MHz, CDCl₃) -149.0 (m, 2F), -157.8 (m, 2F). ¹³C NMR (125 MHz, CDCl₃) 147.9, 125.9, 125.3, 124.2, 123.0, 115.4, 76.8, 32.0, 30.9, 26.2, 23.0, 14.3. HRMS calcd for C₃₀H₃₂F₄O₂ (M⁺) 500.2333, found 500.2329.

1,2,3,4-Tetrafluoro-7,10-dioctyltetracene (5c): This compound was prepared by following the general procedure described above, employing 4c (0.6 g, 1.08 mmol), benzyltriethylammonium chloride (40 mg), NaOH (50% aqueous, 0.8 mL), CHCl₃ (30 mL).

The common workup, chromatography and recrystallization afforded 0.26 g of 5c as red/orange crystals (45%). mp 86-87 ºC (hexane). ¹H NMR (300 MHz, CDCl₃) 8.63 (s, 2H), 8.60 (s, 2H), 7.19 (s, 2H), 3.10 (t, J = 7.8 Hz, 4H), 1.85 (m, 4H), 1.54 (m, 4H), 1.34 (m, 16), 0.93 (t, J = 6.6 Hz, 6H). ¹⁹F NMR (282 MHz, CDCl₃) -149.5 (m, 2F), -158.4 (m, 2F). ¹³C NMR (100 MHz, CDCl₃) 137.0, 132.1, 129.0, 125.2, 123.6, 120.1, 33.4, 32.2, 30.4, 30.2, 29.8, 29.6, 23.0, 14.4. HRMS calcd for C₃₄H₄₀F₄ (M⁺) 524.3061, found 524.3055.
1,2,3,4-Tetrafluoro-6,11-dioctyltetracene (5d): This compound was prepared by following the general procedure described above, employing 4d (0.65 g, 1.18 mmol), benzyltriethylammonium chloride (40 mg), NaOH (50% aqueous, 0.9 mL), CHCl₃ (40 mL). The common workup, chromatography and recrystallization afforded 0.22 g of 5d as red/orange crystals (35%). mp 114-115 °C (hexane). \(^1\)H NMR (300 MHz, CDCl₃) 8.95 (s, 2H), 8.27 (dd, \(J = 6.9, 3.0\) Hz, 2H) 7.50 (dd, \(J = 6.9, 3.0\) Hz, 2H) 3.66 (t, \(J = 8.4\) Hz, 4H), 1.86 (m, 4H), 1.65 (m, 4H), 1.46 (m, 4H) 1.33 (m, 12H), 0.92 (t, \(J = 6.6\) Hz, 6H). \(^1\)F NMR (282 MHz, CDCl₃) -150.0 (m, 2F), -158.4 (m, 2F). \(^{13}\)C NMR (75 MHz, CDCl₃) 134.7, 129.8, 128.1, 125.8, 125.6, 117.2, 32.1, 31.6, 30.5, 29.7, 29.6, 28.7. HRMS calcd for C₃₄H₄₀F₄ (M⁺) 524.3061, found 524.3068.

6,7-Dibromo-1,4-bis(hexyloxy)naphthalene (3a): A mixture of 6 (4.3 g, 13.6 mmol) and Na₂S₂O₄ (35 g) in 300 mL water and 500 mL ethyl ether was vigorously shaken periodically for about one hour. Organic layer was separated, washed by brine, and dried over Na₂SO₄. The solvent was removed in vacuo, leading to slight yellow solid. After drying in vacuum, the product was used directly in the next step. Under Ar, 250 mL DMF was added to a mixture of the solid product, K₂CO₃ (18 g, 130 mmol), and 18-crown-6 (0.1 g). After stirring for 10 minutes at room temperature, 1-iodohexane (8 mL, 54.2 mmol) was added. The resulting mixture was then heated to 85 °C and stirred at that temperature for 4 days. After cooling, the mixture was poured into water and extracted by CH₂Cl₂. The organic layer was washed by dilute aqueous NH₄Cl solution, water and brine in sequence, and then dried over MgSO₄ and concentrated in vacuo. Purification by column chromatography (silica gel, neat hexane ramping to CH₂Cl₂:hexane = 1:9) and recrystallization from hexane yielded colorless crystals.
(4.7 g, 71%). mp 84-85 °C (hexane). $^1$H NMR (400 MHz, CDCl$_3$) 8.48 (s, 2H), 6.68 (s, 2H), 4.05 (t, $J = 6.8$ Hz, 4H), 1.90 (m, 4H), 1.54 (m, 4H), 1.40 (m, 8H), 0.95 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) 147.8, 127.2, 126.4, 122.2, 105.7, 68.8, 31.8, 29.4, 26.1, 22.8, 14.3. HRMS calcld for C$_{22}$H$_{30}$Br$_2$O$_2$ (M$^+$) 484.0607, found 484.0613.

1,4-Bis(hexyloxy)naphthalene (8): This compound was prepared by following the procedure as described for 3a, employing 1,4-naphthoquinone (14.8 g, 93.5 mmol), Na$_2$S$_2$O$_4$ (76 g), K$_2$CO$_3$ (119 g, 862 mmol), 18-crown-6 (0.13 g), 1-iodohexane (38 ml, 260 mol), and DMF (350 mL). The usual workup and recrystallization (from methanol) gave 21.3 g of 8 as colorless crystals (73%). mp 52-53 °C (methanol). $^1$H NMR (400 MHz, CDCl$_3$) 8.26 (dd, $J = 6.4$, 3.2 Hz, 2H), 7.51 (dd, $J = 6.4$, 3.2 Hz, 2H), 6.70 (s, 2H), 4.09 (t, $J = 6.4$ Hz, 4H), 1.92 (m, 4H), 1.58 (m, 4H), 1.41 (m, 8H), 0.96 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) 149.0, 126.8, 125.8, 122.1, 104.5, 68.7, 31.9, 29.6, 26.2, 22.9, 14.3. HRMS calcld for C$_{22}$H$_{32}$O$_2$ (M$^+$) 328.2397, found 328.2393.

2,3-Dibromo-1,4-bis(hexyloxy)naphthalene (3b): A mixture of 8 (5.19 g, 15.8 mmol) and NBS (6.2 g, 34.8 mmol) in 100 mL CH$_2$Cl$_2$ was stirred at room temperature for 24 h. The reaction mixture was washed with a dilute Na$_2$S$_2$O$_4$ aqueous solution and brine. The organic layer was dried over Na$_2$SO$_4$ and concentrated in vacuo. Purification by column chromatography (Silica gel, hexane:CH$_2$Cl$_2$ = 4:1) afforded a colorless solid (6.65 g, 87%), which is pure enough for next step. A small portion of the product was recrystallized to obtain analytical pure sample for melting point measurement. mp 36-38 °C (methanol). $^1$H NMR (300 MHz, CDCl$_3$) 8.08 (dd, $J = 6.6$, 3.3 Hz, 2H), 7.57 (dd, $J = 6.6$, 3.3 Hz, 2H), 4.06 (t,
$J = 6.6 \text{ Hz, } 4\text{H}), 1.97 \text{ (m, } 4\text{H}), 1.60 \text{ (m, } 4\text{H}), 1.41 \text{ (m, } 8\text{H}), 0.95 \text{ (m, } 6\text{H}). \quad ^{13}\text{C NMR (125 MHz, CDCl}_3) 150.4, 128.7, 127.4, 123.0, 116.6, 74.7, 31.9, 30.4, 25.9, 22.9, 14.3. \quad \text{HRMS calcd for C}_{22}\text{H}_{30}\text{Br}_2\text{O}_2 (M^+) 484.0607, \text{ found 484.0599.}

1,4-Epoxy-1,4-dihydro-6,7-dibromo-1,4-dioctynaphthalene (10a): To a stirred solution of 2,5-dioctylfuran (10.7 g, 36.6 mmol) and 1,2,4,5-tetrabromobenzene (9a) (9.0 g, 22.9 mmol) in 500 mL anhydrous toluene under Ar at 0 °C was added a solution of $n$-butyllithium ($n$-BuLi) (1.6 M in hexane, 18.6 mL, 29.8 mmol) dropwise over 6 h via a syringe pump. After the addition of $n$-BuLi, the reaction mixture was stirred at 0 °C for additional 2 h, and then allowed to warm to room temperature slowly and stirred overnight. The reaction was quenched by the slow addition of methanol (5 mL). The resulting mixture was filtered through a pad of celite. The solvent was removed in vacuo. Purification by column chromatography (silica gel, neat hexane then hexane:CHCl$_3$ = 5:1) yielded colorless oil as clean product (7.75 g, 64%). \text{H NMR (300 MHz, CDCl}_3) 7.31 \text{ (s, } 2\text{H}), 6.74 \text{ (s, } 2\text{H}), 2.19 \text{ (m, } 4\text{H}), 1.57 \text{ (m, } 4\text{H}), 1.29 \text{ (m, } 20\text{H}), 0.90 \text{ (m, } 6\text{H}). \quad ^{13}\text{C NMR (100 MHz, CDCl}_3) 154.2, 145.7, 124.4, 120.5, 91.9, 32.1, 30.3, 29.7, 29.5, 29.4, 24.9, 22.9, 14.4. \quad \text{HRMS calcd for C}_{26}\text{H}_{38}\text{Br}_2\text{O} (M^+) 524.1284, \text{ found 524.1291.}

1,4-Epoxy-1,4-dihydro-6,7-dibromo-5,8-dioctynaphthalene (10b) This compound was prepared by following the procedure as described for 10a, employing the following materials: 1,2,4,5-tetrabromo-3,6-dioctylbenzene (9b) (6.38 g, 10.3 mmol), furan (11 mL), $n$-BuLi (1.6 M in hexane, 7.4 mL, 11.8 mmol), and toluene (150 mL). This reaction was carried out at -30 °C. The common workup and chromatography gave 4.2 g of 10b as a colorless solid (78%),
which is pure enough for next step. A small portion of the product was recrystallized to obtain analytical pure sample for melting point measurement. mp 60-61 °C (methanol). $^1$H NMR (400 MHz, CDCl$_3$) 7.03 (s, 2H), 5.76 (s, 2H), 2.81 (m, 4H), 1.50 (m, 4H), 1.30 (m, 20H) 0.90 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) 147.8, 142.9, 135.1, 124.7, 82.0, 35.0, 32.1, 30.0, 29.8, 29.6, 29.4, 22.9, 14.3. HRMS calcd for C$_{26}$H$_{38}$Br$_2$O (M$^+$) 524.1284, found 524.1279.

2,3-Dibromo-5,8-dioctynaphthalene (3c): Under Ar, TiCl$_4$ (11 mL, 100mmol) was added carefully and slowly to a suspension of zinc dust (10.2 g, 156 mmol) in anhydrous THF (250 mL) at 0 °C. The resulting mixture was heated to reflux for 10 minutes. After cooling back to 0 °C by an ice-water bath, a solution of 10a (7.75 g, 14.7 mmol) in anhydrous THF (100 mL) was added dropwise over a course of 2 h. The reaction mixture was refluxed for 15 h. After cooling, the reaction mixture was poured into 400 g of crushed ice and extracted by CH$_2$Cl$_2$. The organic layer was washed with water and brine, dried over MgSO$_4$, and concentrated in vacuo. Purification by column chromatography (silica gel, hexane) yielded a white solid (6.61g, 88%), which is pure enough for next step. A small portion of the product was recrystallized to obtain analytical pure sample for melting point measurement. mp 50-51 °C (THF/methanol). $^1$H NMR (400 MHz) 8.33 (s, 2H), 7.28 (s, 2H), 2.97 (pt, $J$ = 7.6 Hz, 4H), 1.72 (m, 4H), 1.42 (m, 4H) 1.33 (m, 16H), 0.91 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) 136.5, 132.5, 129.6, 127.1, 121.7, 33.0, 32.1, 30.9, 29.9, 29.7, 29.5, 22.9, 14.3. HRMS calcd for C$_{26}$H$_{38}$Br$_2$ (M$^+$) 508.1335, found 508.1352.

2,3-Dibromo-1,4-dioctynaphthalene (3d): This compound was prepared by following the procedure as described for 3c, employing the following materials: 10b (5.32 g, 10.1 mmol),
TiCl₄ (7.6 mL, 69.3 mmol), zinc (7.15 g, 0.11 mol), THF (200 mL). The usual workup, chromatography and recrystallization (methanol/THF) gave 4.9 g of 3d as a white solid (95%). mp 44-45 °C (THF/methanol). ¹H NMR (400 MHz, CDCl₃) 8.05 (dd, J = 6.4, 3.2 Hz, 2H), 7.55 (dd, J = 6.4, 3.2 Hz, 2H), 3.34 (pt, J = 8.0 Hz, 4H), 1.66 (m, 4H), 1.54 (m, 4H), 1.37 (m, 16H), 0.91 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) 139.2, 131.9, 126.8, 125.7, 125.5, 35.1, 32.1, 30.3, 29.6, 29.5, 22.9, 14.4. HRMS calcd for C₂₆H₃₈Br₂ (M⁺) 508.1335, found 508.1337.
References and Notes:


(11) (a) Bendikov, M.; Duong, H. M.; Starkey, K.; Houk, K. N.; Carter, E. A.; Wudl, F. J. 


(14) Lateral displacements along the short and long molecular axis are referred to as roll and pitch displacement, respectively. Curis, M. D.; Cao, J.; Kampf, J. W. J. Am. Chem. Soc. 2004, 126, 4318.


CHAPTER 3

Synthesis and Characterization of a Novel Poly(iptycene) Ladder Polymer

Adapted from:

Introduction

The term "iptycene" was coined by Hart as the base terminology to describe a family of molecules containing a number of arene units joined together to form the bridges of [2.2.2] bicyclic ring systems.\(^1\) The prefixes (e.g. tri- and penti-) indicate the number of interconnected arene planes. Since the first synthesis of triptycene (Figure 3.1) by Bartlett in 1942,\(^2\) a variety of iptycene molecules have been synthesized and investigated.\(^1,3\) The rigid framework of iptycenes has been useful for the study of intramolecular charge transfer,\(^7\) atropisomerism\(^8\) and molecular gears.\(^9\) Recently, iptycenes and iptycene-containing polymers were found to be able to direct molecular organizations in liquid crystal and polymer matrices, using the minimization of the free volume between the arene rings of iptycene frameworks as an organizational driving force.\(^6c,10\) The insertion of fused iptycene units into a polymer backbone was also found to improve solubility,\(^11,12\) enhance mechanical properties\(^13\) and lower the dielectric constants\(^14\) of the polymer. More interestingly, the incorporation of

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**Figure 3.1.** (A) Molecular structure of triptycene; (B) Schematic representation of internal free volume in triptycene; (C) Space filling mode of triptycene molecule
iptycene units into conjugated polymers improves their solid state luminescence quantum yields, stability, and thereby their exciton transport properties.\textsuperscript{11,15} The latter is the result of the three dimensional shape-persistence of iptycene units, which helps to isolate the polymer backbones from each other to avoid self-quenching often observed in condensed phases.

Although iptycenes and iptycene-containing polymers have been extensively investigated, the reports of polymers composed solely of iptycene scaffolds, which are referred to as poly(iptycene)s, are rare.\textsuperscript{11,16-18} Poly(iptycene), which contains both the rigid iptycene unit and a double-stranded ladder polymer structure, is expected to be a two-dimensional disc with a shape-persistent structure and high degrees of internal free volume.\textsuperscript{11,19} The free volume of these structures has been demonstrated to display unique organization in stretched polymer films.\textsuperscript{18} It has been proposed that interweaving a

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{(A) Space filling model of a poly(iptycene) ladder polymer; (B) Proposed structure of interlocked poly(iptycene) and linear polymer (adapted from ref. 18).}
\end{figure}
poly(iptycene) ladder polymer with a linear polymer can produce an inherently puncture and penetration resistant material (Figure 3.2).

Iptycenes are typically prepared by Diels-Alder (D-A) reactions between anthracene or higher acenes (as the diene) and various dienophiles, such as quinones, arynes (dehydrobenzenes) and benzofused endoxides. The quinone route generally requires multi-step syntheses, and the aryne reactions require harsh conditions and result in low yields. In contrast, the reactions between anthracene derivatives and benzofused endoxides represent an efficient method for preparing triptycene precursors that can be readily dehydrated. Our lab has previously demonstrated that a closely related ladder polymer could be prepared from a triptycene-containing AB-type monomer, which bears both anthracene and endoxide groups. Since AB-type monomers contain both the diene and dienophile, they possess the perfect stoichiometry for a D-A polymerization. In the present paper, we report the synthesis of a new AB-type monomer, 1,4-epoxy-5,12-dihexyloxy-1,4-dihydrotetracene (5) (Scheme 3.1), and its polymerization in a neat melt and under high pressure in solution. A novel poly(iptycene) ladder polymer was successfully prepared from the dehydration of the above D-A polyaddition polymer.

Results and Discussion

Monomer Synthesis

Scheme 3.1 illustrates the synthetic route to 5, an AB-type monomer containing both the anthracene and endoxide functionality, as diene and dienophile, respectively. The 1,4-anthraquinone (1), which was prepared from quinizarin according to a literature procedure,
was converted into 1,4-dihexyloxyanthracene (3) by reduction with sodium dithionate and subsequent alkylation. The hexyloxy side chain was introduced to improve the polymer solubility because aromatic ladder polymers generally have poor solubility in organic solvents.\textsuperscript{19} The brominated intermediate (4) was prepared by stirring a mixture of 3 and N-bromosuccinimide (NBS) in \(N,N\)-dimethylformamide (DMF) at room temperature.\textsuperscript{18} In the presence of excess furan, treatment of 4 with phenyllithium (PhLi) in anhydrous tetrahydrofuran (THF) afforded 5 as slightly yellow needle-like crystals. The yield over five steps is 15%.

**Scheme 3.1. Synthesis of monomers**

\textsuperscript{a} Reagents and conditions: (a) (1) \(\text{NaBH}_4\), MeOH, rt-reflux; (2) HCl, rt. (b) \(\text{Na}_2\text{S}_2\text{O}_4\), \(p\)-dioxane, H\(_2\)O, rt; (c) \(n\)-C\(_6\)H\(_{13}\)Br, K\(_2\)CO\(_3\), KI,18-crown-6, DMF, 85 °C; (d) NBS, DMF, rt; (e) furan, THF, PhLi, 0 °C.

**Syntheses of Model Compounds**

For spectroscopic references, we synthesized model compounds 10 and 11 (Scheme 3.2), which resemble the repeating unit of the initial D-A polyaddition polymer and the
expected poly(iptycene) after dehydration, respectively. The synthetic strategy was adapted from a procedure previously reported by Hart. Compound 8 was prepared by the D-A reaction of anthracene and an aryne generated in-situ from 7. Compound 9 was prepared from 8 by a procedure similar to that used for the synthesis of 5. The final step to model compound 10 involved a D-A reaction between anthracene and endoxide (9), which gave a single adduct

Scheme 3.2. Synthesis of model compounds

\[ \text{Scheme 3.2. Synthesis of model compounds}^a \]

\[ \text{Reagents and conditions: (a) } \text{K}_2\text{CO}_3, n-C_8\text{H}_{13}\text{Br}, 18\text{-crown-6, DMF, } 70 \, ^\circ\text{C}; \text{ (b) anthracene, toluene, } n-\text{BuLi, } 0 \, ^\circ\text{C}; \text{ (c) furan, toluene, } n-\text{BuLi, } -30 \, ^\circ\text{C}; \text{ (d) anthracene, xylene, } 140 \, ^\circ\text{C}; \text{ (e) pyridinium } p\text{-toluenesulfonate, acetic anhydride, } 130 \, ^\circ\text{C}; \text{ (f) xylene, } 140 \, ^\circ\text{C}; \text{ (g) pyridinium } p\text{-toluenesulfonate, acetic anhydride, } 120 \, ^\circ\text{C}. \]

10 in 81% yield. In the \(^1\text{H}\) NMR spectrum of 10 (Figure 3.4), three singlets at 2.22, 4.36 and 5.01 ppm are assigned to the three aliphatic methine protons, respectively. These features are
consistent with the NMR results of previously reported similar molecules,\textsuperscript{4g,4h,4j} which were proposed to form a rigid framework with dihedral angles close to 90° between adjacent sets of nonequivalent bridgehead protons, resulting in almost no coupling. Single crystal x-ray structural analysis confirmed that molecules bearing such NMR spectral features are the exo-adduct of the D-A reaction between anthracene and endoxide.\textsuperscript{21} The dehydration of 10 produced model compound 11, as a white solid. Model compound 13, which resembles the terminal tetracene group of expected poly(iptycene) chain, was prepared in two steps. A D-A reaction between 5 and anthracene afforded the single adduct 12, which demonstrated the similar \textsuperscript{1}H NMR spectral features as 10 and could be attributed as the exo-adduct. Finally, the dehydration of 12 afforded model compound 13 as a yellow solid.

Figure 3.3. DSC trace of monomer 5 showing melt endotherm and thermolysis exotherm.
**Thermal Analysis by Differential Scanning Calorimetry (DSC)**

DSC was used to investigate the onset and breadth of various thermally induced transitions and reactions. Figure 3.3 displays the DSC trace of compound 5, showing the D-A polymerization. On heating 5, a sharp endotherm peak was seen at 67 °C, which corresponds to the melting point of 5. Further heating generated a large broad exotherm peak with onset temperature at 162 °C and maximum at 215 °C, which could be attributed to an 111 kJ/mol exothermicity from the D-A reaction of 5. The large breadth of the exotherm peak indicates the slow rate of the D-A reaction. After heating to 290 °C and cooling to 30 °C, no subsequent crystallization was observed. Furthermore, heating of the sample back to 300 °C did not reveal any endothermic melting or exothermic transitions, indicating that the monomer was entirely consumed in the first heating cycle. Analysis of the DSC sample by gel permeation chromatography (GPC) confirmed that polymerization had occurred, yielding a mixture of oligomers with the number average molecular weight ($M_n$) = 2,800 Da and polydispersity index (PDI) = 2.8.

**Preparation of Polymer P1**

Following the DSC result, we carried out a polymerization of 5 in the neat melt by heating the solid at 170 °C (Scheme 3.3). Unfortunately, only low molecular weight polymers with $M_n$ = 5,400-6,000 Da were obtained. Since iptycene molecules generally have high melting points, the low molecular weight can be attributed to the high melting point of the formed oligomers. Additionally, attempts to polymerize 5 in o-dichlorobenzene at 180 °C under atmospheric pressure only afforded a mixture of oligomers.
It is well known that the application of pressure accelerates some reactions whose transition states present a net contraction in volume.\textsuperscript{22}

\[ \Delta V^1 = -RT(\partial \ln k / \partial P)_T \]

The D-A reaction is strongly pressure accelerated because it has large negative activation volumes $\Delta V^2 (-25 \text{ } -\text{ } -45 \text{ cm}^3 \text{ mol}^{-1})$.\textsuperscript{22d,22e} Hence, the polymerization of 5 under high pressure in the solution phase was investigated,\textsuperscript{18} and the results are summarized in Table 3.1. Four monomer solutions of different concentrations in THF were heated at 145 °C under the pressures of 129–146 Kpsi for 5 hours (Scheme 3.3). As expected, increased pressure yielded polymers (P1, Scheme 3.3) with a higher degree of polymerization, and the higher monomer concentrations led to polymers with higher molecular weight, which is typical for condensation polymerizations. However, the molecular weight could not be further improved by increasing the monomer concentration, because the final reaction mixture from 1.5 M monomer solution was found to be viscous gel-like material. P1 was obtained as a white
solidand is soluble in methylene chloride, chloroform and THF. Both the $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of P1 were identical to those of the polymer obtained from the melt. Figure 3.4 displays the $^1\text{H}$ NMR spectra of P1 and the peak assignments, together with the spectrum of model compound 10. The spectral features of P1 are in accord with those of 10. The broad and unstructured signals of P1 reflect the ribbon structure produced by D-A polymerization with a complex sequence of stereoisomers. Specifically, the asymmetrical broad peak observed at 6.7–7.3 ppm suggests that the D-A polymerization proceeds with the formation of stereoisomers. As indicated earlier, model compound 10 was obtained as single adduct and the endoxide reacts exclusively on the exo surface. The stereochemical disorder in the polymer is therefore likely due to reaction at the nonequivalent faces of the anthracene in 5. This is also consistent with the two broad peaks at 1.8–2.5 ppm, which can be assigned to the methine protons (H\text{d} of P1, Figure 3.4) in different isomeric configurations. Only one singlet
was observed for the corresponding methine proton of 10. A complicated $^{13}$C spectrum of P1, which demonstrates more aromatic carbon atoms than those of one repeating unit, provides further support for isomeric structures in P1. However, the stereochemical possibilities in P1 are numerous and can not be conclusively determined. Although we only observe exo D-A

![Figure 3.5. UV-vis absorption spectra of model compound 10 and polymer P1 ($M_n = 16,400$ Da, PDI = 3.6) measured in methylene chloride.](image)

Table 3.1. Summary of Hyperbaric Polymerization Data

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<th>[M]$^a$ (M)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Pressure (psi)</th>
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<th>PDI</th>
<th>$M_n^b$ (Da)</th>
<th>PDI</th>
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<td>6,100</td>
<td>2.2</td>
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<td>145</td>
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<td>3.3</td>
<td>12,600</td>
<td>2.6</td>
</tr>
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<td>145,800</td>
<td>16,400</td>
<td>3.6</td>
<td>16,300</td>
<td>2.5</td>
</tr>
</tbody>
</table>

$^a$ Monomer concentration. $^b$ Molecular weights determined by GPC in THF against polystyrene standards.
adduct in the synthesis of 10 and 12, the high pressure conditions and other macromolecular structural constraints could lead to some endo D-A product. There are further different orientations of the dienophile (endoxide group) with respect to each face of each diene (anthracene group) for a total of four potential stereoisomers for endo D-A linkage as well as four possible stereoisomers for exo D-A linkage. Upon conversion to P2, both the endo and exo linkage give the same stereoisomers and hence as shown in Figure 3.6, the NMR spectrum of P2 is less complex. Interestingly, the UV–vis absorption spectrum of P1 is almost identical to that of the model compound 10 (Figure 3.5).

**Preparation of Polymer P2**

We have found that the dehydration of a D-A polymer similar to P1 was unsuccessful by either catalytic p-toluenesulfonic acid in toluene or direct thermolysis, and incomplete dehydration and decomposition of the polymer were observed. With careful optimization, the dehydration of P1 was realized by employing pyridinium p-toluenesulfonate and acetic anhydride (Scheme 3.3). Polymer P2 was obtained as light yellow solid with no significant change of molecular weight compared to its precursor polymer P1 (Table 3.1). It is readily soluble in organic solvents including methylene chloride, chloroform and THF, due to both the side chain and three-dimensional iptycene units. Thermogravimetric analysis (TGA) of P2 revealed thermal stability up to 350 °C under helium atmosphere.

Successful dehydration of P1 to P2 was confirmed by comparison of the 1H and 13C NMR spectra of P2 and model compound 11 (Figure 3.6 and Figure 3.7). Compared to P1, the 1H spectrum of P2 is well resolved, partly due to the elimination of stereochemistry by
dehydration. The peak at 7.90 ppm in the $^1$H spectrum of P2 is attributed to the proton on naphthalene unit, and the other two aromatic peaks at 7.36 and 6.95 ppm are assigned to the two aromatic protons on the benzene ring. The signal of bridgehead proton is observed at 5.88 ppm, which is typical for iptycene molecules. The signal at 5.49 ppm in the spectrum of 11 does not have a counterpart in the polymer spectrum because it is from the other bridgehead proton ($H_g$) of 11 (Figure 3.6). Accordingly, the signal at 54.1 ppm in the $^{13}$C spectrum of 11, which is attributed to the above mentioned bridgehead carbon atom ($C_m$), also has no counterpart in the $^{13}$C spectrum of P2 (Figure 3.7). Other peaks observed at 3.93, 2.02, 1.70, 1.52 and 1.06 ppm in the $^1$H spectrum of P2 are assigned to the protons of hexyloxy side

![Figure 3.6. $^1$H NMR (Solvent: CDCl$_3$) spectra of model compound 11 (top) and polymer P2 ($M_n$ = 16,300 Da, PDI = 2.5) (bottom).](image)
Figure 3.7. $^{13}$C NMR (Solvent: CDCl$_3$) spectra of model compound 11 (top) and polymer P2 ($M_n = 16,300$, Da, PDI = 2.5) (bottom).

Figure 3.8. UV–vis absorption spectra of model compound 11 and polymer P2 ($M_n=16,300$ Da, PDI = 2.5) measured in methylene chloride.
Figure 3.9. UV–vis absorption spectra of model compound 13 and low molecular weight polymer P2 ($M_n = 6,000$ Da, PDI = 2.3), with inset showing the proposed structure of polymer with one end group.

More informative results came from the $^{13}$C spectrum of P2, which has an excellent match with that of model compound 11 (Figure 3.7). The P2 spectrum shows signals of eight aromatic carbons and seven saturated carbons, consistent with the structure of repeating unit of the expected poly(iptycene). Based on the $^{13}$C peak assignments of model compound 11, which are made by using the combined techniques of distortionless enhancement by polarization transfer (DEPT) and heteronuclear multiple-bond correlation (HMBC), we can make the complete $^{13}$C peak assignments of P2 as illustrated in Figure 3.7.

Figure 3.8 shows the UV–vis absorption spectra of model compound 11 and P2 in methylene chloride. The spectrum of P2 shows a considerable bathochromic shift of the absorption $\lambda_{\text{max}}$ as compared with compound 11, which may result from the extended hyperconjugation between the arene rings of iptycene units. Interestingly, the UV–vis absorption spectrum of a sample of the low molecular weight P2 ($M_n = 6,000$ Da, PDI = 2.3),
shown in Figure 3.9 together with the spectrum of model compound 13, clearly demonstrates the features of a tetracene unit, which is believed to be the end group of the polymer chain. This feature may be useful for studying the alignment of these polymers in liquid crystals and polymeric matrices.

**Conclusion**

A bifunctional AB-type monomer (5) capable of undergoing D-A polymerization was synthesized and its thermally induced polymerization was investigated by DSC. Polymerization of 5 in the melt phase yielded only low molecular weight D-A polymer. However, running the polymerization under increased pressure in solution yielded polymers (P1) with a higher degree of polymerization. Additionally, a novel poly(iptycene) ladder polymer (P2) was successfully produced from the dehydration of the precursor polymer (P1), employing pyridinium p-toluenesulfonate and acetic anhydride. The structures of both P1 and P2 were assigned by correlating their NMR spectra with model compounds.

**Experimental Section**

**Materials.** Anhydrous THF and toluene were purchased from Mallinckrodt Baker Inc. NBS was recrystallized from water. Anthracene was recrystallized from hexane and furan was distilled from K₂CO₃ prior to use. Compound 1,4-anthraquinone (1) was prepared according to literature procedures. All other chemicals of reagent grade were obtained from Aldrich Chemical Co. or Alfa Aesar, and used without further purification.
General methods and instrumentation. All synthetic manipulations were performed under an argon atmosphere using standard Schlenk techniques unless otherwise noted. High-pressure reactions were carried out on a custom-built isostatic compaction system from Harwood Engineering Company, Inc. (Walpole, MA).\(^\text{18}\) Column chromatography was performed using silica gel (40–63 μm) from SiliCycle. NMR spectra were obtained on Varian Mercury-300 MHz, Bruker Advance-400 MHz or Varian Inova-500 MHz instruments. The \(^1\)H and \(^{13}\)C chemical shifts are given in units of \(\delta\) (ppm) relative to tetramethylsilane (TMS) where \(\delta\) (TMS) = 0, and referenced to residual solvent. Experiments of \(^{13}\)C distortionless enhancement by polarization transfer (DEPT) and \(^1\)H-\(^{13}\)C heteronuclear multiple-bond correlation (HMBC) on compound 11 were carried out on a Varian Inova-500 MHz instrument. High-resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APED II 3T FT-ICR-MS using electron impact ionization (EI). Melting points were measured on a Mel-Temp II apparatus (Laboratory Devices INC) and were not corrected. Polymer molecular weights were determined on a HP series 1100 GPC system in THF (1mg/mL sample concentration) at room temperature vs polystyrene standards. Transition temperatures were determined by DSC using a TA Instruments Q1000 DSC at scan rates of 10 °C/min. TGA was carried out with TA Instruments Q50 under helium at a scan rate of 20 °C/min. UV–vis spectra were obtained from Hewlett-Packard 8452A diode array UV–visible spectrophotometer.

Synthesis of monomer

1,4-Dihydroxyanthracene (2). A solution of \(\text{Na}_2\text{S}_2\text{O}_4\) (30 g) in \(p\)-dioxane (170 mL) and nitrogen-bubbled water (170 mL) was added to 1,4-anthraquinone (8.6 g, 41.3 mmol) under
After the mixture was stirred at 25 °C for 3.5 h, an extra Na₂S₂O₄ (16 g) was added in one portion. The mixture was stirred for an additional 4 h, and then poured into 400 mL water. The precipitate was collected by filtration, washed with water and dried in vacuum, leading to a greenish yellow solid as crude product (7.4 g, 85%), which was used without further purification. mp 170–172 °C. ¹H NMR (300 MHz, DMSO-d₆) 9.57 (s, 2H), 8.66 (s, 2H), 8.08 (dd, J = 6.3, 3.3 Hz, 2H), 7.46 (dd, J = 6.6, 3.3 Hz, 2H), 6.62 (s, 2H). ¹³C NMR (75 MHz, DMSO-d₆) 145.4, 130.5, 128.5, 125.4, 125.2, 120.7, 105.6. HRMS calcd for C₁₄H₁₀O₂ (M⁺) 210.0675, found 210.0665.

1,4-Dihexyloxyanthracene (3). In an oven-dried 250 mL round-bottom flask equipped with a stir bar were combined 2 (4.0 g, 19.0 mmol), 1-bromohexane (9.4 mL, 67.0 mmol), potassium carbonate (21 g, 152.2 mmol), 18-crown-6 (0.1 g) and nitrogen-bubbled DMF (150 mL). The mixture was stirred under Ar at 60 °C for 5 d. After cooling to room temperature, the mixture was poured into 300 mL water and the product was extracted with CH₂Cl₂. The organic layer was washed by dilute NH₄Cl aqueous solution and saturated NaCl aqueous solution, and then dried over MgSO₄. Evaporation of the solvent yielded a brown solid which was recrystallized from methanol to yield yellow needle-like crystals (4.5 g, 63%). mp 69–70 °C (methanol). ¹H NMR (300 MHz, CDCl₃) 8.80 (s, 2H), 8.06 (dd, J = 6.3, 3.3 Hz, 2H), 7.48 (dd, J = 6.3, 3.3 Hz, 2H), 6.60 (s, 2H), 4.16 (t, J = 6.5 Hz, 4H), 2.00 (m, 4H), 1.63 (m, 4H), 1.44 (m, 8H), 0.96 (t, J = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) 149.2, 131.8, 129.0, 126.2, 125.8, 121.2, 102.3, 68.8, 32.1, 29.8, 26.5, 23.1, 14.6. HRMS calcd for C₂₆H₃₄O₂ (M⁺) 378.2553, found 378.2556.
2,3-Dibromo-1,4-dihexyloxyanthracene (4). A mixture of 3 (4.4 g, 11.6 mmol), NBS (4.5 g, 25.3 mmol) and nitrogen-bubbled DMF (90 mL) was stirred under Ar at room temperature for 5 h. The mixture was poured into 450 mL dilute NH₄Cl aqueous solution and the product was extracted by CH₂Cl₂. The extracts were combined and washed by 0.1 N aqueous solution of NaOH, water and saturated NaCl aqueous solution in sequence, and then dried over MgSO₄ and concentrated in vacuo. Purification by column chromatography on silica gel with hexane:CH₂Cl₂ (4:1, v/v) afforded 2.8 g (45%) product as light yellow solid. A small portion of the product was recrystallized to obtain analytical pure sample for melting point measurement. mp 56–57 °C (hexane). ¹H NMR (300 MHz, CDCl₃) 8.65 (s, 2H), 8.05 (dd, J = 6.3, 3.3 Hz, 2H), 7.54 (dd, J = 6.6, 3.3 Hz, 2H), 4.17 (t, J = 6.6 Hz, 4H), 2.05 (m, 4H), 1.68 (m, 4H), 1.46 (m, 8H), 0.97 (t, J = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) 150.7, 132.5, 129.0, 127.1, 126.9, 122.4, 115.3, 74.8, 32.2, 30.7, 26.2, 23.1, 14.6. HRMS calcd for C₂₆H₃₂Br₂O₂ (M⁺) 534.0764, found 534.0785.

1,4-Epoxy-5,12-dihexyloxy-1,4-dihydrotetracene (5). Under Ar, a stirred mixture of 4 (2.8 g, 5.2 mmol), furan (30 mL) and anhydrous THF (80 mL) was cooled by an ice-water bath. A solution of PhLi (4.5 mL, 1.5–1.7 M) was then added dropwise over a course of 5 h. After the addition of PhLi, the mixture was stirred at 0 °C for an additional 2 h, and then allowed to warm to room temperature slowly and stirred overnight. Methanol (2 mL) was added slowly to quench the reaction. The reaction mixture was poured into water and the product was extracted by CH₂Cl₂. The organic layer was washed by saturated NaCl aqueous solution and dried over MgSO₄. Solvent was removed in vacuo. Purification by column chromatography on silica gel with CH₂Cl₂:hexane (2:1, v/v) and recrystallization from hexane afforded the product as slightly yellow needle-like crystals (1.76 g, 76%). mp 62–63 °C (hexane). ¹H
NMR (300 MHz, CDCl₃) 8.58 (s, 2H), 8.00 (dd, $J = 6.3$, 3.3 Hz, 2H), 7.47 (dd, $J = 6.5$, 3.3 Hz, 2H), 6.95 (s, 2H), 6.13 (s, 2H), 4.22 (m, 4H), 1.96 (m, 4H), 1.62 (m, 4H), 1.44 (m, 8H), 0.96 (t, $J = 6.8$ Hz, 6H). $^{13}$C NMR (75 MHz, CDCl₃) 143.0, 140.0, 132.0, 128.6, 127.6, 125.9, 125.7, 121.6, 80.5, 74.2, 31.9, 30.5, 26.1, 22.9, 14.3. HRMS calcd for C₃₀H₃₆O₃ (M⁺) 444.2659, found 444.2658.

**Syntheses of model compounds**

1,2,4,5-Tetrabromo-3,6-dihexyloxybenzene (7). In an oven-dried 500 mL round-bottom flask equipped with a stir bar were combined 1,2,4,5-tetrabromohydroquinone (6) (10.9 g, 25.6 mmol), 1-bromohexane (15 mL, 107 mmol), potassium carbonate (38 g, 275 mmol), 18-crown-6 (0.1 g) and nitrogen-bubbled DMF (290 mL). The mixture was stirred under Ar at 70°C for 5 d. The workup procedure is similar to that of the preparation of 3. Recrystallization from CH₂CH₂/methanol yielded colorless crystals (13.3 g, 88%). mp 50–51°C (CH₂CH₂/methanol). $^1$H NMR (300 MHz, CDCl₃) 3.98 (t, $J = 6.6$ Hz, 4H), 1.88 (m, 4H), 1.51 (m, 4H), 1.38 (m, 8H), 0.93 (t, $J = 6.8$ Hz, 6H). $^{13}$C NMR (75 MHz, CDCl₃) 152.1, 121.6, 73.8, 31.9, 30.1, 25.7, 22.8, 14.3. HRMS calcd for C₁₈H₂₆Br₄O₂ (M⁺) 589.8661, found 589.8677.

2,3-Dibromo-1,4-dihexyloxytriptycene (8). To a stirred solution of 7 (3.0 g, 5.0 mmol) and anthracene (2.1 g, 12 mmol) in anhydrous toluene (180 mL) under Ar at 0°C was added dropwise a solution of n-butyllithium (n-BuLi) (3.5 mL, 1.6 M, 5.6 mmol) over a course of 3.5 h. After the addition of n-BuLi, the reaction mixture was allowed to warm to room temperature slowly and stirred overnight. The mixture was quenched by water, and extracted with diethyl ether. The organic layer was washed with water and saturated NaCl aqueous
solution, and dried over MgSO₄. The solvent was evaporated and the residue was recrystallized in acetone. The colorless crystals (unreacted anthracene) were removed by filtration. The filtrate was concentrated and the residue was chromatographed on silica gel with hexane, affording product as colorless crystals (0.9 g, 29%), which are pure enough for next step. A small portion of the product was recrystallized to obtain analytical pure sample for melting point measurement. mp 73–75 °C (methanol). ¹H NMR (500 MHz, CDCl₃) 7.40 (dd, J = 5.3, 3.3 Hz, 4H), 7.04 (dd, J = 5.5, 3.0 Hz, 4H), 5.75 (s, 2H), 3.94 (t, J = 6.8 Hz, 4H), 1.98 (m, 4H), 1.64 (m, 4H), 1.46 (m, 8H), 0.99 (t, J = 7.0 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) 149.0, 144.6, 139.8, 125.8, 124.1, 118.0, 75.3, 49.0, 32.0, 30.4, 26.1, 22.9, 14.4. HRMS calcd for C₃₂H₃₆Br₂O₂ (M⁺) 610.1077, found 610.1071.

6,11(1',2')-Benzeno-1,4-epoxy-5,12-dihexyloxy-1,4,6,11-tetrahydro-tetracene (9). To a stirred solution of 8 (0.69 g, 1.1 mmol) and furan (8 mL) in anhydrous toluene (80 mL) under Ar at -30 °C was added dropwise a solution of n-BuLi (0.8 mL, 1.6M, 1.3 mmol) over a course of 3 h. After the addition of n-BuLi, the mixture was stirred at -30 °C for an additional 2 h, and then allowed to warm to room temperature slowly and stirred overnight. The reaction mixture was quenched by water and diluted with 150 mL diethyl ether. The product was washed with water and saturated NaCl aqueous solution, and dried over MgSO₄. The solvent was evaporated, and the residue was chromatographed on silica gel with CH₂Cl₂:hexane (1:1, v/v, slowly up to 2:1), affording product as a colorless, highly viscous liquid (0.36 g, 62%). ¹H NMR (300 MHz, CDCl₃) 7.36 (dd, J = 5.1, 3.3 Hz, 4H), 6.98 (m, 6H), 5.82 (pt, 2H), 5.71 (s, 2H), 3.94 (m, 4H), 1.84 (m, 4H), 1.57 (m, 4H), 1.43 (m, 8H), 0.97 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) 146.0, 145.8, 144.6, 142.9, 137.8, 136.5, 125.2, 123.8, 81.0, 74.9, 48.4, 31.9, 30.4, 26.1, 22.9, 14.3. HRMS calcd for C₃₂H₄₀O₃ (M⁺) 520.2972, found 520.2964.
exo-5,16(1',2'):8,13(1'',2'')-Dibenzeno-6,15-epoxy-7,14-dihexyloxy-5,5a,6,8,13,15,15a,16-octahydrohexacene (10). A solution of 9 (0.36 g, 0.7 mmol) and anthracene (0.20 g, 1.1 mmol) in xylene (15 mL) was refluxed for 3 d. The reaction mixture was concentrated and the residue was chromatographed on silica gel with CH₂Cl₂:hexane (1:1, v/v), affording the product as a colorless solid (0.40 g, 81%), which is pure enough for next step. A small portion of product was recrystallized to obtain analytical sample for melting point measurement. mp 108–110 °C (methanol). ¹H NMR (500 MHz, CDCl₃) 7.33 (dd, J = 5.2, 3.2 Hz, 2H), 7.31 (dd, J = 5.2, 3.2 Hz, 2H), 7.28 (dd, J = 5.2, 3.2 Hz, 2H), 7.18 (dd, J = 5.2, 3.2 Hz, 2H), 7.15 (dd, J = 5.2, 3.2 Hz, 2H), 6.98 (m, 4H), 6.93 (dd, J = 5.2, 3.2 Hz, 2H), 6.68 (s, 2H), 5.01 (s, 2H), 4.36 (s, 2H), 3.95 (m, 4H), 2.22 (s, 2H), 1.87 (m, 4H), 1.60 (m, 4H), 1.46 (m, 8H), 1.02 (t, J = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) 145.7, 145.6, 144.2, 142.7, 141.6, 138.2, 135.9, 126.2, 125.9, 125.2, 125.17, 124.0, 123.8, 123.76, 123.68, 80.0, 74.7, 49.2, 48.4, 47.6, 31.9, 30.4, 26.1, 23.0, 14.4. HRMS calcd for C₅₀H₅₀O₃ (M⁺) 698.3754, found 698.3740.

5,16(1',2'):8,13(1'',2'')-Dibenzeno-7,14-dihexyloxy-5,8,13,16-tetrahydrohexacene (11). A mixture of 10 (76 mg, 0.11 mmol), pyridinium p-toluenesulfonate (270 mg, 1.1 mmol) and acetic anhydride (4 mL) was stirred under Ar at 120 °C for 15 h. The mixture was then allowed to cool to room temperature. The white precipitate was collected by filtration, washed thoroughly with methanol and dried in vacuum (55 mg, 74%). A small portion of the product was recrystallized to obtain analytical pure sample for melting point measurement. mp 256–258 °C (methanol). ¹H NMR (500 MHz, CDCl₃) 7.90 (s, 2H), 7.39 (m, 8H), 6.99 (m, 8H), 5.83 (s, 2H), 5.49 (s, 2H), 5.97 (t, J = 6.8 Hz, 4H), 2.03 (m, 4H), 1.69 (m, 4H), 1.50 (m,
8H), 1.03 (t, \( J = 7.0 \) Hz, 6H). \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)) 145.8, 144.9, 144.8, 142.4, 133.3, 125.7, 125.6, 123.9, 123.8, 116.5, 75.9, 54.1, 48.2, 32.1, 30.8, 26.2, 23.0, 14.4. HRMS calcd for C\(_{50}\)H\(_{48}\)O\(_2\) (M\(^+\)) 680.3649, found 680.3667.

**exo-5,16(1’,2’)-Benzeno-6,15-epoxy-7,14-dihexyloxy-5,5a,6,15,15a,16-hexahydronpentacene (12).** A mixture of 5 (88 mg, 0.20 mmol) and anthracene (86 mg, 0.48 mmol) in xylene (5 mL) was refluxed at 140 °C for 3 h. The solvent was then removed in vacuo, and the residue was chromatographed on silica gel with CH\(_2\)Cl\(_2\):hexane (1:2, v/v, slowly up to 1:1), affording product as a colorless solid (100 mg, 81%), which is pure enough for next step. A small portion of the product was recrystallized to obtain analytical pure sample for melting point measurement. mp 77-79 °C (methanol). \(^1\)H NMR (400 MHz, CDCl\(_3\)) 8.66 (s, 2H), 8.03 (dd, \( J = 6.4 \) Hz, 3.2 Hz, 2H), 7.49 (dd, \( J = 6.8 \) Hz, 3.2 Hz, 2H), 7.42 (dd, \( J = 5.2 \) Hz, 3.2 Hz, 2H), 7.33 (dd, \( J = 5.2 \) Hz, 3.2 Hz, 2H), 7.26 (dd, \( J = 5.6 \) Hz, 3.2 Hz, 2H), 7.09 (dd, \( J = 5.6 \) Hz, 3.2 Hz, 2H), 5.40 (s, 2H), 4.58 (s, 2H), 4.26 (m, 4H), 2.62 (s, 2H), 2.03 (m, 4H), 1.71 (m, 4H), 1.52 (m, 8H), 1.06 (t, \( J = 7.0 \) Hz, 6H). \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)) 143.9, 141.5, 141.1, 131.5, 129.4, 128.5, 127.7, 126.3, 126.0, 125.6, 124.1, 123.8, 121.6, 80.1, 73.9, 49.6, 47.7, 31.9, 30.5, 26.1, 22.9, 14.4. HRMS calcd for C\(_{44}\)H\(_{46}\)O\(_3\) (M\(^+\)) 622.3442, found 622.3422.

**5,16(1’,2’)-Benzeno-7,14-dihexyloxy-5,16-dihydrohexacene (13).** A mixture of 12 (0.10 g, 0.16 mmol), pyridinium p-toluenesulfonate (0.40 g, 1.6 mmol) and acetic anhydride (5 mL) was stirred at 120 °C for 13 h. After cooling the mixture to room temperature, the yellow precipitate was collected by filtration and washed thoroughly with methanol (30 mg). The filtrate was concentrated and chromatographed on silica gel with CH\(_2\)Cl\(_2\):hexane (1:4, v/v), leading to the second fraction of product as a yellow solid (30 mg) (total yield = 62%).
small portion of the product was recrystallized to obtain analytical pure sample for melting point measurement. mp 150–152 °C (hexane). $^1$H NMR (400 MHz, CDCl$_3$) 8.82 (s, 2H), 8.15 (s, 2H), 8.00 (dd, $J = 6.4, 3.2$ Hz, 2H), 7.49 (dd, $J = 5.2, 3.2$ Hz, 4H), 7.39 (dd, $J = 6.8, 3.2$ Hz, 2H), 7.09 (dd, $J = 5.6, 3.2$ Hz, 4H), 5.57 (s, 2H), 4.19 (t, $J = 6.8$ Hz, 4H), 2.13 (m, 4H), 1.75 (m, 4H), 1.51 (m, 8H), 1.03 (t, $J = 7.0$ Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) 147.3, 144.1, 140.5, 131.1, 128.8, 126.0, 125.5, 124.9, 124.1, 123.1, 121.4, 116.0, 76.1, 53.9, 32.1, 30.9, 26.2, 23.0, 14.4. HRMS calcd for C$_{44}$H$_{44}$O$_2$ (M$^+$) 604.3336, found 604.3360.

**Synthesis of polymers**

**P1. Procedure for melt polymerization.** Monomer (5) (160 mg, 0.36 mmol) was heated at 160 °C under Ar for 3 d. After cooling, the mixture was dissolved in THF (~1 mL) and the product was precipitated into methanol. The precipitate was collected by centrifuge, washed by methanol and dried in vacuum, leading to a white solid as product (150 mg, $M_n = 5,400$ Da, PDI = 1.9).

**General procedure for solution state polymerization under high pressure.** Under a nitrogen atmosphere in a glove box, a solution of 5 (130 mg) in THF (0.33 mL, 0.88 M) was transferred into a short Teflon® tube (inner diameter = 5 mm), which was sealed by insertion of two glass rods at its ends. The sealed tube was placed into the hypobaric reactor, which was equipped with a thermocouple and a pressure measuring system. The reaction was carried out under a pressure of 139,600 psi at 145 °C for 5 h. After cooling, the reaction mixture was added dropwise to 10 mL methanol, leading to the precipitation of a white solid material. The white precipitate was collected by centrifuge, washed by methanol and dried in
vacuum (110 mg, 85%, $M_n = 9,400$ Da, PDI = 2.7). $^1$H NMR (500 MHz, CDCl$_3$) 6.70–7.32 (m, br, 4H), 4.90 (br, 2H), 4.59 (br, 2H), 3.84 (br, 4H), 2.22 (br, 2H), 2.00 (br, 2H), 1.78 (br, 4H), 1.41 (br, 12H), 0.98 (br, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) 144.4, 142.9, 142.2, 136.1, 133.4, 125.8, 123.6, 80.0, 74.6, 48.7, 41.3, 31.9, 30.4, 26.1, 22.9, 14.3.

**P2. General procedure of the dehydration of P1.** A mixture of P1 (100 mg, $M_n = 16,400$ Da, PDI = 3.63), pyridinium p-toluenesulfonate (580 mg) and acetic anhydride (9 mL) was stirred under Ar at 130 °C for 23 h. After cooling to room temperature, a light yellow solid precipitated. The precipitate was collected by filtration, washed thoroughly by methanol and dried in vacuum, affording a light yellow solid as crude product (84 mg, 87%). Further purification involved the precipitation of a THF solution in methanol, and the solid was collected by centrifuge and dried in vacuum ($M_n = 16,300$ Da, PDI = 2.5). $^1$H NMR (500 MHz, CDCl$_3$) 7.93 (br, 2H), 7.36 (br, 2H), 6.95 (br, 2H), 5.88 (br, 2H), 3.93 (br, 4H), 2.02 (br, 4H), 1.70 (br, 4H), 1.52 (br, 8H), 1.06 (br, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) 145.8, 144.3, 141.7, 132.7, 126.0, 125.8, 123.9, 116.6, 75.9, 48.1, 32.1, 30.8, 26.3, 23.0, 14.4.
References and Notes


CHAPTER 4

Synthesis and Characterization of Triptycene-Containing Polyimides and Polyureas
Introduction

What is Polyimide?

The term “polyimides” refers to a class of heterochain polymers that contain imide group (Figure 4.1) in the main chain.\textsuperscript{1-3} According to the molecular structures, polyimides can be categorized into two general types: linear polyimides, which are made by combining imides into long chains (Figure 4.1 (A)) and, aromatic heterocyclic polyimides, which incorporate benzimide in the backbone (Figure 4.1 (B)). Commercial polyimides, which

\begin{align*}
\text{(A)} & \quad \begin{array}{c}
\text{Ra} \\
\text{N} \\
\text{Ra, Rb, Rc}
\end{array} \\
\text{(B)} & \quad \begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\end{align*}

\begin{align*}
\text{(C)} & \quad \begin{array}{c}
\text{N} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{N} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array} \\
\text{n}
\end{align*}

\begin{align*}
\text{(D)} & \quad \begin{array}{c}
\text{N} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{N} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array} \\
\text{n}
\end{align*}

\textbf{Figure 4.1.} (A) General structure of linear imide functional group; (B) An example of aromatic imide functional group; (C) Molecular structure of polyimide for Kapton and Vespel; (D) Molecular structure of polyimide for Meldin.
include Kapton, Kaptrex, Meldin, Vespel and Plavis (Figure 4.1 (C) and (D)), have been in mass production since 1955. Specifically, aromatic polyimides and other aromatic heterocyclic polymers were intensively investigated during the 1960s in order to obtain high-temperature resistant materials. 

**General Preparation of Polyimides**

The synthesis of polyimides can be dated back to 1908, when Marson Bogert reported the polycondensation of ethers or anhydrides of 4-aminophthalic acid. Since then, many synthetic routes for preparing polyimides have been reported. However, the most common way is the two-stage process of the polyacylation of dianhydrides and diamines. At the first stage, a liquid phase reaction between selected dianhydrides and diamines generates a solution of polyamic acids, the prepolymers of polyimides (Figure 4.2). The second stage of the

![Figure 4.2. Schematic illustration of the formation of polyamic acid at the first stage.](image)

![Figure 4.3. Schematic illustration of the formation of polyimide from polyamic acid.](image)
process involves a chemical cyclization, which is also called imidization (Figure 4.3). This step can be carried out in solution phase with the aid of chemical dehydrating reagents and catalysts. Acetic anhydride/pyridine system is most widely used for chemical imidization, because it does not degrade polyamic acid, even at high temperature, and the reaction can also proceed at rather high rates at substantially low temperatures, beginning with room temperature. In addition, the polyamic acid solution prepared at the first stage is often used to cast various products, such as films, fibers, coatings, and molding powders. In this case, the second stage of the synthesis is carried out in cast products by thermal treatment of polyamic acids, which removes solvents and induces the transformation of polyamic acid to polyimide. In addition to traditional wet chemical polymer manufacturing process, different gas phase methods have also been applied. For example, an alternative polyimide deposition method based on vapor deposition polymerization (VDP) allows formation of solventless films through vacuum co-evaporation of a dianhydride and a diamine. The resultant films are subsequently thermally cured to form a polyimide film and the film properties can be controlled by changing the evaporation rates. It has been reported that the dielectric constant of this polyimide film is lower than that of the one obtained by traditional solution deposition of polyamic acid. Interestingly, a recent report demonstrated that the VDP method could prepare a polyimide thin film via a solution-free process as dielectric layer for organic field effect transistors.

Applications of Polyimides

Polyimides are one of the most important classes of polymers used in the microelectronics and photoelectronics industries. Because of their high thermal stability,
chemical resistance, and good mechanical and electric properties, polyimides are often applied in photoresists, passivation and dielectric films, soft print circuit boards, and alignment films within displays.¹

Polyimides, especially aromatic polyimides, have been well recognized as high thermally stable engineering plastics, and have been widely used as a reliable material.¹,⁷ In the 1960s, polyimides, as well as other heterocyclic and aromatic polymers, were intensively investigated for applications in the aerospace industry.¹-² The aromatic and heterocyclic rings of polyimides offered rigid structures with high glass transition (\(T_g\)) and strong linkages, which allowed good resistance in harsh environment. Recently, the dispersion of carbon nanotubes into polyimides at a relatively low loading level was reported to provide environmentally durable materials with electrical conductivity and excellent thermo-optical properties. These composite materials also exhibited excellent flexibility and stability to harsh mechanical manipulation.⁸ The high thermal stability of polyimides also extended their applications in the automotive industry, which requires organic materials with good thermomechanical properties up to 200-220 °C.¹
In electrical component industries, polyimides are often used for flexible cables and as an insulating film on magnetic wires. For example, in a laptop computer, the cable that connects the main logic board to the display (which must flex every time the laptop is opened or closed) is often a polyimide base with copper conductors. The semiconductor industry uses polyimide as a high-temperature adhesive. Currently there is an increasing demand for insulation of wires working above 180 °C. Polyimide is one of the three heterocyclic polymers widely in use.

Polyimides were introduced for the production of electronic components mainly for passivation at the end of the 1970s. However, they are more interesting as materials for electronic and electro-optical applications because of their excellent processability and dielectric and thermomechanical properties. Currently polyimides have been accepted as dielectrics for the integrated circuits and multichip modulus fabrications, owing to their ease of processing, high thermal stability, low stress/coefficient of thermal expansion, excellent electrical properties, and adhesion to substrates. Kapton pyromellitic
dianhydride/oxydianiline (PMDA/ODA), which has a dielectric constant of 3.2 when measured at 1 MHz, is one of the most widely employed polyimides.\textsuperscript{1-2} However, there is current demand for dielectric materials with dielectric constants approaching 2.0 or below in order to reduce the signal delays, drive voltages, and power consumption of today's high powered integrated circuits.\textsuperscript{13a} Among the various approaches for developing polyimides with lower dielectric constants, the introduction of fluorinated groups into polyimide structures has been most effective. This methodology reduces dielectric constant mainly by reducing the electronic polarizability.\textsuperscript{12} However, the lowest dielectric constant obtained with fluorinated polyimide is about 2.5. Recently, a new concept has been developed with an aim to reduce the dielectric constant below 2.\textsuperscript{13} This concept is based on the generation of nanoscopic porosity in the polyimide films, because the dielectric constant of air is 1. A variety of approaches have been reported for developing porous polyimides, such as the use of foaming agents, the generation of foaming agents from partial degradation, the inclusion of hollow microspheres, and block copolymers with “nanofoam”.\textsuperscript{12c,14} It has been proposed that the void generation allows the formation of dielectric films with dielectric constant ranging between 1 and 2, depending on the ratio of air to polymer.\textsuperscript{2,13a}

The conventional multilayer processing of polyimide films by dry or wet-etch often increases the number of process steps and decreases manufacturing throughput. Photosensitive polyimides could be used to save several steps in the process of microelectronics, because the dielectric has to be patterned in order to obtain the bias needed for the connection.\textsuperscript{1d,2} However, it is still a challenging problem, because the photosensitivity, contrast, control of the thickness, and dielectric constant have yet to be definitely solved.
Probably the most widely known application of polyimides in the electro-optic area is their use as alignment coating for liquid crystal displays (LCDs), because they offer excellent thermal and mechanical properties and provide for stable LC alignment. In the current LCD industry, a polyimide alignment layer, which is unidirectionally rubbed with a cloth, is coated on the top and bottom electrodes of a LCD cell. Rubbing process changes the topography of the film surface and it ensures the chain orientation of the polyimide responsible for the anisotropic orientation of LC molecules, which we have described in Chapter 1. Basically, the LC alignment is a result of interactions between LC molecules and polyimides in the alignment layer surface. The operation of LCDs is based on the uniform alignment of LC molecules and its change upon electric field. Hence, the nature of LC alignment and the electro-optical properties of LCDs are strongly dependent on the chemical and physical features of the polyimide film.

In addition to the applications discussed above, polyimides are also interesting materials for nonlinear optical devices, electroluminescent devices, and optical fiber waveguides.

**Polyurea and Polyurethane**

Polyureas and polyurethanes are extremely versatile classes of polymers. A variety of raw materials, synthetic methodologies, and application technologies have been developed to prepare useful materials for many applications. Initially, their development by Otto Bayer and his colleagues came from the impetus for competing with DuPont’s polyamides and polyesters in the 1940s. Basically, polyurea can be prepared from a polycondensation
reaction between an isocyanate and an amine, and polyurethane is the product of a reaction between an isocyanate and a polyol (Figure 4.5). The first prepared polyureas from hexamethylene diamine and hexamethylene diisocyanate (HDI) were not suitable for the preparation of fibers or thermoplastics. However, the new raw materials developed by I. G. Farben (the predecessor company of Bayer AG) during 1940s afforded various polyurea and polyurethane products such as adhesives, rigid foams, elastomers and coatings. A large number of isocyanates have been developed and are commercially available (Chart 4.1). Furthermore, polyurea and polyurethane coatings/elastomers can also be derived from the reaction product of an isocyanate component and a synthetic resin blend component. The isocyanate can be aromatic or aliphatic in nature, and it can be monomer or polymer (quasi-prepolymer or prepolymer). The resin blend can be made up of amine/hydroxyl-terminated polymer resins

![Figure 4.5. Schematic illustration of the preparation of polyureas and polyurethanes.](image-url)
or chain extenders. Since the 1980s, polyurea and polyurethane have been among the most advanced resins for many applications, especially for modern coatings. In addition, polyureas stand out in industrial coatings for their versatility, strength, moisture insensitivity, heat and fire resistance, and longevity. For example, they are widely used in severe environments owing to their good chemical resistance to hydrocarbons and hydrogen sulfide gas, such as industrial sewage and wastewater coatings for rehabilitation of concrete. The short reaction
time and good adhesion properties of polyureas also enable them to be used as caulk and sealant products. Polyurethanes are generally used as casting materials and foams, and their attractive features include good longevity and relatively low cost. Polyurethane foams are often used as soft fiber stuffing that fills sofas and mattresses and hard fibers are employed to insulate buildings and repair cracks in houses. However, it is important to point out that the preparation of polyurethane requires the use of a catalyst to complete the reaction in a timely manner.

Figure 4.6. Sprayable polyurea coating for roof protection.\textsuperscript{23}
Polyurea/Polyurethane hybrid formulations can be defined as the result of a chemical reaction between an isocyanate and a mixture of polyol and amine reactants. These formulations generally provide an intermediate polyurea that displays many of the same properties of a polyurea. However, hybrid formulations can also display some of the negative problems associated with polyurethane chemistry. In coatings formulation, hybrids generally contain a polyether/polyester polyol and a primary amine resulting in a chemical backbone comprised of amine and hydroxyl functionality.

Iptycene-Containing Polymers

As we described in Chapter 3, iptycene is a class of bridged aromatic molecules with attractive rigid frameworks, unique intramolecular cavities (internal free volume), and exceptional thermal stability. Recently, polymers incorporated with iptycene units in their backbones have been found to exhibit interesting properties, such as improved solubility in common organic solvents, directing polymer chain organizations in liquid crystal, enhanced mechanical properties, and low dielectric constants. These structure-property relationships have inspired us to further investigate the effect of iptycene functionalization on the conventional polymer materials.

Aromatic polyimides have outstanding thermal resistance, good mechanical properties and excellent dielectric properties necessary for use in microelectronics as the interlayer dielectrics in integrated circuit fabrication. However, many aromatic polyimides often suffer from their intractability and poor solubility, leading to poor processability. We attempt to address this issue by incorporating three-dimensional bulky iptycene groups into
the polyimide backbone. In addition to providing solution processable polymers, we envisioned that the high degree of internal free volume induced by iptycene units may lower the dielectric constant of the resulting polymer materials.

Recently, elastomeric-like polyurea and polyurethane attracted attention for their interesting mechanical behavior, which is believed to be related to the microstructure of the polymers. Their mechanical properties at very high strain rates is particularly interesting because it is critical to enhance the structural survivability of polyurea and polyurethane protective coatings during high rate loading events. Previous studies by the Swager and Thomas groups have demonstrated that the sterically interconnected polymer-chain network created by the minimization of the internal free volume of iptycene-containing polyesters significantly enhanced the material's mechanical properties via a molecular threading and molecular interlocking mechanism. Therefore, it is of particular interest to synthesize iptycene-containing polyurea and polyurethane and study the effect of iptycene corporation on the polymer's mechanical properties.

In this chapter, we report the synthesis and characterization of two 2,6-diaminotiptycenes and their application on the synthesis of novel polyimides and polyureas. The typical characterizations of these iptycene-containing polyimides and polyureas are also discussed.
Results and Discussion

Monomer Synthesis

As shown in Scheme 4.1, the synthesis of monomer 2,6-diaminotriptycene (2) was carried out by a nitration of triptycene followed by a reduction of the nitro groups. Nitration of triptycene with nitric acid in acetic anhydride led to a mixture of reaction products, which were identified as 2,6-dinitrotriptycene (1a) as the major production and 2,7-dinitrotriptycene (1b) as the minor one. The separation of these two products was feasible because 1b has better solubility than 1a in benzene and other solvents. The predominant β-nitration was previously attributed to resonance effects, steric factors, and/or strained-ring effects and has been extensively discussed by Klanderman and Perkins. The reduction of dinitrotriptycene to diaminotriptycene was successfully achieved by using hydrazine and

Scheme 4.1. Synthesis of Daminotriptycene 2
Raney nickel, and the product was obtained as a white solid.\textsuperscript{30a,30c,32} Scheme 4.2 shows the synthesis of a second diaminotriptycene (6) via a Diels-Alder (D-A) reaction between anthracene derivative and benzofused 1,4-endoxide, which has been proved to be an efficient way for preparing various iptyocene compounds.\textsuperscript{33} Compound 2,6-diaminoanthracene was prepared in one-step from the reduction of 2,6-diamino-anthraquinone using zinc and sodium hydroxide, according to a previously reported route.\textsuperscript{33} Reaction of 3 with dienophile 4 in 1,2-dichlorobenzene at refluxing temperatures gave a single D-A adduct 5, which was dehydrated in the presence of perchloric acid, leading to diaminotriptycene 6 as a white solid.\textsuperscript{34} Both the monomers were characterized by \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy as well as high resolution mass spectroscopy.

\textbf{Scheme 4.2. Synthesis of Diaminotriptycene 6}

\begin{center}
\includegraphics[width=\textwidth]{Scheme_4.2.png}
\end{center}

\textbf{Polyimide Synthesis}

The preparation of polyimides (PI-2 and PI-6) by a conventional two-step polymerization method, which involves a ring-opening polyaddition and a subsequent ring-
closing imidization, is outlined in Scheme 4.3. In this work, only 4,4’-(hexafluoroisopropylidene)dipthalic anhydride (6FDA), which has been widely used for preparing polyimides as dielectric materials, was employed as the dianhydride monomer, because the trifluoromethyl groups have been proved to lower the dielectric constants\textsuperscript{12} and polyimides prepared from 6FDA have been demonstrated to show excellent thermal and mechanical properties, solubility as well as forming colorless thin films.\textsuperscript{2} Reaction between

Scheme 4.3. Synthesis of Polyimides

\[\text{PA-2 or PA-6} \xrightarrow{\text{acetic anhydride, pyridine, rt-110 °C}} \text{Polyimide}\]

\[\text{PI-2: } M_n = 20.6K \text{ Da}, \text{ PDI} = 1.8\]
\[\text{PI-6: } M_n = 28.9K \text{ Da}, \text{ PDI} = 1.8\]
diaminotriptycene and 6FDA in N-methyl-2-pyrrolidone (NMP) at room temperature led to a viscous solution of polyamic acid (PA-2 and PA-6). The chemical imidization of polyamic acids with a dehydrating reagent such as a mixture of acetic anhydride and pyridine (or triethylamine) was very effective in obtaining the desired polyimides.\textsuperscript{35} Both polyimides were obtained as a white/gray solid. Polyimides often exhibit yellowish to brownish in solid state because of the formation charge-transfer complexes between electron-donating amino units and electron-accepting pyromellitimide or phthalimide units.\textsuperscript{2} For PI-2 and PI-6, the bulky three-dimensional triptycene units may significantly prevent the charge-transfer complex formation.\textsuperscript{24}

**Polyimide characterizations**

The resulting polyimides PI-2 and PI-6 exhibited number-average molecular weight ($M_n$) of 20.6 K Da (polymer disperse index (PDI) = 1.8) and 28.9 K Da (PDI = 1.8), respectively, as measured by gel permeation chromatography (GPC) with respect to polystyrene standards. The structures of the obtained polyimides were verified by Fourier transform infrared spectroscopy (FTIR) and $^1$H NMR spectroscopy. As shown in Figure 4.7 and Figure 4.8, both spectra clearly show the typical IR absorption features of a polyimide. The asymmetric and symmetric stretching modes of imide unit’s carbonyl group of PI-2 are observed at 1785 and 1726 cm$^{-1}$ (for PI-6: 1786 and 1727 cm$^{-1}$), respectively. Other characteristic absorption bands of polymide are observed at 1373/1371 cm$^{-1}$ (stretching vibration of imide C–N bond) and 720/722 cm$^{-1}$ (bending vibration of carbonyl group on imide).\textsuperscript{36} The band at 1479 cm$^{-1}$ of both PI-2 and PI-6’s spectrum can be attributed to the
Figure 4.7. FTIR spectrum of polyimide PI-2.

Figure 4.8. FTIR spectrum of polyimide PI-6.
Figure 4.9. $^1$H NMR spectrum of PI-2 in DMSO-$d_6$ and peak assignment.

skeletal stretching vibration mode of aromatic rings.$^{36c,37}$ Multibands in the range of 1100-1400 cm$^{-1}$ can be contributed by the absorption of C–F vibrations. No observation of characteristic absorption bands of polyamic acid at around 3360 cm$^{-1}$ (N-H stretching vibration) and 1650 cm$^{-1}$ (amide carbonyl stretching vibration) indicates that polyamic acids are completely imidized.$^{36}$

The success of imidization was also evidenced by the NMR spectroscopy studies. Figure 4.9 and Figure 4.10 illustrate the $^1$H NMR spectra of PI-2 and PI-6 in dimethyl-$d_6$ sulfoxide (DMSO-$d_6$), which clearly demonstrate all the peaks of the aromatic protons of polymers’ expected structures. No aromatic carboxylic acid proton peaks and aromatic amide proton peaks were detected, indicating the complete conversion of polyamic acid to polyimide. Complete peak assignments of the $^1$H NMR spectra, which are made by using gradient-
Figure 4.10. $^1$H NMR spectrum of PI-6 in DMSO-$d_6$ and peak assignment.

Figure 4.11. $^{19}$F NMR spectra of PI-2 (A) and PI-6 (B) in DMSO-$d_6$. 
correlation spectroscopy (gCOSY) measurements, are shown in the insets of Figure 4.9 and 4.10. In $^{19}$F NMR measurements, a sharp single peak was observed at –63.2 ppm (Figure 4.11), providing further evidence for the successful synthesis of triptycene-containing polyimides.\textsuperscript{36}

**Thermal Imidization**

A thermal induced imidization of PA-2 was also investigated by FTIR spectroscopy. Figure 4.12 (Part A) shows the IR spectrum of PA-2, which demonstrates the characteristic absorption bands of a polyamic acid. The broad band centered at 3400 cm$^{-1}$ is attributed to the overlap of amide N–H stretching and carboxylic acid O–H stretching vibration modes. The absorption bands of amide C=O stretching and carboxylic acid C=O stretching were observed at 1654 cm$^{-1}$ and 1718 cm$^{-1}$, respectively. The band at 1540 cm$^{-1}$ is assigned to the absorption of amide N–H deformation mode.\textsuperscript{12b,35e,36} The thermal induced imidization was carried out via a stepped thermal curing of a cast film of polyamic acid on silica wafer.\textsuperscript{38} The FTIR spectrum of the resulting polyimide PI-2 is shown in Figure 4.12 (part B), which clearly demonstrated the characteristic bands of polyimide. The small peak at 1858 cm$^{-1}$ was attributed to the symmetrical stretching of carbonyl group of unreacted anhydride group.\textsuperscript{36a,39} In order to further characterize the polymer after thermal curing, the polyimide film was treated with tetrahydrofuran (THF) and the soluble part was purified by precipitation in methanol. Interestingly, this sample exhibited an IR spectrum identical to the one of polyimide prepared from chemical imidization (Figure 4.13). GPC analysis showed that the soluble part of thermally cured film contained polyimide with $M_n = 8.2$ K Da.
Figure 4.12. FTIR spectra of polyamic acid PA-2 (A) and polyimide PI-2 from thermal imidization (B).

Figure 4.13. Comparison of FTIR spectrum of PI-2 prepared from chemical imidization and thermal imidization (soluble part).
**Properties of Polyimides**

The triptycene-containing polyimides exhibited good solubility in various solvents, such as THF, NMP, dimethylacetamide, \(N,N\)-dimethylformamide (DMF), and DMSO at room temperature, partly owing to the incorporation of bulky triptycene units into the polymer main chain.\(^{24}\) Thermal stability of the polyimides were investigated by thermogravimetric analysis (TGA), and the results are displayed in Figure 4.14. TGA tests were run from 30 to 800 °C, at a heating rate of 10 °C/min under nitrogen atmosphere. Both PI-2 and PI-6 showed a weight loss of 5-10% below 400 °C, which may be attributed to the removal of moisture and terminal amine-group.\(^{40}\) The thermal weight loss starting at around 500 °C corresponded to the decomposition of the polymer main chain. This good thermal stability may be due to the presence of rigid triptycene units in the polymer backbone.\(^{34}\) The amount of carbonized residue (char yield) of both PI-2 and PI-6 was about 60% at 800 °C. The high char yields of these polyimides can be ascribed to their high aromatic contents. Differential scanning calorimetry (DSC) studies on PI-2 and PI-6 did not detect any glass transition and melting point up to 350 °C, which indicates these polyimides have excellent thermal properties suitable for high temperature applications.
Figure 4.14. TGA thermograms of polyimide PI-2 and PI-6 obtained at a scan rate of 10 °C/min under nitrogen.

The optical properties of the polyimides were studied using UV-vis spectroscopy. Figure 4.15 illustrates the normalized UV-vis absorption spectra of PI-2 and PI-6 in a chloroform solution and as a cast film on a quartz plate. Both polyimides exhibit absorption bands in the region of 200-350 nm. The films have an onset absorption wavelength at around 330 nm, which is lower than that of Kapton (450 nm). This may be interpreted by the reduction of intermolecular CTC, owing to the bulky triptycene units in the polymer backbone.
Figure 4.15. UV-vis absorption spectra of PI-2 and PI-6 in a chloroform solution (A) and as thin film (B).

Synthesis of polyureas

Similar to aromatic polyamides, aromatic polyureas have been recognized as highly stable materials with high melting temperatures and poor solubility in organic solvents, owing to their high crystallinity caused by strong hydrogen bonding between polymer chains. In this work, we chose methylene diphenyl 4,4'-diisocyanate (MDI) as the diisocyanate for the synthesis of triptycene containing aromatic polyurea. According to the typical synthetic methodology, a mixture of 2,6-diaminotriptycene (2) and MDI in anhydrous DMF was stirred at room temperature for 24 hours, leading to a highly viscous liquid (Scheme 4.4). Quenching the reaction mixture in methanol afforded a white solid material (PU-1) that could not be
easily dissolved in common organic solvents, including DMF. However, the material can be dissolved in DMF and DMSO at elevated temperature. No precipitation or curding were observed for the DMSO solution upon cooling and standing at room temperature for weeks. This enables us to further characterize the resulting polyurea PU-1. Figure 4.17 illustrates the $^1$H NMR spectrum of PU-1, which has excellent match with the expected polymer structure. A complete peak assignment was made with the help of gCOSY NMR measurement, as shown in the inset of Figure 4.16. FTIR spectroscopy study clearly demonstrated the
Figure 4.16. $^1$H NMR spectrum of PU-1 in DMSO-$d_6$ and peak assignment.

Figure 4.17. FTIR spectrum of polyurea PU-1.
characteristic absorption bands of a polyurea (Figure 4.17). The band centered at 3393 cm$^{-1}$ and the strong band at 1660 cm$^{-1}$ can be unambiguously attributed to the N–H stretching mode and the C=O stretching mode of urea units, respectively. The MDI’s methylene (–CH$_2$–) stretching absorption was observed at around 2927 cm$^{-1}$ and the band at 1411 cm$^{-1}$ was attributed to its deformation mode. Multiple bands in the range of 1470-1600 cm$^{-1}$ were contributed by the aromatic ring absorptions and amide II absorptions. GPC analysis indicated PU-1 has a high molecular weight with a large PDI ($M_n = 36.3$ K Da, PDI = 5.0). In order to improve the solubility and processibility, soft segments were induced into the main chain by using two aliphatic diisocyanates, 4,4’-diisocyanatodicyclohexylmethane (H$_{12}$MDI) and hexamethylene diisocyanate (HDI), to synthesize triptycene containing polyureas (Scheme 4.4). Although PU-2 and PU-3 have better solubility than PU-1, only low molecular weight PU-2 and PU-3 were obtained using the similar reaction conditions. This could be attributed to the lower reactivity of aliphatic diisocyanates relative to that of the aromatic diisocyanates. Both PU-2 and PU-3 are characterized by FTIR and $^1$H NMR spectroscopy. Increasing the reaction temperature to 50 °C did not improve the molecular weight. It will be necessary to optimize the reaction conditions for polyurea synthesis from aliphatic diisocyanates in the future. In addition, an application of both aromatic and aliphatic isocyanates in one polyurea system may be of particular interest.

**Conclusion**

Diamine monomer 2 and 6 were successfully synthesized via a direct nitration of triptycene followed by a reduction with hydrazine and a D-A reaction between 1,4-endoxide and diaminoanthracene followed by a strong acid catalyzed dehydration. Their applications in
the synthesis of novel triptycene-containing polyimides and polyureas are investigated and the resulting polymers are characterized. In order to clearly understand the effect of triptycene units on these polymers, it is necessary to further study their properties that are directly related to their specific applications, such as dielectric constants and mechanical properties, and to compare them with corresponding non-iptycene analogues.

Experimental Section

Materials. Anhydrous solvents NMP, pyridine, DMF, and o-dichlorobenzene were purchased from Aldrich Chemical Co. Inc. Known compound 2,6-diaminoanthracene (1) was prepared according to a literature procedure. All other chemicals of reagent grade were obtained from Aldrich Chemical Co. or Alfa Aesar, and used without further purification.

General methods and instrumentation. All synthetic manipulations were performed under an argon atmosphere using standard Schlenk techniques unless otherwise noted. Column chromatography was performed using basic alumina (chromatographic grade, pH: 9.0-10.5, 80-325 mesh) from EMD Chemicals Inc. and silica gel (40–63 µm) from SiliCycle. NMR spectra were obtained on Varian Mercury–300 MHz, Bruker Advance–400 MHz or Varian Inova–500 MHz instruments. The $^1$H and $^{13}$C chemical shifts are given in units of $\delta$ (ppm) relative to tetramethylsilane (TMS) where $\delta$(TMS) = 0, and referenced to residual solvent. $^{19}$F NMR chemical shifts are reported relative to trichlorofluoromethane (CFCl$_3$) ($\delta$(CFCl$_3$) = 0) as the reference. Gradient-correlation spectroscopy NMR spectra were obtained on Varian Inova–500 MHz instrument. High-resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APED II 3T FT-ICR-MS using electron impact ionization (EI) or
electrospray ionization (ESI). Melting points were measured on a Mel-Temp II apparatus (Laboratory Devices Inc.) and were not corrected. Polymer molecular weights were determined on a HP series 1100 GPC system in DMF or THF (1mg/mL sample concentration) vs polystyrene standards. Transition temperatures were determined by DSC using a TA Instruments Q1000 DSC at scan rates of 10 °C/min. TGA was carried out with TA Instruments Q50 under nitrogen at a scan rate of 10 °C/min. UV–vis spectra were obtained from Hewlett-Packard 8452A diode array UV–visible spectrophotometer. Fourier Transform infrared (FTIR) spectra were measured on a Perkin-Elmer model 2000 FTIR spectrophotometer using the Spectrum v. 2.00 software package.

**Syntheses of monomers**

**2,6-Dinitrotriptycene (1a).** A solution of triptycene (13.9 g, 54.6 mmol) in acetic anhydride (280 mL) was cooled by a water bath. Nitric acid (68–70%, 21 mL) was then added dropwise. After addition, the mixture was stirred at room temperature for 2 h and then poured into water. The resulting mixture was stirred vigorously overnight and the precipitate was collected by filtration, washed with water, and dried in vacuum. This slightly yellow solid was added to 250 mL benzene. The solid residue was filtered off and recrystallized from ethyl acetate twice, affording the product as a white solid (6.4 g, 39%). The benzene solution and ethyl acetate solution were combined and concentrated on a rotary evaporator. The residue was purified by column chromatography on basic alumina with benzene and afforded a white solid. Further purification involved a recrystallization from ethyl acetate, leading to a clean white material (1.8 g, 9.7%), which was found to be the minor product - 2,7-dinitrotriptycene. Major product (1a, 2, 6-dinitrotriptycene): mp > 350 °C (ethyl acetate). ¹H NMR (300 MHz,
DMSO-d$_6$ 8.37 (d, $J = 2.4$ Hz, 2H), 8.00 (dd, $J = 8.1, 2.1$ Hz, 2H), 7.75 (d, $J = 8.4$ Hz, 2H), 7.54 (dd, $J = 5.4, 3.3$ Hz, 2H), 7.10 (dd, $J = 5.4, 3.3$ Hz, 2H), 6.18 (s, 2H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) 151.6, 145.9, 145.2, 142.9, 126.1, 125.0, 124.6, 121.8, 119.1, 51.7. HRMS calcd for $C_{20}H_{12}N_2O_4$ (M$^+$) 344.0792, found 344.0781. Minor product (1b, 2,7-dinitrotriptycene): mp 253-255 °C. $^1$H (400 MHz, DMSO-d$_6$) 8.34 (d, $J = 2.4$ Hz, 2H), 7.99 (dd, $J = 8.0, 2.0$, 2H), 7.76 (d, $J = 8.0$ Hz, 2H), 7.55 (m, 2H), 7.10 (m, 2H), 6.20 (s, 1H) 6.15 (s, 1H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) 146.3, 145.2, 143.3, 142.5, 126.1, 125.1, 124.7, 124.6, 121.7, 118.9, 52.1, 51.5. HRMS calcd for $C_{20}H_{12}N_2O_4$ (M$^+$) 344.0792, found 344.0798.

2,6-Diaminotriptycene (2). To a solution of 2,6-dinitrotriptycene (0.22g, 0.64 mmol) in THF (40 mL) was added hydrazine monohydrate (1 mL) and a spatula tip of Raney Ni. The mixture was stirred at 60 °C under Ar for 14 h. After cooling to room temperature, the mixture was filtered through a pad of celite and solvent was removed in vacuo. The residue was treated with CH$_2$Cl$_2$/ethyl acetate (1:1), and the resulting white solid was collected by centrifuge and then dried in a vacuum (0.11 g). The soluble part was concentrated and then purified by column chromatography on silica gel with CH$_2$Cl$_2$/ethyl acetate (2:1, up to 1:1, v/v), affording a white solid as the second part of product (0.06 g. Totally, 0.17 g, 93%). A small portion of the product was recrystallized to obtain analytical pure sample for melting point measurement. mp 219-221 °C (CH$_2$Cl$_2$). $^1$H NMR (400 MHz, DMSO-d$_6$) 7.30 (dd, $J = 5.2, 3.2$ Hz, 2H), 6.97 (d, $J = 8.0$ Hz, 2H), 6.92 (dd, $J = 5.6, 3.2$ Hz, 2H), 6.62 (d, $J = 2.0$ Hz, 2H), 6.09 (dd, $J = 8.4, 5.6$ Hz, 2H), 5.12 (s, 2H), 4.84 (s, 4H). $^{13}$C NMR (100 MHz, DMSO-
exo-2-Amino-5,12(1',2')-(4'-amino)benzeno-6,11-epoxy-5,5a,6,11,11a,12-hexylhydrotetracene (5). A solution of 2,6-diaminoanthracene (3) (0.37 g, 1.8 mmol) and 1,4-dihydro-1,4-epoxynaphthalene (4) (0.28 g, 1.8 mmol) in o-dichlorobenzene (25 mL) was refluxed for 4 d. After cooling to room temperature, the reaction mixture was concentrated by rotary evaporation and the residue was chromatographed on silica gel with CHCl₃:ethyl acetate (1:1, v/v), affording the product as a slightly yellow solid (0.50 g, 80%), which is pure enough for next step. A small portion of the product was recrystallized to obtain analytical pure sample for melting point measurement. mp > 200 oC (CHCl₃/hexane) (decomposed). ¹H NMR (500 MHz, CDCl₃) 7.16 (dd, \( J = 5.5, 3.5 \) Hz, 2H), 7.06 (dd, \( J = 5.5, 3.0 \) Hz, 2H), 7.04 (d, \( J = 8.5 \) Hz, 1H) 6.98 (d, \( J = 7.5 \) Hz, 1H), 6.68 (d, \( J = 2.5 \) Hz, 1H), 6.60 (d, \( J = 2.5 \) Hz, 1H), 6.45 (dd, \( J = 8.0, 2.0 \) Hz, 1H), 6.31 (dd, \( J = 8.0, 2.0 \) Hz, 1H), 4.95 (s, 1H), 4.94 (s, 1H), 4.19 (m, 2H), 3.45 (s, 4H), 2.20 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) 147.2, 147.1, 146.2, 144.6, 144.4, 143.4, 134.6, 131.8, 126.3, 124.2, 124.1, 118.8, 112.1, 112.0, 111.5, 111.3, 81.4, 81.3, 49.5, 48.6, 46.9, 46.8. HRMS calcd for C₂₄H₂₀N₂O [M+1]⁺ 353.1648, found 353.1657.

2-Amino-5,12(1',2')-(4'-amino)benzeno-5,12-dihydrotetracene (6). A mixture of 5 (0.36 g, 1.0 mmol), ethanol (20 mL), and perchloric acid (70%, 4 mL) was refluxed under Ar for 7 h. The mixture was then allowed to cool to room temperature and poured into ice-water (100 mL). The resulting mixture was neutralized with aqueous NaOH solution and extracted with CH₂Cl₂. Organic layers were combined, washed with brine, and dried over anhydrous Na₂SO₄.
Solvent was removed in vacuo and the residue was treated with cold CH$_2$Cl$_2$, and the slight yellow/white solid was collected by filtration and dried in vacuum (0.12 g). Filtrate was concentrated and the residue was purified by column chromatography on silica gel with CH$_2$Cl$_2$:ethyl acetate (7:1, up to 6:1, v:v),affording the second portion of product (0.11 g, totally 0.23 g, 68%). A small portion of the product was recrystallized to obtain analytical pure sample for melting point measurement. mp 233-235 °C (CH$_2$Cl$_2$). $^1$H NMR (500 MHz, CDCl$_3$) 7.71 (s, 2H), 7.69 (dd, $J = 6.0$, 3.5 Hz, 2H), 7.36 (dd, $J = 6.0$, 2.5 Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 6.79 (d, $J = 2.5$ Hz, 2H), 6.30 (dd, $J = 8.0$, 2.5 Hz, 2H), 5.29 (s, 2H), 3.52 (s, 4H). $^{13}$C NMR (125 MHz, CDCl$_3$) 146.6, 144.3, 142.9, 135.1, 131.9, 127.6, 125.6, 124.3, 121.2, 111.6, 111.3, 53.1. HRMS calcd for C$_{24}$H$_{18}$N$_2$ [M+1]$^+$ 335.1543, found 335.1547.

**Polyimide synthesis**

**PI-2:** To a stirred solution of 5 (0.28 g, 1.0 mmol) in 5 ml of NMP was added 4,4'- (hexafluoroisopropylidene)diphthalic anhydride (6FDA) (0.44 g, 1.0 mmol) gradually. The reaction mixture was stirred at the ambient temperature for 24 h to form a viscous liquid. A mixture of pyridine (0.5 mL) and acetic anhydride (1 mL) was added to the above reaction. The resulting mixture was stirred at room temperature for an additional 1 h and then was heated to 110 °C for 4.5 h. After cooling to room temperature, the reaction mixture was poured into methanol (200 mL). The precipitate was collected by filtration and washed thoroughly with methanol. Further purification involved the precipitation of a THF solution in methanol, Soxhlet extraction with methanol for 2 d, and a vacuum drying at 100 °C, leading to a white/gray solid as the product (0.53 g, 78%, $M_n = 20.6$ K Da, PDI = 1.8). $^1$H NMR (400 MHz, DMSO-$d_6$) 8.14 (d, $J = 7.2$ Hz, 2H), 7.94 (s, br, 2H), 7.72 (s, 2H), 7.63 (d, $J = 7.6$ Hz,
2H), 7.55 (s, 2H), 7.53 (s, 4H), 7.11 (d, J = 7.6 Hz, 2H), 7.06 (s, 2H), 5.84 (s, 2H). $^{19}$F NMR (282 MHz, DMSO-$d_6$) –62.7 (s, 6F). FT-IR (KBr) v/cm$^{-1}$: 1785, 1726, 1623, 1478, 1436, 1372, 1298, 1257, 1210, 1142, 1105, 985, 853.

Polyimide film of PI-2 was prepared by casting a solution of polyamic acid in NMP on a silicon wafer at room temperature and then by heating at 80 °C (under Ar), 150 °C (under Ar), 250 °C (under air), and 300 °C (under air) each for 1 h.

PI-6: PI-6 was obtained in a similar manner as that for the synthesis of PI-2, employing 6 (0.25 g, 0.75 mmol), 6FDA (0.32 g, 0.72 mmol), NMP (5 mL), pyridine (0.4 mL), and acetic anhydride (0.8 mL). (0.46 g, 83%, $M_n$ = 28.9 K Da, PDI = 1.8). $^1$H NMR (400 MHz, DMSO-$d_6$) 8.14 (s, br, 2H), 7.97 (s, 2H), 7.94 (br, 2H), 7.80 (s, 2H) 7.72 (s, 2H), 7.69 (s, 2H), 7.62 (s, 2H), 7.43 (s, 2H), 7.16 (d, J = 7.2 Hz, 2H), 5.96 (s, 2H). $^{19}$F NMR (282 MHz, DMSO-$d_6$) –62.7. FT-IR (KBr) v/cm$^{-1}$: 1786, 1727, 1622, 1478, 1434, 1371, 1297, 1257, 1210, 1193, 1143, 1104, 985, 964, 881, 837, 744, 721.

**Polyurea synthesis**

PU-1: To a stirred solution of 2 (0.45 g, 1.6 mmol) in anhydrous DMF (4 mL), which was cooled by an ice-water bath, was added dropwise a solution of MDI (0.40 g, 1.6 mmol) in anhydrous DMF (6 mL) under Ar. The resulting mixture was stirred at room temperature for 24 h, and then quenched by a slow addition to methanol. The white precipitate was collected by filtration, washed with methanol, and dried under a vacuum (0.85 g, 100%) ($M_n$ = 36.3 K Da, PDI = 5.0). $^1$H NMR (400 MHz, DMSO-$d_6$) 8.53 (s, 2H), 8.51 (s, 2H), 7.64 (s, 2H), 7.40 (s, 2H), 7.32 (br, 4H), 7.29 (br, 2H), 7.08 (d, J = 7.6 Hz, 4H), 6.97 (s, 2H), 6.90 (d, J = 7.6 Hz,
2H), 5.75 (s, 2H), 5.49 (s, 2H). FT-IR (KBr) v/cm⁻¹: 3392, 2927, 1660, 1597, 1508, 1475, 1411, 1308, 1233, 1098, 1018, 814, 745, 662.

**PU-2:** This polymer was prepared by following the procedure as described for PU-1, employing 2 (0.28 g, 0.98 mmol), H₂MDI (90%, mixture of isomers, 0.29 g, 0.98 mmol), and DMF (6 mL). A white solid was obtained as the product (0.50g, 89%). (Mₙ = 10.0 K Da, PDI = 1.6). ^1^H NMR (400 MHz, DMSO-d₆) 8.21 (s, 1H), 8.17 (s, 1H), 7.57 (s, 1H), 7.53 (s, 1H), 7.37 (s, 2H), 7.22 (m, 2H), 6.96 (s, 2H), 6.82 (m, 2H), 6.19 (d, J = 5.6 Hz, 1H), 5.93 (d, J = 6.4 Hz, 1H), 5.39 (s, 2H) 1.82 (br, 2H), 1.65 (br, 2H), 1.46 (br, 6H) 1.23 (br, 2H) 1.07 (br, 6H), 0.89 (br, 2H). FT-IR (KBr) v/cm⁻¹: 3339, 2925, 2851, 1661, 1596, 1547, 1478, 1324, 1226, 1151, 1097, 746.

**PU-3:** This polymer was prepared by following the procedure as described for PU-1, employing 2 (0.37 g, 1.30 mmol), HDI (0.22 g, 1.30 mmol), and DMF (9 mL). A white solid was obtained as the product (0.50g, 85%) (Mₙ = 8.3 K Da, PDI = 1.4). ^1^H NMR (400 MHz, DMSO-d₆) 8.27 (s, 2H), 7.57 (s, 2H), 7.37 (s, 2H), 7.21 (d, 2H), 6.95 (s, 2H), 6.83 (d, J = 7.6 Hz, 2H), 6.05 (2, 2H), 5.40 (s, 2H) 3.02 (m, br, 4H), 1.38 (s, br, 4H) 1.25 (s, br, 2H). FT-IR (KBr) v/cm⁻¹: 3315, 2931, 1856, 1654, 1594, 1552, 1477, 1415, 1235, 1094, 818, 749.
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CHAPTER 5

Synthesis and Properties of Fluorene-Iptycene Based Polyheteroarylenes
Introduction

Band Gap Engineering of Conjugated Polymers

Organic $\pi$-conjugated polymers constitute a class of promising semiconducting materials having demonstrated utility in device applications, including light-emitting diodes,$^1$ photovoltaic cells,$^2$ field effect transistors,$^3$ and nonlinear optics.$^4$ In addition, fluorescent conjugated polymers have demonstrated high sensitivity in chemical and biological sensor schemes because of the ability of conjugated polymers to create large signal amplification relative to small molecule chemosensors.$^5$ This property has been proposed to result from the delocalization and rapid diffusion of excitons through polymer chains in solution and in thin films.$^5$

The advantages of conjugated polymers can be attributed to their interesting properties that combine the physical properties of polymers with those of semiconductors to obtain unique and novel materials. Furthermore, it is very attractive for synthetic chemists that their electronic and/or optical properties can be extensively tuned by structure modification.$^6$ An additional advantage of using polymers as sensor materials emerges from the modular nature of polymers; i.e., the structure and sequence of the repeating units within polymers can be widely varied and modified, which allows the polymers to be tailored for diverse targets and potentially achieve high selectivity.

In the field of materials science, band gap engineering is very important because the band gap is one of the most important factors controlling a material’s physical properties. Similarly, band gap engineering of organic $\pi$-conjugated polymers also plays a crucial role in
Figure 5.1. Calculated (frontier) energy levels of oligothiophenes with \( n = 1-4 \) and of polythiophene, where \( E_g = \text{band gap} \).\(^8\)

optimizing the performance of optoelectronic devices. The band gap of conventional inorganic semiconductors is defined as the energy difference between the edges of the conduction band and valence band. The band structure of a conjugated polymer is similar to that of its inorganic analogues, which have their electrons organized in bands rather than in discrete levels, and it originates from the interaction of \( \pi \)-orbitals of the repeating units throughout the polymer backbone (Figure 5.1).\(^6-^8\) Interactions between the \( \pi \)-electrons of neighboring polymer chains lead to a three-dimensional band structure. According to the band theory for inorganic semiconductors, the highest occupied band and the lowest unoccupied band of a conjugated polymer, which originate respectively from mixing of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of each repeating unit, are called the valence band and conduction band of the
polymer, and the energy difference between these two bands is referred to as the band gap \( (E_g) \).  

The band gap of a conjugated polymer is determined by many different parameters, such as bond length alternation, conjugation length, aromaticity, resonance energy, and interring torsion angle.\(^6\)-\(^7\) However, subtle influence on the band gap can be achieved by several synthetic approaches.\(^8\)-\(^10\) The introduction of side groups is the easiest way to manipulate the band gap of a given polymer via mesomeric and induced electron effects.\(^9\) For example, electron-donating groups raise the valence band level and electron-withdrawing groups lower the conduction band level. The most widely used electron withdrawing groups are cyano and nitro groups. Flexible side groups, such as alkoxy and alkyl substituents, are also often employed to improve the solubility of a polymer. Furthermore, the effects of these groups on the polymer’s organization in the solid phase have been demonstrated to significantly influence its electronic and optical properties, which is exemplified by regioregular poly(3-hexyl thiophene).\(^3\)  

Another effective way to manipulate the band structure of a conjugated polymer is the incorporation of donor (electron rich)—acceptor (electron poor) units into the polymer backbone, which has been an important approach to tune conjugated polymers’ electronic and optoelectronic properties.\(^8\),\(^10\)-\(^11\) Polymers with alternating donor and acceptor units are also called push-pull polymers. The low band gaps of push-pull polymers are attributed to the interaction of the donor and acceptor moieties, which enhances the double bond character between repeating units and stabilizes the low band gap quinonoid forms within the polymer.
Recent molecular orbital calculations have shown that the hybridization of the energy levels of the donor and acceptor moieties result in donor–acceptor systems with unusually low HOMO–LUMO separation. If the HOMO levels of the donor and the LUMO levels of the acceptor moiety are close in energy, the resulting band structure will show a low energy gap as illustrated in Figure 5.2. On the other hand, it is also accepted that the band gap of such copolymers can decrease significantly if there is a big difference between the electronegativities of the donor and acceptor moieties.

Figure 5.2. Molecular orbital interaction in donor (D) and acceptor (A) moieties leading to a donor-acceptor monomer with a reduced band gap (adapted from ref. 10b).

Therefore, designing extremely low $E_g$ polymers requires strong donors and acceptors. Commonly employed donors are pyrrole, thiophene, fluorene, phenylene and vinylene, and these electron rich units also allow numerous chemical modifications, leading to various interesting conjugated polymers. The acceptor moieties that have been reported for
low band gap polymers include pyridine,\textsuperscript{16} bithiazole,\textsuperscript{17} naphthoselenadiazole,\textsuperscript{18} indenofluorene,\textsuperscript{19} quinoxaline,\textsuperscript{20} 2,1,3-benzothiadiazole,\textsuperscript{21} and perylene\textsuperscript{22}, with some of their molecular structures shown in Figure 5.3. Further reduction of band gaps by enhancing the strength of donor and acceptor moieties via strong orbital interactions has also been reported. For example, the electron withdrawing power of

![Chemical Structures]

\textit{Figure 5.3. Examples of acceptors for donor-acceptor type conjugated polymers.}

quinoxaline or 2,1,3-benzothiadiazole could be further increased by fusion of another pyrazine or thiadiazone ring onto the vacant sites of the phenyl ring to yield pyrazinoquinoxaline, thiadiazoloquinoxaline and benzobis(thiadiazole)\textsuperscript{23-24}. In short, the concept of donor-acceptor copolymerization offers several possibilities to design conjugated polymers whose electronic properties and band gaps can be tuned by varying the electron donor or acceptor strength of the monomers.

\textbf{Iptycene-Containing Conjugated Polymers}

Iptycenes, especially triptycene and pentiptycene derivatives, have been extensively employed in our laboratory to design and synthesize novel functional materials.\textsuperscript{25} Conjugated polymers containing these rigid, three-dimensional iptycene scaffolds have been found to display improved photostability and quantum yields in the solid state, as well as enhanced
solubility in common organic solvents. These enhancements were proposed to result from spatial isolation of the polymer backbones that significantly reduces interchain interaction in the solid state, which is believed to play a dominant role in determining the thin film optical properties of conjugated polymers. Upon introducing pentiptycene units into the conjugated polymer, the three-dimensional bulky structures sterically isolate the polymer backbones and thereby reduce interchain electron/orbital coupling and self-quenching, which often accompanies these interactions. These features afforded novel, highly-fluorescent conjugated polymers, such as poly(p-phenyleneethynylene)s (PPEs), which have been demonstrated to be ultrasensitive sensory materials. Sensor applications have been developed to take advantage of the ultrasensitive fluorescent quenching response of PPEs to vapors of electron-accepting analytes, such as 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT). The detection mechanism is fluorescence quenching through nonbonding electrostatic associations between the electron-rich polymer and the electron-poor nitroaromatic quenchers. In addition, the rigid elaborated scaffolds also introduce additional free volume in the solid-state material, which facilitates rapid analyte diffusion into the polymer film to achieve faster and larger-amplitude responses. This large free volume inherent to the iptycene scaffolds has also been exploited to achieve enhanced chromophore and liquid crystal alignments.

On the basis of the advantages of iptycene-containing PPEs, we have been interested in extending this design concept into other conjugated systems, which have also shown excellent properties for numerous applications. Polyfluorenes (PFs) have been widely studied for polymer light-emitting diodes (PLEDs) because of their processibility, high quantum yield, and good charge transport properties. However, the PLED application of
PFs often suffers from their poor electron-transporting property, which results in a large
electron-injection barrier and unbalance of charge carrier transport. Recent work found that
copolymerization of fluorene with various electron-accepting and/or electron-transporting
moieties could solve this problem.\textsuperscript{23} Hence, fluorene–acceptor based conjugated copolymers
have attracted considerable attention.\textsuperscript{27} In addition to the improvement of charge injection
and transport, the light-emitting color and efficiency of PLEDs based on the fluorene-acceptor
copolymers were found to be easily tuned by the acceptors. No other polymer class offers the
full range of color with high efficiency, low operating voltage, and high lifetime when applied
in a device configuration. Interestingly, photovoltaic devices with good efficiencies and field
effect transistors with high electron mobility based on these kinds of copolymers were also
recently demonstrated.\textsuperscript{27c-d}

Inspired by the above considerations, we designed and synthesized three fluorene-
iptycene based conjugated polymers, and investigated their properties. In this work, we
present the synthesis of two triptycene-type quinoxaline and thienopyrazine acceptor units and
the synthesis of the corresponding iptycene-type donor-accepter copolymers using
palladium(0)-catalyzed Suzuki coupling reaction. These two copolymers were also compared
with a regular fluorene-triptycene copolymer. The three copolymers have iptycene groups of
different electronic properties installed in each repeating unit, and this unique feature
represents a key difference between them and the previously reported copolymers. This
difference is envisioned to explore both the iptycene “insulation” effect and the tuning of the
band structure of conjugated polymers.
Results and Discussion

Monomer Synthesis

The triptycene-type monomers 2 and 5 were prepared from the condensation of a diketone with corresponding diamines (Scheme 5.1 and 5.2).\textsuperscript{28} The diketone compound 1 was prepared by employing commercially available vinylene carbonate and anthracene, a route that has been previously employed to prepare soluble acene precursors because the diketone functionality can be easily removed by heating or irradiation.\textsuperscript{29} The synthesis of 1 starts from a Diels-Alder reaction of anthracene and vinylene carbonate, followed by a base assisted hydrolysis in a methanol/tetrahydrofuran(THF)/water mixture, leading to the diol product in high yield.\textsuperscript{29d,30} Finally, an activated Swern oxidation using trifluoroacetic anhydride and dimethyl sulfoxide (DMSO) gave the target product 1 as a yellow solid.\textsuperscript{29a,29d,30a,31} Monomer 2 was obtained as a white solid by condensing 1 with 3,6-dibromo-1,2-diaminobenzene, which was prepared from the reduction of dibromobenzothiazole.\textsuperscript{28a,32} A similar condensation between diketone 1 and 3,4-diaminothiophene hydrochloride (3),\textsuperscript{33} which was easily prepared from a nitration of 2,5-dibromothiophene followed by a reduction with tin metal under acidic conditions,\textsuperscript{33a} afforded iptycene type thieno[3,4-b]pyrazine 4 as a white solid. Finally, a typical bromination reaction of 4 with N-bromosuccinimide (NBS) in N,N-dimethylformide (DMF) gave the target thienopyrazine monomer 5 as a bright yellow solid.\textsuperscript{34} All of these new compounds are characterized by \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy, as well as high resolution mass spectroscopy.
Scheme 5.1. Synthesis of triptycene-type quinoxaline 2

Scheme 5.2. Synthesis of triptycene-type thieno[3,4-b]pyrazine monomer 5

Polymer Synthesis

The synthetic strategy employed for the preparation of copolymers is based on the Suzuki reaction, using 9,9-dioctylfluorene-2,7-bis(trimethyleneboronate) as the organoboron reagent. The polymerization was carried out in a mixture of toluene and aqueous potassium.
carbonate (2 M) containing a catalytic amount of tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) and aliquat® 336 (methyltrioctylammonium chloride) under vigorous stirring at 105 °C for 72 h (Scheme 5.3).¹⁷,²⁰,²⁷a,³⁶ For comparison, a copolymer (PFP) containing regular triptycene was also prepared from 1,4-diiodotriptycene (6), which was prepared according to a reported procedure.³⁷ All these copolymers were obtained in high yields and are readily dissolved in common organic solvents, such as chloroform, THF, toluene, and chlorobenzene. After standard purifications and drying, PTP, PTQ and PFTP were obtained as white, greenish yellow and dark red solids, respectively (Figure 5.4), indicating their different photophysical properties. Their molecular weights as determined by Gel permeation

**Scheme 5.3.** Synthesis of fluorene-triptycene based copolymers

PFP: $M_n = 26.9$ K Da, PDI = 2.2

PFTP: $M_n = 11.6$ K Da, PDI = 1.9

PFQ: $M_n = 20.6$ K Da, PDI = 2.3
Figure 5.4. Images of the synthesized fluorene-iptycene based conjugated polymers.

Figure 5.5. $^1$H NMR spectra of the (A) PFTP; (B) PFQ; (C) PFP in CDCl$_3$, in which labels of * and # correspond to CHCl$_3$ and H$_2$O, respectively.
chromatography (GPC) against polystyrene standards are within the range of 12 K—27 K Da, corresponding to degrees of polymerization of about 17—42 units and polydispersity index (PDI) of around 2. The copolymers show high thermal stability, with decomposition temperature up to 400 °C as estimated by thermogravimetric analysis (TGA) (Table 5.1). The molecular structures of these copolymers were verified by 1H NMR spectroscopy (Figure 5.5), and the spectroscopic data are in good agreement with their structures.

**Polymer Characterization**

The normalized optical absorption and fluorescence spectra of PFP, PFQ, and PFTP in dilute chloroform solution are shown in Figure 5.6 and Figure 5.7, respectively. PFP has an absorption maximum at 335 nm corresponding to the π-π* transition of the polymer backbone that is blue-shifted by 50 nm and 17 nm relative to the absorption of PF homopolymer and fluorene-phenylene copolymer, respectively. The impact of steric effects was previously invoked to explain the difference in electronic properties of conjugated polymers that differ only in the shape of the repeating unit, because the steric repulsion between adjacent repeating units tends to increase their torsional angle, leading to weaker conjugation and bigger band gap. In this case, the observed blue shift may arise from the repulsive interaction between the bridgehead hydrogen of triptycene and the C-1 or C-3 hydrogen of fluorene. Both PFQ and PFTP have multiple absorption bands in solution (Figure 5.6), and the highest energy absorption bands at 328 and 345 nm, respectively, may be assigned to the fluorene segments of both polymers. Additional long wavelength bands are observed at 395 and 530 nm for PFQ and PFTP, respectively. The substitution of phenylene by quinoxaline or thienopyrazine units in the polymer backbone is observed to cause a
significant red-shift in the absorption band edge of these polymers relative to PFP. This difference is attributed to the intramolecular charge transfer (ICT) interactions that lead to an increase in the effective conjugation length and a reduction of band gap, because quinoxaline and thienopyrazine are good acceptors. Previous studies by Kitamura and coworkers estimated the LUMO of quinoxaline and thienopyrazine at −0.90 and −1.41 eV, respectively, which indicates that thienopyrazine is a stronger acceptor that is expected to have stronger a ICT interaction than quinoxaline. This is consistent with our observation that PFTP has a larger red-shift than PFQ. However, it is also possible that the (five-membered ring) thiophene of thienopyrazine could result in a smaller torsional angle with fluorene than the (six-membered ring) phenylene of quinoxaline, which enhances the efficiency of ICT

Figure 5.6. Normalized UV-vis absorption spectra of PFP, PFQ and PFTP in chloroform.
interaction and leads to a smaller band gap. The optical band gaps of PFP, PFQ and PFTP, determined from the onset of absorption, are 3.43, 2.84, and 2.02 eV, respectively (Table 5.1).

These three copolymers exhibited different emission colors when in solution, as shown in Figure 5.7. The emission bands of PFP, PFQ and PFTP have maxima at 381, 472, and 622 nm, respectively, roughly corresponding to blue, greenish-blue and red light. Similar to their absorption spectra, this difference in the emission properties between the three copolymers can be understood in terms of the strength of donor-acceptor interaction and/or the increased planarity of thiophene-containing polymers, which leads to longer conjugation length and a smaller band gap. The varied photophysical properties of PFP, PFQ and PFTP also demonstrate that the photophysical properties of fluorene-based copolymers can
be easily tuned using suitable co-monomers, indicating the flexibility of structure manipulation of conjugated polymers. The emission bands of all polymers are relatively narrow, without significant vibronic peaks/shoulders, which may be smeared out by large inhomogeneous optical broadening of polymers. Additionally, the spectra demonstrate significant red-shift of the emission with respect to absorption (Stokes shift), valued at 46, 77, and 92 nm for PFP, PFQ and PFTP, respectively, which indicates the presence of a large conformation difference between the ground and the excited states of the copolymers. This may be explained by the structural twisting of polymer backbone from ground state steric effects, while the polymer backbone at excited state has more quinonoid character, which induces planarization. Furthermore, the progressively larger Stokes shift from PFP, PFQ to PFTP suggests that the Stokes shift is increased by the donor-acceptor charge transfer interactions. Table 5.1 summarizes the quantum yields and fluorescence lifetimes of PFP, PFQ to PFTP, together with other photophysical properties. The large Stokes shifts observed are also consistent with the fluorescence lifetime results (Table 5.1), which indicate that the copolymers have long lived excited states that allow for excitons to be transported to lower energy segments in the polymer chain. The presence of a large Stokes shift in conjugated polymers has been considered as an advantage for designing polymer laser materials because the red-shifted emission will limit self-absorption.
Table 5.1. Summary of Physical Properties of Copolymers PFP, PFQ to PFTP

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Chloroform Solution</th>
<th></th>
<th></th>
<th>Thin film</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\lambda_{\text{em}}$ (nm)</td>
<td>$\tau$ (ns)</td>
<td>$E_{\text{g,op}}$ (eV)</td>
</tr>
<tr>
<td>PFP</td>
<td>335</td>
<td>381</td>
<td>0.48; 100%</td>
<td>3.43</td>
</tr>
<tr>
<td>PFQ</td>
<td>328</td>
<td>472</td>
<td>2.46; 100%</td>
<td>2.84</td>
</tr>
<tr>
<td>PFTP</td>
<td>345</td>
<td>622</td>
<td>2.17; 78%</td>
<td>2.02</td>
</tr>
</tbody>
</table>

$^a$ Fluorescence quantum yield relative to quinine sulfate in 0.1 N H$_2$SO$_4$ aqueous solution ($\Phi_{\text{re}} = 0.54$). $^b$ Fluorescence quantum yield relative to cresyl violet perchlorate in methanol ($\Phi_{\text{re}} = 0.54$). $^c$ Band gap estimated from the onset of absorption spectrum in chloroform. $^d$ Decomposition temperature estimated by TGA analysis.

The absorption and emission spectra of PFP, PFQ and PFTP in the solid state (Figure 5.8 and 5.9) are almost identical to their spectra in solution, indicating the success of polymer chain insulation by iptycene units.$^{25a,25i-3,37}$ Further evidence came from the absence of any shoulder peaks and/or tails at the longer wavelength range, which are often observed for various conjugated polymers and are proposed to result from strong polymer inter-chain interactions, leading to formation of aggregates and excimers.$^{27}$ Figure 5.10 shows the fluorescent images of thin films of PFP, PFQ and PFTP irradiated by a 365 nm UV light. The moderately strong and pure emissions indicate that these copolymers retain their pristine single-chain photophysical properties in a thin film.
Figure 5.8. Normalized UV-vis absorption spectra of PFP, PFQ and PFTP films spin-casted from their chloroform solution.

Figure 5.9. Normalized fluorescence spectra of PFP, PFQ and PFTP films spin-casted from their chloroform solution.
Conclusion

Iptycene type quinoxaline and thienopyrazine monomers (2 and 5) were successfully synthesized via a condensation between 10-dihydro-9,10-ethanoanthracene-11,12-dione (1) and corresponding diamines. Three fluorene-based copolymers (PFTP, PFQ, and PFP) containing different iptycene units were prepared via Suzuki coupling reaction, and they exhibited good solubility in appropriate organic solvents. These copolymers are fluorescent in both solution and the solid state, emitting blue, greenish-blue, and red color, respectively. The difference in absorption/emission spectra was attributed to the donor-acceptor charge transfer interactions and conformation change in the polymer backbone induced by steric effects. Moreover, we clearly demonstrated the insulation effect of iptycene units, which prevented both the aggregation of polymer chain and formation of excimers in the solid state. The future work includes electrochemical studies and further tuning the electronic and optical properties of this class of copolymers.
Experimental Section

Materials. Vinylene carbonate, anthracene, glacial acetic acid, trifluoroacetic anhydride, anhydrous DMSO, metal tin, NBS, 9,9-diocytfluorene-2,7-bis(trimethyleneborate), tetrakis(triphenylphosphine)palladium(0), potassium carbonate, and methyltrioctylammonium chloride (aliquat® 336) were purchased from Alfa Aesar, TCI America, Strem Chemical Inc., or Aldrich Chemical Co., and used without further purification. Anhydrous solvents used in the reactions were purchased from Mallinckrodt Baker Inc. Known compounds 9,10-dihydro-9,10-ethanoanthracene-11,12-dione (1),29-31 3,6-dibromo-1,2-diaminobenzene,28a,32 3,4-diaminothiophene dihydrochloride (3),33a and 1,4-diiodotriptycene (6)37 were prepared according to literature procedures.

General methods and instrumentation. All synthetic manipulations were performed under an argon atmosphere using standard Schlenk techniques unless otherwise noted. Column chromatography was performed using basic alumina (pH: 9.0-10.5; 80-325 mesh) from EMD Chemicals Inc. or silica gel (40–63 µm) from SiliCycle. NMR spectra were obtained on Bruker Advance-400 MHz or Varian Inova-500 MHz instruments. The 1H and 13C chemical shifts are given in units of δ (ppm) relative to tetramethylsilane (TMS) where δ (TMS) = 0 and are referenced to residual solvent. High-resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APED II 3T FT-ICR-MS using electron impact ionization (EI) or electrospray ionization (ESI). Melting points were measured on a Mel-Temp II apparatus (Laboratory Devices INC) and were not corrected. Polymer molecular weights were determined on a HP series 1100 GPC system in THF (1mg/mL sample concentration) at room temperature vs polystyrene standards. TGA was carried out with TA Instruments Q50 under
nitrogen at a scan rate of 10 °C/min. UV–vis spectra were obtained from Hewlett-Packard 8452A diode array UV–visible spectrophotometer. Fluorescence spectra were measured with a SPEX Fluorolog–r2 fluorometer (model FL112, 450W xenon lamp). Fluorescence quantum yields in chloroform solutions were determined relative to quinine sulfate solution in 0.1 N H₂SO₄ or cresyl violet perchlorate in methanol. Time-resolved fluorescence measurements were acquired by exciting the samples with 170 femtosecond pulses at 330, 390, or 530 nm from a Coherent RegA Ti:Sapphire amplifier. The resulting fluorescence was spectrally and temporally resolved with a Hamamatsu C4770 Streak Camera system.

**Synthesis of monomers**

5,12-diaza-6,11-benzeno-1,4-dibromo-6,11-dihydrotetracene (2). A mixture of 9,10-dihydro-9,10-ethanoanthracene-11,12-dione (1) (0.91 g, 3.9 mmol) and 2,3-diamino-1,4-dibromobenzene (1.03 g, 3.9 mmol) in glacial acetic acid (30 mL) and ethanol (30 mL) was heated for 20 h at 125 °C. Solvent was removed in vacuo, and the residue was recrystallized from acetonitrile, affording a white/slightly yellow solid as the product (1.54 g, 85%). Further purification involved column chromatography on silica gel with CH₂Cl₂:hexane (2:5, up to 1:1, v/v), affording a white solid as clean product. mp 292–294 °C (acetonitrile). ¹H NMR (400 MHz, CDCl₃) 7.75 (s, 2H), 7.58 (dd, J = 5.6, 3.2 Hz, 2H), 7.15 (dd, J = 5.6, 3.2 Hz, 2H), 5.85 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) 159.0, 141.7, 138.4, 132.9, 127.1, 125.5, 123.2, 54.8. HRMS calcd for C₂₀H₁₂N₂O₄ [M+H]^+ 462.9440, found 462.9426.

1,4-diaza-5,10-benzeno-5,10-dihydroanthra[2,3-c]thiophene (4). A mixture of 9,10-dihydro-9,10-ethanoanthracene-11,12-dione (1) (0.50 g, 2.1 mmol), 3,4-diaminothiophene
hydrochloride (0.40 g, 2.1 mmol), and CH₃COONa (0.35 g, 4.3 mmol) in glacial acetic acid (20 mL) and ethanol (20 mL) was stirred at 125 °C for 18 h. Solvent was removed in vacuo, and the residue was taken with CH₂Cl₂. The mixture was washed with dilute aqueous NaHCO₃ and saturated aqueous NaCl, dried over Na₂SO₄, and concentrated on a rotary evaporator. Purification by column chromatography on silica gel with CH₂Cl₂:hexane (2:1, v/v) afforded a white solid as the product (0.57 g, 86%), which is pure enough for next step. A small portion of the product was recrystallized to obtain analytical pure sample for melting point measurement. mp > 280 °C (acetonitrile) (decomposed). ¹H NMR (400 MHz, CDCl₃) 7.68 (s, 2H), 7.53 (dd, J = 5.2, 3.2 Hz, 2H), 7.17 (dd, J = 5.6, 3.2 Hz, 2H), 5.47 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) 156.2, 141.3, 140.2, 127.2, 125.2, 116.7, 55.4. HRMS calcd for C₂₀H₁₂N₂S [M+1]⁺ 313.0794, found 313.0790.

1,4-diaza-5,10-benzeno-5,10-dihydroanthra[2,3-c]-(2',5'-dibromo)thiophene (5). A solution of NBS (3.6 g, 20 mmol) in DMF (100 mL) was added drop wise to a solution of 4 (3.0 g, 9.6 mmol) in DMF (250 mL) that was cooled by an ice-water bath. After addition, the ice-water bath was removed and the mixture was allowed to warm to room temperature and stirred for 24 h. The mixture was poured into water (400 mL) and the product was extracted with CHCl₃. Organic layers were combined, washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄, and concentrated by rotary evaporation. The residue was recrystallized from CH₂Cl₂, leading to yellow crystals (3.08 g). Mother liquor from recrystallization was concentrated and purified by column chromatography on silica gel with CH₂Cl₂:hexane (1:1, v/v), affording a second crop of product (0.65 g, totally 3.73 g, 83%). mp > 200 °C (CH₂Cl₂) (decomposed). ¹H NMR (400 MHz, CDCl₃) 7.53 (dd, J = 5.2, 3.2 Hz, 2H), 7.19 (dd, J = 5.6,
3.2 Hz, 2H), 5.60 (s, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) 157.6, 140.7, 138.3, 127.4, 125.3, 103.9, 54.6. HRMS calcd for C$_{20}$H$_{10}$Br$_2$N$_2$S [M+1]$^+$ 468.9004, found 468.8994.

**Polymer synthesis**

**PFQ:** Under Ar, an aqueous solution of potassium carbonate (2 M, 7 mL) was added to a mixture of 9,9-dioctylfluorene-2,7-bis(trimethyleneboronate) (190 mg, 0.34 mmol), compound 2 (158 mg, 0.34 mmol), Pd(PPh$_3$)$_4$ (7.0 mg, 0.006 mmol), Aliquat® 336 (60 mg), and toluene (15 mL) in a 25 mL Schlenk flask, which was equipped with a condenser. The reaction mixture was stirred for 72 h at 105 °C under Ar, and then it was cooled to room temperature and taken with chloroform. The resulting mixture was washed with water and saturated aqueous NaCl, dried over anhydrous Na$_2$SO$_4$, and concentrated on a rotary evaporator. The residue was dissolved in a small amount of chloroform and the solution was precipitated in methanol and acetone. A slightly green solid was collected by centrifugation and dried in a vacuum. (0.23 g, 94% yield). $^1$H NMR (400 MHz, CDCl$_3$), $\delta$(ppm): 7.99 (d, br, 2H), 7.93 (s, br, 2H), 7.83 (s, br, 2H), 7.79 (d, br, 2H), 7.56 (s, br, 4H), 7.18 (s, br, 4H), 5.65 (s, 2H), 2.18 (br, 4H), 1.00-1.50 (m, br, 24H), 0.83 (s, 6H).

**PFTP:** This was prepared according to the procedure described for the synthesis of PFQ using 5 (88.5 mg, 0.19 mmol), 9,9-dioctylfluorene-2,7-bis(trimethyleneboronate) (105 mg, 0.19 mmol), Pd(PPh$_3$)$_4$ (5.0 mg, 0.0043 mmol), Aliquat® 336 (40 mg), aqueous potassium carbonate (2 M, 5 mL), and toluene (10 mL) (110 mg, 84%). $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm): 8.34 (d, br, 2H), 8.03 (s, br, 2H), 7.90 (d, br, 2H), 7.60 (m, br, 4H), 7.22 (s, br, 4H), 5.58 (s, 2H), 2.17 (br, 4H), 1.00-1.30 (s, br, 20H), 0.94 (s, br, 4H), 0.78 (m, br, 6H).
**PFP**: This was prepared according to the procedure described for the synthesis of **PFQ** using 6 (46.4 mg, 0.092 mmol), 9,9-dioctylfluorene-2,7-bis(trimethyleneboronate) (51.0 mg, 0.092 mmol), Pd(PPh$_3$)$_4$ (3.0 mg, 0.0026 mmol), Aliquat$^\circledR$ 336 (20 mg), aqueous potassium carbonate (2 M, 2 mL), and toluene (4 mL) (50 mg, 85%). $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm): 8.06 (d, br, 2H), 7.59 (m, br, 4H), 7.39 (s, br, 4H), 7.27 (overlap with CHCl$_3$ peak, 2H), 7.10 (s, br, 4H), 5.90 (s, 2H), 2.29 (s, br, 4H), 1.10-1.40 (m, br, 20H), 1.00 (S, br, 4H), 0.80 (t, 6H).
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Curriculum Vitae

ZHIHUA CHEN

EDUCATION
2002-2007 Massachusetts Institute of Technology, Cambridge, MA
Candidate for Ph.D., Organic Chemistry
Advisor: Professor Timothy M. Swager
Thesis Title: “Organic Materials with Acenoid and Iptycene Structures”

1999-2002 National University of Singapore, Singapore
M.S., Physical Chemistry

1994-1998 Tsinghua University, Beijing, China
B.S., Chemistry

RESEARCH EXPERIENCE
2002-2007 Massachusetts Institute of Technology, Cambridge, MA
Graduate Research Assistant
♦ Studied fluorene-iptycene based donor-acceptor type conjugated polymers.
♦ Synthesized and characterized iptycene-containing polyimides and polyureas.
♦ Examined the effect of perfluoroalkyl sidechains on the photophysical properties of conjugated polymers.
♦ Synthesized acenequinones as fluorescent dyes for guest-host liquid crystal displays.
♦ Designed and synthesized a novel poly(iptycene) ladder polymer with rigid and shape-persist structure.
♦ Developed a family of solution processable, π-stacking fluorinated tetracene derivatives for organic field effect transistors.

1999-2002 National University of Singapore, Singapore
Graduate Research Assistant
♦ Conducted surface analysis of small molecules on metal and metal oxide single crystal surfaces.

1997-1999 Tsinghua University Beijing, China
Undergraduate Research Assistant
♦ Developed and evaluated a series of La-Ce-Cu three-way-catalysts for controlling emission of exhaust gases from automobiles.

PUBLICATIONS
♦ “Surface functionalization of Ni(111) with acrylate monolayers” Yeo, B.-S.; Chen, Z.; Sim, W.-S. Langmuir 2003, 19, 2787-2794.
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Appendix 1

NMR Spectra for Chapter 1
$^1$H NMR Spectrum of 2

$^{13}$C NMR Spectrum of 2
$^1$H NMR Spectrum of 3

$^{13}$C NMR Spectrum of 3
$^1$H NMR Spectrum of 4 (exo)

$^{13}$C NMR Spectrum of 4 (exo)
$^1$H NMR Spectrum of 4 (endo)

$^{13}$C NMR Spectrum of 4 (endo)
$^1$H NMR Spectrum of 5

$^{13}$C NMR Spectrum of 5
$^1$H NMR Spectrum of 8 (exo)

$^{13}$C NMR Spectrum of 8 (exo)
$^1$H NMR Spectrum of 8 (endo)

$^{13}$C NMR Spectrum of 8 (endo)
$^{1}H$ NMR Spectrum of 10

$^{13}C$ NMR Spectrum of 10
\(^1\)H NMR Spectrum of 11

\(^19\)F NMR Spectrum of 11
$^1$H NMR Spectrum of 12

$^{19}$F NMR Spectrum of 12
$^1$H NMR Spectrum of 7

$^{19}$F NMR Spectrum of 7
$^1$H NMR Spectrum of 13 (exo/endo)

$^{13}$C NMR Spectrum of 13 (exo/endo)
$^1$H NMR Spectrum of 13 (exo/exo)

$^{13}$C NMR Spectrum of 13 (exo/exo)
$^1$H NMR Spectrum of 14

$^{13}$C NMR Spectrum of 14
Appendix 2

NMR Spectra for Chapter 2
$^1$H NMR spectra of 4a

$^19$F NMR spectra of 4a
$^{13}$C NMR spectra of 4a

$^1$H NMR spectra of 5a
$^{19}$F NMR spectra of 5a

$^{13}$C NMR spectra of 5a
$^1$H NMR spectra of 4b

$^{19}$F NMR spectra of 4b
$^{13}$C NMR spectra of 4b

$^1$H NMR spectra of 5b
$^{19}$F NMR spectra of 5b

$^{13}$C NMR spectra of 5b
$^1$H NMR spectra of 4c

$^{19}$F NMR spectra of 4c
$^{13}$C NMR spectra of 4c

$^{1}$H NMR spectra of 5c
$^{19}$F NMR spectra of 5c

$^{13}$C NMR spectra of 5c
$^1$H NMR spectra of 4d

$^{19}$F NMR spectra of 4d
$^{13}$C NMR spectra of 4d

$^1$H NMR spectra of 5d
$^{19}\text{F NMR spectra of 5d}$

$^{13}\text{C NMR spectra of 5d}$
$^1$H NMR spectra of 3a

$^{13}$C NMR spectra of 3a
$^1$H NMR spectra of 8

$^{13}$C NMR spectra of 8
$^1$H NMR spectra of 3b

$^{13}$C NMR spectra of 3b
$^1$H NMR spectra of 10a

$^{13}$C NMR spectra of 10a
$^1$H NMR spectra of 3c

$^{13}$C NMR spectra of 3c
$^1$H NMR spectra of 10b

$^{13}$C NMR spectra of 10b
$^1$H NMR spectra of 3d

$^{13}$C NMR spectra of 3d
Appendix 3

NMR Spectra for Chapter 3
$^1$H NMR spectrum of 2

$^{13}$C NMR spectrum of 2
$^1$H NMR spectrum of 3

$^{13}$C NMR spectrum of 3
$^1$H NMR spectrum of 4

$^{13}$C NMR spectrum of 4
$^{1}$H NMR spectrum of 5

$^{13}$C NMR spectrum of 5
$^1$H NMR spectrum of 7

$^{13}$C NMR spectrum of 7
$^1$H NMR spectrum of 8

$^{13}$C NMR spectrum of 8
$^1\text{H NMR}$ spectrum of 9

$^{13}\text{C NMR}$ spectrum of 9
$^1$H NMR spectrum of 10

$^{13}$C NMR spectrum of 10
$^1$H NMR spectrum of 11

$^{13}$C NMR spectrum of 11
$^1$H NMR spectrum of 12

$^{13}$C NMR spectrum of 12
$^1$H NMR spectrum of 13

$^{13}$C NMR spectrum of 13
$^{13}$C DEPT spectra of 11
$^{1}H^{13}C$ HMBC spectra of 11
Appendix 4

NMR Spectra for Chapter 4
$^1$H NMR spectrum of 1a

$^{13}$C NMR spectrum of 1a
$^1$H NMR spectrum of 1b

$^{13}$C NMR spectrum of 1b
$^1$H NMR spectrum of 2

$^{13}$C NMR spectrum of 2
$^1$H NMR spectrum of 5

$^{13}$C NMR spectrum of 5
$^1$H NMR spectrum of 6

$^{13}$C NMR spectrum of 6
$^1$H NMR spectrum of PI-2

$^1$H NMR spectrum of PI-6
$^1$H gCOSY NMR spectrum of PI-2
$^1$H gCOSY NMR spectrum of PI-6
$^1$H NMR spectrum of PU-1

$^1$H NMR spectrum of PU-2

*: DMF
$^1$H NMR spectrum of PU-3

*: DMF
$^1$H gCOSY NMR spectrum of PU-1
Appendix 5

NMR Spectra for Chapter 5
$^1$H NMR spectrum of 2

$^{13}$C NMR spectrum of 2
$^1$H NMR spectrum of 4

$^{13}$C NMR spectrum of 4
$^1$H NMR spectrum of $5$

$^{13}$C NMR spectrum of $5$
\(^1\text{H NMR spectrum of PFQ\)}

\(^1\text{H NMR spectrum of PFTP\)}
$^1$H NMR spectrum of **PFP**